

PANI /MWCNT incorporated CuO-based Nanocomposite Hybrid Systems for Energy Storage Applications

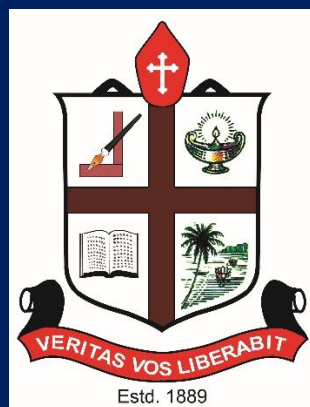
Thesis submitted to the University of Calicut for the Award of
DOCTOR OF PHILOSOPHY IN PHYSICS

By

ANITHA T V

Under the Supervision of

DR. VIMALKUMAR T V



Research and Post-Graduate Department of Physics

St. Thomas College (Autonomous), Thrissur

Kerala- 680 001

JULY 2026

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Dedicated to

My Achan, Amma & Husband...



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CERTIFICATE

This is to certify that the thesis entitled “**PANI/MWCNT incorporated CuO-based Nanocomposite Hybrid Systems for Energy Storage Applications**” is an authentic record of precise research work carried out by Ms. Anitha T V under my guidance and supervision for the partial fulfilment of the award of degree of Doctor of Philosophy in Physics, submitted to University of Calicut and the same has not been submitted elsewhere for any degree or diploma.

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DECLARATION

I hereby declare that the work presented in the thesis entitled “**PANI/MWCNT incorporated CuO-based Nanocomposite Hybrid Systems for Energy Storage Applications**” is based on the original work done by me under the guidance of Dr. Vimalkumar T V, Assistant Professor, Research and Post-Graduate Department of Physics, St. Thomas College (Autonomous), Thrissur, and has not been included in any other thesis submitted previously for the award of any degree. The contents of the thesis have undergone plagiarism check using iThenticate software at C.H.M.K. Library, University of Calicut, and the similarity index was found within the permissible limit. I also declare that the thesis is free from AI generated contents.

Place: Thrissur

Anitha T V

07.07.2026

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Abstract

Development of a cost-effective and an efficient electrode material through a facile and intuitive synthesis route is one of the key points of contention in the area of supercapacitors. This thesis mainly concentrated on the synthesis and characterizations of CuO and PANI/MWCNT incorporated CuO-based nanocomposite hybrid electrode materials. CuO nanostructures are synthesised via a hassle-free hydrothermal method. On the other hand, the PANI/MWCNT incorporated CuO-based ternary/quaternary nanocomposite material is prepared using a one pot chemical oxidative polymerisation method carried out at room temperature, followed by a freeze-drying stage. The crystalline and microstructural, morphological and elemental, thermal properties of the synthesised nanocomposite materials are investigated in detail. Moreover, a comprehensive evaluation is conducted in order to investigate the influence of the transitional metal oxides such as NiO, Co₃O₄ and ZnMn₂O₄ in the electrochemical performance of the ternary CuO/PANI/MWCNT nanocomposite hybrid system. In-depth attention is given to the synergistic interactions between the constituents of composite electrodes that have a crucial role in their electrochemical performance for energy storage applications in terms of specific capacitance, energy density, power density, cyclic stability and rate capacity.

Keywords: Copper oxide, nanocomposite, pseudocapacitor, polyaniline, synergistic effect, hybrid electrodes.

സംഗ്രഹം

ചെലവുകുറഞ്ഞതും ലളിതവും സ്വാഭാവികവുമായ ഗവേഷണ മാർഗം വഴി കാര്യക്ഷമവുമായ ഇലക്ട്രോഡ് പദാർത്ഥങ്ങൾ വികസിപ്പിക്കുക എന്നതാണ് സൂപ്പർ കപ്പാസിറ്റർ മേഖലയിലെ നിലവിൽ നടക്കുന്ന പ്രധാന ഗവേഷണ പ്രവർത്തനങ്ങൾ. ഈ ഗവേഷണ പ്രബന്ധം പ്രധാനമായും കോപ്പർ ഓക്സൈഡ് , PANI/MWCNT എന്നിവ ഉൾപ്പെടുത്തിയ കോപ്പർ ഓക്സൈഡ് അടിസ്ഥാനമാക്കിയ നാനോകമ്പോസിറ്റ് ഹൈബ്രിഡ് ഇലക്ട്രോഡ് പദാർത്ഥങ്ങളുടെ നിർമ്മാണവും തുടർന്നുള്ള ഗവേഷണം അവയുടെ സ്വഭാവവിശകലനത്തിലും വിവിധ ഉത്പന്നനിർമ്മാണത്തിന് പ്രയോജനപ്പെടുത്താവുന്ന രീതിയിലുമാണ്. കോപ്പർ ഓക്സൈഡ് നാനോഘടനകൾ ലളിതമായ ഹൈഡ്രോതെർമൽ രീതിയിലൂടെ തയ്യാറാക്കുന്നു. അതേസമയം, PANI/MWCNT ഉൾപ്പെടുത്തിയ കോപ്പർ ഓക്സൈഡ് അടിസ്ഥാനമാക്കിയ ടെർണറി/ക്വാടേണറി നാനോകമ്പോസിറ്റ് മെറ്റീരിയലുകൾ മൂറിയിലെ താപനിലയിൽ രാസ ഓക്സിഡേറ്റീവ് പോളിമറൈസേഷൻ രീതിയിലൂടെ ആരംഭിച്ച് തുടർന്നുള്ള ഫ്രീസ്-ഡ്രെയിംഗ് ഘട്ടത്തിലൂടെ തയ്യാറാക്കുന്നു. തയ്യാറാക്കിയ നാനോകമ്പോസിറ്റ് പദാർത്ഥങ്ങളുടെ സ്പെട്രോസ്കോപ്പിക് സൂക്ഷ്മഘടനയും, ആകൃതിശാസ്ത്രവും ഘടകവിശകലനവും, താപഗുണങ്ങളും വിശദമായി പരിശോധിക്കുന്നു. കൂടാതെ, NiO, Co₃O₄, ZnMn₂O₄ പോലുള്ള ട്രാൻസിഷണൽ മെറ്റൽ ഓക്സൈഡുകൾ CuO/PANI/MWCNT ടെർണറി നാനോകമ്പോസിറ്റ് ഹൈബ്രിഡ് സിസ്റ്റത്തിന്റെ ഇലക്ട്രോകെമിക്കൽ സ്വഭാവത്തിൽ ഉണ്ടാക്കുന്ന സ്വാധീനം വിലയിരുത്തുന്നതിനായി സമഗ്രമായ വിശകലനം നടത്തുന്നു. സംയുക്ത ഇലക്ട്രോഡുകളുടെ ഘടകങ്ങൾ തമ്മിലുള്ള സഹപ്രവർത്തനങ്ങൾ അവയുടെ ഇലക്ട്രോകെമിക്കൽ പ്രകടനത്തിൽ, അതായത്, പ്രധാനമായും അവയുടെ കപ്പാസിറ്റൻസ്, എനർജി ഡെൻസിറ്റി, പവർ ഡെൻസിറ്റി, സൈക്ലിക് സ്റ്റേബിലിറ്റി, റേറ്റ് കപ്പാസിറ്റി എന്നിവയിൽ വഹിക്കുന്ന നിർണായകമായ പങ്ക് കണ്ടെത്തുന്നതിൽ ആഴത്തിലുള്ള ശ്രദ്ധ കൊടുത്തിരിക്കുന്നു.

Preface

The relentless growth of worldwide population and vigorous use of sustainable energy resources has led the scientific society to passionately work with utmost dedication and focus on the development of highly efficient and reliable energy storage devices. These unwavering efforts fuelled the rapid and effective investigations in the area of Supercapacitors or Ultracapacitors. CuO is one the most promising electrode material with its elemental abundance, non-toxicity and high pseudocapacitive behaviour. However, the few inherent conductivity shortcomings of CuO based electrode material made an effective path for the development of CuO-based nanocomposite hybrid electrode materials with the incorporation of PANI and MWCNTs. This thesis aims to explore the structural, morphological, elemental, thermal and electrochemical properties of CuO and PANI/MWCNT incorporated CuO-based ternary/quaternary nanocomposite hybrid electrode materials. The thesis is categorised into seven chapters and a concise summary of each chapter is presented as follows.

Chapter 1-General introduction focuses on supercapacitors, different electrode materials, synthesis strategies of nanocomposites and the electrochemical analysis techniques. A detailed introduction about supercapacitors, principle and classifications, their advantages and challenges are presented. A comprehensive study on copper oxide, other transitional metal oxides, carbon nanotubes, polyaniline and nanocomposites is also discussed. The electrochemical analysis techniques used for the evaluation of performance of electrode materials are also addressed. The organisation of the thesis and the major objectives of the research is also outlined in the closing remarks of the chapter.

Chapter 2-Synthesis, Characterization, and Supercapacitive Performance of CuO and CuO/PANI/MWCNT Hybrid System deals with the synthesis, structural, morphological, microstructural, and elemental characterizations of CuO and PANI/MWCNT incorporated CuO nanocomposite hybrid electrodes. The chapter discusses the different synthesis strategies and the influence of PANI and MWCNTs on the basic features of CuO electrode materials. The electrochemical performance of CuO

and CuO/PANI/MWCNT nanocomposite hybrid systems are evaluated in both three-electrode and two-electrode configurations.

Chapter 3-Synthesis, Characterization, and Supercapacitive Performance of CuO-NiO/PANI/MWCNT Hybrid System discusses about the synthesis and characterizations of quaternary CuO-NiO/PANI/MWCNT nanocomposite material via structural, morphological and spectroscopic studies. An in-depth examination about the effect of PANI/MWCNT incorporation into the efficient metal oxide nanocomposite CuO-NiO hybrid system through one pot chemical oxidative polymerisation is conducted in detail. The enhanced electrochemical performance of this quaternary nanocomposite is accessed through both three-electrode and two-electrode electrochemical set ups.

Chapter 4-Synthesis, Characterization, and Supercapacitive Performance of CuO-Co₃O₄/PANI/MWCNT Hybrid System deals with the fabrication, characterizations and electrochemical performance evaluation of quaternary nanocomposite CuO-Co₃O₄/PANI/MWCNT hybrid electrode. A comprehensive examination about the synergistic interactions between the four constituents is conducted to evaluate the factors influenced the improved electrochemical performance of the nanocomposite electrode. The supercapacitive performance evaluation of the quaternary composite electrode material is done in both three-electrode and two-electrode configurations.

Chapter 5-Synthesis, Characterization, and Supercapacitive Performance of CuO-ZnMn₂O₄/PANI/MWCNT Hybrid System discusses the synthesis, microstructural, elemental and morphological features of the quaternary CuO-ZnMn₂O₄/PANI/MWCNT nanocomposite electrode material. The study focussed on the influences of binary metal oxide like ZnMn₂O₄ in the CuO-based composite electrode in the enhanced electrochemical performance of the hybrid electrode. The performance investigation of the prepared quaternary composite electrode is done in both three-electrode and two-electrode electrochemical set up.

Chapter 6-Conclusion presents a concise summary of the notable aspects of the overall works and the **Chapter 7-Recommendations** explores the future works and recommendations of the current thesis work in all fields of nanomaterials specifically in energy storage devices.

Research Papers Published

1. Anitha T.V., Gadha Menon K., M.A. Anu, Xavier T.S., T.V. Vimalkumar, In-situ synthesis of Co₃O₄–CuO/PANI/MWCNT nanofibers for high-performance supercapacitor applications, Journal of Physics and Chemistry of Solids, Volume 215, August 2026, 113728, ISSN: 1879-2553 <https://doi.org/10.1016/j.jpcs.2026.113728>.
2. Anitha T.V., Gadha Menon K., Vimalkumar T.V., Merin Tomy, Xavier T.S., Polyaniline/multi-walled carbon nanotube incorporated porous CuO NiO hybrid system for energy storage applications, Journal of Power Sources, Volume 662, 15 January 2026, 238726, ISSN 0378-7753 <https://doi.org/10.1016/j.jpowsour.2025.238726>.
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5. Gadha Menon K., Anitha. T. V., Prabeesh Punathil, T.V. Vimalkumar, Annealing temperature optimization for dip-coated Cu₂SnS₃ thin films: Sustainable pathway to CTS/Zn(O, S) solar cells via numerical simulation, Materials Science and Engineering: B, Volume 314, 2025, 118003, ISSN 0921-5107, <https://doi.org/10.1016/j.mseb.2025.118003>.
6. Merin Tomy, M.A. Anu, Anitha. T. V. , T.V. Vimalkumar, T.S. Xavier, Polyaniline-modified renewable coconut husk-derived activated carbon as an efficient electrode for supercapacitor applications-A sustainable approach, Materials Science and Engineering: B, Volume 321, 2025, 118456, ISSN 0921-5107, <https://doi.org/10.1016/j.mseb.2025.118456>.

7. Anitha. T. V., Thottapuruth Vijayan Vimalkumar, Anna Heba Chakkunny, B. Salameh, A. M. Alsmadi, M. Mathai, Structural and opto-electrical study of as-grown CuS thin film doped with Sn by facile chemical bath deposition for solar cell application AIP Conf. Proc. 2244, 110002 (2020), <https://doi.org/10.1063/5.0009137>.

Research Works Communicated

1. Anitha T.V.^a, Gadha Menon K.^a, M. A. Anu^b, Xavier T. S.^b, T. V. Vimalkumar^{a*}, Enhanced Electrochemical Performance of ZnMn₂O₄-CuO Composite Electrode Integrated with PANI/MWCNT for High- Performance Supercapacitors.

Presentation in National/International **Conferences**

1. *Structural and opto-electrical study of as grown CuS thin film doped with Sn by facile chemical bath deposition for solar cell application* in International Conference on PHYSICS OF MATERIALS & NANOTECHNOLOGY (ICPN-2019) at Mangalore University during September 19-21, 2019.
2. *Tailoring the physical properties of sol-gel dip coated CuO thin films by varying thickness: Investigating its optoelectronic applications* in International Conference on SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS (STAM23) at Mar Athanasius College (Autonomous), Kothamangalam during April 18-20, 2023.
3. *Fe³⁺ Induced Antibacterial Efficacy of Spherical Flower-like CuO Nanoparticles with Enhanced Structural and Optical Properties* in International Conference on Advanced Materials for Sustainability (ICAMS 2023) at School of Physical science, University of Calicut during December 21-23, 2023.
4. *Investigating the effect of Co- and Fe- doping on the surface structural and optical characteristics of CuO micro-flowers* in International Conference on Emerging Trends in Sustainable Energy (ICETSE 2023) at Mercy College, Palakkad during July 24-25, 2023.
5. *Hierarchically porous nano-sized CuO–NiO hybrid system for supercapacitor applications* in International Conference on Advance in Material Science (ICAMS 2025) at St. Dominic's College, Kanjirapally, Kottayam during January 9-10, 2025.

General Introduction

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Worldwide, the awareness of “energy crisis” has led to a series of initiatives and energy management policies in the last decades that have made society to become more focused on energy production and management procedures. Thus, Energy storage devices (ESDs) have gained much interest in the research scenario, thereby more and more works have been centred in recent years on the field of supercapacitors with the aim to fabricate a highly efficient, viable and cost-effective electrode material. Herein, a detailed description of the basics, importance and classifications of the supercapacitors is discussed. An extensive study on the different kinds of charge storage mechanisms involved in the supercapacitors as well as the importance and role of electrode material is also discussed in detail. A brief introduction on metal oxides, carbonaceous compounds and conducting polymers is also given. Moreover, this chapter discusses nanocomposites and their importance and classifications. A detailed description of the important synthesis techniques used in the area of nanomaterials and nanocomposites is also presented. Furthermore, this chapter also deals with the various electrochemical analysis methods used in the field of supercapacitors and discusses their applicability in the area of ESDs. Finally, the organisation of thesis along with the major objectives of the study is described in detail.

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1.1. BACKGROUND

Nowadays, the term ‘energy shortage’ has raised heightened concern among the scientific society due to the uncontrollable deterioration of conventionally used energy sources and unruly expansion of the world population. To balance between the resource and demand ratio in terms of energy, a perfect energy storage system must be put forward. Thus, in the sense of keeping up with the everlasting demand for energy in various day to day scenarios like electronics, grid stabilization, utility vehicles and the automobile industry, scientists took the topic of inventing a powerful, efficient and environmentally viable energy storage system as a hot research material. A perfect energy storage device (ESD) should carry features like remarkable power density and energy density, with a satisfactory life time. Typically used energy storage devices such as batteries, still face the problem of having insufficient power density and short life time due to unwanted heat loss and electrode decay during charging-discharging cycles. On the other hand, the conventional capacitors as an ESD candidate carry sufficient power density but suffer from poor specific energy. Accordingly, the scientific community made a greater focus on the area of supercapacitors (SCs) which can bridge the gap of having an ideal ESD with both high-power density and energy density values (Fig.1.1). Although, supercapacitors are one of the frontier research topics of today, it has a live back history. In the early 1950’s, General electric company engineering workers has started to develop a capacitor with carbon based electrodes and ended up with an electrolytic capacitor fabrication using activated carbon electrode with high specific surface area by Becker in 1957, which he filled for patent [1]. Later, in 1966 Standard Oil of Ohio (SOHIO) Company built a 6V supercapacitor with activated carbon electrode and aqueous sulphuric acid as the electrolyte solution [2]. The first supercapacitor was developed for the military applications in 1982 by Pinnacle Research Institute (PRI), termed as PRI ultracapitors. On behalf of combining both electrolytic and electrochemical features of capacitors, an Electrolytic-Hybrid Electrochemical capacitor was fabricated in 1994 by Evans [1]. However, it is to be noted that before 1990s not much efforts were taken with the aim to reduce the production costs of supercapacitors. B. E. Conway has first talked about pseudocapacitive storage mechanism in supercapacitor field with ruthenium oxide (RuO_2) as electrode material, by 1999. Apart from the carbon based electrodes, the

works were latter started reporting and highlighting the pseudocapacitive nature of metal oxide electrodes, specifically ruthenium oxide (RuO_2), having a specific capacitance of around 2000 F/g [3]. The concept of efficient usage of supercapacitors in hybrid electric vehicles made a breakthrough in their developments with a primary focus on fabricating pseudocapacitive materials having high energy densities compared with conventional double-layer capacitors. On account of multiple oxidation states and quick charging-discharging abilities, transitional metal-based oxides and hydroxides, such as MnO_2 , RuO_2 , NiO , Co_3O_4 , CuO etc., gained elevated priority in the field of SCs [4]. This revitalized scholarly pursuit has enabled advancements in developing high performance supercapacitors with commercial applicability.

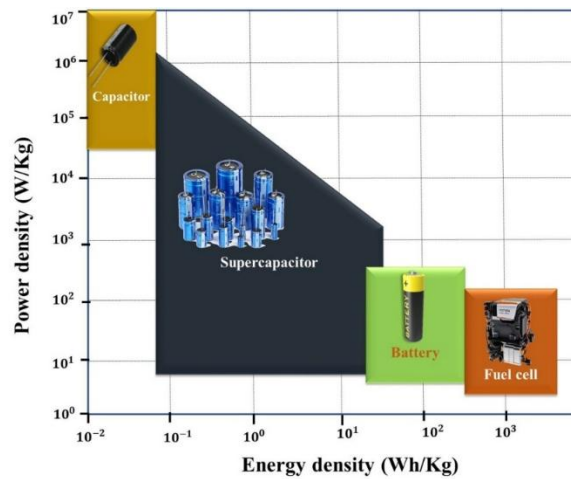


Fig. 1.1. Ragone plot of popular energy storage devices.

1.2. SUPERCAPACITORS

Capacitors known as a conventional ESD with the purpose of storing electrical charges using two parallel plate electrodes separated by a dielectric medium, has been a passive electronic component of electronic circuits. Fig.1.2 shows the schematic structure of an ideal capacitor. The capacitance (C) of this capacitor can be evaluated using the equation;

$$C = \frac{\epsilon_0 A}{d} \quad (1.1)$$

Where ϵ_0 is the dielectric constant, A denotes the surface area of electrodes separated by a distance 'd'. From the above equation, it is clearly observable that the

capacitance value is independent of charge stored ‘q’. Conventional capacitors can be divided into two categories depending on the medium used between electrodes; one is the dielectric capacitors, where the medium is a dielectric material and the second one is the electrolytic capacitor with a solid/liquid ionic conductor between electrodes called as electrolyte. The energy stored in the capacitor can be calculated using the equation;

$$E = \frac{q^2}{2C} \quad (1.2)$$

Therefore, the energy stored in the capacitor is directly linked to the amount of charge stored in that system. The charge stored in conventional capacitors will typically be in the range of some millifarads (in the case of electrolytic capacitors) to the microfarad range (in the case of dielectric capacitors), indicating the poor energy density of the overall system. The power density of the system is evaluated by analysing the total energy stored for a given discharge time. The long discharge time of capacitors make them one of the efficient high power devices [5], [6].

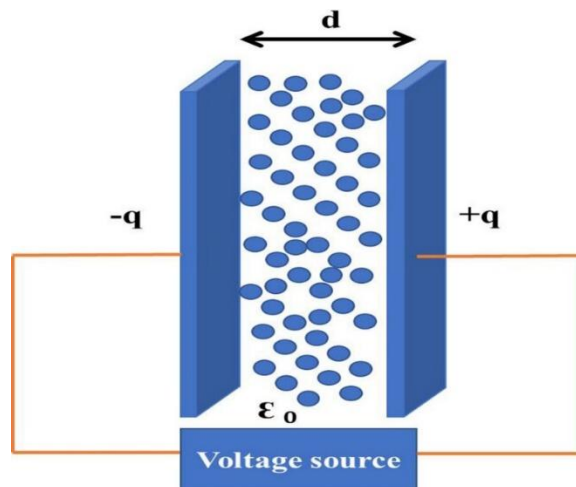


Fig. 1.2. Schematic diagram of a conventional capacitor.

The electrochemical capacitors, commonly known as supercapacitors, are designed to cope with the demerits of both capacitors and batteries, having a remarkable power densities, a rapid charging-discharging process, good durability and higher specific energy value compared with capacitors [7]. The working principle of a supercapacitor is inseparable from the essence of conventional capacitors; usually end up with a capacitance value in the range of Farads (F) leading to the addition of term “super” with their name [8].

A supercapacitor consists of two solid electrodes and an ionic liquid electrolyte solution bath between them. The two electrodes were physically separated using a thin and porous separator material in order to avoid device shortage that may happen due to direct contact, which doesn't hinder the movement of ions. The metallic current collectors used were intended to provide a conductive backbone to the electrodes. The basic design of a supercapacitor is shown in Fig. 1.3.

- **Electrodes:** Electrodes are the most important part of a supercapacitor, which directly influences its overall electrochemical performance, and are generally thin coatings that must be electrically attached to conductive current collectors. The electrode material must be a good ionic conductor and highly resistant to corrosion with long term thermal and chemical stability and superior specific surface area [9].
- **Electrolyte:** Electrolytes are composed of a solvent and dissolved to make the electrodes electrically connected. The conductivity of the electrolyte medium increases with the availability of ions in the solvent. The electrolyte solution directly decides the operational voltage of the cell and the cell power is inversely proportional to ionic resistivity caused by the electrolyte medium in the electrode-electrolyte interface. Depending upon the solvent medium used in electrolytes, three types of electrolyte categories are present: aqueous, organic and ionic liquid electrolytes [10]. The aqueous electrolytes often suffer obstacles related to thermodynamic instability of water beyond the voltage window $\sim 1.23\text{V}$. This water-splitting limit makes the device compromise with its efficiency, energy density and stability. Whereas, the non-aqueous electrolytes like ionic liquids offers wide potential window with significant energy densities [11].
- **Separator:** Separators are components used to physically separate electrodes, but are permeable to electrolyte ions. The separator materials are mostly quite thin and porous nature with good mechanical stability. Separators are made soaked in the electrolyte solution with a high transfer capacity of ionic species. Normally, woven ceramic and glassy fibres and nonwoven polymer films are employed as separators [12]. Poorly designed separators can make negative impacts on the

performance of supercapacitors by cause of their capacity to produce additional resistance in the cell [1].

- **Current collector:** A highly conductive metal foil or spray-painted thin films can serve as current collectors with the function to release/take electrons from/to the external load. Current collectors link the electrode material to the terminals of the capacitor. Commonly used current collector materials are copper, aluminium, nickel, carbon fibre, stainless steel, platinum etc. The selection of current collectors depends on the electrode/electrode material used in the cell. For acidic electrolytes, noncorrosive foils of gold, stainless steel, indium doped titanium oxide and others were commonly used, whereas for alkaline electrolytes, current collector materials like carbon fibre, carbon cloth, nickel foam, etc. were employed. Typically, aluminium based current collectors were chosen for non-aqueous electrolyte medium [13].

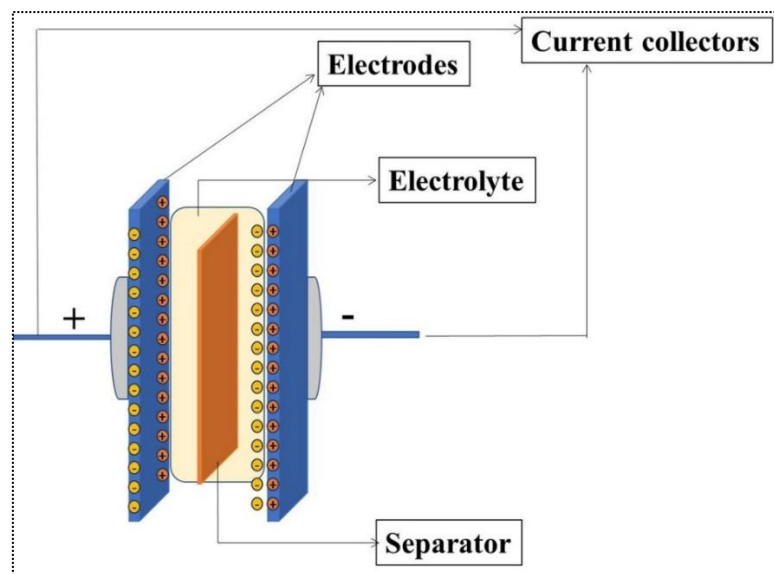


Fig. 1.3. Diagrammatic illustration of supercapacitors.

1.3. CHARGE STORAGE MECHANISMS IN SUPERCAPACITORS

The basic steps that work behind the charge storage mechanism in a supercapacitor can be listed as follows and portrayed in Fig. 1.4;

- ❖ Electrode polarization by an externally applied voltage supply
- ❖ Ionic diffusion in electrolyte solution through the separator
- ❖ Attraction of electrolyte ions in the direction of oppositely polarised electrodes.
- ❖ In the electrode-electrolyte interface, adsorption as well as intercalation of electrolyte ions happen.
- ❖ Ultimately, a double layer arrangement has been formed by the uniform accumulation of equal and opposite charges near the electrode surface, which is attributable to the electrostatic process and electrochemical faradic redox reactions.
- ❖ Penetration of ionic species through the double layer architecture gives rise to pseudocapacitance
- ❖ This electron flow is a representation of charging mode of the capacitor and continues till the potential difference between electrodes matches with the applied voltage.
- ❖ During discharging, electrons flow back to the electron vacancies.

The stability and efficacy of this electrochemical performance in a supercapacitor is greatly determined by its capacity to deliver constant charging/discharging rates over long period of time. The selection of an efficient electrode material with ideal electrode characteristics like good electrical conductivity and surface area as well as satisfactory charge storage mechanisms, is one of the most important deciding factors that impact the efficiency of a supercapacitor device [14].

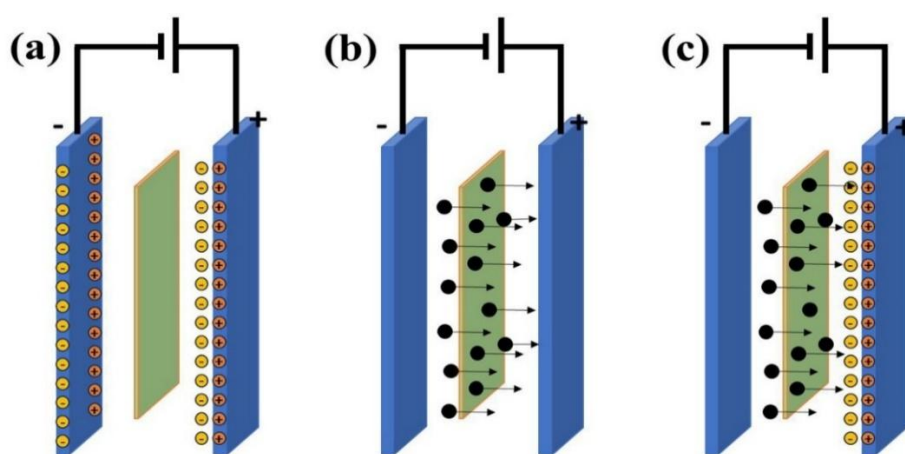


Fig. 1.4. Charge storage mechanisms in supercapacitors through (a) electrostatic charge separation (b) faradic redox reactions (c) electrostatic and electrochemical process.

1.4. TYPES OF SUPERCAPACITORS

Supercapacitors have been mainly divided into three classes namely, electric double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors on the basis of how energy is stored (Fig. 1.5) [15]. EDLCs generally store charges electrostatically or through any non-faradic manner without undergoing any kind of charge transfer at the electrode/electrolyte interface [16]. Activated carbon, carbon nanotubes, graphene, carbon aerogels, carbon foam, and carbon derived carbon are the main classes of EDLC electrode material. When it comes to pseudocapacitors, the charge storage mechanism involves faradic redox reactions and there exists some electrostatic transfer of charge loads between the electrode surface and electrolytes [17]. Metal oxides and conducting polymers are important electrode materials that show pseudocapacitive behaviour. A hybrid supercapacitor is an amalgam of both battery-type electrode having high specific energy and a capacitor-like electrode, having high specific power in one cell [18]. Asymmetric, composite and battery types are three important classes come under hybrid supercapacitors.

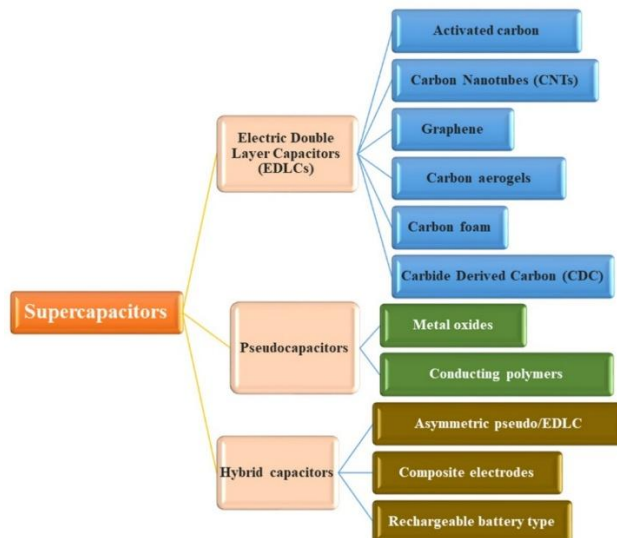


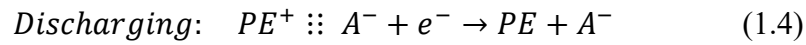
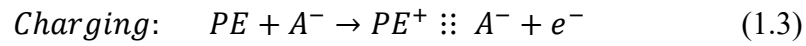
Fig. 1.5. Classification of supercapacitors.

1.4.1. Electric Double-Layer Capacitors (EDLCs)

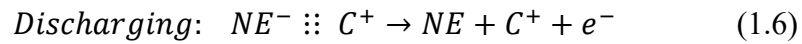
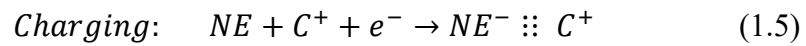
EDLCs are the simplest and most commonly used supercapacitor category using porous carbon-based materials as electrodes, which involves the storage of charges electrostatically without undergoing any kind of faradic processes. Under the externally

applied constant voltage, positive and negative charges get accumulated on the electrode surface. Then, the positive and negative ions get attracted to the oppositely polarised electrodes and make diffusion through the separator and get trapped by the pores of the electrode material, which eventually results in the formation of a monolayer at the electrode-electrolyte interface. The expanded formations of this surface monolayer led to the formation of a secondary diffusion layer in the electrolyte medium. Thus, the combination of surface and diffusion layer causes an electric double layer arrangement in the cell, which can store electrostatic charges. The concept of electric double layer arrangement in the electrode-electrolyte interface was first introduced by Helmholtz, a German scientist, so that the double layer configuration is also called as Helmholtz double-layer. The electrostatic charge storage mechanism in EDLCs is presented in Fig. 1.6. Since there are no transfer of charge loads between the electrode and electrolyte, the charge storage process is highly reversible and has a long-life span. The adsorption and desorption of electrolyte ions in the electrode-electrolyte interface make the foundation for the electrostatic charge storage process of EDLCs, which can be summarised as follows;

At the $+_{ve}$ electrode surface:



At the $-_{ve}$ electrode surface:



where PE and NE represent positive electrode and negative electrode, respectively. Whereas A^- and C^+ denote anion and cation present in the electrolyte. Also, “::” symbolically represents the electrolyte-electrode interface.

The double layer capacitance C_{DL} is estimated using the equation;

$$C_{DL} = \frac{\Delta Q}{\Delta V} \quad (1.7)$$

where ΔQ is the amount of charge stored in EDLC under the potential difference ΔV . EDLCs have quick charge-discharge cycles with good stability, resulting in good power density and cycle life. The performance of EDLCs depend on the porous morphology and surface area of electrode material, electrolyte nature and double layer thickness.

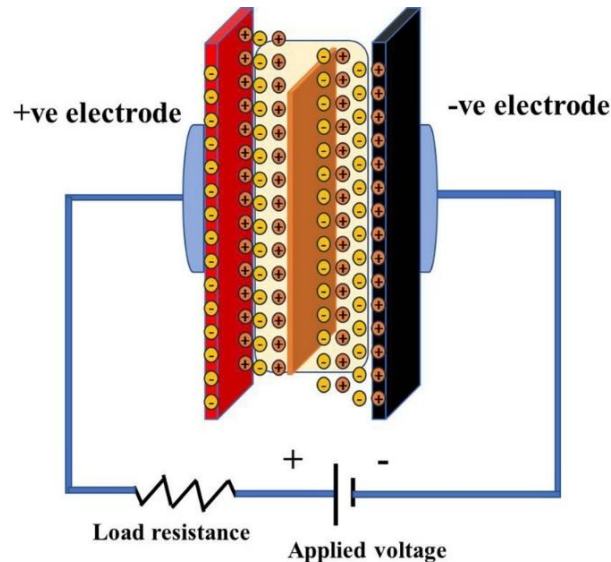


Fig. 1.6. The schematic representation of working principle of EDLCs.

1.4.1.1. Merits and demerits of EDLCs

EDLCs have both merits and demerits which made this class of supercapacitors as a prominent hot research material. Some of the advantages and disadvantages of EDLCs are documented as follows;

- EDLCs exhibits high power density but inferior energy storage capacity.
- EDLCs reports relatively weaker specific capacitance.
- Necessity of porous electrode materials having ideal electrode characteristics with reduced internal resistance value in order to achieve more energy density.
- The charge accumulated on the electrode surface or in the vicinity of electrode surface is the only deciding factor of device performance, not which exhibits in bulk of electrode material.
- The necessity of having an advanced electronic control and easy switching mechanism for the proper functioning of EDLs results in additional energy loss.

1.4.2. Pseudocapacitors

Pseudocapacitors are considered as an alternative form of EDLCs, where the charge storage mechanism involves rapid and reversible faradic redox reactions occurring at the electrode-electrolyte interface, illustrated in Fig. 1.7. Due to the faradic charge storage, pseudocapacitors can store more charge and deliver higher energy density compared to EDLCs.

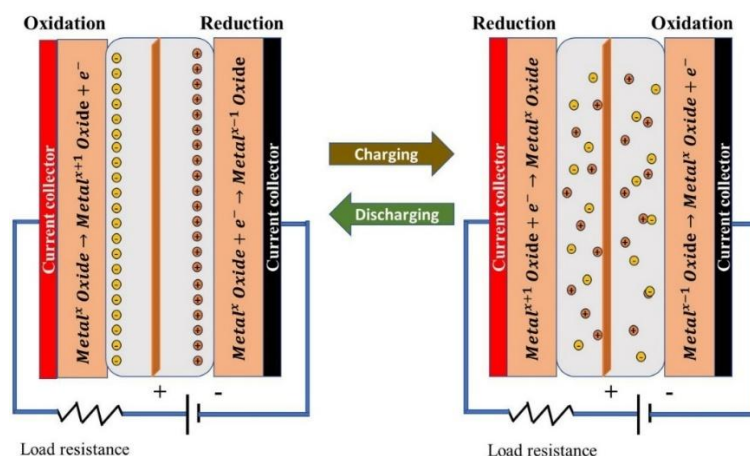


Fig. 1.7. Schematic representation of basic charge storage mechanism of pseudocapacitors.

Broadly, Conway proposed three types of charge storage mechanisms usually occur in pseudocapacitors namely (Fig. 1.8);

- Underpotential deposition: The process in which metal ions get adsorbed on the surface of another metal resulting in the formation of a monolayer due to a strong interaction between them, which is significantly exceeds their oxidation-reduction potential, i.e., deposition of metal ions under deficient potential. Example: deposition of lead ions on the surface of Au electrodes.
- Redox pseudocapacitance: The process of charge storage involving the electrochemical adsorption of electrolyte ions on the electrode surface or on the vicinity of electrode surface. This mechanism of charge storage associates with transfer of charge loads. Example: RuO₂, MnO₂ etc.
- Intercalation pseudocapacitance: The charge storage mechanism is based on the intercalation/de-intercalation of electrolyte ions into the tunnels or interlayers of active material. This mechanism conveyed the charge transfer via a faradic

process without undergoing any crystallographic phase changes. Examples: TiO_2 , Nb_2O_5 etc.

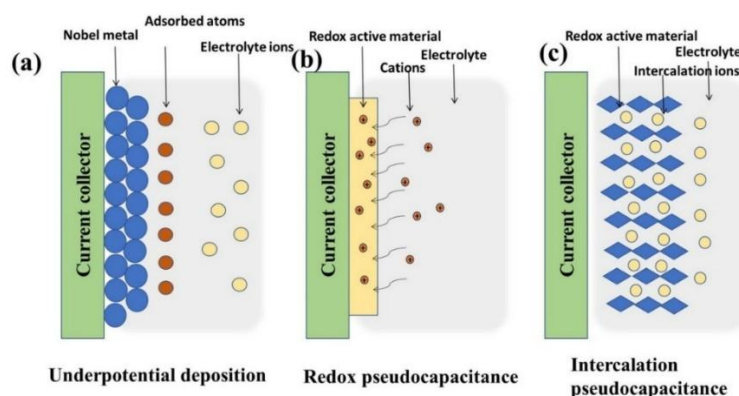


Fig. 1.8. Schematic representation of different types of pseudocapacitors (a) underpotential deposition (b) redox pseudocapacitance (c) intercalation pseudocapacitance.

1.4.2.1. Merits and demerits of pseudocapacitors

Pseudocapacitors are one of the most intensively studied energy storage devices, which have the ability to produce high specific capacitance compared to EDLCs, but have limitations too. Some of them are listed below;

- The performance of pseudocapacitors is limited by the factors like poor electrical conductivity and low accessible surface area.
- In the sense of fabricating metal oxide/hydroxide based pseudocapacitors there is the use of a significant amount of precursor components as well as chemical treatments, which ultimately drive up the cost of large-scale production.
- Need greater control over the synthesis conditions since it greatly influence the particle size and dimensions, and chances of forming agglomerations are relatively high, which eventually results in weak electrical conductivity.

1.4.3. Hybrid supercapacitors

Recently, hybrid supercapacitors have gained much attention among the research community due to their enhanced specific energy without compromising

power density. The commendable specific capacitance value of the hybrid supercapacitor is a result of the electric double layer capacitance produced by the porous carbon-based electrode and pseudocapacitance produced by the metal oxides/hydroxides or conducting polymer electrodes in the same cell. This type of supercapacitor takes the advantage of both EDLCs and pseudocapacitors, involving faradic and non-faradic charge storage mechanisms. The charge storage mechanism in hybrid supercapacitors is represented in Fig. 1.4 (c).

Hybrid supercapacitors have been classified into three main configurations on the basis of electrode arrangement, namely;

- ❖ Asymmetric hybrids: In this configuration, the cell is designed with two dissimilar electrodes, i.e., an EDLC electrode material is used in combination with a pseudocapacitive electrode material.
- ❖ Composite hybrids: In this type of hybrid supercapacitors, electrode material is composed of carbon-based material with the metal oxides and/or conducting polymers. The higher surface area of carbon material helps to enrich the effective contact between pseudocapacitive materials with electrolyte solution.
- ❖ Battery-type hybrids: This class of hybrid supercapacitor involves the use of two different kinds of electrodes; one is supercapacitor type, and the other is battery type. Here, the factors like power density and rate capacity are evaluated on the basis of battery type electrode and energy storage capacity which are determined on the basis of supercapacitor type electrode.

Enhanced specific capacitance and wider voltage range can be achieved using highly stable long-life carbon-based negative electrodes with superior capacitive faradic positive electrodes in aqueous electrolytes. However, the poor rate capacity of a faradic anode material hinders the cell from becoming a high-power hybrid supercapacitor. Thus, in order to overcome this limitation, an efficient mesoporous transitional metal oxide (TMO) or an effective combination of binary TMOs can be used as the faradic electrode material. These forms of electrode material can offer multiple oxidation states and can enrich the redox activities, thereby improving the overall electrochemical performance of the hybrid system.

1.5. ADVANTAGES AND APPLICATIONS OF SUPERCAPACITORS

Supercapacitors are devices which are capable of serve as an intermediate energy storage device between conventional capacitors and batteries. They often offer a satisfactory level of energy storage capacity compared to capacitors and high-power density compared to batteries. Although, the power density of supercapacitors is much higher than that of batteries, they deliver only lower energy densities than batteries, which make them suitable for only high-power applications where energy storage is not very important.

The rapid charging and discharging process is another important aspect of supercapacitor, which makes the charging process of supercapacitor devices easier and quicker. Additionally, the longer cycle life and stability of supercapacitors over ten thousand/fifty thousand repeated cycles make them an inevitable component of energy storage devices like consumer electronics, military, medicinal fields and hybrid automobiles. Moreover, supercapacitors also offer greater safety and thermal stability compared to batteries, without undergoing any kind of deterioration due to corrosion or energy loss.

1.6. ELECTRODE MATERIALS

The electrochemical performance of supercapacitors has been significantly influenced by the proper selection of electrode material and electrolytes. In this regard, there exist enormous research works with the aim to improve the electrochemical activity of electrode material, thereby producing a highly efficient supercapacitor device having excellent power and energy densities, cycle performances and superior lifespan of service. The ideal features of an electrode material are high surface area with porous architecture, good chemical and thermal stability, good ionic and electrical conductivity, low cost and environmental benignity and corrosion resistance. Moreover, the material purity of the electrode is another important factor which decides the performance of the capacitor. The presence of unwanted substances in the electrode composition can results in unnecessary leakage current in the device, which negatively influences its cycle performance and life time through spontaneous discharging.

Additionally, the electrode material's ability to facilitate fast faradic reaction kinetics positively enriches the specific capacitance of the device.

1.6.1. Carbon materials

From an industrialisation perspective, carbon-based electrode materials are the most appropriate ones to be used in energy storage devices. They exhibit many of the desirable electrode properties, that make them outperform over other commonly used materials. Activated carbon, carbon aerogels, carbon nanotubes and graphene, are extensively used electrodes in EDLCs.

Activated carbons (ACs) are the top-priority EDLC material having features like economically and environmentally viable, ease of processing, commendable electrical conductivity and stability. They can be easily synthesised using a carbonization step followed by an activation stage. Another promising EDLC electrode material is carbon aerogels, which are chemically inert and strong electrical conductivity. Graphene based electrode material gained more popularity than other carbon-based electrodes having a theoretical capacitance value of about 550 F/g as well as a theoretical surface area of about 2630 m²/g. The superior surface area and packing density made their surface easily available for electrolyte species. Carbon nanotubes (CNTs) are the widely explored EDLC electrode material having sufficient intertwined mesoporous networks with excellent chemical, thermal and mechanical stability. The mesoporous morphology of CNTs makes their surface easily accessible for electrolyte ions and promotes rapid ionic diffusion, results in lower internal resistance and higher power density.

Generally, carbon-based electrode materials come under the category of materials that are low cost, environmentally benign with abundant reserves. Additionally, the capacitance value of these materials is directly correlated with the total accessible area in the electrode surface rather than the bulk, since the charge storage occurs at the electrode-electrolyte interface through electric double layer formation. But some recent literature has reported that the porosity of the electrode surface is not the only factor which decides the electrochemical performance, as not all the micropores in the electrode surface are actively used by the electrolyte ions [5]. The important factors like power density and energy density have a direct correlation with

the pore size distribution in the electrode material. Therefore, fabricating a carbon-based electrode material having an exceptional surface area with optimal pore size distribution is the pivotal concern for the research community. Moreover, carbon-based electrode in the supercapacitor field offers high power density with commendable cycle, but suffer from low capacitance and energy density values.

1.6.1.1. Carbon nanotubes

Carbon nanotubes are the popular electrode materials used in EDLCs due to their porous morphology with mechanical stability, non-corrosive nature, high thermal stability and capability of functionalization. These materials exhibited a theoretical specific surface area value of about 120-400 m²/g. The intertwined porous architecture with sufficient accessible sites in the CNT surface causes the ionic diffusion to be easier and enhances the double layer formation for efficient electrochemical performances.

Multi-walled carbon nanotubes (MWCNTs) are the carbon-based material made up of sp² hybridised carbon having an elongated cylindrical shape with an average diameter in the range of 3-30 nm. The end part of the tubes is capped by fullerene like nanospheres. Their length may vary with synthesis conditions, indicating that the aspect ratio can vary between ten to ten million [19]. Their structures are like hollow rolled graphite tubes with hexagonal carbon rings as wall builders. Depending upon the arrangements, there exist two types of CNTs namely; single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). As the name indicates, SWCNT consists of only one layer of graphene cylinder whereas MWCNT carries multiple layers of graphene cylinders. Moreover, SWCNTs have a single tube with average diameter around 0.4 nm to 2 nm and MWCNTs have multiple concentric tubes which 0.34 nm apart and average diameter of 2-100 nm. CNTs exhibit more interesting electrical, optical, and structural features than other carbonaceous materials making them appropriate for various applications in biomedical, electrochemical, sensing and opto-electrical fields. CNTs in the field of sensing were more prominent due to their properties like large surface area, sensitivity and fast response time. CNTs are used as electrochemical transducers as well. The unique and ideal electrode features like highly reactive nature, flexible and easily modifiable structures and mechanical stability make

them an efficient electrode material in electrochemical applications. Moreover, studies show that MWCNTs have energy density per mass twice that of SWCNTs [20].

1.6.2. Metal oxides

Metal oxides (MOs) made of transition metal families are very attractive electrode materials used in pseudocapacitors, having the capacity to undergo fast and reversible faradaic redox reactions. They deliver superior capacitance value compared to carbon-based compounds and excellent cycle stability compared to conducting polymers. Consequently, choosing the best faradaic transition metal oxide (TMO) electrode material with multiple oxidation states can enable fast and reversible oxidation and reduction during charging-discharging cycles. RuO_2 is the first TMO used in supercapacitors, which has a theoretical capacitance in the range of 1300-2200 F/g. Unfortunately, the toxic nature and exorbitant cost as a result of rare availability declined considering them as a market-winning electrode material. In the sense of overcoming these dilemmas, the research community has shifted the focus onto another efficient electrode material called MnO_2 because of its low cost and environmentally safe nature. Moreover, MnO_2 carries a theoretical capacitance value of around 1370 F/g, but the practical value is still far below of this. There exist other TMOs like CuO , NiO , Co_3O_4 , Fe_2O_3 etc., which are capable of producing fast and reversible faradaic redox reactions and can be potential supercapacitive electrode materials. Along with transitional metal oxides, chalcogenides, hydroxides, nitrides and their derivative forms are also popular for pseudocapactive behaviour. The structural and morphological properties like dimension, porous nature, and electrode-electrolyte interface chemistry of electrode materials have a strong influence on their electrochemical performances. Ultimately, it is very important to produce an efficient and diligent electrode material for supercapacitor applications.

1.6.2.1. Copper oxide

Among the different TMOs explored for the supercapacitor applications, copper oxide-based electrode material has gained much attention in recent days, due to its exceptional structural, opto-electric and electrochemical properties. Additionally, cost-effectiveness, environmental benignity, ease of synthesis, and ability to produce rapid faradaic redox reactions make them a promising candidate over other popular TMOs.

Generally, copper oxide has three forms; namely the tenorite phase (CuO), cuprite phase (Cu_2O) and a metastable paramelaconite phase (Cu_4O_3) having monoclinic, cubic and tetragonal symmetries, respectively. CuO is a black p-type semiconductor material having plentiful exceptional features like narrow band gap (~ 1.2 eV), high specific surface area, electrochemical activity and chemical stability.

1.6.2.1.1. Structural properties of CuO

CuO has a monoclinic structure with C_{2h}^{62} symmetry and it carries four formula units per one unit cell. Since the coordination number of copper is four, one copper atom is bonded with four neighbour atoms of oxygen in a square planar arrangement along (110) plane (Fig. 1.9). The bond length of Cu-O bonds along (110) plane is $1.88\text{\AA}$ and $1.96\text{\AA}$. In the perpendicular plane, the two Cu-O bonds form an octahedral coordination with much greater bond lengths. In the case of oxygen atoms, it has coordinated with four copper atoms, and shows a distorted tetrahedron. Moreover, oxidation state of oxygen in CuO crystal is Cu^{2+} even though it contains both covalent and ionic bonds [21]. The basic structural parameters of CuO are listed in the table 1.1.

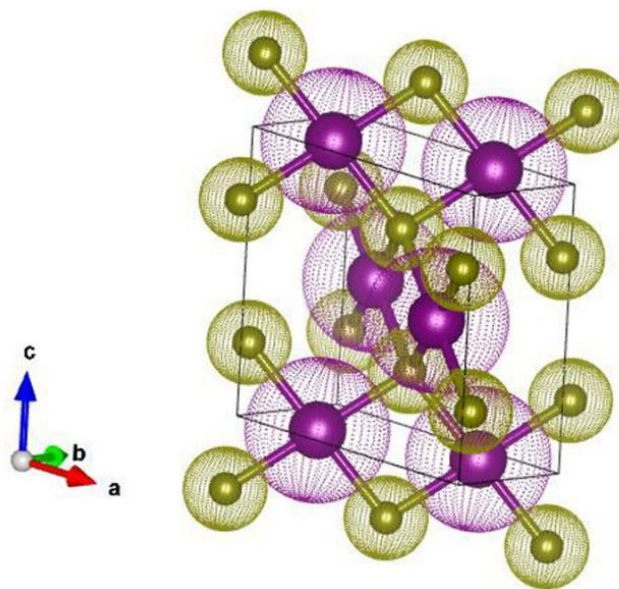


Fig. 1.9. Schematic representation of crystal structure of CuO .

Table 1.1. Basic structural properties of CuO.

Basic Features	Values
Symmetry	Monoclinic
Space group	C_{2h}^6
Lattice parameters	$a=4.683 \text{ \AA}$, $b=3.422 \text{ \AA}$, $c=5.128 \text{ \AA}$, $\alpha=\gamma=90^\circ$, $\beta=99.54^\circ$
Cell volume	$V=81.08 \text{ \AA}^3$
Unit cell content	4 CuO
Molecular weight	79.57
Density	6.515 g/cm^3
Cu-O bond length	$1.96 \text{ \AA}$
O-O bond length	$2.62 \text{ \AA}$
Cu-Cu bond length	$2.90 \text{ \AA}$
Melting point	1201°C

The phonon properties of monoclinic CuO structure were reported in previous literatures, showing the three acoustic and nine optical phonon bands of CuO. The C_{2h}^6 space group of CuO contains two molecules per primitive cell, resulting in Raman active modes as $\Gamma_{\text{RA}} = 4A_u + 5B_u + A_g + 2B_g$. This zone centred Raman active modes are contributed by three Raman active modes ($A_g + 2B_g$), six infrared active modes ($3A_u + 3B_u$) and three acoustic modes ($A_u + 2B_u$) [22].

1.6.2.1.2. Energy band structure of CuO

CuO is a p-type semiconducting material with a narrow indirect band gap. This electronic energy band gap denotes to the energy difference between the valence band maximum and conduction band minimum, both derived from the Cu 3d orbitals. There is an enormous number of theoretical investigations that have been done in order to investigate the electronic band structure of CuO [23], [24]. In spite of the complexities brought out by 3d shell of CuO, there is a conduction band peak at 1.8 eV along with other peaks at 6.8 eV and 10.6 eV, which are aroused due to the fully filled sp orbitals of copper and oxygen [24]. F.P.Koffyberg *et al.* conducted a study on the conduction and valence band edges of CuO and reported that the valence band of CuO resides $\sim 5.42 \text{ eV}$ below the vacuum level contributing to an indirect band gap of 1.35 eV [25].

The theoretical band gap of CuO varies between 0.91 eV-2.74 eV depending upon the method of analysis HSE, OLCAO, LDA+U, SIC LSD, and DFT [26]. The experimental values of indirect band gap ranges between 1.35 eV-1.7 eV for bulk CuO and ranges up to 2.03 eV for CuO thin films. Naveen Kumar *et al.* reported the synthesis of CuO and Cu₂O nanoparticles using sol-gel method and investigated their applicability for solar cell and energy storage devices. They reported a band gap value of 2.18 eV for CuO nanostructures [27]. V. Dhanasekaran *et al.* conducted a study on the optical, electrical and microstructural features of monoclinic CuO nanostructures having ~10 nm size and reported a band gap value of 1.2 eV [28]. The impact of doping on the optical features of CuO was investigated in a few studies and found to have an increase in band gap values. The optical band gap of Ni, Zn and Fe- doped CuO nanostructures was found to be 2.26 eV, 2.12 eV and 2.15 eV [29]. Yunus Akaltun *et al.* studied the influence of film thickness on the optical attributes of CuO and reported a decrease in value of the band gap between 2.03 eV-1.79 eV with the increasing film thickness [30].

1.6.2.1.3. Electrical properties of CuO

The electrical properties of CuO can be described in terms of a few parameters like electron affinity, dielectric constant and carrier mobility. Mark. L. Polak *et al.* investigated the value of electron affinity of CuO using photoelectron spectrum and recorded a value of 1.777 eV [31]. The value of static dielectric constant for CuO thin film has been reported in the range of 12.26 – 13. It is found that this value of dielectric constant varies with film thickness [30]. The carrier mobility of CuO found to be very low with heavy hole effective mass, similar to NiO. Koffyberg *et al.* reported a hole mobility of 0.1 cm²/Vs and introduced the hopping method of conduction in CuO [25].

1.6.2.1.4. Electrochemical properties of CuO

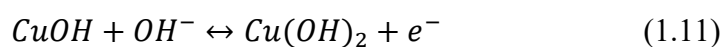
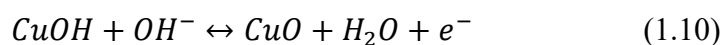
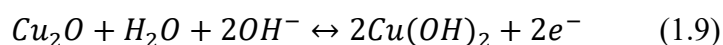
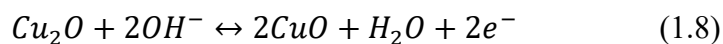
The search for an affordable and environmentally viable electrode material has made the CuO-based supercapacitor area, a frontier of research among the other TMOs. CuO shows rapid and reversible redox activities, which contribute to satisfactory specific capacitance values. The advantage of having various synthesis approaches available to prepare CuO in different morphologies such as nanorods, nanotubes, nanoflowers, nanoflakes, etc., which can improve its capacitance by enriching the

electro-active sites and electron transfer through enhanced surface area. CuO is capable of producing high pseudocapacitive behaviour along with very low internal resistance.

Moreover, some of the unique properties of CuO in electrochemical applications are sorted below;

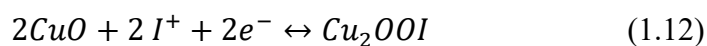
- Tunable electronic configuration of CuO with availability and reversibility of oxidation states.
- Easy to produce different morphologies and different dimensions, which are one of the deciding factors of charge storage mechanism in CuO.
- High thermal and chemical stability make less structural deteriorations in CuO electrodes during repeated charging-discharging process.
- Generally, all TMOs specifically CuO are chemically more stable than many of the popular carbonaceous electrode compounds and is easily associated with other TMOs or polymers or carbon-based compounds to produce more efficient nanocomposite electrode material with enhanced synergistic effects.

The redox activities of CuO in alkaline electrolytes like NaOH/KOH can be as follows [32];

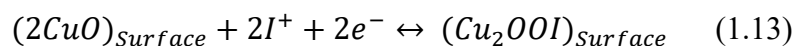


In neutral aqueous electrolytes like Na₂SO₄, there may be two possible charge storage mechanisms occurring in the system [33]:

(1) Intercalation and de-intercalation of cations H⁺ or Na⁺ during redox reactions,



(2) Adsorption of ions into the surface of active material.



Where I can be either H^+ or Na^+ ions.

There are numerous works conducted on the supercapacitive performance of CuO, but capacitance achieved is still only <32% of its theoretical value. Regardless of these fundamental electrochemical properties, CuO suffers very low electronic and ionic conductivity, structural collapse during charge-discharge cycles, minimal energy density and poor cyclic performances. These limitations can be overcome by associating CuO with other guaranteed TMO electrode materials like NiO, Co_3O_4 , $ZnMn_2O_4$, etc., as well as conducting polymers like PANI or carbonaceous compounds like CNTs.

1.6.2.2. Nickel oxide

Ni-based materials, especially NiO, found to have better opportunities in the electrochemical area owing to their specialities like metallic conductivity, ease of synthesis, and high electrochemical activity. In NiO crystal, the elementary distributions of nickel and oxygen atoms are in a stoichiometric ratio of 1:1. The cubic NiO symmetry is formed by the face centred cubic orientation of Ni^{2+} ions with O^{2-} ion in the interstitial sites. The ionic bond between nickel and oxygen through the electrostatic force resulted from the losing and gaining of two electrons by nickel and oxygen, respectively. Basically, NiO is an antiferromagnetic substance and its properties are tuned according to the nickel and oxygen vacancies in the crystal structure. This simple semiconductor material have applicability in areas other than energy storage like sensors, catalysis, batteries and electrochromic devices [34].

NiO is an efficient pseudocapacitor electrode material with a theoretical capacitance of 2573 F/g. The fast and reversible redox activities of NiO led the research community to explore more on the supercapacitor applications of NiO. Depending upon the synthesis method and reaction parameters, different kinds of nanostructures of NiO can be achieved [35], [36], [37], [38]. These nanostructures enhance the surface area and redox active sites of NiO, eventually enhancing the ionic diffusion rate and capacitance. The controlled synthesis of NiO nanostructures with the desirable electrode properties can make it a promising electrode material. However, the low ionic conductivity and declining cycle stability made the pristine NiO based electrode

emerging and less-productive. These shortcomings set the stage for composite electrode materials with the aim to produce high-performance pseudocapacitors.

1.6.2.3. Cobalt oxide

Cobalt oxide (Co_3O_4) is a p-type semiconducting TMO with a direct band gap in the range of 1.48 eV-2.19 eV and a theoretical capacitance of about 890 mAh/g. This low-cost environmental friendly material exhibits other unique properties like high corrosion stability, high surface to volume ratio, and fast and reversible redox features [39]. Co_3O_4 is antiferromagnetic in nature with satisfactory electrical activity. The hollow spinel crystal structure of Co_3O_4 is constituted by the Co^{3+} and Co^{2+} ions located at octahedral 16(d) and tetrahedral 8(a) sites of the lattice, respectively along with the cubic close pack orientation of 32 oxide ions in 32(e) sites. This spinel structure followed by the Co_3O_4 compound having a general compositional formula of AB_2O_4 , in which A represents the +2 charged ions and B represents the +3 charged ions.

Different dimensions and microstructures of Co_3O_4 can be achieved by governing the synthesis strategies. Depending upon the unique morphology attained by the Co_3O_4 nanostructures, the efficacy in electrochemical features can be determined. The redox activities of Co^{2+} and Co^{3+} ions are instrumental in the electrochemical performance of cobalt oxide electrodes. Additionally, the low charge transfer resistance and satisfactory cycle stability make the Co_3O_4 compound a guaranteed electrode material [40]. Apart from the supercapacitor applications, Co_3O_4 is a promising candidate for chemical sensors, photocatalysis, bio-medical field, solar cells and batteries [41], [42], [43].

1.6.2.4. Zinc manganese oxide

Alike cobalt oxide, zinc manganese oxide (ZnMn_2O_4) also has normal spinel symmetry, exhibited in the $\text{I4}_1/\text{amd}$ space group. This mixed metal oxide compound carries a narrow band gap of 1.86 eV. The spinel structure of ZnMn_2O_4 is constituted by the Zn^{2+} and Mn^{3+} ions occupying in the tetragonal and octahedral sites, respectively. The elemental composition of this TMO can be represented by the general formula $(\text{Zn}_{1-x}\text{Mn}_x)(\text{Zn}_x\text{Mn}_{2-x})\text{O}_4$, where x is a parameter that determines the degree of inversion of the compound depending upon the particle size distribution, morphology and

synthesis route and ranges from 0 to 1. In normal spinel structure, Zn orients in the A sites and Mn orients in the B sites of the general spinel AB_2O_4 formula, whereas in the inverse spinel structures, half of the Mn locates in A site and all Zn locates in the B sites. In this $ZnMn_2O_4$ compound, zinc exhibits in single oxidation state, Zn^{2+} and the manganese exhibits in multiple oxidations states like Mn^{2+} and Mn^{3+} . The oxygen element in the compound induces two kinds of vacancies like tetragonal oxygen vacancy with (ZnO_4) unit and octahedral oxygen vacancies with (MnO_6) units [44]. This abundant availability of multivalent cations and anions with oxygen vacancies in the crystal, surpluses its redox activities that eventually enrich the electrochemical features of the ternary metal oxide. Thus, recent research developments focused more on the investigations of $ZnMn_2O_4$ as an efficient electrode material, especially in supercapacitors [45], [46]. This cost effective and environmental friendly ternary metal oxide compound has found potential applications in the other areas like Li-ion batteries, catalysis, gas sensors and biosensors [47], [48], [49], [50].

There is an enormous number of synthesis approaches, namely sol-gel route, hydrothermal method, spin coating, micro-emulsion method, etc., available for the preparation of $ZnMn_2O_4$ in various nanostructures [47], [49], [51]. Depending upon the morphological variations of this ternary metal oxide such as changes in pore size, pore volume and surface area, the electrochemical performance of the electrode material also undergoes fluctuations. The $ZnMn_2O_4$ compound with porous morphology can exhibit superior specific capacitance and rate capacity better than binary metal oxides [52]. The porous architecture not only enhances the surface area of electrode surface but also helps to overcome the mechanical stress arises during the multiple charge/discharge cycles. The spinel crystal structure of $ZnMn_2O_4$ provides a strong and efficient mechanical durability that protect the $ZnMn_2O_4$ -based electrode material from voluminous expansion or structural deteriorations during rapid and repeated charge-discharge cycles. Moreover, the synergistic redox contributions from Zn and Mn and the improved electrical conductivity of this ternary metal oxide compared with other Mn-based metal oxides increase the charge storage capacity of the electrode material. These commendable attributes make $ZnMn_2O_4$ a superbly multifaceted electrode element with high capacitance and cyclic performance over energy storage devices [44].

1.6.3. Conducting polymers

Until the middle of the 20th century, organic polymers were considered to be only insulating and anti-corrosive materials and were inclusively used in the application areas of plastics and insulators. Conducting polymers (CPs), the well-known Nobel prize-winning materials, came to the light of research after the discovery of polyacetylene in the year 1958. The outstanding works of Alan G. McDiarmid, Hideki Shirakawa, and Alan J. Heeger in polyacetylene material doped with iodine led to a breakthrough in the field of CPs and won the Nobel prize in Chemistry for the year 2000 [53]. CPs possess superior properties like low specific density, cost effectiveness, ease of processing, tuneable electrical conductivity, anti-resistivity and excellent electrochemical properties, making them an inevitable candidate in the field of electrochemistry [54], [55]. Due to these exceptional features, researchers found many possible areas of applications for CPs in LEDs [56], electromagnetic shielding [57], sensors [58], transistors [59], supercapacitors [60], electrochromic gadgets [61] and corrosion resistance [62]. Polyacetylene (PA), Polyaniline (PANI), Polypyrroles (PPy), Polythiophenes (PTh), Polyindole (PIn), and Polyphenylene Vinylenes (PPV) are examples of conducting polymers. Among these, PA is the earliest conducting polymer with the highest electrical conductivity and simple molecular structure, but suffers from limitations like insoluble nature, infusibility and low environmental stability [63].

The electrical conductivity of CPs is basically derived from their electronic structure which led to the concept of intrinsically conducting polymers (ICPs) in which a conjugated structure exists along with polymer backbone. This π -conjugated chain is formed due to the overlapping and delocalization of unpaired electrons of carbon, which is the core foundation for the electrochemical redox properties of CPs. This impressive and unparalleled trait of CPs made them a guaranteed member in the supercapacitor applications.

The intrinsic electrical conductivity of CPs was found to rely on the factors like;

- Amount of charge carriers

- Enhancement in carrier mobility due to overlapping of orbits
- Charge hopping among polymeric chains
- Degree of π conjugation

The conductivity range of conducting polymers can be schematically represented as in Fig. 1.10.

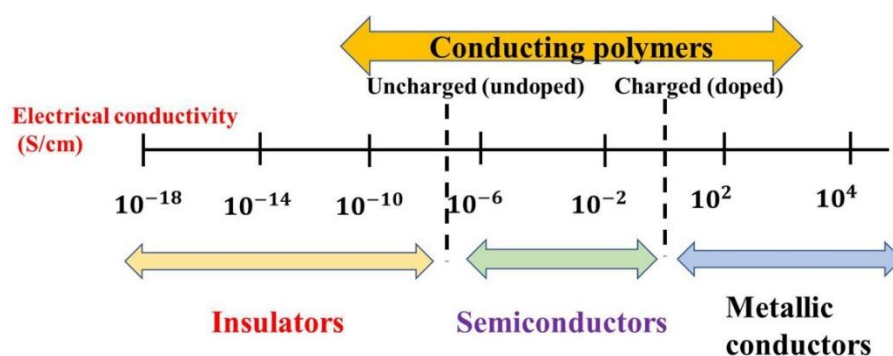


Fig. 1.10. Electrical conductivity chart for insulators, semiconductors, conductors and conducting polymers.

The intrinsic and extrinsic physical-chemical properties of CPs are mostly derived in the synthesis stage itself, making a clear dependence on various synthesis parameters like the nature of dopant, doping percentage, synthesis time and temperature, monomer concentration, and solution pH. Due to the fact of having the limitation of poor mechanical strength of CPs, research was focused on the key strategies to improve their mechanical stability of them. Some of the important strategies employed for this purpose were in-situ synthesis assisted with thermoplastic materials [64], producing composite/ hybrid compounds [65], metallic nanoparticle incorporation into polymeric chains [66], and use of polymeric/hydrogel type template in the synthesis stage [67].

1.6.3.1. Polyaniline

Polyaniline (PANI) is one of the oldest synthetic polymer materials, well recognised since the 19th century. The oxidation of aniline resulted in the production of “aniline black”, popularly used in textiles as a dye from the year 1835. From 20th century, the scientific community made efforts to explore the molecular structure and intermediate forms of aniline black. Moreover, Green and Woodhead found the four forms of PANI: protoemeraldine, emeraldine, pernigraniline, and nigraniline, through

their enormous efforts during the years 1910-1912 [68], [69]. The breakthrough in the history of PANI started after MacDiarmid synthesised green colour PANI in 1985, through chemical oxidation of aniline monomer with ammonium persulphate as oxidant in aqueous HCl medium. This green PANI powder showed an electrical conductivity in the range of 10 S/cm. After this game changer innovation, PANI acquired a special position in the field of CPs because of its properties like simple synthesis routes, cost effectiveness, environmental benignity, unique protonation mechanisms and ease of tuning physical characteristics through managing oxidation and protonation stages.

PANI has a very complex molecular structure consisting of an alternative arrangement of both benzene rings and nitrogen atoms. PANI is commonly a phenyl-based polymer with flexible –NH groups attached on both ends of phenyl rings in the polymer chain. These chemically active –NH groups are responsible for the oxidation and protonation phases of PANI and are the deciding factor of many physical and chemical properties as well. The nitrogen atoms in the polymer chain can exist in two different forms; one is sp^2 hybridised imine state and other is sp^3 hybridised amine state. Depending upon the level of oxidation, PANI has two forms; a fully reduced form and a fully oxidised form, as shown in figure 1.11.

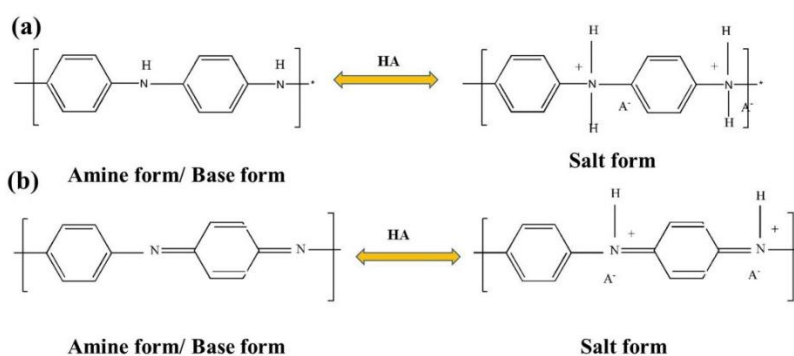


Fig. 1.11. (a) The fully reduced form and (b) fully oxidised form of PANI.

In the fully reduced form of PANI, the polymer chain consists of benzenoid rings and amine group of nitrogen, whereas, in the fully oxidised form of PANI polymer chain is composed of both benzenoid and quinoid rings along with imine state of nitrogen. Nitrogen atom can be existed as protonated or non-protonated states depending on the solution pH. The non-protonated amine state is termed as the base form of PANI. The fully reduced state, referred to as leucoemeraldine (light yellow), is a non-conducting state of PANI composed of a benzenoid ring with hydrogen bonded

nitrogen atoms seen in the base form. The fully oxidised pernigraniline (violet) is another non-conducting form of PANI with quinoid rings, and no hydrogen atoms are present in the base form. The intermediate state between these two forms is called emeraldine (green), which is a conducting state of PANI with both benzenoid and quinoid rings (Fig. 1.12). The ratio between the parameters m and n decides the redox states of PANI, which is 1:0 for leucoemeraldine, 0:1 for pernigraniline and 1:1 for emeraldine forms. Thus, it is important to regulate the proportion between benzenoid and quinoid rings as emeraldine state to achieve the electrochemically active PANI state.

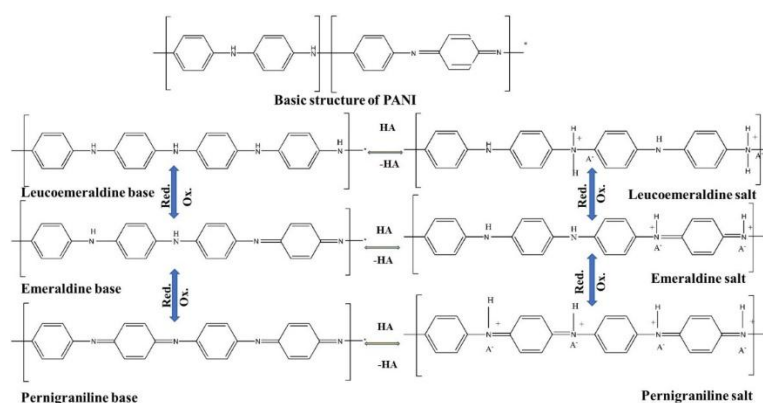
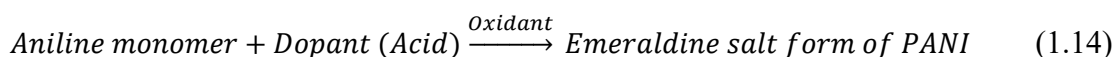


Fig. 1.12. Different states of PANI and their conversion process.

The PANI synthesis can be done using any of the two major synthesis strategies under acidic conditions, chemical synthesis and electrochemical synthesis. The chemical synthesis involves the direct oxidation of aniline monomer in the presence of chemical oxidants. The electrochemical synthesis doesn't use any oxidants, but involves the generation of active species on the surface of the electrode under an applied voltage that causes electron transfer between the substrate and electrode.

1.6.3.1.1. Chemical synthesis of PANI

The chemical synthesis of PANI in its emeraldine salt form involves dissolving of the aniline monomer in any of the aqueous acidic medium like HCl, H₂SO₄, HBr etc. and allowing it to undergo chemical polymerisation when an oxidant solution is added to the parent mixture. The green colour insoluble PANI residue obtained has to be filtered and washed before the drying procedure. Thus, the polymerisation and doping processes have occurred in the same acidic medium, simultaneously. The synthesis strategy can be summarised as follows;



This chemical oxidation method of PANI synthesis is influenced by various synthesis parameters like;

- Concentration of oxidant
- Nature and pH of medium
- Reaction time
- Reaction temperature
- Monomer to oxidant proportion

Although, chemical synthesis is the most suitable synthesis procedure of PANI in large scale applications, many other synthesis approaches like interfacial polymerisation [70], microemulsion polymerisation [71], enzymatic synthesis [72] and solid state synthesis [73] are also discussed in the studies.

1.6.3.1.2. Conducting mechanism in PANI

The electrical conductivity of conducting polymers is primarily arises from the transportation of quasi particles like solitons, polarons and bipolarons, which are created under protonation. Solitons are the charge carriers in degenerate CPs, whereas in non-degenerate CPs, the charge transportation is facilitated by polarons and bipolarons. The solitons are formed when one of the carbon atoms fails to delocalise its electron with adjacent atoms, resulting in the formation of a new π bond in the polymer chain and the radical moves through the chains. Polarons are quasi particles having charge $\pm e$ formed when a conducting polymer is doped with an electron acceptor. This doping cause some of the carbon atoms to get a positive charge (polaron) and it tries to couple with the unpaired electron in the soliton. The distance between the hole and the coupled electron varies as the concentration of dopants changes. As the concentration increases above a certain limit, two polarons are created and coupled to form a bipolaron having a charge of $\pm 2e$. In polarons, the energy gap between the highest occupied molecular orbit (HOMO) of valence band and the lowest unoccupied molecular orbit (LUMO) of the conduction band decreases. Whereas, in the case of bipolarons, this band gap between HOMO and LUMO orbitals gets reduced further due to the combined energy of two polarons, resulting in the enhancement of electrical conductivity to the next level [74].

Out of three different oxidation states of PANI, the emeraldine base (EB) form is the only conducting state of PANI. Protonation of imine nitrogen in the polymer chain is the way to make EB form to conduct when transformed in to emeraldine salt (ES) state. The proton doping indicates doping of base PANI with the help of any protonic acids like HCl, H₂SO₄, HBr, H₃PO₄, etc., to synthesis protonated PANI, is generally called as PANI salt form or emeraldine salt form. The unpaired or unreacted counter ion (negative ion) of the protonic acid medium occurs in the vicinity of polymer chain for establishing the electrical neutrality. The polarity and nature of counter ion, electrical conductivity can be tuned by reducing the band gap. Moreover, the lone pair, polarons or bipolarons play a significant role in the electrical conductivity of PANI, which can enhance the conductivity of PANI up to the range of 10¹⁰ S/cm [75].

The electrical conductivity of PANI depends on the following factors [76], [77];

- The length of polymeric chain and its crystallinity
- Nature of dopant and degree of doping
- Temperature
- Synthesis conditions like monomer concentration, monomer to oxidant ratio, reaction time and temperature
- Presence of substitution elements in the polymer chains

Alike other CPs, PANI is one of the potential electrode materials for pseudocapacitors having high theoretical capacitance of 3407 F/g, good electroactivity, and high electrical conductivity. The major drawback of PANI is its low cycle life due to the fact that the repeated charging-discharging causes unnecessary contraction and expansion of polymer chains. The electrochemical efficacy of PANI is mainly focused on the morphology and oxidation states of PANI, which depend on the grade of doping level as well as the size of the dopant [78]. Compared to carbonaceous compounds, PANI-based supercapacitors can deliver more energy but have poor charge density. Furthermore, during the charging of electrode material, polymers get attracted to the negative ions of the electrolyte and undergo oxidation, while during discharging polymers get reduced. Even though doping of PANI can improve the mechanical stability of the compound, the large scale of doping can result in volume changes and lead to a mechanical breakdown of electrode materials [75]. Thus, a major drawback of PANI-based supercapacitors is their poor mechanical stability and shorter life span.

This can be minimized by the strategy of making a hybrid/ composite material combining PANI with any of the carbonaceous compounds or inorganic oxides or hydroxides.

1.6.4. Composite electrodes

Although TMOs are good electrode material for the better improvement in energy density and power density in the supercapacitor field, since they can deliver high specific capacitance values compared to carbonaceous compounds, they still face a major drawback of inefficiency in carrying the capacitance over elevated sweep rates. In practical applications, bare metal oxides hinder their potentialities due to poor electrical conductivity except for RuO_2 , which resulted in increased series and charge transfer resistances of the electrode and thus ended up with a large IR drop, especially at higher current densities. Moreover, metal oxides usually face issues like mechanical strain during repeated charge discharge cycles, leading to crack formation in the electrode surface which will adversely affect the long-term stability of the supercapacitor [79]. Thus, in the sense to mitigating these flaws it is obvious to think about a versatile composite electrode material that combines metal oxides with carbonaceous compounds, which can sort out the limitations faced by both the individual components. These composite electrodes are developed with an aim to provide an efficient electrode stuff with high energy and power densities, cyclic stability and rate capacity. In such metal oxide-carbon composite framework, carbon-based material provides a basic physical support as well as a conductive pathway for the metal oxide part. The major charge and energy storage contributions carried by the metal oxide component through its multiple electro-active sites can be supported by the high electrical conductivity, power density and rate capacity of the carbon part. The synergistic effects produced by the composite electrode material can also result in declined material production cost.

Apart from metal oxide-carbon combination in composite electrodes, there is also another area combining metal oxides with conducting polymers as well. CPs are also one of the highly preferred electrode materials in the supercapacitor field, since they deliver high electrical conductivity, are cheap and easy to produce and have high electro-activity. Among various CPs, PANI is one of the most studied pseudocapacitor electrode materials with a high theoretical capacitance. However, the substandard

mechanical stability of PANI led to its marginal structural degradations during repeated charge/discharge cycle tests, eventually ended up in attenuated capacitance retention. Thus, these structural shortcomings of PANI can adversely affect the long-term stability of the metal oxide-PANI composite also. To straighten out these stability shortcomings, it is very much logical to associate this metal oxide-CP composite material with any of the structurally robust material like carbon-based compounds.

1.6.4.1. Transition metal oxide composites

TMOs like RuO_2 , MnO_2 , NiO , CuO , Co_3O_4 , TiO_2 , etc., are the most potential pseudocapacitive electrode materials that carry efficient electrochemical activity with a high theoretical capacitance. Although TMOs deliver high electrochemical performance, their intrinsically poor ionic conductivity results in reduced specific capacitance and rate capacity in real time applications. Thus, combining two or more metal oxides with multiple oxidation states can be used as one of the beneficial strategies to proffer the inherent limitations of a single metal oxide electrode system and can deliberately improve the specific capacitance as well as energy densities. Taking RuO_2 electrode as an example, it can be seen that designing an electrode material combining RuO_2 with other transitional metal oxides like TiO_2 , SnO_2 , CaO , MoO_3 and VO_x can produce a marginal improvement in the surface area of the electrode surface and can positively influence its electrochemical performances [80] [81]. W.Sugimoto *et al.* conducted a study on the charge storage capacities of a rutile type RuO_2 - VO_2 composite solution prepared via polymerizable-complex method for electrochemical applications and found an exceptional improvement in the electrochemical performance in the composite material compared with pure RuO_2 and attained a specific capacitance value more than 1200 F/g [82]. The conductivity issues prevailed within the NiO electrode matrix were compromised with the addition of the promising RuO_2 in order to fabricate composite electrode surface and ended up with an improved surface area, pseudocapacitive behaviour and wider operational voltage window also [83]. En-Hui Liu *et al.* aimed to decrease the large series resistance values of MnO_2 electrodes that limit their electrochemical performance by producing a NiO/MnO_2 composite electrode material with a high surface area of about 130-190 m^2/g and attained a specific capacitance of about 453 F/g at a scan rate of 10 mV/s [84]. In order to utilise the synergistic effects of two pseudocapacitive TMOs, Mohamed Racik K *et al.* prepared manganese oxide decorated CuO composite electrode materials for

supercapacitor applications and found an enhancement in the specific capacitance values for the composite electrode compared to pure CuO and MnO₂ electrodes [85]. CuO-based electrode materials find an improvement in pseudocapacitive behaviour with other TMOs and achieved a greater attention among the researchers in recent years [86], [87], [88]. There are also reports on the production of ternary metal oxide combinations such as ZnO-NiO-CuO, Co₃O₄-CuO-NiO, CuO/Ag/Co₃O₄ mixed oxide electrodes as an efficient candidate for supercapacitor applications [89], [90], [91]. A hierarchical combination of mixed metal oxides has been expected to deliver better pseudocapacitive performance using improvised porosity and surface features that are created through their synergistic interactions among individual metal oxide components.

1.6.4.2. Polymer composites

Enormous progress in the area of pseudocapacitors has been made in the last decade with the advent of the possibility of making metal oxide-conducting polymer composite electrode with the aim of flourishing the pseudocapacitor area with low cost and highly efficient electrode materials. Metal oxides and conducting polymers were the most exploited electrode materials in the area of pseudocapacitors. But both suffer numerous shortcomings when performed individually such as lower electronic and ionic conductivities for metal oxides as well as structural instabilities for conducting polymers that results in declined specific capacitance and rate capacities in their individual performances. Thus, a successful combination of these metal oxides with conducting polymers can be make a fruitful electrode surface in pseudocapacitor area. Ran Lui *et al.* tried to prepare RuO₂/(3,4-ethylenedioxythiophene) (PEDOT) nanotubes via electropolymerisation and found an improved specific capacitance and rate capacity of the electrode material. They proved that the PEDOT nanotubes served as a template for the growth of RuO₂ nanostructures and provided a better porous surface for the electrochemical performance of the composite material [92]. The support of high electroconductive materials like CPs helps to improve the poorer ionic conductivity suffered by the metal oxides like MnO₂ by creating an electro-active atmosphere for the better electrochemical performance of the metal oxides with various oxidation states [93], [94]. CuO with conducting polymer composite materials is also one of the hot research areas among the scientific world since the effective utilisation of pseudocapacitive behaviour of CuO can be enhanced with the conducting mechanism

offered by the CPs. Murat Ates *et al.* electrochemically synthesised three different combinations of CP-CuO composite electrodes involving three different CPs such as PANI, PEDOT and PPy. The PANI/CuO composite electrode attained the highest capacitance value of about 286.35 F/g at a scan rate of 20 mV/s compared with PEDOT/CuO and PPy/CuO composites [95]. Some research findings on CuO and PANI combination suggests that the polymerisation of aniline along with the dispersed CuO nanostructures can twice the storage capacity and rate capacity of the composite electrodes [96]. Other than the energy storage area, the CuO/PANI composite material is used in other applications such as electromagnetic interference shielding, sensors, solar cells and water treatments [97], [98], [99], [100]. Sayed Mohammed Adman *et al.* synthesised a symmetric supercapacitor device using PANI decorated NiO-CuO composite as an electrode material and achieved a specific capacitance of about 157.50 F/g with 65% capacitance retention over 10000 charge/discharge cycles. They found the highest energy density of about 35 Wh/Kg and power density of about 1326.31 W/Kg [101]. Thus, the often conductivity challenges prevailed in metal oxide electrode species are somewhat minimised by making fruitful stoichiometric combinations with highly conductive substances like CPs.

1.6.4.3. Metal oxide-conducting polymer-carbon based composite electrodes

In the last decade, researchers are found to have gained greater interest in the ternary or quaternary composite electrode materials involving any of the carbon-based EDLC material, metal oxides and CPs. The low-cost, abundant nature of metal oxides offering multiple oxidation states with high theoretical capacitance in the supercapacitor area are but backstepped in the supercapacitor field due to their often-insufficient conductivity challenges. These issues are found to have improvised with the help of a conductive pathway offered by any of the CPs that can also serve as a pseudocapacitive supplementer. However, the inherent mechanical and structural instabilities faced by the CPs like PANI make them an unstable electrode surface during repeated charge/discharge cycles. Thus, the metal oxide-CP composite electrode surfaces should be supported by a material having high structural integrity and electrochemical capacity. Thus, the introduction of any of the carbonaceous compounds like graphene oxide (GO), reduced GO (r-GO), CNTs, and carbon aerogels with high structural stability along with sufficient specific surface area and porosity into the metal

oxide-CP matrix can effectively improve the performance of ternary/quaternary composite electrodes. There are enormous efforts that have been put forward by the scientists in recent years in the sense of exploiting different kinds of metal oxide, CPs and carbon compounds. Murat Ates *et al.* compared the supercapacitive performance of rGO/RuO₂, rGO/PANI, PANI/RuO₂ and rGO/RuO₂/PANI nanocomposites synthesised using the in situ polymerisation method and reported the highest value of specific capacitance of about 723.09 F/g at 2 mV/s for the ternary rGO/RuO₂/PANI nanocomposite than other binary composites [102]. A similar kind of study was conducted by Murat Ates *et al.* replacing PANI with another conducting polymer polyvinylcarbazole (PVK) and achieved a maximum capacitance value of about 2698 F/g at a scan rate of 2 mV/s [103]. The role and importance of conducting polymer on the same matrix produced using the same synthesis method can be differentiated from these studies. A robust supercapacitor device fabricated using a ternary nanocomposite electrode involving 70% of MnO₂ nanorods, PANI and GO, and achieved a capacitance of about 512 F/g at a current density of 0.25 A/g with 97% capacitive retention over 5100 cycles. The improved performance of ternary composite electrode can be the result of the conductive framework provided by the PANI and enhanced electroactive surface sites offered by the GO, eventually resulting in the enhanced energy and charge storage rates [104]. Yingying Huang *et al.* studied the electrochemical performance of MnO₂/PANI/MWCNT nanocomposite and reported a specific capacitance of about 395 F/g at the current density of 1 A/g [105]. The hierarchical NiO/PANI/MWCNT core-shell composite delivered good electrochemical performances compared to its individual contributions [106], [107]. The MWCNT incorporated wool-ball-like CuO@NiO hybrid ternary composite electrodes were synthesised via a solvothermal route with a high surface area of about 262 m²/g and delivered a capacitance of about 786 F/g at a current density of 2 A/g [108]. The quaternary nanocomposite electrode CuO@NiO/PANI/MWCNT exhibited high supercapacitive performance and reported a specific capacitance of about 1372 F/g with 83% capacitance retention over 1500 cycles [109]. The enhanced electrochemical performance of ternary/quaternary nanocomposite electrodes involving different metal oxides, CPs and carbon compounds can be attributed to their well utilised synergistic interactions along with the structural and morphological improvisations brought in the composite matrix by the individual components that lead to a marginal reduction in the charge transfer resistance of the electrode material through the improved electrochemical reactions.

1.7. NANOCOMPOSITES

Nanocomposites are materials constituted with multiple phases in which any one, two or three dimensions lie in the nanometer regime. When size of the material is reduced to the nanometer range, there is a possibility to create phase interfaces which have a direct influence on the material properties. Nanocomposites have many advantages like high surface area, improved optical properties and enhanced mechanical features compared to other classes of composite materials. These materials can be prepared using metallic, non-metallic or polymeric materials using various synthesis methods. The nanocomposite is a broadened area comprising one dimensional, two-dimensional, three-dimensional and amorphous materials in which dissimilar components distinctively mixed together in the nanometer range. The major three classifications of the nanocomposite materials are listed in Fig. 1.13. Metal oxide nanocomposites (MONCs) are one of the important classes of nanocomposites that come under all these three major categories and come with exceptional structural, morphological, optical and electrical characteristics. The exceptional features offered by the nanocomposite materials are not only the result of properties of its individual components but also its morphological as well as interfacial attributes. These unique characteristics exhibited by the nanocomposites make them a viable candidate in many applications like sensors, supercapacitors, photovoltaics, non-linear optics catalyst, and battery cathode materials [110].

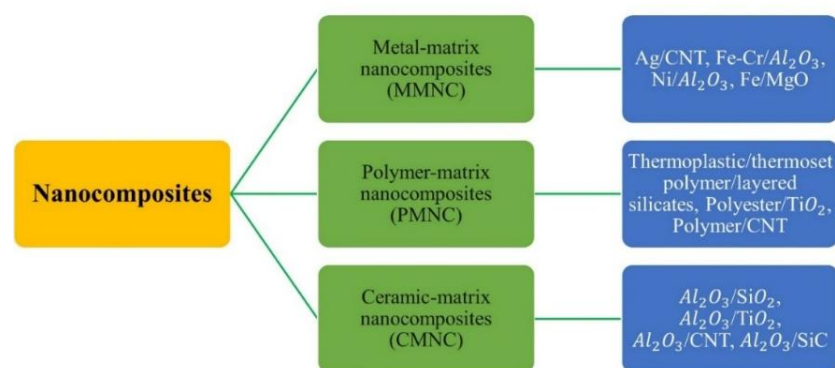


Fig. 1.13. Classification of nanocomposites with their examples.

1.7.1. Synthesis strategies for nanocomposites

The size and dimensions of nanocomposites have a critical role in their structural, morphological, optical, electrical and magnetic properties. Thus, the

strategies employed for the synthesis of nanocomposites must be chosen appropriately since they have a direct influence on their basic characteristics. One of the types of classification in the synthesis methods is mainly in three sections, namely solution-based synthesis, vapor phase synthesis and gas phase synthesis. Another popular categorisation of synthesis methods is the top-down approach and bottom-up approach, as listed in the Fig.1.14. Chemical and physical methods of synthesis come under these two major classifications. Physical methods usually produce a bulk number of products, but the uniformity in the size and dimensions of the end product is not guaranteed. There are numerous kinds of chemical/wet methods used for the synthesis of nanocomposites, among them three of the simple, cost effective and efficient methods that are commonly used are the co-precipitation method, the sol-gel method and the hydrothermal method.

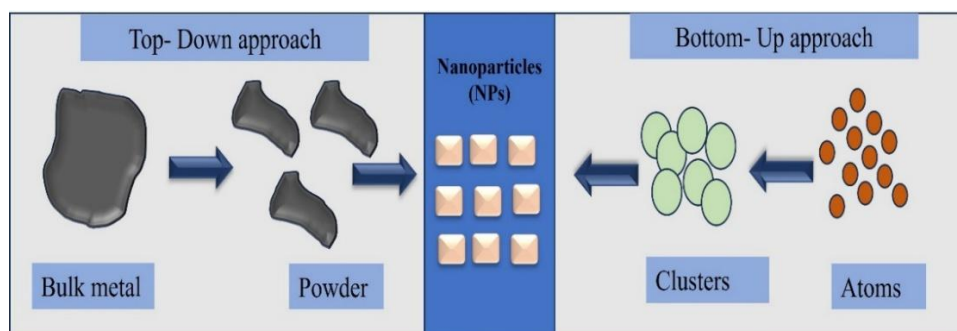


Fig. 1.14. Two different approaches of nanocomposite synthesis methods.

1.7.1.1. Co-precipitation method

Co-precipitation is a simple and effective synthesis approach used for the production of metal oxide nanostructures, metal oxide-metal oxide and metal oxide-ceramic nanocomposites. In this method, usually an insoluble precipitate product is created within the basic solution. Inorganic salts are used as precursor material and they are allowed to dissolve in any of the solvents, like water, to obtain a homogeneous solution of intended precursor. The end product from the precursor solution is produced after a critical concentration of reactants are reached followed by nucleation and growth phases, and will usually be in a hydroxide/oxalate form. This hydroxide/oxalate precipitate is then filtered and washed thoroughly before getting decomposed in to the metal oxide state under high thermal conditions. The reaction conditions like pH of the solution, temperature and molar ratios of precursors etc. has a greater influence on the

size, dimensions and uniformity of the precipitate product. The precipitation agents commonly used in these synthesis methods are NaOH, KOH, Na₂CO₃, NH₃, etc., and are the deciding factor of solution pH [111]. The uniformity of the precipitate production without any sort of agglomerations or structural defects can be assured with the help of external agents like surfactants in the synthesis procedures. This simple synthesis method carries other advantages, like economical, flexibility, acute control over the size and shape of final product and mass output.

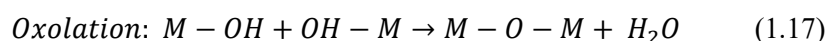
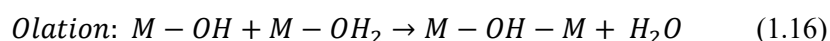
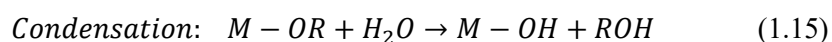
The usual steps involved in a simple co-precipitation approach of nanocomposite/nanoparticle synthesis are mentioned below;

- I. **Preparation of precursor solution** by dissolving the metal salts in water or any other solvents.
- II. **Mixing** the constituents thoroughly using constant stirring until a homogeneous solution is obtained.
- III. **Addition of precipitation agent** to the precursor solution for the initiation of precipitation process.
- IV. **Aging and stirring** constantly to assure the uniform and complete particle growth to occur.
- V. **Filtering and washing** the end product for the complete removal of impurities and unreacted salts using water and ethanol.
- VI. **Drying and annealing** the precipitate in high thermal conditions to improve the crystallinity and purity of the final product.

1.7.1.2. Sol-gel method

Sol-gel method is one of the simplest and efficient bottom-up approaches commonly used for the synthesis of metal oxides, metal oxide nanocomposites, ceramic powders and inorganic/organic hybrid matrices. The approach works on the principle of conversion of the solution or sol phase of a precursor into the gel phase of the intended product with high purity and uniformity. Sol-gel process is composed of two important stages: hydrolysis and condensation [111]. In the hydrolysis stage, the water or alcohol solvents initiate the breaking of alkoxy group -OR from the metal oxide precursors and get replaced by the hydroxyl groups OH. The solution pH, reaction temperature, concentration of precursors, nature of solvent and alkyl groups are some

of the deciding factors of hydrolysis process. In the condensation or polycondensation stage, M-OH bonds formed during the hydrolysis process is allowed to undergo two reactions called ololation and/or oxolation. As the name indicates, oxolation is the stage in which ‘oxo’ bridges were developed between the metal cations (M-O-M) and ololation is the stage in which ‘ol’ bridge were built in connection with the metal cations (M-OH-M) [112].



The so-called gel formed during the condensation stage is allowed to age naturally for the complete product formation with high structural and phase purity. A drying procedure was set after this basic sol-gel processes for the removal of impurities and excess water or volatile solvents that may be trapped in the porous networks of the product. Depending upon the drying conditions, the obtained gel can be in various forms called xerogels and aerogels. The complete nanoparticle formation is happening during the calcination process.

Some of the advantageous of sol-gel synthesis methods are;

- Ease of synthesis of metal oxide nanoparticles and metal oxide nanocomposites
- Low-cost and high compositional control.
- Ability to achieve intended product at high purity and homogeneity
- Ability to tune the structural and morphological features by optimising factors like solution pH, reaction temperature, concentration of precursors etc.
- Ease of producing thin films of amorphous materials.

1.7.1.3. Hydrothermal method

The hydrothermal method is one of the simplest, efficient and low-cost synthesis methods used for the synthesis of metal oxides, which uses water as the solvent medium. In the historical view, German geologist Karl Emil von Schafhäütl

was the one who tried the first hydrothermal synthesis of microscopic quartz crystals with the help of a pressure cooker [113]. In this method, a high pressure and temperature was set as the synthesis conditions which helps to dissolve and recrystallize the metal ions in the aqueous solvent. The reaction temperature is mostly selected above 100 °C, and the closed atmosphere makes the pressure conditions as desired. This common synthesis method is efficient in making metal oxide composites as well with high purity and crystallinity, without using any toxic elements. Autoclaves are commonly used equipment for conducting this kind of synthesis method and the internal structure of an autoclave is presented in Fig. 1.15. This method of synthesis offers promising advantages like affordability of production in large scales, good control over the material stoichiometry without much agglomerative structures, and extreme purity [114]. Moreover, this synthesis approach is suitable for researchers in tuning the properties of metal oxides, hydroxides, nitrides, etc., or any kind of complex compounds according to the desired applications by governing the material sources and synthesis conditions with or without templates [44].

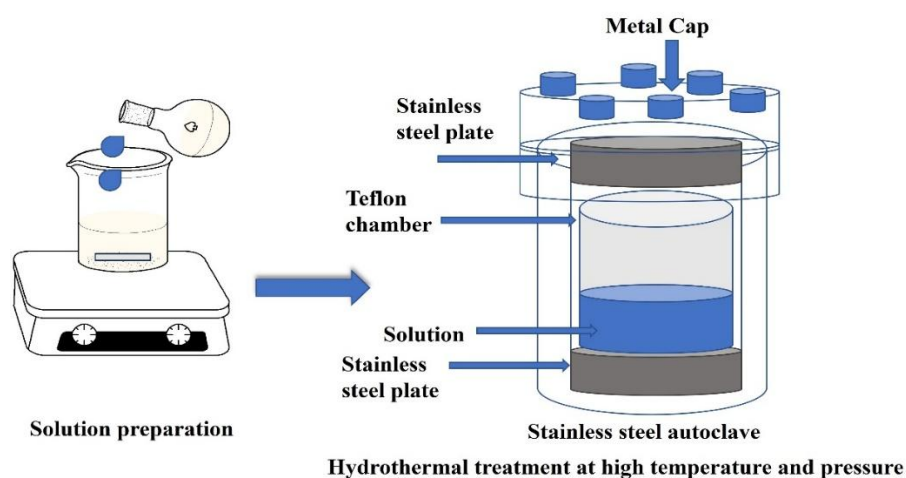


Fig. 1.15. The synthesis procedure of hydrothermal method and the parts of a stainless-steel autoclave.

The material synthesis through the hydrothermal method usually deals with two stages; nucleation and growth. These two stages are mainly controlled by the process called supersaturation; it is the ratio between actual concentration of species to the saturation concentration of species in the solution. The process of nucleation starts when the supersaturation stage is achieved, where the solute particles get precipitated into small cluster units. Following the nucleation stage, the incorporation of growth

units consecutively occurs, and growth stage get initiated [115]. These stages of hydrothermal treatment are illustrated in Fig. 1.16.

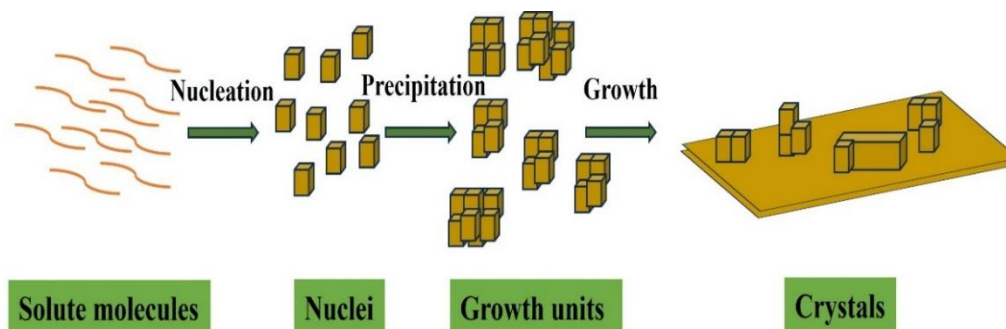


Fig. 1.16. Schematic representation of crystal growth procedure under hydrothermal method.

Hydrothermal method has several other advantages like [114];

- Simple and cost-effective pollution free approach.
- Time and energy saving method.
- Extreme control over shape and stoichiometry of the compound.
- Good nucleation control.
- Highly crystalline end product with desirable physio-chemical properties.

It is one of the common practices in this synthesis method to use any kind of surfactants, capping agents or other supportive additives to the reaction mixture with an aim to tune the size/shape or other characteristics of the final product [116]. Other than these additives, reaction temperature, pressure as well as reaction duration has a direct influence on the particle size/shape or morphology of the products [117].

1.7.1.4. Lyophilization

Lyophilization or freeze-drying is one of the common drying techniques used to remove unwanted/ unreacted organics from the intended final product. This procedure deals with the sublimation of sol-gel product at lower pressure for the complete removal of liquid phases from the sample. At this acute lower pressure stage, the capillary forces appearing in the product will be in their lowest value, so that this drying process can be completed with minimal shrinkage or breaking of the product networks. This method is commonly used for gel species which are unstable at high

temperature drying conditions and ensures the long-term life of the synthesised nanomaterial. During the whole process of drying, the sol gel suspension is kept frozen which causes a uniformity in the process. Mostly, in the liquid-phase drying processes, the particles in the top most layer of suspension are dried first and cause them to behave like an inhibition layer over the other particles existing in the lower parts of the suspension from drying properly [118]. Thus, lyophilization is an optimal drying process which ensures the uniform drying of the whole sample and also aids in increasing the porosity in the surface of the sample that can ensure its increased surface area and mesoporous nature. In addition to that, the synthesis or formation temperature region is a crucial factor for the conductive nature of polymer preparations. That is, CPs like PANI become highly conductive only at the lower temperatures [119]. There are also reports suggesting the formation of improved polyaniline networks with minimal defects at the sub-zero level reaction temperatures [120]. Jundale *et al.* conducted a study on the polyaniline nanofibers that reinforced the CuO nanoparticles to form a nanocomposite film prepared via the in situ polymerisation method at 0°C [121].

1.8. ELECTROCHEMICAL ANALYSIS

The performance of supercapacitors is based on the essential features like specific capacitance, power and energy densities, cyclic performance and life time. To characterise the capacitor performance, it has to be evaluated in two different configurations: the two-electrode configuration and the three-electrode configuration. In the three-electrode configuration, as the name indicates three electrodes are needed for the performance evaluation: one is a working electrode made up of the prepared electrode material, second one is a reference electrode and the last one is a counter or auxiliary electrode. These three electrodes are connected to a potentiostat for analysing the variation of current with different scan rates or the variation of potential of electrode with different current densities. Usually used reference electrodes are silver chloride electrodes or saturated calomel electrode, with the function of controlling the potential of working electrode. The counter electrodes are used to complete the electrical circuit and maintain electrical neutrality. Moreover, it also serves as a protector for the working electrode from other unintended potential changes occurring in the system. The working electrodes are fabricated using an active material slurry prepared with the help of a binder compound and activated carbon in a polymer solvent. Example of counter electrodes are platinum and graphite electrodes. In the two-electrode configuration,

only working electrode and the counter electrode are used. The schematic representation of both configurations is presented in Fig. 1.17. In both configurations, the suitability of the prepared electrode material is tested through three major electrochemical techniques:

1. Cyclic voltammetry (CV)
2. Galvanostatic charge-discharge (GCD)
3. Electrochemical impedance spectroscopy (EIS)

The obtained data from all these characterisation techniques were graphically represented for the performance analysis of intended supercapacitor material.

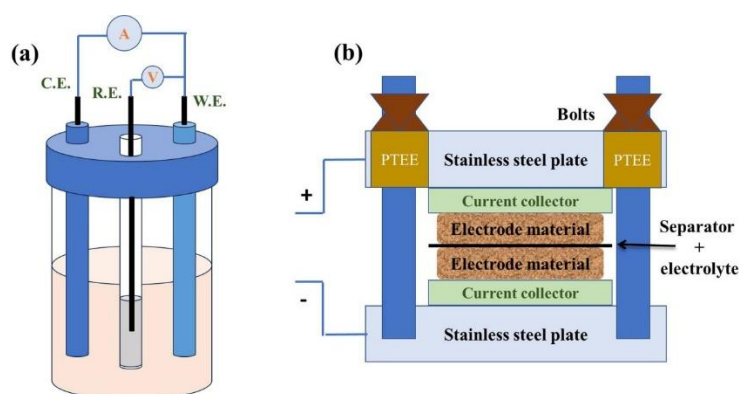


Fig. 1.17. Schematic representation of (a) three-electrode cell configuration (b) two-electrode cell configuration.

1.8.1. Cyclic Voltammetry (CV)

Cyclic voltammetry is the first method used to evaluate the electrochemical performance of electrode material, which effectively records the redox behaviour of the electrode material. During this analysis, a potential is applied to the working electrode with respect to the reference electrode having fixed potential resulting in a linear potential sweep happening between the two fixed potentials. Additionally, in this test, a positive sweep rate (dV/dt) is first applied (charging) within the potential limit and then reversing the voltage sweep (discharging) after reaching the maximum range of potential, during which the obtained current is recorded. Thus, the CV curve represents the variation of time dependent current within the fixed potential window. A typical CV response of electrode material in the three-electrode configuration is presented in (Fig. 1.18 (a)), where E_{pa} and E_{pc} represent anodic peak potential and cathodic peak

potential, i_{pa} and i_{pc} denote anodic peak current and cathodic peak current, respectively. The CV curve of an ideal capacitor is of rectangular shape and that of EDLCs carry a deformed rectangular shape, whereas pseudocapacitors presents a different shaped CV curve with oxidation and reduction peaks (Fig. 1.18 (b)).

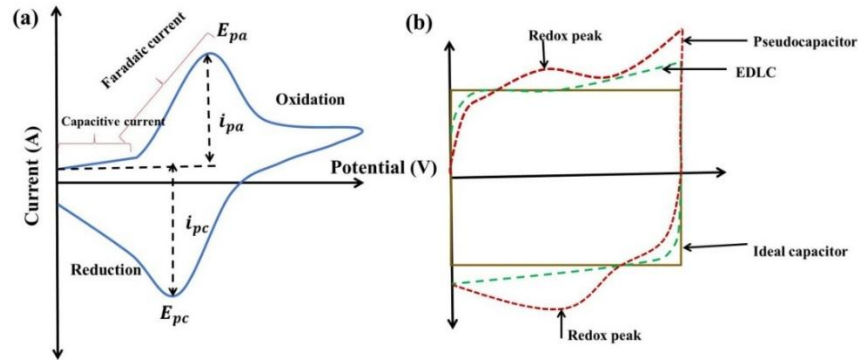


Fig. 1.18. (a) Typical CV response of an electrode material in a supercapacitor device (b) CV curve of ideal capacitor, EDLC, pseudocapacitor.

The specific capacitance (C_s) can be evaluated from CV curve in the three-electrode configuration using the equation;

$$C_s = \frac{A}{2mk\Delta v} \quad (1.18)$$

The specific capacitance in the two-electrode configuration can be estimated using the following equation;

$$C_s = \frac{A}{mk\Delta v} \quad (1.19)$$

where k denotes scan rate, A represents area under the curve equal to $\int I dV$, m is the active mass of electrode material and ΔV is the potential window.

1.8.2. Galvanostatic Charge-Discharge (GCD)

The galvanostatic charge-discharge method is the most important technique in the supercapacitor performance analysis, and is considered the most appropriate way to evaluate specific capacitance and cyclic performance of the working electrode or device. In this method, variation of potential with respect to time within a pre-fixed voltage limits are studied for different applied current densities. This process involves the charging and discharging of electrode material within the potential window. The voltage responses vary linearly with time, producing a triangular shape for the GCD

curve. The difference in GCD response of ideal capacitors, pseudocapacitors and EDLCs are schematically represented in Fig. 1.19. The deviation of the GCD curve of pseudocapacitor from the triangular shape can be attributed to its faradic redox properties. The initial ohmic drop in the discharge part of the GCD curve is due to the internal resistance in the system.

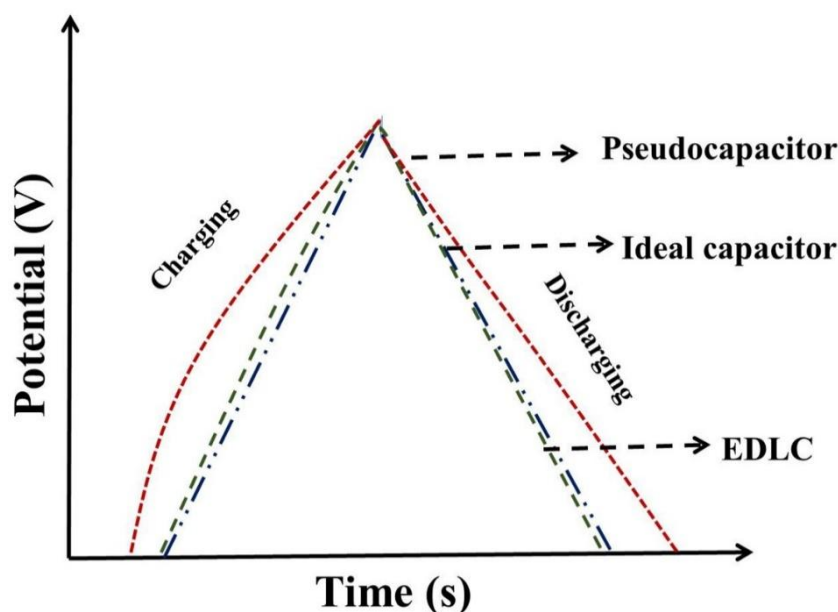


Fig. 1.19. GCD curve of ideal capacitor, pseudocapacitor and EDLC.

The specific capacitance of electrode in the three-electrode configuration can be estimated using the following equation;

$$C_s = \frac{i \Delta t}{m \Delta v} \quad (1.20)$$

The specific capacitance of device in the two-electrode configuration can be evaluated using the following equation;

$$C_s = 2 * \frac{i \Delta t}{m \Delta v} \quad (1.21)$$

Where i is the value of average cathodic current and Δt represents the discharge time.

1.8.3. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopic analysis is used to evaluate the interfacial properties connected with reactions happening at the electrode-electrolyte interface. In this test, a small amplitude AC current is supplied to the electrode

configuration over the frequency range of 10 mHz to 100kHz. The impedance value obtained from this study is the combined result of solution resistance (R_s), charge transfer resistance (R_{ct}), electrochemical double-layer capacitance and reactance in the system. The Nyquist plot from EIS data is a graph plotted between real impedance (Z) and imaginary impedance (Z'), as shown in Fig. 1.20.

The value of X-intercept at the high frequency region in the impedance spectra corresponds to equivalent series resistance (ESR) which represents the solution resistance of electrolyte in the system. The diameter of semi-circle arc in the high frequency region denotes the charge transfer resistance that occurs at the electrode-electrolyte interface. The linear portion in the low frequency region is the indication of ideal capacitive behaviour. The straight line which makes an angle 45° with the X-axis is called as Warburg line representing the ionic diffusion in the interface.

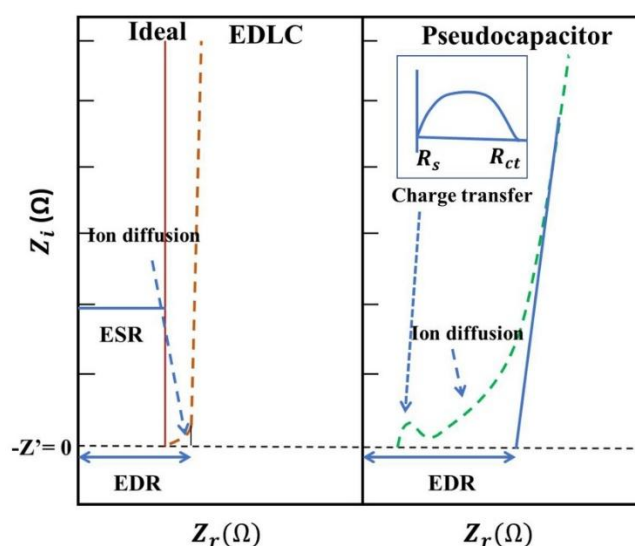


Fig. 1.20. Nyquist plot of ideal capacitor, EDLC and pseudocapacitor.

1.8.4. Cycle stability

Cycle stability of an electrode material is used to evaluate its long-term performance as a supercapacitor device. Cycle stability is typically measured using the GCD technique, which determines the extent to which the prepared electrode material can withstand. Usually, cycle performance leads to electrode degradation, initiates corrosion and increases ESR values, ultimately causing a decline in specific capacitance.

1.8.5. Specific energy and specific power

The specific energy and specific power are the two important parameters which determine the efficiency of the supercapacitor for practical uses. The energy density (E_d) in Wh/kg and power density (P_d) in W/kg was evaluated using the equations (1.22) and (1.23), respectively.

$$E_d = \frac{0.5}{3.6} C_s (\Delta V)^2 \quad (1.22)$$

$$P_d = \frac{E_d}{\Delta t} * 3600 \quad (1.23)$$

From the equation, it is clear that the value of energy density directly depends on specific capacitance and potential window. Thus, to improve the specific capacitance, we have to focus on appropriate choice of electrode material, whereas the potential window is associated with the electrolyte. From equation (1.1), it is evident that specific capacitance can be improved either by increasing the surface area of electrode material or by decreasing the electrode separation. Power density of the supercapacitor is influenced by the discharge time.

1.9. CHALLENGES OF SUPERCAPCITORS

Supercapacitors have become an inevitable part of world's energy management systems since they are found to have exceptional roles in the fields of transportation, automobiles, industrial and medical scenarios, and consumer electronics. However, its large-scale commercialization still faces some shortcomings as:

- The storage capacity of supercapacitors still come under a subject of concern, since its energy density is not much high as the conventional batteries.
- Lower energy density causes a bulkier appearance in the supercapacitor device.
- The voltage rate of supercapacitors is very limited, i.e., less than 2.7 V, leading to a need for a large number of series connections for commercial applications. Moreover, the consistency of voltage in each series connections must be guaranteed as there is a lot of charge-discharge cycles during working.

- Even though high-power density and cycle life is the major advantage of supercapacitors, it is limited for industrial applications.
- Cost of production is high.
- Requirement of additional infrastructures for proper installation.
- Drawback of self-discharging about 10-40% in a day.

Thus, numerous studies are being carried out in this area to develop a novel and high-performance electrode material with an excellent surface area and a proper choice of electrolyte medium is required to establish a better potential window, leading to an efficient supercapacitor device with high storage capacity.

1.10. WHY HYBRID SUPERCAPCITORS- A BRIEF INTRODUCTION

Hybrid capacitors with their enhanced specific capacitance and energy densities without compromising the power capacities are one of the frontier research trends in the modern scientific community. The superior specific capacitance is the result of contributions from both EDLC material and pseudocapacitor material. The incorporation of both types of electrode material can enhance the surface-to-volume ratio of the combined product, which can positively enrich the electrochemical performances. The charge storage mechanism of EDLCs lie in its intrinsic electronic structure and charge partition depth, whereas that of pseudocapacitors are based on the redox activities between the electrode and the electrolyte in the electro-active sites. The combination of these processes contributes to the charge storage mechanism of hybrid supercapacitors [18]. The hybrid supercapacitors can store a large amount of charge at elevated power densities, so that they can be considered to be a reciprocal choice compared with batteries. The major advantage of the development of the hybrid supercapacitors is the hope of achieving enhanced energy density up to 20-30 W h/Kg, rapid redox activities, good cycle performance and an extensive life span. The choice of electrode material in the hybrid supercapacitors is based on coupling different kinds of EDLCs as well as pseudocapacitive elements like carbon nanotubes, graphene, reduced graphene oxides, activated carbon, conducting polymers and metal oxides. The combination of these materials can overshadow the individual limitations faced by each component and result in higher capacitance with extended stability and affordability. Here, the EDLC material supplies high power density, whereas the pseudocapacitive

element contributes higher energy density, resulting in the uplifted electrochemical parameters that approaches the characteristics of an ideal electrode. [122].

The hybrid electrode material combining metal oxide, conducting polymer and any carbonaceous compound can enrich the supercapacitive performance. Here, the conducting polymer can undergo redox activities along with metal oxides, which provide a chance for achieving higher capacitance. Furthermore, the introduction of carbon compounds like CNTs can ensure the structural stability of pseudocapacitive element and also results in overall enhancement in the specific surface area of the hybrid electrode, which eventually make a smooth contact between pseudocapacitor components and electrolyte. Although the risk of leakage introduced by the pseudocapacitive components through the faradaic reactions, that can be counterbalanced with the help of the EDLC material, which stabilizes the charge storage mechanism and suppresses the self-discharge limitations- provided the hybrid material is engineered properly. These combinations of electrode materials have the capacity to produce specific capacitance in between 100-800 F/g. But they face some limitations too as listed below [122];

- ❖ Lack of power proficiency.
- ❖ Need safe operation and control.
- ❖ Need an extremely efficient synthesis method that can produce porous architecture.
- ❖ Superior control over each element of the hybrid composition is required to achieve desirable electrochemical properties.

1.11. SCOPE AND OBJECTIVES OF PRESENT STUDY

The fabrication of a sustainable, high-performance and eco-conscious electrode material for the supercapacitor applications is the major objective of this work. This thesis work is concentrated on the synthesis, structural and morphological characterisations and electrochemical performance evaluation of CuO-based composite/hybrid electrodes. The metal oxides and binary metal oxide composites were synthesised using hydrothermal method and their hybrid systems with PANI and MWCNTs were prepared using chemical oxidative synthesis followed by lyophilisation technique. The electrochemical performance of the fabricated hybrid electrode

materials was evaluated in both the three-electrode configuration and the two-electrode symmetric configuration. The prominent objectives of the thesis are:

- To synthesise and characterise CuO nanomaterial and CuO/PANI/MWCNT hybrid material using hydrothermal and chemical oxidative polymerisation routes for energy storage applications.
- To synthesise and characterise CuO-NiO nanocomposite and CuO-NiO/PANI/MWCNT hybrid material using hydrothermal and chemical oxidative polymerisation routes for energy storage applications.
- To synthesise and characterise CuO-Co₃O₄ nanocomposite and CuO-Co₃O₄/PANI/MWCNT hybrid material using hydrothermal and chemical oxidative polymerisation routes for energy storage applications.
- To synthesise and characterise CuO-ZnMn₂O₄ nanocomposite and CuO-ZnMn₂O₄/PANI/MWCNT hybrid material using hydrothermal chemical oxidative polymerisation routes for energy storage applications.
- Evaluation of the electrochemical performance of CuO-based composite/hybrid electrode materials in a symmetric two-electrode configuration set up.

1.12. ORGANISATION OF THESIS WORK

Energy storage devices are one of the prominent research areas in the 21st century, due to the everlasting demand for energy in the world. Supercapacitors with superior power densities, rapid charge-discharge cycles and commendable cycle life compared to conventional capacitors and batteries offer a potential candidate to meet the energy demand and supply of the world population. Thus, wise selection and fabrication of efficient and high-performance electrode material for designing supercapacitor devices is a crucial attribute in the area of energy storage devices. The thesis is intended to fabricate CuO-based metal oxide/PANI/MWCNT hybrid systems as a cost-effective and eco-conscious high performance electrode material. A brief and concise introduction about the scope and need of energy storage devices, different kinds of supercapacitors and electrode materials, their various synthesis approaches and electrochemical analysis are discussed in this chapter. Chapter 2 concentrated on the synthesis, structural and morphological investigations and electrochemical

performance evaluation of pristine CuO and CuO/PANI/MWCNT composite as an efficient electrode material. The synthesis, structural and morphological investigations and electrochemical performance investigations of CuO-NiO nanocomposite and CuO-NiO/PANI/MWCNT hybrid electrode material in both the three-electrode and the two-electrode symmetric device configurations are thoroughly discussed in chapter 3. Chapter 4 focuses on the synthesis, characterisations and electrochemical performance investigations of CuO-Co₃O₄ nanocomposite and CuO-Co₃O₄/PANI/MWCNT hybrid material in both the three-electrode and the two-electrode symmetric device configurations. The fabrication and detailed characterisations of CuO-ZnMn₂O₄ nanocomposite and CuO-ZnMn₂O₄/PANI/MWCNT hybrid material are discussed in detail in chapter 5. The electrochemical performance of the prepared electrode materials is also explored in this chapter. Chapter 6 presents the overall inferences and conclusions obtained from the studies performed, and chapter 7 discusses some of the future perspectives and recommendations of the works conducted in this thesis.

1.13. REFERENCES

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Synthesis, Characterization, and Supercapacitive Performance of CuO and CuO/PANI/MWCNT Hybrid System

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Efficient energy storage mechanism became an intricate and vital part of global sustainable energy management in light of ever-increasing mass energy demand across the world. Supercapacitors gained much attention on account of its high-power density and faster charge-discharge capacities over the conventional capacitors and batteries, which are typically ruling among Energy Storage Devices (ESDs). CuO is the one among the electrochemically active TMOs considered to be promising substitute for commercial ones in supercapacitor field, carrying high theoretical capacitance along with other oddities like low cost, environmental friendliness, sufficient stability, and high intrinsic activity. Owing to its shortcomings like poor electrical conductivity and specific surface area, the actual electrochemical activity of copper oxide is still far lower. Metal oxides and conducting polymers are combined with carbonaceous materials like MWCNTs can become a profitable composite electrode material to enhance the pseudocapacitive performance because of their combined synergetic effects. Within this context, a surfactant free approach to CuO synthesis through hydrothermal method is discussed and compared its electrochemical performance with the CuO/PANI/MWCNT composite electrode synthesised via one pot in-situ polymerisation method.

