

STUDIES ON NOVEL ELECTRODE MATERIALS FOR ENERGY APPLICATIONS

*Thesis Submitted to the University of Calicut for the
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By

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Dedicated to my family...

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Preface

Conducting polymers have emerged as an important class of functional materials due to their unique combination of electrical conductivity, redox activity, and structural versatility. Their tuneable physicochemical properties make them promising candidates for applications in energy storage, sensing, optoelectronics, and electromagnetic interference shielding. However, achieving high electrochemical stability, wide operating potential windows, and scalable synthesis remains a significant challenge. My research focuses on addressing these limitations through rational molecular design and controlled structural engineering, aiming to develop robust, multifunctional conducting polymer systems suitable for advanced aqueous energy and electronic applications.

The thesis is divided into a total of 5 chapters.

Chapter 1 provides a detailed introduction to conducting polymers with special emphasis on polyaniline, including a brief literature review. This section covers various aspects related to polyaniline and polyaniline/hydrogel systems, including synthesis methods and their applications. Additionally, a brief description of the electrochemistry of conducting polymers, highlighting their reaction-driven biomimetic properties are also presented.

Chapter 2 provides a concise overview of materials employed, characterization techniques applied, and methodologies adopted for the current research. This section also offers a detailed explanation of the various electrochemical techniques, such as cyclic voltammetry,

chronopotentiometry, GCD, and EIS studies employed in the presented work.

Chapter 3 reports the development of a covalently integrated polyaniline (PANI) and nitrogen-doped reduced graphene oxide (N-rGO) macromolecular system for supercapacitor applications. PANI was chemically anchored onto N-rGO through amide linkages to overcome chain degradation, entanglement, and poor cyclic stability. N-rGO acts as a conductive template that promotes ordered polymer growth, reduces aggregation, buffers volume changes, and enhances charge transport. Nitrogen doping further improves conductivity and wettability, and introduces additional redox-active sites. The optimized composite exhibits enhanced specific capacitance, rate capability, and cycling stability, demonstrating the effectiveness of covalent hybridization for robust and high-performance aqueous supercapacitor electrodes.

Chapter 4 builds upon the N-mrGO-PANI system by introducing sulfur as an additional co-dopant to further enhance electrochemical performance and structural stability. While nitrogen doping improved conductivity and interfacial interactions with PANI, sulfur incorporation was proposed to generate additional redox-active centres within the rGO lattice and increase the Faradaic contribution. Sulfur doping also creates distinct chemical environments capable of reversible redox activity, facilitating improved charge transfer and ion diffusion. A covalently functionalized PANI system integrated with sulfur and nitrogen co-doped rGO was designed, synthesized, and systematically characterized to evaluate the effect of dual heteroatom incorporation. The results demonstrate that targeted atomic-level modification through S and N co-doping synergistically enhances structural integrity, interfacial

interactions, and overall electrochemical performance of the hybrid electrode.

Chapter 5 addresses the persistent limitation of narrow operating potential windows in conducting polymers within aqueous electrolytes, where oxygen and hydrogen evolution reactions lead to irreversible degradation and restrict device voltage. It also tackles the challenges of complex, costly functionalization routes that often disrupt π -conjugation and reduce electrical performance. To overcome these constraints, a new conducting polymer family based on P4PDA was developed. The incorporation of an azo linkage into the backbone functions as a proton sink and electron-withdrawing unit, lowering local HOMO energy and shifting charge storage toward intrinsic backbone redox processes rather than water-driven interfacial reactions. The polymers were synthesized via a simple, scalable one-pot process in aqueous medium using readily available monomers, enabling direct incorporation of functional groups such as -OH, -OMe, -COOH, and -SH without multistep reactions. This backbone engineering strategy resulted in stable and unusually wide electrochemical windows up to 2.5 V in acidic electrolytes and 2.7 V in LiClO₄, establishing a versatile and scalable platform for electrochemically stable conducting polymers in aqueous systems.

Chapter 6 provides a comprehensive summary of the major findings and highlights of the present work. This chapter also outlines the future outlook of the present investigation, particularly focusing on the development of various biomimetic devices.

LIST OF ABBREVIATIONS

APS	<i>Ammonium Persulphate</i>
AR	<i>Analytical Reagent</i>
B	<i>Boron</i>
CE	<i>Coulombic Efficiency</i>
CNT	<i>Carbon Nanotube</i>
CPs	<i>Conducting Polymers</i>
C_{SP}	<i>Specific Capacitance</i>
$CuCl_2$	<i>Copper (II) Chloride</i>
CV	<i>Cyclic Voltammetry</i>
DCC	<i>N, N'-Dicyclohexylcarbodiimide</i>
DMAP	<i>4-(Dimethylamino)pyridine</i>
DMF	<i>N, N-Dimethyl Formamide</i>
DMSO	<i>Dimethyl Sulfoxide</i>
EAP	<i>Electrochemically Active Polymers</i>
EDAX	<i>Energy Dispersive X-ray Analysis</i>
EDLC	<i>Electrochemical Double Layer Capacitor</i>
EDX / EDS	<i>Energy-dispersive X-ray Spectroscopy</i>
EIS	<i>Electrochemical Impedance Spectroscopy</i>
EMI	<i>Electromagnetic interference</i>
ESR	<i>Electron Spin Resonance Spectroscopy</i>
FESEM	<i>Field Emission Scanning Electron Microscopy</i>
FT-Raman	<i>Fourier Transform-Raman Spectroscopy</i>
FTIR	<i>Fourier Transform Infra-Red Spectroscopy</i>
GCD	<i>Galvanostatic Charge-Discharge</i>
GCE	<i>Glassy Carbon Electrode</i>
GO	<i>Graphene Oxide</i>
H_2O_2	<i>Hydrogen Peroxide</i>
H_2CrO_4	<i>Chromic Acid</i>
H_2SO_4	<i>Sulfuric Acid</i>
HCl	<i>Hydrochloric Acid</i>
HOMO	<i>Highest Occupied Molecular Orbital</i>
HR-TEM	<i>High-Resolution Transmission Electron Microscopy</i>

<i>ID/IG</i>	<i>Intensity ratio of D-band to G-band</i>
<i>IR drop</i>	<i>Internal Resistance (Ohmic) drop</i>
<i>KMnO₄</i>	<i>Potassium Permanganate</i>
<i>LEDs</i>	<i>Light-Emitting Devices / Diodes</i>
<i>Li-ion</i>	<i>Lithium-ion</i>
<i>LUMO</i>	<i>Lowest Unoccupied Molecular Orbital</i>
<i>mGO</i>	<i>Modified Graphene Oxide</i>
<i>MLG</i>	<i>Multilayer Graphene</i>
<i>N</i>	<i>Nitrogen</i>
<i>NaNO₂</i>	<i>Sodium Nitrite</i>
<i>N-mrGO</i>	<i>Nitrogen-doped Modified Reduced Graphene Oxide</i>
<i>NMP</i>	<i>N-Methyl-2-pyrrolidone</i>
<i>N-rGO</i>	<i>Nitrogen-doped Reduced Graphene Oxide</i>
<i>P</i>	<i>Phosphorus</i>
<i>P4PDP</i>	<i>Poly(4-(phenyldiazenyl)aniline)</i>
<i>PANI</i>	<i>Polyaniline</i>
<i>PPy</i>	<i>Polypyrrole</i>
<i>PTh</i>	<i>Polythiophene</i>
<i>Q</i>	<i>Quinonoid ring</i>
<i>rGO</i>	<i>Reduced Graphene Oxide</i>
<i>Rs</i>	<i>Solution Resistance</i>
<i>S</i>	<i>Sulfur</i>
<i>SEM</i>	<i>Scanning Electron Microscopy</i>
<i>SN-mrGO</i>	<i>Sulfur and Nitrogen co-doped Modified Reduced Graphene Oxide</i>
<i>SN-mrGO-PANI</i>	<i>S and N co-doped mGO-Polyaniline Composite</i>

Chapter 1

Introduction

Conducting polymers enable tunable electrical transport through π -conjugated backbones and reversible doping. This work addresses intrinsic instability and limited processability in polyaniline by integrating heteroatom-engineered graphene derivatives and designing structurally versatile azo-linked polymers, establishing stable, multifunctional platforms for high-performance electrochemical energy storage and advanced electronic applications.

1.1 Conducting Polymers

Conducting polymers (CPs) are a class of organic polymers that exhibit the property of electrical conductivity^[1]. They have the potential to be used in many technologies, including energy storage devices^[2], optoelectronics^[3], actuators^[4], sensors^[5], radiation detectors^[6], Schottky diodes^[7], anti-electrostatic materials^[8], electromagnetic interference (EMI) shielding^[9], smart textiles^[10], field-effect transistors^[11], photocatalysts^[12], solar cells^[13], electrochromic devices^[14] etc. Further, CPs play a key role in the slow transition from a fossil fuel-driven society to a sustainable society since they show promising potential in the field of energy storage as well as renewable energy production. The ease of synthesis, environmental stability, flexibility, lightweight, versatility, etc, led to an exponential growth of CP research.



Figure 1.1: *The winners of the Nobel Prize in Chemistry 2000.*

Polymers were long believed to be electrical insulators until a paradigm shift occurred after the serendipitous synthesis of a silvery polyacetylene film by Hideki Shirakawa using an excess of Ziegler-Natta catalyst. Although the pristine polyacetylene film only had limited conductivity,

the breakthrough came in 1977 when Alan G. MacDiarmid and Alan J. Heeger demonstrated that chemical doping of polyacetylene with electron acceptors such as iodine, bromine, or chlorine resulted in an increase in electrical conductivity by several orders of magnitude^[15]. This discovery established that the electrical properties of conjugated polymers can be dramatically tuned through doping, laying the foundation for the field of conducting polymers. In recognition of this, Shirakawa, MacDiarmid, and Heeger were jointly awarded the Nobel Prize in Chemistry in 2000.

Before the discovery of polyacetylene, there were also some early reports regarding organic conducting materials. In 1862, H. Letheby electrically oxidized aniline in H_2SO_4 and obtained a partially conducting material, which is most probably polyaniline (PANI)^[16]. K. Bechgaard and D. Jerome discovered another conductive material that consists of large cyclic conjugated systems arranged as stacks of coins that act as donors and inorganic acceptors. Even though polyacetylene is not the first conducting organic material, it opened up a new field of CPs for research^[17].

Following the discovery of conducting polyacetylene, a series of CPs were discovered in the next decade, including polypyrrole (PPy)^[18], polythiophene (PTh)^[19], poly(p-phenylene)^[20], polyaniline (PANI)^[21], poly(p-phenylene vinylene)^[22], poly(benzodifurandione)^[23], etc., and the structures of these polymers are given in Figure 1.2. The most important feature of all these polymers is the presence of alternating single and double (or triple) bonds along the polymer chain backbone; hence, they are also known as π -conjugated polymers.

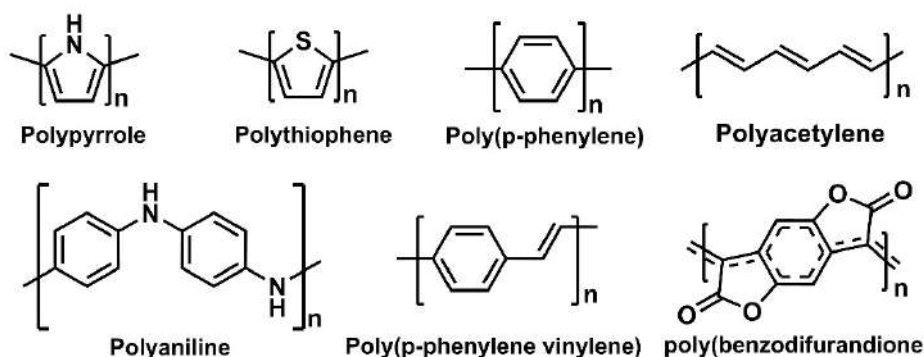


Figure 1.2: Structure of polypyrrole (PPy), polythiophene (PTh), poly(*p*-phenylene), polyacetylene, polyaniline (PANI), poly (*p*-phenylene vinylene), and poly(benzodifurandione)

The attention on synthetic metals or CPs increased further with the discovery of new properties and applications. The electroluminescent property of poly(*p*-phenylene vinylene) was discovered by Friend et al. and is used as an active light-emitting layer in polymer light-emitting diodes.^[24] The field of organic photovoltaics was opened up by Heeger et al. in 1995 with bulk-heterojunction polymer solar cells based on poly(*p*-phenylene vinylene) and fullerene derivatives.^[25] These discoveries further strengthened the research on CPs.

Even though CPs are extensively used for many applications, they have some limitations too. Poor electrochemical stability, low processability, low conductivity compared to metallic conductors, and tedious and costly steps involved in functionalization are some of the major limitations of CPs. The recent discovery of a new *n*-type solution-processable conducting polymer, poly(benzodifurandione), signifies the need to develop new CPs to meet the demands of the research community^[26]. In this thesis, we mainly focus on improving the electrochemical stability of PANI so that it can be used as an electrode

material for supercapacitor applications and also addressing the difficulties in functionalizing CPs by introducing a new set of polymers to the class of conducting polymers, which are easy to functionalize.

1.1.1 Conductivity of Conducting Polymers

In CPs, all the atoms along the backbone of the polymer chain are sp^2 hybridized. The unhybridized p-orbital in each of the atoms will be perpendicular to the polymer chain and parallel to each other. These p-orbitals can laterally overlap with any of the adjacent atom's p-orbital to form a π -bond. Ultimately, every p-orbital in the polymer backbone will be delocalized due to the lateral overlapping to both sides. The overlapping produces band-like structures similar to metals and semiconductors. The conductivity range of CPs, along with other conductive materials, is given in Figure 1.3, and the band structure of CPs, along with insulators and conductors, is given in Figure 1.4.

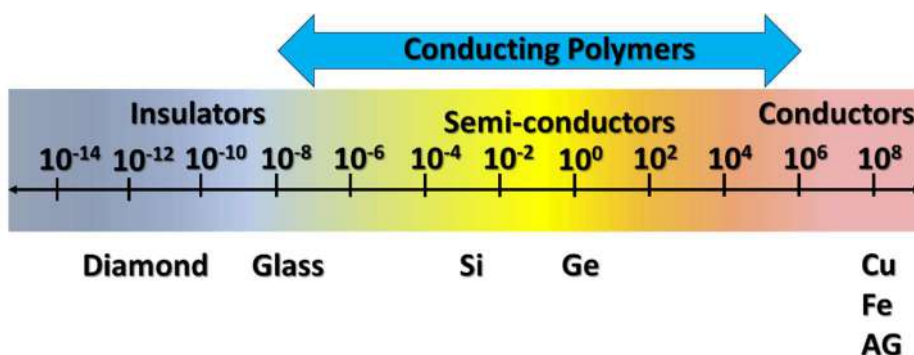


Figure 1.3: *Conductivity range of CPs along with some common materials*

The conduction of electricity in materials is primarily due to the presence of freely moving electrons in them. The electron present in the outermost shell of a material is considered as the electron in the valence band. The

electron in the conduction band has higher energy than that of an electron in the valence band, and these electrons are also responsible for the conduction of electricity. The energy difference between these two bands is known as the band gap energy, and materials are classified into insulator, semiconductor, and conductor according to the structure of the band gap. For conjugated polymers, the Highest Occupied Molecular Orbital (HOMO) is considered as the valence band, and the Lowest Unoccupied Molecular Orbital (LUMO) is considered as the conduction band. The energy difference between the HOMO and LUMO is the band gap energy. In the case of conducting polymers, the delocalization increases the energy of HOMO and decreases the energy of LUMO.

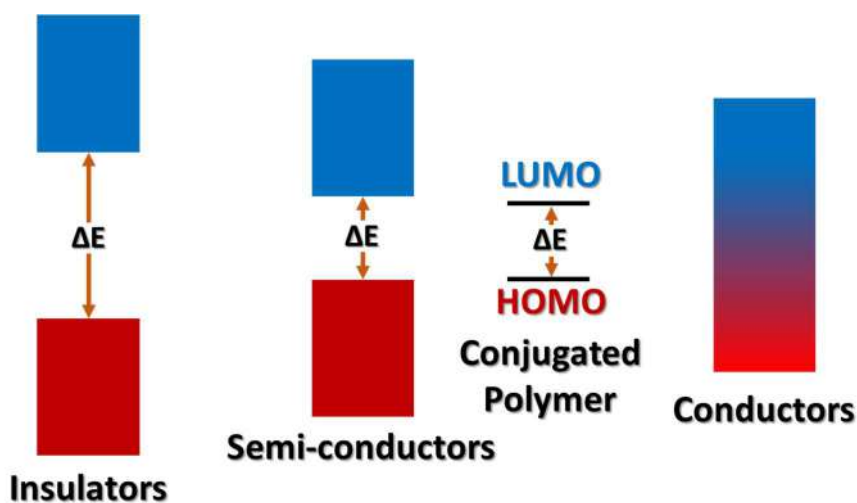


Figure 1.4: Band gap energy diagram of insulators, semiconductors, conjugated polymers, and conductors.

1.1.2 Types of Conducting Polymers

Electrochemically active polymers (EAP) can be classified into two types based on the mode of charge propagation, and they are ion-conducting polymers^[27] and electron-conducting polymers^[1]. The type

of charge propagation in the polymer merely depends on its chemical structure. In an ion-conducting polymer, the charge conduction is due to the movement of ions present in the structure. Polyaryl sulfone, polystyrene, and polyaryl ketone are some well-known examples of these ion-conducting polymers. The electron-conducting polymers conduct charge due to the movement of electrons through the polymer chain. The electron-conducting polymers can be further divided based on the mode of electron transport. (i) The electrons are transported as a result of electron transfer reactions between neighboring localized redox sites. Poly(tetracyanoquinodimethane), poly(viologens), etc., are some examples belonging to this group. (ii) The electron transfer occurs through the conjugated double bonds present in the polymer backbone.

1.1.3 Doping and Dedoping in Conducting Polymers

The CPs in their undoped state exhibit very low conductivity, and their electrochemical activities are also very poor. To be used as a substitute for semiconductor material, the conjugated polymer should be made conductive by introducing charge carriers into the polymer chain. The charge carriers are introduced by oxidizing or reducing the CPs with charge transfer reagents, and this process is known as doping, which significantly alters the electrochemical properties of the CPs. In CPs, doping is the process of increasing the conductivity, and a dopant is the chemical agent responsible for doping.

The doping of CPs with a charge transfer reagent has a significant effect on their electrical properties. With the increased number of charge carriers, there will be a change in the Fermi level of the CPs^[28]. This alteration in the Fermi level can lead to increased conductivity as a

greater number of charge carriers are available to facilitate the movement of charge through the polymer chain.

The doping in inorganic materials is normally referred to as the addition or removal of electrons from the conduction band. The incorporation of a negative charge in the valence band is called n-doping, and the incorporation of holes in the valence band is known as p-doping. In the case of CPs, the dopant's role can be either releasing the electrons to the CP backbone or withdrawing electrons from the CP backbone. As the term doping is borrowed from inorganic materials, the classification of doping in inorganic materials can also be applied to doping in CPs. The addition of electrons to the LUMO of CPs is called n-doping, and the removal of electrons from the HOMO is called p-doping. The properties of CPs are greatly affected by the type of dopants used because the size and mobility of the dopants have a direct effect on their conductivity.

1.1.4 Charge Carriers in Conducting Polymers

For a rigid semiconductor system, the addition of electrons to the conduction band and the removal of an electron from the valence band occur without any deformation in the crystalline structure. On the other hand, for CPs, the removal or addition of electrons causes a chain deformation around the charge with the cost of energy, thereby putting the charge in a lower energy state^[29]. The size of the lattice deformation is usually determined by elastic deformation energy, and the lattice deformation can extend up to approximately 20 monomer units. This localized charged particle, along with the deformed chain together, is known as a polaron and is also defined as an electron dressed by a phonon cloud. If two charges are bound together in a common distorted chain, then it is known as a bipolaron. Even though the coulombic

interactions tend to repel the charges, they are bound together by chain deformation. The energy required to form two distinct chain deformations rather than a single one is greater than the Coulomb energy gained by their separation. Polarons are similar to electrons since they have a charge of 1 and a spin of $\frac{1}{2}$. Bipolarons have a zero spin and are doubly charged, mainly due to the pairing of the electrons. For all conjugated conducting polymers, except for polyacetylene, polarons and bipolarons are the entities through which the charge transport is accomplished. They can travel along the chain as an entity, with the atoms in the path changing their positions so that the deformation travels with the electron or hole^[30]. It should also be noted that p-type doping produces positive polarons and bipolarons (Figure 1.5) and n-type doping produces negative polarons and bipolarons (Figure 1.6).

In polyacetylene, a distinctive class of charge carriers emerges as a result of doping, known as solitons.^[31] Solitons are localized distortions in the polymer chain, arising due to the presence of an additional electron or hole. These solitons can move through the polymer chain more easily compared to polarons and bipolarons since they do not require the movement of any atoms, but only need the rearrangement of bonds. The structure of different solitons formed is given in Figure 1.7.

Doping in polymers can be accomplished chemically, electrochemically, and photochemically, as well as by charge injection at the interface^[32]. In the case of electrochemical or chemical doping, the induced electrical conductivity is permanent until the charge carriers are purposely removed by dedoping, i.e., by reversing the electrochemical reactions, or until the charge carriers are chemically compensated.

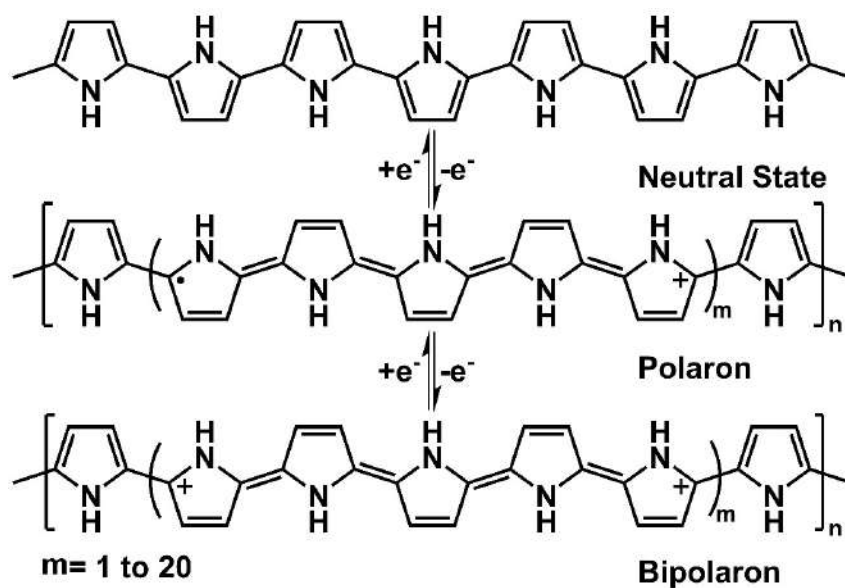


Figure 1.5: Structure of polaron and bipolaron formed in a polythiophene chain during p-type doping

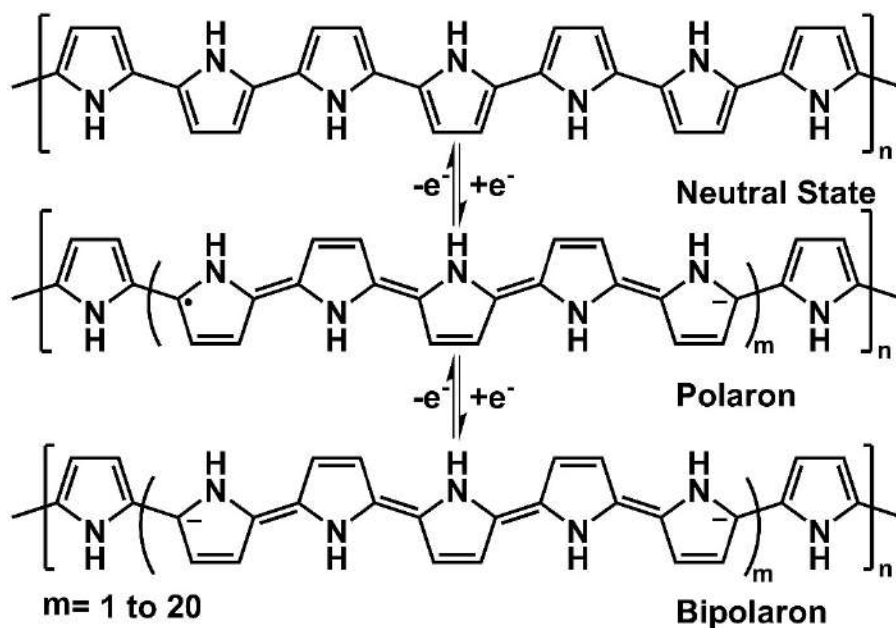


Figure 1.6: Structure of polaron and bipolaron formed in a polythiophene chain during n-type doping.

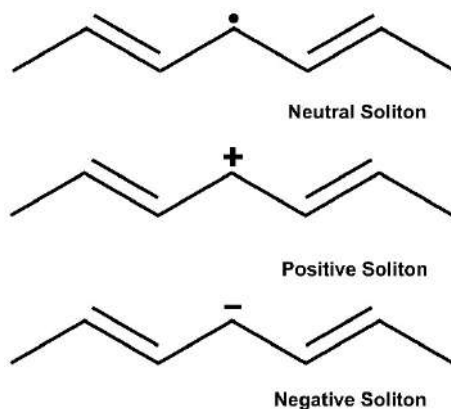


Figure 1.7: *Structure of different solitons formed in polyacetylene.*

The doping process is completely reversible, i.e. CPs can be converted into a completely insulating state, and this process is termed dedoping. Dedoping can be achieved by exposing the oxidatively doped polymer to electron donors or by exposing the reductively doped polymer to an electron acceptor. This forms the basics of the application of CPs as electrodes for energy storage devices.

1.1.5 Charge-Transport in Conducting Polymers

The understanding of the fundamental processes taking place at atomic scales to mesoscopic scales is an important aspect of material development. The charge-transport properties of CPs are explained by adapting different models, often developed for semiconducting materials. The structure of CPs is very complex compared to that of inorganic semiconductors, which contain strongly localized atoms. In contrast, CPs consist of polymer chains with a high degree of conformational freedom, and the individual chains only exhibit weak interactions between them, making the structure very complex. In CPs, the charge carriers not only hop between defects but also between

different chains. The conductivity of CPs is commonly explained by the following theories.

Band Theory

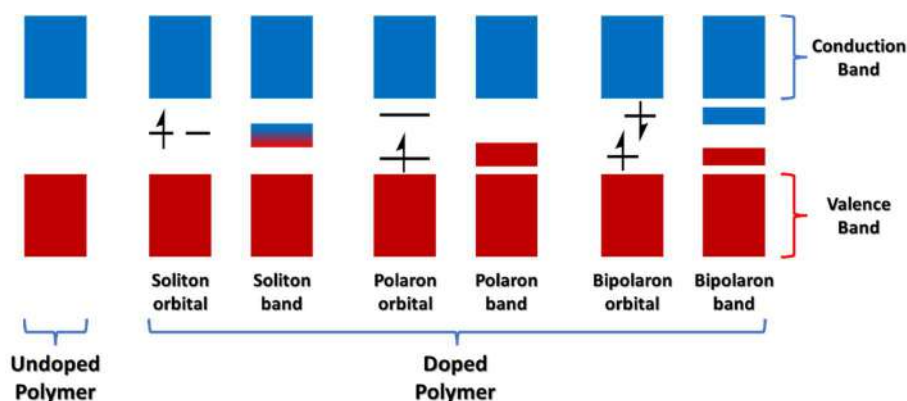


Figure 1.8: *Orbital and band structure of soliton, polaron, and bipolaron*

The electrical conductivity of CPs can be explained by applying band theory to solitons, polarons, and bipolarons. The band gap energy of the undoped state of CP is the same as that of a semiconductor; hence, an electron can jump from HOMO to LUMO if sufficient energy is given. In the case of polaron, the energy of HOMO is increased, making the band gap energy less than that of the undoped state. The bipolaron, on the other hand, has an even smaller band gap energy compared to that of a polaron since the coupling of two polarons further decreases band gap energy due to the increase in the energy of HOMO and a decrease in the energy of LUMO. In the case of a soliton, a degenerate state exists due to the isolation of two-phased bonding electrons having indistinguishable energy states, resulting in the formation of a soliton band^[33]. The band structure of different types of charge carriers is given in Figure 1.8.

Variable Range Hopping Model (Mott's model)

Variable Range Hopping Model^[34] is used to explain the conductivity dependence of amorphous materials and organic conjugated polymers on temperature. According to Mott's model, the charge carriers can hop between distortions having different energies by the absorption of phonons. The decrease in temperature causes a decrease in thermal energy (k_B), resulting in a decrease in the number of available energy states nearby, and this increases the mean range of hopping. The expression for conductivity is as follows:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T}{T_0} \right)^\gamma \right] \quad (\text{eq. 1.1})$$

The exponent $\gamma = \frac{1}{4}$ for hopping in three dimensions, $\gamma = \frac{1}{3}$ for hopping in two dimensions and $\gamma = \frac{1}{2}$ for hopping in one dimension. If the decay of the electronic wavefunction with distance r is given by $e^{(-r/L_{loc})}$, where the L_{loc} is the localisation length, then T_0 is given by

$$k_B T_0 \sim 16 / (N(E_F) L_{loc}^3) \quad (\text{eq. 1.2})$$

where $N(E_F)$ is the density of localised states at the Fermi level. The σ_0 is the prefactor.

At sufficiently elevated temperatures, the value of $\gamma = 1$ and the conductivity would exhibit a straightforward activated pattern as described in Equation (1.1), because the hopping occurs predominantly to the nearest neighbors. This pattern is also applicable for electron

movement through thermal excitation into a conduction band, characterized by extended states in a crystalline semiconductor. In such instances, the conductivity would roughly correspond to the quantity of electrons excited across the semiconductor's energy gap^[35].

Schaefer-Siebert-Roth Model

The electrical conductivity of CPs is explained by Mott in terms of average hopping distance and localization length. In contrast to Mott's model, Schaefer-Siebert-Roth model explains the conductivity in terms of conjugation length and localization length^[36]. Upon doping a CP, breakage of the π -bond and formation of charge carriers occur, and this, in turn, creates different conjugation lengths along the polymer backbone^[37].

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T}{T_0} \right)^{-\gamma} \right] \quad (\text{eq. 1.3})$$

Where the exponent γ depends on the density of the Fermi level and has with value $\frac{1}{4} \leq \gamma \leq \frac{1}{2}$, σ_0 and T_0 depends on the localization length.

1.2 Polyaniline

Polyaniline (PANI) is one of the most studied CPs owing to its ease of synthesis, low cost, high electrical conductivity, environmental stability, and biocompatibility. Among CPs, PANI has the longest history and can probably be traced back 180 years to the experiments of Runge^[38] in 1834 about a dark green powder formed when a mixture of aniline nitrate and CuCl_2 are heated together. Fritzsche^[21] in 1840 noted the formation of green precipitate on oxidation of the salt of aniline with H_2CrO_4 . Letheby in 1984 reported a blue product formation at the anode on electrolysis of aniline sulfate. The research of Runge, Fritzsche, and

Letheby on aniline black during the 19th century shed light on the redox properties and acid-base properties.

The term ‘polyaniline’ was first used by Brown et al. in the middle of the 19th century in their article regarding the vapor phase oxidation of aniline^[39]. In the 1960s, Josefowicz et al. reported that carefully synthesized emeraldine salt of polyaniline shows conductivity^[40], a decade before the discovery of the first intrinsically conductive polymer (halogen-doped polyacetylene)^[15, 41]. In the middle of the 1980s, MacDiarmid et al.^[42] and Travers et al.^[43] simultaneously reported that acid doping in the emeraldine form of PANI dramatically increased the conductivity by an order of 10-fold. This breakthrough discovery placed PANI into the family of intrinsically conducting polymers.

1.2.1 Structure of Polyaniline

PANI is a homopolymer having aniline as the repeating unit. The molecular structure of PANI consists of quinoid or benzenoid or both of them in different proportions. The PANI can exist in many structures depending on the level of oxidation. The pernigraniline state is the fully oxidized structure, and it consists of only quinoid structures. The fully reduced structure is called leucoemeraldine, which only consists of benzenoid units. The emeraldine form consists of ~50% quinoid structures and ~50% benzenoid units. The emeraldine form of PANI is the most conductive among different structures. The structure of PANI in different oxidation states is given in Figure 1.9

The fully oxidized and reduced structures of PANI are insulators in nature, and the conducting form of PANI is any other state in between the pernigraniline and leucoemeraldine. The PANI has many more

structures in between the fully oxidized and reduced structures according to the x:y ratio (where x represents the benzenoid and y represents the quinoid structure), in which quinoid and benzenoid rings are present. The x:y ratio of fully oxidized pernigraniline is 0:1, fully reduced leucoemeraldine is 1:0, and half-reduced/oxidized emeraldine is 1:1.

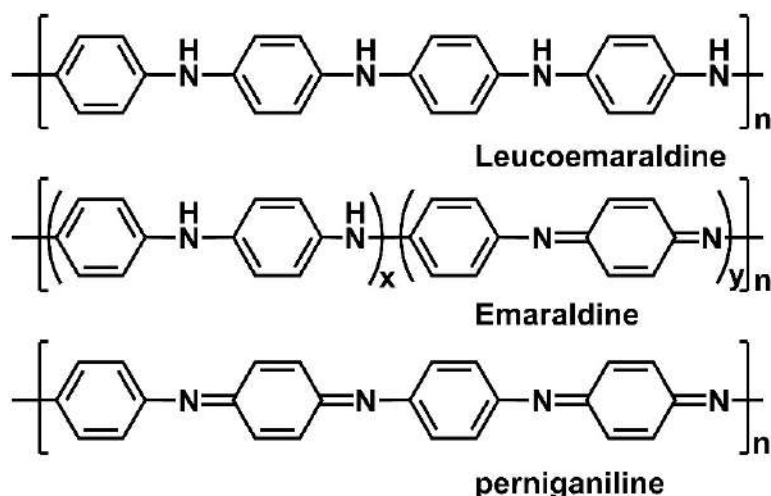


Figure 1.9: Structure of polyaniline in different oxidation states.

1.2.2 Doping in Polyaniline

There are three different oxidation states for PANI. Fully reduced leucoemeraldine, half oxidized emeraldine, and fully oxidized pernigraniline. The emeraldine base is the most stable oxidation form among the three forms. The doping of emeraldine base with protic acid converts it to emeraldine salt. This process results in an increase in conductivity due to the formation of charge carriers in the polymer chain backbone. This protonation process does not alter the number of π -electrons in the polymer backbone but induces delocalized charge carriers through structural reorganization. The process of doping in PANI is depicted in Figure 1.10

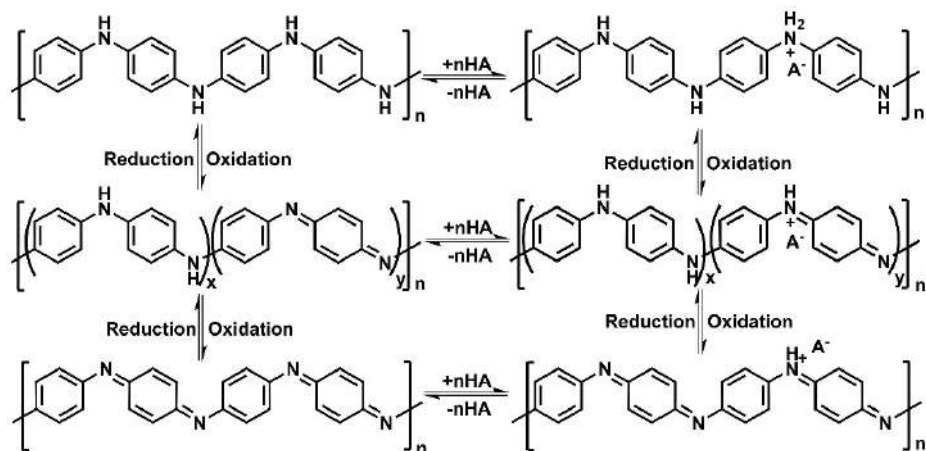


Figure 1.10: Doping of polyaniline in different oxidation states.

Different strategies have been developed for the doping of PANI to tune the electrical conductivity and functional properties. Doping with protic inorganic acid results in the highly conducting PANI but suffers from low mechanical stability and processability. The limitations of protic inorganic acids are addressed by using bulky protic organic acids. The doping with organic acids results in a more mechanically stable and processable PANI without compromising on conductivity.

Doping of PANI with the applied potential is another well-known method known as electrochemical doping. This method allows precise control over the doping level through an applied potential. The electrochemical doping is suitable for energy storage as well as sensing applications.

The self-doping methodology is an advanced strategy for doping PANI. In this, acidic functional groups are attached directly to the polymer chain backbone or side chains. The acidic functional groups act as an internal proton source, and this improves the conductivity stability over a wide pH range.

1.2.3 Synthesis of Polyaniline

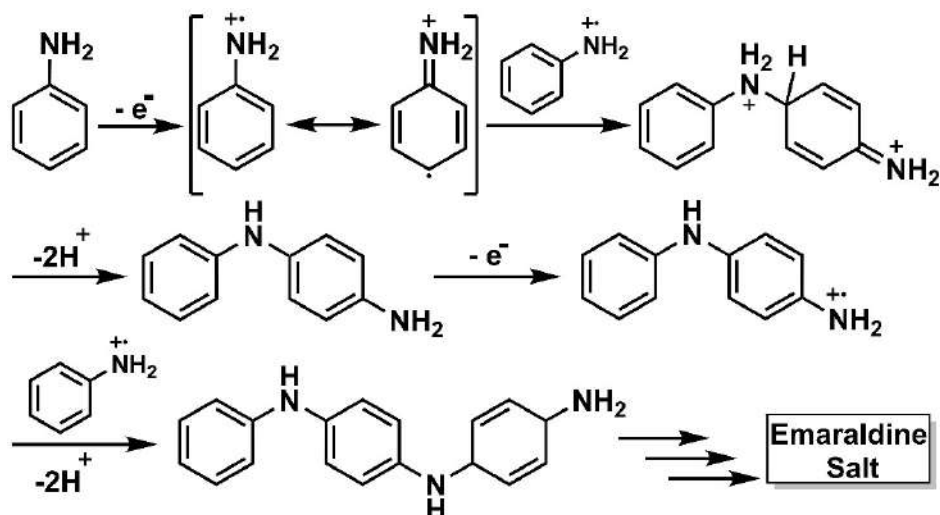


Figure 1.11: Mechanism of Polyaniline synthesis

Many methods, such as Chemical Oxidation, Electrochemical polymerization, Template-Assisted Synthesis, Interfacial polymerization, Ultrasonication-Assisted Synthesis, Microwave-Assisted Synthesis, Photochemical Synthesis, Enzymatic polymerization, Solid-State polymerization, and Combination Methods, are available for the synthesis of PANI. Among the different methods, the polymerization through chemical oxidation is the most widely used protocol. In this thesis, we also adopted the chemical oxidation method to prepare the CPs. The mechanism of polymerization is given in Figure 1.11.

1.2.4 Applications of Polyaniline

The history of PANI dates back to 1834. The interest in the PANI-related research showed an exponential growth after the discovery of its

conductivity. The main advantages of PANI include ease of synthesis, environmental stability, tunable electrical conductivity, and unique redox characteristics. These properties make PANI an ideal candidate for different applications.

The properties of PANI were optimized by adopting different synthetic strategies to meet the needs of specific applications, and some of these applications are as follows:

Sensors

The sensitivity of PANI to the surrounding environments and conditions allows it to be used as a highly selective and sensitive sensor for gases, pH, hazardous chemicals, etc. The sensors play a crucial role in the early detection of diseases, safety systems, early pollutant warning systems, etc.

Anticorrosion Coatings

The PANI has a high chemical resistance property. This high tolerance to chemicals makes it an ideal candidate for the use of anticorrosion coatings on the metal surfaces. PANI layers protect metal surfaces by preventing contact with corrosive agents. The PANI anticorrosion layer is extensively used to increase the life span of metals used in extreme environments like marine, chemical processing units, automobile parts, and sometimes in spacecraft.

Light-Emitting Devices

The PANI itself is not typically used as an emissive layer in light-emitting devices (LEDs). The PANI serves as an electron-blocking layer or as a hole transport material in LEDs. PANI facilitates charge transport

and injection, thereby improving the life span, efficiency, and stability of the LEDs.

Biosensors

The PANI has the inherent ability to sense the presence of biomolecules. The redox-active or the proton-responsive nature of the PANI backbone allows it to interact with biomolecules. Appropriate modifications allow it to achieve selectivity and be used as biosensors and play a vital role in environmental monitoring, healthcare, and biotechnology. Surface functionalization of PANI with biomarkers offers sensors with high precision and a high-sensitivity device.

Electromagnetic Interference Shielding

PANI-based composites are good at absorbing or reflecting electromagnetic waves. PANI shields are effectively used for protecting sensitive electronic components from external electromagnetic waves and signal interferences. PANI EMI shields have potential applications in aerospace, automobile electronics, medical devices, etc.

Smart Textiles

The conductive nature of PANI is used to convert ordinary textiles into smart textiles by integrating electronic functionalities with simple coating technology. The PANI coatings can help to integrate sensors for health monitoring applications, energy storage systems for wearable electronics, actuators to give physical stimuli, etc.

Water Treatment

PANI-based materials can be used to purify water by removing impurities from the water via adsorption or degradation, or by simple

filtration. The surface modification of PANI allows selective adsorption of heavy metals or pathogens from polluted water.

Anti-Static Materials

Incorporating PANI into insulating polymers or any coatings will result in imparting anti-static properties to the particular material. The conducting nature of PANI can effectively prevent the buildup of static charges on the surface of materials, which causes problems in sensitive electronic manufacturing and some chemical processes.

Drug-Delivery Systems

The easy and precise control of drug-releasing kinetics of PANI makes it an ideal candidate for drug delivery systems. The sensitivity of PANI towards pH, temperature, or electrical stimuli can be utilized for the controlled release of drugs to the target areas. The biocompatibility and safe metabolic products make PANI ideal for biomedical applications.

Electrochromic Devices

The reversible color changing of PANI concerning potential variations makes it an ideal candidate for electrochromic devices. The electrochromic property of PANI can be used in smart windows to regulate the transmission of sunlight. PANI can also be used for low-power consumption and high contrast screens with very fast response time.

Artificial Muscles

PANI and PANI-based materials can change the volume or length in response to an electrical signal mimicking the muscle function. The actuation of PANI finds application in systems where precise control of

movements is required. Fast response time, biocompatibility, and high mechanical stability allow PANI-based materials to be used in soft robotics, prosthetic limbs, biomedical engineering applications, and microfluid pumps.

Energy Storage Devices

The PANI has some unique redox properties, making it an ideal candidate for an electrode material for various energy storage devices like supercapacitors, lithium-ion batteries, fuel cells, etc. The electrode based on PANI-related materials is known to have high capacitance and high-rate capability, and this allows it to charge/discharge faster.

1.3 Graphene and Graphene-Derived Materials

Carbon is one of the most versatile elements in the periodic table because of its capability to exist in diverse allotropes ranging from zero-dimensional fullerenes to three-dimensional graphite or diamond. Among these, the two-dimensional form has gained much attention because of its exceptional electrical and mechanical properties. The discovery of graphene opened up a new pathway towards functionalized 2D materials. These derivatives, mainly graphene oxide (GO), reduced graphene oxide (rGO), heteroatom-doped rGO, graphite oxide, few-layer and multi-layer graphene, fluorographene, graphene quantum dots, etc., retain many of the unique properties of graphene in addition to their own features. Each material in the graphene family possesses distinctive properties arising from modifications of the sp^2 -hybridised carbon network.

Graphene

Graphene is a single layer of sp^2 -hybridised carbon atoms. The layers are formed from 6-membered rings. The structure of graphene is given in Figure 1.12. Each carbon atom is bonded with 3 other carbon atoms through σ -bonds. Each carbon atom has a unhybridized p-orbital (p_z) perpendicular to the plane, and these p_z orbitals laterally overlap with the p_z orbitals of neighboring carbon atoms, forming a continuous π -conjugated network. The continuous π -conjugated network is responsible for the unique electrical and mechanical properties of the graphene. Despite these remarkable properties, its chemical inertness, low dispersibility, and high tendency to aggregate make it difficult to use directly.

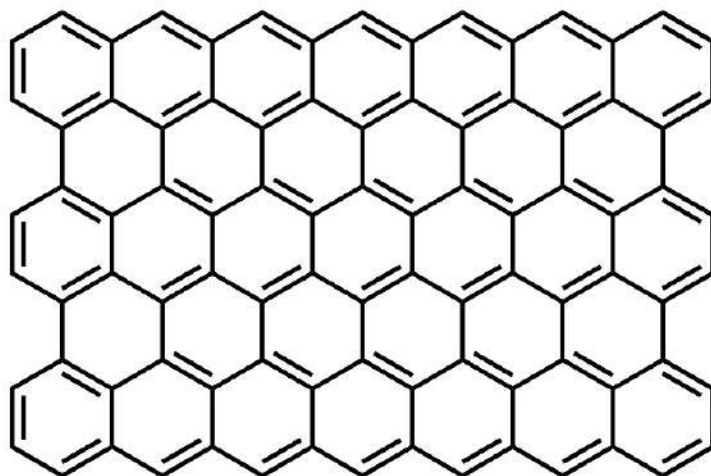


Figure 1.12: *Structure of graphene*

Graphene oxide

GO is also a layered form of carbon. It is formed by the introduction of oxygen functionalities to the graphene structure. Common oxygen functional groups added are hydroxyl (-OH) and epoxide (-O-) groups on the basal plane, and carbonyl (C=O) and carboxyl (-COOH) groups at the edges. Introduction of functionalities converts sp^2 carbons to sp^3 carbons. This disturbs the π -conjugation and makes the GO semiconducting in nature. GO is mostly prepared by oxidative exfoliation of graphite using strong oxidizing agents. The Hummers' method is the most extensively used synthetic approach for the preparation of GO. The presence of functional groups makes the GO hydrophilic in nature.

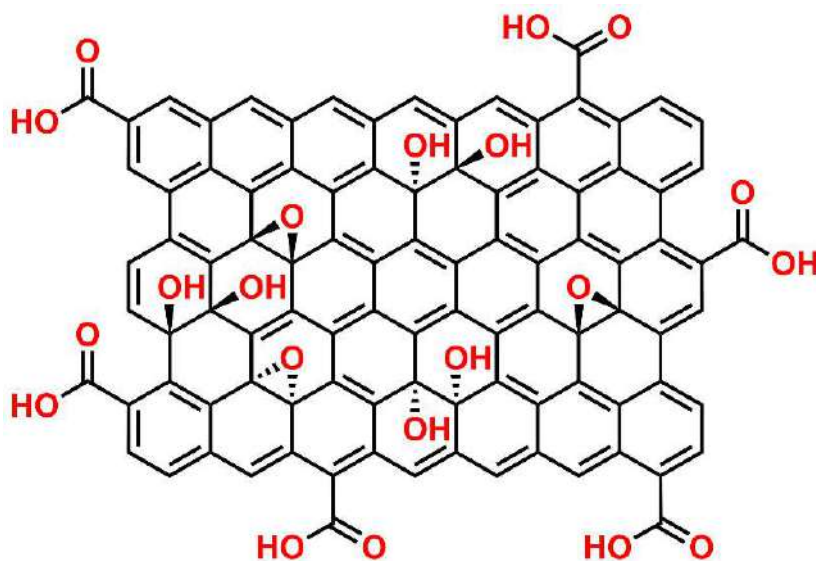


Figure 1.13: *Structure of GO*

Few-Layer and Multilayer Graphene (FLG and MLG)

Graphene is most often obtained not as a perfect monolayer but as few-layer (2-10 layers) or multilayer (>10 layers) stacks. These layered

systems exhibit properties that deviate from those of monolayer graphene due to interlayer interactions, such as modified band structure, reduced charge mobility, and decreased optical transparency.

