

Synthesis, Characterization and Applications of Photocatalytic Nanomaterials

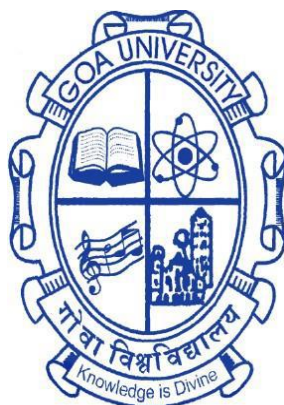
A THESIS SUBMITTED IN PARTIAL FULFILMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in Chemistry

IN THE SCHOOL OF CHEMICAL SCIENCES

GOA UNIVERSITY



By

Manisha Ratan Mhalsekar

DCT's Dhempe College of Arts and Science, Miramar, Panaji, Goa

Under

Cluster Research Centre in Chemistry, Government College of Arts,
Science and Commerce, Khandola, Marcela, Goa

May 2025

DECLARATION

I, Manisha R. Mhalsekar, hereby declare that this thesis represents work that has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

Place: Panaji.

Date:

Manisha R. Mhalsekar

CERTIFICATE

I, hereby certify that the above Declaration of the candidate, Manisha R. Mhalsekar, is true and the work was carried out under my supervision.

Prof. Vrinda Borker

Guide

Retired-Professor (Chemistry),
Dhempe College of Arts and Science,
Miramar, Panaji Goa, 403001.

Prof. Purnakala Samant

Co-guide

Principal and Professor (Chemistry),
Government College of Arts, Science and
Commerce, Khandola, Marcela, Goa,
403107.

Acknowledgment

The current research endeavour was accomplished with the assistance of several experts, advisors and well-wishers. I'll always be indebted to their unstinted support and motivation throughout my career.

Firstly, I extend humble gratitude to my research guide and advisor, Prof. Vrinda Borker (Rtd.Professor, Dhempe College, Miramar), for her tireless support and supervision at every stage of my research. She has been instrumental in inculcating the scientific temperament and knowledge in me. Also, deepest gratitude goes to my co-guide Prof. Purnakala Samant (Principal, Govt. College, Khandola) for timely, fruitful discussions and mentoring.

Further, I owe sincere thanks to my subject experts, Prof. V.M.S. Verenkar (Dean-SCS) and Prof. Sunder Dhuri (Registrar-GU), School of Chemical Sciences, Goa University, for their rich and expert technical recommendations during my PhD course.

My sincere gratitude goes to Principal Prof. (Dr) P.S.Ramu Murthy, Dhempe College Miramar, for administrative and laboratory facility support.

I also acknowledge Dr. Bidhan Shinkre (Research Dean), School of Chemical Sciences, Goa University, for the Departmental Research Committee (DRC) proceedings.

I'll always be in debt to my HODs of Chemistry, Dhempe College, Mrs.Varsha Virginkar and Ms.Deepa Audi, for their wholehearted help and motivation during my PhD course

I would like to thank 'Dempo Charities Trust' and 'Directorate of Higher Education' for supporting my PhD through the FDP programme.

Heartfelt thanks to all my dear colleagues, Dr. Chandan, Dr. Bhanudas, Dr.Priyanka, Dr.Durga, Ms.Dipika, Ms.Arati, Dr.Rajashri, Dr.Geeta, Dr.Satu, Dr.Shambu, Dr.Shashank and Ms.Shubhlakshmi for their overwhelming voluntary help and moral support.

My due gratitude goes to my fellow research colleagues, Ms.Firdaus, Ms.Sanjali, Ms.Mangala, Mr.Pranav, Ms.Medha, Mr.Shubankar for creating a friendly atmosphere.

I extend gratitude to the Cluster Research Centre in Chemistry-Govt. College-Khandola, Sophisticated Analytical Instrument Facility (SAIF), IIT-Bombay & Kanpur, Chemistry Department at Govt. College Khandola, DST-FIST Lab-Jaysingpur-College, Jaysingpur, for providing advanced instrumental facilities for material characterization. Thanks to MCL at Goa University and CSIF at the BITS Pilani Goa campus.

My due thanks to Prof. N. N. Ghosh (BITS Pilani-Goa) for providing technical inputs and extending instrumental facilities for my research work. My humble and earnest gratitude goes to Prof. T. Maruyama, Meijo University-Japan for providing Raman and XPS data.

I also acknowledge all the non-teaching staff at Dhempe College for their wholehearted help.

On a personal front, I owe hearty thanks to my mother, husband, in-laws, brother, son and other family members for their unconditional support and affection. Finally, I thank almighty god for showering all good blessings on me.

Once again, thank you all..!.