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2.1. INTRODUCTION

Energy generation and storage has turned into a key focus area all over the world due to the ever-rising global energy demand as a result of marginal population increase. Rechargeable batteries are considered to be leading energy storage system prevailing among the ESDs due to their high energy density, but they holding the limitations of deprived life duration and specific power as well as lack of availability for proper recycling and disposal systems after life-end. Insubstantial storage capacity and over-sized appearance unambiguously hinder fuel cells from becoming an efficient alternative for batteries. Moreover, the conventional capacitor lack its electrochemical performance in consequence of deficient specific energy[1]. To date, an enormous amount of effort has been carried out by the scientific community in search of a viable candidate in the area of ESDs that can bridge the gap between rechargeable batteries and conventional capacitors. SCs has become a potential contender in this scenario, possessing high power density and modest specific energy, and possibly having longer cycle life in comparison with batteries [2], [3], [4]. However, real-time power and energy efficacy of SCs are far beneath from the expectations and so the need for a convenient and travel-friendly, flexible future generation SCs with commendable energy-power efficiencies are still unmet.

The selection and design of appropriate electrode material is a key factor for acquiring satisfactory electrochemical performances from the storage system. Enriched electrical conductivity and ionic mobility, ease of fabrication, economically viable, and porous architecture are some of the key criteria to be emphasised while selecting an electrode material in supercapacitor context [5]. Literally, the casting of electrode material is the bottom-line of supercapacitor performances to attain admirable capacitance values. Transitional metal oxides (TMOs) are one of the promising candidates in the category of electrode material exhibiting attractive electrochemical achievements in the past few decades [6], [7], [8], [9]. TMOs carry higher specific capacitance values as result of their significant redox behaviour compared with carbon based electrode materials, ends up in notable capacitance and electrochemical stability [10]. Therefore, economical and environmentally viable metal oxide energy storage systems are found to be on the rise, in response to keeping the balance between energy demand and consumption in the modern society. Notably, amid of all 3d-TMOs such

as Fe, Co, Ni, Zn and Ti based, Cu-based electrode material achieved better attention due to its chemical stability, rich reserve and pseudocapacitive nature [11].

2.1.1. Electrochemical performance of CuO - A literature survey

Even though, all oxide forms of copper are being attractive materials in the stream of research, cupric oxide (CuO) has found as a hopeful material for the fabrication of supercapacitor working electrodes. As yet, theoretical capacitance of CuO found to attain a commendable value of 1800 F/g which is almost comparable with that of hydrated ruthenium oxide working electrodes (~ 2200 F/g) [12]. Supercapacitive performance of CuO can be well-tuned by optimising its morphology, crystallinity, surface area, and particle size [13], [14], [15]. Wide variety of CuO nanostructures, for example, nanorods [16], nanoflakes [17], nanotubes [18], nanowires [19], nanoflowers [20], [21], and nanoparticles [22] has been already synthesised. In recent years, different variety of synthetic approaches such as sol-gel method [23], hydrothermal method [24], co-precipitation [25], microwave irradiation [26], electrodeposition method [27], solvothermal method [28], chemical bath deposition [29], have been reported intensively to synthesise CuO nanoparticles with different morphologies.

Many researches have been conducted on the pseudocapacitive performance of CuO-based SCs. Even though, copper chalcogenide based pseudocapacitors is a potential member in the electrochemical field, because of their poor electrical conductivity, structural collapse during charge-discharge cycles, and minimal energy density, production of CuO electrode with remarkable energy density and capacitance are still in urgent demand [30]. Deepak P Dubal *et al.* synthesised cauliflower-like CuO with a surface area ~ 49 m²/g, showed a specific capacitance of 179 F/g in 1 M Na₂SO₄ electrolyte solution [13]. Seyyed E. Moosavifard *et al.* designed a 3D highly ordered nanoporous CuO framework exhibiting an excellent electrochemical performance with a specific capacitance value of 431 F/g at 3.5 mA/cm² [31]. Yu Xin Zhang *et al.* fabricated mesoporous CuO using wet chemical method and reported a capacitance value of about 137 F/g in 6 M KOH solution [32]. A trouble-free chemical synthesis of 3D-flower-like CuO nanostructures was proposed by S. K. Shinde *et al.* and acquired a capacitance of about 498 F/g at a current density of 5 mV/s [33]. Deepak P. Dubal *et*

al. reported a surfactant assisted chemical bath deposition method of CuO thin film fabrication and obtained a specific capacitance value of 396 F/g at current density 5 mV/s for CuO nanobuds [34]. V. Senthilkumar *et al.* reported a comparative supercapacitive performance of binder-free CuO nanoplates and binder assisted bud- and flower-shaped CuO nanostructures and obtained a high specific capacitance value of about 536 F/g at current density 2 A/g with 94% capacity retention over 2000 cycles for CuO nanoplates [35]. Lakshmi Kunhikrishnan *et al.* prepared sphere-like CuO nanostructures via CTAB-assisted co-precipitation method and reported a capacitance value of 468 F/g at a scan rate of 5 mV/s with a capacity retention of 94% after 2000 CV cycles [36]. Another appropriate strategy to improve the electrochemical performance of metal oxides is to try doping with productive transitional metal ions which can effectively alter the electronic structure of host material and eventually improve the conductivity of the matrix. Wenbo Lv *et al.* discussed the effect of Mo-doping in CuO nanosheets synthesised via a simple hydrothermal route and attained a specific capacitance value of about 1392 F/g at 2 A/g. The work concludes with the practical possibility of Mo-CuO composite electrode as a promising candidate in ESDs with an excellent energy density of 36 Wh/ kg at 810 W/ Kg [37]. Faiza Iram *et al.* incorporated transition metals such as Zn, Mn, Ni individually in to the CuO matrix via co-precipitation method and reported a higher capacitance value of 507 F/g at 5 mV/s for the Ni- doped CuO sample, since the Ni doped sample exhibited better surface area compared with others [38]. A facile co-precipitation method was used by Manika Chaudhary *et al.* for the synthesis of pure and Co and Fe doped CuO nanostructures and achieved a specific capacitance values of about 114 F/g, 136 F/g and 170 F/g for CuO, Co-doped CuO and Fe-doped CuO, respectively at 0.5 A/g [39]. Mohan-Reddy Pallavolu *et al.* synthesised Al-doped CuO nanoflakes via co-precipitation method and reported a maximum of 272 C/g at 1 A/g for the 5 wt% doped CuO with 99% capacity retention over 5000 charge/discharge cycles [30]. The one of the major drawbacks suffered by metal oxides in the electrochemical field is lesser active mass utilization by the electrolyte, owing to their poor porous structure which declines the accessible sites in the electrode-electrolyte interface [40]. Better choice of current collecting substrates like Ni foam, copper foam and copper foils can efficiently overcome this problem by providing greater electrochemical active contact area which undoubtedly complimenting the effective utilization of active electrode material. Guiling Wang *et*

al. prepared CuO nanosheets directly grown on Ni foam via template-free grown method. The study showed that an array of CuO nanosheets have been uniformly arranged over the Ni foam with a thickness of 5 μm and achieved a specific capacitance value of 569 F/g at a current density of 5 mA/cm^2 in KOH electrolyte [41]. Yunhu Li *et al.* directly grown CuO nanostructures on copper foam and got a higher capacitance value of about 212 F/g at a current density of 0.41 mA/cm^2 for CuO nanosheets [40]. In spite of all these efforts, the best reported specific capacitance value of CuO electrode is still far less than its theoretical value, which provides more opportunities for further research on this material [5].

2.1.2. CuO-based ternary nanocomposites- An overview

The electrochemical performance of CuO-based SCs usually suffers from the limitations like inferior electrical conductivity and structural stability in the course of consecutive charge/discharge cycles. These shortcomings can be minimised by fabricating a potential hybrid composite system integrating CuO with conducting polymers as well as any carbonaceous materials. At present, hybrid composite electrodes are broadly studied on account of their probable utilities. Metal oxides/hydroxides, conducting polymers (CPs) and carbon-related materials are the key elements that prevailed in the field of SCs [42], [43]. A wise combination of these elements can produce exceptional outcomes in this area. Nowadays, CP-TMO combinations are extensively explored by the researchers in order to overcome the mechanical instabilities and agglomeration issues that typically decline the supercapacitor performances [44], [45], [46], [47]. Carbon- based electrode materials such as activated carbon, multi-walled carbon nanotubes (MWCNTs) and graphene having higher specific surface area can be incorporated with TMOs to trigger their pseudocapacitive performances through synergistic effects [48]. For instance, Chandan Kumar Maity *et al.* reported the one pot synthesis of N-rGo/ZnO-CuO nanocomposite and exhibited a specific capacitance value of 1075 F/g at current density 1 A/g in 1M KOH with 88% capacitance retention [49]. Moreover, Nadia Boutaleb *et al.* synthesised ternary nanocomposite of polyaniline@TiO₂-CuO through a facile method followed by in-situ polymerisation and evaluated the electrochemical performance of the hybrid system. This work reports an areal capacitance of 296.7 mF/cm^2 at 1 mA/cm^2 with 88% capacity retention over 1500 cycles [50]. Yingying Huang *et al.* worked on the

preparation of MnO₂/PANI/MWCNT ternary nanocomposite electrode via chemical method and acquired a specific capacitance of about 395 F/g at a current density of 1 A/g having 72% retention after 1000 cycles of charging and discharging [51]. Among CuO-based composite electrodes, a few efforts have been reported regarding the CuO-MWCNT binary nanocomposites for the improved electrochemical performances. Rini Paulose *et al.* tried CuO-MWCNT preparation using the in-situ co-precipitation technique and achieved a specific capacitance of about 452.8 F/g at scan rate 10 mV/s [52]. A study on the fabrication of CuO mesocrystal/ MWCNT composite as an anode material in lithium ion batteries was reported by Junmin Xu *et al.* and revealed a commendable reversible capacitance of 1.11 mA h cm⁻² at 0.39 mA/cm² for the hybrid system after 400 cycles [53]. Niaz Ahmad Niaz *et al.* explored the electrochemical behaviour of CuO/MWCNT composite and reported a specific capacitance value of 810 mA h g⁻¹ with 80.86 % coulombic efficiency [54]. Shivaprasad Chalawadi *et al.* explored the hydrogen gas sensing application of CuO/PANI/MWCNT ternary nanocomposite using green synthesis method and the hybrid exhibited a detection of H₂ gas in concentrations ranging from 110 to 2 ppm at temperatures of 200 and 250 °C [55].

2.2. EXPERIMENTAL SECTION

2.2.1. Synthesis materials

Copper nitrate trihydrate (Cu(NO₃)₂·3 H₂O), urea (CH₄N₂O), ammonium persulfate (APS) ((NH₄)₂S₂O₈) and aniline hydrochloride (C₆H₅NH₂·HCl), analytical grade hydrochloric acid (HCl), sodium sulphate (Na₂SO₄), sodium dodecyl sulphate (CH₃(CH₂)₁₁OSO₃Na) (SDS, > 98%) and de-ionised (DI) water were purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, OD × L = 6 – 9 nm × 5 μm), polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standard and utilized without any further purifications. Distilled ethanol was used for cleaning purposes.

2.2.2. Synthesis of CuO nanostructures

Spherical flower-like CuO nanostructures were synthesised by a simple hydrothermal route. The synthesis process was carried out in a way similar with one previously reported chemical method with slightly different reaction conditions [56]. Initially, 0.3 M copper nitrate trihydrate was dissolved in 50 ml of deionised water which was kept under constant stirring for 30 minutes. Later, 0.6 g of $\text{CO}(\text{NH}_2)_2$ was mixed into the above solution without disturbing the stirring process. Subsequently, the whole 50 ml solution was shifted to a well-cleaned 100 ml Teflon-lined autoclave and which was later kept in laboratory oven at temperature $180\text{ }^\circ\text{C}$ with reaction time of 24 hours. After the reaction, the sample was preferred to cool spontaneously and collected the black powder by the process of centrifugation. The obtained product was washed 4-5 times in distilled water and twice with ethanol. Finally, the obtained powders were dried in an oven at $80\text{ }^\circ\text{C}$ for 5 hours before further analyses and use. The whole synthesis process is schematically represented in Fig. 2.1.

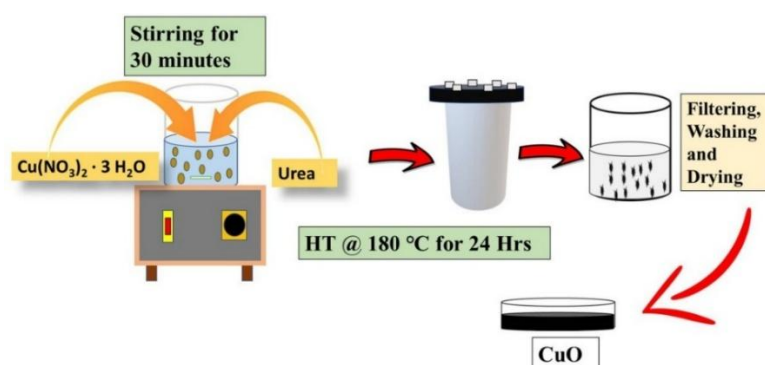


Fig. 2. 1. Schematic representation of CuO preparation.

2.2.3. Synthesis of polyaniline

The synthesis procedure of PANI was followed by a previously reported work with minor modifications in the process conditions [57]. Initially, 2 g of aniline hydrochloride was dissolved in 20 ml of 1 M HCl solution under constant stirring. Simultaneously, 4.04 g of APS was dissolved in 20 ml of 1 M HCl solution in another beaker under stirring. After continuous 30 minutes of stirring, the APS mixture was added drop by drop wise to the aniline hydrochloride solution, and continued the stirring for 2 hours. Thereafter, the whole solution preserved in dark for 24 hours. The

dark green residue obtained from the procedure was then filtered and washed thoroughly with water and ethanol for removing all the unreacted components and excess acids from the product. After that, the as-obtained slurry was stored in cold press in - 120 °C for 1 hour before freeze drying at - 70 °C for 48 hours. A completely dried dark green powder was collected after the freeze-drying process; this is the final PANI nanostructure.

2.2.4. Synthesis of CuO/PANI/MWCNT ternary nanocomposite

The CuO/PANI/MWCNT ternary nanocomposite was prepared by one pot in-situ polymerisation method. First of all, 0.4 g of aniline hydrochloride and 1 g of APS were separately dissolved in 15 ml of 1 M HCl solution. Then, 0.03 g of MWCNT was dispersed in a solvent containing 3 g of SDS and 50 ml DI water under ultra-sonication for 2 hrs. After which the already prepared solution of aniline hydrochloride was added drop by drop to the MWCNT solution under continuous stirring process. Later, 30 mg of as-synthesised CuO nanostructures were added to the aniline-MWCNT mixture and continued the stirring process for 1 hr. Here, the specific weight of metal oxides and all other molar ratios were selected after primary trials, and the chosen ratios were kept the optimum balance between structural properties and ideal electrode characteristics. Then, the APS solution was introduced slowly to the above-mentioned solution and kept for 3 hours constant stirring. The obtained dark green solution was then maintained undisturbed for 24 hours in the dark room at room temperature for the complete polymerisation to occur. Thereafter, the collected dark green residue is subjected to thorough washing using distilled water and ethanol for 5-6 times until all the unwanted species were washed out. After that, the as-obtained slurry was preserved under cold press in - 120 °C for 1 hour before freeze drying at - 70 °C for 48 hours. After completing the freeze-drying stage, a wholly dried dark green powder was collected; this is the final CuO/PANI/MWCNT ternary nanocomposite. This product is named as CPM for the convenience.

2.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, AERIS Research (Source: Cu K α)). Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany)

was employed to determine the vibrational modes of the as-synthesised samples. Fourier transform infrared (FTIR) spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using ZnSe crystal. The surface morphology and elemental composition were done using a combination of High- Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

2.2.6. Electrode preparation and electrochemical studies

The electrochemical features of as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt % of active material, 10 wt % of polyvinylidene fluoride (PVDF) and 10 wt % of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly onto a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in working electrode was 1.5 mg cm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of as-synthesised samples. The as-prepared samples were subjected to studies such as cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) in an operating potential window of 0-0.8 V.

The specific capacitance (F/g) of fabricated electrode materials can be evaluated from the CV curve and GCD plot using the following equations (2.1) and (2.2), respectively;

$$C_s = \frac{\int_{V_1}^{V_2} I(V) dV}{2 K (V_2 - V_1) m} \quad (2.1)$$

$$C_s = \frac{I \Delta t}{m \Delta V} \quad (2.2)$$

Where V_1 and V_2 are the cutoff potentials (volts) in the graph, $I(V)$ is the value of voltametric current (A) in each potential, m indicates the active mass of material (g), $V_2 - V_1$ describes the potential window of CV curve, Δt denotes the discharge time (s) and K signifies the scan rate value in mV/s.

In order to explore the real-time electrochemical performance of the materials, a two-electrode symmetric cell device was used. The gel-type slurry was prepared in a similar manner of three electrode system and pasted in to two pre-cleaned stainless-steel substrates of dimension $2 \times 3 \text{ cm}^2$, which were served as positive and negative electrodes. A filter paper dipped in 1 M Na_2SO_4 electrolyte solution was kept in between these uniformly coated stainless steel electrodes as a separator. The schematic representation of symmetric supercapacitor device was shown in Fig. 2.2.

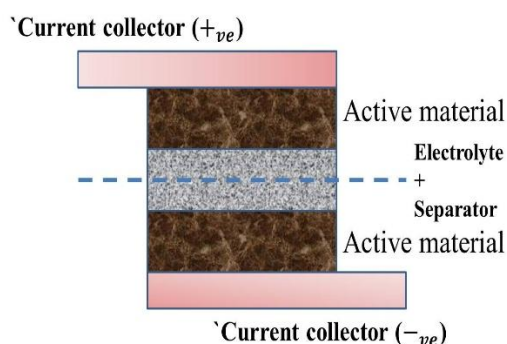


Fig. 2.2. Schematic representation of symmetric supercapacitor device.

The specific capacitance (F/g) can be estimated from the CV and GCD curves of symmetric two-electrode configurations as follows;

$$C_s = \frac{\int_{V_1}^{V_2} I(V) dV}{K (V_2 - V_1) m} \quad (2.3)$$

$$C_s = 2 \frac{I \Delta t}{m \Delta V} \quad (2.4)$$

Where V_1 and V_2 are the cutoff potentials (Volts) in the graph, $I(V)$ is the value of voltametric current (A) in each potential, m indicates the active mass of material (g),

$V_2 - V_1$ describes the potential window of CV curve, Δt denotes the discharge time (s) and K signifies the scan rate value in mV/s. The energy density (E_d) in Wh/kg and power density (P_d) in W/kg was evaluated using the equations (2.5) and (2.6), respectively.

$$E_d = \frac{0.5}{3.6} C_s (\Delta V)^2 \quad (2.5)$$

$$P_d = \frac{E_d}{\Delta t} * 3600 \quad (2.6)$$

The cyclic performance of the electrode materials was conducted at 10 mA applied current for 50000 cycles of charge/discharge in a potential range of 0-0.8 V. The charge storage mechanism of an electrode material can be explained using Dunn's method. According to this, there is possibility of two-type of charge storage mechanisms to happen in a working electrode.

- 1) Capacitive contribution: This is surface controlled charge storage mechanism happens in the surface of electrode material. This type of contribution enables fast charging and discharging and is directly proportional to scan rate (v).
- 2) Diffusive contribution: This is diffusion-controlled charge storage mechanism involving diffusion of ionic carriers in to the bulk of material and is proportional to the square root of scan rate ($v^{1/2}$).

The total current in the electrode system is directly proportional to the scan rate in such a way that;

$$i = av^b \quad (2.7)$$

Where a and b are changeable parameters. The value of b equivalent to the value of slope in $\log v$ vs. $\log i$ graph. From the value of b , the major contributor of capacitive current in the system can be estimated. If the value of b approaches to 0.5, the major charge storage mechanism in the system will be diffusion controlled, whereas if the b value closes to 1, the charge storage mechanism is surface-controlled.

Thus,

$$i = i_{\text{capacitive}} + i_{\text{diffusive}} \quad (2.8)$$

$$i = k_1 v + k_2 v^{1/2} \quad (2.9)$$

$$\frac{i}{v^{1/2}} = k_1 v^{1/2} + k_2 \quad (2.10)$$

Where the parameters k_1 and k_2 can be obtained from the slope and intercept values in the $v^{1/2}$ and $i/v^{1/2}$ plot. The individual capacitive and diffusive contributions can be estimated using the following equations;

$$\text{capacitive contribution (\%)} = \frac{i_{\text{capacitive}}}{i_{\text{capacitive}} + i_{\text{diffusive}}} * 100 \quad (2.11)$$

$$\text{diffusive contribution (\%)} = 100 - \text{capacitive contribution (\%)} \quad (2.12)$$

The columbic efficiency of working electrode can be estimated using the equation;

$$\eta (\%) = \frac{t_d}{t_c} * 100 \quad (2.13)$$

Where t_d and t_c are the discharging and charging times in seconds, respectively.

2.3. RESULTS AND DISCUSSION

2.3.1. X-Ray diffraction (XRD)

Structural characteristics of the obtained CuO, PANI, MWCNT and CuO/PANI/MWCNT were executed by X-ray diffraction with $\text{CuK}\alpha$ radiation of 0.154 nm wavelength. Fig. 2.3 displays the XRD profile of CuO, PANI, MWCNT and CPM which are continuously scanned from 10° to 80° with scanning step of 0.04. The XRD image of CuO shows sharp and narrow diffraction peaks at 32.69° , 35.45° , 35.69° , 38.88° , 38.92° , 48.92° , 53.44° , 58.44° , 61.65° , 66.09° , 66.39° , 68.18° , 2θ were indexed to planes (110), (002), (-111), (200), (111), (-202), (020), (202), (-113), (02-2), (-311), (220) respectively and have shown absolute match with the monoclinic symmetry of tenorite phase of copper oxide having space group C2/c (15) (JCPDS Card no: 80-0076) [58]. No other peaks of supplementary phases were detected, which evince the purity of sample. The intense and furthest tapered behaviour of each peak in the pattern describes the extreme crystallinity of the so-obtained product. The XRD plot of PANI shows characteristic peaks at angles 14.19° , 20.4° , and 25.18° , which are correspond to the crystallographic lattice planes (010), (100), and (110) of PANI in emerald salt form (JCPDS – 060-1167). In case of MWCNT, diffraction peaks were observed at 25.82°

and 42.99° attributed to the (002) and (100) planes of the hexagonal graphite form of MWCNTs (JCPDS-98 005-2230) [52]. The XRD profile of CuO/PANI/MWCNT ternary nanocomposite presents characteristic peaks of PANI, MWCNT and CuO distinctively. The diffraction peaks observed at 14.72° , 19.89° correspond to PANI, whereas the peak at 25.93° becomes representative of PANI/MWCNT combination. Moreover, the peak at 43.05° ascribed to (100) plane of MWCNT. All the dominant peaks of the monoclinic CuO crystal structure were also present in its ternary nanocomposite at 32.41° , 35.40° , 38.71° , 48.75° , 61.61° , 66.48° and 67.96° can be attributed to the planes (110), (002), (200), (-202), (-113), (-311), and (220), respectively. The diffraction peaks of CuO shows small shifts due to the presence of PANI/MWCNT, which confirms the effective fixing of CuO on to the surface of MWCNT that ultimately induce strains to the lattice of CuO [60], [61]. The reason for the decrease in peak intensity of CuO phase in the composite XRD data can be possibly due to the presence of carboxylic and hydroxyl parts. The dominant functional groups present in the ternary composite can effectively slow down proper crystallisation and growth of metal oxides [54].

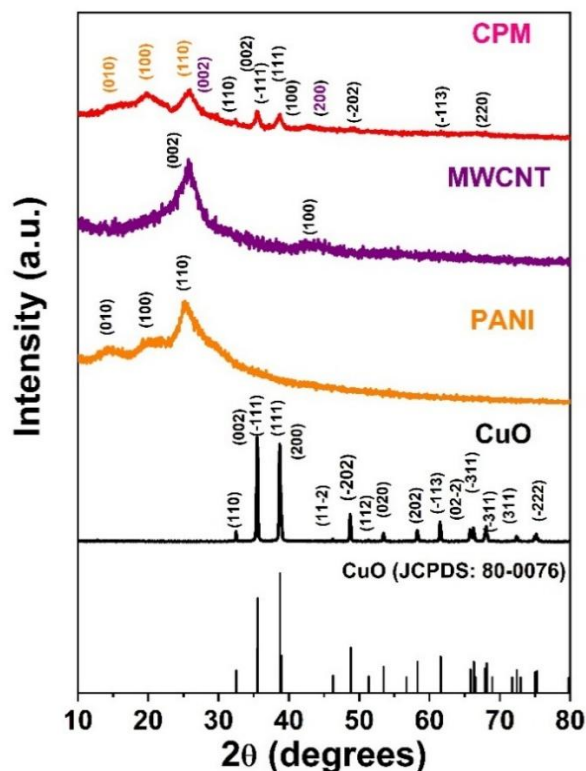


Fig. 2.3. The XRD graph of pure CuO, PANI, MWCNT and CPM nanostructures.

2.3.2. Raman spectroscopy

Raman Spectroscopy is a powerful method to get detailed information about chemical bonds, crystal structure, and phases of the materials synthesised. The three Raman peak positions at 299 cm^{-1} , 349 cm^{-1} and 631 cm^{-1} which are dominant in the spectra are in parallel with the Raman active bands of the monoclinic structure of CuO with C_{2h}^6 (c^2/c) space group. CuO primitive cell consists of two molecular units with 12 vibrational modes. Among these, three are Raman active modes (A_g+2B_g) [62]. Here, Fig. 2.4 (a) illustrates the Raman profile of so-synthesised CuO nanostructures having one dominant peak at 299 cm^{-1} which can be ascribed to the asymmetric stretching mode (A_g) arising due to the in/out phase rotation of CuO structure. Along with that, there exhibit peaks at 349 cm^{-1} and 631 cm^{-1} , which corresponds to the well-known bending mode B_g^1 and symmetric oxygen stretching B_g^2 modes of monoclinic CuO nanostructure. Aside from these three preeminent vibrational modes, a broad peak appears at wavenumber 1133 cm^{-1} , belonging to the multiphonon band of CuO connected with the inharmonic coupling between phonons in polar solids [63]. Moreover, no modes correspond to impurity phases or any possible secondary phases were identified in the spectra. Fig. 2.4 (b) presents the Raman spectrum of ternary nanocomposite CPM, showing an exact combination of prominent modes of CuO, PANI and MWCNT [10], [64], [65], listed in the Table 2.1. The D band (disorder band) of MWCNT were due to lattice defect of the phonon mode of vibration from MWCNT surface and G band (graphite band) resulted from the C–C (vibrational modes) and double-degenerate phonon modes of E_{2g} symmetry of MWCNT. Both these bands undergone slighter shift, which are probably due to the better incorporation of PANI with MWCNT. The G' band that appeared in the spectrum is an overtone of the D band and is associated with stacking alignment of graphene layers [66]. The less intense A_g , and B_g^2 vibration modes of CuO are clearly visible in the spectra.

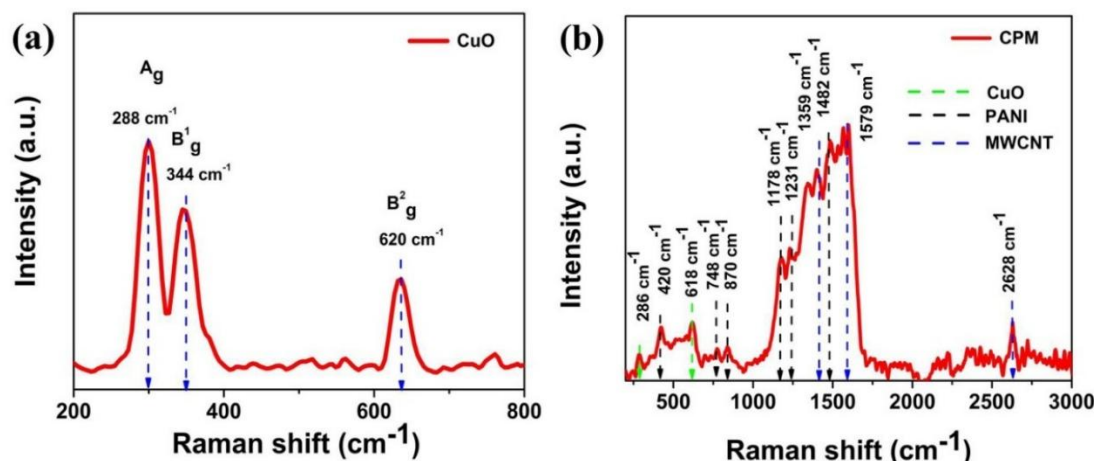


Fig. 2.4. Raman spectra of as-synthesised (a) CuO and CPM nanostructures.

Table 2.1. List of assignments of dominant characteristic bands appeared in CPM nanocomposite

Raman modes (cm ⁻¹)	Assignments
286 cm ⁻¹	A _g mode of monoclinic CuO
618 cm ⁻¹	B _g ² mode of monoclinic CuO
420 cm ⁻¹	Out of plane C–H wag in bi-polaronic
748 cm ⁻¹	Imine deformation of quinoid ring
870 cm ⁻¹	Ring deformation of benzenoid ring in emeraldine salt
1178 cm ⁻¹	C–H bending of benzenoid ring
1231 cm ⁻¹	C–H bending of quinoid ring
1482 cm ⁻¹	C=N stretching in quinoid ring
1359 cm ⁻¹	D- band of MWCNT
1579 cm ⁻¹	G-band of MWCNT
2628 cm ⁻¹	G' band of MWCNT

2.3.3. FT-IR spectroscopy

The FT-IR spectroscopy helps to detect the fundamental molecular vibrations of functional groups that occur in a material; also, it can be easily observe the minor structural changes that may happen in material compositions. Fig.2.7. (a) illustrates the FTIR spectral image of CuO spherical nanostructures. The adsorption

peaks at 596 cm^{-1} , 541 cm^{-1} , and 414 cm^{-1} were confirmed the formation of the monoclinic crystal structure of CuO flower-like nanostructures (shown in the inset of Fig. 2.5. (a)). These three bands in the fingerprint area of IR spectrum assigned to the Cu-O stretching modes along $[-202]$ and $[202]$ planes [67]. Upon comparison with previous literatures [68] [69], slight shift in the characteristics peaks can be ascribed to size-induced lattice variations as well as stress and defects appeared in the crystal structure [70]. The additional bands that appeared in the range of $800\text{--}1300\text{ cm}^{-1}$ were connected with OH bending vibration and C–H stretching, which indicate the presence of hydroxyl group [71]. Besides these dominant bands, no infrared active modes associated with other phases of copper oxide, like band at 615 cm^{-1} associated with Cu_2O , appeared in the spectrum which thereupon affirm the exceptionally pure tenorite phase of copper oxide [72]. In the case of FT-IR spectra of CPM nanocomposite (shown in Fig.2.5. (b)), a numerous number of vibrational modes appear representing the correct formation of CuO/PANI/MWCNT, which are listed in Table 2.2 [73], [74]. The minor shifts in the characteristic peaks of quinoid and benzenoid rings of PANI may attributed to the interactions like hydrogen bonding between NH group of PANI and metal oxide surface [75].

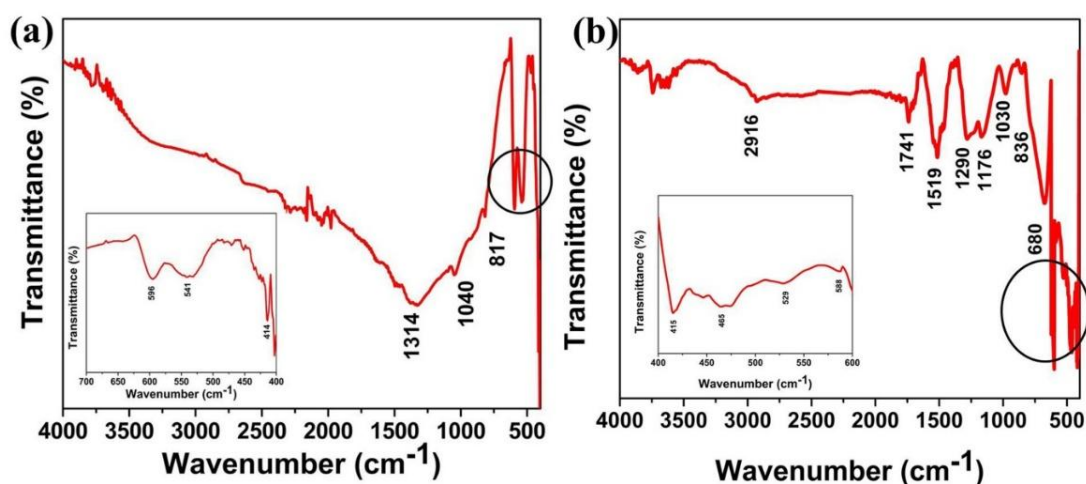


Fig. 2.5. FT-IR spectra of (a) CuO nanostructure and (b) CPM (insets shows the enlarged image of FTIR spectrum of (a) CuO in the wavenumber range $700\text{--}400\text{ cm}^{-1}$ (b) CPM in the wavenumber range $600\text{--}400\text{ cm}^{-1}$).

Table 2.2. List of peaks in FT-IR spectrum of CPM and its assignments.

FT-IR peaks	Assignments
2916 cm ⁻¹	asymmetric/ symmetric methylene stretching bands from PANI
1741 cm ⁻¹	stretch mode of carboxylic groups in MWCNT
1519 cm ⁻¹	C=C stretching in quinoid ring of PANI
1290 cm ⁻¹	C-N for aromatic amines in the polaron structure of conducting PANI
1176 cm ⁻¹	characteristic band of the protonated form of conducting PANI
1030 cm ⁻¹	due to protonated imine group in PANI
836 cm ⁻¹	out of plane C-H bending vibration.
400-600 cm ⁻¹	stretching vibrations of Cu-O

2.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The surface morphology of the CuO nanostructures was assessed with the help of FESEM, as shown in Fig. 2.6. Size determination of grains was established with the help of ImageJ software. From the inspection of Fig. 2.6 (a) and (b), it can be easily perceived that the CuO powders were constituted of well-defined spherical marigold flower-like structures having an average diameter of $10 \pm 2 \mu\text{m}$. Moreover, the high magnification FESEM image (Fig. 2.6 (c)) clearly shows that each spherical micro-flower was composed of several dozens of well-organized nanopetals. The densely packed nanopetals are interconnected together to form a 3D-flower like architecture. Each petal-like CuO structure has a length of $\sim 450 \text{ nm}$, width $\sim 200 \text{ nm}$ and thickness about $\sim 70 \text{ nm}$. The uniform distribution of nanopetals to form the marigold flower-like structure with abundant tiny pores and crevices in between contribute to the enhancement in volumetric specific surface area, which eventually induce a positive impact on the electrochemical capacity of pristine CuO. The quantitative elemental composition survey was carried out using EDS technique, which is plotted in Fig. 2.6

(d). The CuO exhibited a Cu:O ratio of 53.81 : 46.19 in EDS data, which is in accordance with the stoichiometry distribution of cupric oxide [76].

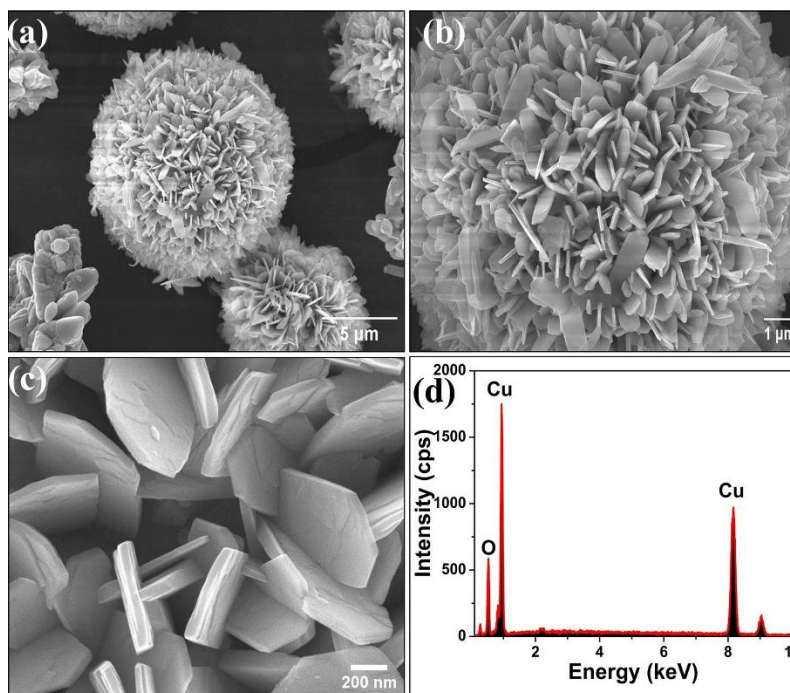


Fig. 2.6. (a-c) Low magnification SEM images of as-prepared CuO (d) EDS spectrum of CuO.

Furthermore, EDS chemical mapping was employed for the close interrogation of material to ascertain its chemical nature. Unsurprisingly, a sectional inspection of the EDS images in Fig. 2.7 revealed the homogeneous distributions of Cu and O atoms in the CuO crystal lattice, as understood from the chemical synthesis.

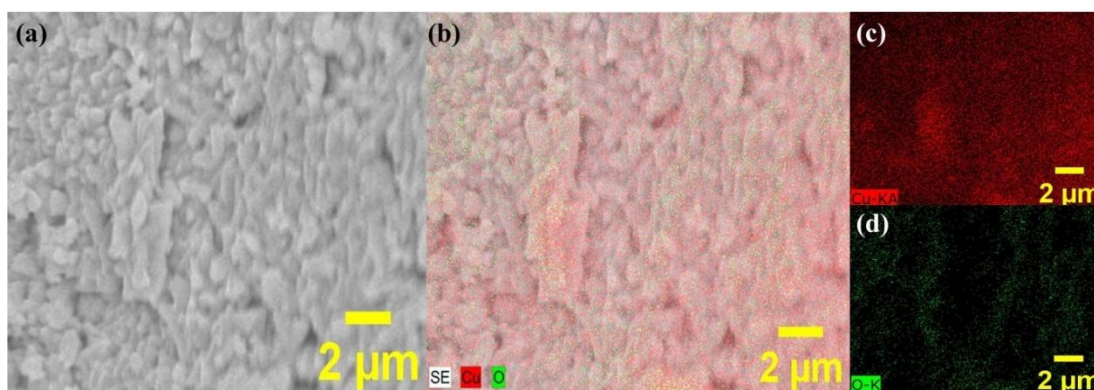


Fig. 2.7 (a) SEM and (b) EDS mapping images of CuO nanostructures, (c & d) elemental distribution of Cu and O in the area shown in images a.

The morphological analysis of CuO/PANI/MWCNT ternary nanocomposites was presented in Fig. 2.8 (a-c). The low magnification SEM images display a spongy appearance of nanocomposite with large number of porous frameworks. The voluminous pores in between the interconnected regions of composite will surely strengthen their effective surface area and boost its electrochemical performances. The incorporation of MWCNT to CuO transformed the spherical flower-like morphology of CuO in to a 3-D porous framework of several interconnected electro-conducting groups, which enables a smooth and productive contact between electrode material and electrolyte [54]. These conductive networks facilitated better ionic transportations and leading to superior electrochemical performance. There may be a synergistic effect of CuO, PANI and MWCNT in the matrix through hydrogen bond and $\pi - \pi^*$ interactions and which can mutually boost the overall electric conductivity and electrochemical performance of nanocomposite electrode [42]. The EDS plot of CPM was displayed in Fig.2.8 (d), clearly showing the presence of carbon, nitrogen, oxygen and copper in the composite. It is visible that the carbon content (76.98 wt%) is the dominating one compared with the metal oxide part.

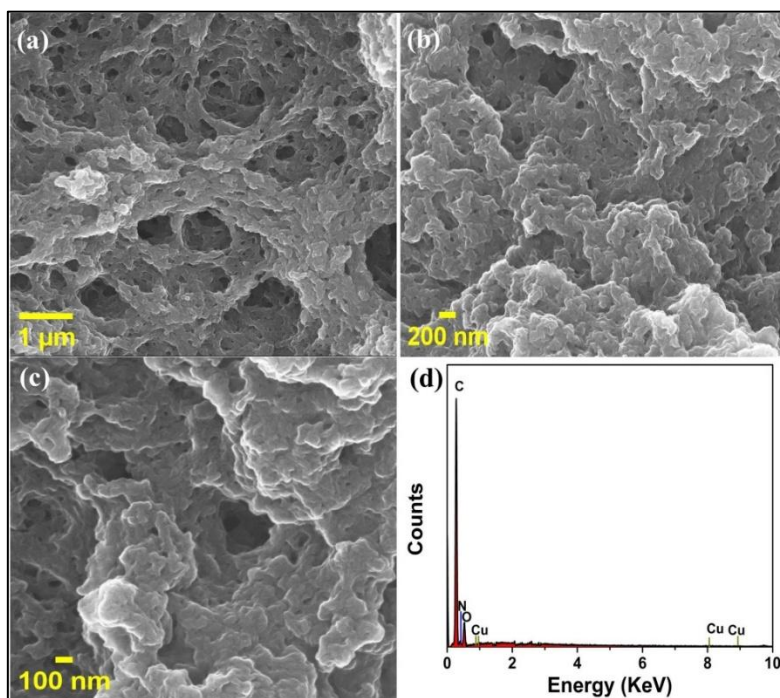


Fig. 2.8. (a-c) Low magnification SEM images (d) EDS spectrum of CPM.

The EDS mapping images of CPM nanocomposite was presented in Fig. 2.9 (a-b). The distinctive elemental distribution was shown in Fig.2.9 (c-f), indicating the presence of elements C, N, O and Cu in the composite matrix.

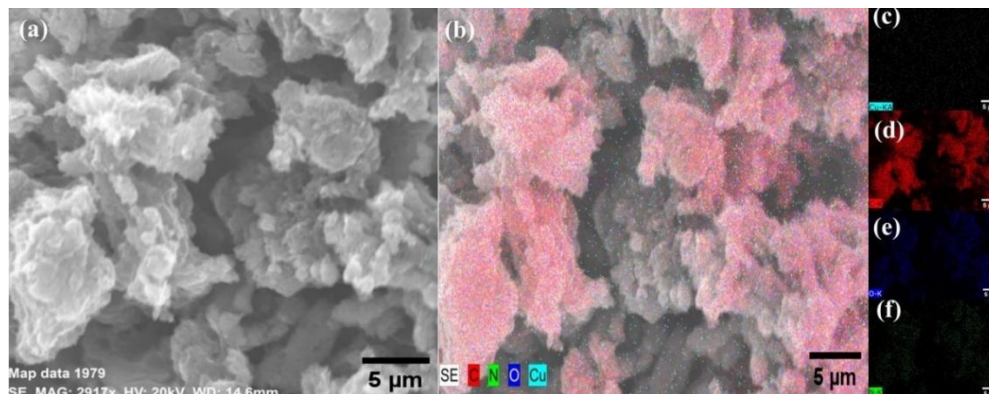


Fig. 2.9 (a) SEM and (b) EDS mapping images of CPM nanocomposites, (c-f) elemental distribution of C, N, O and Cu in the area shown in images (a & b).

2.3.5. High Resolution Transmission electron micrographs (HR-TEM)

In conjunction with FESEM analysis, the morphology of pristine CuO was more inspected using HRTEM imaging techniques, as presented in Fig. 2.10. Fig. 2.10 (a-b) shows the HRTEM image of CuO with their corresponding SAED pattern. The SAED patterns discerned to the fact that the prepared samples were in monoclinic phase of copper oxide, which is in good accordance with the inferences from XRD. Almost all the prominent peaks of monoclinic CuO symmetry can be well indexed to the rings observed in SAED plot. The lattice resolved TEM images in Fig. 2.10 (c-f) presents the planes (-111), (111), (110), and (-202) with their measured d-spacing values 0.253 nm, 0.235 nm, 0.272 nm, and 0.185 nm respectively. These calculated d-spacing outcomes were satisfactory with those in the SAED pattern. Besides, lattice resolved TEM image of plane (111) with d value 0.232 nm and its corresponding profile plot image were illustrated in Fig. 2.10 (g-h). From the aforementioned experimental analysis including XRD, HRTEM, SAED, FFT and profile plot, d-spacing value for the dominant plane (111) were compared and presented in Table 2.3.

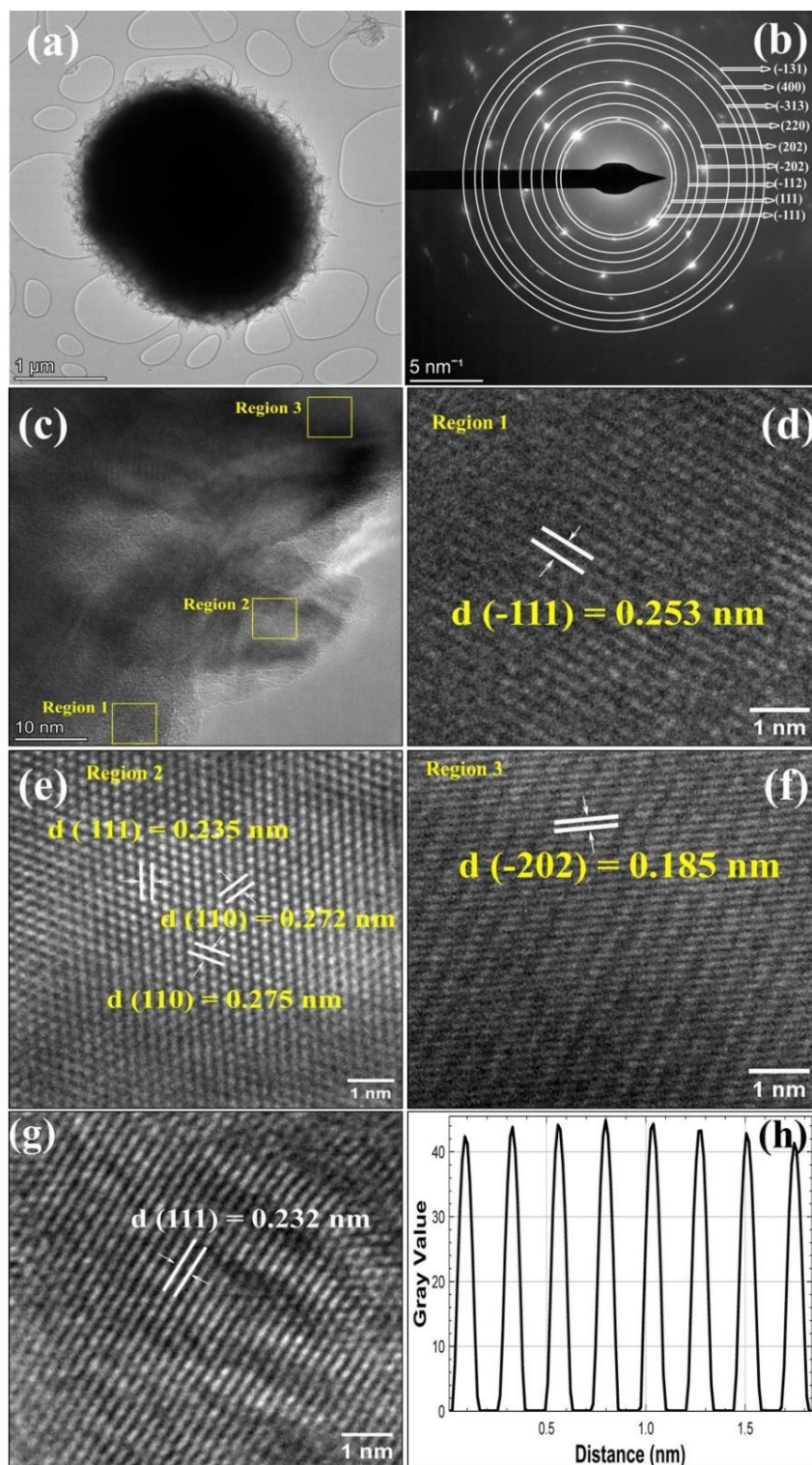


Fig. 2.10 (a) TEM images of CuO nanostructures (b) selected area diffraction patterns of CuO (c-f) lattice resolved HRTEM images of CuO (g-h) lattice resolved HRTEM image of plane (111) and its corresponding profile plot.

Table 2.3. Comparison of d-spacing values of crystal plane (111).

Plane	d_{XRD} (nm)	d_{SAED} (nm)	d_{HRTEM} (nm)	d_{FFT} (nm)	$d_{\text{profile plot}}$ (nm)
(111)	0.232	0.238	0.232	0.23	0.229

The microstructural features of CuO/PANI/MWCNT were further examined by TEM, HR-TEM and SAED images shown in Fig. 2.11. The TEM image of CPM (shown in Fig. 2.11 (a)), presents a fibrous framework of all the constituents as similar as in the FESEM images. The MWCNT network shown in the HR-TEM image, displayed in Fig. 2.11 (b), possess an average diameter of 8-10 nm. Lattice fringes of CPM composite was clearly presented in Fig. 2.11 (c), consist of fringes having d-spacing value of about 0.252 nm attributed to the (111) plane of CuO. The SAED pattern of nanocomposite (Fig. 2.11 (d)) displays brighter concentric rings that correspond to the polycrystalline nature of CPM composite.

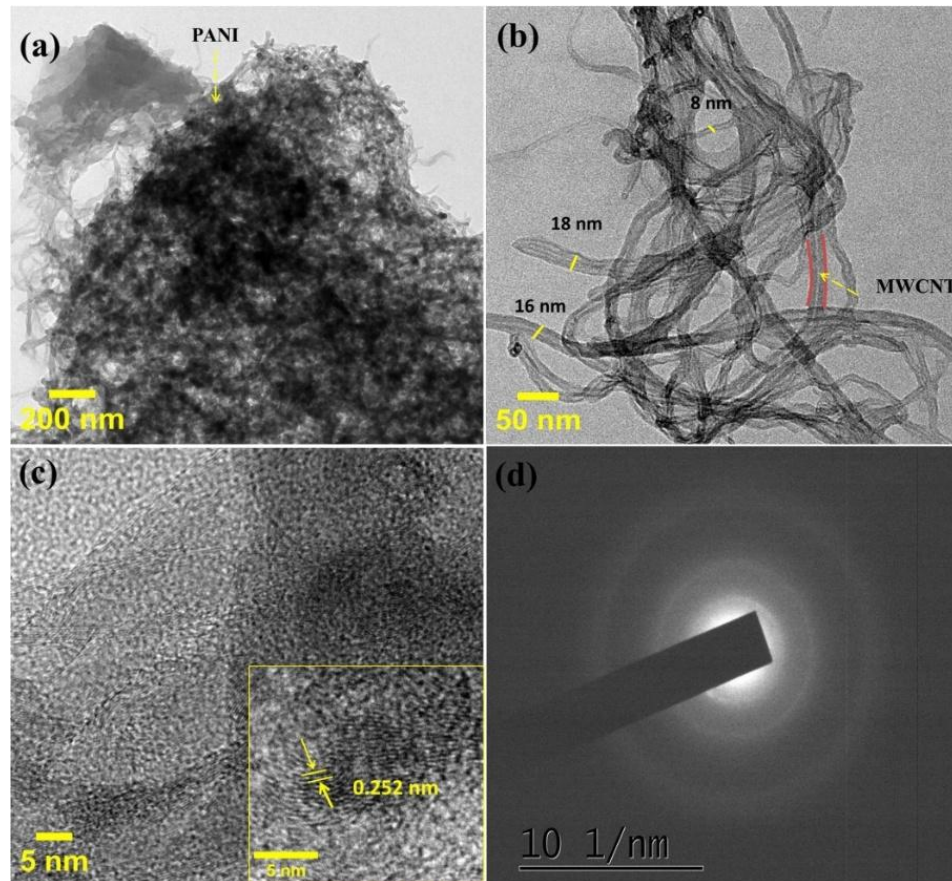


Fig. 2.11 (a) TEM images (b) HR-TEM images (c) lattice resolved HRTEM images (inset shows the lattice fringes of (111) plane of CuO) (d) selected area diffraction patterns of CPM nanocomposite.

2.3.6. X-Ray Photoelectron Spectroscopy (XPS)

The XPS analysis of pure CuO and CuO/PANI/MWCNT composite were conducted to examine the chemical composition, oxidation states and chemical states of the material. Fig. 2.12 (a) shows the XPS survey of CuO with characteristic peaks of Cu 2p and O 1s. Fig 2.12 (b-c) presents the high resolution spectra of elements Cu and O. The peaks observed at 933.8 eV and 953.5 eV (Fig 2.12 (b)) correspond to the Cu 2p_{3/2} and Cu 2p_{1/2} states of Cu²⁺ in CuO nanostructure. A spin energy separation of 19.7 eV was observed between the states [37]. Moreover, the three satellite peaks spotted at 941.3 eV, 943.6 eV and 962.5 eV were also detected, which confirms the formation of the CuO nanostructures. In the elemental XPS spectrum of O 1s (Fig. 2.12 (c)), a peak at 529.7 eV can be attributed to the Cu-O bond. Furthermore, the peak at 531.2 eV corresponds to the oxygen vacancies (V_o) present in the lattice [78].

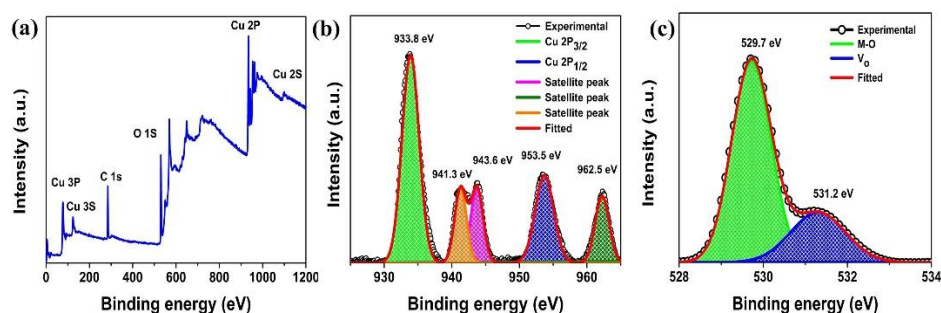


Fig. 2.12. (a) XPS survey spectrum and XPS elemental spectra of (b) Cu 2p and (c) O 1s in CuO nanostructures.

The survey scan of CuO/PANI/MWCNT was presented in Fig. 2.13 (a), having characteristic peaks of Cu 2p, O 1s, C 1s, and N 1s, which confirm the elemental blend of CuO with PANI and MWCNT. The peaks located at 284.3 eV, 285.1 eV and 287.4 eV of the C 1s core level spectrum shown in Fig. 2.13 (b) can be attributed to Sp² carbon bonding, Sp³ carbon bonding and >C=O- bond of C 1s state [79]. The XPS spectra of N 1s displayed in Fig. 2.13 (c), presents three prominent peaks at 399 eV, 400.1 eV and 401.6 eV representing benzenoid imine (=N-H-), positively charged imine (-N-H-), and protonated amine (-N-H⁺-) of PANI [80]. The high-intense notable peaks of benzenoid imine and -N-H- bond indicate the occurrence of healthy interactions between PANI and MWCNT. In Fig. 2.13 (d), the major peaks of Cu²⁺ states were located at 933.6 eV and 953.5 eV representing Cu 2p_{3/2} and Cu 2p_{1/2}. The energy gap of 19.9 eV between these spin energy coupling orbits confirms the presence

of Cu^{2+} , thereby the occurrence of CuO form in the ternary composite. Along with this, two shake-up peaks were also observed at 943.3 eV and 963.2 eV [49]. In the case of O1s in CPM composites (Fig. 2.13 (e)), peaks were observed at 531.5 eV and 532.5 eV, correspond to oxygen vacancies and M-OH bonds, respectively [78].

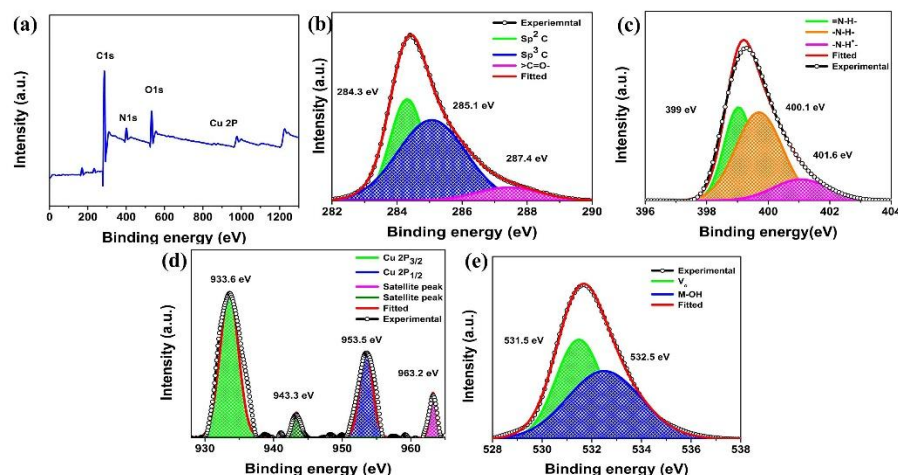


Fig. 2.13. (a) XPS survey spectrum and XPS elemental spectra of (b) C 1S, (c) N 1S (d) Cu 2P (e) O 1s of CPM nanocomposite.

2.3.7. Brunauer-Emmett-Teller (BET) analysis

Figure 2.14 (a-b) shows the N_2 adsorption-desorption isotherm plot and pore size distribution (PSD) of CuO nanostructures. The Brunauer-Emmett-Teller (BET) method was carried out for the tabulation of specific surface area and Barrett-Joyner-Halenda (BJH) equation was employed for the PSD calculations. The BET specific surface area of the CuO product was estimated as $\sim 29.29 \text{ m}^2/\text{g}$. The plateau region in the isotherm plot relates to the monolayer coverage of surface area, whereas the steep portion gives details about the initial level of adsorption and surface accessibility [38]. The plot indicates that the adsorption isotherm of CuO is type IV with H3 hysteresis according to IUPAC classification, which commonly occurs in mesoporous materials. The results show that the sample material has a network of interconnected pores having pore diameters in the domain of 2-50 nm. The PSD of CuO nanostructures in the Fig. 2.14 (b) confirm the mesoporous nature with an average pore volume and diameter of $\sim 0.097 \text{ cm}^3/\text{g}$ and 12.89 nm respectively. The PSD maxima of the sample centered at two different pore radii, which are $\sim 1.26 \text{ nm}$ and $\sim 5.62 \text{ nm}$. Here, the nanopetal like CuO particles interconnected unevenly to create tiny pores in between to form the microflower architecture. This type of surface morphology with sufficient surface area

and well-developed pore structures are commendably compliments the electrochemical performance of the prepared product since the pore channels can themselves act as a clear route for the active electrolyte transport and boosts the electrochemical reactions by providing more and more active sites. The N₂ adsorption-desorption isotherm plot and pore size distribution (PSD) of CuO/PANI/MWCNT composite were shown in Fig. 2.14 (c-d). The average specific surface area of the composite was $\sim 48 \text{ m}^2/\text{g}$. The plot indicates that the adsorption isotherm of the composite is also type IV with H3 hysteresis. The results show that the composite material has a network of interconnected pores having pore diameter in the domain of 2-50 nm. The PSD of composite material shown in the Fig. 2.14 (d) confirms the mesoporous nature with an average pore volume and diameter of $\sim 0.33 \text{ cm}^3/\text{g}$ and 8.7 nm respectively. The moderate increase of surface area of the composite material, despite the intrinsically high surface area of MWCNTs, may due to the encapsulation of metal oxides and PANI over the surface of nanotubes of MWCNTs. As evidenced by SEM and TEM observations, this coating can partially block the accessible pores of composite material and eventually limits the contribution of MWCNTs to the effective BET surface area.

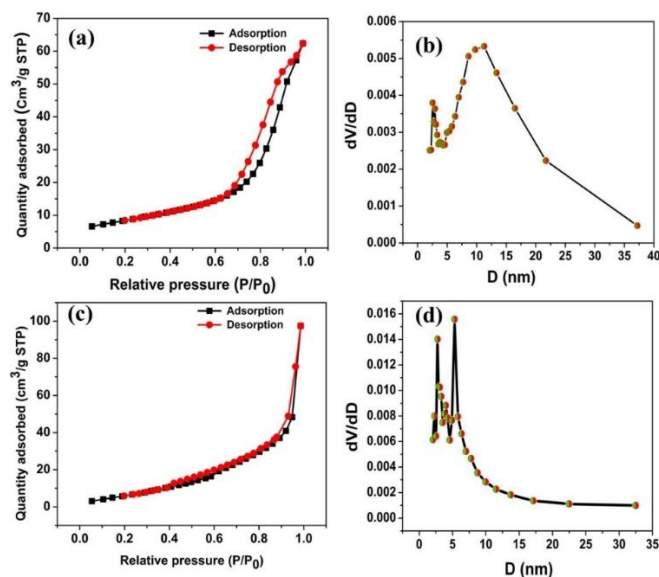


Fig. 2.14. N₂ adsorption-desorption isotherm plot and the pore size distribution graph of (a,b) CuO (c,d) CPM composite.

2.3.8. Thermo-gravimetric Analysis (TGA)

Thermal stability of electrode material is an indispensable quality for attaining authentic supercapacitors [81]. The thermal stability of synthesised materials was

investigated through TGA-DTA analysis, presented in Fig. 2. 15. The reasonable thermal stability of CuO and MWCNTs were evident from the plot, since the total weight loss are only 7.18% and 6.19% for CuO and MWCNTs over 700 °C, respectively. The TGA curves of PANI and CuO/PANI/MWCNT show three step decomposition process. From the room temperature to 150 °C, both PANI and CPM samples suffers a weight loss of about 12 %, which is accounted for the loss of moisture from the materials [82]. The second stage of decomposition phase starts from a temperature of 150 °C to 340 °C, a weight loss of about 38% for PANI and 35 % for CPM happened due to elimination of acid components (HCl) and the initial thermal decomposition of PANI in to its monomer, oligomer, dimer, and trimmer forms. In the third and most significant stage of decomposition, the real breakdown of PANI happens and suffers a weight loss of 12% for CPM and 19% for PANI until the temperature 530 °C, attributable to thermal decomposition of oligomer, dimers, and trimmer forms of PANI [83]. At 700 °C, a residue mass of PANI and CPM were estimated to be 35.82 % and 28.25 %, indicating the improved thermal stability of CuO/PANI/MWCNT than that of PANI due to the synergistic effects of CuO and MWCNTs. The strong interactions of thermally resistant CuO with PANI, combined with the mechanical strength of MWCNTs contributes to the effective enrichment in the thermal stability of composite system [84], [85].

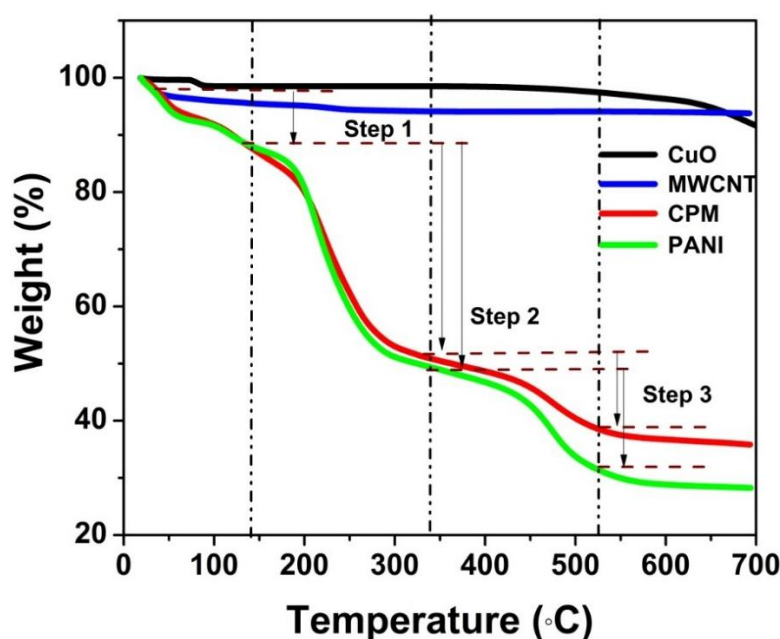


Fig. 2.15. Thermogravimetric analysis of CuO, MWCNT, PANI and CPM composite.

2.3.9. Electrochemical studies

2.3.9.1. Cyclic voltammetry (CV)

The cyclic voltammetry (CV) of as-synthesised materials was established to evaluate the supercapacitive performance and their corresponding potentiality in the energy storage field. Initially, the performance of CuO as working electrode was studied using two different electrolytes – an alkaline electrolyte (5M NaOH) and a non-corrosive neutral electrolyte (1M Na₂SO₄). Fig. 2.16 shows the respective cyclic voltammetric curves of CuO in three electrode configurations with electrolytes- NaOH and Na₂SO₄. The electrochemical performance of CuO with NaOH electrolyte were analysed in voltage window of 0-0.45 V, whereas the same with Na₂SO₄ in a potential range of 0-0.8 V. From the figure, it is evident that the performance with NaOH electrolyte does not produce significant capacitance value compared with that of Na₂SO₄. pH factor has greater influence in the charge transfer mechanisms in the electrochemical set up since it alters the ionic conductivity and mobility of charge carriers [86]. Here, the area under the CV curve produced by the electrode material with alkaline electrolyte is very low compared with that of with the neutral medium, which implies that CuO suffered greater charge transfer resistance with alkaline electrolytes. Hence, further electrochemical studies were executed in Na₂SO₄ electrolyte to get better results.

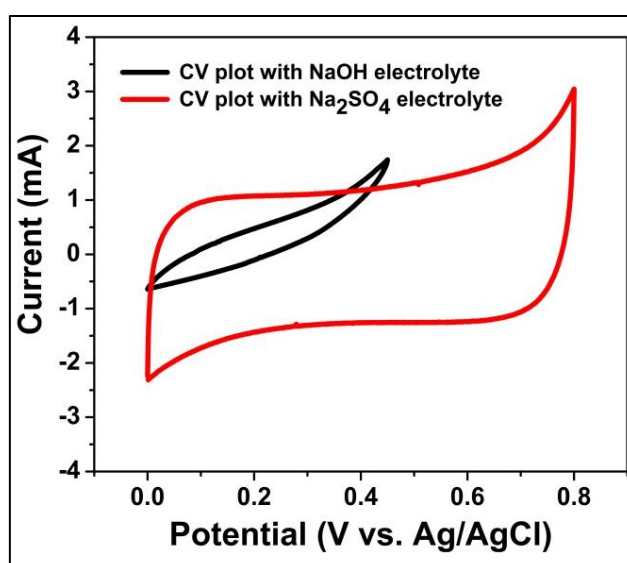


Fig. 2.16. CV curves of CuO electrode with two different electrolytes at 10 mV/s.

The detailed electrochemical measurements of electrode materials were carried out in a three-electrode configuration using 1M Na₂SO₄ as electrolyte solution. Fig. 2.17 depicts the cyclic voltammetry graph of CuO and CuO/PANI/MWCNT electrodes at distinct scan rates from 5-100 mV/s in a voltage window of 0 - 0.8 V. Unsurprisingly, the voltametric current was increasing with the scan rate which is a key feature of an ideal capacitor [87].

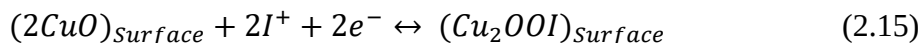
The CV curve of CuO follows a shape seemingly close to an ideal rectangular one without any noticeable redox peaks, whereas that of the composite electrode presents a quasi-rectangular shape. The non-rectangular shape of CV curves clearly indicates that both the materials possess very distinctive capacitive characteristics from that of electric double layer capacitors. The composite sample exhibits a pair of redox peaks at (0.43/0.2 V) at lower scan rates due to the presence of PANI. This redox peak can be attributed to the leucoemeraldine (LE) transition to Emeraldine (E) in PANI samples [88]. There is a redox peak shift while increasing scan rates, which indicates that MWCNTs and PANI enhanced the redox properties of the nanocomposite.

In neutral aqueous electrolytes like Na₂SO₄, there may be two possible charge storage mechanisms occur in the system [13]:

(1) Intercalation and de-intercalation of cations H⁺ or Na⁺ during redox reactions,



(2) Adsorption of ions into the surface of active material.



Where I can be either H⁺ or Na⁺ ions. Here, the quasi-rectangular CV curves of samples shown in Fig. 2.17 points to the process of charge storage through intercalation and de-intercalation of ions in the active materials. Furthermore, shape of a voltametric plot is deeply influenced by the nanostructure of material, its specific surface area and porosity [34]. Unsurprisingly, with the scan rates increase, the area under the CV curves also increases. The direct proportionality of voltametric current with the scan rates is one of fundamental characters of ideal capacitor [89]. At lower scan rates, ionic diffusion process is enriched due to greater access of active pores in electrode material

by the electrolyte ions complimenting the insertion process of protons, which eventually enhances the redox reactions [90].

The CuO working electrode showed a specific capacitance of 123 F/g at a scan rate of 10 mV/s and 47 F/g at a scan rate of 100 mV/s. The CuO/PANI/MWCNT nanocomposite delivered a capacitance value of 478 F/g at 10 mV/s and 106 F/g at 100 mV/s. Higher value C_s at lower scan rates (< 30 mV/s) is the indication of maximum use of active surface area by the ions for charge storage occurred at lower scan rates [91]. From the comparison of CV curves of CuO and the composite electrode materials (Fig. 2.17 (c)), it can be seen that there is an effective increase of voltametric current in the case of nanocomposite material compared with pure CuO. The increase in current indicates the better utilisation of electrode material through effective ionic diffusion, as a consequence of the enhanced surface area and porosity of nanocomposite. In addition to large surface area, occurrence of uniform and stable pore structure also makes remarkable advantage in its electrochemical properties. The pore network present in CuO/PANI/MWCNT allows smooth mass transport of ionic or electronic charge carriers and also raises the accessibility of electrode material to the electrolyte medium. Generally, in the case of mesoporous materials, the effect of large number accessible electro-active areas is directly correlated with its capacitive currents [92].

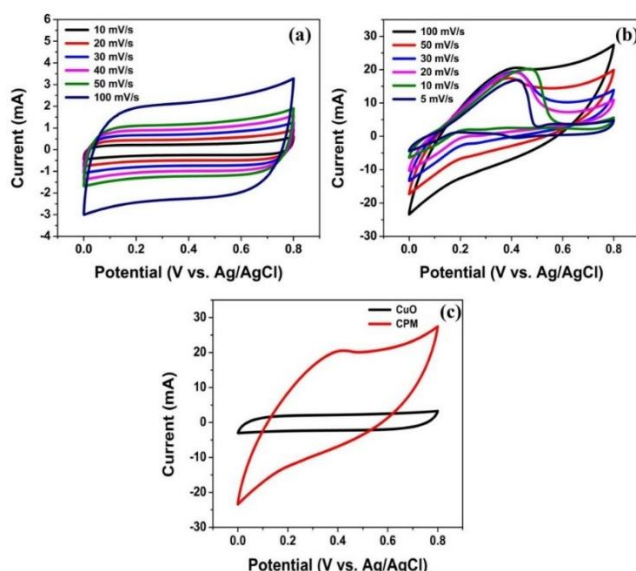


Fig. 2.17. CV plot of (a) CuO electrode and (b) CPM composite electrode at varying scan rates, (c) comparison of CV cure of CuO and CPM at a scan rate of 100 mV/s.

Equations (2.6-2.11) were utilised to figure out the capacitive and diffusion-controlled contributions, which are separate and actively present at each potential, involve in the total current production during the electrochemical reactions. Fig. 2.18 deals with the charge storage mechanism analysis of pristine CuO using power law and Dunn's method. The plot between scan rate and peak current at a specific potential 0.4 V, as shown in Fig. 2.18 (a), shows the linearity in the fitted data with a value of slope approaching to one. Thus, the dominance of capacitive contribution in the overall charge storage mechanism is confirmed. This capacitive contribution mainly arises from the surface-controlled redox reactions results in faster reaction kinetics. The surface-controlled pseudocapacitance can lead to efficient and reliable energy storage capacities with remarkable cyclic performances [93]. The $v^{1/2}$ vs. $i/v^{1/2}$ plot helps to estimate values of k_1 and k_2 , thereby distinguishing between the capacitive and diffusive controlled contributions in percentage (Fig. 2.18 (b)). The calculated values of k_1 and k_2 are 3.01 and -2.95, respectively. The analysis indicated that the surface-controlled redox reactions were 85 % for the CuO working electrode at 10 mV/s (Fig. 2.18 (c)). The shaded region shows the diffusion-controlled contribution in the storage mechanism at lower scan rate. It is noticeable that with the increasing scan rates, the diffusion part contribution gets diminished and recorded as 2 % at 100 mV/s (Fig. 2.18 (d)), can be attributed that the time at the higher scan rates were enough to occur the diffusion/intercalation of electrolyte ions [94].

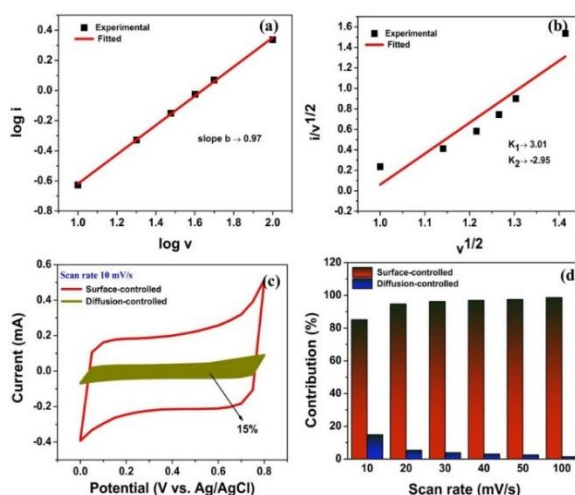


Fig. 2.18 (a) scan rate vs. peak current plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ diagram (c) decoupling of diffusion and capacitive contribution in CuO working electrode at scan rate 10 mV/s (d) capacity contribution analysis of CuO at varying scan rates.

The diffusive and capacitive contributions in the CPM working electrode were evaluated using power law and Dunn's method, were portrayed in Fig. 2.19. The linear plot between scan rate and peak current 0.4 V was observed in the Fig. 2.19 (a), suggesting a slope of 0.66. This indicates the importance of both capacitive and diffusive contributions in the overall charge storage, with slighter major part from the surface-controlled redox reactions since the value of b higher than five. The values of parameters k_1 and k_2 were found to be 2.130 and -15.58, respectively estimated from the plot between $v^{1/2}$ and $i/v^{1/2}$ (Fig. 2.19 (b)). Using these parameters the capacitive and diffusive contributions in the CPM working electrode were distinguished and presented in Fig. 2.19 (c). The shaded region indicates the diffusive contribution as 13 % at a scan rate of 10 mV/s. Just like CuO, CPM electrode also shows a decline of diffusive contribution part with increasing scan rates (Fig. 2.19 (d)).

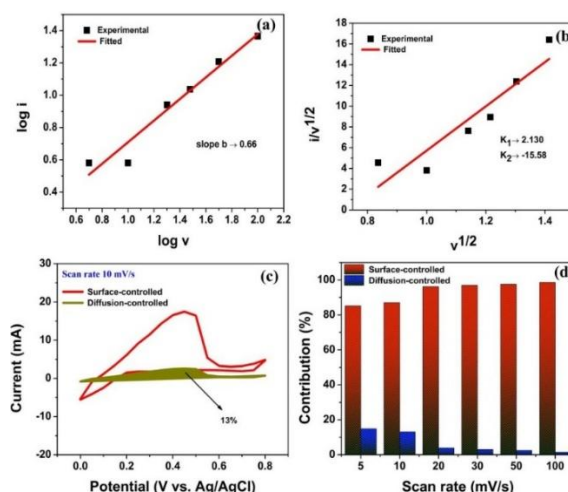


Fig. 2.19 (a) scan rate vs. peak current plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ diagram (c) decoupling of diffusion and capacitive contribution in CPM working electrode at scan rate 10 mV/s (d) capacity contribution analysis of CPM composite at varying scan rates.

2.3.9.2. Galvanostatic charge/discharge (GCD) studies

The electrochemical performance of CuO and CuO/PANI/MWCNT electrodes was then determined with constant galvanostatic charge/discharge (GCD) measurements at discrete current densities, which is shown in Fig. 2.20 (a,b). The GCD curves show good symmetry having nearly ideal triangular shapes at all current densities, which exemplifies the notable capacitive response of both electrode materials for supercapacitor applications [35]. A small voltage drop was visible in the discharge

curves of composite sample, possibly due to the internal resistance of the electrode material. Additionally, PANI based electrode materials have visible influence on this IR drop [95]. The higher discharge time of the composite electrode in comparison with pure CuO, indicating the enhanced electrochemical behaviour. The calculated values of specific capacitance are plotted in the Fig. 2.20 (c,d). At current densities of 0.3 A/g, 0.5 A/g, 2 A/g and 3 A/g, CuO electrode obtained capacitance values of 141 F/g, 94 F/g, 70 F/g, and 67 F/g respectively. Whereas, the composite electrode obtained capacitance values of 516 F/g, 259 F/g, 113 F/g, and 20 F/g at current densities 0.5 A/g, 1 A/g, 3 A/g and 5 A/g, respectively. The sharp decline of specific capacitance values at higher current densities may due to the ineffective utilization of deeper active sites, as ions lack sufficient time to diffuse and transport under rapid cycling conditions. In addition, the major two elements in the composite material, that is CuO and PANI, were pseudocapacitive and inherently have slow charge storage mechanism compared to double-layer charging, which limits the rate capacity of composite electrode. This improved specific capacitance of composite sample is the result of combined features of metal oxide, PANI and MWCNT, owing to the fact that PANI and MWCNT framework together provides a conductive pathway in the overall electrochemical process. The efficient and uniform growth of PANI over the surface of CuO and the sufficient supply of electro-active sites by MWCNT were positively enriched the electrochemical behaviour of the ternary composite electrode. Although the capacitance value of electrode material gets improved by the incorporation of PANI and MWCNT, it is still less compared to the theoretical capacitance of CuO, likely due to the presence of electrochemically inactive “dead mass”. The structural instability of PANI, which undergoes swelling and contraction during cycling may cause obstacles to the ionic transport and reduces the active participation of electrode material. Furthermore, the interfacial resistance created in hybrid material combined with their relatively thicker composite layers restricts deeper penetration of electrolyte ions into the active sites of CuO.

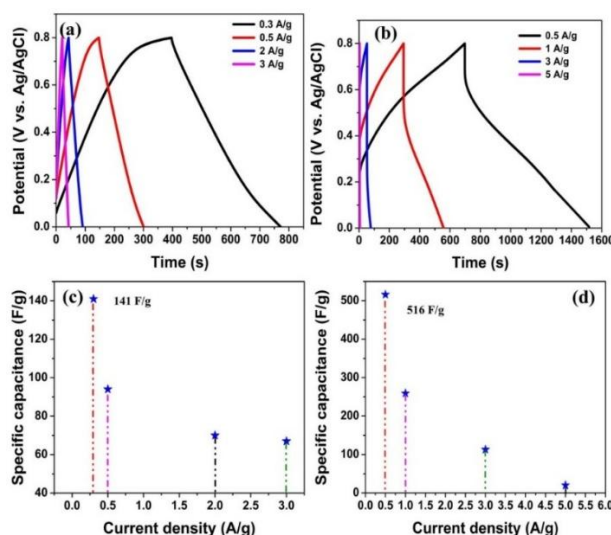


Fig. 2.20. GCD graph of (a) CuO electrode and (b) CPM composite electrode at varying current densities, variation of specific capacitance with current density for (c) CuO and (d) CPM electrodes.

2.3.9.3. Electrochemical impedance spectroscopy (EIS)

The EIS study of the CuO and CPM electrodes, in terms of the Nyquist diagram, was conducted in the frequency window of 100 kHz to 100 mHz with an AC voltage of 10 mV to investigate the complex interfacial electronic features at the electrode-electrolyte juncture, which was illustrated in Fig. 2.21 (a). Unsurprisingly, the Nyquist plot presents a distorted semicircle in the higher frequency region tailed by a straight spike in the lower frequency side. The depressed semicircle is a clear indication of redox reactions taken place between Cu^{2+} and Cu^+ . The supercapacitive behaviour of CuO electrode is evidently seen from the sharp increase of imaginary part of impedance in the lower frequency side. The EIS data of both electrodes were fitted with the help of EIS spectrum analyser software, shown in Fig. 2.21 (b,c) and the corresponding equivalent Randles circuit is presented in the inset of Fig. 2.21 (b,c). The circuit formed by the combination of components corresponds to solution resistance (R_s), charge-transfer resistance (R_{ct}), Warburg resistance (Z_w), and constant phase element (CPE). Z_w referred to the impedance during the mass transport of redox species to the electrode surface. R_{ct} related to the kinetics of the electrochemical system assuming that the redox species are not getting absorbed to the surface of electrode and it determines the amount of resistance suffered by the electrons flow at the electrode/electrolyte intersection. The CPE value specify the low-frequency pseudo-capacitance and double layer capacitance

[96]. The value of solution resistance is revealed from the initial intercept value of semi-circle curve to the real axis, whereas the R_{ct} values are interpreted from the impedance arc diameter. The EIS analyser software was used to evaluate values for R_s , R_{ct} , CPE, and n of CuO and CuO/PANI/MWCNT electrodes, which are tabularized in table 2.4. Lower values of R_s and R_{ct} of the composite electrode point out the improved ionic conduction and electrolyte diffusion throughout the configuration, which eventually announces the better electrochemical properties of the composite material.

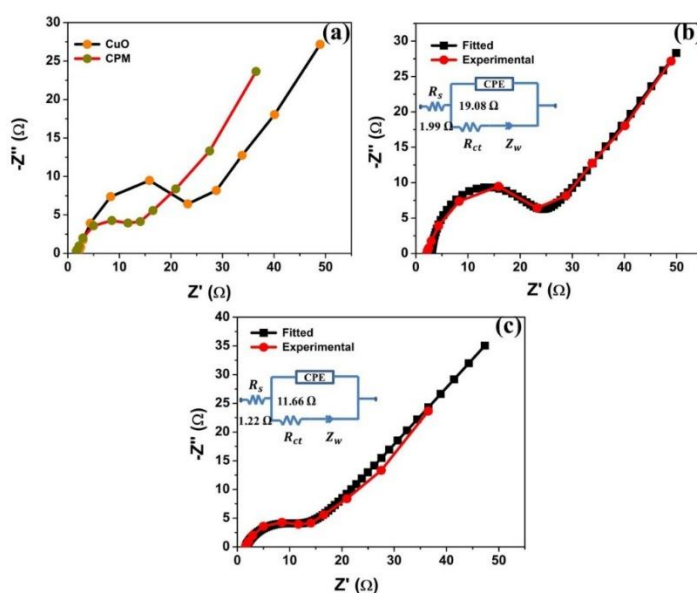


Fig. 2.21. Nyquist plot of (a) CuO and CPM electrodes, best fitted Nyquist plot of (b) CuO and (c) CPM (insets shows the equivalent electric circuit of fitted plot).

Table 2.4. Equivalent Randles circuit fitted data from the EIS study.

Sample	R_s (Ω)	R_{ct} (Ω)	W	CPE	n
CuO	1.99	19.08	22.75	0.00057	0.943
CPM	1.22	11.66	33.72	0.00049	0.688

2.3.9.4. Cycle stability

The cycle stability of CuO and CPM electrodes for 5000 cycles was explored in three-electrode configuration for current density of 3 A/g and displayed in Fig. 2.22. CuO shows a gradual increase of specific capacitance in the initial cycles and found to have stable capacitance retention of 97% after 1200 cycles. In the case of CPM, after

the initial 5 cycles the electrode shows excellent capacitance retention of 95 % over 5000 cycles. The initial increment in capacitance may be ascribed to the activation period for the electrodes [97]. Even though, the capacitive retention efficiency of the composite electrode is little bit less than that of pure CuO, the graph itself shows that CPM material presents much better stability over 5000 charge/discharge cycles without any deviations from the capacitance value in each cycle. The high capacitance retention of prepared electrodes hints that the materials do not undergo any surface structural deformations even after 5000 continuous charge-discharge cycles.

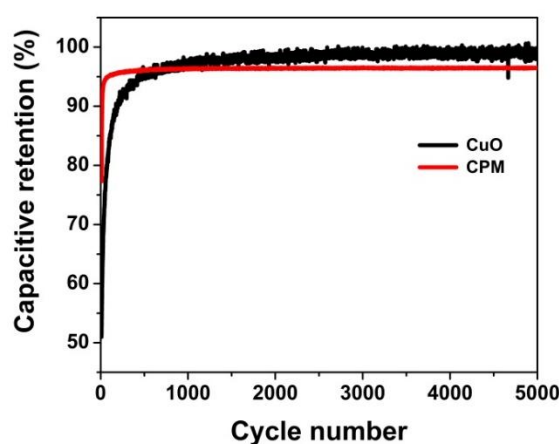


Fig. 2.22. Cycling life test of CuO and CPM electrodes for 5000 cycles at a current density of 3 A/g.

2.3.9.5. Electrochemical performance of CuO and CuO/PANI/MWCNT ternary nanocomposite in symmetric two-electrode configuration

A symmetric supercapacitor device set up with two-electrode configuration was used to test the practical possibilities of CuO and CPM electrode materials. Fig. 2.23 (a) shows the CV curve fabricated device with CuO as the active material for different scan rates. The material presents a quasi-rectangular shaped CV curve similar to that in the three-electrode set up, indicating the pseudocapacitive behaviour of the material. The GCD plots (Fig. 2.23 (b)) showcased a very close triangular shaped charge/discharge graphs with small amount of IR drop for all the current densities. The material exhibited a specific capacitance of 83 F/g at 0.5 A/g, 56 F/g at 0.8 A/g, 52 F/g at 1 A/g, and 25 F/g at 2 A/g (shown in Fig. 2.23 (c)). The coulombic efficiency of CuO working electrode at various current densities were calculated using the equation (2.

12), shown in Fig. 2.23 (d). The material shows relatively better coulombic performance over increasing current densities. The Ragone plot (PD vs. ED curve) of CuO electrode was shown in Fig. 2.23 (e) and made comparison with the standard Ragone plot [4]. The CuO electrode shows a maximum energy density of 7.37 Wh/Kg and power density of ~ 402 W/Kg. The sample exhibited relatively better energy density and power density compared with the conventional batteries, which indicates the utilization of as-synthesised CuO material for electrode fabrication in electrochemical systems are very promising. The capacitance retention of CuO-based device was evaluated for 50000 charge/discharge cycles at a discharge current of 10 mA is shown in Fig. 2.23 (f). The material shows high retention efficiency of about 99% over 50000 cycles, but the overall stability of capacitance was diminished after 20000 cycles. As the cycle number increases, material suffers some kind of capacitance deviation in each cycle.

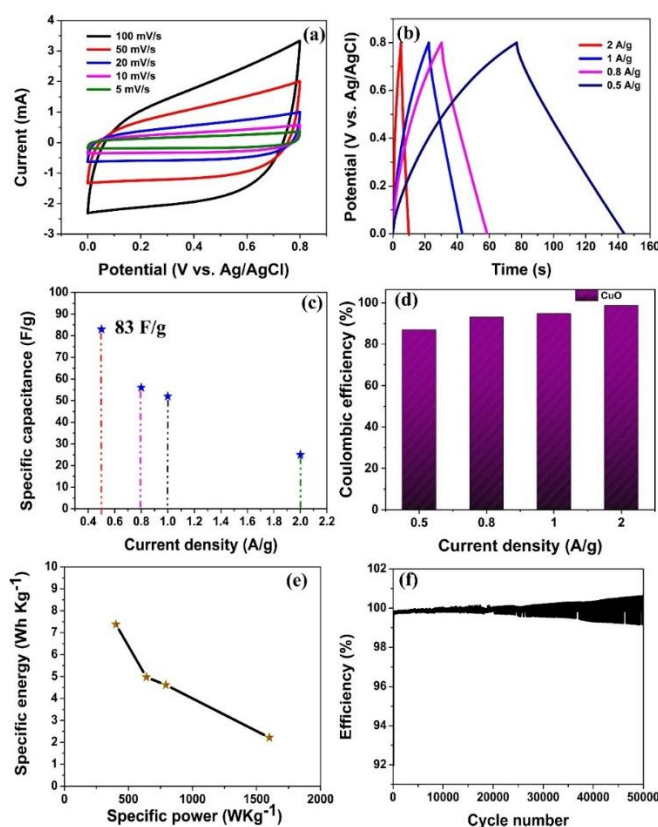


Fig. 2.23 (a) CV (b) GCD plots of CuO composite in two electrode configuration (c) calculated specific capacitance from GCD (d) Ragone plot (e) coulombic efficiency analysis and (f) cycle stability of CuO composite in 50000 cycles.

The device performance of symmetric supercapacitor with CPM nanocomposite as working electrode in a two-electrode configuration was systematically investigated, was depicted in Fig. 2.24. The CV profiles of CPM composite displayed quasi-rectangular shape with a pair of distinct redox peaks at potentials (0.2V, 0.42V), reflecting the contributions from PANI (Fig. 2.24(a)). The redox peaks get shifted to (0.32 V, 0.53 V) as the scan rate increases to 100 mV/s, which reveals the kinetic influences in the electrochemical performances. The GCD analysis, shown in Fig. 2.24 (b), indicates the nearly triangular shape for all the charge-discharge curves at varying current densities. The specific capacitance value of CPM working electrode estimated from GCD data was portrayed in Fig. 2.24 (c), showing a specific capacitance value of 115 F/g at a current density of 1 A/g. The coulombic efficiency of CPM electrode at various current densities were evaluated and displayed in Fig. 2.24 (d). The device showed reasonable coulombic efficiency values at all current densities. Fig. 2.24 (e) shows the energy-power characteristic of device using Ragone plot, highlighting a specific energy of CPM composite of about 10.22 Wh/Kg at a specific power of 866 W/Kg. Moreover, the maximum power density of composite electrode is found to be 4788 W/Kg at an energy density of 1.5 Wh/Kg. The capacitance retention of CPM-based device was evaluated for 50000 charge/discharge cycles at a discharge current of 15 mA is shown in Fig. 2.24 (f). The material shows retention efficiency of about 87.8% over 50000 cycles which is found to be lower than that of pristine CuO, but the overall stability of capacitance surpasses that of CuO. The CPM electrode showed relatively consistent efficiency over 50000 cycles without any degradation over the repeated charge-discharge cycles.

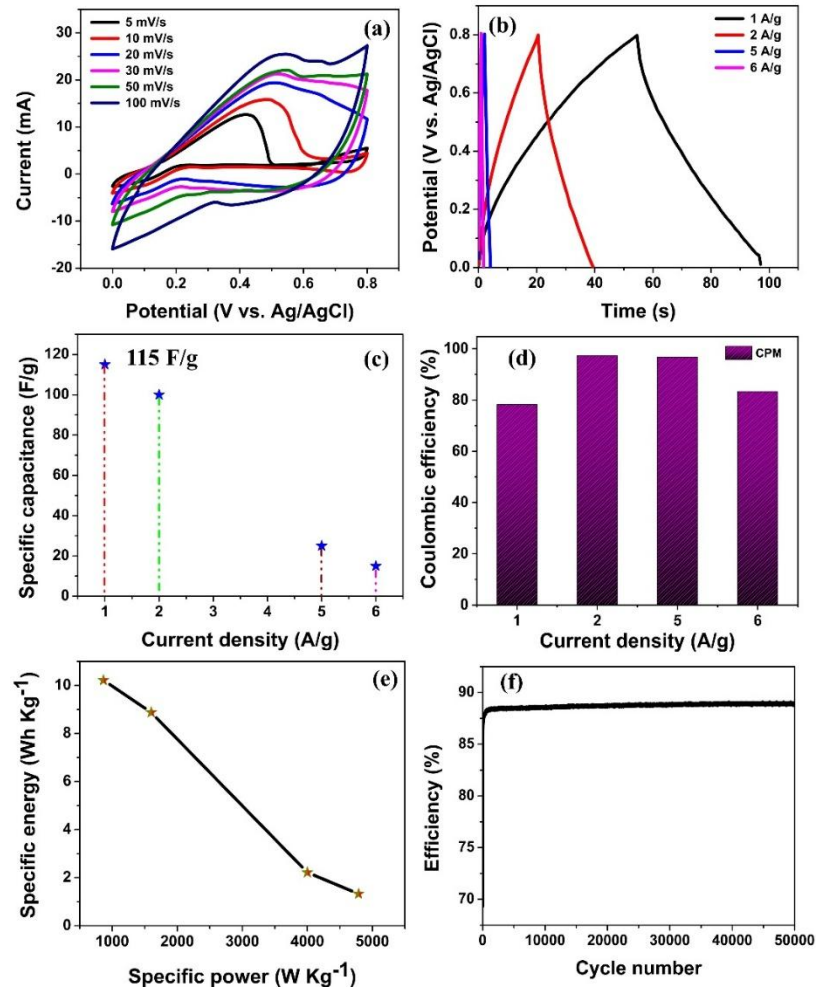


Fig. 2.24 (a) CV (b) GCD plots of CPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) Ragone plot (e) coulombic efficiency analysis and (f) cycle stability of CPM composite in 50000 cycles.

2.4. CONCLUSION

In this work, pristine CuO and CuO/PANI/MWCNT nanocomposites were fabricated by facile hydrothermal and freeze drying assisted in-situ polymerisation methods, respectively. Structural, morphological, thermal stability and optical features of both CuO and composite samples were evaluated using XRD, FT-IR, Raman, FESEM-EDS, HRTEM, XPS, BET and TGA. The electrochemical performance of pure CuO and ternary composite electrodes were analysed using both three and two- electrode configurations. The ternary composite attained a commendable supercapacitor performance, characterised with a specific capacitance of 516 F/g at 0.5 A/g. This improved specific capacitance of composite sample is the result of combined features of metal oxide, PANI and MWCNT, owing to the fact that PANI and MWCNT framework together provides a conductive pathway in the overall electrochemical process. The highly conductive polymer PANI improved the stability of the ternary nanocomposite by providing a good adhesion between CuO and MWCNT, without compromising the overall electrochemical behaviour, owing to the combined synergistic effects of all components in the composite.

Table 2.5. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CuO	123	10	94	0.5	64	10	83	1
CPM	478	10	516	0.5	102	10	115	1

2.5. REFERENCES

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Synthesis, Characterization, and Supercapacitive Performance of CuO-NiO/PANI/MWCNT Hybrid System

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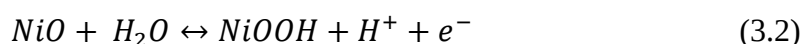
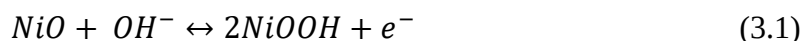
Transitional metal oxides exhibiting diverse oxidation states have been entrenched for their pseudocapacitive nature, enabling their higher specific capacitance values in light of proficient redox reactions. However, the poor intrinsic electric conductivity, lower cationic-anionic diffusion and lesser stability of TMOs limit its specific capacitance value far from its actual theoretical values. These inherent problems associated with TMOs pave the way of incorporating one TMO with another TMO to create an efficient electro-active hybrid nanocomposite system. The composite electrodes fabricated with the appropriate choice of materials can overcome the entire shortcomings inherited by their constituent materials with the help of the combined synergetic effects. Herein, one of the most sought-after metal oxides, NiO was selected as the supportive transition metal oxide and has been introduced in to the CuO/PANI/MWCNT ternary system via in-situ polymerisation for the better electrochemical performance. This quaternary hybrid system is composed of two electrochemically vibrant metal oxides (CuO and NiO) backed by the inevitable collaborator MWCNT as a source of ample electrochemically active contact area as well as stronger electrical conductor, blended with PANI as a productive stability enhancer. The structural, morphological and optical interpretations of this quaternary nanocomposite system were discussed with the help of XRD, RAMAN spectroscopy, FESEM-EDS, HRTEM, XPS, BET and TGA analyses. The electrochemical performance of the proposed hybrid system was evaluated in detail.

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3.1. INTRODUCTION

Nonetheless, commercial SCs predominantly rely on high power nanoporous carbon-based materials and usually deliver lower energy density compared with batteries. The electrode material is the most important factor which greatly influences the electrochemical performance of the supercapacitor. The electrochemically active sites on the electrode surface greatly influence the supercapacitor performance, which ultimately raise the substantial interest of mesoporous materials in this field. Transitional metal oxides (TMOs), commonly mesoporous in nature, range from single metal oxides to quaternary metal oxides and have been a research hotspot in recent years due to their fast and plentiful faradic redox reactions, which eventually compliment their commendable specific capacitance and energy density [1], [2].

Accordingly, a perfect choice of electrode material can be formed by an excellent blend of three important groups of electrode material such as carbonaceous compounds, transitional metal oxides (TMOs)/ hydroxides, and conducting polymers. From this perceptive, we have already combined MWCNT as a source of carbonaceous compound with the metal oxide CuO and PANI as a conducting polymer. Apart from these, a recent trend for further improvement of the electrochemical performance of CuO, is preparing electroactive hybrid materials of CuO with other TMOs such as MnO₂, ZnO, NiO, TiO₂ and Co₃O₄ for the electrochemical studies [3], [4], [5], [6], [7]. Among these, NiO is one of the popular TMO candidates in the field of SCs with peculiar properties like environmental friendliness, non-toxic nature and high theoretical capacitance (~ 2584 F/g) [8]. NiO offers more commercial advantages over other TMOs, because their cost-effectiveness and ease of preparation. Nevertheless, NiO possess exceptional electrical conductivity and electrochemical activity, which supplements its performance in the field of supercapacitors. Moreover, lattice of NiO contributes more electrochemical active sites in NiO-based nanocomposites, which eventually improves the charge transfer strength of electrode material [9]. The two possible charge storage mechanisms followed in a NiO based electrode material can be described as follows;



Accordingly, it is assumed that a productive combination of CuO with NiO will be a worthy tactic, which can improve its electrochemical performances by providing high specific surface area and electrical conductivity [6], [10]. Thus, the fruitful formation of CuO-NiO nanocomposite results in improved specific capacitance and long-term cyclic stability compared with individual metal oxides, making it a viable electrode material for SC applications. Moreover, this highly porous nanostructured electro-active TMO hybrid system can be well-supported by a solid electric conductor having a better surface area such as MWCNT and a stability enhancer like PANI. PANI will make a better adhesion of TMOs combo with MWCNTs, eventually leading to a stable quaternary nanocomposite for better electrochemical performance of electrode material. Thus, the CuO-NiO/PANI/MWCNT quaternary nanocomposite hybrid system can be effectively used as exceptional electrode material in the area of supercapacitor.

3.1.1. NiO-based supercapacitors- An overview

Among the popular TMOs like ruthenium oxide, iron oxide, zinc oxide, magnesium oxide etc., NiO is one of the cost-effective promising electrode candidates in the supercapacitor world. The high theoretical capacitance, thermal stability, low toxicity and apparently large pseudo-capacitive nature of NiO material made them a viable member in the category of efficient electrode materials [11]. The surface morphology and active surface area have a positive role in the electrochemical performance of NiO. Sumanta Kumar Meher *et al.* fabricated a pine-cone nanostructured NiO powder via a hydrothermally heat-treated precipitation method involving CTAB as a template material. This NiO electrode material exhibited a maximum specific capacitance of 337 F/g at a scan rate of 2 mV/s with capacitive retention of 99% after 100 charge/discharge cycles [12]. Kamantchi Kamaraj Purushothaman *et al.* synthesised nanosheet-assembled NiO microstructure via hydrothermal route and reported a specific capacitance of 989 F/g at scan rate of 3 mV/s with 97% capacitance retention after 1000 charge/discharge cycles [11]. Zeheng Yang *et al.* fabricated multishelled hollow NiO nanospheres by layer-by-layer self-assembly. The double shelled NiO exhibited a surface area of $\sim 92.99 \text{ m}^2/\text{g}$ and delivered a specific

capacitance of 612.5 F/g at a current density of 0.5 A/g [13]. Muhamed Shareef Kolathodi *et al.* synthesised NiO nanofibers via electrospinning technique followed by an annealing stage. They tried an asymmetric supercapacitor device with this NiO nanofibers and reported a gravimetric capacitance of 141 F/g and energy density of 43.75 Wh/kg [14]. Jinping Chen *et al.* reported hydrothermal synthesis of Al-doped NiO nanosheet arrays and exhibited a superior specific capacitance of 2253 ± 105 F/g at 1 A/g [15]. P.E. Saranya *et al.* synthesised pure and Ce-doped NiO via sol-gel method. The Ce-1% doped NiO sample showed a flower-like nanostructure with a surface area of $226.6 \text{ m}^2 \text{ g}^{-1}$ and offered capacitance of 2444 F/g at a scan rate of 5 mV/s, which is three times higher than that of pure NiO [16]. NiO-based binary and ternary nanocomposite electrode materials are also widely used in the supercapacitor field [17], [18], [19]. Shabhe Haider *et al.* tried the synthesis of PANI/NiO/Graphene using the wet chemical polymerisation method and studied its electrochemical performance in a neutral hybrid gel polymer mix of PVA/Na₂SO₄. The symmetric supercapacitor device based on the synthesised nanocomposite showed a specific capacitance of 152 F/g with energy density of 59.41 W h/kg at a high-power density of 850 W/kg [20]. Bal Sydulu Singu *et al.* synthesised NiO-PANI nanocomposite via in-situ aqueous oxidative polymerisation and showed the uniform distribution of NiO nanosheets over the nanofibrous PANI framework. Moreover, this nanocomposite delivered a specific capacitance of 514 F/g at 1 mV/s [21]. The NiO/carbon composite was fabricated by Subbukali Vijayakumar *et al.* with the help of starch as a stabilizing agent. The NiO/C composite calcinated at 500 °C showed a higher specific capacitance of 644 F/g at scan rate 2 mV/s compared with those composites prepared at 400 °C and 600 °C [22]. Junjiao Chen *et al.* reported a NiO@MnO₂ core/shell nanocomposite via two-step method and presented the growth of nanosheet like MnO₂ particles over the NiO nanotubes. The combined composite electrode delivered a capacitance of 266.7 F/g at 0.5 A/g [23]. The NiO-ZnO/GO nanocomposite was prepared by Raphael M. Obodo *et al.* using co-precipitation method and reported a capacitance of 1690 F/g for 1:1/GO sample at a scan rate of 10 mV/s [24]. Therefore, these previous literatures confirm that NiO is a hopeful electrode material that can make more improvement in electrochemical properties of CuO.

3.1.2. CuO-NiO nanocomposite as an efficient electrode material- A literature survey

Recently, multicomponent electrode preparation has been explored widely in the area of supercapacitors, owing to the fact that the both individual electrochemical contributions and synergistic effects of constituents can make efficient and productive electrode materials. CuO-NiO nanocomposite network is one of the extensively studied combination as a feasible electrochemically active capacitor [25], [26]. For instance, Yu Xin Zhang *et al.* investigated the synthesis and morphological evolution of CuO-NiO micropolyhedrons prepared by a simple precipitation method followed by calcination stages. The composite showed a specific capacitance of 370 F/g at current density of 2 mA/cm² in a three electrode system [27]. It has been observed that the electrochemical performance of the CuO-NiO composite micro polyhedrons is directly connected with its structural and morphological properties rather than its surface area. Thus, an appropriate pore size and surface morphology build more productive diffusion paths for the electrolyte ions, resulting in their enhanced intercalation and overall faradaic reactions. Recently, Siyi Xiao *et al.* prepared a wheat like CuO-NiO composite by a two-step electrochemical deposition and showed that the CuO-NiO composite attained an areal capacitance value 10.63 times higher than that of pure CuO [28]. They tested the specific capacitance and capacitive retention rate of the electrode materials before and after the incorporation of nickel oxide signifying that the synergistic effect between CuO and NiO enhances the electrochemical outcomes of the CuO/NiO composite materials. The structural, morphological and optical properties of CuO, NiO, and CuO-NiO composites were studied in detail by E. Arulkumar *et al.* They concluded that the improvement of specific capacitance of the composite electrode is the direct consequence of spherical CuO being strongly bound to NiO to enrich the surface area of the composite. The composite electrode delivered an energy density of 4.24Wh kg⁻¹ at a power density of 10.67 kW kg⁻¹ [29]. Sujit Chatterjee *et al.* synthesised CuO-NiO composite via hydrothermal route followed by calcination and found a combination ratio of (CuO)₅₀(NiO)₅₀ reached the highest capacitance of 35.63 F/g at current density 0.3 A/g. This CuO-NiO composite presented a 3D hierarchical morphology due to the aggregation of thin nanosheets [6]. Behnam Chameh *et al.* reported a study on the electrochemical performance of Cu-MOF-derived CuO/NiO and

CuO/NiO/Ni₃(VO₄)₂ composites. They observed a maximum capacity of 37.04 C/g in 3M LiOH electrolyte solution for the ternary composite at a gravimetric current of 2 A/g [30]. The electrochemical performance of ternary ZnO-CuO-NiO mixed metal oxides prepared by a simple gel combustion method was investigated by R. Packiaraj *et al.* and showed an outstanding capacitance of 1831 F/g at 1 A/g, which is much higher than single and binary metal oxides. The asymmetric supercapacitor device designed with the mixed metal oxides exhibited a power density of 5672 W/Kg with a specific energy density of 15.7 W h /Kg [31]. These eminent works on CuO-NiO based electrode materials have proved that this metal oxide combination can be a potential choice for fabricating high performance supercapacitors.

3.1.3. CuO-NiO/PANI/MWCNT hybrid systems for supercapacitor applications

Recent researches on the supercapacitor have been more focused on the preparation of hybrid electrode materials combining the metal oxides, conductive polymers and carbon compounds. Metal oxides are themselves a viable member of pseudocapacitors due to their excellent theoretical capacitance and power density. Also, conducting polymers like polyaniline have good capacitive response and exceptional electrical conductivity. Carbonaceous compounds like graphene and CNTs are well-renowned for their superior mechanical and chemical stability along with high surface area. Specifically noteworthy is the fruitful combination of TMOs with PANI as well as CNTs, resulting in a fertile base given by its distinctive contributions coupled with the synergistic effects that make them a promising member in energy storage applications. For instance, Vijay Kakani *et al.* prepared CuO/NiO/r-GO composite by ultrasonication and reported a capacitance of 220 F/g at a current density of 0.5 A/g. The enhancement of electrochemical performance of composite were attributed to the availability of multi-oxidation states and the uniform growth of CuO/NiO composite onto the surface of nitrogen doped graphene facilitates rapid charge storage in the system [32]. Elumalai Arulkumar *et al.* reported facile synthesis of CuO/NiO/rGO with varying rGO ratios and showed that the CNR-(50:50) electrode got a maximum specific capacitance of 302 F/g at 10 mV/s [33]. H₂O₂ supported hydrothermal and microwave preparation of CuO/NiO/MWCNT electrode material was discussed in a recent literature reported by Sannasi Veeman *et al.* and showed a specific capacitance of 581.3

F/g at 1 A/g for the ternary electrode [34]. Also, Sayed Mohammed Adnan *et al.* explored the NiO-CuO decorated PANI nanocomposite as a symmetric supercapacitor device with 69 % capacity retention over 10000 charge/discharge cycles [35]. Recently, Manash J. Baruah *et al.* reported the first work on ethanol-assisted in-situ stimulated synthesis of graphene oxide supported CuO/NiO nanoparticles and resulted in increased surface area of the composite [36]. Mahasweta Chatterjee *et al.* synthesised wool ball-like CuO/NiO/MWCNT hybrid system and explored its supercapacitive performance. They reported a specific capacitance of 786 F/g at 0.6 A/g for the optimised ternary composite. This fusion of binary TMOs in to MWCNTs improved the surface area, electrical conductivity as well as charge transfer properties of the whole system [37]. To the best of our knowledge, the only one work based on CuO-NiO/PANI/MWCNT quaternary composite was done by Ishita Chakraborty *et al.* and reported a maximum capacitance of 1372 F/g at 5 mV/s having 83% capacitance retention after 1500 cycles of charge/discharge, making them a potential electrode material [38]. Here, the porous nanoarchitecture and availability of multiple oxidation states of both metal oxides have enriched electro-active sites in the electrode surfaces. Additionally, the double role of PANI as a pseudocapacitive material as well as a conductive binder results in an enhanced mechanical stability of the electrode material. Moreover, MWCNT provides a potential conductive framework that eventually facilitates the charge transfer features of the material.

3.2. EXPERIMENTAL SECTION

3.2.1. Synthesis materials

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$), ammonium persulfate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and aniline hydrochloride ($\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$), analytical grade hydrochloric acid (HCl), sodium sulphate (Na_2SO_4), sodium dodecyl sulphate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) (SDS, > 98%), nickel nitrate ($(\text{NiNO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), de-ionised (DI) water were purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, $OD \times L = 6 - 9 \text{ nm} \times 5 \mu\text{m}$), Polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP), activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standards

and utilized without any further purifications. Distilled ethanol was used for cleaning purpose.

3.2.2. Synthesis of NiO

The NiO nanoparticles were prepared via a similar surfactant-free hydrothermal process with the same reaction conditions of CuO synthesis. Firstly, 1.45 g of nickel nitrate was dissolved in 50 ml of de-ionised water. Later, 1 M NaOH solution was added to the precursor solution under constant stirring. The whole solution was then transported to the autoclave setup and kept in the oven under 180 °C for 24 hours. When the reaction conditions met, the resultant solution from the reactor was filtered and washed thoroughly using DI water and ethanol. The obtained light green NiO precipitate was then shifted to an oven at 80 °C for 6 hours to get the purified NiO nanoparticles.

3.2.3. Synthesis of CuO-NiO nanocomposite

The CuO-NiO nanocomposite was processed using the hydrothermal method without employing any additives of surfactants. Initially, 10mM nickel nitrate was allowed to dissolve completely in 50 ml of DI water via a continuous stirring process. Later, the previously prepared CuO nanoparticles (40 mg) were allowed to disperse in the above-mentioned nickel precursor solution. Then, 0.6 mM urea was added to the solution without disturbing the stirring process until a clear homogeneous solution is attained. The whole 50 ml solution was then transferred to an autoclave and set to keep in the oven at 180 °C for 24 hours to complete the synthesis process. The earned precipitates after hydrothermal reaction were washed multiple times with DI water and ethanol for the removal of unreacted substances from the resultant. Later, the obtained precipitate was sent to an oven at 80 °C for 6 hours to get the CuO-NiO nanocomposite.

3.2.4. Synthesis of NiO/PANI/MWCNT ternary nanocomposite and CuO-NiO/PANI/MWCNT quaternary nanocomposite

The NiO/PANI/MWCNT ternary nanocomposite was prepared using a similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO with 30 mg of as-prepared NiO and the final product is named as NPM for the convenience.

The CuO-NiO/PANI/MWCNT quaternary nanocomposite was prepared in the similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO with 30 mg of as-prepared CuO-NiO nanocomposite and the final product is named as CNPM for the convenience.

3.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, Aeris Research (Source: Cu K α)). Fullprof Suite software was used for Rietveld analysis. Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany) was employed to determine the vibrational modes of the as-synthesised samples. Fourier Transform Infrared (FTIR) spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using ZnSe crystal. The surface morphology and elemental composition were done using a combination of High- Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of a TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

3.2.6. Electrode preparation and electrochemical studies

The electrochemical features of as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt% of active material, 10 wt% of polyvinylidene fluoride (PVDF) and 10 wt% of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly in to a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in the working electrode was 1.28 mg cm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as

reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of as-synthesised samples.

3.3. RESULTS AND DISCUSSION

3.3.1. X-Ray diffraction (XRD)

Structural and microstructural features of as-prepared materials were examined using X-ray diffractometer. The XRD profiles of NiO and CuO-NiO nanoparticles along with that of already prepared CuO for comparison are displayed in Fig. 3.1(a). All the dominant peaks of NiO can be well indexed by comparing with their standard JCPDS (cubic NiO -47-1049). The crystallographic scattering peaks were observed at 37.08°, 43.20°, 62.94°, 75.37° and 79.45° which are corresponds to (111), (200), (220), (113) and (222) planes of cubic NiO [39]. The XRD pattern of CuO-NiO nanocomposite was found to be a correct blend of monoclinic CuO and cubic NiO crystal structures. Even though CuO reflections were more prominent in the XRD pattern of the composite, NiO peaks were also easily detectable, which clearly indicated that both CuO and NiO phases were grown freely in the synthesis stage [40]. No additional peaks or phases were detected in any of the XRD patterns. Fig. 3.1 (b) shows the XRD patterns of newly synthesised NiO/PANI/MWCNT and CuO/NiO/PANI/MWCNT in the region 10°-90° along with those of PANI, MWCNT, and CPM for confirming the correct formation of composites. From the figure, it is very clear that the three very distinctive peaks that appeared in the XRD data of NPM composite at 37.14°, 43.09°, and 62.62° were correspond to the NiO phase. For CNPM composite, all the peaks in between 30°-90° were assigned to the presence of CuO-NiO composite in the hybrid system. Also, the three peaks at 14.71°, 19.66° and 25.32° in CNPM were corresponded to (011), (020), and (200) reflections of emeraldine salt form of PANI. No peak correspond to MWCNT was visible in the XRD spectrum of NPM, maybe due to its coincidence with the broad bump of PANI in the 20-30° region. The peak at 25.75° in CNPM composite can be a resultant of (200) plane of PANI and (002) plane of MWCNT, can be a result of interaction between both PANI and MWCNT. Thus, from the XRD analysis itself, the correct formation of NiO, CuO-NiO, NPM and CNPM nanostructures were validated. The charge transfer interactions among metal

oxides, PANI and MWCNT leading to alterations in chain packing and configurations, may be resulted in gentle shifts in the peak positions [41].

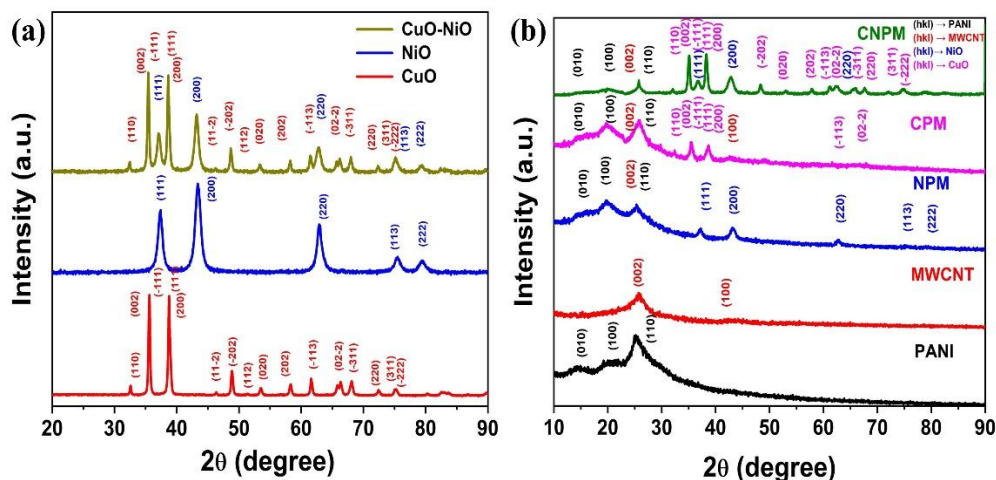


Fig. 3.1. XRD patterns of (a) CuO, NiO, CuO-NiO nanoparticles and (b) PANI, MWCNT, CPM, NPM, and CNPM composites.

3.3.2. Raman Spectroscopy

The room temperature Raman analysis of prepared composites was performed for the further structural confirmations, presented in Fig. 3.2. The Raman spectra of NiO (Fig. 3.2 (a)) show two dominant bands at 513 cm^{-1} and 1017 cm^{-1} , which are imputed to the LO and 2LO phonon modes of NiO, respectively. These LO phonon energies were fairly in agreement with previous reports [39], [42]. The Raman spectrum of CuO-NiO nanocomposite (shown in Fig. 3.2 (b)) delivers an exact combination of Raman active bands of pristine CuO and NiO nanostructures which precisely confirms the successful composite formation of CuO with NiO [10], [40]. The Raman spectra of ternary and quaternary composites, NPM and CNPM were shown in Fig. 3.2 (c,d). The low intense bands at 413 cm^{-1} and 522 cm^{-1} confirm the presence of NiO in the NPM composite, which can be attributed to TO modes and LO modes. In the case of CNPM composite, 277 cm^{-1} , 420 cm^{-1} , and 535 cm^{-1} Raman modes were accounted for the A_g mode of CuO and TO and LO modes of NiO, respectively. The Raman active mode of PANI and MWCNTs were noted and listed in Table 3.1 with their corresponding peak assignments [43].

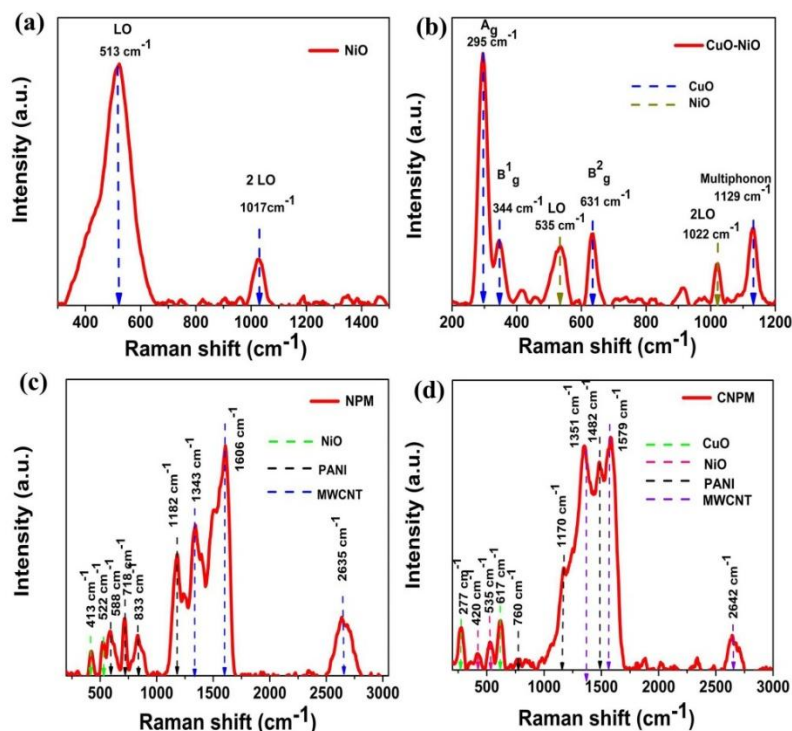


Fig. 3.2. Raman profiles of pristine (a) NiO (b) CuO-NiO (c) NPM (d) CNPM composites.

Table 3.1. List of assignments of dominant characteristic bands appeared in Raman spectra of NPM and CNPM nanocomposite.

Raman modes		Assignments
NPM	CNPM	
-	277 cm ⁻¹	A _g mode of monoclinic CuO
413 cm ⁻¹	420 cm ⁻¹	TO mode of NiO
522 cm ⁻¹	535 cm ⁻¹	LO mode of NiO
718 cm ⁻¹	760 cm ⁻¹	Raman active mode of PANI
-	617 cm ⁻¹	B _g ² mode of monoclinic CuO
833 cm ⁻¹	-	Ring deformation of benzenoid ring in emeraldine salt form of PANI
1182 cm ⁻¹	1170 cm ⁻¹	C-H bending of benzenoid ring in PANI
-	1482 cm ⁻¹	C=N stretching in quinoid ring in PANI
1343 cm ⁻¹	1351 cm ⁻¹	D- band of MWCNT
1606 cm ⁻¹	1579 cm ⁻¹	G-band of MWCNT
2635 cm ⁻¹	2642 cm ⁻¹	G' band of MWCNT

3.3.3. FT-IR spectroscopy

The chemical structures of the composites formed during mutual interactions and bonds were investigated through FT-IR spectra, shown in Fig. 3.3. The small absorption peaks at 3745 cm^{-1} attributed to the vibrational stretching of O-H bonds, whereas the peak at 2969 cm^{-1} ascribed to C-H stretching in CH-Cl groups. The band at 1514 cm^{-1} corresponds to hydrogen bonded carbonyl groups, and C-O stretching is indicated through the peak at 1161 cm^{-1} . The bands that appeared at 423 cm^{-1} , 484 cm^{-1} and 603 cm^{-1} (shown in Fig. 3.3 (a)) correspond to the vibrational stretching of Ni-O bonds. As shown in Fig. 3.3 (b), the absorption bands in between $400\text{--}650\text{ cm}^{-1}$ can be a blend of CuO and NiO nanostructures [39], [44]. In NPM and CNPM composites, bands corresponding to metal oxide bonds were appeared between the wavelengths $400\text{--}700\text{ cm}^{-1}$. The other peaks presented in the range of $680\text{--}4000\text{ cm}^{-1}$ can be of pristine PANI and MWCNTs, listed in Table 3.2. The slight variation of peaks positions metal oxides, PANI and MWCNTs indicates the effective interactions between PANI and MWCNTs resulted in polarity changes or metal oxide and MWCNTs causes lowering of vibrational energies [45].