Graphane

Graphane is a fully hydrogenated derivative of graphene, in which each carbon atom is bonded to a hydrogen atom, converting the hybridization from sp^2 to sp^3 . This eliminates the delocalized π -conjugation, making graphane an insulating material.

Fluorographene and Other Halogenated Graphenes

Similar to graphane, graphene can be functionalised with halogens, the most studied being fluorographene, in which each carbon atom is bonded to a fluorine atom. This results in a chemically stable and insulating material with unique surface chemistry and potential for further derivatization. Chlorinated and brominated graphenes represent additional halogenated variants, although they are less stable.

Reduced Graphene Oxide (rGO)

The rGO is the reduced form of GO. Some of the oxygen functionalities are removed from the surface of GO to obtain rGO. The removal restores some of the lost π -conjugation, making the rGO more conducting compared to GO. Some of the methods employed to convert the GO to rGO are as follows.

Chemical Reduction: GO is reduced chemically with the help of reducing agents like hydrazine hydrate, sodium borohydride, ascorbic acid, or hydroquinone.

Thermal Reduction: With the help of high temperature, the oxygen functional groups are removed.

Electrochemical reduction: The GO is reduced by applying a cathodic potential in a suitable electrolyte, offering a green and controllable method.

During the reduction of GO, not all functional groups are removed, nor the lattice defects are restored, and hence rGO possesses distinctive properties compared to both GO and graphene.

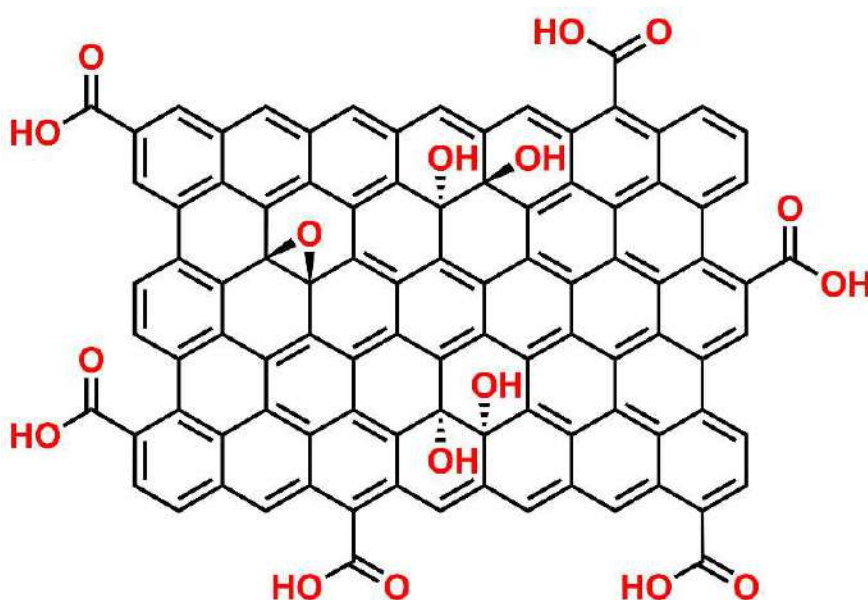


Figure 1.14: *Structure of GO*

Heteroatom-Doped rGO

Hetero atom doped rGO is a special type of rGO in which some of the carbon atoms are replaced with hetero atoms. The doping in rGO can lead to changes in the electronic state. The common atoms used for doping are Nitrogen (N), Sulfur (S), Boron (B), Phosphorous (P), etc.

1.4 Supercapacitors

Production and storage of energy are an important necessity of a modern energy-driven society. The extensive use of fossil fuels for day-to-day energy needs has a severe effect on the environment, and this urges the need for renewable energy sources. The storage devices play a key role in the transformation of a fossil fuel-dependent society to a renewable energy-dependent society.

There are mainly three types of energy storage devices that are used extensively, and they are batteries, supercapacitors, and fuel cells. Batteries and supercapacitors are available in all sizes and hence are used in portable devices as well as in stationary ones. On the other hand, the fuel cells are comparatively larger and, hence, are mainly used for stationary applications.

Supercapacitors are energy storage devices believed to bridge the gap between traditional capacitors and batteries. Supercapacitors and batteries mainly differ in their energy storage mechanisms. Batteries store energy via Faradaic reactions, and supercapacitors store energy via a non-Faradaic process. The batteries have a very high energy density, but they suffer from low power density. On the contrary, supercapacitors have a very high-power density but have lower energy density than batteries.

Depending on the mechanism involved in the energy storage, the supercapacitors are broadly divided into electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. The first EDLC (Electric Double-Layer Capacitor) was demonstrated by H. I. Becker in 1957, and the first supercapacitor device was fabricated by Standard Oil Company

in 1971 for commercial application. In EDLCs, charge storage occurs through the formation of static electricity in the electrodes, and there is no charge transfer reaction between the electrode and electrolyte, meaning that charging/discharging involves only non-Faradaic reactions. Since no Faradaic reaction is involved in EDLCs, the charge/discharge process is very fast, and there is no associated volume change, resulting in high power density and long cycle life.

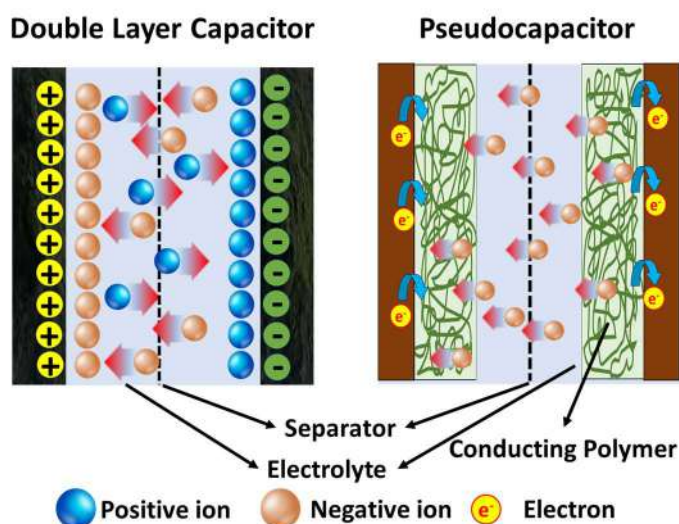


Figure 1.15: Graphical representation of EDLC and pseudocapacitor during the charging process.

Pseudocapacitor, also called Faraday quasi-capacitor, was first proposed by Conway in 1951. The pseudocapacitor differs from EDLC in the storage mechanism. In pseudocapacitors, the energy storage mechanism involves both the reversible adsorption of ions onto the surface of the active material as well as the redox reaction between the ions in the electrolyte and active material. When a potential is applied, the ions in the electrolyte diffuse towards the surface of the active material and from there they will enter into the bulk of the active material as a result of

redox reactions at the interface, resulting in the storage of large amounts of energy compared to the EDLCs. The Graphical representation of EDLC and pseudocapacitor during the charging process is shown in Figure 1.15.

The main challenge in designing a supercapacitor electrode is that no single material can provide all the required properties. Carbon-based materials have very high-power density and very long cycle life, but suffer from low energy density and low capacitance retention rate. Metal oxides and CPs, on the other hand, have high specific capacitance arising from their pseudocapacitive nature and moderately high energy density. Their main limitation is poor cycle life and comparatively lower power density. In order to overcome these shortcomings, these materials have been combined through different strategies to utilize their synergistic effect.

The CPs are promising materials for supercapacitor electrodes because of their advantages like ease of synthesis, low cost, redox properties, etc. The main limitation of CPs when used as an electrode material is their poor cyclic stability. The poor cyclic stability arises from structural degradation caused by continuous charge/discharge cycles. The main strategy employed to overcome this limitation is by making composites with different carbon materials like GO, rGO, graphene, carbon nanotube (CNT), etc.

The composite of GO and PANI has gained significant attention as a supercapacitor electrode material. The abundant oxygen functionalities present in GO form strong non-covalent interactions with the PANI chains. These interactions reduce the chain entanglement of PANI chains by allowing them to grow on the surface of GO in an ordered manner.

Less entangled chains are more stable when subjected to continuous charge/discharge cycles. As a result, GO/PANI composites demonstrate promising specific capacitance and cycling stability, making them a valuable candidate for energy storage applications.

Li et al. report a three-step synthesis of covalently-grafted polyaniline/GO nanocomposites featuring uniform nanorod-like PANI grown on GO sheets. The fabricated supercapacitor device achieved a specific capacitance of 442 F g^{-1} at 1 A g^{-1} . The energy density and power density of the device are calculated to be 9.6 Wh kg^{-1} and 3468 W kg^{-1} , respectively^[44].

Zhang et al. synthesized GO/PANI composites via a one-step electrochemical co-deposition method using varying GO concentrations. Microscopy revealed PANI nanofibers coating and intercalating GO sheets. Using 10 mg L^{-1} GO, they have achieved a specific capacitance of 1136.4 F g^{-1} at 1 mV s^{-1} . The cyclic stability is found to be 89% after 1000 cycles. Results demonstrate GO/PANI's potential as a high-performance, stable, and eco-friendly supercapacitor electrode material^[45]. Gui et al. prepared a PANI/GO composite by varying the ratio. They have obtained a distinctive *Mace-like* morphology, which increases the specific surface area and conductivity of the composite. The device exhibits a specific capacitance of 355.2 F g^{-1} at 0.5 A g^{-1} . The material exhibited a capacitive retention of 80.46% after 1000 cycles.

Mitchell *et al.* synthesized multilayer films of PANI and GO on indium tin oxide (ITO) electrodes via electropolymerization and dip coating for supercapacitor applications. GO was prepared chemically, and its formation was confirmed by XRD. Electrochemical evaluation in $1 \text{ M H}_2\text{SO}_4$ revealed that PANI-GO multilayers exhibited a significantly

higher specific capacitance (429 F g^{-1}) than pure PANI films (201 F g^{-1}) at a discharge current of 1 mA. The enhancement was attributed to GO's large surface area, oxygen-containing functional groups, and synergistic interactions with PANI, which improved active-site availability and ion diffusion. The electrodes demonstrated stable cycling over 1000 charge-discharge cycles, indicating potential for high-performance energy storage devices^[46].

Liu *et al.* reported a carboxyl-functionalized GO (CFGO)/PANI composite synthesized via *in situ* polymerization after oxalic acid treatment to convert GO's basal plane, oxygenated groups into carboxyl groups. This modification improved bonding between GO and PANI, creating a stable, compact architecture that enhanced electron transport and active material utilisation. Electrodes in 1 M H_2SO_4 showed a specific capacitance of 525 F g^{-1} at 0.3 A g^{-1} , surpassing CFGO/PANI (262 F g^{-1}), GO/PANI (323 F g^{-1}), and pure PANI (295 F g^{-1}). Cycling at 1 A g^{-1} retained 91% capacitance (476 F g^{-1}) after 200 cycles. The composite's structure suppressed PANI wire entanglement and improved electrochemical stability, making it a promising high-performance supercapacitor electrode^[47].

Li *et al.* synthesized hierarchical GO/PANI nanocomposites on flexible substrates via one-step interfacial electrochemical polymerization at a water/chloroform interface. Uniform PANI nanorods anchored onto GO formed a 3D nanostructure, enhancing ion diffusion and structural stability. The resulting flexible all-solid-state supercapacitor delivered a high specific capacitance of 1095 F g^{-1} at 1 A g^{-1} , excellent cycling retention (91.1% after 1000 cycles), energy density of 24.3 Wh kg^{-1} , and maximum power density of 28.1 kW kg^{-1} . Strong π - π interactions

between GO and PANI, combined with the hierarchical architecture, yielded superior rate capability, mechanical flexibility, and stability, outperforming many previous carbon-based/PANI devices^[48].

Bharadiya *et al.* synthesized GO wrapped PANI nanorods via in situ oxidative polymerization using nitric acid as a proton donor. Morphological analyses (FESEM, TEM) showed increased nanorod formation with GO concentration, with monolayer and multilayer GO sheets wrapping PANI. PANI/GO10 exhibited the highest specific capacitance (276 F g^{-1} by CV; 246 F g^{-1} by GCD at 0.1 A g^{-1}) and retained 80% after 500 cycles, outperforming pure PANI. Structural studies confirmed partial GO reduction, increased d-spacing, and strong PANI-GO interaction. EIS revealed reduced equivalent series resistance with GO content. The synergy enhanced capacitance, conductivity, and cycling stability, making PANI/GO promising for supercapacitors^[49].

M. Manoj *et al.* synthesized polyaniline-GO nanocomposites via a simple in-situ oxidative polymerization method, where GO sheets act as templates for the ordered growth of PANI nanorods, enhancing surface area and conductivity. Electrochemical studies using 1 M LiClO_4 in acetonitrile showed a high specific capacitance of 810 F g^{-1} at 0.2 A g^{-1} in a three-electrode configuration. In a two-electrode setup with an organic electrolyte ($0\text{-}2.5 \text{ V}$), the device achieved 230 F g^{-1} at 3 A g^{-1} , 175 F g^{-1} at 4 A g^{-1} , and 132 F g^{-1} at 5 A g^{-1} . Cycling stability tests at 5 A g^{-1} demonstrated 84.8% capacitance retention after 1000 cycles, indicating excellent durability. The high capacitance is attributed to the ordered nanorod growth over GO sheets, which improves the effective surface area and electrical conductivity. This study highlights the potential of cost-effective, simply synthesized PANI-GO composites for

high-power supercapacitor applications with strong performance and stability^[50].

Çıplak et al. synthesized a GO/PANI nanocomposite via a green, one-step *in situ* polymerization using dodecyl benzene sulfonic acid (DBSA) as dopant and stabilizer to enhance processability and electrochemical performance for supercapacitor applications. Uniform ultrafine PANI coatings were achieved on GO nanosheets by optimizing the aniline/GO ratio. In a two-electrode configuration, the optimized GO/PANI8 electrode delivered a high specific capacitance of 269.3 F g⁻¹ at 1 A g⁻¹. It also exhibited excellent cyclic stability, retaining 81.3 % of its capacitance after 10,000 charge-discharge cycles. The strong PANI-GO interaction, DBSA doping, and improved dispersibility contributed to enhanced ion transport, charge transfer, and homogeneous electrode coating. The results highlight that organic acid-doped GO/PANI nanocomposites can surpass many inorganic acid-doped counterparts, making them promising candidates for high-performance, processable supercapacitor electrodes^[51].

Male et al. synthesized PANI-GO hybrid composites via an interfacial polymerization pathway, where PANI nanofibers were intercalated into and coated over GO layers, yielding a semi-crystalline material with high conductivity (1.7 S cm⁻¹). The PANI-GO electrode exhibited a specific capacitance of 346 F g⁻¹, energy density of 17 Wh kg⁻¹, and power density of 316 W kg⁻¹ at 0.5 A g⁻¹. Even at 2.5 A g⁻¹, values of 242 F g⁻¹, 12 Wh kg⁻¹, and 1579 W kg⁻¹ were achieved. The composite maintained 84 % capacitance retention after 1000 cycles, outperforming pure PANI (280 F g⁻¹). Electrochemical impedance spectroscopy revealed low solution resistance (0.98 Ω), ESR (5 Ω), and a small time constant (0.9

ms), indicating fast charge-discharge capability. The synergistic effect of GO's mechanical strength and conductivity with PANI's pseudocapacitance enhanced performance, making PANI-GO a promising supercapacitor electrode material^[52].

Guiheng Xu et al. have prepared a GO/PANI composite using supercritical CO₂-assisted polymerisation. They have achieved a uniform PANI dispersion. The synthesised composite showed a capacitance value of 425 F g⁻¹ at 0.2 A g⁻¹. The material exhibited superior rate capability and cyclic stability compared to bare PANI and GO.

To further improve conductivity and charge transport, reduced graphene oxide (rGO) has increasingly replaced GO in PANI-based composites. The partial restoration of the sp² carbon network in rGO significantly enhances electrical conductivity, enabling more efficient electron transfer. When combined with PANI, rGO serves as a conductive backbone that improves rate capability, mitigates structural degradation during cycling, and enhances overall electrochemical stability, thereby addressing key limitations of pristine PANI electrodes.

Pawar et al. have prepared a rGO/PANI composite thin films through a successive ionic layer adsorption and reaction (SILAR) technique. They have prepared a flexible asymmetric solid-state supercapacitor using the thin film. The material exhibited a high capacitance of 710 F g⁻¹ and retained 91% after 5000 cycles^[53].

Ladrón-de-Guevara et al. have developed a cost-effective method to prepare rGO/PANI composite. In this, the GO is reduced using an infrared laser to produce rGO. The rGO thus obtained was highly porous in nature and also had high conductivity. The PANI coating enhanced the pseudocapacitance. The material exhibited a capacitance of 42 F g⁻¹ at

0.18 A g⁻¹. The material also exhibited a cyclic stability of 84% after 2000 cycles^[54].

Wang et al. reported an eco-friendly methodology to fabricate rGO/PANI composites. Polyphenols from green tea were used for the reduction of GO. Amine groups were introduced to rGO using the Mannich reaction, and later PANI was attached to these amino groups. The optimized electrode achieved a capacitance of 732 mF cm⁻² at 0.5 mA cm⁻². The electrodes also retained 90.3% of their initial capacitance after 1000 cycles^[55].

A three-dimensional rGO/PANI composite has been prepared by Xiaodong Hong et al. A diffusion-driven layer-by-layer assembly technique was employed for the synthesis of 3D porous rGO. PANI coated on the 3D rGO was used as the electrode material. The electrode exhibited a capacitance of 438.8 F g⁻¹ at 0.5 A g⁻¹. The capacitive retention of the material was 76.5% after 2000 cycles^[56].

Thanks to progress like this, combining PANI with heteroatom-doped reduced graphene oxide creates powerful composites for supercapacitor electrodes. Nitrogen, sulfur, boron, or phosphorus added into rGO changes how electrons move, increases surface attraction to ions, and brings extra spots where energy-storing reactions happen - so more charge gets stored. With PANI present, these modified rGO layers act as strong backbones: they carry current well, join easily in chemical activity, and hold up even when stress builds during repeated cycles. Unlike basic GO/PANI mixes, the doped version moves electricity much faster, links tighter with PANI molecules, beats regular rGO/PANI by enabling stronger faradaic contributions, and opens paths so ions reach

deeper zones. Together, their joint strengths turn them into top candidates whenever long-lasting, high-output supercapacitors are needed.

Macherla et al. reported an N-doped rGO/PANI flexible electrode for supercapacitor applications. N-rGO acted as a template for PANI to grow, and this helped the formation of long interconnected nanostructures. The fabricated device exhibited a capacitance of 322 F g^{-1} at 1 A g^{-1} . The device also retained 93% of its initial capacitance after 1000 cycles. The energy density and power density of the device were calculated to be 27.95 Wh kg^{-1} and 780.12 W kg^{-1} , respectively^[57].

Salehi et al. synthesized an S-doped rGO/PANI supercapacitor electrode. The S doping was achieved through a hydrothermal method. An asymmetric device was fabricated with this material. The device exhibited a capacitance of 1662.13 F g^{-1} . The energy density and power density of the device were calculated to be 17.5 Wh kg^{-1} and 356 W kg^{-1} , respectively. The device also retained 82% of its initial capacitance after 250 cycles^[58].

1.5 Electromagnetic Interference (EMI) Shielding

The unavoidable dependence of modern society on technology is causing an exponential growth in electronic devices, wireless communications, and high-frequency integrated circuits. These technologies offer convenience and enhanced productivity, but also introduce new challenges like electromagnetic interference (EMI). The disturbance in the operation of a device due to the unwanted electromagnetic radiation from another source is termed EMI^[59]. Signal degradation, data loss, or malfunction of devices due to EMI can cause serious threats in critical

sectors such as aerospace, healthcare, defense, and automotive electronics. As devices become more sensitive and smaller, and as the operating frequency increases, they become more susceptible to EMI^[60].

EMI can originate from both natural and man-made sources. Lightning, solar flares, and electrostatic discharges are examples of natural sources, while electric motors, power lines, mobile phones, Wi-Fi, radios, and microwave ovens are examples of man-made sources. One of the most studied and effective ways to tackle EMI is by shielding it using suitable materials.

The EMI shielding is mainly done by reflecting or absorbing the electromagnetic waves using suitable materials. The total shielding effectiveness (SE_T) is measured in decibels (dB), and it is the sum of reflection (SE_R), absorption (SE_A) and multiple internal reflection (SE_M)(Equation 1.4)^[61]. The schematic diagram of EMI shielding is depicted in Figure 1.16.

$$SE_T = SE_R + SE_A + SE_M \quad (\text{eq. 1.4})$$

(i) Reflection

It is one of the mechanisms involved in EMI shielding. The electromagnetic waves will get reflected when they encounter the surface of a conducting material, like metals or conducting polymers. The charge carriers present on the surface of the material will interact with the electric field of the incoming electromagnetic wave. This causes the charge carriers to oscillate and produce an opposing magnetic field that

reflects the incoming radiation. The extent of reflection is directly proportional to the conductivity of the surface and the frequency of the incoming wave. Metals are highly reflective due to their high conductivity. On the other hand, conducting polymers reflect the electromagnetic waves in their conducting form. In conducting polymers, the π -conjugated system and the charge carriers formed from doping are responsible for the effective reflection^[62]. Reflection is considered the first line of defense since it reduces the intensity of incoming electromagnetic radiation before absorption or internal scattering mechanisms^[63].

(ii) Absorption

It is the second major mechanism involved in EMI shielding. The dissipation of the energy of the incoming electromagnetic wave occurs in the bulk rather than on the surface. The process of absorption involves the generation of heat from the incoming radiation. The absorption of a material is dominant when it has permanent electric or magnetic dipoles, moderate conductivity, and high dielectric or magnetic losses. The dipoles interact with the alternating electric or magnetic field of the incoming electromagnetic waves, and this results in internal friction, causing the energy to dissipate as heat^[64]. Absorption is dominant when the thickness of the material is high and when the frequency of the incoming radiation is high^[64c].

(iii) Multiple Internal Reflection

Multiple internal reflection is the third mechanism involved in EMI shielding. The incoming electromagnetic waves undergo repeated scattering and internal reflections within the internal structure of the material. This mechanism is dominant in materials having porous,

layered, fibrous, or heterogeneous microstructures. This mechanism does not dissipate any direct energy of the incoming radiation, but it increases the path length of the incoming radiation in the bulk of the material, hence increasing the probability of being absorbed^[65].

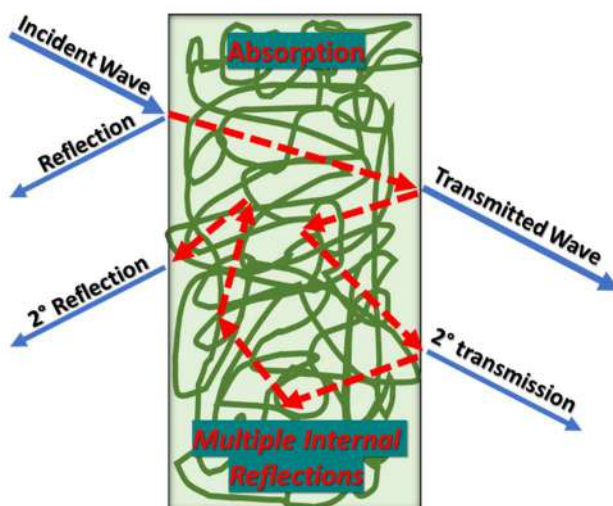


Figure 1.16: Schematic representation of EMI shielding in a conducting polymer.

There has been growing research into using conducting polymers as promising materials for EMI shielding because they possess the characteristics of being lightweight, flexible, and tunable in their electrical properties. With the incorporation of magnetic or dielectric nanofillers, these polymers are able to create synergistic properties, leading to improved absorption-based shielding performance. Therefore, conducting polymer-based systems offer a promising avenue towards next-generation light and efficient EMI shielding materials.

Yanjun et al. prepared semiconducting wood/polyaniline (PANI) composites by in situ polymerization, where aniline monomer was embedded in wood veneer to make it electrically conductive while

preserving the natural wood structure. Composites showed electromagnetic shielding effectiveness ranging from 30 to 60 dB. FTIR and XRD confirmed interactions of PANI and wood and increased crystallinity without structural deterioration^[66].

Khasim et al. have synthesized para-Toluene Sulphonic Acid (p-TSA) doped polyaniline-graphene nanoplatelet (PANI-GRNP) composite films through in situ polymerization. Structural and morphological polymerization (SEM, FTIR, XRD, Raman, TGA) ensured uniform GRNP dispersion and excellent PANI-GRNP interactions, resulting in improved conductivity and dielectric properties. Electrical conductivity was enhanced by almost five times upon p-TSA doping owing to π - π conjugation and a higher density of charge carriers. In the X-band (8-12 GHz), a shielding effectiveness of -14.5 dB (>95% absorption) was observed for 10 wt% GRNP, which was characterized by absorption. The composites also demonstrated enhanced thermal stability and low skin depth, and hence, they are potential materials for use as EMI shields^[67].

Iqbal et al. prepared barium ferrite encapsulated polythiophene (BaFe₁₂O₁₉/PTh) nanocomposites through in situ emulsion polymerization to examine electromagnetic interference shielding. SEM and TEM confirmed-shell structure with BaFe₁₂O₁₉ nanoparticles encapsulated uniformly by PTh. Phase purity was confirmed by XRD, while VSM measurement demonstrated higher ferromagnetic behavior with NC-100 (BaFe₁₂O₁₉:PTh = 1:1), giving a magnetic moment of 25.78 emu/g and coercivity of 2.5 kOe. Electrical conductivity was maximum at 2.71 S/cm for NC-50. Thermal studies established higher stability compared to pure PTh. The composite NC-100 provided better

microwave shielding effectiveness of 43.27 dB at 11.65 GHz due to synergistic dielectric as well as magnetic loss^[68].

Gill et al. prepared graphene-encapsulated polypyrrole-graphene (PG) nanocomposites by in situ chemical oxidative polymerization and explored their electromagnetic interference (EMI) shielding efficiency in the X-band (8.2-12.4 GHz). The highest efficiency was attained with 0.2 wt% graphene incorporation (PG2), showing shielding effectiveness due to absorption (SEA) of ~33 dB and minor reflection (<1 dB)^[69].

Rahal et al. demonstrated carbon quantum dots (CQDs) application in microwave shielding for the first time by synthesizing nanocomposites of polypyrrole/CQD (PPyCQD) using in situ polymerization. Structural, morphological, and electrical analysis (XRD, FTIR, UV-Vis, AFM, SEM, and DC conductivity) established the high PPy-CQD interaction, smoother morphology, and conductivity improvement with improved loading of CQDs. Microwave absorption in the 2-8 GHz range revealed remarkable improvement over pure PPy. The PPyCQD200 composite recorded a minimum reflection loss of -32.8 dB at a thickness of 5.5 mm, while 25% loading realized -27.8 dB at 6.93 GHz with 2.34 GHz bandwidth. The cooperative dielectric loss and interfacial polarization make PPyCQDs light-weight, eco-friendly microwave absorbers^[70].

Madhusudhana et al. prepared polypyrrole/graphite (PPy/G) nanocomposites by in situ chemical oxidative polymerization of pyrrole in the presence of green tea extract as a reducing medium for Fe³⁺ ions. Structural (XRD, FTIR) and morphological (SEM) analysis verified the incorporation of graphite in the form of successful graphite incorporation and altered PPy microstructure, with MSNG2 (10 wt% G) presenting dense morphology. UV-vis spectrum showed high absorption throughout

the visible spectrum. Dielectric and AC conductivity measurements presented increased charge transfer and small polaron hopping, with the maximum conductivity in MSNG2. Electromagnetic interference shielding effectiveness measurements in the Ku-band (12-18 GHz) exhibited better shielding effectiveness (10-18 dB), which was predominantly absorption, focusing on PPy/G composites as low-weight, low-cost material opportunities for dielectric and EMI shielding applications^[71].

Luo et al. prepared reduced graphene oxide/strontium ferrite/polyaniline (R-GO/SF/PANI) nanocomposites by in situ polymerization and characterized their structural, magnetic, and microwave absorption characteristics. XRD, FTIR, TEM, Raman, and VSM polymerizations proved phase-pure $\text{SrFe}_{12}\text{O}_{19}$ nanoparticles uniformly dispersed on R-GO sheets and surrounded by PANI chains, along with intensive interfacial interactions and charge transfer. The composites exhibited tunable permittivity and promoted dielectric/magnetic losses. R-GO/SF/PANI showed superior microwave absorption, reaching the maximum reflection loss of -45.0 dB at 16.08 GHz with 5.48 GHz bandwidth at 1.5 mm thickness. These findings feature R-GO/SF/PANI as thin, light, and high-performance electromagnetic interference absorbers^[72].

Bhardwaj et al. prepared surfactant-assisted polypyrrole (PPy) composites with amine-functionalized multiwalled carbon nanotubes (AMWCNTs), graphene, and a hybrid carbon assemblage (HCA) through sodium lauryl sulfate-dopant-assisted in situ emulsion polymerization. Confirmation of intensive PPy-carbon interactions, smaller particle size, and enhanced chain packing was achieved through

structural (XRD, FTIR) and morphological (SEM) analysis. Dielectric analysis showed increased polarization and charge transfer across the interface, resulting in better impedance matching and high dielectric loss. EMI shielding polymerization in the Ku-band range of 12.4-18 GHz exhibited attenuation levels ranging from -28.8 dB (PPy) to -79.9 dB (PPy-HCA), which were dominated by absorption. The findings point toward PPy-carbon allotrope composites as light-weight effective absorbers for EMI shielding and stealth applications^[73].

Kumar et al. prepared ferrite-polyaniline (PANI) nanocomposites and ferrite-PANI coated fabrics by in situ polymerization of $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 0.4$) nanoparticles, which were synthesized by sol-gel. XRD established spinel phase formation with a crystallite size ranging from 20 to 30 nm, whereas SEM-EDS confirmed homogeneous distribution within the PANI matrix. Magnetic analysis demonstrated saturation magnetisation growing up to $\text{Zn} = 0.3$ before it fell off. At X-band (8.2-12.4 GHz), composites with 50 wt% ferrite registered 60 dB shielding effectiveness ($>99.9\%$ attenuation), which was dominated by absorption. Ferrite-PANI-coated fabrics of thickness 0.30 mm had 40-48 dB shielding, showing lightweight, flexible, and effective EMI shielding for real-world applications^[74].

Kulkarni et al. prepared porous polythiophene (PTh) thin films by a straightforward room-temperature chemical oxidative polymerization method and studied their electromagnetic interference (EMI) shielding and microwave absorption characteristics in the Ku-band (12-18 GHz). Structural and morphological polymerizations (XRD, FESEM, TEM, FTIR, XPS) identified porous fiber-like PTh with nanoscale characteristics. Interestingly, the films showed double negative (DNG)

behavior by simultaneously having negative permittivity and permeability. The optimized film (0.2 M thiophene) exhibited a lowest reflection loss of -44.41 dB at 17.54 GHz (99.99% absorption) with shielding effectiveness of -18 dB at 16.3 GHz at a mere thickness of 5.31 μm , demarcating lightweight, high-performance absorption-dominated shielding^[75].

Gahlout et al. optimized synthesis parameters of polypyrrole (PPy) in a systematic way for increased electromagnetic interference (EMI) shielding in the X-band (8.2 - 12.4 GHz). With the variation of oxidant (FeCl_3) concentration, dopant concentration, and dopant type, they reported that a ratio of 1:2:1 pyrrole: oxidant: dopant using sodium lauryl sulfate (SLS) provided the best conductivity (42 S/cm) and shielding effectiveness (-126 dB). FTIR validated better conjugation and reduced defect centers under optimum conditions, while TGA and XRD identified stable thermal and structural properties. EMI shielding was dominated by absorption, and hence, PPy-SLS was a high-performance, corrosion-resistant, and light-weight alternative to metals for useful EMI shielding applications^[76].

1.6 Objectives and Scope of the Present Work

Conducting polymers (CPs) are promising electrode materials for supercapacitor applications owing to their low cost, ease of synthesis, and pseudocapacitive charge storage. However, their practical application is limited by two persistent challenges: poor cyclic stability arising from structural degradation during repeated charge/discharge cycles, and the difficulty of tuning their physicochemical properties through functionalization, which typically requires costly reagents or

multistep reactions. This thesis addresses both limitations through two complementary strategies.

The specific objectives of this work are:

1. To covalently functionalize polyaniline (PANI) with nitrogen-doped reduced graphene oxide (N-mrGO) via an amide linkage, in order to stabilize the PANI chains, reduce rGO sheet aggregation, and improve cyclic stability and electrochemical performance.
2. To further enhance this system through sulfur and nitrogen co-doping of the reduced graphene oxide (SN-mrGO), introducing additional non-covalent interactions and pseudocapacitive contributions.
3. To fabricate and evaluate symmetric supercapacitor devices using the optimized PANI/heteroatom-doped rGO composites, assessing specific capacitance, rate capability, cyclic stability, and energy/power density.
4. To design and synthesize a new class of conjugated polymers via a simple, scalable one-pot polymerization in aqueous medium, incorporating diverse functional groups (-OH, -OMe, -COOH, -SH) to enable fine control over physicochemical and electrochemical properties without multistep synthesis.
5. To evaluate the electrochemical performance of this new polymer family as supercapacitor electrode materials, with particular attention to their unusually wide operating potential window (~ 2.5 V) in aqueous electrolytes.

6. To investigate the electromagnetic interference (EMI) shielding performance of the new polymer family, establishing their multifunctional potential for advanced energy and electronic applications.

Together, these objectives progress from improving an established conducting polymer (PANI) through composite engineering, to the rational design of a new, inherently more stable and versatile conducting polymer platform — establishing strategies applicable to next-generation aqueous energy storage and electromagnetic shielding materials.

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Chapter 2

Materials and methods

A concise overview of materials employed, characterization techniques applied, and methodologies adopted for the current research. This section also offers a detailed explanation of the various electrochemical techniques, such as cyclic voltammetry, chronopotentiometry, GCD, and EIS studies employed in the presented work.

2.1 Materials

The list of chemicals utilised in this research work is given in Table 2.1. All the chemicals were used as received, except aniline. The aniline was distilled under reduced pressure and stored below 10 °C before use. Double-distilled water was employed for all the experiments.

Table 2.1: *List of chemicals and source.*

Consumables	Source
Aniline AR	Merck, India
Anthranilic acid	Sigma Aldrich, USA
2-Aminophenol	Himedia, India
o-Anisidine	Sigma Aldrich, USA
2-Aminothiophenol	TCI Chemicals, Japan
Dicyclohexylcarbodiimide	TCI Chemicals, Japan
4-(Dimethylamino)pyridine	TCI Chemicals, Japan
Ammonium persulphate	Merck, India
Graphite Powder	Sigma Aldrich, USA
Potassium permanganate	Merck, India
Sodium nitrite	Merck, India
Sodium nitrate	Himedia, India
N, N-Dimethyl formamide	Merck, India
Dimethyl sulfoxide	Merck, India
N-Methyl-2-pyrrolidone	Himedia, India
Hydrochloric acid	Merck, India
Carbon conductive paste	MG Chemicals, USA
Sulfuric acid	Merck, India

2.2 Methods

2.2.1 Synthesis of Graphene Oxide (GO)

GO was synthesised via the modified Hummers' method^[1]. In a typical reaction, 5 g of graphitic powder, 2.5 g of NaNO_2 , and 120 mL of H_2SO_4 were taken in a 1000 mL beaker. It was then kept in an ice bath of 0 °C and stirred for 30 min. To the resulting mixture, 15 g of KMnO_4 was added very slowly with constant stirring, and after the addition, the ice bath was removed, and the reaction mixture was further stirred for another 8 hr until a thick grey paste was obtained. 200 mL of distilled water was then added, causing an increase in temperature to 98 °C. After 1 hr of stirring, the mixture was further diluted to 800 mL and 33% H_2O_2 was added till the colour changed to a bright yellow colour. The resultant yellow solution was then filtered and washed with 5% HCl to remove SO_4^{2-} ions, followed by distilled water to remove Cl^- ions. After washing, it was dried in a vacuum oven at 60 °C to obtain GO.

2.2.2 Covalent Functionalization of Graphene Oxide

Steglich esterification reaction was employed to functionalise GO with aniline through an amide bond^[2]. Initially, 200 mg of graphene oxide was dispersed in 100 mL of dry N, N-Dimethyl formamide (DMF), and 10 mmol of aniline was added to it and stirred for 30 minutes. To the resulting mixture, 10 mmol of N,N'-dicyclohexylcarbodiimide (DCC) and 1 mmol of 4-(dimethylamino)pyridine (DMAP) dissolved in 20 mL of DMF were charged. The reaction mixture was then heated to 50 °C and stirred for 72 hr. After the completion of the reaction, the reaction mixture was filtered, washed with plenty of DMF followed by ethanol,

and dried in a vacuum oven at 60 °C overnight to obtain modified graphene oxide (mGO). The reaction is depicted in Figure 2.1.

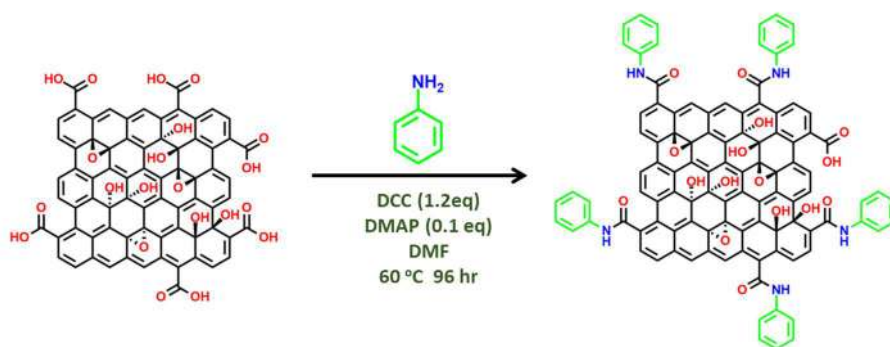


Figure 2.1: *Covalent Functionalization of GO*

2.2.3 Simultaneous Reduction and Doping of Modified Graphene Oxide

200 mg of mGO were dispersed in 70 mL of distilled water by sonicating for 1 hour. To this dispersion, 5 g of the doping agent was added and then stirred for 20 minutes. The resultant mixture was transferred to a Teflon-lined autoclave and heated at 180 °C for 24 hr. After the completion of the reaction, the autoclave was allowed to cool down to room temperature. The product was then filtered, washed thoroughly with distilled water, and dried at 60 °C in a vacuum oven overnight to obtain heteroatom-doped modified reduced graphene oxide. Urea was used as a doping agent to dope with nitrogen, and thiourea was used as a doping agent to dope with both nitrogen and sulfur^[3]. The nitrogen-doped modified reduced graphene oxide is named as N-mrGO, and the sulfur and nitrogen co-doped modified reduced graphene oxide is named as SN-mrGO.

2.2.4 Incorporating Polyaniline to N-mrGO/SN-mrGO

200 mg of N-mrGO/SN-mrGO was taken in a round-bottom flask, and 70 mL of 1M H₂SO₄ was added. The mixture was sonicated for 1 hr to get a homogeneous dispersion. 1 eq. of aniline was added and stirred for 30 minutes by keeping in an ice bath. To the resulting mixture, 1.25 eq. of Ammonium persulphate (APS) dissolved in 30 mL of 1M H₂SO₄ was added dropwise over 30 minutes. The reaction mixture was further stirred for 12 hr by maintaining the temperature at 0 °C. The product was filtered, washed with distilled water followed by acetone, and then dried in a vacuum oven at 60 °C. For mGO and mrGO, 5 mmol of aniline was used, and the samples were named as mGO-PANI and mrGO-PANI, respectively^[4]. In the case of N-mrGO, 5 mmol, 7.5 mmol, and 10 mmol of aniline were used, and the samples were named N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10, respectively. Similarly, for SN-mrGO 5 mmol, 7.5 mmol, and 10 mmol and aniline were used, and the samples were named SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10, respectively.

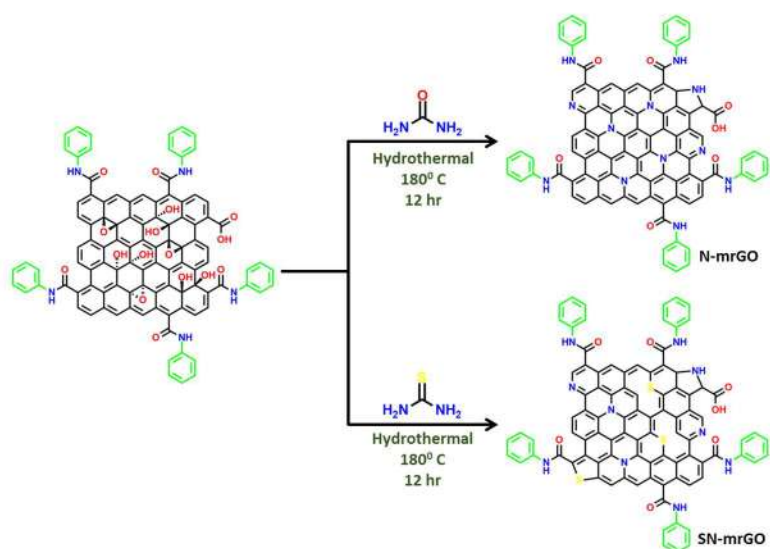


Figure 2.2: Simultaneous reduction and hetero-atom doping of mGO

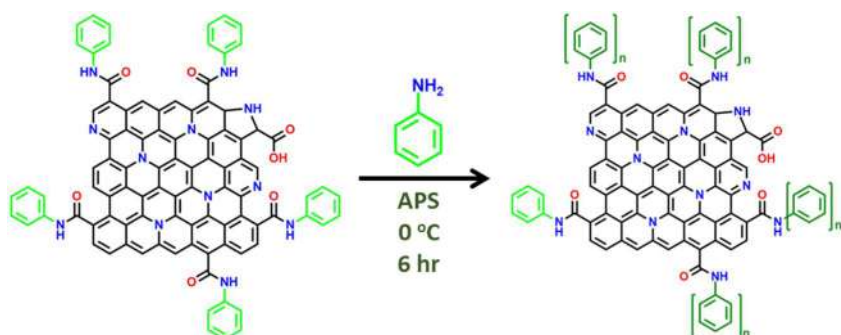


Figure 2.3: Incorporating PANI to N-mrGO

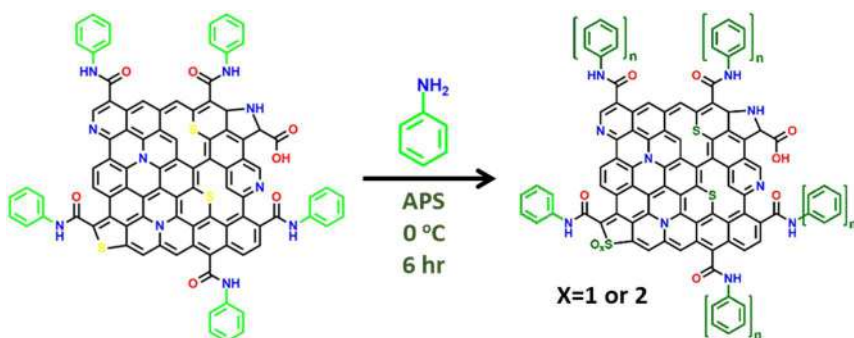


Figure 2.3: *Incorporating PANI to SN-mrGO*

2.2.5 Synthesis of Poly(4-(phenyldiazenyl)aniline) (P4PDP) and Its Derivatives.

The polymer P4PDA and its ortho-substituted derivatives were synthesized; the unsubstituted parent polymer is designated PH, while the -COOH, -OH, -OMe, and -SH substituted analogues are designated PCOOH, POH, POME, and PSH, respectively. In the synthesis of P4PDA and its derivatives, 25 mL of 35% HCl is added to 100 mL of distilled water. To the resultant solution, 10 mmol of the corresponding ortho derivative of aniline is added and cooled to 0 °C by placing it in an ice bath. 10 mmol of NaNO₂ dissolved in 20 mL of distilled water, and then added dropwise to the above solution with continuous stirring. After stirring for 10 minutes, 10 mmol of aniline is added dropwise, and the mixture is kept for an additional 20 minutes. Finally, 12.5 mmol of ammonium persulfate (APS) dissolved in 50 mL of distilled water is added very slowly over 30 minutes, and the reaction is maintained for 15 hours with constant stirring while maintaining a temperature of 0 °C. After the completion of the reaction, the product is filtered, washed with water, and acetone to remove oligomers, unreacted monomers, and salts. The polymer obtained is then dried in a vacuum oven overnight at 60 °C. The different ortho substituents of aniline used were -H, -COOH, -OH, -OMe, and -SH. The corresponding polymers were designated as PH, PCOOH, POH, POME, and PSH, respectively. Monomers used for synthesis are aniline, 2-aminophenol, 2-aminothiophenol, 2-anthranilic acid, and o-anisidine, and the corresponding polymers are named PH, POH, PSH, PCOOH, and POME, respectively. The synthesis procedure is represented in Figure 2.4.

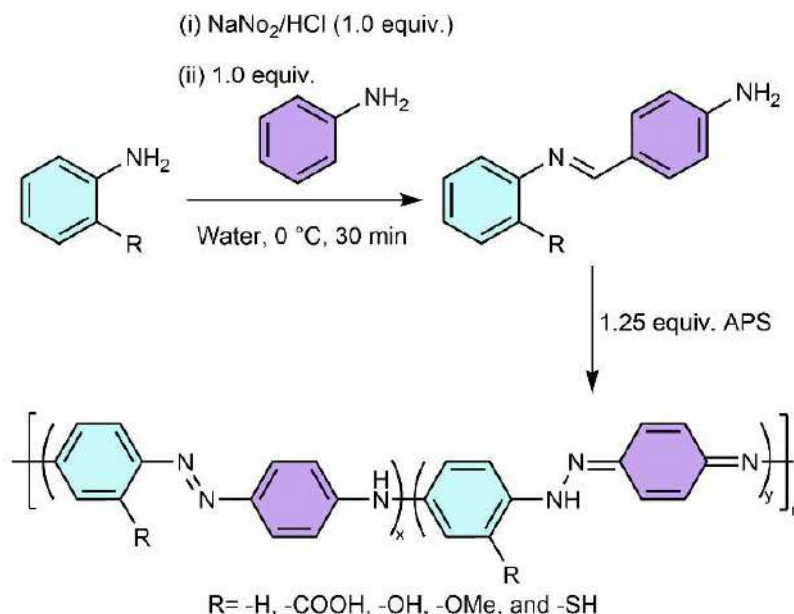


Figure 2.4: *Synthesis of poly(4-(phenyldiazenyl) aniline) and its derivatives.*

2.2.6 Calculations of Electrochemical Performance

The equation for the calculation of specific capacitance (C_{SP}) from CV is given as^[5]:

$$C_{\text{sp}} = \frac{\int Idv}{2vm\Delta V} \quad (2.1)$$

Where C_{sp} (Fg^{-1}) is the capacitance, $\int Idv$ is the area under the curve, v is the scan rate, m is the active mass of the material, and ΔV is the potential window.

The equation for the calculation of specific capacitance (C_{SP}) from Galvanostatic Charge-Discharge (GCD) is given as:

$$C_{\text{sp}} = \frac{I\Delta t}{m\Delta V} \quad (2.2)$$

Where C_{sp} (Fg^{-1}) is the capacitance, I is the current, Δt is the discharge time, m is the active mass of the material, and ΔV is the potential window.

The energy density (E) is the amount of energy stored per unit mass and is calculated using the equation 2.3 from the GCD.

$$E = \frac{1}{2} C \Delta V^2 \quad (2.3)$$

Where E (W h kg^{-1}) is the energy density, C_{sp} is the specific capacitance (F g^{-1}), and ΔV is the potential window.

Power density (P) is the rate at which a device can release or absorb energy per unit mass is calculated using the equation eq. 2.4 from the GCD.

$$P = E / \Delta t \quad (2.4)$$

Where E (W h kg^{-1}) is the energy density, Δt is the discharge time, and P (kW kg^{-1}) is the power density.

