

Synthesis of Metal Oxides Based Photocatalysts for the Removal of Organic Pollutants from Waste Water



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DOCTOR OF PHILOSOPHY

By

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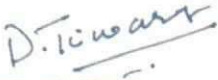
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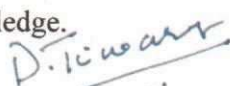
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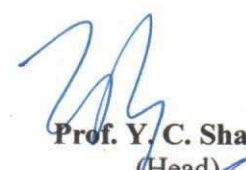
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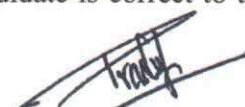

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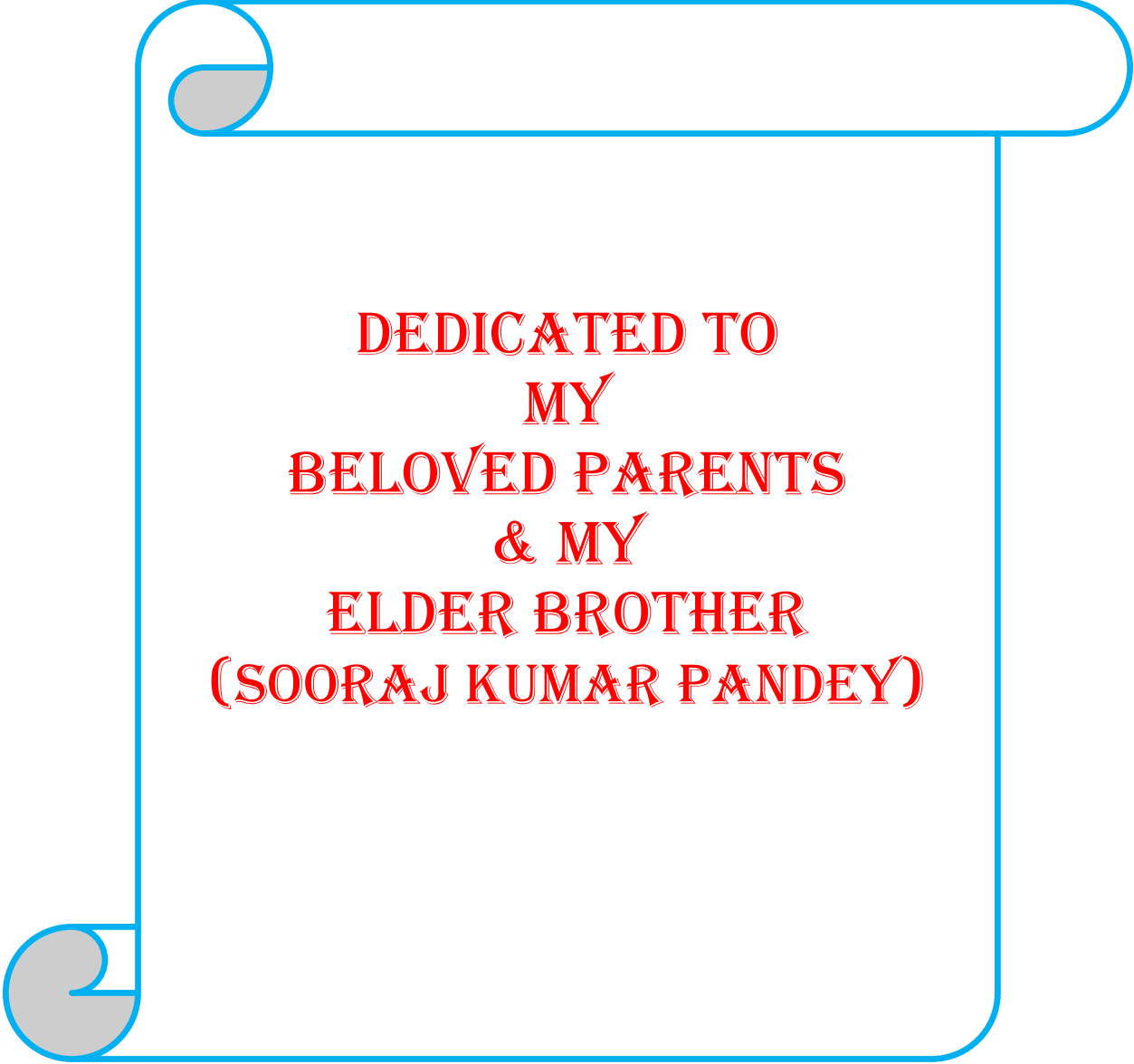
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**DEDICATED TO
MY
BELOVED PARENTS
& MY
ELDER BROTHER
(SOORAJ KUMAR PANDEY)**