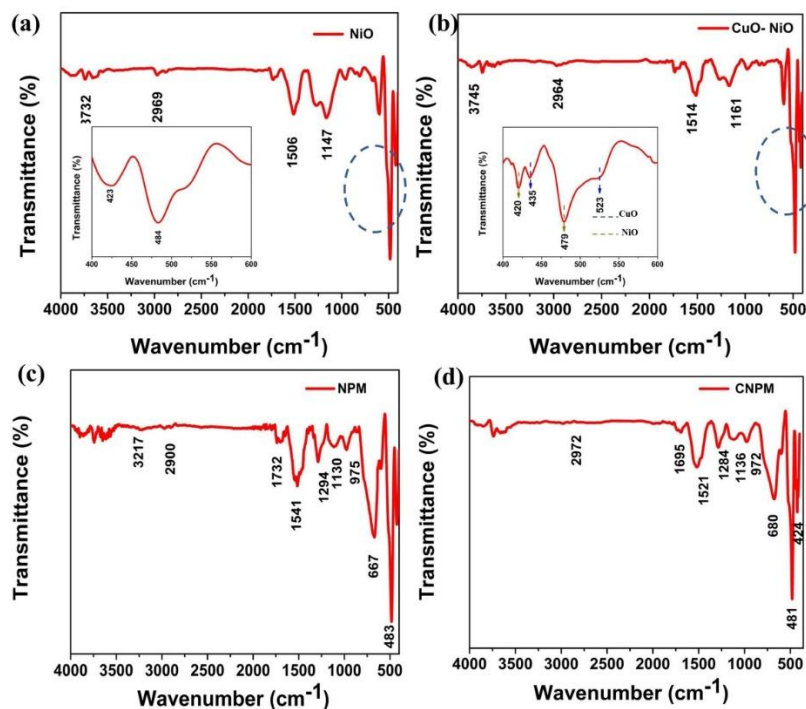


Fig. 3.3. FT-IR spectra of (a) NiO (b) CuO-NiO (c) NPM (d) CNPM nanocomposites. (inset shows the zoomed spectra of NiO and CuO-NiO in the range $400\text{--}600\text{ cm}^{-1}$ as marked in its corresponding figures 3.3 (a) and (b)).

Table 3.2. List of FT-IR bands and its assignments appeared in NPM and CNPM composites.

FT-IR bands		Assignments
NPM	CNPM	
3217	-	O-H bonds due to existence of water molecules
2900	2972	asymmetric/ symmetric methylene stretching bands from PANI
1732	1675	stretch mode of carboxylic groups in MWCNT
1541	1521	C=C stretching in quinoid ring of PANI
1294	1284	C-N for aromatic amines in the polaron structure of conducting PANI
1130	1136	characteristic band of the protonated form of conducting PANI
975	972	characteristic peaks of mono substituted benzene, indicates the formation of PANI
667	671	Characteristic peak of Ni-O
483	481	Characteristic peak of Ni-O
-	424	Characteristic peak of Cu-O

3.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The morphological appearances of the materials were inspected by FESEM images. The surface morphology of NiO sample was portrayed in Fig. 3.4 (a,b,c); it carried an irregular pattern of nanoflakes distribution with some sort of agglomerated clumps in between. The flakes possess very small dimensions approximately 10 nm average thicknesses. On the other hand, SEM images of the CuO-NiO composite revealed the formation of rice-like nanoparticles, displayed in Fig. 3.4 (d,e,f). It is to be noted that

the sizes of these rice-like particles are relatively small and emanating with a considerable number of tiny porous spaces that can be unquestionably profitable for the electrochemical capacity of the prepared sample [46]. The incorporation of NiO into CuO has effectively transformed the flake-like morphology of CuO into very minute rice-like particles with several minute pores. The average size of uniformly distributed rice-like composite particles is estimated as ~ 95 nm length, ~ 38 nm width and ~ 6 nm thickness. The morphological investigations of NPM composite is presented in Fig. 3.6 (g,h,i). The composite exhibited a nanofibrous texture with several intertwined frameworks, having an average diameter of 55 nm. The PANI/MWCNT growth over NiO nanoflakes, make complete fibrillar morphology without any kind of agglomerations or appearance of flakes of NiO in the composite system. The diameter of these fibres was higher than the pristine PANI fibres as well as the nanotubes of MWCNTs, indicating the grafting of PANI over the MWCNT tubes [47]. The CNPM composite shows a nanotubular morphology (Fig. 3.6(j,k,l)) resemble to that of MWCNTs; however, the average diameter of tubes was increased to 34 nm, likely due to the successful growth and wrapping of PANI over MWCNT surfaces. The originally smooth surface of MWCNT tubes were obscured as the nanofibrous PANI with agglomerated protrusions was linked to the MWCNT surfaces, contributing to the observed increase in average diameter of tubules. The metal oxides become morphologically indistinct due to the uniform interactive growth of PANI and MWCNT over the metal oxides. Moreover, the highly voluminous pores exhibited within the composite made it to have an effective specific surface area, thereby facilitating the productive contact between the electrode surface and electrolyte ions. This overall structural configuration in the composite provides more and more conductive pathways, which led to a better electrochemical performance of the hybrid system.

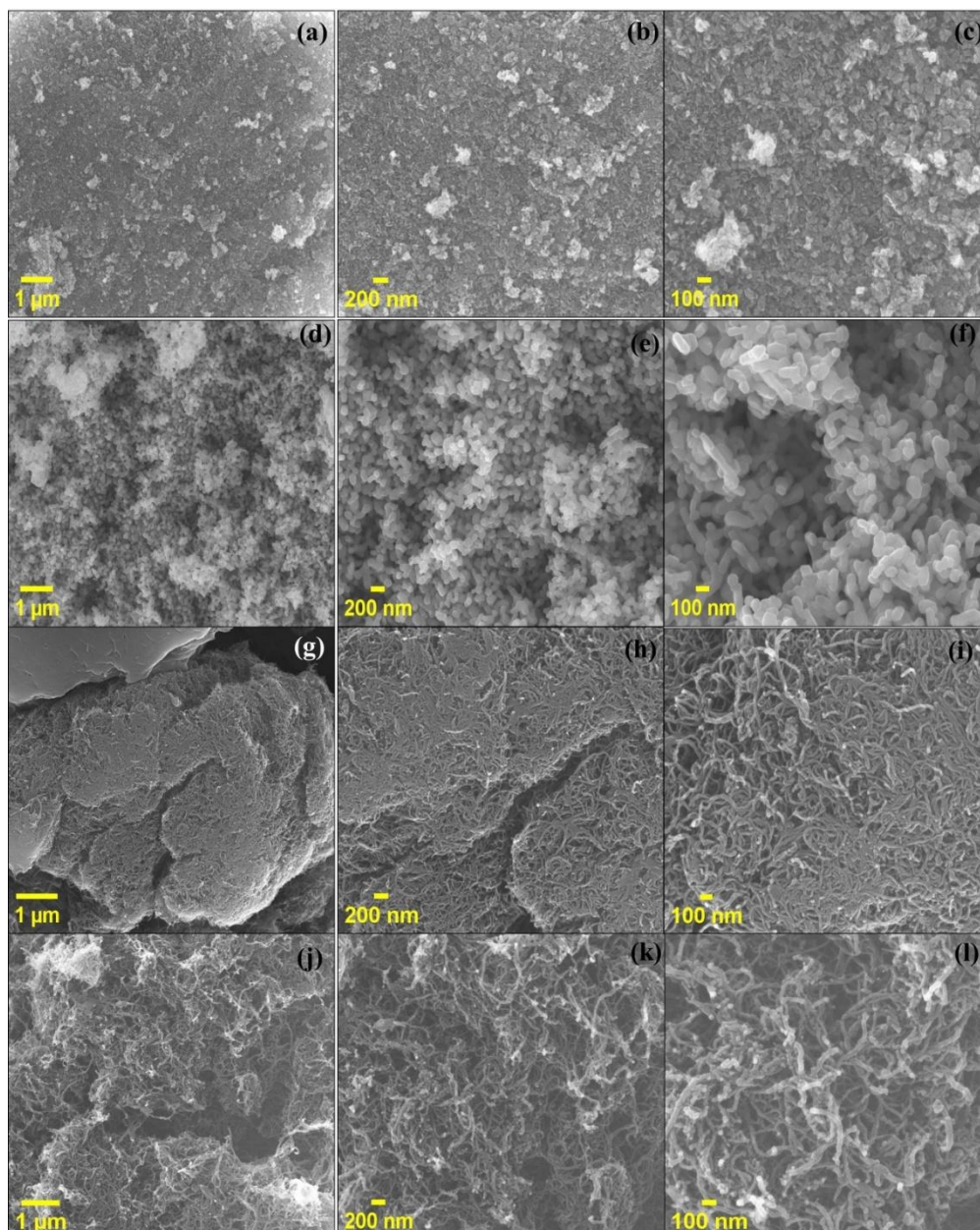


Fig. 3.4. SEM micrographs of (a,b,c) NiO (d,e,f) CuO-NiO (g,h,i) NPM (j,k,l) CNPM nanocomposites.

The compositional evaluations of the composites were performed using conventional energy dispersive spectroscopy (EDS), as shown in Fig. 3.5. The existence of elements like nickel and oxygen was obviously visible in the spectra of NiO, displayed in Fig. 3.5 (a). Similarly, the EDS spectrum of CuO-NiO (Fig. 3.5 (b)) reveals the distinct peaks of elements like copper, nickel and oxygen, confirming the successful integration of these constituents in the composite material. The successful formation of both NPM and CNPM composites were confirmed through the EDS

spectra presented in Fig. 3.5 (c-d). In the NPM composite, detection of elements C, N, Ni, and O verifies the incorporation of PANI/MWCNT in to NiO, whereas the presence of additional signal of Cu in the CNPM confirms the successful interaction of CuO-NiO with PANI/MWCNTs. The atomic mass ratio of these detected elements was tabulated in Table 3.3. The atomic concentrations of all elements that appeared in each synthesised materials were further validate the precise formation of intended composites. The equal amount of elements Cu and Ni, with nearly double amount of the oxygen validates the successful formation of CuO-NiO composite. The relatively lower atomic ratio of Ni in CNPM composite as compared with other detected elements, supports the observed less intense peaks of NiO in the XRD pattern of the composite.

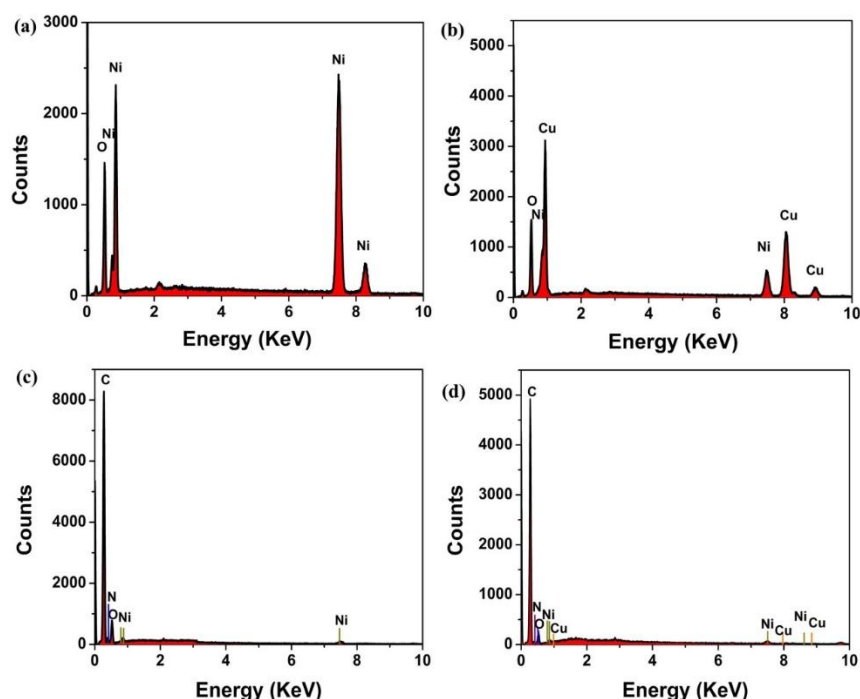


Fig. 3.5. EDS spectra of (a) NiO, (b) CuO-NiO, (c) NPM, and (d) CNPM composites.

Table 3.3. Elemental data of NiO, CuO-NiO, NPM, and CNPM composites obtained from EDS analysis.

Sample	Atomic ratio (%)				
	Cu	O	Ni	C	N
NiO	-	41.82	58.18	-	-
CuO-NiO	27.95	46.84	25.21	-	-
NPM	-	15.02	8.80	65.12	11.06
CNPM	7.09	11.14	3.21	70.58	7.98

The corresponding elemental mapping images of NiO, CuO-NiO, NPM and CNPM composites were displayed in Fig. 3.6, Fig. 3.7, Fig. 3.8, and Fig. 3.9 which further confirms the occurrence and uniform distribution of intended elements in each sample. The yellow regions observed in the EDS map of NiO (Fig. 3.6 (b)) confirm the richness of NiO. In the case of CuO-NiO, EDS map shown in Fig. 3.7 (b) shows the lighter blue and yellow regions of CuO and NiO in the composite system. The rich elemental presence of carbon in both NPM and CNPM composites (Fig. 3.8 & 3.9) confirms the presence of MWCNTs, while the nitrogen distributions were also evident, indicating that PANI was grafted over the CNT surface during composite formation. From the EDS map of NPM (Fig. 3.8 (b)), it is evident that the PANI and MWCNT growth of made the NiO presence as indistinct. Thus, the Cu, Ni, and O elemental distributions along with the contributions of PANI and MWCNTs (Fig. 3.9 (b)) ascertain the successful formation of quaternary CuO-NiO/PANI/MWCNT composite.

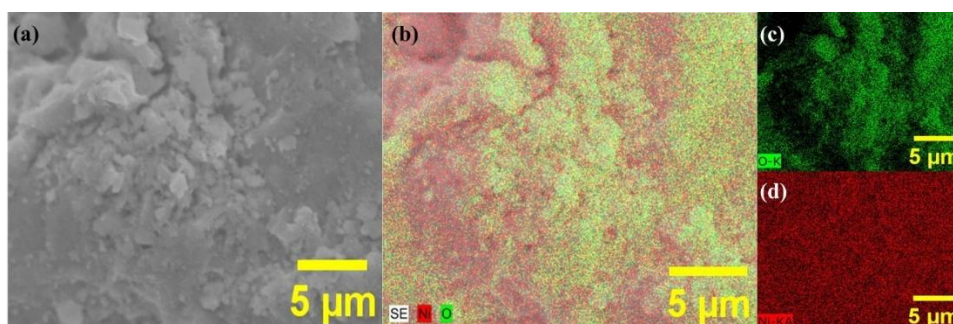


Fig. 3.6. (a) SEM image, (b) EDS mapping of NiO nanostructures, and (c-d) selective elemental distribution for the area shown in image (a).

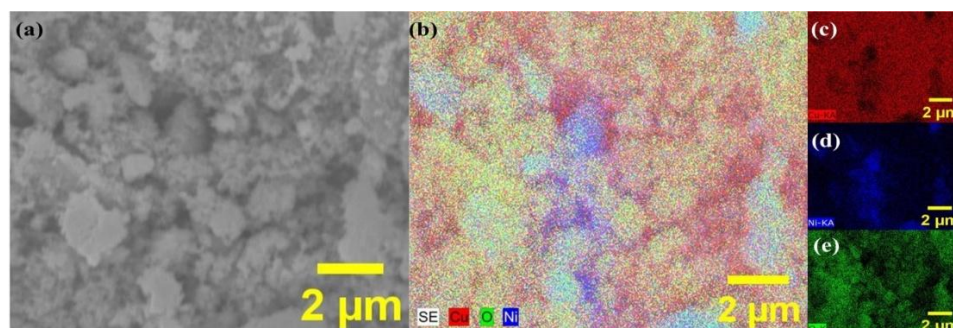


Fig. 3.7. (a) SEM image, (b) EDS mapping CuO-NiO nanocomposites, and (c-e) selective elemental distribution for the area shown in image (a).

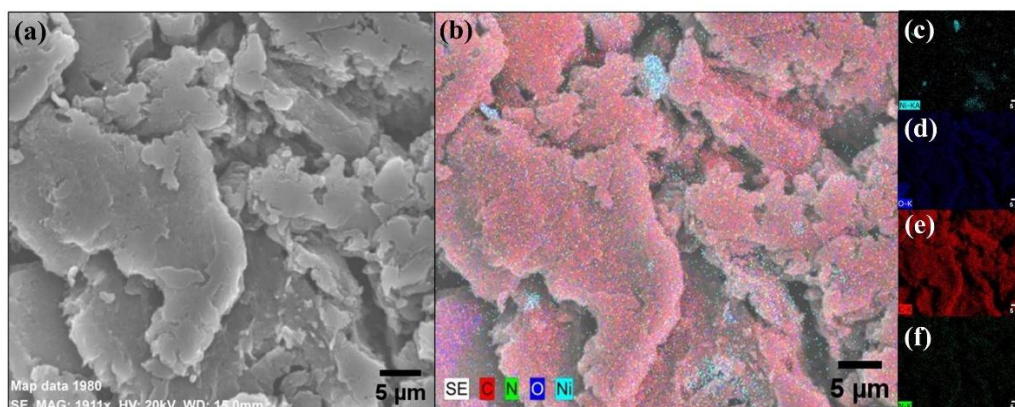


Fig. 3.8. (a) SEM image, (b) EDS mapping of NPM composites, and (c-f) selective elemental distribution for the area shown in image (a).

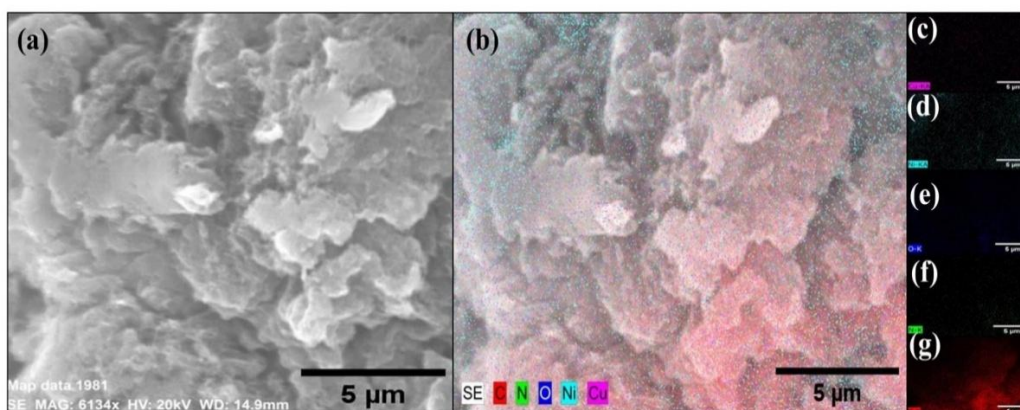


Fig. 3.9. (a) SEM image, (b) EDS mapping of CNPM composites, and (c-g) selective elemental distribution for the area shown in image (a).

3.3.5. High Resolution Transmission electron micrographs (HR-TEM)

The microstructural features of CuO-NiO/PANI/MWCNT composites were investigated through TEM, HRTEM images (Fig. 3.10), intended to get more comprehensive information about the structural features. The TEM images shown in Fig. 3.10 (a,b), presents a tubular morphology of composite, consistent with FESEM findings. The increase in tubular diameter can be understood from the TEM image shown in Fig. 3.10 (b), attributable to the wrapping of PANI over the MWCNT tubules, a process reported in polymer-CNTs frameworks [48]. The CuO-NiO nanoparticles can be distinctly visible from the HRTEM image, presented in Fig. 3.10 (c), which has an average diameter of 8.22 nm, matches with dimensions commonly seen for metal oxides introduced within polymer frameworks. The crystallographic d-spacing measurement shown in Fig. 3.10 (d), align with the dominant (110) plane of CuO nanostructures.

Furthermore, from the fig. 3.10 (e), it is evident that the composite consists of several intertwined nanotubes with varying diameter, i.e., a kind of structural modification persuaded by the extent of PANI grafting over MWCNTs. The SAED pattern of composite displayed in Fig. 3.10 (f) consists of concentric rings indicating the polycrystalline nature of the sample.

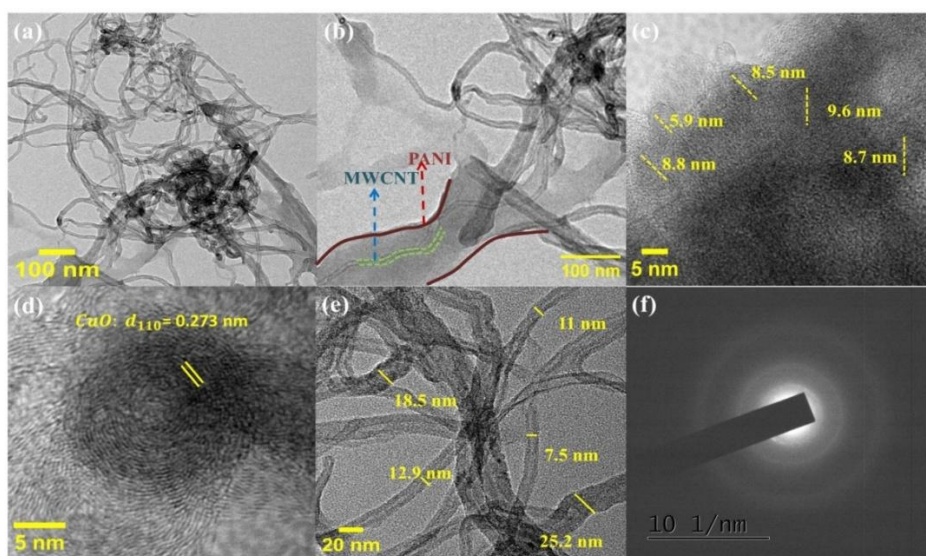


Fig. 3.10. (a,b) TEM micrograph (c,d,e) HRTEM images (f) SAED pattern of CNPM composites.

3.3.6. X-Ray Photoelectron spectroscopy (XPS)

The compositional analysis and elemental confirmations of the quaternary nanocomposite CNPM examined using XPS profiles and are shown in Fig. 3.11. The survey spectrum (Fig. 3.11 (a)) confirms the co-existence of Cu, Ni, C, O, and N in the material. The high resolution XPS spectra of C 1s (Fig. 3.11 (b)) can be deconvoluted to four major and minor peaks at 284.3 eV, 285.2 eV, 286.8 eV, and 289.7 eV. The high intense major peak at 284.3 eV can be attributed to the sp^2 hybridised carbon ($C=C$) in the graphitic structure of MWCNTs. The second major peak at 285.2 eV corresponds to contributions from both sp^3 hybridised carbon ($C-C$) at the MWCNT surface as well as $C-N$ components present in the PANI structure [49]. The less intense peak at 286.8 eV ascribed to carbon atoms bound to functional groups like hydroxyl groups ($C-OH$). The final peak with higher binding energy and low intensity appeared at 289.7 eV, attributed to the carbon atoms connected with bipolaronic nitrogen cations ($C=N^+$) in PANI [50].

The N 1s core level spectrum shown in Fig. 3.11 (c) fitted with three dominant peaks with binding energies of 399 eV, 399.7 eV, and 401.1 eV, in which the major contribution was from both the amine groups (—N—H—) and imine groups (=N—H—) of emeraldine base appeared at 399.7 eV and 399 eV, respectively. The low intense high binding energy peak at 401.1 eV, attributed to generated iminium ions ($\text{—N}^+=$), which were created due to the interaction between MWCNT and PANI through $\pi - \pi^*$ conjugation [47]. The O 1s spectrum (Fig. 3.11 (d)) can be deconvoluted to four peaks at binding energies 530.6 eV, 531.2 eV, 532.4 eV and 534.2 eV. The broad peak at 530.6 eV corresponds to lattice oxygen involved in metal oxide bonds such as Ni-O and Cu-O bonds. Also the presence of C—O and C=O bonds in the composites was confirmed through this peak [32]. The peaks at 531.2 eV and 532.4 eV related to oxygen vacancies and metal-hydroxyl bonds present in the lattice, respectively [51]. The presence of H_2O or $\text{CO}_2/\text{CO}_3^{2-}$ species has resulted in the less intense peak at 534.2 eV [52]. The Cu 2p core level spectrum is presented in Fig. 3.11 (e). The two prominent peaks that appeared at 933.6 eV and 953.6 eV represent the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ orbits, respectively. The energy gap of 20 eV between these spin energies coupling orbits confirms the presence of Cu^{2+} , thereby the occurrence of CuO form in the quaternary composite. Along with this, two shake-up peaks were also located at 943.1 eV and 963.3 eV [53]. The minor shifts in the binding energies of Cu^{2+} in the composite compared with that of the CuO sample suggests the effective interactions of metal oxides with MWCNTs and the PANI matrix. The two main peaks of Ni 2P state, shown in Fig. 3.11 (f), observed at binding energies 855.5 eV and 873.4 eV, were ascribed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ orbits of Ni^{2+} species [32]. The spin orbit coupling energy band gap of these orbits found to be 17.9 eV, along with two satellite peaks for each main peak.

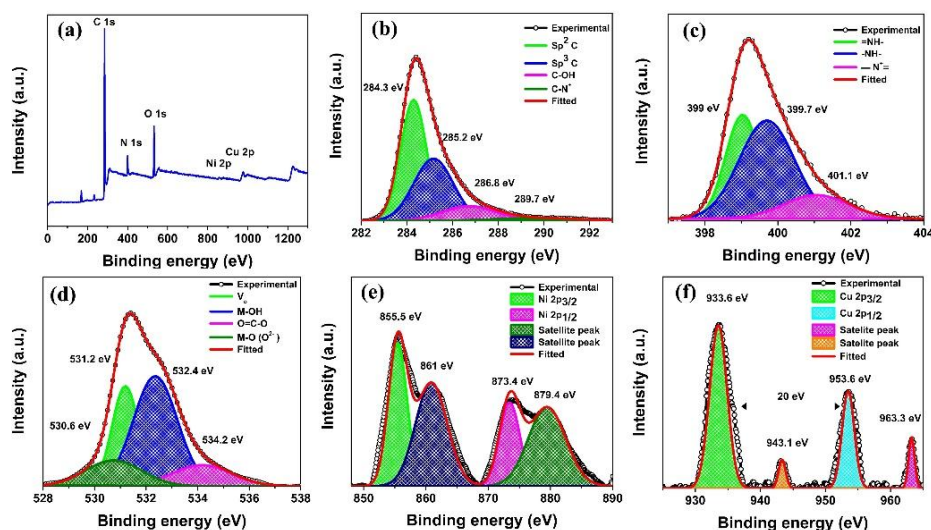


Fig. 3.11. (a) XPS survey spectrum and XPS elemental core spectra of (b) C 1s and (c) N 1s (d) O 1s, (e) Cu 2p, and (f) Ni 2p of CNPM nanocomposite.

3.3.7. Brunauer-Emmett-Teller (BET) analysis

The electrochemical performance of the materials is strongly associated with their specific surface area and inner porous textural. Fig. 3.12 shows the N₂ adsorption-desorption isotherms and pore size distribution (PSD) plots of NiO, CuO-NiO, NPM and CNPM nanocomposites. The steep region in the isotherm plot generally gives the information about initial level adsorption that occurs during nitrogen contact and availability of active surface adsorption sites [54]. Like CuO, the mesoporous nature of NiO was inferred from its type IV adsorption behaviour in adsorption – desorption isotherm with H3 hysteresis loop ranges from 0.8-1 (P/P₀), presented in Fig. 3.12 (a). Brunauer-Emmett-Teller (BET) surface area of NiO sample was approximated to be 21 m²/g. The pore size distribution (shown in the inset of Fig. 3. 12 (a)) lies in the mesoporous range with a pore radius of ~ 6.42 nm and pore volume of ~ 0.087 cm³/g. In the case of CuO-NiO composite, the BET specific surface area from the N₂ adsorption-desorption isotherm was estimated as ~ 45 m²/g. The isotherm plot of nanocomposite, displayed in Fig. 3.12 (b) shows type IV isotherm performance with a hysteresis loop between 0.65-1 (P/P₀), which is frequently seen in mesoporous materials. In the inset of Fig. 3.12 (b), the pore size distribution image of CuO-NiO composite is presented. The average pore radius and volume are tabulated as 9.12 nm and 0.146 cm³/g. The higher value of surface area and smaller pore sites for the CuO-NiO composite when compared with

the pristine CuO and NiO, will create a large amount of pore channels for the adequate diffusion and active transportation of electrolyte [55], [56]. In the case of NPM, adsorption-desorption isotherm plot, shown in Fig. 3.12 (c) illustrates the H3 hysteresis loop ranging between 0.55-1 (P/P_0) with type IV adsorption nature, having a BET surface area of 57 m^2/g . The average pore radius and volume are tabulated as 11.5 nm and 0.061 cm^3/g . Meanwhile, CNPM composite behaves like type IV mesoporous materials having H2 hysteresis loop, with a highest surface area of about 81 m^2/g (Fig. 3.12 (d)). The average pore radius and volume are tabulated as 13.2 nm and 0.178 cm^3/g . The synergism between MWCNTs and PANI, along with metal oxide composites results in the enhancement of the specific surface area of the quaternary hybrid system. Although there is an improvement in the surface area of CNPM, the surface encapsulation of nanotubes by the metal oxides and PANI, as confirmed by SEM/TEM observations, limits the accessibility of active centres and certain pores, thereby hinders their contribution to surface area.

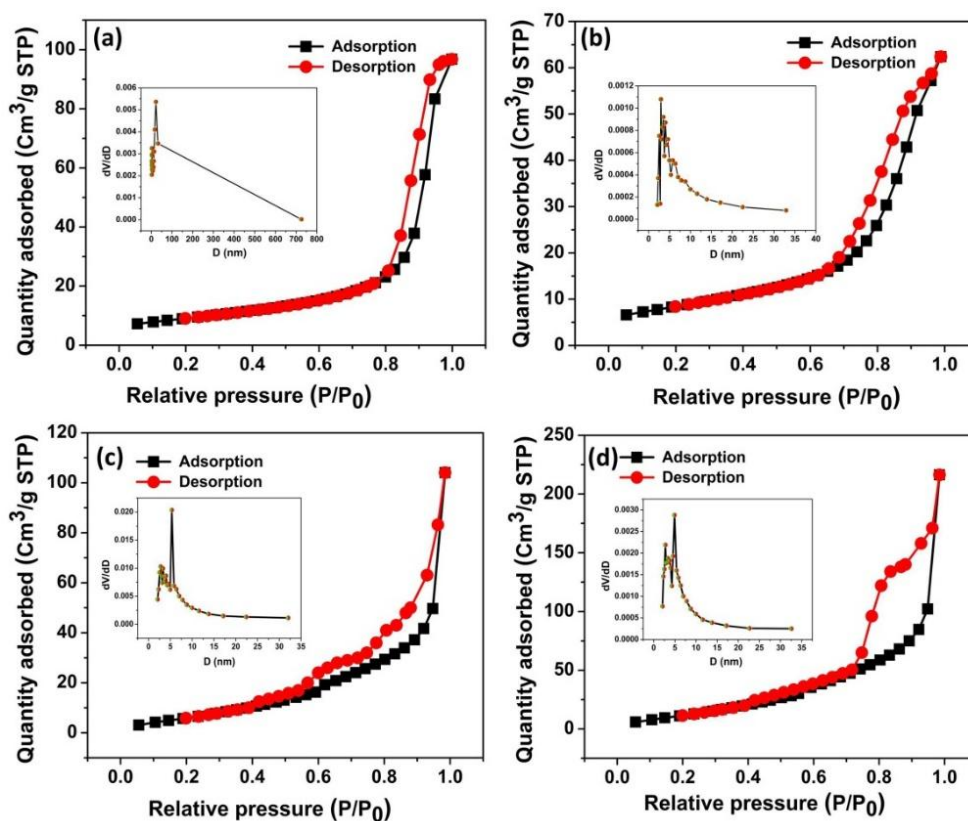


Fig. 3.12. The N_2 adsorption-desorption isothermal plots of (a) NiO (b) CuO-NiO (c) NPM and (d) CNPM nanocomposites. Inset shows the corresponding PSD plots.

3.3.8. Thermo-gravimetric Analysis (TGA)

The thermal stability of the CuO-NiO/PANI/MWCNT quaternary composite was investigated using thermogravimetric data presented in Fig. 3.13. The composite undergoes significant weight loss through mainly three steps of decomposition. In the initial stage, CNPM lose its weight by 8.12% until the temperature reaches 100 °C, which corresponds to the loss of absorbed water molecules from the surface. The second noticeable weight loss of 28.75% was attributed to the removal of acid elements from the composite and the degradation of polymer into monomers, oligomers, trimmers, and dimers between the temperature range 168 °C to 321 °C. The CNPM composite underwent a weight loss of about 11.78% until the temperature reaches 522 °C in the final stage of decomposition, which is accountable for the degradation of polymer backbones [57]. In the end, 46.30% of residual CNPM survived the thermal degradation, which is significantly higher than that of pristine PANI, indicates the positive effects of synergistic interactions between metal oxides, PANI and MWCNTs. The stronger network of metal oxides having high thermal resistance with PANI can effectively prevent the early decomposition of composite material, while the structural integrity of MWCNTs effectively delays the decomposition by efficiently dissipating heat energy [38], [58].

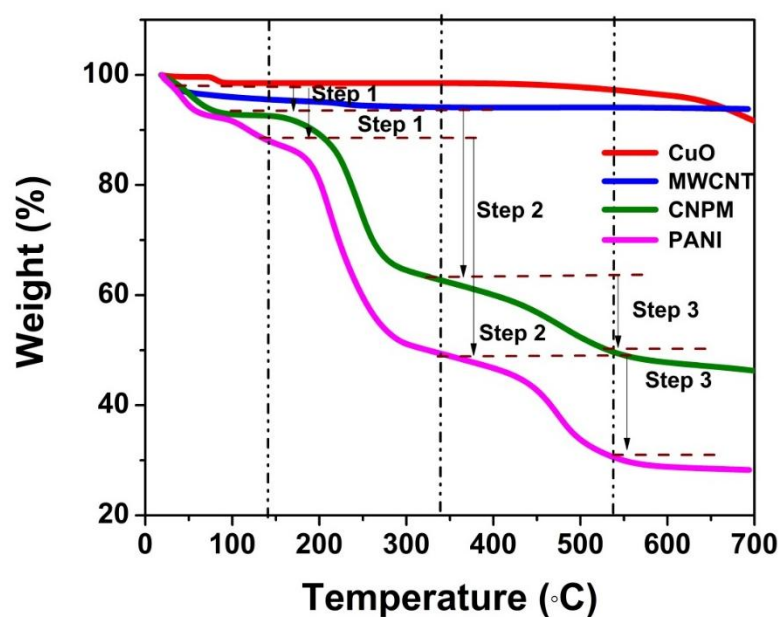


Fig. 3.13. Thermogravimetric analysis of CuO, MWCNT, PANI and CuO-NiO/PANI/MWCNT composite.

3.3.9. Electrochemical studies

3.3.9.1. Cyclic voltammetry (CV)

The electrochemical performance of the samples was evaluated in a three-electrode configuration with 1M Na₂SO₄ as the electrolyte medium. Fig. 3.14 (a,b,c,d) illustrates the cyclic voltammetry (CV) plots of NiO, CuO-NiO, NPM and CNPM composites with scan rates varying from 2 mV/s to 100 mV/s in a potential range of 0-0.8 V. The non-rectangular shape of CV curves clearly indicates that all the samples possess very distinctive capacitive characteristics from that of electric double layer capacitors [59]. The direct proportionality between voltametric current and scan rates is clear from the plots, which is one of the fundamental characteristic of an ideal capacitor [60].

Furthermore, nanosize and structure, surface area, and porous nature significantly configure the voltametric performance of a material [61]. Thus, compared with CV curves of pure metal oxides, the PANI and MWCNT incorporation makes the marginal shape change in CV plot of composites. As similar as CPM composite, the NPM and CNPM composites exhibit a pair of redox peaks at lower scan rates due to the presence of PANI. For NPM, the redox peaks were located at (0.37 V, 0.2 V) and for CNPM peaks were at (0.42 V, 0.18 V) at 10 mV/s. This redox peak can be attributed to the leucoemeraldine (LE) transition to Emeraldine (E) in PANI samples [62]. There is redox peak shift for the NPM and CNPM composites as similar to CPM, while increasing scan rates, which indicates that MWCNTs and PANI enhanced the redox properties of the nanocomposite. The increase in current indicates the better utilisation of electrode material through effective ionic diffusion, as a consequence of enhanced surface area and porosity of the nanocomposite. The good current response in composite electrodes is a clear indication of their better conductivity with lower internal resistance. Moreover, the metal oxide attachments with MWCNTs beneficially avoids the aggregation of CNTs, and the PANI coatings over the metal oxide-MWCNT composite system can effectively enhance ionic conductivity through the hybrid composite through synergistic effects [63].

Fig. 3.14 (e) shows the comparative CV curve analysis of CuO, NiO, CuO-NiO, CPM, NPM and CNPM composites at 100 mV/s, showing the capacitive current

increase of quaternary CNPM composite compared with the pristine CuO, resulting in the enhance specific capacitance of composite. The enhancement in specific capacitance values can be easily interpreted using the Fig. 3.14 (f), making a comparative analysis of capacitance values of all nanostructures at 10 mV/s. In addition to large surface area, occurrence robust pore structure makes remarkable advantage in its electrochemical properties. The pore network presents in CNPM allows smooth mass transport of ionic or electronic charge carriers and also raise the accessibility of electrode material to the electrolyte medium, compared with their binary and ternary counter parts. Generally, in the case of mesoporous materials, the effect of large number accessible electro-active areas is directly correlated with its capacitive currents [64].

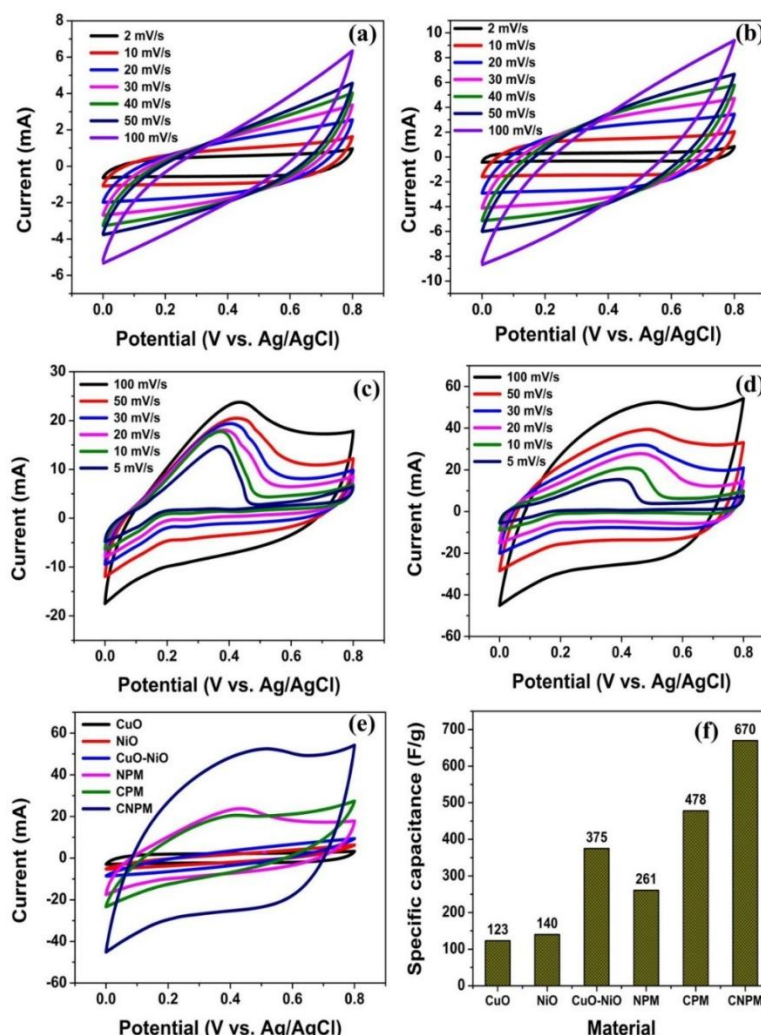


Fig. 3.14. CV curves of (a) NiO (b) CuO-NiO (c) NPM (d) CNPM, comparison of (e) CV curves of CuO, NiO, CuO-NiO, CPM, NPM and CNPM nanocomposites at 100 mV/s (f) specific capacitance of CuO, NiO, CuO-NiO, CPM, NPM and CNPM nanocomposites at 10 mV/s.

The charge storage mechanisms involved in the electrochemical performance of CNPM working electrode was estimated using Dunn method (Fig. 3.15). Fig. 3.15 (a) shows the $\log v$ vs. $\log i$ plot drawn using the data obtained from CV at 0.4 V. The value of 'b' obtained from this plot was 0.83, which indicates the dominance of capacitive controlled storage reactions. The value of parameters k_1 and k_2 were evaluated from the $v^{1/2}$ vs. $i/v^{1/2}$ plot and are used to estimate the current contributions (Fig. 3.15 (b)). The estimated current contributions involving diffusive and surface-controlled reactions in the CNPM working electrode at a scan rate of 10 mV/s were evaluated and portrayed in Fig. 3.15 (c). This decoupling of respective contributions helps to identify the exact reactions involved in the charge storage mechanism, suggesting a dominance of surface-controlled current part in the electrochemical performance of CNPM composite. The variation of current contributions at each scan rates was evaluated and presented in Fig. 3.15 (d), indicating the decrease of diffusive capacitance contributions at higher scan rates. The surface-controlled current contribution is 77 % at 10 mV/s and reaches to 98.8 % at 100 mV/s.

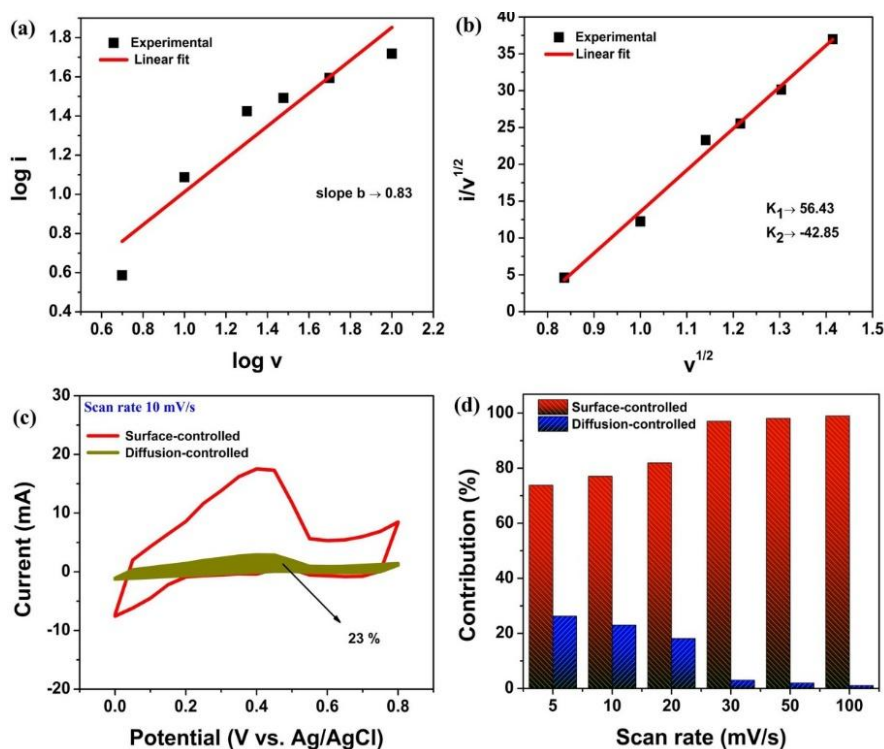


Fig. 3.15. (a) $\log v$ vs. $\log i$ plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ plot (c) decoupling of capacitive and diffusive current contributions at scan rate 10 mV/s (d) Histograms of diffusive and capacitive contributions of CNPM working electrode at varying scan rates.

3.3.9.2. Galvanostatic charge/discharge (GCD) studies

For the better electrochemical analysis of prepared working electrodes, galvanostatic charge/discharge (GCD) measurements were taken at different current densities. Fig. 3.16 (a,b,c,d) presents the GCD curves of the as-synthesised NiO, CuO-NiO, NPM, CNPM composites in the potential window of 0-0.8 V. All GCD curves showed good symmetry with nearly triangular shape, remarking good capacitive behaviour of materials even at higher current densities. Acute control over the active mass is crucial in the electrochemical performance of the system, since the mass directly correlates with the specific surface area [65]. The specific capacitance of NiO was 192.7 F/g, 137 F/g, 31 F/g and 28 F/g for currents densities of 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. The C_s values of CuO-NiO composite were 622 F/g, 258 F/g, 143.7 F/g and 120 F/g for currents densities of 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. Unsurprisingly, the PANI-MWCNT incorporated composite electrode materials displayed better capacitance compared with their binary counterparts. The NPM electrode exhibits specific capacitance values of 346 F/g, 261 F/g, 185 F/g, and 186 F/g at current densities of 0.5 A/g, 1 A/g, 3 A/g and 5 A/g, respectively. Whereas, the CNPM composite attained capacitance values of 775 F/g, 410 F/g, 262 F/g and 123 F/g at 1 A/g, 2 A/g, 3 A/g and 7 A/g, respectively. Fig. 3.16 (e) presents the comparative GCD curves of CuO, NiO, CuO-NiO, CPM, NPM, and CNPM composites at a current density of 1 A/g. The enhancement in the discharging time of CNPM was clearly noticeable from this plot. A comparison of specific capacitance values of CuO, NiO, CuO-NiO, CPM, NPM, and CNPM materials at various current densities was portrayed in Fig. 3.16 (f). The remarkable capacitance behaviour of CNPM nanocomposite can be the contribution of its surface area and porosity, which facilitates accessible active surface for enhanced penetration of electrolyte ions to the working electrode matrix. The mesoporous morphology of CNPM with commendable surface area assures the fair distribution of electrolyte solution and fast ionic diffusion through the pores. During charging/discharging, mesoporous structure of CNPM offers lower internal resistance, thereby quick ionic transport in the system. The possibility of ionic trapping in the pores are less compared with microporous materials, eventually upturn the capacitance values and corresponding energy-power densities even at higher charging/discharging rates [66].

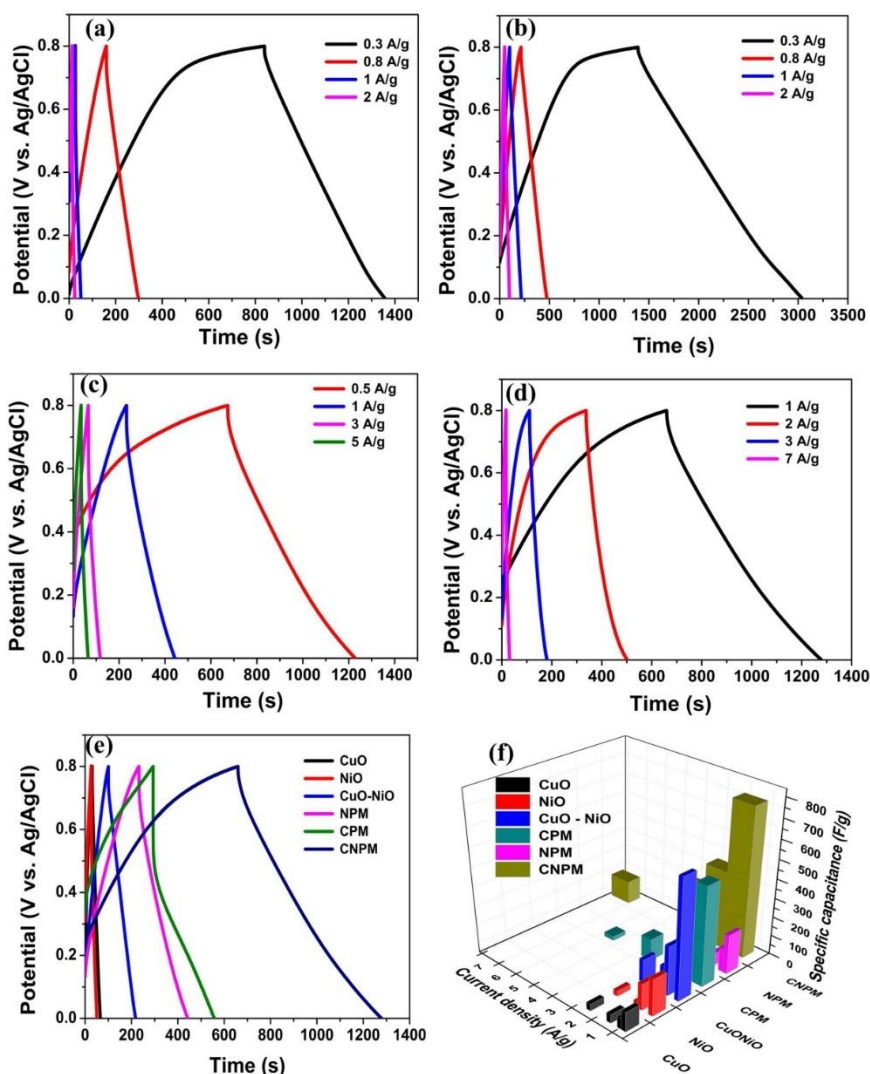


Fig. 3.16. GCD curves of (a) NiO (b) CuO-NiO (c) NPM (d) CNPM (e) comparison of charge-discharge curves of CuO, NiO, CuO-NiO, CPM, NPM, CNPM composites at current density of 1 A/g, (f) variation of specific capacitance with current density of CuO, NiO, CuO-NiO, CPM, NPM, CNPM composites.

3.3.9.3. Electrochemical impedance spectroscopy (EIS)

The Nyquist impedance plot of electrode materials from EIS measurements are shown in Fig. 3.17, which is done in a frequency range of 100 kHz to 100 mHz with a signal amplitude of 10 mV. The best fitted Nyquist plots of NiO, CuO-NiO, NPM, and CNPM composites evaluated through EIS analyser software, were shown in Fig. 3.17 (a-d). All the EIS curves presents a distorted semicircle in the high frequency region and a linear behaviour in lower frequency region (Fig. 3.17 (e)). The arc portion results from the redox reactions that happened in the electrode-electrolyte interface, whereas the linear edge in lower frequency area specifies the supercapacitive behaviour of as-

prepared working electrodes. The R_s , R_{ct} , CPE, W and n values of each electrode materials were calculated using EIS spectrum analyser software, are tabulated in Table 3.4. The Nyquist plot of the quaternary CNPM composite displayed almost a straight line nature with very small semicircle in the higher frequency region. The lower values of R_s and R_{ct} for the CNPM composite electrode undoubtedly indicate the enhancement of ion accessibility, owing to its very low internal resistance, resulted in increased electrical conductivity in the configuration [67].

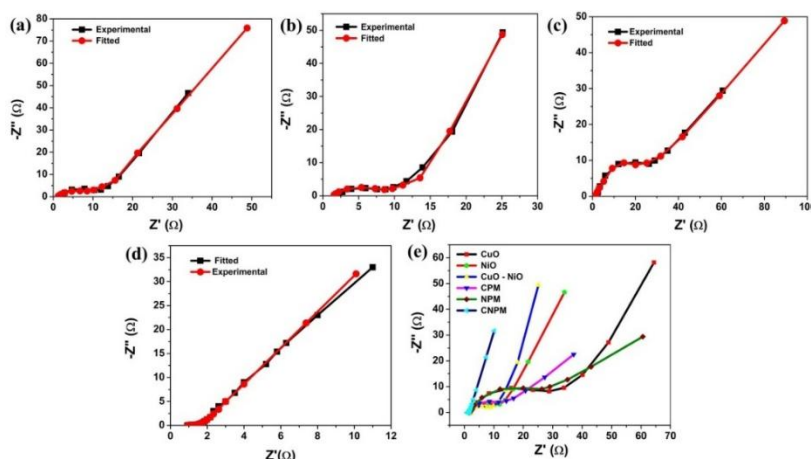


Fig. 3.17. (a) The best fitted Nyquist plot of as-prepared (a) NiO, (b) CuO-NiO, (c) NPM (d) CNPM (e) comparison of Nyquists plots of all nanostructures.

Table 3.4. The R_s , R_{ct} , CPE, W and n values of as-synthesised CuO, NiO, CuO-NiO, CPM, NPM, CNPM nanocomposites.

	Sample					
	CuO	NiO	CuO-NiO	CPM	NPM	CNPM
$R_s (\Omega)$	2	1.85	1.69	1.22	1.39	0.99
$R_{ct} (\Omega)$	29.30	10.29	6.00	11.66	21.72	1.42
W	22.75	32.35	23.653	33.72	55.84	10.68
CPE	0.00057	0.00042	0.00018	0.0049	0.00046	0.00008
n	0.943	0.666	0.736	0.688	0.660	0.563

3.3.9.4. Cycle stability

The capacitance retention analysis of CNPM nanocomposite were investigated for 5000 consecutive cycles at a current density of 7 A/g, depicted in Fig. 3.18. There is a gradual decrease in capacitance value for the initial 500 cycles, probably due to the active phase of the working electrode [68]. The sample exhibited a commendable capacity retention of about ~ 97.3 % for the remaining charge-discharge cycles. The noticeable capacitance retention of composite accounts that the material doesn't suffer

any kind of structural deformations despite of repeated charge-discharge operations. Typically, the frequent insertion/extraction of charge carriers into/from the electrode surface causes harmful mechanical degradation of the active material. In contrast, the CNPM nanocomposite with mesoporous architecture and rich interconnected porosity made them compactable to overcome the mechanical strains with its everlasting mechanical flexibility [64], [69].

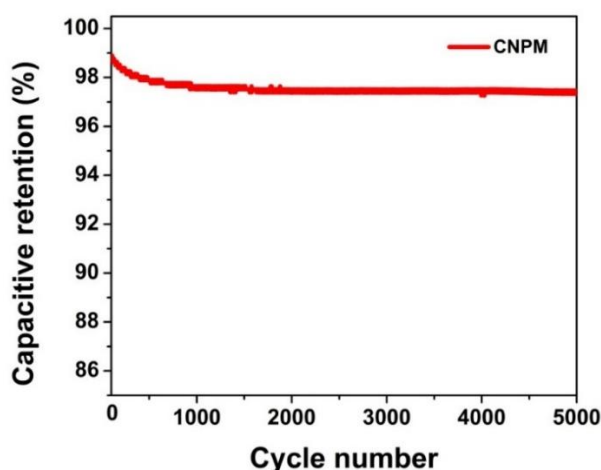


Fig. 3.18. Cycle stability of CNPM working electrode over 5000 cycles.

3.3.9.5. Electrochemical performance of CuO-NiO/PANI/MWCNT quaternary nanocomposite in symmetric two-electrode configuration

A symmetric supercapacitor device set up with a two-electrode configuration was used to test the practical possibilities of CNPM composite electrode. Fig. 3.19 (a) shows the CV curve fabricated device with CNPM as the active material for different scan rates. The material presents a quasi-rectangular shaped CV curve without any noticeable redox peaks, indicating the pseudocapacitive behaviour of the material. The GCD plots (Fig. 3.19 (b)) showcased a very close triangular shaped charge/discharge graphs with IR drop for all the current densities. The material exhibited a specific capacitance of 457 F/g at 1 A/g, 270 F/g at 2 A/g, 113 F/g at 3 A/g and 75 F/g at 5 A/g (shown in Fig. 3.19 (c)). The high value of specific capacitance for the quaternary composite is probably because of the nano-sized porous infrastructure of mixed oxides involved in the composite electrode and the enhanced conductivity, stability and surface area contributed from the PANI and MWCNT counterparts. PANI being a conducting polymer that can serve not only as a binder between the CuO, NiO, and MWCNT

components, but also as a member involved in the redox reactions as well. The satisfactory coulombic efficiency values were obtained for CNPM working electrode, which is presented in Fig. 3.19 (d). The Ragone plot (PD vs. ED curve) of composite electrode was shown in Fig. 3.19 (e) and made a comparison with the standard Ragone plot [70]. The CNPM electrode shows a maximum energy density of 40.62 Wh/Kg and power density of ~ 786 W/Kg. The sample exhibited relatively better energy density and power density compared with the conventional batteries, which indicates the utilization of this quaternary composite electrode for electrode fabrication in electrochemical systems are very promising. The capacitance retention was evaluated for 50000 charge/discharge cycles at a discharge current of 10 mA is shown in Fig. 3.19 (f). The quaternary composite material shows high retention efficiency of about 99.7% over 50000 cycles, which shows its excellent stability and compatibility as potential electrode stuff in energy storage applications.

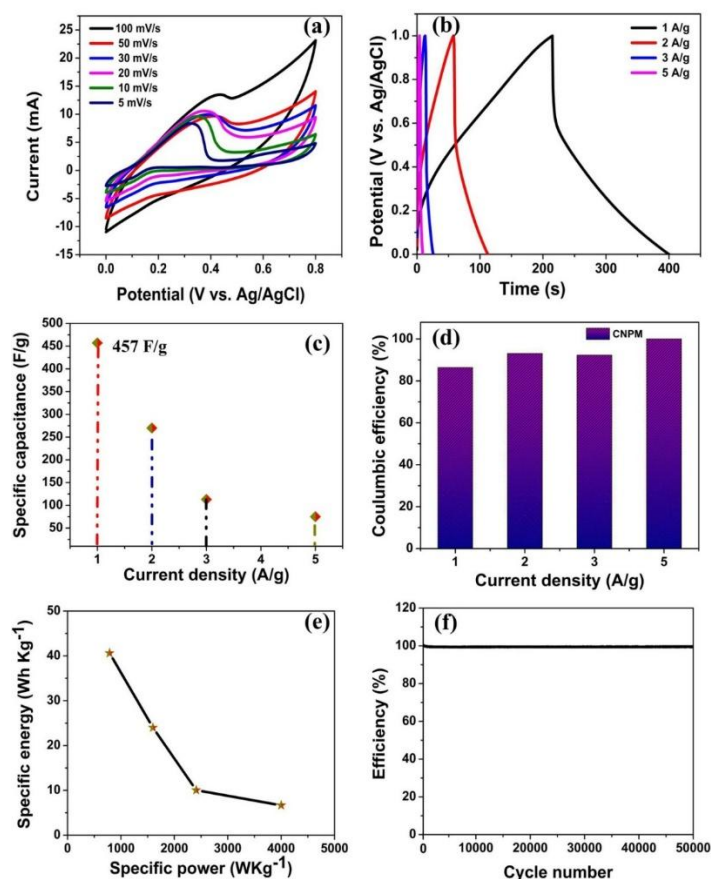


Fig. 3.19. (a) CV (b) GCD plots of CNPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) columbic efficiency analysis (e) Ragone plot and (f) cycle stability of CNPM composite in 50000 cycles.

3.4. CONCLUSION

The CuO-NiO/PANI/MWCNT nanocomposites were prepared using the freeze-drying assisted synthesis method. The chemical oxidative polymerisation of aniline followed by a freeze-drying stage along with already prepared metal oxide composites such as CuO-NiO and MWCNTs forms a feasible method for synthesising CuO-NiO/PANI/MWCNT composites. The structural, morphological, optical and thermal properties of the prepared nanocomposite was evaluated using XRD, Raman, FT-IR, FESEM-HRTEM with EDS, BET and TGA. All these characteristics confirmed the intended formation of nanocomposite with satisfactory properties beneficial for the supercapacitive performances. The electrochemical performance of CNPM working electrode was studied initially in a three configuration. An excellent specific capacitance value of about 775 F/g was reported at a current density of 1 A/g. A symmetric supercapacitor device was established using CNPM working electrode in a two-electrode configuration and it has attained a remarkable energy density of 40.62 Wh/Kg at the power density of ~786 W/Kg. The synergistic interaction between PANI and MWCNTs in the presence of binary metal oxide composites has resulted in improvement of electrochemical performance of the quaternary composite compared with that of its individual components.

Table 3.5. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CuO-NiO/PANI/MWCNT	670	10	775	1	364	10	457	1

3.5. REFERENCE

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Synthesis, Characterization, and Supercapacitive Performance of CuO-Co₃O₄/PANI/MWCNT Hybrid System

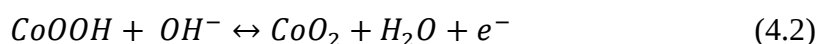
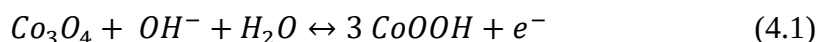
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Owing to the best strategies for improving the characteristics of supercapacitors such as better energy density and long cycle life, it is important to choose impressive composite electrode materials wisely that can supplement both highly porous active structures combined with large accessible spots for ionic species and also can enhance the overall pseudocapacitive nature. Cobaltite oxide (Co₃O₄) is one of the recently explored electrode materials in the area of high-performance supercapacitors on account of its high predicted capacitance and favorable pseudocapacitive behavior. Introduction of Co₃O₄ in to the ternary CuO/PANI/MWCNT hybrid system can enhance the electrochemical performance caused by the peculiar properties of Co₃O₄ such as good efficiency, long term stability and corrosion free nature. The effective combination of binary TMOs (CuO and Co₃O₄) into the PANI/MWCNT environment surpasses the electrochemical performance of the combined quaternary system. The structural, morphological understandings and thermal stability of the combined hybrid system are interpreted with XRD, FESEM-EDS, HRTEM, XPS, BET, RAMAN and TGA. The electrochemical performance of the hybrid system is examined using both three and two electrode configurations.

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4.1. INTRODUCTION

In the current era, metal oxide NPs have gained much attention due to their intriguing properties like significant electrical and chemical properties, high surface-to-volume ratios, and ease of preparation. Along with the recent trend for further improvement of the electrochemical performance of CuO, researchers are preparing electro-active hybrid materials of CuO with other TMOs. Among the popular TMOs predominantly prevailing in the scientific community, cobalt oxide NPs are well-known for applications like catalysis, magnetic fluids, sensors, and energy storage devices [1], [2], [3], [4]. Cobalt oxide exists in various forms like cobaltous oxide (CoO), cobaltic oxide (Co₂O₃) and cobaltite oxide (Co₃O₄), in which the black antiferromagnetic tricovalent tetraoxide (Co₃O₄) found an esteemed position in the field of supercapacitor applications [5]. Co₃O₄ is the least explored one type of electrode material in the electrochemical field, having AB₂O₄ spinel structure along with high theoretical capacitance (~ 3560 F/g) and excellent intercalative pseudocapacitive features. The Co₃O₄ electrode material has been found to have good reversible specific capacity, corrosion resistance and long term stability [6]. The possible charge storage mechanisms followed in a Co₃O₄ based electrode material can be described as follows;



4.1.1. Cobaltite oxide (Co₃O₄): An emerging electrode material

Owing to the properties like high predicted specific capacitance and potential pseudocapacitance properties, Co₃O₄ becomes a viable electrode material in energy storage applications. There are a few previous reports focusing on the electrochemical performance of Co₃O₄ [7], [8], [9]. R. R. Samal *et al.* discussed the anionic and cationic surfactant assisted hydrothermal synthesis of cobalt oxide and explored the electrochemical performance of these cobalt oxide nanoflakes in a three-electrode configuration. They reported a higher capacitance of 777.45 F/g, energy density of 32.66 W h/Kg and powder density of 39.8 kW/Kg for CTAB-assisted Co₃O₄ nanoflakes [5]. An ultra-layered porous Co₃O₄ structures synthesised through the precipitation method has delivered a specific capacitance of 548 F/g at a current density of 8 A/g

with 68% capacitance retention [10]. Badreah Ali Al Jahdaly *et al.* employed phytosynthesis assisted with marine red algae extract as a stabilizing agent for the preparation of Co₃O₄ NPs. The activated carbon/ Co₃O₄ symmetric device designed was established a specific capacitance of 182 F/g at a current density of 1 A/g [11]. Juan Xu *et al.* prepared Co₃O₄ nanotubes via annealing a chemically deposited cobalt hydroxide in an anionic aluminium oxide template. The electrochemical measurements of these Co₃O₄ nanotubes show a specific capacitance value of 574 F/g at 0.1 A/g [12]. Gwang –Su Jang *et al.* reported the electrochemical performance of hydrothermally prepared Co₃O₄ nanorods and stacked NPs. The stack like NPs exhibited a capacitance of 226.3 F/g at a scan rate 10 mV/s in a 6M KOH electrolyte solution. During calcination at high temperature, the surface morphology of the synthesised cobalt oxides has changed to morous category, eventually leading to a better ionic transport through the electrode surface [13]. Unfortunately, the specific capacitance and cycling stability of Co₃O₄ is still very beyond the theoretical value by cause of the limitations like poor electrical conductivity and surface area. Till now, various strategies have been developed by researchers in order to overcome the aforementioned drawbacks. One among the powerful strategies was to establish a metal dopant in to the environment of Co₃O₄ [14], [15], [16]. Faizal Ali *et al.* studied the effect of chromium in the electrochemical performance of cobalt oxide nanostructures by varying the doping percentage from 1 to 10. The Cr 6%-doped Co₃O₄ sample exhibited specific capacitance of 1283 F/g at 5 mV/s in 3M KOH electrolyte solution. The excessive doping of chromium will adversely affect the electrode performance, since it covers the electro-active sites in the lattice of cobalt oxides [17]. Shude Liu *et al.* discussed the electrochemical potential of oxygen deficient Cu-doped Co₃O₄ nanocrystals and designed an asymmetric supercapacitor with O_v-Cu-Co₃O₄@C electrode having a high energy density of 64.1 W h kg⁻¹ at 800 W kg⁻¹. Moreover, the occurrence of Cu dopants and O vacancies in the composite electrode synergistically enhanced the accessible electro-active sites, yielding refined redox chemistry [18].

4.1.2. CuO-Co₃O₄ composite electrodes for supercapacitor applications

Even though, metal doping as well as changing preparation conditions in the synthesis of CuO has improved its pseudocapitance compared with the pristine CuO,

it still suffers capacity decay due to sluggish charge transportation in the electrochemical system. So as to alleviate these limitations, another strategy of developing a hetero-structure with enriched electro-active sites by combining highly conductive and electrochemically active TMO material like Co₃O₄ with CuO is implemented [19], [20]. S. Balasundari *et al.* prepared CuO-Co₃O₄ via a precipitation method followed by the microwave assisted hydrothermal technique. The composite electrode exhibited a specific capacitance of 586 C/g with cyclic reversibility of 113.6% under a high current density of 20 A g⁻¹ after 5000 cycles. The robust synergistic effects between CuO and Co₃O₄ and their potential redox reactions during the charging and discharging process significantly enhance the electrochemical property of the electrode [21]. Recently, Ke Xue *et al.* have grown CuO/Co₃O₄ material directly onto nickel foam by combining electrodeposition and SILAR methods. They prepared spherical and wheat-like nanocomposites and exploited its electrochemical performances. The wheat-like CuO/Co₃O₄ has acquired high specific capacity and stability [22]. K. Athira *et al.* have hydrothermally synthesised CuO/Co₃O₄ nanocomposite and studied its electrochemical performance. The composite electrode material exhibited a specific capacitance of 860 F/g at 2 A/g [23].

4.1.3. CuO-Co₃O₄/PANI/MWCNT quaternary hybrid electrode material as a potential member in ESDs

The next productive strategy for the enhancement of the electrochemical performance of CuO-Co₃O₄ composite is to make them combined with PANI and MWCNTs, which eventually lead to a quaternary hybrid electrode material. There are only a few reports on this electrode combination based on CuO, Co₃O₄, PANI and MWCNTs. S. Prabhu *et al.* used the hydrothermal method for the preparation of 3D flower-like CuO/Co₃O₄/r-GO heterostructure and the as-prepared electrode has shown a high surface area resulting in more interfacial contact area between the electrode surface and electrolyte ions, thereby the excellent electrochemical performance is attained [24]. Bairui Thao *et al.* fabricated Ni foam supported CuO/Co₃O₄/r-GO composite electrode and the asymmetric supercapacitor device based on the as-synthesised composite delivered a specific capacitance of 660.5 F/g at 2 A/g with 92.3% capacity retention [25]. Yingmeng Zhang *et al.* prepared sandwiched CuO/Co₃O₄ nanosphere/RGO composite and explored the electrochemical performance of the as-

synthesised 3D-composite structure. The sandwiched nature of CuO/Co₃O₄ nanospheres on to the layers of RGO has avoided the aggregate formation among both RGO and CuO/Co₃O₄ nanospheres, which leads to enhanced conductivity and electrochemical performance of the electrode. The electrode material exhibited a reversible capacitance of 847 mA.h.g⁻¹ after 200 cycles at 20 mA/g [26]. To the best of our knowledge, there are no literatures on CuO-Co₃O₄/PANI/MWCNT quaternary composites for any sort of applications.

4.2. EXPERIMENTAL SECTION

4.2.1. Synthesis materials

Copper nitrate trihydrate (Cu(NO₃)₂.3H₂O), urea (CH₄N₂O), ammonium persulfate (APS) ((NH₄)₂S₂O₈), aniline hydrochloride (C₆H₅NH₂.HCl), analytical grade hydrochloric acid (HCl), sodium sulphate (Na₂SO₄), sodium dodecyl sulphate (CH₃(CH₂)₁₁OSO₃Na) (SDS, > 98%), cobalt nitrate ((CoNO₃)₂.6H₂O), ammonia solution (25%) and de-ionised (DI) water were purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, OD × L = 6 – 9 nm × 5 μm), polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standard and utilized without any further purifications. Distilled ethanol was used for cleaning purposes.

4.2.2. Synthesis of Co₃O₄

The Co₃O₄ nanoparticles were prepared via similar surfactant-free hydrothermal process with the similar reaction conditions of the CuO synthesis. Firstly, 0.1M of cobalt nitrate was dissolved in 75 ml de-ionised water. Later, 10 ml ammonia solution was added to the precursor solution to achieve a pH in the range of 8-10 under constant stirring. 0.003 M urea was added to the whole solution before transferring it into the autoclave setup and kept in the oven under 180 °C for 24 hours. When the reaction conditions met, the resultant solution from the reactor was filtered and washed thoroughly using DI water and ethanol. The obtained Co₃O₄ precipitate was then shifted to an oven at 80 °C for 6 hours to get the purified Co₃O₄ nanoparticles.

4.2.3. Synthesis of CuO-Co₃O₄ nanocomposite

The CuO-Co₃O₄ nanocomposite was processed using the hydrothermal method without employing any additives or surfactants. Initially, 0.1 M cobalt nitrate was allowed to dissolve completely in 30 ml of DI water via a continuous stirring process. Later, the previously prepared CuO nanoparticles (40 mg) were allowed to disperse in the above-mentioned precursor solution. Later, a 20 ml of ammonia solution was added drop wise to the whole solution. Then, 0.6 mM urea was added to the solution without disturbing the stirring process till a clear homogeneous solution was attained. The whole 50 ml solution was then transferred to an autoclave and set to keep in an oven at 180 °C for 24 hours to complete the synthesis process. The earned precipitates after hydrothermal reaction were washed multiple times with DI water and ethanol for the removal of the unwanted/unreacted substances from the resultant. Later, the obtained precipitate was transferred to oven at 80 °C for 6 hours to get the CuO-Co₃O₄ nanocomposite.

4.2.4. Synthesis of Co₃O₄/PANI/MWCNT ternary nanocomposite and CuO- Co₃O₄/PANI/MWCNT quaternary nanocomposite

The Co₃O₄/PANI/MWCNT ternary nanocomposite was prepared in a similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared Co₃O₄ and the final product is named CoPM for convenience.

The CuO-Co₃O₄/PANI/MWCNT quaternary nanocomposite was prepared in a similar synthesis procedure as CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared CuO-Co₃O₄ nanocomposite and the final product is named CCoPM for convenience.

4.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, Aeris Research (Source: Cu K α)). Fullprof Suite software was used for Rietveld analysis. Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany) was employed to determine the vibrational modes of the as-synthesised samples. Fourier Transform Infrared (FTIR)

spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using a ZnSe crystal. The surface morphology and elemental composition were done using a combination of High-Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of a TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

4.2.6. Electrode preparation and electrochemical studies

The electrochemical features of as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt % of active material, 10 wt % of polyvinylidene fluoride (PVDF) and 10 wt % of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly in to a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in the working electrode was 1.7 mgcm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of as-synthesised samples.

4.3. RESULTS AND DISCUSSION

4.3.1. X-Ray diffraction (XRD)

The structure and phase purity of materials were examined using X-ray diffractometer. The XRD profiles of Co₃O₄ and CuO-Co₃O₄ nanoparticles along with that of already prepared CuO for comparison are displayed in Fig. 4.1(a). Both Co₃O₄ and CuO-Co₃O₄ materials show their polycrystalline nature. All the dominant peaks of Co₃O₄ can be well indexed by comparing them with the corresponding JCPDS (No.-

43-1003). The crystallographic scattering peaks are observed at 18.88°, 31.16°, 36.73°, 38.55°, 44.60°, 55.72°, 59.24°, and 65.15° which correspond to (111), (220), (311), (222), (400), (422), (511) and (440) planes of the face centred cubic Co₃O₄ [12]. Moreover, no peaks of secondary phases like CoO or impurity peaks are observed in the XRD profile of Co₃O₄, which validate the formation of pristine cubic Co₃O₄ with preferential plane growth in the (311) direction. The XRD pattern of CuO-Co₃O₄ nanocomposite is found to be an exact mix of the monoclinic CuO and the cubic Co₃O₄ crystal structures, which clearly indicate that both CuO and Co₃O₄ phases are grown freely in the synthesis stage. Fig. 4.1 (b) shows the XRD patterns of the newly synthesised CoPM and CCoPM in the region 10°-90° along with those of PANI, MWCNT, and CPM for confirming the exact formation of the composites. The CoPM composite consists of peaks correspond to cubic Co₃O₄ phase in the 30°-90° region, even though their intensity get diminished owing to the dominance of PANI and MWCNT parts. The crystallographic plane (111) of Co₃O₄ is not appeared in the spectra because of the three dominant peaks of PANI observed in that region. Furthermore, the slight peaks shifts seen in the peak positions of the cubic Co₃O₄ can be attributed to their interaction with PANI-MWCNTs. For CCoPM composite, all the peaks in between 30°-90° are assigned to the presence of CuO-Co₃O₄ composite in the hybrid system. Also, the three peaks at 14.71°, 20.06° and 25.18° in XRD are correspond to (011), (020), and (200) crystallographic planes of emeraldine salt. No peak corresponding to MWCNT is visible in the XRD spectra of CoPM and CCoPM, which may be due to its peak coincidence with the broad bump of PANI in the 20-30° region. Thus, the formation of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanostructures is substantiated from the XRD data. The charge transfer interactions among the metal oxides, PANI and MWCNT leading to alterations in chain packing and configurations, may result in gentle shifts in the peak positions [27].

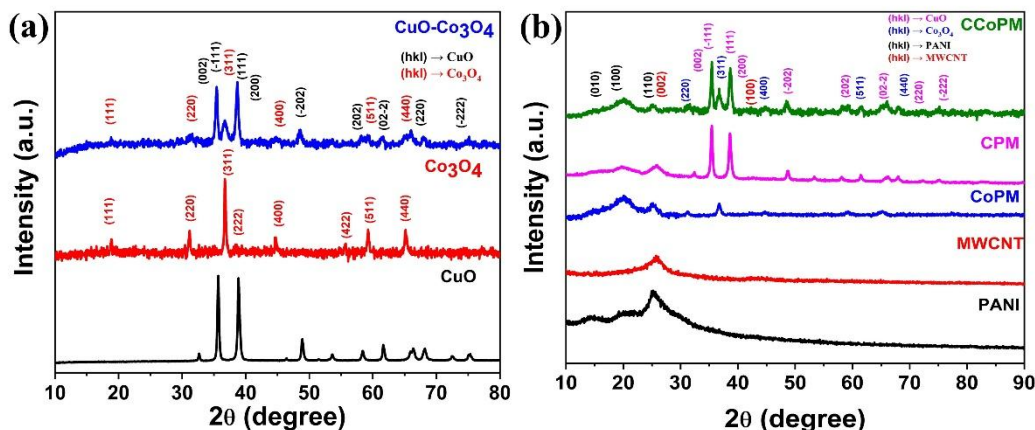


Fig. 4.1. XRD patterns of (a) CuO, Co₃O₄, CuO-Co₃O₄ nanoparticles and (b) PANI, MWCNT, CoPM, CPM, and CCoPM composites.

4.3.2. Raman spectroscopy

The Raman spectral evaluation was carried out to identify the structural purity and secondary or impurity phases in the composites. Fig. 4.2 (a) portrays the Raman spectra of Co₃O₄ nanoparticles having prominent bands at 194 cm⁻¹, 483 cm⁻¹, 520 cm⁻¹, 615 cm⁻¹, and 687 cm⁻¹, corresponding to F_{1g}, E_g, F_{2g}, F_{3g} and A_{1g} modes of spinel Co₃O₄ structure, which are consistent with previous reports [28]. The most intense Raman shift at 687 cm⁻¹ is attributed to the vibrational modes of octahedral units of Co₃⁺ ions. The Raman spectra of CuO-Co₃O₄ composite is displayed in Fig. 4.2 (b), presenting a blend of the Raman active modes of both monoclinic CuO and cubic Co₃O₄ [29]. The ternary composite CoPM shows Raman modes combining modes of individual constituents, as shown in Fig. 4.2 (c). Along with the E_g and F_{2g} modes of spinel Co₃O₄, characteristic modes of PANI and MWCNT were appeared in the spectra. The Raman shifts at 1346 cm⁻¹, 1599 cm⁻¹, and 2687 cm⁻¹ were ascribed to the D, G and 2D bands of MWCNTs. The lattice defects of phonon mode of vibrations in MWCNT surface cause the D mode, whereas the vibrations of C-C bond (sp² carbon atoms) in the graphitic layer result in the G band in the Raman spectra [30]. The shifts at 710 cm⁻¹, 816 cm⁻¹, and 1187 cm⁻¹ correspond to the characteristic peaks of the emeraldine salt form of PANI molecules. The Raman spectra of the quaternary composite CCoPM is displayed in Fig. 4.2 (d). The A_g and B_g modes of CuO at 289 cm⁻¹ and 618 cm⁻¹ and F_{2g} and F_{3g} modes of Co₃O₄ at 512 cm⁻¹ and 601 cm⁻¹ clearly confirm the presence of CuO-Co₃O₄ nanocomposite in the hybrid matrix. Unlike, the

CoPM sample, the CCoPM composite displayed the three intense shifts at 1183 cm⁻¹, 1342 cm⁻¹ and 1607 cm⁻¹ which indicated the synergistic combinational effects of PANI and MWCNT along with other less intense modes of both PANI and MWCNTs in the hybrid system. The peak intensity of Raman active modes of PANI molecules was lesser in the CoPM compared with that of in the CCoPM composite. Additionally, even though the characteristic peaks of PANI and MWCNTs were visible in both composites, there was an observable overlap of major MWCNT peaks with those of PANI. The PANI dominations in the Raman spectra were due to the lower MWCNT content in the sample as well as the inability of the laser beam to penetrate into the darker materials [31]. The observed small shifts in the quaternary composite are attributed to the effective interaction between PANI, MWCNT and metal oxides.

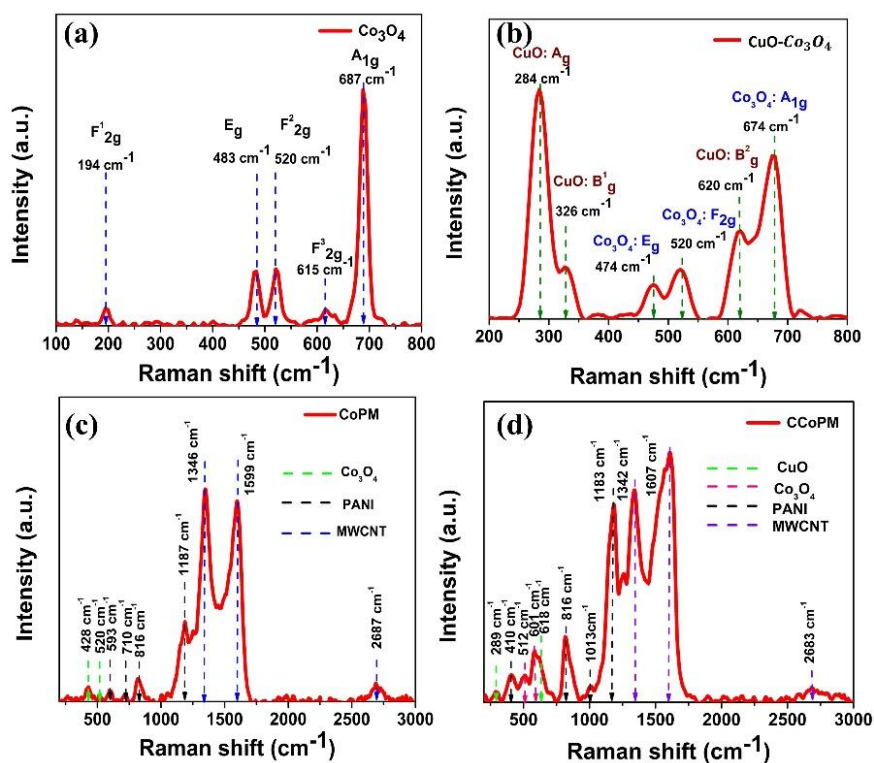


Fig. 4.2. Raman profiles of pristine (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM composites.

4.3.3. FT-IR spectroscopy

The crystal structure and molecular bonding in the prepared composites were then identified using FT-IR spectra, shown in Fig. 4.3. The FT-IR spectrum of the Co₃O₄ nanostructure has shown in the Fig. 4.3 (a) displays two prominent peaks of

spinel Co₃O₄ at 655 cm⁻¹ and 568 cm⁻¹. The peak at 655 cm⁻¹ ascribed to the stretching mode of ABO, where B represents the Co³⁺ in the tetrahedral hole in the Co₃O₄ lattice, whereas the peak at 568 cm⁻¹ related to the OB₃ stretching mode where B represents Co²⁺ in the octahedral hole [13], [32]. The peak at 1510 cm⁻¹ attributed to the stretching vibrational mode of O-H bond, whereas the peak at 1163 cm⁻¹ represents the stretching vibrational modes of C-O bonds [32]. In the Fig. 4.3 (b), there are peaks corresponding to both CuO and Co₃O₄ crystal structures. The peaks representing Co₃O₄ were appeared at 677 cm⁻¹ and 574 cm⁻¹, whereas the peak of Cu-O bond was occurred at 438 cm⁻¹. The peak at 2920 cm⁻¹ corresponds to stretching modes of O-H bonds, while the peak at 1452 cm⁻¹ attributed to vibrations of H₂O molecules [33]. The other less intense peaks in the range of 900-1300 cm⁻¹ represent the carbonyl groups [5]. The FT-IR spectra of CoPM and CCoPM nanocomposites are presented in Fig. 4.3 (c-d), highlighting the prominent modes of PANI, MWCNTs and metal oxides illustrated in Table 4.1.

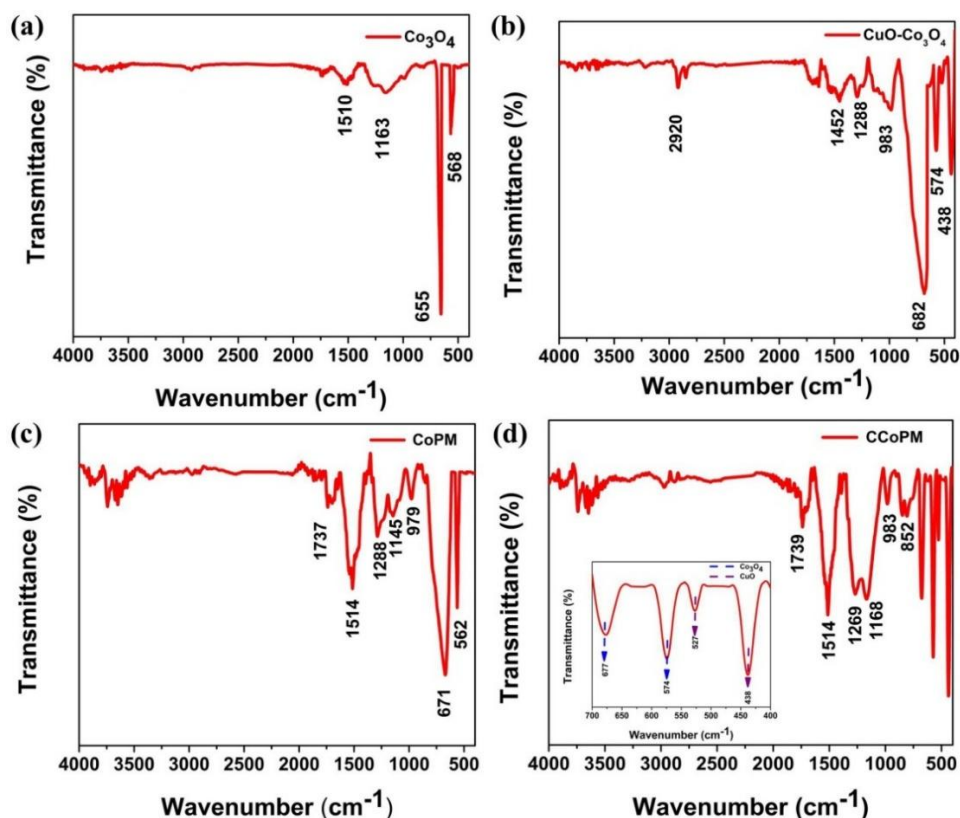


Fig. 4.3. FT-IR spectra of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM nanocomposites. (inset shows the zoomed spectra of CCoPM in the range 400-700 cm⁻¹ as marked in its corresponding figures 4.3 (d))

Table 4.1. List of peaks in FT-IR spectrum of CoPM and CCoPM nanocomposites and its corresponding assignments

FT-IR peaks		Assignments
CoPM	CCoPM	
1737 cm ⁻¹	1739 cm ⁻¹	stretch mode of carboxylic groups in MWCNT
1514 cm ⁻¹	1514 cm ⁻¹	C=C stretching in quinoid ring of PANI
1288 cm ⁻¹	1269 cm ⁻¹	C-N for aromatic amines in the polaron structure of conducting PANI
1145 cm ⁻¹	1168 cm ⁻¹	characteristic band of the protonated form of conducting PANI
972 cm ⁻¹	983 cm ⁻¹	due to protonated imine group in PANI
-	852 cm ⁻¹	Out of plane C-H bending vibration.
671 cm ⁻¹ & 569 cm ⁻¹	677 cm ⁻¹ & 574 cm ⁻¹	stretching modes of Co ₃ O ₄
-	527 cm ⁻¹ & 438 cm ⁻¹	stretching vibrations of Cu-O

4.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The surface morphological evolutions of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites were systematically investigated through FESEM-EDS analysis, portrayed in Fig. 4.4. The low and high magnification SEM images of Co₃O₄ shown in Fig. 4.4 (a-c) present a heterogenous distribution of several octahedral and diamond-like nanoparticles. The octahedral shaped nanoparticle carries a side length of around 128 nm, whereas the diamond-like particles have dimensions around 200 nm. The overall uneven distribution of these mixed shaped particles resulted in minimal pores in the morphology. In contrast, the morphological case of CuO-Co₃O₄ nanocomposites, a porous network of uniformly distributed bulky nanospheres interspersed with diamond-shaped nanoparticles, probably Co₃O₄ particles over the surfaces can be seen (Fig. 4.4 (d-f)). The sphere carries an average diameter of 940 nm, whereas the diamonds like structures over the sphere surfaces have a side length in the range of 20 to 35 nm. The porous architecture of this nanocomposite can contribute to enhancement in its specific surface area, thereby improving the material's

supercapacitive performances. The incorporation of PANI and MWCNTs into the Co₃O₄ nanosystem, has induced visible morphological modifications like the transformation of octahedral shaped particle of Co₃O₄ into an agglomerated form combining the polymer networks and tubular morphology of MWCNTs (Fig. 4.4 (g-i)). The overall agglomerated morphology of the ternary CoPM composite has been limited by beneficial pores. In the instance of CCoPM quaternary composite, several voluminous pores can be seen along with the fibrillar morphology, which can positively enrich the effective surface area of composite (Fig. 4.4 (j-l)). The interconnected thick fibres carry an average diameter of about 42 nm. From the lower magnification SEM micrographs (Fig. 4.4 (j)), it is easily understood that the grafting of PANI over the MWCNT surfaces in the presence of CuO-Co₃O₄ made the metal oxides morphologically indistinct. The highly substantial porous infrastructure made the composite capable for the electrochemical applications.

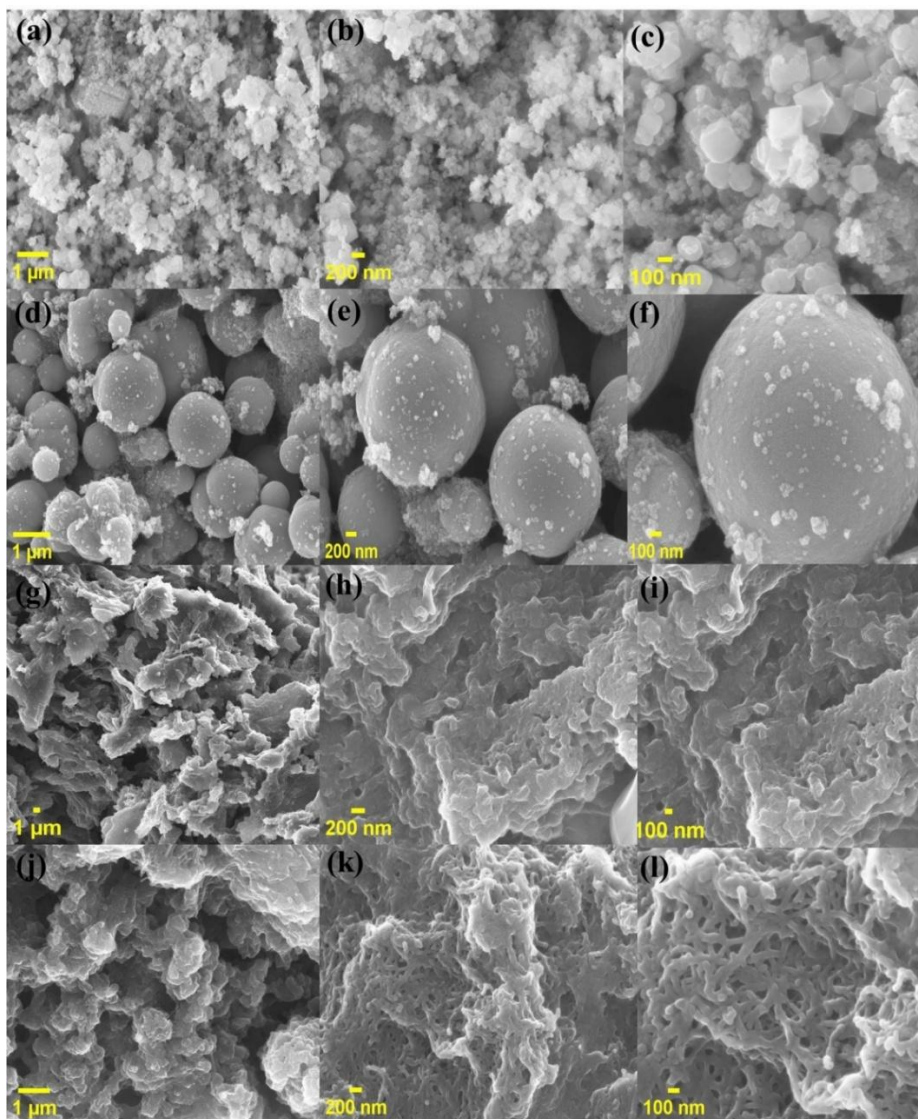


Fig. 4.4. FESEM micrographs of (a,b,c) Co₃O₄ (d,e,f) CuO-Co₃O₄ (g,h,i) CoPM (j,k,l) CCoPM nanocomposites.

The elemental composition of the prepared composites was done using conventional energy dispersive spectroscopy (EDS), as shown in Fig. 4.5. The co-existence of elements like cobalt and oxygen is clearly visible in the spectra of Co₃O₄, displayed in Fig. 4.5 (a). Also, the EDS plot of CuO-Co₃O₄ (Fig. 4.5 (b)) shows the noticeable peaks of constituents like copper, cobalt and oxygen, validating the exact formation of these elements in the material. In the EDS spectrum of CoPM, the presence of elements C, N, Co, and O verifies effective introduction of PANI/MWCNT combination into Co₃O₄, as shown in Fig. 4.5 (c). From the EDS image of CCoPM shown in Fig. 4.5 (d), the co-existence of Cu, Co, N, C and oxygen clearly confirmed the formation of the quaternary CCoPM composite. The atomic mass concentrations of

the constituent elements are listed in Table 4.2. The atomic concentrations of each constituent element in the synthesised material were validated to ensure the formation of planned compounds. The relatively higher atomic presence of carbon was observed in the ternary and quaternary composites, indicating the synergistic interactions of PANI and MWCNTs.

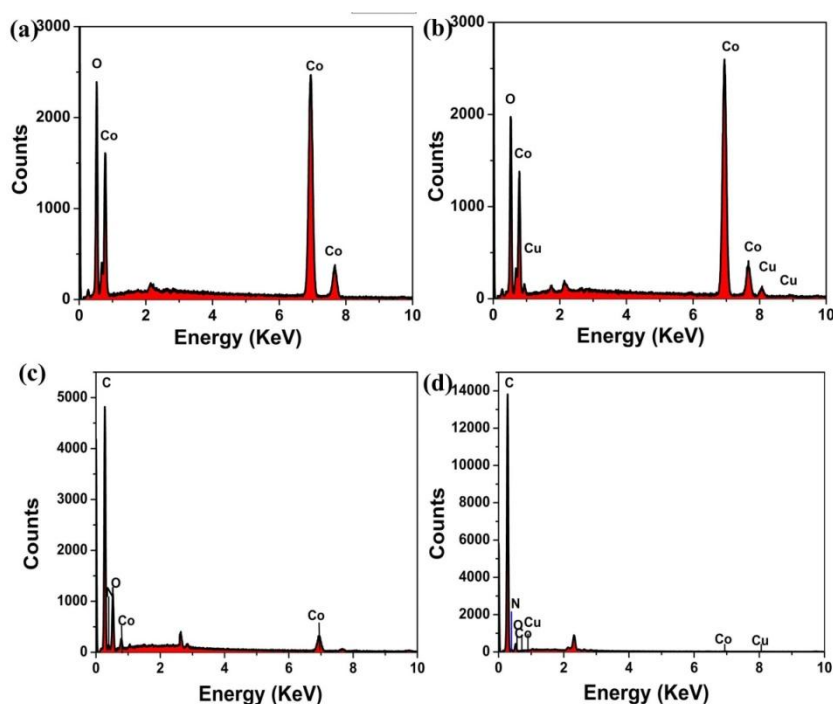


Fig. 4.5. EDS spectra of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM nanocomposites.

Table 4.2. Elemental data of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM composites obtained from EDS analysis.

Sample	Atomic ratio (%)				
	Cu	O	Co	C	N
Co ₃ O ₄	-	54.21	45.79	-	-
CuO- waCo ₃ O ₄	17.25	43.64	39.11	-	-
CoPM	-	17.03	13.80	59.73	9.44
CCoPM	8.12	11.11	7.31	57.64	15.82

The elemental mapping images of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites are shown in the following figures (Fig. 4.6, Fig. 4.7, Fig. 4.8, Fig. 4.9). The yellowish colour over the whole material surface is clear evidence for the

uniform distribution of cobalt and oxygen in Co₃O₄ (Fig. 4.6). The co-existence of CuO and Co₃O₄ were validated from the EDS map of CuO-Co₃O₄ shown in Fig. 4.7. In the case of CoPM composite, the co-existence of Co₃O₄, PANI and MWCNTs were observable at the first glance itself (Fig. 4.8). However, some kind of uneven distribution of carbon is seen in the EDS map, suggesting some heterogeneity in the synthesis process. The domination of the element carbon is evident in the EDS mapping image of CCoPM (Fig. 4.9), as suggested by the EDS data. But the existence of cobalt oxide, copper oxide and PANI were also suggested by the corresponding EDS elemental distribution images.

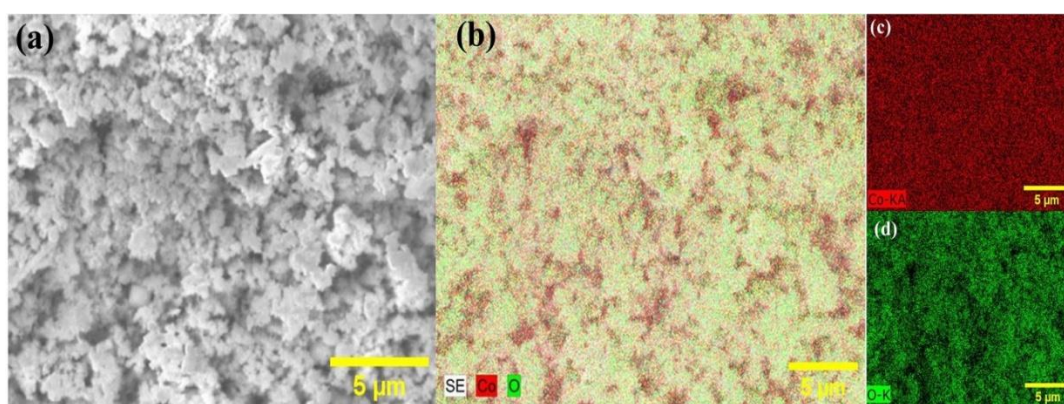


Fig. 4.6. (a) SEM image, (b) EDS mapping of Co₃O₄ nanostructures, and (c-d) selective elemental distribution for the area shown in image (a).

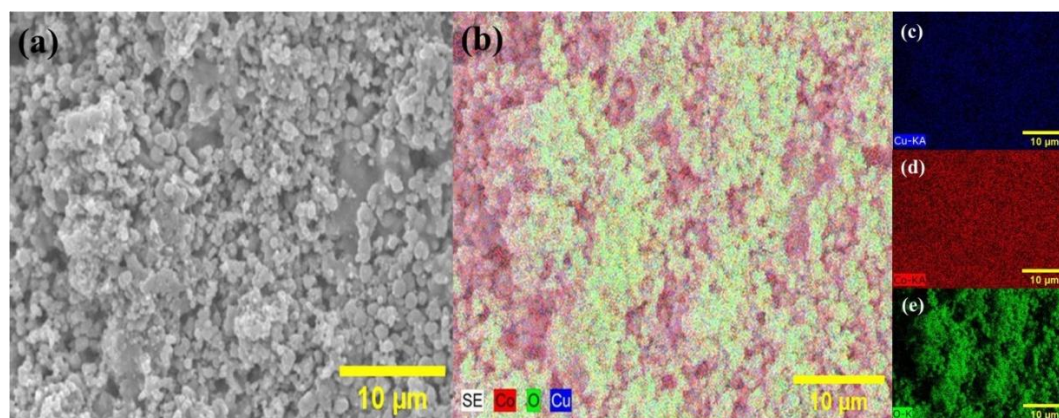


Fig. 4.7. (a) SEM image, (b) EDS mapping CuO-Co₃O₄ nanocomposites, and (c-e) selective elemental distribution for the area shown in image (a).

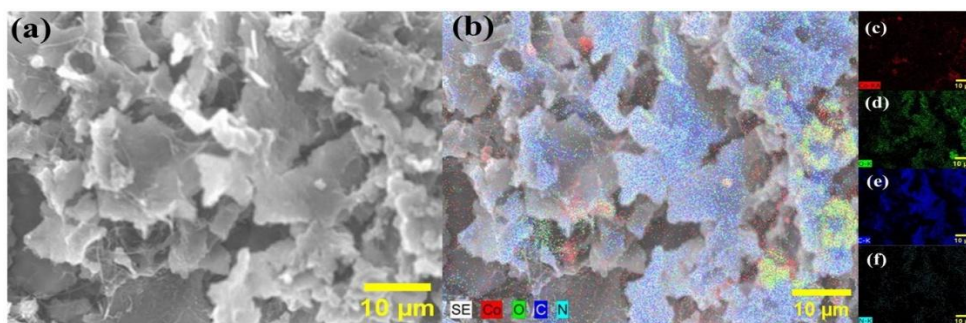


Fig. 4.8. (a) SEM image, (b) EDS mapping CoPM nanocomposites, and (c-f) selective elemental distribution for the area shown in image (a).

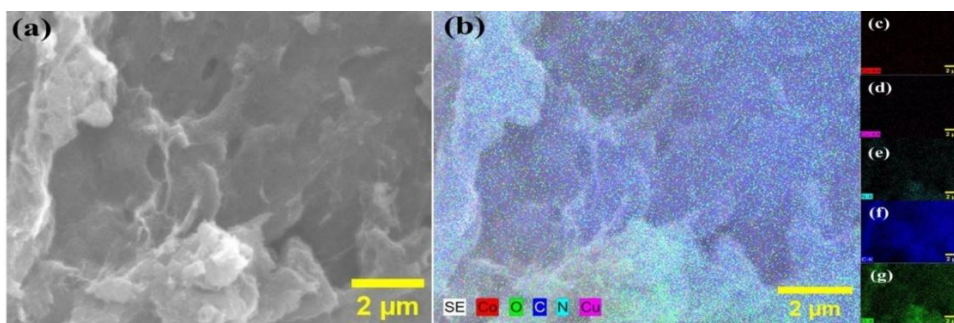


Fig. 4.9. (a) SEM image, (b) EDS mapping CCoPM nanocomposites, and (c-g) selective elemental distribution for the area shown in image (a).

4.3.5. High Resolution Transmission electron micrographs (HR-TEM)

The microstructural properties of the CCoPM composite were further investigated using TEM, HRTEM-SAED analyses, depicted in Fig. 4.10. The TEM images shown in Fig. 4.10 (a,b), illustrates the presence of PANI grafted MWCNTs integrated with the metal oxide phases. The PANI grafted tubules have a greater average diameter compared with the unmodified MWCNTs. The CuO existence is substantiated from the HRTEM image shown in Fig. 4.10 (c), showing the dominant crystallographic (111) and (-111) planes within the composite. The homogenous distribution of metal oxide particles within the composite was evident from the HRTEM image shown in Fig. 4.10 (d), with the particle size distribution histogram plot shown in the inset of Fig. 4.10(d). The HRTEM image of lumps that appeared in the fibrous network was attributable to the (200) plane of MWCNTs (Fig. 4.10 (e)). The SAED pattern displayed in Fig. 4.10 (f) shows the polycrystalline nature of the sample.

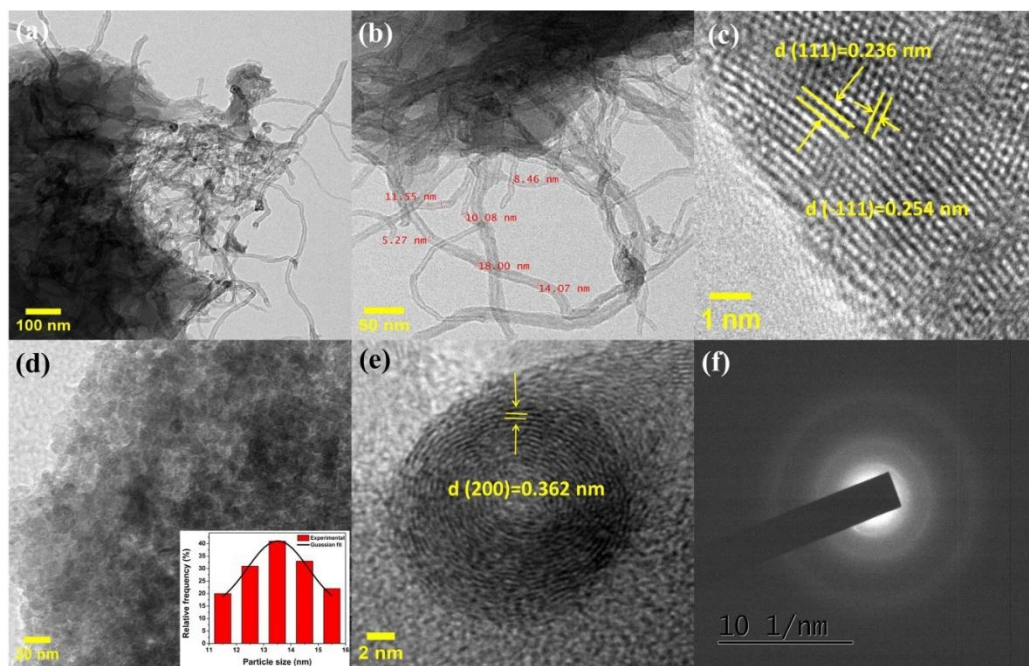


Fig. 4.10. (a,b) TEM micrograph (c,d,e) HRTEM images (f) SAED pattern of CCoPM composites.

4.3.6. X-Ray Photoelectron spectroscopy (XPS)

The elemental compositions and chemical oxidative states of the quaternary CCoPM nanocomposite were investigated through XPS studies, which are presented in Fig. 4.11. The survey spectra of the composite are shown in Fig. 4.11 (a), having the evidence of elements C, N, O, Cu, and Co in the matrix, without any impurity elements. The spectral resolution of the C 1s state is presented in Fig.4.11 (b), which is associated with three peaks after deconvolution at binding energies 284.3 eV, 285.2 eV, and 286.4 eV. The intense peak of core level C 1s at 284.3 eV was allocated to the sp² C atoms. The peak at 285.2 eV was responsible for sp³ C atoms as well as indicating the carbon-nitrogen binding through C=N bonds [34]. While, the less intense peak at 286.4 eV can be associated with both C-N bonds in the composites, proving the effective interaction between PANI and MWCNTs [35]. The core level spectrum of the O 1s orbital level is shown in Fig. 4.11 (c), which is deconvoluted to four major and minor peaks at 529.1 eV, 531.3 eV, 532.2 eV, and 534.6 eV. The less intense peak at lower binding energy 529.1 eV was the representation of both metal-oxygen bonds arising from CuO and Co₃O₄ crystals as well as C-O/C=O bonds [34], while the intense peak at 531.3 eV was associated with oxygen vacancies prevailing in the whole hybrid composite [36]. The

high intense broad peak at 532.2 eV was responsible for the adsorbed –OH functional groups on the composite surfaces. The minor peak at the higher binding energy position was associated with O=C-O bondings resulted from the PANI/MWCNT intercalations [37]. The deconvoluted N 1s spectra was displayed in Fig. 4.11 (d), demonstrating three equal intense peaks located at the binding energies 399 eV, 399.6 eV and 401 eV associated with emeraldine form of PANI. The peak at 399 eV was associated with the quinoid imine ring (=N-H-), whereas peak at 399.6 eV arose from the presence of benzenoid amine ring (-N-H-). The third peak at higher binding energy is responsible for -N-H⁺- bonds in the composite [38]. The existence of CuO in the composite system was identified from the core level spectra of Cu 2p, displayed in Fig. 4.11 (e). The two characteristic peaks located at 933.3 eV and 953.4 eV were attributed to Cu 2p_{3/2} and Cu 2p_{1/2} orbits of Cu²⁺ states of CuO, with a spin orbit coupling energy band gap of 20.1 eV. The two satellite peaks that appeared at 943.4 eV and 963.2 eV further confirm the presence of CuO phase in the composite [24], [34]. In the meantime, the characteristic peaks of Co 2p phase of Co₃O₄ were identified from the high resolution XPS spectra presented in Fig. 4.11 (f). The two major peaks appeared at 782.5 eV and 797.8 eV were attributed to the Co³⁺ 2p_{3/2} and Co³⁺ 2p_{1/2} orbital levels of Co³⁺ oxidation state, along with their obvious shake-up peaks at 787 eV and 802.2 eV [13].

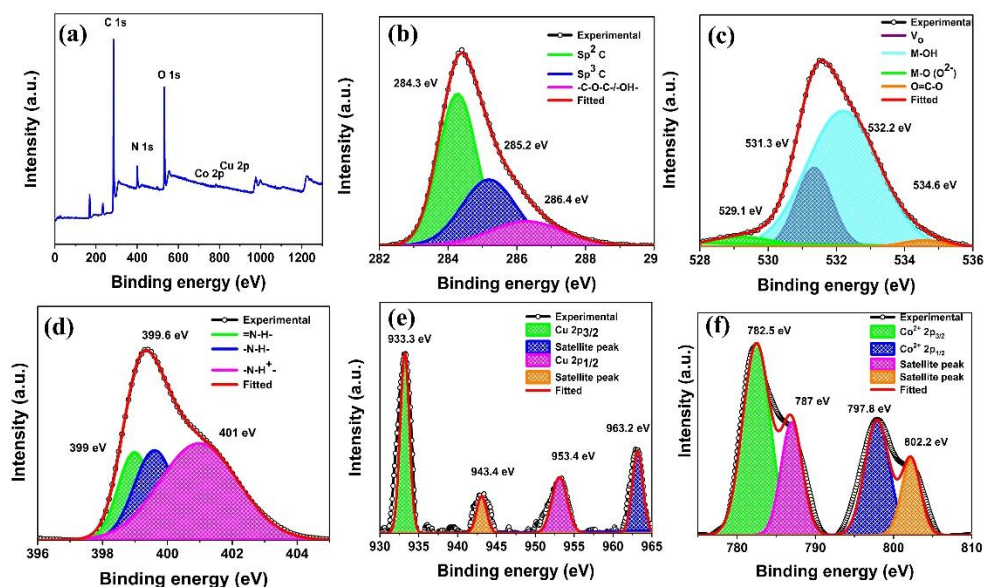


Fig. 4.11. (a) XPS survey spectrum and XPS elemental core spectra of (b) C 1s and (c) O 1s (d) N 1s, (e) Cu 2p, and (f) Co 2p states of CCoPM nanocomposite.

4.3.7. Brunauer-Emmett-Teller (BET) analysis

The specific surface area and pore size distribution of Co₃O₄, CuO-Co₃O₄, CoPM, and CCoPM nanocomposites were estimated using Brunauer-Emmett-Teller analysis and are presented in Fig. 4.12. From the N₂ adsorption-desorption isotherm plot of Co₃O₄ which is shown in Fig. 4.12 (a), it is interpreted that the material exhibits type IV adsorption behaviour with a H3 hysteresis loop ranging from 0.5-1 (P/P₀). Co₃O₄ shows mesoporous nature with a BET surface area of about ~12.3 m²/g. The pore radius and pore volume of Co₃O₄ estimated from the pore size distribution (PSD) plot shown in the inset of Fig. 4.12 (a) is 5.22 nm and 0.014 cm³/g, respectively. The adsorption-desorption plot of CuO-Co₃O₄ nanocomposite (Fig. 4.12 (b)) concluded the type IV adsorption behaviour of composite with H3 hysteresis loop between 0.5-1 (P/P₀). The specific surface area was estimated to be 61 m²/g. The mesoporous nature of this composite was visible from the PSD plot shown in the inset figure with a pore radius and volume of about 1.12 nm and 0.038 cm³/g, respectively. The CoPM composite sample exhibits a type IV adsorption isotherm with H3 hysteresis loop ranges 0.6-0.9 (P/P₀) with a surface area of 34 m²/g, which is shown in Fig. 4.12 (c). From the PSD plot shown in the inset figure, the pore radius and volume were estimated to be 4.32 nm and 0.049 cm³/g. In the case of the quaternary CCoPM composite, the N₂ adsorption-desorption isotherm plot (Fig. 4.12 (d)) shows a type IV adsorption nature with a H3 hysteresis loop ranges between 0.5-1 (P/P₀). The mesoporous nature of the composite sample was inferred from the PSD plot (inset figure in Fig. 4.12 (d)) with a pore radius and volume of 1.51 nm and 0.081 cm³/g, respectively. The BET surface area of the quaternary composite is about 100.1 m²/g. While the contribution of PANI is essential in terms of electrical conductivity, but its coating over the nanotubes can cause a reduction in the active porosity of MWCNTs, despite the inherently high surface area of the nanotubes. The CCoPM composite, having a greater specific surface area and well-established mesoporous structure, which can eventually turn up the electrochemical performance of the composite electrode.

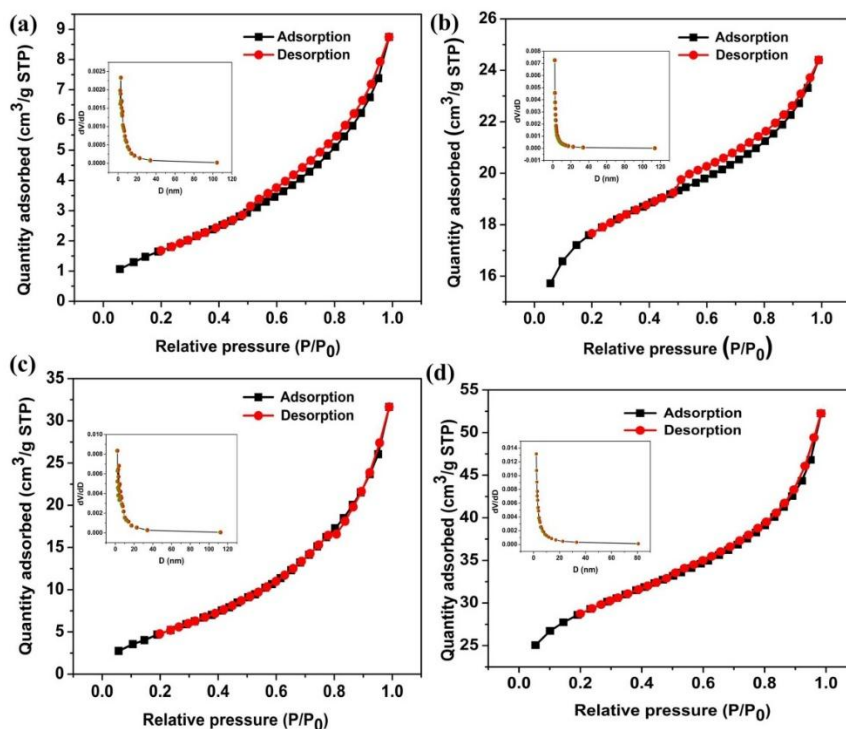


Fig. 4.12. The N₂ adsorption-desorption isothermal plots of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM and (d) CCoPM nanocomposites. Inset shows the corresponding PSD plots.

4.3.8. Thermo-gravimetric Analysis (TGA)

The thermal stability of composite material is one of the significant features that affects the electrochemical performances of the system. Fig. 4.13 shows the thermogravimetric analysis results of the CCoPM composite. The thermal stability of CCoPM can be explained through three main steps of decomposition, similar to PANI. In the first stage, complete release of water molecules accounts for a weight loss of 8.23% at a temperature of 111 °C. Due to the thermal decomposition of polymer molecules, the composite material underwent a weight loss of about 36% until the temperature reaches 324 °C. The release of acid dopants from the composite also contributed to this loss of mass. In the final step, CCoPM losses weight by 11.56% at 525 °C attributable for the complete degradation of polymer components [41], [42]. A final residue of about 40 % was retained by the CCoPM composite at the end of thermal process, which is much higher than that of pure PANI. Thus, the individual contributions from each constituent made the CCoPM composite material a capable member in the area of electrode materials. The excellent thermal stability and robust structure of MWCNTs benefit the overall heat resistance of composite material, while

the metal oxides serve as a thermal barrier contributing to the effective durability of material [43], [44].

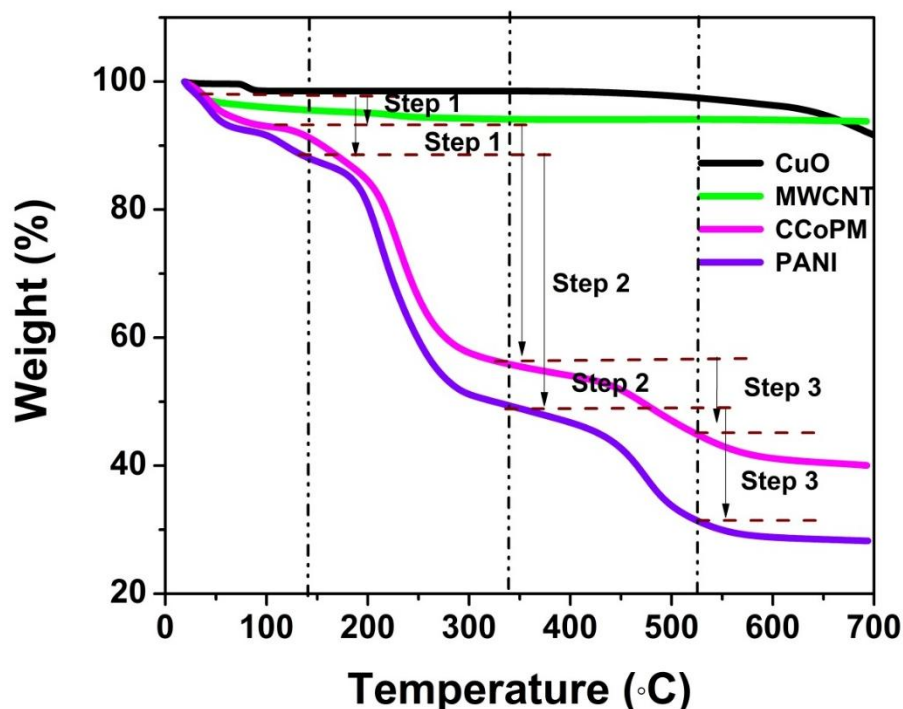


Fig. 4.13. Thermogravimetric analysis of CuO, MWCNT, PANI and CCoPM composite.

4.3.9. Electrochemical studies

4.3.9.1. Cyclic voltammetry (CV)

The electrochemical performance of the prepared Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites was evaluated using the conventional three-electrode cell configuration. Fig. 4.14 illustrates the cyclic voltametric curves of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM working electrodes in a potential window of 0-0.8 V at different scan rates from 5 mV/s to 100 mV/s. The CV curves of Co₃O₄ displayed in Fig. 4.14 (a) show quasi-rectangular shape current responses, confirming the pseudocapacitive nature of Co₃O₄. Undoubtedly, the capacitive current increases with scan rates, suggesting its remarkable reversibility of charge-discharge response. The CV curve retained its shape during each oxidation and reduction processes even though the sweep rate got amplified. Alike Co₃O₄, the CuO-Co₃O₄ composite also displayed a quasi-rectangular CV curve without any noticeable redox peaks (Fig. 4.14 (b)). However, the CV curves of CuO-Co₃O₄ composite yield larger integral area compared with Co₃O₄

and CuO electrodes, indicating the better electrochemical reaction activities of the composite and upgraded specific capacitance values due to the combined contributions of CuO and Co₃O₄. The cyclic voltametric responses of CoPM and CCoPM composites are portrayed in Fig. 4.14 (c-d). The CoPM ternary composite exhibits a non-rectangular CV curve with a pair of noticeable redox peaks at (0.19V, 0.4V). The area under the current response of the CoPM composite was relatively higher than Co₃O₄, due to the impact of electrochemical features of PANI and MWCNTs. The CV profiles of the CCoPM show the highest current response as anticipated compared with the other nanostructures, suggesting the contributions of CuO, Co₃O₄, PANI and MWCNTs get effectively used to get a refined electrochemical performance. The redox peaks in this quaternary composite are not distinguishable as much as in the CV plot of CoPM. As the scan rates get multiplied, there is a slight shift in the redox peaks to higher and lower potentials due to the restriction of diffusion rate to showcase that the electronic neutralisation generally occurs during redox reactions [45]. Higher current response is an indication of lower internal resistance suffered by the composite working electrode, leading to a better electrical conductivity. As the scan rate increases, the integral area that quantifies the capacitance value of the electrode material also increases. But, the overall specific capacitance value declines with sweep rate due to the fact that at higher scan rates the electrolyte ions interact only with the electrode surface, while at lower scan rates a greater number of ions make contact and interact with the interior of the electrode material [46]. This is a clear indication of the dependence of electrochemical performance of a working electrode on its morphology. Fig. 4.14 (e) shows the comparative analysis of the current response of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM and CCoPM working electrodes at a sweep rate of 100 mV/s. The enhanced current response of the quaternary composite electrode is evident from the analysis profile, leading to an achievement of maximum specific capacitance of about 592 F/g by this composite electrode at 10 mV/s (Fig. 4.14 (f)). The incorporation of PANI and MWCNTs provide a conductive bridge for the electrolyte ions to easily enter to the interior of the composite electrode, leading to a faster electronic transportation and enhancement in the supercapacitance of the material. The binary metal oxide combination CuO-Co₃O₄ bounds to PANI and MWCNT linkages in the way to overcome the drawbacks arise due to agglomerations in the morphology. These integrated effects resulted in the formation of a unique porous architecture with better

active surface area for the quaternary composite, effectively enriches its capacitance value compared to individual counterparts.