2.2.7 General Characterizations

Fourier Transform Infra-Red Spectroscopy (FTIR)

The structural characteristics of the prepared samples were investigated using Fourier-transform infrared (FTIR) spectroscopy. The samples were mixed with potassium bromide (KBr) to form transparent pellets suitable for analysis. FTIR spectroscopy detects the vibrational modes of chemical bonds, providing detailed information on the functional groups, bonding interactions, and molecular structure of the material. The spectra of all samples were recorded over a range of $4000\text{-}500 \text{ cm}^{-1}$, capturing both high- and low-frequency vibrational modes relevant to the polymer

backbone and side groups. Measurements were performed using a JASCO FTIR-4600 spectrometer under controlled conditions to ensure reproducible and accurate spectral data.

UV-Visible spectroscopy

The optical absorption properties of the synthesised samples were investigated using UV-Visible (UV-Vis) spectroscopy. This technique is based on the principle of electronic transitions between molecular orbitals, where photons in the ultraviolet and visible regions of the electromagnetic spectrum are absorbed by the material, promoting electrons from lower-energy orbitals to higher-energy orbitals. UV-Vis spectroscopy provides information on the electronic structure, degree of conjugation, and possible interactions within the polymer chains. It is a widely used, non-destructive, and qualitative method for probing both the presence and relative concentration of chromophoric groups in a sample. The measurements in this study were performed using a JASCO UV-Visible spectrophotometer under standard experimental conditions, ensuring consistent and reliable absorption spectra for all samples analysed.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to record the physical changes associated with temperature. The thermal degradation of the prepared samples was measured by monitoring the change in mass with respect to temperature in the N₂ atmosphere. All the measurements were done in a temperature range of 30 °C to 650 °C at the heating rate of 10 °C min⁻¹ using a Perkin Elmer TGA analyser. The spectrum was plotted with temperature on the x-axis and % weight loss on the y-axis.

Field Emission Scanning Electron Microscopy (FESEM)

The topographic and morphological characterisation of the prepared samples was analysed by Field Emission Scanning Electron Microscopy (FESEM). In FESEM, the surface of the samples was scanned using a focused beam of electrons, and the resulting secondary electrons, backscattered electrons, and characteristic X-rays produced are processed to generate the surface image of the sample. All the samples were analysed using the ZEISS Gemini SEM 300 FESEM.

Energy-dispersive X-ray spectroscopy (EDAX analysis)

The elemental composition of the samples was analysed using EDX analysis. In EDX, the X-rays are produced when a beam of electron beam hits the surface of the material. The wavelength of the X-ray produced will be characteristic of the elements present. The EDX analysis of all the samples was recorded along with the SEM analysis.

Transmission Electron Microscopy (TEM)

Transition electron microscopy (TEM) is a high-resolution imaging technique used to study the morphology, composition, crystallinity, etc., of materials. It uses a high-energy electron beam for imaging. The electron beam scattering through a very thin film of the sample is utilised to generate high-resolution images.

X-ray Photoelectron Spectroscopy (XPS)

The elemental composition and binding energy of electrons present on the surface of the samples were analysed using X-ray photoelectron spectroscopy (XPS). XPS is a surface qualitative technique, and it uses the principle of the photoelectric effect. It can be used to study the

elemental composition of ~10 nm (~30 atomic layers) of a given sample. The sample measurements were carried out in the Omicron Nanotechnology XPS instrument.

FT-Raman Spectroscopy

Fourier Transform-Raman Spectroscopy is a technique to identify the structural fingerprint of a molecule or a material by determining the modes of vibrations. Raman spectroscopy works on the principle of inelastic scattering of photons from the sample. The measurements were carried out in the WITec alpha300RA Raman system with a 532 nm DPSS laser.

Electron Spin Resonance Spectroscopy (ESR)

The unpaired electron species in the prepared samples were analysed using electron spin resonance (ESR) spectroscopy. ESR is a sensitive technique that detects paramagnetic centres, such as radicals or transition metal ions, by measuring the resonant absorption of microwave radiation in the presence of an external magnetic field. It provides information on the electronic environment, spin density, and distribution of unpaired electrons in a material. The ESR spectra of all samples were recorded using a JEOL JES FA200 ESR spectrometer under standard experimental conditions, ensuring accurate characterisation of the paramagnetic species and their interactions within the polymer matrix.

2.2.8 Electrochemical Characterizations

Different electrochemical techniques, such as Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Galvanostatic Charge-Discharge (GCD), were used to evaluate the electrochemical properties of the samples employed in this research work. A Zenner

Zennium Pro galvanostat/potentiostat electrochemical workstation (Germany), along with Thales XT software, was used for all electrochemical experiments. For all experiments conducted, Ag/AgCl was used as the reference electrode, Pt as the counter electrode, and the material coated on a Glassy carbon electrode as the working electrode.

Preparation of Working Electrode

For all the electrochemical analyses, a sample coated onto a Glassy Carbon Electrode (GCE) was employed as the working electrode. First, the GCE was thoroughly cleaned using a microfiber cloth and alumina powder to obtain a clean surface. The sample for analysis was then weighed and mixed with conducting carbon powder in a 2:1 ratio, dispersed in isopropanol, and the required amount was drop-casted onto the GCE. The GCE drop-casted with the sample was then dried in a vacuum oven for 30 minutes at 50 °C.

Cyclic Voltammetry

The electron transfer behaviour of the prepared material was evaluated using cyclic voltammetry (CV), a widely used electrochemical technique for probing redox properties and electron transfer kinetics. In CV, the potential of the working electrode is swept linearly over time in a triangular waveform, while the resulting current is recorded. The observed anodic peak current (i_{pa}) corresponds to the oxidation of electroactive species, while the cathodic peak current (i_{pc}) corresponds to the reduction. The peak potentials (E_{pa} and E_{pc}) provide information about the thermodynamics of the redox processes.

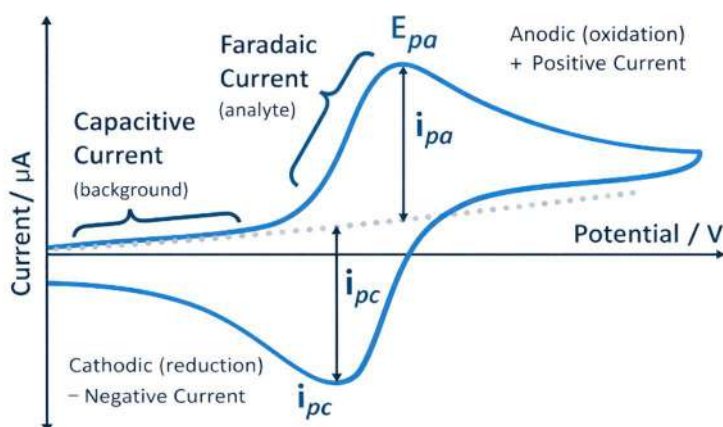


Figure 2.5: *Cyclic voltammogram*

The Figure 2.5 illustrates these features: the initial capacitive current arises from the charging of the electrical double layer, while the faradaic current reflects the electron transfer reactions of the analyte. The separation between anodic and cathodic peaks indicates the reversibility of the redox process. The area under the peaks is proportional to the charge involved, and the shape of the voltammogram can reveal whether the process is diffusion-controlled or surface-confined. Figure 2.6 depicts a typical cyclic voltammogram, highlighting the capacitive background, faradaic currents, peak currents, and corresponding potentials for both oxidation and reduction processes, providing a comprehensive understanding of the electrochemical behaviour of the material.

Galvanostatic Charge Discharge

GCD is a widely used electrochemical technique for assessing the charge-storage characteristics of materials, particularly in supercapacitors, batteries, and other energy storage devices. In GCD measurements, a constant current is applied to the material, and the

resulting potential response is recorded over time. During the charging process, a positive current drives the accumulation of charge within the material, increasing its potential. Once the potential reaches a predetermined upper limit, the current is reversed to a negative value, initiating the discharge process. The constant current is maintained throughout the discharge until the potential drops back to the lower set value. This sequence of charge and discharge produces a potential versus time curve that reflects the material's electrochemical behaviour. Analysis of the GCD profile allows for the extraction of critical parameters, including specific capacitance or capacity, energy density, power density, and coulombic efficiency. Additionally, repeated cycling through GCD experiments provides information on the cycle life and stability of the material under operational conditions. The shape and symmetry of the charge-discharge curves also indicate resistive losses, internal resistance, and charge-transfer kinetics. Overall, GCD is a fundamental method for characterizing energy storage materials and comparing their performance under standardised conditions, offering direct insights into both practical and theoretical electrochemical properties.

Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful technique used to study the electrochemical behaviour of materials, interfaces, and electrochemical systems. It is mostly used to study the electrical behaviour, charge transfer, ion diffusion, and kinetics of electrochemical reactions and processes. In an EIS analysis, the current response is measured when a small AC voltage is applied to the system. The impedance is then analysed as a function of applied frequency. The data obtained from EIS is normally plotted as Nyquist

plots (imaginary vs. real impedance). EIS spectra of all the samples were recorded at an open circuit voltage with an amplitude of 10 mV for a sinusoidal wave and in a frequency range of 1 Hz to 100 kHz. Zmann software was used to fit the experimental data.

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Chapter 3

Covalently Bonded Polyaniline-Nitrogen Doped rGO Macromolecules for Superior Supercapacitors with Enhanced Energy Density and Long-Term Cyclic Stability

This chapter reports a covalently integrated polyaniline (PANI)/nitrogen-doped reduced graphene oxide (N-rGO) macromolecular system for supercapacitors. Amide anchoring enhances structural stability and charge transport, while N-rGO improves conductivity, wettability, and redox activity. The optimized composite delivers high capacitance, excellent rate capability, and superior cycling stability in aqueous electrolytes.

3.1 Introduction

Supercapacitors stand as a promising candidate in the realm of energy storage devices. They offer distinct advantages over traditional batteries in terms of power density and cycle life¹. Their superior power density, intermediate energy density, and fast charge/discharge cycles make them ideal for various applications spanning from automotive to portable electronics³⁻⁸. CPs⁹ and 2D carbon materials like graphene^{10, 11}, GO¹⁴, rGO¹⁶, CNT¹⁸, etc., are the most explored materials for the supercapacitor electrodes. CPs have the advantage of moderately high energy density and specific capacitance, but suffer from low power density and poor cycle life. On the other hand, 2D carbon materials offer high-power density and long cycle life, but suffer from low energy density and specific capacitance²⁰.

PANI is a promising electrode material owing to its ease of synthesis, high theoretical capacitance, and environmental stability, but its low-rate capability and poor cyclic stability remain major drawbacks. The issues associated with PANI mainly arise from the chain degradation during continuous cycling and self-interactions from chain entanglement. The common strategy employed to overcome these problems is to design composites to utilize the synergistic effect²¹⁻²⁴. However, such composites often compromise one property to improve another due to weak non-covalent interactions and limited stability^{25, 26}.

The ease of synthesis, scalability, high conductivity, and close resemblance to the properties and structure of graphene make rGO an ideal candidate for forming composites with PANI. PANI can reduce the aggregation of rGO sheets caused by strong π - π interactions, which

would otherwise lead to a loss of surface area and subsequently affect its surface-related properties.

In our present work, a dual strategy is employed to design a PANI and N-doped rGO (N-rGO) based macromolecular system for supercapacitor applications. The system consists of PANI attached to N-rGO sheets via amide bonds between carboxylic acid groups of N-rGO and amino groups of PANI. The N-rGO acts as a soft template for the ordered growth of PANI, reducing chain entanglement and stabilizing the volume change of PANI chains during charge/discharge, thereby enhancing cyclic stability and energy storage capability. Nitrogen doping improves the conductivity, generates redox centers, increases wettability, improves charge transport, imparts a partial pseudocapacitive behavior without lattice distortion, introducing favorable non-covalent interactions with PANI. This dual approach is expected to provide a stable and high-performance electrode for a supercapacitor, motivating the detailed investigations presented in this chapter, and this work is published in the *Journal of Power Sources*²⁷.

3.2 Result and Discussion

The detailed synthetic procedure adopted is presented in Chapter 2. The synthesis scheme of the material is shown in Figure 3.1. The GO is synthesized by the modified Hummers' method. In the next step, the aniline monomer is attached to the carboxylic acid groups of GO through an amide bond using Steglich amidation, with DCC/DMAP as coupling agents. The reaction mechanism is presented in Figure 3.2. The basic conditions maintained during the coupling reaction ensure that no aniline oligomers are formed. After successfully attaching aniline to GO, the

material undergoes simultaneous reduction and doping via a hydrothermal method, with urea serving as both the reducing agent and nitrogen source. Finally, PANI is attached to N-mrGO using ammonium peroxydisulfate as the oxidizing agent for polymerization.

3.2.1 Structural, Spectroscopic, and Thermal Characterization

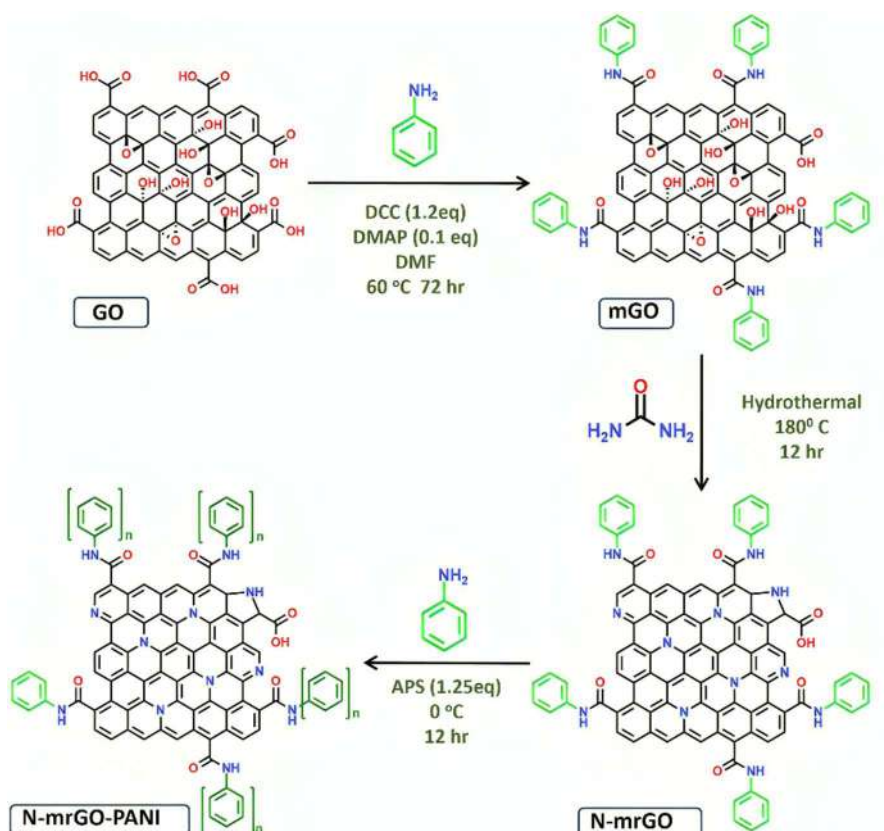


Figure 3.1: Synthesis scheme of N-mrGO-PANI

FTIR spectra were recorded to identify functional groups and to confirm the presence of chemical modifications. The results are presented in Figure 3.3. The FTIR spectrum of GO and mGO has the characteristic

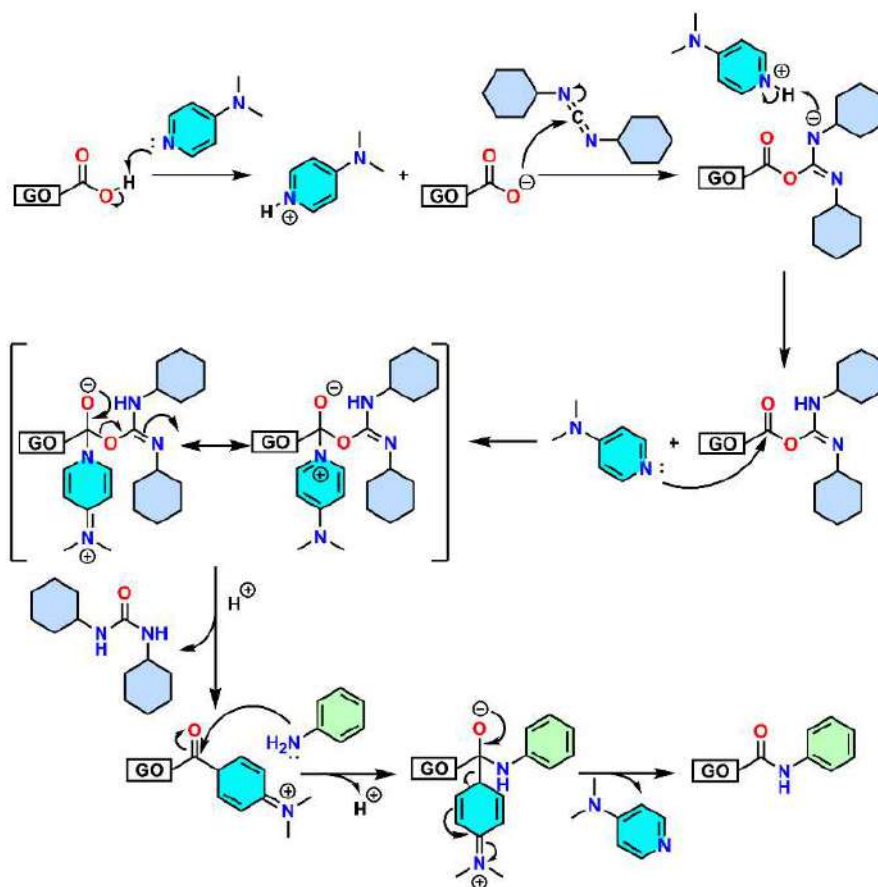


Figure 3.2: Mechanism of Steglich amidation for the coupling of GO with aniline

peaks at 1742, 1635, and 1401 cm^{-1} corresponding to C=O stretching, C=C stretching, and O-H bending respectively^{28, 29}. In addition to the characteristic peaks of GO, a new peak appeared at 1568 cm^{-1} for mGO corresponding to the amide bond stretching, confirming the successful attachment of aniline to the GO through an amide bond³⁰⁻³². The spectra of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 have two prominent peaks at 1587 and 1486 cm^{-1} corresponding to benzenoid and quinonoid stretching peaks, and this confirms the incorporation of PANI into the N-mrGO. The other prominent peaks present are at 1297,

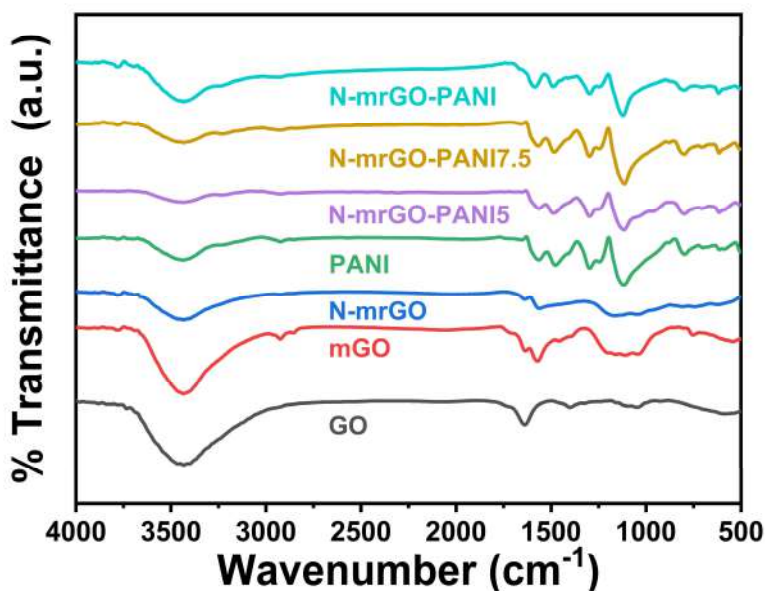


Figure 3.3: FTIR spectra of GO, mGO, N-mrGO, PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10.

1243, and 1120 cm^{-1} corresponding to C-N stretching of the quinonoid ring, C-N stretching of the benzenoid ring, and Q=N=Q stretching, respectively (where Q is the quinonoid ring) ³³.

The electronic structure of the samples was analyzed using UV-Visible spectra. The spectra are shown in Figure 3.4. The GO shows a peak at 274 nm, and a shoulder peak at 340 nm, which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the C=O bond. The mGO obtained by attaching an aniline to the GO through an amide bond shows two peaks. The first peak at 263 nm, corresponding to the $\pi \rightarrow \pi^*$, shows a blue shift compared to that of GO. This is due to the strong electron-withdrawing nature of the new amide bond formed. The second peak at 480 nm, assigned to $n \rightarrow \pi^*$, shows a red shift, and this is because of the strong $n \rightarrow \pi^*$ transitions

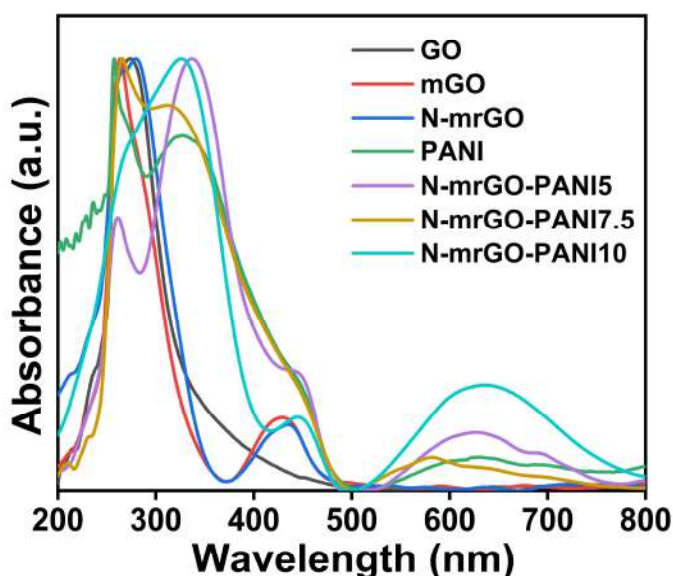


Figure 3.4: UV-Visible spectra of GO, mGO, N-mrGO, PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10.

present in the amide bond³⁴. These changes in electronic spectra further confirm the formation of a new amide bond between the GO and aniline.

The N-mrGO shows two peaks similar to those of GO and mGO. The $\pi \rightarrow \pi^*$ transition peak appears around 280 nm, which shows a red shift when compared with that in mGO, and this is because of the increase in conjugation due to the removal of oxygen functionalities during reduction. The $n \rightarrow \pi^*$ transition appears at 481 nm, like mGO. The UV-Visible spectra of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 are similar to that of PANI and have three peaks around ~327 nm, ~447 nm, and ~627 nm corresponding to $\pi \rightarrow \pi^*$, $\pi \rightarrow$ polaron transition, and Polaron $\rightarrow \pi^*$ transition³⁵.

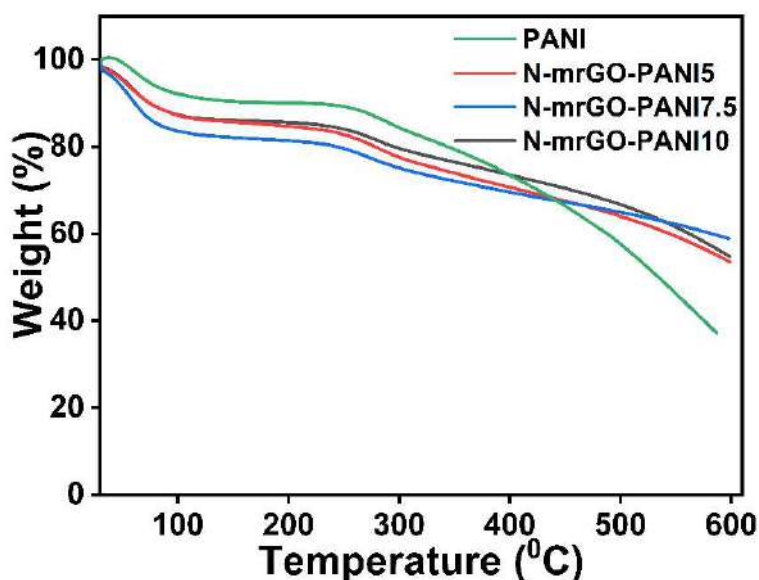


Figure 3.5: TGA of PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10

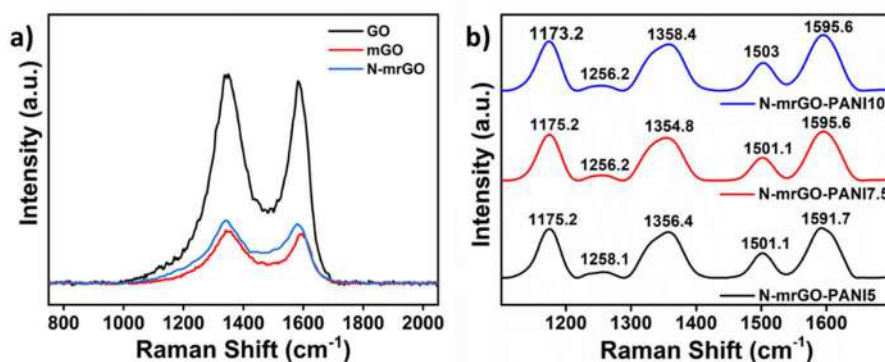


Figure 3.6: (a) FT-Raman spectra of GO, mGO, and N-mrGO, and (b) FT-Raman of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10.

The thermal stability of PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 was analyzed using TGA over the temperature range of 30 °C to 600 °C and is given in Figure 3.5. All samples exhibited three

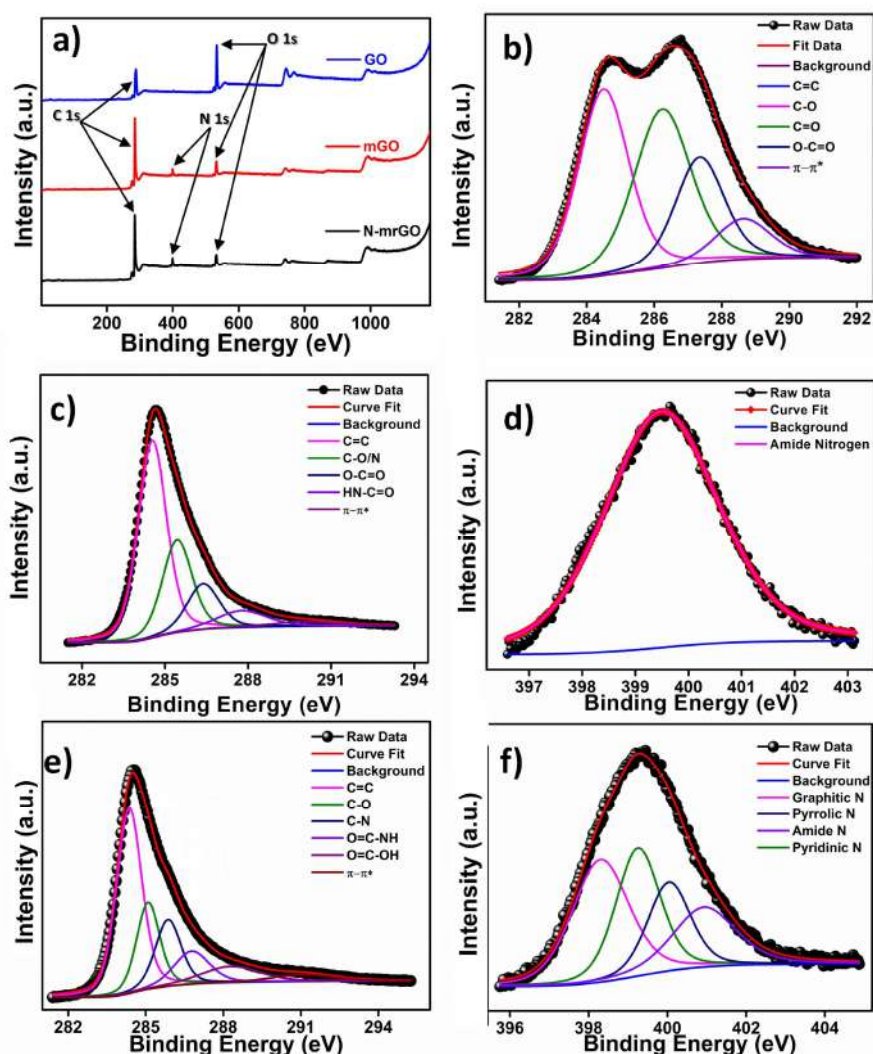


Figure 3.7. (a) XPS survey spectrum of GO, mGO and N-mrGO. Deconvoluted XPS spectra of (b) C 1s of GO, (c) C 1s of mGO, (d) N 1s of mGO, (e) C 1s of N-mrGO and (f) N 1s of N-mrGO.

distinct stages of weight loss during thermal degradation³⁶. The initial weight loss observed up to 100 °C is attributed to the evaporation of water molecules. The second stage, beginning around 240 °C, corresponds to the release of dopant ions from the PANI chains. The final

stage, starting at approximately 300 °C, is due to the thermo-oxidative decomposition of the PANI backbone. The residual mass after decomposition was 37.2%, 54.8%, 53.5%, and 58.4% for PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10, respectively. These results indicate that the thermal stability of PANI is enhanced upon covalent functionalization with N-doped rGO. This improvement suggests increased structural stability of the polymer chains in the synthesized composites, as expected.

The chemical structure of the prepared samples was further analyzed using FT-Raman spectroscopy, and the spectra are presented in Figure 3.6. The Raman spectra of GO, mGO, and N-mrGO consist of a G-band around $\sim 1585\text{ cm}^{-1}$ and a D-band at around $\sim 1349\text{ cm}^{-1}$. In the Raman spectrum of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 consists peaks at $\sim 1595\text{ cm}^{-1}$, $\sim 1503\text{ cm}^{-1}$, $\sim 1358\text{ cm}^{-1}$, $\sim 1256\text{ cm}^{-1}$, and $\sim 1171\text{ cm}^{-1}$ corresponding to stretching vibration of C=C, deformation of N-H in semi-quinonoid structure, vibration of C-N in polaronic structure, vibration associated with deformation of benzene structure, and in-plane bending of C-H in the semi-quinonoid or benzene respectively³⁷. The G-band and D-band were not visible in the PANI grafted samples because of the excess amount of polyaniline present.

The elemental composition of the synthesized materials was evaluated with the high-resolution X-ray photoelectron spectroscopy (XPS) and is shown in Figure 3.7. The XPS survey spectrum of GO, mGO, and N-mrGO reveals two prominent peaks: C 1s ($\sim 284.5\text{ eV}$) and O 1s ($\sim 399.5\text{ eV}$)³⁷. However, mGO and N-mrGO exhibit an additional N 1s peak at approximately 532.5 eV. In mGO, this N 1s peak arises from the formation of new amide bonds, which again confirms the amide bond

formation, while in N-mrGO, this results from amide bonds and doped nitrogen in mrGO sheets^{38, 39}.

Further analysis of GO's C 1s spectra reveals distinct components, including -C=C- (284.55 eV), -C-O (286.25 eV), -C=O (287.35 eV), -O-C=O (288.7 eV), and $\pi \rightarrow \pi^*$ shake-up satellite peak (288.7 eV)⁴⁰. Deconvoluting the C 1s XPS spectrum of mGO reveals peaks at 284.6, 285.5, 286.4, 287.8, and 290.2 eV, corresponding to -C=C-, -C-O-, -COOH, -CONH-, and π - π^* transition, respectively. Notably, the N 1s spectrum of mGO shows a single peak at 399.5 eV, attributed to amide bond nitrogen⁴⁰. In the case of N-mrGO, its C 1s spectrum is deconvoluted into C=C, -C-O-, -C-N, -NH-C=O, -O-C=O, and $\pi \rightarrow \pi^*$ shake-up satellite peak at 284.4, 285.1, 285.9, 286.8, 288.3, and 291.2 eV, respectively. Significantly, the relative intensity of the -C=C- peak increases in N-mrGO after simultaneous reduction and doping compared to the -C-O and -O-C=O peaks. The deconvoluted N 1s spectrum of N-mrGO reveals three additional peaks relative to mGO at 398.3, 399.2, 400.0, and 400.9 eV, corresponding to graphitic nitrogen, pyrrolic nitrogen, amide nitrogen, and pyridinic nitrogen, respectively. These peaks validate the doping of rGO with nitrogen⁴¹⁻⁴³.

3.2.2 Morphological Analysis

The surface morphology of the synthesized materials was studied using FE-SEM, and the results are presented in Figure 3.8. The FE-SEM of N-mrGO revealed sheet structures with wrinkles or folds, which indicates the formation of less aggregated sheets. The FE-SEM images of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 have revealed

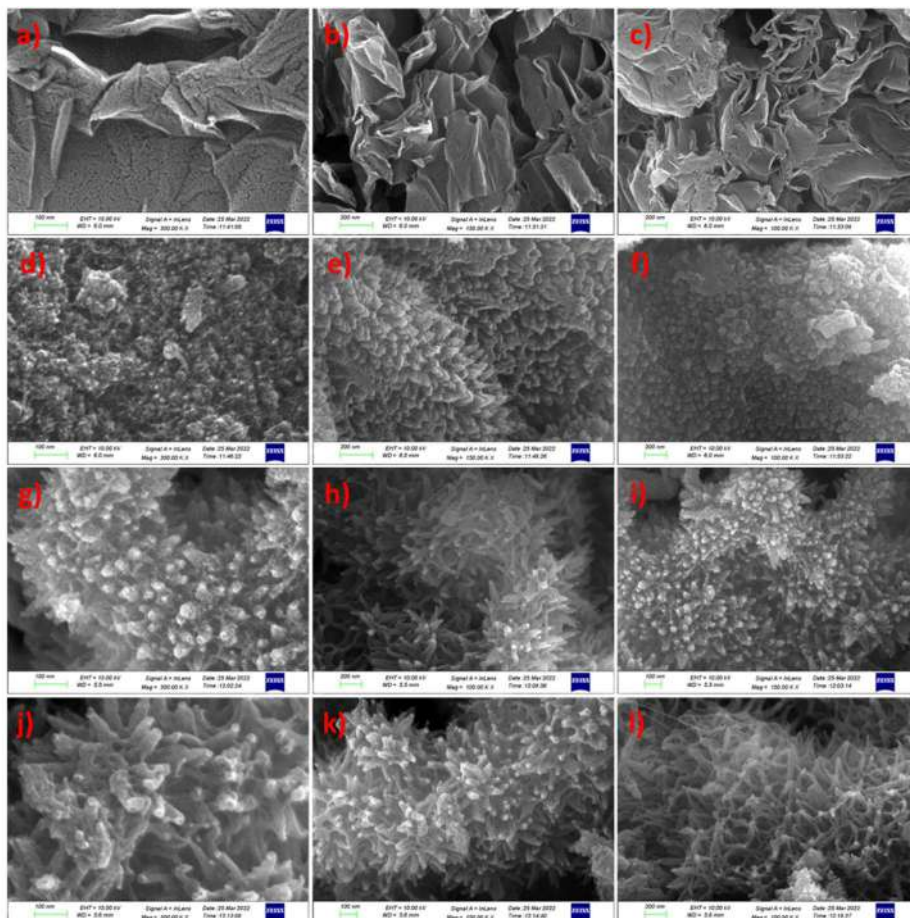


Figure 3.8: FE-SEM images at different magnifications of (a-c) N-mrGO, (d-f) N-mrGO-PANI5, (g-i) N-mrGO-PANI7.5, and (j-l) N-mrGO-PANI10.

a coral-like morphology similar to that of PANI. The images also suggest that the PANI chains formed during the polymerization completely cover the N-mrGO surfaces^{44, 45}. The coral-like morphology also helps in better ion diffusion.

The High-Resolution Transmission Electron Microscopy (HR-TEM) analysis further supports the morphological characteristics observed in the FE-SEM results, and the results are presented in Figure 3.9. The N-mrGO samples exhibit transparent and wrinkled sheet-like structures,

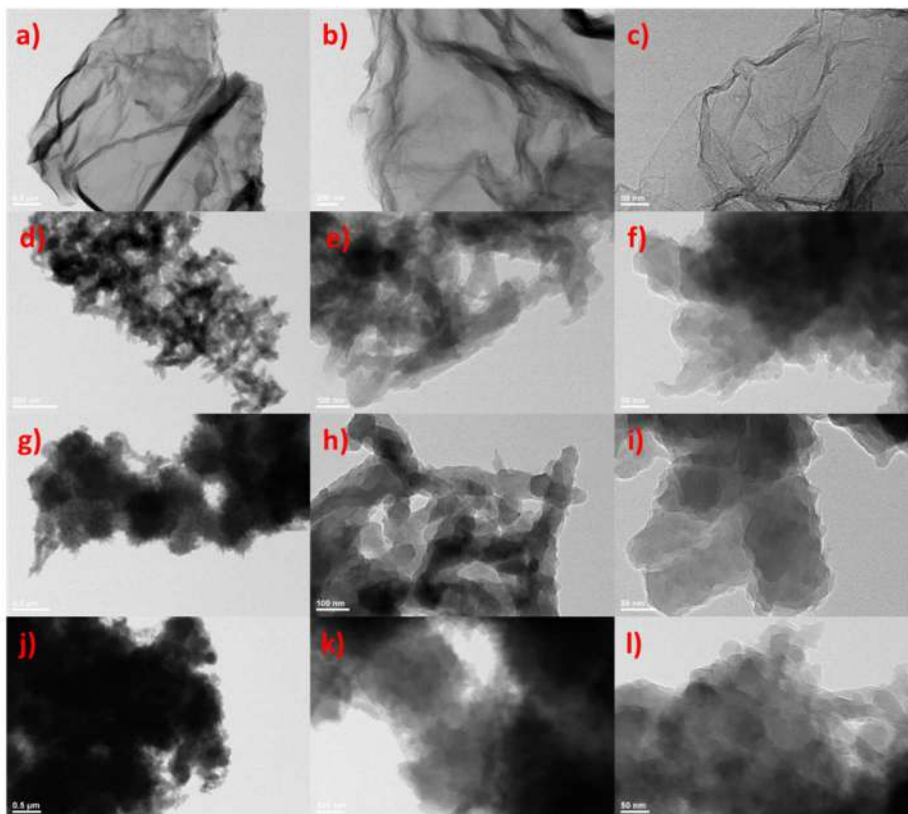


Figure 3.9: HR-TEM images at different magnifications of (a-c) N-mrGO, (d-f) N-mrGO-PANI5, (g-i) N-mrGO-PANI7.5, and (j-l) N-mrGO-PANI10.

which are characteristic of nitrogen-doped rGO. In the case of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10, the HR-TEM images clearly reveal a coral-like morphology of PANI with a porous nature^{46, 47}. These results further confirm the uniform distribution of PANI on the surface of N-mrGO⁴⁸.

3.2.3 Electrochemical Analysis

The electrochemical analysis of the synthesized materials was conducted using a three-electrode configuration comprising Ag/AgCl as the reference electrode, platinum (Pt) as the counter electrode, active

material coated onto a glassy carbon electrode (GCE) as the working electrode, and 1M H₂SO₄ as the electrolyte. CV was performed within a

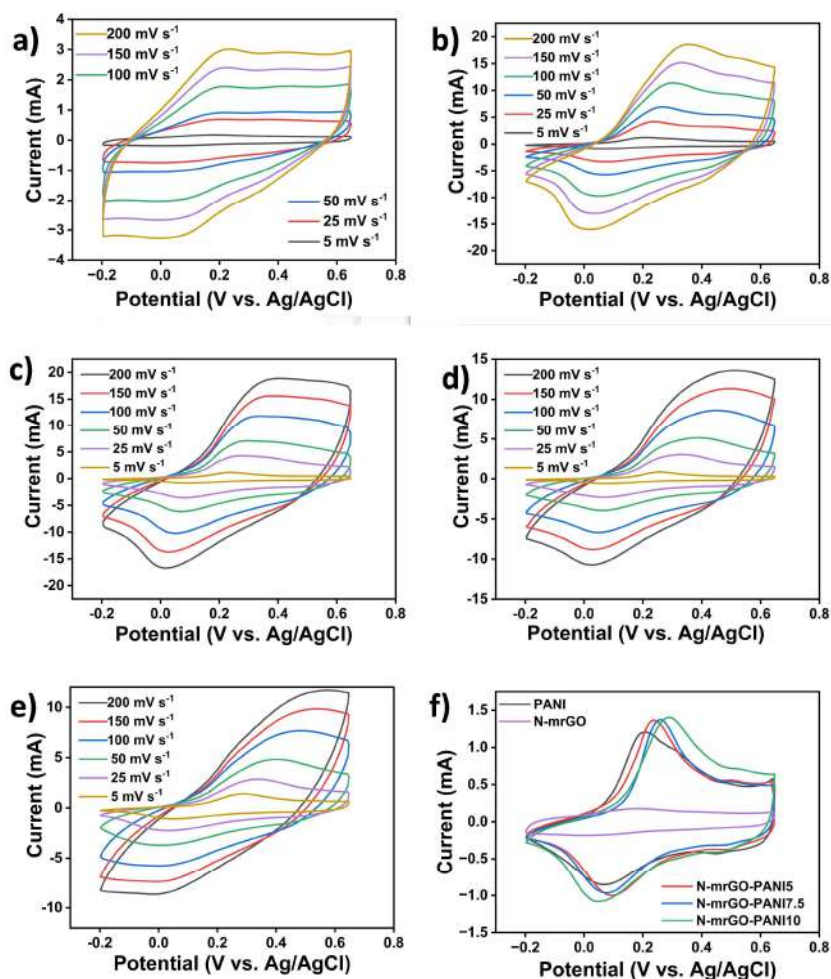


Figure 3.10: CV recorded in different scan rates of (a) N-mrGO, (b) PANI, (c) N-mrGO-PANI5, (d) N-mrGO-PANI7.5, (e) N-mrGO-PANI10, (f) CV of PANI, N-mrGO, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 at a scan rate of 5 mV s^{-1} .

potential window of -0.2 to 0.65 V to evaluate the redox behavior of the samples. The CV curves recorded at various scan rates are shown in

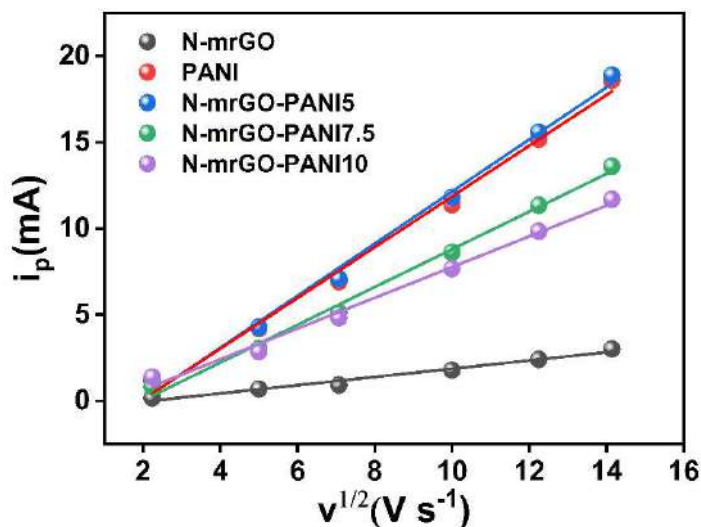


Figure 3.11: Plot of peak current vs. the square root of scan rate

Table 3.1: Linear fitting parameters of peak current (i_p) versus square root of scan rate ($v^{1/2}$) for N-mrGO, PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10

Sample	Intercept	Slope	R ²
N-mrGO	-5.22×10^{-4}	2.39×10^{-4}	0.97442
PANI	-0.00286	0.00147	0.99031
N-mrGO-PANI5	-0.00296	0.00151	0.9926
N-mrGO-PANI7.5	-0.00215	0.00109	0.99283
N-mrGO-PANI10	-0.00115	8.91421E-4	0.98942

Figure 3.10. The CV of N-mrGO deviates from the typical rectangular shape characteristic of EDLC-type materials and displays a pair of redox peaks, attributed to the presence of nitrogen dopants that introduce redox

centers on the rGO. In contrast, the CV profiles of N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 resemble that of pristine PANI, exhibiting two distinct sets of redox peaks corresponding to the reversible transitions between leucoemeraldine and emeraldine, and emeraldine and pernigraniline oxidation states of PANI^{44, 49}.

The peak current (i_p) versus the square root of the scan rate ($v^{1/2}$) was plotted for N-mrGO, PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10⁵⁰. The linear relationship observed in each case indicates that the redox process in all the materials is diffusion-controlled. Among the samples, N-mrGO-PANI5 exhibited the highest slope (0.00151), suggesting enhanced electrochemical activity and more efficient charge transport. However, with increasing PANI content, the slope gradually decreases, indicating higher internal resistance and diffusion limitations. The high R^2 values (> 0.97) for all samples confirm the strong linear correlation.