CONTENTS

No.	Topic	Page No.
1.	Chapter-1: Introduction	1-29
1.1	Brief overview of photocatalytic nanomaterials	1
1.2	Types of Photocatalyst	3
1.3	The basic principle of semiconductor metal oxide-based photocatalysis: A model dye degradation	3
1.4	Factors Influencing Photocatalysis	5
1.5	ZnO and TiO ₂ -based Photocatalysts	5
1.6	Aim and objective of current research	7
1.7	Literature review: Photocatalytic nanomaterials	8
	1.7.1 Cerium-doped Zinc oxide nanomaterials for photocatalytic degradation of methylene blue and textile dye	8
	1.7.2 Rare earth metal ion-doped Zinc oxide nanomaterials for photocatalytic degradation of organic dyes	11
	1.7.3 Anatase titanium dioxide nanomaterial for photodegradation of drug and dye molecules	14
	1.7.4 Multiwalled carbon nanotube/titanium dioxide composite for photocatalytic organic synthesis	15
1.8	Material characterization techniques	17
	References	20
2.	Chapter-2: Synthesis of cerium-doped zinc oxide nanomaterials, characterization and photocatalytic degradation studies of methylene blue and textile industry Red CL-5B dye	30-60
2.1	Introduction	30
2.2	Experimental	31
	2.2.1 Preparation of Ce _x Zn _{1-x} O nanomaterials	31
2.3	Characterization techniques	32
2.4	Photocatalytic organic dye degradation studies	33
2.5	Textile Industry Red CL-5B dye degradation studies	35
2.6	Results and discussions	35
	2.6.1 Chemical composition of oxides and codes	35
	2.6.2 IR studies	36

2.6.3 Thermal analysis of precursor	37
2.6.4 X-ray Diffraction studies	38
2.6.5 Nitrogen adsorption-desorption studies	40
2.6.6 X-ray photoelectron spectroscopy studies	41
2.6.7 UV-visible DRS: Light absorption and band gap	42
2.6.8 Photoluminescence: Spectral emission analysis	44
2.6.9 Microstructural studies: SEM/HRTEM/EDAX	45
2.7 Photocatalytic studies	48
2.7.1 Photocatalytic degradation of methylene blue dye	48
2.7.2 pH-dependent photocatalytic methylene blue dye degradation studies	50
2.7.3 Photocatalytic degradation of textile industry Red CL-5B dye	51
2.7.4 Recyclability of photocatalyst	53
2.7.5 Reactive species trapping experiment	54
2.8 Proposed mechanism for photocatalytic dye degradation	55
2.9 Conclusions	57
References	59
3. Chapter-3: Synthesis of rare-earth metal ion (Nd/Sm/Dy/Ho)-doped zinc oxide nanomaterials, characterization and photocatalytic degradation of Rhodamine B and Red CL-5B dye	61-109
3.1 Introduction	61
3.2 Experimental: Materials and Methods	63
3.2.1 Materials	63
3.2.2 Preparation of $M_xZn_{1-x}O$ materials from M^{3+}/Zn -oxalate precursor	63
3.2.3 Preparation of hydrazinated $M_xZn_{1-x}O$ from M^{3+}/Zn -oxalate hydrazinate precursor	64
3.3 Characterization techniques	65
3.4 UV-visible DRS studies: Light absorption and band gap	66
3.5 Photoluminescence studies	67
3.6 Photocatalytic studies: Rhodamine B and Red CL 5B dye degradation	67
3.7 LC-MS studies: Identification of Rhodamine B degradants	68
3.8 Results and Discussion	69

3.8.1	Modification of precursors by hydrazine and its influence on material properties	69
3.8.2	IR studies	70
3.8.3	Thermal analysis of precursor	71
3.8.4	X-ray diffraction studies	72
3.8.5	Nitrogen adsorption-desorption studies	76
3.8.6	Microstructural studies: SEM/TEM/EDAX/SAED	78
3.8.7	X-ray photoelectron spectroscopy studies	83
3.8.8	Raman studies	85
3.8.9	UV-visible absorption and band gap energy	86
3.9	Photoluminescence studies	88
3.10	Dielectric studies	93
3.11	Electrical conductivity	94
3.12	Correlation between structural and charge separation in photocatalyst	95
3.13	Photocatalytic degradation activity of Rhodamine B and Red CL-5B dye	96
3.13.1	Effect of catalyst quantity	96
3.13.2	Effect of pH	97
3.13.3	Effect of $M_xZn_{1-x}O$ catalyst	98
3.13.4	Photocatalytic degradation studies of Red CL-5B dye	99
3.14	Reactive species trapping experiment	100
3.15	Proposed mechanism for photocatalytic degradation of dyes	101
3.16	LC-MS studies: Identification of Rhodamine B (RhB) degradants	102
3.17	Recyclability of photocatalyst	104
3.18	Conclusions	105
	References	107
4.	Chapter-4: Synthesis of anatase titanium dioxide nanomaterial, characterization and photocatalytic degradation studies	110-146
4.1	Introduction	110
4.2	Materials and Methods	112
4.2.1	Chemicals	112
4.2.2	Preparation of TiO_2 nanomaterial via β -CD-based precursor method	112