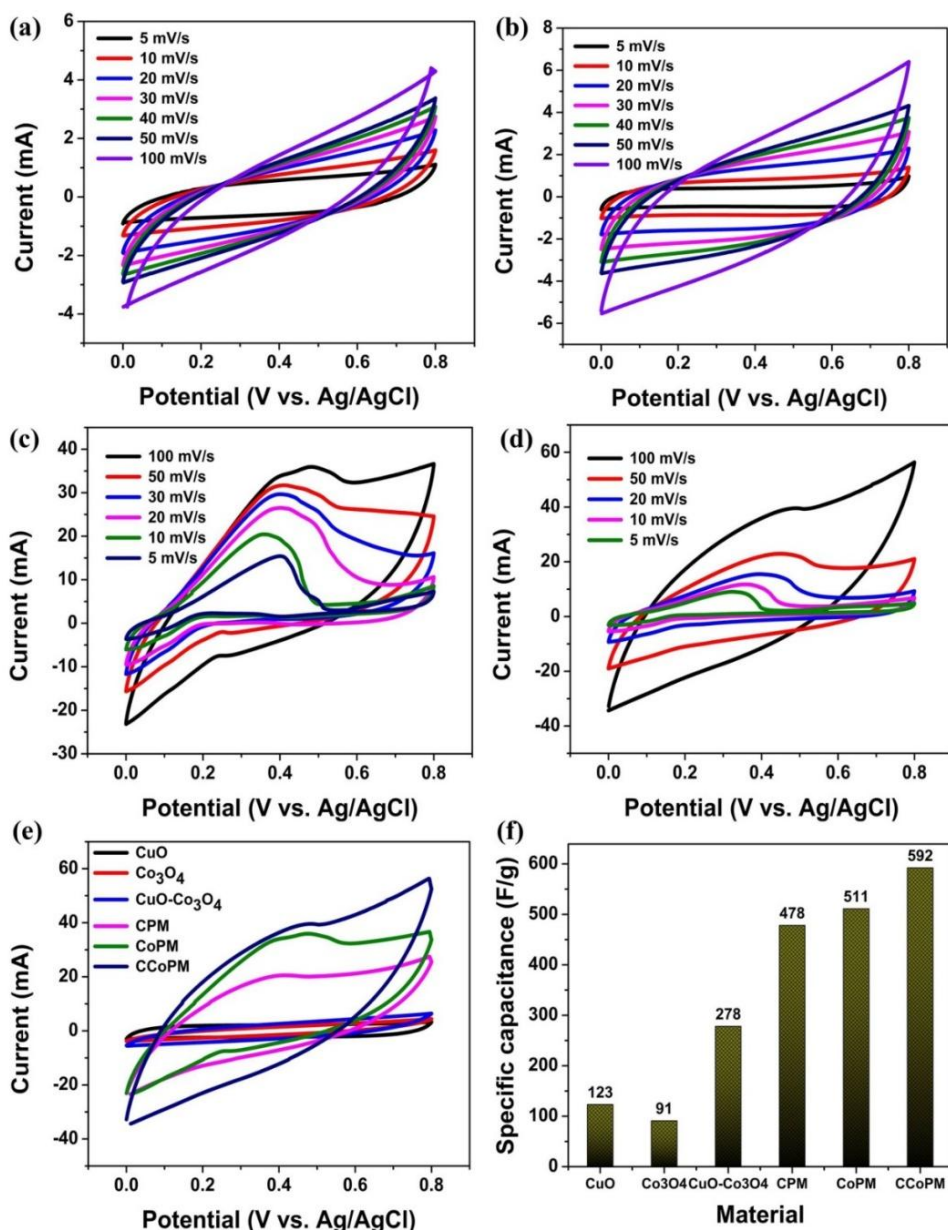


Fig. 4.14. CV curves of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM, comparison of (e) CV curves of CuO, Co₃O₄, CuO- Co₃O₄, CPM, CoPM and CCoPM nanocomposites at 100 mV/s (f) specific capacitance of CuO, Co₃O₄, CuO- Co₃O₄, CPM, CoPM and CCoPM nanocomposites at 10 mV/s.

The kinetics of capacitive performance of the CCoPM composite electrode was then elucidated using power law. Fig. 4.15 (a) portrays the linear relation between scan rate and anodic current with a slope value of about 0.84, indicating prominence of surface-controlled capacitive contributions in the charge storage

mechanism. The $v^{1/2}$ vs. $i/v^{1/2}$ graph shown in Fig. 4.15 (b) helps to evaluate the capacitive and diffusive contribution parameters k_1 and k_2 . The obtained values of k_1 and k_2 were 33.576 and -24.192, respectively. The capacitive contribution due to the effect of surface-controlled redox reactions was found to be 90% for the CCoPM electrode at the sweep rate of 10 mV/s (Fig. 4.15 (c)). The shaded region in Fig. 4.15 (c) illustrates the diffusive contribution in the current response of the composite electrode at 10 mV/s. With the amplification in sweep rate, the surface-controlled capacitive contribution enriched to 98 % at 100 mV/s (Fig. 4.15 (d)). The electrochemical performance arises from the redox reactions happening at the surface or near surface regions of the electrode usually results in faster kinetics and better cyclic performance [47].

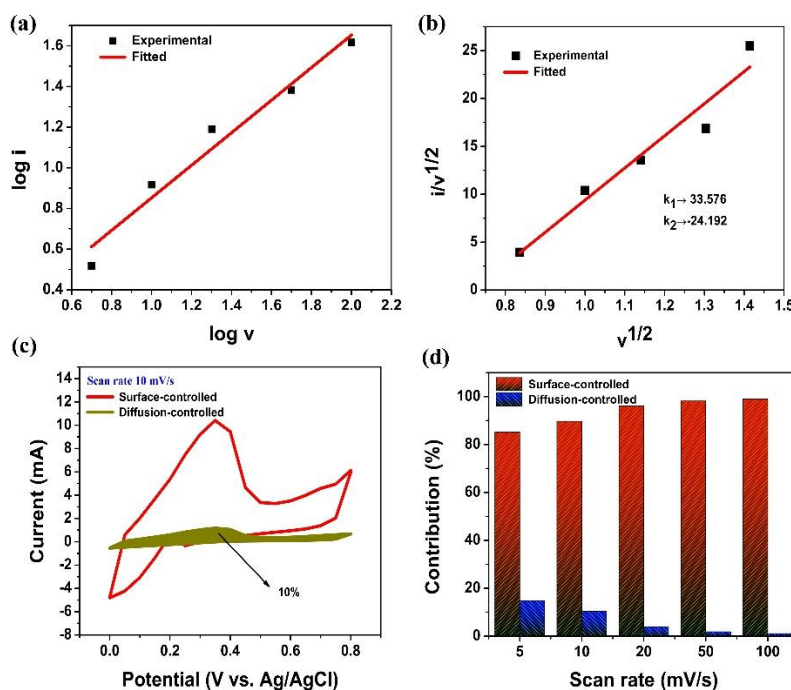


Fig. 4.15 (a) $\log v$ vs. $\log i$ plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ plot (c) decoupling of capacitive and diffusive current contributions at scan rate 10 mV/s (d) Histograms of diffusive and capacitive contributions of CCoPM working electrode at varying scan rates.

4.3.9.2. Galvanostatic charge/discharge (GCD) studies

The electrochemical features of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites were further tested with GCD measurements conducted at different current densities, shown in Fig. 4.16 (a-e). The non-linear appearance of GCD curves

suggests the pseudocapacitive behaviour of all the composite electrodes. The Co₃O₄ working electrode shows a non-linear GCD curve with small IR drops as a consequence of internal resistance suffered by the working electrode during the reaction activities (Fig. 4.16 (a)). The discharge curve of CuO-Co₃O₄ (as seen in Fig. 4.16 (b)) found to be much longer compared to pristine CuO and Co₃O₄, results in better capacitance values. The specific capacitance of Co₃O₄ electrode was found to be 264 F/g, 220 F/g, 198 F/g, and 73 F/g and that was for CuO-Co₃O₄ was found to be 383 F/g, 230 F/g, 150 F/g and 83 F/g, at current densities of 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. The GCD plots of CoPM and CCoPM nanocomposites are displayed in Fig. 4.16 (c-d), with relatively less IR drop in the discharge process indicating better electronic conductivity as well as lower energy loss in the electrode material [46]. The specific capacitance value of CoPM electrode was found to be 446 F/g, 243 F/g, 99 F/g, and 35 F/g at current densities 1 A/g, 2 A/g, 3 A/g and 5 A/g, respectively, whereas CCoPM electrode exhibited specific capacitance values of 647 F/g, 525 F/g, 334 F/g, and 115 F/g at current densities 1 A/g, 2 A/g, 3 A/g and 4 A/g, respectively. The GCD response of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM and CCoPM nanocomposites is compared in Fig. 4. 16 (e) at a current density of 1 A/g, presents the enhanced electrochemical performance of CCoPM composite with the longest discharge time favourable for energy storage applications. The specific capacitance values attained for CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM and CCoPM working electrodes were compared diagrammatically in Fig. 4.16 (f). The almost symmetrical triangular shaped GCD curve of the CCoPM composite reveals the total capacitance performance as a sum of both pseudocapacitive contributions from metal oxides, PANI and the double layer capacitive contribution from MWCNTs [45]. The distinctive porous morphology formed due to the synergistic interaction of PANI-MWCNT frameworks with the binary metal oxides, resulting in productive electrochemical features of the quaternary composite electrode. Moreover, the PANI particles grafted over the metal oxide-MWCNT surfaces can access more electrolyte ions and actively participate in the redox reactions [46].

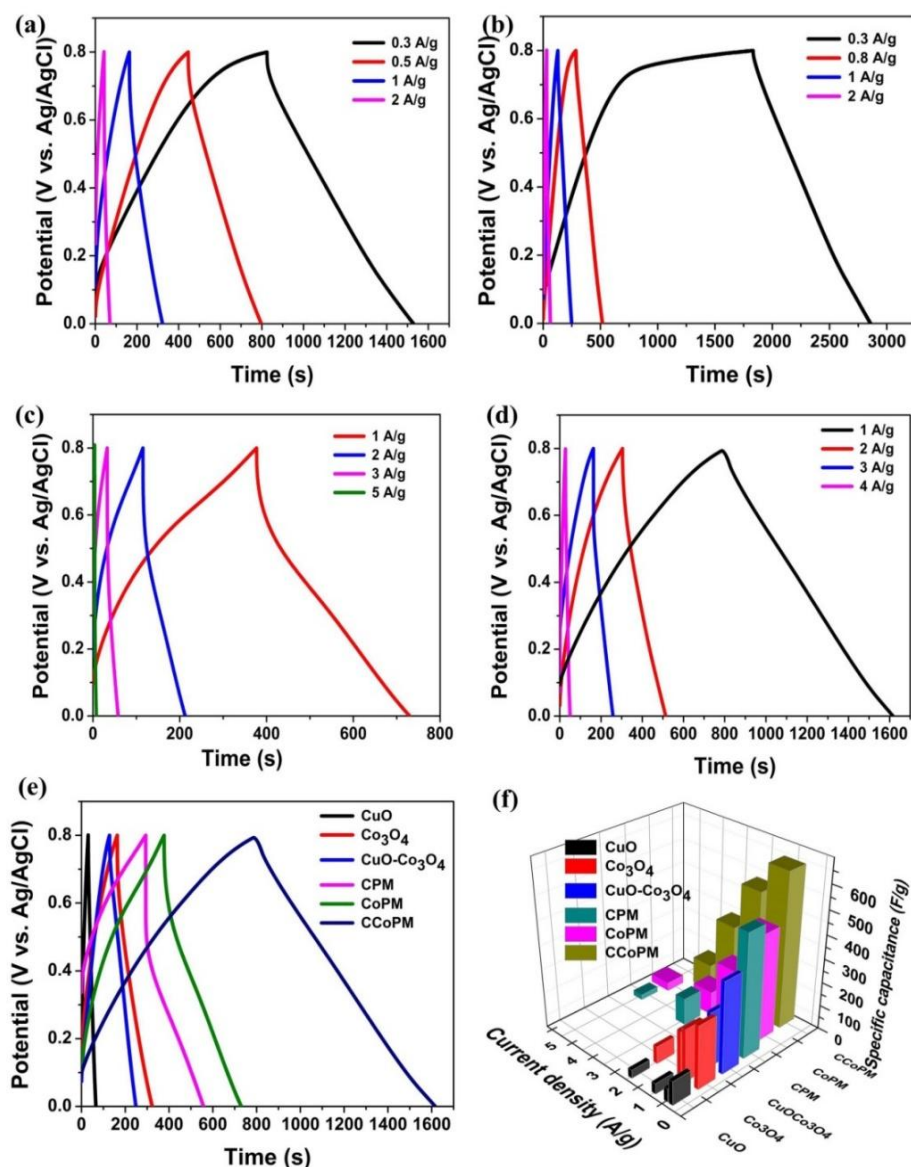


Fig. 4.16. GCD curves of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM (e) comparison of charge-discharge curves of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM, CCoPM composites at current density of 1 A/g, (f) variation of specific capacitance with current density of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM, CCoPM composites.

4.3.9.3. Electrochemical impedance spectroscopy (EIS)

The best approach to study the electrical conductivity, internal structure and charge transport processes exhibited by working electrodes is to conduct an EIS analysis, as shown in Fig. 4. 17. The Nyquist plots of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM working electrodes are individually portrayed in Fig. 4.17 (a-d). The Nyquist plots of Co₃O₄ and CuO-Co₃O₄ electrodes exhibit a distorted semi-circle region in the high frequency region and a linear portion in low frequency region, as expected for a

pseudocapacitive material, whereas the CoPM and CCoPM composite working electrodes displayed a very faint semi-circle arc in the high frequency region (Fig. 4.17 (e)). The best fitted EIS spectra are also visible in each EIS plots correspond to the equivalent electrical circuit combining elements such as R_s , R_{ct} , CPE and W. The values of these EIS parameters are tabulated in Table 4.3. The quaternary composite electrode CCoPM exhibited the lowest charge transfer resistance value, suggesting the high charge transport rate of this electrode material, which eventually resulted in its better electrochemical performance.

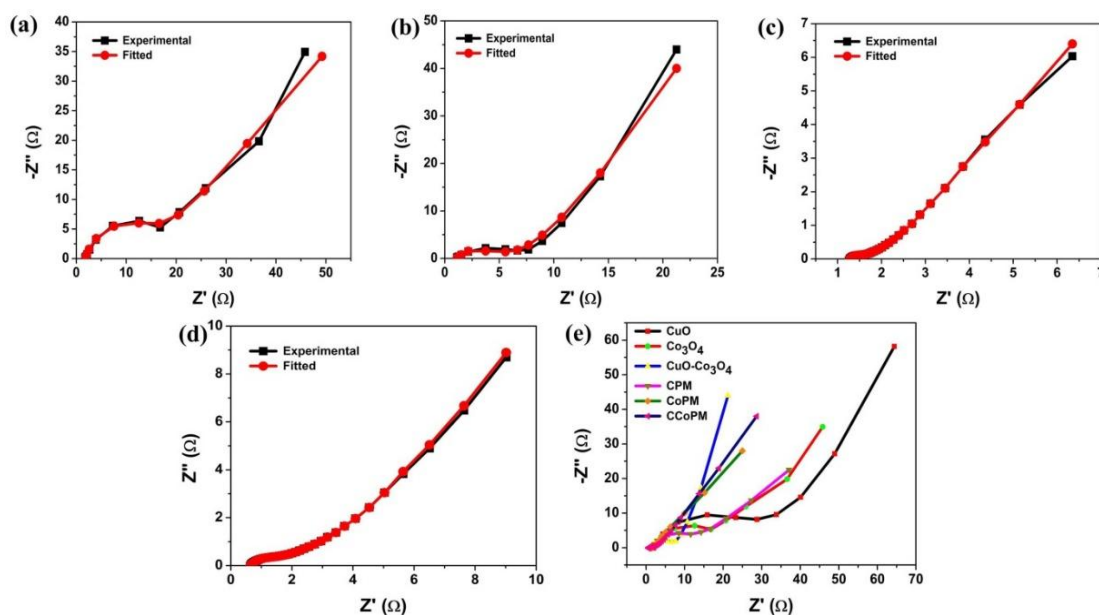


Fig. 4.17 (a) The best fitted Nyquist plot of as-prepared (a) Co₃O₄, (b) CuO-Co₃O₄, (c) CoPM (d) CCoPM (e) comparison of Nyquists plots of all nanostructures.

Table 4.3. The R_s , R_{ct} , CPE, W and n values of as-synthesised CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM, CCoPM nanocomposites.

	Sample					
	CuO	Co ₃ O ₄	CuO-Co ₃ O ₄	CPM	CoPM	CCoPM
R_s (Ω)	2	1.81	1.13	1.22	1.25	0.66
R_{ct} (Ω)	29.30	14.42	3.13	11.66	1.63	1.31
W	22.75	27.09	38.54	33.72	41.34	40.68
CPE	0.00057	0.00049	0.00002	0.0049	0.00004	0.00008
n	0.943	0.799	0.960	0.688	0.980	0.963

4.3.9.4. Cycle stability

The cycle stability of the CCoPM composite in the three-electrode cell configuration was evaluated over 5000 repeated charge-discharged cycles at a current density of 8 A/g. Fig. 4.18 shows that the quaternary composite sustains 98.7% of capacitance during the continuous charge-discharge cycles. The exclusive porous morphology with a larger specific surface area of the CCoPM working electrode contributed to its enhanced electro-active sites and fast charge transport along with rapid charge storage kinetics, which ultimately resulted in its better cyclic performance. This proves the efficiency of the CCoPM composite as a potential electrode material in the field of energy storage devices.

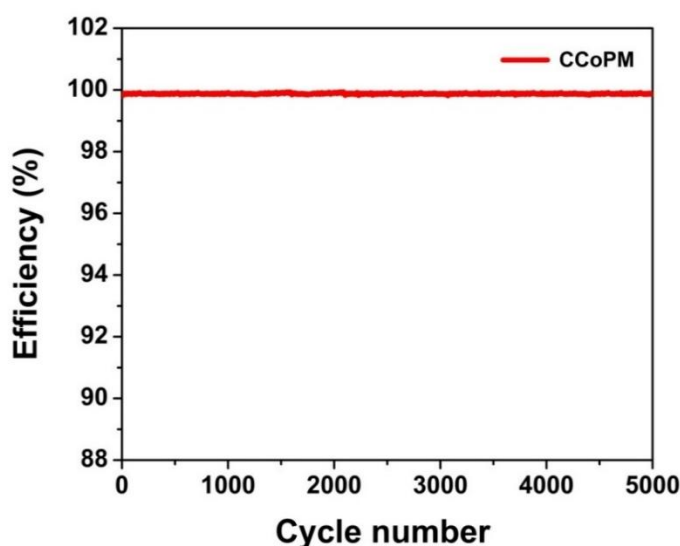


Fig.4.18. Cycle stability of CCoPM working electrode over 5000 cycles.

4.3.9.5. Electrochemical performance of CuO-Co₃O₄/PANI/MWCNT quaternary nanocomposite in symmetric two-electrode configuration

The electrochemical performance of a symmetrical supercapacitor device is evaluated using CCoPM as the working material and 1M Na₂SO₄ as the electrolyte in a two-electrode cell assembly. The real-time device-level performance of this configuration was analysed in the optimised potential window of 0-0.8V. Fig. 4.19 (a) illustrates the cyclic voltametric profiles of the CCoPM electrode at various sweep rates ranges from 5 mV/s to 100 mV/s. The CV response curve of the CCoPM exhibits a quasi-rectangular shape with a pair of redox peaks at (0.17 V, 0.39 V). Alike the three-

electrode configuration responses, the peaks got slighter shifts as the scan rates increased and at 100 mV/s, the redox peaks appeared at (0.31 V ,0.5 V). The GCD curves of CCoPM composite electrodes were analysed at different current densities of 1A/g, 2 A/g, 3A/g and 5 A/g, shown in Fig. 4.19 (b). All the GCD curves presented almost symmetrical charge-discharge behaviour with small IR loss, consistent with the three-electrode results. The specific capacitance values of CCoPM electrode evaluated from the GCD plots are 405 F/g, 335 F/g, 202 F/g, and 87.5 F/g at current densities of 1A/g, 2 A/g, 3A/g and 5 A/g, respectively (Fig. 4.19 (c)). The coulombic efficiency of electrode performance at various current densities is investigated and portrayed in Fig. 4. 19 (d), suggesting satisfactory cycle performance of CCoPM electrode at all current densities. The electrochemical performance of an electrode material is further characterised by its energy density and power density values. The Ragone plot of CCoPM electrode is depicted in Fig. 4.19 (e), exhibiting a highest specific energy of 36 Wh/Kg at a specific power of 800 W/Kg. The remarkable specific energy is attributed to the combined contributions from double-layer nature and redox reactions. The electrode material showed a better power density of 4022 W/Kg at a current density of 5 A/g. The long-term cycle stability of CCoPM electrode was investigated through conducting GCD test of the electrode over continuous 50000 cycles at a current density of 10 A/g. Fig. 4.19 (f) shows the capacity retention capacity of the composite electrode during 50000 charge-discharge cycles, upholds 93.2% capacitance retention. This suggests that the quaternary composite doesn't undergo any kind of structural deformations over the repeated charging and discharging processes. Thus, the overall enhancement in electrochemical performance of the quaternary nanocomposite including the constituents CuO, Co₃O₄, PANI and MWCNTs can be ascribed to the profitable surface area of the material formed due to the synergistic interactions between individual constituents. The exclusive porous networks formed during the synthesis stage, particularly during the active polymerisation phase, lead to the generation of more and more electro-active sites. The productive utilisation of these active sites by both electrostatic and surface controlled redox reactions resulted in enrichment of the overall electrochemical performance [46].

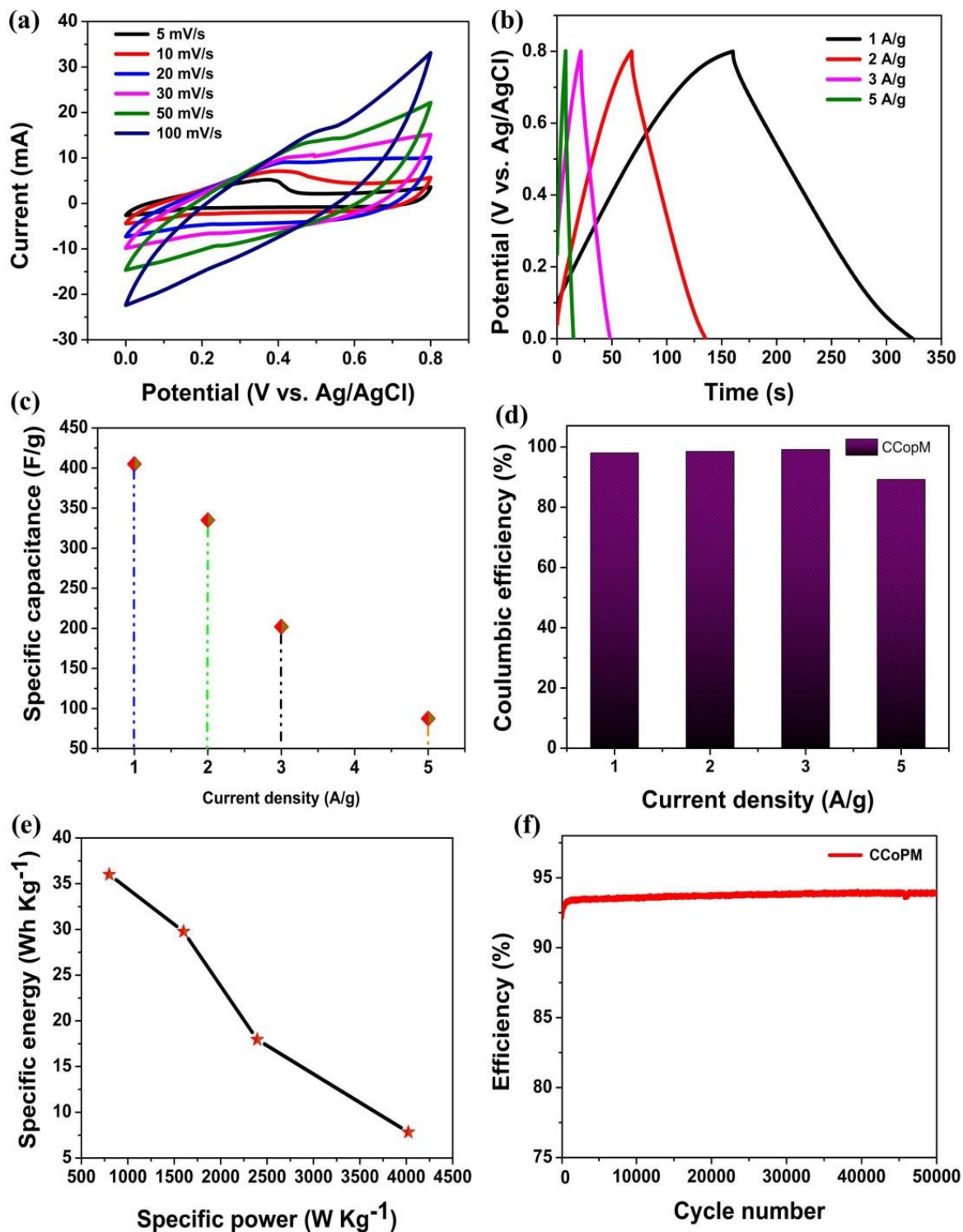


Fig. 4.19. (a) CV (b) GCD plots of CCoPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) columbic efficiency analysis (e) Ragone plot and (f) cycle stability of CCoPM composite in 50000 cycles.

4.4. CONCLUSION

The Co₃O₄, CuO-Co₃O₄, Co₃O₄/PANI/MWCNT and CuO-Co₃O₄/PANI/MWCNT nanocomposites were successfully synthesised using hydrothermal and one-pot chemical polymerisation methods, respectively. The intended formation of ternary and quaternary nanocomposites was confirmed with the help of XRD, FT-IR, Raman, FESEM-EDS, HRTEM, and BET characterisation techniques. The thermal stability and compositional analysis are further evaluated using TGA and XPS techniques. The electrochemical features of the prepared nanostructures were studied in three-electrode cell arrangement, showed a superior specific capacitance value of 647 F/g at a current density of 1 A/g for the CCoPM composite electrode, with marginal charge transfer resistance and better cycle performances. The device-level performance of the CCoPM electrode was analysed by fabricating a symmetric supercapacitor device in the two-electrode cell assembly. The CCoPM composite achieved a remarkable specific energy of about 36 Wh/Kg at a power density of 800 W/Kg. The composite electrode exhibited a 93.2% capacitive retention over 50000 continuous charge-discharge cycles. The binary metal oxide combination CuO-Co₃O₄ bounds to PANI and MWCNT, resulting in the formation of a unique porous architecture with better active surface area for the quaternary composite, effectively enriching its capacitance value compared to individual counterparts.

Table 4.4. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CCoPM	592	10	647	1	351	10	405	1

4.5. REFERENCES

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Synthesis, Characterization, and Supercapacitive Performance of CuO-ZnMn₂O₄/PANI/MWCNT Hybrid System

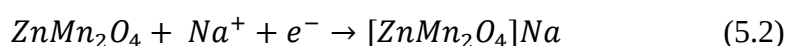
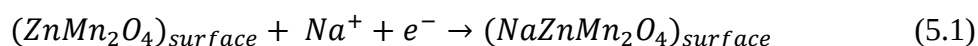
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The effectual strategy of incorporating two TMOs together in order to attain a well-behaved supercapacitor has created an opportunity for combining a ternary metal oxide ZnMn₂O₄ with the binary metal oxide CuO. The multiple valence states offered by the element Mn in the ZnMn₂O₄ help to provide plenty of redox active sites during chemical reactions, making the compound an imminent member in the supercapacitor scenario. Even though, Mn- based compounds have already been well-established in the supercapacitor field, ZnMn₂O₄ is one of the least explored ones. The CuO-ZnMn₂O₄ nanocomposite can become a potential candidate in the supercapacitor field by taking advantage of multiple valence states offered from both CuO and ZnMn₂O₄ compounds resulting in the improved electrochemical efficiency of the electrode material. The incorporation of these TMO nanocomposites with the PANI/MWCNT combination can qualitatively and quantitatively benefit the overall electrochemical performance of the quaternary electrode material. Herein, a detailed evaluation concerning the potentiality of CuO-ZnMn₂O₄/PANI/MWCNT hybrid system in the supercapacitor field is discussed.

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5.1. INTRODUCTION

The major challenge faced by the supercapacitors is often its low energy density compared with batteries. The scientific world is still working on the area of the supercapacitors to alleviate this major drawback with various strategies, in the sense of improving the electrochemical features of electrode materials. Without sacrificing power density, there is much effort has been employed to improve the charge storage mechanisms of electrode materials in supercapacitor scenarios. By addressing the drawbacks of widely used electrode materials, researchers are trying to explore a new category of potential electrode materials which are economical, environmentally benign, and having the potential to meet ever-lasting needs of an energy-demanding world. Among the various Mn-based TMOs, zinc manganese oxide (ZnMn₂O₄) is a bimetallic TMO having spinel type structure with high electrical conductivity and a band gap of 1.86 eV, which are widely used in areas like catalysis, sensors, energy storage devices [1], [2], [3]. In the AB₂O₄ spinel structure of ZnMn₂O₄ (ZMO) compound, the divalent Zn²⁺ and the trivalent Mn³⁺ ions occupy in the tetrahedral and octahedral sites, respectively [4]. In this structure, oxygen ions produce two types of vacancies such as tetrahedral vacancy and octahedral vacancy. The possible charge storage mechanisms of ZMO in neutral electrolytes like Na₂SO₄ can be as follows [5];



The intriguing attributes of ZnMn₂O₄ electrode material such as its spinel architecture with significant internal spaces that can accommodate more electrolyte ions, availability of larger accessible electro-active sites, and excellent pseudocapacitive nature, made it a potential choice for fabricating a nanocomposite with CuO [6].

5.1.1. ZnMn₂O₄ – A potential electrode material

Despite the fact that ZMO has many potential electrochemical features like high theoretical capacitance (1152 F/g), it is the least studied in the supercapacitor field as compared with its applicability in Li-ion batteries. The electrochemical performances of ZMO-based electrodes are substantially guided by few factors like surface area and

porosity, morphology and purity. One of the best methods to improve the device performance is to fabricate a porous nano-network to the electrode material in order to enrich electro-active sites, thereby enhancing rapid ionic diffusion. For instance, Yanping Gao *et al.* reported preparation of porous ZMO microstructures via calcination and the optimised ZMO material prepared at calcination conditions of 450 °C for 6 h achieved a specific capacitance of 1093 F/g 1 A/g. Heterolite structured ZMO prepared by the hydrothermal route and achieved a specific capacitance of 675 F/g at a scan rate of 5 mV/s [7]. M. Puratchi Mani *et al.* prepared a cubic-like ZMO electrode material using the double hydroxide-mediated hydrothermal method and showed a battery-type faradic behaviour of ZMO electrode having a capacitance of 776 F/g at a scan rate of 5 mV/s in a 2 M KOH electrolyte along with a capacitive retention of 91.7% over 5000 cycles [8]. There were works on Ni substituted ZMO nanospheres prepared via sol-gel auto-combustion method. As the Ni incorporation increases there is a phase transition of material from tetragonal to cubic crystal structure along with the enhancement in electrochemical features [9]. Recently, P. Deva *et al.* reported a mesoporous ZMO preparation using citric acid-mediated sol gel auto-combustion approach. The spinel ZMO electrode material showed an impressive electrochemical performance with a specific capacitance of 417.5 F/g at current density 1 A/g. The enhancement in supercapacitive properties of ZMO electrode material is attributed to the increased surface area and ionic conductivity along with commendable mechanical stability [10].

5.1.2. CuO-ZnMn₂O₄ nanocomposite: A short introduction

Another effective strategy widely used for improving the electrochemical performance of TMOs is to make nanocomposites with other TMOs in order to use the benefit of their synergistic effects along with their individual contributions. ZMO has been extensively studied in the form of its composite electrode form as a suitable option in supercapacitors [11], [12], [13]. For instance, Veeman Sannasi *et al.* prepared ZMO/Mn₂O₃ composite by ultrasonication and microwave irradiation assisted hydrothermal routes. The four ‘petal’ and six ‘petal’ flower-like morphology of composite materials were evident in the morphological analyses. The as-synthesised composite electrode exhibited a specific capacitance of 380 F/g at current density of 0.5 A/g [14]. Cathodic electrosynthesis of ZMO/Mn₃O₄ nanostructures was reported by Bahareh Ameri *et al.* and showed that the nano rod-like composite material exhibited a

maximum storage capacity of 321.34 F/g [15]. Thus, CuO with ZMO can be effectively used as a potential composite electrode material for improving the electrochemical performance. There were only few studies on the structural, optical, physicochemical and electrochemical performances of CuO/ZMO composite [16]. Recently, Liping Qin *et al.* reported improved electrode performance of CuO/ZMO composite as a cathode material in Zn-ion batteries. The composite displayed a capacity of 118 mAh/g at 2 A/g along having an efficiency of more than 96% [17].

5.1.3. CuO-ZnMn₂O₄/PANI/MWCNT quaternary hybrid system as a potential electrode material

Although significant improvement in electrochemical performance has been acquired through fabricating binary nanocomposites, challenges remain in securing high energy density and long cycle life, especially at higher current densities. Thus, studies focusing on the innovative strategies to enrich the ionic conductivity and structural integrity of the CuO-ZMO-based electrodes by linking them with conducting polymers like PANI and well-known carbon compounds must be adopted. A few studies on ZMO-carbon compounds were previously reported with an aim to elevate the electrode porosity and surface area, intercalation sites and rapid charge transport kinetics. For instance, a recent work was published on the synthesis of pure ZMO and ZMO/graphene composites using the combustion method and reported a high specific capacitance of 783 F/g for ZMO/rGO electrode at a scan rate of 5 mV/s which can be due to the highly porous structure of composite along with high surface area, which allows the easy penetration of ions [18]. Recently, a similar composite material ZMO/rGO with a needle-like nanostructure was produced by Pitcheri Rosaiah *et al.* using hydrothermal route and attained a specific capacitance of 628 F/g at 1 A/g. The asymmetric supercapacitor device designed with the as-synthesised material showed an energy density of 40.2 W h/Kg at a power density of 1125 W/Kg [19]. Chen Zhang *et al.* investigated the electrochemical performance of ZMO/GO composite electrode fabricated using electrospinning technique followed by annealing and reported the highest specific capacitance of 1489.5 F/g at 1 A/g for 0.3 wt% GO-ZMO sample [20]. The incorporation of conducting polymer polypyrrole and graphene in ZMO was studied in detail by Haiyan Gao *et al.* and observed a significant decrease in charge transfer impedance of the composite material due to the synergistic effects of rGO and

PPy [21]. According to our understanding, there is no published works on CuO-ZnMn₂O₄/PANI/MWCNT quaternary hybrid composite in energy storage applications.

5.2. EXPERIMENTAL SECTION

5.2.1. Synthesis materials

Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), urea (CH₄N₂O), ammonium persulfate (APS) ((NH₄)₂S₂O₈) and aniline hydrochloride (C₆H₅NH₂·HCl), analytical grade hydrochloric acid (HCl), sodium sulphate (Na₂SO₄), sodium dodecyl sulphate (CH₃(CH₂)₁₁OSO₃Na) (SDS, > 98%), manganese chloride tetrahydrate (MnCl₂·4H₂O), Zinc acetate dihydrate (Zn (CH₃CO₂)₂·2H₂O), sodium hydroxide (NaOH), potassium hydroxide (KOH), deionised (DI) water was purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, $OD \times L = 6 - 9 \text{ nm} \times 5 \mu\text{m}$), Polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standard and utilized without any further purifications. Distilled ethanol was used for cleaning purpose.

5.2.2. Synthesis of ZnMn₂O₄

The ZnMn₂O₄ nanoparticles were prepared via a similar surfactant-free hydrothermal process with the same reaction conditions of CuO synthesis. Firstly, 4 M manganese chloride tetrahydrate and 2 M Zinc acetate dehydrate were simultaneously dissolved in 40 ml of deionised water. Later, a 20 ml NaOH:KOH solution was prepared in another beaker in a molar ratio of 1:2. The mixed hydroxide solution was slowly added to the precursor solution under constant stirring until a brownish yellow solution is formed. The whole solution was then transported to the autoclave setup and kept in the oven under 180 °C for 24 hours. When the reaction conditions met, the resultant solution from the reactor was filtered and washed thoroughly using DI water and ethanol. The obtained brownish ZnMn₂O₄ precipitate was then shifted to an oven at 80 °C for 6 hours to get the purified ZnMn₂O₄ nanoparticles.

5.2.3. Synthesis of CuO-ZnMn₂O₄ nanocomposite

The CuO-ZnMn₂O₄ nanocomposite was processed using the hydrothermal method without employing any additives of surfactants. Initially, 0.2 M manganese chloride tetrahydrate and 0.1 M zinc acetate dihydrate were allowed to dissolve completely in 30 ml of DI water via a continuous stirring process. Later, the previously prepared CuO nanoparticles (40 mg) were allowed to disperse in the above-mentioned precursor solution. Then, a 20 ml of 0.5 M NaOH: 1M KOH solution was prepared in another beaker. The mixed hydroxide solution was slowly added to the precursor solution under constant stirring until a brownish solution was attained. The whole 50 ml solution was then transferred to an autoclave and set to keep in oven at 180 °C for 24 hours completing the synthesis process. The earned precipitates after hydrothermal reaction were washed multiple times with DI water and ethanol for the removal of unwanted/unreacted substances from the resultant. Later, the obtained precipitate was sent to oven at 80 °C for 6 hours to get the CuO-ZnMn₂O₄ nanocomposite.

5.2.4. Synthesis of ZnMn₂O₄/PANI/MWCNT ternary nanocomposite and CuO- ZnMn₂O₄/PANI/MWCNT quaternary nanocomposite

The ZnMn₂O₄/PANI/MWCNT ternary nanocomposite was prepared in the similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared ZnMn₂O₄ and the final product is named as ZPM for the convenience.

The CuO-ZnMn₂O₄/PANI/MWCNT quaternary nanocomposite was prepared in the similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared CuO-ZnMn₂O₄ nanocomposite and the final product is named as CZPM for convenience.

5.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, Aeris Research (Source: Cu K α)). Fullprof Suite software was used for Rietveld analysis. Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany) was employed to determine the

vibrational modes of the as-synthesised samples. Fourier transform infrared (FTIR) spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using ZnSe crystal. The surface morphology and elemental composition were done using a combination of High- Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

5.2.6. Electrode preparation and electrochemical studies

The electrochemical features of the as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt. % of the active material, 10 wt. % of polyvinylidene fluoride (PVDF) and 10 wt. % of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly in to a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in working electrode was 1.25 mg cm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of the as-synthesised samples.

5.3. RESULTS AND DISCUSSION

5.3.1. X-Ray diffraction (XRD)

The material purity and structural features of ZnMn₂O₄, CuO-ZnMn₂O₄, ZPM and CZPM nanocomposites were evaluated using powder X-ray spectrometer and displayed in Fig. 5.1. In order to confirm the adequate formation of the composites,

XRD profiles of CuO, CPM, PANI, and MWCNTs are also presented in the Fig. 5.1 (a). From the figure, it is evident that ZnMn₂O₄ compound with the tetragonal crystal structure was successfully formed, with no evidence of any kind of secondary or impurity phases (JCPDS No. 24-1133, space group: I41/amd). The major intense diffraction peaks obtained at 2 θ values 18.17°, 29.25°, 31.25°, 32.90°, 36.38°, 44.81°, 59.03°, and 60.72° were assigned to the crystal planes (101), (112), (200), (103), (211), (220), (321), and (224), respectively [6]. The XRD pattern of CuO-ZnMn₂O₄ nanocomposite showed a combination of all prominent peaks of both the monoclinic CuO and the tetragonal ZnMn₂O₄. The PANI-MWCNT incorporated materials (shown in Fig. 5.1 (b)), particularly ZPM, displayed a complete blend of dominant peaks of PANI at 2 θ values of 19.45° and 25.14° along with several prominent diffraction planes of ZnMn₂O₄ located at 17.01°, 29.27°, 31.31°, 32.97°, and 36.79° [22]. In the case of XRD pattern of quaternary nanocomposite CZPM, PANI dominated nature was apparent at a glance, accompanied with some of the major crystallographic diffraction peaks of both CuO and ZnMn₂O₄ phases. The dominant peak of MWCNT in the 25.8°-26° range is not clearly visible in the XRD spectra of both ZPM and CZPM, but a low intense bump of MWCNT at 42.92° was observed [23]. The minor peak shifts in the XRD profiles of both ternary and quaternary nanocomposites can be attributed to the synergistic interactions between PANI-MWCNT with metal oxides, which are expected to surplus the overall electrochemical performance of the composites.

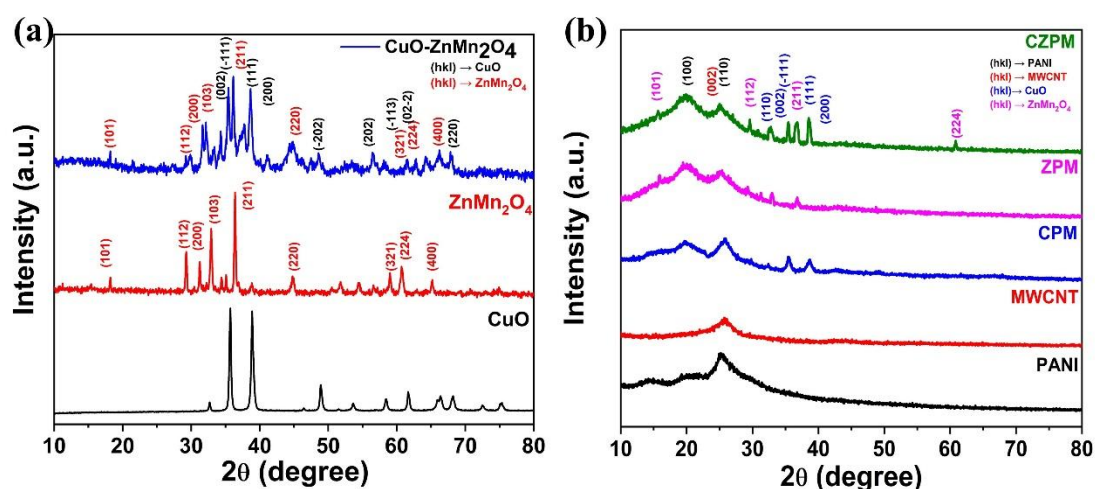


Fig. 5.1. XRD patterns of (a) CuO, ZnMn₂O₄, CuO-ZnMn₂O₄ nanoparticles and (b) PANI, MWCNT, CPM, ZPM, and CZPM composites.

5.3.2. Raman spectroscopy

The Raman spectra of ZnMn₂O₄, CuO-ZnMn₂O₄, ZPM and CZPM composites are carried out to evaluate the structural integrity and phase purity, which is presented in Fig. 5.2. According to group analysis, the spinel ZnMn₂O₄ structure has 10 Raman active modes as follows;

$$T = 2 A_{1g} + 3 B_{1g} + B_{2g} + 4 E_g \quad (5.3)$$

Among these Raman modes, the as-synthesised ZnMn₂O₄ material showed Raman peaks at 317 cm⁻¹, 368 cm⁻¹, and 665 cm⁻¹ which are consistent with previous reports of the tetragonal ZnMn₂O₄ nanomaterials, as seen in Fig. 5.2 (a) [24]. The strong peak at 665 cm⁻¹ can be attributed to A_{1g} symmetry [25]. The Raman spectra of CuO-ZnMn₂O₄ composite exhibits consistent peaks corresponding to both CuO and ZnMn₂O₄, confirms the occurrence of both components in the composite material (Fig. 5.2 (b)). The intense Raman modes at 298 cm⁻¹ and 629 cm⁻¹ were attributed to the A_g and B_g² symmetries of CuO [26], while the modes at 317 cm⁻¹, 368 cm⁻¹, 474 cm⁻¹, 593 cm⁻¹, and 660 cm⁻¹ represented the Raman active modes of tetragonal ZnMn₂O₄. Fig. 5.2 (c) presents the Raman spectra of ternary ZPM nanocomposite, evidencing the exact formation of PANI, MWCNT and ZnMn₂O₄ in the composite with their corresponding characteristic peaks. The list of Raman active modes and their corresponding attributes are listed in Table 5.1. The enhancement in peak intensity of the band at 1591 cm⁻¹ in the composite material is related to the effective interaction between carbonyl functional groups of MWCNTs with the quinoid rings in PANI. The noticeable bands at 1338 cm⁻¹ and 1591 cm⁻¹, can be attributable to the synergistic π-π interactions between MWCNTs and PANI fibres [27].

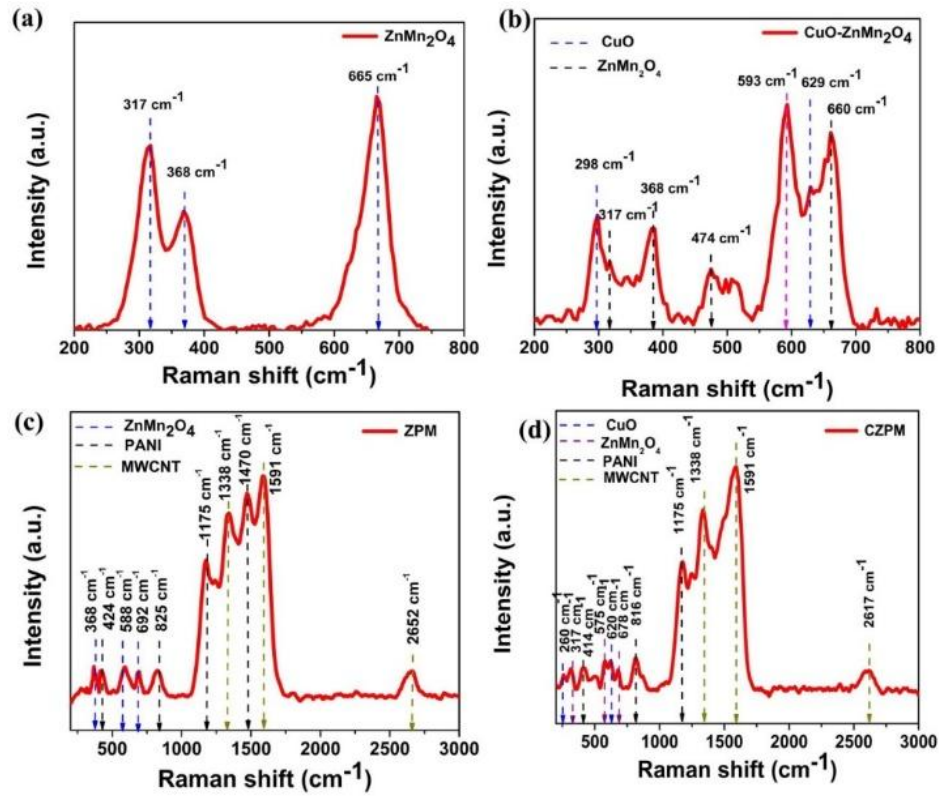


Fig. 5.2. Raman profiles of pristine (a) ZnMn₂O₄ (b) CuO-ZnMn₂O₄ (c) ZPM (d) CZPM composites.

Table 5.1. List of assignments of dominant characteristic bands appeared in Raman spectra of ZPM and CZPM nanocomposite.

Raman modes		Assignments
ZPM	CZPM	
-	260 cm ⁻¹	A _g mode of monoclinic CuO
368 cm ⁻¹	317 cm ⁻¹	Raman active mode of tetragonal ZnMn ₂ O ₄
424 cm ⁻¹	414 cm ⁻¹	Out of plane C-H wag in bipolaronic
588 cm ⁻¹	575 cm ⁻¹	Raman active mode of tetragonal ZnMn ₂ O ₄
-	620 cm ⁻¹	B _g ² mode of monoclinic CuO
692 cm ⁻¹	678 cm ⁻¹	A _g mode of tetragonal ZnMn ₂ O ₄

825 cm ⁻¹	816 cm ⁻¹	Ring deformation of benzenoid ring in emeraldine salt form of PANI
1175 cm ⁻¹	1175 cm ⁻¹	C-H bending of benzenoid ring in PANI
1470 cm ⁻¹	-	C=N stretching in quinoid ring in PANI
1338 cm ⁻¹	1338 cm ⁻¹	D- band of MWCNT
1591 cm ⁻¹	1591 cm ⁻¹	G-band of MWCNT
2652 cm ⁻¹	2617 cm ⁻¹	G' band of MWCNT

5.3.3. FT-IR spectroscopy

The FT-IR spectra of ZnMn₂O₄, CuO- ZnMn₂O₄, ZPM, and CZPM composites are shown in Fig. 5.3, in the aim of focusing more on their microstructural features and molecular bonds. In the Fig. 5.3 (a), FT-IR spectrum of ZnMn₂O₄ is presented. The three sharp and intense observed peaks in the wavenumber range 500-700 cm⁻¹ were attributed to the M-O and M-O-M bonds of the tetragonal ZMO structure (M=Zn,Mn) [7]. The weak band at 1732 cm⁻¹ corresponds to vibrational modes of carbonyl groups and 1110 cm⁻¹ linked with the bending vibration peak of residual water molecules [28]. The FT-IR spectra of CuO-ZMO nanocomposite are displayed in Fig. 5.3 (b), presenting two intense peaks of ZnMn₂O₄ at 628 cm⁻¹ and 520 cm⁻¹ and a characteristic peak of Cu-O bond at 434 cm⁻¹. The vibrational modes of carbonyl groups and bending mode of water molecules were appeared in the composite material also. The peak at 2924 cm⁻¹ attributed to the stretching vibrational mode of O-H bond [7]. The ternary and quaternary composites, ZPM and CZPM, reveal an integration of vibrational peaks of metal oxides, PANI and MWCNTs. The characteristic peaks of each constituent and their corresponding peak assignments are listed in Table 5.2.

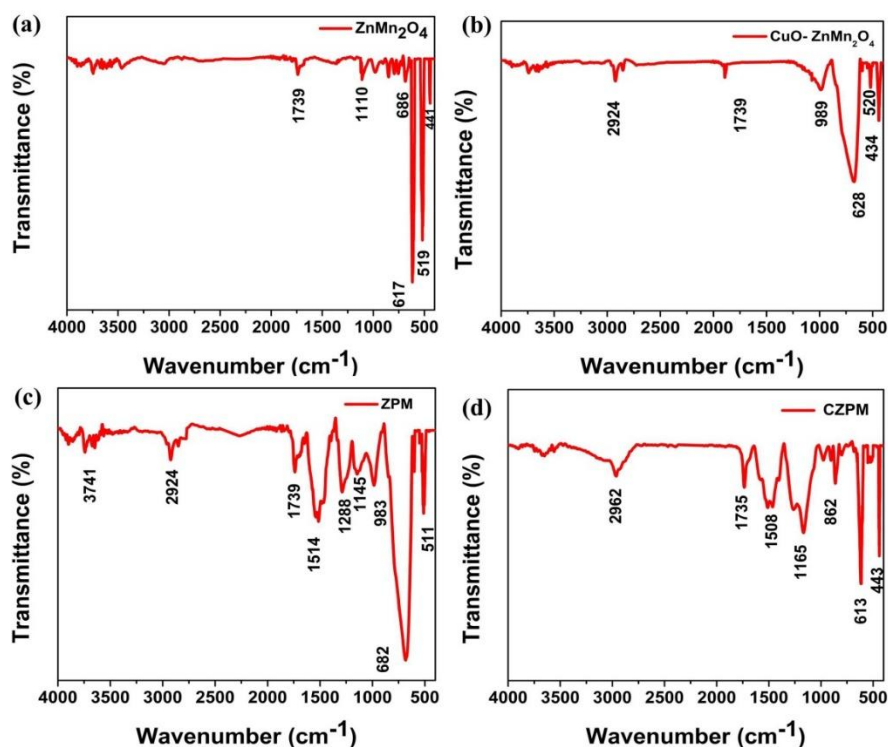


Fig. 5. 3. FT-IR spectra of (a) ZnMn₂O₄ (b) CuO- ZnMn₂O₄ (c) ZPM (d) CZPM nanocomposites.

Table 5.2. List of peaks in FT-IR spectrum of ZPM and CZPM nanocomposites and its corresponding assignments.

FT-IR peaks		Assignments
ZPM	CZPM	
3741 cm ⁻¹		stretching vibrational mode of O-H bond
2924 cm ⁻¹	2962 cm ⁻¹	stretching vibrational mode of O-H bond
1739 cm ⁻¹	1735 cm ⁻¹	stretch mode of carboxylic groups in MWCNT
1514 cm ⁻¹	1508 cm ⁻¹	C=C stretching in quinoid ring of PANI
1288 cm ⁻¹	1296 cm ⁻¹	C-N for aromatic amines in the polaron structure of conducting PANI

1145 cm ⁻¹	1165 cm ⁻¹	characteristic band of the protonated form of conducting PANI
983 cm ⁻¹	972 cm ⁻¹	due to protonated imine group in PANI
-	862 cm ⁻¹	out-of plane C–H bending vibration.
682 cm ⁻¹ & 511 cm ⁻¹	613 cm ⁻¹	stretching modes of ZMO
-	443 cm ⁻¹	stretching vibrations of Cu–O

5.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The morphological and elemental investigations of the synthesised ZMO, CuO-ZMO, ZPM and CZPM composites were done using FESEM-EDS analyses, which are depicted in Fig. 5.4. The ZMO material displayed a heterogeneous distribution of several flake-like and diamond-like nanostructures (shown in Fig. 5.4 (a-c)). This irregular configuration of nanostructures carries some kind of porous spaces thought the surfaces. In the highly magnified images (Fig. 5.4 (c)), a few nanotube-like structures were also seen in certain regions. The CuO-ZMO composite carries a nanotubular morphology with some sort of nanoparticles over the tube surfaces (Fig. 5.4 (d-e)). The nanoflake structure of CuO underwent modification in to the tubular form with some diamond shaped ZMO particles scattered over tube surfaces to form the complete symmetry of CuO-ZMO composite. The FESEM image of the ZPM composite has shown in Fig. 5.10 (g-i), portrayed an agglomerative framework of nanotubules interspersed with some voluminous porous regions. The fibres viewed as some interconnected networks got attached together as a result of enhance PANI wrapping over MWCNT surfaces. This agglomerative nature made the metal oxide nanoparticles morphologically indistinct. The surface modification of CuO-ZMO composite through the incorporation of PANI and MWCNTs was analysed through SEM images shown in Fig. 5.10 (j-l). The CZPM nanocomposite presents nanofibrillar texture with large voluminous pores in between, creating an effective contact area for

electrochemical reactions. The average diameter of these fibres was estimated to be 32 nm, highlighting the synergistic interaction between PANI and MWCNTs.

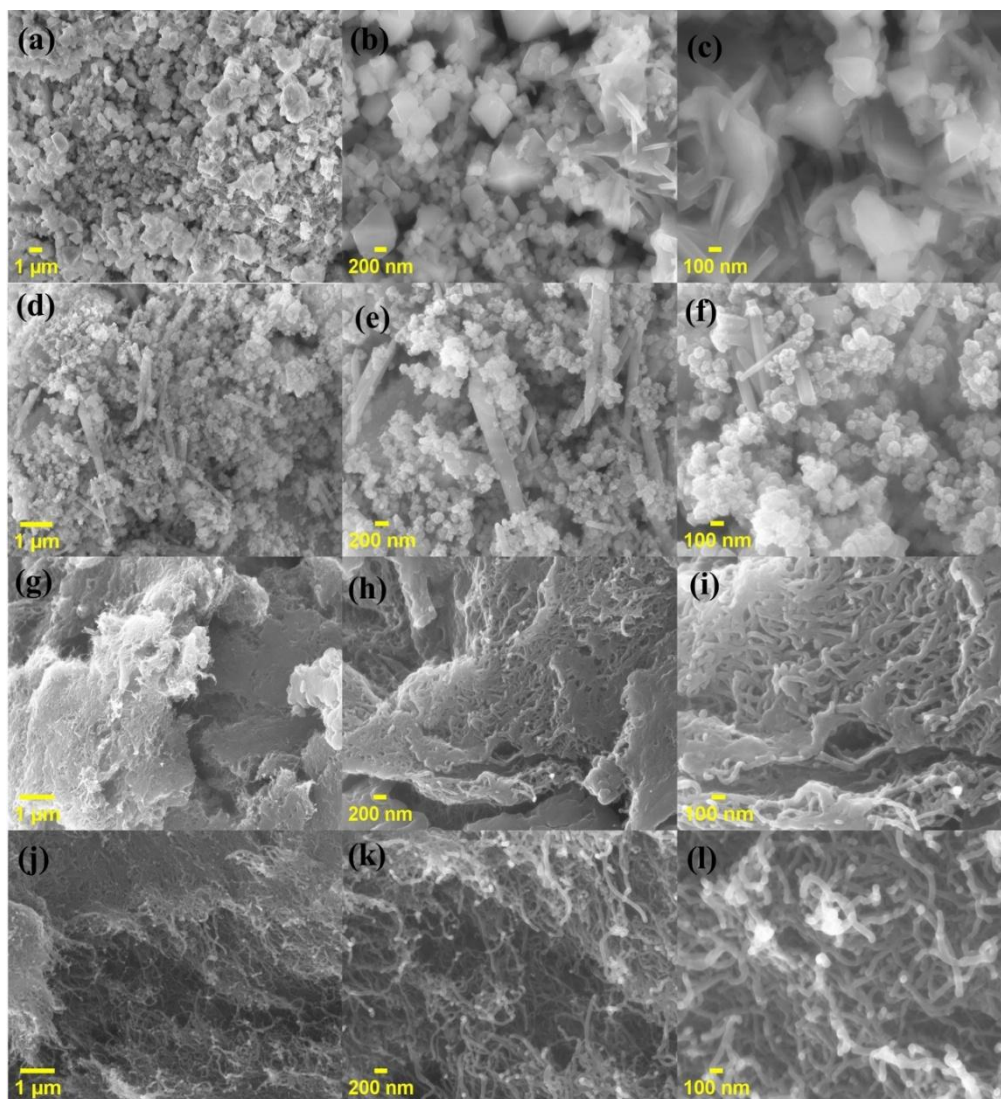


Fig. 5.4. FESEM micrographs of (a,b,c) ZnMn₂O₄ (d,e,f) CuO- ZnMn₂O₄ (g,h,i) ZPM (j,k,l) CZPM nanocomposites.

The EDS spectra of ZMO, CuO-ZMO, ZPM and CZPM composites are presented in Fig. 5.5. The existence of elements Zn, Mn and O in the material confirms the intended formation of ZnMn₂O₄ (Fig. 5.4(a)). The EDS spectrum of CuO-ZMO composite, shown in Fig. 5.5 (b), carries the element Cu in addition to Zn, Mn and O, which clearly validates the exact formation of CuO-ZMO composites. The incorporation of PANI and MWCNTs in to the matrix of ZMO and CuO-ZMO materials was confirmed through the presence of C and N in the ZPM and CZPM composites, respectively (Fig. 5.5 (c-d)). The atomic concentrations of constituents in

each composite material were displayed in Table 5.3. The expected elemental formation of all composites was verified with the help of this tabular data.

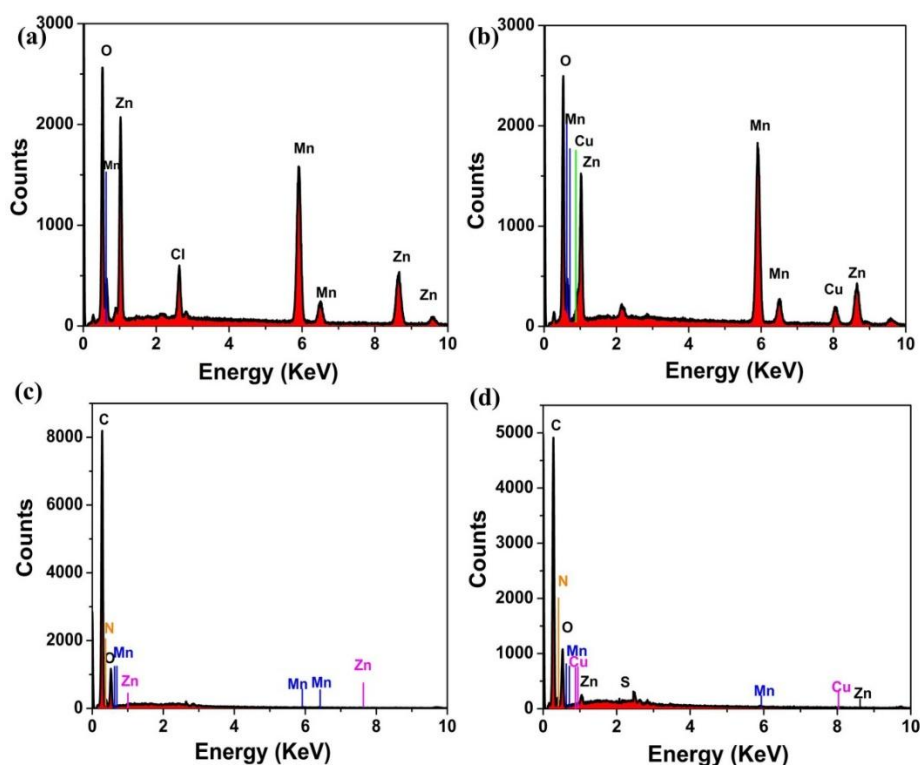


Fig. 5.5. EDS spectra of (a) ZnMn₂O₄ (b) CuO- ZnMn₂O₄ (c) ZPM (d) CZPM nanocomposites.

Table 5.3. Elemental data of ZnMn₂O₄, CuO- ZnMn₂O₄, ZPM and CZPM composites obtained from EDS analysis.

Sample	Atomic ratio (%)					
	Cu	O	Zn	Mn	C	N
ZnMn ₂ O ₄	-	54.11	17.45	28.44	-	-
CuO- ZnMn ₂ O ₄	22.14	43.12	11.14	23.60	-	-
ZPM	-	23.14	8.05	18.46	41.23	9.12
CZPM	12.02	10.13	5.21	17.19	47.63	7.82

The EDS mapping of ZMO, CuO-ZMO, ZPM and CZPM nanocomposites is portrayed in Fig. 5.6, Fig. 5.7, Fig. 5.8, and Fig. 5.9 respectively. From Fig. 5.6, the white colour region evidences the exact formation of ZnMn₂O₄. The excess amount of oxygen in the compound was clear from the selective elemental images. In the case of

CuO-ZMO composites, the homogeneous distribution of elements Cu, Zn, Mn and O is clearly visible at first glance (Fig. 5.7). The elemental mapping image of ZPM composite presented in Fig. 5.8 indicated the predominance of carbon over the other elements like nitrogen, copper, zinc, manganese and oxygen. Similarly, from the EDS map of the CZPM composite (Fig. 5.9) a higher contribution of carbon from both PANI and MWCNTs was noticed. The effective interaction between PANI and MWCNTs was noticed. The effective interaction between PANI and MWCNTs was undeniable from the presence of nitrogen in the vicinity of carbon atoms.

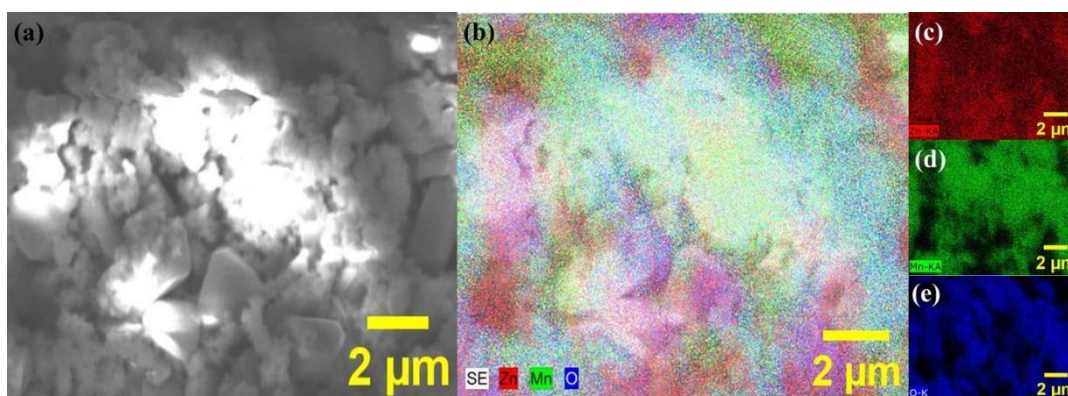


Fig. 5.6. (a) SEM image, (b) EDS mapping of ZnMn₂O₄ nanostructures, and (c-e) selective elemental distribution for the area shown in image (a).

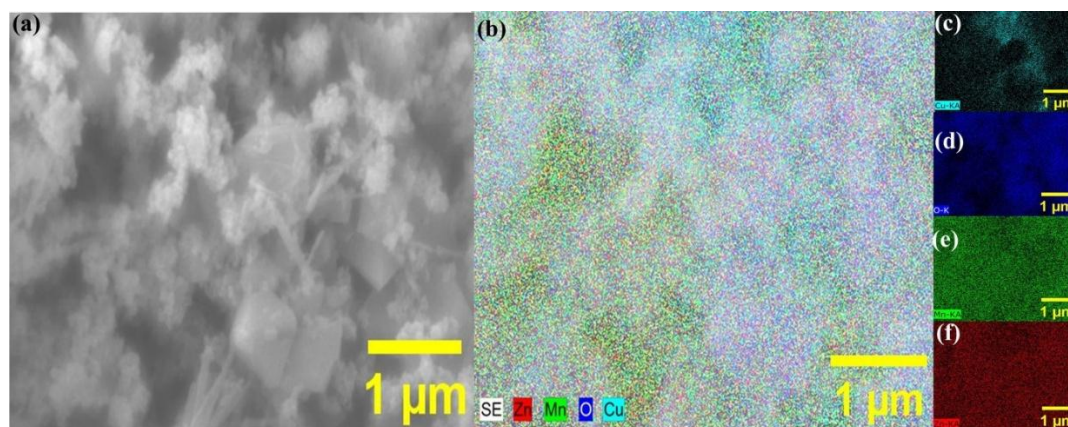


Fig. 5.7. (a) SEM image, (b) EDS mapping of CuO-ZnMn₂O₄ nanostructures, and (c-f) selective elemental distribution for the area shown in image (a).

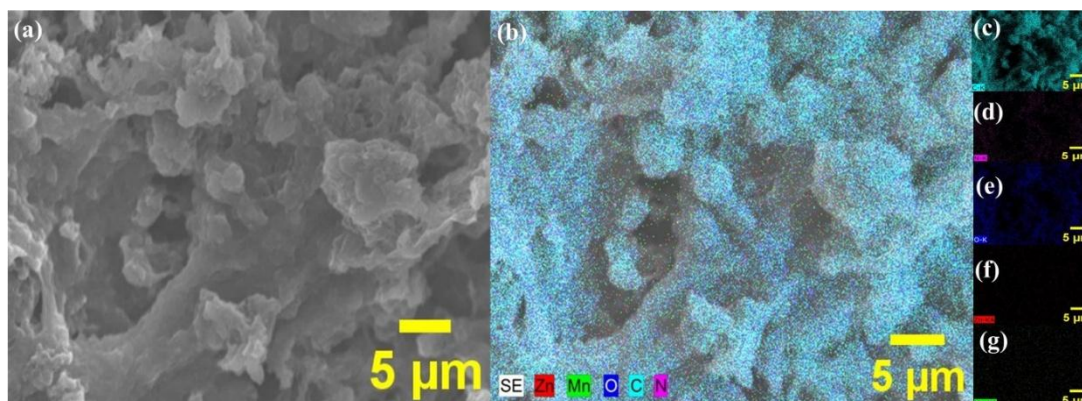


Fig. 5.8. (a) SEM image, (b) EDS mapping of ZPM nanostructures, and (c-g) selective elemental distribution for the area shown in image (a).

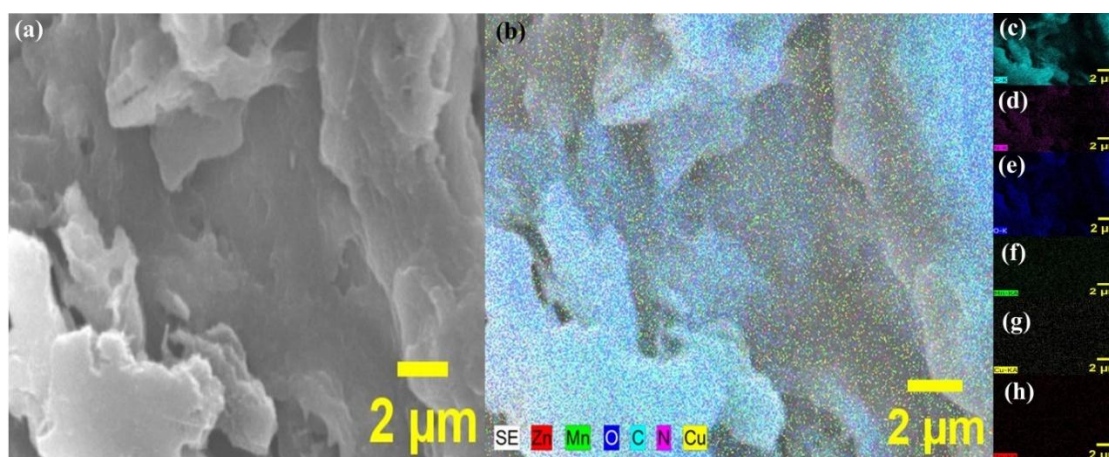


Fig. 5.9. (a) SEM image, (b) EDS mapping of CZPM nanostructures, and (c-h) selective elemental distribution for the area shown in image (a).

5.3.5. High Resolution Transmission electron micrographs (HR-TEM)

The microstructural characteristics of the quaternary CuO-ZnMn₂O₄/PANI/MWCNT hybrid composite were investigated through the TEM, HRTEM-SAED images shown in Fig. 5.10. From Fig. 5.10 (a-b), it is obviously inferred the co-existence of CuO-ZMO with PANI and MWCNTs in the composite system. The HRTEM image shown in Fig. 5.10(c), it is undeniable about the wrapping of PANI around the tubular texture of MWCNTs through their synergistic interactions. The average diameter of these rough interconnected fibrillar networks was estimated to be 17.5 to 20 nm. From Fig. 5.10(d), the presence of metal oxide particles along with PANI and MWCNT contributions was verified from the identification of dominant crystallographic planes in the HRTEM images. The inner-outer diameter of fibres was

analysed to prove the PANI wrapping on the MWCNT surfaces during polymerisation. The SAED pattern of CZPM composite is presented in Fig. 5.10 (f), shows the concentric rings that substantiates the polycrystalline nature of composite.

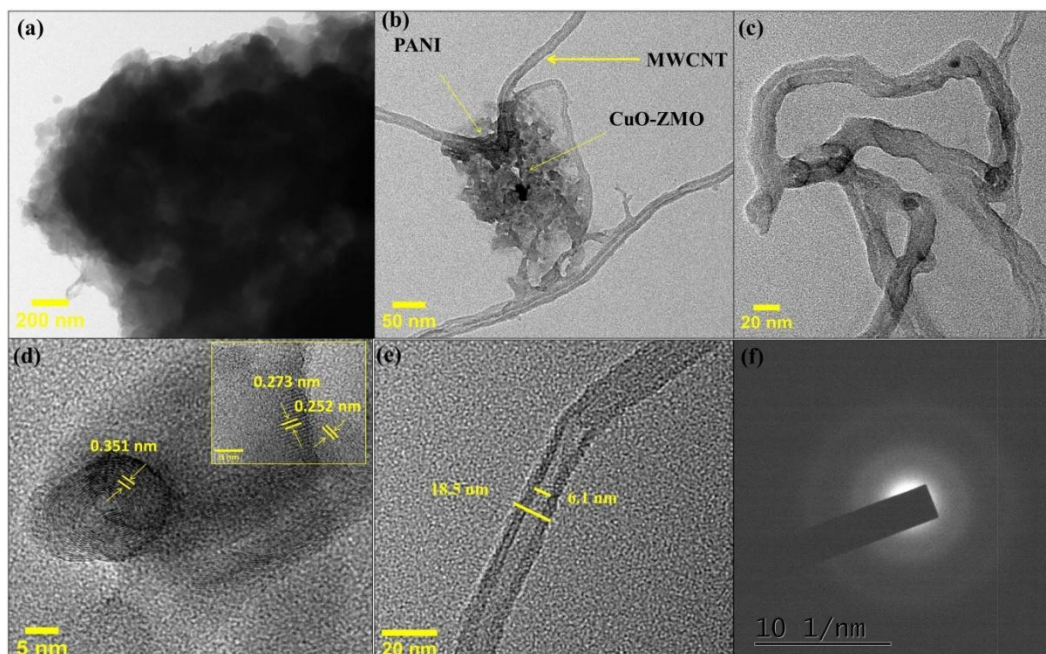


Fig. 5.10. (a,b,c) TEM micrograph (d,e) HRTEM images (f) SAED pattern of CZPM composites. Inset figure in Fig. 5.10 (d) shows crystallographic planes of nanostructures in the composite.

5.3.6. X-Ray Photoelectron spectroscopy (XPS)

The compositional analysis and identification of chemical oxidation states in the composites were carried out using X-ray photoelectron spectra, as presented in Fig. 5.11. The survey spectrum shown in Fig. 5.11 (a) confirms the presents of the elements C, N, O, Zn, Mn, and Cu in the quaternary CZPM composite. The core level spectra of C 1s displayed in Fig. 5.11 (b) is deconvoluted to three major peaks located at binding energies 284.5 eV, 286.2 eV, and 287.6 eV which can be assigned to the sp^2 hybridized Carbon atoms, C=O, and C-OH bonds, respectively [29]. Higher intensity of sp^2 hybridised carbon atoms is a clear indication of grafting of PANI over MWCNTs, since conductive PANI polymers consists of an abundant amount of C=C bonds [30]. The core level XPS spectra of N 1s shown in Fig. 5.11 (c) deconvoluted to three peaks at 399.2 eV, 401 eV, and 403.6 eV. The high intense peak at lower binding energy of 399.2 eV can be attributed to the neutral amine groups (-N-H-) present in the PANI, whereas

protonated imine groups are responsible for the peak at 401 eV. The less intense peak at 403.6 eV assigned to the protonated amine groups [31]. The protonated nitrogen in the composite is an clear indication of the high conductive nature of PANI [32]. This ionic nitrogen presence can be due to the effective interaction of PANI and MWCNTs through π - π^* conjugation [33]. The XPS spectrum of Zn 2p is shown in Fig. 5. 11 (c) featuring the characteristic peaks at binding energies 1022 eV and 1046 eV, allocated to the Zn 2p_{3/2} and Zn 2p_{1/2} orbits, respectively [34]. The oxidation states of Mn 2P was revealed through analysing the core level XPS spectrum presented in Fig. 5.11 (d). The two peaks at 641.9 eV and 652.9 eV were corresponds to the Mn 2p_{3/2} and Mn 2p_{1/2} orbitals, respectively. There exists one satellite peak at 643.6 eV, confirming the existence of Mn³⁺ and Mn²⁺ ions in the composite [35]. The characteristic peaks of Cu 2p_{3/2} and Cu 2p_{1/2} were located at the binding energies 932.8 eV and 952.7 eV along with three shake up peaks (shown in Fig. 5.11 (e)) [36]. The core level XPS spectrum of O 1s is shown in Fig. 5. 11 (e), having three deconvoluted peaks at 531.3 eV, 532.6 eV and 534.6 eV representing oxgen vacancies, metal-hydroxyl bonds and carbon oxygen bonds (O=C-O), respectively [34], [37].

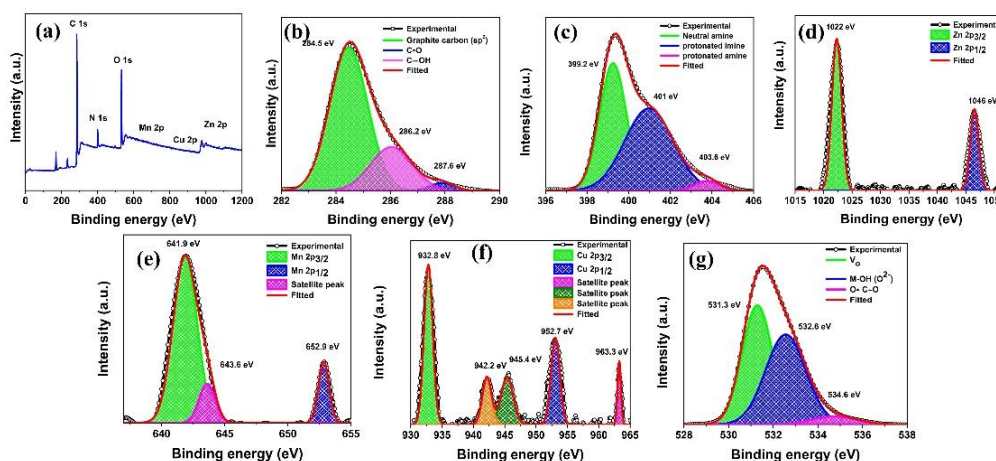


Fig. 5.11. (a) XPS survey spectrum and XPS elemental core spectra of (b) C 1s and (c) N 1s (d) Zn 2p and (e) Mn 2p (f) Cu 2p (g) O 1s states of CZPM nanocomposite.

5.3.7. Brunauer-Emmett-Teller (BET) analysis

The specific surface area and pore size distribution of ZMO, CuO-ZMO, ZPM, and CZPM nanocomposites were estimated using Brunauer-Emmett-Teller analysis and are presented in Fig. 5.12. From the N₂ adsorption-desorption isotherm plot of ZMO which is shown in Fig. 5.12 (a), it is inferred that the material exhibits type IV

adsorption behaviour with a H3 hysteresis loop ranging from 0.6-0.95 (P/P_0). The type IV adsorption isotherms were usually exhibited by mesoporous species in which the adsorption nature is determined generally by the interaction between adsorbent and adsorptive [27]. In addition, the shape of hysteresis loops is also crucial in describing the metastability of the adsorption process. ZMO shows mesoporous nature with a BET surface area of about $\sim 8 \text{ m}^2/\text{g}$. The pore radius and pore volume of ZMO estimated from the pore size distribution (PSD) plot and are shown in the inset of Fig. 5.12 (a) is 3.12 nm and $0.012 \text{ cm}^3/\text{g}$, respectively. The adsorption-desorption plot of CuO-ZMO nanocomposite (Fig. 5.12 (b)) concluded the type IV adsorption isotherm with H3 hysteresis loop between 0.4-1 (P/P_0). The specific surface area was estimated to be $68 \text{ m}^2/\text{g}$. The mesoporous nature of this composite was visible from the PSD plot shown in the inset figure with a pore radius and volume of about 12.1 nm and $0.86 \text{ cm}^3/\text{g}$, respectively. The ZPM composite sample exhibits a type IV adsorption isotherm with H3 hysteresis loop ranges 0.8-1 (P/P_0) with a surface area of $14 \text{ m}^2/\text{g}$, which is shown in Fig. 5.12 (c). From the PSD plot shown in the inset figure, the pore radius and volume were estimated to be 6.14 nm and $0.043 \text{ cm}^3/\text{g}$. In the case of the quaternary CZPM composite, the N_2 adsorption-desorption isotherm plot (Fig. 5.12 (d)) shows a H1 hysteresis loop ranges between 0.79-1 (P/P_0). The mesoporous nature of the composite sample was inferred from the PSD plot (inset figure in Fig. 5.12 (d)) with a pore radius and volume of 16.12 nm and $0.91 \text{ cm}^3/\text{g}$, respectively. The BET surface area of the quaternary composite is about $114 \text{ m}^2/\text{g}$. The inbuilt greater surface area of MWCNTs with tubular morphology as well as the fibrous conductive frameworks of PANI themselves can effectively contribute to the overall surface area of the composite system. Additionally, the PANI/MWCNT incorporation can make porous interconnected networks throughout the composite, as visible in the SEM micrographs, which can increase electrolyte penetration to the electrode surface. The CZPM composite having a larger specific surface area and pore structure can effectively enhance the electrochemically active sites between the electrode-electrolyte interface and surpasses the ionic migrations in the system, which can eventually turn up the electrochemical performance of the composite electrode.

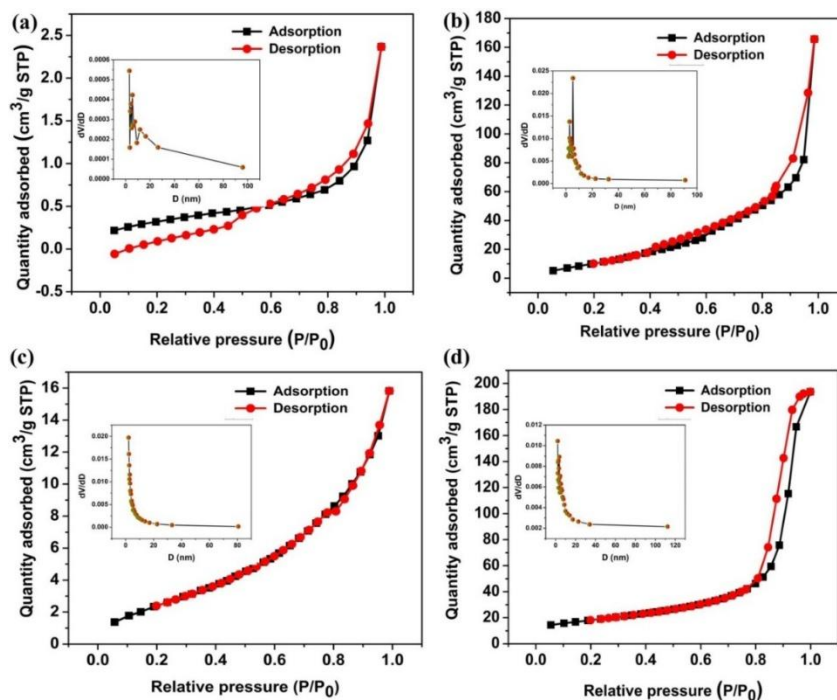


Fig. 5.12. The N₂ adsorption-desorption isothermal plots of (a) ZnMn₂O₄ (b) CuO-ZnMn₂O₄ (c) ZPM and (d) CZPM nanocomposites. Inset shows the corresponding PSD plots.

5.3.8. Thermo-gravimetric Analysis (TGA)

The stability of CZPM quaternary composite under thermal test was conducted using TGA analysis, portrayed in Fig. 5.13. The CZPM composite material suffers three stages of decomposition which results in marginal weight loss over temperature exposure. The complete release of water molecules from the composite material resulted in a weight loss of about 5.65% at a temperature of 97 °C. In the second stage, due to the removal of acid components as well as the initiation of polymer degradation contributes to a significant loss of about 34.5% at 337 °C. Final degradation of polymer backbones accounts for a weight loss of about 10% until the temperature 569 °C [38], [39]. The substantial amount of the final residual part of CZPM indicates the enhanced thermal stability of the quaternary composite when compared with pristine PANI, due to the significant thermal strength contributed from the metal oxides and MWCNTs. The metal oxides carry commendable thermal resistance and their strong bond with PANI make the decomposition process slower and lesser [40]. Moreover, the higher stability and mechanical strength of carbon compounds like MWCNTs under thermal stress delayed the temperature breakdown of composite [41].

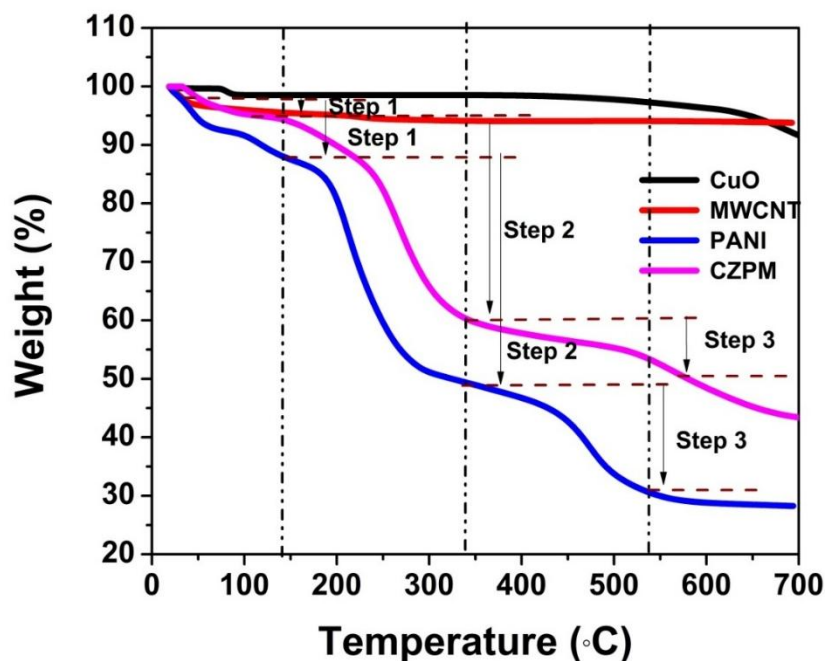


Fig. 5.13. Thermogravimetric analysis of CuO, MWCNT, PANI and CZPM composite.

5.3.9. Electrochemical studies

5.3.9.1. Cyclic voltammetry (CV)

To access the electrochemical performance of ZMO, CuO-ZMO, ZPM, and CZPM nanocomposite, cyclic voltametric analysis was conducted in a three-electrode system at different scan rates ranging from 5 mV/s to 100 mV/s, shown in Fig. 5.14. The CV measurements were taken in the optimised potential window of 0-0.8V with 1M Na₂SO₄ as the electrolyte solution. ZMO electrode material exhibited CV curves having geometry much deviated from the ideal rectangular shape, suggests its pseudocapacitive nature (Fig. 5.14 (a)). Although, the integral area which quantifies the current responses has escalated with the increasing sweep rate, the total areal current response at each scan rate remained significantly low compared to that of pristine CuO. The CV profile of CuO-ZMO nanocomposite electrode material is displayed in Fig. 5.14 (b), shows the quasi-rectangular shape of CV curves without any noticeable redox peaks. The visible broadening of CV loops with sweep rate without disturbing its shape is a clear indication of the excellent rate capacity and reversibility of cyclic performance. The increase in current responses with sweep rate is attributable to the faster transport of electrically active species from the electrolyte ions to electrode

surfaces [42]. The CV curves of ternary-quaternary nanocomposites ZPM and CZPM are depicted in Fig. 5.14 (c-d). Both the composite electrodes showed a quasi-rectangular shaped current response with distinct redox peaks. The redox peaks in the CV curve of ZPM sample were appeared at potentials (0.17V, 0.37V) ascribed to the exchange of emeraldine and lucoemeraldine states in PANI [43]. A slighter shift in redox peak positions of ZPM was observed when sweep rate got amplified. The quaternary composite electrode material exhibited a non-rectangular CV curve with a pair of redox peaks at potentials (0.15 V, 0.42 V) at the lower scan rate and went through major shifts in position to a potential pair (0.22 V, 0.57 V) as the sweep rate reached 100 mV/s, which indicated that the PANI and MWCNT incorporation has effectively improved the redox properties of the composite. Noteworthy, the obvious enrichment in current response of CZPM with the increasing scan rates without deforming its shape indicates the high rate capacity and reversibility of the composite [27]. The enhanced capacitive performance of CZPM electrode material is clearly understood from the comparative CV analysis of CuO, ZMO, CZMO, CPM, ZPM and CZPM at the scan rate 100 mV/s, is portrayed in Fig. 5.14 (e). The specific capacitance values obtained from the cyclic voltametric analysis are presented through histogram in Fig. 5.14 (f), showing the remarkable electrochemical performance of CZPM working electrode aroused from the synergistic effects between CuO-ZMO, PANI and MWCNTs within the composite [44]. Undoubtedly, the total specific capacitance of composite electrode can be attributable to the combined influence of electric double layer capacitance and pseudocapacitance. The tubular morphology and porous architecture of the metal oxide anchored PANI-MWCNT system enabled faster ionic transport and kinetics through improved electrical conductivity [45].

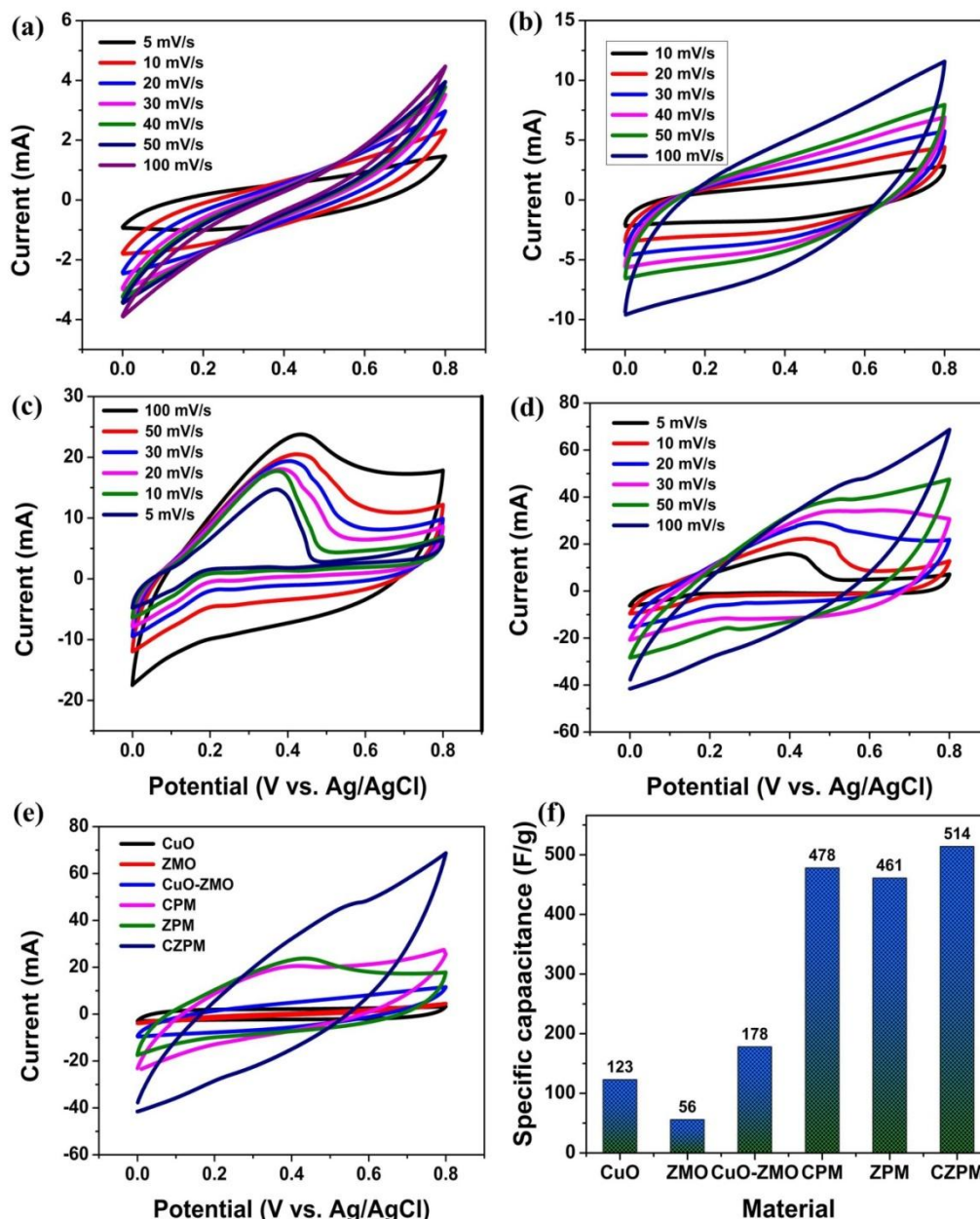


Fig. 5.14. CV curves of (a) ZMO (b) CuO-ZMO (c) ZPM (d) CZPM, comparison of (e) CV curves of CuO, ZMO, CuO- ZMO, CPM, ZPM and CZPM nanocomposites at 100 mV/s (f) specific capacitance of CuO, ZMO, CuO- ZMO, CPM, CZPM and CZPM nanocomposites at 10 mV/s.

The reaction kinetics that occurred during the charge storage mechanism in the CZPM composite electrode is analysed using Dunn's method. The linearity between scan rate and anodic current response at a potential of 0.4 V was observed in Fig. 5.15 (a). The anodic slope value obtained from the plot was 0.83. From $v^{1/2}$ vs. $i/v^{1/2}$ graph (Fig. 5.15 (b)), the coefficient values k_1 and k_2 were extracted and used for the estimation of surface-controlled capacitive contribution and diffusion-controlled

contributions in the total capacitive current response of CZPM electrode. There is a slight deviation from the linearity in the data showing the relation between the square root of the scan rate and peak current. Fig. 5.15 (c) illustrates the separate contribution analysis in the current response of CZPM electrode at the scan rate of 10 mV/s. The shaded region indicates the diffusion-controlled capacitive contribution to the overall current response. As the sweep rate increased, the surface-controlled capacitive contributions became predominant compared to diffusion-controlled redox reactions and achieved a value of 98% at 100 mV/s (Fig. 5.15 (d)).

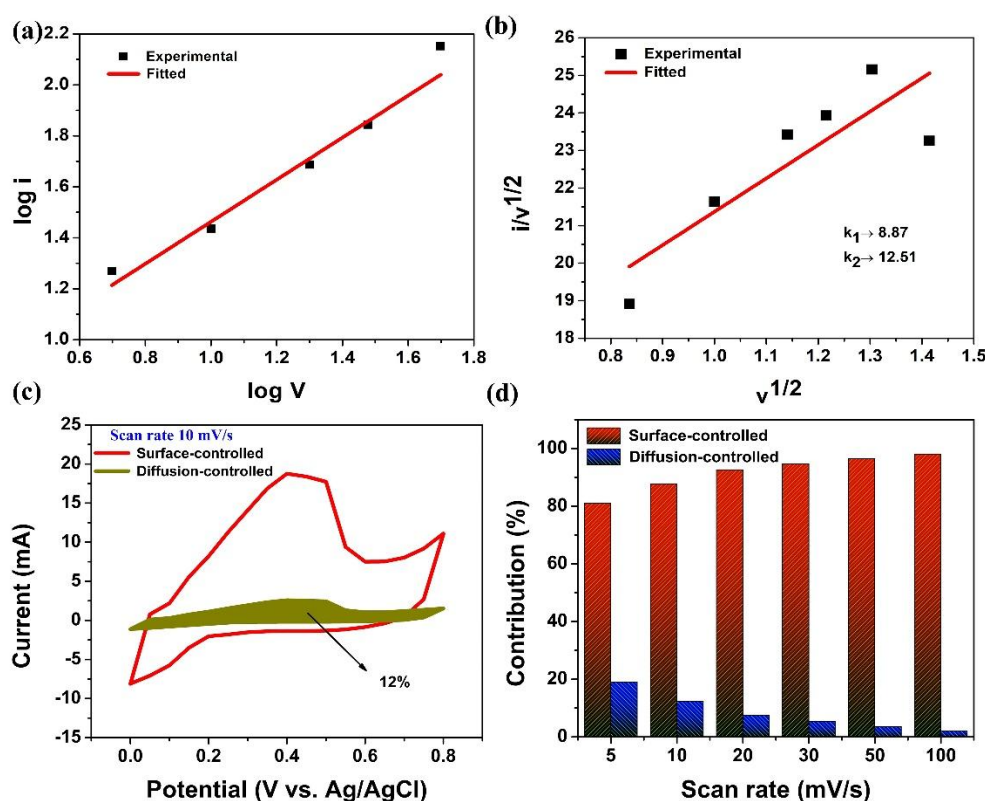


Fig. 5.15. (a) $\log v$ vs. $\log i$ plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ plot (c) decoupling of capacitive and diffusive current contributions at scan rate 10 mV/s (d) Histograms of diffusive and capacitive contributions of CZPM working electrode at varying scan rates.

5.3.9.2. Galvanostatic charge/discharge (GCD) studies

To probe more thoroughly into the electrochemical dynamics of the synthesised ZMO, CuO-ZMO, ZPM, and CZPM composites, GCD studies were conducted. Fig. 5.16 (a-b) shows the GCD profiles of ZMO and CuO-ZMO nanostructures in the optimised potential range of 0-0.8V. The symmetric shapes of GCD curves in all current

densities indicate the satisfactory reversibility of electrodes. The discharging time of CuO-ZMO working electrode is found to be more than that of ZMO electrode. The calculated specific capacitance of ZMO electrode were 114 F/g, 78 F/g, 37 F/g, and 23 F/g, whereas that of CuO-ZMO were found to be 310 F/g, 264 F/g, 50 F/g and 22 F/g at current densities 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. The GCD profiles of ZMO/PANI/MWCNT and CuO-ZMO/PANI/MWCNT electrode are depicted in Fig. 5.16 (c-d). Each electrode shows symmetric shape in GCD curves with improved discharging time compared to their individual counterparts. The low IR drops in all electrode material is one of the beneficial feature of energy storage devices which minimises the heat dissipation during continuous charge-discharge cycles [46]. The specific capacitance values of ZPM and CZPM electrodes were 438 F/g, 345 F/g, 93.75 F/g, and 81.25 F/g, and 693 F/g, 527 F/g, 248 F/g, and 169 F/g at current densities of 1 A/g, 2A/g, 3 A/g, and 5 A/g, respectively. The comparison of the discharging time of CuO, ZMO, CuO-ZMO, CPM, ZPM, and CZPM electrodes at a current density of 1 A/g is displayed in Fig. 5.16 (e). The longest discharging time of the quaternary composite is a clear indication of its enhanced specific capacitance, which can be understood from the histogram presented in Fig. 5.16 (f). The improved performance of this composite electrode is attributable to its beneficial porous structure. More specifically, the uniform growth of PANI over the surface of binary metal oxide composite anchored MWCNTs creates more number of active sites in the electrode surface for achieving faster redox reactions, as well as PANI has built a conductive pathway in the system by improving the electrical contact between metal oxides and MWCNTs [27].

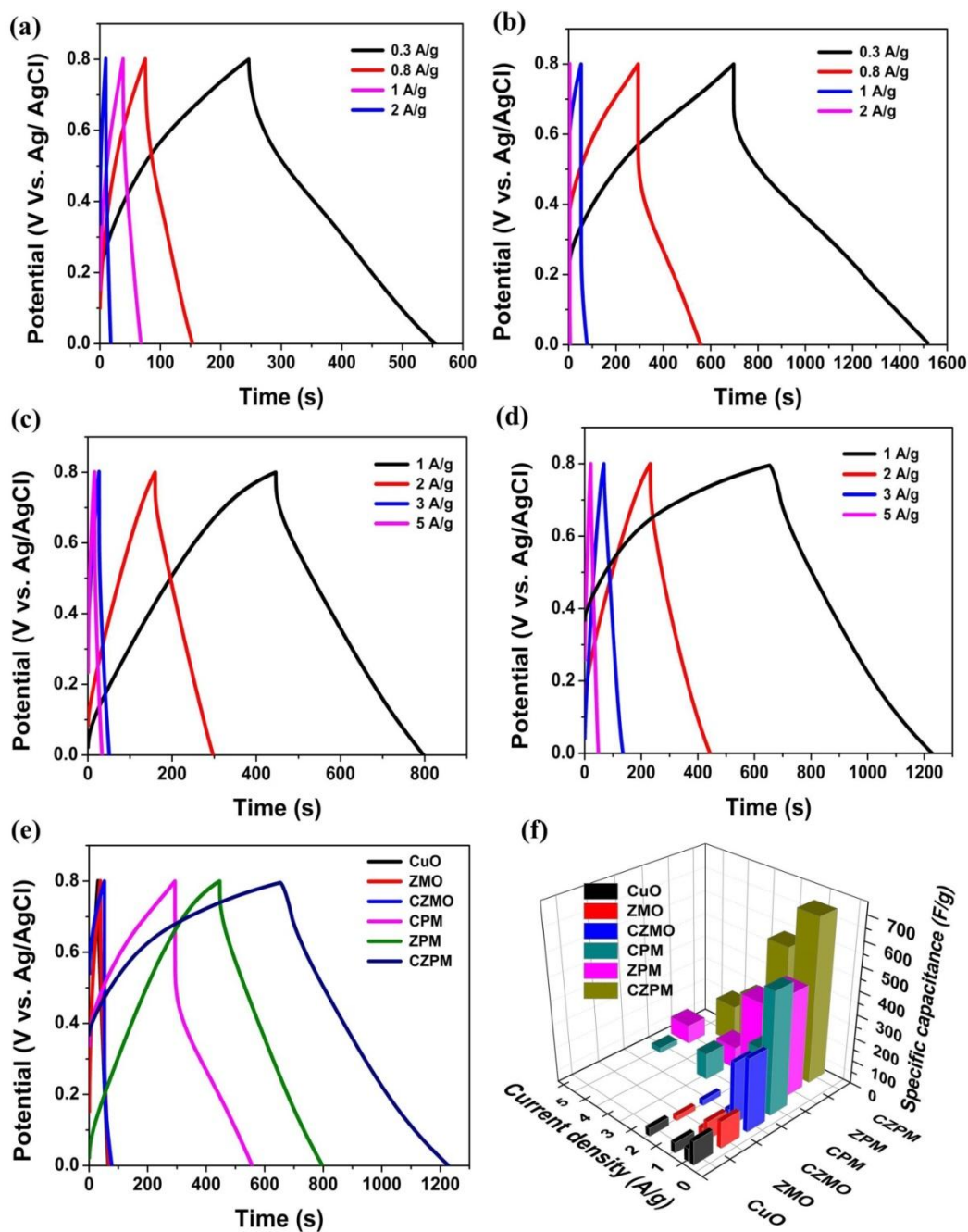


Fig. 5.16. GCD curves of (a) ZMO (b) CuO-ZMO (c) ZPM (d) CZPM (e) comparison of charge-discharge curves of CuO, ZMO, CuO-ZMO, CPM, ZPM, CZPM composites at current density of 1 A/g, (f) variation of specific capacitance with current density of CuO, ZMO, CuO-ZMO, CPM, ZPM, CZPM composites.

5.3.9.3. Electrochemical impedance spectroscopy (EIS)

The EIS studies of working electrodes were conducted with the intention to get deeper insight about the electrochemical features like ionic and electrical conductivity, internal and charge transport resistances, and interfacial process. Fig. 5.17 illustrates the Nyquist plots of ZMO, CuO-ZMO, ZPM and CZPM composite electrodes. The

ZMO and CuO-ZMO electrodes exhibit a well-defined distorted semi-circle arc in the high frequency region followed by a linear steep region in the lower frequency range (Fig. 5.17 (a-b)). The semi-circle portion in Nyquist plot is ascribed to the charge accumulation in the electrode-electrolyte interface, whereas the linear portion in the lower frequency range indicates the diffusion of electrolyte ions into the electrode material [42]. In the Nyquist plots of ZPM and CZPM electrodes there are no noticeable frequency dependent semi-circle portion, shown in Fig. 5.17 (c-d). The lower charge transfer resistance of composite electrodes is the combined effects of MWCNTs and metal oxides, where PANI usually suffered by high transfer resistance [47]. The comparison of Nyquist plots is shown in Fig. 5.17 (e), indicates the improved electrochemical features of the quaternary composite. The Nyquist plots of ZMO, CuO-ZMO, ZPM, and CZPM composite electrodes are best fitted using an equivalent circuit diagram combining R_s , R_{ct} , CPE and W components and the values of these parameters are presented in Table 5.4. The lower values of Warburg resistance are attributed to the shorter ionic diffusion path lengths exhibited by the composite electrode as a direct consequence of its advantageous porous morphology [46]. The lower values of charge transfer resistance offered by the quaternary composite electrode material are a clear indication of the potential application of this material in the field of energy storage devices.

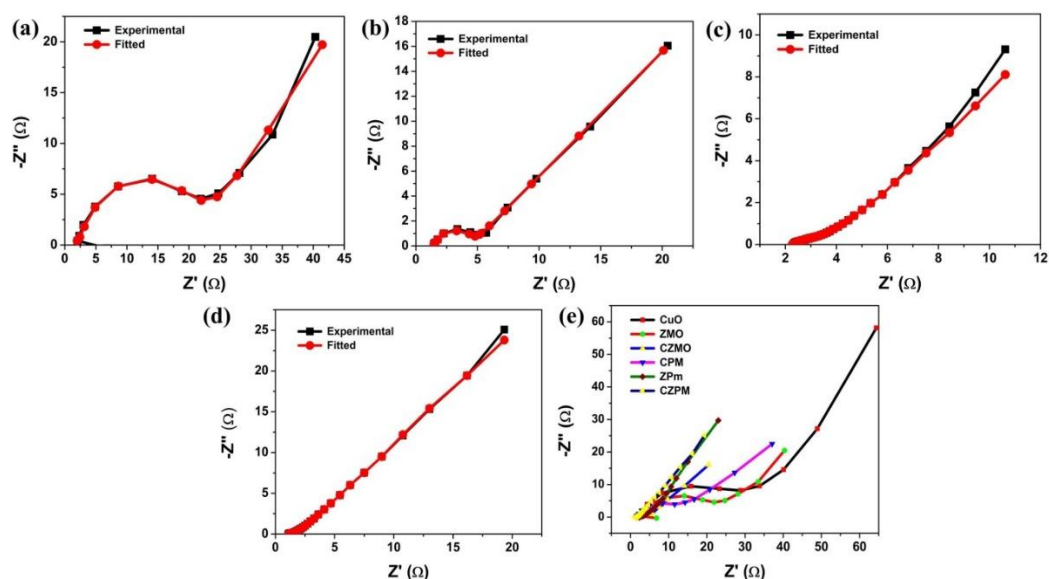


Fig. 5.17. (a) The best fitted Nyquist plot of as-prepared (a) ZMO, (b) CuO-ZMO, (c) ZPM (d) CZPM (e) comparison of Nyquists plots of all nanostructures.

Table 5.4. The R_s , R_{ct} , CPE, W and n values of as-synthesised CuO, ZMO, CuO-ZMO, CPM, ZPM, CZPM nanocomposites.

	Sample					
	CuO	ZnMn ₂ O ₄	CuO-ZnMn ₂ O ₄	CPM	ZPM	CZPM
R_s (Ω)	2	1.85	2.19	1.22	2.32	1.12
R_{ct} (Ω)	29.30	20.59	2.25	11.66	2.89	1.65
W	22.75	15.55	12.42	33.72	21.14	16.18
CPE	0.00057	0.00041	0.00006	0.0049	0.00067	0.00009
n	0.943	0.696	1.005	0.688	0.947	0.903

5.3.9.4. Cycle stability

The cyclic stability is a crucial factor in determining the efficiency of the power delivering capacity of supercapacitor. Generally, EDLCs like MWCNTs exhibit high cycle stability due to the absence of pseudocapacitive effects, while the pseudocapacitors like metal oxides and conducting polymers express low cyclic stability caused by their reversible redox reactions always results in increased series resistance and declined capacitive performances. Therefore a suitable combination of these two categories can overcome the issues related with the cyclic performances of the electrode material [46]. The long-term cycle stability of quaternary CZPM composite electrode was tested over 5000 charge-discharge cycles in a three-electrode system at a current density of 7 A/g and presented in Fig. 5.18 (a). From the figure, it is evident that the CZPM composite delivered an excellent capacitive retention of about 99.8% after 5000 cycles, due to the combined contributions of MWCNTs and metal oxides. This remarkable cyclic performance of composite electrode over 5000 repeated charge-discharge cycles is a clearly verified with the help of post-cycling SEM image, shown in Fig. 5.18 (b). The structural integrity of the electrode surface is evident from the SEM images, may attributed to the combined effect of inherently structural robustness of metal oxides and MWCNT, which doesn't allow any kind of structural or volume changes during continuous reversible redox reactions.

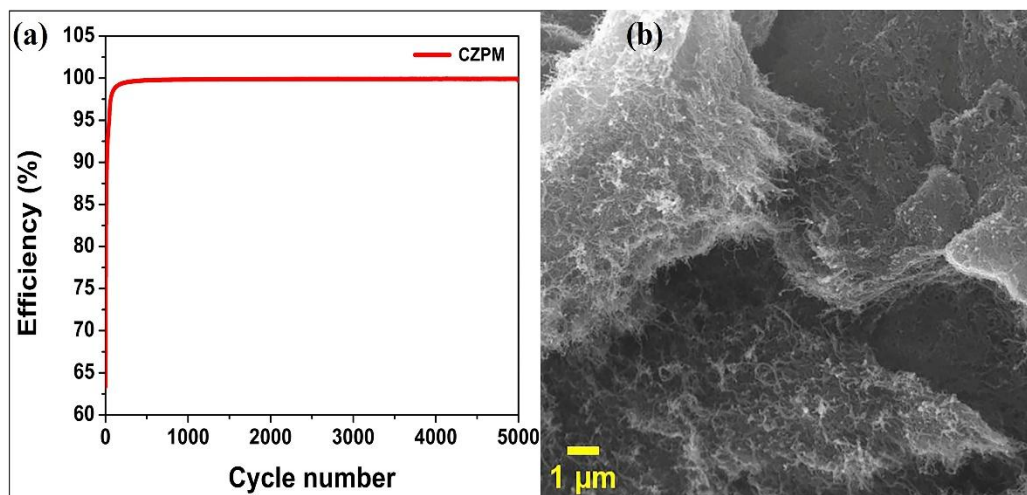


Fig. 5.18. (a) Cycle stability of CZPM working electrode over 5000 cycles (b) post-cycling SEM image of CZPM working electrode.

5.3.9.5. Electrochemical performance of CuO-ZnMn₂O₄/PANI/MWCNT ternary nanocomposite in symmetric two-electrode configuration

A symmetric supercapacitor device is fabricated with two-electrode cell assembly with 1 M Na₂SO₄ as electrolyte. The device performance of CZPM composite electrode is evaluated within the optimised potential window 0-0.8V. Fig. 5.19 (a) depicts the CV profiles of CZPM electrode at various scan rates ranges from 5 mV/s to 100 mV/s. The non-rectangular CV curve shape with noticeable redox peaks at potentials (0.17 V, 0.38 V), can be attributed to the redox transitions between emeraldine and lucoemeraldine forms of PANI [44]. The redox current response of the composite electrode increases as the sweep rate increases indicating the good rate capacity of the CZPM electrode material. The synergistic impacts of PANI and MWCNTs over the metal oxide combination results in improvement in the redox properties of the composite, leading to slighter shifts in redox peak positions in higher current densities. The GCD measurements of CZPM symmetric device at varying current densities are presented in Fig. 5.19 (b). The symmetrical charge and discharge response with small ohmic drop in the analysis data signify the high capacitive reversibility of the working electrode. The maximum capacitance delivered by the

composite electrode was 205 F/g at a current density of 1 A/g (Fig. 5.19 (c)), can be ascribed to the combined effect of double layer capacitance and pseudocapacitance. The pronounced reduction in the specific capacitance value of the electrode material in the symmetric two-electrode configuration, compared to three-electrode configuration, ascribed to the sluggish ionic transport inherent in the ZMO's because of their spinel structure along with other risk factors like internal resistance effects and restricted electrolyte accessibility in the full cell performance level. The coulombic efficiency of composite electrode was evaluated from the GCD results and portrayed in Fig. 5.19 (d). The CZPM composite electrode displayed fair columbic efficiency values for all the current densities points to the improved performance of composite material. The noticeable electrochemical performance of this composite electrode with satisfactory coulombic efficiency can be attributable to its advantageous structure as well as capacitive contributions from each one of its constituents. The specific power and specific energy are the crucial parameters in the electrochemical field, which delve deeper in to the practical applicability of composite electrode over other conventional capacitors. The Ragone plot expressing the variation of energy density with power density is presented in Fig. 5.19 (e), which shows a high energy density of CZPM electrode of about 18.22 Wh/Kg at a current density of 1 A/g. The maximum power density obtained by the CZPM symmetric device was 1111 W/Kg at 5 A/g. Fortunately, the prepared quaternary composite exhibited almost 100% of initial capacity over 50000 repeated charge-discharge cycles, as understood from Fig. 5.19 (f). The exceptional morphology of quaternary composite prevents the unwanted agglomeration or structural/voluminous deteriorations may happen during the long-term cycling process, resulted in the commendable structural stability of the electrode.

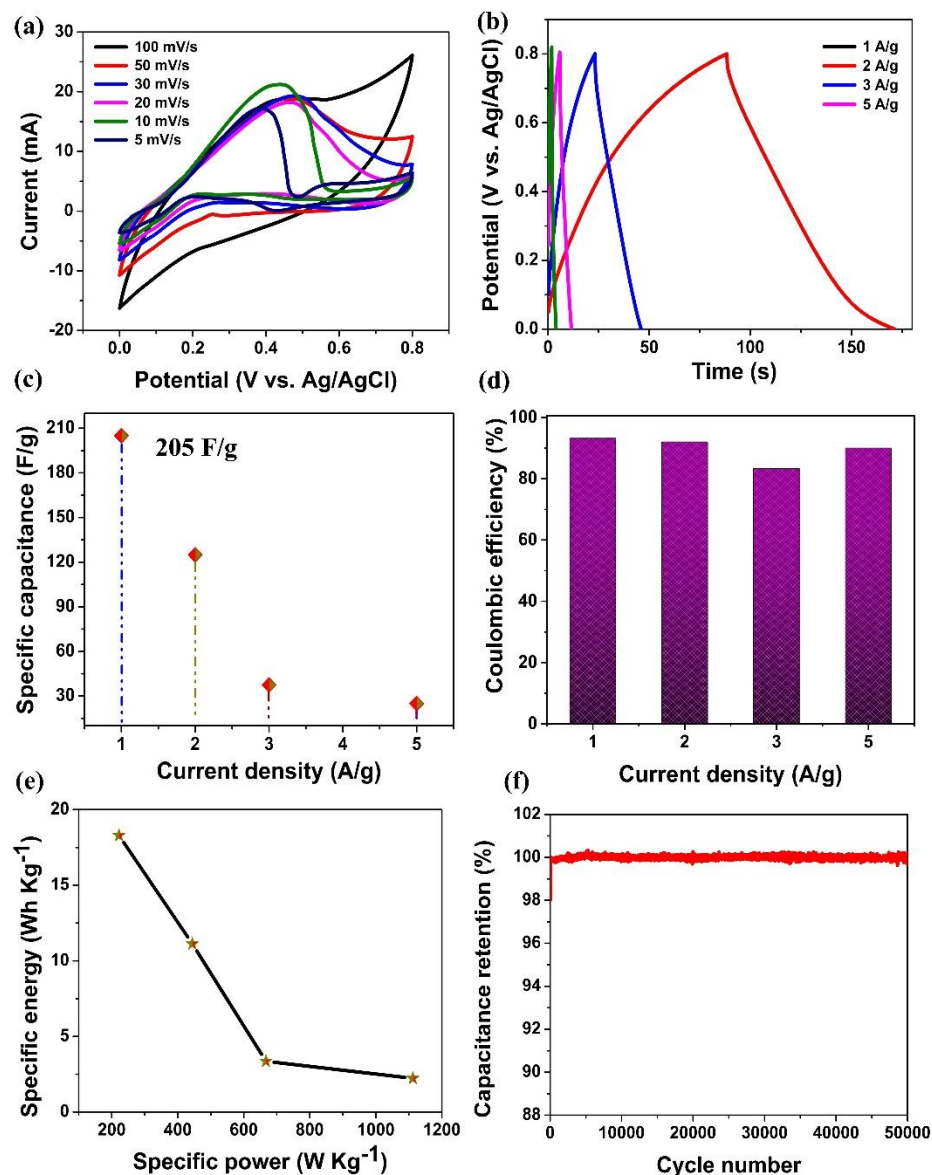


Fig. 5.19. (a) CV (b) GCD plots of CZPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) coulombic efficiency analysis (e) Ragone plot and (f) cycle stability of CZPM composite in 50000 cycles.

5.4. CONCLUSION

The ZMO, CuO-ZMO, ZPM and CZPM composite material were fabricated through hydrothermal and freeze drying assisted one pot chemical polymerisation method exhibited exceptional surface morphologies and electrochemical features. The quaternary composite electrode material achieved a maximum capacitance of 693 F/g at a current density of 1 A/g, attributed to the productive synergism between constituent elements such as CuO, ZMO, PANI and MWCNT resulted in the unique porous morphology with high specific surface area. In particular, the electrode material maintained a capacitive retention of 100% over 50000 cycles in the two-electrode cell assembly with satisfactory energy density of 18.22 Wh/Kg. Furthermore, the incorporation of metal oxides in to the PANI-MWCNT bounded framework prevents the volume expansions or structural deformations during long term cycling. The assured electrochemical performance with excellent specific capacitance and cyclic performances of CZPM composite electrode make them a potential choice as working electrode in the energy storage devices.

Table 5.5. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CZPM	514	10	693	1	197	10	205	1

5.5. REFERENCE

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Conclusion

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This chapter summarizes the thesis with some of the essential points and core insights derived from the research work. The essential and concise views associated with each chapter is discussed shortly. The importance of a ternary/quaternary CuO-based nanocomposite hybrid electrode material in the supercapacitor area is expressed in the chapter.

=====

Energy storage and management have become one of the major concerns in the present society since the relentless growth of world population and unending demand of energy is multiplying day by day. This led to dangerous effects on world economy and made the research community to discover a highly efficient and reliable energy storage devices. Supercapacitors have become a prominent area of research based on the current scenario and specifically scientists concentrated more on to hybrid electrode materials that can cover all aspects of ESDs like high specific capacitance, energy density, power density, cyclic stability and rate capacity. The search for an alternative approach to overcome the inherent insufficiency of ionic conductivity in CuO electrodes is become a hot research area. The thesis work had made an effort to synthesis an efficient, reliable and high performing hybrid supercapacitor electrode material for energy storage applications.

Chapter 1 deals with the concise introduction about importance of ESDs, supercapacitors and its classifications, different kinds of electrode materials and electrochemical analysis. A comprehensive analysis about the properties of CuO and a brief introduction on carbon-based electrode materials and conducting polymers specifically polyaniline is also given.

Chapter 2 presents the synthesis of CuO nanostructures via simple hydrothermal method and a detailed evaluation of its structural, morphological, elemental and thermal properties is also presented. The ternary CuO/PANI/MWCNT nanocomposite was synthesised through one pot chemical oxidative polymerisation method followed by lyophilization process. The influence of PANI and MWCNT incorporation into CuO is studied in detail through structural and spectroscopic analyses. The enhancement in the electrochemical performance of ternary nanocomposite electrode was observed when compared with that of pure CuO electrode indicating the synergistic effects between CuO, PANI and MWCNTs. The conductive pathway provided by PANI and the improved surface area and mechanical strength provided by MWCNTs made the composite to become a potential electrode material.

The synthesis and characterizations of quaternary CuO-NiO/PANI/MWCNT nanocomposite is discussed in **chapter 3**. The preparation of this quaternary nanocomposite was done using one pot chemical oxidation polymerisation followed by lyophilization and influence of NiO in to the CuO/PANI/MWCNT hybrid system

was evaluated using structural, morphological, elemental and thermal characterization techniques. The improvement in surface area and porosity of the composite material was observed. The enhancement in the electrochemical performance of quaternary CuO-NiO/PANI/MWCNT nanocomposite hybrid electrode was recorded in comparison with CuO, NiO, CuO-NiO, CuO/PANI/MWCNT and NiO/PANI/MWCNT electrodes. The synergistic interactions between the individual constituents and their individual contributions made the composite electrode more efficient and reliable. The composite electrode delivered highest specific capacitance with high percentage of capacitive retention efficiency.

Chapter 4 discusses synthesis, characterizations and electrochemical performance evaluation of quaternary composite CuO-Co₃O₄/PANI/MWCNT hybrid electrode material. The introduction of cobalt oxide into the composite has resulted in improved surface and morphological features and thereby the electrochemical performance of quaternary composite electrode has improved compared to CuO, Co₃O₄, CuO-Co₃O₄, CuO/PANI/MWCNT and Co₃O₄/PANI/MWCNT electrodes. The high pseudocapacitive capacity of cobalt oxide along with the individual contributions of PANI and MWCNTs has made the quaternary composite as a viable electrode material in supercapacitor applications.

The synthesis and structural, morphological, elemental and thermal characterizations of CuO-ZnMn₂O₄/PANI/MWCNT quaternary composite was presented in **chapter 5**. The synthesis of CuO-ZnMn₂O₄/PANI/MWCNT quaternary composite via chemical oxidative polymerization method and its electrochemical performance evaluation with both three-electrode and two-electrode configurations were discussed in detail. The improvement of electrochemical capacities of composite electrode through the incorporation of zinc manganese oxide and individual as well as synergistic contributions of CuO, PANI and MWCNTs has made the quaternary composite as an efficient electrode material with high capacitive retention efficiency.