The charge storage mechanism of the N-mrGO-PANI electrodes was analyzed using Dunn's model⁵¹. The capacitive (surface-controlled) and diffusion-controlled contributions were quantitatively separated using this method. At 25 mV s^{-1} , all samples exhibit mixed charge storage behavior. This indicates that fast surface redox reactions and ion diffusion into the bulk of the active material coexist together. For all electrode material, the capacitive contribution increases progressively with scan rate ($5\text{-}200 \text{ mV s}^{-1}$), and the diffusion-controlled contribution decreases. This reflects kinetic limitations on ion diffusion at higher scan rates and the dominance of surface-controlled processes. N-mrGO-PANI7.5 displays the highest capacitive contribution across the entire scan-rate range, reaching $\sim 75\%$ at $\geq 100 \text{ mV s}^{-1}$, indicating an optimal

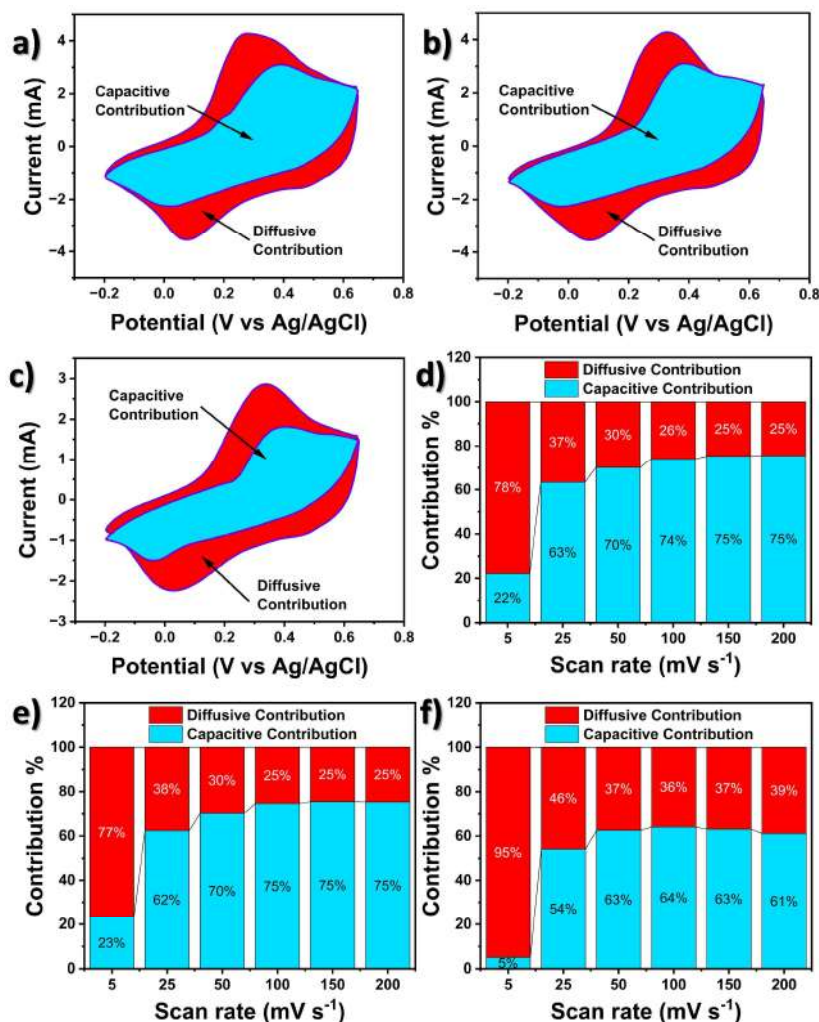


Figure 3.12: Calculations performed using Dunn's model showing the separation of capacitive and diffusive contributions at a scan rate of 25 mV/s for (a) N-mrGO-PANI5, (b) N-mrGO-PANI7.5, and (c) N-mrGO-PANI10. The capacitive and diffusive contributions at various scan rates (d) N-mrGO-PANI5, (e) N-mrGO-PANI7.5, and (f) N-mrGO-PANI10.

balance between electroactive surface area and ion transport pathways. In comparison, N-mrGO-PANI5 shows relatively higher diffusion control at low scan rates. The N-mrGO-PANI10 is predominantly diffusion-controlled at low scan rate (~95% at 5 mV s⁻¹) and retains a

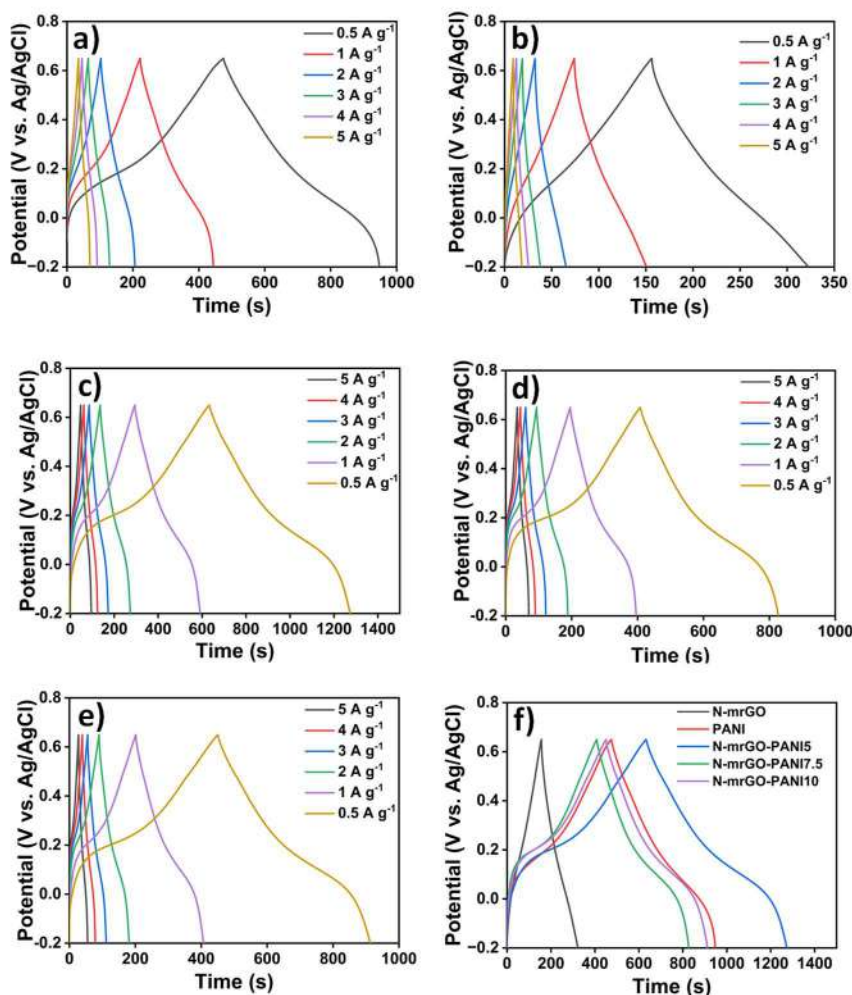


Figure 3.13: GCD curves of (a) *N*-mrGO, (b) PANI, (c) *N*-mrGO-PANI5, (d) *N*-mrGO-PANI7.5, (e) *N*-mrGO-PANI10, (f) GCD of *N*-mrGO-PANI5, *N*-mrGO-PANI7.5, and *N*-mrGO-PANI10 at a current density of 0.5 A g^{-1} .

lower capacitive fraction even at higher scan rates, indicating restricted on accessibility due to excessive PANI loading.

The electrochemical performance of the samples was further evaluated using GCD measurements. The GCD curves of *N*-mrGO, PANI, *N*-mrGO-PANI5, *N*-mrGO-PANI7.5, and *N*-mrGO-PANI10 at different

current densities are shown in Figure 3.13. All the samples exhibited nearly triangular GCD profiles, indicating excellent capacitive behavior and good electrochemical reversibility. The PANI and PANI-containing samples show slight deviation from the ideal triangular shape because of their pseudocapacitive nature⁵².

Among the different samples, N-mrGO-PANI5 showed the longest discharge time, reflecting its superior specific capacitance. The superior performance can be attributed to the better chain stabilization and reduced chain entanglement by N-mrGO sheets. In the case of N-mrGO-PANI7.5 and N-mrGO-PANI10, there is a slight reduction in discharge time, and this is due to the poor chain stabilization as the PANI content increases. The specific capacitance values of N-mrGO, PANI, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 are calculated as 189.87, 557.66, 748.97, 486.35, and 536.50 F g⁻¹, respectively. These results confirm that the PANI loading in N-mrGO-PANI5 yields an optimal balance between conductivity, redox activity, and ion accessibility⁵³.

3.2.4 Supercapacitor Device Performance

A symmetric coin-cell type supercapacitor was fabricated using N-mrGO-PANI5 and 1M H₂SO₄ as the electrolyte. The potential window for the measurement was set at 0.0 V to 0.8 V as obtained from the three-electrode measurement. The CV of the device were recorded at different scan rates and the results are presented in Figure 3.14a. The shape of the CVs is not varying as the scan increases, and this indicates that the device has an excellent rate capability^{54, 55}. GCD measurements of the device

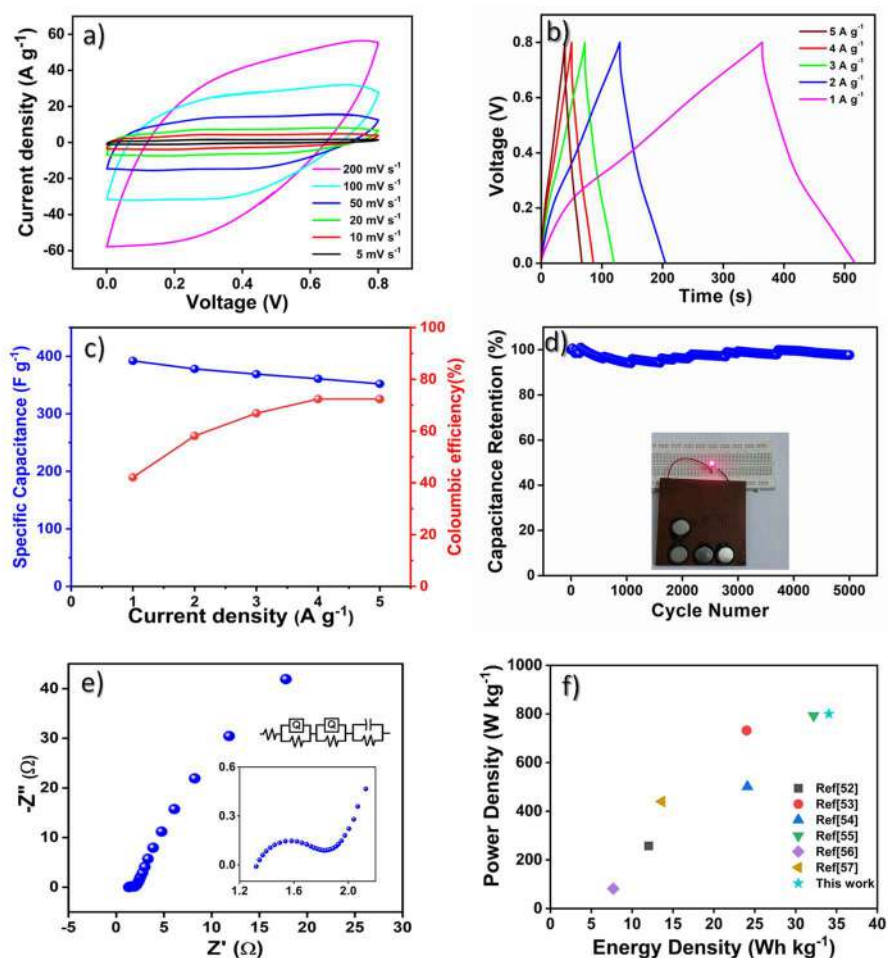


Figure 3.14: Electrochemical characterization of fabricated symmetrical supercapacitor device (a) CV recorded in different scan rates, (b) GCD recorded at different current densities, (c) Specific capacitance at different current densities calculated from GCD, (d) Cyclic stability of symmetric device, (e) Nyquist plot, (f) Ragone Plot.

were carried out at different current densities and the results are represented in Figure 3.14b. The specific capacitance of the device was calculated from the GCD curve and is represented in Figure 3.14c. The capacitance from different current densities indicates that the device also

Table 3.2. Fitted EIS parameters of the device.

Element	Parameter	Value
Solution resistance	Rs	1.303 Ω
Interfacial branch	R1	0.569 Ω
	Q1	$4.185 \times 10^{-3} \text{ S s}^n$
	n1	0.602
Diffusion branch	R2	$9.08 \times 10^6 \Omega$
	Q2	0.616 S s^n
	n2	0.56
Low-frequency branch	R3	119.2 Ω
	C	0.397 F

exhibited a high-rate capability of 89.8%. Further both the energy density and power density were calculated. The device exhibited a moderately high energy density of 34.071 Wh kg⁻¹ and a high-power density of 800 W kg⁻¹.

The coulombic efficiency (CE) of the device at different current densities was also calculated. The results are represented in Figure 3.14c. The CE increases with an increase in current density, starting from 42% at 1 A/g and reaching a stable value of ~72% at 4-5 A/g. This trend indicates reduced charge losses at higher currents, suggesting improved reversibility and stable charge/discharge processes.

Conducting polymers used as supercapacitor electrodes generally exhibit poor cyclic stability due to repeated swelling and shrinkage of polymer chains during redox processes, which causes mechanical degradation and

loss of electrical integrity. This inherent instability leads to progressive capacitance fading and limits their long-term practical application. In

Table 3.3: Comparison of our work with similar supercapacitor electrode materials.

System	Specific Capacitance (F g ⁻¹)	Power Density (W kg)	Energy Density (Wh kg)	Cyclic Stability	Reference
N-rGO/PANI	346.3 (1 A g ⁻¹)	257.9	12.02	81.3% (5000 cycles)	²
rGO/PANI	97 (1 A g ⁻¹)	732	24	82% (5000 cycles)	¹²
Ionic liquid/RGO/PANI	791 (1 A g ⁻¹)	501	24.1	91.5% (1000 cycles)	¹³
PANI/ 3-D graphene	789.9 (1 A g ⁻¹)	793.3	32.2	90% (5000 cycles)	¹⁵
PANI/rGO	409 (1 A g ⁻¹)	81.8	7.7	87% (5000 cycles)	¹⁷
PANI/N-graphene	808.7 (1 A g ⁻¹)	440	13.63	96% (5000 cycles)	¹⁹
This Work	383.3 (1 A g⁻¹)	800	34.071	97.64% (5000 cycles)	--

contrast, the material developed in this work shows significantly enhanced cyclic stability. The fabricated device retains 97.64% of its capacitance after 5000 charge-discharge cycles, clearly demonstrating an excellent cycle life and improved structural robustness compared to

conventional conducting polymer-based supercapacitors. A slight decrease in capacitance retention was observed around 1000 cycles, which is attributed to the mechanical stress associated with the repeated swelling and shrinking of the conducting polymer during redox cycling⁵⁶. With further cycling, the polymer matrix gradually relaxes, leading to the opening of additional pores and improved electrolyte penetration into the electrode bulk. This enhanced ion accessibility results in a subsequent increase in capacitance.

The Nyquist plot of the device is shown in Figure 3.14e, and the corresponding electrochemical impedance spectroscopy (EIS) data were fitted with the equivalent circuit $R_s-(R_1\parallel Q_1)-(R_2\parallel Q_2)-(R_3\parallel C)$. The fitted parameters are summarized in Table 3.2. The high-frequency region of the Nyquist plot displays a semicircle, whereas the low-frequency region shows a linear tail. The low solution resistance ($R_s=1.30\ \Omega$) indicates good electrolyte conductivity and effective electrode–electrolyte contact. The small charge-transfer resistance ($R_1=0.57\ \Omega$) reflects efficient electron transport, while the depressed semicircle ($n_1=0.60$) is attributed to surface heterogeneity arising from the porous macromolecular network. The second element ($Q_2=0.56$) suggests Warburg-type diffusion behavior, consistent with ion transport within the composite matrix, although the large error in R_2 indicates a predominantly diffusion-controlled process rather than a well-defined resistance. At low frequencies, the large capacitance ($C=0.40\ \text{F}$) and long relaxation time highlight the significant charge-storage contribution from both PANI pseudocapacitance and the double-layer capacitance of N-doped rGO. The performance of the device is compared with similar materials, and the results are summarized in Table 3.3. For further clarity the results also plotted as a Ragone plot (Figure 3.14f).

3.3 Conclusion

This chapter presents the successful synthesis and detailed investigation of a covalently functionalized hybrid electrode material. PANI was successfully attached to N doped rGO through an amide linkage. The materials were analyzed using FTIR, UV-Vis, Raman, XPS, SEM, TEM, and TGA analyses. The materials demonstrated improved structural integrity and thermal stability compared to pristine PANI and N-mrGO. To evaluate the effect of PANI content, three different compositions, N-mrGO-PANI5, N-mrGO-PANI7.5, and N-mrGO-PANI10 were systematically synthesized and studied.

Electrochemical performance was studied using CV, GCD, peak current versus square root of scan rate analysis, and Dunn's model. The results indicate that the charge storage mechanism arises from surface-controlled capacitive processes and diffusion-controlled faradaic reactions. Among the three compositions, N-mrGO-PANI5 exhibited the highest specific capacitance and superior rate capability, attributed to the optimized PANI loading and efficient charge transfer at the PANI/N-mrGO interface.

The N-mrGO-PANI5 was then used for the fabrication of a symmetric supercapacitor device. The device delivered a high specific capacitance of 392 F g^{-1} at a current density of 1 A g^{-1} and retained 89.8% of its capacitance at 5 A g^{-1} , demonstrating excellent rate capability. Long-term cycling studies showed a high capacitance retention of 97.64% after 5000 charge/discharge cycles. The EIS analysis confirmed low internal resistance and efficient ion transport of the device. Furthermore, the device achieved a high energy density of 34.07 Wh kg^{-1} along with a

power density of 800 W kg⁻¹. This study indicates that covalent functionalization of PANI with N-mrGO as an effective strategy for developing highly stable and high-performance supercapacitor electrodes.

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Chapter 4

Polyaniline-Functionalized Sulfur and Nitrogen Co-Doped rGO: Towards Sustainable, Ultra-Stable Supercapacitors with Superior Energy Density and High Retention Rate

This chapter extends the N-mrGO–PANI system by incorporating sulfur co-doping to enhance electrochemical performance and stability. Sulfur introduces additional redox-active sites and improves charge transfer and ion diffusion. The covalently integrated S,N co-doped rGO/PANI hybrid demonstrates synergistically enhanced structural integrity, interfacial interaction, and overall electrode performance.

4.1 Introduction

The N-mrGO-PANI systems described in Chapter 3 showcased excellent energy storage properties compared to the previously reported PANI/rGO systems. The enhancement in electrode performance can be attributed to the dual strategy employed to stabilize the polymer chain. In this chapter, we propose the introduction of S as an additional dopant to further enhance the redox properties of rGO and structural stability of PANI, utilizing additional non-covalent interactions. The N doping improves electronic conductivity and introduces favorable interactions between PANI and rGO. The introduction of S as a co-dopant can create additional redox-active centers within the rGO lattice and thereby increase the Faradaic contribution^{1, 2}. S doping also introduces distinct chemical environments capable of participating in reversible redox processes, which will facilitate improved charge transfer and ion diffusion.

In this chapter, a PANI covalently functionalised with S and N co-doped rGO system is designed, synthesized, and systematically characterized to study the effect of dual heteroatom incorporation on the structural features, interfacial interactions, and electrochemical response. The study aims to utilize the synergistic effects of S and N doping and to demonstrate how targeted atomic-level modifications can be used to progressively improve the performance of PANI/rGO electrodes⁴.

4.2 Results and Discussions

The detailed procedure adopted for the synthesis of S and N co-doped rGO functionalised with PANI is given in Chapter 2. The synthetic

scheme is presented in Figure 4.1. GO was synthesized from graphite powder using a modified Hummers' method. Aniline was then linked to GO through an amide linkage between the carboxylic acid groups of GO and the amine groups of aniline. Steglich amidation, a mild and efficient method for amide bond formation using DCC/DMAP as coupling agents, was employed to carry out the amide coupling reaction. The detailed mechanism is given in Figure 3.2.

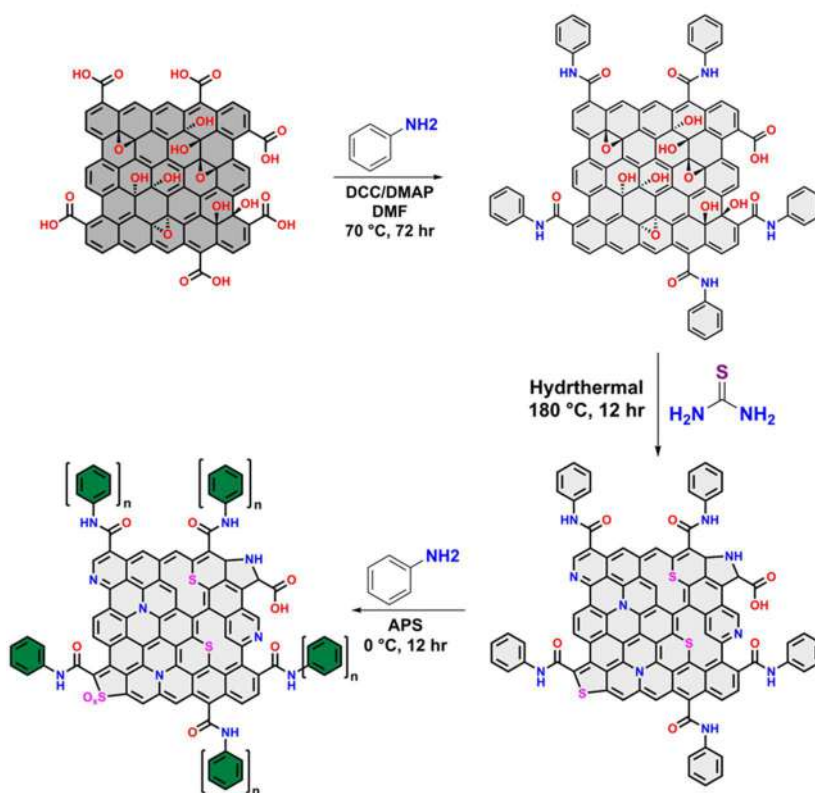


Figure 4.1: *Synthesis scheme of SN-mrGO-PANI.*

4.2.1 Structural and Spectroscopic Characterization

The vibrational frequencies of different functional groups present in the materials were investigated using FT-IR spectroscopy. Figure 4.2 shows

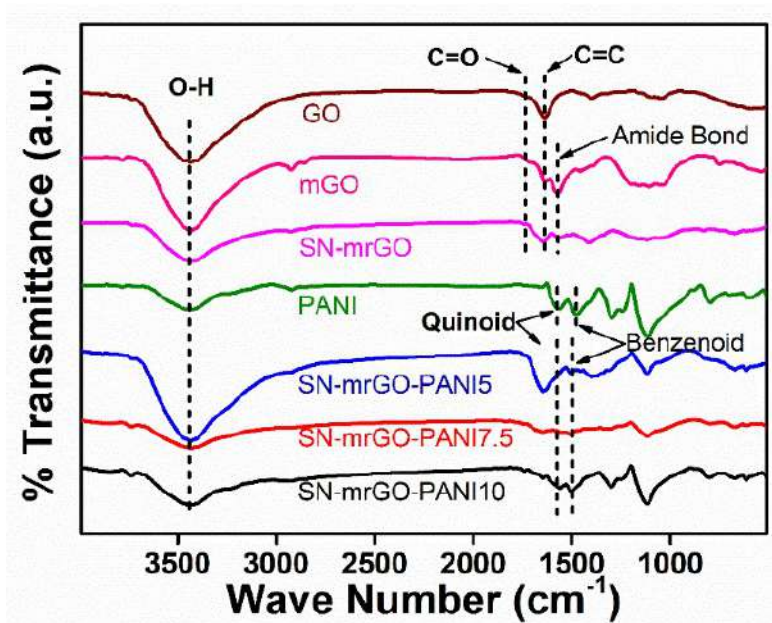


Figure 4.2: FTIR spectra of GO, mGO, SN-mrGO, PANI SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10.

the FT-IR spectrum of PANI, GO, mGO, SN-mrGO, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10. The GO shows bands at 1725, 1637, 1401, and 1092 cm^{-1} corresponding to C=O, C=C, O-H bending, and C-O-C bending vibrations, respectively⁷. The spectrum of mGO has all the major absorption peaks of GO. In addition to this, mGO has a new peak that appeared at 1570 cm^{-1} corresponding to the formation of a new amide bond, indicating the successful functionalization of GO with aniline monomer. PANI shows the characteristic bands at 1565, 1476, 1295, and 1121 cm^{-1} corresponding to quinoid stretching, benzenoid stretching, C-N-C stretching, and N-H bending, respectively. FT-IR spectra of SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 retain the major absorption peaks of PANI with a small shift in intensities. The shifting of peaks confirms the

successful incorporation of polyaniline into SN-mrGO. It can also be seen that the peaks corresponding to SN-mrGO are masked by pristine PANI peaks⁹⁻¹².

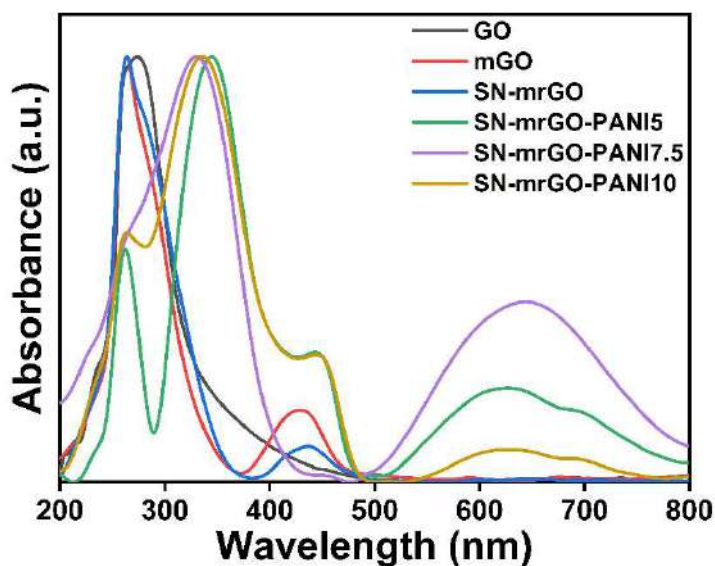


Figure 4.3: UV-Visible spectra of GO, mGO, SN-mrGO, PANI, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10.

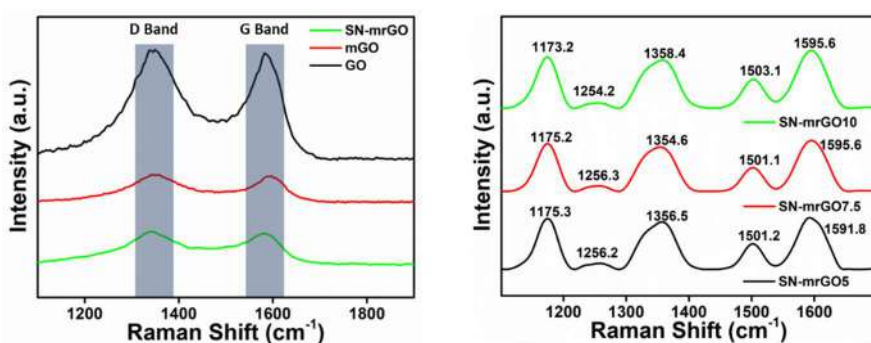


Figure 4.4: FT-Raman spectra of GO, mGO, SN-mrGO, PANI, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10.

The electronic structure of the samples was analyzed using UV-visible spectroscopy, and the spectra are given in Figure 4.3. The UV-visible spectrum of GO shows peaks at 274 nm and 334 nm, and is assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The corresponding peaks of mGO were observed at 263 nm and 429 nm, respectively. The $n \rightarrow \pi^*$ transition in mGO shows a noticeable red shift due to the amide bond, which further confirms the amide bond formation between GO and aniline. The SN-mrGO also showed two peaks in the UV-Vis spectrum similar to those of GO and mGO. The peak at 264 nm corresponds to $\pi \rightarrow \pi^*$ and the peak at 437 nm corresponds to the $n \rightarrow \pi^*$ transition, respectively. The $n \rightarrow \pi^*$ transition in SN-mrGO is further redshifted compared to mGO due to the increase in extended conjugation through the removal of oxygen functionalities during hydrothermal reduction. The UV-visible spectra of SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 are similar to that of PANI and have three peaks around ~ 327 nm, ~ 447 nm, and ~ 627 nm corresponding to $\pi \rightarrow \pi^*$, $\pi \rightarrow \text{polaron}$, and $\text{polaron} \rightarrow \pi^*$ ¹⁴.

The chemical structure of the prepared samples was analyzed using FT-Raman analysis, and the results are presented in Figure 4.4. The FT-Raman spectra of GO, mGO, and SN-mrGO D-band and G-band are around ~ 1580 and 1350 cm^{-1} , and the values are listed in Table 4.1. The D-band in the spectra originates from the defects, and the G-band originates from the in-plane vibrations of C=C in the graphitic structure. The I_D/I_G ratio of GO, mGO, and SN-mrGO remained unchanged, indicating that the defects in the samples were not significantly altered during functionalization and reduction. In the functionalization process, the monomer is added primarily to the carboxylic acid groups in the periphery of the GO sheet, which does not affect existing defects. However, during the reduction process, the removal of oxygen functional

groups typically decreases defect density, while heteroatom doping introduces additional defects. These opposing effects balance out, resulting in a stable I_D/I_G ratio. After incorporating PANI into SN-mrGO, the FT-Raman spectra showed characteristic peaks of PANI around $\sim 1171\text{ cm}^{-1}$, $\sim 1256\text{ cm}^{-1}$, $\sim 1358\text{ cm}^{-1}$, $\sim 1503\text{ cm}^{-1}$, and $\sim 1595\text{ cm}^{-1}$, which correspond respectively to the in-plane bending of C-H in the semi-quinoid or benzene structures, vibration associated with deformation of the benzene structure, vibration of C-N in the polaronic structure, deformation of N-H in the semi-quinoid structure, and stretching vibration of C=C. It should also be noted that after incorporation, the D band and G band are not observed, indicating that the SN-mrGO is completely covered by PANI chains.

High-resolution XPS spectra were recorded to examine the formation of the amide bond between rGO and aniline, as well as to study the doping of S and N to the carbon skeleton of mrGO. The XPS analysis results were presented in Figure 4.5. In the XPS survey spectrum (Figure 4.5a) of GO, only C 1s and O 1s are detected. On the other hand, for mGO, in addition to C 1s and O 1s, a new signal appears around 399.5 eV corresponding to N 1s, indicating successful coupling of aniline monomer to the GO through an amide bond. After simultaneous reduction and doping of the mGO, the XPS survey spectrum of SN-mrGO, in addition to C 1s, O1s, and N 1s, a new peak appears corresponding to S 2p, indicating the successful doping.

The deconvoluted C 1s spectra (Figure 4.5b) of mGO contain four peaks at 284.55 eV, 285.45 eV, 286.4 eV, and 288.2 eV corresponding to C=C, C-O, -CONH-, and -COOH, respectively¹⁶. The deconvoluted spectra of N 1s of mGO (Figure 4.5c) show only a single peak at 399.53 eV

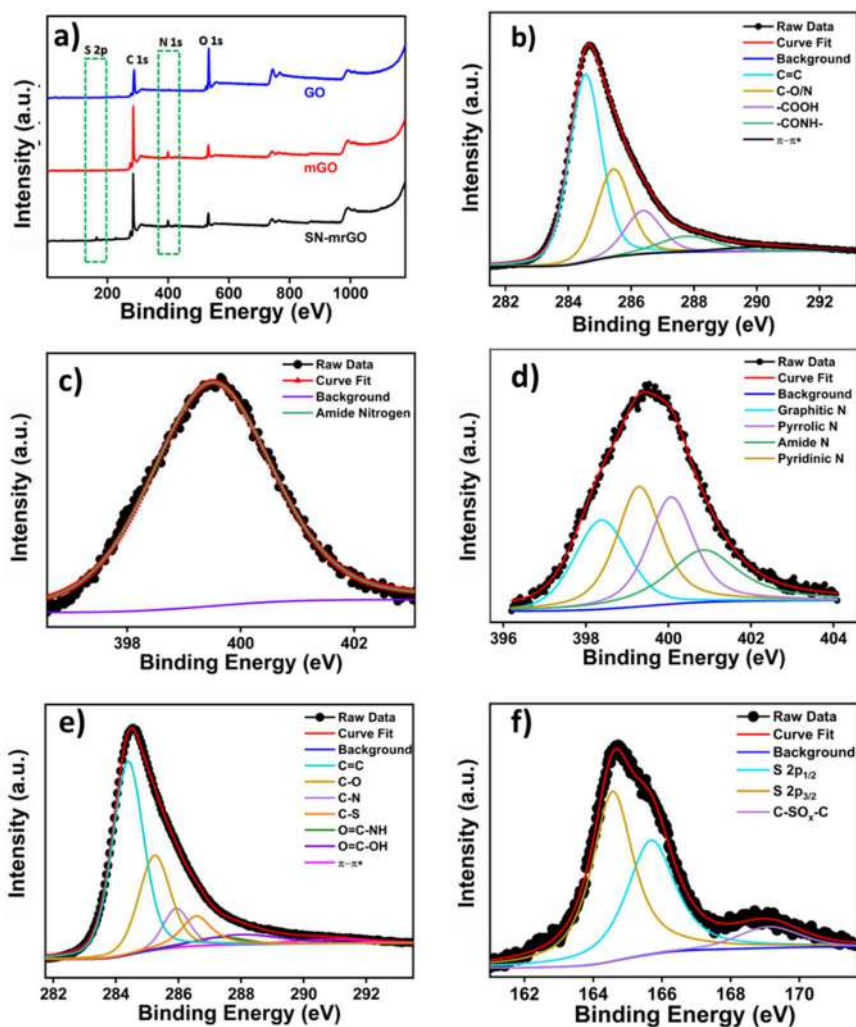


Figure. 4.5: (a) XPS survey spectrum of GO, mGO, and SN-mrGO (b-c) C 1s and N 1s spectrum of mGO (d-f) C 1s, N 1s and S 2p spectrum of SN-mrGO.

corresponding to the amide bond. After the simultaneous reduction and doping of mGO, the deconvoluted C 1s spectra of SN-mrGO (Figure 4.5d) show peaks at 284.4 eV, 285.5 eV, 285.95 eV, 286.6 eV, 287.3 eV, and 288.3 eV corresponding to C=C, -C-O-, -C-N-, -C-S-, -CONH-, and -

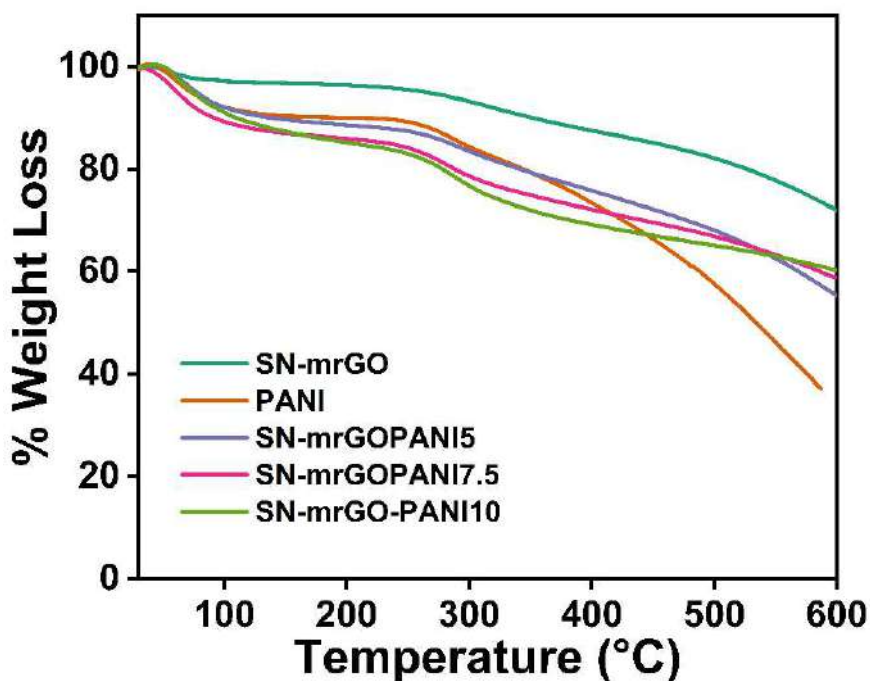


Figure 4.6: TGA curve of SN-mrGO, PANI, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10.

COOH, respectively. The deconvolution of N 1s (Figure 4.5e) shows four peaks at 398.39 eV, 399.29 eV, 400.07 eV, and 400.85 eV which can be attributed to graphitic N, pyridinic N, pyrrolic N, and amide N respectively and the S 2p spectrum after deconvolution (Figure 4.5f) shows three peaks at 164.57 eV, 165.7 eV and 169.15 eV corresponding to $2p_{3/2}$, $2p_{1/2}$ and $-C-SO_x-C$ species¹⁷ indicating the incorporation of N and S onto the carbon skeleton of mrGO.

The thermal stability of SN-mrGO, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 was examined with TGA in N_2 atmosphere, and the resulting thermograms are represented in Figure 4.6. The thermogram of SN-rGO shows a loss of about 4% between 80 °C

and 120 °C due to the desorption of water. No additional weight loss is observed up to 250 °C, indicating good thermal stability under inert conditions in this range. A gradual weight loss of about 25% is observed from 250 °C to 600 °C, which is due to the loss of oxygen functionalities, partial pyrolysis of the rGO framework, and decomposition of residual organic species or labile S/N-containing moieties associated with the S, N co-doping. SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 exhibited a three-stage mass loss, similar to PANI. All the materials exhibited an initial mass loss of about 10%, corresponding to the removal of moisture. No significant mass loss is observed up to ~220 °C, indicating good thermal stability of the macromolecular system in this range. The loss of dopants and oligomers is observed between 260 °C and 320 °C, with a loss of about 10% for PANI and SN-mrGO-PANI5, and about 15% for SN-mrGO-PANI7.5 and SN-mrGO-PANI10. Beyond 320 °C, degradation of the polymer backbone becomes dominant, leading to a further mass loss of about 47%, 24.6%, 16.3%, and 14.8% for PANI, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10, respectively. The corresponding residual weights at 600 °C are 37%, 55.4%, 58.7%, and 60.2%. The thermal stability of the studied materials is observed to increase with an increase in PANI loading. All show improved thermal stability compared to PANI.

4.2.2 Morphological and Elemental Analysis.

The surface morphologies of SN-mrGO, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 were analyzed using FESEM and HRTEM. The results are presented in Figure 4.7 and Figure 4.8, respectively. The FESEM image of SN-mrGO shows a wrinkled sheet-like structure, and this structure is also clearly visible in TEM.

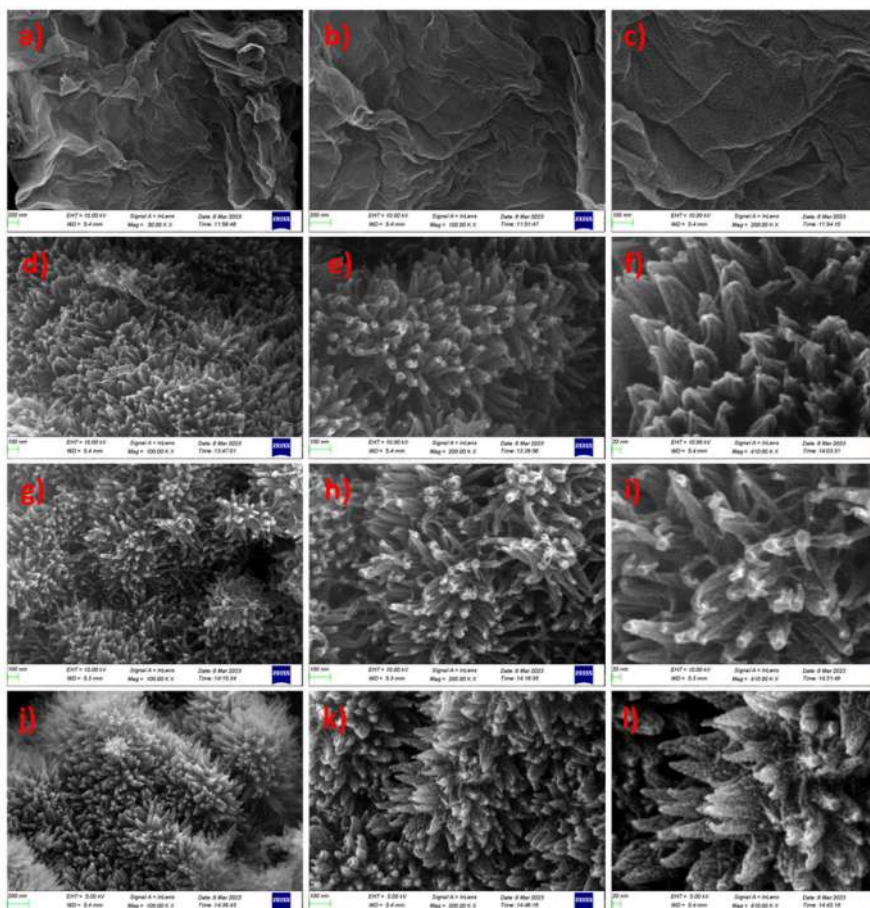


Figure 4.7: FE-SEM images at different magnifications of (a-c) SN-mrGO, (d-f) SN-mrGO-PANI5, (g-i) SN-mrGO-PANI7.5, and (j-l) SN-mrGO-PANI10 are presented.

The FESEM images of SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 at different magnifications are shown in Figure 4.7 c-l. All of the material has a coral-like hierarchical nanostructure associated with short nanowires. These nanostructures enable better surface reactions, thereby enhancing the capacitance. The TEM images of SN-mrGO, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10

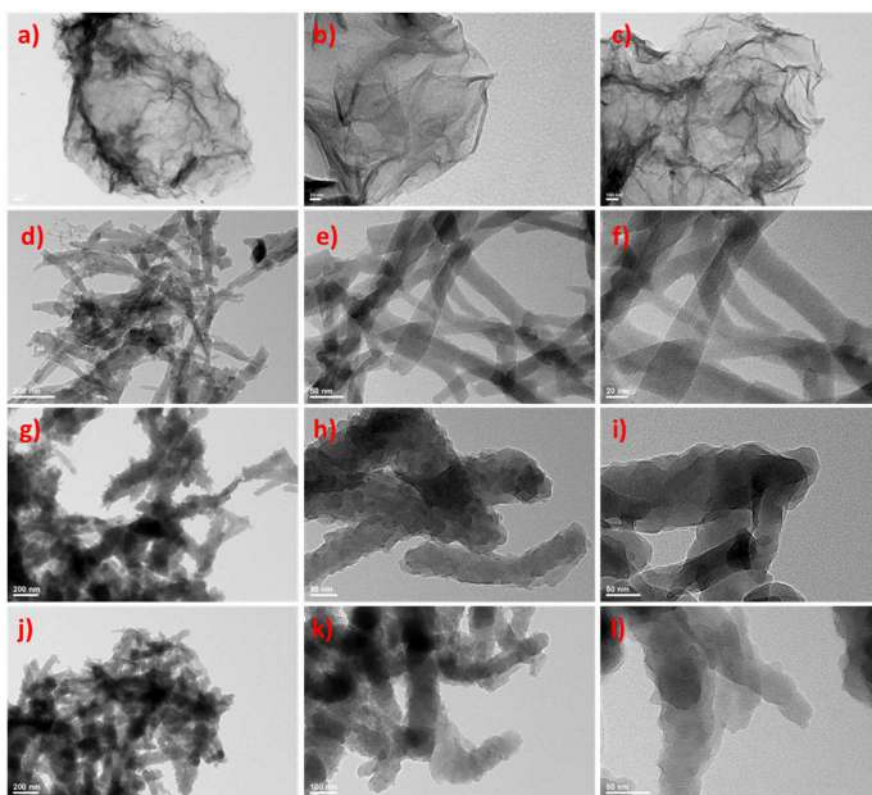


Figure 4.8: HR-TEM images at different magnifications of (a-c) SN-mrGO, (d-f) SN-mrGO-PANI5, (g-i) SN-mrGO-PANI7.5, and (j-l) SN-mrGO-PANI10.

at different magnifications are shown in Figure 4.8 c-l. The results are in good agreement with the morphological characteristics of FESEM images and show the presence of mesopores in the material. The elemental analysis of the SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 is carried out using Energy Dispersive X-ray Analysis (EDAX) measurements. The elemental analysis spectrum obtained from the HRTEM analysis is presented in Figure 4.9. The results confirm the presence of C, N, S, and O in the surface of the

material. The detected elements are distributed on the surface of the material uniformly.

4.2.3 Electrochemical Analysis

The electrochemical characteristics of the materials are analyzed using CV in a three-electrode setup, with Ag/AgCl as the reference electrode, Pt as the counter electrode, and the material coated on a glassy carbon electrode as the working electrode. In all the measurements, 1M H₂SO₄ is used as the electrolyte. The CVs are recorded at a scan rate ranging from 5 mV s⁻¹ to 200 mV s⁻¹. The corresponding CVs obtained are presented in Figure 4.10. The CV curve of SN-mrGO showed a notable deviation from the ideal rectangular shape observed for GO and rGO¹⁸, instead a set of redox peaks are observe. This indicates that, in addition to electrochemical double-layer formation, charge storage also involves Faradaic processes. The Faradaic, or pseudocapacitive, behavior of SN-mrGO arises from the doped S and N, as expected.

The CV of PANI exhibits two sets of redox peaks corresponding to the leucoemeraldine ↔ emeraldine and emeraldine ↔ pernigraniline transition¹⁹. Similarly, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 also display a similar CV with two sets of redox peaks. The oxidation peaks shift toward more positive potentials, while the reduction peaks shift toward more negative potentials.

To better understand the different factors contributing to the electrode's capacitance, we analyzed the CVs of SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 using Dunn's method (Figure 4.11)²⁰. It has seen observed that with the increase of scan rate from 5 to 200 mVs⁻¹, the capacitive contribution increases. This indicates that the

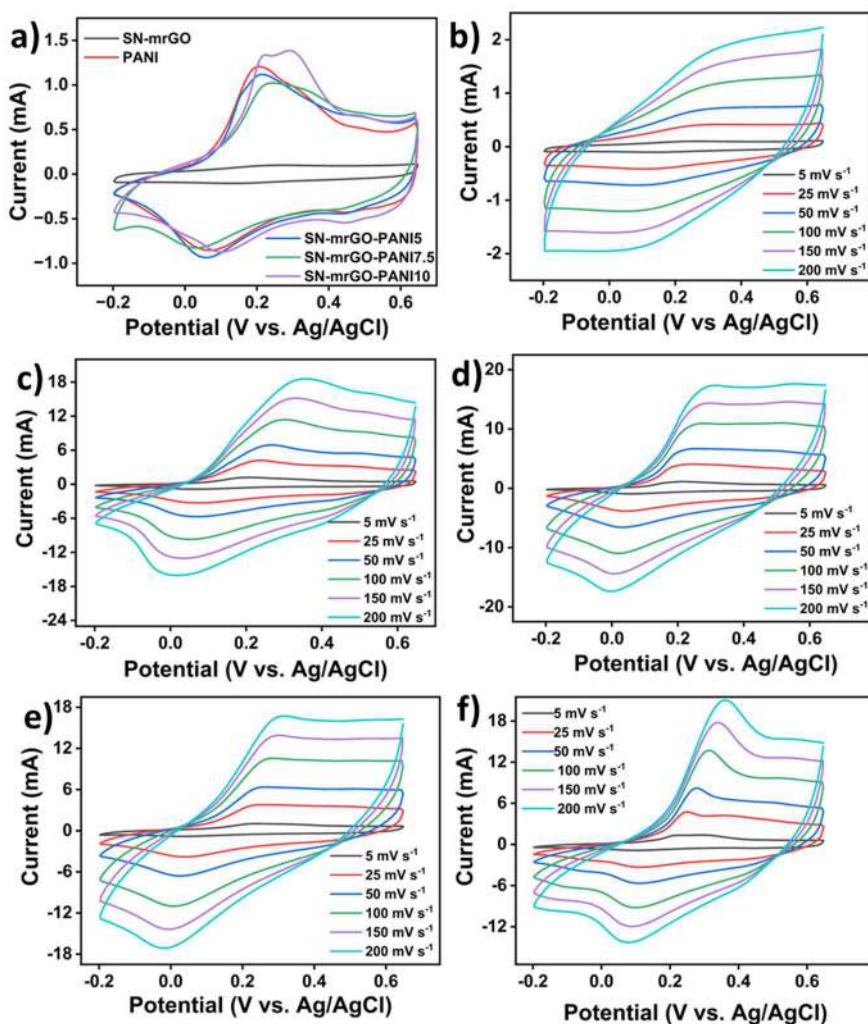


Figure 4.10: (a) CV of PANI, SN-mrGO, SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 at a scan rate of 5 mV s⁻¹. CV recorded in different scan rates of (b) SN-mrGO, (c) PANI, (d) SN-mrGO-PANI5, (e) SN-mrGO-PANI7.5, and (f) SN-mrGO-PANI10.

capacitance mainly arises from surface contribution rather than bulk at higher scan rates. The high capacitive contribution also indicates that the electrodes have high-rate capability.

