

**SYNTHESIS, CHARACTERIZATION AND
APPLICATIONS OF LANTHANIDE NANO
PARTICLES DOPED ON ZnO, TiO₂, SiO₂.**



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Registration No: 042-Ph.D- CHEM-GCU-09

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**DEPARTMENT OF CHEMISTRY
GC UNIVERSITY LAHORE-PAKISTAN**

**SYNTHESIS, CHARACTERIZATION AND
APPLICATIONS OF LANTHANIDE NANO
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RESEARCH COMPLETION CERTIFICATE

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I, Farhat Anwar, Reg. No. 042-Ph.D-CHEM-GCU-09 scholar of Ph.D. in the subject of Chemistry for the session 2010-2014 hereby declare that the matter printed in the thesis titled " **SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF LANTHANIDE NANO PARTICLES DOPED ON ZnO, TiO₂, SiO₂**" is my own work and has not been printed, published and submitted as research work, thesis or publication in any form in any University, Research Institution in Pakistan or Abroad.

Dated: _____

Signature of Deponent

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Farhat Anwar

DEDICATION

***To my parents whose wishes and prayers have taken
me wherever I have managed to go, to my beloved Son
Abdul Hannan and my little darling Yusra Abid.***

ABSTRACT

Three sets of *nanoparticles* (*ZnO*, *Gd/ZnO*, *Sm/ZnO*, *La/ZnO*), (*TiO₂*, *Gd/TiO₂*, *Sm/TiO₂*, *La/TiO₂*) and (*SiO₂*, *Gd/SiO₂*, *Sm/SiO₂*, *La/SiO₂*) were fabricated by sol-gel method using appropriate precursors with and without using surfactant (Sodium Dodecyl Sulphate) below its CMC value. The synthesized samples were characterized by *Thermogravimetric Analysis/Differential scanning calorimetry* (TGA/DSC) for their thermal properties, by scanning electron microscopy (SEM) for morphology of nanoparticles, by Transmission electron microscopy (TEM) for particle size, by *X-Ray Diffraction* (XRD) for crystal structure and crystallite size, and *Fourier Transform Infrared Spectroscopy* (FTIR) was used to analyze metal-oxygen bonding and functional groups. All characterization techniques confirmed the synthesis of nanoparticles. The average size of all nanoparticles was observed below 30nm and results obtained from TEM and XRD for particle size are in agreement with each other. *Solid phase UV-visible absorption spectrophotometer* (SPS) analysis was performed to study optical band gap of metal oxide nanoparticles and effect of doping on the band gap of nanoparticles. It was observed that band gap of undoped nanoparticles were higher than the band gap of same material in bulk form and band gap of lanthanide doped nanomaterials was less than undoped material. The observed optical band gap value for ZnO was 3.62eV, for TiO₂ was 3.69eV and for SiO₂ was 3.58eV. Catalytic activity was done by photodegradation of a highly neurotoxic, industrial pollutant Methylene Blue at different reaction conditions for time intervals 30 minutes, 60 minutes and 120 minutes using UV-light, Sunlight and dark. The photocatalytic degradation of MB was studied by using UV-Vis spectrophotometer in kinetic mode and first order rate constant (k) was calculated. Maximum degradation (26.146%) with k-value 0.1031 Sec⁻¹ was made Gd/ZnO nanoparticles after 120 minute reaction in UV-light. It was also observed that photodegradation activity of Gd/ZnO, Sm/ZnO and Sm/TiO₂ was approximately equal with a slight difference. Also SiO₂ and Ln (Ln= Gd,Sm,La) doped SiO₂ have lower catalytic degradation activity as compared to (*ZnO*, *Gd/ZnO*, *Sm/ZnO*, *La/ZnO*) and (*TiO₂*, *Gd/TiO₂*, *Sm/TiO₂*, *La/TiO₂*). Results suggested that these nanoparticles may be envisaged for the treatment of waste water.

THE MAIN OBJECTIVE OF THE PRESENT PhD THESIS

From Literature it has been investigated that nanomaterials are flatterer vital due to their catalytic, optical and electrical applications in whole world now a days. However Pakistan is a country that is not faring that well in this aspect of technology despite of having better infrastructure for synthesis and applications of nanotechnology and there is a need to develop new technologies and materials by utilizing available resources to meet the upcoming environmental and energy challenges and to gain economic benefits. So the present research work include synthesis of nanoparticles using cheapest precursor salts, optimum fabrication conditions, and greater efficiency along with subsequent objectives, which mainly are;

- Fabrication of transition metal oxide nanoparticles (ZnO, TiO₂, SiO₂).
- Doping of transition metal oxide nanoparticles with lanthanide where (Ln= Gd, Sm and La).
- Selection of suitable method for nanoparticles fabrication.
- Controlled conditions of pH, temperature and heating time.
- Characterization of nanoparticles by TEM, SEM, XRD, TGA, FTIR, UV-Visible.
- Particular precursor concentration and surfactants to check the:
 - (a) Primary particle size and morphology of nanoparticles.
 - (b) Crystal Phase of material, crystallite size and Crystallite shape.
 - (c) Optical properties of the obtained nanoparticles to make development solar cell fabrication.
 - (d) The investigation of the catalysis by degradation of organic dye.
 - (e) The photocatalytic activity in the frame of change of fabrication media, catalysis conditions, and catalysis time period.
 - (f) Study of first order rate constant value and %age degradation of organic dye.
 - (g) The correlation between the catalysts, activity-morpho-structural properties.

ORGANIZATION OF THE REPORT

This thesis has been prearranged in five chapters. The chapter 1 is about the introduction of nanotechnology and nanomaterials and different characterization methods. Chapter 2 contains a pertinent literature review on transition metal oxides and lanthanide doped nanoparticles. Chapter 3 deals with the fabrication procedures and chemicals and materials used in this research work. Chapter 4 presents the experimental results and discussion on the synthesis of nanoparticles in which the structural characterization of samples has been carried out by X-rays diffraction (XRD), UV-VIS Spectroscopy Scanning electron Microscope (SEM), and Transmission Electron Microscopy (TEM), catalytic and optical study of the nanoparticles. Chapter 5 contains the conclusions for the experimental research work and suggestions for future work.

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List of Abbreviations

eV	electron volt
SDS	Sodium Dodecyle sulphate
CMC	Critical micelle concentration
λ_{\max}	Lambda max
Θ	Braggs angel
nm	nanometer
ppm	parts per million
FWHM	Full width half maxima
M.B	Methylene Blue
ln	log natural
UV	Ultraviolet
min	minutes
k	first order rate constant
A	Absorption
t	thickness of thin layer
Vis	Visible
MHz	Megahertz
%age	percentage
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
EDX	Energy Dispersive X-Rays
TGA	Thermo Gravimetric Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
Ln	Lanthanides
La	Lanthanum
Sm	Samarium
Gd	Gadolinium
ZnO	Zinc Oxide
TiO ₂	Titanium Oxide
SiO ₂	Silicon Oxide

INTRODUCTION

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