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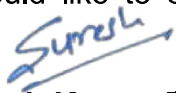
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ABBREVIATIONS

AOPs	Advance Oxidation Processes
ASP	Activated Sludge Process
MBR	Membrane Bioreactor
POPs	Persistent Organic Pollutants
USEPA	United State Environmental Protection Agency
ROS	Reactive Oxygen Species
VB	Valence Band
CB	Conduction Band
UV	Ultra Violet
MG	Malachite Green
RhB	Rhodamine B
PNP	Para nitrophenol
NaBH₄	Sodium Borohydride
HR-XRD	High Resolution X-ray Diffraction
FT-IR	Fourier Transform Infrared
TEM	Transmission Electron Microscopy
FE-SEM	Field Emission Scanning Electron Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
FEG	Field Emission Gun
XPS	X-ray Photoelectron Spectroscopy
UV-Vis DRS	Ultra Violet-Visible Diffuse Reflectance Spectra

PL	Photoluminescence
TOF	Turn Over Frequency
AR Grade	Analytical Reagent Grade
BET	Brunauer - Emmette – Teller
O₂^{•-}	Anionic superoxide radical
•OOH	Hydroperoxyl radical
OH[•]	Hydroxyl radical
OH⁻	Hydroxyl ion
NPs	Nanoparticles
SC	Semiconductor
SAED	Selected Area Electron Diffraction
BJH	Barret-Joyner-Halenda
PBQ	Para-benzoquinone
IPA	Iso-propyl alcohol
KI	Potassium iodide
AgNO₃	Silver nitrate

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PREFACE

In the current scenario the water contamination is a serious problem for the whole of the biota, and it tends to increase continuously with the advancement in industrialization, urbanization and growing population. Water is of utmost importance to sustain life on the earth surface. Unfortunately, there is limited source of fresh water available on the earth's surface. Moreover, industrial, agricultural and domestic activities consume a large fraction of available water; these activities also play major role in contamination of water since they generate large amount of waste water which contains various types of pollutants. Based on the physical and chemical properties of the pollutants they may be classified as physical, chemical and biological contaminants. Chemical contaminants in water may be organic, inorganic (metal ions) and radioactive wastes. The organic contaminant released from various industries contains a broad variety of organic compounds such as dyes, phenols, pharmaceuticals, cosmetic products, microplastics, polymers etc. In order to treat these organics from waste water various remediation techniques have already been running since past several decades such as filtration, adsorption, biological treatment, electrocatalysis and photocatalysis. However, among all these treatment techniques, photocatalysis is one of the most efficient, economic and environment friendly (green) technique to treat waste water. The potential successes of photocatalysis mainly rely on designing suitable semiconductor material as a photocatalyst that can absorb suitable light with simultaneous generation of excitons (electron and hole pairs). These photogenerated electron and holes may react with acceptor and donor species (generally O_2 and H_2O) and generate reactive species which helps in the breakdown of the harmful organics. Although, there are various types of transition metal oxides like TiO_2 , ZnO , Fe_2O_3 , WO_3 , NiO etc. that have been

used as photocatalysts but the main drawbacks of using individual semiconductor as photocatalysts is that they poorly utilize solar light and suffer from fast electron (e^-) hole (h^+) recombination which suppresses the photocatalytic efficiency of the semiconductor. In order to solve this problem various types of binary and ternary heterojunction semiconductor photocatalysts have been designed and developed.