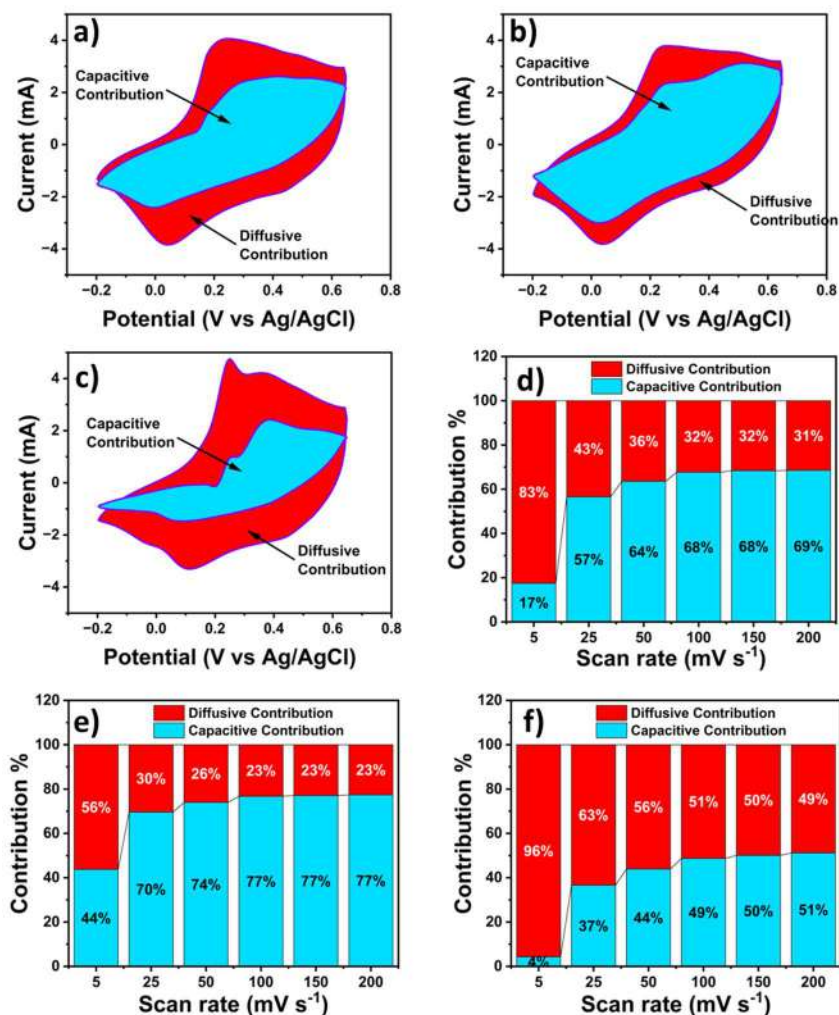


Figure 4.11: Capacitive and diffusive contributions calculated using Dunn's model at a scan rate of 25 mV/s for (a) SN-mrGO-PANI5, (b) SN-mrGO-PANI7.5, and (c) SN-mrGO-PANI10. The capacitive and diffusive contributions at various scan rates for (d) SN-mrGO-PANI5, (e) SN-mrGO-PANI7.5, and (f) SN-mrGO-PANI10.

The GCD measurements of SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 at different current densities were carried out to evaluate their potential as electrode materials for supercapacitor

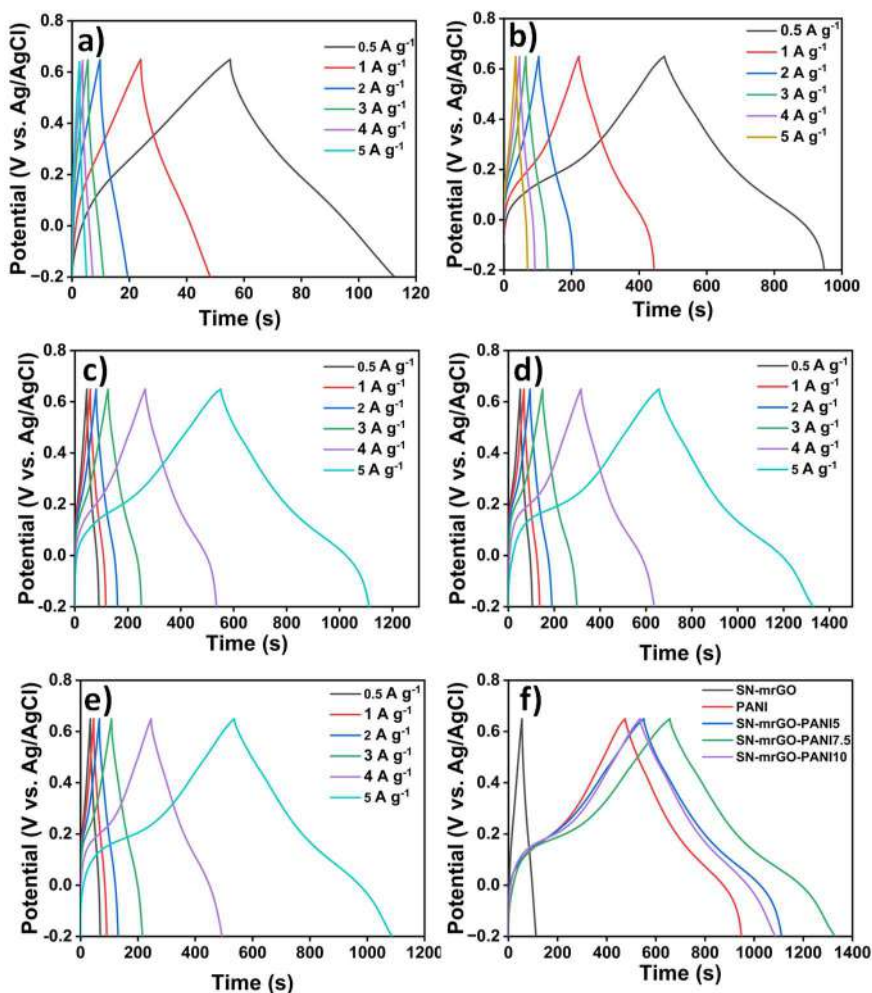


Figure. 4.12: GCD curves of (a) SN-mrGO, (b) PANI, (c) SN-mrGO-PANI5, (d) SN-mrGO-PANI7.5, (e) SN-mrGO-PANI7.10, (f) GCD of SN-mrGO-PANI5, SN-mrGO-PANI7.5, and SN-mrGO-PANI10 at a current density of 0.5 A g^{-1} .

applications, the results are shown in Figure 4.12. The GCD curves exhibit nearly triangular shapes with minimal IR (internal resistance) drop, indicating good capacitive behavior and low internal resistance. The specific capacitances calculated from the GCD curves are presented

in Figure 4.13a. it can be seen that SN-mrGO-PANI7.5 demonstrated the highest specific capacitance of 398.4 F g⁻¹. The cyclic stability of the materials was further assessed through GCD measurements at a current density of 5 A g⁻¹ over 2000 cycles. Consistent with the capacitance results, SN-mrGO-PANI7.5 also exhibited the highest stability, retaining 91.91% of its initial capacitance.

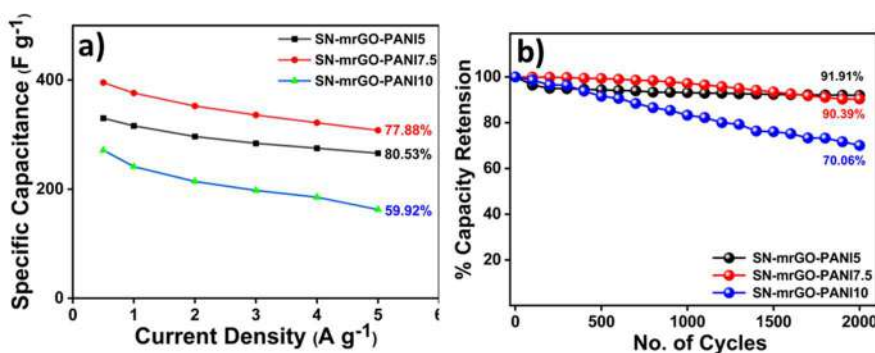


Figure. 4.13: a) Specific capacitance of SN-mGO-PANI5, SN-mGO-PANI7.5, and SN-mGO-PANI10 at different current densities for three-electrode configuration. b) Cyclic stability of SN-mGO-PANI5, SN-mGO-PANI7.5, and SN-mGO-PANI10 in three electrode configuration.

A well-ordered polymer chain can be prepared by using soft templates like rGO. This can lead to the formation of better-accessible redox sites and promote fast diffusion through the polymer network, leading to high specific capacitance and cyclic stability^{21,22}. It is known that polyaniline-based materials with more chemical interaction shows improved performance²³⁻²⁵. It should also be noted that the π - π interaction is not very advantageous for polyaniline since the π -electron system is already electron-rich²⁶. When rGO is used as the template, π - π interaction

between the polymer chain is the more prominent interaction, which is not very beneficial for the electrochemical performance.

Hence, we doped rGO with a heteroatom to introduce more non-covalent interaction between the polyaniline chain and rGO sheet rather than just π - π interaction. Further, we covalently grafted the polyaniline chain to S and N-doped rGO sheet since a strong covalent interaction can increase the electrochemical performance and cyclic stability to a greater extent²⁷. Among the three compositions studied, SN-mrGO-PANI10, though it contained more PANI content, exhibited less specific capacitance, which is because to less chain stabilization and higher self-interactions²⁸ SN-mrGO-PANI7.5, with maximum chain stabilization, has extraordinarily high cyclic stability, has been proven to be the best-performing supercapacitor electrode in our studies.

4.2.4 Supercapacitor Device Performance

Since the SN-mrGO-PANI7.5 has the best supercapacitive performance we have selected this material to fabricate a symmetric supercapacitor device. Electrochemical properties of the device are further studied with CV, GCD, and EIS by fabricating a symmetric supercapacitor device. The results are presented in Figure 4.14. The CVs (Figure 4.14a) were recorded with in a potential window of 0 V to 0.8 V. The deviation of the CV loop from the rectangular shape indicates that the charge storage is mainly due to the pseudocapacitive nature of the device^{29, 30}. The capacitance from CV is calculated and found to be 591 F g⁻¹ at a scan rate of 5 mV s⁻¹ (Figure 4.14b).

The GCD curves of the device was also recorded and presented in Figure 4.14c. Nearly triangular GCD curves indicate that the material has a

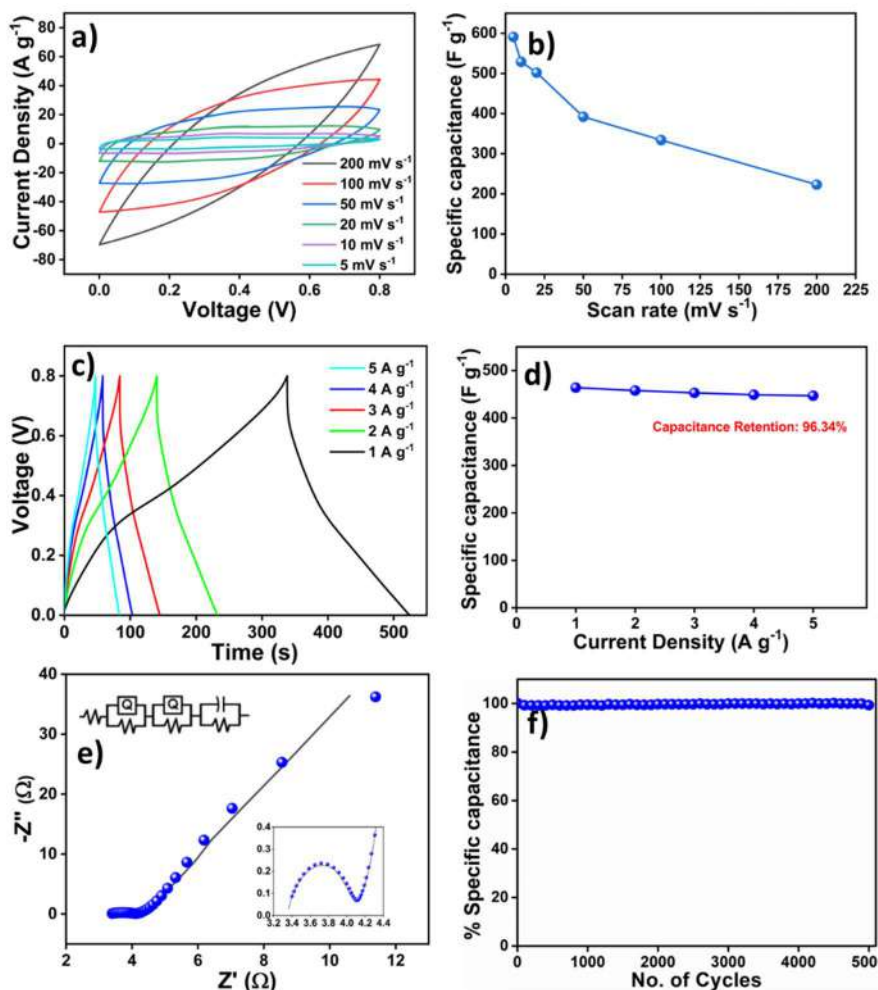


Figure 4.14: Electrochemical characteristics of fabricated device a) CVs, b) capacitance at different scan rates, c) GCD curves, d) Capacitance at different current densities, e) EIS of the device, and f) cyclic stability up to 5000 cycles.

greater reversibility and a capacitive nature³¹. The capacitance values calculated from the GCD curves of the device are 464 F g^{-1} , 458 F g^{-1} , 453 F g^{-1} , 449 F g^{-1} , and 447 F g^{-1} at a current density of 1, 2, 3, 4, and 5 A g^{-1} , respectively (Figure 4.14d). The device shows a higher capacitive retention of 96.34 % even at a higher current density of 5 A g^{-1} . The

Table 4.2: Comparison Table

System	Capacitance	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Cyclic Stability	Ref.
N-rGO/PANI	346.3 at 1 A g ⁻¹	12.02	257.9	81.3% (5000 cycles)	³
rGO/PANI	97 at 1 A g ⁻¹	24	732	82% (5000 cycles)	⁵
Ionic liquid-modified rGO/PANI	791 at 1 A g ⁻¹	24.1	501	91.5% (5000 cycles)	⁶
PANI/3-D graphene	789.9 at 1 A g ⁻¹	32.2	793.3	90% (5000 cycles)	⁸
PANI/rGO	409 at 1 A g ⁻¹	7.7	81.8	87% (5000 cycles)	¹³
PANI/N-graphene	808.7 at 1 A g ⁻¹	13.63	440	96% (5000 cycles)	¹⁵
This Work	464 at 1 A g⁻¹	41.28	799.3	99.35% (5000 cycles)	-

energy density and power density of the device were also calculated and found to be 41.28 Wh kg⁻¹ and 799.3 W kg⁻¹. The very high energy

density and power density extend the range of possible applications for the device, making it capable of replacing batteries in grid energy storage, regenerative braking systems, and uninterruptible power systems. The energy density of the fabricated device is also very close to the energy density of Li-ion batteries, hence effectively bridging the gap between capacitors and batteries.

The cyclic stability of the device is also a crucial factor for real-world applications, and our system is found to be highly stable with 99.35% even after 5000 cycles (Figure 4.14f). A comparison table comprising the performance of similar materials is given in Table 4.2, and the corresponding Ragone plot is represented in Figure 4.15.

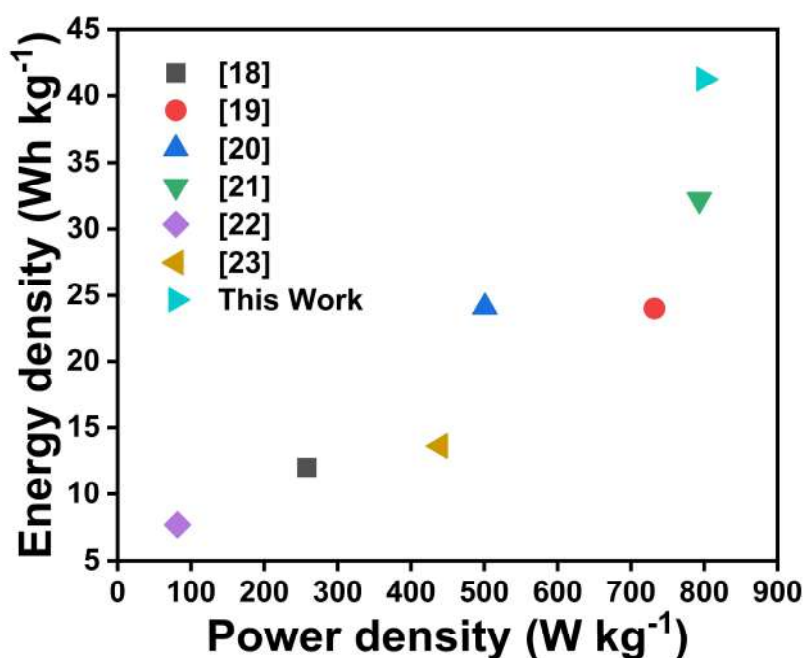


Figure 4.15: Ragone plot

4.3 Conclusions

In this chapter, a high-performance supercapacitor electrode based on the covalent functionalization strategy of PANI with S and N co-doped rGO via amide bond has been demonstrated. The covalent strategy directly addresses the inherent limitations of individual components. The poor cyclic stability of CP-based electrodes and the relatively low specific capacitance and energy density of rGO-based materials was mainly focused. The formation of a macromolecular network effectively suppresses PANI backbone degradation arising from repetitive volumetric expansion/contraction during charge-discharge cycling. It also reduced the restacking and aggregation of rGO sheets, thereby minimizing active surface area loss.

Structural and chemical analyses with FTIR, UV-Vis, Raman, and XPS confirms the successful covalent coupling between PANI and SN-mrGO, along with effective heteroatom doping. The TGA analysis depict the enhanced thermal stability of the covalently functionalized composites. The SEM and TEM reveal a coral like morphology, favorable for the ion transport and electron conduction. Electrochemical investigations carried out using CV, GCD, peak current versus $v^{1/2}$ analysis, and Dunn's model. The analysis clearly demonstrates the synergistic contribution of EDLC and pseudocapacitive charge-storage mechanisms in the SN-mrGO-PANI system.

Among the three compositions investigated, SN-mrGO-PANI7.5 exhibits the most balanced electrochemical performance. The PANI loading was optimal in this composition and this maximizes redox activity without compromising ion diffusion or electrical conductivity. Using this optimized composition, a symmetric supercapacitor device

was fabricated. The performance of the device was evaluated using CV, GCD, EIS, and cyclic stability studies. The device delivers a high specific capacitance of 464 F g^{-1} at 1 A g^{-1} , a power density of 799.3 W kg^{-1} , and an energy density of 41.28 Wh kg^{-1} . Notably, the device retains 99.35% of its initial capacitance after 5000 charge/discharge cycles, representing exceptional cyclic stability for a PANI-based supercapacitor.

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Chapter 5

Poly[4-(phenyldiazenyl)aniline] and Its Derivatives: A New Family of Backbone-Engineered Conducting Polymers with Wider Electrochemical Potential Windows and Intrinsic Derivatization Capabilities.

This chapter overcomes the narrow potential windows and degradation of conducting polymers in aqueous electrolytes by developing a new P4PDA-based polymer family. An azo linkage lowers HOMO energy and shifts redox activity to the backbone. A scalable one-pot synthesis enables functionalization, achieving a stable electrochemical window of 2.7 V.

5.1 Introduction

Despite the long history of conducting polymers¹, achieving stable operation over a wide potential window in aqueous systems still remains unresolved. Electrochemical devices utilizing aqueous electrolytes are inherently constrained by oxygen and hydrogen evolution reactions (OER and HER)², which limits the voltage range. Conducting polymers undergo an irreversible reaction with OER and HER, leading to rapid performance degradation³. At the same time, the ease of functionalization also remains a major bottleneck and limits its wider applications⁴. Tuning mechanical or chemical properties through functionalization usually requires multistep reactions and expensive reagents, increasing material cost and limiting scalability. The chemical modifications of CPs often compromise their electrical properties because of the steric interactions that distort the π -conjugation of the polymer backbone⁵. Together, these limitations prevent conducting polymers from realizing their full potential in practical, large-scale applications⁶.

In this chapter, we present a new polymer P4PDA and its ortho-substituted derivatives were synthesized; the unsubstituted parent polymer is designated PH, while the -COOH, -OH, -OMe, and -SH substituted analogues are designated PCOOH, POH, POME, and PSH, respectively. In the synthesis of P4PDA and its derivatives, 25 mL of 35% HCl is added to 100 mL of distilled water. The azo linkage acts as a proton sink during oxidation and simultaneously withdraws electron density from adjacent carbon atoms, thereby lowering the local HOMO energy⁷. Consequently, charge storage predominantly occurs within the polymer backbone rather than through interfacial Faradaic processes

involving water oxidation, enabling stable operation over wider potential windows in aqueous electrolytes^{8,9}.

In this work, a well-known monomer, 4PDA, is strategically employed to enable facile derivatization and a one-pot polymerization process. The functional group versatility is demonstrated by incorporating diverse functional groups, like -OH, -OMe, -COOH, and -SH. These groups are introduced directly without multistep reactions or expensive reagents. The polymers are synthesized through a simple one-pot, sequential process in an aqueous medium (1 M HCl). This methodology supports scalability and low-cost production. As a result of this backbone engineering strategy, the polymers exhibit a stable, wide operation potential window of 2.5 V in aqueous acidic electrolytes such as 1 M H₂SO₄ and MSA, and extending to 2.7 V in 1 M LiClO₄. These results establish a scalable design framework for a new CP that combines a wider potential window, electrochemical stability, and versatile chemical tunability in aqueous systems.

5.2 Result and Discussion

A detailed synthetic procedure adopted for the synthesis of the new polymer is presented in Chapter 2. In the monomer synthesis strategy, two aniline units are involved, and it is depicted in Figure 5.1. In aniline 1 (A1) and aniline 2 (A2), *ortho* and *meta* positions are available for functional group substitution. The *para* position in A2 is not available, as it is required for polymerization chain growth. Introduction of functional groups at the *ortho* position of A1 and the *meta* position of A2 leads to steric interactions similar to those present in PANI. These steric interactions can disrupt the extended π -conjugation along the polymer

backbone. During the diazotization reaction of the *meta* derivatives of A1, as shown in Scheme 5.1 and Scheme 5.2, more than one product forms, depending on the directing nature of the functional group. This leads to an additional step for monomer isolation and further purification. Therefore, the only suitable position for introducing a functional group is the *ortho* position of A2. Hence, an *ortho*-substituted aniline derivative was used as A2 to introduce functional groups into the polymer chain backbone.

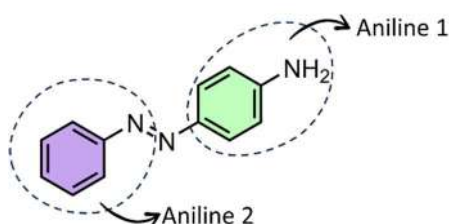
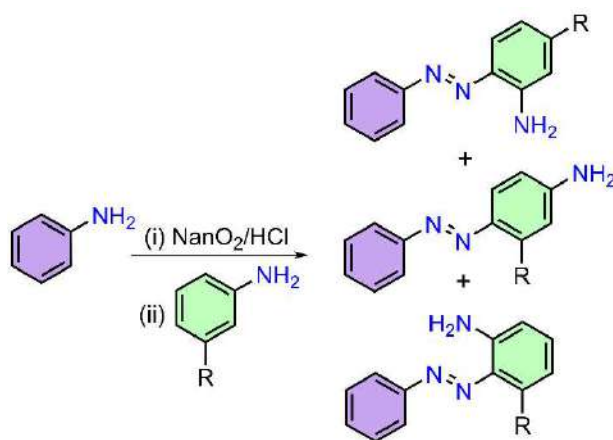
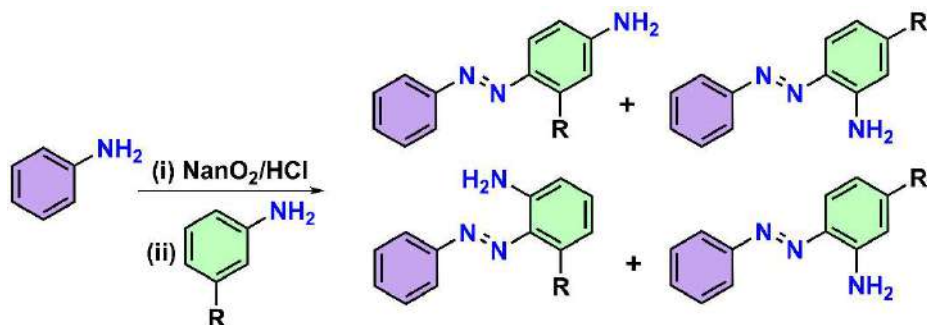


Figure 5.1: Structure of 4PDA.



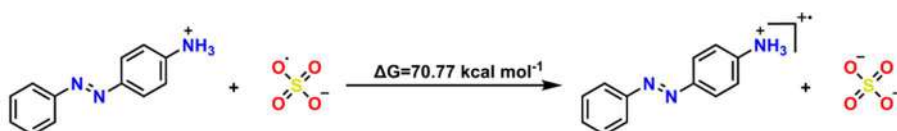
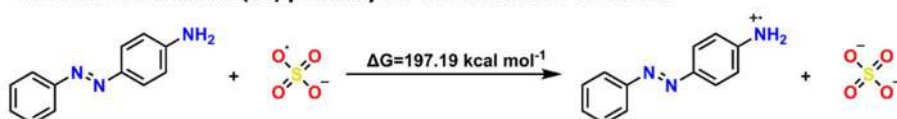
Scheme 5.1: Side reaction for *ortho*-*para* directing substituents.



Scheme 5.2: Side reaction for meta-directing substituents.

5.2.1 Theoretical and Computational Studies

The electron transfer (ET) pathway for the formation of radical



The hydrogen atom transfer (HAT) pathway for the formation of radical

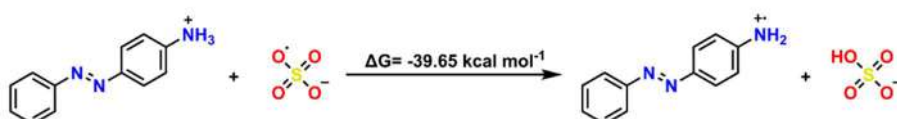
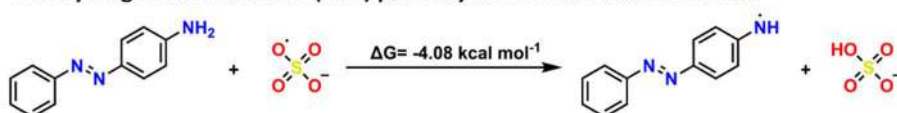


Figure 5.2: Gibbs free energy profiles for the four possible radical formation pathways considered in this study.

The mechanism of polymerization reaction was investigated using density functional theory (DFT) calculations using the BP86/6-31+G(d, p) level theory¹⁰. The structures were optimized, and vibrational

frequency calculations were performed to confirm true minima and to obtain Gibbs free energies. Radical formation was first examined by comparing electron transfer (ET) and hydrogen atom transfer (HAT) pathways from protonated and non-protonated 4PDA¹¹. The calculated Gibbs free energies for ET from non-protonated and protonated 4PDA are 197.19 and 70.77 kcal mol⁻¹, respectively. This indicates that ET is energetically unfavorable. In contrast, the Gibbs free energies for HAT from protonated and non-protonated aniline are -4.08 and -39.65 kcal mol⁻¹, respectively, demonstrating that HAT is energetically favored. The HAT emerges as the dominant radical formation pathway, with protonation significantly lowering the energetic barrier relative to electron transfer. The Gibbs free energy landscape for the four possible pathways is presented in Figure 5.2.

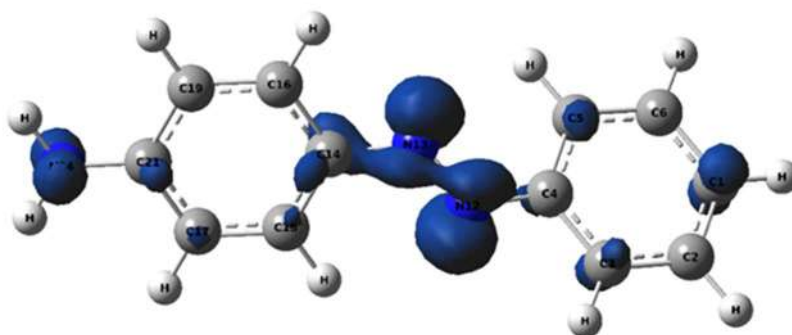


Figure 5.3: *Spin density diagram of the 4PDA radical cation.*

The spin density diagram of the 4PDA radical cation is presented in Figure 5.3. The spin density diagram indicates that the unpaired electron is primarily localized on the nitrogen atoms of the azo (-N=N-) linkage¹². Among the two benzene rings, the highest spin density is observed at the C1 carbon, which is para to the azo linkage on the aniline ring.

Significant spin density is also observed on the amine nitrogen atom¹³. The resonance structure of the 4PDA radical cation is given in Figure 5.4. Nitrogens in the azo bond are less likely to participate directly in coupling reactions because such interactions would disrupt the conjugation between the two aromatic rings, which is energetically unfavorable. Instead, the coupling reaction is more likely to occur between the amine nitrogen and the C1 carbon of another radical species. However, direct coupling between two amine nitrogen atoms is less probable due to the electrostatic repulsion between the positively charged nitrogen centers in the radical cations¹⁴.

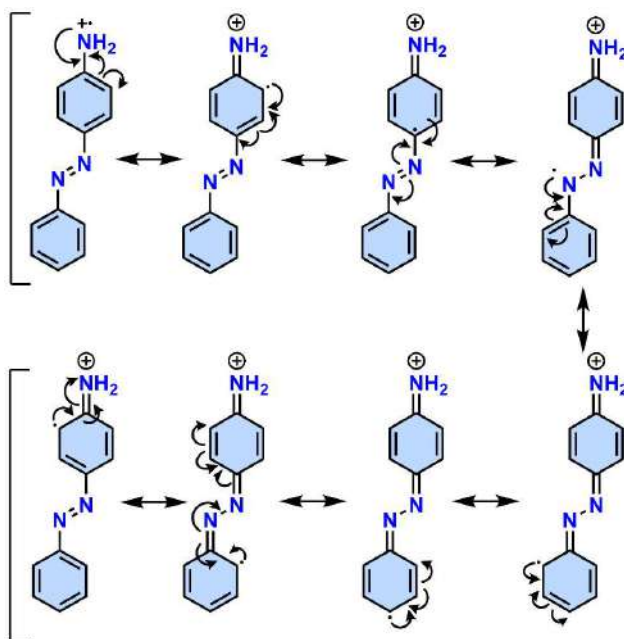


Figure 5.4: *Resonance stabilization of the 4PDA radical cation.*

The resonance structures of the radical cation are shown in Figure 5.4. These canonical forms rationalize the preferential localization of the unpaired electron on specific carbon and nitrogen centers, as discussed in the preceding section. The resonance picture, therefore, directly

supports the identification of C1, C3, C5, N12, N13, C17, C19, and N24 as the most electron-rich sites of the radical cation.

From this distribution, it follows that radical coupling is most likely to proceed via interaction between the nitrogen atom N24 of one radical and a carbon center with high electron density on another radical species. Such N-C coupling pathways are consistent with both the resonance stabilization of the radical cation and the requirement to maintain conjugation along the polymer backbone.

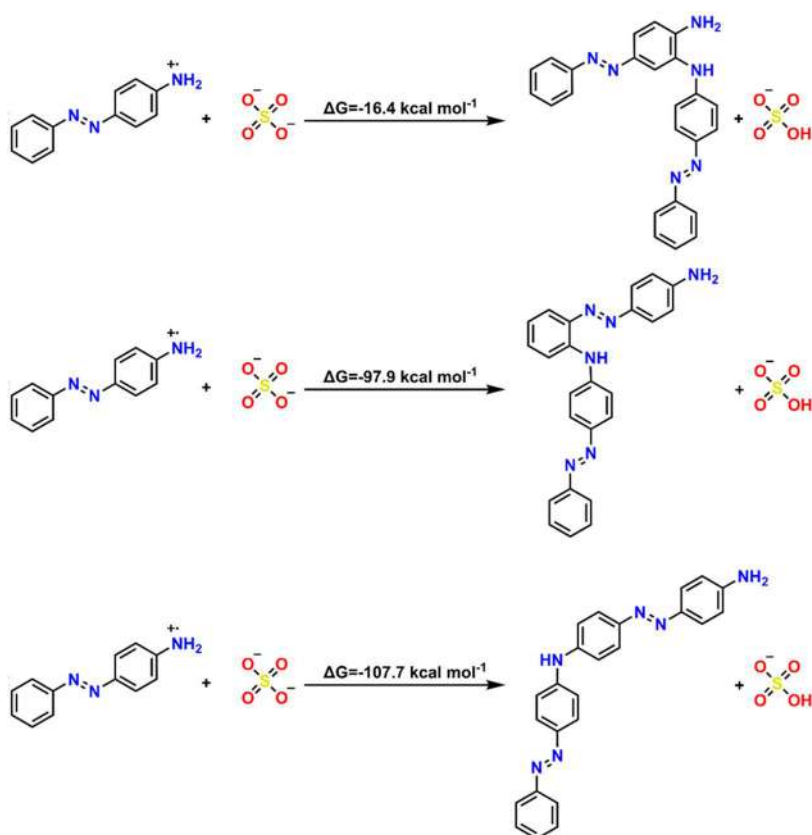


Figure 5.5: Calculated Gibbs free energy changes (ΔG) for the relative thermodynamic favorability of the possible coupling pathways.

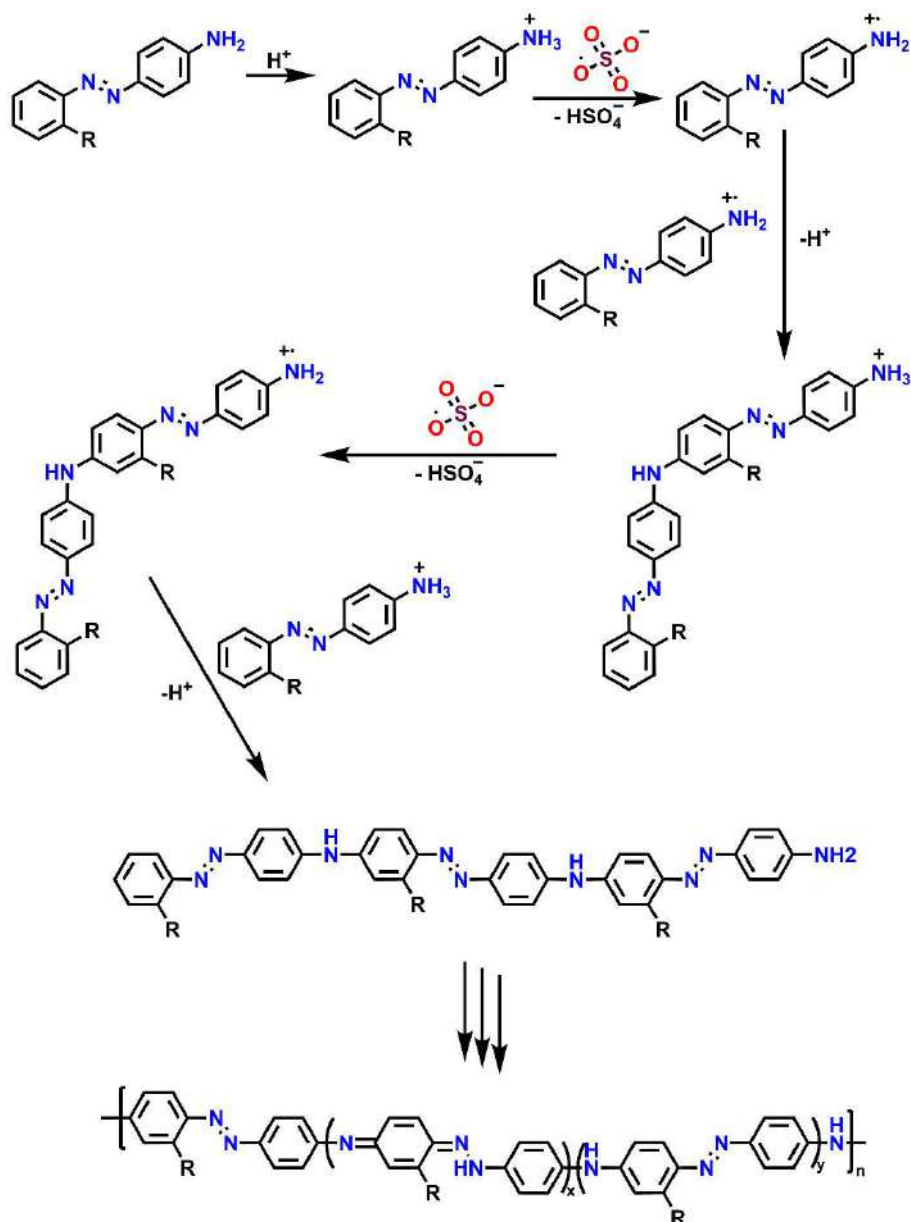


Figure 5.6: Proposed oxidative polymerization mechanism of the synthesized polymers.

Although several coupling pathways are theoretically possible, C-C and N-N coupling are not observed during polymer formation. C-C coupling is disfavored as it disrupts aromaticity and leads to non-conjugated,

sterically strained structures that are energetically unstable. Similarly, N-N coupling is unfavorable due to the poor stability of N-N bonds under oxidative acidic conditions. This is because such coupling would terminate conjugation rather than extend the polymer backbone. Consequently, N-C coupling is selectively favored, as it preserves aromaticity and enables efficient π -conjugation along the growing polymer chain.

The Gibbs free energies associated with coupling between N24 and the high-spin-density sites, namely C1, C5, C17, C13, and C19, were calculated, and the results are summarized in Figure 5.5. The calculated Gibbs free energy changes are $-16.4 \text{ kcal mol}^{-1}$ for coupling between N24 and C17/C19, $-97.9 \text{ kcal mol}^{-1}$ for coupling between N24 and C3/C5, and $-107.7 \text{ kcal mol}^{-1}$ for coupling between N24 and C1. Among the pathways considered, coupling through C1 is therefore the most energetically favorable, indicating that this pathway is the most feasible during chain propagation. Based on these energetic trends, the coupling mechanism proposed from the DFT calculations is illustrated in Figure 5.6.

5.2.2 Structural and Spectroscopic Characterization

The vibrational characteristics of the polymers were examined using Fourier transform infrared spectroscopy. The spectra are presented in Figure 5.7. The spectra of the polymers show two strong peaks around ~ 1585 and $\sim 1490 \text{ cm}^{-1}$, corresponding to the quinoid and benzenoid stretching vibrations, respectively¹⁵. All the substituents stabilize the quinoid segment, and hence they show a red shift compared to the quinoid stretching of PH. The -OMe group donates electron density,

while -OH and -SH donate electron density as well as form hydrogen bonding with the iminium nitrogen. In the case of -COOH, even though it is electron-withdrawing, it forms strong hydrogen bonding; hence, a red shift is observed. The substitution reduces the π - π stacking due to steric effects; hence, the benzenoid bands show a blue shift compared to PH. The -N=N- stretching of the azo group appears as a shoulder peak adjacent to the strong benzenoid stretching¹⁶. This band also shows a red shift compared to unsubstituted PH, which can be attributed to hydrogen bonding and conjugation effects.

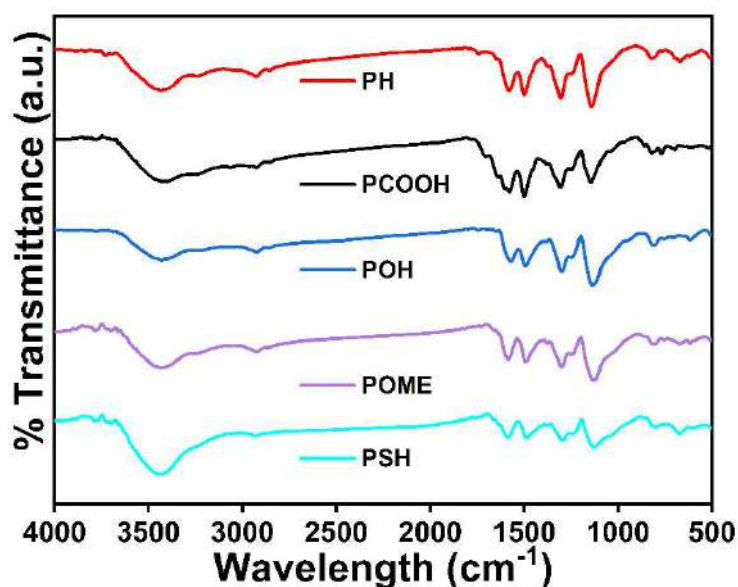


Figure 5.7: FTIR spectra of the synthesized polymers.

In addition to the benzenoid and quinoid peaks, the spectra have prominent peaks present at around ~ 1305 , 1245 , and ~ 1140 cm^{-1} , which give insights into the proton doping present.¹⁷ The band at ~ 1305 cm^{-1} is assigned to the C-N stretching vibration of benzenoid amine units,

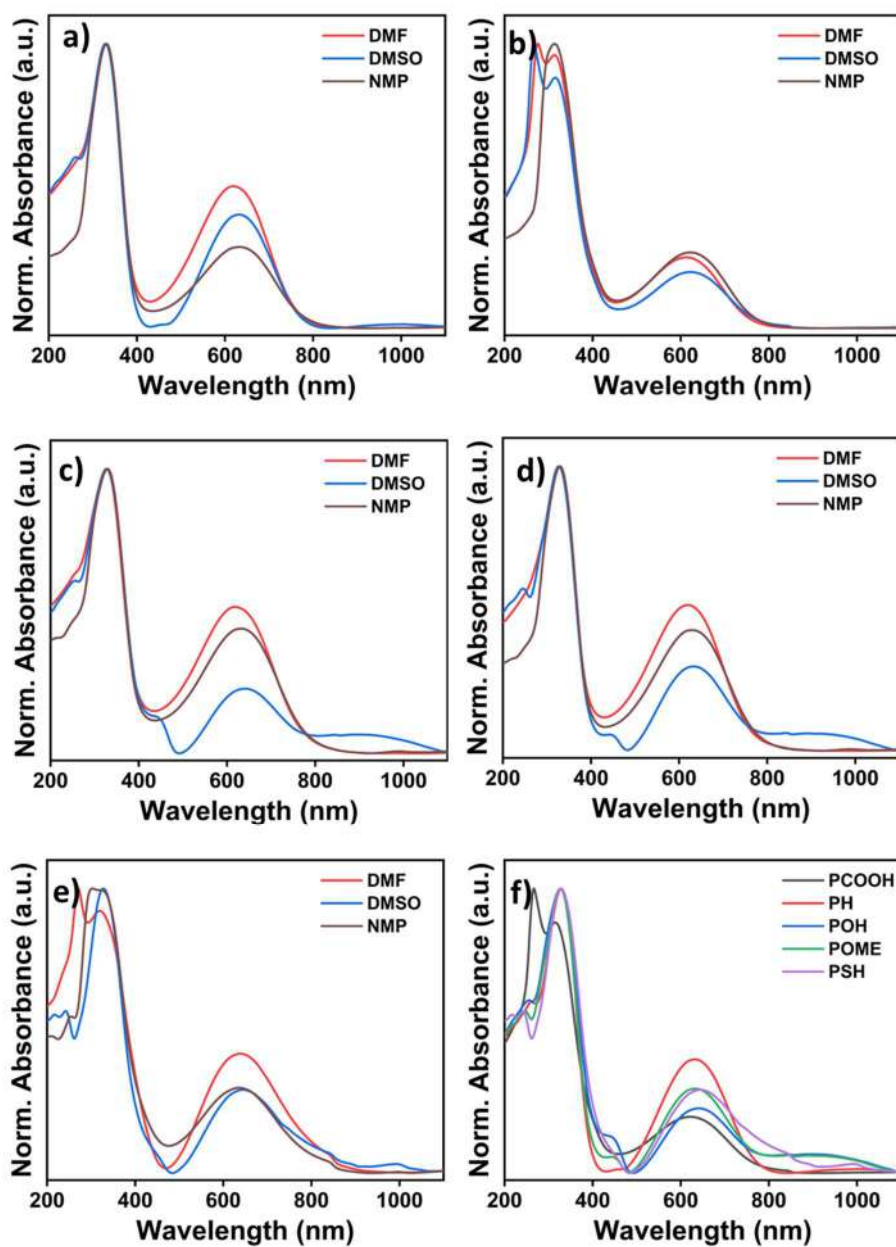


Figure 5.8: UV-visible absorption spectra of (a-e) PH, PCOOH, POH, POME, and PSH, respectively, recorded in DMSO, DMF, and NMP, (f) UV-visible absorption spectra of all polymers studied in DMSO.

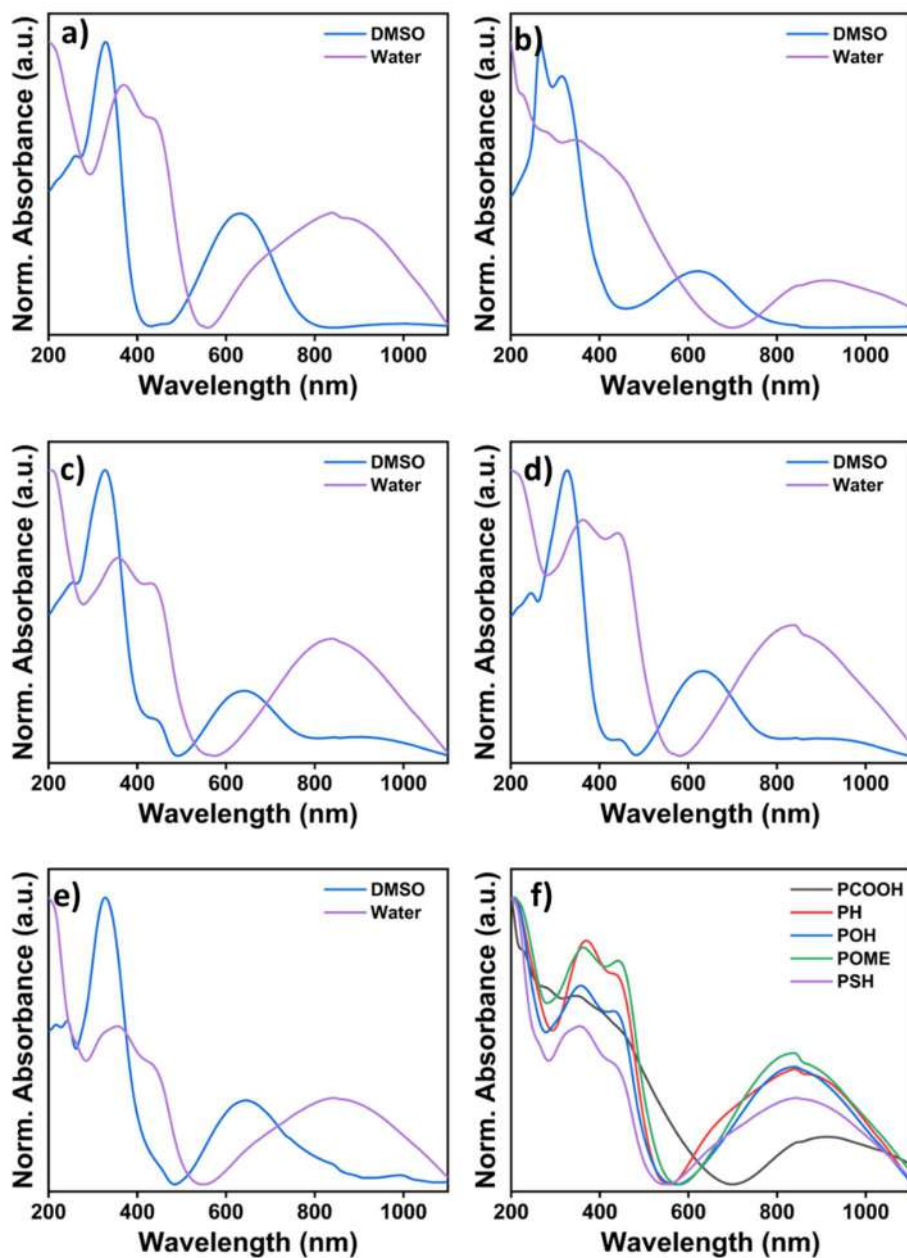


Figure 5.9: UV-visible absorption spectra of (a-e) PH, PCOOH, POH, POME, and PSH, respectively, recorded in DMSO and H_2O , (f) Comparative spectra of all polymers in H_2O .

whereas the band at $\sim 1245\text{ cm}^{-1}$ corresponds to the C-N⁺ stretching of protonated imine sites, resulting in the generation of polaronic charge carriers¹⁸. The intense band observed at $\sim 1141\text{ cm}^{-1}$ is assigned to the polaron delocalization or electronic-like band, which arises from strong coupling between vibrational modes and delocalized charge carriers along the conjugated backbone. These three bands confirm the protonation of the polymer chain and its delocalization¹⁹.