To conclude, the thesis emphasis on the synthesis and electrochemical performance evaluation of CuO and PANI/MWCNT incorporated CuO-based nanocomposite hybrid electrode materials. The influence of PANI and MWCNTs in the electrode fabrication was discussed in detail. The improvement in the electrochemical performance of electrode prepared through the introduction of metal oxides like NiO,

Co_3O_4 and ZnMn_2O_4 is accessed and found a marginal enhancement in the specific capacitance, energy density, power density and cyclic stability of the electrode materials.

Recommendations

Some future aspects of the current research are presented. We foresee the vast areas to explore in this area of metal oxide-based nanocomposite materials in the optoelectronic applications particularly in energy storage devices.

Transitional metal oxides are always a promising electrode material in the field of supercapacitors. Among which CuO gained much more attraction in recent years as a viable electrode candidate for pseudocapacitors. This is predominantly due to its advantageous like low cost, environmental benignity, elemental abundance, high theoretical specific capacitance and availability of oxidation states for fast redox activities. However, the inherent conductivity issues faced by the CuO-based electrodes can be minimised by combining it with other carbonaceous compounds and conducting polymers. The current research focused on to the synthesis of CuO electrode via simple hydrothermal route and extensively studied its structural, microstructural, morphological, elemental and thermal properties using various characterisation techniques. Electrochemical properties of the CuO electrode revealed the insufficiency of specific capacitance, energy density, power density and cyclic stability features of pure CuO. Thus, the study paved way to synthesis and analysis the electrochemical potentialities of PANI/MWCNT incorporated CuO-based nanocomposite hybrid electrode materials via one pot chemical oxidative polymerisation method followed by freeze drying condition. Further improvement in the electrochemical properties like specific capacitance, energy density, power density, cycle stability and rate capacity of the nanocomposite electrodes was done by the introduction of other transitional metal oxides like NiO, Co₃O₄, and ZnMn₂O₄.

In addition to the different aspects of CuO-based nanocomposites discussed in the current work, attempts can be put forward to study the optical, dielectric and magnetic properties of these composites, which are still remain underexplored. The molar proportions between CuO and other metal oxides, metal oxide composites and MWCNT or PANI and MWCNT can be altered and studied. Moreover, the synthesis method of these composite electrodes can be refined using other sophisticated bottom-up synthesis approaches for exploring the possibility of increasing active surface area and porosity of electrode surface with an aim to improve the ionic diffusions through the electrode-electrolyte interface.

In addition to NiO, Co₃O₄, and ZnMn₂O₄, other transitional metal oxides like MnO₂, V₂O₅, TiO₂, ZnO etc. can be tried with CuO for making potential nanocomposite electrodes. Furthermore, there is another possibility to use

heteroatom-functionalised carbon which has the capacity to undergo redox activities and produce pseudocapacitance replacing MWCNTs.

In the sense to reduce the cost of production, the expensive carbon-based compound like MWCNT can be replaced by biomass derived carbon precursors. The electrochemical performance of synthesised CuO-based nanocomposite electrode material can be improved by examine more about the features like interfacial properties, charge collection and transport capacities, defect states etc.

The achieved potential (0.8 V) in the aqueous electrolyte is comparatively low, which demands a lot of series connections in practical scenarios. Thus, there is an open chance to make attempts to increase the potential window by using different non-aqueous or polymer electrolytes with different mole percent. Based on few studies, there is a possibility to increase the device performance by matching pore size of electrode surface and ionic size of electrolytes.

Like metal oxide-based electrode material, same synthesis and electrochemical analyses can be extended to metal sulphides also since they also have ability to attain high specific capacitance and cycle stability. Furthermore, there is also a possibility to attempt theoretical simulations and interpretations about the charge storage mechanisms involved in the electrode working to improve and optimise the device performance.

Fabrication of flexible supercapacitor devices that can withstand all external mechanical deformations is one of the important innovations of present research society in the area of smart energy storage devices. Also, the production of microsupercapacitors based on this CuO-based composite electrodes can be attempted. Therefore, more sophisticated production techniques like ink jet printing or roll-roll printing can be implemented for the fabrication of flexible and wearable devices based on this PANI/MWCNT incorporated CuO-based composite electrodes.

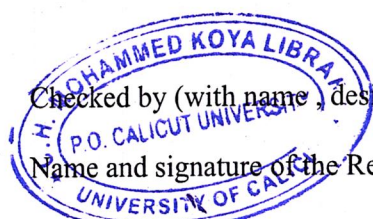


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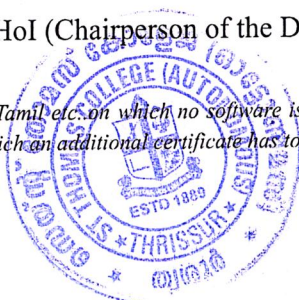
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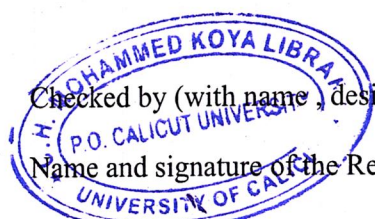
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Abstract

Development of a cost-effective and an efficient electrode material through a facile and intuitive synthesis route is one of the key points of contention in the area of supercapacitors. This thesis mainly concentrated on the synthesis and characterizations of CuO and PANI/MWCNT incorporated CuO-based nanocomposite hybrid electrode materials. CuO nanostructures are synthesised via a hassle-free hydrothermal method. On the other hand, the PANI/MWCNT incorporated CuO-based ternary/quaternary nanocomposite material is prepared using a one pot chemical oxidative polymerisation method carried out at room temperature, followed by a freeze-drying stage. The crystalline and microstructural, morphological and elemental, thermal properties of the synthesised nanocomposite materials are investigated in detail. Moreover, a comprehensive evaluation is conducted in order to investigate the influence of the transitional metal oxides such as NiO, Co₃O₄ and ZnMn₂O₄ in the electrochemical performance of the ternary CuO/PANI/MWCNT nanocomposite hybrid system. In-depth attention is given to the synergistic interactions between the constituents of composite electrodes that have a crucial role in their electrochemical performance for energy storage applications in terms of specific capacitance, energy density, power density, cyclic stability and rate capacity.

Keywords: Copper oxide, nanocomposite, pseudocapacitor, polyaniline, synergistic effect, hybrid electrodes.



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സംഗ്രഹം

ചെലവുകുറഞ്ഞതും ലളിതവും സ്വാഭാവികവുമായ ഗവേഷണ മാർഗം വഴി കാര്യക്ഷമവുമായ ഇലക്ട്രോഡ് പദാർത്ഥങ്ങൾ വികസിപ്പിക്കുക എന്നതാണ് സൂപ്പർ കപ്പാസിറ്റർ മേഖലയിലെ നിലവിൽ നടക്കുന്ന പ്രധാന ഗവേഷണ പ്രവർത്തനങ്ങൾ. ഈ ഗവേഷണ പ്രബന്ധം പ്രധാനമായും കോപ്പർ ഓക്സൈഡ്, PANI/MWCNT എന്നിവ ഉൾപ്പെടുത്തിയ കോപ്പർ ഓക്സൈഡ് അടിസ്ഥാനമാക്കിയ നാനോകമ്പോസിറ്റ് ഹൈബ്രിഡ് ഇലക്ട്രോഡ് പദാർത്ഥങ്ങളുടെ നിർമ്മാണവും തുടർന്നുള്ള ഗവേഷണം അവയുടെ സ്വാഭാവികലനത്തിലും വിവിധ ഉത്പന്നനിർമ്മാണത്തിന് പ്രയോജനപ്പെടുത്താവുന്ന രീതിയിലുമാണ്. കോപ്പർ ഓക്സൈഡ് നാനോഘടനകൾ ലളിതമായ ഹൈഡ്രോതെർമൽ രീതിയിലൂടെ തയ്യാറാക്കുന്നു. അതേസമയം, PANI/MWCNT ഉൾപ്പെടുത്തിയ കോപ്പർ ഓക്സൈഡ് അടിസ്ഥാനമാക്കിയ ടെർണറി/ക്വാടേണറി നാനോകമ്പോസിറ്റ് മെറ്റീരിയലുകൾ മുറിയിലെ താപനിലയിൽ രാസ ഓക്സിഡേറ്റീവ് പോളിമറൈസേഷൻ രീതിയിലൂടെ ആരംഭിച്ച് തുടർന്നുള്ള ഫ്രീസ്-ഡ്രെയിംഗ് ഘട്ടത്തിലൂടെ തയ്യാറാക്കുന്നു. തയ്യാറാക്കിയ നാനോകമ്പോസിറ്റ് പദാർത്ഥങ്ങളുടെ സ്പെട്രോസ്കോപ്പിക് സൂക്ഷ്മഘടനയും, ആകൃതിശാസ്ത്രവും ഘടകവിശകലനവും, താപഗുണങ്ങളും വിശദമായി പരിശോധിക്കുന്നു. കൂടാതെ, NiO, Co₃O₄, ZnMn₂O₄ പോലുള്ള ട്രാൻസിഷണൽ മെറ്റൽ ഓക്സൈഡുകൾ CuO/PANI/MWCNT ടെർണറി നാനോകമ്പോസിറ്റ് ഹൈബ്രിഡ് സിസ്റ്റത്തിന്റേ ഇലക്ട്രോകെമിക്കൽ സ്വാഭാവത്തിൽ ഉണ്ടാക്കുന്ന സ്വാധീനം വിലയിരുത്തുന്നതിനായി സമഗ്രമായ വിശകലനം നടത്തുന്നു. സംയുക്ത ഇലക്ട്രോഡുകളുടെ ഘടകങ്ങൾ തമ്മിലുള്ള സഹപ്രവർത്തനങ്ങൾ അവയുടെ ഇലക്ട്രോകെമിക്കൽ പ്രകടനത്തിൽ, അതായത്, പ്രധാനമായും അവയുടെ കപ്പാസിറ്റൻസ്, എനർജി ഡെൻസിറ്റി, പവർ ഡെൻസിറ്റി, സൈക്ലിക് സ്റ്റേബിലിറ്റി, റേറ്റ് കപ്പാസിറ്റി എന്നിവയിൽ വഹിക്കുന്ന നിർണായകമായ പങ്ക് കണ്ടെത്തുന്നതിൽ ആഴത്തിലുള്ള ശ്രദ്ധ കൊടുത്തിരിക്കുന്നു.

കീവേഡുകൾ: കോപ്പർ ഓക്സൈഡ്, നാനോകോമ്പോസിറ്റ്, പ്സ്യൂഡോകാപാസിറ്റർ, പോളിയിനിലിൻ, സഹപ്രവർത്തന ഫലം, ഹൈബ്രിഡ് ഇലക്ട്രോഡുകൾ.


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General Introduction

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Worldwide, the awareness of “energy crisis” has led to a series of initiatives and energy management policies in the last decades that have made society to become more focused on energy production and management procedures. Thus, Energy storage devices (ESDs) have gained much interest in the research scenario, thereby more and more works have been centred in recent years on the field of supercapacitors with the aim to fabricate a highly efficient, viable and cost-effective electrode material. Herein, a detailed description of the basics, importance and classifications of the supercapacitors is discussed. An extensive study on the different kinds of charge storage mechanisms involved in the supercapacitors as well as the importance and role of electrode material is also discussed in detail. A brief introduction on metal oxides, carbonaceous compounds and conducting polymers is also given. Moreover, this chapter discusses nanocomposites and their importance and classifications. A detailed description of the important synthesis techniques used in the area of nanomaterials and nanocomposites is also presented. Furthermore, this chapter also deals with the various electrochemical analysis methods used in the field of supercapacitors and discusses their applicability in the area of ESDs. Finally, the organisation of thesis along with the major objectives of the study is described in detail.

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1.1. BACKGROUND

Nowadays, the term ‘energy shortage’ has raised heightened concern among the scientific society due to the uncontrollable deterioration of conventionally used energy sources and unruly expansion of the world population. To balance between the resource and demand ratio in terms of energy, a perfect energy storage system must be put forward. Thus, in the sense of keeping up with the everlasting demand for energy in various day to day scenarios like electronics, grid stabilization, utility vehicles and the automobile industry, scientists took the topic of inventing a powerful, efficient and environmentally viable energy storage system as a hot research material. A perfect energy storage device (ESD) should carry features like remarkable power density and energy density, with a satisfactory life time. Typically used energy storage devices such as batteries, still face the problem of having insufficient power density and short life time due to unwanted heat loss and electrode decay during charging-discharging cycles. On the other hand, the conventional capacitors as an ESD candidate carry sufficient power density but suffer from poor specific energy. Accordingly, the scientific community made a greater focus on the area of supercapacitors (SCs) which can bridge the gap of having an ideal ESD with both high-power density and energy density values (Fig.1.1). Although, supercapacitors are one of the frontier research topics of today, it has a live back history. In the early 1950’s, General electric company engineering workers has started to develop a capacitor with carbon based electrodes and ended up with an electrolytic capacitor fabrication using activated carbon electrode with high specific surface area by Becker in 1957, which he filled for patent [1]. Later, in 1966 Standard Oil of Ohio (SOHIO) Company built a 6V supercapacitor with activated carbon electrode and aqueous sulphuric acid as the electrolyte solution [2]. The first supercapacitor was developed for the military applications in 1982 by Pinnacle Research Institute (PRI), termed as PRI ultracapitors. On behalf of combining both electrolytic and electrochemical features of capacitors, an Electrolytic-Hybrid Electrochemical capacitor was fabricated in 1994 by Evans [1]. However, it is to be noted that before 1990s not much efforts were taken with the aim to reduce the production costs of supercapacitors. B. E. Conway has first talked about pseudocapacitive storage mechanism in supercapacitor field with ruthenium oxide (RuO_2) as electrode material, by 1999. Apart from the carbon based electrodes, the

works were latter started reporting and highlighting the pseudocapacitive nature of metal oxide electrodes, specifically ruthenium oxide (RuO_2), having a specific capacitance of around 2000 F/g [3]. The concept of efficient usage of supercapacitors in hybrid electric vehicles made a breakthrough in their developments with a primary focus on fabricating pseudocapacitive materials having high energy densities compared with conventional double-layer capacitors. On account of multiple oxidation states and quick charging-discharging abilities, transitional metal-based oxides and hydroxides, such as MnO_2 , RuO_2 , NiO , Co_3O_4 , CuO etc., gained elevated priority in the field of SCs [4]. This revitalized scholarly pursuit has enabled advancements in developing high performance supercapacitors with commercial applicability.

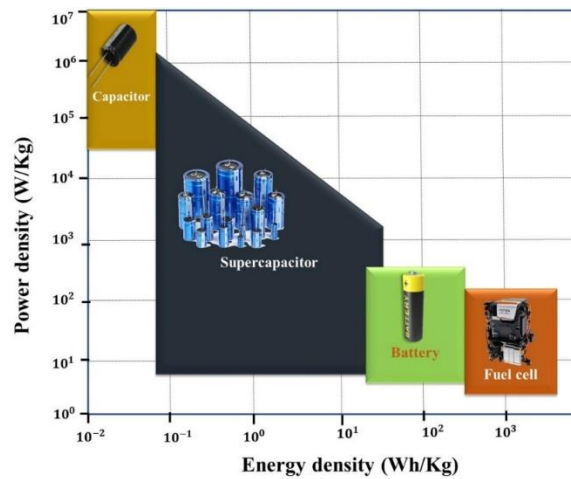


Fig. 1.1. Ragone plot of popular energy storage devices.

1.2. SUPERCAPACITORS

Capacitors known as a conventional ESD with the purpose of storing electrical charges using two parallel plate electrodes separated by a dielectric medium, has been a passive electronic component of electronic circuits. Fig.1.2 shows the schematic structure of an ideal capacitor. The capacitance (C) of this capacitor can be evaluated using the equation;

$$C = \frac{\epsilon_0 A}{d} \quad (1.1)$$

Where ϵ_0 is the dielectric constant, A denotes the surface area of electrodes separated by a distance 'd'. From the above equation, it is clearly observable that the

capacitance value is independent of charge stored ‘q’. Conventional capacitors can be divided into two categories depending on the medium used between electrodes; one is the dielectric capacitors, where the medium is a dielectric material and the second one is the electrolytic capacitor with a solid/liquid ionic conductor between electrodes called as electrolyte. The energy stored in the capacitor can be calculated using the equation;

$$E = \frac{q^2}{2C} \quad (1.2)$$

Therefore, the energy stored in the capacitor is directly linked to the amount of charge stored in that system. The charge stored in conventional capacitors will typically be in the range of some millifarads (in the case of electrolytic capacitors) to the microfarad range (in the case of dielectric capacitors), indicating the poor energy density of the overall system. The power density of the system is evaluated by analysing the total energy stored for a given discharge time. The long discharge time of capacitors make them one of the efficient high power devices [5], [6].

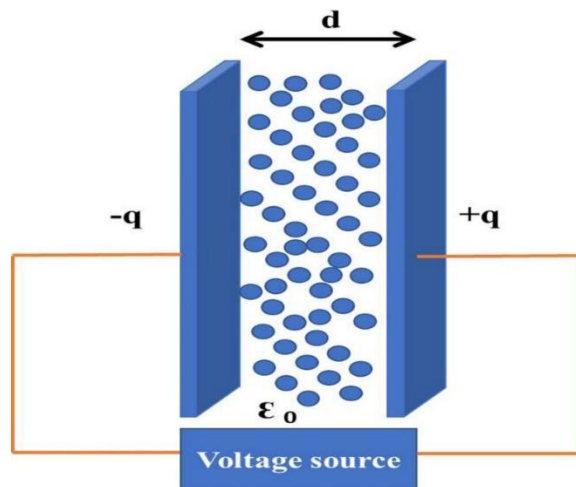


Fig. 1.2. Schematic diagram of a conventional capacitor.

The electrochemical capacitors, commonly known as supercapacitors, are designed to cope with the demerits of both capacitors and batteries, having a remarkable power densities, a rapid charging-discharging process, good durability and higher specific energy value compared with capacitors [7]. The working principle of a supercapacitor is inseparable from the essence of conventional capacitors; usually end up with a capacitance value in the range of Farads (F) leading to the addition of term “super” with their name [8].

A supercapacitor consists of two solid electrodes and an ionic liquid electrolyte solution bath between them. The two electrodes were physically separated using a thin and porous separator material in order to avoid device shortage that may happen due to direct contact, which doesn't hinder the movement of ions. The metallic current collectors used were intended to provide a conductive backbone to the electrodes. The basic design of a supercapacitor is shown in Fig. 1.3.

- **Electrodes:** Electrodes are the most important part of a supercapacitor, which directly influences its overall electrochemical performance, and are generally thin coatings that must be electrically attached to conductive current collectors. The electrode material must be a good ionic conductor and highly resistant to corrosion with long term thermal and chemical stability and superior specific surface area [9].
- **Electrolyte:** Electrolytes are composed of a solvent and dissolved to make the electrodes electrically connected. The conductivity of the electrolyte medium increases with the availability of ions in the solvent. The electrolyte solution directly decides the operational voltage of the cell and the cell power is inversely proportional to ionic resistivity caused by the electrolyte medium in the electrode-electrolyte interface. Depending upon the solvent medium used in electrolytes, three types of electrolyte categories are present: aqueous, organic and ionic liquid electrolytes [10]. The aqueous electrolytes often suffer obstacles related to thermodynamic instability of water beyond the voltage window $\sim 1.23\text{V}$. This water-splitting limit makes the device compromise with its efficiency, energy density and stability. Whereas, the non-aqueous electrolytes like ionic liquids offers wide potential window with significant energy densities [11].
- **Separator:** Separators are components used to physically separate electrodes, but are permeable to electrolyte ions. The separator materials are mostly quite thin and porous nature with good mechanical stability. Separators are made soaked in the electrolyte solution with a high transfer capacity of ionic species. Normally, woven ceramic and glassy fibres and nonwoven polymer films are employed as separators [12]. Poorly designed separators can make negative impacts on the

performance of supercapacitors by cause of their capacity to produce additional resistance in the cell [1].

- **Current collector:** A highly conductive metal foil or spray-painted thin films can serve as current collectors with the function to release/take electrons from/to the external load. Current collectors link the electrode material to the terminals of the capacitor. Commonly used current collector materials are copper, aluminium, nickel, carbon fibre, stainless steel, platinum etc. The selection of current collectors depends on the electrode/electrode material used in the cell. For acidic electrolytes, noncorrosive foils of gold, stainless steel, indium doped titanium oxide and others were commonly used, whereas for alkaline electrolytes, current collector materials like carbon fibre, carbon cloth, nickel foam, etc. were employed. Typically, aluminium based current collectors were chosen for non-aqueous electrolyte medium [13].

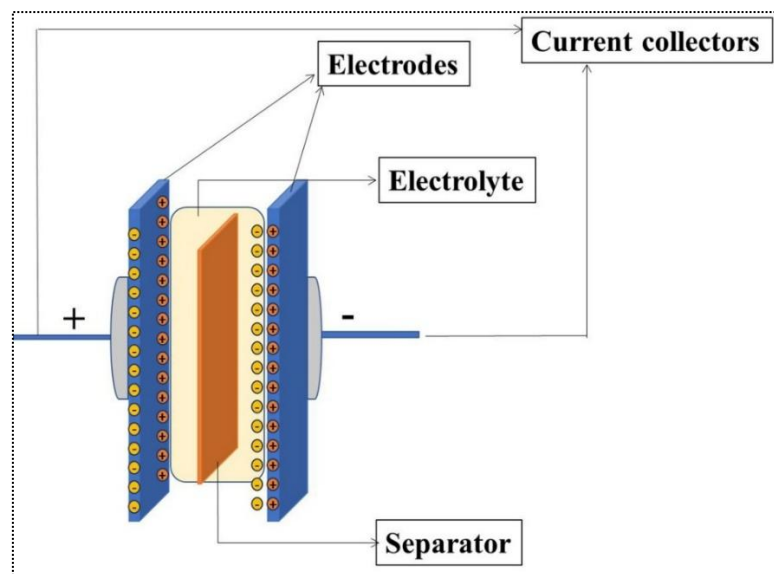


Fig. 1.3. Diagrammatic illustration of supercapacitors.

1.3. CHARGE STORAGE MECHANISMS IN SUPERCAPACITORS

The basic steps that work behind the charge storage mechanism in a supercapacitor can be listed as follows and portrayed in Fig. 1.4;

- ❖ Electrode polarization by an externally applied voltage supply
- ❖ Ionic diffusion in electrolyte solution through the separator
- ❖ Attraction of electrolyte ions in the direction of oppositely polarised electrodes.
- ❖ In the electrode-electrolyte interface, adsorption as well as intercalation of electrolyte ions happen.
- ❖ Ultimately, a double layer arrangement has been formed by the uniform accumulation of equal and opposite charges near the electrode surface, which is attributable to the electrostatic process and electrochemical faradic redox reactions.
- ❖ Penetration of ionic species through the double layer architecture gives rise to pseudocapacitance
- ❖ This electron flow is a representation of charging mode of the capacitor and continues till the potential difference between electrodes matches with the applied voltage.
- ❖ During discharging, electrons flow back to the electron vacancies.

The stability and efficacy of this electrochemical performance in a supercapacitor is greatly determined by its capacity to deliver constant charging/discharging rates over long period of time. The selection of an efficient electrode material with ideal electrode characteristics like good electrical conductivity and surface area as well as satisfactory charge storage mechanisms, is one of the most important deciding factors that impact the efficiency of a supercapacitor device [14].

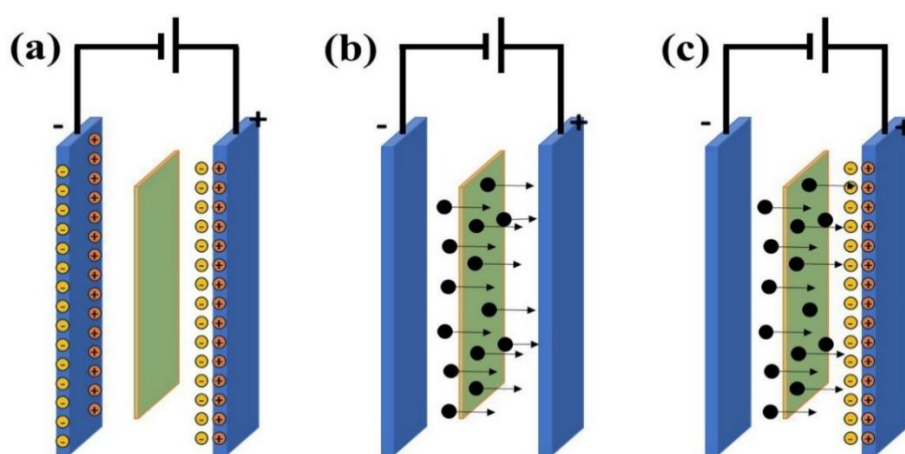


Fig. 1.4. Charge storage mechanisms in supercapacitors through (a) electrostatic charge separation (b) faradic redox reactions (c) electrostatic and electrochemical process.

1.4. TYPES OF SUPERCAPACITORS

Supercapacitors have been mainly divided into three classes namely, electric double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors on the basis of how energy is stored (Fig. 1.5) [15]. EDLCs generally store charges electrostatically or through any non-faradic manner without undergoing any kind of charge transfer at the electrode/electrolyte interface [16]. Activated carbon, carbon nanotubes, graphene, carbon aerogels, carbon foam, and carbon derived carbon are the main classes of EDLC electrode material. When it comes to pseudocapacitors, the charge storage mechanism involves faradic redox reactions and there exists some electrostatic transfer of charge loads between the electrode surface and electrolytes [17]. Metal oxides and conducting polymers are important electrode materials that show pseudocapacitive behaviour. A hybrid supercapacitor is an amalgam of both battery-type electrode having high specific energy and a capacitor-like electrode, having high specific power in one cell [18]. Asymmetric, composite and battery types are three important classes come under hybrid supercapacitors.

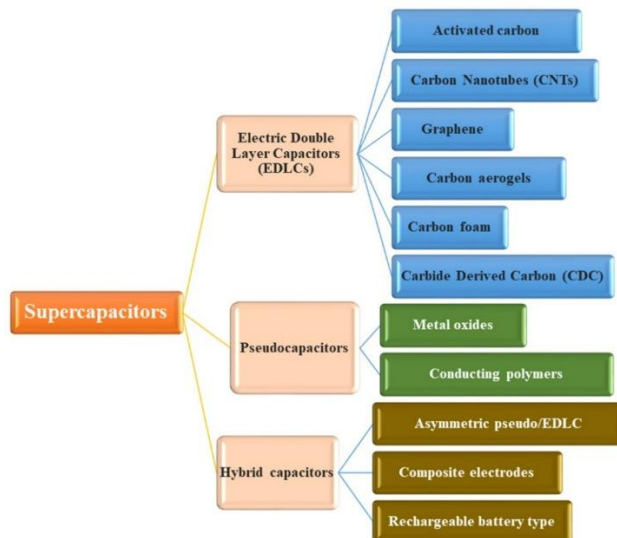


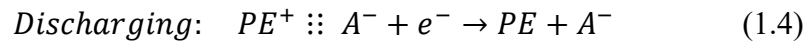
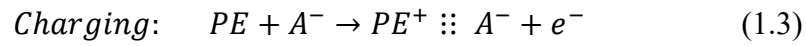
Fig. 1.5. Classification of supercapacitors.

1.4.1. Electric Double-Layer Capacitors (EDLCs)

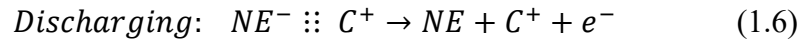
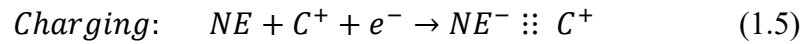
EDLCs are the simplest and most commonly used supercapacitor category using porous carbon-based materials as electrodes, which involves the storage of charges electrostatically without undergoing any kind of faradic processes. Under the externally

applied constant voltage, positive and negative charges get accumulated on the electrode surface. Then, the positive and negative ions get attracted to the oppositely polarised electrodes and make diffusion through the separator and get trapped by the pores of the electrode material, which eventually results in the formation of a monolayer at the electrode-electrolyte interface. The expanded formations of this surface monolayer led to the formation of a secondary diffusion layer in the electrolyte medium. Thus, the combination of surface and diffusion layer causes an electric double layer arrangement in the cell, which can store electrostatic charges. The concept of electric double layer arrangement in the electrode-electrolyte interface was first introduced by Helmholtz, a German scientist, so that the double layer configuration is also called as Helmholtz double-layer. The electrostatic charge storage mechanism in EDLCs is presented in Fig. 1.6. Since there are no transfer of charge loads between the electrode and electrolyte, the charge storage process is highly reversible and has a long-life span. The adsorption and desorption of electrolyte ions in the electrode-electrolyte interface make the foundation for the electrostatic charge storage process of EDLCs, which can be summarised as follows;

At the $+_{ve}$ electrode surface:



At the $-_{ve}$ electrode surface:



where PE and NE represent positive electrode and negative electrode, respectively. Whereas A^- and C^+ denote anion and cation present in the electrolyte. Also, “::” symbolically represents the electrolyte-electrode interface.

The double layer capacitance C_{DL} is estimated using the equation;

$$C_{DL} = \frac{\Delta Q}{\Delta V} \quad (1.7)$$

where ΔQ is the amount of charge stored in EDLC under the potential difference ΔV . EDLCs have quick charge-discharge cycles with good stability, resulting in good power density and cycle life. The performance of EDLCs depend on the porous morphology and surface area of electrode material, electrolyte nature and double layer thickness.

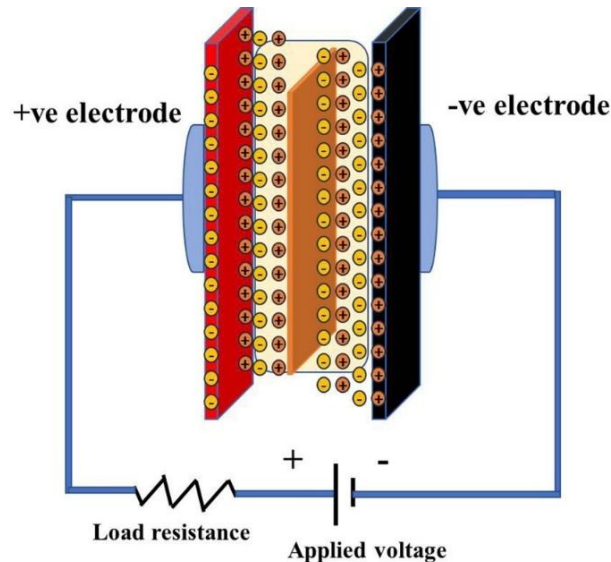


Fig. 1.6. The schematic representation of working principle of EDLCs.

1.4.1.1. Merits and demerits of EDLCs

EDLCs have both merits and demerits which made this class of supercapacitors as a prominent hot research material. Some of the advantages and disadvantages of EDLCs are documented as follows;

- EDLCs exhibits high power density but inferior energy storage capacity.
- EDLCs reports relatively weaker specific capacitance.
- Necessity of porous electrode materials having ideal electrode characteristics with reduced internal resistance value in order to achieve more energy density.
- The charge accumulated on the electrode surface or in the vicinity of electrode surface is the only deciding factor of device performance, not which exhibits in bulk of electrode material.
- The necessity of having an advanced electronic control and easy switching mechanism for the proper functioning of EDLs results in additional energy loss.

1.4.2. Pseudocapacitors

Pseudocapacitors are considered as an alternative form of EDLCs, where the charge storage mechanism involves rapid and reversible faradic redox reactions occurring at the electrode-electrolyte interface, illustrated in Fig. 1.7. Due to the faradic charge storage, pseudocapacitors can store more charge and deliver higher energy density compared to EDLCs.

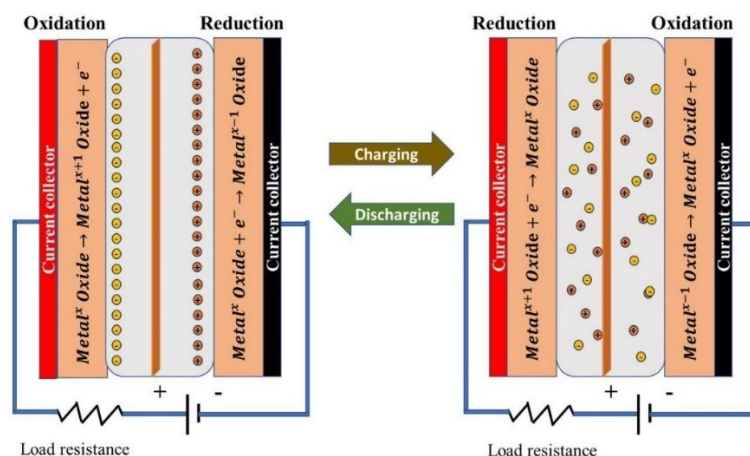


Fig. 1.7. Schematic representation of basic charge storage mechanism of pseudocapacitors.

Broadly, Conway proposed three types of charge storage mechanisms usually occur in pseudocapacitors namely (Fig. 1.8);

- Underpotential deposition: The process in which metal ions get adsorbed on the surface of another metal resulting in the formation of a monolayer due to a strong interaction between them, which is significantly exceeds their oxidation-reduction potential, i.e., deposition of metal ions under deficient potential. Example: deposition of lead ions on the surface of Au electrodes.
- Redox pseudocapacitance: The process of charge storage involving the electrochemical adsorption of electrolyte ions on the electrode surface or on the vicinity of electrode surface. This mechanism of charge storage associates with transfer of charge loads. Example: RuO_2 , MnO_2 etc.
- Intercalation pseudocapacitance: The charge storage mechanism is based on the intercalation/de-intercalation of electrolyte ions into the tunnels or interlayers of active material. This mechanism conveyed the charge transfer via a faradic

process without undergoing any crystallographic phase changes. Examples: TiO_2 , Nb_2O_5 etc.

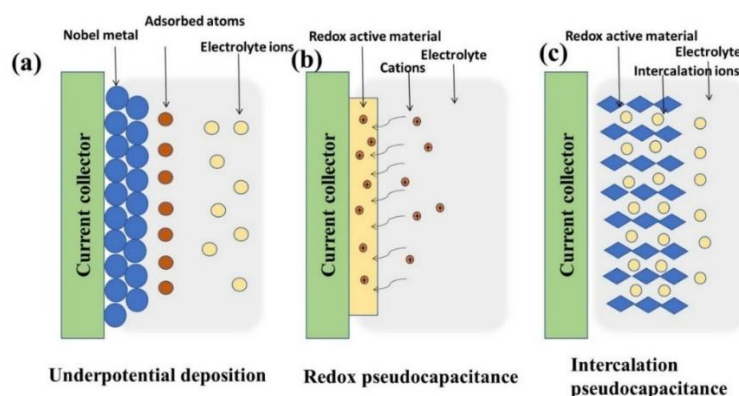


Fig. 1.8. Schematic representation of different types of pseudocapacitors (a) underpotential deposition (b) redox pseudocapacitance (c) intercalation pseudocapacitance.

1.4.2.1. Merits and demerits of pseudocapacitors

Pseudocapacitors are one of the most intensively studied energy storage devices, which have the ability to produce high specific capacitance compared to EDLCs, but have limitations too. Some of them are listed below;

- The performance of pseudocapacitors is limited by the factors like poor electrical conductivity and low accessible surface area.
- In the sense of fabricating metal oxide/hydroxide based pseudocapacitors there is the use of a significant amount of precursor components as well as chemical treatments, which ultimately drive up the cost of large-scale production.
- Need greater control over the synthesis conditions since it greatly influence the particle size and dimensions, and chances of forming agglomerations are relatively high, which eventually results in weak electrical conductivity.

1.4.3. Hybrid supercapacitors

Recently, hybrid supercapacitors have gained much attention among the research community due to their enhanced specific energy without compromising

power density. The commendable specific capacitance value of the hybrid supercapacitor is a result of the electric double layer capacitance produced by the porous carbon-based electrode and pseudocapacitance produced by the metal oxides/hydroxides or conducting polymer electrodes in the same cell. This type of supercapacitor takes the advantage of both EDLCs and pseudocapacitors, involving faradic and non-faradic charge storage mechanisms. The charge storage mechanism in hybrid supercapacitors is represented in Fig. 1.4 (c).

Hybrid supercapacitors have been classified into three main configurations on the basis of electrode arrangement, namely;

- ❖ Asymmetric hybrids: In this configuration, the cell is designed with two dissimilar electrodes, i.e., an EDLC electrode material is used in combination with a pseudocapacitive electrode material.
- ❖ Composite hybrids: In this type of hybrid supercapacitors, electrode material is composed of carbon-based material with the metal oxides and/or conducting polymers. The higher surface area of carbon material helps to enrich the effective contact between pseudocapacitive materials with electrolyte solution.
- ❖ Battery-type hybrids: This class of hybrid supercapacitor involves the use of two different kinds of electrodes; one is supercapacitor type, and the other is battery type. Here, the factors like power density and rate capacity are evaluated on the basis of battery type electrode and energy storage capacity which are determined on the basis of supercapacitor type electrode.

Enhanced specific capacitance and wider voltage range can be achieved using highly stable long-life carbon-based negative electrodes with superior capacitive faradic positive electrodes in aqueous electrolytes. However, the poor rate capacity of a faradic anode material hinders the cell from becoming a high-power hybrid supercapacitor. Thus, in order to overcome this limitation, an efficient mesoporous transitional metal oxide (TMO) or an effective combination of binary TMOs can be used as the faradic electrode material. These forms of electrode material can offer multiple oxidation states and can enrich the redox activities, thereby improving the overall electrochemical performance of the hybrid system.

1.5. ADVANTAGES AND APPLICATIONS OF SUPERCAPACITORS

Supercapacitors are devices which are capable of serve as an intermediate energy storage device between conventional capacitors and batteries. They often offer a satisfactory level of energy storage capacity compared to capacitors and high-power density compared to batteries. Although, the power density of supercapacitors is much higher than that of batteries, they deliver only lower energy densities than batteries, which make them suitable for only high-power applications where energy storage is not very important.

The rapid charging and discharging process is another important aspect of supercapacitor, which makes the charging process of supercapacitor devices easier and quicker. Additionally, the longer cycle life and stability of supercapacitors over ten thousand/fifty thousand repeated cycles make them an inevitable component of energy storage devices like consumer electronics, military, medicinal fields and hybrid automobiles. Moreover, supercapacitors also offer greater safety and thermal stability compared to batteries, without undergoing any kind of deterioration due to corrosion or energy loss.

1.6. ELECTRODE MATERIALS

The electrochemical performance of supercapacitors has been significantly influenced by the proper selection of electrode material and electrolytes. In this regard, there exist enormous research works with the aim to improve the electrochemical activity of electrode material, thereby producing a highly efficient supercapacitor device having excellent power and energy densities, cycle performances and superior lifespan of service. The ideal features of an electrode material are high surface area with porous architecture, good chemical and thermal stability, good ionic and electrical conductivity, low cost and environmental benignity and corrosion resistance. Moreover, the material purity of the electrode is another important factor which decides the performance of the capacitor. The presence of unwanted substances in the electrode composition can results in unnecessary leakage current in the device, which negatively influences its cycle performance and life time through spontaneous discharging.

Additionally, the electrode material's ability to facilitate fast faradic reaction kinetics positively enriches the specific capacitance of the device.

1.6.1. Carbon materials

From an industrialisation perspective, carbon-based electrode materials are the most appropriate ones to be used in energy storage devices. They exhibit many of the desirable electrode properties, that make them outperform over other commonly used materials. Activated carbon, carbon aerogels, carbon nanotubes and graphene, are extensively used electrodes in EDLCs.

Activated carbons (ACs) are the top-priority EDLC material having features like economically and environmentally viable, ease of processing, commendable electrical conductivity and stability. They can be easily synthesised using a carbonization step followed by an activation stage. Another promising EDLC electrode material is carbon aerogels, which are chemically inert and strong electrical conductivity. Graphene based electrode material gained more popularity than other carbon-based electrodes having a theoretical capacitance value of about 550 F/g as well as a theoretical surface area of about 2630 m²/g. The superior surface area and packing density made their surface easily available for electrolyte species. Carbon nanotubes (CNTs) are the widely explored EDLC electrode material having sufficient intertwined mesoporous networks with excellent chemical, thermal and mechanical stability. The mesoporous morphology of CNTs makes their surface easily accessible for electrolyte ions and promotes rapid ionic diffusion, results in lower internal resistance and higher power density.

Generally, carbon-based electrode materials come under the category of materials that are low cost, environmentally benign with abundant reserves. Additionally, the capacitance value of these materials is directly correlated with the total accessible area in the electrode surface rather than the bulk, since the charge storage occurs at the electrode-electrolyte interface through electric double layer formation. But some recent literature has reported that the porosity of the electrode surface is not the only factor which decides the electrochemical performance, as not all the micropores in the electrode surface are actively used by the electrolyte ions [5]. The important factors like power density and energy density have a direct correlation with

the pore size distribution in the electrode material. Therefore, fabricating a carbon-based electrode material having an exceptional surface area with optimal pore size distribution is the pivotal concern for the research community. Moreover, carbon-based electrode in the supercapacitor field offers high power density with commendable cycle, but suffer from low capacitance and energy density values.

1.6.1.1. Carbon nanotubes

Carbon nanotubes are the popular electrode materials used in EDLCs due to their porous morphology with mechanical stability, non-corrosive nature, high thermal stability and capability of functionalization. These materials exhibited a theoretical specific surface area value of about 120-400 m²/g. The intertwined porous architecture with sufficient accessible sites in the CNT surface causes the ionic diffusion to be easier and enhances the double layer formation for efficient electrochemical performances.

Multi-walled carbon nanotubes (MWCNTs) are the carbon-based material made up of sp² hybridised carbon having an elongated cylindrical shape with an average diameter in the range of 3-30 nm. The end part of the tubes is capped by fullerene like nanospheres. Their length may vary with synthesis conditions, indicating that the aspect ratio can vary between ten to ten million [19]. Their structures are like hollow rolled graphite tubes with hexagonal carbon rings as wall builders. Depending upon the arrangements, there exist two types of CNTs namely; single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). As the name indicates, SWCNT consists of only one layer of graphene cylinder whereas MWCNT carries multiple layers of graphene cylinders. Moreover, SWCNTs have a single tube with average diameter around 0.4 nm to 2 nm and MWCNTs have multiple concentric tubes which 0.34 nm apart and average diameter of 2-100 nm. CNTs exhibit more interesting electrical, optical, and structural features than other carbonaceous materials making them appropriate for various applications in biomedical, electrochemical, sensing and opto-electrical fields. CNTs in the field of sensing were more prominent due to their properties like large surface area, sensitivity and fast response time. CNTs are used as electrochemical transducers as well. The unique and ideal electrode features like highly reactive nature, flexible and easily modifiable structures and mechanical stability make

them an efficient electrode material in electrochemical applications. Moreover, studies show that MWCNTs have energy density per mass twice that of SWCNTs [20].

1.6.2. Metal oxides

Metal oxides (MOs) made of transition metal families are very attractive electrode materials used in pseudocapacitors, having the capacity to undergo fast and reversible faradaic redox reactions. They deliver superior capacitance value compared to carbon-based compounds and excellent cycle stability compared to conducting polymers. Consequently, choosing the best faradaic transition metal oxide (TMO) electrode material with multiple oxidation states can enable fast and reversible oxidation and reduction during charging-discharging cycles. RuO_2 is the first TMO used in supercapacitors, which has a theoretical capacitance in the range of 1300-2200 F/g. Unfortunately, the toxic nature and exorbitant cost as a result of rare availability declined considering them as a market-winning electrode material. In the sense of overcoming these dilemmas, the research community has shifted the focus onto another efficient electrode material called MnO_2 because of its low cost and environmentally safe nature. Moreover, MnO_2 carries a theoretical capacitance value of around 1370 F/g, but the practical value is still far below of this. There exist other TMOs like CuO , NiO , Co_3O_4 , Fe_2O_3 etc., which are capable of producing fast and reversible faradaic redox reactions and can be potential supercapacitive electrode materials. Along with transitional metal oxides, chalcogenides, hydroxides, nitrides and their derivative forms are also popular for pseudocapactive behaviour. The structural and morphological properties like dimension, porous nature, and electrode-electrolyte interface chemistry of electrode materials have a strong influence on their electrochemical performances. Ultimately, it is very important to produce an efficient and diligent electrode material for supercapacitor applications.

1.6.2.1. Copper oxide

Among the different TMOs explored for the supercapacitor applications, copper oxide-based electrode material has gained much attention in recent days, due to its exceptional structural, opto-electric and electrochemical properties. Additionally, cost-effectiveness, environmental benignity, ease of synthesis, and ability to produce rapid faradaic redox reactions make them a promising candidate over other popular TMOs.

Generally, copper oxide has three forms; namely the tenorite phase (CuO), cuprite phase (Cu₂O) and a metastable paramelaconite phase (Cu₄O₃) having monoclinic, cubic and tetragonal symmetries, respectively. CuO is a black p-type semiconductor material having plentiful exceptional features like narrow band gap (~1.2 eV), high specific surface area, electrochemical activity and chemical stability.

1.6.2.1.1. Structural properties of CuO

CuO has a monoclinic structure with C_{2h}^{62} symmetry and it carries four formula units per one unit cell. Since the coordination number of copper is four, one copper atom is bonded with four neighbour atoms of oxygen in a square planar arrangement along (110) plane (Fig. 1.9). The bond length of Cu-O bonds along (110) plane is 1.88Å and 1.96Å. In the perpendicular plane, the two Cu-O bonds form an octahedral coordination with much greater bond lengths. In the case of oxygen atoms, it has coordinated with four copper atoms, and shows a distorted tetrahedron. Moreover, oxidation state of oxygen in CuO crystal is O^{2-} even though it contains both covalent and ionic bonds [21]. The basic structural parameters of CuO are listed in the table 1.1.

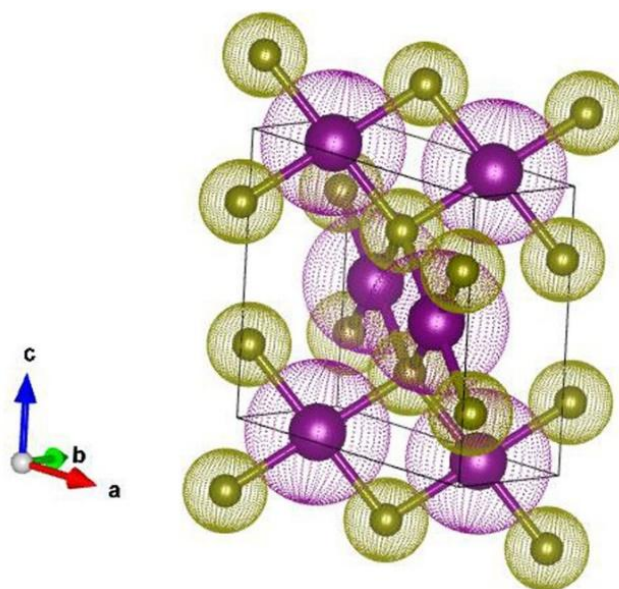


Fig. 1.9. Schematic representation of crystal structure of CuO.

Table 1.1. Basic structural properties of CuO.

Basic Features	Values
Symmetry	Monoclinic
Space group	C_{2h}^6
Lattice parameters	$a=4.683 \text{ \AA}$, $b=3.422 \text{ \AA}$, $c=5.128 \text{ \AA}$, $\alpha=\gamma=90^\circ$, $\beta=99.54^\circ$
Cell volume	$V=81.08 \text{ \AA}^3$
Unit cell content	4 CuO
Molecular weight	79.57
Density	6.515 g/cm^3
Cu-O bond length	$1.96 \text{ \AA}$
O-O bond length	$2.62 \text{ \AA}$
Cu-Cu bond length	$2.90 \text{ \AA}$
Melting point	1201°C

The phonon properties of monoclinic CuO structure were reported in previous literatures, showing the three acoustic and nine optical phonon bands of CuO. The C_{2h}^6 space group of CuO contains two molecules per primitive cell, resulting in Raman active modes as $\Gamma_{\text{RA}} = 4A_u + 5B_u + A_g + 2B_g$. This zone centred Raman active modes are contributed by three Raman active modes ($A_g + 2B_g$), six infrared active modes ($3A_u + 3B_u$) and three acoustic modes ($A_u + 2B_u$) [22].

1.6.2.1.2. Energy band structure of CuO

CuO is a p-type semiconducting material with a narrow indirect band gap. This electronic energy band gap denotes to the energy difference between the valence band maximum and conduction band minimum, both derived from the Cu 3d orbitals. There is an enormous number of theoretical investigations that have been done in order to investigate the electronic band structure of CuO [23], [24]. In spite of the complexities brought out by 3d shell of CuO, there is a conduction band peak at 1.8 eV along with other peaks at 6.8 eV and 10.6 eV, which are aroused due to the fully filled sp orbitals of copper and oxygen [24]. F.P.Koffyberg *et al.* conducted a study on the conduction and valence band edges of CuO and reported that the valence band of CuO resides $\sim 5.42 \text{ eV}$ below the vacuum level contributing to an indirect band gap of 1.35 eV [25].

The theoretical band gap of CuO varies between 0.91 eV-2.74 eV depending upon the method of analysis HSE, OLCAO, LDA+U, SIC LSD, and DFT [26]. The experimental values of indirect band gap ranges between 1.35 eV-1.7 eV for bulk CuO and ranges up to 2.03 eV for CuO thin films. Naveen Kumar *et al.* reported the synthesis of CuO and Cu₂O nanoparticles using sol-gel method and investigated their applicability for solar cell and energy storage devices. They reported a band gap value of 2.18 eV for CuO nanostructures [27]. V. Dhanasekaran *et al.* conducted a study on the optical, electrical and microstructural features of monoclinic CuO nanostructures having ~10 nm size and reported a band gap value of 1.2 eV [28]. The impact of doping on the optical features of CuO was investigated in a few studies and found to have an increase in band gap values. The optical band gap of Ni, Zn and Fe- doped CuO nanostructures was found to be 2.26 eV, 2.12 eV and 2.15 eV [29]. Yunus Akaltun *et al.* studied the influence of film thickness on the optical attributes of CuO and reported a decrease in value of the band gap between 2.03 eV-1.79 eV with the increasing film thickness [30].

1.6.2.1.3. Electrical properties of CuO

The electrical properties of CuO can be described in terms of a few parameters like electron affinity, dielectric constant and carrier mobility. Mark. L. Polak *et al.* investigated the value of electron affinity of CuO using photoelectron spectrum and recorded a value of 1.777 eV [31]. The value of static dielectric constant for CuO thin film has been reported in the range of 12.26 – 13. It is found that this value of dielectric constant varies with film thickness [30]. The carrier mobility of CuO found to be very low with heavy hole effective mass, similar to NiO. Koffyberg *et al.* reported a hole mobility of 0.1 cm²/Vs and introduced the hopping method of conduction in CuO [25].

1.6.2.1.4. Electrochemical properties of CuO

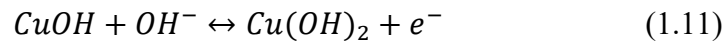
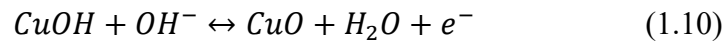
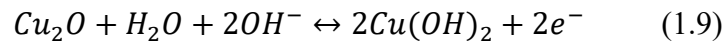
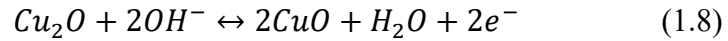
The search for an affordable and environmentally viable electrode material has made the CuO-based supercapacitor area, a frontier of research among the other TMOs. CuO shows rapid and reversible redox activities, which contribute to satisfactory specific capacitance values. The advantage of having various synthesis approaches available to prepare CuO in different morphologies such as nanorods, nanotubes, nanoflowers, nanoflakes, etc., which can improve its capacitance by enriching the

electro-active sites and electron transfer through enhanced surface area. CuO is capable of producing high pseudocapacitive behaviour along with very low internal resistance.

Moreover, some of the unique properties of CuO in electrochemical applications are sorted below;

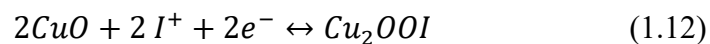
- Tunable electronic configuration of CuO with availability and reversibility of oxidation states.
- Easy to produce different morphologies and different dimensions, which are one of the deciding factors of charge storage mechanism in CuO.
- High thermal and chemical stability make less structural deteriorations in CuO electrodes during repeated charging-discharging process.
- Generally, all TMOs specifically CuO are chemically more stable than many of the popular carbonaceous electrode compounds and is easily associated with other TMOs or polymers or carbon-based compounds to produce more efficient nanocomposite electrode material with enhanced synergistic effects.

The redox activities of CuO in alkaline electrolytes like NaOH/KOH can be as follows [32];

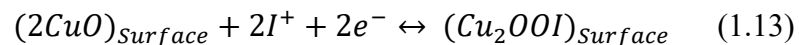


In neutral aqueous electrolytes like Na₂SO₄, there may be two possible charge storage mechanisms occurring in the system [33]:

(1) Intercalation and de-intercalation of cations H⁺ or Na⁺ during redox reactions,



(2) Adsorption of ions into the surface of active material.



Where I can be either H^+ or Na^+ ions.

There are numerous works conducted on the supercapacitive performance of CuO, but capacitance achieved is still only <32% of its theoretical value. Regardless of these fundamental electrochemical properties, CuO suffers very low electronic and ionic conductivity, structural collapse during charge-discharge cycles, minimal energy density and poor cyclic performances. These limitations can be overcome by associating CuO with other guaranteed TMO electrode materials like NiO, Co_3O_4 , $ZnMn_2O_4$, etc., as well as conducting polymers like PANI or carbonaceous compounds like CNTs.

1.6.2.2. Nickel oxide

Ni-based materials, especially NiO, found to have better opportunities in the electrochemical area owing to their specialities like metallic conductivity, ease of synthesis, and high electrochemical activity. In NiO crystal, the elementary distributions of nickel and oxygen atoms are in a stoichiometric ratio of 1:1. The cubic NiO symmetry is formed by the face centred cubic orientation of Ni^{2+} ions with O^{2-} ion in the interstitial sites. The ionic bond between nickel and oxygen through the electrostatic force resulted from the losing and gaining of two electrons by nickel and oxygen, respectively. Basically, NiO is an antiferromagnetic substance and its properties are tuned according to the nickel and oxygen vacancies in the crystal structure. This simple semiconductor material have applicability in areas other than energy storage like sensors, catalysis, batteries and electrochromic devices [34].

NiO is an efficient pseudocapacitor electrode material with a theoretical capacitance of 2573 F/g. The fast and reversible redox activities of NiO led the research community to explore more on the supercapacitor applications of NiO. Depending upon the synthesis method and reaction parameters, different kinds of nanostructures of NiO can be achieved [35], [36], [37], [38]. These nanostructures enhance the surface area and redox active sites of NiO, eventually enhancing the ionic diffusion rate and capacitance. The controlled synthesis of NiO nanostructures with the desirable electrode properties can make it a promising electrode material. However, the low ionic conductivity and declining cycle stability made the pristine NiO based electrode

emerging and less-productive. These shortcomings set the stage for composite electrode materials with the aim to produce high-performance pseudocapacitors.

1.6.2.3. Cobalt oxide

Cobalt oxide (Co_3O_4) is a p-type semiconducting TMO with a direct band gap in the range of 1.48 eV-2.19 eV and a theoretical capacitance of about 890 mAh/g. This low-cost environmental friendly material exhibits other unique properties like high corrosion stability, high surface to volume ratio, and fast and reversible redox features [39]. Co_3O_4 is antiferromagnetic in nature with satisfactory electrical activity. The hollow spinel crystal structure of Co_3O_4 is constituted by the Co^{3+} and Co^{2+} ions located at octahedral 16(d) and tetrahedral 8(a) sites of the lattice, respectively along with the cubic close pack orientation of 32 oxide ions in 32(e) sites. This spinel structure followed by the Co_3O_4 compound having a general compositional formula of AB_2O_4 , in which A represents the +2 charged ions and B represents the +3 charged ions.

Different dimensions and microstructures of Co_3O_4 can be achieved by governing the synthesis strategies. Depending upon the unique morphology attained by the Co_3O_4 nanostructures, the efficacy in electrochemical features can be determined. The redox activities of Co^{2+} and Co^{3+} ions are instrumental in the electrochemical performance of cobalt oxide electrodes. Additionally, the low charge transfer resistance and satisfactory cycle stability make the Co_3O_4 compound a guaranteed electrode material [40]. Apart from the supercapacitor applications, Co_3O_4 is a promising candidate for chemical sensors, photocatalysis, bio-medical field, solar cells and batteries [41], [42], [43].

1.6.2.4. Zinc manganese oxide

Alike cobalt oxide, zinc manganese oxide (ZnMn_2O_4) also has normal spinel symmetry, exhibited in the $\text{I4}_1/\text{amd}$ space group. This mixed metal oxide compound carries a narrow band gap of 1.86 eV. The spinel structure of ZnMn_2O_4 is constituted by the Zn^{2+} and Mn^{3+} ions occupying in the tetragonal and octahedral sites, respectively. The elemental composition of this TMO can be represented by the general formula $(\text{Zn}_{1-x}\text{Mn}_x)(\text{Zn}_x\text{Mn}_{2-x})\text{O}_4$, where x is a parameter that determines the degree of inversion of the compound depending upon the particle size distribution, morphology and

synthesis route and ranges from 0 to 1. In normal spinel structure, Zn orients in the A sites and Mn orients in the B sites of the general spinel AB_2O_4 formula, whereas in the inverse spinel structures, half of the Mn locates in A site and all Zn locates in the B sites. In this $ZnMn_2O_4$ compound, zinc exhibits in single oxidation state, Zn^{2+} and the manganese exhibits in multiple oxidations states like Mn^{2+} and Mn^{3+} . The oxygen element in the compound induces two kinds of vacancies like tetragonal oxygen vacancy with (ZnO_4) unit and octahedral oxygen vacancies with (MnO_6) units [44]. This abundant availability of multivalent cations and anions with oxygen vacancies in the crystal, surpluses its redox activities that eventually enrich the electrochemical features of the ternary metal oxide. Thus, recent research developments focused more on the investigations of $ZnMn_2O_4$ as an efficient electrode material, especially in supercapacitors [45], [46]. This cost effective and environmental friendly ternary metal oxide compound has found potential applications in the other areas like Li-ion batteries, catalysis, gas sensors and biosensors [47], [48], [49], [50].

There is an enormous number of synthesis approaches, namely sol-gel route, hydrothermal method, spin coating, micro-emulsion method, etc., available for the preparation of $ZnMn_2O_4$ in various nanostructures [47], [49], [51]. Depending upon the morphological variations of this ternary metal oxide such as changes in pore size, pore volume and surface area, the electrochemical performance of the electrode material also undergoes fluctuations. The $ZnMn_2O_4$ compound with porous morphology can exhibit superior specific capacitance and rate capacity better than binary metal oxides [52]. The porous architecture not only enhances the surface area of electrode surface but also helps to overcome the mechanical stress arises during the multiple charge/discharge cycles. The spinel crystal structure of $ZnMn_2O_4$ provides a strong and efficient mechanical durability that protect the $ZnMn_2O_4$ -based electrode material from voluminous expansion or structural deteriorations during rapid and repeated charge-discharge cycles. Moreover, the synergistic redox contributions from Zn and Mn and the improved electrical conductivity of this ternary metal oxide compared with other Mn-based metal oxides increase the charge storage capacity of the electrode material. These commendable attributes make $ZnMn_2O_4$ a superbly multifaceted electrode element with high capacitance and cyclic performance over energy storage devices [44].

1.6.3. Conducting polymers

Until the middle of the 20th century, organic polymers were considered to be only insulating and anti-corrosive materials and were inclusively used in the application areas of plastics and insulators. Conducting polymers (CPs), the well-known Nobel prize-winning materials, came to the light of research after the discovery of polyacetylene in the year 1958. The outstanding works of Alan G. McDiarmid, Hideki Shirakawa, and Alan J. Heeger in polyacetylene material doped with iodine led to a breakthrough in the field of CPs and won the Nobel prize in Chemistry for the year 2000 [53]. CPs possess superior properties like low specific density, cost effectiveness, ease of processing, tuneable electrical conductivity, anti-resistivity and excellent electrochemical properties, making them an inevitable candidate in the field of electrochemistry [54], [55]. Due to these exceptional features, researchers found many possible areas of applications for CPs in LEDs [56], electromagnetic shielding [57], sensors [58], transistors [59], supercapacitors [60], electrochromic gadgets [61] and corrosion resistance [62]. Polyacetylene (PA), Polyaniline (PANI), Polypyrroles (PPy), Polythiophenes (PTh), Polyindole (PIn), and Polyphenylene Vinylenes (PPV) are examples of conducting polymers. Among these, PA is the earliest conducting polymer with the highest electrical conductivity and simple molecular structure, but suffers from limitations like insoluble nature, infusibility and low environmental stability [63].

The electrical conductivity of CPs is basically derived from their electronic structure which led to the concept of intrinsically conducting polymers (ICPs) in which a conjugated structure exists along with polymer backbone. This π -conjugated chain is formed due to the overlapping and delocalization of unpaired electrons of carbon, which is the core foundation for the electrochemical redox properties of CPs. This impressive and unparalleled trait of CPs made them a guaranteed member in the supercapacitor applications.

The intrinsic electrical conductivity of CPs was found to rely on the factors like;

- Amount of charge carriers

- Enhancement in carrier mobility due to overlapping of orbits
- Charge hopping among polymeric chains
- Degree of π conjugation

The conductivity range of conducting polymers can be schematically represented as in Fig. 1.10.

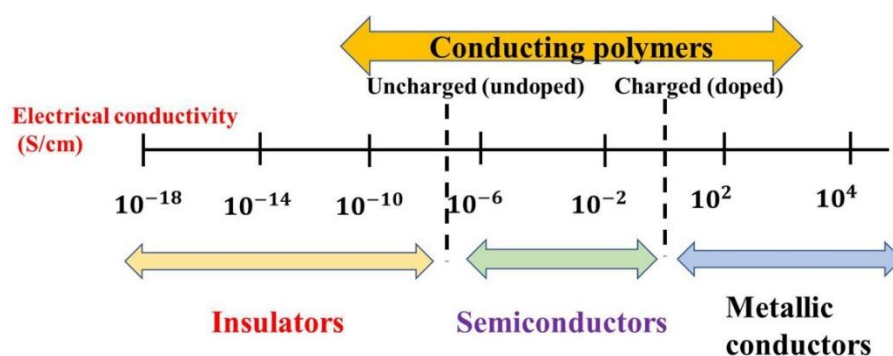


Fig. 1.10. Electrical conductivity chart for insulators, semiconductors, conductors and conducting polymers.

The intrinsic and extrinsic physical-chemical properties of CPs are mostly derived in the synthesis stage itself, making a clear dependence on various synthesis parameters like the nature of dopant, doping percentage, synthesis time and temperature, monomer concentration, and solution pH. Due to the fact of having the limitation of poor mechanical strength of CPs, research was focused on the key strategies to improve their mechanical stability of them. Some of the important strategies employed for this purpose were in-situ synthesis assisted with thermoplastic materials [64], producing composite/ hybrid compounds [65], metallic nanoparticle incorporation into polymeric chains [66], and use of polymeric/hydrogel type template in the synthesis stage [67].

1.6.3.1. Polyaniline

Polyaniline (PANI) is one of the oldest synthetic polymer materials, well recognised since the 19th century. The oxidation of aniline resulted in the production of “aniline black”, popularly used in textiles as a dye from the year 1835. From 20th century, the scientific community made efforts to explore the molecular structure and intermediate forms of aniline black. Moreover, Green and Woodhead found the four forms of PANI: protoemeraldine, emeraldine, pernigraniline, and nigraniline, through

their enormous efforts during the years 1910-1912 [68], [69]. The breakthrough in the history of PANI started after MacDiarmid synthesised green colour PANI in 1985, through chemical oxidation of aniline monomer with ammonium persulphate as oxidant in aqueous HCl medium. This green PANI powder showed an electrical conductivity in the range of 10 S/cm. After this game changer innovation, PANI acquired a special position in the field of CPs because of its properties like simple synthesis routes, cost effectiveness, environmental benignity, unique protonation mechanisms and ease of tuning physical characteristics through managing oxidation and protonation stages.

PANI has a very complex molecular structure consisting of an alternative arrangement of both benzene rings and nitrogen atoms. PANI is commonly a phenyl-based polymer with flexible –NH groups attached on both ends of phenyl rings in the polymer chain. These chemically active –NH groups are responsible for the oxidation and protonation phases of PANI and are the deciding factor of many physical and chemical properties as well. The nitrogen atoms in the polymer chain can exist in two different forms; one is sp^2 hybridised imine state and other is sp^3 hybridised amine state. Depending upon the level of oxidation, PANI has two forms; a fully reduced form and a fully oxidised form, as shown in figure 1.11.

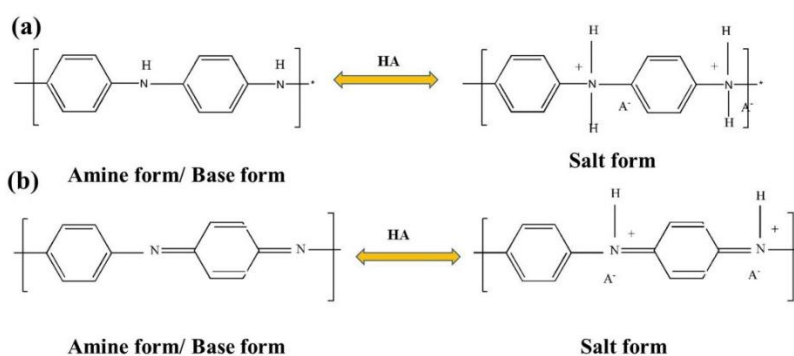


Fig. 1.11. (a) The fully reduced form and (b) fully oxidised form of PANI.

In the fully reduced form of PANI, the polymer chain consists of benzenoid rings and amine group of nitrogen, whereas, in the fully oxidised form of PANI polymer chain is composed of both benzenoid and quinoid rings along with imine state of nitrogen. Nitrogen atom can be existed as protonated or non-protonated states depending on the solution pH. The non-protonated amine state is termed as the base form of PANI. The fully reduced state, referred to as leucoemeraldine (light yellow), is a non-conducting state of PANI composed of a benzenoid ring with hydrogen bonded

nitrogen atoms seen in the base form. The fully oxidised pernigraniline (violet) is another non-conducting form of PANI with quinoid rings, and no hydrogen atoms are present in the base form. The intermediate state between these two forms is called emeraldine (green), which is a conducting state of PANI with both benzenoid and quinoid rings (Fig. 1.12). The ratio between the parameters m and n decides the redox states of PANI, which is 1:0 for leucoemeraldine, 0:1 for pernigraniline and 1:1 for emeraldine forms. Thus, it is important to regulate the proportion between benzenoid and quinoid rings as emeraldine state to achieve the electrochemically active PANI state.

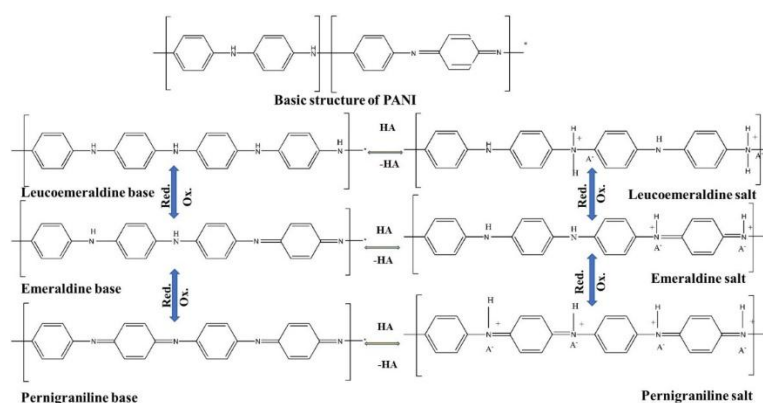
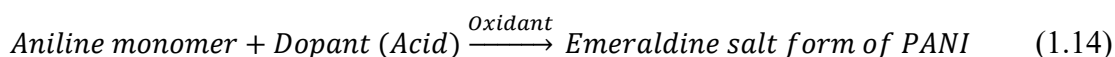


Fig. 1.12. Different states of PANI and their conversion process.

The PANI synthesis can be done using any of the two major synthesis strategies under acidic conditions, chemical synthesis and electrochemical synthesis. The chemical synthesis involves the direct oxidation of aniline monomer in the presence of chemical oxidants. The electrochemical synthesis doesn't use any oxidants, but involves the generation of active species on the surface of the electrode under an applied voltage that causes electron transfer between the substrate and electrode.

1.6.3.1.1. Chemical synthesis of PANI

The chemical synthesis of PANI in its emeraldine salt form involves dissolving of the aniline monomer in any of the aqueous acidic medium like HCl, H₂SO₄, HBr etc. and allowing it to undergo chemical polymerisation when an oxidant solution is added to the parent mixture. The green colour insoluble PANI residue obtained has to be filtered and washed before the drying procedure. Thus, the polymerisation and doping processes have occurred in the same acidic medium, simultaneously. The synthesis strategy can be summarised as follows;



This chemical oxidation method of PANI synthesis is influenced by various synthesis parameters like;

- Concentration of oxidant
- Nature and pH of medium
- Reaction time
- Reaction temperature
- Monomer to oxidant proportion

Although, chemical synthesis is the most suitable synthesis procedure of PANI in large scale applications, many other synthesis approaches like interfacial polymerisation [70], microemulsion polymerisation [71], enzymatic synthesis [72] and solid state synthesis [73] are also discussed in the studies.

1.6.3.1.2. Conducting mechanism in PANI

The electrical conductivity of conducting polymers is primarily arises from the transportation of quasi particles like solitons, polarons and bipolarons, which are created under protonation. Solitons are the charge carriers in degenerate CPs, whereas in non-degenerate CPs, the charge transportation is facilitated by polarons and bipolarons. The solitons are formed when one of the carbon atoms fails to delocalise its electron with adjacent atoms, resulting in the formation of a new π bond in the polymer chain and the radical moves through the chains. Polarons are quasi particles having charge $\pm e$ formed when a conducting polymer is doped with an electron acceptor. This doping cause some of the carbon atoms to get a positive charge (polaron) and it tries to couple with the unpaired electron in the soliton. The distance between the hole and the coupled electron varies as the concentration of dopants changes. As the concentration increases above a certain limit, two polarons are created and coupled to form a bipolaron having a charge of $\pm 2e$. In polarons, the energy gap between the highest occupied molecular orbit (HOMO) of valence band and the lowest unoccupied molecular orbit (LUMO) of the conduction band decreases. Whereas, in the case of bipolarons, this band gap between HOMO and LUMO orbitals gets reduced further due to the combined energy of two polarons, resulting in the enhancement of electrical conductivity to the next level [74].

Out of three different oxidation states of PANI, the emeraldine base (EB) form is the only conducting state of PANI. Protonation of imine nitrogen in the polymer chain is the way to make EB form to conduct when transformed in to emeraldine salt (ES) state. The proton doping indicates doping of base PANI with the help of any protonic acids like HCl, H₂SO₄, HBr, H₃PO₄, etc., to synthesis protonated PANI, is generally called as PANI salt form or emeraldine salt form. The unpaired or unreacted counter ion (negative ion) of the protonic acid medium occurs in the vicinity of polymer chain for establishing the electrical neutrality. The polarity and nature of counter ion, electrical conductivity can be tuned by reducing the band gap. Moreover, the lone pair, polarons or bipolarons play a significant role in the electrical conductivity of PANI, which can enhance the conductivity of PANI up to the range of 10¹⁰ S/cm [75].

The electrical conductivity of PANI depends on the following factors [76], [77];

- The length of polymeric chain and its crystallinity
- Nature of dopant and degree of doping
- Temperature
- Synthesis conditions like monomer concentration, monomer to oxidant ratio, reaction time and temperature
- Presence of substitution elements in the polymer chains

Alike other CPs, PANI is one of the potential electrode materials for pseudocapacitors having high theoretical capacitance of 3407 F/g, good electroactivity, and high electrical conductivity. The major drawback of PANI is its low cycle life due to the fact that the repeated charging-discharging causes unnecessary contraction and expansion of polymer chains. The electrochemical efficacy of PANI is mainly focused on the morphology and oxidation states of PANI, which depend on the grade of doping level as well as the size of the dopant [78]. Compared to carbonaceous compounds, PANI-based supercapacitors can deliver more energy but have poor charge density. Furthermore, during the charging of electrode material, polymers get attracted to the negative ions of the electrolyte and undergo oxidation, while during discharging polymers get reduced. Even though doping of PANI can improve the mechanical stability of the compound, the large scale of doping can result in volume changes and lead to a mechanical breakdown of electrode materials [75]. Thus, a major drawback of PANI-based supercapacitors is their poor mechanical stability and shorter life span.

This can be minimized by the strategy of making a hybrid/ composite material combining PANI with any of the carbonaceous compounds or inorganic oxides or hydroxides.

1.6.4. Composite electrodes

Although TMOs are good electrode material for the better improvement in energy density and power density in the supercapacitor field, since they can deliver high specific capacitance values compared to carbonaceous compounds, they still face a major drawback of inefficiency in carrying the capacitance over elevated sweep rates. In practical applications, bare metal oxides hinder their potentialities due to poor electrical conductivity except for RuO_2 , which resulted in increased series and charge transfer resistances of the electrode and thus ended up with a large IR drop, especially at higher current densities. Moreover, metal oxides usually face issues like mechanical strain during repeated charge discharge cycles, leading to crack formation in the electrode surface which will adversely affect the long-term stability of the supercapacitor [79]. Thus, in the sense to mitigating these flaws it is obvious to think about a versatile composite electrode material that combines metal oxides with carbonaceous compounds, which can sort out the limitations faced by both the individual components. These composite electrodes are developed with an aim to provide an efficient electrode stuff with high energy and power densities, cyclic stability and rate capacity. In such metal oxide-carbon composite framework, carbon-based material provides a basic physical support as well as a conductive pathway for the metal oxide part. The major charge and energy storage contributions carried by the metal oxide component through its multiple electro-active sites can be supported by the high electrical conductivity, power density and rate capacity of the carbon part. The synergistic effects produced by the composite electrode material can also result in declined material production cost.

Apart from metal oxide-carbon combination in composite electrodes, there is also another area combining metal oxides with conducting polymers as well. CPs are also one of the highly preferred electrode materials in the supercapacitor field, since they deliver high electrical conductivity, are cheap and easy to produce and have high electro-activity. Among various CPs, PANI is one of the most studied pseudocapacitor electrode materials with a high theoretical capacitance. However, the substandard

mechanical stability of PANI led to its marginal structural degradations during repeated charge/discharge cycle tests, eventually ended up in attenuated capacitance retention. Thus, these structural shortcomings of PANI can adversely affect the long-term stability of the metal oxide-PANI composite also. To straighten out these stability shortcomings, it is very much logical to associate this metal oxide-CP composite material with any of the structurally robust material like carbon-based compounds.

1.6.4.1. Transition metal oxide composites

TMOs like RuO_2 , MnO_2 , NiO , CuO , Co_3O_4 , TiO_2 , etc., are the most potential pseudocapacitive electrode materials that carry efficient electrochemical activity with a high theoretical capacitance. Although TMOs deliver high electrochemical performance, their intrinsically poor ionic conductivity results in reduced specific capacitance and rate capacity in real time applications. Thus, combining two or more metal oxides with multiple oxidation states can be used as one of the beneficial strategies to proffer the inherent limitations of a single metal oxide electrode system and can deliberately improve the specific capacitance as well as energy densities. Taking RuO_2 electrode as an example, it can be seen that designing an electrode material combining RuO_2 with other transitional metal oxides like TiO_2 , SnO_2 , CaO , MoO_3 and VO_x can produce a marginal improvement in the surface area of the electrode surface and can positively influence its electrochemical performances [80] [81]. W.Sugimoto *et al.* conducted a study on the charge storage capacities of a rutile type RuO_2 - VO_2 composite solution prepared via polymerizable-complex method for electrochemical applications and found an exceptional improvement in the electrochemical performance in the composite material compared with pure RuO_2 and attained a specific capacitance value more than 1200 F/g [82]. The conductivity issues prevailed within the NiO electrode matrix were compromised with the addition of the promising RuO_2 in order to fabricate composite electrode surface and ended up with an improved surface area, pseudocapacitive behaviour and wider operational voltage window also [83]. En-Hui Liu *et al.* aimed to decrease the large series resistance values of MnO_2 electrodes that limit their electrochemical performance by producing a NiO/MnO_2 composite electrode material with a high surface area of about 130-190 m^2/g and attained a specific capacitance of about 453 F/g at a scan rate of 10 mV/s [84]. In order to utilise the synergistic effects of two pseudocapacitive TMOs, Mohamed Racik K *et al.* prepared manganese oxide decorated CuO composite electrode materials for

supercapacitor applications and found an enhancement in the specific capacitance values for the composite electrode compared to pure CuO and MnO₂ electrodes [85]. CuO-based electrode materials find an improvement in pseudocapacitive behaviour with other TMOs and achieved a greater attention among the researchers in recent years [86], [87], [88]. There are also reports on the production of ternary metal oxide combinations such as ZnO-NiO-CuO, Co₃O₄-CuO-NiO, CuO/Ag/Co₃O₄ mixed oxide electrodes as an efficient candidate for supercapacitor applications [89], [90], [91]. A hierarchical combination of mixed metal oxides has been expected to deliver better pseudocapacitive performance using improvised porosity and surface features that are created through their synergistic interactions among individual metal oxide components.

1.6.4.2. Polymer composites

Enormous progress in the area of pseudocapacitors has been made in the last decade with the advent of the possibility of making metal oxide-conducting polymer composite electrode with the aim of flourishing the pseudocapacitor area with low cost and highly efficient electrode materials. Metal oxides and conducting polymers were the most exploited electrode materials in the area of pseudocapacitors. But both suffer numerous shortcomings when performed individually such as lower electronic and ionic conductivities for metal oxides as well as structural instabilities for conducting polymers that results in declined specific capacitance and rate capacities in their individual performances. Thus, a successful combination of these metal oxides with conducting polymers can be make a fruitful electrode surface in pseudocapacitor area. Ran Lui *et al.* tried to prepare RuO₂/(3,4-ethylenedioxythiophene) (PEDOT) nanotubes via electropolymerisation and found an improved specific capacitance and rate capacity of the electrode material. They proved that the PEDOT nanotubes served as a template for the growth of RuO₂ nanostructures and provided a better porous surface for the electrochemical performance of the composite material [92]. The support of high electroconductive materials like CPs helps to improve the poorer ionic conductivity suffered by the metal oxides like MnO₂ by creating an electro-active atmosphere for the better electrochemical performance of the metal oxides with various oxidation states [93], [94]. CuO with conducting polymer composite materials is also one of the hot research areas among the scientific world since the effective utilisation of pseudocapacitive behaviour of CuO can be enhanced with the conducting mechanism

offered by the CPs. Murat Ates *et al.* electrochemically synthesised three different combinations of CP-CuO composite electrodes involving three different CPs such as PANI, PEDOT and PPy. The PANI/CuO composite electrode attained the highest capacitance value of about 286.35 F/g at a scan rate of 20 mV/s compared with PEDOT/CuO and PPy/CuO composites [95]. Some research findings on CuO and PANI combination suggests that the polymerisation of aniline along with the dispersed CuO nanostructures can twice the storage capacity and rate capacity of the composite electrodes [96]. Other than the energy storage area, the CuO/PANI composite material is used in other applications such as electromagnetic interference shielding, sensors, solar cells and water treatments [97], [98], [99], [100]. Sayed Mohammed Adman *et al.* synthesised a symmetric supercapacitor device using PANI decorated NiO-CuO composite as an electrode material and achieved a specific capacitance of about 157.50 F/g with 65% capacitance retention over 10000 charge/discharge cycles. They found the highest energy density of about 35 Wh/Kg and power density of about 1326.31 W/Kg [101]. Thus, the often conductivity challenges prevailed in metal oxide electrode species are somewhat minimised by making fruitful stoichiometric combinations with highly conductive substances like CPs.

1.6.4.3. Metal oxide-conducting polymer-carbon based composite electrodes

In the last decade, researchers are found to have gained greater interest in the ternary or quaternary composite electrode materials involving any of the carbon-based EDLC material, metal oxides and CPs. The low-cost, abundant nature of metal oxides offering multiple oxidation states with high theoretical capacitance in the supercapacitor area are but backstepped in the supercapacitor field due to their often-insufficient conductivity challenges. These issues are found to have improvised with the help of a conductive pathway offered by any of the CPs that can also serve as a pseudocapacitive supplementer. However, the inherent mechanical and structural instabilities faced by the CPs like PANI make them an unstable electrode surface during repeated charge/discharge cycles. Thus, the metal oxide-CP composite electrode surfaces should be supported by a material having high structural integrity and electrochemical capacity. Thus, the introduction of any of the carbonaceous compounds like graphene oxide (GO), reduced GO (r-GO), CNTs, and carbon aerogels with high structural stability along with sufficient specific surface area and porosity into the metal

oxide-CP matrix can effectively improve the performance of ternary/quaternary composite electrodes. There are enormous efforts that have been put forward by the scientists in recent years in the sense of exploiting different kinds of metal oxide, CPs and carbon compounds. Murat Ates *et al.* compared the supercapacitive performance of rGO/RuO₂, rGO/PANI, PANI/RuO₂ and rGO/RuO₂/PANI nanocomposites synthesised using the in situ polymerisation method and reported the highest value of specific capacitance of about 723.09 F/g at 2 mV/s for the ternary rGO/RuO₂/PANI nanocomposite than other binary composites [102]. A similar kind of study was conducted by Murat Ates *et al.* replacing PANI with another conducting polymer polyvinylcarbazole (PVK) and achieved a maximum capacitance value of about 2698 F/g at a scan rate of 2 mV/s [103]. The role and importance of conducting polymer on the same matrix produced using the same synthesis method can be differentiated from these studies. A robust supercapacitor device fabricated using a ternary nanocomposite electrode involving 70% of MnO₂ nanorods, PANI and GO, and achieved a capacitance of about 512 F/g at a current density of 0.25 A/g with 97% capacitive retention over 5100 cycles. The improved performance of ternary composite electrode can be the result of the conductive framework provided by the PANI and enhanced electroactive surface sites offered by the GO, eventually resulting in the enhanced energy and charge storage rates [104]. Yingying Huang *et al.* studied the electrochemical performance of MnO₂/PANI/MWCNT nanocomposite and reported a specific capacitance of about 395 F/g at the current density of 1 A/g [105]. The hierarchical NiO/PANI/MWCNT core-shell composite delivered good electrochemical performances compared to its individual contributions [106], [107]. The MWCNT incorporated wool-ball-like CuO@NiO hybrid ternary composite electrodes were synthesised via a solvothermal route with a high surface area of about 262 m²/g and delivered a capacitance of about 786 F/g at a current density of 2 A/g [108]. The quaternary nanocomposite electrode CuO@NiO/PANI/MWCNT exhibited high supercapacitive performance and reported a specific capacitance of about 1372 F/g with 83% capacitance retention over 1500 cycles [109]. The enhanced electrochemical performance of ternary/quaternary nanocomposite electrodes involving different metal oxides, CPs and carbon compounds can be attributed to their well utilised synergistic interactions along with the structural and morphological improvisations brought in the composite matrix by the individual components that lead to a marginal reduction in the charge transfer resistance of the electrode material through the improved electrochemical reactions.

1.7. NANOCOMPOSITES

Nanocomposites are materials constituted with multiple phases in which any one, two or three dimensions lie in the nanometer regime. When size of the material is reduced to the nanometer range, there is a possibility to create phase interfaces which have a direct influence on the material properties. Nanocomposites have many advantages like high surface area, improved optical properties and enhanced mechanical features compared to other classes of composite materials. These materials can be prepared using metallic, non-metallic or polymeric materials using various synthesis methods. The nanocomposite is a broadened area comprising one dimensional, two-dimensional, three-dimensional and amorphous materials in which dissimilar components distinctively mixed together in the nanometer range. The major three classifications of the nanocomposite materials are listed in Fig. 1.13. Metal oxide nanocomposites (MONCs) are one of the important classes of nanocomposites that come under all these three major categories and come with exceptional structural, morphological, optical and electrical characteristics. The exceptional features offered by the nanocomposite materials are not only the result of properties of its individual components but also its morphological as well as interfacial attributes. These unique characteristics exhibited by the nanocomposites make them a viable candidate in many applications like sensors, supercapacitors, photovoltaics, non-linear optics catalyst, and battery cathode materials [110].

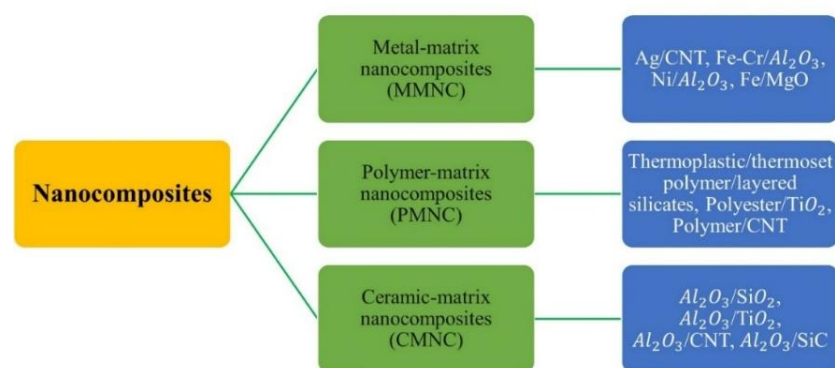


Fig. 1.13. Classification of nanocomposites with their examples.

1.7.1. Synthesis strategies for nanocomposites

The size and dimensions of nanocomposites have a critical role in their structural, morphological, optical, electrical and magnetic properties. Thus, the

strategies employed for the synthesis of nanocomposites must be chosen appropriately since they have a direct influence on their basic characteristics. One of the types of classification in the synthesis methods is mainly in three sections, namely solution-based synthesis, vapor phase synthesis and gas phase synthesis. Another popular categorisation of synthesis methods is the top-down approach and bottom-up approach, as listed in the Fig.1.14. Chemical and physical methods of synthesis come under these two major classifications. Physical methods usually produce a bulk number of products, but the uniformity in the size and dimensions of the end product is not guaranteed. There are numerous kinds of chemical/wet methods used for the synthesis of nanocomposites, among them three of the simple, cost effective and efficient methods that are commonly used are the co-precipitation method, the sol-gel method and the hydrothermal method.

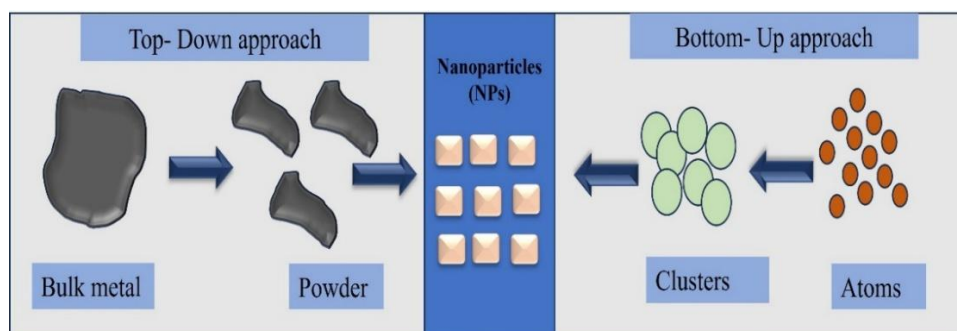


Fig. 1.14. Two different approaches of nanocomposite synthesis methods.

1.7.1.1. Co-precipitation method

Co-precipitation is a simple and effective synthesis approach used for the production of metal oxide nanostructures, metal oxide-metal oxide and metal oxide-ceramic nanocomposites. In this method, usually an insoluble precipitate product is created within the basic solution. Inorganic salts are used as precursor material and they are allowed to dissolve in any of the solvents, like water, to obtain a homogeneous solution of intended precursor. The end product from the precursor solution is produced after a critical concentration of reactants are reached followed by nucleation and growth phases, and will usually be in a hydroxide/oxalate form. This hydroxide/oxalate precipitate is then filtered and washed thoroughly before getting decomposed in to the metal oxide state under high thermal conditions. The reaction conditions like pH of the solution, temperature and molar ratios of precursors etc. has a greater influence on the

size, dimensions and uniformity of the precipitate product. The precipitation agents commonly used in these synthesis methods are NaOH, KOH, Na_2CO_3 , NH_3 , etc., and are the deciding factor of solution pH [111]. The uniformity of the precipitate production without any sort of agglomerations or structural defects can be assured with the help of external agents like surfactants in the synthesis procedures. This simple synthesis method carries other advantages, like economical, flexibility, acute control over the size and shape of final product and mass output.

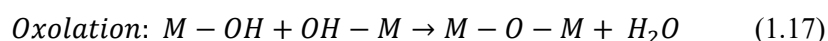
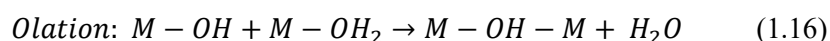
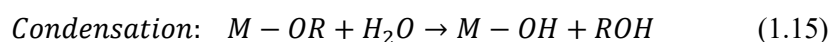
The usual steps involved in a simple co-precipitation approach of nanocomposite/nanoparticle synthesis are mentioned below;

- I. **Preparation of precursor solution** by dissolving the metal salts in water or any other solvents.
- II. **Mixing** the constituents thoroughly using constant stirring until a homogeneous solution is obtained.
- III. **Addition of precipitation agent** to the precursor solution for the initiation of precipitation process.
- IV. **Aging and stirring** constantly to assure the uniform and complete particle growth to occur.
- V. **Filtering and washing** the end product for the complete removal of impurities and unreacted salts using water and ethanol.
- VI. **Drying and annealing** the precipitate in high thermal conditions to improve the crystallinity and purity of the final product.

1.7.1.2. Sol-gel method

Sol-gel method is one of the simplest and efficient bottom-up approaches commonly used for the synthesis of metal oxides, metal oxide nanocomposites, ceramic powders and inorganic/organic hybrid matrices. The approach works on the principle of conversion of the solution or sol phase of a precursor into the gel phase of the intended product with high purity and uniformity. Sol-gel process is composed of two important stages: hydrolysis and condensation [111]. In the hydrolysis stage, the water or alcohol solvents initiate the breaking of alkoxy group -OR from the metal oxide precursors and get replaced by the hydroxyl groups OH. The solution pH, reaction temperature, concentration of precursors, nature of solvent and alkyl groups are some

of the deciding factors of hydrolysis process. In the condensation or polycondensation stage, M-OH bonds formed during the hydrolysis process is allowed to undergo two reactions called ololation and/or oxolation. As the name indicates, oxolation is the stage in which ‘oxo’ bridges were developed between the metal cations (M-O-M) and ololation is the stage in which ‘ol’ bridge were built in connection with the metal cations (M-OH-M) [112].



The so-called gel formed during the condensation stage is allowed to age naturally for the complete product formation with high structural and phase purity. A drying procedure was set after this basic sol-gel processes for the removal of impurities and excess water or volatile solvents that may be trapped in the porous networks of the product. Depending upon the drying conditions, the obtained gel can be in various forms called xerogels and aerogels. The complete nanoparticle formation is happening during the calcination process.

Some of the advantageous of sol-gel synthesis methods are;

- Ease of synthesis of metal oxide nanoparticles and metal oxide nanocomposites
- Low-cost and high compositional control.
- Ability to achieve intended product at high purity and homogeneity
- Ability to tune the structural and morphological features by optimising factors like solution pH, reaction temperature, concentration of precursors etc.
- Ease of producing thin films of amorphous materials.

1.7.1.3. Hydrothermal method

The hydrothermal method is one of the simplest, efficient and low-cost synthesis methods used for the synthesis of metal oxides, which uses water as the solvent medium. In the historical view, German geologist Karl Emil von Schafhäütl

was the one who tried the first hydrothermal synthesis of microscopic quartz crystals with the help of a pressure cooker [113]. In this method, a high pressure and temperature was set as the synthesis conditions which helps to dissolve and recrystallize the metal ions in the aqueous solvent. The reaction temperature is mostly selected above 100 °C, and the closed atmosphere makes the pressure conditions as desired. This common synthesis method is efficient in making metal oxide composites as well with high purity and crystallinity, without using any toxic elements. Autoclaves are commonly used equipment for conducting this kind of synthesis method and the internal structure of an autoclave is presented in Fig. 1.15. This method of synthesis offers promising advantages like affordability of production in large scales, good control over the material stoichiometry without much agglomerative structures, and extreme purity [114]. Moreover, this synthesis approach is suitable for researchers in tuning the properties of metal oxides, hydroxides, nitrides, etc., or any kind of complex compounds according to the desired applications by governing the material sources and synthesis conditions with or without templates [44].

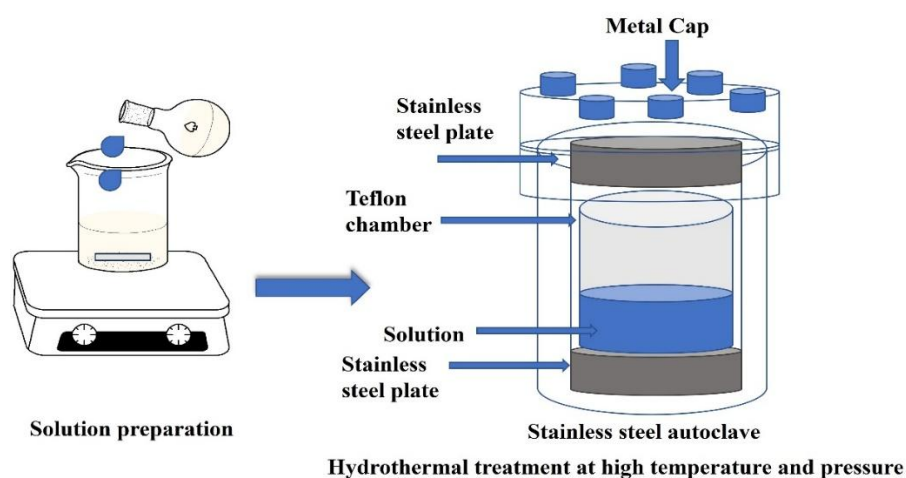


Fig. 1.15. The synthesis procedure of hydrothermal method and the parts of a stainless-steel autoclave.

The material synthesis through the hydrothermal method usually deals with two stages; nucleation and growth. These two stages are mainly controlled by the process called supersaturation; it is the ratio between actual concentration of species to the saturation concentration of species in the solution. The process of nucleation starts when the supersaturation stage is achieved, where the solute particles get precipitated into small cluster units. Following the nucleation stage, the incorporation of growth

units consecutively occurs, and growth stage get initiated [115]. These stages of hydrothermal treatment are illustrated in Fig. 1.16.

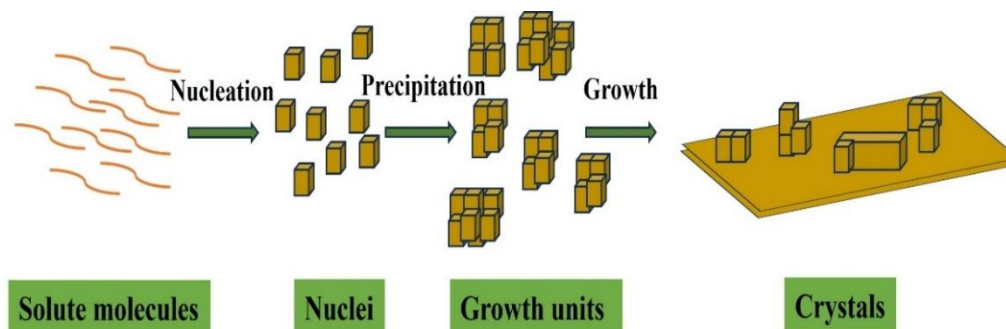


Fig. 1.16. Schematic representation of crystal growth procedure under hydrothermal method.

Hydrothermal method has several other advantages like [114];

- Simple and cost-effective pollution free approach.
- Time and energy saving method.
- Extreme control over shape and stoichiometry of the compound.
- Good nucleation control.
- Highly crystalline end product with desirable physio-chemical properties.

It is one of the common practices in this synthesis method to use any kind of surfactants, capping agents or other supportive additives to the reaction mixture with an aim to tune the size/shape or other characteristics of the final product [116]. Other than these additives, reaction temperature, pressure as well as reaction duration has a direct influence on the particle size/shape or morphology of the products [117].

1.7.1.4. Lyophilization

Lyophilization or freeze-drying is one of the common drying techniques used to remove unwanted/ unreacted organics from the intended final product. This procedure deals with the sublimation of sol-gel product at lower pressure for the complete removal of liquid phases from the sample. At this acute lower pressure stage, the capillary forces appearing in the product will be in their lowest value, so that this drying process can be completed with minimal shrinkage or breaking of the product networks. This method is commonly used for gel species which are unstable at high

temperature drying conditions and ensures the long-term life of the synthesised nanomaterial. During the whole process of drying, the sol gel suspension is kept frozen which causes a uniformity in the process. Mostly, in the liquid-phase drying processes, the particles in the top most layer of suspension are dried first and cause them to behave like an inhibition layer over the other particles existing in the lower parts of the suspension from drying properly [118]. Thus, lyophilization is an optimal drying process which ensures the uniform drying of the whole sample and also aids in increasing the porosity in the surface of the sample that can ensure its increased surface area and mesoporous nature. In addition to that, the synthesis or formation temperature region is a crucial factor for the conductive nature of polymer preparations. That is, CPs like PANI become highly conductive only at the lower temperatures [119]. There are also reports suggesting the formation of improved polyaniline networks with minimal defects at the sub-zero level reaction temperatures [120]. Jundale *et al.* conducted a study on the polyaniline nanofibers that reinforced the CuO nanoparticles to form a nanocomposite film prepared via the in situ polymerisation method at 0°C [121].

1.8. ELECTROCHEMICAL ANALYSIS

The performance of supercapacitors is based on the essential features like specific capacitance, power and energy densities, cyclic performance and life time. To characterise the capacitor performance, it has to be evaluated in two different configurations: the two-electrode configuration and the three-electrode configuration. In the three-electrode configuration, as the name indicates three electrodes are needed for the performance evaluation: one is a working electrode made up of the prepared electrode material, second one is a reference electrode and the last one is a counter or auxiliary electrode. These three electrodes are connected to a potentiostat for analysing the variation of current with different scan rates or the variation of potential of electrode with different current densities. Usually used reference electrodes are silver chloride electrodes or saturated calomel electrode, with the function of controlling the potential of working electrode. The counter electrodes are used to complete the electrical circuit and maintain electrical neutrality. Moreover, it also serves as a protector for the working electrode from other unintended potential changes occurring in the system. The working electrodes are fabricated using an active material slurry prepared with the help of a binder compound and activated carbon in a polymer solvent. Example of counter electrodes are platinum and graphite electrodes. In the two-electrode configuration,

only working electrode and the counter electrode are used. The schematic representation of both configurations is presented in Fig. 1.17. In both configurations, the suitability of the prepared electrode material is tested through three major electrochemical techniques:

1. Cyclic voltammetry (CV)
2. Galvanostatic charge-discharge (GCD)
3. Electrochemical impedance spectroscopy (EIS)

The obtained data from all these characterisation techniques were graphically represented for the performance analysis of intended supercapacitor material.

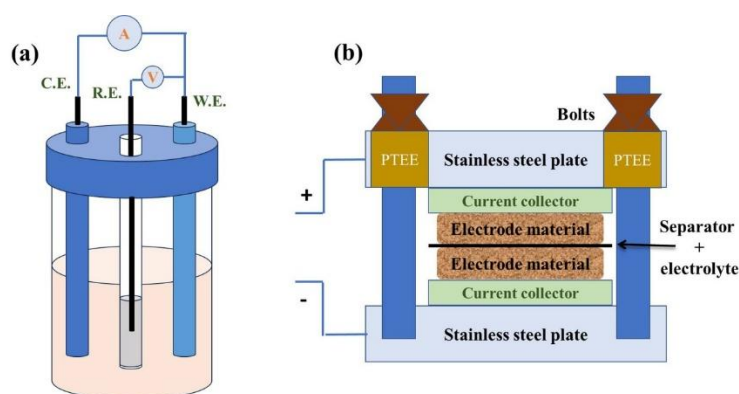


Fig. 1.17. Schematic representation of (a) three-electrode cell configuration (b) two-electrode cell configuration.

1.8.1. Cyclic Voltammetry (CV)

Cyclic voltammetry is the first method used to evaluate the electrochemical performance of electrode material, which effectively records the redox behaviour of the electrode material. During this analysis, a potential is applied to the working electrode with respect to the reference electrode having fixed potential resulting in a linear potential sweep happening between the two fixed potentials. Additionally, in this test, a positive sweep rate (dV/dt) is first applied (charging) within the potential limit and then reversing the voltage sweep (discharging) after reaching the maximum range of potential, during which the obtained current is recorded. Thus, the CV curve represents the variation of time dependent current within the fixed potential window. A typical CV response of electrode material in the three-electrode configuration is presented in (Fig. 1.18 (a)), where E_{pa} and E_{pc} represent anodic peak potential and cathodic peak

potential, i_{pa} and i_{pc} denote anodic peak current and cathodic peak current, respectively. The CV curve of an ideal capacitor is of rectangular shape and that of EDLCs carry a deformed rectangular shape, whereas pseudocapacitors presents a different shaped CV curve with oxidation and reduction peaks (Fig. 1.18 (b)).

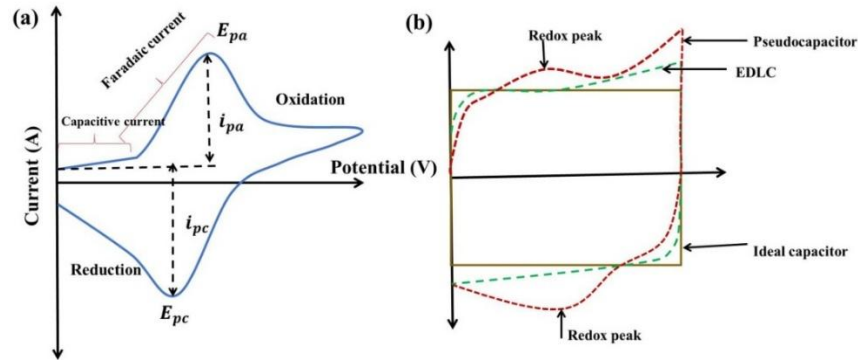


Fig. 1.18. (a) Typical CV response of an electrode material in a supercapacitor device (b) CV curve of ideal capacitor, EDLC, pseudocapacitor.

The specific capacitance (C_s) can be evaluated from CV curve in the three-electrode configuration using the equation;

$$C_s = \frac{A}{2mk\Delta v} \quad (1.18)$$

The specific capacitance in the two-electrode configuration can be estimated using the following equation;

$$C_s = \frac{A}{mk\Delta v} \quad (1.19)$$

where k denotes scan rate, A represents area under the curve equal to $\int I dV$, m is the active mass of electrode material and ΔV is the potential window.

1.8.2. Galvanostatic Charge-Discharge (GCD)

The galvanostatic charge-discharge method is the most important technique in the supercapacitor performance analysis, and is considered the most appropriate way to evaluate specific capacitance and cyclic performance of the working electrode or device. In this method, variation of potential with respect to time within a pre-fixed voltage limits are studied for different applied current densities. This process involves the charging and discharging of electrode material within the potential window. The voltage responses vary linearly with time, producing a triangular shape for the GCD

curve. The difference in GCD response of ideal capacitors, pseudocapacitors and EDLCs are schematically represented in Fig. 1.19. The deviation of the GCD curve of pseudocapacitor from the triangular shape can be attributed to its faradic redox properties. The initial ohmic drop in the discharge part of the GCD curve is due to the internal resistance in the system.

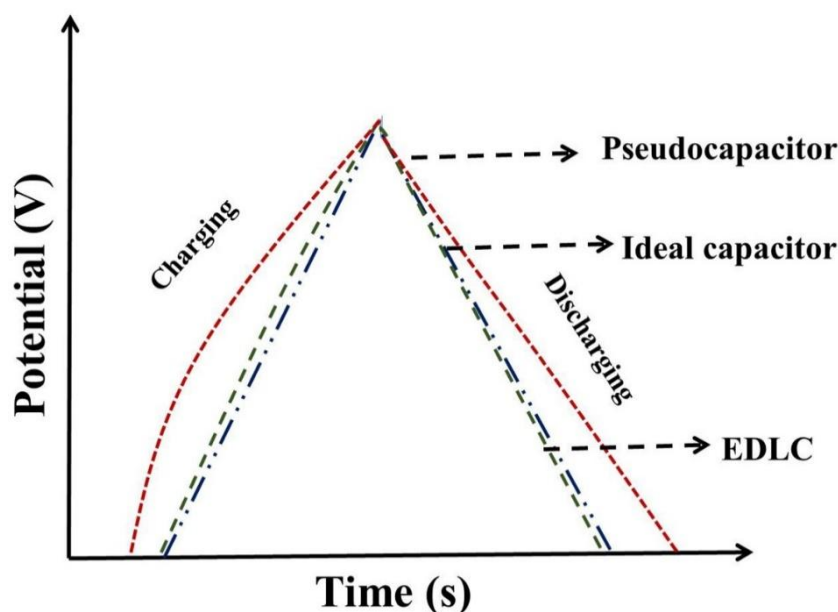


Fig. 1.19. GCD curve of ideal capacitor, pseudocapacitor and EDLC.

The specific capacitance of electrode in the three-electrode configuration can be estimated using the following equation;

$$C_s = \frac{i \Delta t}{m \Delta v} \quad (1.20)$$

The specific capacitance of device in the two-electrode configuration can be evaluated using the following equation;

$$C_s = 2 * \frac{i \Delta t}{m \Delta v} \quad (1.21)$$

Where i is the value of average cathodic current and Δt represents the discharge time.

1.8.3. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopic analysis is used to evaluate the interfacial properties connected with reactions happening at the electrode-electrolyte interface. In this test, a small amplitude AC current is supplied to the electrode

configuration over the frequency range of 10 mHz to 100kHz. The impedance value obtained from this study is the combined result of solution resistance (R_s), charge transfer resistance (R_{ct}), electrochemical double-layer capacitance and reactance in the system. The Nyquist plot from EIS data is a graph plotted between real impedance (Z) and imaginary impedance (Z'), as shown in Fig. 1.20.

The value of X-intercept at the high frequency region in the impedance spectra corresponds to equivalent series resistance (ESR) which represents the solution resistance of electrolyte in the system. The diameter of semi-circle arc in the high frequency region denotes the charge transfer resistance that occurs at the electrode-electrolyte interface. The linear portion in the low frequency region is the indication of ideal capacitive behaviour. The straight line which makes an angle 45° with the X-axis is called as Warburg line representing the ionic diffusion in the interface.

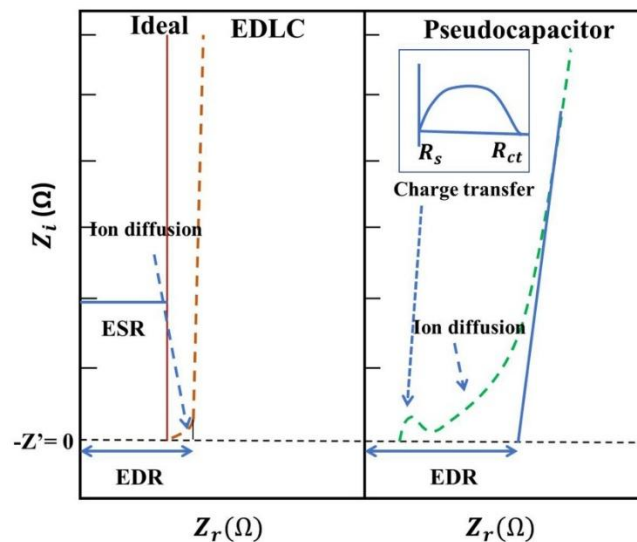


Fig. 1.20. Nyquist plot of ideal capacitor, EDLC and pseudocapacitor.

1.8.4. Cycle stability

Cycle stability of an electrode material is used to evaluate its long-term performance as a supercapacitor device. Cycle stability is typically measured using the GCD technique, which determines the extent to which the prepared electrode material can withstand. Usually, cycle performance leads to electrode degradation, initiates corrosion and increases ESR values, ultimately causing a decline in specific capacitance.

1.8.5. Specific energy and specific power

The specific energy and specific power are the two important parameters which determine the efficiency of the supercapacitor for practical uses. The energy density (E_d) in Wh/kg and power density (P_d) in W/kg was evaluated using the equations (1.22) and (1.23), respectively.

$$E_d = \frac{0.5}{3.6} C_s (\Delta V)^2 \quad (1.22)$$

$$P_d = \frac{E_d}{\Delta t} * 3600 \quad (1.23)$$

From the equation, it is clear that the value of energy density directly depends on specific capacitance and potential window. Thus, to improve the specific capacitance, we have to focus on appropriate choice of electrode material, whereas the potential window is associated with the electrolyte. From equation (1.1), it is evident that specific capacitance can be improved either by increasing the surface area of electrode material or by decreasing the electrode separation. Power density of the supercapacitor is influenced by the discharge time.

1.9. CHALLENGES OF SUPERCAPCITORS

Supercapacitors have become an inevitable part of world's energy management systems since they are found to have exceptional roles in the fields of transportation, automobiles, industrial and medical scenarios, and consumer electronics. However, its large-scale commercialization still faces some shortcomings as:

- The storage capacity of supercapacitors still come under a subject of concern, since its energy density is not much high as the conventional batteries.
- Lower energy density causes a bulkier appearance in the supercapacitor device.
- The voltage rate of supercapacitors is very limited, i.e., less than 2.7 V, leading to a need for a large number of series connections for commercial applications. Moreover, the consistency of voltage in each series connections must be guaranteed as there is a lot of charge-discharge cycles during working.

- Even though high-power density and cycle life is the major advantage of supercapacitors, it is limited for industrial applications.
- Cost of production is high.
- Requirement of additional infrastructures for proper installation.
- Drawback of self-discharging about 10-40% in a day.

Thus, numerous studies are being carried out in this area to develop a novel and high-performance electrode material with an excellent surface area and a proper choice of electrolyte medium is required to establish a better potential window, leading to an efficient supercapacitor device with high storage capacity.

1.10. WHY HYBRID SUPERCAPCITORS- A BRIEF INTRODUCTION

Hybrid capacitors with their enhanced specific capacitance and energy densities without compromising the power capacities are one of the frontier research trends in the modern scientific community. The superior specific capacitance is the result of contributions from both EDLC material and pseudocapacitor material. The incorporation of both types of electrode material can enhance the surface-to-volume ratio of the combined product, which can positively enrich the electrochemical performances. The charge storage mechanism of EDLCs lie in its intrinsic electronic structure and charge partition depth, whereas that of pseudocapacitors are based on the redox activities between the electrode and the electrolyte in the electro-active sites. The combination of these processes contributes to the charge storage mechanism of hybrid supercapacitors [18]. The hybrid supercapacitors can store a large amount of charge at elevated power densities, so that they can be considered to be a reciprocal choice compared with batteries. The major advantage of the development of the hybrid supercapacitors is the hope of achieving enhanced energy density up to 20-30 W h/Kg, rapid redox activities, good cycle performance and an extensive life span. The choice of electrode material in the hybrid supercapacitors is based on coupling different kinds of EDLCs as well as pseudocapacitive elements like carbon nanotubes, graphene, reduced graphene oxides, activated carbon, conducting polymers and metal oxides. The combination of these materials can overshadow the individual limitations faced by each component and result in higher capacitance with extended stability and affordability. Here, the EDLC material supplies high power density, whereas the pseudocapacitive

element contributes higher energy density, resulting in the uplifted electrochemical parameters that approaches the characteristics of an ideal electrode. [122].

The hybrid electrode material combining metal oxide, conducting polymer and any carbonaceous compound can enrich the supercapacitive performance. Here, the conducting polymer can undergo redox activities along with metal oxides, which provide a chance for achieving higher capacitance. Furthermore, the introduction of carbon compounds like CNTs can ensure the structural stability of pseudocapacitive element and also results in overall enhancement in the specific surface area of the hybrid electrode, which eventually make a smooth contact between pseudocapacitor components and electrolyte. Although the risk of leakage introduced by the pseudocapacitive components through the faradaic reactions, that can be counterbalanced with the help of the EDLC material, which stabilizes the charge storage mechanism and suppresses the self-discharge limitations- provided the hybrid material is engineered properly. These combinations of electrode materials have the capacity to produce specific capacitance in between 100-800 F/g. But they face some limitations too as listed below [122];

- ❖ Lack of power proficiency.
- ❖ Need safe operation and control.
- ❖ Need an extremely efficient synthesis method that can produce porous architecture.
- ❖ Superior control over each element of the hybrid composition is required to achieve desirable electrochemical properties.

1.11. SCOPE AND OBJECTIVES OF PRESENT STUDY

The fabrication of a sustainable, high-performance and eco-conscious electrode material for the supercapacitor applications is the major objective of this work. This thesis work is concentrated on the synthesis, structural and morphological characterisations and electrochemical performance evaluation of CuO-based composite/hybrid electrodes. The metal oxides and binary metal oxide composites were synthesised using hydrothermal method and their hybrid systems with PANI and MWCNTs were prepared using chemical oxidative synthesis followed by lyophilisation technique. The electrochemical performance of the fabricated hybrid electrode

materials was evaluated in both the three-electrode configuration and the two-electrode symmetric configuration. The prominent objectives of the thesis are:

- To synthesise and characterise CuO nanomaterial and CuO/PANI/MWCNT hybrid material using hydrothermal and chemical oxidative polymerisation routes for energy storage applications.
- To synthesise and characterise CuO-NiO nanocomposite and CuO-NiO/PANI/MWCNT hybrid material using hydrothermal and chemical oxidative polymerisation routes for energy storage applications.
- To synthesise and characterise CuO-Co₃O₄ nanocomposite and CuO-Co₃O₄/PANI/MWCNT hybrid material using hydrothermal and chemical oxidative polymerisation routes for energy storage applications.
- To synthesise and characterise CuO-ZnMn₂O₄ nanocomposite and CuO-ZnMn₂O₄/PANI/MWCNT hybrid material using hydrothermal chemical oxidative polymerisation routes for energy storage applications.
- Evaluation of the electrochemical performance of CuO-based composite/hybrid electrode materials in a symmetric two-electrode configuration set up.

1.12. ORGANISATION OF THESIS WORK

Energy storage devices are one of the prominent research areas in the 21st century, due to the everlasting demand for energy in the world. Supercapacitors with superior power densities, rapid charge-discharge cycles and commendable cycle life compared to conventional capacitors and batteries offer a potential candidate to meet the energy demand and supply of the world population. Thus, wise selection and fabrication of efficient and high-performance electrode material for designing supercapacitor devices is a crucial attribute in the area of energy storage devices. The thesis is intended to fabricate CuO-based metal oxide/PANI/MWCNT hybrid systems as a cost-effective and eco-conscious high performance electrode material. A brief and concise introduction about the scope and need of energy storage devices, different kinds of supercapacitors and electrode materials, their various synthesis approaches and electrochemical analysis are discussed in this chapter. Chapter 2 concentrated on the synthesis, structural and morphological investigations and electrochemical

performance evaluation of pristine CuO and CuO/PANI/MWCNT composite as an efficient electrode material. The synthesis, structural and morphological investigations and electrochemical performance investigations of CuO-NiO nanocomposite and CuO-NiO/PANI/MWCNT hybrid electrode material in both the three-electrode and the two-electrode symmetric device configurations are thoroughly discussed in chapter 3. Chapter 4 focuses on the synthesis, characterisations and electrochemical performance investigations of CuO-Co₃O₄ nanocomposite and CuO-Co₃O₄/PANI/MWCNT hybrid material in both the three-electrode and the two-electrode symmetric device configurations. The fabrication and detailed characterisations of CuO-ZnMn₂O₄ nanocomposite and CuO-ZnMn₂O₄/PANI/MWCNT hybrid material are discussed in detail in chapter 5. The electrochemical performance of the prepared electrode materials is also explored in this chapter. Chapter 6 presents the overall inferences and conclusions obtained from the studies performed, and chapter 7 discusses some of the future perspectives and recommendations of the works conducted in this thesis.

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Synthesis, Characterization, and Supercapacitive Performance of CuO and CuO/PANI/MWCNT Hybrid System

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Efficient energy storage mechanism became an intricate and vital part of global sustainable energy management in light of ever-increasing mass energy demand across the world. Supercapacitors gained much attention on account of its high-power density and faster charge-discharge capacities over the conventional capacitors and batteries, which are typically ruling among Energy Storage Devices (ESDs). CuO is the one among the electrochemically active TMOs considered to be promising substitute for commercial ones in supercapacitor field, carrying high theoretical capacitance along with other oddities like low cost, environmental friendliness, sufficient stability, and high intrinsic activity. Owing to its shortcomings like poor electrical conductivity and specific surface area, the actual electrochemical activity of copper oxide is still far lower. Metal oxides and conducting polymers are combined with carbonaceous materials like MWCNTs can become a profitable composite electrode material to enhance the pseudocapacitive performance because of their combined synergetic effects. Within this context, a surfactant free approach to CuO synthesis through hydrothermal method is discussed and compared its electrochemical performance with the CuO/PANI/MWCNT composite electrode synthesised via one pot in-situ polymerisation method.

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2.1. INTRODUCTION

Energy generation and storage has turned into a key focus area all over the world due to the ever-rising global energy demand as a result of marginal population increase. Rechargeable batteries are considered to be leading energy storage system prevailing among the ESDs due to their high energy density, but they holding the limitations of deprived life duration and specific power as well as lack of availability for proper recycling and disposal systems after life-end. Insubstantial storage capacity and over-sized appearance unambiguously hinder fuel cells from becoming an efficient alternative for batteries. Moreover, the conventional capacitor lack its electrochemical performance in consequence of deficient specific energy[1]. To date, an enormous amount of effort has been carried out by the scientific community in search of a viable candidate in the area of ESDs that can bridge the gap between rechargeable batteries and conventional capacitors. SCs has become a potential contender in this scenario, possessing high power density and modest specific energy, and possibly having longer cycle life in comparison with batteries [2], [3], [4]. However, real-time power and energy efficacy of SCs are far beneath from the expectations and so the need for a convenient and travel-friendly, flexible future generation SCs with commendable energy-power efficiencies are still unmet.

The selection and design of appropriate electrode material is a key factor for acquiring satisfactory electrochemical performances from the storage system. Enriched electrical conductivity and ionic mobility, ease of fabrication, economically viable, and porous architecture are some of the key criteria to be emphasised while selecting an electrode material in supercapacitor context [5]. Literally, the casting of electrode material is the bottom-line of supercapacitor performances to attain admirable capacitance values. Transitional metal oxides (TMOs) are one of the promising candidates in the category of electrode material exhibiting attractive electrochemical achievements in the past few decades [6], [7], [8], [9]. TMOs carry higher specific capacitance values as result of their significant redox behaviour compared with carbon based electrode materials, ends up in notable capacitance and electrochemical stability [10]. Therefore, economical and environmentally viable metal oxide energy storage systems are found to be on the rise, in response to keeping the balance between energy demand and consumption in the modern society. Notably, amid of all 3d-TMOs such

as Fe, Co, Ni, Zn and Ti based, Cu-based electrode material achieved better attention due to its chemical stability, rich reserve and pseudocapacitive nature [11].

2.1.1. Electrochemical performance of CuO - A literature survey

Even though, all oxide forms of copper are being attractive materials in the stream of research, cupric oxide (CuO) has found as a hopeful material for the fabrication of supercapacitor working electrodes. As yet, theoretical capacitance of CuO found to attain a commendable value of 1800 F/g which is almost comparable with that of hydrated ruthenium oxide working electrodes (~ 2200 F/g) [12]. Supercapacitive performance of CuO can be well-tuned by optimising its morphology, crystallinity, surface area, and particle size [13], [14], [15]. Wide variety of CuO nanostructures, for example, nanorods [16], nanoflakes [17], nanotubes[18], nanowires[19], nanoflowers[20], [21], and nanoparticles [22] has been already synthesised. In recent years, different variety of synthetic approaches such as sol-gel method [23], hydrothermal method [24], co-precipitation [25], microwave irradiation [26], electrodeposition method [27], solvothermal method [28], chemical bath deposition [29], have been reported intensively to synthesise CuO nanoparticles with different morphologies.