4.3	Characterization techniques	113
4.4	Photocatalytic degradation of Paracetamol drug molecule	114
4.5	Photocatalytic degradation of Rhodamine B dye molecule	114
4.6	Results and discussion	116
	4.6.1 Possible mechanism for the formation of nanosized TiO ₂	116
	4.6.2 IR and thermal analysis of precursor	117
	4.6.3 XRD phase analysis	118
	4.6.4 BET Surface analysis	123
	4.6.5 X-ray photoelectron spectroscopy studies	126
	4.6.6 Raman analysis	127
	4.6.7 Microstructural analysis (SEM/TEM/EDAX/PSD)	128
	4.6.8 UV-vis absorption studies and band gap	131
	4.6.9 Photoluminescence studies	133
4.7	Photodegradation of Rhodamine B (Rh B) model dye molecule	134
4.8	Application of Photocatalyst: Photodegradation of Paracetamol molecule	136
	4.8.1 Effect of types of catalyst	138
	4.8.2 Effect of concentration of catalyst	139
	4.8.3 Effect of pH of paracetamol solution	140
4.9	Reactive species trapping experiment.	141
4.10	Liquid chromatography-Mass spectrometry (LC-MS) studies : Identification of Paracetamol drug molecule degradants	142
4.11	Conclusions	144
	References	145
5	Chapter-5: Synthesis, characterization and application of MWCNT/TiO₂ composite material for the photocatalytic reduction of benzophenone to benzopinacol	147-184
5.1	Introduction	147
5.2	Materials and Methods	149
	5.2.1 Chemicals	149
	5.2.2 Preparation of MWCNT/TiO ₂ composite materials	149
5.3	Characterization techniques	150
5.4	Photocatalytic organic reaction experimental set-up	151

5.5	Results and discussion	153
5.5.1	Precursor Layer Coating method of composite preparation	153
5.5.2	FTIR studies	153
5.5.3	Thermal Analysis (TGA-DSC)	155
5.5.4	X-ray diffraction studies	156
5.5.5	Surface analysis	158
5.5.6	Microstructural analysis (SEM/PSD/ EDAX/ TEM)	160
5.5.7	UV-visible DRS light absorption studies	163
5.5.8	Photoluminescence studies	165
5.5.9	X-ray Photoelectron spectroscopy studies	166
5.5.10	Raman studies	169
5.6	Photocatalytic activity of X%-MWCNT/TiO ₂	171
5.6.1	Photocatalytic synthesis of Benzopinacol in UV and sunlight	171
5.6.2	Proton Chemical Shift Assignment for synthesised benzopinacol	174
5.7	Reactive species trapping experiment.	175
5.8	Proposed Mechanism for photocatalytic synthesis of benzopinacol from benzophenone catalysed by photocatalyst	177
5.9	Plausible role of composite materials for improved photocatalytic activity	178
5.10	Conclusions	180
	References	181
6	Chapter-6: Summary and future scope of research work	185-187
7	List of Publications and Oral Presentations	188

LIST OF TABLES

Table No	Content	Page No
Table 2.1:	Chemical composition of material, material code, moles of Ce doped in ZnO, average crystallite size estimated from XRD-Scherrer formula, calculated lattice parameters (a, c), and BET- surface area	41
Table 2.2:	Comparative photodegradation efficiencies of reported Ce-doped ZnO with that of CZ5 material	53
Table 3.1:	Compilation of synthesized material compositions and their codes	65
Table 3.2:	Compilation of IR bands of precursor and their $M_xZn_{1-x}O$ material	71
Table 3.3:	Compilation of material composition, assigned codes, observed lattice parameters a and c, Scherrer average crystallite size (D_{avg}), strain (ϵ) and dislocation density (δ)	75
Table 3.4:	Material code, surface area, total pore volume and mean pore diameter values	77
Table 3.5:	Elemental composition by EDAX showing the weight (%) and atomic (%) for $M_xZn_{1-x}O$ samples	82
Table 3.6:	Compilation of band gap values of $M_xZn_{1-x}O$ materials	87
Table 3.7:	Compilation of PL emissions due to different elements doped ZnO	93
Table 4.1:	Comparative data of TH, 1DT, 2DT and 3DT materials phases formed at different annealed temperatures and their crystallite sizes	120
Table 4.2:	Rietveld analysis data for sample 2DT	122
Table 4.3:	Sample codes, BET-specific surface area, total pore volume, and mean pore diameter	125
Table 4.4:	Compilation of particle size (Scherrer), calculated band gap energy from UV-visible DRS (Tauc-method) and based on particle size using equation 4	132
Table 5.1:	Compilation of composite composition, assigned codes, BET-specific surface area, Total pore volume, and Mean pore diameter values	160
Table 5.2:	Compilation of XPS BE (eV) of Ti, O and C for bare TiO_2 and 6CT	168
Table 5.3:	% Yield of benzopinacol from benzophenone in the presence of sunlight and photocatalyst	172
Table 5.4:	% Yield of benzopinacol from benzophenone in the presence of UV light and photocatalyst	173