The UV-visible absorption spectra of the polymers were recorded in different polar aprotic solvents (Dimethyl sulfoxide (DMSO), DMF, and N-Methyl-2-pyrrolidone (NMP)) and polar protic solvents (H₂O), to better understand the intrinsic electronic structure of the polymers and their solvent-dependent charge states²⁰. The spectra are presented in Figures 5.8 and 5.9, respectively.

In polar aprotic solvents, all polymers exhibit two absorption peaks. The high-energy peak around $\sim 320\text{ nm}$ is assigned to the π - π^* transition of the benzenoid units, and the peak around $\sim 630\text{ nm}$ is assigned to the excitonic or benzenoid to quinoid transitions associated with extended conjugation²¹. The spectra recorded in DMF and NMP are identical, implying that these solvents do not facilitate any protonation or perturb the electronic state and therefore reflect the intrinsic ground-state electronic structure.

In DMSO, the spectra of POH, POME, and PSH show a slight variation compared to the spectra obtained in DMF and NMP. The peaks corresponding to the π - π^* transition and the excitonic or benzenoid to quinoid transitions remain the same, but have an additional shoulder peak around $\sim 440\text{ nm}$, whereas they remain optically silent in DMF and NMP²².

The protonation effect of the polymers was evaluated by recording the spectra in H₂O and is given in Figure 5.9. In H₂O, the $\pi \rightarrow \pi^*$ transition shows a red shift, and two new peaks emerge as a result of protonation. The new peak around ~ 620 nm is assigned to the polaron (exciton $\rightarrow$ polaron) transitions arising from protonation of the imine nitrogen sites, and the peak around ~ 900 nm is assigned to the bipolaronic or free-carrier absorption associated with highly delocalized charged states. These spectral changes indicate the formation of protonated and charge-delocalized species promoted by hydrogen bonding and solvent acidity.

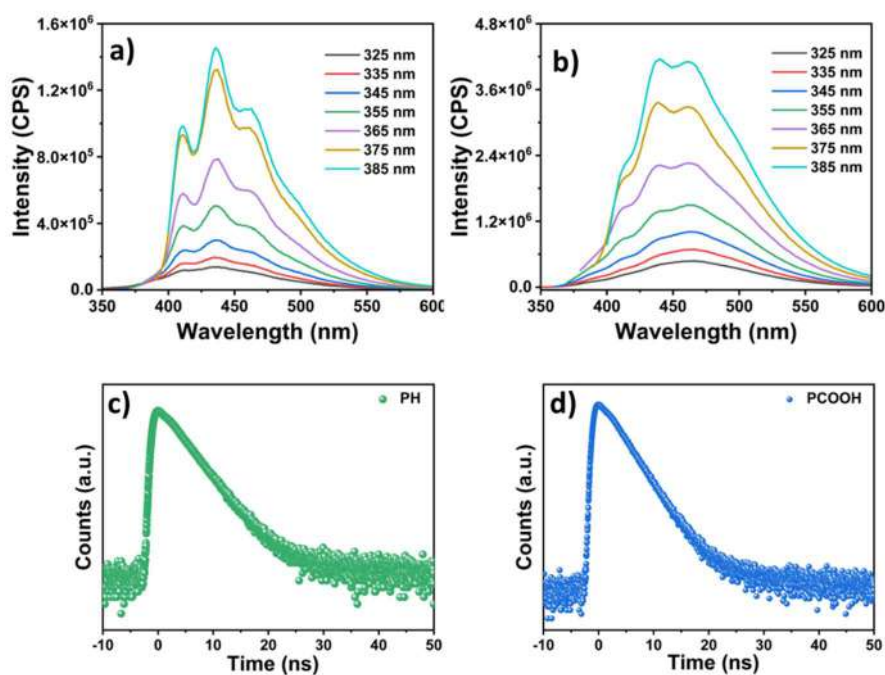


Figure 5.10: Fluorescence spectra of a) PH in NMP, b) PCOOH in NMP, and Photoluminescence decay curves of c) PCOOH, d) PH.

Florescence property is only observed for PH and PCOOH^{23, 24}. The fluorescence emission spectra of PH and PCOOH were recorded in NMP

over the 350-600 nm range using excitation wavelengths between 325 and 385 nm, and the results are given in Figure 5.10 (a-b). The emission peaks of both PH and PCOOH do not have any shift with respect to the change in excitation wavelength. The intensity of the emission peak, on the other hand, had a noticeable increase with an increase in the excitation wavelength^{25, 26}. This excitation-wavelength-independent emission behavior indicates the presence of a rapid internal conversion mechanism to a common lowest excited emissive state before the radiative transition, and this is in accordance with ²⁷. This observation also suggests the absence of excitation-selective emissive sites or heterogeneous chromophore domains in the polymers.

PCOOH exhibited a significantly higher fluorescence intensity than PH under identical experimental conditions and concentration. The emission intensity of PCOOH was increased from approximately 4.76×10^5 to 4.16×10^6 counts per second (CPS) as the excitation wavelength was increased from 325 to 385 nm, whereas PH showed a comparatively lower increase from 1.39×10^5 to 1.95×10^6 counts per second (CPS). The higher emission intensity of PCOOH indicates a higher effective fluorescence efficiency relative to PH.

Both polymers displayed three well-defined emission bands, indicative of vibronically resolved π - π^* transitions of the conjugated backbone²⁸. For PCOOH, emission maxima were observed at approximately 415, 440, and 461 nm, whereas PH exhibited corresponding peaks at around 410, 436, and 461 nm. The slight red shift of the lower-wavelength emission bands in PCOOH relative to PH suggests that the carboxyl group stabilizes the excitation and also improves the solvent-polymer interaction. The presence of similar vibronic features in both polymers

suggests that the fundamental emissive backbone remains unchanged, while functionalization only alters the excited-state energetics²⁸.

A notable difference between the two polymers is the broadness of their emission profiles. PCOOH exhibited a very broad fluorescence emission nearly covering the entire visible region, whereas the emission of PH was comparatively narrower. The broader emission in PCOOH indicates an increased electronic and conformational heterogeneity in the excited state, likely arising from hydrogen-bonding interactions between the carboxyl groups and NMP, as well as increased structural flexibility induced by functionalization. The absence of excitation-dependent peak shifts indicates that these emissive states are energetically coupled and relax to a common emissive minimum rather than behaving as independent chromophoric domains.

The fluorescence studies reveal excitation-wavelength-independent emission with well-defined vibronic features and broad visible-range fluorescence, indicating stable and energetically coupled emissive states. The combination of broadband emission and consistent photophysical behavior under varying excitation conditions suggests their potential suitability for future applications requiring robust optical responses, such as fluorescence-based sensing, optoelectronic devices, and light-harvesting systems, while also providing insight into the influence of backbone functionalization on excited-state dynamics.

Time-resolved fluorescence measurements were performed to investigate the excited-state dynamics of PH and PCOOH in NMP, and the results are given in Figure 5.10 (c-d). The fluorescence decay profiles of both polymers were fitted using a mono-exponential decay model, indicating the presence of a dominant emissive excited state with

negligible contribution from secondary decay pathways. The fluorescence lifetimes were determined to be 3.76 ns for PH and 3.87 ns for PCOOH, and the close similarity of these values suggests that

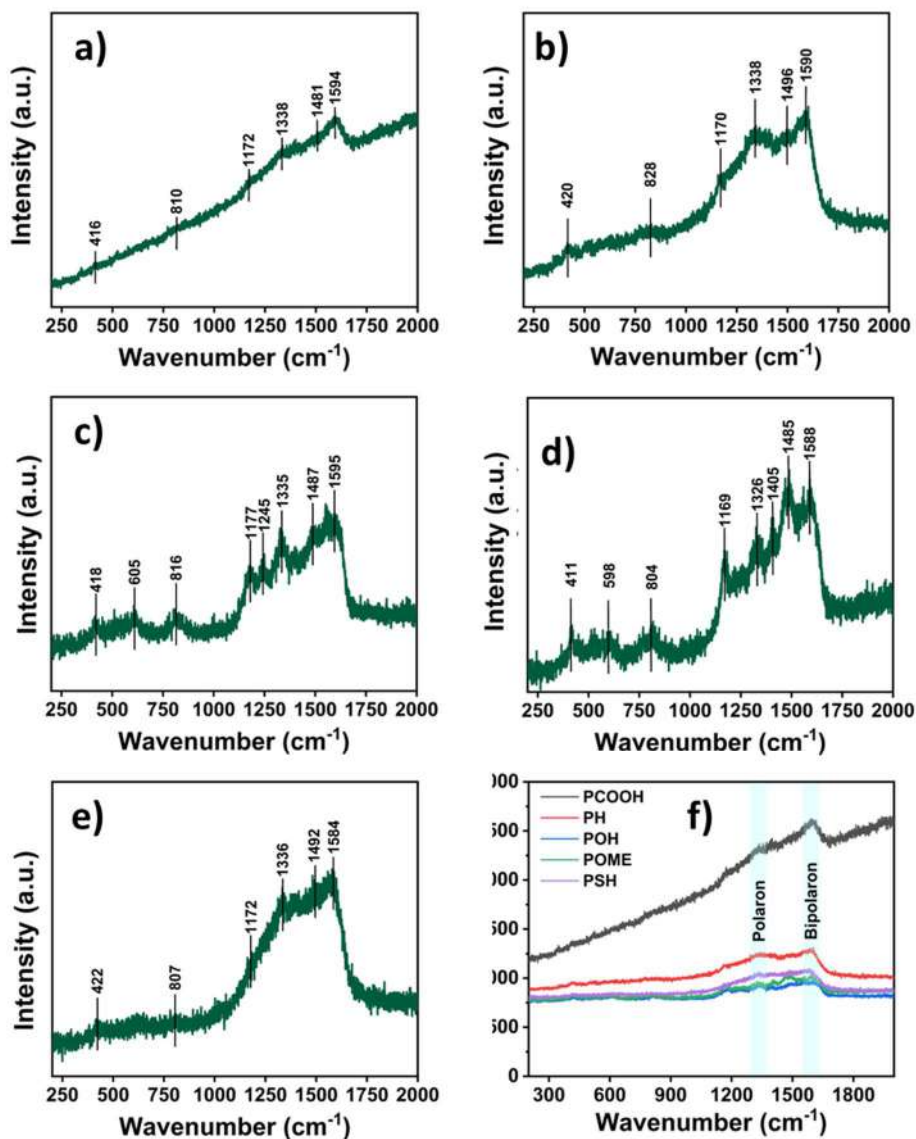


Figure 5.11: FT Raman spectra of the synthesized polymers.

functionalization does not significantly alter the intrinsic radiative relaxation timescale of the conjugated backbone²⁹. Accordingly, the differences observed in this steady-state emission intensity and spectral breadth are attributed primarily to variations in excited-state stabilization and non-radiative decay processes rather than the formation of distinct emissive states. The mono-exponential decay behavior, together with excitation-wavelength-independent emission, confirms radiative recombination from a well-defined lowest excited state, reflecting stable and reproducible photophysical behavior under variable excitation conditions.

The Raman spectra of the polymers are presented in Figure 5.11. The Raman spectra exhibit the characteristic vibrational features of conducting polymers. This confirms the preservation of the conjugated backbone after polymerization. All samples show prominent bands in the regions ~ 1150 - 1200 , ~ 1320 - 1340 , ~ 1480 - 1500 , and ~ 1580 - 1600 cm^{-1} , which are assigned to C-H bending of quinoid units, C-N $\bullet^+$ stretching associated with polarons, C=N/C=C stretching of quinoid rings, and C=C stretching of benzenoid rings, respectively³⁰. The bands are broad in nature and have higher intensity than that of base line. This indicates structural disorder and strong electron-phonon coupling found in partially oxidized and doped conducting polymers²⁹.

The PH shows a moderately intense polaron band at 1338 cm^{-1} . This indicates a balanced benzenoid-quinoid structure. In contrast, the PCOOH shows an enhancement in the Raman intensity, mainly in the polaronic and quinoid bands at 1338 cm^{-1} and 1496 cm^{-1} , respectively. It also has additional bands at 420 cm^{-1} and 828 cm^{-1} corresponding to ring deformations in the polymer chain. This is attributed to the increased

charge localization and stabilization of polarons/bipolarons by the electron-withdrawing -COOH. The POH spectrum has the polaron peak at 1338 cm^{-1} with moderate intensity and is attributed to the hydrogen-bonding interactions of the hydroxyl group. For POME, the lower intensity of the polaron band at 1326 cm^{-1} compared to the intensity of the benzenoid/quinoid band at 1485 cm^{-1} reflects decreased doping and increased localization of the π -electrons. The PSH displays less pronounced polaronic bands at 1336 cm^{-1} due to the weak electronic interaction of the thiol group with the polymer chain, hence its weak charge-carrier stabilization^{31,32}.

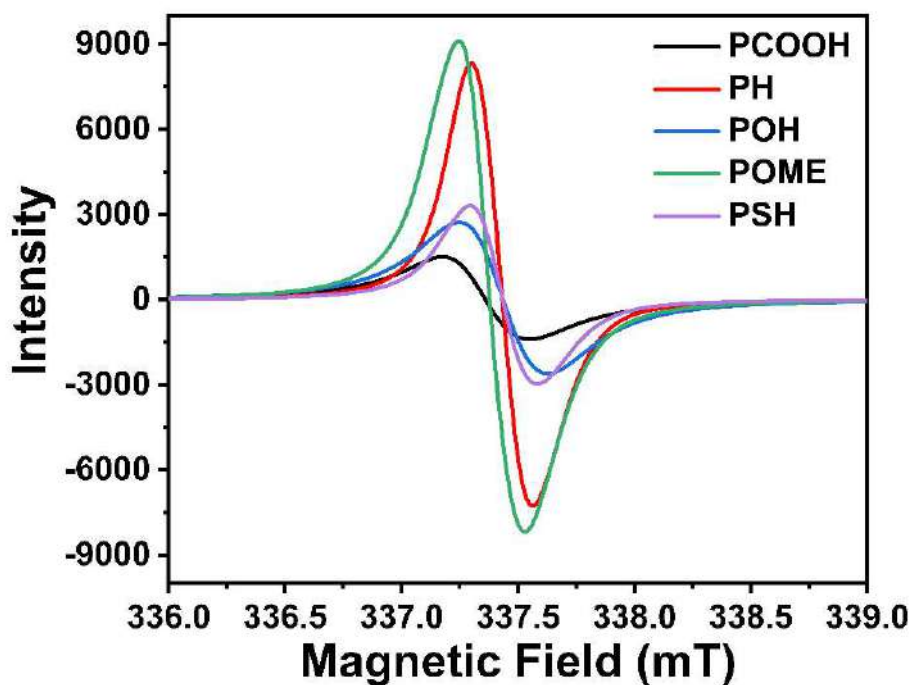


Figure 5.12: ESR spectra of PCOOH, PH, POH, POME, and PSH.

The comparative intensity plot of the Raman spectra of the polymers is shown in Figure 5.11f. PCOOH and PH have the highest Raman intensity among the polymers. The POH, POME, and PSH display comparatively

lower intensities. The PH and PCOOH have fluorescence properties, which increase the Raman intensity by introducing a fluorescence background. Also, under near-resonance conditions, the Raman effects are enhanced through resonance. The resonance enhancement preferentially amplifies bands strongly coupled with the electronic structures, like polaron and bipolaron. The Raman analysis confirms that the functionalization changes the electronic structure of the polymers. It is also evident that the polaron/bipolaron formation is favored by the electron-withdrawing substituents, and the electron-donating groups suppress the formation.

ESR spectroscopy was employed to evaluate the nature of charge carriers and spin delocalization in the synthesized polymers. The spectra are presented in Figure 5.12, and the ESR parameters are given in Table 5.1. All spectra were recorded under identical experimental conditions, including microwave power, modulation amplitude, and temperature.

Table 5.1: *ESR parameters of the synthesized polymers, including g-factor, peak-to-peak linewidth (ΔH_{pp}), and asymmetry parameter (a/b).*

Sample Name	g-factor	ΔH_{pp}	a/b
PCOOH	2.00156	0.3723	1.077646
PH	2.00081	0.2685	1.145337
POH	2.00155	0.3785	1.046802
POME	2.00151	0.2808	1.113188
PSH	2.00167	0.2868	1.112639

All polymers exhibit a single, broad ESR signal centered at a g -value close to the free-electron value ($g \approx 2.002$), confirming that the paramagnetic species are predominantly carbon-centered π -radical polarons. The absence of additional resonance features or hyperfine splitting indicates a homogeneous spin population with substantial delocalization along the conjugated polymer backbone, which is characteristic of doped conducting polymers³³.

The peak-to-peak linewidth (ΔH_{pp}) displays dependence on the nature of the substituent³⁴. The PH and POME exhibit comparatively narrower linewidths, indicative of enhanced polaron delocalization and reduced spin-spin interactions. The POH and PCOOH show broader ESR lines, and is attributed to the increased structural disorder and partial localization of charge carriers due to hydrogen-bonding interactions. The PSH has an intermediate linewidth, which is consistent with the polarizable S atom promoting delocalization while introducing moderate spin-orbit coupling effects³⁵.

All the spectra have Dysonian line shapes, as reflected by asymmetry (a/b) values greater than one. This confirms the conducting nature of the polymers³⁶. Higher a/b values observed for PH, POME, and PSH suggest relatively higher charge carrier mobility, whereas lower values for POH and PCOOH indicate reduced electronic transport, consistent with their broader linewidths.

The ESR results indicate that the chemical modification of the polymer backbone does not alter the fundamental nature of the charge carriers but significantly influences the extent of spin delocalization and electronic transport through substituent-induced structural and electronic effects.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface elemental composition and doping characteristics of the synthesized polymers³⁷. The survey spectra are presented in Figure 5.13. The survey spectrum of PH, PCOOH, POH, POME, and PSH exhibits prominent C 1s and N 1s peaks in all samples, confirming the formation of the conjugated polymer backbone. O 1s signals are also present in all the samples. The signals are arising from O containing functional groups, polymer chain backbone, and from SO_4^{2-} . To clearly visualize low-intensity elemental features, the survey spectra were plotted using a logarithmic intensity scale. Although all polymers were synthesized in 1 M HCl, differences are observed in the retention of chloride counterions. Cl 2p signals are detected for PH, POME, and PSH, which are attributed to chloride ions incorporated during acid-mediated polymerization and protonation of the polymer backbone. In contrast, Cl 2p peaks are absent in both PCOOH and POH. The absence of chloride in POH can be associated with the increased hydrophilicity and hydrogen-bonding capability introduced by the hydroxyl substituent, which may facilitate the removal of weakly bound anions during post-synthesis washing without necessarily suppressing effective backbone protonation.

The S 2p signals of sulfur are observed in PH, POH, POME, and PSH. For PH, POH, and POME, these peaks are attributed primarily to residual sulfate species originating from ammonium persulfate used as the

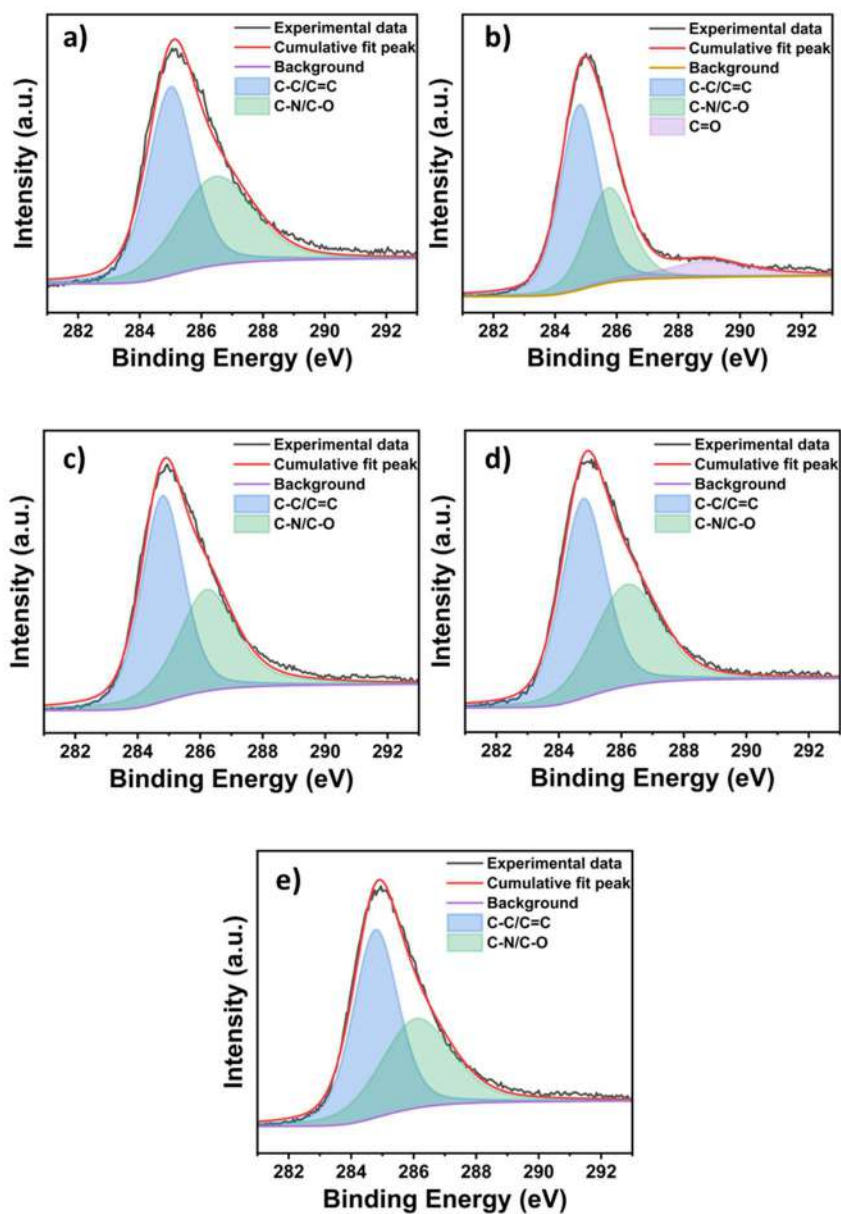


Figure 5.14. High-resolution $C\ 1s$ XPS spectra of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH. All spectra were charge-corrected with respect to the $C-C/C=C$ peak at 284.8 eV.

oxidant during polymerization. The PSH additionally contains S contributions from the thiol substituent. Notably, S 2p signals are entirely absent in PCOOH, indicating minimal incorporation or retention of sulfate species at the polymer surface. The absence of both Cl 2p and S 2p signals in PCOOH suggests the presence of a fundamentally different charge compensation mechanism. This observation correlates with its significantly lower electrical conductivity ($\sim 10^{-5}$ S cm $^{-1}$) relative to the other samples (10^{-2} - 10^{-3} S cm $^{-1}$), as well as its inferior EMI shielding performance (will be discussed later in this chapter).

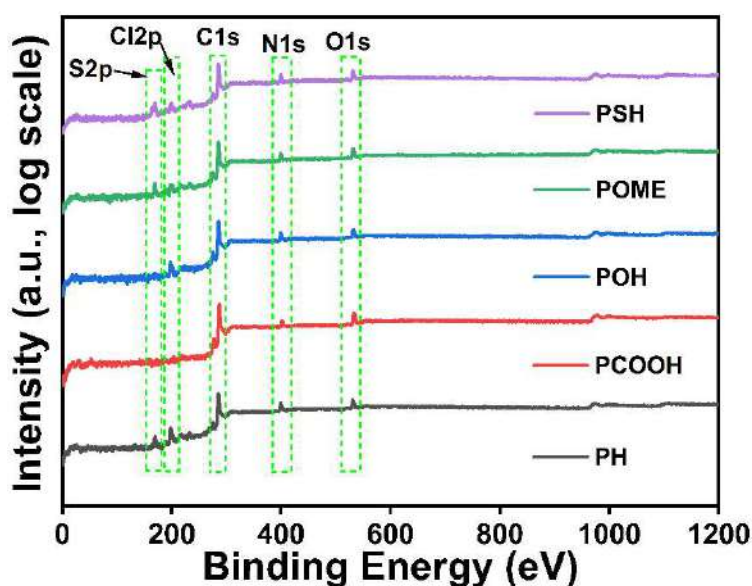


Figure 5.13: XPS survey spectra of PH, PCOOH, POH, POME, and PSH.

Overall, the survey spectra reveal systematic differences in counter-ion retention and surface chemistry as a function of ortho-substitution; however, the survey analysis alone cannot distinguish between different nitrogen chemical states or degrees of protonation, necessitating detailed

deconvolution of the high-resolution core-level spectra, particularly the N 1s region, to elucidate the nature of charge carriers and protonation in these polymers.

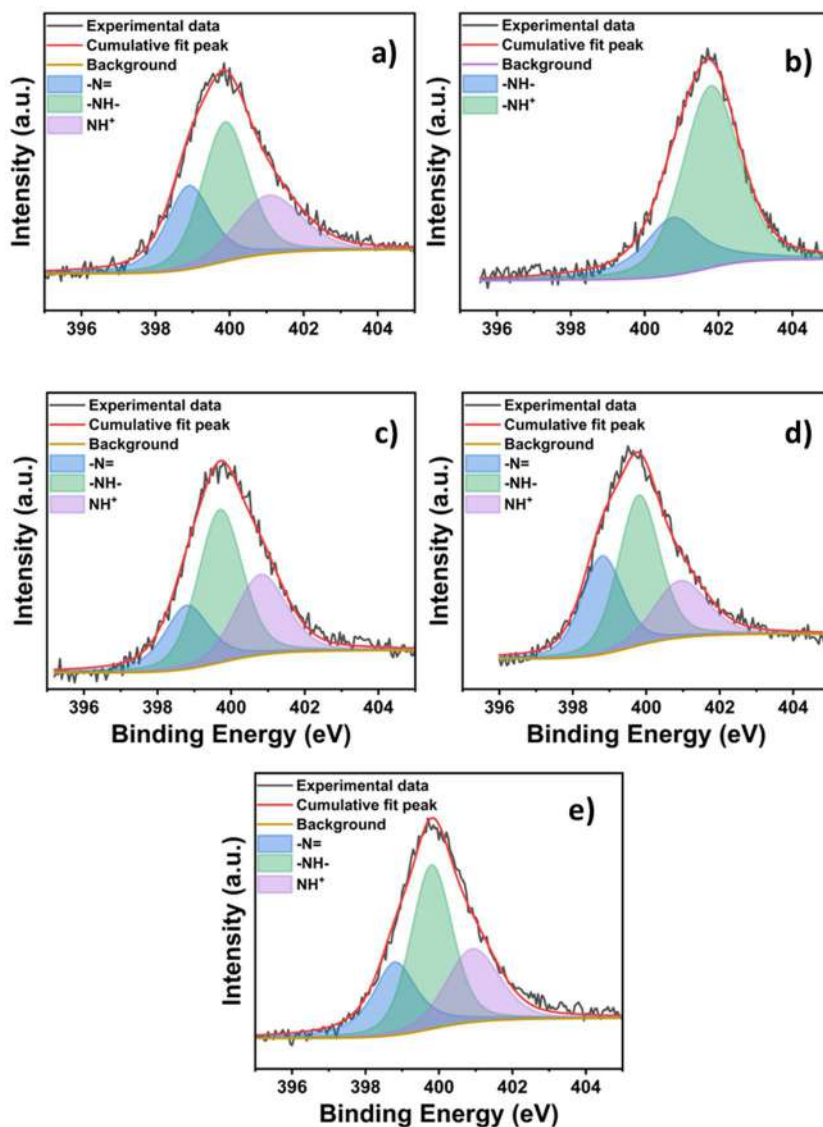


Figure 5.15. High-resolution N 1s X-ray photoelectron spectra of the conducting polymers: (a) PH, (b) PCOOH, (c) POH, (d) POME and (e) PSH.

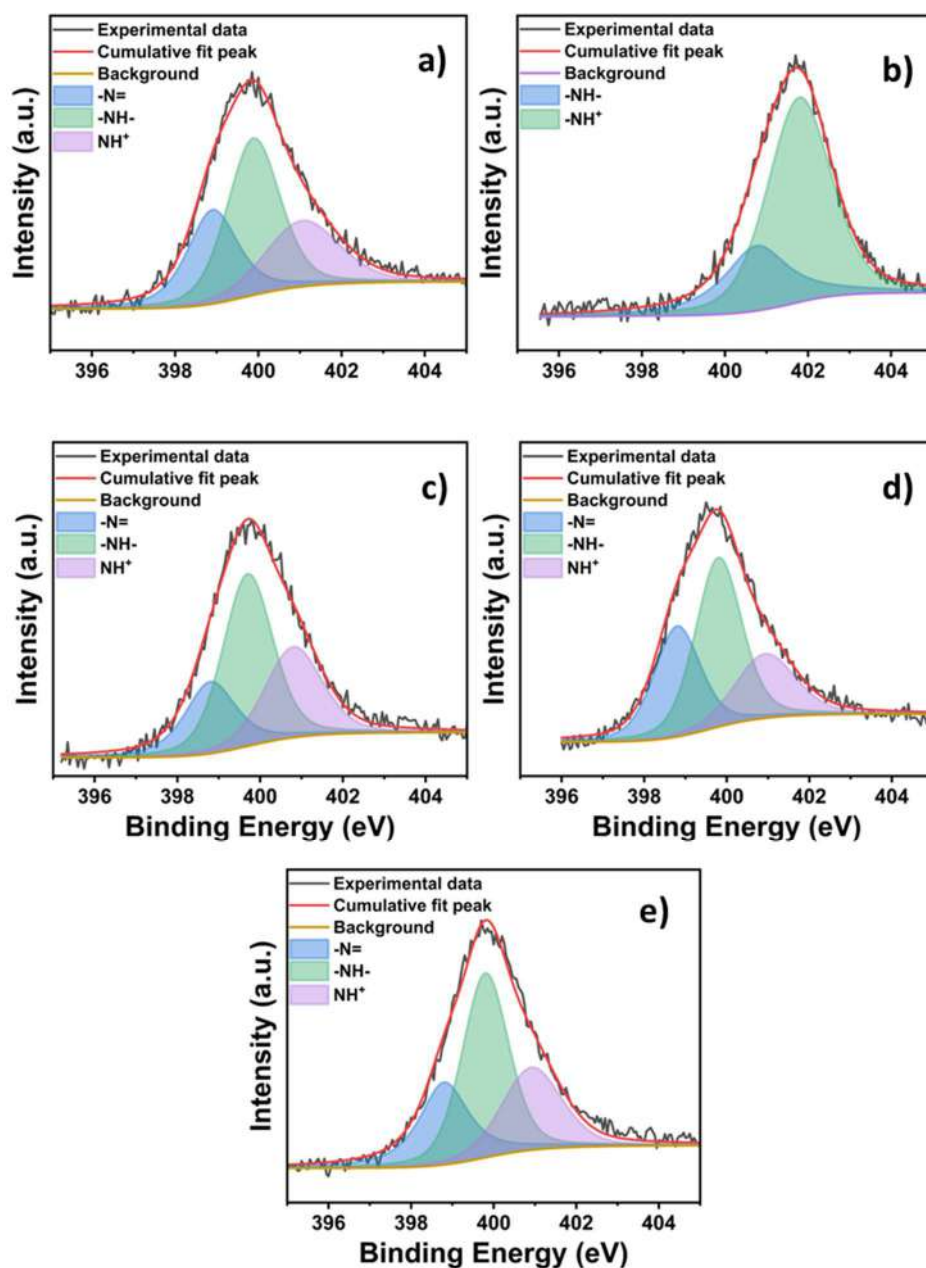


Figure 5.15. High-resolution $N\ 1s$ X-ray photoelectron spectra of the conducting polymers: (a) PH, (b) PCOOH, (c) POH, (d) POME and (e) PSH.

The high-resolution C 1s XPS spectra of PH, PCOOH, POH, POME, and PSH were deconvoluted to analyze the carbon chemical environments associated with the polymers. The deconvoluted spectra are presented in Figure 5.14. For all polymers, the C 1s spectra were fitted using two components centered at 284.8 eV and 285.60 eV. The peak at 284.8 eV corresponds to C-C and C=C bonds of the polymer backbone. The peak at 285.6 eV is assigned to the C-N and C-O. The C-N bond is associated with the aniline units, and the C-O bonds are from the oxygen-containing substituents and dopants.

In the case of PCOOH, an additional peak is observed at 288.95 eV, which is characteristic of carbonyl carbon (C=O) of carboxylic acid. This peak confirms the -COOH functional group in the polymer. The carbonyl peak is not detected in PH, POH, POME, and PSH, indicating the absence of carboxyl-type carbon in these polymers. The absence of well-resolved asymmetry or additional shoulders in the experimental spectra, separate deconvolution of C-S or C-O contributions was not performed, as their expected binding energies overlap significantly with the C-N/C-O peak in the ~285.6 - 286.0 eV region.

The high-resolution N 1s spectra of PH, PCOOH, POH, POME, and PSH were deconvoluted to analyze the nitrogen chemical states and protonation behavior of the polymer backbone. The deconvoluted spectra are presented in Figure 5.15. For PH, POH, POME, and PSH, the N 1s spectra are deconvoluted into three components centered at 398.5 eV, 399.6 eV, and 401.1 eV, corresponding to imine nitrogen (-N=), amine nitrogen (-NH-), and protonated nitrogen species, respectively.

The presence of protonated nitrogen confirms successful acid doping during polymerization in 1 M HCl.

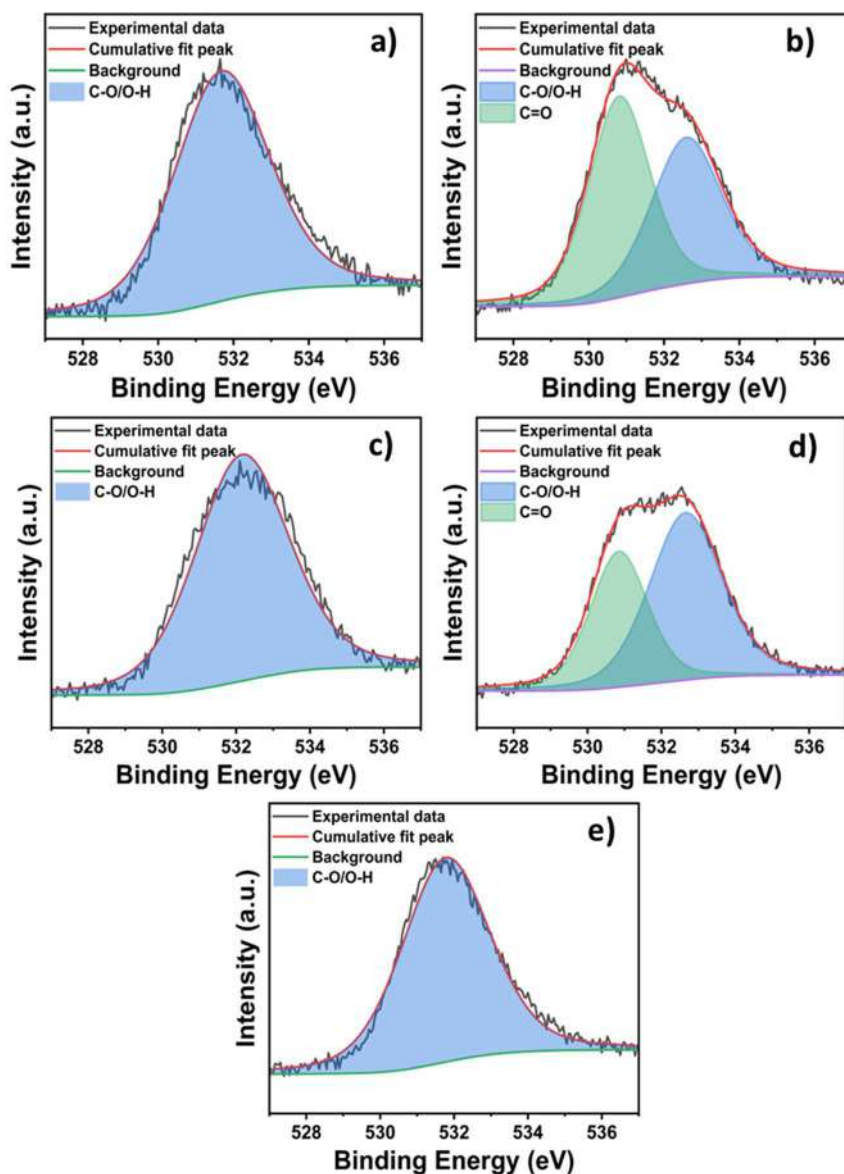


Figure 5.16. High-resolution O 1s X-ray photoelectron spectra of the conducting polymers: (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH.

In contrast, the N 1s spectrum of PCOOH exhibits a distinctly different behavior, characterized by the absence of an imine nitrogen component and the presence of a dominant protonated nitrogen peak, and amine nitrogen. This indicates that protonated nitrogen species constitute the predominant nitrogen environment in PCOOH. The absence of the imine component is attributed to strong localization and stabilization of protonated nitrogen through internal interactions with the carboxylic acid functionality, which suppresses the formation of distinct quinoid imine environments. No π - π^* peaks were observed in the N 1s spectra, which is consistent with predominantly protonated and disordered nature of the polymer backbones.

The high-resolution O 1s X-ray photoelectron spectra of PH, PCOOH, POH, POME, and PSH were analyzed to elucidate the chemical environments of oxygen from both functional groups and residual counterions introduced during polymerization. The deconvoluted spectra are presented in Figure 5.16.

In the case of PH and PSH, the O 1s signal arises predominantly from residual sulfate counterions originating from ammonium persulfate used as the oxidant during polymerization. Accordingly, their O 1s spectra could be adequately described by a single broad component centered around ~531 - 532 eV.

POH exhibits a dominant O 1s component at higher binding energy (~532.5 - 533 eV), which is attributed to the hydroxyl (C-O / O-H) functionality introduced by ortho substitution. The predominance of the

hydroxyl-related oxygen indicates that oxygen in POH is largely associated with the polymer backbone rather than counterions.

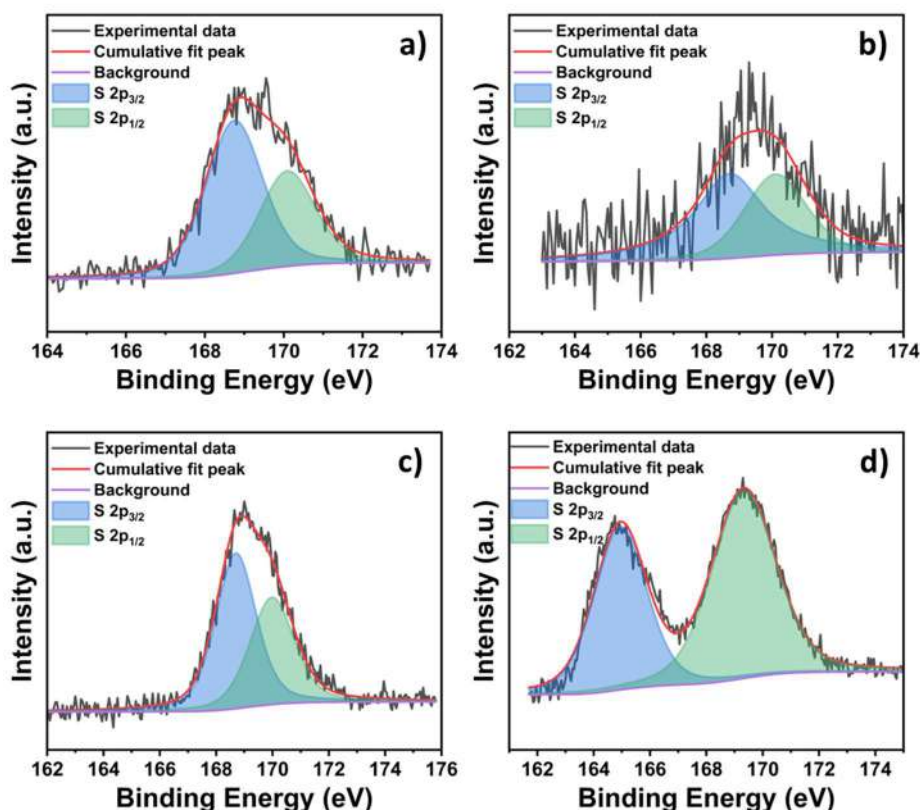


Figure 5.17. High-resolution *S* 2*p* X-ray photoelectron spectra of the conducting polymers: (a) PH, (b) POH, (c) POME, and (d) PSH.

For POME, the O 1*s* spectrum could be resolved into two components of comparable intensity. The lower binding energy peak at ~531 eV is assigned to oxygen in residual sulfate counterions. The higher binding energy component at ~533 eV corresponds to the methoxy (C-O-C) oxygen. The comparable contributions of these two components are attributed to surface enrichment of sulfate species.

PCOOH displays a distinctly different O 1s spectral profile, which necessitates deconvolution into two intrinsic components. The lower binding energy peak at 530.8 eV corresponds to carbonyl (C=O) oxygen. The higher binding energy peak at 532.6 eV is attributed to hydroxyl (C-O / O-H) oxygen of the carboxylic acid group. The absence of a sulfate-related peak in PCOOH is consistent with the lack of S 2p and Cl 2p signals; this indicates that charge compensation occurs predominantly through internal interactions rather than external counterions.

The high-resolution S 2p X-ray photoelectron spectra of PH, POH, POME, and PSH were analyzed to identify the chemical states of S present in the polymers. The deconvoluted spectra are presented in Figure 5.17. S in these systems originates either from residual sulfate counterions introduced during polymerization using ammonium persulfate or, in the case of PSH, from the intrinsic thiol substituent. For PCOOH, no S 2p signal was detected, which is consistent with the absence of sulfate and chloride counterions in this polymer.

The S 2p spectra of PH, POH and POME exhibit a single S chemical environment, which could be fitted with one spin-orbit doublet in the binding energy range of ~168 - 170 eV. This doublet corresponds to highly oxidized S (S^{6+}) in sulfate (SO_4^{2-}) species, confirming the presence of residual sulfate counterions associated with acid doping during polymerization. No low-binding-energy S components were observed in these samples, indicating the absence of S incorporated into the polymer backbone.

In contrast, the S 2p spectrum of PSH displays two distinct S contributions that are clearly evident even in the raw spectrum (Figure 5.17d). Accordingly, the spectrum was deconvoluted using two spin-

orbit doublets. The lower binding energy doublet, with the S 2p_{3/2} component centered at 164.85 eV, is attributed to thiol (-SH) S associated with the ortho-thiol substituent in PSH. The higher binding energy doublet, with the S 2p_{3/2} component at 169.3 eV, corresponds to sulfate S originating from residual sulfate counterions. The coexistence of these two S environments indicates that both intrinsic thiol groups and external sulfate counterions contribute to the S 2p signal in PSH.

5.2.3 Thermal characterization

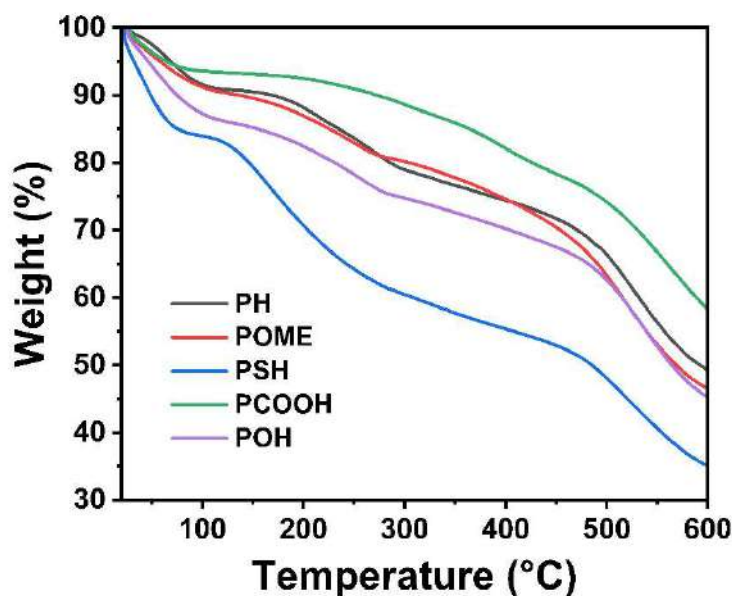


Figure 5.18: TGA curves of PCOOH, PH, POH, POME, and PSH.

The thermal properties of the polymers were investigated using TGA. The corresponding thermograms are presented in Figure 5.18. The TGA profiles of all polymers exhibit three distinct weight-loss regions, indicating multistep thermal degradation behavior typical of conducting polymers³⁸. The first weight-loss step, observed below ~120 °C,

corresponds to the removal of physically adsorbed and hydrogen-bonded moisture.

The second weight-loss region, occurring in the temperature range of approximately 200-300 °C, is attributed to the loss of dopant anions and degradation of low molecular weight oligomers. This region is characterized by a slow mass loss, suggesting progressive de-doping rather than direct backbone cleavage. The final weight-loss stage, initiated above 350 °C, corresponds to irreversible polymer backbone degradation involving chain scission and oxidative decomposition. This stage governs the ultimate thermal endurance of the materials. The weight percentage of residue remaining at 600 °C is 58.1%, 49.2%, 46.4%, 45.2%, and 35.1% for PCOOH, PH, POH, POME, and PSH, respectively. The high residual mass yield of PCOOH indicates enhanced char-forming ability, likely arising from intermolecular hydrogen bonding and acid-assisted crosslinking, which stabilize the polymer matrix at elevated temperatures. Conversely, PSH exhibits the lowest residual mass, suggesting rapid mass loss once degradation is initiated, possibly due to the formation of volatile S-containing fragments and poor char stability.

DTG analysis of the polymers provides further information about the degradation kinetics and enables the determination of the maximum Polymer Degradation Temperature (PDT_{max}). The DTG curves of the polymers are represented in Figure 5.19a. The PDT_{max} values were found to be 330 °C, 389 °C, 305 °C, 294 °C, and 402 °C for PCOOH, PH, POH, POME, and PSH, respectively. The lower PDT_{max} observed for POME indicates that the methoxy substitution facilitates earlier backbone degradation. The PSH exhibits the highest PDT_{max} , indicating a delayed

onset of backbone degradation. It should be noted that this delayed degradation does not translate into improved high-temperature survivability, as evidenced by its poor residual mass.

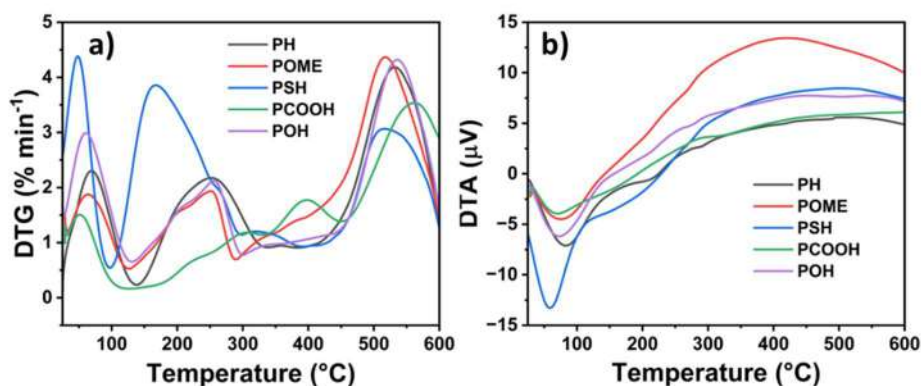


Figure 5.19: (a) DTG, and (b) DTA curves of PCOOH, PH, POH, POME, and PSH.