Many researches have been conducted on the pseudocapacitive performance of CuO-based SCs. Even though, copper chalcogenide based pseudocapacitors is a potential member in the electrochemical field, because of their poor electrical conductivity, structural collapse during charge-discharge cycles, and minimal energy density, production of CuO electrode with remarkable energy density and capacitance are still in urgent demand [30]. Deepak P Dubal *et al.* synthesised cauliflower-like CuO with a surface area ~ 49 m²/g, showed a specific capacitance of 179 F/g in 1 M Na₂SO₄ electrolyte solution [13]. Seyyed E. Moosavifard *et al.* designed a 3D highly ordered nanoporous CuO framework exhibiting an excellent electrochemical performance with a specific capacitance value of 431 F/g at 3.5 mA/cm² [31]. Yu Xin Zhang *et al.* fabricated mesoporous CuO using wet chemical method and reported a capacitance value of about 137 F/g in 6 M KOH solution [32]. A trouble-free chemical synthesis of 3D-flower-like CuO nanostructures was proposed by S. K. Shinde *et al.* and acquired a capacitance of about 498 F/g at a current density of 5 mV/s [33]. Deepak P. Dubal *et*

al. reported a surfactant assisted chemical bath deposition method of CuO thin film fabrication and obtained a specific capacitance value of 396 F/g at current density 5 mV/s for CuO nanobuds [34]. V. Senthilkumar *et al.* reported a comparative supercapacitive performance of binder-free CuO nanoplates and binder assisted bud- and flower-shaped CuO nanostructures and obtained a high specific capacitance value of about 536 F/g at current density 2 A/g with 94% capacity retention over 2000 cycles for CuO nanoplates [35]. Lakshmi Kunhikrishnan *et al.* prepared sphere-like CuO nanostructures via CTAB-assisted co-precipitation method and reported a capacitance value of 468 F/g at a scan rate of 5 mV/s with a capacity retention of 94% after 2000 CV cycles [36]. Another appropriate strategy to improve the electrochemical performance of metal oxides is to try doping with productive transitional metal ions which can effectively alter the electronic structure of host material and eventually improve the conductivity of the matrix. Wenbo Lv *et al.* discussed the effect of Mo-doping in CuO nanosheets synthesised via a simple hydrothermal route and attained a specific capacitance value of about 1392 F/g at 2 A/g. The work concludes with the practical possibility of Mo-CuO composite electrode as a promising candidate in ESDs with an excellent energy density of 36 Wh/ kg at 810 W/ Kg [37]. Faiza Iram *et al.* incorporated transition metals such as Zn, Mn, Ni individually in to the CuO matrix via co-precipitation method and reported a higher capacitance value of 507 F/g at 5 mV/s for the Ni- doped CuO sample, since the Ni doped sample exhibited better surface area compared with others [38]. A facile co-precipitation method was used by Manika Chaudhary *et al.* for the synthesis of pure and Co and Fe doped CuO nanostructures and achieved a specific capacitance values of about 114 F/g, 136 F/g and 170 F/g for CuO, Co-doped CuO and Fe-doped CuO, respectively at 0.5 A/g [39]. Mohan-Reddy Pallavolu *et al.* synthesised Al-doped CuO nanoflakes via co-precipitation method and reported a maximum of 272 C/g at 1 A/g for the 5 wt% doped CuO with 99% capacity retention over 5000 charge/discharge cycles [30]. The one of the major drawbacks suffered by metal oxides in the electrochemical field is lesser active mass utilization by the electrolyte, owing to their poor porous structure which declines the accessible sites in the electrode-electrolyte interface [40]. Better choice of current collecting substrates like Ni foam, copper foam and copper foils can efficiently overcome this problem by providing greater electrochemical active contact area which undoubtedly complimenting the effective utilization of active electrode material. Guiling Wang *et*

al. prepared CuO nanosheets directly grown on Ni foam via template-free grown method. The study showed that an array of CuO nanosheets have been uniformly arranged over the Ni foam with a thickness of 5 μm and achieved a specific capacitance value of 569 F/g at a current density of 5 mA/cm^2 in KOH electrolyte [41]. Yunhu Li *et al.* directly grown CuO nanostructures on copper foam and got a higher capacitance value of about 212 F/g at a current density of 0.41 mA/cm^2 for CuO nanosheets [40]. In spite of all these efforts, the best reported specific capacitance value of CuO electrode is still far less than its theoretical value, which provides more opportunities for further research on this material [5].

2.1.2. CuO-based ternary nanocomposites- An overview

The electrochemical performance of CuO-based SCs usually suffers from the limitations like inferior electrical conductivity and structural stability in the course of consecutive charge/discharge cycles. These shortcomings can be minimised by fabricating a potential hybrid composite system integrating CuO with conducting polymers as well as any carbonaceous materials. At present, hybrid composite electrodes are broadly studied on account of their probable utilities. Metal oxides/hydroxides, conducting polymers (CPs) and carbon-related materials are the key elements that prevailed in the field of SCs [42], [43]. A wise combination of these elements can produce exceptional outcomes in this area. Nowadays, CP-TMO combinations are extensively explored by the researchers in order to overcome the mechanical instabilities and agglomeration issues that typically decline the supercapacitor performances [44], [45], [46], [47]. Carbon- based electrode materials such as activated carbon, multi-walled carbon nanotubes (MWCNTs) and graphene having higher specific surface area can be incorporated with TMOs to trigger their pseudocapacitive performances through synergistic effects [48]. For instance, Chandan Kumar Maity *et al.* reported the one pot synthesis of N-rGo/ZnO-CuO nanocomposite and exhibited a specific capacitance value of 1075 F/g at current density 1 A/g in 1M KOH with 88% capacitance retention [49]. Moreover, Nadia Boutaleb *et al.* synthesised ternary nanocomposite of polyaniline@TiO₂-CuO through a facile method followed by in-situ polymerisation and evaluated the electrochemical performance of the hybrid system. This work reports an areal capacitance of 296.7 mF/cm^2 at 1 mA/cm^2 with 88% capacity retention over 1500 cycles [50]. Yingying Huang *et al.* worked on the

preparation of MnO₂/PANI/MWCNT ternary nanocomposite electrode via chemical method and acquired a specific capacitance of about 395 F/g at a current density of 1 A/g having 72% retention after 1000 cycles of charging and discharging [51]. Among CuO-based composite electrodes, a few efforts have been reported regarding the CuO-MWCNT binary nanocomposites for the improved electrochemical performances. Rini Paulose *et al.* tried CuO-MWCNT preparation using the in-situ co-precipitation technique and achieved a specific capacitance of about 452.8 F/g at scan rate 10 mV/s [52]. A study on the fabrication of CuO mesocrystal/ MWCNT composite as an anode material in lithium ion batteries was reported by Junmin Xu *et al.* and revealed a commendable reversible capacitance of 1.11 mA h cm⁻² at 0.39 mA/cm² for the hybrid system after 400 cycles [53]. Niaz Ahmad Niaz *et al.* explored the electrochemical behaviour of CuO/MWCNT composite and reported a specific capacitance value of 810 mA h g⁻¹ with 80.86 % coulombic efficiency [54]. Shivaprasad Chalawadi *et al.* explored the hydrogen gas sensing application of CuO/PANI/MWCNT ternary nanocomposite using green synthesis method and the hybrid exhibited a detection of H₂ gas in concentrations ranging from 110 to 2 ppm at temperatures of 200 and 250 °C [55].

2.2. EXPERIMENTAL SECTION

2.2.1. Synthesis materials

Copper nitrate trihydrate (Cu(NO₃)₂·3 H₂O), urea (CH₄N₂O), ammonium persulfate (APS) ((NH₄)₂S₂O₈) and aniline hydrochloride (C₆H₅NH₂·HCl), analytical grade hydrochloric acid (HCl), sodium sulphate (Na₂SO₄), sodium dodecyl sulphate (CH₃(CH₂)₁₁OSO₃Na) (SDS, > 98%) and de-ionised (DI) water were purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, OD × L = 6 – 9 nm × 5 μm), polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standard and utilized without any further purifications. Distilled ethanol was used for cleaning purposes.

2.2.2. Synthesis of CuO nanostructures

Spherical flower-like CuO nanostructures were synthesised by a simple hydrothermal route. The synthesis process was carried out in a way similar with one previously reported chemical method with slightly different reaction conditions [56]. Initially, 0.3 M copper nitrate trihydrate was dissolved in 50 ml of deionised water which was kept under constant stirring for 30 minutes. Later, 0.6 g of $\text{CO}(\text{NH}_2)_2$ was mixed into the above solution without disturbing the stirring process. Subsequently, the whole 50 ml solution was shifted to a well-cleaned 100 ml Teflon-lined autoclave and which was later kept in laboratory oven at temperature 180°C with reaction time of 24 hours. After the reaction, the sample was preferred to cool spontaneously and collected the black powder by the process of centrifugation. The obtained product was washed 4-5 times in distilled water and twice with ethanol. Finally, the obtained powders were dried in an oven at 80°C for 5 hours before further analyses and use. The whole synthesis process is schematically represented in Fig. 2.1.

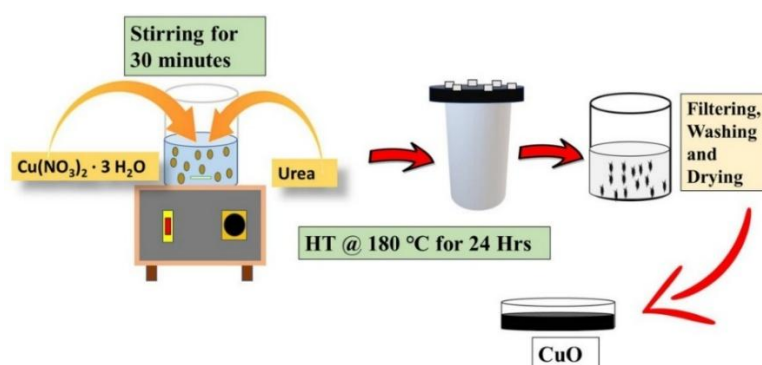


Fig. 2. 1. Schematic representation of CuO preparation.

2.2.3. Synthesis of polyaniline

The synthesis procedure of PANI was followed by a previously reported work with minor modifications in the process conditions [57]. Initially, 2 g of aniline hydrochloride was dissolved in 20 ml of 1 M HCl solution under constant stirring. Simultaneously, 4.04 g of APS was dissolved in 20 ml of 1 M HCl solution in another beaker under stirring. After continuous 30 minutes of stirring, the APS mixture was added drop by drop wise to the aniline hydrochloride solution, and continued the stirring for 2 hours. Thereafter, the whole solution preserved in dark for 24 hours. The

dark green residue obtained from the procedure was then filtered and washed thoroughly with water and ethanol for removing all the unreacted components and excess acids from the product. After that, the as-obtained slurry was stored in cold press in - 120 °C for 1 hour before freeze drying at - 70 °C for 48 hours. A completely dried dark green powder was collected after the freeze-drying process; this is the final PANI nanostructure.

2.2.4. Synthesis of CuO/PANI/MWCNT ternary nanocomposite

The CuO/PANI/MWCNT ternary nanocomposite was prepared by one pot in-situ polymerisation method. First of all, 0.4 g of aniline hydrochloride and 1 g of APS were separately dissolved in 15 ml of 1 M HCl solution. Then, 0.03 g of MWCNT was dispersed in a solvent containing 3 g of SDS and 50 ml DI water under ultra-sonication for 2 hrs. After which the already prepared solution of aniline hydrochloride was added drop by drop to the MWCNT solution under continuous stirring process. Later, 30 mg of as-synthesised CuO nanostructures were added to the aniline-MWCNT mixture and continued the stirring process for 1 hr. Here, the specific weight of metal oxides and all other molar ratios were selected after primary trials, and the chosen ratios were kept the optimum balance between structural properties and ideal electrode characteristics. Then, the APS solution was introduced slowly to the above-mentioned solution and kept for 3 hours constant stirring. The obtained dark green solution was then maintained undisturbed for 24 hours in the dark room at room temperature for the complete polymerisation to occur. Thereafter, the collected dark green residue is subjected to thorough washing using distilled water and ethanol for 5-6 times until all the unwanted species were washed out. After that, the as-obtained slurry was preserved under cold press in - 120 °C for 1 hour before freeze drying at - 70 °C for 48 hours. After completing the freeze-drying stage, a wholly dried dark green powder was collected; this is the final CuO/PANI/MWCNT ternary nanocomposite. This product is named as CPM for the convenience.

2.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, AERIS Research (Source: Cu K α)). Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany)

was employed to determine the vibrational modes of the as-synthesised samples. Fourier transform infrared (FTIR) spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using ZnSe crystal. The surface morphology and elemental composition were done using a combination of High- Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

2.2.6. Electrode preparation and electrochemical studies

The electrochemical features of as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt % of active material, 10 wt % of polyvinylidene fluoride (PVDF) and 10 wt % of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly onto a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in working electrode was 1.5 mg cm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of as-synthesised samples. The as-prepared samples were subjected to studies such as cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) in an operating potential window of 0-0.8 V.

The specific capacitance (F/g) of fabricated electrode materials can be evaluated from the CV curve and GCD plot using the following equations (2.1) and (2.2), respectively;

$$C_s = \frac{\int_{V_1}^{V_2} I(V) dV}{2 K (V_2 - V_1) m} \quad (2.1)$$

$$C_s = \frac{I \Delta t}{m \Delta V} \quad (2.2)$$

Where V_1 and V_2 are the cutoff potentials (volts) in the graph, $I(V)$ is the value of voltametric current (A) in each potential, m indicates the active mass of material (g), $V_2 - V_1$ describes the potential window of CV curve, Δt denotes the discharge time (s) and K signifies the scan rate value in mV/s.

In order to explore the real-time electrochemical performance of the materials, a two-electrode symmetric cell device was used. The gel-type slurry was prepared in a similar manner of three electrode system and pasted in to two pre-cleaned stainless-steel substrates of dimension $2 \times 3 \text{ cm}^2$, which were served as positive and negative electrodes. A filter paper dipped in 1 M Na_2SO_4 electrolyte solution was kept in between these uniformly coated stainless steel electrodes as a separator. The schematic representation of symmetric supercapacitor device was shown in Fig. 2.2.

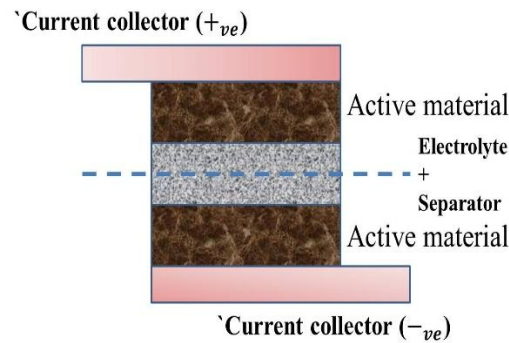


Fig. 2.2. Schematic representation of symmetric supercapacitor device.

The specific capacitance (F/g) can be estimated from the CV and GCD curves of symmetric two-electrode configurations as follows;

$$C_s = \frac{\int_{V_1}^{V_2} I(V) dV}{K (V_2 - V_1) m} \quad (2.3)$$

$$C_s = 2 \frac{I \Delta t}{m \Delta V} \quad (2.4)$$

Where V_1 and V_2 are the cutoff potentials (Volts) in the graph, $I(V)$ is the value of voltametric current (A) in each potential, m indicates the active mass of material (g),

$V_2 - V_1$ describes the potential window of CV curve, Δt denotes the discharge time (s) and K signifies the scan rate value in mV/s. The energy density (E_d) in Wh/kg and power density (P_d) in W/kg was evaluated using the equations (2.5) and (2.6), respectively.

$$E_d = \frac{0.5}{3.6} C_s (\Delta V)^2 \quad (2.5)$$

$$P_d = \frac{E_d}{\Delta t} * 3600 \quad (2.6)$$

The cyclic performance of the electrode materials was conducted at 10 mA applied current for 50000 cycles of charge/discharge in a potential range of 0-0.8 V. The charge storage mechanism of an electrode material can be explained using Dunn's method. According to this, there is possibility of two-type of charge storage mechanisms to happen in a working electrode.

- 1) Capacitive contribution: This is surface controlled charge storage mechanism happens in the surface of electrode material. This type of contribution enables fast charging and discharging and is directly proportional to scan rate (v).
- 2) Diffusive contribution: This is diffusion-controlled charge storage mechanism involving diffusion of ionic carriers in to the bulk of material and is proportional to the square root of scan rate ($v^{1/2}$).

The total current in the electrode system is directly proportional to the scan rate in such a way that;

$$i = av^b \quad (2.7)$$

Where a and b are changeable parameters. The value of b equivalent to the value of slope in $\log v$ vs. $\log i$ graph. From the value of b , the major contributor of capacitive current in the system can be estimated. If the value of b approaches to 0.5, the major charge storage mechanism in the system will be diffusion controlled, whereas if the b value closes to 1, the charge storage mechanism is surface-controlled.

Thus,

$$i = i_{\text{capacitive}} + i_{\text{diffusive}} \quad (2.8)$$

$$i = k_1 v + k_2 v^{1/2} \quad (2.9)$$

$$\frac{i}{v^{1/2}} = k_1 v^{1/2} + k_2 \quad (2.10)$$

Where the parameters k_1 and k_2 can be obtained from the slope and intercept values in the $v^{1/2}$ and $i/v^{1/2}$ plot. The individual capacitive and diffusive contributions can be estimated using the following equations;

$$\text{capacitive contribution (\%)} = \frac{i_{\text{capacitive}}}{i_{\text{capacitive}} + i_{\text{diffusive}}} * 100 \quad (2.11)$$

$$\text{diffusive contribution (\%)} = 100 - \text{capacitive contribution (\%)} \quad (2.12)$$

The columbic efficiency of working electrode can be estimated using the equation;

$$\eta (\%) = \frac{t_d}{t_c} * 100 \quad (2.13)$$

Where t_d and t_c are the discharging and charging times in seconds, respectively.

2.3. RESULTS AND DISCUSSION

2.3.1. X-Ray diffraction (XRD)

Structural characteristics of the obtained CuO, PANI, MWCNT and CuO/PANI/MWCNT were executed by X-ray diffraction with $\text{CuK}\alpha$ radiation of 0.154 nm wavelength. Fig. 2.3 displays the XRD profile of CuO, PANI, MWCNT and CPM which are continuously scanned from 10° to 80° with scanning step of 0.04. The XRD image of CuO shows sharp and narrow diffraction peaks at 32.69° , 35.45° , 35.69° , 38.88° , 38.92° , 48.92° , 53.44° , 58.44° , 61.65° , 66.09° , 66.39° , 68.18° , 2θ were indexed to planes (110), (002), (-111), (200), (111), (-202), (020), (202), (-113), (02-2), (-311), (220) respectively and have shown absolute match with the monoclinic symmetry of tenorite phase of copper oxide having space group C2/c (15) (JCPDS Card no: 80-0076) [58]. No other peaks of supplementary phases were detected, which evince the purity of sample. The intense and furthest tapered behaviour of each peak in the pattern describes the extreme crystallinity of the so-obtained product. The XRD plot of PANI shows characteristic peaks at angles 14.19° , 20.4° , and 25.18° , which are correspond to the crystallographic lattice planes (010), (100), and (110) of PANI in emerald salt form (JCPDS – 060-1167). In case of MWCNT, diffraction peaks were observed at 25.82°

and 42.99° attributed to the (002) and (100) planes of the hexagonal graphite form of MWCNTs (JCPDS-98 005-2230) [52]. The XRD profile of CuO/PANI/MWCNT ternary nanocomposite presents characteristic peaks of PANI, MWCNT and CuO distinctively. The diffraction peaks observed at 14.72° , 19.89° correspond to PANI, whereas the peak at 25.93° becomes representative of PANI/MWCNT combination. Moreover, the peak at 43.05° ascribed to (100) plane of MWCNT. All the dominant peaks of the monoclinic CuO crystal structure were also present in its ternary nanocomposite at 32.41° , 35.40° , 38.71° , 48.75° , 61.61° , 66.48° and 67.96° can be attributed to the planes (110), (002), (200), (-202), (-113), (-311), and (220), respectively. The diffraction peaks of CuO shows small shifts due to the presence of PANI/MWCNT, which confirms the effective fixing of CuO on to the surface of MWCNT that ultimately induce strains to the lattice of CuO [60], [61]. The reason for the decrease in peak intensity of CuO phase in the composite XRD data can be possibly due to the presence of carboxylic and hydroxyl parts. The dominant functional groups present in the ternary composite can effectively slow down proper crystallisation and growth of metal oxides [54].

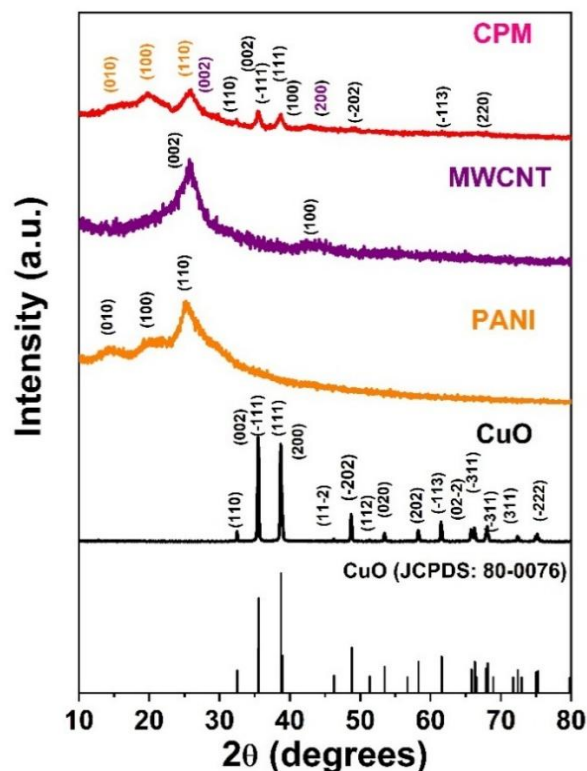


Fig. 2.3. The XRD graph of pure CuO, PANI, MWCNT and CPM nanostructures.

2.3.2. Raman spectroscopy

Raman Spectroscopy is a powerful method to get detailed information about chemical bonds, crystal structure, and phases of the materials synthesised. The three Raman peak positions at 299 cm^{-1} , 349 cm^{-1} and 631 cm^{-1} which are dominant in the spectra are in parallel with the Raman active bands of the monoclinic structure of CuO with C_{2h}^6 (c^2/c) space group. CuO primitive cell consists of two molecular units with 12 vibrational modes. Among these, three are Raman active modes (A_g+2B_g) [62]. Here, Fig. 2.4 (a) illustrates the Raman profile of so-synthesised CuO nanostructures having one dominant peak at 299 cm^{-1} which can be ascribed to the asymmetric stretching mode (A_g) arising due to the in/out phase rotation of CuO structure. Along with that, there exhibit peaks at 349 cm^{-1} and 631 cm^{-1} , which corresponds to the well-known bending mode B_g^1 and symmetric oxygen stretching B_g^2 modes of monoclinic CuO nanostructure. Aside from these three preeminent vibrational modes, a broad peak appears at wavenumber 1133 cm^{-1} , belonging to the multiphonon band of CuO connected with the inharmonic coupling between phonons in polar solids [63]. Moreover, no modes correspond to impurity phases or any possible secondary phases were identified in the spectra. Fig. 2.4 (b) presents the Raman spectrum of ternary nanocomposite CPM, showing an exact combination of prominent modes of CuO, PANI and MWCNT [10], [64], [65], listed in the Table 2.1. The D band (disorder band) of MWCNT were due to lattice defect of the phonon mode of vibration from MWCNT surface and G band (graphite band) resulted from the C–C (vibrational modes) and double-degenerate phonon modes of E_{2g} symmetry of MWCNT. Both these bands undergone slighter shift, which are probably due to the better incorporation of PANI with MWCNT. The G' band that appeared in the spectrum is an overtone of the D band and is associated with stacking alignment of graphene layers [66]. The less intense A_g , and B_g^2 vibration modes of CuO are clearly visible in the spectra.

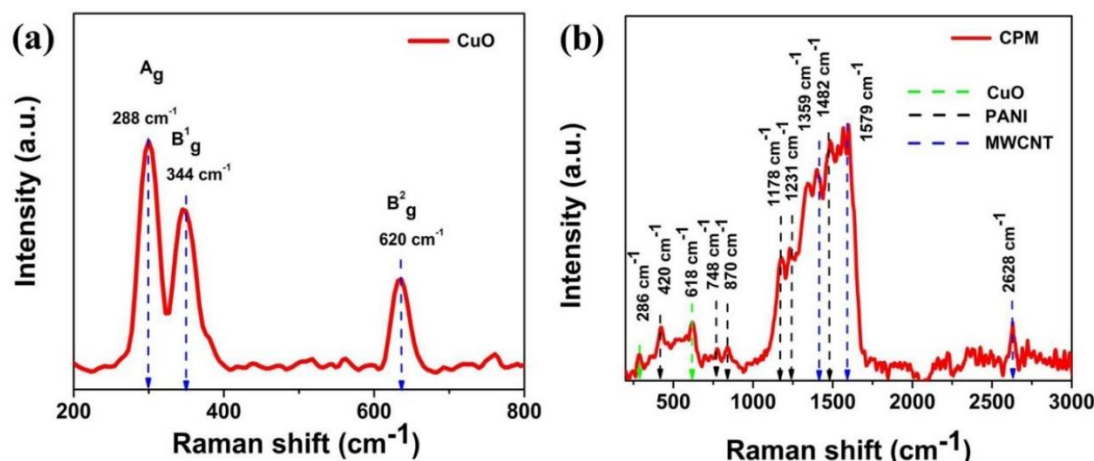


Fig. 2.4. Raman spectra of as-synthesised (a) CuO and CPM nanostructures.

Table 2.1. List of assignments of dominant characteristic bands appeared in CPM nanocomposite

Raman modes (cm ⁻¹)	Assignments
286 cm ⁻¹	A _g mode of monoclinic CuO
618 cm ⁻¹	B _g ² mode of monoclinic CuO
420 cm ⁻¹	Out of plane C–H wag in bi-polaronic
748 cm ⁻¹	Imine deformation of quinoid ring
870 cm ⁻¹	Ring deformation of benzenoid ring in emeraldine salt
1178 cm ⁻¹	C–H bending of benzenoid ring
1231 cm ⁻¹	C–H bending of quinoid ring
1482 cm ⁻¹	C=N stretching in quinoid ring
1359 cm ⁻¹	D- band of MWCNT
1579 cm ⁻¹	G-band of MWCNT
2628 cm ⁻¹	G' band of MWCNT

2.3.3. FT-IR spectroscopy

The FT-IR spectroscopy helps to detect the fundamental molecular vibrations of functional groups that occur in a material; also, it can be easily observe the minor structural changes that may happen in material compositions. Fig.2.7. (a) illustrates the FTIR spectral image of CuO spherical nanostructures. The adsorption

peaks at 596 cm^{-1} , 541 cm^{-1} , and 414 cm^{-1} were confirmed the formation of the monoclinic crystal structure of CuO flower-like nanostructures (shown in the inset of Fig. 2.5. (a)). These three bands in the fingerprint area of IR spectrum assigned to the Cu-O stretching modes along $[-202]$ and $[202]$ planes [67]. Upon comparison with previous literatures [68] [69], slight shift in the characteristics peaks can be ascribed to size-induced lattice variations as well as stress and defects appeared in the crystal structure [70]. The additional bands that appeared in the range of $800\text{--}1300\text{ cm}^{-1}$ were connected with OH bending vibration and C–H stretching, which indicate the presence of hydroxyl group [71]. Besides these dominant bands, no infrared active modes associated with other phases of copper oxide, like band at 615 cm^{-1} associated with Cu_2O , appeared in the spectrum which thereupon affirm the exceptionally pure tenorite phase of copper oxide [72]. In the case of FT-IR spectra of CPM nanocomposite (shown in Fig.2.5. (b)), a numerous number of vibrational modes appear representing the correct formation of CuO/PANI/MWCNT, which are listed in Table 2.2 [73], [74]. The minor shifts in the characteristic peaks of quinoid and benzenoid rings of PANI may attributed to the interactions like hydrogen bonding between NH group of PANI and metal oxide surface [75].

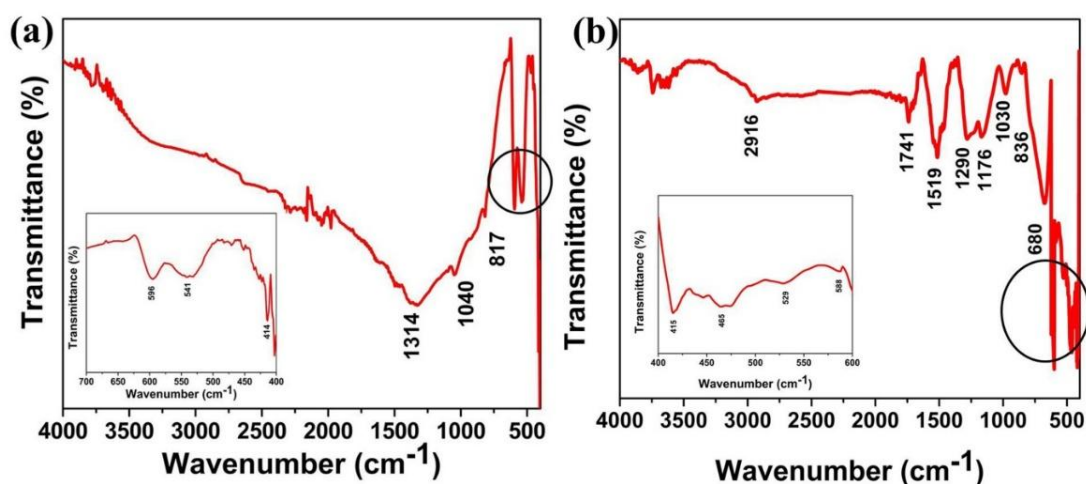


Fig. 2.5. FT-IR spectra of (a) CuO nanostructure and (b) CPM (insets shows the enlarged image of FTIR spectrum of (a) CuO in the wavenumber range $700\text{--}400\text{ cm}^{-1}$ (b) CPM in the wavenumber range $600\text{--}400\text{ cm}^{-1}$).

Table 2.2. List of peaks in FT-IR spectrum of CPM and its assignments.

FT-IR peaks	Assignments
2916 cm ⁻¹	asymmetric/ symmetric methylene stretching bands from PANI
1741 cm ⁻¹	stretch mode of carboxylic groups in MWCNT
1519 cm ⁻¹	C=C stretching in quinoid ring of PANI
1290 cm ⁻¹	C-N for aromatic amines in the polaron structure of conducting PANI
1176 cm ⁻¹	characteristic band of the protonated form of conducting PANI
1030 cm ⁻¹	due to protonated imine group in PANI
836 cm ⁻¹	out of plane C-H bending vibration.
400-600 cm ⁻¹	stretching vibrations of Cu-O

2.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The surface morphology of the CuO nanostructures was assessed with the help of FESEM, as shown in Fig. 2.6. Size determination of grains was established with the help of ImageJ software. From the inspection of Fig. 2.6 (a) and (b), it can be easily perceived that the CuO powders were constituted of well-defined spherical marigold flower-like structures having an average diameter of $10 \pm 2 \mu\text{m}$. Moreover, the high magnification FESEM image (Fig. 2.6 (c)) clearly shows that each spherical micro-flower was composed of several dozens of well-organized nanopetals. The densely packed nanopetals are interconnected together to form a 3D-flower like architecture. Each petal-like CuO structure has a length of $\sim 450 \text{ nm}$, width $\sim 200 \text{ nm}$ and thickness about $\sim 70 \text{ nm}$. The uniform distribution of nanopetals to form the marigold flower-like structure with abundant tiny pores and crevices in between contribute to the enhancement in volumetric specific surface area, which eventually induce a positive impact on the electrochemical capacity of pristine CuO. The quantitative elemental composition survey was carried out using EDS technique, which is plotted in Fig. 2.6

(d). The CuO exposed a Cu:O ratio of 53.81 : 46.19 in EDS data, which is in accordance with the stoichiometry distribution of cupric oxide [76].

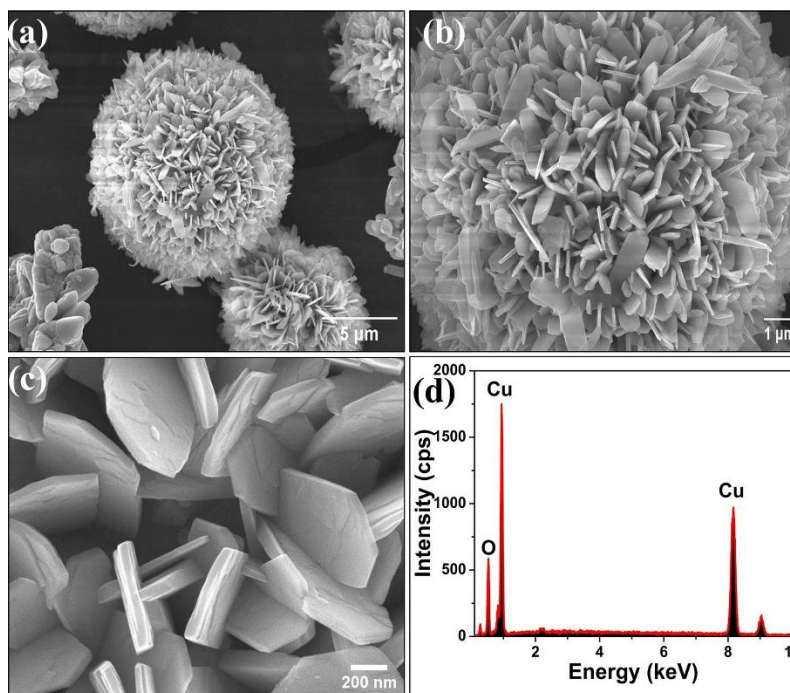


Fig. 2.6. (a-c) Low magnification SEM images of as-prepared CuO (d) EDS spectrum of CuO.

Furthermore, EDS chemical mapping was employed for the close interrogation of material to ascertain its chemical nature. Unsurprisingly, a sectional inspection of the EDS images in Fig. 2.7 revealed the homogeneous distributions of Cu and O atoms in the CuO crystal lattice, as understood from the chemical synthesis.

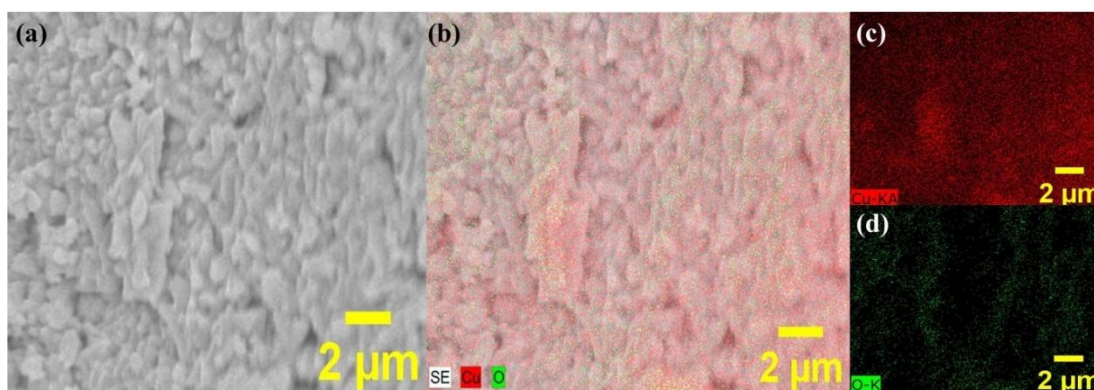


Fig. 2.7 (a) SEM and (b) EDS mapping images of CuO nanostructures, (c & d) elemental distribution of Cu and O in the area shown in images a.

The morphological analysis of CuO/PANI/MWCNT ternary nanocomposites was presented in Fig. 2.8 (a-c). The low magnification SEM images display a spongy appearance of nanocomposite with large number of porous frameworks. The voluminous pores in between the interconnected regions of composite will surely strengthen their effective surface area and boost its electrochemical performances. The incorporation of MWCNT to CuO transformed the spherical flower-like morphology of CuO in to a 3-D porous framework of several interconnected electro-conducting groups, which enables a smooth and productive contact between electrode material and electrolyte [54]. These conductive networks facilitated better ionic transportations and leading to superior electrochemical performance. There may be a synergistic effect of CuO, PANI and MWCNT in the matrix through hydrogen bond and $\pi - \pi^*$ interactions and which can mutually boost the overall electric conductivity and electrochemical performance of nanocomposite electrode [42]. The EDS plot of CPM was displayed in Fig.2.8 (d), clearly showing the presence of carbon, nitrogen, oxygen and copper in the composite. It is visible that the carbon content (76.98 wt%) is the dominating one compared with the metal oxide part.

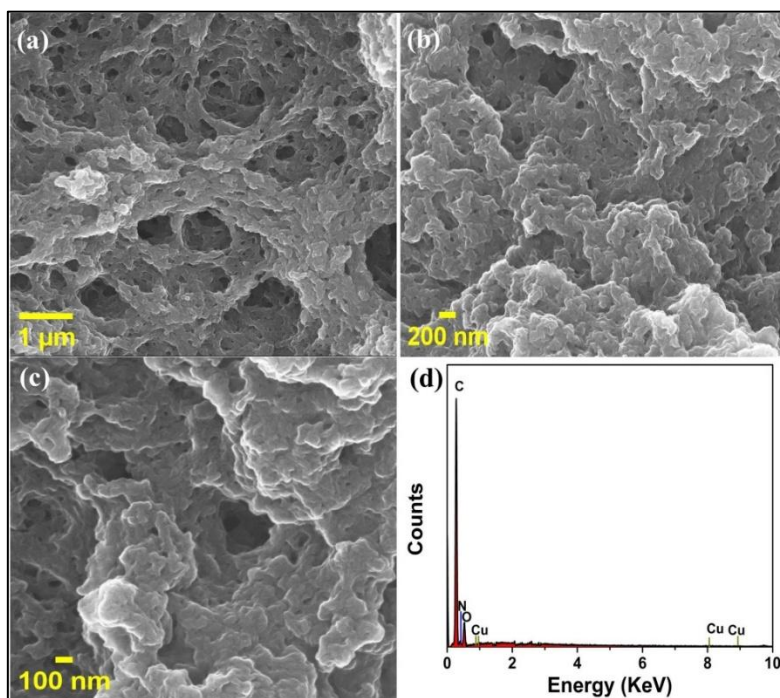


Fig. 2.8. (a-c) Low magnification SEM images (d) EDS spectrum of CPM.

The EDS mapping images of CPM nanocomposite was presented in Fig. 2.9 (a-b). The distinctive elemental distribution was shown in Fig.2.9 (c-f), indicating the presence of elements C, N, O and Cu in the composite matrix.

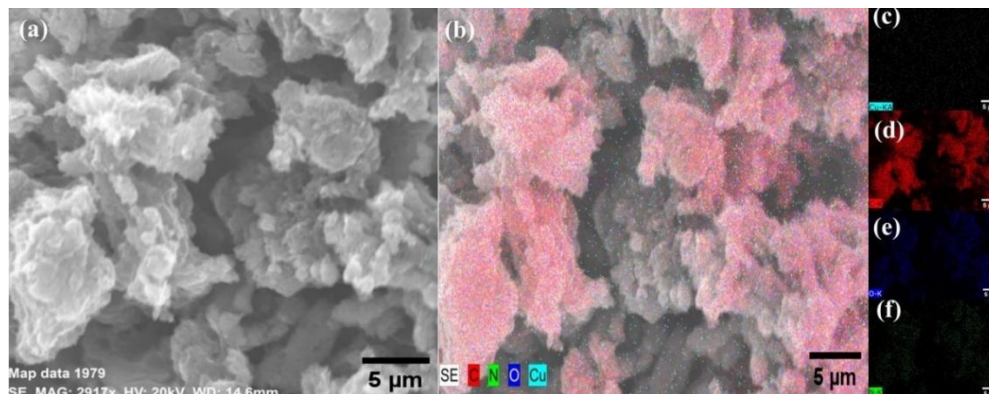


Fig. 2.9 (a) SEM and (b) EDS mapping images of CPM nanocomposites, (c-f) elemental distribution of C, N, O and Cu in the area shown in images (a & b).

2.3.5. High Resolution Transmission electron micrographs (HR-TEM)

In conjunction with FESEM analysis, the morphology of pristine CuO was more inspected using HRTEM imaging techniques, as presented in Fig. 2.10. Fig. 2.10 (a-b) shows the HRTEM image of CuO with their corresponding SAED pattern. The SAED patterns discerned to the fact that the prepared samples were in monoclinic phase of copper oxide, which is in good accordance with the inferences from XRD. Almost all the prominent peaks of monoclinic CuO symmetry can be well indexed to the rings observed in SAED plot. The lattice resolved TEM images in Fig. 2.10 (c-f) presents the planes (-111), (111), (110), and (-202) with their measured d-spacing values 0.253 nm, 0.235 nm, 0.272 nm, and 0.185 nm respectively. These calculated d-spacing outcomes were satisfactory with those in the SAED pattern. Besides, lattice resolved TEM image of plane (111) with d value 0.232 nm and its corresponding profile plot image were illustrated in Fig. 2.10 (g-h). From the aforementioned experimental analysis including XRD, HRTEM, SAED, FFT and profile plot, d-spacing value for the dominant plane (111) were compared and presented in Table 2.3.

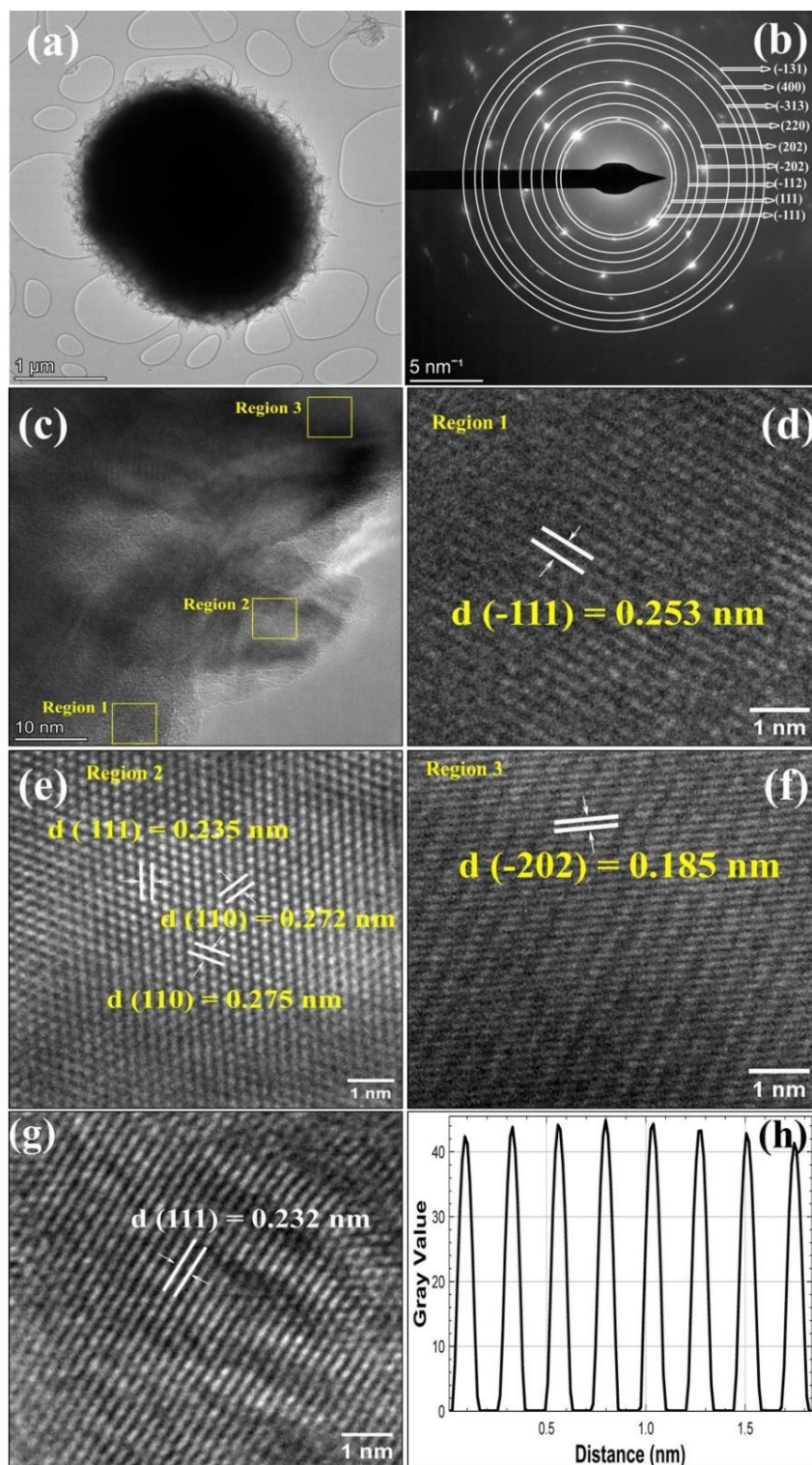


Fig. 2.10 (a) TEM images of CuO nanostructures (b) selected area diffraction patterns of CuO (c-f) lattice resolved HRTEM images of CuO (g-h) lattice resolved HRTEM image of plane (111) and its corresponding profile plot.

Table 2.3. Comparison of d-spacing values of crystal plane (111).

Plane	d_{XRD} (nm)	d_{SAED} (nm)	d_{HRTEM} (nm)	d_{FFT} (nm)	$d_{\text{profile plot}}$ (nm)
(111)	0.232	0.238	0.232	0.23	0.229

The microstructural features of CuO/PANI/MWCNT were further examined by TEM, HR-TEM and SAED images shown in Fig. 2.11. The TEM image of CPM (shown in Fig. 2.11 (a)), presents a fibrous framework of all the constituents as similar as in the FESEM images. The MWCNT network shown in the HR-TEM image, displayed in Fig. 2.11 (b), possess an average diameter of 8-10 nm. Lattice fringes of CPM composite was clearly presented in Fig. 2.11 (c), consist of fringes having d-spacing value of about 0.252 nm attributed to the (111) plane of CuO. The SAED pattern of nanocomposite (Fig. 2.11 (d)) displays brighter concentric rings that correspond to the polycrystalline nature of CPM composite.

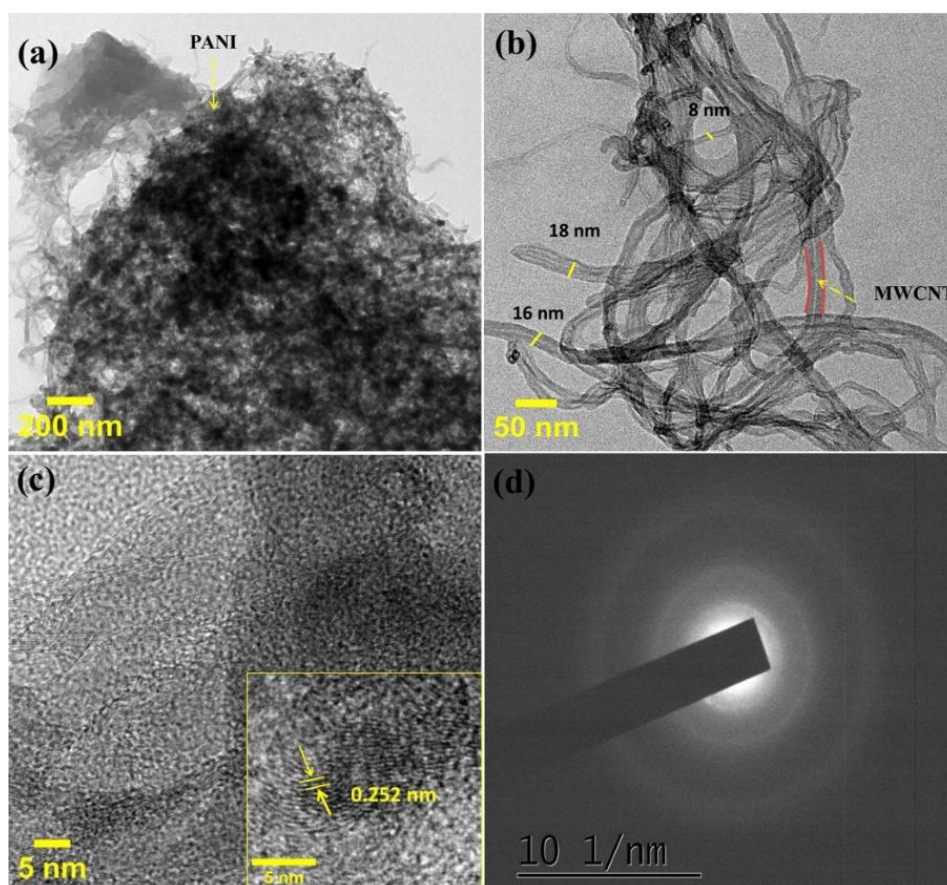


Fig. 2.11 (a) TEM images (b) HR-TEM images (c) lattice resolved HRTEM images (inset shows the lattice fringes of (111) plane of CuO) (d) selected area diffraction patterns of CPM nanocomposite.

2.3.6. X-Ray Photoelectron Spectroscopy (XPS)

The XPS analysis of pure CuO and CuO/PANI/MWCNT composite were conducted to examine the chemical composition, oxidation states and chemical states of the material. Fig. 2.12 (a) shows the XPS survey of CuO with characteristic peaks of Cu 2p and O 1s. Fig 2.12 (b-c) presents the high resolution spectra of elements Cu and O. The peaks observed at 933.8 eV and 953.5 eV (Fig 2.12 (b)) correspond to the Cu 2p_{3/2} and Cu 2p_{1/2} states of Cu²⁺ in CuO nanostructure. A spin energy separation of 19.7 eV was observed between the states [37]. Moreover, the three satellite peaks spotted at 941.3 eV, 943.6 eV and 962.5 eV were also detected, which confirms the formation of the CuO nanostructures. In the elemental XPS spectrum of O 1s (Fig. 2.12 (c)), a peak at 529.7 eV can be attributed to the Cu-O bond. Furthermore, the peak at 531.2 eV corresponds to the oxygen vacancies (V_o) present in the lattice [78].

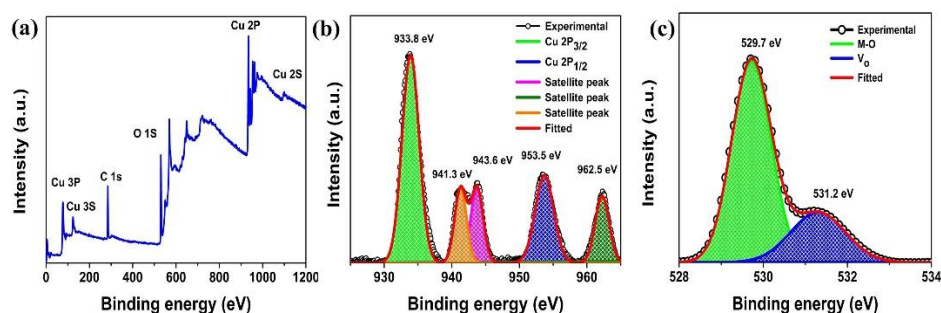


Fig. 2.12. (a) XPS survey spectrum and XPS elemental spectra of (b) Cu 2p and (c) O 1s in CuO nanostructures.

The survey scan of CuO/PANI/MWCNT was presented in Fig. 2.13 (a), having characteristic peaks of Cu 2p, O 1s, C 1s, and N 1s, which confirm the elemental blend of CuO with PANI and MWCNT. The peaks located at 284.3 eV, 285.1 eV and 287.4 eV of the C 1s core level spectrum shown in Fig. 2.13 (b) can be attributed to Sp² carbon bonding, Sp³ carbon bonding and >C=O- bond of C 1s state [79]. The XPS spectra of N 1s displayed in Fig. 2.13 (c), presents three prominent peaks at 399 eV, 400.1 eV and 401.6 eV representing benzenoid imine (=N-H-), positively charged imine (-N-H-), and protonated amine (-N-H⁺-) of PANI [80]. The high-intense notable peaks of benzenoid imine and -N-H- bond indicate the occurrence of healthy interactions between PANI and MWCNT. In Fig. 2.13 (d), the major peaks of Cu²⁺ states were located at 933.6 eV and 953.5 eV representing Cu 2p_{3/2} and Cu 2p_{1/2}. The energy gap of 19.9 eV between these spin energy coupling orbits confirms the presence

of Cu^{2+} , thereby the occurrence of CuO form in the ternary composite. Along with this, two shake-up peaks were also observed at 943.3 eV and 963.2 eV [49]. In the case of O1s in CPM composites (Fig. 2.13 (e)), peaks were observed at 531.5 eV and 532.5 eV, correspond to oxygen vacancies and M-OH bonds, respectively [78].

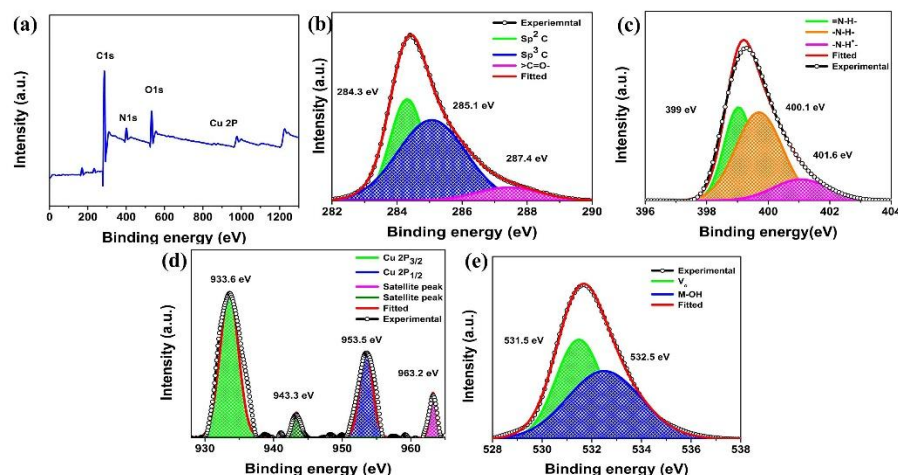


Fig. 2.13. (a) XPS survey spectrum and XPS elemental spectra of (b) C 1S, (c) N 1S (d) Cu 2P (e) O 1s of CPM nanocomposite.

2.3.7. Brunauer-Emmett-Teller (BET) analysis

Figure 2.14 (a-b) shows the N_2 adsorption-desorption isotherm plot and pore size distribution (PSD) of CuO nanostructures. The Brunauer-Emmett-Teller (BET) method was carried out for the tabulation of specific surface area and Barrett-Joyner-Halenda (BJH) equation was employed for the PSD calculations. The BET specific surface area of the CuO product was estimated as $\sim 29.29 \text{ m}^2/\text{g}$. The plateau region in the isotherm plot relates to the monolayer coverage of surface area, whereas the steep portion gives details about the initial level of adsorption and surface accessibility [38]. The plot indicates that the adsorption isotherm of CuO is type IV with H3 hysteresis according to IUPAC classification, which commonly occurs in mesoporous materials. The results show that the sample material has a network of interconnected pores having pore diameters in the domain of 2-50 nm. The PSD of CuO nanostructures in the Fig. 2.14 (b) confirm the mesoporous nature with an average pore volume and diameter of $\sim 0.097 \text{ cm}^3/\text{g}$ and 12.89 nm respectively. The PSD maxima of the sample centered at two different pore radii, which are $\sim 1.26 \text{ nm}$ and $\sim 5.62 \text{ nm}$. Here, the nanopetal like CuO particles interconnected unevenly to create tiny pores in between to form the microflower architecture. This type of surface morphology with sufficient surface area

and well-developed pore structures are commendably compliments the electrochemical performance of the prepared product since the pore channels can themselves act as a clear route for the active electrolyte transport and boosts the electrochemical reactions by providing more and more active sites. The N₂ adsorption-desorption isotherm plot and pore size distribution (PSD) of CuO/PANI/MWCNT composite were shown in Fig. 2.14 (c-d). The average specific surface area of the composite was $\sim 48 \text{ m}^2/\text{g}$. The plot indicates that the adsorption isotherm of the composite is also type IV with H3 hysteresis. The results show that the composite material has a network of interconnected pores having pore diameter in the domain of 2-50 nm. The PSD of composite material shown in the Fig. 2.14 (d) confirms the mesoporous nature with an average pore volume and diameter of $\sim 0.33 \text{ cm}^3/\text{g}$ and 8.7 nm respectively. The moderate increase of surface area of the composite material, despite the intrinsically high surface area of MWCNTs, may due to the encapsulation of metal oxides and PANI over the surface of nanotubes of MWCNTs. As evidenced by SEM and TEM observations, this coating can partially block the accessible pores of composite material and eventually limits the contribution of MWCNTs to the effective BET surface area.

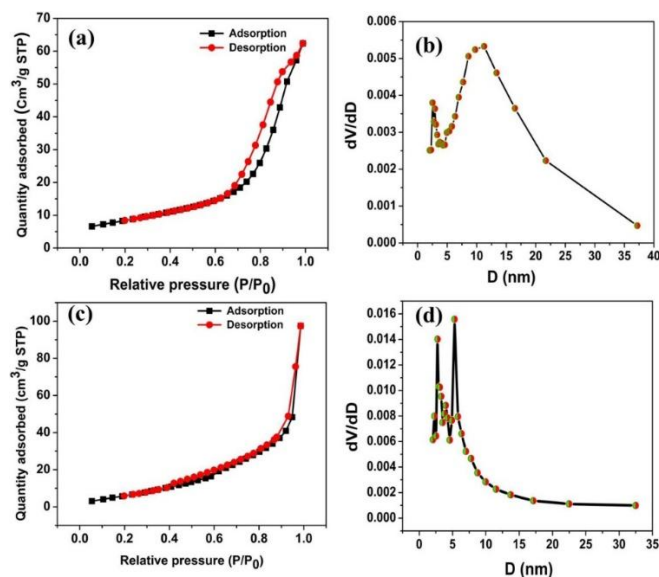


Fig. 2.14. N₂ adsorption-desorption isotherm plot and the pore size distribution graph of (a,b) CuO (c,d) CPM composite.

2.3.8. Thermo-gravimetric Analysis (TGA)

Thermal stability of electrode material is an indispensable quality for attaining authentic supercapacitors [81]. The thermal stability of synthesised materials was

investigated through TGA-DTA analysis, presented in Fig. 2. 15. The reasonable thermal stability of CuO and MWCNTs were evident from the plot, since the total weight loss are only 7.18% and 6.19% for CuO and MWCNTs over 700 °C, respectively. The TGA curves of PANI and CuO/PANI/MWCNT show three step decomposition process. From the room temperature to 150 °C, both PANI and CPM samples suffers a weight loss of about 12 %, which is accounted for the loss of moisture from the materials [82]. The second stage of decomposition phase starts from a temperature of 150 °C to 340 °C, a weight loss of about 38% for PANI and 35 % for CPM happened due to elimination of acid components (HCl) and the initial thermal decomposition of PANI in to its monomer, oligomer, dimer, and trimmer forms. In the third and most significant stage of decomposition, the real breakdown of PANI happens and suffers a weight loss of 12% for CPM and 19% for PANI until the temperature 530 °C, attributable to thermal decomposition of oligomer, dimers, and trimmer forms of PANI [83]. At 700 °C, a residue mass of PANI and CPM were estimated to be 35.82 % and 28.25 %, indicating the improved thermal stability of CuO/PANI/MWCNT than that of PANI due to the synergistic effects of CuO and MWCNTs. The strong interactions of thermally resistant CuO with PANI, combined with the mechanical strength of MWCNTs contributes to the effective enrichment in the thermal stability of composite system [84], [85].

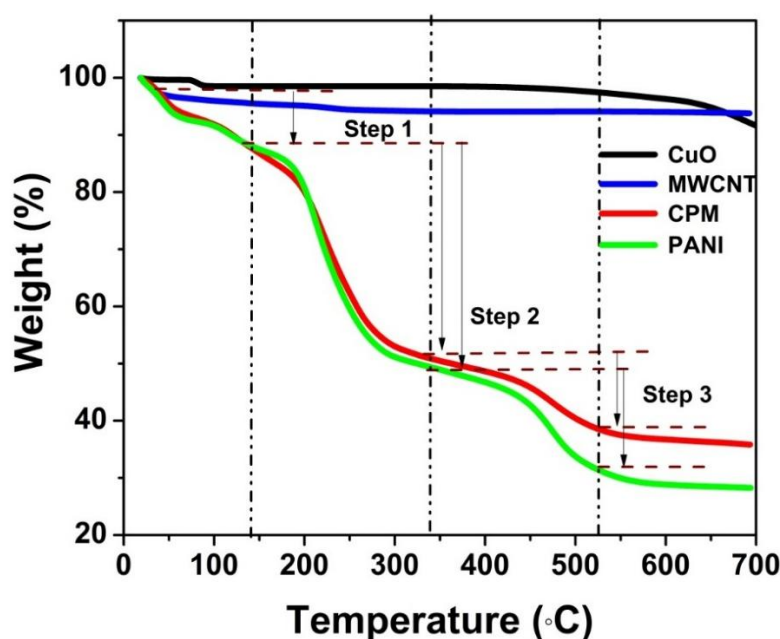


Fig. 2.15. Thermogravimetric analysis of CuO, MWCNT, PANI and CPM composite.

2.3.9. Electrochemical studies

2.3.9.1. Cyclic voltammetry (CV)

The cyclic voltammetry (CV) of as-synthesised materials was established to evaluate the supercapacitive performance and their corresponding potentiality in the energy storage field. Initially, the performance of CuO as working electrode was studied using two different electrolytes – an alkaline electrolyte (5M NaOH) and a non-corrosive neutral electrolyte (1M Na₂SO₄). Fig. 2.16 shows the respective cyclic voltammetric curves of CuO in three electrode configurations with electrolytes- NaOH and Na₂SO₄. The electrochemical performance of CuO with NaOH electrolyte were analysed in voltage window of 0-0.45 V, whereas the same with Na₂SO₄ in a potential range of 0-0.8 V. From the figure, it is evident that the performance with NaOH electrolyte does not produce significant capacitance value compared with that of Na₂SO₄. pH factor has greater influence in the charge transfer mechanisms in the electrochemical set up since it alters the ionic conductivity and mobility of charge carriers [86]. Here, the area under the CV curve produced by the electrode material with alkaline electrolyte is very low compared with that of with the neutral medium, which implies that CuO suffered greater charge transfer resistance with alkaline electrolytes. Hence, further electrochemical studies were executed in Na₂SO₄ electrolyte to get better results.

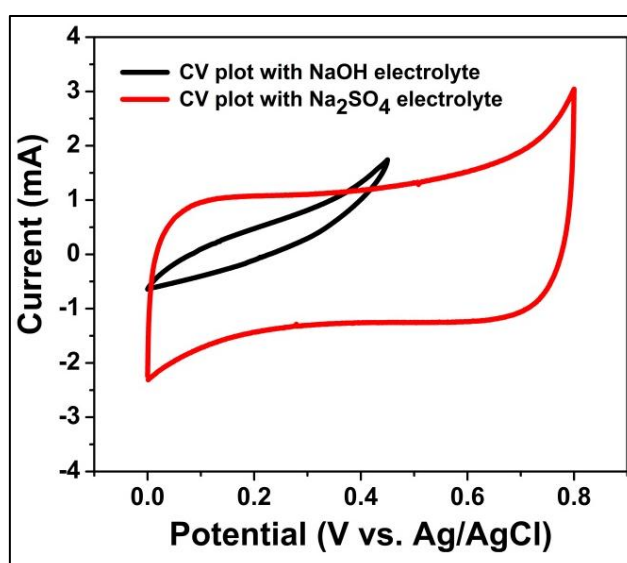


Fig. 2.16. CV curves of CuO electrode with two different electrolytes at 10 mV/s.

The detailed electrochemical measurements of electrode materials were carried out in a three-electrode configuration using 1M Na₂SO₄ as electrolyte solution. Fig. 2.17 depicts the cyclic voltammetry graph of CuO and CuO/PANI/MWCNT electrodes at distinct scan rates from 5-100 mV/s in a voltage window of 0 - 0.8 V. Unsurprisingly, the voltametric current was increasing with the scan rate which is a key feature of an ideal capacitor [87].

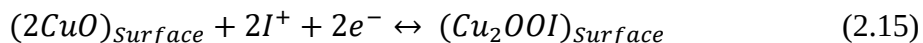
The CV curve of CuO follows a shape seemingly close to an ideal rectangular one without any noticeable redox peaks, whereas that of the composite electrode presents a quasi-rectangular shape. The non-rectangular shape of CV curves clearly indicates that both the materials possess very distinctive capacitive characteristics from that of electric double layer capacitors. The composite sample exhibits a pair of redox peaks at (0.43/0.2 V) at lower scan rates due to the presence of PANI. This redox peak can be attributed to the leucoemeraldine (LE) transition to Emeraldine (E) in PANI samples [88]. There is a redox peak shift while increasing scan rates, which indicates that MWCNTs and PANI enhanced the redox properties of the nanocomposite.

In neutral aqueous electrolytes like Na₂SO₄, there may be two possible charge storage mechanisms occur in the system [13]:

(1) Intercalation and de-intercalation of cations H⁺ or Na⁺ during redox reactions,



(2) Adsorption of ions into the surface of active material.



Where I can be either H⁺ or Na⁺ ions. Here, the quasi-rectangular CV curves of samples shown in Fig. 2.17 points to the process of charge storage through intercalation and de-intercalation of ions in the active materials. Furthermore, shape of a voltametric plot is deeply influenced by the nanostructure of material, its specific surface area and porosity [34]. Unsurprisingly, with the scan rates increase, the area under the CV curves also increases. The direct proportionality of voltametric current with the scan rates is one of fundamental characters of ideal capacitor [89]. At lower scan rates, ionic diffusion process is enriched due to greater access of active pores in electrode material

by the electrolyte ions complimenting the insertion process of protons, which eventually enhances the redox reactions [90].

The CuO working electrode showed a specific capacitance of 123 F/g at a scan rate of 10 mV/s and 47 F/g at a scan rate of 100 mV/s. The CuO/PANI/MWCNT nanocomposite delivered a capacitance value of 478 F/g at 10 mV/s and 106 F/g at 100 mV/s. Higher value C_s at lower scan rates (< 30 mV/s) is the indication of maximum use of active surface area by the ions for charge storage occurred at lower scan rates [91]. From the comparison of CV curves of CuO and the composite electrode materials (Fig. 2.17 (c)), it can be seen that there is an effective increase of voltametric current in the case of nanocomposite material compared with pure CuO. The increase in current indicates the better utilisation of electrode material through effective ionic diffusion, as a consequence of the enhanced surface area and porosity of nanocomposite. In addition to large surface area, occurrence of uniform and stable pore structure also makes remarkable advantage in its electrochemical properties. The pore network present in CuO/PANI/MWCNT allows smooth mass transport of ionic or electronic charge carriers and also raises the accessibility of electrode material to the electrolyte medium. Generally, in the case of mesoporous materials, the effect of large number accessible electro-active areas is directly correlated with its capacitive currents [92].

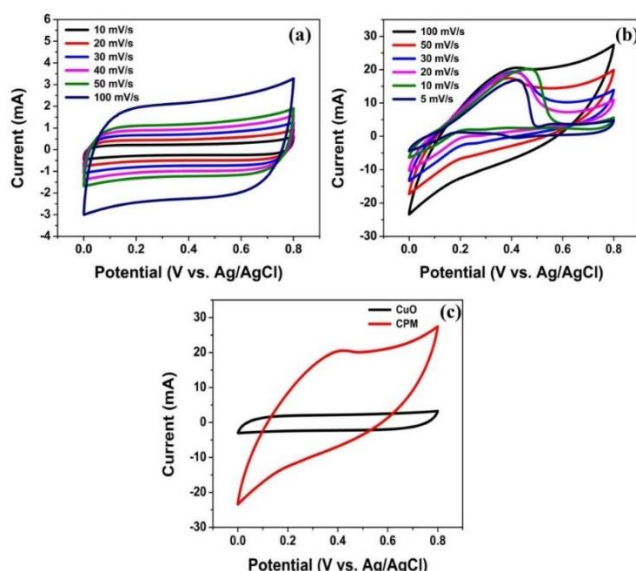


Fig. 2.17. CV plot of (a) CuO electrode and (b) CPM composite electrode at varying scan rates, (c) comparison of CV cure of CuO and CPM at a scan rate of 100 mV/s.

Equations (2.6-2.11) were utilised to figure out the capacitive and diffusion-controlled contributions, which are separate and actively present at each potential, involve in the total current production during the electrochemical reactions. Fig. 2.18 deals with the charge storage mechanism analysis of pristine CuO using power law and Dunn's method. The plot between scan rate and peak current at a specific potential 0.4 V, as shown in Fig. 2.18 (a), shows the linearity in the fitted data with a value of slope approaching to one. Thus, the dominance of capacitive contribution in the overall charge storage mechanism is confirmed. This capacitive contribution mainly arises from the surface-controlled redox reactions results in faster reaction kinetics. The surface-controlled pseudocapacitance can lead to efficient and reliable energy storage capacities with remarkable cyclic performances [93]. The $v^{1/2}$ vs. $i/v^{1/2}$ plot helps to estimate values of k_1 and k_2 , thereby distinguishing between the capacitive and diffusive controlled contributions in percentage (Fig. 2.18 (b)). The calculated values of k_1 and k_2 are 3.01 and -2.95, respectively. The analysis indicated that the surface-controlled redox reactions were 85 % for the CuO working electrode at 10 mV/s (Fig. 2.18 (c)). The shaded region shows the diffusion-controlled contribution in the storage mechanism at lower scan rate. It is noticeable that with the increasing scan rates, the diffusion part contribution gets diminished and recorded as 2 % at 100 mV/s (Fig. 2.18 (d)), can be attributed that the time at the higher scan rates were enough to occur the diffusion/intercalation of electrolyte ions [94].

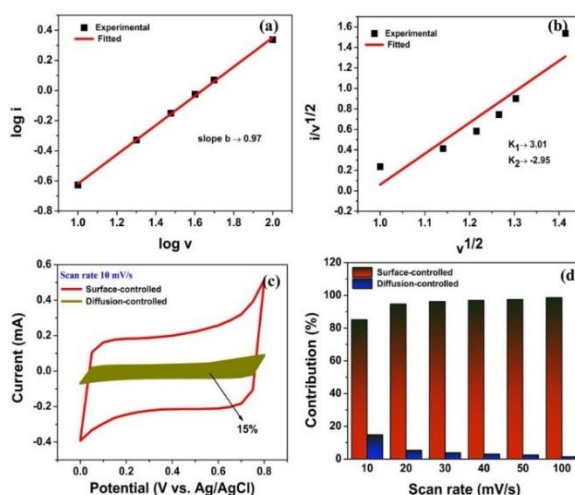


Fig. 2.18 (a) scan rate vs. peak current plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ diagram (c) decoupling of diffusion and capacitive contribution in CuO working electrode at scan rate 10 mV/s (d) capacity contribution analysis of CuO at varying scan rates.

The diffusive and capacitive contributions in the CPM working electrode were evaluated using power law and Dunn's method, were portrayed in Fig. 2.19. The linear plot between scan rate and peak current 0.4 V was observed in the Fig. 2.19 (a), suggesting a slope of 0.66. This indicates the importance of both capacitive and diffusive contributions in the overall charge storage, with slighter major part from the surface-controlled redox reactions since the value of b higher than five. The values of parameters k_1 and k_2 were found to be 2.130 and -15.58, respectively estimated from the plot between $v^{1/2}$ and $i/v^{1/2}$ (Fig. 2.19 (b)). Using these parameters the capacitive and diffusive contributions in the CPM working electrode were distinguished and presented in Fig. 2.19 (c). The shaded region indicates the diffusive contribution as 13 % at a scan rate of 10 mV/s. Just like CuO, CPM electrode also shows a decline of diffusive contribution part with increasing scan rates (Fig. 2.19 (d)).

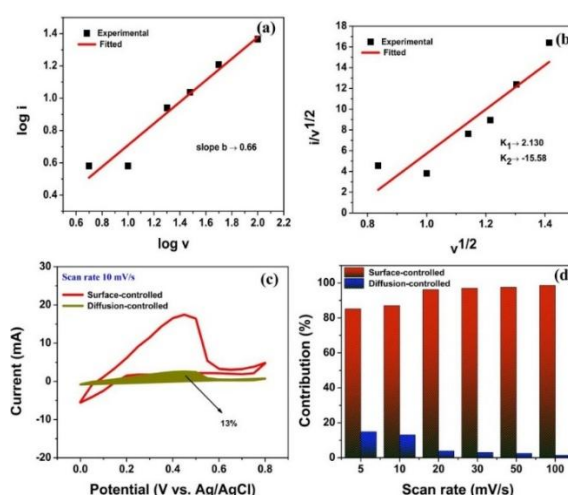


Fig. 2.19 (a) scan rate vs. peak current plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ diagram (c) decoupling of diffusion and capacitive contribution in CPM working electrode at scan rate 10 mV/s (d) capacity contribution analysis of CPM composite at varying scan rates.

2.3.9.2. Galvanostatic charge/discharge (GCD) studies

The electrochemical performance of CuO and CuO/PANI/MWCNT electrodes was then determined with constant galvanostatic charge/discharge (GCD) measurements at discrete current densities, which is shown in Fig. 2.20 (a,b). The GCD curves show good symmetry having nearly ideal triangular shapes at all current densities, which exemplifies the notable capacitive response of both electrode materials for supercapacitor applications [35]. A small voltage drop was visible in the discharge

curves of composite sample, possibly due to the internal resistance of the electrode material. Additionally, PANI based electrode materials have visible influence on this IR drop [95]. The higher discharge time of the composite electrode in comparison with pure CuO, indicating the enhanced electrochemical behaviour. The calculated values of specific capacitance are plotted in the Fig. 2.20 (c,d). At current densities of 0.3 A/g, 0.5 A/g, 2 A/g and 3 A/g, CuO electrode obtained capacitance values of 141 F/g, 94 F/g, 70 F/g, and 67 F/g respectively. Whereas, the composite electrode obtained capacitance values of 516 F/g, 259 F/g, 113 F/g, and 20 F/g at current densities 0.5 A/g, 1 A/g, 3 A/g and 5 A/g, respectively. The sharp decline of specific capacitance values at higher current densities may due to the ineffective utilization of deeper active sites, as ions lack sufficient time to diffuse and transport under rapid cycling conditions. In addition, the major two elements in the composite material, that is CuO and PANI, were pseudocapacitive and inherently have slow charge storage mechanism compared to double-layer charging, which limits the rate capacity of composite electrode. This improved specific capacitance of composite sample is the result of combined features of metal oxide, PANI and MWCNT, owing to the fact that PANI and MWCNT framework together provides a conductive pathway in the overall electrochemical process. The efficient and uniform growth of PANI over the surface of CuO and the sufficient supply of electro-active sites by MWCNT were positively enriched the electrochemical behaviour of the ternary composite electrode. Although the capacitance value of electrode material gets improved by the incorporation of PANI and MWCNT, it is still less compared to the theoretical capacitance of CuO, likely due to the presence of electrochemically inactive “dead mass”. The structural instability of PANI, which undergoes swelling and contraction during cycling may cause obstacles to the ionic transport and reduces the active participation of electrode material. Furthermore, the interfacial resistance created in hybrid material combined with their relatively thicker composite layers restricts deeper penetration of electrolyte ions into the active sites of CuO.

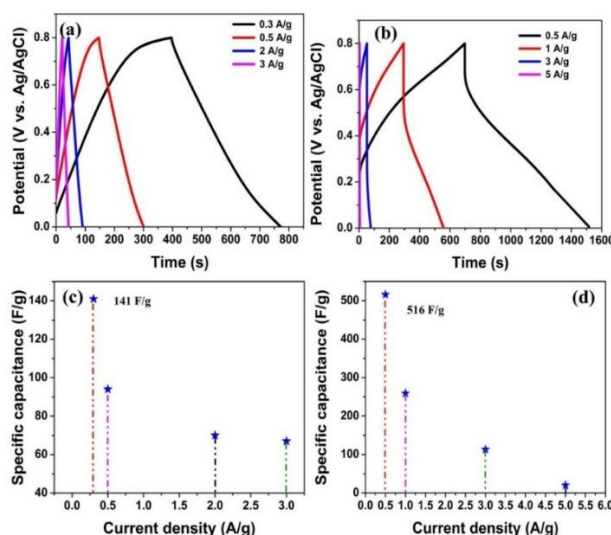


Fig. 2.20. GCD graph of (a) CuO electrode and (b) CPM composite electrode at varying current densities, variation of specific capacitance with current density for (c) CuO and (d) CPM electrodes.

2.3.9.3. Electrochemical impedance spectroscopy (EIS)

The EIS study of the CuO and CPM electrodes, in terms of the Nyquist diagram, was conducted in the frequency window of 100 kHz to 100 mHz with an AC voltage of 10 mV to investigate the complex interfacial electronic features at the electrode-electrolyte juncture, which was illustrated in Fig. 2.21 (a). Unsurprisingly, the Nyquist plot presents a distorted semicircle in the higher frequency region tailed by a straight spike in the lower frequency side. The depressed semicircle is a clear indication of redox reactions taken place between Cu^{2+} and Cu^+ . The supercapacitive behaviour of CuO electrode is evidently seen from the sharp increase of imaginary part of impedance in the lower frequency side. The EIS data of both electrodes were fitted with the help of EIS spectrum analyser software, shown in Fig. 2.21 (b,c) and the corresponding equivalent Randles circuit is presented in the inset of Fig. 2.21 (b,c). The circuit formed by the combination of components corresponds to solution resistance (R_s), charge-transfer resistance (R_{ct}), Warburg resistance (Z_w), and constant phase element (CPE). Z_w referred to the impedance during the mass transport of redox species to the electrode surface. R_{ct} related to the kinetics of the electrochemical system assuming that the redox species are not getting absorbed to the surface of electrode and it determines the amount of resistance suffered by the electrons flow at the electrode/electrolyte intersection. The CPE value specify the low-frequency pseudo-capacitance and double layer capacitance

[96]. The value of solution resistance is revealed from the initial intercept value of semi-circle curve to the real axis, whereas the R_{ct} values are interpreted from the impedance arc diameter. The EIS analyser software was used to evaluate values for R_s , R_{ct} , CPE, and n of CuO and CuO/PANI/MWCNT electrodes, which are tabularized in table 2.4. Lower values of R_s and R_{ct} of the composite electrode point out the improved ionic conduction and electrolyte diffusion throughout the configuration, which eventually announces the better electrochemical properties of the composite material.

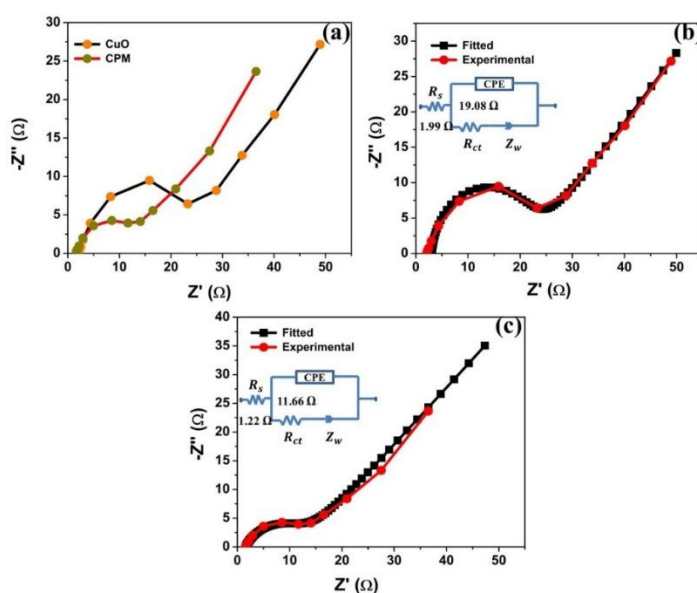


Fig. 2.21. Nyquist plot of (a) CuO and CPM electrodes, best fitted Nyquist plot of (b) CuO and (c) CPM (insets shows the equivalent electric circuit of fitted plot).

Table 2.4. Equivalent Randles circuit fitted data from the EIS study.

Sample	R_s (Ω)	R_{ct} (Ω)	W	CPE	n
CuO	1.99	19.08	22.75	0.00057	0.943
CPM	1.22	11.66	33.72	0.00049	0.688

2.3.9.4. Cycle stability

The cycle stability of CuO and CPM electrodes for 5000 cycles was explored in three-electrode configuration for current density of 3 A/g and displayed in Fig. 2.22. CuO shows a gradual increase of specific capacitance in the initial cycles and found to have stable capacitance retention of 97% after 1200 cycles. In the case of CPM, after

the initial 5 cycles the electrode shows excellent capacitance retention of 95 % over 5000 cycles. The initial increment in capacitance may be ascribed to the activation period for the electrodes [97]. Even though, the capacitive retention efficiency of the composite electrode is little bit less than that of pure CuO, the graph itself shows that CPM material presents much better stability over 5000 charge/discharge cycles without any deviations from the capacitance value in each cycle. The high capacitance retention of prepared electrodes hints that the materials do not undergo any surface structural deformations even after 5000 continuous charge-discharge cycles.

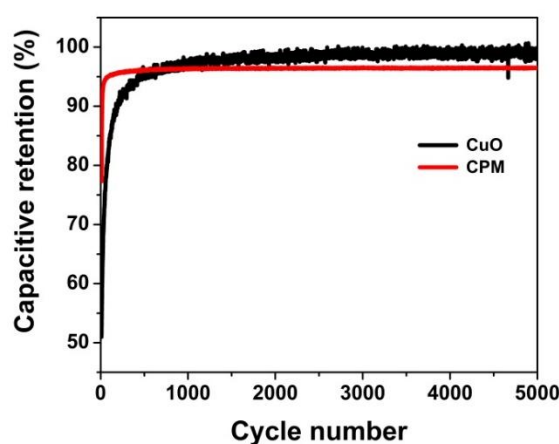


Fig. 2.22. Cycling life test of CuO and CPM electrodes for 5000 cycles at a current density of 3 A/g.

2.3.9.5. Electrochemical performance of CuO and CuO/PANI/MWCNT ternary nanocomposite in symmetric two-electrode configuration

A symmetric supercapacitor device set up with two-electrode configuration was used to test the practical possibilities of CuO and CPM electrode materials. Fig. 2.23 (a) shows the CV curve fabricated device with CuO as the active material for different scan rates. The material presents a quasi-rectangular shaped CV curve similar to that in the three-electrode set up, indicating the pseudocapacitive behaviour of the material. The GCD plots (Fig. 2.23 (b)) showcased a very close triangular shaped charge/discharge graphs with small amount of IR drop for all the current densities. The material exhibited a specific capacitance of 83 F/g at 0.5 A/g, 56 F/g at 0.8 A/g, 52 F/g at 1 A/g, and 25 F/g at 2 A/g (shown in Fig. 2.23 (c)). The coulombic efficiency of CuO working electrode at various current densities were calculated using the equation (2.

12), shown in Fig. 2.23 (d). The material shows relatively better coulombic performance over increasing current densities. The Ragone plot (PD vs. ED curve) of CuO electrode was shown in Fig. 2.23 (e) and made comparison with the standard Ragone plot [4]. The CuO electrode shows a maximum energy density of 7.37 Wh/Kg and power density of ~ 402 W/Kg. The sample exhibited relatively better energy density and power density compared with the conventional batteries, which indicates the utilization of as-synthesised CuO material for electrode fabrication in electrochemical systems are very promising. The capacitance retention of CuO-based device was evaluated for 50000 charge/discharge cycles at a discharge current of 10 mA is shown in Fig. 2.23 (f). The material shows high retention efficiency of about 99% over 50000 cycles, but the overall stability of capacitance was diminished after 20000 cycles. As the cycle number increases, material suffers some kind of capacitance deviation in each cycle.

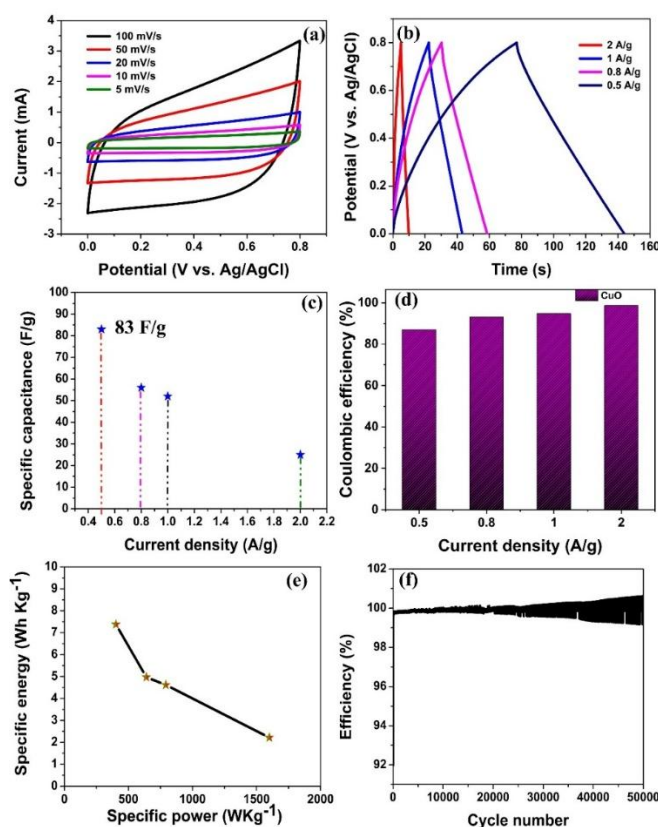


Fig. 2.23 (a) CV (b) GCD plots of CuO composite in two electrode configuration (c) calculated specific capacitance from GCD (d) Ragone plot (e) coulombic efficiency analysis and (f) cycle stability of CuO composite in 50000 cycles.

The device performance of symmetric supercapacitor with CPM nanocomposite as working electrode in a two-electrode configuration was systematically investigated, was depicted in Fig. 2.24. The CV profiles of CPM composite displayed quasi-rectangular shape with a pair of distinct redox peaks at potentials (0.2V, 0.42V), reflecting the contributions from PANI (Fig. 2.24(a)). The redox peaks get shifted to (0.32 V, 0.53 V) as the scan rate increases to 100 mV/s, which reveals the kinetic influences in the electrochemical performances. The GCD analysis, shown in Fig. 2.24 (b), indicates the nearly triangular shape for all the charge-discharge curves at varying current densities. The specific capacitance value of CPM working electrode estimated from GCD data was portrayed in Fig. 2.24 (c), showing a specific capacitance value of 115 F/g at a current density of 1 A/g. The coulombic efficiency of CPM electrode at various current densities were evaluated and displayed in Fig. 2.24 (d). The device showed reasonable coulombic efficiency values at all current densities. Fig. 2.24 (e) shows the energy-power characteristic of device using Ragone plot, highlighting a specific energy of CPM composite of about 10.22 Wh/Kg at a specific power of 866 W/Kg. Moreover, the maximum power density of composite electrode is found to be 4788 W/Kg at an energy density of 1.5 Wh/Kg. The capacitance retention of CPM-based device was evaluated for 50000 charge/discharge cycles at a discharge current of 15 mA is shown in Fig. 2.24 (f). The material shows retention efficiency of about 87.8% over 50000 cycles which is found to be lower than that of pristine CuO, but the overall stability of capacitance surpasses that of CuO. The CPM electrode showed relatively consistent efficiency over 50000 cycles without any degradation over the repeated charge-discharge cycles.

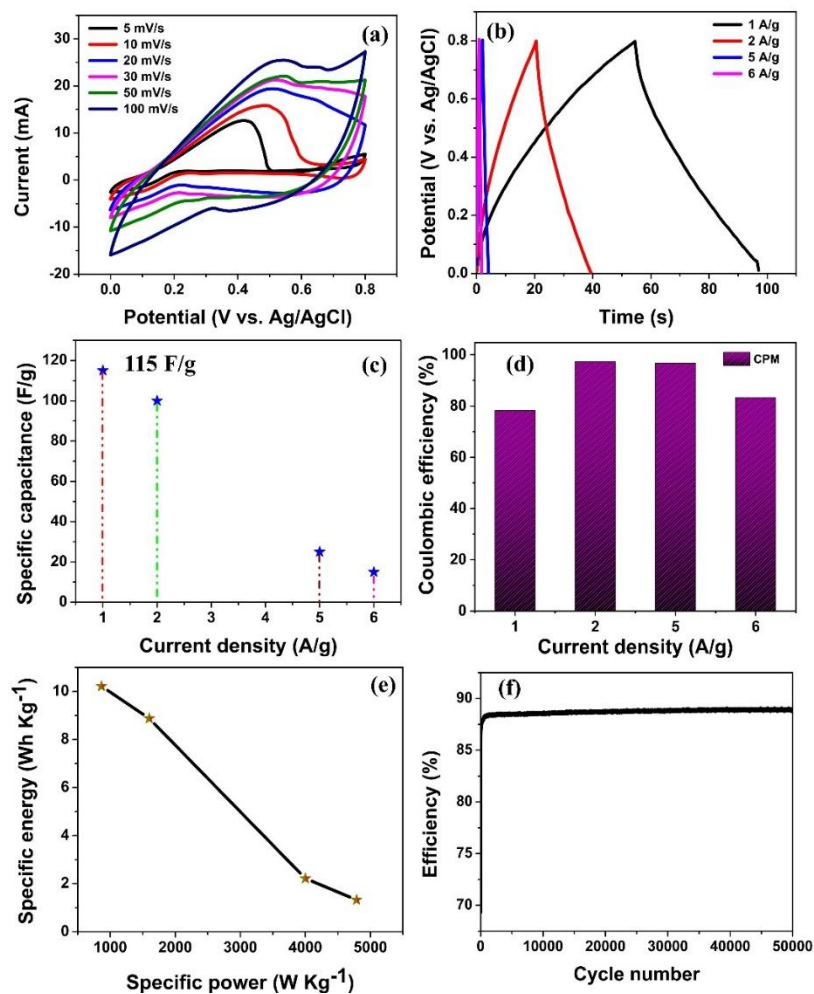


Fig. 2.24 (a) CV (b) GCD plots of CPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) Ragone plot (e) coulombic efficiency analysis and (f) cycle stability of CPM composite in 50000 cycles.

2.4. CONCLUSION

In this work, pristine CuO and CuO/PANI/MWCNT nanocomposites were fabricated by facile hydrothermal and freeze drying assisted in-situ polymerisation methods, respectively. Structural, morphological, thermal stability and optical features of both CuO and composite samples were evaluated using XRD, FT-IR, Raman, FESEM-EDS, HRTEM, XPS, BET and TGA. The electrochemical performance of pure CuO and ternary composite electrodes were analysed using both three and two- electrode configurations. The ternary composite attained a commendable supercapacitor performance, characterised with a specific capacitance of 516 F/g at 0.5 A/g. This improved specific capacitance of composite sample is the result of combined features of metal oxide, PANI and MWCNT, owing to the fact that PANI and MWCNT framework together provides a conductive pathway in the overall electrochemical process. The highly conductive polymer PANI improved the stability of the ternary nanocomposite by providing a good adhesion between CuO and MWCNT, without compromising the overall electrochemical behaviour, owing to the combined synergistic effects of all components in the composite.

Table 2.5. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CuO	123	10	94	0.5	64	10	83	1
CPM	478	10	516	0.5	102	10	115	1

2.5. REFERENCES

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Synthesis, Characterization, and Supercapacitive Performance of CuO-NiO/PANI/MWCNT Hybrid System

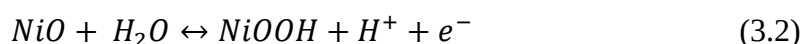
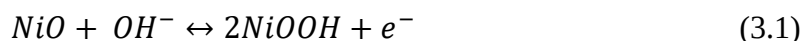
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Transitional metal oxides exhibiting diverse oxidation states have been entrenched for their pseudocapacitive nature, enabling their higher specific capacitance values in light of proficient redox reactions. However, the poor intrinsic electric conductivity, lower cationic-anionic diffusion and lesser stability of TMOs limit its specific capacitance value far from its actual theoretical values. These inherent problems associated with TMOs pave the way of incorporating one TMO with another TMO to create an efficient electro-active hybrid nanocomposite system. The composite electrodes fabricated with the appropriate choice of materials can overcome the entire shortcomings inherited by their constituent materials with the help of the combined synergetic effects. Herein, one of the most sought-after metal oxides, NiO was selected as the supportive transition metal oxide and has been introduced in to the CuO/PANI/MWCNT ternary system via in-situ polymerisation for the better electrochemical performance. This quaternary hybrid system is composed of two electrochemically vibrant metal oxides (CuO and NiO) backed by the inevitable collaborator MWCNT as a source of ample electrochemically active contact area as well as stronger electrical conductor, blended with PANI as a productive stability enhancer. The structural, morphological and optical interpretations of this quaternary nanocomposite system were discussed with the help of XRD, RAMAN spectroscopy, FESEM-EDS, HRTEM, XPS, BET and TGA analyses. The electrochemical performance of the proposed hybrid system was evaluated in detail.

3.1. INTRODUCTION

Nonetheless, commercial SCs predominantly rely on high power nanoporous carbon-based materials and usually deliver lower energy density compared with batteries. The electrode material is the most important factor which greatly influences the electrochemical performance of the supercapacitor. The electrochemically active sites on the electrode surface greatly influence the supercapacitor performance, which ultimately raise the substantial interest of mesoporous materials in this field. Transitional metal oxides (TMOs), commonly mesoporous in nature, range from single metal oxides to quaternary metal oxides and have been a research hotspot in recent years due to their fast and plentiful faradic redox reactions, which eventually compliment their commendable specific capacitance and energy density [1], [2].

Accordingly, a perfect choice of electrode material can be formed by an excellent blend of three important groups of electrode material such as carbonaceous compounds, transitional metal oxides (TMOs)/ hydroxides, and conducting polymers. From this perceptive, we have already combined MWCNT as a source of carbonaceous compound with the metal oxide CuO and PANI as a conducting polymer. Apart from these, a recent trend for further improvement of the electrochemical performance of CuO, is preparing electroactive hybrid materials of CuO with other TMOs such as MnO₂, ZnO, NiO, TiO₂ and Co₃O₄ for the electrochemical studies [3], [4], [5], [6], [7]. Among these, NiO is one of the popular TMO candidates in the field of SCs with peculiar properties like environmental friendliness, non-toxic nature and high theoretical capacitance (~ 2584 F/g) [8]. NiO offers more commercial advantages over other TMOs, because their cost-effectiveness and ease of preparation. Nevertheless, NiO possess exceptional electrical conductivity and electrochemical activity, which supplements its performance in the field of supercapacitors. Moreover, lattice of NiO contributes more electrochemical active sites in NiO-based nanocomposites, which eventually improves the charge transfer strength of electrode material [9]. The two possible charge storage mechanisms followed in a NiO based electrode material can be described as follows;



Accordingly, it is assumed that a productive combination of CuO with NiO will be a worthy tactic, which can improve its electrochemical performances by providing high specific surface area and electrical conductivity [6], [10]. Thus, the fruitful formation of CuO-NiO nanocomposite results in improved specific capacitance and long-term cyclic stability compared with individual metal oxides, making it a viable electrode material for SC applications. Moreover, this highly porous nanostructured electro-active TMO hybrid system can be well-supported by a solid electric conductor having a better surface area such as MWCNT and a stability enhancer like PANI. PANI will make a better adhesion of TMOs combo with MWCNTs, eventually leading to a stable quaternary nanocomposite for better electrochemical performance of electrode material. Thus, the CuO-NiO/PANI/MWCNT quaternary nanocomposite hybrid system can be effectively used as exceptional electrode material in the area of supercapacitor.

3.1.1. NiO-based supercapacitors- An overview

Among the popular TMOs like ruthenium oxide, iron oxide, zinc oxide, magnesium oxide etc., NiO is one of the cost-effective promising electrode candidates in the supercapacitor world. The high theoretical capacitance, thermal stability, low toxicity and apparently large pseudo-capacitive nature of NiO material made them a viable member in the category of efficient electrode materials [11]. The surface morphology and active surface area have a positive role in the electrochemical performance of NiO. Sumanta Kumar Meher *et al.* fabricated a pine-cone nanostructured NiO powder via a hydrothermally heat-treated precipitation method involving CTAB as a template material. This NiO electrode material exhibited a maximum specific capacitance of 337 F/g at a scan rate of 2 mV/s with capacitive retention of 99% after 100 charge/discharge cycles [12]. Kamantchi Kamaraj Purushothaman *et al.* synthesised nanosheet-assembled NiO microstructure via hydrothermal route and reported a specific capacitance of 989 F/g at scan rate of 3 mV/s with 97% capacitance retention after 1000 charge/discharge cycles [11]. Zeheng Yang *et al.* fabricated multishelled hollow NiO nanospheres by layer-by-layer self-assembly. The double shelled NiO exhibited a surface area of $\sim 92.99 \text{ m}^2/\text{g}$ and delivered a specific

capacitance of 612.5 F/g at a current density of 0.5 A/g [13]. Muhamed Shareef Kolathodi *et al.* synthesised NiO nanofibers via electrospinning technique followed by an annealing stage. They tried an asymmetric supercapacitor device with this NiO nanofibers and reported a gravimetric capacitance of 141 F/g and energy density of 43.75 Wh/kg [14]. Jinping Chen *et al.* reported hydrothermal synthesis of Al-doped NiO nanosheet arrays and exhibited a superior specific capacitance of 2253 ± 105 F/g at 1 A/g [15]. P.E. Saranya *et al.* synthesised pure and Ce-doped NiO via sol-gel method. The Ce-1% doped NiO sample showed a flower-like nanostructure with a surface area of $226.6 \text{ m}^2 \text{ g}^{-1}$ and offered capacitance of 2444 F/g at a scan rate of 5 mV/s, which is three times higher than that of pure NiO [16]. NiO-based binary and ternary nanocomposite electrode materials are also widely used in the supercapacitor field [17], [18], [19]. Shabhe Haider *et al.* tried the synthesis of PANI/NiO/Graphene using the wet chemical polymerisation method and studied its electrochemical performance in a neutral hybrid gel polymer mix of PVA/Na₂SO₄. The symmetric supercapacitor device based on the synthesised nanocomposite showed a specific capacitance of 152 F/g with energy density of 59.41 W h/kg at a high-power density of 850 W/kg [20]. Bal Sydulu Singu *et al.* synthesised NiO-PANI nanocomposite via in-situ aqueous oxidative polymerisation and showed the uniform distribution of NiO nanosheets over the nanofibrous PANI framework. Moreover, this nanocomposite delivered a specific capacitance of 514 F/g at 1 mV/s [21]. The NiO/carbon composite was fabricated by Subbukali Vijayakumar *et al.* with the help of starch as a stabilizing agent. The NiO/C composite calcinated at 500 °C showed a higher specific capacitance of 644 F/g at scan rate 2 mV/s compared with those composites prepared at 400 °C and 600 °C [22]. Junjiao Chen *et al.* reported a NiO@MnO₂ core/shell nanocomposite via two-step method and presented the growth of nanosheet like MnO₂ particles over the NiO nanotubes. The combined composite electrode delivered a capacitance of 266.7 F/g at 0.5 A/g [23]. The NiO-ZnO/GO nanocomposite was prepared by Raphael M. Obodo *et al.* using co-precipitation method and reported a capacitance of 1690 F/g for 1:1/GO sample at a scan rate of 10 mV/s [24]. Therefore, these previous literatures confirm that NiO is a hopeful electrode material that can make more improvement in electrochemical properties of CuO.

3.1.2. CuO-NiO nanocomposite as an efficient electrode material- A literature survey

Recently, multicomponent electrode preparation has been explored widely in the area of supercapacitors, owing to the fact that the both individual electrochemical contributions and synergistic effects of constituents can make efficient and productive electrode materials. CuO-NiO nanocomposite network is one of the extensively studied combination as a feasible electrochemically active capacitor [25], [26]. For instance, Yu Xin Zhang *et al.* investigated the synthesis and morphological evolution of CuO-NiO micropolyhedrons prepared by a simple precipitation method followed by calcination stages. The composite showed a specific capacitance of 370 F/g at current density of 2 mA/cm² in a three electrode system [27]. It has been observed that the electrochemical performance of the CuO-NiO composite micro polyhedrons is directly connected with its structural and morphological properties rather than its surface area. Thus, an appropriate pore size and surface morphology build more productive diffusion paths for the electrolyte ions, resulting in their enhanced intercalation and overall faradaic reactions. Recently, Siyi Xiao *et al.* prepared a wheat like CuO-NiO composite by a two-step electrochemical deposition and showed that the CuO-NiO composite attained an areal capacitance value 10.63 times higher than that of pure CuO [28]. They tested the specific capacitance and capacitive retention rate of the electrode materials before and after the incorporation of nickel oxide signifying that the synergistic effect between CuO and NiO enhances the electrochemical outcomes of the CuO/NiO composite materials. The structural, morphological and optical properties of CuO, NiO, and CuO-NiO composites were studied in detail by E. Arulkumar *et al.* They concluded that the improvement of specific capacitance of the composite electrode is the direct consequence of spherical CuO being strongly bound to NiO to enrich the surface area of the composite. The composite electrode delivered an energy density of 4.24Wh kg⁻¹ at a power density of 10.67 kW kg⁻¹ [29]. Sujit Chatterjee *et al.* synthesised CuO-NiO composite via hydrothermal route followed by calcination and found a combination ratio of (CuO)₅₀(NiO)₅₀ reached the highest capacitance of 35.63 F/g at current density 0.3 A/g. This CuO-NiO composite presented a 3D hierarchical morphology due to the aggregation of thin nanosheets [6]. Behnam Chameh *et al.* reported a study on the electrochemical performance of Cu-MOF-derived CuO/NiO and

CuO/NiO/Ni₃(VO₄)₂ composites. They observed a maximum capacity of 37.04 C/g in 3M LiOH electrolyte solution for the ternary composite at a gravimetric current of 2 A/g [30]. The electrochemical performance of ternary ZnO-CuO-NiO mixed metal oxides prepared by a simple gel combustion method was investigated by R. Packiaraj *et al.* and showed an outstanding capacitance of 1831 F/g at 1 A/g, which is much higher than single and binary metal oxides. The asymmetric supercapacitor device designed with the mixed metal oxides exhibited a power density of 5672 W/Kg with a specific energy density of 15.7 W h /Kg [31]. These eminent works on CuO-NiO based electrode materials have proved that this metal oxide combination can be a potential choice for fabricating high performance supercapacitors.

3.1.3. CuO-NiO/PANI/MWCNT hybrid systems for supercapacitor applications

Recent researches on the supercapacitor have been more focused on the preparation of hybrid electrode materials combining the metal oxides, conductive polymers and carbon compounds. Metal oxides are themselves a viable member of pseudocapacitors due to their excellent theoretical capacitance and power density. Also, conducting polymers like polyaniline have good capacitive response and exceptional electrical conductivity. Carbonaceous compounds like graphene and CNTs are well-renowned for their superior mechanical and chemical stability along with high surface area. Specifically noteworthy is the fruitful combination of TMOs with PANI as well as CNTs, resulting in a fertile base given by its distinctive contributions coupled with the synergistic effects that make them a promising member in energy storage applications. For instance, Vijay Kakani *et al.* prepared CuO/NiO/r-GO composite by ultrasonication and reported a capacitance of 220 F/g at a current density of 0.5 A/g. The enhancement of electrochemical performance of composite were attributed to the availability of multi-oxidation states and the uniform growth of CuO/NiO composite onto the surface of nitrogen doped graphene facilitates rapid charge storage in the system [32]. Elumalai Arulkumar *et al.* reported facile synthesis of CuO/NiO/rGO with varying rGO ratios and showed that the CNR-(50:50) electrode got a maximum specific capacitance of 302 F/g at 10 mV/s [33]. H₂O₂ supported hydrothermal and microwave preparation of CuO/NiO/MWCNT electrode material was discussed in a recent literature reported by Sannasi Veeman *et al.* and showed a specific capacitance of 581.3

F/g at 1 A/g for the ternary electrode [34]. Also, Sayed Mohammed Adnan *et al.* explored the NiO-CuO decorated PANI nanocomposite as a symmetric supercapacitor device with 69 % capacity retention over 10000 charge/discharge cycles [35]. Recently, Manash J. Baruah *et al.* reported the first work on ethanol-assisted in-situ stimulated synthesis of graphene oxide supported CuO/NiO nanoparticles and resulted in increased surface area of the composite [36]. Mahasweta Chatterjee *et al.* synthesised wool ball-like CuO/NiO/MWCNT hybrid system and explored its supercapacitive performance. They reported a specific capacitance of 786 F/g at 0.6 A/g for the optimised ternary composite. This fusion of binary TMOs in to MWCNTs improved the surface area, electrical conductivity as well as charge transfer properties of the whole system [37]. To the best of our knowledge, the only one work based on CuO-NiO/PANI/MWCNT quaternary composite was done by Ishita Chakraborty *et al.* and reported a maximum capacitance of 1372 F/g at 5 mV/s having 83% capacitance retention after 1500 cycles of charge/discharge, making them a potential electrode material [38]. Here, the porous nanoarchitecture and availability of multiple oxidation states of both metal oxides have enriched electro-active sites in the electrode surfaces. Additionally, the double role of PANI as a pseudocapacitive material as well as a conductive binder results in an enhanced mechanical stability of the electrode material. Moreover, MWCNT provides a potential conductive framework that eventually facilitates the charge transfer features of the material.

3.2. EXPERIMENTAL SECTION

3.2.1. Synthesis materials

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$), ammonium persulfate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and aniline hydrochloride ($\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$), analytical grade hydrochloric acid (HCl), sodium sulphate (Na_2SO_4), sodium dodecyl sulphate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) (SDS, > 98%), nickel nitrate ($(\text{NiNO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), de-ionised (DI) water were purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, $\text{OD} \times \text{L} = 6 - 9 \text{ nm} \times 5 \mu\text{m}$), Polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP), activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standards

and utilized without any further purifications. Distilled ethanol was used for cleaning purpose.

3.2.2. Synthesis of NiO

The NiO nanoparticles were prepared via a similar surfactant-free hydrothermal process with the same reaction conditions of CuO synthesis. Firstly, 1.45 g of nickel nitrate was dissolved in 50 ml of de-ionised water. Later, 1 M NaOH solution was added to the precursor solution under constant stirring. The whole solution was then transported to the autoclave setup and kept in the oven under 180 °C for 24 hours. When the reaction conditions met, the resultant solution from the reactor was filtered and washed thoroughly using DI water and ethanol. The obtained light green NiO precipitate was then shifted to an oven at 80 °C for 6 hours to get the purified NiO nanoparticles.

3.2.3. Synthesis of CuO-NiO nanocomposite

The CuO-NiO nanocomposite was processed using the hydrothermal method without employing any additives of surfactants. Initially, 10mM nickel nitrate was allowed to dissolve completely in 50 ml of DI water via a continuous stirring process. Later, the previously prepared CuO nanoparticles (40 mg) were allowed to disperse in the above-mentioned nickel precursor solution. Then, 0.6 mM urea was added to the solution without disturbing the stirring process until a clear homogeneous solution is attained. The whole 50 ml solution was then transferred to an autoclave and set to keep in the oven at 180 °C for 24 hours to complete the synthesis process. The earned precipitates after hydrothermal reaction were washed multiple times with DI water and ethanol for the removal of unreacted substances from the resultant. Later, the obtained precipitate was sent to an oven at 80 °C for 6 hours to get the CuO-NiO nanocomposite.

3.2.4. Synthesis of NiO/PANI/MWCNT ternary nanocomposite and CuO-NiO/PANI/MWCNT quaternary nanocomposite

The NiO/PANI/MWCNT ternary nanocomposite was prepared using a similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO with 30 mg of as-prepared NiO and the final product is named as NPM for the convenience.

The CuO-NiO/PANI/MWCNT quaternary nanocomposite was prepared in the similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO with 30 mg of as-prepared CuO-NiO nanocomposite and the final product is named as CNPM for the convenience.

3.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, Aeris Research (Source: Cu K α)). Fullprof Suite software was used for Rietveld analysis. Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany) was employed to determine the vibrational modes of the as-synthesised samples. Fourier Transform Infrared (FTIR) spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using ZnSe crystal. The surface morphology and elemental composition were done using a combination of High- Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of a TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

3.2.6. Electrode preparation and electrochemical studies

The electrochemical features of as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt% of active material, 10 wt% of polyvinylidene fluoride (PVDF) and 10 wt% of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly in to a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in the working electrode was 1.28 mg cm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as

reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of as-synthesised samples.

3.3. RESULTS AND DISCUSSION

3.3.1. X-Ray diffraction (XRD)

Structural and microstructural features of as-prepared materials were examined using X-ray diffractometer. The XRD profiles of NiO and CuO-NiO nanoparticles along with that of already prepared CuO for comparison are displayed in Fig. 3.1(a). All the dominant peaks of NiO can be well indexed by comparing with their standard JCPDS (cubic NiO -47-1049). The crystallographic scattering peaks were observed at 37.08°, 43.20°, 62.94°, 75.37° and 79.45° which are corresponds to (111), (200), (220), (113) and (222) planes of cubic NiO [39]. The XRD pattern of CuO-NiO nanocomposite was found to be a correct blend of monoclinic CuO and cubic NiO crystal structures. Even though CuO reflections were more prominent in the XRD pattern of the composite, NiO peaks were also easily detectable, which clearly indicated that both CuO and NiO phases were grown freely in the synthesis stage [40]. No additional peaks or phases were detected in any of the XRD patterns. Fig. 3.1 (b) shows the XRD patterns of newly synthesised NiO/PANI/MWCNT and CuO/NiO/PANI/MWCNT in the region 10°-90° along with those of PANI, MWCNT, and CPM for confirming the correct formation of composites. From the figure, it is very clear that the three very distinctive peaks that appeared in the XRD data of NPM composite at 37.14°, 43.09°, and 62.62° were correspond to the NiO phase. For CNPM composite, all the peaks in between 30°-90° were assigned to the presence of CuO-NiO composite in the hybrid system. Also, the three peaks at 14.71°, 19.66° and 25.32° in CNPM were corresponded to (011), (020), and (200) reflections of emeraldine salt form of PANI. No peak correspond to MWCNT was visible in the XRD spectrum of NPM, maybe due to its coincidence with the broad bump of PANI in the 20-30° region. The peak at 25.75° in CNPM composite can be a resultant of (200) plane of PANI and (002) plane of MWCNT, can be a result of interaction between both PANI and MWCNT. Thus, from the XRD analysis itself, the correct formation of NiO, CuO-NiO, NPM and CNPM nanostructures were validated. The charge transfer interactions among metal

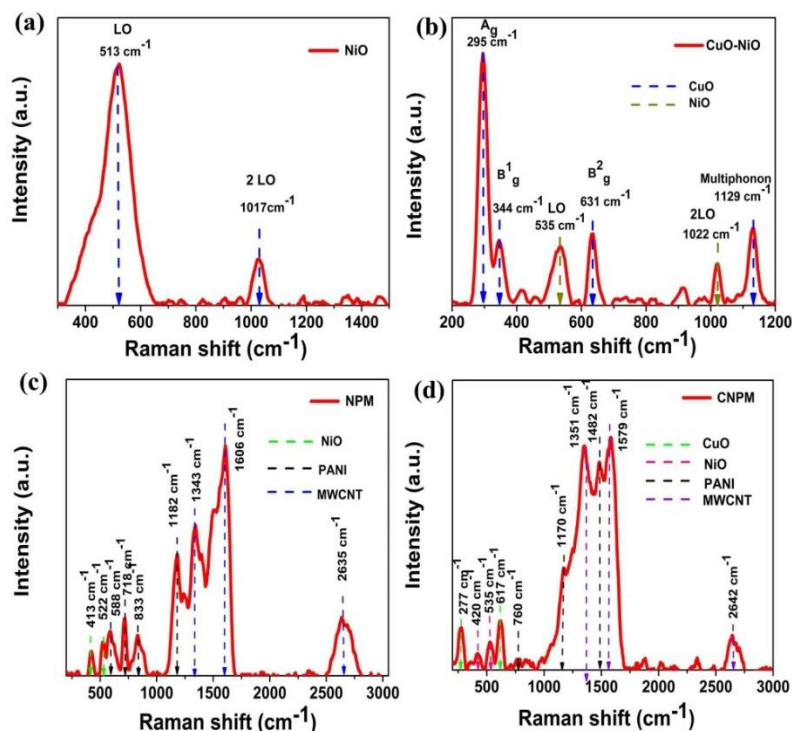


Fig. 3.2. Raman profiles of pristine (a) NiO (b) CuO-NiO (c) NPM (d) CNPM composites.

Table 3.1. List of assignments of dominant characteristic bands appeared in Raman spectra of NPM and CNPM nanocomposite.

Raman modes		Assignments
NPM	CNPM	
-	277 cm ⁻¹	A _g mode of monoclinic CuO
413 cm ⁻¹	420 cm ⁻¹	TO mode of NiO
522 cm ⁻¹	535 cm ⁻¹	LO mode of NiO
718 cm ⁻¹	760 cm ⁻¹	Raman active mode of PANI
-	617 cm ⁻¹	B _g ² mode of monoclinic CuO
833 cm ⁻¹	-	Ring deformation of benzenoid ring in emeraldine salt form of PANI
1182 cm ⁻¹	1170 cm ⁻¹	C-H bending of benzenoid ring in PANI
-	1482 cm ⁻¹	C=N stretching in quinoid ring in PANI
1343 cm ⁻¹	1351 cm ⁻¹	D- band of MWCNT
1606 cm ⁻¹	1579 cm ⁻¹	G-band of MWCNT
2635 cm ⁻¹	2642 cm ⁻¹	G' band of MWCNT

3.3.3. FT-IR spectroscopy

The chemical structures of the composites formed during mutual interactions and bonds were investigated through FT-IR spectra, shown in Fig. 3.3. The small absorption peaks at 3745 cm^{-1} attributed to the vibrational stretching of O-H bonds, whereas the peak at 2969 cm^{-1} ascribed to C-H stretching in CH-Cl groups. The band at 1514 cm^{-1} corresponds to hydrogen bonded carbonyl groups, and C-O stretching is indicated through the peak at 1161 cm^{-1} . The bands that appeared at 423 cm^{-1} , 484 cm^{-1} and 603 cm^{-1} (shown in Fig. 3.3 (a)) correspond to the vibrational stretching of Ni-O bonds. As shown in Fig. 3.3 (b), the absorption bands in between $400\text{--}650\text{ cm}^{-1}$ can be a blend of CuO and NiO nanostructures [39], [44]. In NPM and CNPM composites, bands corresponding to metal oxide bonds were appeared between the wavelengths $400\text{--}700\text{ cm}^{-1}$. The other peaks presented in the range of $680\text{--}4000\text{ cm}^{-1}$ can be of pristine PANI and MWCNTs, listed in Table 3.2. The slight variation of peaks positions metal oxides, PANI and MWCNTs indicates the effective interactions between PANI and MWCNTs resulted in polarity changes or metal oxide and MWCNTs causes lowering of vibrational energies [45].

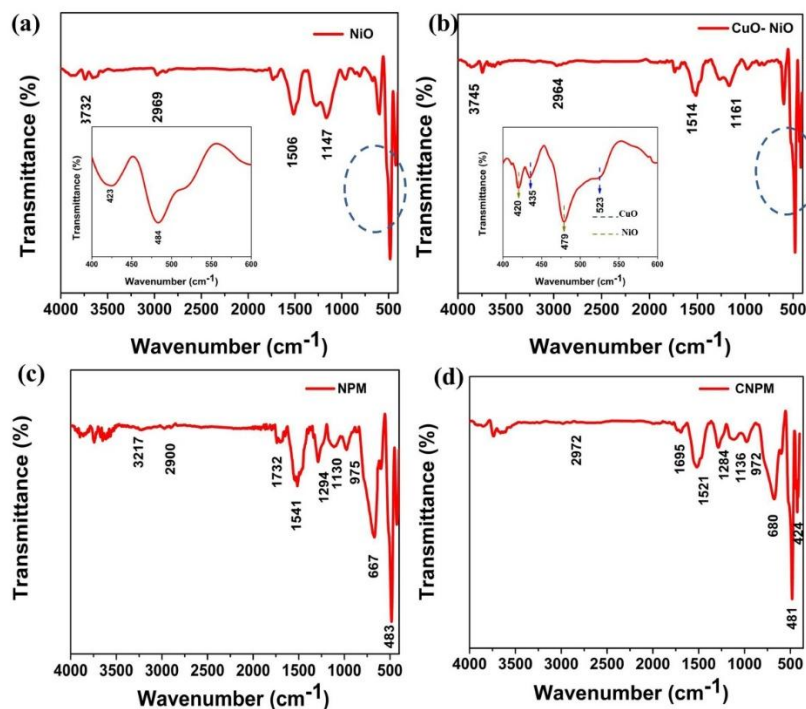


Fig. 3.3. FT-IR spectra of (a) NiO (b) CuO-NiO (c) NPM (d) CNPM nanocomposites. (inset shows the zoomed spectra of NiO and CuO-NiO in the range $400\text{--}600\text{ cm}^{-1}$ as marked in its corresponding figures 3.3 (a) and (b)).

Table 3.2. List of FT-IR bands and its assignments appeared in NPM and CNPM composites.

FT-IR bands		Assignments
NPM	CNPM	
3217	-	O-H bonds due to existence of water molecules
2900	2972	asymmetric/ symmetric methylene stretching bands from PANI
1732	1675	stretch mode of carboxylic groups in MWCNT
1541	1521	C=C stretching in quinoid ring of PANI
1294	1284	C-N for aromatic amines in the polaron structure of conducting PANI
1130	1136	characteristic band of the protonated form of conducting PANI
975	972	characteristic peaks of mono substituted benzene, indicates the formation of PANI
667	671	Characteristic peak of Ni-O
483	481	Characteristic peak of Ni-O
-	424	Characteristic peak of Cu-O

3.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The morphological appearances of the materials were inspected by FESEM images. The surface morphology of NiO sample was portrayed in Fig. 3.4 (a,b,c); it carried an irregular pattern of nanoflakes distribution with some sort of agglomerated clumps in between. The flakes possess very small dimensions approximately 10 nm average thicknesses. On the other hand, SEM images of the CuO-NiO composite revealed the formation of rice-like nanoparticles, displayed in Fig. 3.4 (d,e,f). It is to be noted that

the sizes of these rice-like particles are relatively small and emanating with a considerable number of tiny porous spaces that can be unquestionably profitable for the electrochemical capacity of the prepared sample [46]. The incorporation of NiO into CuO has effectively transformed the flake-like morphology of CuO into very minute rice-like particles with several minute pores. The average size of uniformly distributed rice-like composite particles is estimated as ~ 95 nm length, ~ 38 nm width and ~ 6 nm thickness. The morphological investigations of NPM composite is presented in Fig. 3.6 (g,h,i). The composite exhibited a nanofibrous texture with several intertwined frameworks, having an average diameter of 55 nm. The PANI/MWCNT growth over NiO nanoflakes, make complete fibrillar morphology without any kind of agglomerations or appearance of flakes of NiO in the composite system. The diameter of these fibres was higher than the pristine PANI fibres as well as the nanotubes of MWCNTs, indicating the grafting of PANI over the MWCNT tubes [47]. The CNPM composite shows a nanotubular morphology (Fig. 3.6(j,k,l)) resemble to that of MWCNTs; however, the average diameter of tubes was increased to 34 nm, likely due to the successful growth and wrapping of PANI over MWCNT surfaces. The originally smooth surface of MWCNT tubes were obscured as the nanofibrous PANI with agglomerated protrusions was linked to the MWCNT surfaces, contributing to the observed increase in average diameter of tubules. The metal oxides become morphologically indistinct due to the uniform interactive growth of PANI and MWCNT over the metal oxides. Moreover, the highly voluminous pores exhibited within the composite made it to have an effective specific surface area, thereby facilitating the productive contact between the electrode surface and electrolyte ions. This overall structural configuration in the composite provides more and more conductive pathways, which led to a better electrochemical performance of the hybrid system.