Herein, this thesis we have reported three different binary combination of heterojunction photocatalysts, which includes g-C₃N₄/NiO, Ag/NiO and NiS/ZnO, these photocatalysts were synthesized by following hydrothermal and sol-gel routes, as prepared catalysts were characterized by different analytical and spectroscopic techniques to assess the differences between them. Further the synthesized photocatalysts were employed over the photocatalytic removal of malachite green (MG), rhodamine B (RhB) and p-nitrophenol (PNP). The formed heterojunction nanocomposites following step scheme “S-scheme” (S-scheme is just a pathway of charge migration between two semiconductor photocatalyst in such a way that it looks like “S” letter of the English alphabet) or type II mechanism in different samples exhibit significant improvement towards the photocatalytic removal of organic pollutants (MG, RhB and PNP).

This thesis is divided into six chapters; the brief description about each chapter is as follows

The **chapter 1** of the thesis consists of a detailed introduction about various types of pollutants (mainly organic pollutants) present in water and some useful methods available for their removal by highlighting heterogeneous photocatalysis has also been discussed in subsequent sections. This chapter also includes the literature survey on different types of photocatalyst used in this thesis. Last section of this chapter consists of the objectives of this thesis.

Chapter 2 deals with the materials, methods and characterization techniques which were

used during our entire work. The first section of this chapter discusses about the materials used and experimental procedure followed to synthesize different photocatalysts used to carry out research work presented in this thesis. Next section consists of the discussion about different analytical and spectroscopic techniques used to characterize the synthesized materials. This chapter also discusses about protocols followed during photocatalytic degradation experiment.

Chapter 3 mainly investigates the synthesis of heterostructured g-C₃N₄/NiO nanocomposites by hydrothermal route. The prepared nanocomposites have been analyzed by various characterization techniques like XRD, FT-IR, TEM, FE-SEM, XPS, UV-Vis DRS, and B.E.T. etc. The photocatalytic activity of the synthesized samples is evaluated by applying the photocatalysts for the removal of malachite green (MG) dye from water. How the different loading amount of g-C₃N₄ over NiO affects the photocatalytic performance is also studied in this chapter. The kinetic study of all the prepared photocatalyst toward the degradation of MG is also presented.

Chapter 4 deals with the study of the photocatalytic behavior of Ag/NiO nanocomposites. The nanocomposites are synthesized by sol-gel method followed by ultrasonic dispersion. The structural and morphological study of the prepared nanocomposite photocatalysts were carried out from the XRD, TEM and FE-SEM results whereas the chemical state is determined with the help of XPS data. In this chapter the photocatalysts are applied for the degradation of rhodamine B (RhB) and it was found that the Ag/NiO (6 wt% loading of Ag) nanocomposite removes the highest percentage of the RhB dye. The chapter also discusses about the scavenger experiment which is carried out to demonstrate the reactive intermediate species involved during the photocatalytic process.

Chapter 5 discusses about the preparation of NiS, ZnO and NiS/ZnO (12, 14 and 16

mol% of NiS) catalysts. In order to confirm the formation of the desired photocatalysts, the samples were characterized by different available analytical techniques such as XRD, TEM, FE-SEM, XPS etc. The optical band gaps of the nanoparticles are also calculated with the help of Tauc relation by using absorbance data obtained from UV-Vis DRS. The efficiency of the synthesized catalysts is evaluated by the photocatalytic removal of p-nitrophenol (PNP) and RhB dye. The photoluminescence (PL) study of the photocatalysts is also given in the current chapter to know the charge recombination process in them. The discussion about the plausible mechanism which takes place during the photocatalysis is also given in this chapter.

Chapter 6 consists of the complete summary of this thesis along with the short discussion about the scope of the work ahead.