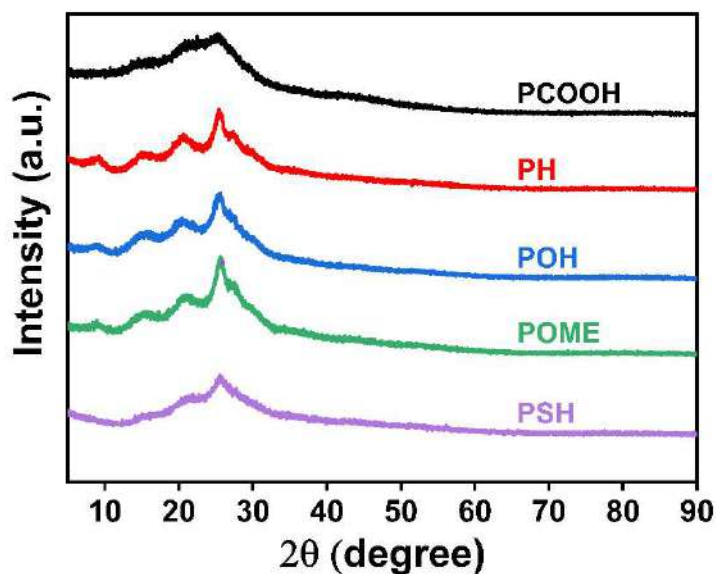


Figure 5.20. XRD patterns of PH, PCOOH, POH, POME, and PSH

The XRD spectra of the polymers are presented in Figure 5.20. All five polymers exhibit three characteristic diffraction peaks centered at approximately 15°, 20.5°, and 25.6°. These reflections are broad in nature, indicating the absence of long-range crystalline order. This also confirms the amorphous to nature of the polymers.

The broad peak at 25.6° is associated with interchain π - π stacking or short-range ordering between conjugated polymer chains. The reflections at ~20.5° and ~15° arise from the periodicities related to polymer backbone spacing and side-group-induced packing distances. These peaks indicates that the fundamental backbone structure remains similar across PH, PCOOH, POH, POME, and PSH. The small variations in broadenings of peaks across different samples indicates that substituent effects primarily influence short-range ordering rather than inducing crystallinity.

5.2.4 Morphological and Elemental Analysis

The surface morphology and elemental composition of all the polymers were examined using FESEM coupled with EDAX. The resulting FESEM images and EDAX spectra of the polymers are presented in Figures 5.21 to 5.25. The FESEM images at different magnifications reveal that all the polymers have heterogeneous morphologies with irregular flakes and granular features, indicating the absence of long-range structural ordering. No significant morphology-specific trends are observed among the polymers, suggesting that functional group substitution does not alter the overall surface texture at the microscale.

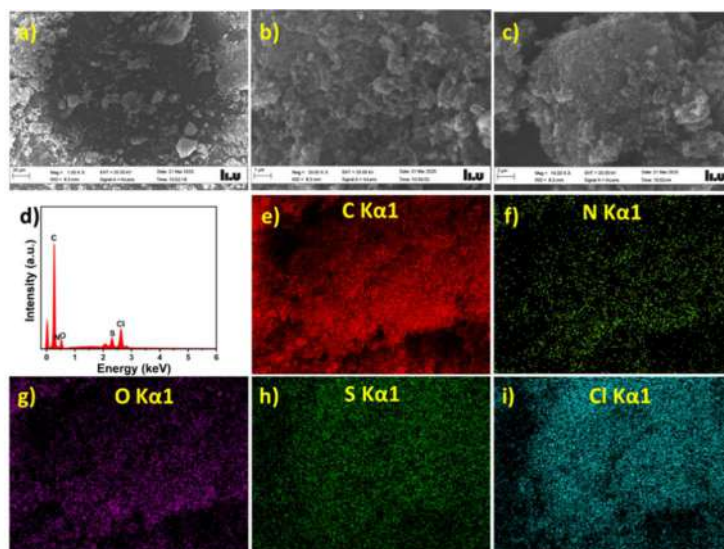


Figure 5.21: (a-c) FE-SEM images of PH at different magnifications, d) EDAX spectrum of PH. Elemental mapping images of PH: e) carbon, f) nitrogen, g) oxygen, h) sulfur, and i) chlorine.

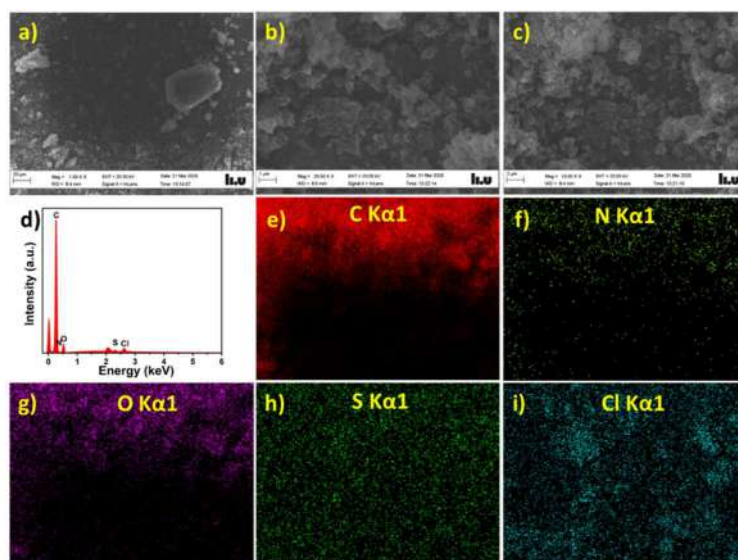


Figure 5.22: (a-c) FE-SEM images of PCOOH at different magnifications, d) EDAX spectrum of PCOOH. Elemental mapping images of PH e) carbon, f) nitrogen, g) oxygen, h) sulfur, and i) chlorine.

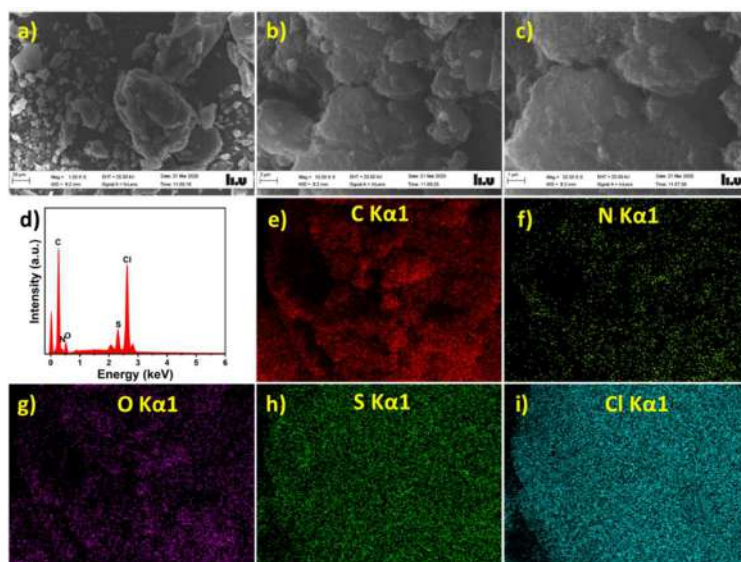


Figure 5.23: (a-c) FE-SEM images of POH at different magnifications, d) EDAX spectrum of POH. Elemental mapping images of POH: e) carbon, f) nitrogen, g) oxygen, h) sulfur, and i) chlorine.

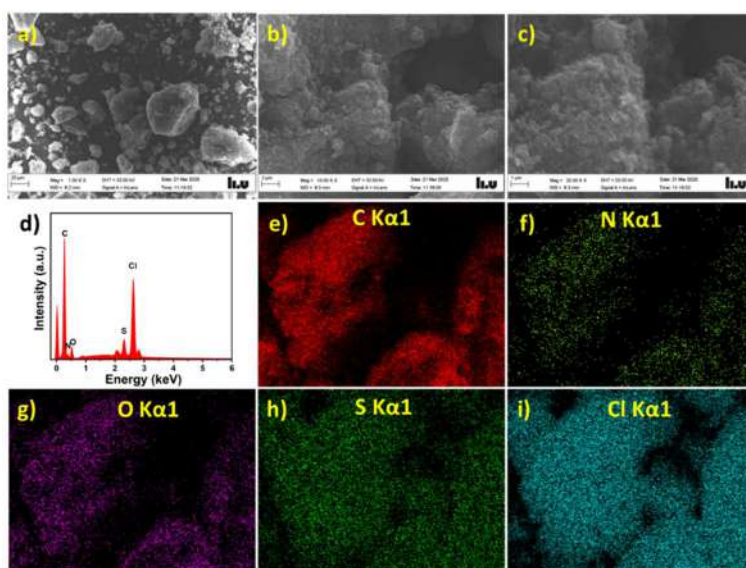


Figure 5.24: (a-c) FE-SEM images of POME at different magnifications, d) EDAX spectrum of POME. Elemental mapping images of POME: e) carbon, f) nitrogen, g) oxygen, h) sulfur, and i) chlorine.

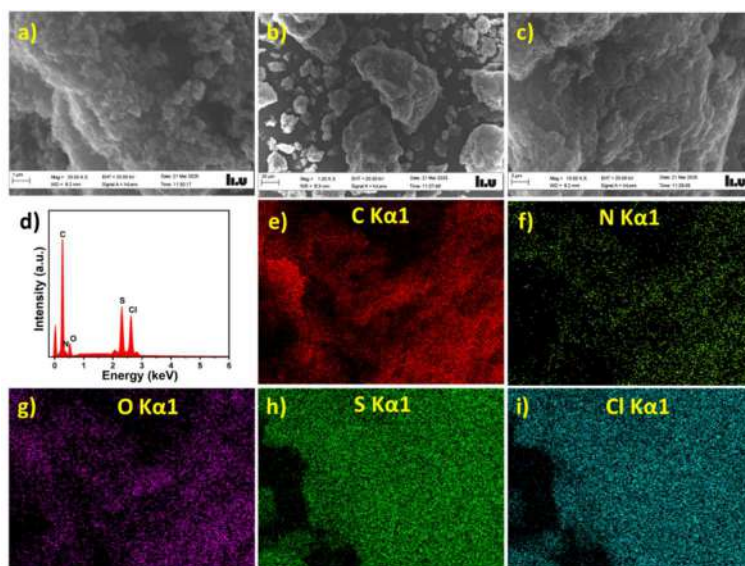


Figure 5.25: (a-c) FE-SEM images of PSH at different magnifications, d) EDAX spectrum of PSH. Elemental mapping images of PSH: e) carbon, f) nitrogen, g) oxygen, h) sulfur, and i) chlorine.

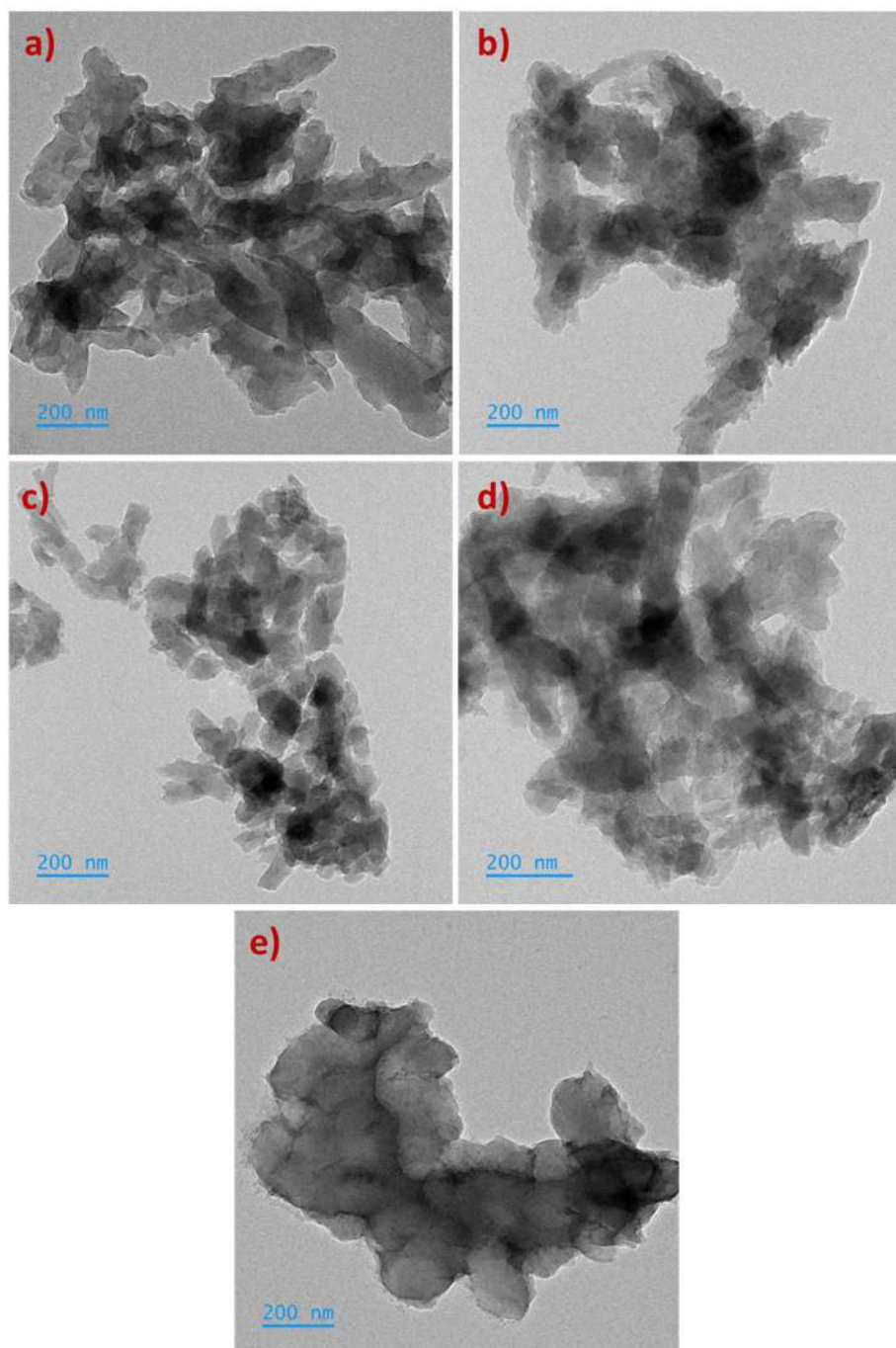


Figure 5.26. TEM images of PH, PCOOH, POH, POME, and PSH recorded at identical magnification (scale bar: 200 nm).

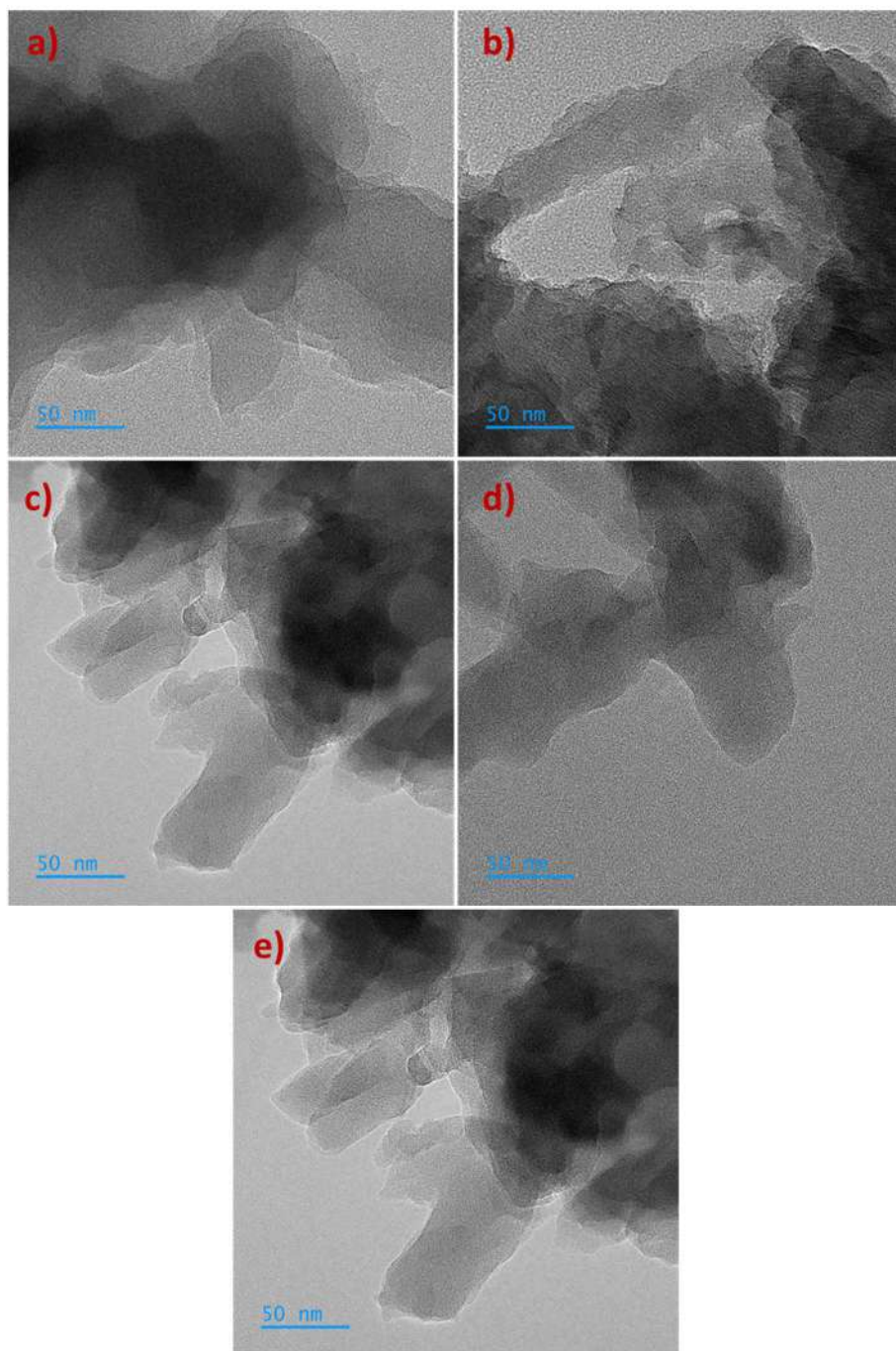


Figure 5.27. High-magnification TEM images of PH, PCOOH, POH, POME, and PSH showing agglomerated particulate morphology (scale bar: 50 nm).

The elemental composition of the polymers was further studied using EDAX analysis. The EDAX shows the presence of C, N, O, Cl, and S. Further, the elemental mapping reveals a largely homogeneous spatial distribution of the detected elements across the analyzed regions, suggesting uniform incorporation during polymerization.

The EDAX is a bulk-sensitive technique with a significantly larger information depth compared to XPS. The absence of Cl in PCOOH and POH, and the absence of S in PCOOH as observed by XPS, indicates surface-level de-doping or loss of weakly bound counter-ions from the outermost layers. Therefore, the combined EDAX and XPS results demonstrate a depth-dependent distribution of dopant species, which is governed by the type of functional groups. The EDAX confirmed bulk incorporation, and the XPS provided the surface-specific chemical information.

TEM images of PH, PCOOH, POH, POME, and PSH recorded at identical magnifications (200 nm scale) are given in Figure 5.26, and Figure 5.27 shows the microstructures at a lower magnification corresponding to a 50 nm scale. In both cases, all polymers exhibit agglomerated assemblies composed of randomly sized particles without any well-defined or ordered nanostructures. The overall morphology remains comparable across all the polymers. The observed agglomerated morphology is consistent with the SEM analysis, confirming that it is an intrinsic characteristic of the polymer materials. Consequently, the morphological similarity across the polymers suggests that the differences in electrochemical performance primarily arise from variations in chemical functionality rather than from morphological effects.

5.2.5 Electrical, Dielectric, and Magnetic Properties

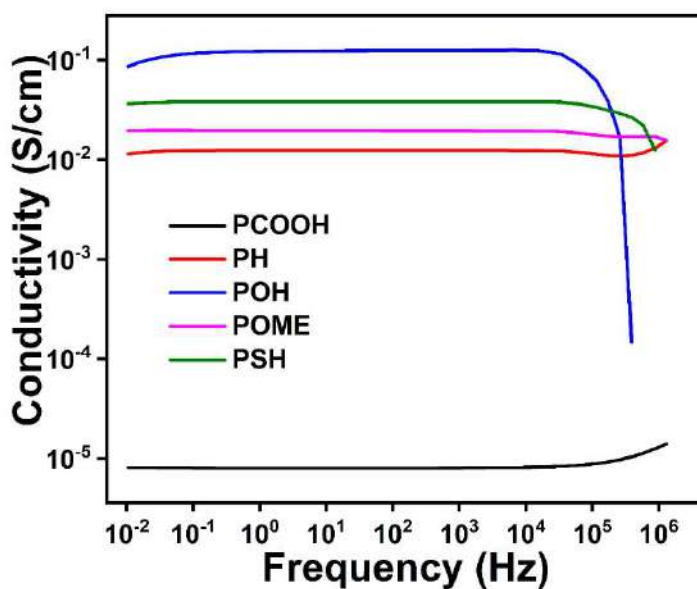


Figure 5.28: *AC conductivity with respect to frequency of PCOOH, PH, POH, POME, and PSH.*

Table 5.2: σ_{dc} of the polymer samples

Sample	σ_{dc} (S cm ⁻¹)
PCOOH	8.02×10^{-6}
PH	1.2×10^{-2}
POH	1.2×10^{-1}
POME	1.9×10^{-2}
PSH	3.8×10^{-2}

The frequency-dependent conductivity of the samples was measured from 10^{-2} Hz to 10^6 Hz and is presented in Figure 5.28. The dielectric behavior of the samples indicates different charge transport mechanisms for the polymers. In the lower frequency range, all the samples show frequency-independent behavior, resulting in a plateau region corresponding to DC conductivity (σ_{dc}). The σ_{dc} values obtained from this frequency-independent plateau region are presented in Table 5.2. Among the samples, POH exhibited the highest conductivity, while PCOOH showed the lowest. These results suggest that polymers with electron-donating functional groups (-OH, -OMe, and -SH) enhance conductivity, whereas the electron-withdrawing group (-COOH) reduces the conductivity.

At higher frequencies, PCOOH, PH, and POME exhibit increasing conductivity due to enhanced charge mobility and reduced interfacial polarization effects. However, POH and PSH show a notable deviation from this ideal behavior, with conductivity decreasing as the frequency increases. This deviation is attributed to dipolar relaxation losses associated with the -OH and -SH functional groups. At higher frequencies, these polar groups are unable to align with the rapidly oscillating electric field, leading to energy loss and reduced ionic mobility. The energy drops result from a phase mismatch caused by the lag in dipolar alignment with the oscillating field, leading to dielectric relaxation and dissipation of energy in the form of heat^{39, 40}.

The dielectric constant (ϵ') of the samples was investigated as a function of frequency and is presented in Figure 5.29a. PCOOH exhibited the lowest ϵ' across all frequencies, which is attributed to its limited polarization due to the inability of its dipoles to rapidly align with the

alternating electric field. In contrast, POME showed the highest ϵ' , indicating superior polarizability. POH and PSH exhibited moderate ϵ' values due to the sluggish polarization behavior of hydroxyl and thiol functional groups. This sluggish nature is also reflected in their frequency-dependent conductivity. The ϵ' of PH was moderately low, as expected, due to the absence of any polarizable functional groups⁴¹.

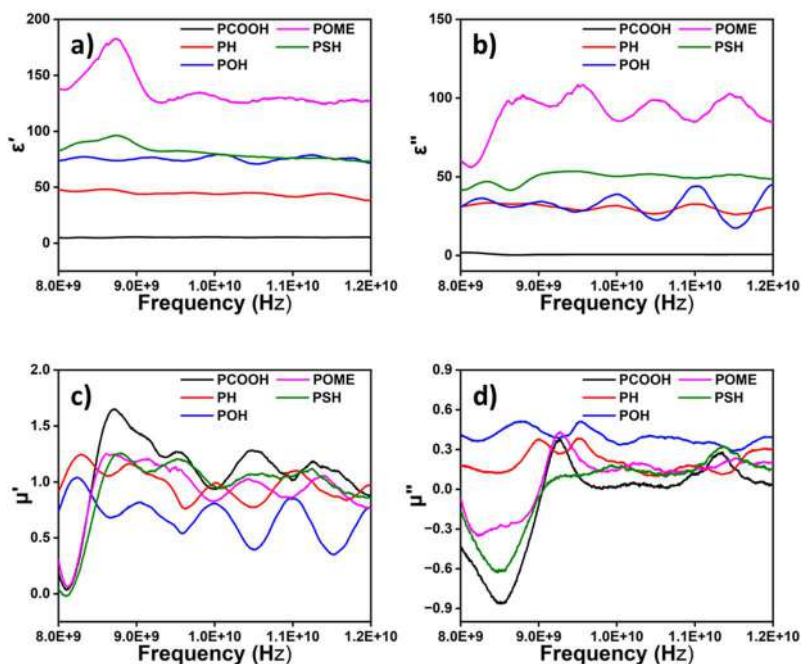


Figure 5.29: Frequency-dependent dielectric and magnetic response of PH, PCOOH, POH, POME, and PSH: (a) real part of dielectric permittivity (ϵ') versus frequency, (b) imaginary part of dielectric permittivity (ϵ'') versus frequency, (c) real part of magnetic permeability (μ') versus frequency, and (d) imaginary part of magnetic permeability (μ'') versus frequency

The dielectric loss (ϵ'') of the samples was further studied as a function of frequency. The results are shown in Figure 5.29b. The results highlight

the influence of the nature of functional groups on energy dissipation. The dielectric loss values follow the order: POME ($\epsilon'' \approx 100$) > PSH ($\epsilon'' \approx 40$) > POH $\approx$ PH ($\epsilon'' \approx 30$) > PCOOH ($\epsilon'' \approx 5$). POME exhibited the highest ϵ'' across the entire frequency range, indicating significant energy loss via dipolar relaxation and interfacial polarization mechanisms^{41, 42}.

POME and POH displayed a wave-like variation with multiple peaks across the X-band, unlike the frequency-independent behavior observed for PSH, PH, and PCOOH. The wave-like ϵ'' in POME and POH suggests the presence of multiple relaxation processes. The methoxy group (-OMe) in POME possesses a strong and permanent dipole moment, enhancing dipolar polarization and segmental motion, which leads to localized resonance phenomena at distinct frequencies, resulting in the observed wave-like pattern. POH, with its hydroxyl group (-OH), likely exhibits hydrogen-bonded segmental dynamics or heterogeneous environments, giving rise to multiple relaxation processes at different frequencies.

PSH, PH, and PCOOH exhibit nearly a flat ϵ'' profile, indicating a weak, frequency-independent dipolar contribution. Therefore, the energy loss in these samples is not primarily due to polarization effects but rather due to ohmic conduction and non-relaxing dipoles. In the case of PCOOH, the lowest ϵ'' is attributed to stiffening of the polymer matrix caused by strong hydrogen bonding, which suppresses dipole mobility and leads to minimal relaxation losses.

Magnetic permeability measurements were also conducted in the X-band, and the results are presented in Figures 5.29c and 5.29d. All samples exhibited microwave permeability, arising from magnetic moments. The plots show a wave-like appearance, indicating the

presence of diverse heterogeneous interfacial surfaces. Regardless of the functional groups present, the functionalization had little effect on the overall magnetic permeability values.

5.2.6 EMI Shielding Performance

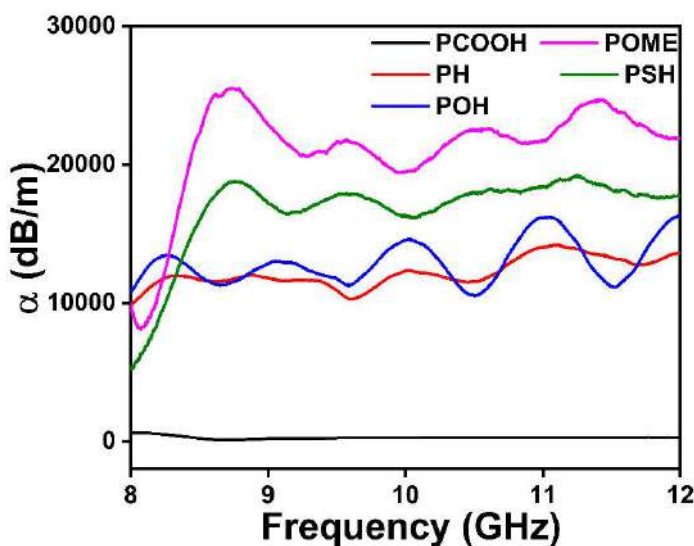


Figure 5.30: Frequency dependence of the attenuation constant (α) for PH and its functionalized derivatives PCOOH, POH, POME, and PSH.

A combination of effective impedance matching with free space and favorable electromagnetic loss governs microwave (MW) absorber performance. The intrinsic ability of a material to dissipate incident MW radiation is commonly evaluated using the attenuation constant (α), where a higher α reflects a greater capacity for electromagnetic energy attenuation within the material. The attenuation constant versus frequency plot of the polymers is presented in Figure 5.30. The attenuation constant is defined as:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \sqrt{\mu''\varepsilon'' - \mu'\varepsilon' \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu''\varepsilon'' + \mu'\varepsilon')^2}} \quad (5.1)$$

Where f is the frequency and c is the velocity of light.

Among the polymers, POME exhibits the highest attenuation constant, which can be attributed to the synergistic contribution of enhanced electrical conductivity and strong dielectric polarization, leading to pronounced MW energy dissipation. PH, POH, and PSH also display comparatively high α values, indicating effective attenuation behavior dominated primarily by polarization-related loss mechanisms. In contrast, PCOOH shows a markedly low attenuation constant, suggesting inefficient MW energy dissipation arising from weak relaxation and conduction losses. It should be noted that a high attenuation constant alone does not guarantee superior MW absorption performance. MW absorption efficiency is strongly influenced by impedance matching between the absorber and free space, which governs the extent of MW entry into the material. Consequently, optimal MW absorbers must achieve a balanced combination of high attenuation capability and appropriate impedance matching to realize effective MW absorption^{43, 44}.

The EMI shielding effectiveness of the synthesized polymers was examined in the X-band (8-12 GHz). The results are presented in Figure 5.31. The shielding effectiveness (SE_T), expressed in decibels (dB), measures the reduction in the energy of electromagnetic (EM) waves upon interaction with a shielding material. The total shielding effectiveness (SE_T) represents the overall energy loss of EM waves as they pass through the shielding material. The SE_T is defined as:

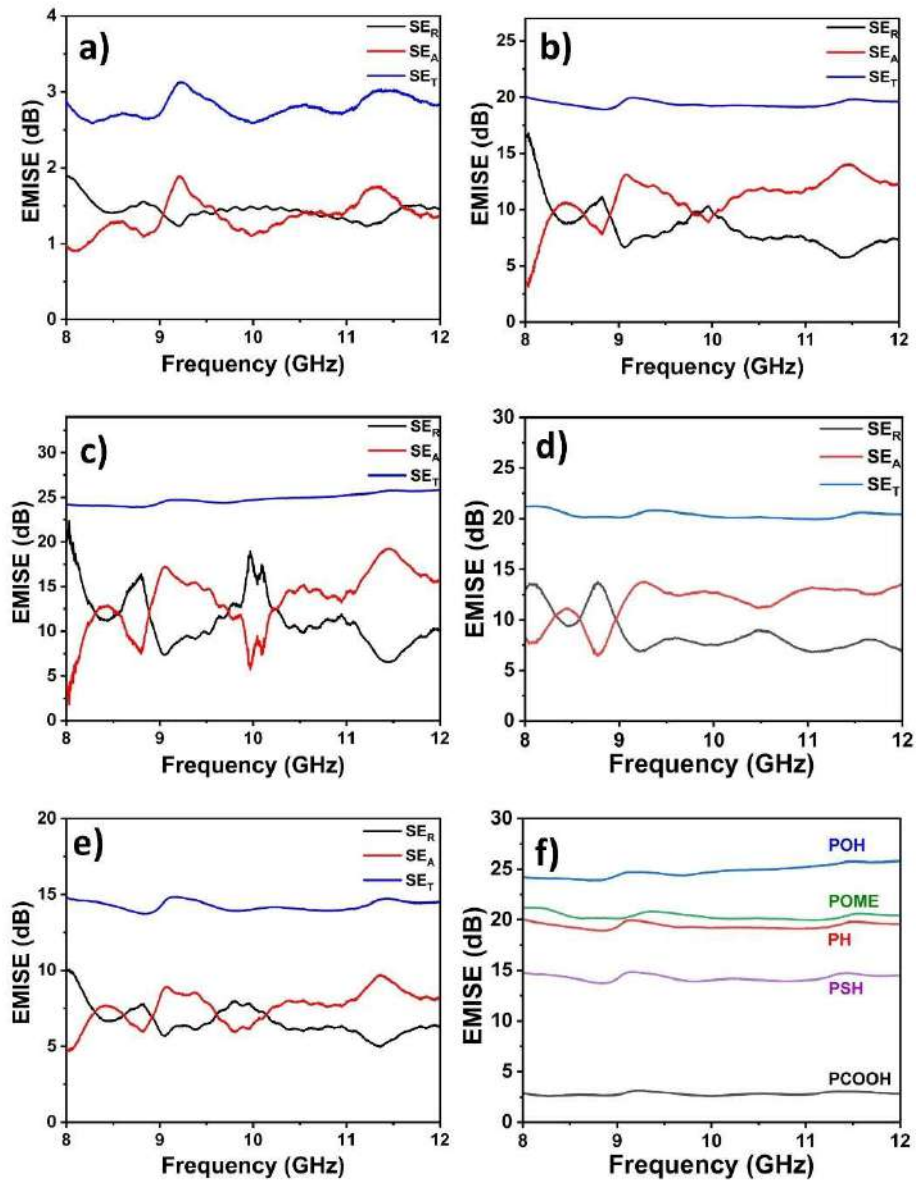


Figure 5.31: EMI shielding effectiveness of a) PCOOH, b) PH, c) POH, d) POME, e) PSH, and f) comparison of SE_T.

$$SE_T = -10 \log \left(\frac{P_t}{P_i} \right) \quad (5.2)$$

where P_t and P_i are the powers of the transmitted and incident electromagnetic waves, respectively. The SE_T was further decomposed into reflection (SE_R) and absorption (SE_A) using relations 5.3& 5.4 and is represented in Figure 5.31 a-e.

$$SE_R = -10 \log(1 - R) \quad (5.3)$$

$$SE_A = -10 \log\left(\frac{T}{1-R}\right) \quad (5.4)$$

The total shielding effectiveness (SE_T), along with the deconvoluted SE_R and SE_A components, was analyzed for all samples. Among them, PCOOH exhibited the lowest EMI shielding efficiency, with a maximum SE_T of 3.1 dB across the entire frequency range. This indicates that most of the incident EM waves passed through the sample with minimal absorption or reflection. The poor shielding performance is attributed to the low conductivity of PCOOH, suggesting an insufficient charge carrier density to effectively attenuate the incoming EM radiation.

In contrast, POH exhibited the highest EMI shielding efficiency, with a maximum SE_T of 25.8 dB, predominantly driven by SE_A , which contributed 22.3 dB. The superior performance of POH is attributed to the highly polarizing hydroxyl group and the high concentration of charge carriers, as indicated by its high electrical conductivity. POME showed the second-highest shielding efficiency with a SE_T of 21.2 dB, where SE_A was again the dominant mechanism, contributing 13.3 dB. The presence of the methoxy functional group likely enhances charge carrier mobility, thereby improving absorption efficiency. PH exhibited an SE_T of 20 dB, closely comparable to POME. Although PH has higher electrical conductivity than POME, the enhanced polarizing effect of the methoxy group in POME contributes to its better performance. PSH

showed a moderate EMI shielding efficiency of 14.9 dB, primarily due to absorption-driven, like the other samples. Its lower performance can be attributed to its relatively low conductivity and the weak polarizing nature of the thiol group. The comparative SET plot clearly reveals the trend in EMI shielding performance as:



This correlates well with the conductivity values obtained from broadband dielectric spectra. This trend confirms that the EMI shielding efficiency of the polymers primarily depends on their electrical conductivity and the nature of the substituent functional groups present in the polymer structure.

5.2.7 Electrochemical Analysis

The CVs of PH, PCOOH, POH, POME, and PSH recorded in 1 M H₂SO₄ are given in Figure 5.32. All polymers exhibited a stable and much wider potential window of -1.0 V to 1.5 V. There was no observable hydrogen or oxygen evolution across this potential window. One of the remarkable results of our studies is this wider potential window, indicating good electrochemical stability under acidic aqueous conditions for our newly synthesized polymers⁴⁵.

The peak current, i_{pa} , and i_{pc} from the CV recorded at 10 mV s⁻¹ in 1 M H₂SO₄ are given in Table 5.3. The CV of PH recorded at 10 mV s⁻¹ shows two well-resolved oxidation peaks at 0.33 V and 0.53 V, with corresponding reduction peaks at 0.44 and -0.1 V. The first oxidation peak and the corresponding reduction peaks are much wider compared to the second redox peaks, suggesting kinetics or structural heterogeneity

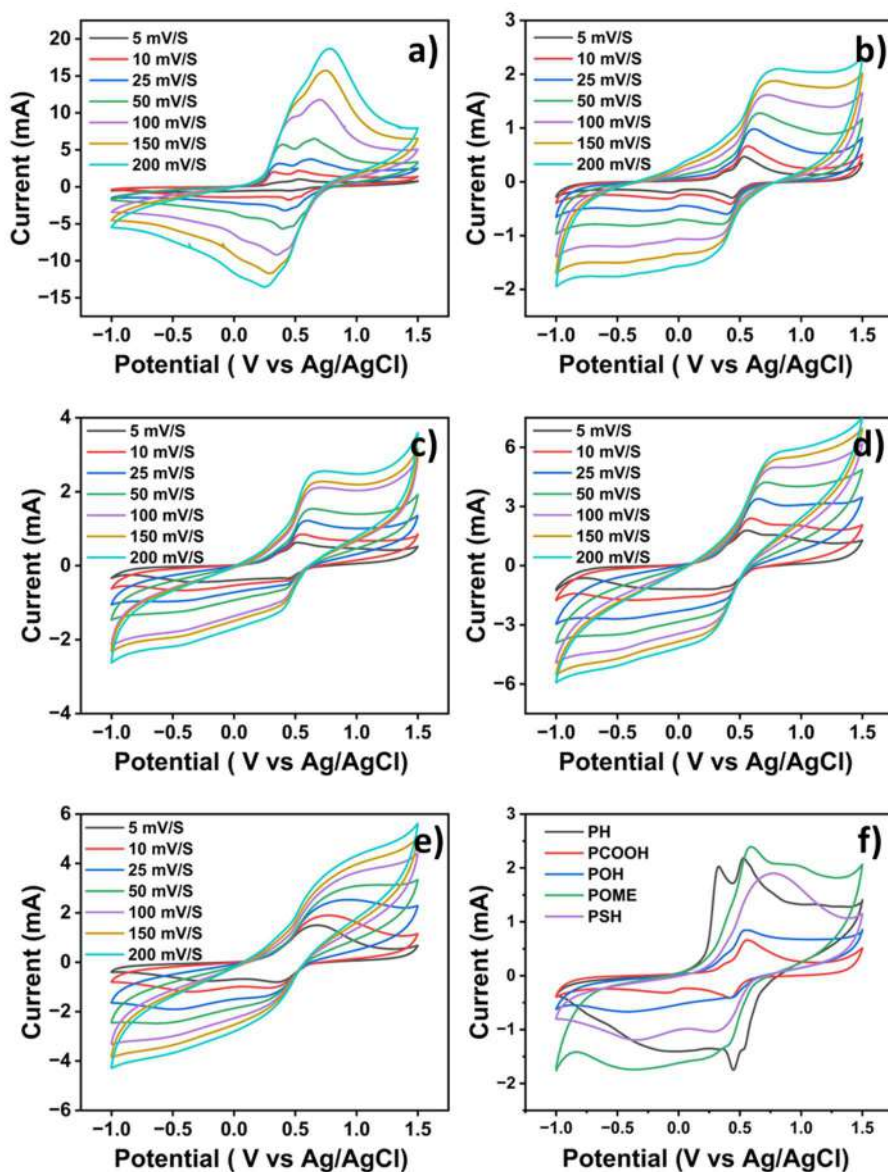


Figure 5.32: CV of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH recorded at different scan rates in 1 M H_2SO_4 , (f) a comparative cyclic voltammogram of all polymers recorded at a fixed scan rate of 10 mV s^{-1} .

associated with deeply reduced states. This redox behavior is characteristic of polyaniline-type systems and is associated with transitions between different oxidation states of the polymer backbone.

Table 5.3: Oxidation (i_{pa}) and reduction peak (i_{pc}) potentials CVs of PH, PCOOH, POH, POME, and PSH recorded in 1 M H_2SO_4 at a scan rate of 10 mV s^{-1} .

Polymer	i_{pa-1} (V)	i_{pa-2} (V)	i_{pc-1} (V)	i_{pc-2} (V)
PH	0.33	0.53	0.44	-0.10
PCOOH	0.39	0.56	0.42	-0.11
POH	0.39	0.56	0.42	-0.42
POME	0.40	0.58	0.42	0.20
PSH	0.79	-	0.31	-0.38

The functionalized polymers retain similar electrochemical behavior. The CVs of PCOOH and POH recorded at 10 mV s^{-1} exhibit oxidation peaks at approximately 0.39 V that appear as shoulders, followed by a strong oxidation peak at 0.56 V. The corresponding first reduction peak is observed at 0.42 V for both polymers. The second peaks are observed at -0.11 V for PCOOH and at -0.42 V for POH. The shoulder-type oxidation peaks indicate a partial overlap of redox processes, reflecting the influence of polar substituents on the electronic structure of the polymer.

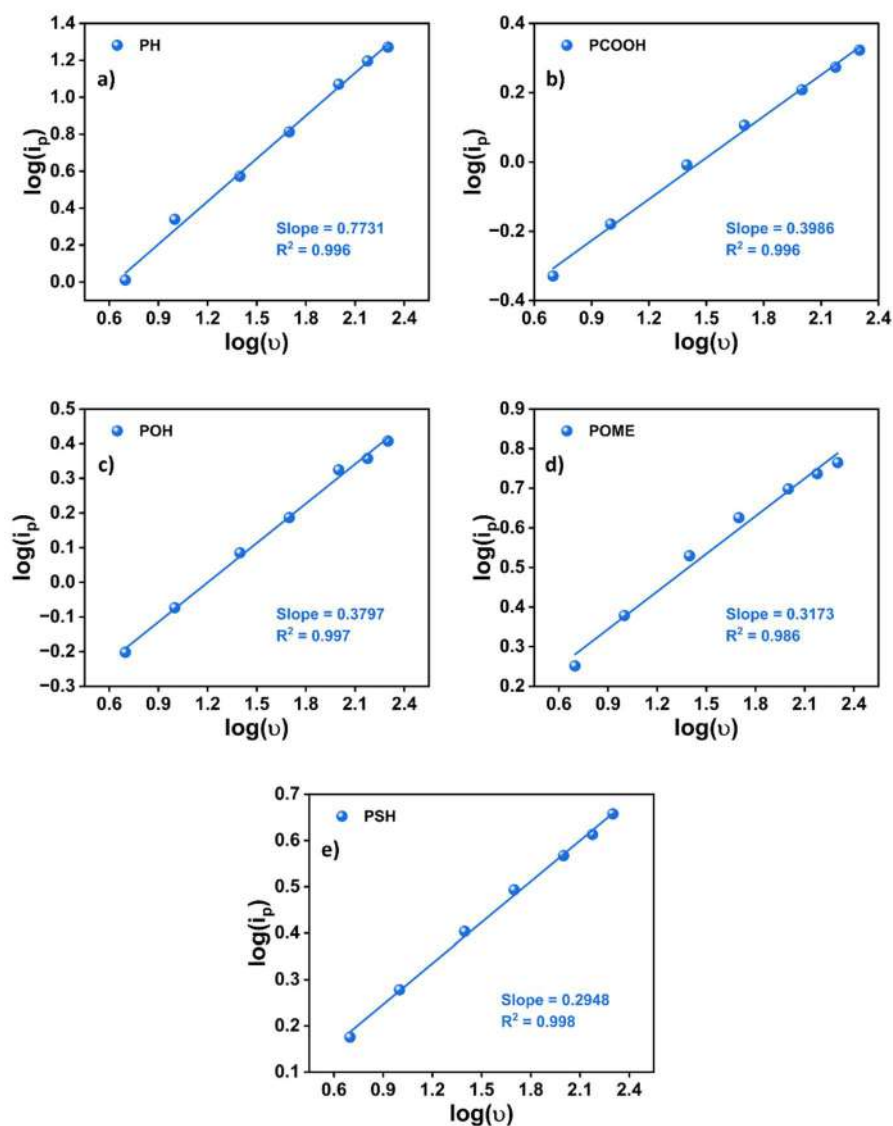


Figure 5.33: $\log(i_p)$ versus $\log(v)$ plots of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH in 1 M H_2SO_4

POME displays a more complex electrochemical response, with multiple oxidation peaks at approximately 0.40 V appearing as a shoulder, 0.58 V, and 0.98 V. The corresponding reduction peaks at around 0.42 V, 0.20 V, and -0.33 V. The appearance of an additional high-potential oxidation

process suggests stabilization of higher oxidation states by the electron-donating methoxy group.

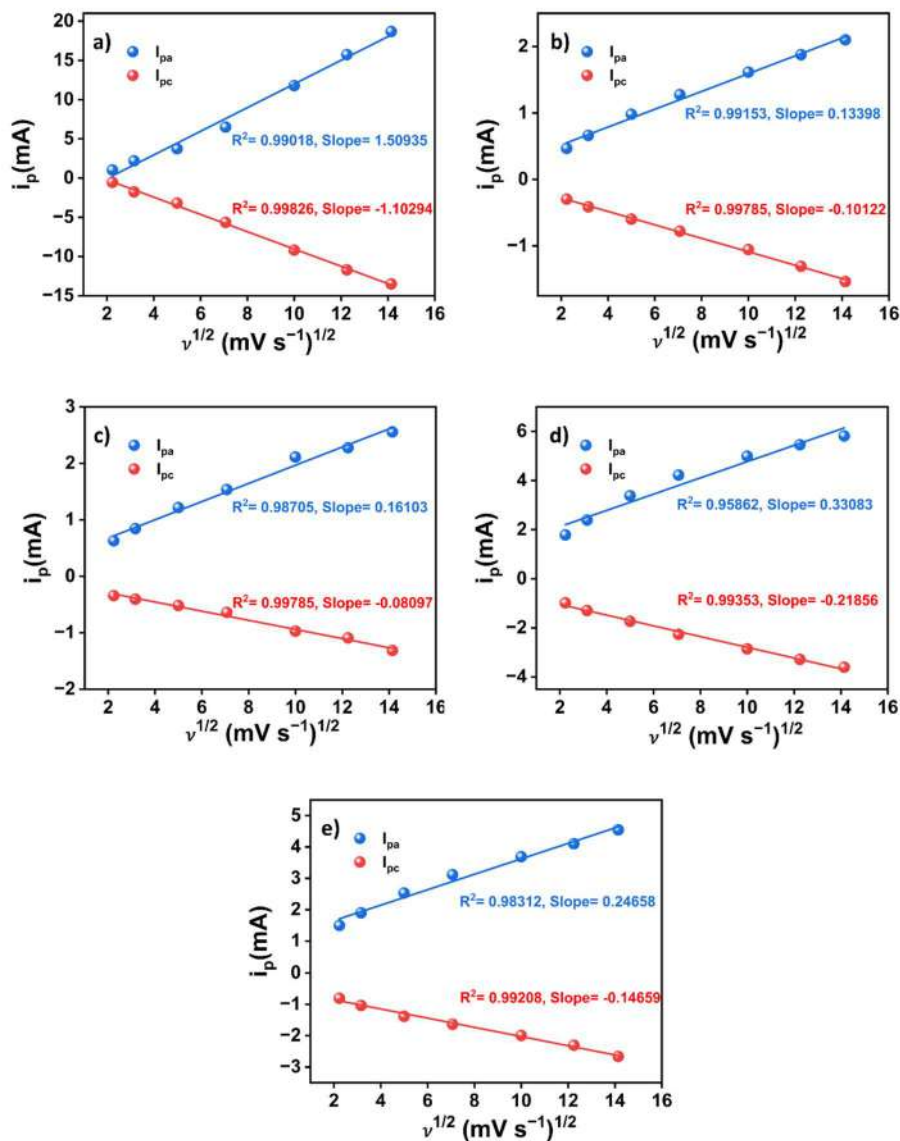


Figure 5.34: Dependence of the anodic and cathodic peak currents on the square root of scan rate for (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH recorded in 1 M H_2SO_4 .