LIST OF FIGURES

Figure No.	Caption	Page No
Figure 1.1:	Schematic diagram showing the mechanism of model photocatalyst activated by light energy and electron transfer pathways	4
Figure 2.1:	Schematic diagram of the reactor set-up for photocatalytic degradation of dye molecules	34
Figure 2.2:	Infrared spectra of samples CZ0, CZ3, and CZ5 (a) cerium-zinc-succinate precursor (b) Ce/Zn-oxides	36
Figure 2.3:	TGA-DSC thermograms of cerium-zinc-succinate precursor	37
Figure 2.4:	XRD patterns of CZ0, CZ1,CZ2,CZ3,CZ4, CZ5,CZ6 and CZ7 materials. Inset picture: Observed shift in peak position for samples CZ0, CZ3, CZ5 and CZ7	39
Figure 2.5:	Adsorption/desorption isotherms for (a) CZ0, and (b) CZ7	40
Figure 2.6:	XPS spectra of CZ5 (a) Survey spectrum (b) Zn 2p (c) O1s and (d) Ce 3d	42
Figure 2.7:	(a) UV-visible absorption spectra for samples CZ0 to CZ7 (b) Tauc plots for samples CZ0 to CZ7	43
Figure 2.8:	(a) PL intensity versus wavelength (b) PL intensity versus energy (eV) of samples CZ0 to CZ7	45
Figure 2.9:	SEM images of (a) CZ0 and (b) CZ5 materials	45
Figure 2.10:	HR-TEM images of (a) CZ0 and (b) CZ5 materials	46
Figure 2.11:	Particle size distribution of (a) CZ0 and (b) CZ5	47
Figure 2.12:	EDAX spectrum of CZ5 material	47
Figure 2.13:	(a) % MB degradation efficiency profiles for photocatalysts (CZ0 to CZ7) (b) UV-visible absorbance spectra of MB dye recorded at time points for CZ5 (c) % MB degradation in UV and sunlight at 120 min time point for photocatalyst (CZ0 to CZ7) (d) $\ln(C_0/C_t)$ versus time plot for calculating the rate constant for photocatalyst (CZ0 to CZ7)	50
Figure 2.14:	pH-dependent % degradation profiles of MB dye	51

Figure 2.15:	% Degradation of Red CL-5B dye for Blank, CZ0, CZ3 and CZ5 materials in (a) UV light and (b) Sunlight	52
Figure 2.16:	(a) % Degradation of Red CL-5B dye for 4 cycles at time points 0, 10, 20, 30, 40 and 50 min. (b) FESEM of catalyst CZ5 before photoactivity (c) FESEM of catalyst CZ5 after 4 th photoactivity cycle	54
Figure 2.17:	Trapping of charged species by scavengers	55
Figure 2.18:	Schematic diagram depicting the mechanism of methylene blue and Red CL-5B dye degradation on Ce-doped ZnO photocatalyst in the presence of light	56
Figure 3.1:	Synthesis scheme for $M_xZn_{1-x}O$ ($x=0.05, 0.1$) via M/Zn-oxalate (MZOx1 and MZOx2) and hydrazine-M/Zn-oxalate (MZOxHz1 and MZOxHz2) precursors	64
Figure 3.2:	IR spectra (a) Precursors: NZOx1, NZOx2, NZOxHz1, and NZOxHz2 and (b) Nd/Zn-oxides: NZO1, NZO2, NZOH1 and NZOH2.	70
Figure 3.3:	TGA – DTA thermograms of (a) NZOx2 (b) NZOxHz2 precursor.	72
Figure 3.4:	XRD patterns of (a) $Nd_xZn_{1-x}O$ (b) $Sm_xZn_{1-x}O$ (c) $Dy_xZn_{1-x}O$ (d) $Ho_xZn_{1-x}O$ where $x=0.05$ and 0.1 prepared from oxalate and oxalate-hydrazinate precursors	73
Figure 3.5:	XRD patterns of NZO1, NZO2, NZOH1 and NZOH2 with an inset picture showing the peak shift effect due to Nd^{3+} doping in ZnO	75
Figure 3.6:	BET adsorption-desorption isotherms along with BJH plots for (a) NZO2 and (b) NZOH2	77
Figure 3.7:	SEM images of (a) NZO2 (b) NZOH2	78
Figure 3.8:	SEM images of $M_xZn_{1-x}O$, ($M=Nd/Sm/Dy/Ho$, $x = 0.1$)	79
Figure 3.9:	TEM images (a) NZO2 and (b) NZOH2	80
Figure 3.10	TEM images (a) SZO2 (b) DZO2 and (c) HZO2	80
Figure 3.11:	Particle size distribution of (a) NZO2 and (b) NZOH2	81
Figure 3.12:	SAED patterns of (a) NZO2 and (b) NZOH2	81
Figure 3.13:	EDAX spectra of (a) NZO2 (b) SZO2 (c) DZO2 and (d) HZO2	82
Figure 3.14:	XPS Survey scan of $M_xZn_{1-x}O$ samples	84