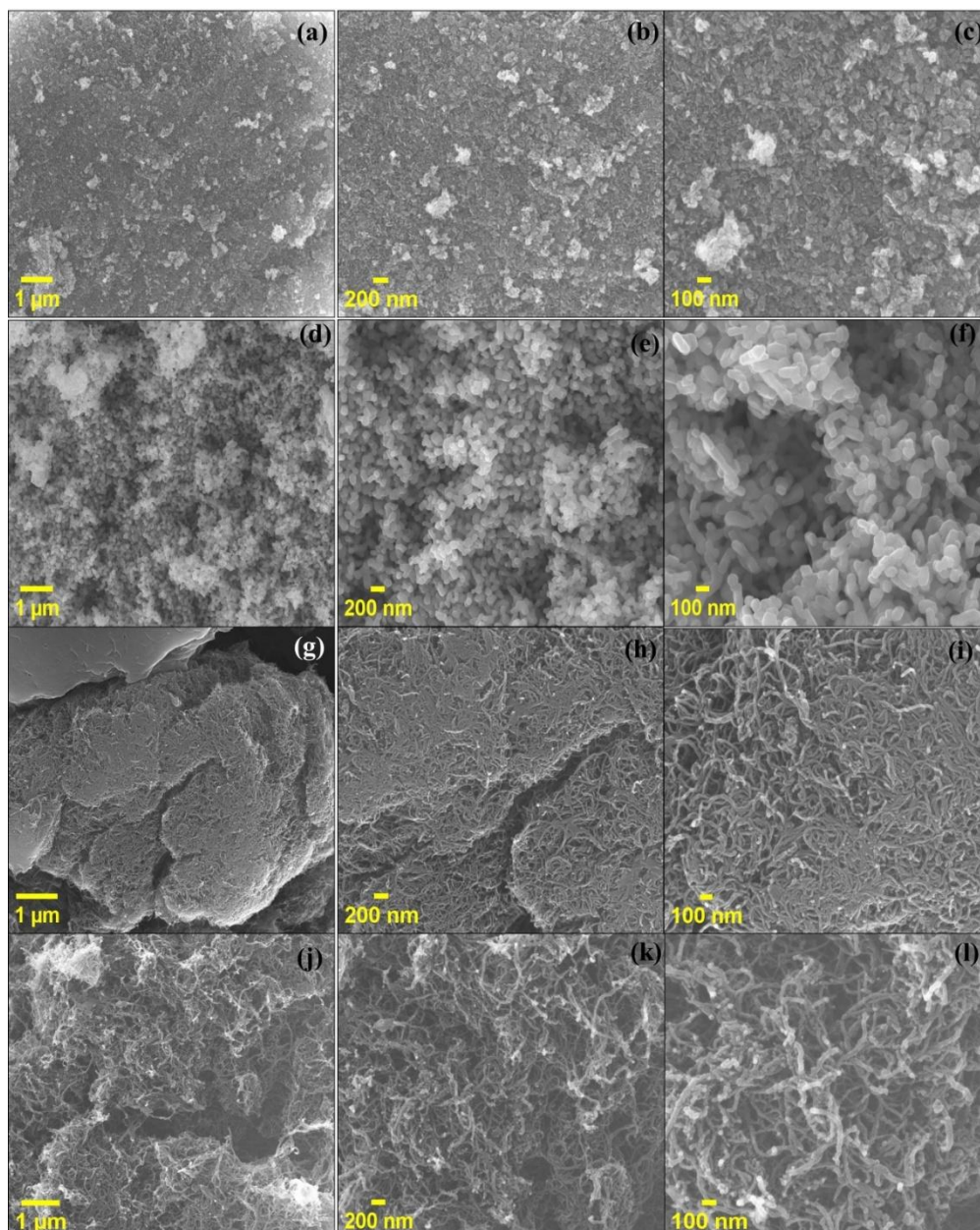


Fig. 3.4. SEM micrographs of (a,b,c) NiO (d,e,f) CuO-NiO (g,h,i) NPM (j,k,l) CNPM nanocomposites.

The compositional evaluations of the composites were performed using conventional energy dispersive spectroscopy (EDS), as shown in Fig. 3.5. The existence of elements like nickel and oxygen was obviously visible in the spectra of NiO, displayed in Fig. 3.5 (a). Similarly, the EDS spectrum of CuO-NiO (Fig. 3.5 (b)) reveals the distinct peaks of elements like copper, nickel and oxygen, confirming the successful integration of these constituents in the composite material. The successful formation of both NPM and CNPM composites were confirmed through the EDS

spectra presented in Fig. 3.5 (c-d). In the NPM composite, detection of elements C, N, Ni, and O verifies the incorporation of PANI/MWCNT in to NiO, whereas the presence of additional signal of Cu in the CNPM confirms the successful interaction of CuO-NiO with PANI/MWCNTs. The atomic mass ratio of these detected elements was tabulated in Table 3.3. The atomic concentrations of all elements that appeared in each synthesised materials were further validate the precise formation of intended composites. The equal amount of elements Cu and Ni, with nearly double amount of the oxygen validates the successful formation of CuO-NiO composite. The relatively lower atomic ratio of Ni in CNPM composite as compared with other detected elements, supports the observed less intense peaks of NiO in the XRD pattern of the composite.

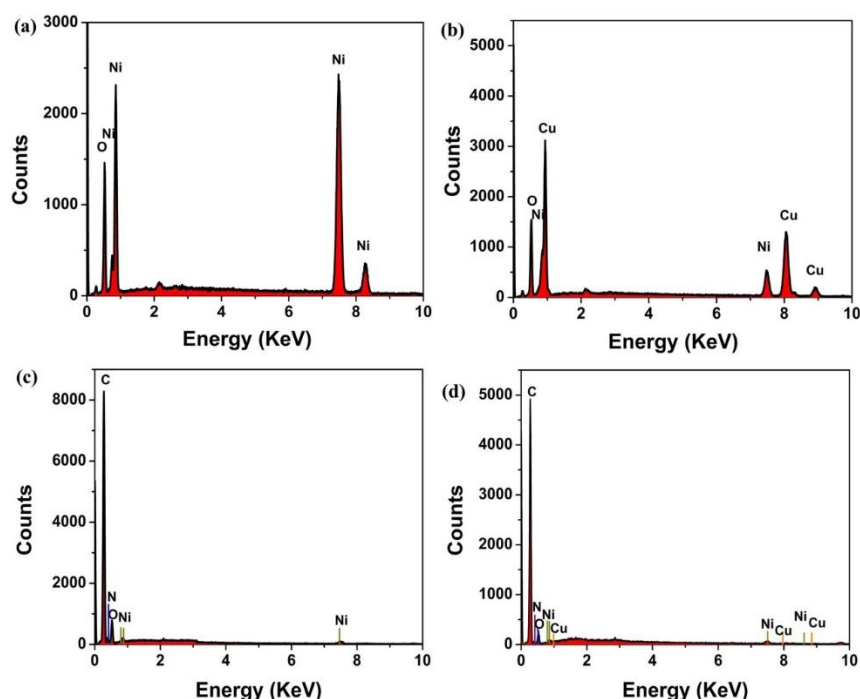


Fig. 3.5. EDS spectra of (a) NiO, (b) CuO-NiO, (c) NPM, and (d) CNPM composites.

Table 3.3. Elemental data of NiO, CuO-NiO, NPM, and CNPM composites obtained from EDS analysis.

Sample	Atomic ratio (%)				
	Cu	O	Ni	C	N
NiO	-	41.82	58.18	-	-
CuO-NiO	27.95	46.84	25.21	-	-
NPM	-	15.02	8.80	65.12	11.06
CNPM	7.09	11.14	3.21	70.58	7.98

The corresponding elemental mapping images of NiO, CuO-NiO, NPM and CNPM composites were displayed in Fig. 3.6, Fig. 3.7, Fig. 3.8, and Fig. 3.9 which further confirms the occurrence and uniform distribution of intended elements in each sample. The yellow regions observed in the EDS map of NiO (Fig. 3.6 (b)) confirm the richness of NiO. In the case of CuO-NiO, EDS map shown in Fig. 3.7 (b) shows the lighter blue and yellow regions of CuO and NiO in the composite system. The rich elemental presence of carbon in both NPM and CNPM composites (Fig. 3.8 & 3.9) confirms the presence of MWCNTs, while the nitrogen distributions were also evident, indicating that PANI was grafted over the CNT surface during composite formation. From the EDS map of NPM (Fig. 3.8 (b)), it is evident that the PANI and MWCNT growth of made the NiO presence as indistinct. Thus, the Cu, Ni, and O elemental distributions along with the contributions of PANI and MWCNTs (Fig. 3.9 (b)) ascertain the successful formation of quaternary CuO-NiO/PANI/MWCNT composite.

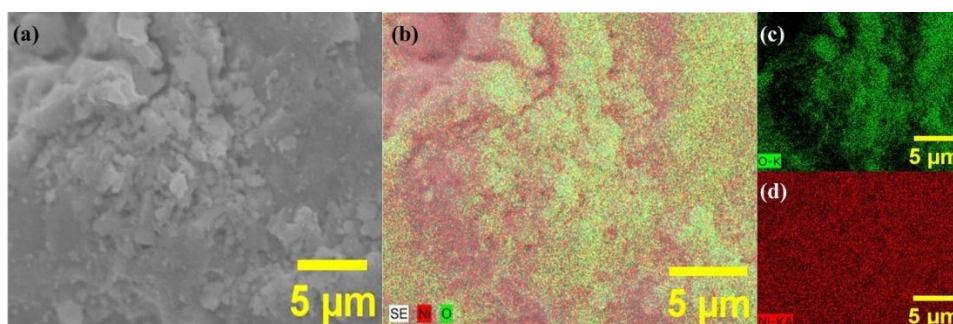


Fig. 3.6. (a) SEM image, (b) EDS mapping of NiO nanostructures, and (c-d) selective elemental distribution for the area shown in image (a).

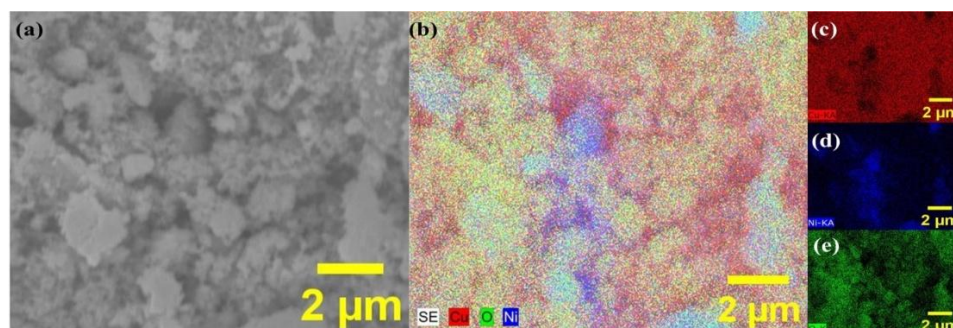


Fig. 3.7. (a) SEM image, (b) EDS mapping CuO-NiO nanocomposites, and (c-e) selective elemental distribution for the area shown in image (a).

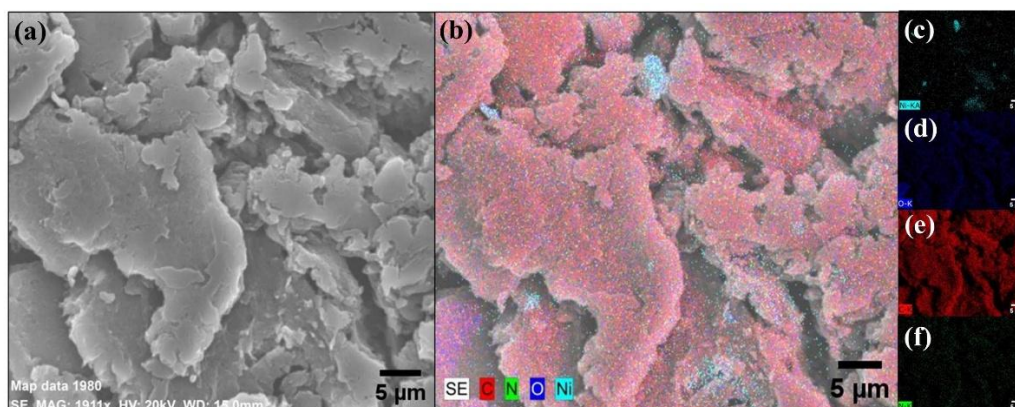


Fig. 3.8. (a) SEM image, (b) EDS mapping of NPM composites, and (c-f) selective elemental distribution for the area shown in image (a).

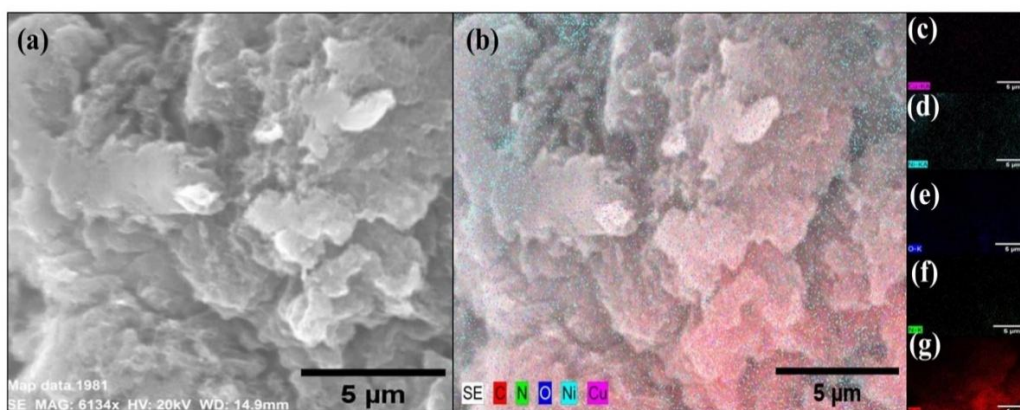


Fig. 3.9. (a) SEM image, (b) EDS mapping of CNPM composites, and (c-g) selective elemental distribution for the area shown in image (a).

3.3.5. High Resolution Transmission electron micrographs (HR-TEM)

The microstructural features of CuO-NiO/PANI/MWCNT composites were investigated through TEM, HRTEM images (Fig. 3.10), intended to get more comprehensive information about the structural features. The TEM images shown in Fig. 3.10 (a,b), presents a tubular morphology of composite, consistent with FESEM findings. The increase in tubular diameter can be understood from the TEM image shown in Fig. 3.10 (b), attributable to the wrapping of PANI over the MWCNT tubules, a process reported in polymer-CNTs frameworks [48]. The CuO-NiO nanoparticles can be distinctly visible from the HRTEM image, presented in Fig. 3.10 (c), which has an average diameter of 8.22 nm, matches with dimensions commonly seen for metal oxides introduced within polymer frameworks. The crystallographic d-spacing measurement shown in Fig. 3.10 (d), align with the dominant (110) plane of CuO nanostructures.

Furthermore, from the fig. 3.10 (e), it is evident that the composite consists of several intertwined nanotubes with varying diameter, i.e., a kind of structural modification persuaded by the extent of PANI grafting over MWCNTs. The SAED pattern of composite displayed in Fig. 3.10 (f) consists of concentric rings indicating the polycrystalline nature of the sample.

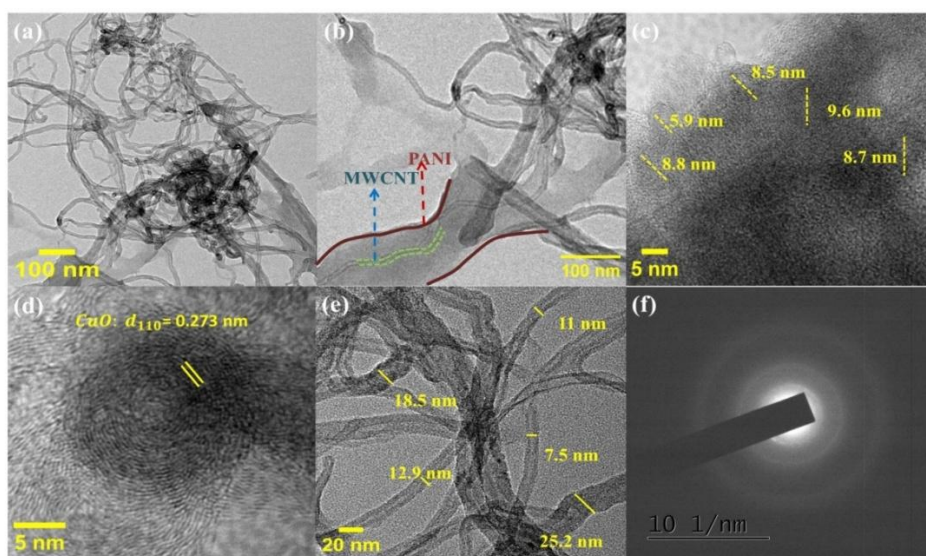


Fig. 3.10. (a,b) TEM micrograph (c,d,e) HRTEM images (f) SAED pattern of CNPM composites.

3.3.6. X-Ray Photoelectron spectroscopy (XPS)

The compositional analysis and elemental confirmations of the quaternary nanocomposite CNPM examined using XPS profiles and are shown in Fig. 3.11. The survey spectrum (Fig. 3.11 (a)) confirms the co-existence of Cu, Ni, C, O, and N in the material. The high resolution XPS spectra of C 1s (Fig. 3.11 (b)) can be deconvoluted to four major and minor peaks at 284.3 eV, 285.2 eV, 286.8 eV, and 289.7 eV. The high intense major peak at 284.3 eV can be attributed to the sp^2 hybridised carbon ($C=C$) in the graphitic structure of MWCNTs. The second major peak at 285.2 eV corresponds to contributions from both sp^3 hybridised carbon ($C-C$) at the MWCNT surface as well as $C-N$ components present in the PANI structure [49]. The less intense peak at 286.8 eV ascribed to carbon atoms bound to functional groups like hydroxyl groups ($C-OH$). The final peak with higher binding energy and low intensity appeared at 289.7 eV, attributed to the carbon atoms connected with bipolaronic nitrogen cations ($C=N^+$) in PANI [50].

The N 1s core level spectrum shown in Fig. 3.11 (c) fitted with three dominant peaks with binding energies of 399 eV, 399.7 eV, and 401.1 eV, in which the major contribution was from both the amine groups ($-\text{N}-\text{H}-$) and imine groups ($=\text{N}-\text{H}-$) of emeraldine base appeared at 399.7 eV and 399 eV, respectively. The low intense high binding energy peak at 401.1 eV, attributed to generated iminium ions ($-\text{N}^+=$), which were created due to the interaction between MWCNT and PANI through $\pi - \pi^*$ conjugation [47]. The O 1s spectrum (Fig. 3.11 (d)) can be deconvoluted to four peaks at binding energies 530.6 eV, 531.2 eV, 532.4 eV and 534.2 eV. The broad peak at 530.6 eV corresponds to lattice oxygen involved in metal oxide bonds such as Ni-O and Cu-O bonds. Also the presence of C—O and C=O bonds in the composites was confirmed through this peak [32]. The peaks at 531.2 eV and 532.4 eV related to oxygen vacancies and metal-hydroxyl bonds present in the lattice, respectively [51]. The presence of H_2O or $\text{CO}_2/\text{CO}_3^{2-}$ species has resulted in the less intense peak at 534.2 eV [52]. The Cu 2p core level spectrum is presented in Fig. 3.11 (e). The two prominent peaks that appeared at 933.6 eV and 953.6 eV represent the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ orbits, respectively. The energy gap of 20 eV between these spin energies coupling orbits confirms the presence of Cu^{2+} , thereby the occurrence of CuO form in the quaternary composite. Along with this, two shake-up peaks were also located at 943.1 eV and 963.3 eV [53]. The minor shifts in the binding energies of Cu^{2+} in the composite compared with that of the CuO sample suggests the effective interactions of metal oxides with MWCNTs and the PANI matrix. The two main peaks of Ni 2P state, shown in Fig. 3.11 (f), observed at binding energies 855.5 eV and 873.4 eV, were ascribed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ orbits of Ni^{2+} species [32]. The spin orbit coupling energy band gap of these orbits found to be 17.9 eV, along with two satellite peaks for each main peak.

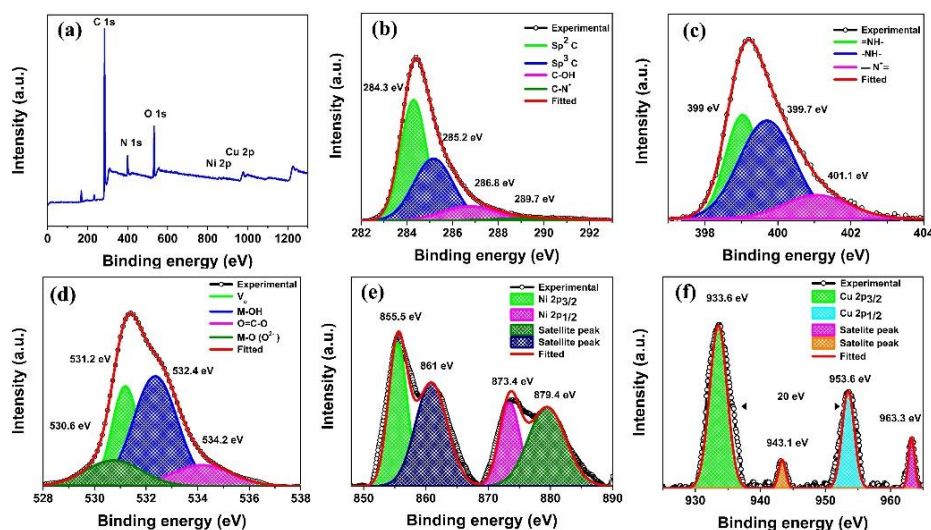


Fig. 3.11. (a) XPS survey spectrum and XPS elemental core spectra of (b) C 1s and (c) N 1s (d) O 1s, (e) Cu 2p, and (f) Ni 2p of CNPM nanocomposite.

3.3.7. Brunauer-Emmett-Teller (BET) analysis

The electrochemical performance of the materials is strongly associated with their specific surface area and inner porous textural. Fig. 3.12 shows the N₂ adsorption-desorption isotherms and pore size distribution (PSD) plots of NiO, CuO-NiO, NPM and CNPM nanocomposites. The steep region in the isotherm plot generally gives the information about initial level adsorption that occurs during nitrogen contact and availability of active surface adsorption sites [54]. Like CuO, the mesoporous nature of NiO was inferred from its type IV adsorption behaviour in adsorption – desorption isotherm with H3 hysteresis loop ranges from 0.8-1 (P/P₀), presented in Fig. 3.12 (a). Brunauer-Emmett-Teller (BET) surface area of NiO sample was approximated to be 21 m²/g. The pore size distribution (shown in the inset of Fig. 3. 12 (a)) lies in the mesoporous range with a pore radius of ~ 6.42 nm and pore volume of ~ 0.087 cm³/g. In the case of CuO-NiO composite, the BET specific surface area from the N₂ adsorption-desorption isotherm was estimated as ~ 45 m²/g. The isotherm plot of nanocomposite, displayed in Fig. 3.12 (b) shows type IV isotherm performance with a hysteresis loop between 0.65-1 (P/P₀), which is frequently seen in mesoporous materials. In the inset of Fig. 3.12 (b), the pore size distribution image of CuO-NiO composite is presented. The average pore radius and volume are tabulated as 9.12 nm and 0.146 cm³/g. The higher value of surface area and smaller pore sites for the CuO-NiO composite when compared with

the pristine CuO and NiO, will create a large amount of pore channels for the adequate diffusion and active transportation of electrolyte [55], [56]. In the case of NPM, adsorption-desorption isotherm plot, shown in Fig. 3.12 (c) illustrates the H3 hysteresis loop ranging between 0.55-1 (P/P_0) with type IV adsorption nature, having a BET surface area of 57 m^2/g . The average pore radius and volume are tabulated as 11.5 nm and 0.061 cm^3/g . Meanwhile, CNPM composite behaves like type IV mesoporous materials having H2 hysteresis loop, with a highest surface area of about 81 m^2/g (Fig. 3.12 (d)). The average pore radius and volume are tabulated as 13.2 nm and 0.178 cm^3/g . The synergism between MWCNTs and PANI, along with metal oxide composites results in the enhancement of the specific surface area of the quaternary hybrid system. Although there is an improvement in the surface area of CNPM, the surface encapsulation of nanotubes by the metal oxides and PANI, as confirmed by SEM/TEM observations, limits the accessibility of active centres and certain pores, thereby hinders their contribution to surface area.

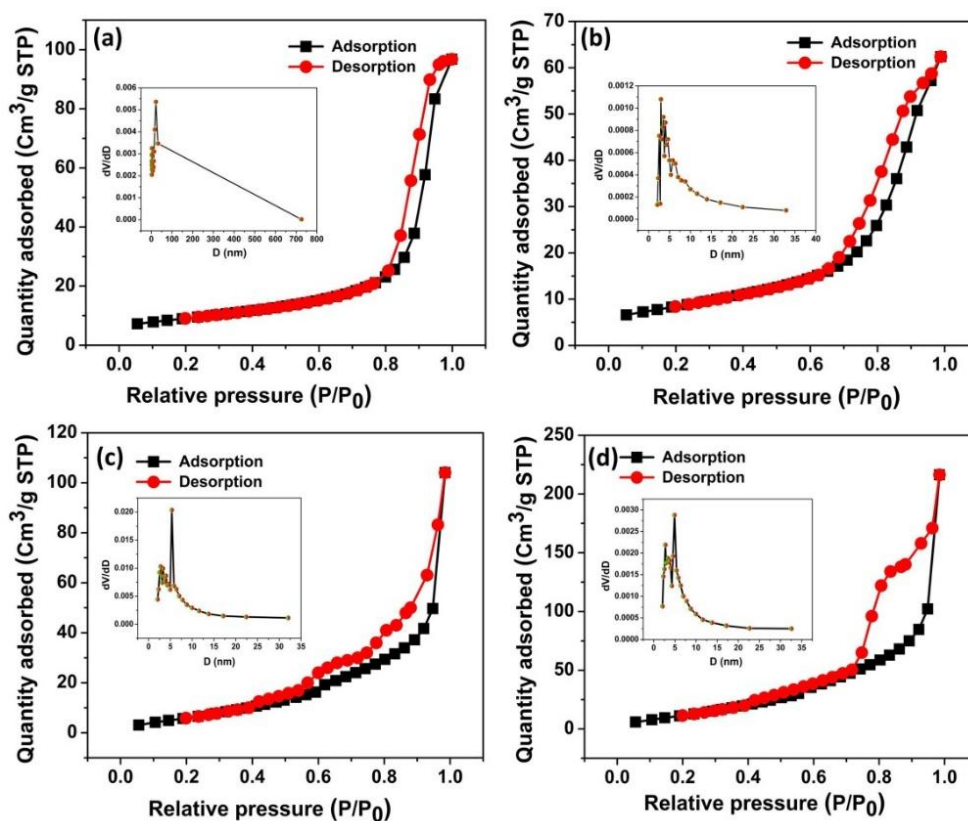


Fig. 3.12. The N_2 adsorption-desorption isothermal plots of (a) NiO (b) CuO-NiO (c) NPM and (d) CNPM nanocomposites. Inset shows the corresponding PSD plots.

3.3.8. Thermo-gravimetric Analysis (TGA)

The thermal stability of the CuO-NiO/PANI/MWCNT quaternary composite was investigated using thermogravimetric data presented in Fig. 3.13. The composite undergoes significant weight loss through mainly three steps of decomposition. In the initial stage, CNPM lose its weight by 8.12% until the temperature reaches 100 °C, which corresponds to the loss of absorbed water molecules from the surface. The second noticeable weight loss of 28.75% was attributed to the removal of acid elements from the composite and the degradation of polymer into monomers, oligomers, trimmers, and dimers between the temperature range 168 °C to 321 °C. The CNPM composite underwent a weight loss of about 11.78% until the temperature reaches 522 °C in the final stage of decomposition, which is accountable for the degradation of polymer backbones [57]. In the end, 46.30% of residual CNPM survived the thermal degradation, which is significantly higher than that of pristine PANI, indicates the positive effects of synergistic interactions between metal oxides, PANI and MWCNTs. The stronger network of metal oxides having high thermal resistance with PANI can effectively prevent the early decomposition of composite material, while the structural integrity of MWCNTs effectively delays the decomposition by efficiently dissipating heat energy [38], [58].

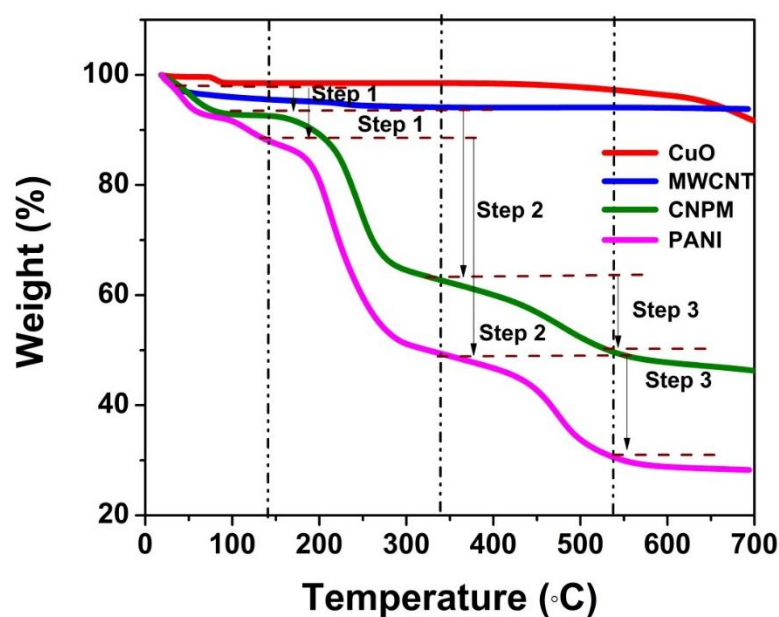


Fig. 3.13. Thermogravimetric analysis of CuO, MWCNT, PANI and CuO-NiO/PANI/MWCNT composite.

3.3.9. Electrochemical studies

3.3.9.1. Cyclic voltammetry (CV)

The electrochemical performance of the samples was evaluated in a three-electrode configuration with 1M Na₂SO₄ as the electrolyte medium. Fig. 3.14 (a,b,c,d) illustrates the cyclic voltammetry (CV) plots of NiO, CuO-NiO, NPM and CNPM composites with scan rates varying from 2 mV/s to 100 mV/s in a potential range of 0-0.8 V. The non-rectangular shape of CV curves clearly indicates that all the samples possess very distinctive capacitive characteristics from that of electric double layer capacitors [59]. The direct proportionality between voltametric current and scan rates is clear from the plots, which is one of the fundamental characteristic of an ideal capacitor [60].

Furthermore, nanosize and structure, surface area, and porous nature significantly configure the voltametric performance of a material [61]. Thus, compared with CV curves of pure metal oxides, the PANI and MWCNT incorporation makes the marginal shape change in CV plot of composites. As similar as CPM composite, the NPM and CNPM composites exhibit a pair of redox peaks at lower scan rates due to the presence of PANI. For NPM, the redox peaks were located at (0.37 V, 0.2 V) and for CNPM peaks were at (0.42 V, 0.18 V) at 10 mV/s. This redox peak can be attributed to the leucoemeraldine (LE) transition to Emeraldine (E) in PANI samples [62]. There is redox peak shift for the NPM and CNPM composites as similar to CPM, while increasing scan rates, which indicates that MWCNTs and PANI enhanced the redox properties of the nanocomposite. The increase in current indicates the better utilisation of electrode material through effective ionic diffusion, as a consequence of enhanced surface area and porosity of the nanocomposite. The good current response in composite electrodes is a clear indication of their better conductivity with lower internal resistance. Moreover, the metal oxide attachments with MWCNTs beneficially avoids the aggregation of CNTs, and the PANI coatings over the metal oxide-MWCNT composite system can effectively enhance ionic conductivity through the hybrid composite through synergistic effects [63].

Fig. 3.14 (e) shows the comparative CV curve analysis of CuO, NiO, CuO-NiO, CPM, NPM and CNPM composites at 100 mV/s, showing the capacitive current

increase of quaternary CNPM composite compared with the pristine CuO, resulting in the enhance specific capacitance of composite. The enhancement in specific capacitance values can be easily interpreted using the Fig. 3.14 (f), making a comparative analysis of capacitance values of all nanostructures at 10 mV/s. In addition to large surface area, occurrence robust pore structure makes remarkable advantage in its electrochemical properties. The pore network presents in CNPM allows smooth mass transport of ionic or electronic charge carriers and also raise the accessibility of electrode material to the electrolyte medium, compared with their binary and ternary counter parts. Generally, in the case of mesoporous materials, the effect of large number accessible electro-active areas is directly correlated with its capacitive currents [64].

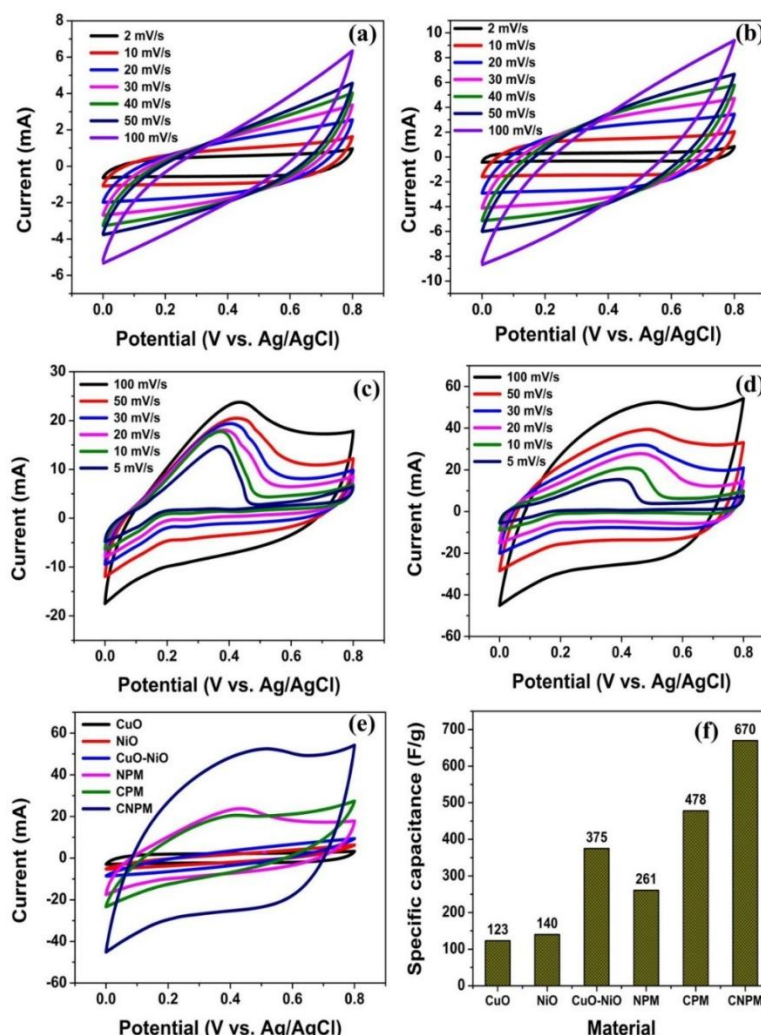


Fig. 3.14. CV curves of (a) NiO (b) CuO-NiO (c) NPM (d) CNPM, comparison of (e) CV curves of CuO, NiO, CuO-NiO, CPM, NPM and CNPM nanocomposites at 100 mV/s (f) specific capacitance of CuO, NiO, CuO-NiO, CPM, NPM and CNPM nanocomposites at 10 mV/s.

The charge storage mechanisms involved in the electrochemical performance of CNPM working electrode was estimated using Dunn method (Fig. 3.15). Fig. 3.15 (a) shows the $\log v$ vs. $\log i$ plot drawn using the data obtained from CV at 0.4 V. The value of 'b' obtained from this plot was 0.83, which indicates the dominance of capacitive controlled storage reactions. The value of parameters k_1 and k_2 were evaluated from the $v^{1/2}$ vs. $i/v^{1/2}$ plot and are used to estimate the current contributions (Fig. 3.15 (b)). The estimated current contributions involving diffusive and surface-controlled reactions in the CNPM working electrode at a scan rate of 10 mV/s were evaluated and portrayed in Fig. 3.15 (c). This decoupling of respective contributions helps to identify the exact reactions involved in the charge storage mechanism, suggesting a dominance of surface-controlled current part in the electrochemical performance of CNPM composite. The variation of current contributions at each scan rates was evaluated and presented in Fig. 3.15 (d), indicating the decrease of diffusive capacitance contributions at higher scan rates. The surface-controlled current contribution is 77 % at 10 mV/s and reaches to 98.8 % at 100 mV/s.

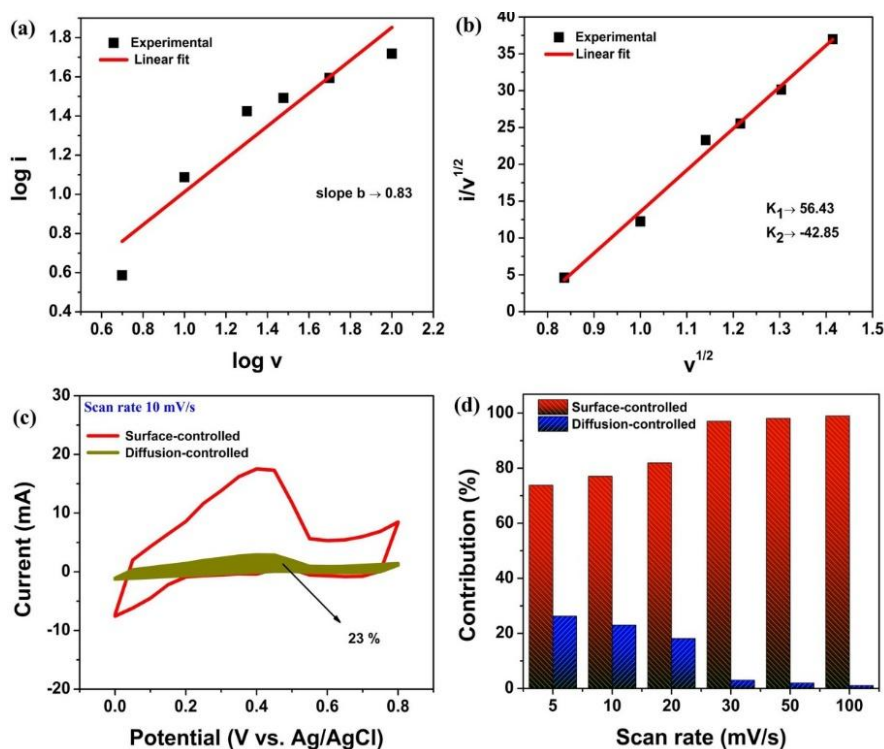


Fig. 3.15. (a) $\log v$ vs. $\log i$ plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ plot (c) decoupling of capacitive and diffusive current contributions at scan rate 10 mV/s (d) Histograms of diffusive and capacitive contributions of CNPM working electrode at varying scan rates.

3.3.9.2. Galvanostatic charge/discharge (GCD) studies

For the better electrochemical analysis of prepared working electrodes, galvanostatic charge/discharge (GCD) measurements were taken at different current densities. Fig. 3.16 (a,b,c,d) presents the GCD curves of the as-synthesised NiO, CuO-NiO, NPM, CNPM composites in the potential window of 0-0.8 V. All GCD curves showed good symmetry with nearly triangular shape, remarking good capacitive behaviour of materials even at higher current densities. Acute control over the active mass is crucial in the electrochemical performance of the system, since the mass directly correlates with the specific surface area [65]. The specific capacitance of NiO was 192.7 F/g, 137 F/g, 31 F/g and 28 F/g for currents densities of 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. The C_s values of CuO-NiO composite were 622 F/g, 258 F/g, 143.7 F/g and 120 F/g for currents densities of 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. Unsurprisingly, the PANI-MWCNT incorporated composite electrode materials displayed better capacitance compared with their binary counterparts. The NPM electrode exhibits specific capacitance values of 346 F/g, 261 F/g, 185 F/g, and 186 F/g at current densities of 0.5 A/g, 1 A/g, 3 A/g and 5 A/g, respectively. Whereas, the CNPM composite attained capacitance values of 775 F/g, 410 F/g, 262 F/g and 123 F/g at 1 A/g, 2 A/g, 3 A/g and 7 A/g, respectively. Fig. 3.16 (e) presents the comparative GCD curves of CuO, NiO, CuO-NiO, CPM, NPM, and CNPM composites at a current density of 1 A/g. The enhancement in the discharging time of CNPM was clearly noticeable from this plot. A comparison of specific capacitance values of CuO, NiO, CuO-NiO, CPM, NPM, and CNPM materials at various current densities was portrayed in Fig. 3.16 (f). The remarkable capacitance behaviour of CNPM nanocomposite can be the contribution of its surface area and porosity, which facilitates accessible active surface for enhanced penetration of electrolyte ions to the working electrode matrix. The mesoporous morphology of CNPM with commendable surface area assures the fair distribution of electrolyte solution and fast ionic diffusion through the pores. During charging/discharging, mesoporous structure of CNPM offers lower internal resistance, thereby quick ionic transport in the system. The possibility of ionic trapping in the pores are less compared with microporous materials, eventually upturn the capacitance values and corresponding energy-power densities even at higher charging/discharging rates [66].

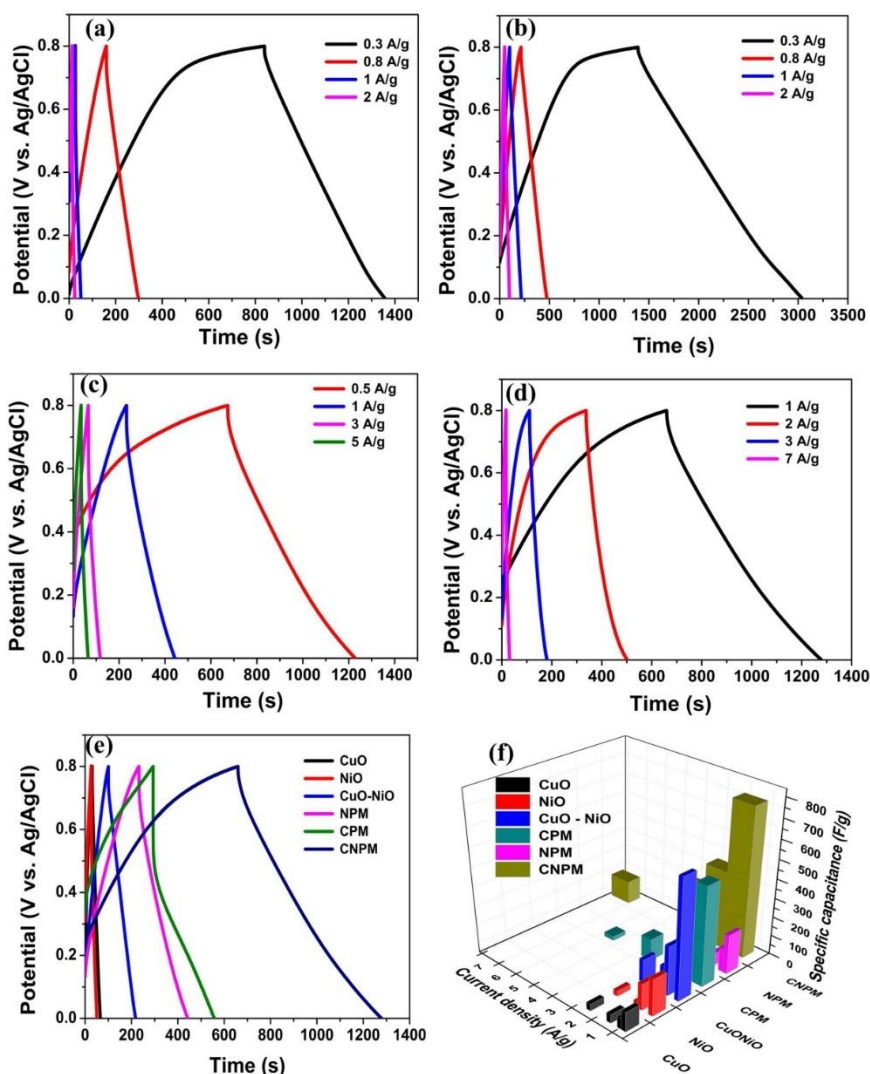


Fig. 3.16. GCD curves of (a) NiO (b) CuO-NiO (c) NPM (d) CNPM (e) comparison of charge-discharge curves of CuO, NiO, CuO-NiO, CPM, NPM, CNPM composites at current density of 1 A/g, (f) variation of specific capacitance with current density of CuO, NiO, CuO-NiO, CPM, NPM, CNPM composites.

3.3.9.3. Electrochemical impedance spectroscopy (EIS)

The Nyquist impedance plot of electrode materials from EIS measurements are shown in Fig. 3.17, which is done in a frequency range of 100 kHz to 100 mHz with a signal amplitude of 10 mV. The best fitted Nyquist plots of NiO, CuO-NiO, NPM, and CNPM composites evaluated through EIS analyser software, were shown in Fig. 3.17 (a-d). All the EIS curves presents a distorted semicircle in the high frequency region and a linear behaviour in lower frequency region (Fig. 3.17 (e)). The arc portion results from the redox reactions that happened in the electrode-electrolyte interface, whereas the linear edge in lower frequency area specifies the supercapacitive behaviour of as-

prepared working electrodes. The R_s , R_{ct} , CPE, W and n values of each electrode materials were calculated using EIS spectrum analyser software, are tabulated in Table 3.4. The Nyquist plot of the quaternary CNPM composite displayed almost a straight line nature with very small semicircle in the higher frequency region. The lower values of R_s and R_{ct} for the CNPM composite electrode undoubtedly indicate the enhancement of ion accessibility, owing to its very low internal resistance, resulted in increased electrical conductivity in the configuration [67].

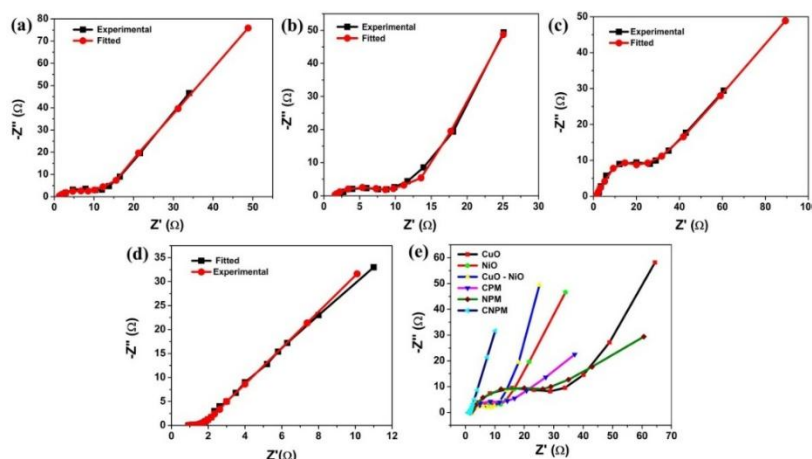


Fig. 3.17. (a) The best fitted Nyquist plot of as-prepared (a) NiO, (b) CuO-NiO, (c) NPM (d) CNPM (e) comparison of Nyquists plots of all nanostructures.

Table 3.4. The R_s , R_{ct} , CPE, W and n values of as-synthesised CuO, NiO, CuO-NiO, CPM, NPM, CNPM nanocomposites.

	Sample					
	CuO	NiO	CuO-NiO	CPM	NPM	CNPM
$R_s (\Omega)$	2	1.85	1.69	1.22	1.39	0.99
$R_{ct} (\Omega)$	29.30	10.29	6.00	11.66	21.72	1.42
W	22.75	32.35	23.653	33.72	55.84	10.68
CPE	0.00057	0.00042	0.00018	0.0049	0.00046	0.00008
n	0.943	0.666	0.736	0.688	0.660	0.563

3.3.9.4. Cycle stability

The capacitance retention analysis of CNPM nanocomposite were investigated for 5000 consecutive cycles at a current density of 7 A/g, depicted in Fig. 3.18. There is a gradual decrease in capacitance value for the initial 500 cycles, probably due to the active phase of the working electrode [68]. The sample exhibited a commendable capacity retention of about ~ 97.3 % for the remaining charge-discharge cycles. The noticeable capacitance retention of composite accounts that the material doesn't suffer

any kind of structural deformations despite of repeated charge-discharge operations. Typically, the frequent insertion/extraction of charge carriers into/from the electrode surface causes harmful mechanical degradation of the active material. In contrast, the CNPM nanocomposite with mesoporous architecture and rich interconnected porosity made them compactable to overcome the mechanical strains with its everlasting mechanical flexibility [64], [69].

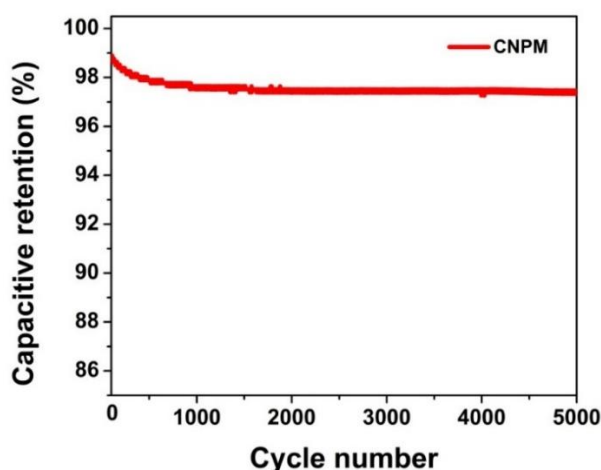


Fig. 3.18. Cycle stability of CNPM working electrode over 5000 cycles.

3.3.9.5. Electrochemical performance of CuO-NiO/PANI/MWCNT quaternary nanocomposite in symmetric two-electrode configuration

A symmetric supercapacitor device set up with a two-electrode configuration was used to test the practical possibilities of CNPM composite electrode. Fig. 3.19 (a) shows the CV curve fabricated device with CNPM as the active material for different scan rates. The material presents a quasi-rectangular shaped CV curve without any noticeable redox peaks, indicating the pseudocapacitive behaviour of the material. The GCD plots (Fig. 3.19 (b)) showcased a very close triangular shaped charge/discharge graphs with IR drop for all the current densities. The material exhibited a specific capacitance of 457 F/g at 1 A/g, 270 F/g at 2 A/g, 113 F/g at 3 A/g and 75 F/g at 5 A/g (shown in Fig. 3.19 (c)). The high value of specific capacitance for the quaternary composite is probably because of the nano-sized porous infrastructure of mixed oxides involved in the composite electrode and the enhanced conductivity, stability and surface area contributed from the PANI and MWCNT counterparts. PANI being a conducting polymer that can serve not only as a binder between the CuO, NiO, and MWCNT

components, but also as a member involved in the redox reactions as well. The satisfactory coulombic efficiency values were obtained for CNPM working electrode, which is presented in Fig. 3.19 (d). The Ragone plot (PD vs. ED curve) of composite electrode was shown in Fig. 3.19 (e) and made a comparison with the standard Ragone plot [70]. The CNPM electrode shows a maximum energy density of 40.62 Wh/Kg and power density of ~ 786 W/Kg. The sample exhibited relatively better energy density and power density compared with the conventional batteries, which indicates the utilization of this quaternary composite electrode for electrode fabrication in electrochemical systems are very promising. The capacitance retention was evaluated for 50000 charge/discharge cycles at a discharge current of 10 mA is shown in Fig. 3.19 (f). The quaternary composite material shows high retention efficiency of about 99.7% over 50000 cycles, which shows its excellent stability and compatibility as potential electrode stuff in energy storage applications.

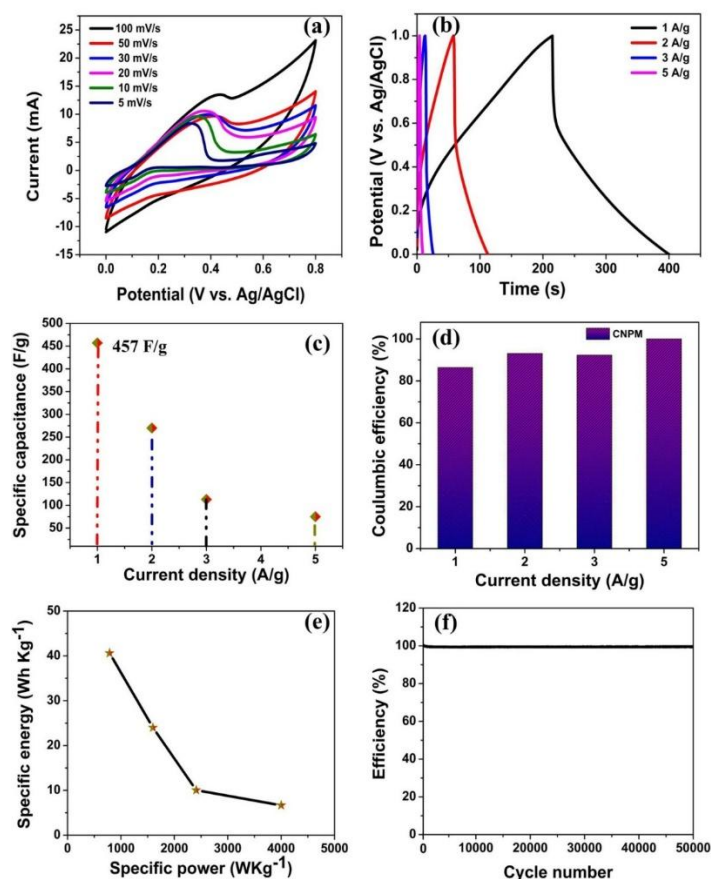


Fig. 3.19. (a) CV (b) GCD plots of CNPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) columbic efficiency analysis (e) Ragone plot and (f) cycle stability of CNPM composite in 50000 cycles.

3.4. CONCLUSION

The CuO-NiO/PANI/MWCNT nanocomposites were prepared using the freeze-drying assisted synthesis method. The chemical oxidative polymerisation of aniline followed by a freeze-drying stage along with already prepared metal oxide composites such as CuO-NiO and MWCNTs forms a feasible method for synthesising CuO-NiO/PANI/MWCNT composites. The structural, morphological, optical and thermal properties of the prepared nanocomposite was evaluated using XRD, Raman, FT-IR, FESEM-HRTEM with EDS, BET and TGA. All these characteristics confirmed the intended formation of nanocomposite with satisfactory properties beneficial for the supercapacitive performances. The electrochemical performance of CNPM working electrode was studied initially in a three configuration. An excellent specific capacitance value of about 775 F/g was reported at a current density of 1 A/g. A symmetric supercapacitor device was established using CNPM working electrode in a two-electrode configuration and it has attained a remarkable energy density of 40.62 Wh/Kg at the power density of ~786 W/Kg. The synergistic interaction between PANI and MWCNTs in the presence of binary metal oxide composites has resulted in improvement of electrochemical performance of the quaternary composite compared with that of its individual components.

Table 3.5. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CuO-NiO/PANI/MWCNT	670	10	775	1	364	10	457	1

3.5. REFERENCE

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Synthesis, Characterization, and Supercapacitive Performance of CuO-Co₃O₄ /PANI/MWCNT Hybrid System

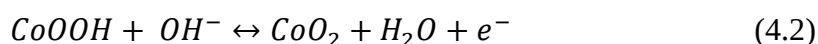
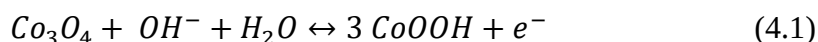
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Owing to the best strategies for improving the characteristics of supercapacitors such as better energy density and long cycle life, it is important to choose impressive composite electrode materials wisely that can supplement both highly porous active structures combined with large accessible spots for ionic species and also can enhance the overall pseudocapacitive nature. Cobaltite oxide (Co₃O₄) is one of the recently explored electrode materials in the area of high-performance supercapacitors on account of its high predicted capacitance and favorable pseudocapacitive behavior. Introduction of Co₃O₄ in to the ternary CuO/PANI/MWCNT hybrid system can enhance the electrochemical performance caused by the peculiar properties of Co₃O₄ such as good efficiency, long term stability and corrosion free nature. The effective combination of binary TMOs (CuO and Co₃O₄) into the PANI/MWCNT environment surpasses the electrochemical performance of the combined quaternary system. The structural, morphological understandings and thermal stability of the combined hybrid system are interpreted with XRD, FESEM-EDS, HRTEM, XPS, BET, RAMAN and TGA. The electrochemical performance of the hybrid system is examined using both three and two electrode configurations.

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4.1. INTRODUCTION

In the current era, metal oxide NPs have gained much attention due to their intriguing properties like significant electrical and chemical properties, high surface-to-volume ratios, and ease of preparation. Along with the recent trend for further improvement of the electrochemical performance of CuO, researchers are preparing electro-active hybrid materials of CuO with other TMOs. Among the popular TMOs predominantly prevailing in the scientific community, cobalt oxide NPs are well-known for applications like catalysis, magnetic fluids, sensors, and energy storage devices [1], [2], [3], [4]. Cobalt oxide exists in various forms like cobaltous oxide (CoO), cobaltic oxide (Co₂O₃) and cobaltite oxide (Co₃O₄), in which the black antiferromagnetic tricovalent tetraoxide (Co₃O₄) found an esteemed position in the field of supercapacitor applications [5]. Co₃O₄ is the least explored one type of electrode material in the electrochemical field, having AB₂O₄ spinel structure along with high theoretical capacitance (~ 3560 F/g) and excellent intercalative pseudocapacitive features. The Co₃O₄ electrode material has been found to have good reversible specific capacity, corrosion resistance and long term stability [6]. The possible charge storage mechanisms followed in a Co₃O₄ based electrode material can be described as follows;



4.1.1. Cobaltite oxide (Co₃O₄): An emerging electrode material

Owing to the properties like high predicted specific capacitance and potential pseudocapacitance properties, Co₃O₄ becomes a viable electrode material in energy storage applications. There are a few previous reports focusing on the electrochemical performance of Co₃O₄ [7], [8], [9]. R. R. Samal *et al.* discussed the anionic and cationic surfactant assisted hydrothermal synthesis of cobalt oxide and explored the electrochemical performance of these cobalt oxide nanoflakes in a three-electrode configuration. They reported a higher capacitance of 777.45 F/g, energy density of 32.66 W h/Kg and powder density of 39.8 kW/Kg for CTAB-assisted Co₃O₄ nanoflakes [5]. An ultra-layered porous Co₃O₄ structures synthesised through the precipitation method has delivered a specific capacitance of 548 F/g at a current density of 8 A/g

with 68% capacitance retention [10]. Badreah Ali Al Jahdaly *et al.* employed phytosynthesis assisted with marine red algae extract as a stabilizing agent for the preparation of Co₃O₄ NPs. The activated carbon/ Co₃O₄ symmetric device designed was established a specific capacitance of 182 F/g at a current density of 1 A/g [11]. Juan Xu *et al.* prepared Co₃O₄ nanotubes via annealing a chemically deposited cobalt hydroxide in an anionic aluminium oxide template. The electrochemical measurements of these Co₃O₄ nanotubes show a specific capacitance value of 574 F/g at 0.1 A/g [12]. Gwang –Su Jang *et al.* reported the electrochemical performance of hydrothermally prepared Co₃O₄ nanorods and stacked NPs. The stack like NPs exhibited a capacitance of 226.3 F/g at a scan rate 10 mV/s in a 6M KOH electrolyte solution. During calcination at high temperature, the surface morphology of the synthesised cobalt oxides has changed to morous category, eventually leading to a better ionic transport through the electrode surface [13]. Unfortunately, the specific capacitance and cycling stability of Co₃O₄ is still very beyond the theoretical value by cause of the limitations like poor electrical conductivity and surface area. Till now, various strategies have been developed by researchers in order to overcome the aforementioned drawbacks. One among the powerful strategies was to establish a metal dopant in to the environment of Co₃O₄ [14], [15], [16]. Faizal Ali *et al.* studied the effect of chromium in the electrochemical performance of cobalt oxide nanostructures by varying the doping percentage from 1 to 10. The Cr 6%-doped Co₃O₄ sample exhibited specific capacitance of 1283 F/g at 5 mV/s in 3M KOH electrolyte solution. The excessive doping of chromium will adversely affect the electrode performance, since it covers the electro-active sites in the lattice of cobalt oxides [17]. Shude Liu *et al.* discussed the electrochemical potential of oxygen deficient Cu-doped Co₃O₄ nanocrystals and designed an asymmetric supercapacitor with O_v-Cu-Co₃O₄@C electrode having a high energy density of 64.1 W h kg⁻¹ at 800 W kg⁻¹. Moreover, the occurrence of Cu dopants and O vacancies in the composite electrode synergistically enhanced the accessible electro-active sites, yielding refined redox chemistry [18].

4.1.2. CuO-Co₃O₄ composite electrodes for supercapacitor applications

Even though, metal doping as well as changing preparation conditions in the synthesis of CuO has improved its pseudocapitance compared with the pristine CuO,

it still suffers capacity decay due to sluggish charge transportation in the electrochemical system. So as to alleviate these limitations, another strategy of developing a hetero-structure with enriched electro-active sites by combining highly conductive and electrochemically active TMO material like Co₃O₄ with CuO is implemented [19], [20]. S. Balasundari *et al.* prepared CuO-Co₃O₄ via a precipitation method followed by the microwave assisted hydrothermal technique. The composite electrode exhibited a specific capacitance of 586 C/g with cyclic reversibility of 113.6% under a high current density of 20 A g⁻¹ after 5000 cycles. The robust synergistic effects between CuO and Co₃O₄ and their potential redox reactions during the charging and discharging process significantly enhance the electrochemical property of the electrode [21]. Recently, Ke Xue *et al.* have grown CuO/Co₃O₄ material directly onto nickel foam by combining electrodeposition and SILAR methods. They prepared spherical and wheat-like nanocomposites and exploited its electrochemical performances. The wheat-like CuO/Co₃O₄ has acquired high specific capacity and stability [22]. K. Athira *et al.* have hydrothermally synthesised CuO/Co₃O₄ nanocomposite and studied its electrochemical performance. The composite electrode material exhibited a specific capacitance of 860 F/g at 2 A/g [23].

4.1.3. CuO-Co₃O₄/PANI/MWCNT quaternary hybrid electrode material as a potential member in ESDs

The next productive strategy for the enhancement of the electrochemical performance of CuO-Co₃O₄ composite is to make them combined with PANI and MWCNTs, which eventually lead to a quaternary hybrid electrode material. There are only a few reports on this electrode combination based on CuO, Co₃O₄, PANI and MWCNTs. S. Prabhu *et al.* used the hydrothermal method for the preparation of 3D flower-like CuO/Co₃O₄/r-GO heterostructure and the as-prepared electrode has shown a high surface area resulting in more interfacial contact area between the electrode surface and electrolyte ions, thereby the excellent electrochemical performance is attained [24]. Bairui Thao *et al.* fabricated Ni foam supported CuO/Co₃O₄/r-GO composite electrode and the asymmetric supercapacitor device based on the as-synthesised composite delivered a specific capacitance of 660.5 F/g at 2 A/g with 92.3% capacity retention [25]. Yingmeng Zhang *et al.* prepared sandwiched CuO/Co₃O₄ nanosphere/RGO composite and explored the electrochemical performance of the as-

synthesised 3D-composite structure. The sandwiched nature of CuO/Co₃O₄ nanospheres on to the layers of RGO has avoided the aggregate formation among both RGO and CuO/Co₃O₄ nanospheres, which leads to enhanced conductivity and electrochemical performance of the electrode. The electrode material exhibited a reversible capacitance of 847 mA.h.g⁻¹ after 200 cycles at 20 mA/g [26]. To the best of our knowledge, there are no literatures on CuO-Co₃O₄/PANI/MWCNT quaternary composites for any sort of applications.

4.2. EXPERIMENTAL SECTION

4.2.1. Synthesis materials

Copper nitrate trihydrate (Cu(NO₃)₂.3H₂O), urea (CH₄N₂O), ammonium persulfate (APS) ((NH₄)₂S₂O₈), aniline hydrochloride (C₆H₅NH₂.HCl), analytical grade hydrochloric acid (HCl), sodium sulphate (Na₂SO₄), sodium dodecyl sulphate (CH₃(CH₂)₁₁OSO₃Na) (SDS, > 98%), cobalt nitrate ((CoNO₃)₂.6H₂O), ammonia solution (25%) and de-ionised (DI) water were purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, OD × L = 6 – 9 nm × 5 μm), polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standard and utilized without any further purifications. Distilled ethanol was used for cleaning purposes.

4.2.2. Synthesis of Co₃O₄

The Co₃O₄ nanoparticles were prepared via similar surfactant-free hydrothermal process with the similar reaction conditions of the CuO synthesis. Firstly, 0.1M of cobalt nitrate was dissolved in 75 ml de-ionised water. Later, 10 ml ammonia solution was added to the precursor solution to achieve a pH in the range of 8-10 under constant stirring. 0.003 M urea was added to the whole solution before transferring it into the autoclave setup and kept in the oven under 180 °C for 24 hours. When the reaction conditions met, the resultant solution from the reactor was filtered and washed thoroughly using DI water and ethanol. The obtained Co₃O₄ precipitate was then shifted to an oven at 80 °C for 6 hours to get the purified Co₃O₄ nanoparticles.

4.2.3. Synthesis of CuO-Co₃O₄ nanocomposite

The CuO-Co₃O₄ nanocomposite was processed using the hydrothermal method without employing any additives or surfactants. Initially, 0.1 M cobalt nitrate was allowed to dissolve completely in 30 ml of DI water via a continuous stirring process. Later, the previously prepared CuO nanoparticles (40 mg) were allowed to disperse in the above-mentioned precursor solution. Later, a 20 ml of ammonia solution was added drop wise to the whole solution. Then, 0.6 mM urea was added to the solution without disturbing the stirring process till a clear homogeneous solution was attained. The whole 50 ml solution was then transferred to an autoclave and set to keep in an oven at 180 °C for 24 hours to complete the synthesis process. The earned precipitates after hydrothermal reaction were washed multiple times with DI water and ethanol for the removal of the unwanted/unreacted substances from the resultant. Later, the obtained precipitate was transferred to oven at 80 °C for 6 hours to get the CuO-Co₃O₄ nanocomposite.

4.2.4. Synthesis of Co₃O₄/PANI/MWCNT ternary nanocomposite and CuO- Co₃O₄/PANI/MWCNT quaternary nanocomposite

The Co₃O₄/PANI/MWCNT ternary nanocomposite was prepared in a similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared Co₃O₄ and the final product is named CoPM for convenience.

The CuO-Co₃O₄/PANI/MWCNT quaternary nanocomposite was prepared in a similar synthesis procedure as CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared CuO-Co₃O₄ nanocomposite and the final product is named CCoPM for convenience.

4.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, Aeris Research (Source: Cu K α)). Fullprof Suite software was used for Rietveld analysis. Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany) was employed to determine the vibrational modes of the as-synthesised samples. Fourier Transform Infrared (FTIR)

spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using a ZnSe crystal. The surface morphology and elemental composition were done using a combination of High-Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of a TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

4.2.6. Electrode preparation and electrochemical studies

The electrochemical features of as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt % of active material, 10 wt % of polyvinylidene fluoride (PVDF) and 10 wt % of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly in to a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in the working electrode was 1.7 mgcm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of as-synthesised samples.

4.3. RESULTS AND DISCUSSION

4.3.1. X-Ray diffraction (XRD)

The structure and phase purity of materials were examined using X-ray diffractometer. The XRD profiles of Co₃O₄ and CuO-Co₃O₄ nanoparticles along with that of already prepared CuO for comparison are displayed in Fig. 4.1(a). Both Co₃O₄ and CuO-Co₃O₄ materials show their polycrystalline nature. All the dominant peaks of Co₃O₄ can be well indexed by comparing them with the corresponding JCPDS (No.-

43-1003). The crystallographic scattering peaks are observed at 18.88°, 31.16°, 36.73°, 38.55°, 44.60°, 55.72°, 59.24°, and 65.15° which correspond to (111), (220), (311), (222), (400), (422), (511) and (440) planes of the face centred cubic Co₃O₄ [12]. Moreover, no peaks of secondary phases like CoO or impurity peaks are observed in the XRD profile of Co₃O₄, which validate the formation of pristine cubic Co₃O₄ with preferential plane growth in the (311) direction. The XRD pattern of CuO-Co₃O₄ nanocomposite is found to be an exact mix of the monoclinic CuO and the cubic Co₃O₄ crystal structures, which clearly indicate that both CuO and Co₃O₄ phases are grown freely in the synthesis stage. Fig. 4.1 (b) shows the XRD patterns of the newly synthesised CoPM and CCoPM in the region 10°-90° along with those of PANI, MWCNT, and CPM for confirming the exact formation of the composites. The CoPM composite consists of peaks correspond to cubic Co₃O₄ phase in the 30°-90° region, even though their intensity get diminished owing to the dominance of PANI and MWCNT parts. The crystallographic plane (111) of Co₃O₄ is not appeared in the spectra because of the three dominant peaks of PANI observed in that region. Furthermore, the slight peaks shifts seen in the peak positions of the cubic Co₃O₄ can be attributed to their interaction with PANI-MWCNTs. For CCoPM composite, all the peaks in between 30°-90° are assigned to the presence of CuO-Co₃O₄ composite in the hybrid system. Also, the three peaks at 14.71°, 20.06° and 25.18° in XRD are correspond to (011), (020), and (200) crystallographic planes of emeraldine salt. No peak corresponding to MWCNT is visible in the XRD spectra of CoPM and CCoPM, which may be due to its peak coincidence with the broad bump of PANI in the 20-30° region. Thus, the formation of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanostructures is substantiated from the XRD data. The charge transfer interactions among the metal oxides, PANI and MWCNT leading to alterations in chain packing and configurations, may result in gentle shifts in the peak positions [27].

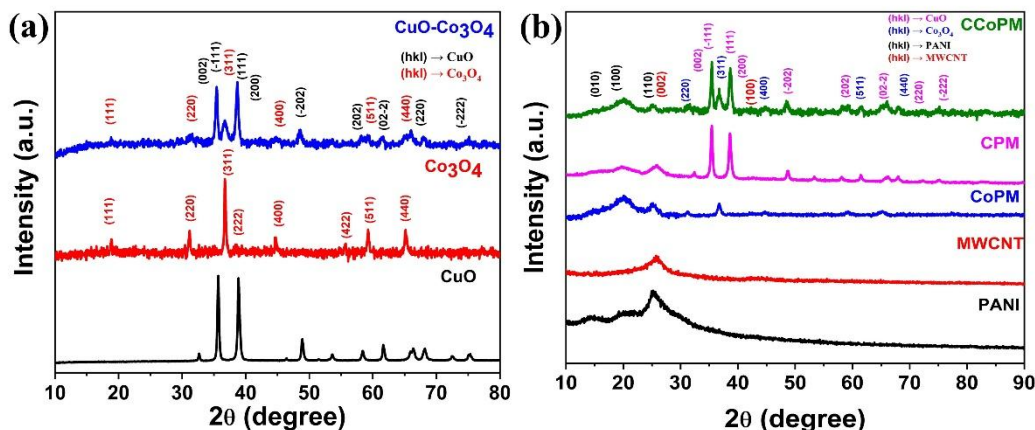


Fig. 4.1. XRD patterns of (a) CuO, Co₃O₄, CuO-Co₃O₄ nanoparticles and (b) PANI, MWCNT, CoPM, CPM, and CCoPM composites.

4.3.2. Raman spectroscopy

The Raman spectral evaluation was carried out to identify the structural purity and secondary or impurity phases in the composites. Fig. 4.2 (a) portrays the Raman spectra of Co₃O₄ nanoparticles having prominent bands at 194 cm⁻¹, 483 cm⁻¹, 520 cm⁻¹, 615 cm⁻¹, and 687 cm⁻¹, corresponding to F_{1g}, E_g, F_{2g}, F_{3g} and A_{1g} modes of spinel Co₃O₄ structure, which are consistent with previous reports [28]. The most intense Raman shift at 687 cm⁻¹ is attributed to the vibrational modes of octahedral units of Co₃⁺ ions. The Raman spectra of CuO-Co₃O₄ composite is displayed in Fig. 4.2 (b), presenting a blend of the Raman active modes of both monoclinic CuO and cubic Co₃O₄ [29]. The ternary composite CoPM shows Raman modes combining modes of individual constituents, as shown in Fig. 4.2 (c). Along with the E_g and F_{2g} modes of spinel Co₃O₄, characteristic modes of PANI and MWCNT were appeared in the spectra. The Raman shifts at 1346 cm⁻¹, 1599 cm⁻¹, and 2687 cm⁻¹ were ascribed to the D, G and 2D bands of MWCNTs. The lattice defects of phonon mode of vibrations in MWCNT surface cause the D mode, whereas the vibrations of C-C bond (sp² carbon atoms) in the graphitic layer result in the G band in the Raman spectra [30]. The shifts at 710 cm⁻¹, 816 cm⁻¹, and 1187 cm⁻¹ correspond to the characteristic peaks of the emeraldine salt form of PANI molecules. The Raman spectra of the quaternary composite CCoPM is displayed in Fig. 4.2 (d). The A_g and B_g modes of CuO at 289 cm⁻¹ and 618 cm⁻¹ and F_{2g} and F_{3g} modes of Co₃O₄ at 512 cm⁻¹ and 601 cm⁻¹ clearly confirm the presence of CuO-Co₃O₄ nanocomposite in the hybrid matrix. Unlike, the

CoPM sample, the CCoPM composite displayed the three intense shifts at 1183 cm⁻¹, 1342 cm⁻¹ and 1607 cm⁻¹ which indicated the synergistic combinational effects of PANI and MWCNT along with other less intense modes of both PANI and MWCNTs in the hybrid system. The peak intensity of Raman active modes of PANI molecules was lesser in the CoPM compared with that of in the CCoPM composite. Additionally, even though the characteristic peaks of PANI and MWCNTs were visible in both composites, there was an observable overlap of major MWCNT peaks with those of PANI. The PANI dominations in the Raman spectra were due to the lower MWCNT content in the sample as well as the inability of the laser beam to penetrate into the darker materials [31]. The observed small shifts in the quaternary composite are attributed to the effective interaction between PANI, MWCNT and metal oxides.

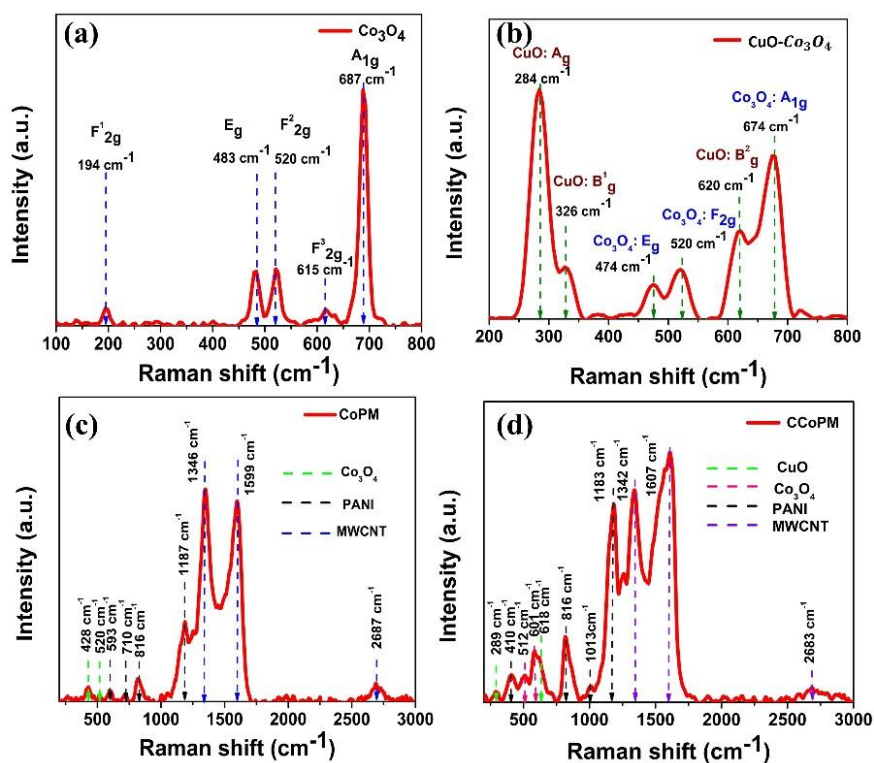


Fig. 4.2. Raman profiles of pristine (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM composites.

4.3.3. FT-IR spectroscopy

The crystal structure and molecular bonding in the prepared composites were then identified using FT-IR spectra, shown in Fig. 4.3. The FT-IR spectrum of the Co₃O₄ nanostructure has shown in the Fig. 4.3 (a) displays two prominent peaks of

spinel Co₃O₄ at 655 cm⁻¹ and 568 cm⁻¹. The peak at 655 cm⁻¹ ascribed to the stretching mode of ABO, where B represents the Co³⁺ in the tetrahedral hole in the Co₃O₄ lattice, whereas the peak at 568 cm⁻¹ related to the OB₃ stretching mode where B represents Co²⁺ in the octahedral hole [13], [32]. The peak at 1510 cm⁻¹ attributed to the stretching vibrational mode of O-H bond, whereas the peak at 1163 cm⁻¹ represents the stretching vibrational modes of C-O bonds [32]. In the Fig. 4.3 (b), there are peaks corresponding to both CuO and Co₃O₄ crystal structures. The peaks representing Co₃O₄ were appeared at 677 cm⁻¹ and 574 cm⁻¹, whereas the peak of Cu-O bond was occurred at 438 cm⁻¹. The peak at 2920 cm⁻¹ corresponds to stretching modes of O-H bonds, while the peak at 1452 cm⁻¹ attributed to vibrations of H₂O molecules [33]. The other less intense peaks in the range of 900-1300 cm⁻¹ represent the carbonyl groups [5]. The FT-IR spectra of CoPM and CCoPM nanocomposites are presented in Fig. 4.3 (c-d), highlighting the prominent modes of PANI, MWCNTs and metal oxides illustrated in Table 4.1.

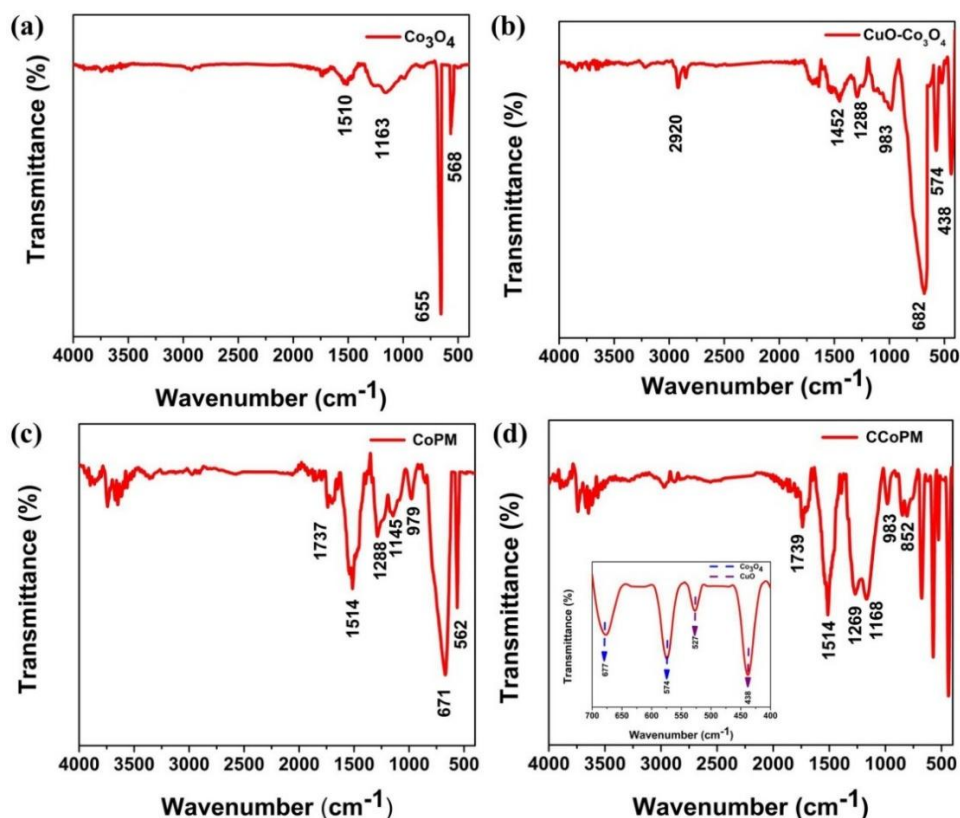


Fig. 4.3. FT-IR spectra of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM nanocomposites. (inset shows the zoomed spectra of CCoPM in the range 400-700 cm⁻¹ as marked in its corresponding figures 4.3 (d))

Table 4.1. List of peaks in FT-IR spectrum of CoPM and CCoPM nanocomposites and its corresponding assignments

FT-IR peaks		Assignments
CoPM	CCoPM	
1737 cm ⁻¹	1739 cm ⁻¹	stretch mode of carboxylic groups in MWCNT
1514 cm ⁻¹	1514 cm ⁻¹	C=C stretching in quinoid ring of PANI
1288 cm ⁻¹	1269 cm ⁻¹	C-N for aromatic amines in the polaron structure of conducting PANI
1145 cm ⁻¹	1168 cm ⁻¹	characteristic band of the protonated form of conducting PANI
972 cm ⁻¹	983 cm ⁻¹	due to protonated imine group in PANI
-	852 cm ⁻¹	Out of plane C-H bending vibration.
671 cm ⁻¹ & 569 cm ⁻¹	677 cm ⁻¹ & 574 cm ⁻¹	stretching modes of Co ₃ O ₄
-	527 cm ⁻¹ & 438 cm ⁻¹	stretching vibrations of Cu-O

4.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The surface morphological evolutions of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites were systematically investigated through FESEM-EDS analysis, portrayed in Fig. 4.4. The low and high magnification SEM images of Co₃O₄ shown in Fig. 4.4 (a-c) present a heterogenous distribution of several octahedral and diamond-like nanoparticles. The octahedral shaped nanoparticle carries a side length of around 128 nm, whereas the diamond-like particles have dimensions around 200 nm. The overall uneven distribution of these mixed shaped particles resulted in minimal pores in the morphology. In contrast, the morphological case of CuO-Co₃O₄ nanocomposites, a porous network of uniformly distributed bulky nanospheres interspersed with diamond-shaped nanoparticles, probably Co₃O₄ particles over the surfaces can be seen (Fig. 4.4 (d-f)). The sphere carries an average diameter of 940 nm, whereas the diamonds like structures over the sphere surfaces have a side length in the range of 20 to 35 nm. The porous architecture of this nanocomposite can contribute to enhancement in its specific surface area, thereby improving the material's

supercapacitive performances. The incorporation of PANI and MWCNTs into the Co₃O₄ nanosystem, has induced visible morphological modifications like the transformation of octahedral shaped particle of Co₃O₄ into an agglomerated form combining the polymer networks and tubular morphology of MWCNTs (Fig. 4.4 (g-i)). The overall agglomerated morphology of the ternary CoPM composite has been limited by beneficial pores. In the instance of CCoPM quaternary composite, several voluminous pores can be seen along with the fibrillar morphology, which can positively enrich the effective surface area of composite (Fig. 4.4 (j-l)). The interconnected thick fibres carry an average diameter of about 42 nm. From the lower magnification SEM micrographs (Fig. 4.4 (j)), it is easily understood that the grafting of PANI over the MWCNT surfaces in the presence of CuO-Co₃O₄ made the metal oxides morphologically indistinct. The highly substantial porous infrastructure made the composite capable for the electrochemical applications.

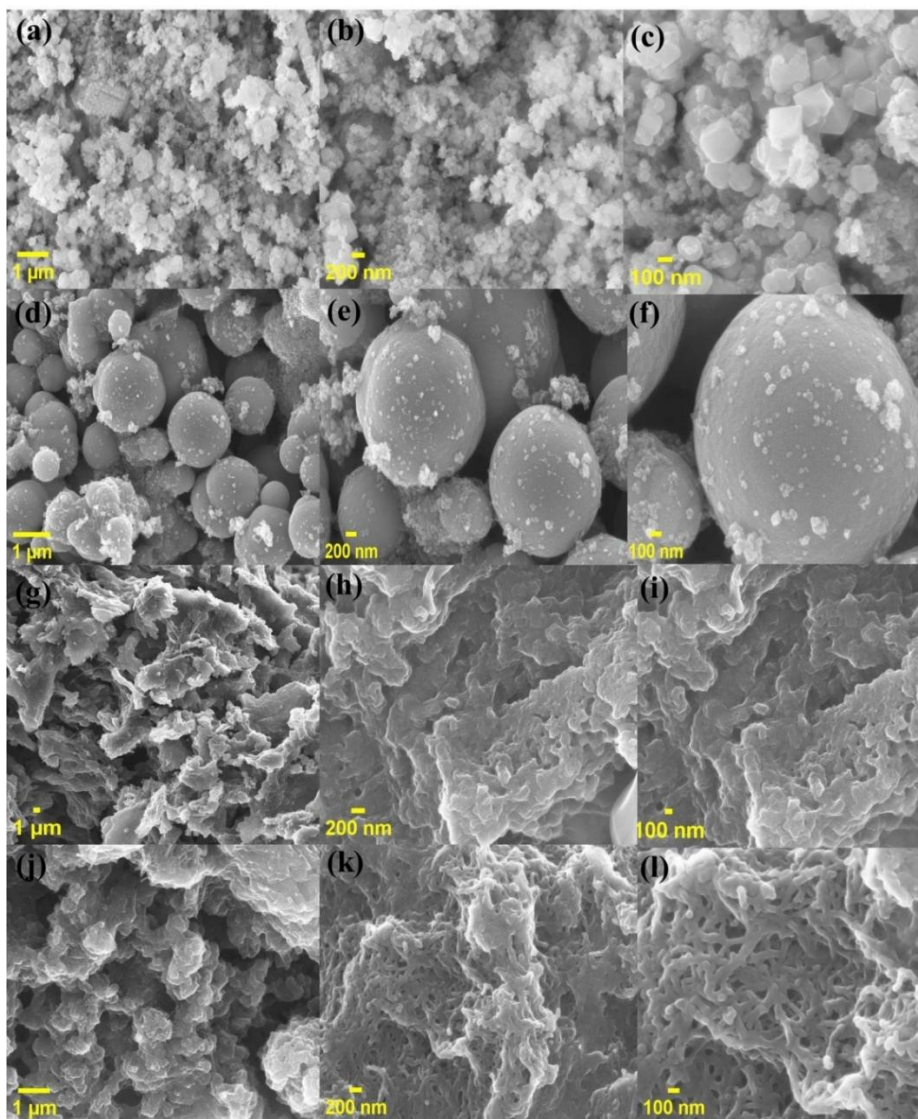


Fig. 4.4. FESEM micrographs of (a,b,c) Co₃O₄ (d,e,f) CuO-Co₃O₄ (g,h,i) CoPM (j,k,l) CCoPM nanocomposites.

The elemental composition of the prepared composites was done using conventional energy dispersive spectroscopy (EDS), as shown in Fig. 4.5. The co-existence of elements like cobalt and oxygen is clearly visible in the spectra of Co₃O₄, displayed in Fig. 4.5 (a). Also, the EDS plot of CuO-Co₃O₄ (Fig. 4.5 (b)) shows the noticeable peaks of constituents like copper, cobalt and oxygen, validating the exact formation of these elements in the material. In the EDS spectrum of CoPM, the presence of elements C, N, Co, and O verifies effective introduction of PANI/MWCNT combination into Co₃O₄, as shown in Fig. 4.5 (c). From the EDS image of CCoPM shown in Fig. 4.5 (d), the co-existence of Cu, Co, N, C and oxygen clearly confirmed the formation of the quaternary CCoPM composite. The atomic mass concentrations of

the constituent elements are listed in Table 4.2. The atomic concentrations of each constituent element in the synthesised material were validated to ensure the formation of planned compounds. The relatively higher atomic presence of carbon was observed in the ternary and quaternary composites, indicating the synergistic interactions of PANI and MWCNTs.

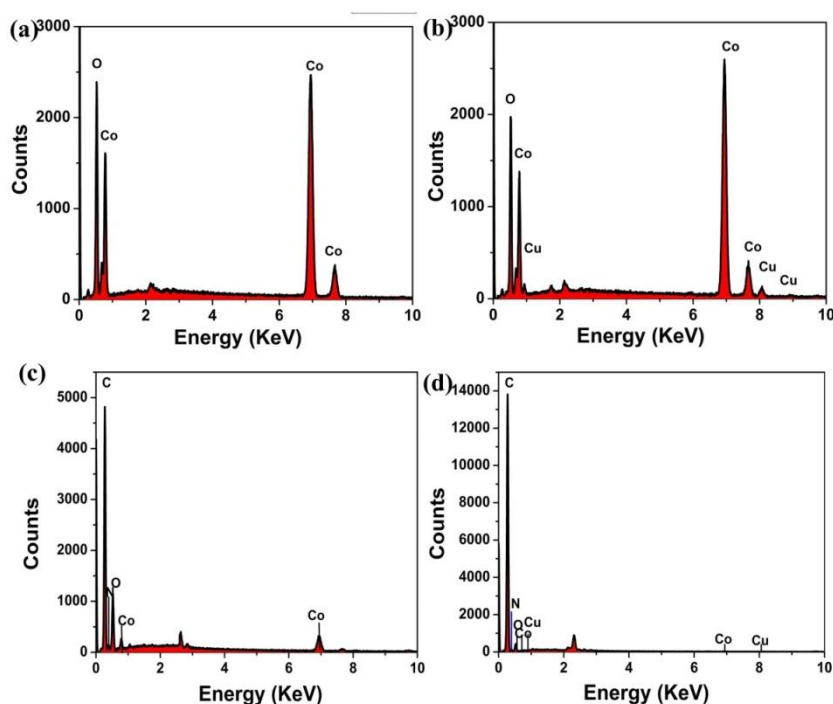


Fig. 4.5. EDS spectra of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM nanocomposites.

Table 4.2. Elemental data of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM composites obtained from EDS analysis.

Sample	Atomic ratio (%)				
	Cu	O	Co	C	N
Co ₃ O ₄	-	54.21	45.79	-	-
CuO- waCo ₃ O ₄	17.25	43.64	39.11	-	-
CoPM	-	17.03	13.80	59.73	9.44
CCoPM	8.12	11.11	7.31	57.64	15.82

The elemental mapping images of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites are shown in the following figures (Fig. 4.6, Fig. 4.7, Fig. 4.8, Fig. 4.9). The yellowish colour over the whole material surface is clear evidence for the

uniform distribution of cobalt and oxygen in Co₃O₄ (Fig. 4.6). The co-existence of CuO and Co₃O₄ were validated from the EDS map of CuO-Co₃O₄ shown in Fig. 4.7. In the case of CoPM composite, the co-existence of Co₃O₄, PANI and MWCNTs were observable at the first glance itself (Fig. 4.8). However, some kind of uneven distribution of carbon is seen in the EDS map, suggesting some heterogeneity in the synthesis process. The domination of the element carbon is evident in the EDS mapping image of CCoPM (Fig. 4.9), as suggested by the EDS data. But the existence of cobalt oxide, copper oxide and PANI were also suggested by the corresponding EDS elemental distribution images.

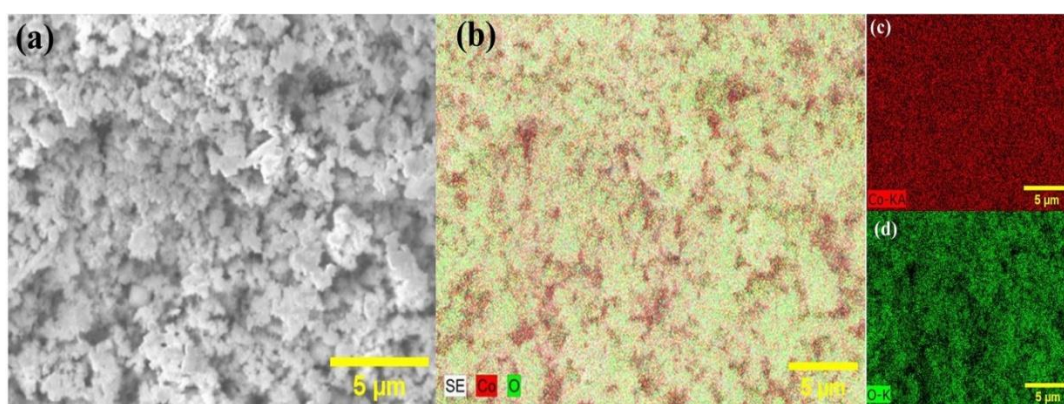


Fig. 4.6. (a) SEM image, (b) EDS mapping of Co₃O₄ nanostructures, and (c-d) selective elemental distribution for the area shown in image (a).

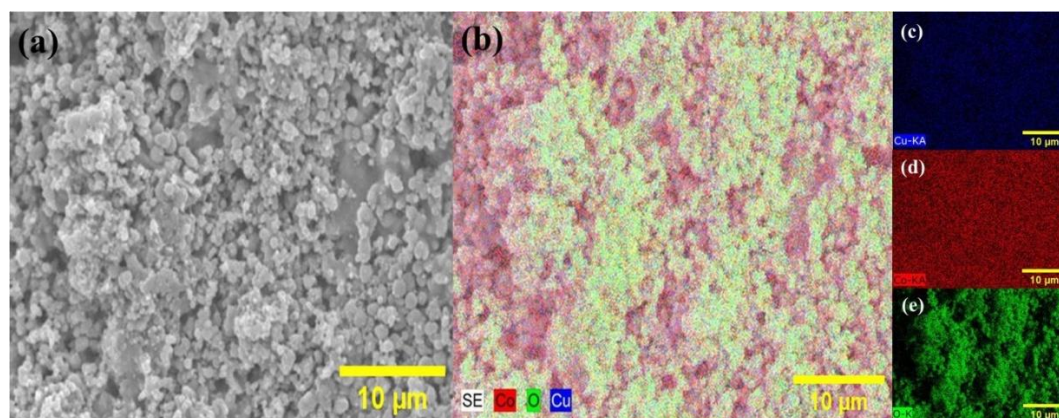


Fig. 4.7. (a) SEM image, (b) EDS mapping CuO-Co₃O₄ nanocomposites, and (c-e) selective elemental distribution for the area shown in image (a).

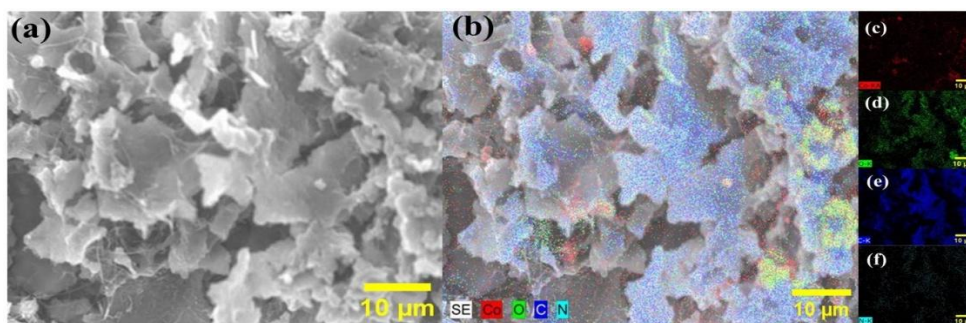


Fig. 4.8. (a) SEM image, (b) EDS mapping CoPM nanocomposites, and (c-f) selective elemental distribution for the area shown in image (a).

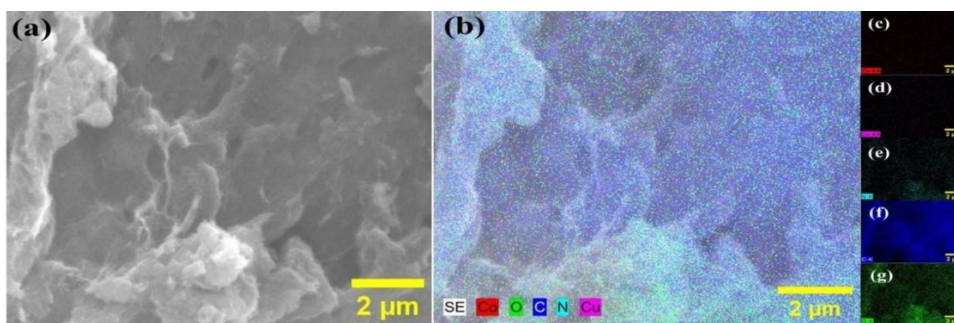


Fig. 4.9. (a) SEM image, (b) EDS mapping CCoPM nanocomposites, and (c-g) selective elemental distribution for the area shown in image (a).

4.3.5. High Resolution Transmission electron micrographs (HR-TEM)

The microstructural properties of the CCoPM composite were further investigated using TEM, HRTEM-SAED analyses, depicted in Fig. 4.10. The TEM images shown in Fig. 4.10 (a,b), illustrates the presence of PANI grafted MWCNTs integrated with the metal oxide phases. The PANI grafted tubules have a greater average diameter compared with the unmodified MWCNTs. The CuO existence is substantiated from the HRTEM image shown in Fig. 4.10 (c), showing the dominant crystallographic (111) and (-111) planes within the composite. The homogenous distribution of metal oxide particles within the composite was evident from the HRTEM image shown in Fig. 4.10 (d), with the particle size distribution histogram plot shown in the inset of Fig. 4.10(d). The HRTEM image of lumps that appeared in the fibrous network was attributable to the (200) plane of MWCNTs (Fig. 4.10 (e)). The SAED pattern displayed in Fig. 4.10 (f) shows the polycrystalline nature of the sample.

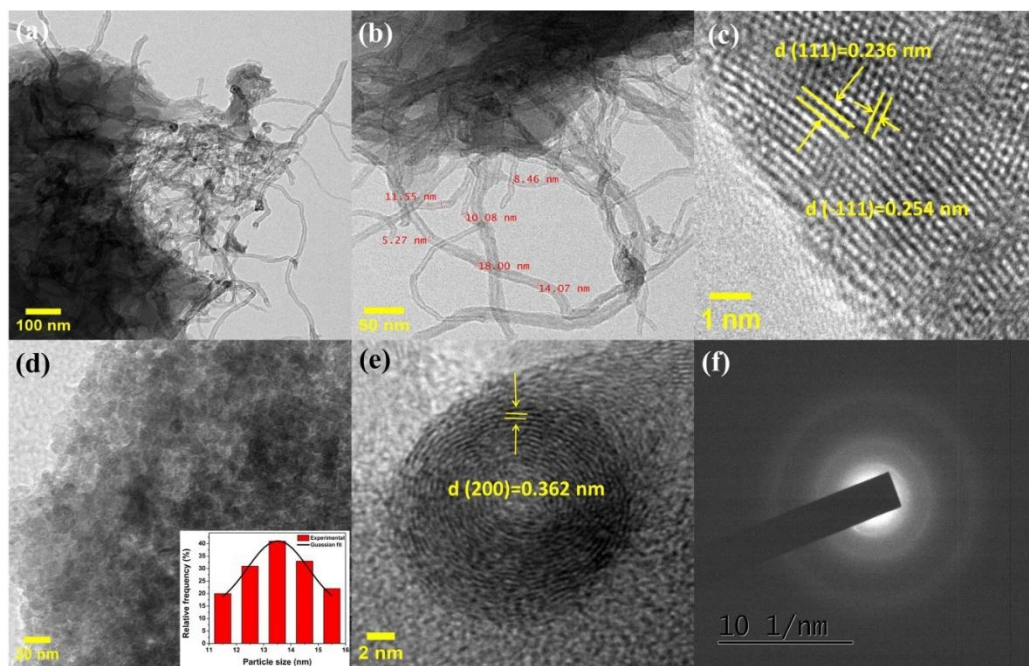


Fig. 4.10. (a,b) TEM micrograph (c,d,e) HRTEM images (f) SAED pattern of CCoPM composites.

4.3.6. X-Ray Photoelectron spectroscopy (XPS)

The elemental compositions and chemical oxidative states of the quaternary CCoPM nanocomposite were investigated through XPS studies, which are presented in Fig. 4.11. The survey spectra of the composite are shown in Fig. 4.11 (a), having the evidence of elements C, N, O, Cu, and Co in the matrix, without any impurity elements. The spectral resolution of the C 1s state is presented in Fig.4.11 (b), which is associated with three peaks after deconvolution at binding energies 284.3 eV, 285.2 eV, and 286.4 eV. The intense peak of core level C 1s at 284.3 eV was allocated to the sp² C atoms. The peak at 285.2 eV was responsible for sp³ C atoms as well as indicating the carbon-nitrogen binding through C=N bonds [34]. While, the less intense peak at 286.4 eV can be associated with both C-N bonds in the composites, proving the effective interaction between PANI and MWCNTs [35]. The core level spectrum of the O 1s orbital level is shown in Fig. 4.11 (c), which is deconvoluted to four major and minor peaks at 529.1 eV, 531.3 eV, 532.2 eV, and 534.6 eV. The less intense peak at lower binding energy 529.1 eV was the representation of both metal-oxygen bonds arising from CuO and Co₃O₄ crystals as well as C-O/C=O bonds [34], while the intense peak at 531.3 eV was associated with oxygen vacancies prevailing in the whole hybrid composite [36]. The

high intense broad peak at 532.2 eV was responsible for the adsorbed –OH functional groups on the composite surfaces. The minor peak at the higher binding energy position was associated with O=C-O bondings resulted from the PANI/MWCNT intercalations [37]. The deconvoluted N 1s spectra was displayed in Fig. 4.11 (d), demonstrating three equal intense peaks located at the binding energies 399 eV, 399.6 eV and 401 eV associated with emeraldine form of PANI. The peak at 399 eV was associated with the quinoid imine ring (=N-H-), whereas peak at 399.6 eV arose from the presence of benzenoid amine ring (-N-H-). The third peak at higher binding energy is responsible for -N-H⁺- bonds in the composite [38]. The existence of CuO in the composite system was identified from the core level spectra of Cu 2p, displayed in Fig. 4.11 (e). The two characteristic peaks located at 933.3 eV and 953.4 eV were attributed to Cu 2p_{3/2} and Cu 2p_{1/2} orbits of Cu²⁺ states of CuO, with a spin orbit coupling energy band gap of 20.1 eV. The two satellite peaks that appeared at 943.4 eV and 963.2 eV further confirm the presence of CuO phase in the composite [24], [34]. In the meantime, the characteristic peaks of Co 2p phase of Co₃O₄ were identified from the high resolution XPS spectra presented in Fig. 4.11 (f). The two major peaks appeared at 782.5 eV and 797.8 eV were attributed to the Co³⁺ 2p_{3/2} and Co³⁺ 2p_{1/2} orbital levels of Co³⁺ oxidation state, along with their obvious shake-up peaks at 787 eV and 802.2 eV [13].

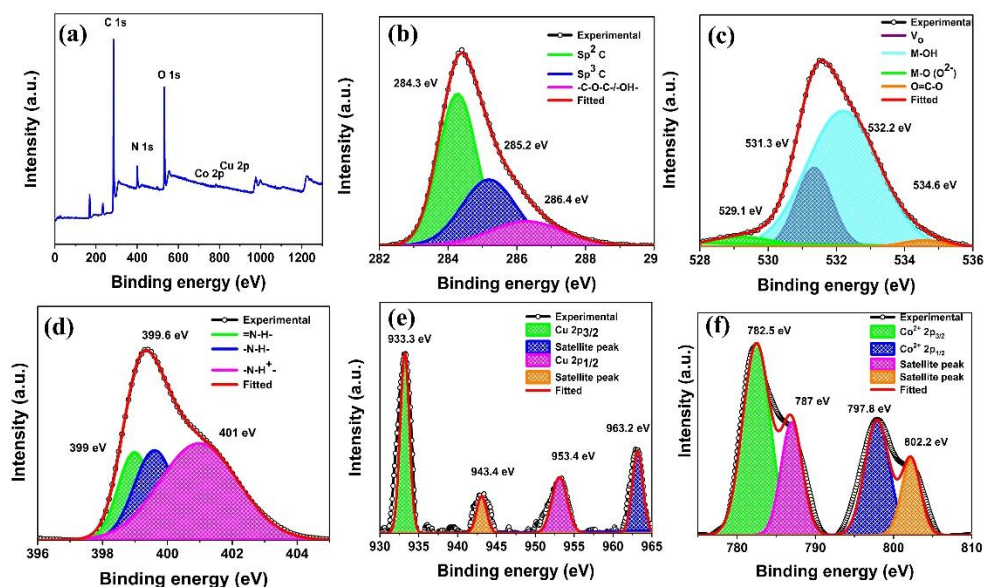


Fig. 4.11. (a) XPS survey spectrum and XPS elemental core spectra of (b) C 1s and (c) O 1s (d) N 1s, (e) Cu 2p, and (f) Co 2p states of CCoPM nanocomposite.

4.3.7. Brunauer-Emmett-Teller (BET) analysis

The specific surface area and pore size distribution of Co₃O₄, CuO-Co₃O₄, CoPM, and CCoPM nanocomposites were estimated using Brunauer-Emmett-Teller analysis and are presented in Fig. 4.12. From the N₂ adsorption-desorption isotherm plot of Co₃O₄ which is shown in Fig. 4.12 (a), it is interpreted that the material exhibits type IV adsorption behaviour with a H3 hysteresis loop ranging from 0.5-1 (P/P₀). Co₃O₄ shows mesoporous nature with a BET surface area of about ~12.3 m²/g. The pore radius and pore volume of Co₃O₄ estimated from the pore size distribution (PSD) plot shown in the inset of Fig. 4.12 (a) is 5.22 nm and 0.014 cm³/g, respectively. The adsorption-desorption plot of CuO-Co₃O₄ nanocomposite (Fig. 4.12 (b)) concluded the type IV adsorption behaviour of composite with H3 hysteresis loop between 0.5-1 (P/P₀). The specific surface area was estimated to be 61 m²/g. The mesoporous nature of this composite was visible from the PSD plot shown in the inset figure with a pore radius and volume of about 1.12 nm and 0.038 cm³/g, respectively. The CoPM composite sample exhibits a type IV adsorption isotherm with H3 hysteresis loop ranges 0.6-0.9 (P/P₀) with a surface area of 34 m²/g, which is shown in Fig. 4.12 (c). From the PSD plot shown in the inset figure, the pore radius and volume were estimated to be 4.32 nm and 0.049 cm³/g. In the case of the quaternary CCoPM composite, the N₂ adsorption-desorption isotherm plot (Fig. 4.12 (d)) shows a type IV adsorption nature with a H3 hysteresis loop ranges between 0.5-1 (P/P₀). The mesoporous nature of the composite sample was inferred from the PSD plot (inset figure in Fig. 4.12 (d)) with a pore radius and volume of 1.51 nm and 0.081 cm³/g, respectively. The BET surface area of the quaternary composite is about 100.1 m²/g. While the contribution of PANI is essential in terms of electrical conductivity, but its coating over the nanotubes can cause a reduction in the active porosity of MWCNTs, despite the inherently high surface area of the nanotubes. The CCoPM composite, having a greater specific surface area and well-established mesoporous structure, which can eventually turn up the electrochemical performance of the composite electrode.

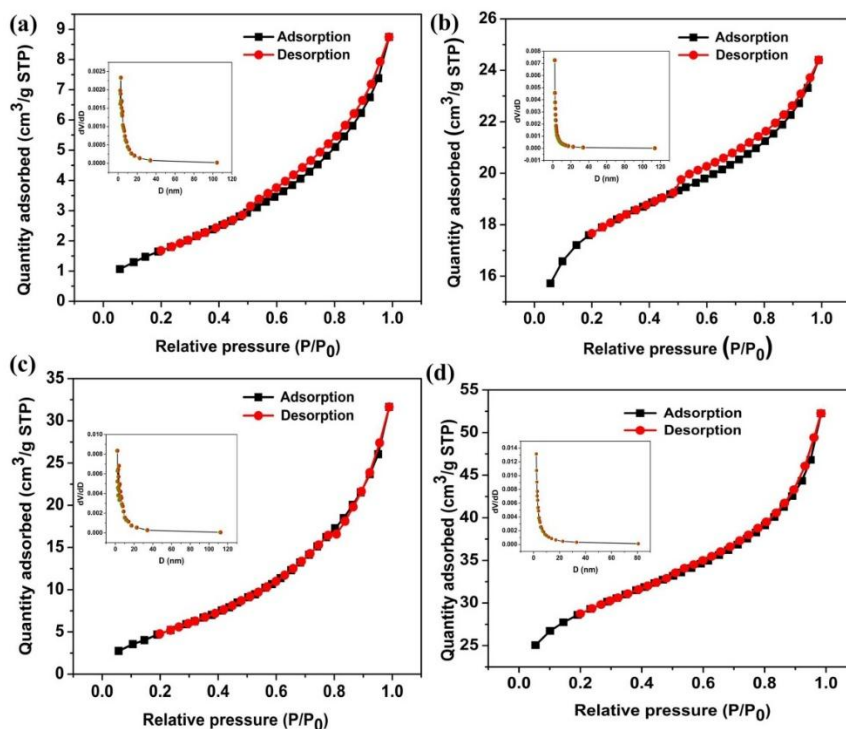


Fig. 4.12. The N₂ adsorption-desorption isothermal plots of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM and (d) CCoPM nanocomposites. Inset shows the corresponding PSD plots.

4.3.8. Thermo-gravimetric Analysis (TGA)

The thermal stability of composite material is one of the significant features that affects the electrochemical performances of the system. Fig. 4.13 shows the thermogravimetric analysis results of the CCoPM composite. The thermal stability of CCoPM can be explained through three main steps of decomposition, similar to PANI. In the first stage, complete release of water molecules accounts for a weight loss of 8.23% at a temperature of 111 °C. Due to the thermal decomposition of polymer molecules, the composite material underwent a weight loss of about 36% until the temperature reaches 324 °C. The release of acid dopants from the composite also contributed to this loss of mass. In the final step, CCoPM losses weight by 11.56% at 525 °C attributable for the complete degradation of polymer components [41], [42]. A final residue of about 40 % was retained by the CCoPM composite at the end of thermal process, which is much higher than that of pure PANI. Thus, the individual contributions from each constituent made the CCoPM composite material a capable member in the area of electrode materials. The excellent thermal stability and robust structure of MWCNTs benefit the overall heat resistance of composite material, while

the metal oxides serve as a thermal barrier contributing to the effective durability of material [43], [44].

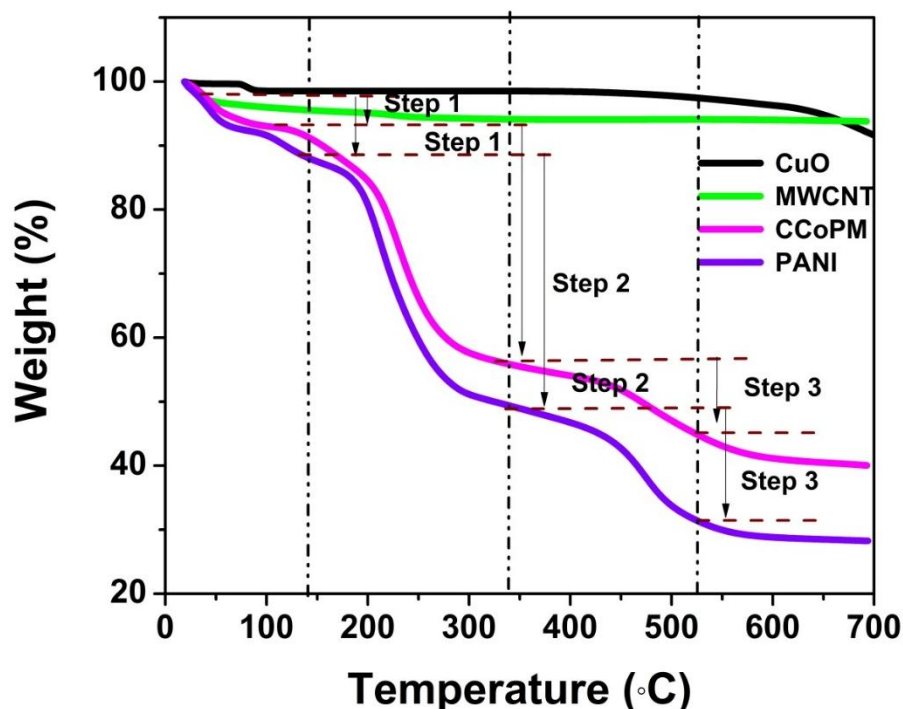


Fig. 4.13. Thermogravimetric analysis of CuO, MWCNT, PANI and CCoPM composite.

4.3.9. Electrochemical studies

4.3.9.1. Cyclic voltammetry (CV)

The electrochemical performance of the prepared Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites was evaluated using the conventional three-electrode cell configuration. Fig. 4.14 illustrates the cyclic voltametric curves of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM working electrodes in a potential window of 0-0.8 V at different scan rates from 5 mV/s to 100 mV/s. The CV curves of Co₃O₄ displayed in Fig. 4.14 (a) show quasi-rectangular shape current responses, confirming the pseudocapacitive nature of Co₃O₄. Undoubtedly, the capacitive current increases with scan rates, suggesting its remarkable reversibility of charge-discharge response. The CV curve retained its shape during each oxidation and reduction processes even though the sweep rate got amplified. Alike Co₃O₄, the CuO-Co₃O₄ composite also displayed a quasi-rectangular CV curve without any noticeable redox peaks (Fig. 4.14 (b)). However, the CV curves of CuO-Co₃O₄ composite yield larger integral area compared with Co₃O₄

and CuO electrodes, indicating the better electrochemical reaction activities of the composite and upgraded specific capacitance values due to the combined contributions of CuO and Co₃O₄. The cyclic voltametric responses of CoPM and CCoPM composites are portrayed in Fig. 4.14 (c-d). The CoPM ternary composite exhibits a non-rectangular CV curve with a pair of noticeable redox peaks at (0.19V, 0.4V). The area under the current response of the CoPM composite was relatively higher than Co₃O₄, due to the impact of electrochemical features of PANI and MWCNTs. The CV profiles of the CCoPM show the highest current response as anticipated compared with the other nanostructures, suggesting the contributions of CuO, Co₃O₄, PANI and MWCNTs get effectively used to get a refined electrochemical performance. The redox peaks in this quaternary composite are not distinguishable as much as in the CV plot of CoPM. As the scan rates get multiplied, there is a slight shift in the redox peaks to higher and lower potentials due to the restriction of diffusion rate to showcase that the electronic neutralisation generally occurs during redox reactions [45]. Higher current response is an indication of lower internal resistance suffered by the composite working electrode, leading to a better electrical conductivity. As the scan rate increases, the integral area that quantifies the capacitance value of the electrode material also increases. But, the overall specific capacitance value declines with sweep rate due to the fact that at higher scan rates the electrolyte ions interact only with the electrode surface, while at lower scan rates a greater number of ions make contact and interact with the interior of the electrode material [46]. This is a clear indication of the dependence of electrochemical performance of a working electrode on its morphology. Fig. 4.14 (e) shows the comparative analysis of the current response of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM and CCoPM working electrodes at a sweep rate of 100 mV/s. The enhanced current response of the quaternary composite electrode is evident from the analysis profile, leading to an achievement of maximum specific capacitance of about 592 F/g by this composite electrode at 10 mV/s (Fig. 4.14 (f)). The incorporation of PANI and MWCNTs provide a conductive bridge for the electrolyte ions to easily enter to the interior of the composite electrode, leading to a faster electronic transportation and enhancement in the supercapacitance of the material. The binary metal oxide combination CuO-Co₃O₄ bounds to PANI and MWCNT linkages in the way to overcome the drawbacks arise due to agglomerations in the morphology. These integrated effects resulted in the formation of a unique porous architecture with better

active surface area for the quaternary composite, effectively enriches its capacitance value compared to individual counterparts.

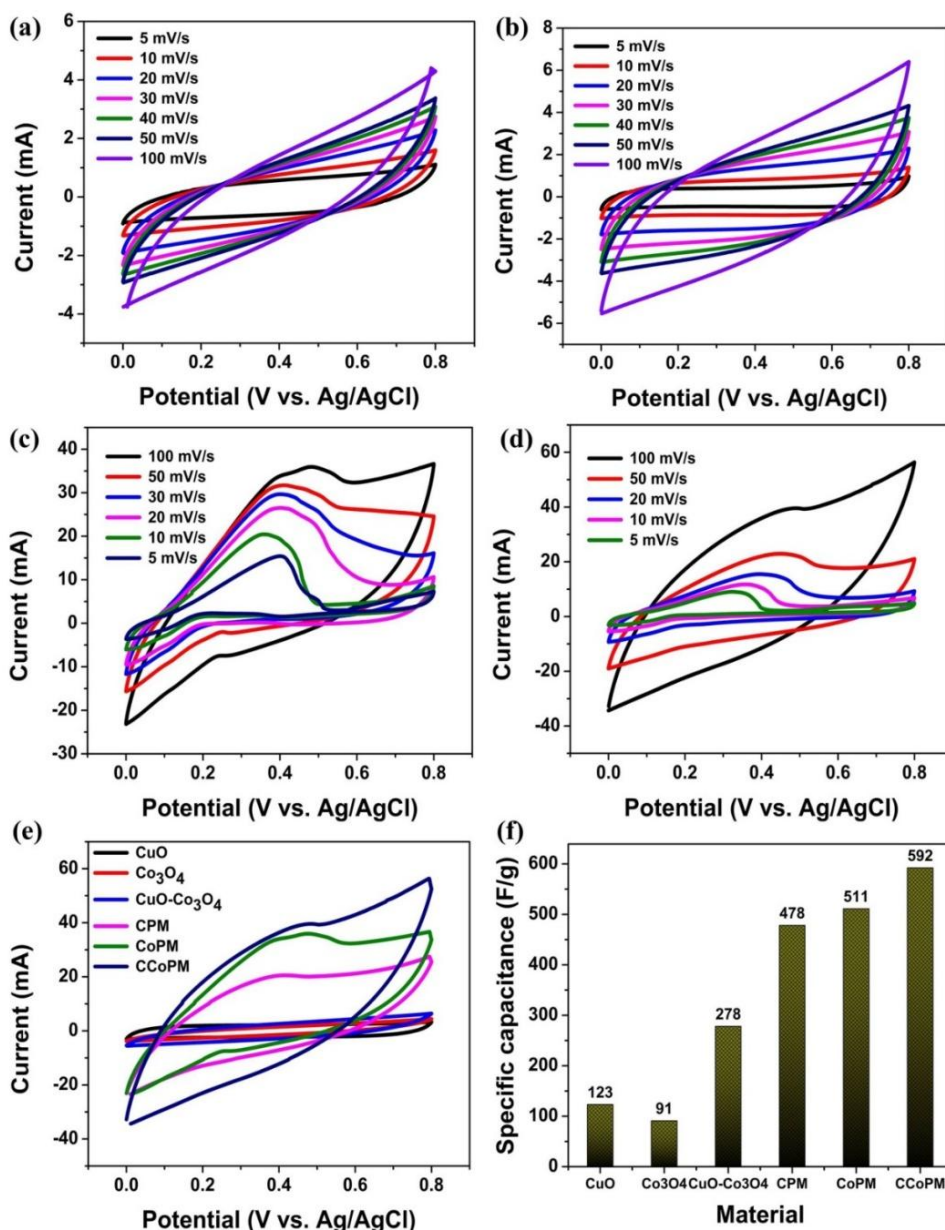


Fig. 4.14. CV curves of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM, comparison of (e) CV curves of CuO, Co₃O₄, CuO- Co₃O₄, CPM, CoPM and CCoPM nanocomposites at 100 mV/s (f) specific capacitance of CuO, Co₃O₄, CuO- Co₃O₄, CPM, CoPM and CCoPM nanocomposites at 10 mV/s.

The kinetics of capacitive performance of the CCoPM composite electrode was then elucidated using power law. Fig. 4.15 (a) portrays the linear relation between scan rate and anodic current with a slope value of about 0.84, indicating prominence of surface-controlled capacitive contributions in the charge storage

mechanism. The $v^{1/2}$ vs. $i/v^{1/2}$ graph shown in Fig. 4.15 (b) helps to evaluate the capacitive and diffusive contribution parameters k_1 and k_2 . The obtained values of k_1 and k_2 were 33.576 and -24.192, respectively. The capacitive contribution due to the effect of surface-controlled redox reactions was found to be 90% for the CCoPM electrode at the sweep rate of 10 mV/s (Fig. 4.15 (c)). The shaded region in Fig. 4.15 (c) illustrates the diffusive contribution in the current response of the composite electrode at 10 mV/s. With the amplification in sweep rate, the surface-controlled capacitive contribution enriched to 98 % at 100 mV/s (Fig. 4.15 (d)). The electrochemical performance arises from the redox reactions happening at the surface or near surface regions of the electrode usually results in faster kinetics and better cyclic performance [47].

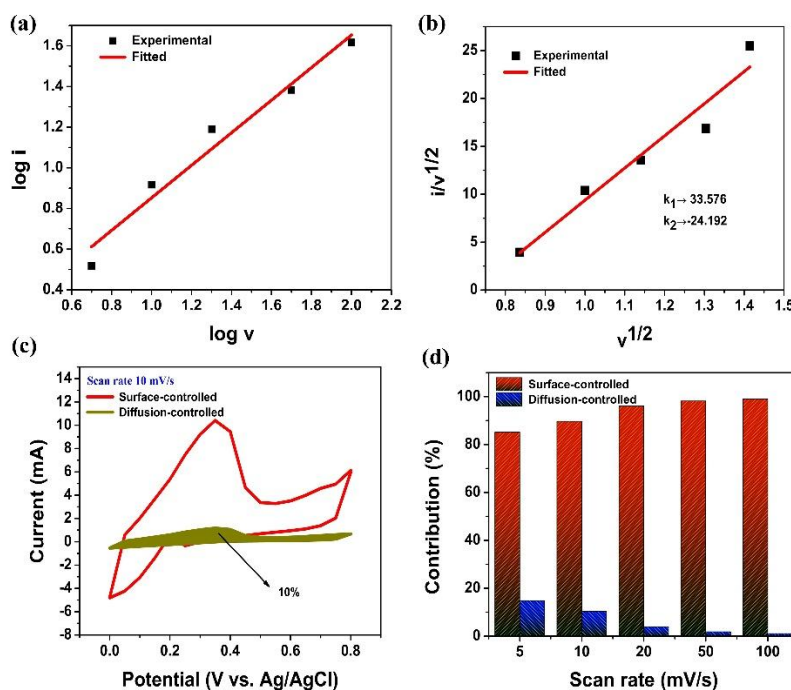


Fig. 4.15 (a) log v vs. log i plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ plot (c) decoupling of capacitive and diffusive current contributions at scan rate 10 mV/s (d) Histograms of diffusive and capacitive contributions of CCoPM working electrode at varying scan rates.