In contrast, PSH exhibits a single broad oxidation peak centered at approximately 0.79 V and broad reduction peaks at 0.31 V and -0.38 V, indicating merged or suppressed redox transitions. The second reduction peaks of all polymers and the third reduction peak of POME are broad in nature, suggesting kinetically slower processes associated with the most reduced states.

Table 5.4: Kinetic parameters from peak current versus square root of scan rate plots and *b*-values derived from $\log(i_p)$ versus $\log(v)$ analysis in 1 M H_2SO_4 .

Polymer	Peak type	(i _p vs √v)		(log-log)	
		Slope	R ²	b-value	R ²
PH	Anodic	1.51	0.99	0.7731	0.996
	Cathodic	-1.1	0.998	-	-
PCOOH	Anodic	0.133	0.991	0.3986	0.996
	Cathodic	-0.101	0.998	-	-
POH	Anodic	0.161	0.987	0.3797	0.997
	Cathodic	-0.08	0.997	-	-
POME	Anodic	0.331	0.958	0.3173	0.986
	Cathodic	-0.218	0.994	-	-
PSH	Anodic	0.247	0.983	0.2948	0.998

Polymer	Peak type	(i _p vs √v)		(log-log)	
		Slope	R ²	b-value	R ²
	Cathodic	-0.147	0.992	-	-

Table 5.5: Kinetic parameters from peak current versus square root of scan rate plots and b-values derived from $\log(i_p)$ versus $\log(v)$ analysis in 1 M MSA.

Polymer	Peak type	(i _p vs √v)		(log-log)	
		Slope	R ²	b-value	R ²
PH	Anodic	0.178	0.987	0.299	0.998
	Cathodic	-0.152	0.984	-	-
PCOOH	Anodic	0.072	0.999	0.459	0.998
	Cathodic	-0.051	0.984	-	-
POH	Anodic	0.266	0.994	0.305	0.995
	Cathodic	-0.224	0.996		
POME	Anodic	0.154	0.993	0.322	0.994
	Cathodic	-0.127	0.957	-	-
PSH	Anodic	0.157	0.98	0.254	0.991
	Cathodic	-0.186	0.942	-	-

The scan-rate-dependent analysis of CVs indicates a clear difference in the charge-storage kinetics for different functional groups. The b-value analysis plot and Randles-Ševčík analysis plots are given in Figures 5.33 and 5.34, respectively, and the data are summarized in Table 5.4. For all polymers, the anodic peak current exhibits a linear dependence on the square root of scan rate. This indicates that the process involved is diffusion-controlled. However, the b-values obtained from $\log(i_p)$ versus $\log(v)$ plots show significant variation for polymers containing different functional groups. The PH has a b-value of 0.77, suggesting mixed charge-storage behavior with a significant surface-controlled contribution. In the case of PCOOH, POH, POME, and PSH, the b-values in the lower range of 0.29 - 0.40 indicate dominant diffusion-controlled kinetics. This transition from mixed to diffusion-limited behavior suggests that the strong influence of functional groups on ion transport and charge-compensation mechanisms in acidic media.

Figure 5.37 shows the CVs of polymers recorded in 1 M MSA at various scan rates ranging from 5 to 200 mV s^{-1} . All polymers exhibit stable electrochemical responses across a wide potential window of -1.0 V to 1.5 V, identical to that observed in 1 M H_2SO_4 , indicating good electrochemical stability of the polymer backbones in aqueous organic acid. The CV shows an increase in peak current and moderate peak broadening as the scan rate increases. Showing diffusion-controlled process in all polymers

The redox processes of all the polymers were compared by plotting the CVs at a scan rate of 10 mV s^{-1} , and the results are presented in Table 5.6. In contrast to H_2SO_4 , the redox peaks of all polymers in MSA are

less resolved. This is because of the larger size of counterions penetrating into the polymer matrix. Each polymer exhibits two sets of redox peaks. The first oxidation peak appears as a shoulder, indicating partial overlap of redox transitions. The corresponding reduction peaks occur at positive and negative potentials, with a broad low-potential reduction peak for all polymers. This broadening suggests a slower kinetics and/or structural rearrangements associated with the deeply reduced states.

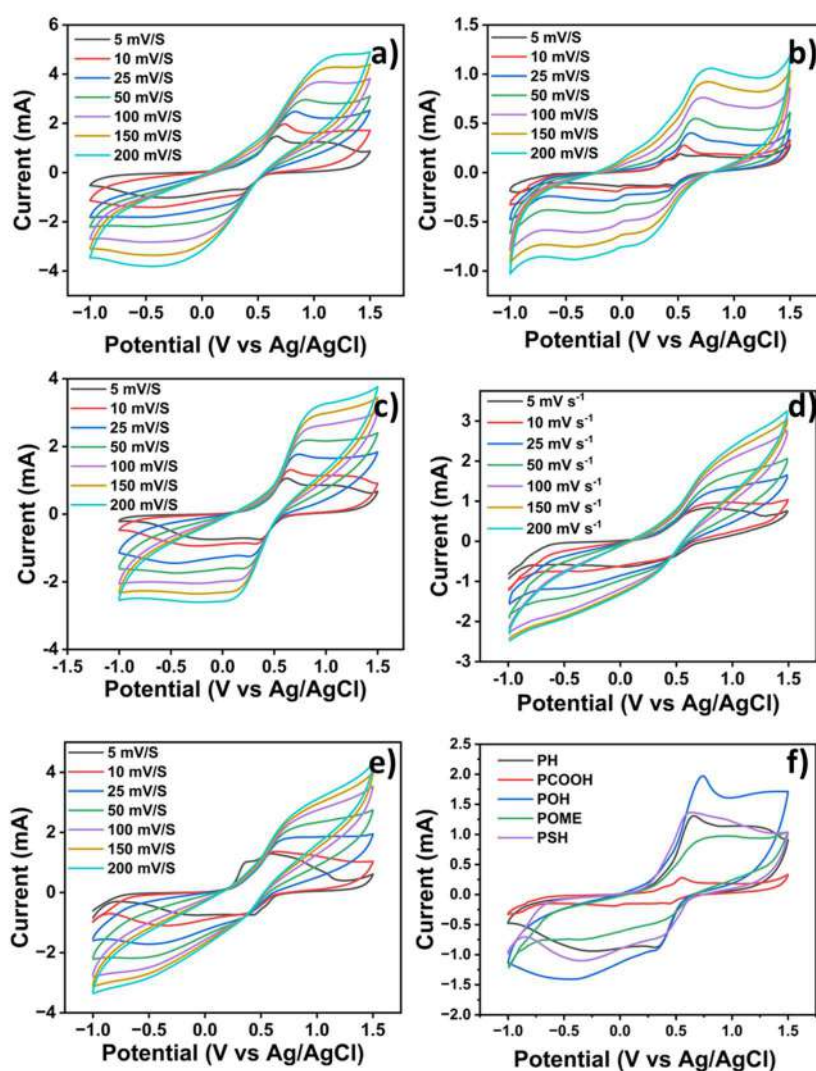


Figure 5.35: CV of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH recorded at different scan rates in 1 M MSA, (f) a comparative cyclic voltammogram of all polymers recorded at a fixed scan rate of 10 $mV s^{-1}$.

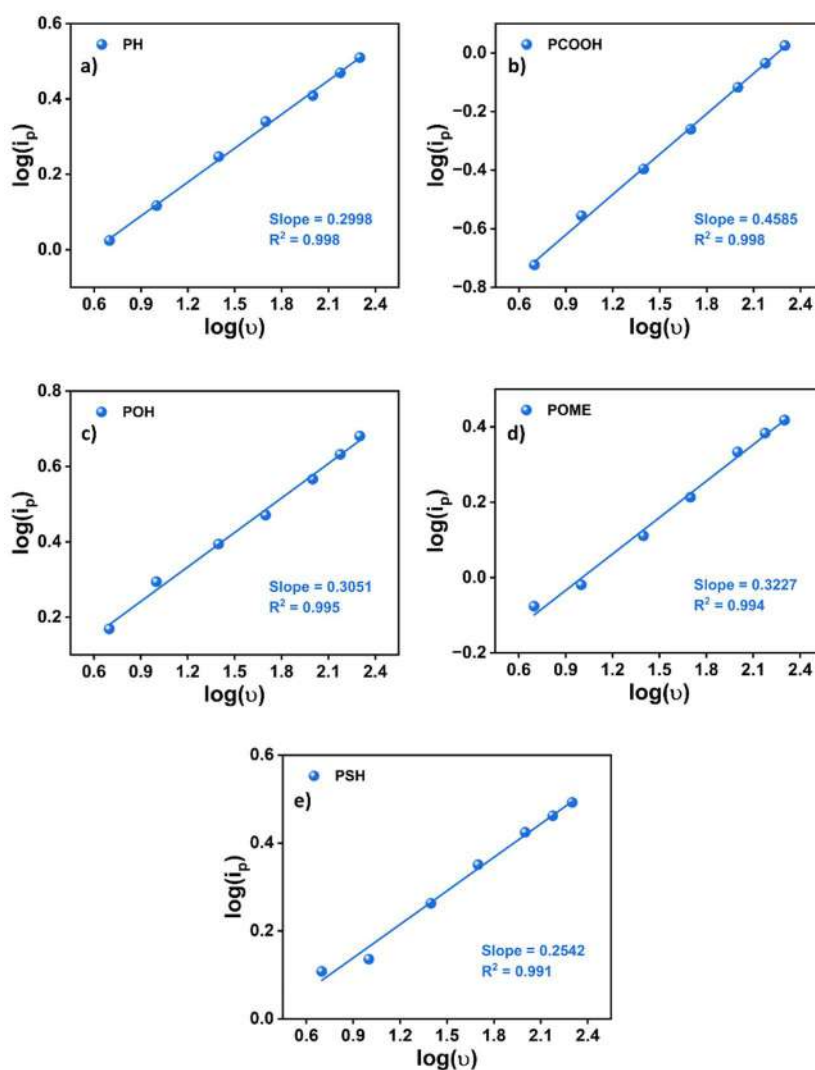


Figure 5.36: $\log(i_p)$ versus $\log(v)$ plots of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH in 1 M MSA.

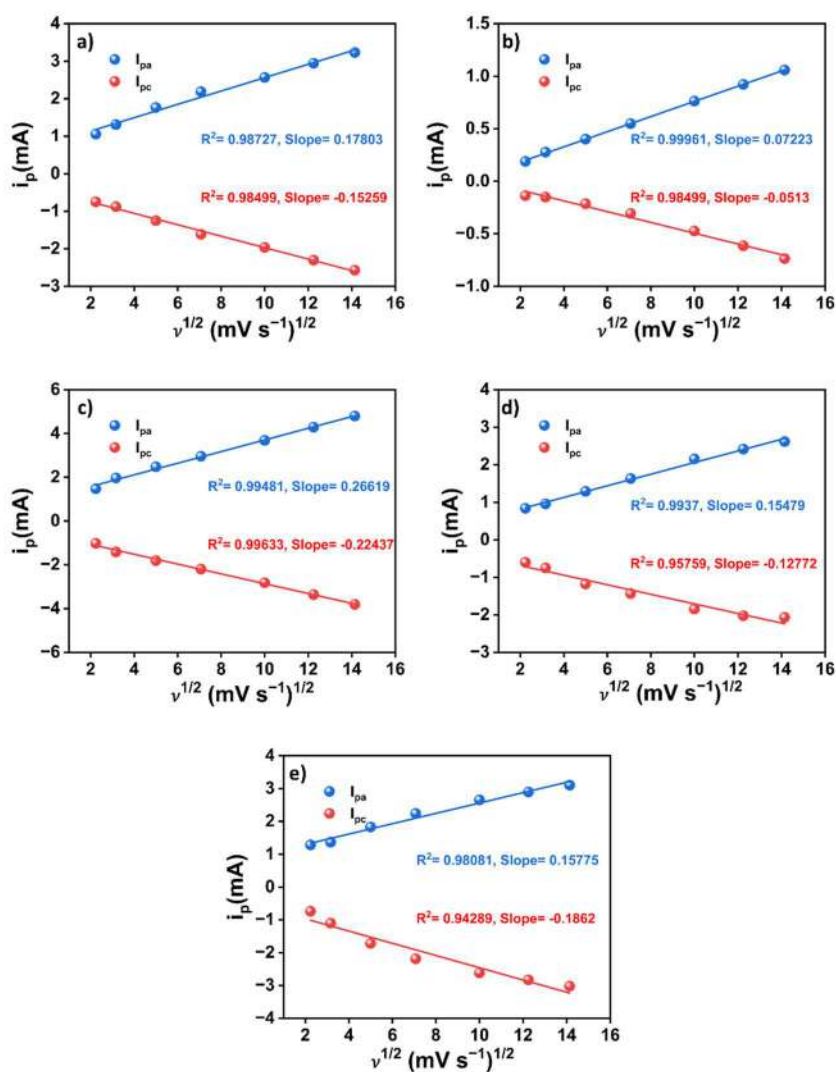


Figure 5.37: The anodic and cathodic peak currents vs. the square root of scan rate for (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH recorded in 1 M MSA.

The charge-storage kinetics of the polymers were studied by plotting i_p versus $\sqrt{v}$ and the $\log(i_p)$ versus $\log(v)$, and are shown in Figures 5.36 and 5.37, respectively. The kinetic parameters obtained from these plots are summarized in Table 5.5. The high linearity observed in both

analyses indicates the involvement of diffusion-controlled processes. The results indicate that replacing H_2SO_4 with MSA preserves the electrochemical stability and redox activity of the polymers while modifying the peak resolution and charge-transport dynamics.

Table 5.6: Oxidation (i_{pa}) and reduction peak (i_{pc}) potentials CVs of PH, PCOOH, POH, POME, and PSH recorded in 1 M MSA at a scan rate of 10 mV s^{-1} .

Polymer	i_{pa-1} (V)	i_{pa-2} (V)	i_{pc-1} (V)	i_{pc-2} (V)
PH	0.65	1.23	0.33	-0.23
PCOOH	0.55	0.89	0.44	-0.05
POH	0.74	1.28	0.35	-0.39
POME	0.085	-	0.35	-0.34
PSH	0.63	-0.93	0.37	-0.35

The electrochemical response of the polymers was studied in 1 M LiClO_4 solution in aqueous medium to evaluate the redox properties of the polymers in neutral conditions. Compared to acidic electrolytes, all the polymers have a wider electrochemically stable potential window of -1.2 V to 1.5 V, indicating enhanced electrochemical stability in the neutral medium.

The CVs of polymers were recorded in 1 M LiClO_4 . Figure 5.38f represents the CVs of polymers at a scan rate of 10 mV s^{-1} . All polymers have two oxidation and two reduction peaks, indicating a two-step redox

process. PH shows the first redox couple at ~ 0.02 V, followed by a second redox process centered around 0.53-0.58 V. The functionalized polymers have shifts in the redox peaks. PCOOH has positive shifts in

Table 5.7: Kinetic parameters from peak current versus square root of scan rate plots and b -values derived from $\log(i_p)$ versus $\log(v)$ analysis in 1 M LiClO₄.

Polymer	Peak type	(i _p vs $\sqrt{v}$)		(log-log)	
		Slope	R ²	b-value	R ²
PH	Anodic	0.134	0.992	0.5637	0.997
	Cathodic	-0.1351	0.999	-	-
PCOOH	Anodic	0.278	0.995	0.6037	0.999
	Cathodic	-0.226	0.997	-	-
POH	Anodic	0.205	0.995	0.503	0.997
	Cathodic	-0.162	0.997	-	-
POME	Anodic	0.289	0.996	0.5291	0.994
	Cathodic	-0.328	0.992	-	-
PSH	Anodic	0.154	0.99	0.4658	0.974
	Cathodic	-0.192	0.998	-	-

the oxidation peaks, along with a large separation in the corresponding reduction peaks. This suggests stabilized oxidation states and slower reduction kinetics. POH and PSH show negative second reduction peaks

(-0.70 V and -0.78 V, respectively), indicating kinetically slow reduction processes. POME has a positive shift of the first reduction peak, and other peaks similar to those of PH. The observation of two redox couples

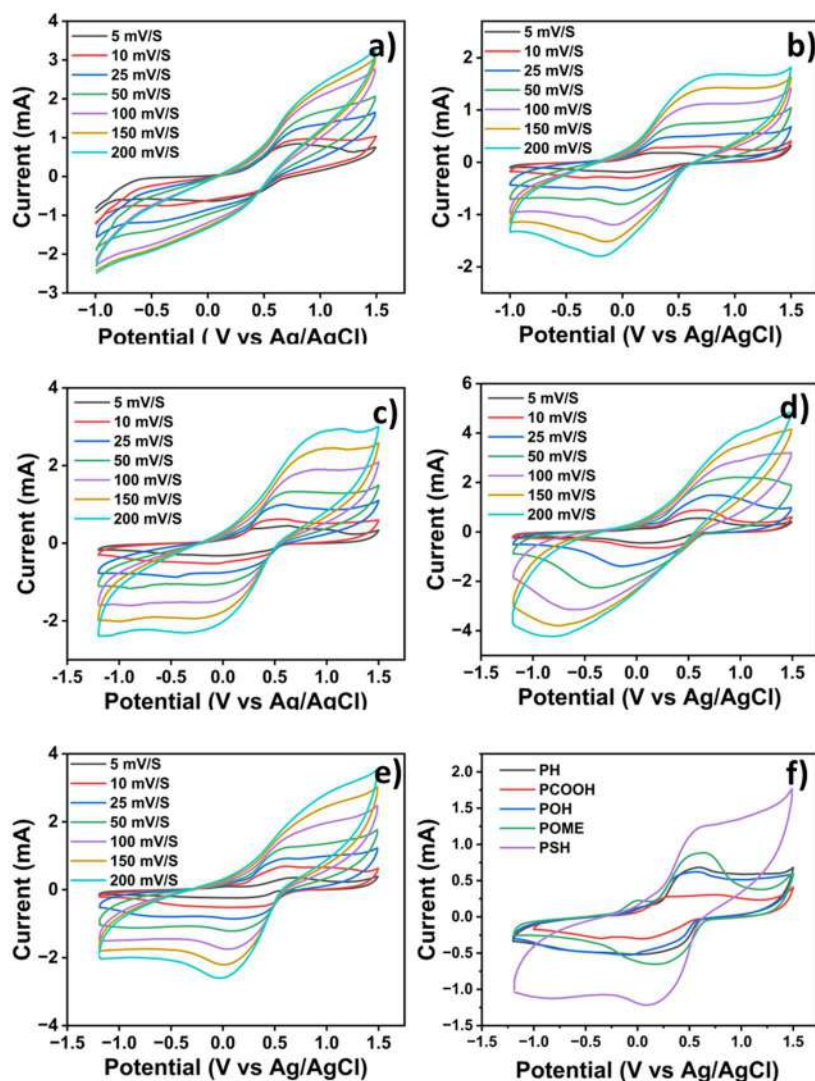


Figure 5.38: CV of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH recorded at different scan rates in 1 M LiClO₄, (f) a comparative cyclic voltammogram of all polymers recorded at a fixed scan rate of 10 mV s⁻¹.

in LiClO_4 confirms the presence of a stable multistep redox process with substituent-dependent processes⁴⁶.

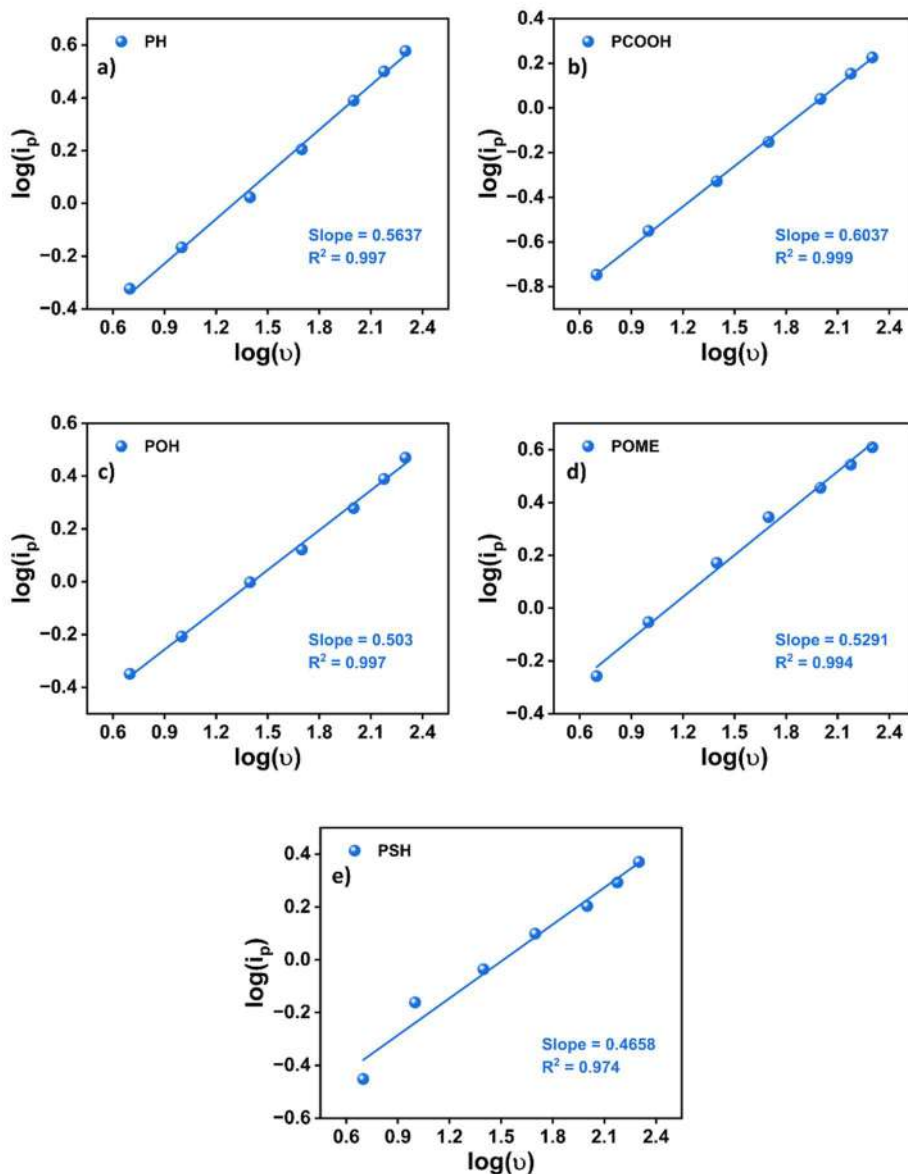


Figure 5.39: $\log(i_p)$ versus $\log(v)$ plots of (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH in 1 M LiClO_4 .

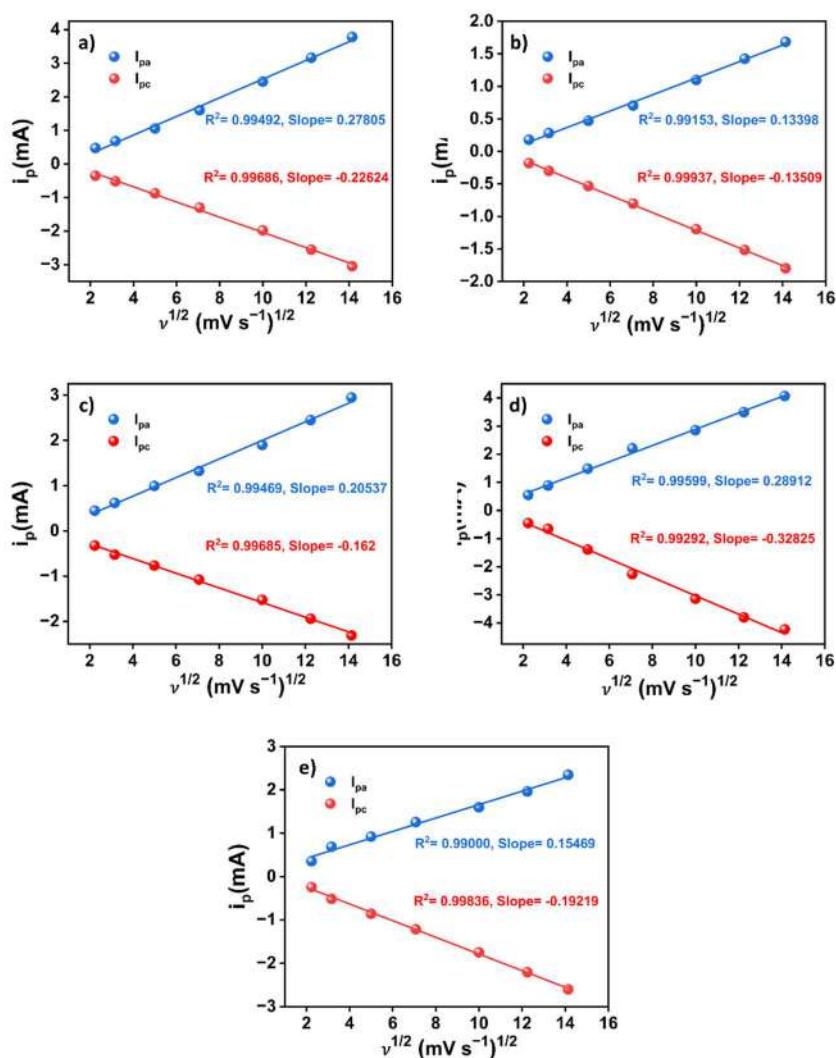


Figure 5.40: Dependence of the anodic and cathodic peak currents on the square root of scan rate for (a) PH, (b) PCOOH, (c) POH, (d) POME, and (e) PSH recorded in 1 M LiClO₄.

The square root of the scan-rate dependence of the anodic peak currents reveals a strong linear relationship between the peak current. The square root of the scan rate for all polymers, with R^2 exceeding 0.99. The corresponding plots are presented in Figure 5.40. This behavior indicates

a significant diffusion-controlled contribution to the redox processes in LiClO_4 electrolyte. To further quantify the charge-storage mechanism, b -values were extracted from $\log(i_p)$ versus $\log(v)$ plots using the anodic peak currents, as shown in Figure 5.39. The obtained b -values range from 0.47 to 0.60, as presented in Table 5.7, and all exhibit excellent linearity ($R^2 \geq 0.97$).

Table 5.8: Oxidation (i_{pa}) and reduction peak (i_{pc}) potentials CVs of PH, PCOOH, POH, POME, and PSH recorded in 1 M LiClO_4 at a scan rate of 10 mV s^{-1} .

Polymer	i_{pa-1} (V)	i_{pa-2} (V)	i_{pc-1} (V)	i_{pc-2} (V)
PH	0.02	0.58	0.02	0.53
PCOOH	0.29	0.78	0.04	-0.35
POH	0.04	0.57	-0.07	-0.7
POME	-0.01	0.64	0.18	-0.44
PSH	0.17	0.56	0.01	-0.78

The b -values close to 0.5 across the polymer series indicate that the electrochemical response in LiClO_4 is predominantly governed by diffusion-limited ion transport within the polymer films, with only a minor contribution from surface-controlled capacitive processes. Among the polymers, PCOOH displays the highest b -value, suggesting relatively enhanced ion accessibility and reduced diffusion limitations, likely due to increased hydrophilicity and stronger polymer-electrolyte

interactions. In contrast, PSH exhibits the lowest b -value, reflecting greater diffusion resistance, possibly arising from specific interactions or local structural constraints within the polymer matrix.

In summary, the electrochemical behavior of the five polymers was systematically examined in three aqueous electrolytes, namely 1 M H_2SO_4 , 1 M MSA, and 1 M LiClO_4 , to elucidate the influence of electrolyte acidity, ion size, and ion-polymer interactions on redox activity and charge-storage mechanisms. In acidic electrolytes (H_2SO_4 and MSA), all polymers exhibit multiple and comparatively sharper redox characteristics arising from proton-coupled doping-dedoping processes. The high proton mobility facilitates rapid charge compensation, leading to higher peak currents and enhanced pseudocapacitive contributions. Among the two acids, H_2SO_4 results in more pronounced redox activity, whereas MSA results in broader peaks due to the bulkier methyl sulfonate anion and its slower transport, while still maintaining stable electrochemical behavior. In contrast, the neutral electrolyte (1 M LiClO_4) yields a distinctly different response, characterized by a wider stable potential window, a single pair of broad redox peaks, and reduced current density, reflecting the suppression of proton-assisted redox transitions and the dominance of diffusion-controlled charge compensation by hydrated Li^+ and ClO_4^- ions. Scan-rate dependent analysis further corroborates this electrolyte-dependent behavior, with higher b -values in acidic media indicating increased surface-controlled and pseudocapacitive contributions, whereas b -values close to 0.5 in LiClO_4 , together with the linear dependence of peak current on the square root of scan rate, confirm diffusion-limited charge storage. Functional group substitution further modulates these trends by altering polymer hydrophilicity and ion accessibility. The polar

substituents promote relatively improved electrochemical activity, particularly in neutral and weakly acidic environments, and the bulkier or strongly interacting groups impose greater diffusion limitations.

5.2.8 Supercapacitor Device Performance

A symmetric supercapacitor device was fabricated using PH as the electrode material to carry out a preliminary analysis check its feasibility for future energy storage applications. 1 M H_2SO_4 is used as the electrolyte. The device was operated within a potential window of 0 V - 2.5 V. The device is fabricated of PH as an electrode material for future energy storage applications. This study also highlights its potential for further performance enhancement through material and device engineering. The CV profiles of the symmetric device are shown in Figure 5.41. The device exhibited a stable capacitive behavior across the wider potential window without any evident features associated with OER or HER.

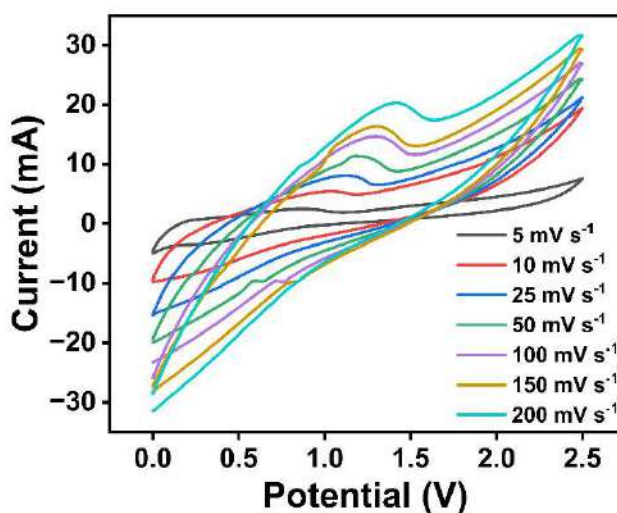


Figure 5.41: CV of the symmetric PH-based supercapacitor.

The GCD performance of the symmetric supercapacitor device is shown in Figure 5.42a.

The electrochemical performance of the fabricated device is modest and not exceptional. This is consistent with its material design. The supercapacitor electrode was fabricated using just the conducting polymer alone. We did not employ any material or electrode engineering strategies such as composite formation or nano-structuring. Consequently, the performance of the electrode is purely from the conducting polymer alone. In the absence of any material engineering, the conducting polymer electrodes have limited performance because of the limited electrical conductivity, restricted ion diffusion, and poor mechanical stability during prolonged charge/discharge cycles. These limitations of conducting-polymer-based electrodes are responsible for the moderate electrochemical performance of the supercapacitor device. The capacitance of the fabricated device was calculated and is 94 F g^{-1} at 1 A g^{-1} . The energy density and power density of the device were also calculated and are 49 Wh kg^{-1} and 1.0 kW kg^{-1} , respectively.

The primary objective of this preliminary study is not for performance optimization, but to demonstrate that the newly developed polymers can function as an active electrode material in energy storage devices. The material can also operate stably over a wide potential window in an aqueous electrolyte. The operation within a wide voltage window of 2.5 V is particularly significant, as the energy density is directly related to the square of the operating voltage. Therefore, even moderate improvement in the potential window can translate into enhanced energy density when higher cell voltages are accessible. A wider operating window in aqueous electrolytes also improves safety compared to

organic or ionic liquid-based systems. The electrochemical stability of the device suggests that these advantages can be further exploited through material and device engineering strategies in future studies.

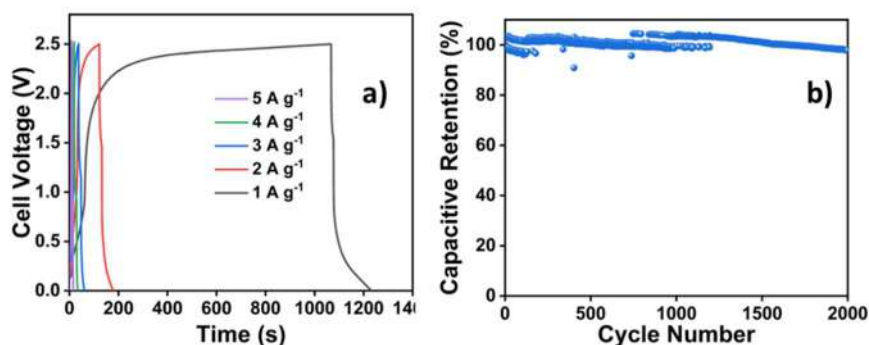


Figure 5.42: (a) Galvanostatic charge-discharge (GCD) profiles of the symmetric PH-based supercapacitor measured in 1 M H₂SO₄, and (b) cyclic stability performance of the device evaluated at a current density of 5 A g⁻¹.

5.3 Conclusion

This work reports the design, synthesis, and comprehensive characterization of a new family of conducting polymers. The polymers were synthesized via a simple, one-pot polymerization process in an aqueous acidic medium. The versatility in functional group attachment in the polymer backbone is demonstrated by introducing -OH, -OMe, -COOH, and -SH functional groups as representative examples without requiring any post-polymerization modification. Structural and chemical characterizations were done using FTIR, UV-Vis, fluorescence and lifetime measurements, ESR, XPS, and Raman analysis, while morphological features were examined using SEM/EDX and TEM. Thermal stability was evaluated by TGA, DTG, and DTA.

Electrochemical characterization of the polymers was investigated through cyclic voltammetry, b-value analysis, and scan-rate-dependent studies. The incorporation of an azo linkage within the conjugated backbone was shown to act as a proton sink and electron-withdrawing unit, stabilizing polaron and bipolaron formation and shifting charge storage from interfacial water-driven Faradaic reactions to intrinsic backbone redox processes. As a result, the polymers exhibit wide potential windows in different electrolytes. In aqueous acidic electrolytes such as 1 M H₂SO₄ and 1 M MSA, the potential window is estimated to be as wide as 2.5 V and extending to 2.7 V in 1 M LiClO₄, which is uncommon in conducting polymers in aqueous systems. A symmetric supercapacitor device fabricated using the polymer PH exhibits stable capacitive behavior over wide voltage windows of up to 2.5 V in 1 M H₂SO₄, with good reversibility and sustained cycling stability, confirming reliable device-level performance. The device exhibited a capacitance of 94 F g⁻¹ at 1 A g⁻¹. The energy density and power density of the device are found to be 49 Wh kg⁻¹ and 1.0 kW kg⁻¹, respectively.

In addition to the electrochemical performance, the polymers were evaluated for frequency-dependent electrical conductivity, dielectric constant, dielectric loss, magnetic permeability, attenuation constant, and electromagnetic interference shielding effectiveness. The results reveal clear structure-property relationships linking backbone design and functional groups to charge transport, polarization losses, and absorption-dominated EMI shielding performance. Together, these findings establish a scalable and chemically versatile framework for more processable multifunctional conducting polymers that integrate wide electrochemical stability with energy storage and EMI shielding capabilities in aqueous environments.

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Chapter 6

Conclusion

This thesis advances conducting polymers for aqueous energy storage through two strategies: covalent functionalization of polyaniline with heteroatom-doped rGO to enhance stability and performance, and rational design of an azo-linked polymer family with wide potential windows, facile functionalization, and multifunctional electrochemical, dielectric, optical, and electromagnetic properties.

6.1 Summary

CPs have gained significant research interest because of their unique electrochemical properties. CPs are extensively studied for their applications in the energy storage field. Even though they have many advantages, their intrinsic properties pose some challenges. Electrochemical stability, operating potential window, and chemical versatility are the main concerns associated with CPs. This thesis systematically addresses the key limitations associated with CPs for aqueous energy-storage devices. The work progresses from covalently functionalizing PANI to the rational design of a new CP family that overcomes the challenges associated with conventional CPs.

In the first part of the thesis, PANI is covalently functionalized with hetero-atom-doped rGO. In Chapter 1, PANI is covalently attached to N-doped rGO through an amide linkage. The PANI is effectively stabilized through non-covalent interactions from N-mrGO. Also, PANI reduced the aggregation of the rGO sheets, thereby increasing the active surface area. The optimized N-mrGO-PANI5 had structural stability as well as improved electrochemical performance. Later, N-mrGO-PANI5 is made into an electrode, and a symmetrical supercapacitor device is fabricated using 1 M H₂SO₄ as the electrolyte. The fabricated device exhibited high specific capacitance, excellent rate capability, and long cycle life. The device also had high energy density and moderately high-power density.

In Chapter 2, the N-mrGO-PANI system is further improved by co-doping with S. The S doping introduced additional non-covalent interactions and imparted an additional pseudocapacitive nature to the rGO. SN-mrGO-PANI7.5 showed the optimized performance. A symmetrical supercapacitor is fabricated using the optimized material,

and its performance is evaluated. The device exhibited improved specific capacitance, rate capability, cycle life, energy density, and power density. Collectively, Chapters 1 and 2 established that the covalent functionalization of PANI with hetero-atom-doped rGO is an effective and robust strategy for improving the performance of PANI-based electrodes for energy storage applications.

The studies in Chapters 1 and 2 proved improvements in the performance of PANI-based electrode materials. Further improvement of the system was hindered by the limited potential window of the system in aqueous environments and the difficulties in the functionalization of the polymers. OER and HER pose major challenges in aqueous systems. Also, costly monomers or complex organic reactions limited the functionalization of CPs for tuning their properties.

In Chapter 3, a new family of CPs was rationally designed and synthesized. The polymers were synthesized by a simple one-pot methodology. In addition to this, the reaction was also carried out in an aqueous medium, offering the advantages of scalability, cost-effectiveness, and processability. The incorporation of an azo linkage within the conjugated backbone acted as a proton sink and an electron-withdrawing unit. This stabilizes polaron and bipolaron formation and shifts the charge storage from interfacial water-driven Faradaic reactions to intrinsic backbone redox processes. As a result, the polymers exhibit wide potential windows in different electrolytes. In aqueous acidic electrolytes such as 1 M H_2SO_4 and 1 M MSA, the potential window is estimated to be as wide as 2.5 V and extends to 2.7 V in 1 M LiClO_4 , which is uncommon for conducting polymers in aqueous systems. A symmetric supercapacitor device fabricated using the polymer PH

exhibits stable capacitive behavior over wide voltage windows of up to 2.5 V in 1 M H₂SO₄.

Furthermore, readily available aniline derivatives were used to incorporate different functional groups into the polymer chain backbone. This eliminated the need to use multistep synthesis or expensive reagents. The functionalization allowed efficient tuning of the physicochemical, electrochemical, and dielectric properties. The materials also showcased a clear dependence of frequency-dependent conductivity, dielectric behavior, and absorption-dominated electromagnetic interference shielding effectiveness on the functional group present. The results establish a new versatile multifunctional CP system that addresses the key limitations encountered by currently available CPs.

Overall, this thesis demonstrates a clear advancement of PANI-based electrodes through covalent functionalization. Secondly, a new CP family is rationally designed to overcome the limitations associated with existing CPs. The findings provide a next-generation CP system suitable for advanced aqueous energy and electronic applications.

6.2 Future Outlook

In this thesis, we have successfully developed a covalent functionalization method for PANI to address its inherent limitations, and also developed a new CP. These two outcomes of this thesis extend beyond the scope of supercapacitors and span energy, sensing, electronics, and multifunctional material platforms.

The covalent functionalization of PANI with heteroatom-doped rGO was proven to be an efficient and generalizable method for other conducting

polymers as well. The strategy can be effectively utilized for electrode engineering in future applications. This methodology successfully demonstrated a reduction in polymer chain degradation during continuous charge/discharge cycles and reduced the aggregation of rGO sheets. This allows the methodology to be adopted for high-mass-loading supercapacitor electrodes, since stability is an important factor. These materials are also promising electrode materials for flexible electrodes, as the covalent bonds can better tolerate mechanical stress compared to composites formed by physical mixing.



The macromolecular structure of the heteroatom-doped rGO/PANI system can also be utilised for hybrid energy storage systems. Stable pseudocapacitance and fast charge transport are the key features required for hybrid energy storage devices. In addition to this, heteroatom-doped rGO has active sites that can be utilized for electrocatalysis, including oxygen reduction, OER, and HER. The PANI present in the material can effectively act as a redox mediator or a conductive filler for electrocatalysis applications.

The new family of CP has opened up a wider application horizon because of its easy synthesis, large potential window in aqueous systems, and multifunctional properties. The wide potential window of the P4PDP in

aqueous electrolyte make it a promising candidate for future applications in high-voltage aqueous supercapacitors. The large operating window is directly related to the high energy density of the device. This feature also helps the polymers to be used in redox flow batteries and electrochemical actuators.

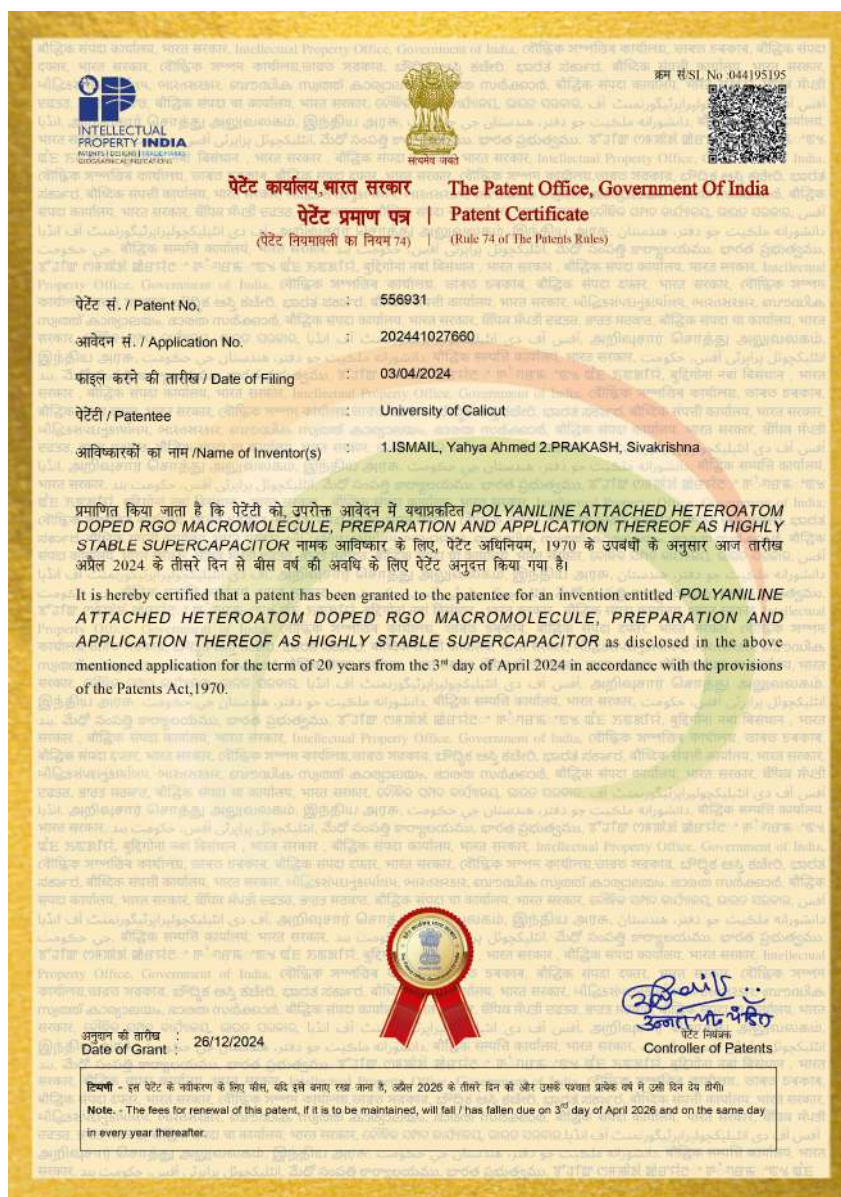
The possibility of direct functionalization of the polymer chain backbone makes P4PDP and its derivatives suitable for electrochemical sensing. The fluorescence properties of PH and PCOOH also showcase the extent of tunability through functionalization. The fluorescence properties of the polymers can also be utilized for fluorescence sensing applications. Tuning the emission band gap opens up new opportunities for these polymers to be used in light-emitting diode (LED) and optoelectronic applications.

The polymers were also observed to have dielectric responsive nature and EMI shielding performance. These properties make them ideal for EMI shielding coatings, lightweight radar-absorbing materials, and electronic packaging. The one-pot synthesis methodology, aqueous synthesis medium, and cost-effective materials make them suitable for large-scale applications.

Beyond energy and electronics, the presence of redox-active azo linkages and heteroatom-containing functional groups opens avenues for electrocatalysis and photocatalysis, where charge delocalization and tunable electronic density are critical. These polymers may also find applications in smart multifunctional systems, combining energy storage, EMI shielding, and sensing within a single material platform.

Altogether, the polymer design rules developed here constitute a universal platform for next-generation conducting polymers with universal electrochemical stability, optical functionality, and electromagnetic tunability, which are both processable and low-cost.

Patent



**“POLYANILINE ATTACHED HETEROATOM DOPED RGO
MACROMOLECULE, PREPARATION AND APPLICATION THEREOF
AS HIGHLYSTABLE SUPERCAPACITOR”**

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List Of Publications



Material Research Bulletin

***Sivakrishna Prakash, Roopasri
Rajamani, PM Anjana, RB Rakhi Yahya
A Ismail.***



Journal of Power Sources

***Sivakrishna Prakash, Roopasri
Rajamani, SM Varghese, RB Rakhi
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***Lijin Rajan, Toribio F Otero,
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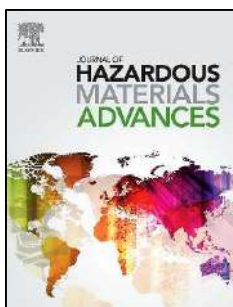
International Journal of Biological Macromolecules.

***Athira Ajayan, Lijin Rajan,
Sivakrishna Prakash, Yahya A Ismail***



Next materials

*Roopasri Rajamani, **Sivakrishna Prakash**, Yahya A Ismail*



Journal of Hazardous Materials Advances

*P Sowmya, Linda Williams, **Sivakrishna Prakash**, Abraham Joseph*



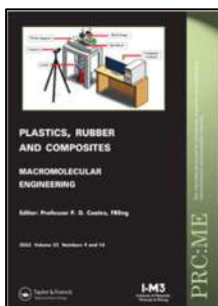
Journal of Solid State Chemistry

*P Sowmya, **Sivakrishna Prakash**, Abraham Joseph*



RSC Advances

*P Sowmya, **Sivakrishna Prakash**, Abraham Joseph*



Plastics, Rubber and Composites

Roopasri Rajamani, Sivakrishna

Prakash, Yahya A Ismail

Presentations

Paper presentation (poster) in Advanced Materials Synthesis, Characterization and Application (AMSCA 2023), International Conference organized by the Dept. of Physics, Savitribai Phule Pune University.

Paper presentation (poster) in Frontiers in Chemical Sciences (FCS 2024), Conference organized by the Department of Chemistry, University of Calicut.