Figure 3.15:	XPS spectra of NZOH2 (a) Survey scan (b) HR-XPS: Zn 2p (c) O 1s (d) Nd 3d.	84
Figure 3.16:	Raman spectra of ZnO, NZO2, SZO2, DZO2 and HZO2 materials	85
Figure 3.17:	UV-visible light absorption spectra of $M_xZn_{1-x}O$ where [M = (a) Nd (b) Sm (c) Dy (d) Ho and x= 0.05 and 0.1] materials	87
Figure 3.18:	Comparative bandgap (E_g) of $M_xZn_{1-x}O$ materials	88
Figure 3.19:	PL emission spectra for MZO1, MZO2, MZOH1 and MZOH2 materials	90
Figure 3.20:	PL emission spectra of NZO1, NZO2, NZOH1 and NZOH2 (a) PL-intensity versus emitted wavelength (b) PL-intensity versus energy (c) FWHM of blue PL peak at $\lambda = 468$ nm (d) Mechanism showing various electronic transitions in $M_xZn_{1-x}O$	92
Figure 3.21:	Comparative dielectric constant plots of NZO2 and NZOH2 samples	94
Figure 3.22:	Conductivity recorded against the temperature scale ($^{\circ}C$) for NZO2 and NZOH2 samples.	95
Figure 3.23:	Effect of catalyst concentration on the % degradation efficiency	97
Figure 3.24:	Effect of pH on the % degradation efficiency of catalyst	98
Figure 3.25:	Effect of type of catalyst (MZO2) on the % degradation efficiency	99
Figure 3.26:	Percentage degradation efficiency of Red CL 5B dye in (a) UV light and (b) sunlight	99
Figure 3.27:	Trapping of charged species	100
Figure 3.28:	Schematic diagram showing the photocatalytic process, charge mobility, formation of the reactive species and degradation of dye molecule over the photocatalyst	101
Figure 3.29:	LC-MS spectrum of Rh B solution (a) Chromatogram before Rh B solution (b) MS spectrum of Rh B solution before degradation (c) Chromatogram of Rh B after degradation (d) MS spectrum of degradant-1 with $m/z=415$ and (e) MS spectrum of degradant-2 with $m/z=117$	103
Figure 3.30:	Recyclability test for photocatalyst	104
Figure 4.1:	The schematic diagram depicting the synthesis of TiO_2 using β -CD	112
Figure 4.2:	Molecular structure of Rhodamine B dye molecule	115