4.3.9.2. Galvanostatic charge/discharge (GCD) studies

The electrochemical features of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM nanocomposites were further tested with GCD measurements conducted at different current densities, shown in Fig. 4.16 (a-e). The non-linear appearance of GCD curves

suggests the pseudocapacitive behaviour of all the composite electrodes. The Co₃O₄ working electrode shows a non-linear GCD curve with small IR drops as a consequence of internal resistance suffered by the working electrode during the reaction activities (Fig. 4.16 (a)). The discharge curve of CuO-Co₃O₄ (as seen in Fig. 4.16 (b)) found to be much longer compared to pristine CuO and Co₃O₄, results in better capacitance values. The specific capacitance of Co₃O₄ electrode was found to be 264 F/g, 220 F/g, 198 F/g, and 73 F/g and that was for CuO-Co₃O₄ was found to be 383 F/g, 230 F/g, 150 F/g and 83 F/g, at current densities of 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. The GCD plots of CoPM and CCoPM nanocomposites are displayed in Fig. 4.16 (c-d), with relatively less IR drop in the discharge process indicating better electronic conductivity as well as lower energy loss in the electrode material [46]. The specific capacitance value of CoPM electrode was found to be 446 F/g, 243 F/g, 99 F/g, and 35 F/g at current densities 1 A/g, 2 A/g, 3 A/g and 5 A/g, respectively, whereas CCoPM electrode exhibited specific capacitance values of 647 F/g, 525 F/g, 334 F/g, and 115 F/g at current densities 1 A/g, 2 A/g, 3 A/g and 4 A/g, respectively. The GCD response of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM and CCoPM nanocomposites is compared in Fig. 4. 16 (e) at a current density of 1 A/g, presents the enhanced electrochemical performance of CCoPM composite with the longest discharge time favourable for energy storage applications. The specific capacitance values attained for CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM and CCoPM working electrodes were compared diagrammatically in Fig. 4.16 (f). The almost symmetrical triangular shaped GCD curve of the CCoPM composite reveals the total capacitance performance as a sum of both pseudocapacitive contributions from metal oxides, PANI and the double layer capacitive contribution from MWCNTs [45]. The distinctive porous morphology formed due to the synergistic interaction of PANI-MWCNT frameworks with the binary metal oxides, resulting in productive electrochemical features of the quaternary composite electrode. Moreover, the PANI particles grafted over the metal oxide-MWCNT surfaces can access more electrolyte ions and actively participate in the redox reactions [46].

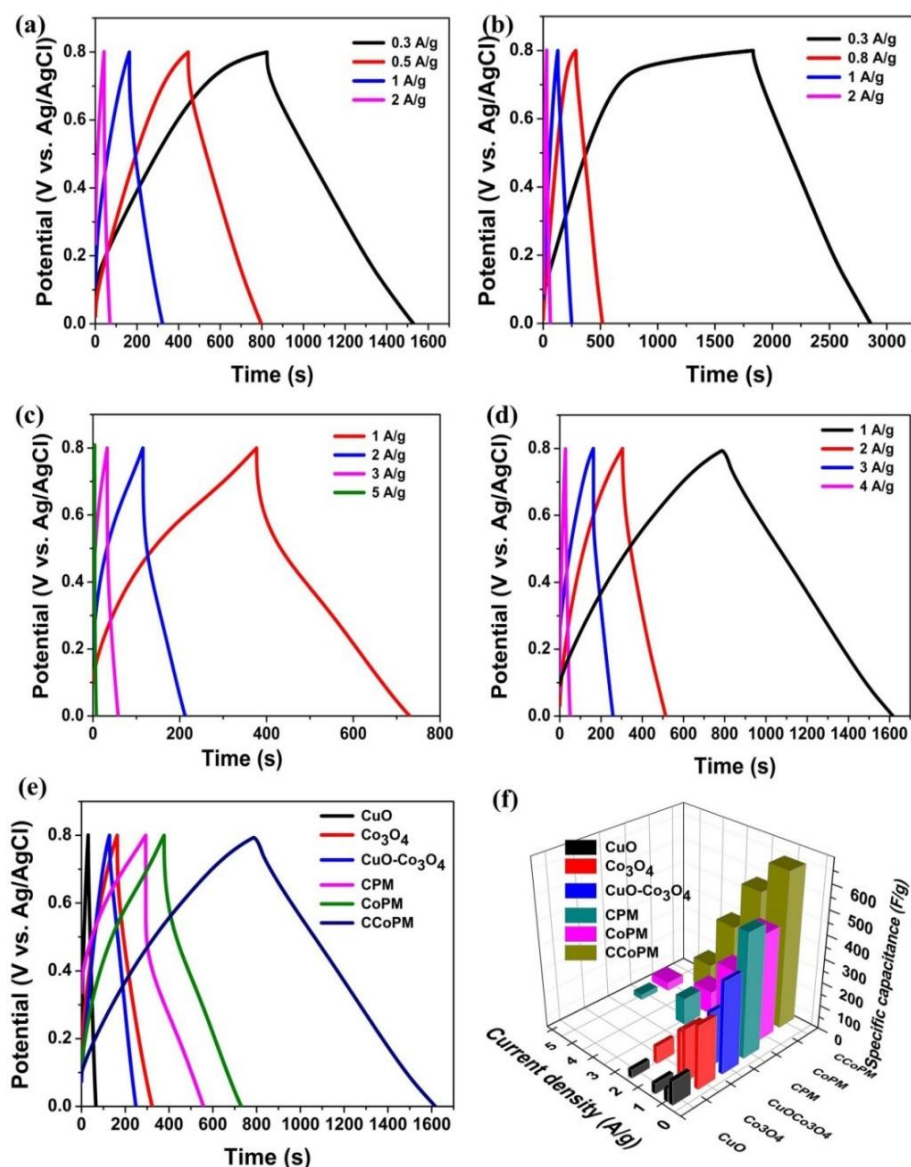


Fig. 4.16. GCD curves of (a) Co₃O₄ (b) CuO-Co₃O₄ (c) CoPM (d) CCoPM (e) comparison of charge-discharge curves of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM, CCoPM composites at current density of 1 A/g, (f) variation of specific capacitance with current density of CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM, CCoPM composites.

4.3.9.3. Electrochemical impedance spectroscopy (EIS)

The best approach to study the electrical conductivity, internal structure and charge transport processes exhibited by working electrodes is to conduct an EIS analysis, as shown in Fig. 4. 17. The Nyquist plots of Co₃O₄, CuO-Co₃O₄, CoPM and CCoPM working electrodes are individually portrayed in Fig. 4.17 (a-d). The Nyquist plots of Co₃O₄ and CuO-Co₃O₄ electrodes exhibit a distorted semi-circle region in the high frequency region and a linear portion in low frequency region, as expected for a

pseudocapacitive material, whereas the CoPM and CCoPM composite working electrodes displayed a very faint semi-circle arc in the high frequency region (Fig. 4.17 (e)). The best fitted EIS spectra are also visible in each EIS plots correspond to the equivalent electrical circuit combining elements such as R_s , R_{ct} , CPE and W. The values of these EIS parameters are tabulated in Table 4.3. The quaternary composite electrode CCoPM exhibited the lowest charge transfer resistance value, suggesting the high charge transport rate of this electrode material, which eventually resulted in its better electrochemical performance.

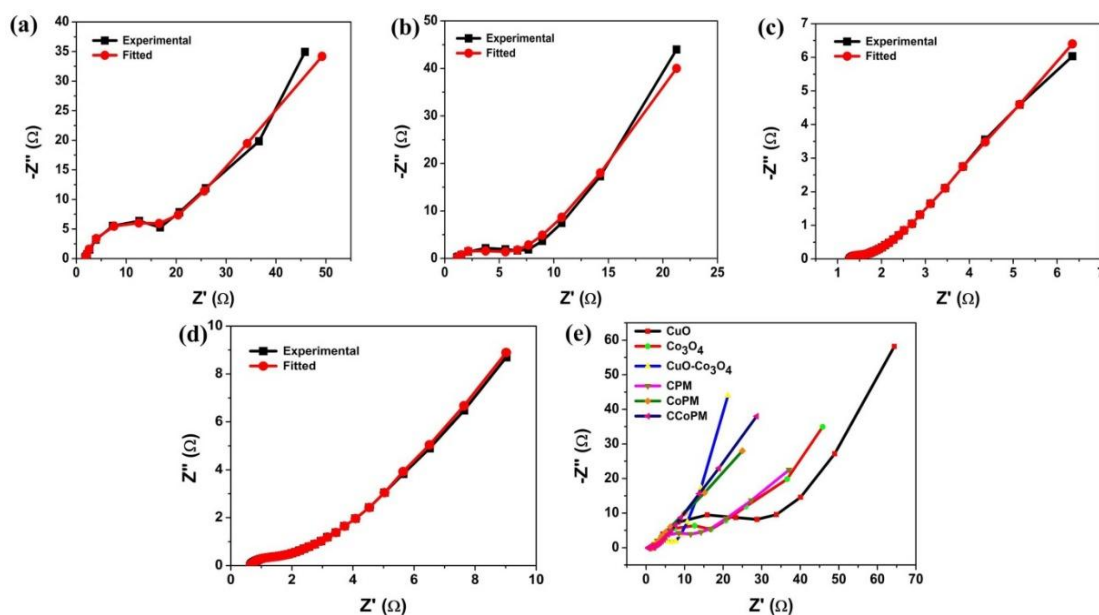


Fig. 4.17 (a) The best fitted Nyquist plot of as-prepared (a) Co₃O₄, (b) CuO-Co₃O₄, (c) CoPM (d) CCoPM (e) comparison of Nyquists plots of all nanostructures.

Table 4.3. The R_s , R_{ct} , CPE, W and n values of as-synthesised CuO, Co₃O₄, CuO-Co₃O₄, CPM, CoPM, CCoPM nanocomposites.

	Sample					
	CuO	Co ₃ O ₄	CuO-Co ₃ O ₄	CPM	CoPM	CCoPM
R_s (Ω)	2	1.81	1.13	1.22	1.25	0.66
R_{ct} (Ω)	29.30	14.42	3.13	11.66	1.63	1.31
W	22.75	27.09	38.54	33.72	41.34	40.68
CPE	0.00057	0.00049	0.00002	0.0049	0.00004	0.00008
n	0.943	0.799	0.960	0.688	0.980	0.963

4.3.9.4. Cycle stability

The cycle stability of the CCoPM composite in the three-electrode cell configuration was evaluated over 5000 repeated charge-discharged cycles at a current density of 8 A/g. Fig. 4.18 shows that the quaternary composite sustains 98.7% of capacitance during the continuous charge-discharge cycles. The exclusive porous morphology with a larger specific surface area of the CCoPM working electrode contributed to its enhanced electro-active sites and fast charge transport along with rapid charge storage kinetics, which ultimately resulted in its better cyclic performance. This proves the efficiency of the CCoPM composite as a potential electrode material in the field of energy storage devices.

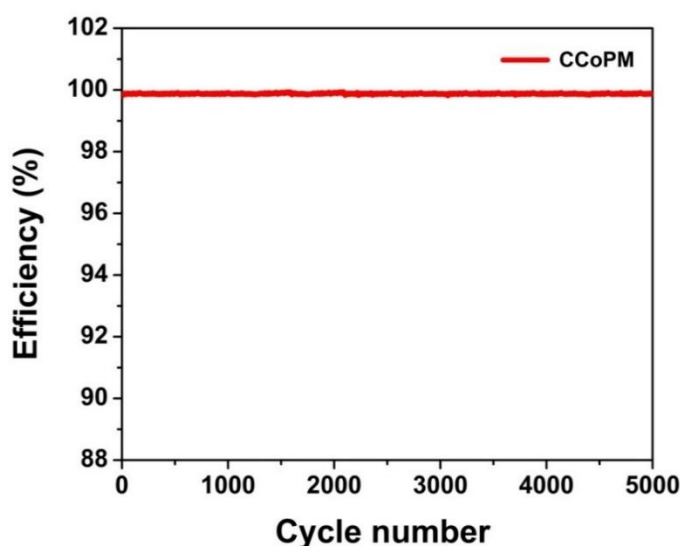


Fig.4.18. Cycle stability of CCoPM working electrode over 5000 cycles.

4.3.9.5. Electrochemical performance of CuO-Co₃O₄/PANI/MWCNT quaternary nanocomposite in symmetric two-electrode configuration

The electrochemical performance of a symmetrical supercapacitor device is evaluated using CCoPM as the working material and 1M Na₂SO₄ as the electrolyte in a two-electrode cell assembly. The real-time device-level performance of this configuration was analysed in the optimised potential window of 0-0.8V. Fig. 4.19 (a) illustrates the cyclic voltametric profiles of the CCoPM electrode at various sweep rates ranges from 5 mV/s to 100 mV/s. The CV response curve of the CCoPM exhibits a quasi-rectangular shape with a pair of redox peaks at (0.17 V, 0.39 V). Alike the three-

electrode configuration responses, the peaks got slighter shifts as the scan rates increased and at 100 mV/s, the redox peaks appeared at (0.31 V ,0.5 V). The GCD curves of CCoPM composite electrodes were analysed at different current densities of 1A/g, 2 A/g, 3A/g and 5 A/g, shown in Fig. 4.19 (b). All the GCD curves presented almost symmetrical charge-discharge behaviour with small IR loss, consistent with the three-electrode results. The specific capacitance values of CCoPM electrode evaluated from the GCD plots are 405 F/g, 335 F/g, 202 F/g, and 87.5 F/g at current densities of 1A/g, 2 A/g, 3A/g and 5 A/g, respectively (Fig. 4.19 (c)). The coulombic efficiency of electrode performance at various current densities is investigated and portrayed in Fig. 4. 19 (d), suggesting satisfactory cycle performance of CCoPM electrode at all current densities. The electrochemical performance of an electrode material is further characterised by its energy density and power density values. The Ragone plot of CCoPM electrode is depicted in Fig. 4.19 (e), exhibiting a highest specific energy of 36 Wh/Kg at a specific power of 800 W/Kg. The remarkable specific energy is attributed to the combined contributions from double-layer nature and redox reactions. The electrode material showed a better power density of 4022 W/Kg at a current density of 5 A/g. The long-term cycle stability of CCoPM electrode was investigated through conducting GCD test of the electrode over continuous 50000 cycles at a current density of 10 A/g. Fig. 4.19 (f) shows the capacity retention capacity of the composite electrode during 50000 charge-discharge cycles, upholds 93.2% capacitance retention. This suggests that the quaternary composite doesn't undergo any kind of structural deformations over the repeated charging and discharging processes. Thus, the overall enhancement in electrochemical performance of the quaternary nanocomposite including the constituents CuO, Co₃O₄, PANI and MWCNTs can be ascribed to the profitable surface area of the material formed due to the synergistic interactions between individual constituents. The exclusive porous networks formed during the synthesis stage, particularly during the active polymerisation phase, lead to the generation of more and more electro-active sites. The productive utilisation of these active sites by both electrostatic and surface controlled redox reactions resulted in enrichment of the overall electrochemical performance [46].

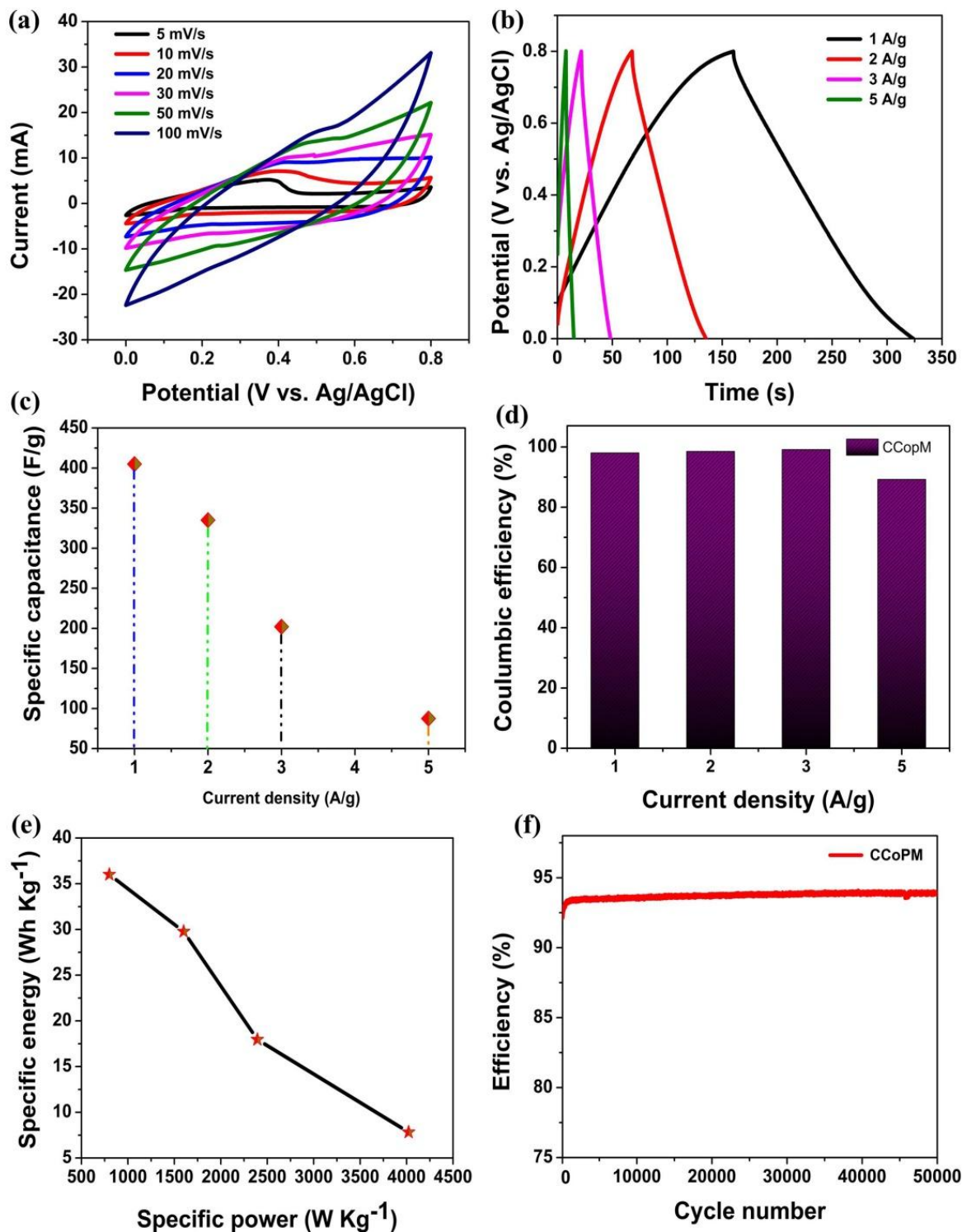


Fig. 4.19. (a) CV (b) GCD plots of CCoPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) columbic efficiency analysis (e) Ragone plot and (f) cycle stability of CCoPM composite in 50000 cycles.

4.4. CONCLUSION

The Co₃O₄, CuO-Co₃O₄, Co₃O₄/PANI/MWCNT and CuO-Co₃O₄/PANI/MWCNT nanocomposites were successfully synthesised using hydrothermal and one-pot chemical polymerisation methods, respectively. The intended formation of ternary and quaternary nanocomposites was confirmed with the help of XRD, FT-IR, Raman, FESEM-EDS, HRTEM, and BET characterisation techniques. The thermal stability and compositional analysis are further evaluated using TGA and XPS techniques. The electrochemical features of the prepared nanostructures were studied in three-electrode cell arrangement, showed a superior specific capacitance value of 647 F/g at a current density of 1 A/g for the CCoPM composite electrode, with marginal charge transfer resistance and better cycle performances. The device-level performance of the CCoPM electrode was analysed by fabricating a symmetric supercapacitor device in the two-electrode cell assembly. The CCoPM composite achieved a remarkable specific energy of about 36 Wh/Kg at a power density of 800 W/Kg. The composite electrode exhibited a 93.2% capacitive retention over 50000 continuous charge-discharge cycles. The binary metal oxide combination CuO-Co₃O₄ bounds to PANI and MWCNT, resulting in the formation of a unique porous architecture with better active surface area for the quaternary composite, effectively enriching its capacitance value compared to individual counterparts.

Table 4.4. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CCoPM	592	10	647	1	351	10	405	1

4.5. REFERENCES

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Synthesis, Characterization, and Supercapacitive Performance of CuO-ZnMn₂O₄/PANI/MWCNT Hybrid System

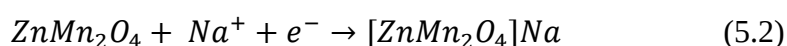
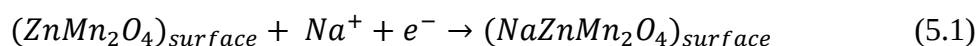
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The effectual strategy of incorporating two TMOs together in order to attain a well-behaved supercapacitor has created an opportunity for combining a ternary metal oxide ZnMn₂O₄ with the binary metal oxide CuO. The multiple valence states offered by the element Mn in the ZnMn₂O₄ help to provide plenty of redox active sites during chemical reactions, making the compound an imminent member in the supercapacitor scenario. Even though, Mn- based compounds have already been well-established in the supercapacitor field, ZnMn₂O₄ is one of the least explored ones. The CuO-ZnMn₂O₄ nanocomposite can become a potential candidate in the supercapacitor field by taking advantage of multiple valence states offered from both CuO and ZnMn₂O₄ compounds resulting in the improved electrochemical efficiency of the electrode material. The incorporation of these TMO nanocomposites with the PANI/MWCNT combination can qualitatively and quantitatively benefit the overall electrochemical performance of the quaternary electrode material. Herein, a detailed evaluation concerning the potentiality of CuO-ZnMn₂O₄/PANI/MWCNT hybrid system in the supercapacitor field is discussed.

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5.1. INTRODUCTION

The major challenge faced by the supercapacitors is often its low energy density compared with batteries. The scientific world is still working on the area of the supercapacitors to alleviate this major drawback with various strategies, in the sense of improving the electrochemical features of electrode materials. Without sacrificing power density, there is much effort has been employed to improve the charge storage mechanisms of electrode materials in supercapacitor scenarios. By addressing the drawbacks of widely used electrode materials, researchers are trying to explore a new category of potential electrode materials which are economical, environmentally benign, and having the potential to meet ever-lasting needs of an energy-demanding world. Among the various Mn-based TMOs, zinc manganese oxide (ZnMn₂O₄) is a bimetallic TMO having spinel type structure with high electrical conductivity and a band gap of 1.86 eV, which are widely used in areas like catalysis, sensors, energy storage devices [1], [2], [3]. In the AB₂O₄ spinel structure of ZnMn₂O₄ (ZMO) compound, the divalent Zn²⁺ and the trivalent Mn³⁺ ions occupy in the tetrahedral and octahedral sites, respectively [4]. In this structure, oxygen ions produce two types of vacancies such as tetrahedral vacancy and octahedral vacancy. The possible charge storage mechanisms of ZMO in neutral electrolytes like Na₂SO₄ can be as follows [5];



The intriguing attributes of ZnMn₂O₄ electrode material such as its spinel architecture with significant internal spaces that can accommodate more electrolyte ions, availability of larger accessible electro-active sites, and excellent pseudocapacitive nature, made it a potential choice for fabricating a nanocomposite with CuO [6].

5.1.1. ZnMn₂O₄ – A potential electrode material

Despite the fact that ZMO has many potential electrochemical features like high theoretical capacitance (1152 F/g), it is the least studied in the supercapacitor field as compared with its applicability in Li-ion batteries. The electrochemical performances of ZMO-based electrodes are substantially guided by few factors like surface area and

porosity, morphology and purity. One of the best methods to improve the device performance is to fabricate a porous nano-network to the electrode material in order to enrich electro-active sites, thereby enhancing rapid ionic diffusion. For instance, Yanping Gao *et al.* reported preparation of porous ZMO microstructures via calcination and the optimised ZMO material prepared at calcination conditions of 450 °C for 6 h achieved a specific capacitance of 1093 F/g 1 A/g. Heterolite structured ZMO prepared by the hydrothermal route and achieved a specific capacitance of 675 F/g at a scan rate of 5 mV/s [7]. M. Puratchi Mani *et al.* prepared a cubic-like ZMO electrode material using the double hydroxide-mediated hydrothermal method and showed a battery-type faradic behaviour of ZMO electrode having a capacitance of 776 F/g at a scan rate of 5 mV/s in a 2 M KOH electrolyte along with a capacitive retention of 91.7% over 5000 cycles [8]. There were works on Ni substituted ZMO nanospheres prepared via sol-gel auto-combustion method. As the Ni incorporation increases there is a phase transition of material from tetragonal to cubic crystal structure along with the enhancement in electrochemical features [9]. Recently, P. Deva *et al.* reported a mesoporous ZMO preparation using citric acid-mediated sol gel auto-combustion approach. The spinel ZMO electrode material showed an impressive electrochemical performance with a specific capacitance of 417.5 F/g at current density 1 A/g. The enhancement in supercapacitive properties of ZMO electrode material is attributed to the increased surface area and ionic conductivity along with commendable mechanical stability [10].

5.1.2. CuO-ZnMn₂O₄ nanocomposite: A short introduction

Another effective strategy widely used for improving the electrochemical performance of TMOs is to make nanocomposites with other TMOs in order to use the benefit of their synergistic effects along with their individual contributions. ZMO has been extensively studied in the form of its composite electrode form as a suitable option in supercapacitors [11], [12], [13]. For instance, Veeman Sannasi *et al.* prepared ZMO/Mn₂O₃ composite by ultrasonication and microwave irradiation assisted hydrothermal routes. The four ‘petal’ and six ‘petal’ flower-like morphology of composite materials were evident in the morphological analyses. The as-synthesised composite electrode exhibited a specific capacitance of 380 F/g at current density of 0.5 A/g [14]. Cathodic electrosynthesis of ZMO/Mn₃O₄ nanostructures was reported by Bahareh Ameri *et al.* and showed that the nano rod-like composite material exhibited a

maximum storage capacity of 321.34 F/g [15]. Thus, CuO with ZMO can be effectively used as a potential composite electrode material for improving the electrochemical performance. There were only few studies on the structural, optical, physicochemical and electrochemical performances of CuO/ZMO composite [16]. Recently, Liping Qin *et al.* reported improved electrode performance of CuO/ZMO composite as a cathode material in Zn-ion batteries. The composite displayed a capacity of 118 mAh/g at 2 A/g along having an efficiency of more than 96% [17].

5.1.3. CuO-ZnMn₂O₄/PANI/MWCNT quaternary hybrid system as a potential electrode material

Although significant improvement in electrochemical performance has been acquired through fabricating binary nanocomposites, challenges remain in securing high energy density and long cycle life, especially at higher current densities. Thus, studies focusing on the innovative strategies to enrich the ionic conductivity and structural integrity of the CuO-ZMO-based electrodes by linking them with conducting polymers like PANI and well-known carbon compounds must be adopted. A few studies on ZMO-carbon compounds were previously reported with an aim to elevate the electrode porosity and surface area, intercalation sites and rapid charge transport kinetics. For instance, a recent work was published on the synthesis of pure ZMO and ZMO/graphene composites using the combustion method and reported a high specific capacitance of 783 F/g for ZMO/rGO electrode at a scan rate of 5 mV/s which can be due to the highly porous structure of composite along with high surface area, which allows the easy penetration of ions [18]. Recently, a similar composite material ZMO/rGO with a needle-like nanostructure was produced by Pitcheri Rosaiah *et al.* using hydrothermal route and attained a specific capacitance of 628 F/g at 1 A/g. The asymmetric supercapacitor device designed with the as-synthesised material showed an energy density of 40.2 W h/Kg at a power density of 1125 W/Kg [19]. Chen Zhang *et al.* investigated the electrochemical performance of ZMO/GO composite electrode fabricated using electrospinning technique followed by annealing and reported the highest specific capacitance of 1489.5 F/g at 1 A/g for 0.3 wt% GO-ZMO sample [20]. The incorporation of conducting polymer polypyrrole and graphene in ZMO was studied in detail by Haiyan Gao *et al.* and observed a significant decrease in charge transfer impedance of the composite material due to the synergistic effects of rGO and

PPy [21]. According to our understanding, there is no published works on CuO-ZnMn₂O₄/PANI/MWCNT quaternary hybrid composite in energy storage applications.

5.2. EXPERIMENTAL SECTION

5.2.1. Synthesis materials

Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), urea (CH₄N₂O), ammonium persulfate (APS) ((NH₄)₂S₂O₈) and aniline hydrochloride (C₆H₅NH₂·HCl), analytical grade hydrochloric acid (HCl), sodium sulphate (Na₂SO₄), sodium dodecyl sulphate (CH₃(CH₂)₁₁OSO₃Na) (SDS, > 98%), manganese chloride tetrahydrate (MnCl₂·4H₂O), Zinc acetate dihydrate (Zn (CH₃CO₂)₂·2H₂O), sodium hydroxide (NaOH), potassium hydroxide (KOH), deionised (DI) water was purchased from Merck India Pvt. Ltd. Multi-walled carbon nanotubes (MWCNTs, > 95%, $OD \times L = 6 - 9 \text{ nm} \times 5 \mu\text{m}$), Polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and activated carbon were purchased from Sigma-Aldrich. All the chemicals used were analytical standard and utilized without any further purifications. Distilled ethanol was used for cleaning purpose.

5.2.2. Synthesis of ZnMn₂O₄

The ZnMn₂O₄ nanoparticles were prepared via a similar surfactant-free hydrothermal process with the same reaction conditions of CuO synthesis. Firstly, 4 M manganese chloride tetrahydrate and 2 M Zinc acetate dehydrate were simultaneously dissolved in 40 ml of deionised water. Later, a 20 ml NaOH:KOH solution was prepared in another beaker in a molar ratio of 1:2. The mixed hydroxide solution was slowly added to the precursor solution under constant stirring until a brownish yellow solution is formed. The whole solution was then transported to the autoclave setup and kept in the oven under 180 °C for 24 hours. When the reaction conditions met, the resultant solution from the reactor was filtered and washed thoroughly using DI water and ethanol. The obtained brownish ZnMn₂O₄ precipitate was then shifted to an oven at 80 °C for 6 hours to get the purified ZnMn₂O₄ nanoparticles.

5.2.3. Synthesis of CuO-ZnMn₂O₄ nanocomposite

The CuO-ZnMn₂O₄ nanocomposite was processed using the hydrothermal method without employing any additives of surfactants. Initially, 0.2 M manganese chloride tetrahydrate and 0.1 M zinc acetate dihydrate were allowed to dissolve completely in 30 ml of DI water via a continuous stirring process. Later, the previously prepared CuO nanoparticles (40 mg) were allowed to disperse in the above-mentioned precursor solution. Then, a 20 ml of 0.5 M NaOH: 1M KOH solution was prepared in another beaker. The mixed hydroxide solution was slowly added to the precursor solution under constant stirring until a brownish solution was attained. The whole 50 ml solution was then transferred to an autoclave and set to keep in oven at 180 °C for 24 hours completing the synthesis process. The earned precipitates after hydrothermal reaction were washed multiple times with DI water and ethanol for the removal of unwanted/unreacted substances from the resultant. Later, the obtained precipitate was sent to oven at 80 °C for 6 hours to get the CuO-ZnMn₂O₄ nanocomposite.

5.2.4. Synthesis of ZnMn₂O₄/PANI/MWCNT ternary nanocomposite and CuO- ZnMn₂O₄/PANI/MWCNT quaternary nanocomposite

The ZnMn₂O₄/PANI/MWCNT ternary nanocomposite was prepared in the similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared ZnMn₂O₄ and the final product is named as ZPM for the convenience.

The CuO-ZnMn₂O₄/PANI/MWCNT quaternary nanocomposite was prepared in the similar synthesis procedure of CuO/PANI/MWCNT, replacing the 30 mg of CuO addition by 30 mg of as-prepared CuO-ZnMn₂O₄ nanocomposite and the final product is named as CZPM for convenience.

5.2.5. Instruments and material characterisation

The crystallographic structural details were investigated using X-Ray diffraction technique (PANALYTICAL, Aeris Research (Source: Cu K α)). Fullprof Suite software was used for Rietveld analysis. Raman spectroscopy with an excitation wavelength of 532 nm (WiTec alpha 300, Germany) was employed to determine the

vibrational modes of the as-synthesised samples. Fourier transform infrared (FTIR) spectrum was recorded using FTIR - Shimadzu IR affinity model 1s fitted with Attenuated Total Reflectance (ATR) mode using ZnSe crystal. The surface morphology and elemental composition were done using a combination of High- Resolution Transmission Electron Microscopy (HRTEM) (Thermofisher Talos F200 S) and Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SIGMA HV- Carl zeiss with Bruker Quantax 200- Z10 EDS Detector). The X-ray photoelectric spectroscopy was carried out using a Thermo scientific K-alpha X-ray photoelectron spectrometer. The N₂ adsorption-desorption isotherm was conducted by Brunauer-Emmett-Teller (BET) technique with the help of TB440A surface area analyser. The thermo-gravimetric analysis (TGA) was performed with the help of SDT Q600 V20.9 Build 20 analyser in the temperature range of RT-700 °C at a heating rate of 100 °C /min.

5.2.6. Electrode preparation and electrochemical studies

The electrochemical features of the as-synthesised samples were investigated using Ivium CompactStat electrochemical workstation. In the three-electrode configuration, the slurry for working electrode fabrication was prepared by mixing 80 wt. % of the active material, 10 wt. % of polyvinylidene fluoride (PVDF) and 10 wt. % of activated carbon in N-methyl pyrrolidine (NMP). The obtained gel-type solution was pasted uniformly in to a 1 × 1 cm² pre-cleaned stainless-steel substrate and kept at 60 °C for 6 hours. The effective active mass load in working electrode was 1.25 mg cm⁻². The three-electrode system was arranged with Ag/AgCl electrode and platinum electrode as reference and counter electrodes, respectively. 1M Na₂SO₄ solution was preferred as the electrolyte medium to characterise the electrochemical performance of the as-synthesised samples.

5.3. RESULTS AND DISCUSSION

5.3.1. X-Ray diffraction (XRD)

The material purity and structural features of ZnMn₂O₄, CuO-ZnMn₂O₄, ZPM and CZPM nanocomposites were evaluated using powder X-ray spectrometer and displayed in Fig. 5.1. In order to confirm the adequate formation of the composites,

XRD profiles of CuO, CPM, PANI, and MWCNTs are also presented in the Fig. 5.1 (a). From the figure, it is evident that ZnMn₂O₄ compound with the tetragonal crystal structure was successfully formed, with no evidence of any kind of secondary or impurity phases (JCPDS No. 24-1133, space group: I41/amd). The major intense diffraction peaks obtained at 2 θ values 18.17 °, 29.25 °, 31.25 °, 32.90 °, 36.38 °, 44.81°, 59.03 °, and 60.72 ° were assigned to the crystal planes (101), (112), (200), (103), (211), (220), (321), and (224), respectively [6]. The XRD pattern of CuO-ZnMn₂O₄ nanocomposite showed a combination of all prominent peaks of both the monoclinic CuO and the tetragonal ZnMn₂O₄. The PANI-MWCNT incorporated materials (shown in Fig. 5.1 (b)), particularly ZPM, displayed a complete blend of dominant peaks of PANI at 2 θ values of 19.45 ° and 25.14 ° along with several prominent diffraction planes of ZnMn₂O₄ located at 17.01 °, 29.27 °, 31.31 °, 32.97 °, and 36.79° [22]. In the case of XRD pattern of quaternary nanocomposite CZPM, PANI dominated nature was apparent at a glance, accompanied with some of the major crystallographic diffraction peaks of both CuO and ZnMn₂O₄ phases. The dominant peak of MWCNT in the 25.8°-26° range is not clearly visible in the XRD spectra of both ZPM and CZPM, but a low intense bump of MWCNT at 42.92 ° was observed [23]. The minor peak shifts in the XRD profiles of both ternary and quaternary nanocomposites can be attributed to the synergistic interactions between PANI-MWCNT with metal oxides, which are expected to surplus the overall electrochemical performance of the composites.

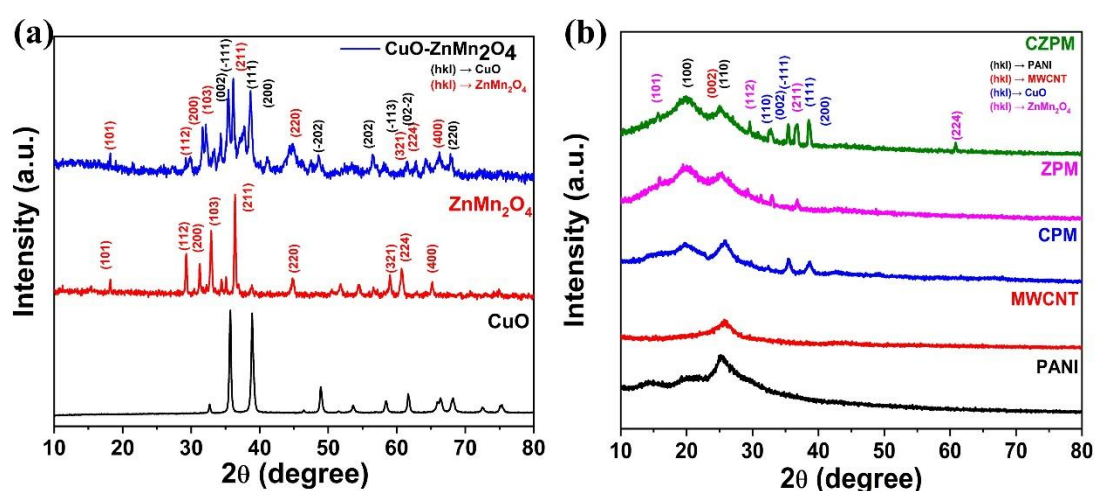


Fig. 5.1. XRD patterns of (a) CuO, ZnMn₂O₄, CuO-ZnMn₂O₄ nanoparticles and (b) PANI, MWCNT, CPM, ZPM, and CZPM composites.

5.3.2. Raman spectroscopy

The Raman spectra of ZnMn₂O₄, CuO-ZnMn₂O₄, ZPM and CZPM composites are carried out to evaluate the structural integrity and phase purity, which is presented in Fig. 5.2. According to group analysis, the spinel ZnMn₂O₄ structure has 10 Raman active modes as follows;

$$T = 2 A_{1g} + 3 B_{1g} + B_{2g} + 4 E_g \quad (5.3)$$

Among these Raman modes, the as-synthesised ZnMn₂O₄ material showed Raman peaks at 317 cm⁻¹, 368 cm⁻¹, and 665 cm⁻¹ which are consistent with previous reports of the tetragonal ZnMn₂O₄ nanomaterials, as seen in Fig. 5.2 (a) [24]. The strong peak at 665 cm⁻¹ can be attributed to A_{1g} symmetry [25]. The Raman spectra of CuO-ZnMn₂O₄ composite exhibits consistent peaks corresponding to both CuO and ZnMn₂O₄, confirms the occurrence of both components in the composite material (Fig. 5.2 (b)). The intense Raman modes at 298 cm⁻¹ and 629 cm⁻¹ were attributed to the A_g and B_g² symmetries of CuO [26], while the modes at 317 cm⁻¹, 368 cm⁻¹, 474 cm⁻¹, 593 cm⁻¹, and 660 cm⁻¹ represented the Raman active modes of tetragonal ZnMn₂O₄. Fig. 5.2 (c) presents the Raman spectra of ternary ZPM nanocomposite, evidencing the exact formation of PANI, MWCNT and ZnMn₂O₄ in the composite with their corresponding characteristic peaks. The list of Raman active modes and their corresponding attributes are listed in Table 5.1. The enhancement in peak intensity of the band at 1591 cm⁻¹ in the composite material is related to the effective interaction between carbonyl functional groups of MWCNTs with the quinoid rings in PANI. The noticeable bands at 1338 cm⁻¹ and 1591 cm⁻¹, can be attributable to the synergistic π-π interactions between MWCNTs and PANI fibres [27].

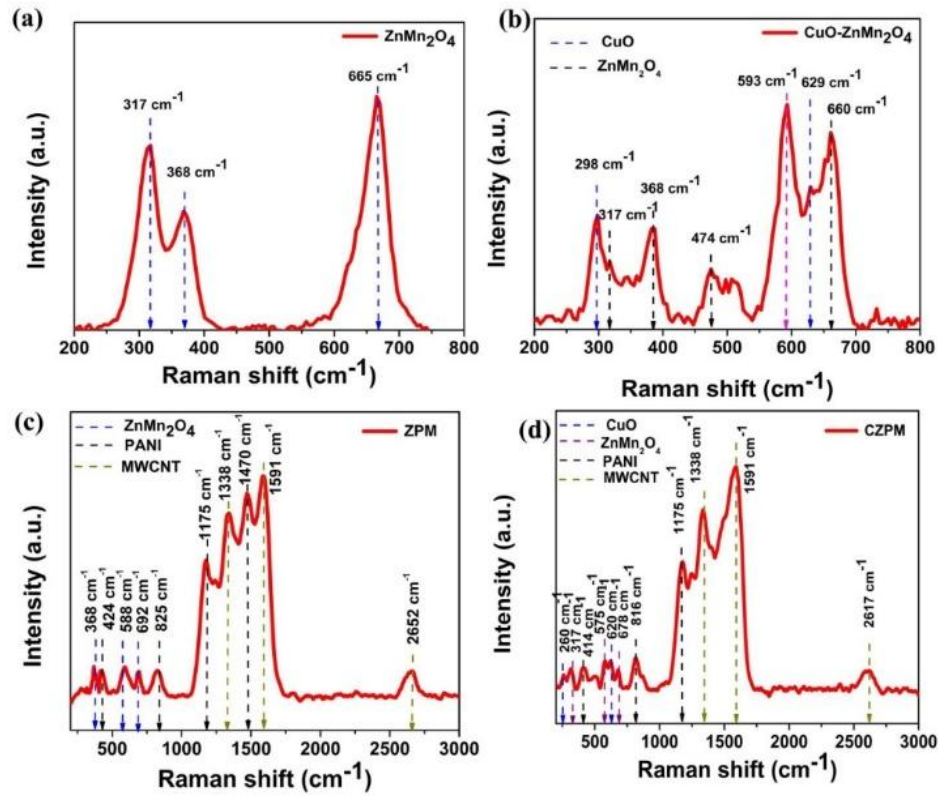


Fig. 5.2. Raman profiles of pristine (a) ZnMn₂O₄ (b) CuO-ZnMn₂O₄ (c) ZPM (d) CZPM composites.

Table 5.1. List of assignments of dominant characteristic bands appeared in Raman spectra of ZPM and CZPM nanocomposite.

Raman modes		Assignments
ZPM	CZPM	
-	260 cm ⁻¹	A _g mode of monoclinic CuO
368 cm ⁻¹	317 cm ⁻¹	Raman active mode of tetragonal ZnMn ₂ O ₄
424 cm ⁻¹	414 cm ⁻¹	Out of plane C-H wag in bipolaronic
588 cm ⁻¹	575 cm ⁻¹	Raman active mode of tetragonal ZnMn ₂ O ₄
-	620 cm ⁻¹	B _g ² mode of monoclinic CuO
692 cm ⁻¹	678 cm ⁻¹	A _g mode of tetragonal ZnMn ₂ O ₄

825 cm ⁻¹	816 cm ⁻¹	Ring deformation of benzenoid ring in emeraldine salt form of PANI
1175 cm ⁻¹	1175 cm ⁻¹	C-H bending of benzenoid ring in PANI
1470 cm ⁻¹	-	C=N stretching in quinoid ring in PANI
1338 cm ⁻¹	1338 cm ⁻¹	D- band of MWCNT
1591 cm ⁻¹	1591 cm ⁻¹	G-band of MWCNT
2652 cm ⁻¹	2617 cm ⁻¹	G' band of MWCNT

5.3.3. FT-IR spectroscopy

The FT-IR spectra of ZnMn₂O₄, CuO- ZnMn₂O₄, ZPM, and CZPM composites are shown in Fig. 5.3, in the aim of focusing more on their microstructural features and molecular bonds. In the Fig. 5.3 (a), FT-IR spectrum of ZnMn₂O₄ is presented. The three sharp and intense observed peaks in the wavenumber range 500-700 cm⁻¹ were attributed to the M-O and M-O-M bonds of the tetragonal ZMO structure (M=Zn,Mn) [7]. The weak band at 1732 cm⁻¹ corresponds to vibrational modes of carbonyl groups and 1110 cm⁻¹ linked with the bending vibration peak of residual water molecules [28]. The FT-IR spectra of CuO-ZMO nanocomposite are displayed in Fig. 5.3 (b), presenting two intense peaks of ZnMn₂O₄ at 628 cm⁻¹ and 520 cm⁻¹ and a characteristic peak of Cu-O bond at 434 cm⁻¹. The vibrational modes of carbonyl groups and bending mode of water molecules were appeared in the composite material also. The peak at 2924 cm⁻¹ attributed to the stretching vibrational mode of O-H bond [7]. The ternary and quaternary composites, ZPM and CZPM, reveal an integration of vibrational peaks of metal oxides, PANI and MWCNTs. The characteristic peaks of each constituent and their corresponding peak assignments are listed in Table 5.2.

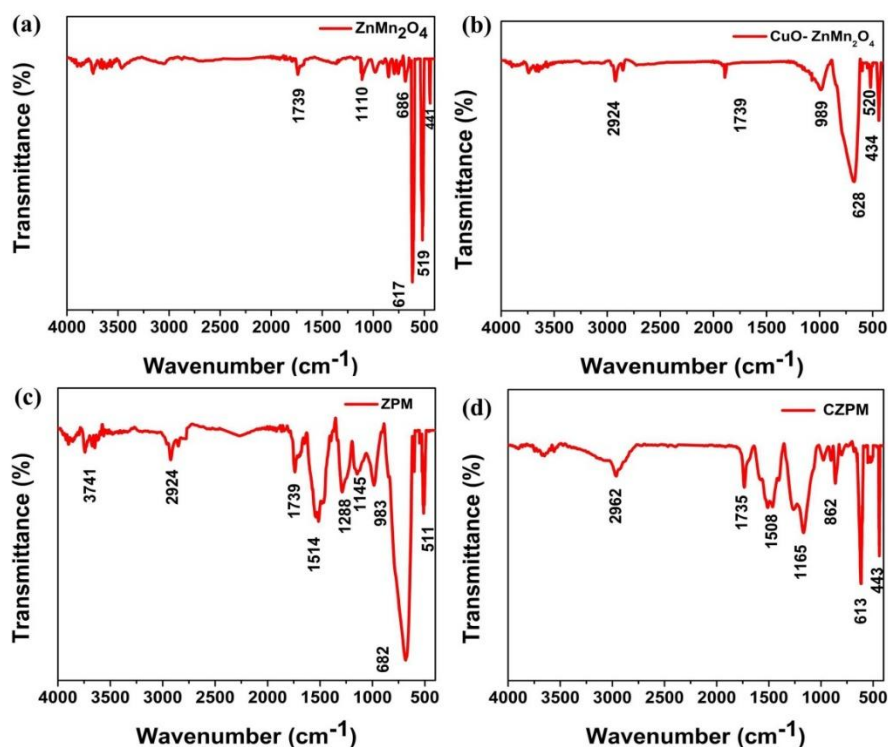


Fig. 5. 3. FT-IR spectra of (a) ZnMn₂O₄ (b) CuO- ZnMn₂O₄ (c) ZPM (d) CZPM nanocomposites.

Table 5.2. List of peaks in FT-IR spectrum of ZPM and CZPM nanocomposites and its corresponding assignments.

FT-IR peaks		Assignments
ZPM	CZPM	
3741 cm ⁻¹		stretching vibrational mode of O-H bond
2924 cm ⁻¹	2962 cm ⁻¹	stretching vibrational mode of O-H bond
1739 cm ⁻¹	1735 cm ⁻¹	stretch mode of carboxylic groups in MWCNT
1514 cm ⁻¹	1508 cm ⁻¹	C=C stretching in quinoid ring of PANI
1288 cm ⁻¹	1296 cm ⁻¹	C-N for aromatic amines in the polaron structure of conducting PANI

1145 cm ⁻¹	1165 cm ⁻¹	characteristic band of the protonated form of conducting PANI
983 cm ⁻¹	972 cm ⁻¹	due to protonated imine group in PANI
-	862 cm ⁻¹	out-of plane C–H bending vibration.
682 cm ⁻¹ & 511 cm ⁻¹	613 cm ⁻¹	stretching modes of ZMO
-	443 cm ⁻¹	stretching vibrations of Cu–O

5.3.4. Field Emission Scanning Electron Microscopic images (FESEM) and elemental mapping

The morphological and elemental investigations of the synthesised ZMO, CuO-ZMO, ZPM and CZPM composites were done using FESEM-EDS analyses, which are depicted in Fig. 5.4. The ZMO material displayed a heterogeneous distribution of several flake-like and diamond-like nanostructures (shown in Fig. 5.4 (a-c)). This irregular configuration of nanostructures carries some kind of porous spaces thought the surfaces. In the highly magnified images (Fig. 5.4 (c)), a few nanotube-like structures were also seen in certain regions. The CuO-ZMO composite carries a nanotubular morphology with some sort of nanoparticles over the tube surfaces (Fig. 5.4 (d-e)). The nanoflake structure of CuO underwent modification in to the tubular form with some diamond shaped ZMO particles scattered over tube surfaces to form the complete symmetry of CuO-ZMO composite. The FESEM image of the ZPM composite has shown in Fig. 5.10 (g-i), portrayed an agglomerative framework of nanotubules interspersed with some voluminous porous regions. The fibres viewed as some interconnected networks got attached together as a result of enhance PANI wrapping over MWCNT surfaces. This agglomerative nature made the metal oxide nanoparticles morphologically indistinct. The surface modification of CuO-ZMO composite through the incorporation of PANI and MWCNTs was analysed through SEM images shown in Fig. 5.10 (j-l). The CZPM nanocomposite presents nanofibrillar texture with large voluminous pores in between, creating an effective contact area for

electrochemical reactions. The average diameter of these fibres was estimated to be 32 nm, highlighting the synergistic interaction between PANI and MWCNTs.

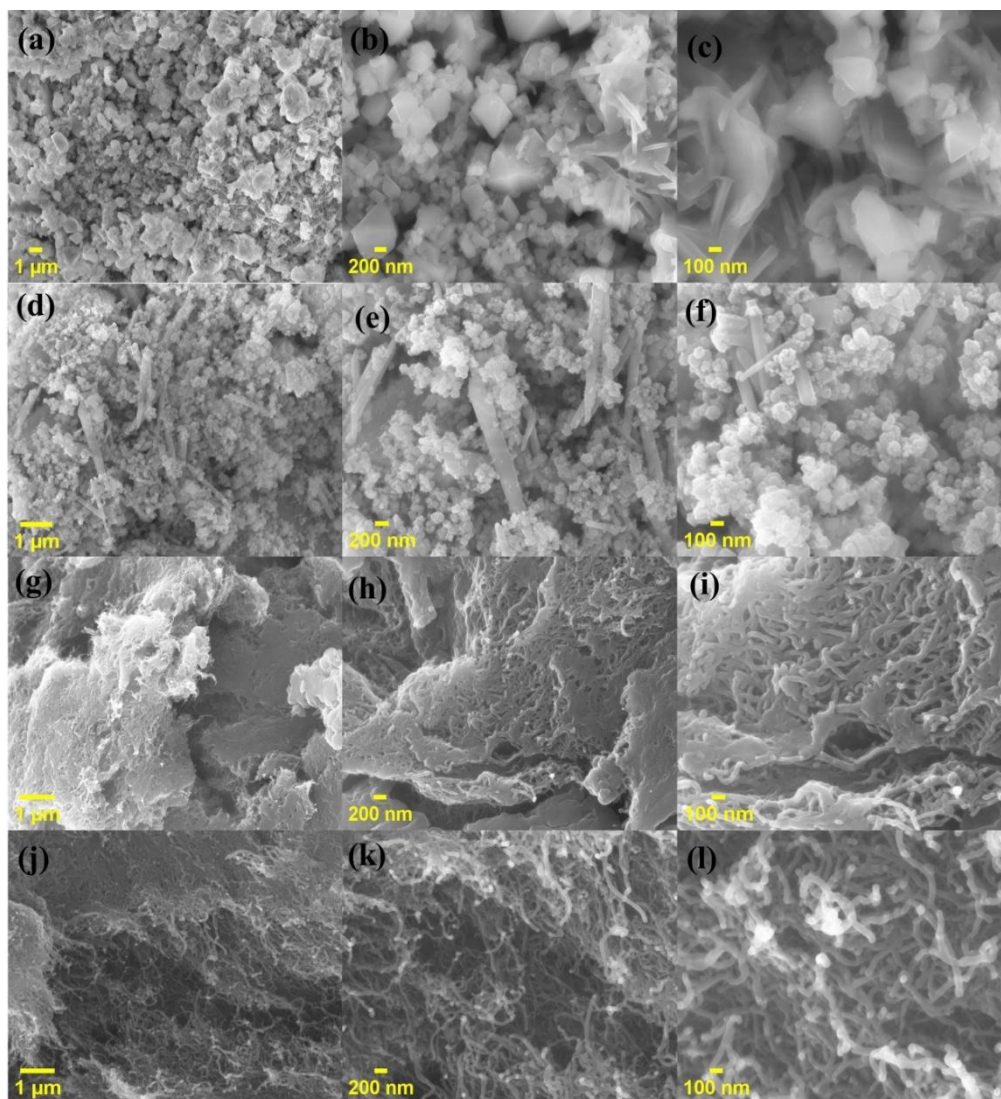


Fig. 5.4. FESEM micrographs of (a,b,c) ZnMn₂O₄ (d,e,f) CuO- ZnMn₂O₄ (g,h,i) ZPM (j,k,l) CZPM nanocomposites.

The EDS spectra of ZMO, CuO-ZMO, ZPM and CZPM composites are presented in Fig. 5.5. The existence of elements Zn, Mn and O in the material confirms the intended formation of ZnMn₂O₄ (Fig. 5.4(a)). The EDS spectrum of CuO-ZMO composite, shown in Fig. 5.5 (b), carries the element Cu in addition to Zn, Mn and O, which clearly validates the exact formation of CuO-ZMO composites. The incorporation of PANI and MWCNTs in to the matrix of ZMO and CuO-ZMO materials was confirmed through the presence of C and N in the ZPM and CZPM composites, respectively (Fig. 5.5 (c-d)). The atomic concentrations of constituents in

each composite material were displayed in Table 5.3. The expected elemental formation of all composites was verified with the help of this tabular data.

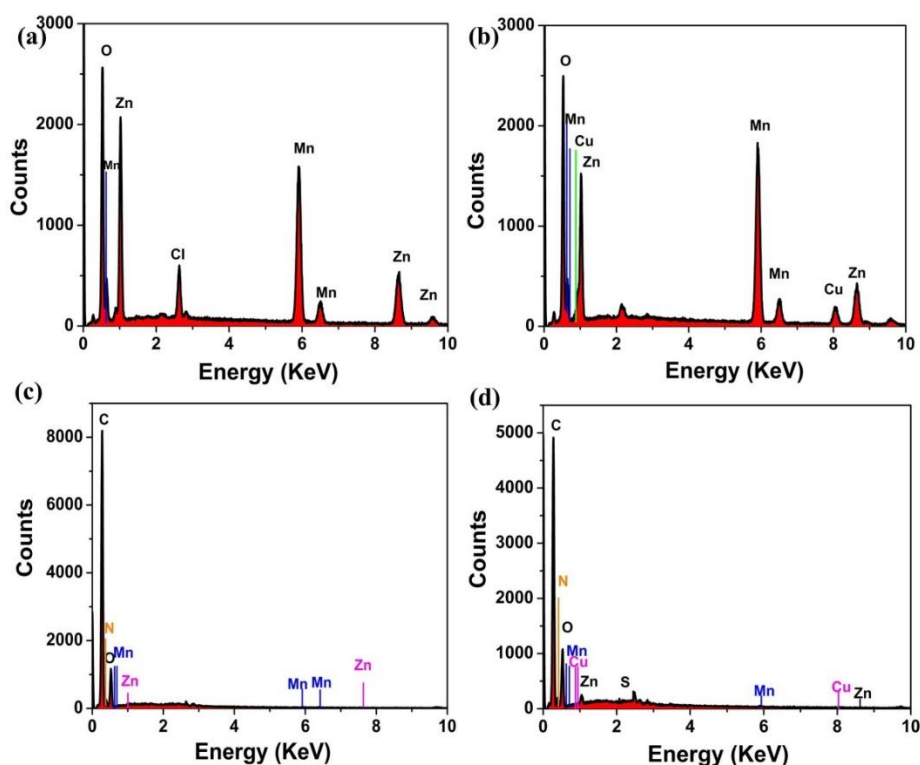


Fig. 5.5. EDS spectra of (a) ZnMn₂O₄ (b) CuO- ZnMn₂O₄ (c) ZPM (d) CZPM nanocomposites.

Table 5.3. Elemental data of ZnMn₂O₄, CuO- ZnMn₂O₄, ZPM and CZPM composites obtained from EDS analysis.

Sample	Atomic ratio (%)					
	Cu	O	Zn	Mn	C	N
ZnMn ₂ O ₄	-	54.11	17.45	28.44	-	-
CuO- ZnMn ₂ O ₄	22.14	43.12	11.14	23.60	-	-
ZPM	-	23.14	8.05	18.46	41.23	9.12
CZPM	12.02	10.13	5.21	17.19	47.63	7.82

The EDS mapping of ZMO, CuO-ZMO, ZPM and CZPM nanocomposites is portrayed in Fig. 5.6, Fig. 5.7, Fig. 5.8, and Fig. 5.9 respectively. From Fig. 5.6, the white colour region evidences the exact formation of ZnMn₂O₄. The excess amount of oxygen in the compound was clear from the selective elemental images. In the case of

CuO-ZMO composites, the homogeneous distribution of elements Cu, Zn, Mn and O is clearly visible at first glance (Fig. 5.7). The elemental mapping image of ZPM composite presented in Fig. 5.8 indicated the predominance of carbon over the other elements like nitrogen, copper, zinc, manganese and oxygen. Similarly, from the EDS map of the CZPM composite (Fig. 5.9) a higher contribution of carbon from both PANI and MWCNTs was noticed. The effective interaction between PANI and MWCNTs was noticed. The effective interaction between PANI and MWCNTs was undeniable from the presence of nitrogen in the vicinity of carbon atoms.

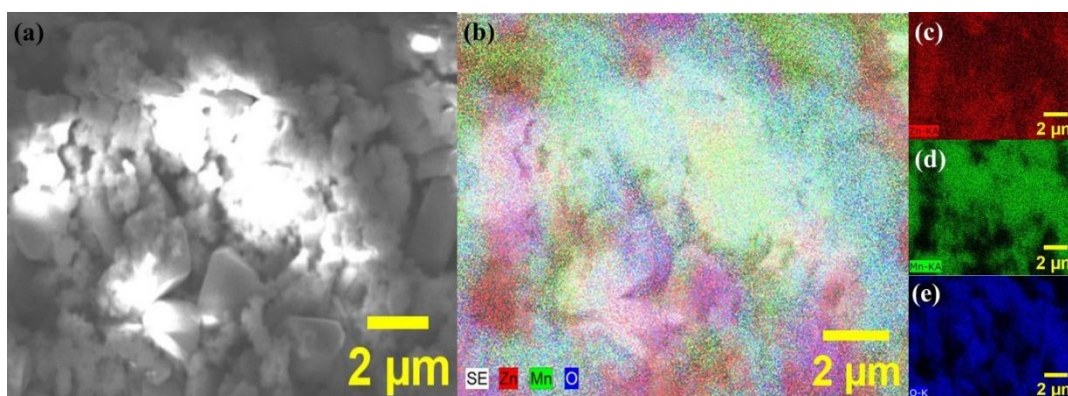


Fig. 5.6. (a) SEM image, (b) EDS mapping of ZnMn₂O₄ nanostructures, and (c-e) selective elemental distribution for the area shown in image (a).

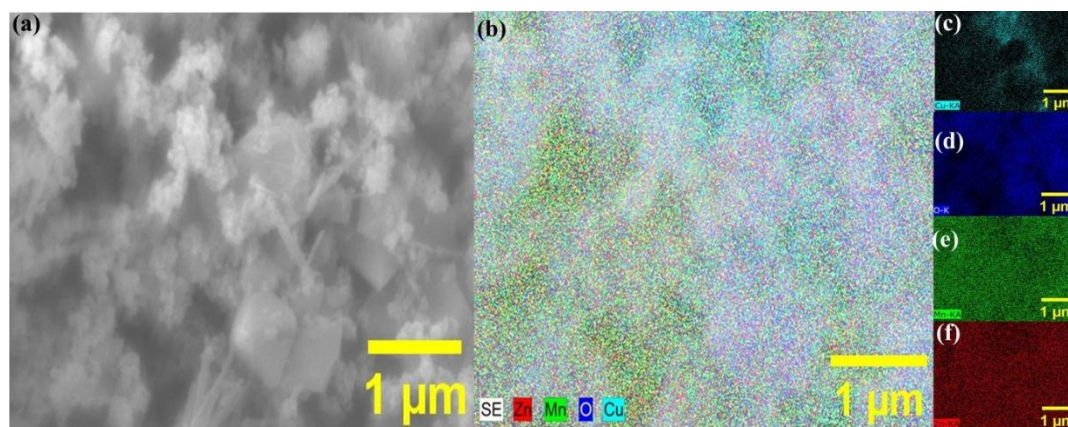


Fig. 5.7. (a) SEM image, (b) EDS mapping of CuO-ZnMn₂O₄ nanostructures, and (c-f) selective elemental distribution for the area shown in image (a).

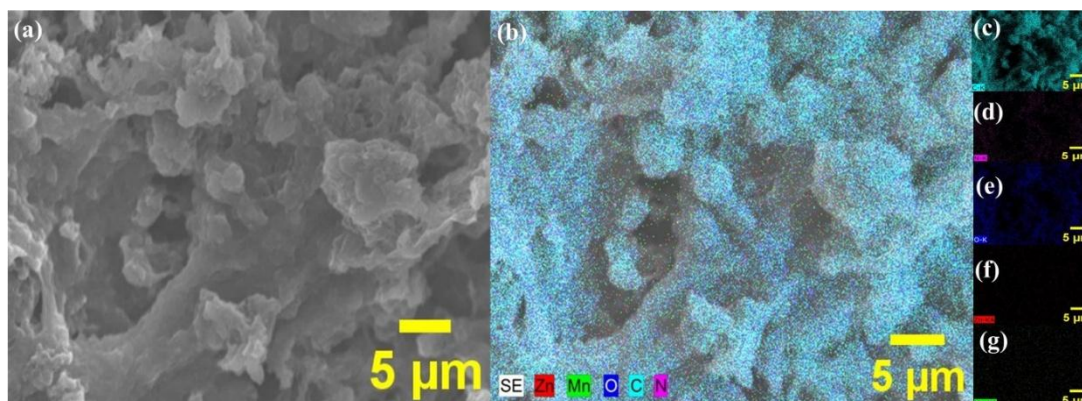


Fig. 5.8. (a) SEM image, (b) EDS mapping of ZPM nanostructures, and (c-g) selective elemental distribution for the area shown in image (a).

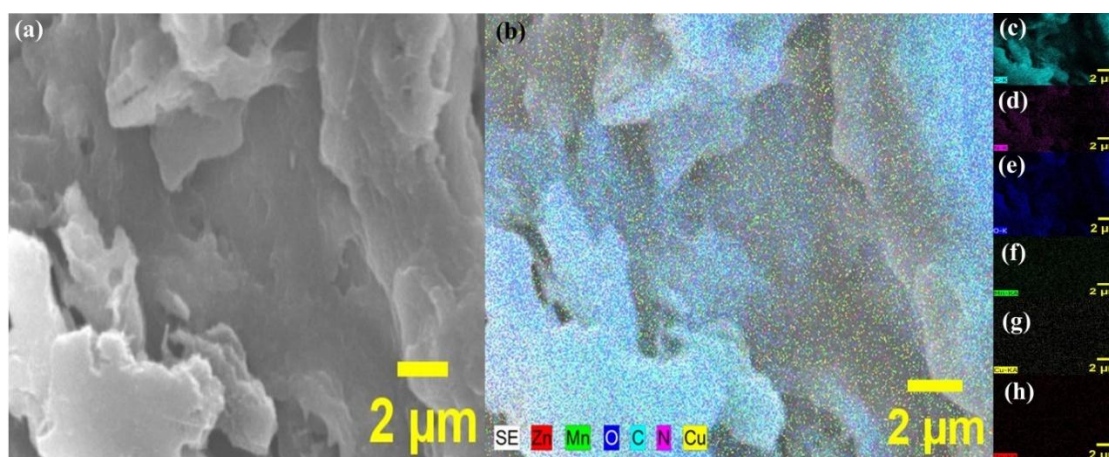


Fig. 5.9. (a) SEM image, (b) EDS mapping of CZPM nanostructures, and (c-h) selective elemental distribution for the area shown in image (a).

5.3.5. High Resolution Transmission electron micrographs (HR-TEM)

The microstructural characteristics of the quaternary CuO-ZnMn₂O₄/PANI/MWCNT hybrid composite were investigated through the TEM, HRTEM-SAED images shown in Fig. 5.10. From Fig. 5.10 (a-b), it is obviously inferred the co-existence of CuO-ZMO with PANI and MWCNTs in the composite system. The HRTEM image shown in Fig. 5.10(c), it is undeniable about the wrapping of PANI around the tubular texture of MWCNTs through their synergistic interactions. The average diameter of these rough interconnected fibrillar networks was estimated to be 17.5 to 20 nm. From Fig. 5.10(d), the presence of metal oxide particles along with PANI and MWCNT contributions was verified from the identification of dominant crystallographic planes in the HRTEM images. The inner-outer diameter of fibres was

analysed to prove the PANI wrapping on the MWCNT surfaces during polymerisation. The SAED pattern of CZPM composite is presented in Fig. 5.10 (f), shows the concentric rings that substantiates the polycrystalline nature of composite.

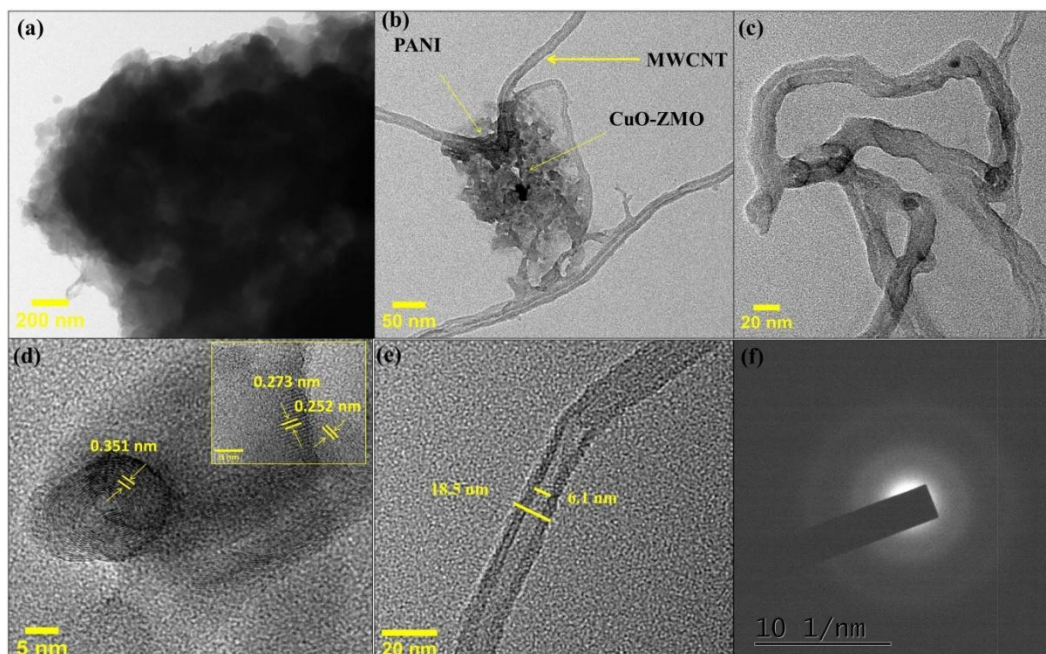


Fig. 5.10. (a,b,c) TEM micrograph (d,e) HRTEM images (f) SAED pattern of CZPM composites. Inset figure in Fig. 5.10 (d) shows crystallographic planes of nanostructures in the composite.

5.3.6. X-Ray Photoelectron spectroscopy (XPS)

The compositional analysis and identification of chemical oxidation states in the composites were carried out using X-ray photoelectron spectra, as presented in Fig. 5.11. The survey spectrum shown in Fig. 5.11 (a) confirms the presents of the elements C, N, O, Zn, Mn, and Cu in the quaternary CZPM composite. The core level spectra of C 1s displayed in Fig. 5.11 (b) is deconvoluted to three major peaks located at binding energies 284.5 eV, 286.2 eV, and 287.6 eV which can be assigned to the sp^2 hybridized Carbon atoms, C=O, and C-OH bonds, respectively [29]. Higher intensity of sp^2 hybridised carbon atoms is a clear indication of grafting of PANI over MWCNTs, since conductive PANI polymers consists of an abundant amount of C=C bonds [30]. The core level XPS spectra of N 1s shown in Fig. 5.11 (c) deconvoluted to three peaks at 399.2 eV, 401 eV, and 403.6 eV. The high intense peak at lower binding energy of 399.2 eV can be attributed to the neutral amine groups (-N-H-) present in the PANI, whereas

protonated imine groups are responsible for the peak at 401 eV. The less intense peak at 403.6 eV assigned to the protonated amine groups [31]. The protonated nitrogen in the composite is an clear indication of the high conductive nature of PANI [32]. This ionic nitrogen presence can be due to the effective interaction of PANI and MWCNTs through π - π^* conjugation [33]. The XPS spectrum of Zn 2p is shown in Fig. 5. 11 (c) featuring the characteristic peaks at binding energies 1022 eV and 1046 eV, allocated to the Zn 2p_{3/2} and Zn 2p_{1/2} orbits, respectively [34]. The oxidation states of Mn 2P was revealed through analysing the core level XPS spectrum presented in Fig. 5.11 (d). The two peaks at 641.9 eV and 652.9 eV were corresponds to the Mn 2p_{3/2} and Mn 2p_{1/2} orbitals, respectively. There exists one satellite peak at 643.6 eV, confirming the existence of Mn³⁺ and Mn²⁺ ions in the composite [35]. The characteristic peaks of Cu 2p_{3/2} and Cu 2p_{1/2} were located at the binding energies 932.8 eV and 952.7 eV along with three shake up peaks (shown in Fig. 5.11 (e)) [36]. The core level XPS spectrum of O 1s is shown in Fig. 5. 11 (e), having three deconvoluted peaks at 531.3 eV, 532.6 eV and 534.6 eV representing oxgen vacancies, metal-hydroxyl bonds and carbon oxygen bonds (O=C-O), respectively [34], [37].

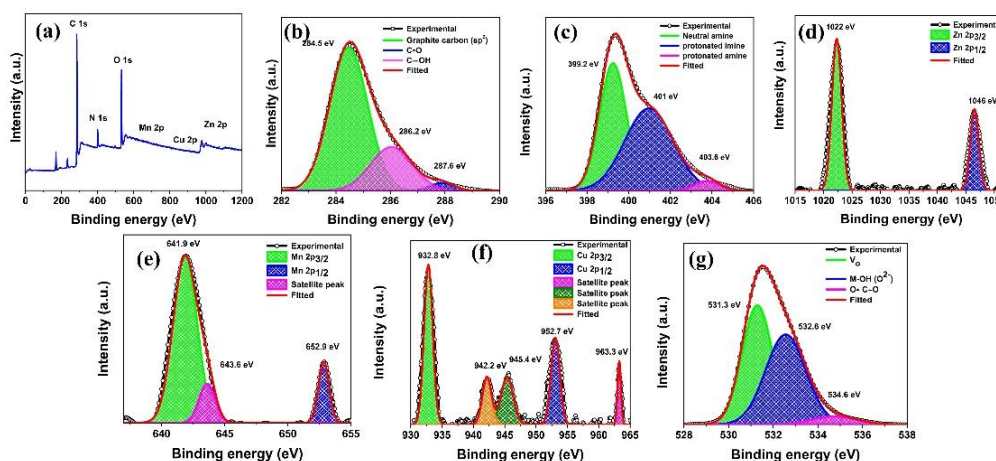


Fig. 5.11. (a) XPS survey spectrum and XPS elemental core spectra of (b) C 1s and (c) N 1s (d) Zn 2p and (e) Mn 2p (f) Cu 2p (g) O 1s states of CZPM nanocomposite.

5.3.7. Brunauer-Emmett-Teller (BET) analysis

The specific surface area and pore size distribution of ZMO, CuO-ZMO, ZPM, and CZPM nanocomposites were estimated using Brunauer-Emmett-Teller analysis and are presented in Fig. 5.12. From the N₂ adsorption-desorption isotherm plot of ZMO which is shown in Fig. 5.12 (a), it is inferred that the material exhibits type IV

adsorption behaviour with a H3 hysteresis loop ranging from 0.6-0.95 (P/P_0). The type IV adsorption isotherms were usually exhibited by mesoporous species in which the adsorption nature is determined generally by the interaction between adsorbent and adsorptive [27]. In addition, the shape of hysteresis loops is also crucial in describing the metastability of the adsorption process. ZMO shows mesoporous nature with a BET surface area of about $\sim 8 \text{ m}^2/\text{g}$. The pore radius and pore volume of ZMO estimated from the pore size distribution (PSD) plot and are shown in the inset of Fig. 5.12 (a) is 3.12 nm and $0.012 \text{ cm}^3/\text{g}$, respectively. The adsorption-desorption plot of CuO-ZMO nanocomposite (Fig. 5.12 (b)) concluded the type IV adsorption isotherm with H3 hysteresis loop between 0.4-1 (P/P_0). The specific surface area was estimated to be $68 \text{ m}^2/\text{g}$. The mesoporous nature of this composite was visible from the PSD plot shown in the inset figure with a pore radius and volume of about 12.1 nm and $0.86 \text{ cm}^3/\text{g}$, respectively. The ZPM composite sample exhibits a type IV adsorption isotherm with H3 hysteresis loop ranges 0.8-1 (P/P_0) with a surface area of $14 \text{ m}^2/\text{g}$, which is shown in Fig. 5.12 (c). From the PSD plot shown in the inset figure, the pore radius and volume were estimated to be 6.14 nm and $0.043 \text{ cm}^3/\text{g}$. In the case of the quaternary CZPM composite, the N_2 adsorption-desorption isotherm plot (Fig. 5.12 (d)) shows a H1 hysteresis loop ranges between 0.79-1 (P/P_0). The mesoporous nature of the composite sample was inferred from the PSD plot (inset figure in Fig. 5.12 (d)) with a pore radius and volume of 16.12 nm and $0.91 \text{ cm}^3/\text{g}$, respectively. The BET surface area of the quaternary composite is about $114 \text{ m}^2/\text{g}$. The inbuilt greater surface area of MWCNTs with tubular morphology as well as the fibrous conductive frameworks of PANI themselves can effectively contribute to the overall surface area of the composite system. Additionally, the PANI/MWCNT incorporation can make porous interconnected networks throughout the composite, as visible in the SEM micrographs, which can increase electrolyte penetration to the electrode surface. The CZPM composite having a larger specific surface area and pore structure can effectively enhance the electrochemically active sites between the electrode-electrolyte interface and surpasses the ionic migrations in the system, which can eventually turn up the electrochemical performance of the composite electrode.

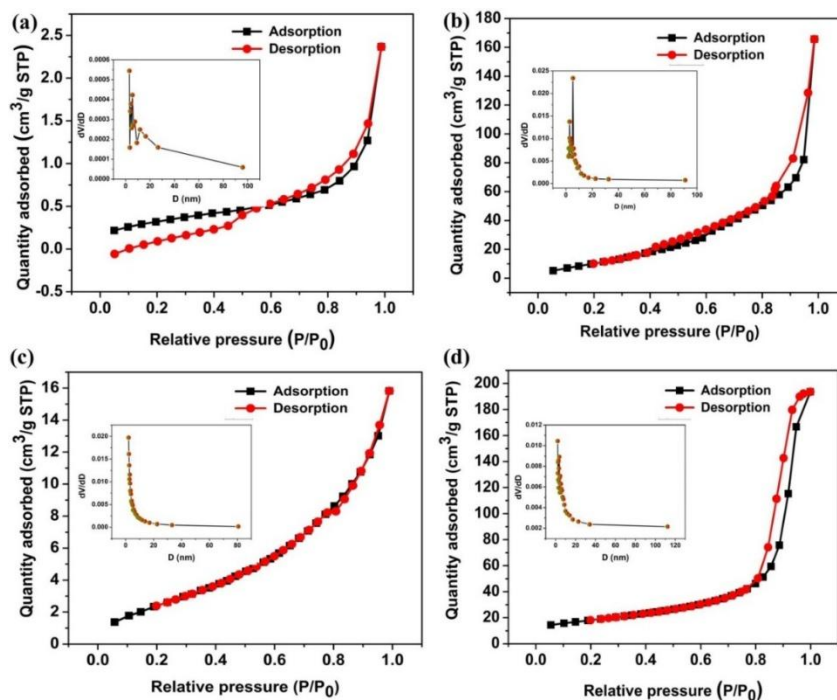


Fig. 5.12. The N₂ adsorption-desorption isothermal plots of (a) ZnMn₂O₄ (b) CuO-ZnMn₂O₄ (c) ZPM and (d) CZPM nanocomposites. Inset shows the corresponding PSD plots.

5.3.8. Thermo-gravimetric Analysis (TGA)

The stability of CZPM quaternary composite under thermal test was conducted using TGA analysis, portrayed in Fig. 5.13. The CZPM composite material suffers three stages of decomposition which results in marginal weight loss over temperature exposure. The complete release of water molecules from the composite material resulted in a weight loss of about 5.65% at a temperature of 97 °C. In the second stage, due to the removal of acid components as well as the initiation of polymer degradation contributes to a significant loss of about 34.5% at 337 °C. Final degradation of polymer backbones accounts for a weight loss of about 10% until the temperature 569 °C [38], [39]. The substantial amount of the final residual part of CZPM indicates the enhanced thermal stability of the quaternary composite when compared with pristine PANI, due to the significant thermal strength contributed from the metal oxides and MWCNTs. The metal oxides carry commendable thermal resistance and their strong bond with PANI make the decomposition process slower and lesser [40]. Moreover, the higher stability and mechanical strength of carbon compounds like MWCNTs under thermal stress delayed the temperature breakdown of composite [41].

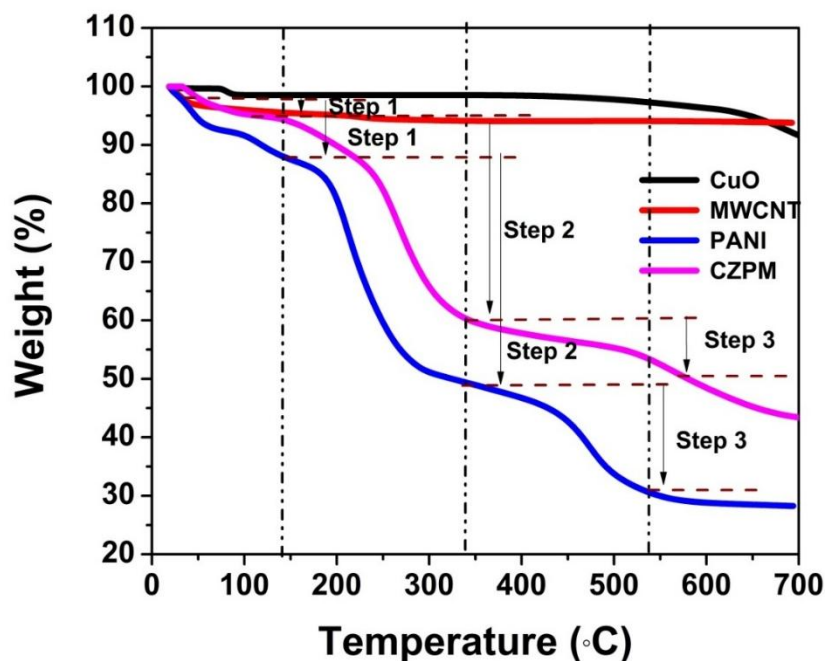


Fig. 5.13. Thermogravimetric analysis of CuO, MWCNT, PANI and CZPM composite.

5.3.9. Electrochemical studies

5.3.9.1. Cyclic voltammetry (CV)

To access the electrochemical performance of ZMO, CuO-ZMO, ZPM, and CZPM nanocomposite, cyclic voltametric analysis was conducted in a three-electrode system at different scan rates ranging from 5 mV/s to 100 mV/s, shown in Fig. 5.14. The CV measurements were taken in the optimised potential window of 0-0.8V with 1M Na₂SO₄ as the electrolyte solution. ZMO electrode material exhibited CV curves having geometry much deviated from the ideal rectangular shape, suggests its pseudocapacitive nature (Fig. 5.14 (a)). Although, the integral area which quantifies the current responses has escalated with the increasing sweep rate, the total areal current response at each scan rate remained significantly low compared to that of pristine CuO. The CV profile of CuO-ZMO nanocomposite electrode material is displayed in Fig. 5.14 (b), shows the quasi-rectangular shape of CV curves without any noticeable redox peaks. The visible broadening of CV loops with sweep rate without disturbing its shape is a clear indication of the excellent rate capacity and reversibility of cyclic performance. The increase in current responses with sweep rate is attributable to the faster transport of electrically active species from the electrolyte ions to electrode

surfaces [42]. The CV curves of ternary-quaternary nanocomposites ZPM and CZPM are depicted in Fig. 5.14 (c-d). Both the composite electrodes showed a quasi-rectangular shaped current response with distinct redox peaks. The redox peaks in the CV curve of ZPM sample were appeared at potentials (0.17V, 0.37V) ascribed to the exchange of emeraldine and lucoemeraldine states in PANI [43]. A slighter shift in redox peak positions of ZPM was observed when sweep rate got amplified. The quaternary composite electrode material exhibited a non-rectangular CV curve with a pair of redox peaks at potentials (0.15 V, 0.42 V) at the lower scan rate and went through major shifts in position to a potential pair (0.22 V, 0.57 V) as the sweep rate reached 100 mV/s, which indicated that the PANI and MWCNT incorporation has effectively improved the redox properties of the composite. Noteworthy, the obvious enrichment in current response of CZPM with the increasing scan rates without deforming its shape indicates the high rate capacity and reversibility of the composite [27]. The enhanced capacitive performance of CZPM electrode material is clearly understood from the comparative CV analysis of CuO, ZMO, CZMO, CPM, ZPM and CZPM at the scan rate 100 mV/s, is portrayed in Fig. 5.14 (e). The specific capacitance values obtained from the cyclic voltametric analysis are presented through histogram in Fig. 5.14 (f), showing the remarkable electrochemical performance of CZPM working electrode aroused from the synergistic effects between CuO-ZMO, PANI and MWCNTs within the composite [44]. Undoubtedly, the total specific capacitance of composite electrode can be attributable to the combined influence of electric double layer capacitance and pseudocapacitance. The tubular morphology and porous architecture of the metal oxide anchored PANI-MWCNT system enabled faster ionic transport and kinetics through improved electrical conductivity [45].

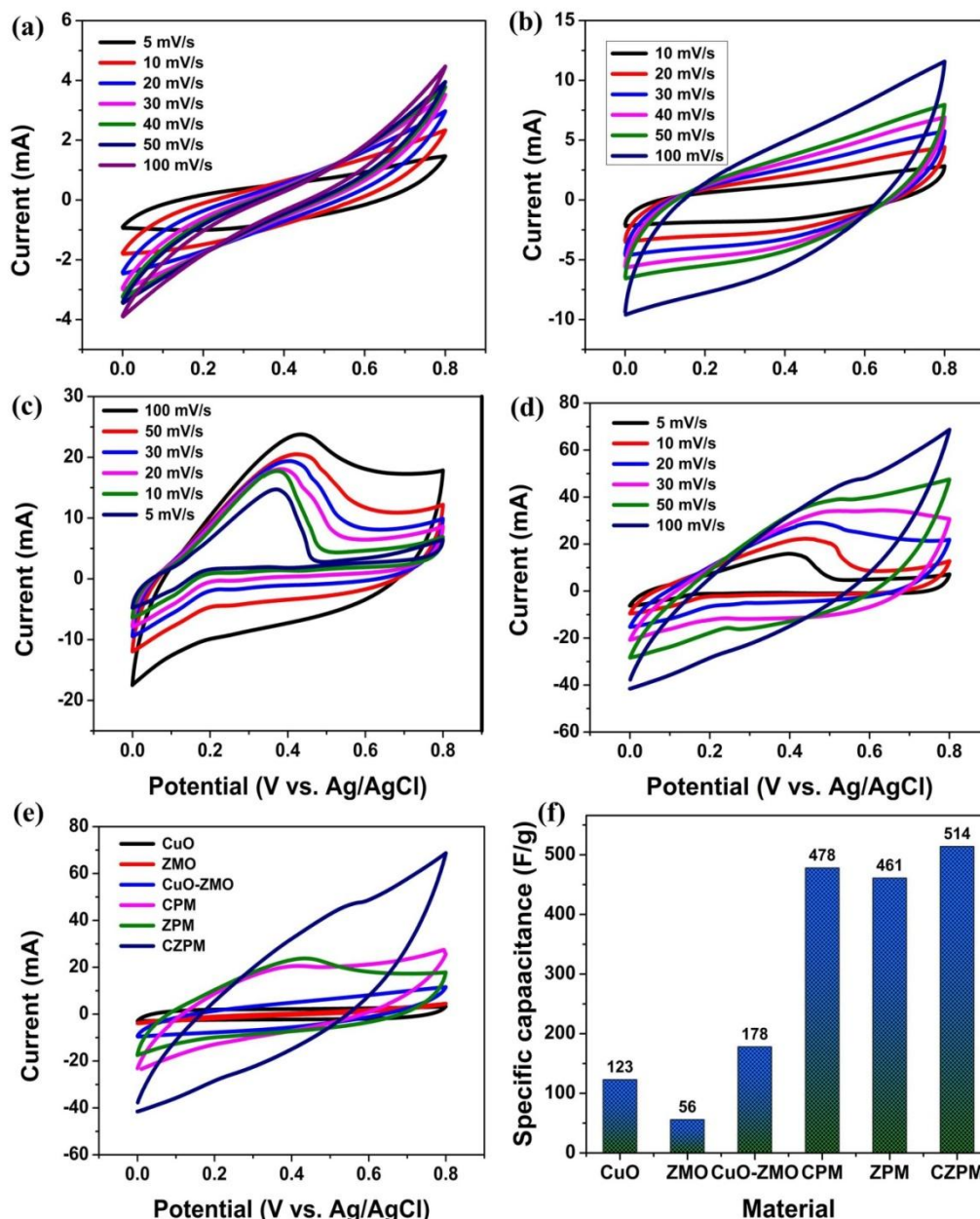


Fig. 5.14. CV curves of (a) ZMO (b) CuO-ZMO (c) ZPM (d) CZPM, comparison of (e) CV curves of CuO, ZMO, CuO- ZMO, CPM, ZPM and CZPM nanocomposites at 100 mV/s (f) specific capacitance of CuO, ZMO, CuO- ZMO, CPM, CZPM and CZPM nanocomposites at 10 mV/s.

The reaction kinetics that occurred during the charge storage mechanism in the CZPM composite electrode is analysed using Dunn's method. The linearity between scan rate and anodic current response at a potential of 0.4 V was observed in Fig. 5.15 (a). The anodic slope value obtained from the plot was 0.83. From $v^{1/2}$ vs. $i/v^{1/2}$ graph (Fig. 5.15 (b)), the coefficient values k_1 and k_2 were extracted and used for the estimation of surface-controlled capacitive contribution and diffusion-controlled

contributions in the total capacitive current response of CZPM electrode. There is a slight deviation from the linearity in the data showing the relation between the square root of the scan rate and peak current. Fig. 5.15 (c) illustrates the separate contribution analysis in the current response of CZPM electrode at the scan rate of 10 mV/s. The shaded region indicates the diffusion-controlled capacitive contribution to the overall current response. As the sweep rate increased, the surface-controlled capacitive contributions became predominant compared to diffusion-controlled redox reactions and achieved a value of 98% at 100 mV/s (Fig. 5.15 (d)).

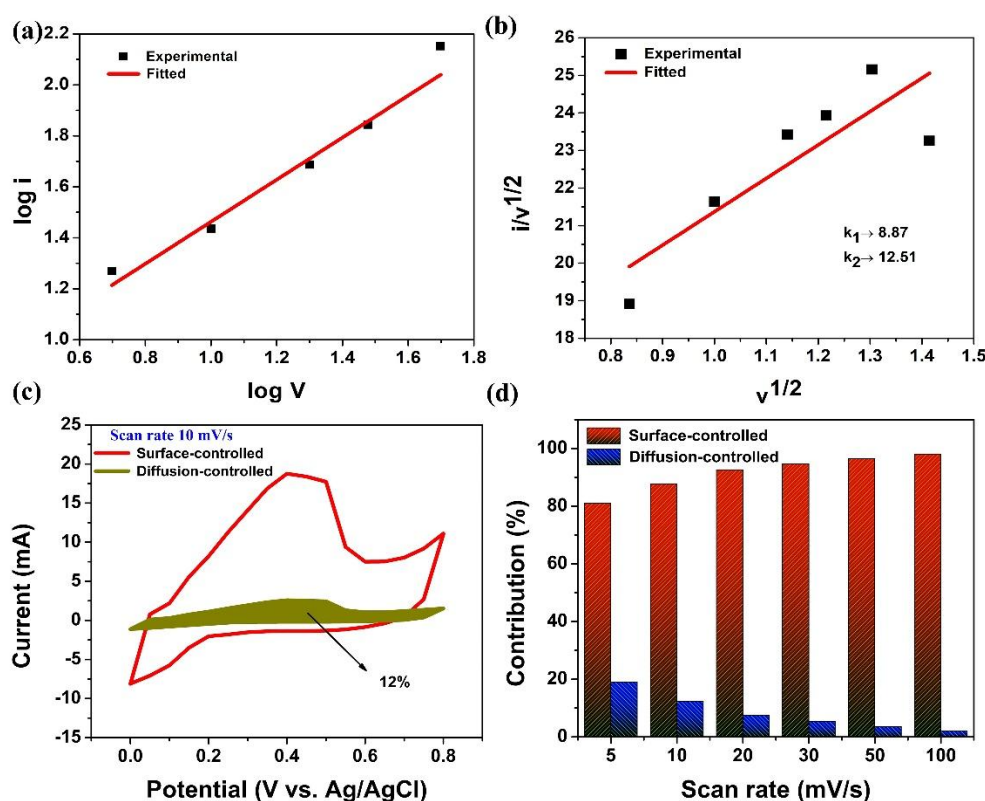


Fig. 5.15. (a) $\log v$ vs. $\log i$ plot (b) $v^{1/2}$ vs. $i/v^{1/2}$ plot (c) decoupling of capacitive and diffusive current contributions at scan rate 10 mV/s (d) Histograms of diffusive and capacitive contributions of CZPM working electrode at varying scan rates.

5.3.9.2. Galvanostatic charge/discharge (GCD) studies

To probe more thoroughly into the electrochemical dynamics of the synthesised ZMO, CuO-ZMO, ZPM, and CZPM composites, GCD studies were conducted. Fig. 5.16 (a-b) shows the GCD profiles of ZMO and CuO-ZMO nanostructures in the optimised potential range of 0-0.8V. The symmetric shapes of GCD curves in all current

densities indicate the satisfactory reversibility of electrodes. The discharging time of CuO-ZMO working electrode is found to be more than that of ZMO electrode. The calculated specific capacitance of ZMO electrode were 114 F/g, 78 F/g, 37 F/g, and 23 F/g, whereas that of CuO-ZMO were found to be 310 F/g, 264 F/g, 50 F/g and 22 F/g at current densities 0.3 A/g, 0.8 A/g, 1 A/g and 2 A/g, respectively. The GCD profiles of ZMO/PANI/MWCNT and CuO-ZMO/PANI/MWCNT electrode are depicted in Fig. 5.16 (c-d). Each electrode shows symmetric shape in GCD curves with improved discharging time compared to their individual counterparts. The low IR drops in all electrode material is one of the beneficial feature of energy storage devices which minimises the heat dissipation during continuous charge-discharge cycles [46]. The specific capacitance values of ZPM and CZPM electrodes were 438 F/g, 345 F/g, 93.75 F/g, and 81.25 F/g, and 693 F/g, 527 F/g, 248 F/g, and 169 F/g at current densities of 1 A/g, 2A/g, 3 A/g, and 5 A/g, respectively. The comparison of the discharging time of CuO, ZMO, CuO-ZMO, CPM, ZPM, and CZPM electrodes at a current density of 1 A/g is displayed in Fig. 5.16 (e). The longest discharging time of the quaternary composite is a clear indication of its enhanced specific capacitance, which can be understood from the histogram presented in Fig. 5.16 (f). The improved performance of this composite electrode is attributable to its beneficial porous structure. More specifically, the uniform growth of PANI over the surface of binary metal oxide composite anchored MWCNTs creates more number of active sites in the electrode surface for achieving faster redox reactions, as well as PANI has built a conductive pathway in the system by improving the electrical contact between metal oxides and MWCNTs [27].

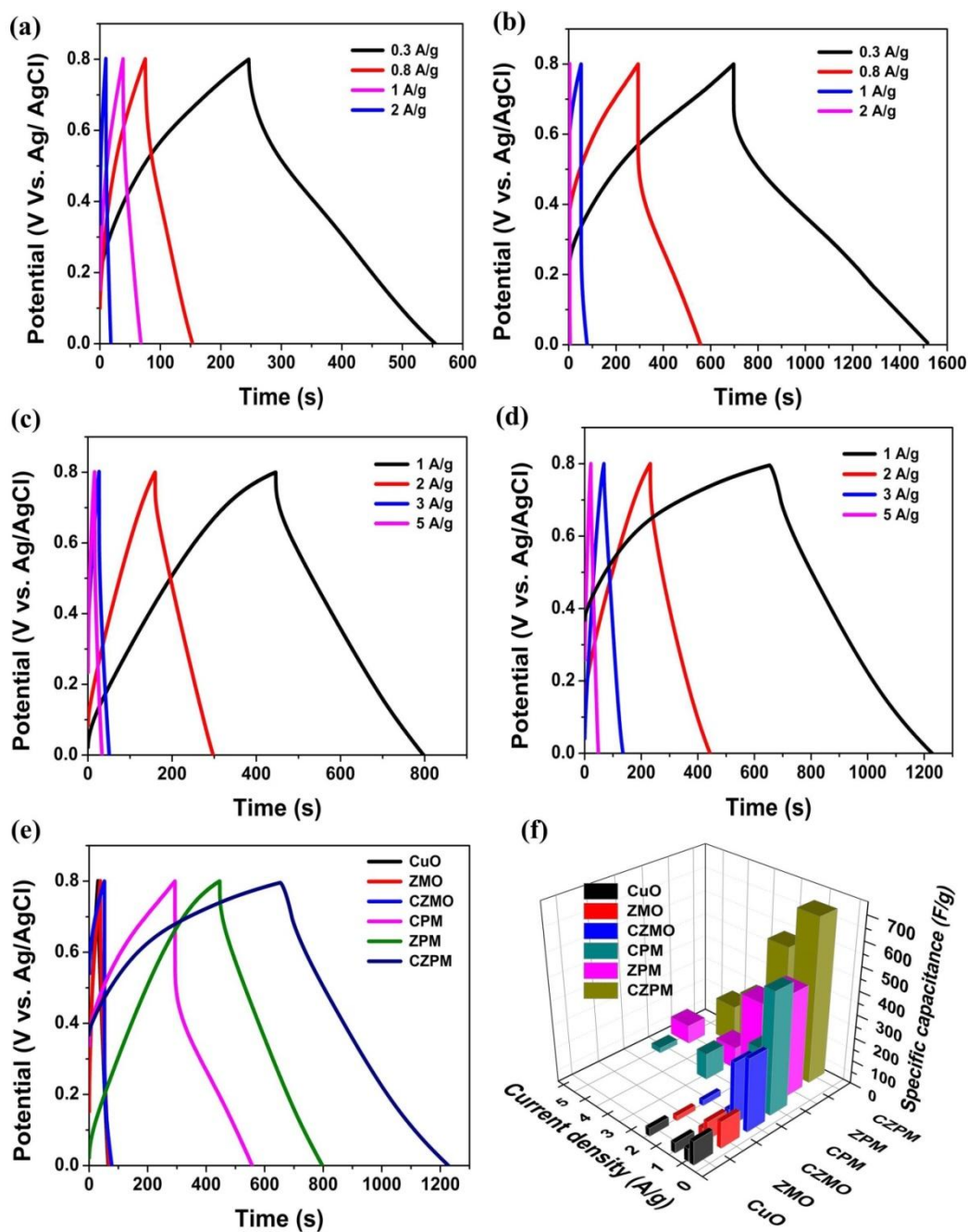


Fig. 5.16. GCD curves of (a) ZMO (b) CuO-ZMO (c) ZPM (d) CZPM (e) comparison of charge-discharge curves of CuO, ZMO, CuO-ZMO, CPM, ZPM, CZPM composites at current density of 1 A/g, (f) variation of specific capacitance with current density of CuO, ZMO, CuO-ZMO, CPM, ZPM, CZPM composites.

5.3.9.3. Electrochemical impedance spectroscopy (EIS)

The EIS studies of working electrodes were conducted with the intention to get deeper insight about the electrochemical features like ionic and electrical conductivity, internal and charge transport resistances, and interfacial process. Fig. 5.17 illustrates the Nyquist plots of ZMO, CuO-ZMO, ZPM and CZPM composite electrodes. The

ZMO and CuO-ZMO electrodes exhibit a well-defined distorted semi-circle arc in the high frequency region followed by a linear steep region in the lower frequency range (Fig. 5.17 (a-b)). The semi-circle portion in Nyquist plot is ascribed to the charge accumulation in the electrode-electrolyte interface, whereas the linear portion in the lower frequency range indicates the diffusion of electrolyte ions into the electrode material [42]. In the Nyquist plots of ZPM and CZPM electrodes there are no noticeable frequency dependent semi-circle portion, shown in Fig. 5.17 (c-d). The lower charge transfer resistance of composite electrodes is the combined effects of MWCNTs and metal oxides, where PANI usually suffered by high transfer resistance [47]. The comparison of Nyquist plots is shown in Fig. 5.17 (e), indicates the improved electrochemical features of the quaternary composite. The Nyquist plots of ZMO, CuO-ZMO, ZPM, and CZPM composite electrodes are best fitted using an equivalent circuit diagram combining R_s , R_{ct} , CPE and W components and the values of these parameters are presented in Table 5.4. The lower values of Warburg resistance are attributed to the shorter ionic diffusion path lengths exhibited by the composite electrode as a direct consequence of its advantageous porous morphology [46]. The lower values of charge transfer resistance offered by the quaternary composite electrode material are a clear indication of the potential application of this material in the field of energy storage devices.

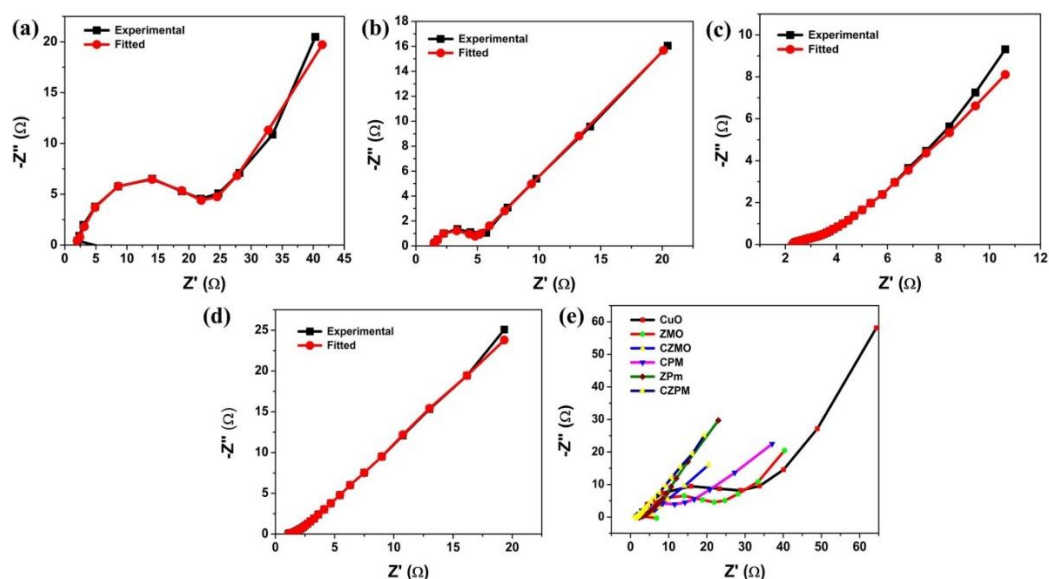


Fig. 5.17. (a) The best fitted Nyquist plot of as-prepared (a) ZMO, (b) CuO-ZMO, (c) ZPM (d) CZPM (e) comparison of Nyquists plots of all nanostructures.

Table 5.4. The R_s , R_{ct} , CPE, W and n values of as-synthesised CuO, ZMO, CuO-ZMO, CPM, ZPM, CZPM nanocomposites.

	Sample					
	CuO	ZnMn ₂ O ₄	CuO-ZnMn ₂ O ₄	CPM	ZPM	CZPM
R_s (Ω)	2	1.85	2.19	1.22	2.32	1.12
R_{ct} (Ω)	29.30	20.59	2.25	11.66	2.89	1.65
W	22.75	15.55	12.42	33.72	21.14	16.18
CPE	0.00057	0.00041	0.00006	0.0049	0.00067	0.00009
n	0.943	0.696	1.005	0.688	0.947	0.903

5.3.9.4. Cycle stability

The cyclic stability is a crucial factor in determining the efficiency of the power delivering capacity of supercapacitor. Generally, EDLCs like MWCNTs exhibit high cycle stability due to the absence of pseudocapacitive effects, while the pseudocapacitors like metal oxides and conducting polymers express low cyclic stability caused by their reversible redox reactions always results in increased series resistance and declined capacitive performances. Therefore a suitable combination of these two categories can overcome the issues related with the cyclic performances of the electrode material [46]. The long-term cycle stability of quaternary CZPM composite electrode was tested over 5000 charge-discharge cycles in a three-electrode system at a current density of 7 A/g and presented in Fig. 5.18 (a). From the figure, it is evident that the CZPM composite delivered an excellent capacitive retention of about 99.8% after 5000 cycles, due to the combined contributions of MWCNTs and metal oxides. This remarkable cyclic performance of composite electrode over 5000 repeated charge-discharge cycles is a clearly verified with the help of post-cycling SEM image, shown in Fig. 5.18 (b). The structural integrity of the electrode surface is evident from the SEM images, may attributed to the combined effect of inherently structural robustness of metal oxides and MWCNT, which doesn't allow any kind of structural or volume changes during continuous reversible redox reactions.

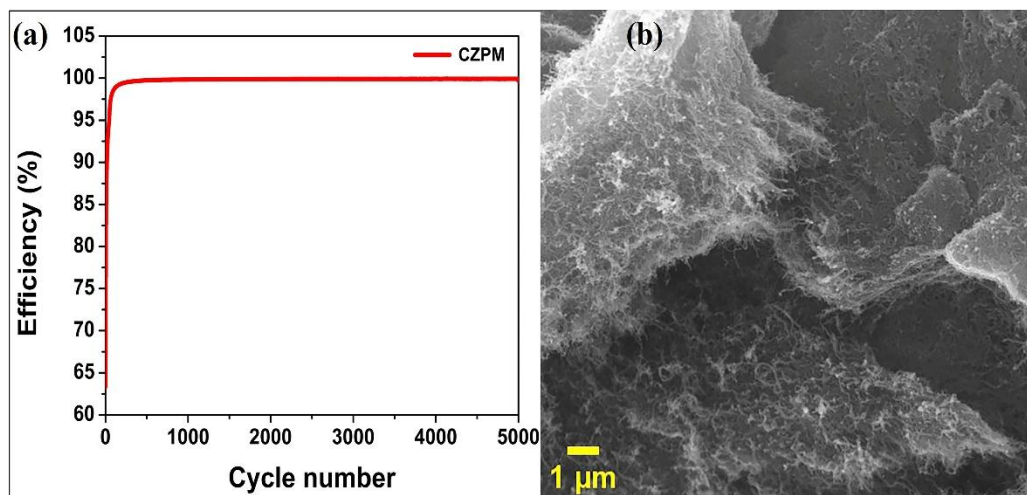


Fig. 5.18. (a) Cycle stability of CZPM working electrode over 5000 cycles (b) post-cycling SEM image of CZPM working electrode.

5.3.9.5. Electrochemical performance of CuO-ZnMn₂O₄/PANI/MWCNT ternary nanocomposite in symmetric two-electrode configuration

A symmetric supercapacitor device is fabricated with two-electrode cell assembly with 1 M Na₂SO₄ as electrolyte. The device performance of CZPM composite electrode is evaluated within the optimised potential window 0-0.8V. Fig. 5.19 (a) depicts the CV profiles of CZPM electrode at various scan rates ranges from 5 mV/s to 100 mV/s. The non-rectangular CV curve shape with noticeable redox peaks at potentials (0.17 V, 0.38 V), can be attributed to the redox transitions between emeraldine and lucoemeraldine forms of PANI [44]. The redox current response of the composite electrode increases as the sweep rate increases indicating the good rate capacity of the CZPM electrode material. The synergistic impacts of PANI and MWCNTs over the metal oxide combination results in improvement in the redox properties of the composite, leading to slighter shifts in redox peak positions in higher current densities. The GCD measurements of CZPM symmetric device at varying current densities are presented in Fig. 5.19 (b). The symmetrical charge and discharge response with small ohmic drop in the analysis data signify the high capacitive reversibility of the working electrode. The maximum capacitance delivered by the

composite electrode was 205 F/g at a current density of 1 A/g (Fig. 5.19 (c)), can be ascribed to the combined effect of double layer capacitance and pseudocapacitance. The pronounced reduction in the specific capacitance value of the electrode material in the symmetric two-electrode configuration, compared to three-electrode configuration, ascribed to the sluggish ionic transport inherent in the ZMO's because of their spinel structure along with other risk factors like internal resistance effects and restricted electrolyte accessibility in the full cell performance level. The coulombic efficiency of composite electrode was evaluated from the GCD results and portrayed in Fig. 5.19 (d). The CZPM composite electrode displayed fair columbic efficiency values for all the current densities points to the improved performance of composite material. The noticeable electrochemical performance of this composite electrode with satisfactory coulombic efficiency can be attributable to its advantageous structure as well as capacitive contributions from each one of its constituents. The specific power and specific energy are the crucial parameters in the electrochemical field, which delve deeper in to the practical applicability of composite electrode over other conventional capacitors. The Ragone plot expressing the variation of energy density with power density is presented in Fig. 5.19 (e), which shows a high energy density of CZPM electrode of about 18.22 Wh/Kg at a current density of 1 A/g. The maximum power density obtained by the CZPM symmetric device was 1111 W/Kg at 5 A/g. Fortunately, the prepared quaternary composite exhibited almost 100% of initial capacity over 50000 repeated charge-discharge cycles, as understood from Fig. 5.19 (f). The exceptional morphology of quaternary composite prevents the unwanted agglomeration or structural/voluminous deteriorations may happen during the long-term cycling process, resulted in the commendable structural stability of the electrode.

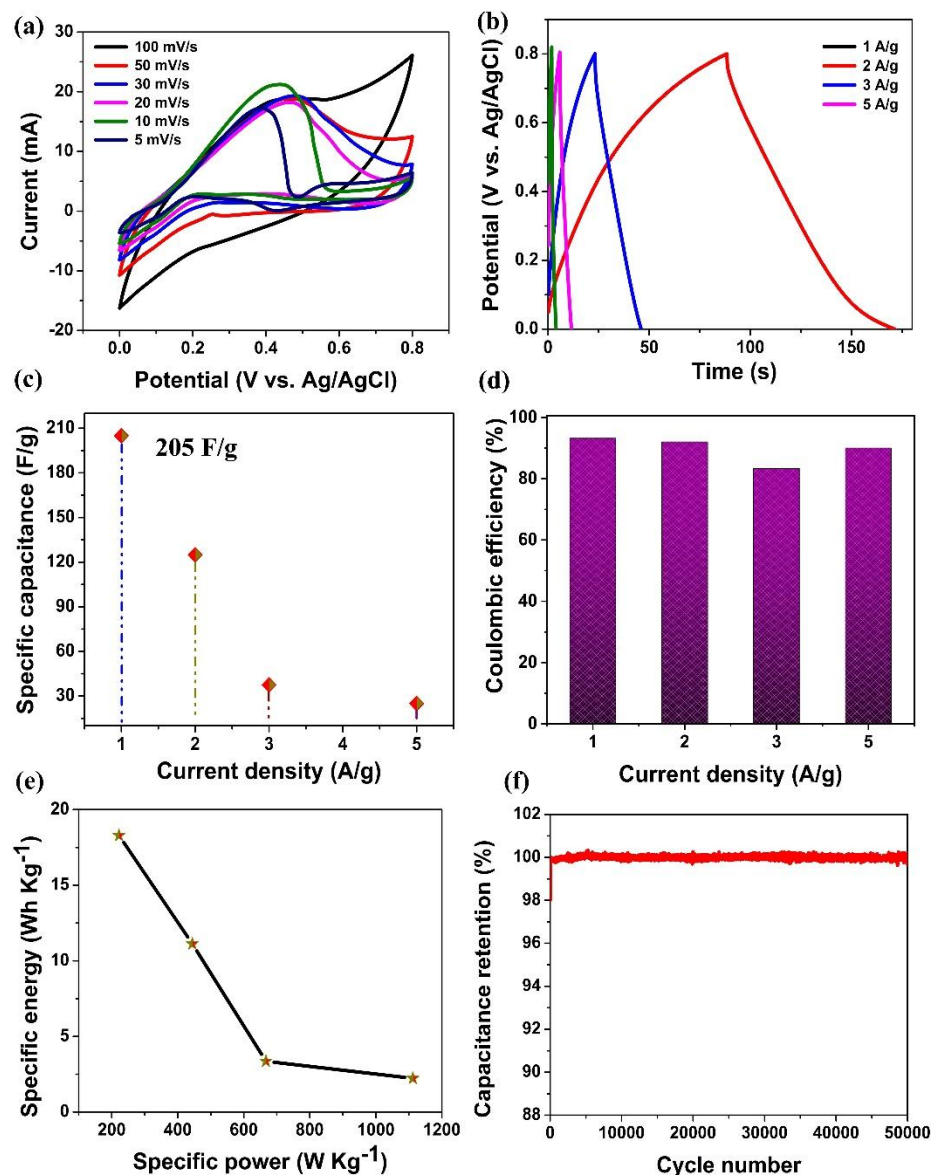


Fig. 5.19. (a) CV (b) GCD plots of CZPM composite in two electrode configuration (c) calculated specific capacitance from GCD (d) coulombic efficiency analysis (e) Ragone plot and (f) cycle stability of CZPM composite in 50000 cycles.

5.4. CONCLUSION

The ZMO, CuO-ZMO, ZPM and CZPM composite material were fabricated through hydrothermal and freeze drying assisted one pot chemical polymerisation method exhibited exceptional surface morphologies and electrochemical features. The quaternary composite electrode material achieved a maximum capacitance of 693 F/g at a current density of 1 A/g, attributed to the productive synergism between constituent elements such as CuO, ZMO, PANI and MWCNT resulted in the unique porous morphology with high specific surface area. In particular, the electrode material maintained a capacitive retention of 100% over 50000 cycles in the two-electrode cell assembly with satisfactory energy density of 18.22 Wh/Kg. Furthermore, the incorporation of metal oxides in to the PANI-MWCNT bounded framework prevents the volume expansions or structural deformations during long term cycling. The assured electrochemical performance with excellent specific capacitance and cyclic performances of CZPM composite electrode make them a potential choice as working electrode in the energy storage devices.

Table 5.5. Comparison of specific capacitance values estimated from CV and GCD measurements in both three- and two-electrode configurations.

Material	Three-electrode configuration				Two-electrode configuration			
	CV		GCD		CV		GCD	
	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)	Specific capacitance (F/g)	Scan rate (mV/s)	Specific capacitance (F/g)	Current density (A/g)
CZPM	514	10	693	1	197	10	205	1

5.5. REFERENCE

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Conclusion

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This chapter summarizes the thesis with some of the essential points and core insights derived from the research work. The essential and concise views associated with each chapter is discussed shortly. The importance of a ternary/quaternary CuO-based nanocomposite hybrid electrode material in the supercapacitor area is expressed in the chapter.

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Energy storage and management have become one of the major concerns in the present society since the relentless growth of world population and unending demand of energy is multiplying day by day. This led to dangerous effects on world economy and made the research community to discover a highly efficient and reliable energy storage devices. Supercapacitors have become a prominent area of research based on the current scenario and specifically scientists concentrated more on to hybrid electrode materials that can cover all aspects of ESDs like high specific capacitance, energy density, power density, cyclic stability and rate capacity. The search for an alternative approach to overcome the inherent insufficiency of ionic conductivity in CuO electrodes is become a hot research area. The thesis work had made an effort to synthesis an efficient, reliable and high performing hybrid supercapacitor electrode material for energy storage applications.

Chapter 1 deals with the concise introduction about importance of ESDs, supercapacitors and its classifications, different kinds of electrode materials and electrochemical analysis. A comprehensive analysis about the properties of CuO and a brief introduction on carbon-based electrode materials and conducting polymers specifically polyaniline is also given.

Chapter 2 presents the synthesis of CuO nanostructures via simple hydrothermal method and a detailed evaluation of its structural, morphological, elemental and thermal properties is also presented. The ternary CuO/PANI/MWCNT nanocomposite was synthesised through one pot chemical oxidative polymerisation method followed by lyophilization process. The influence of PANI and MWCNT incorporation into CuO is studied in detail through structural and spectroscopic analyses. The enhancement in the electrochemical performance of ternary nanocomposite electrode was observed when compared with that of pure CuO electrode indicating the synergistic effects between CuO, PANI and MWCNTs. The conductive pathway provided by PANI and the improved surface area and mechanical strength provided by MWCNTs made the composite to become a potential electrode material.

The synthesis and characterizations of quaternary CuO-NiO/PANI/MWCNT nanocomposite is discussed in **chapter 3**. The preparation of this quaternary nanocomposite was done using one pot chemical oxidation polymerisation followed by lyophilization and influence of NiO in to the CuO/PANI/MWCNT hybrid system

was evaluated using structural, morphological, elemental and thermal characterization techniques. The improvement in surface area and porosity of the composite material was observed. The enhancement in the electrochemical performance of quaternary CuO-NiO/PANI/MWCNT nanocomposite hybrid electrode was recorded in comparison with CuO, NiO, CuO-NiO, CuO/PANI/MWCNT and NiO/PANI/MWCNT electrodes. The synergistic interactions between the individual constituents and their individual contributions made the composite electrode more efficient and reliable. The composite electrode delivered highest specific capacitance with high percentage of capacitive retention efficiency.

Chapter 4 discusses synthesis, characterizations and electrochemical performance evaluation of quaternary composite CuO-Co₃O₄/PANI/MWCNT hybrid electrode material. The introduction of cobalt oxide into the composite has resulted in improved surface and morphological features and thereby the electrochemical performance of quaternary composite electrode has improved compared to CuO, Co₃O₄, CuO-Co₃O₄, CuO/PANI/MWCNT and Co₃O₄/PANI/MWCNT electrodes. The high pseudocapacitive capacity of cobalt oxide along with the individual contributions of PANI and MWCNTs has made the quaternary composite as a viable electrode material in supercapacitor applications.

The synthesis and structural, morphological, elemental and thermal characterizations of CuO-ZnMn₂O₄/PANI/MWCNT quaternary composite was presented in **chapter 5**. The synthesis of CuO-ZnMn₂O₄/PANI/MWCNT quaternary composite via chemical oxidative polymerization method and its electrochemical performance evaluation with both three-electrode and two-electrode configurations were discussed in detail. The improvement of electrochemical capacities of composite electrode through the incorporation of zinc manganese oxide and individual as well as synergistic contributions of CuO, PANI and MWCNTs has made the quaternary composite as an efficient electrode material with high capacitive retention efficiency.

To conclude, the thesis emphasis on the synthesis and electrochemical performance evaluation of CuO and PANI/MWCNT incorporated CuO-based nanocomposite hybrid electrode materials. The influence of PANI and MWCNTs in the electrode fabrication was discussed in detail. The improvement in the electrochemical performance of electrode prepared through the introduction of metal oxides like NiO,

Co_3O_4 and ZnMn_2O_4 is accessed and found a marginal enhancement in the specific capacitance, energy density, power density and cyclic stability of the electrode materials.

Recommendations

Some future aspects of the current research are presented. We foresee the vast areas to explore in this area of metal oxide-based nanocomposite materials in the optoelectronic applications particularly in energy storage devices.

Transitional metal oxides are always a promising electrode material in the field of supercapacitors. Among which CuO gained much more attraction in recent years as a viable electrode candidate for pseudocapacitors. This is predominantly due to its advantageous like low cost, environmental benignity, elemental abundance, high theoretical specific capacitance and availability of oxidation states for fast redox activities. However, the inherent conductivity issues faced by the CuO-based electrodes can be minimised by combining it with other carbonaceous compounds and conducting polymers. The current research focused on to the synthesis of CuO electrode via simple hydrothermal route and extensively studied its structural, microstructural, morphological, elemental and thermal properties using various characterisation techniques. Electrochemical properties of the CuO electrode revealed the insufficiency of specific capacitance, energy density, power density and cyclic stability features of pure CuO. Thus, the study paved way to synthesis and analysis the electrochemical potentialities of PANI/MWCNT incorporated CuO-based nanocomposite hybrid electrode materials via one pot chemical oxidative polymerisation method followed by freeze drying condition. Further improvement in the electrochemical properties like specific capacitance, energy density, power density, cycle stability and rate capacity of the nanocomposite electrodes was done by the introduction of other transitional metal oxides like NiO, Co₃O₄, and ZnMn₂O₄.

In addition to the different aspects of CuO-based nanocomposites discussed in the current work, attempts can be put forward to study the optical, dielectric and magnetic properties of these composites, which are still remain underexplored. The molar proportions between CuO and other metal oxides, metal oxide composites and MWCNT or PANI and MWCNT can be altered and studied. Moreover, the synthesis method of these composite electrodes can be refined using other sophisticated bottom-up synthesis approaches for exploring the possibility of increasing active surface area and porosity of electrode surface with an aim to improve the ionic diffusions through the electrode-electrolyte interface.

In addition to NiO, Co₃O₄, and ZnMn₂O₄, other transitional metal oxides like MnO₂, V₂O₅, TiO₂, ZnO etc. can be tried with CuO for making potential nanocomposite electrodes. Furthermore, there is another possibility to use

heteroatom-functionalised carbon which has the capacity to undergo redox activities and produce pseudocapacitance replacing MWCNTs.

In the sense to reduce the cost of production, the expensive carbon-based compound like MWCNT can be replaced by biomass derived carbon precursors. The electrochemical performance of synthesised CuO-based nanocomposite electrode material can be improved by examine more about the features like interfacial properties, charge collection and transport capacities, defect states etc.

The achieved potential (0.8 V) in the aqueous electrolyte is comparatively low, which demands a lot of series connections in practical scenarios. Thus, there is an open chance to make attempts to increase the potential window by using different non-aqueous or polymer electrolytes with different mole percent. Based on few studies, there is a possibility to increase the device performance by matching pore size of electrode surface and ionic size of electrolytes.

Like metal oxide-based electrode material, same synthesis and electrochemical analyses can be extended to metal sulphides also since they also have ability to attain high specific capacitance and cycle stability. Furthermore, there is also a possibility to attempt theoretical simulations and interpretations about the charge storage mechanisms involved in the electrode working to improve and optimise the device performance.

Fabrication of flexible supercapacitor devices that can withstand all external mechanical deformations is one of the important innovations of present research society in the area of smart energy storage devices. Also, the production of microsupercapacitors based on this CuO-based composite electrodes can be attempted. Therefore, more sophisticated production techniques like ink jet printing or roll-roll printing can be implemented for the fabrication of flexible and wearable devices based on this PANI/MWCNT incorporated CuO-based composite electrodes.