

Nano Crystal Semiconductor Synthesis, Characterisation and Photodegradation

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adjudge of the degree of*

DOCTOR OF PHILOSOPHY IN CHEMISTRY

BINU NAUFAL



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CERTIFICATE

This is to certify that the thesis entitled “Nano crystal semiconductor synthesis characterisation and photodegradation” submitted by Mr. Binu Naufal to the University of Calicut for the award for the degree of Doctor of Philosophy in Chemistry, is a record of precise research work carried out at the department of Chemistry, University of Calicut under my guidance and supervision. The contents of the thesis have been checked for plagiarism using the software ‘Urkund’ and similarity index falls under permissible limit. I further certify that the thesis or part has not previously formed the basis for the award of any degree, diploma, fellowship, associateship or any other similar title of any other universities or institutions.

Calicut University
January 2018

Dr. Pradeepan Periyat

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The adjudicators of the thesis entitled “Nano crystal semiconductor synthesis characterisation and photodegradation” submitted by Mr. Binu Naufal, have not suggested any major changes in the scientific content, results and interpretations. However some typographic errors and mild corrections suggested by the examiners are incorporated in the revised thesis.

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January 2018

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I hereby declare that the matter embodied in the thesis is the result of studies carried out by me at the Department of Chemistry, University of Calicut, under the supervision of **Dr. PradeepanPeriyat**, Assistant Professor, Department of Chemistry, University of Calicut and the same has not previously formed the basis for the award of any degree or diploma. Whenever the work described or cited is based on the findings of other researchers, due acknowledgement is made in keeping with the general practice of reporting scientific observations.

Binu Naufal

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***To
The Society***

*“Anyone who can solve the problems of water will be worthy of two
Nobel prizes-
one for peace and one for science”*

-John. F. Kennedy

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GLOSSARY

TP	:	Titanium tetra isopropoxide
AC	:	Acetic acid
TSm1	:	1% Samarium doped TiO ₂
TSm2	:	2% Samarium doped TiO ₂
TSm5	:	5% Samarium doped TiO ₂
TSm10	:	10% Samarium doped TiO ₂
TDy0.5	:	0.5% Dysprosium doped TiO ₂
TDy1	:	1% Dysprosium doped TiO ₂
TDy2	:	2% Dysprosium doped TiO ₂
TDy5	:	5% Dysprosium doped TiO ₂
TDy10	:	10% Dysprosium doped TiO ₂
TYb1	:	1% Ytterbium doped TiO ₂
TYb2	:	2% Ytterbium doped TiO ₂
TYb5	:	5% Ytterbium doped TiO ₂
TYb10	:	10% Ytterbium doped TiO ₂
TNd0.5	:	0.5% Neodymium doped TiO ₂
TNd1	:	1% Neodymium doped TiO ₂
TNd2	:	2% Neodymium doped TiO ₂
TNd5	:	5% Neodymium doped TiO ₂
TNd10	:	10% Neodymium doped TiO ₂

TEr0.5	:	0.5% Erbium doped TiO ₂
TEr1	:	1% Erbium doped TiO ₂
TEr2	:	2% Erbium doped TiO ₂
TEr5	:	5% Erbium doped TiO ₂
TEr10	:	10% Erbium doped TiO ₂
FT IR	:	Fourier transform infrared spectroscopy
XRD	:	X-Ray diffraction
DRS	:	Diffuse reflectance spectra
DSC	:	Differential scanning calorimetry
XPS	:	X-Ray photoelectron spectroscopy
SEM	:	Scanning electron microscope
EDS	:	Energy dispersive spectroscopy
TEM	:	Transmission electron microscope
BET	:	Brunaur-Emmett-Teller
PL	:	Photo luminescence
MB	:	Methylene blue
CB	:	Conduction band
VB	:	Valance band
UV	:	Ultra violet
TOC	:	Total organic carbon

ABSTRACT

Nanocrystalline semiconductor oxide TiO_2 and various rare earth metal ions (Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+} and Nd^{3+}) doped TiO_2 were synthesized using a modified sol-gel method. All these materials were well characterised with different techniques such as FT-IR, XRD, Raman spectroscopy, DRS, XPS, SEM and TEM. The photocatalytic activity of nanocrystalline TiO_2 and various rare earth metal ions (Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+} and Nd^{3+}) doped TiO_2 were systematically studied as function of temperature under both UV and sunlight. Chapter 1 explains the subject of nano science and nanomaterials, an introduction to semiconducting nanocrystalline TiO_2 , objective and overview of the current thesis. Chapter 2 explains the materials and methods used for carrying out the research work. The working chapter 3, 4, 5, 6 and 7 explains the systematic study on the effect of various rare earth metal ion dopants (Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+} and Nd^{3+}) on nanocrystalline TiO_2 and its photocatalytic activity. Chapter 8 explains the successful demonstration of the self-cleaning and pesticide degradation application of the Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+} and Nd^{3+} doped TiO_2 photocatalyst discussed in chapter 3, 4, 5, 6 and 7 for two practical applications. In first application, a self-cleaning coatings on glass bottle were developed using the above TiO_2 photocatalyst to demonstrate the self-cleaning application of TiO_2 photocatalyst by purifying the organic dye contaminated water under the UV and normal sunlight. In second application explains the degradation of an organo chlorine pesticide “karate” commonly used by the farmers of

Kerala using the Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+} and Nd^{3+} doped TiO_2 photocatalyst. Self-cleaning and degradation activity of pesticide by using above TiO_2 photocatalyst was more effective in sunlight than UV light. These study shows the possibility of using Sm^{3+} , Dy^{3+} , Er^{3+} , Yb^{3+} and Nd^{3+} doped TiO_2 photocatalyst for the practical and industrial applications such as self-cleaning coatings, decomposition of organic pesticides, water purification *etc.*

1 Chapter

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Chapter

**Samarium ion (Sm^{3+})
doped TiO_2 synthesis,
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