Figure 4.3:	Schematic diagram of the photocatalytic reactor used for dye/drug degradation activity	115
Figure 4.4:	(a) Hydrogen bonded β -CD and $\text{TiO}(\text{OH})_2$ (b) FTIR of precursor (c) FTIR spectra of annealed sample TH, 1DT, 2DT and 3DT (d) TGA-DTA profiles of 2DT precursor	118
Figure 4.5:	XRD diffraction patterns of (a) TH, 1DT, 2DT and 3DT (b) Sample TH annealed at 450, 500 and 600 °C (c) Sample 2DT annealed at 450, 500 and 600 °C (d) Rietveld analysis of 2DT	120
Figure 4.6:	Detailed Rietveld XRD pattern of sample 2DT	121
Figure 4.7:	BET adsorption-desorption isotherms for (a) TH (b) 1DT (c) 2DT and (d) 3DT	124
Figure 4.8:	BJH plots for pore size distribution for (a) TH (b) 1DT (c) 2DT and (d) 3DT	124
Figure 4.9:	Observed trends for (a) surface area, (b) total pore volume and (c) mean pore diameter for samples TH, 1DT, 2DT and 3DT	126
Figure 4.10:	XPS of 2DT material (a) Survey scan (b) O 1s (c) Ti 2p	126
Figure 4.11:	(a) Raman spectra (b) Enlarged Raman spectra of TH, 1DT, 2DT and 3DT	127
Figure 4.12:	FE-SEM images of (a) TH and (b) 2DT	128
Figure 4.13:	Particle size distribution of (a) TH and (b) 2DT	129
Figure 4.14:	EDAX of 2DT sample	129
Figure 4.15:	(a-d) TEM images (e) SAED (f,g) HR-TEM images of TH	130
Figure 4.16:	(a-d) TEM images (e) SAED (f,g) HR-TEM images of 2DT	131
Figure 4.17:	(a) Diffuse Reflectance UV–vis absorption spectra and (b) Band gap based on Tauc plots for TiO_2 samples: TH, 1DT, 2DT and 3DT.	133
Figure 4.18:	PL spectra of TiO_2 samples: TH, 1DT, 2DT and 3DT	134
Figure 4.19:	%Photodegradation of Rhodamine B (a) in UV light and (b) Kinetic plots	135

Figure 4.20:	Photocatalytic degradation activity of paracetamol over TH and 2DT in UV and sunlight.	137
Figure 4.21:	Effect of types of catalyst (1DT, 2DT and 3DT) on photocatalytic activity	138
Figure 4.22:	Effect of concentration of photocatalyst (2DT) (60 mg, 80 mg, 100 mg and 120 mg) on photocatalytic activity	139
Figure 4.23:	Effect of pH of paracetamol solution (pH2, pH4, pH7, pH8, pH10) on photocatalytic activity	140
Figure 4.24:	Reactive species trapping experiment	141
Figure 4.25:	LC-MS spectra of paracetamol solution (a) Chromatogram before degradation of paracetamol solution, (b) MS of paracetamol before degradation, (c) Chromatogram after degradation of paracetamol solution, (d) MS spectrum of degradant-1 with m/z=126 and (e) MS spectrum of degradant-2 with m/z=116	143
Figure 5.1:	Schematic diagram depicting the preparation of MWCNT/TiO ₂ composite materials by precursor-layer-coating (PLC) method	150
Figure 5.2:	Schematic diagram of the reactor used for the photocatalytic conversion of benzophenone to benzopinacol	152
Figure 5.3:	IR spectra for (a) synthesized precursor and (b) precursor heated at 250, 350, 450 and 550 °C temperatures, MWCNT and carbopol polymer	154
Figure 5.4:	TGA-DSC thermogram of 2CT precursor	155
Figure 5.5:	XRD diffractograms of (a) MWCNT (b) TiO ₂ (c) precursor annealed at different temperatures and (d) Composite materials-2CT, 4CT, 6CT and 8CT	158
Figure 5.6:	Adsorption-desorption isotherms and BJH plots of (a) TiO ₂ (b) 8CT	159
Figure 5.7:	FE-SEM images (a,b) TiO ₂ and (c,d) 6CT composite material	161
Figure 5.8:	Particle size distribution of bare TiO ₂ material	161
Figure 5.9:	EDAX spectrum of 6CT sample showing the presence of C, O and Ti peaks	162
Figure 5.10:	HR-TEM images 6CT: (a-f) MWCNT coated with TiO ₂ , (g) of TiO ₂ (h) Lattice fringes of MWCNT and (i) SAED images of composite	163

Figure 5.11:	(a) UV-visible absorption spectra and (b) Tauc plots of T, 2CT, 4CT, 6CT, and 8CT	164
Figure 5.12:	PL spectra of bare TiO ₂ (T), MWCNT (C) and composites-2CT, 4CT, 6CT and 8CT	166
Figure 5.13:	XPS of T, 2CT, 4CT, 6CT and 8CT (a) Survey scan (b) Ti 2p, (c) O 1s (d) C 1s	167
Figure 5.14:	High-resolution XPS spectra of bare TiO ₂ : (a) Ti (b) O and 6CT : (c) Ti (d) O (e) C	169
Figure 5.15:	Raman spectra of (a) TiO ₂ , MWCNT, 2CT, 4CT, 6CT and 8CT (b) Peak shift in D and G bands of MWCNT present in 2CT, 4CT, 6CT and 8CT	170
Figure 5.16:	Illustrating the reaction product % yield comparison for blank, MWCNT, T, 2CT, 4CT, 6CT and 8CT irradiated with (a) sunlight and (b) UV light	174
Figure 5.17:	Structure of benzopinacol	174
Figure 5.18:	¹ H NMR proton chemical shift assignment	175
Figure 5.19:	Photocatalytic reaction efficiency (% RE) in terms of % yield plotted against each charge scavenger	176
Figure 5.20:	Schematic diagram of the proposed model for the electron transfer from TiO ₂ to MWCNT composite materials across heterojunction for enhanced photocatalytic activity	179

LIST OF ABBREVIATIONS

FTIR	:	Fourier transform Infra-red
XRD	:	X-ray powder diffraction
XPS	:	X-ray photoelectron spectroscopy
PL	:	Photoluminescence
DRS	:	Diffuse reflectance spectroscopy
UV	:	Ultra-violet
BJH	:	Barret-Joyner-Halenda
BET	:	Brunauer-Emmett-Teller
TGA	:	Thermogravimetric analyzer
DTA	:	Differential thermal analyzer
DSC	:	Differential scanning calorimeter
SEM	:	Scanning electron microscopy
TEM	:	Transmission electron microscopy
EDAX	:	Electron diffraction absorption X-rays
FWHM	:	Full-width half maxima
CB	:	Conduction band
VB	:	Valance band
HR	:	High resolution
HT	:	High temperature
RE	:	Rare earth
BE	:	Binding energy
eV	:	Electron volt
MWCNT	:	Multi-walled carbon nanotubes
Rh B	:	Rhodamine B
MB	:	Methylene blue
JCPDS	:	Joint Committee on Powder Diffraction Studies
ICDD	:	International Centre for Diffraction Data
PLC	:	Precursor Layer Coating
TiP	:	Titanium isopropoxide

ABSTRACT

The current research deals with the synthesis and characterization of ZnO and TiO₂-based nanomaterials, which are useful for photocatalytic applications. In this perspective, a series of Ce-doped ZnO, (Nd/Sm/Dy/Ho)-doped ZnO, anatase TiO₂, and MWCNT/TiO₂ composite materials were prepared and investigated for their potential photocatalytic applications. The Ce_xZn_{1-x}O (where: x=0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07 moles) nanomaterials were prepared via Ce/Zn-succinate precursor method and evaluated for Methylene blue (MB) and Red CL-5B dye photodegradation activities in Uv and sunlight. The M_xZn_{1-x}O, (where, M=Nd/ Sm/Dy/Ho and x = 0.05 and 0.1 moles) were prepared from the thermal decomposition of M/Zn-oxalate and oxalate-hydrazinate precursor. The materials were compared for their photocatalytic dye degradation and photoluminescence (PL) properties. Photoactive anatase TiO₂ nanomaterial was synthesized from a novel beta-cyclodextrin-titanyl-oxy hydroxide precursor, suitable for degradation of Rhodamine-B dye and Paracetamol drug molecule on irradiation with Uv-visible light. Also, composite material, X%-MWCNT/TiO₂, where X = 0, 2, 4, 6, and 8% w/w was conveniently fabricated via the precursor-layer-coating (PLC) method, which was beneficial in the hetero-photocatalytic benzopinacol synthesis on irradiation with UV and sunlight. All synthesized materials were appropriately characterized by IR, XRD, nitrogen gas adsorption-desorption, XPS, SEM, HR-TEM, EDAX, Raman, photoluminescence (PL), and Uv-visible absorption (Uv-vis DRS) techniques. The (Ce/Nd/Sm/Dy/Ho) doped ZnO materials crystallized in single-phase ZnO hexagonal wurtzite structures. The metal ion dopant was successfully incorporated in the lattice position of ZnO, which was confirmed by XRD, XPS, and EDAX studies. A simple and 2-step method was adopted to produce anatase TiO₂ nano-powder employing cyclodextrin-based complex precursors. The MWCNT/TiO₂ composite material was characterized by SEM/HR-TEM and EDAX techniques, which revealed the shape, size, and morphology of particles. Surface analysis indicated mesoporous materials with high specific surface areas along with varied pore diameters and distributions. XPS studies proved the elemental composition, chemical bonding, and proportionate elemental estimation in the materials. The metal ion doped-ZnO exhibited enhanced Uv-visible light absorption properties, reduced band gap energies and shift in absorption edges towards the visible region. The Ce_xZn_{1-x}O materials displayed excellent photodegradation of MB and Red CL-5B dye with mineralization, a high rate of degradation, nearly eight times faster compared to pure ZnO in both UV and sunlight. The

Nd/ZnO material, obtained from hydrazinated Nd-Zn-oxalate precursor, showed improved PL intensities (1.5 times) with a narrow bandwidth (~ 15 nm). From the comparative dye degradation profiles obtained for $M_xZn_{1-x}O$, where ($M=Nd/Sm/Dy/Ho$), Ho-doped ZnO showed the highest photoactivity for Rhodamine-B and Red CL-5B dye. The improved charge transfer, creation of cationic vacancies that act as electron-trap sites and retarded rate of (e^-h^+) pair recombination. The pure anatase TiO_2 catalyst was evaluated for photodegradation of Rhodamine-B and Paracetamol molecules. The comparative LC-MS studies were performed on Paracetamol solution before and after the addition of TiO_2 catalyst irradiated with Uv. The MWCNT/ TiO_2 composite materials exhibited excellent photocatalytic organic synthesis activity with high conversion efficiency for benzopinacol in Uv and sunlight. The formation of heterojunctions and synergistic effects between TiO_2 and MWCNT were responsible for the dramatic increase in photocatalytic activity. Herein, simple, cost-effective, and highly efficient procedures were developed for the synthesis of photocatalytic materials and systematically characterized to understand the structure-property relationship and successfully evaluated for environmental pollution remediation, photoluminescence, and photocatalytic organic synthesis applications. Hence, these materials can be strongly advocated in the treatment of effluents, optical sensors, and organic synthesis.

Chapter-1:

Introduction

1.1 Brief overview of photocatalytic nanomaterials

Material science encompasses diverse topics and plays a pivotal role in inventing various scientific technologies. The increasing demand for modern smart devices and confronting environmental issues are well catered by novel materials [1–3]. Hydrogen energy production, artificial photosynthesis, and abatement of environmental pollution are some of the hallmark discoveries based on photocatalytic materials [4–6]. The light absorption and energy transformation by a material is the most attractive and thriving area in photocatalysis. The sunlight-induced processes are preferred over others because they offer several advantages such as being inexpensive, auto-functioning, eco-friendly and utilisation of abundantly available solar energy. Photocatalysis, photovoltaics, and photo-electrocatalysis are important technologies that harness light and convert it into other useful energy sources [7,8].

In nature, a model photocatalytic reaction occurs in the green plant leaves, and the process is known as photosynthesis, wherein the carbon dioxide and water are converted into carbohydrates (energy source) and oxygen is released into the environment. The term “photocatalysis” is a combination of two Greek words “photo” and “katalyo”, which means “light” and “to decompose or break down”, respectively. Scientifically, the photocatalyst is a material which is activated by incident light/photon energy and in turn accelerates the rate of reaction without undergoing any chemical change at the end of the process, and the phenomenon is known as photocatalysis [9]. The idea of photocatalysis was first proposed by Edmond Becquerel in 1839. He studied the natural photosynthesis process and its mechanism in microorganisms [10]. For the first time in 1911, the word “Photocatalyst” appeared in a scientific paper [11]. Later, the bleaching of Prussian blue dye solution by ZnO photocatalyst on irradiation with light was reported [12]. A few years later, TiO₂ was investigated as a photocatalyst to bleach dyes in the presence of O₂ [13]. In 1968, the oxygen gas evolution on TiO₂ was discovered by shining light on the TiO₂ photocatalyst at Bell Scientific Laboratory [14]. Later, Honda and Fujishima introduced the concept of sustainable energy production, wherein they demonstrated the splitting of water molecules (photolysis) into hydrogen gas (fuel) and oxygen on irradiation of light over TiO₂ photocatalyst [15]. Since then, a large volume of research articles and theories has been proposed by several scientific groups. In the recent past large number of scientific works have been devoted to the preparation of innovative photocatalytic materials and

processes to tackle the energy and environmental pollution crises. The term photocatalysis, defined by the International Union of Pure and Applied Chemistry (IUPAC) was confined to changes in reaction rates that occur in the presence of a semiconductor (photocatalyst) and light illumination.

Annually, global organic dye production is pegged at about ~700000 tons, of which about 20% of dyes make their way into the ecosystem and pose a hazard to human health and the environment [16]. In this regard, the decomposition of these dyes is vital to safeguard our ecosystem. These chemicals are very detrimental to the environment and should be reduced to very low concentrations (< 1 ppm) during the effluent treatment [17].

Amongst all photocatalysts, metal oxides are prolific materials with unmatched technological relevance [18]. The wide-range photo-applications are owed to their excellent physico-chemical properties, low cost and high stability [19]. However, factors like wide band gap, low absorption of visible light (sunlight), and rapid recombination of generated charge pairs have been limiting its practical applicability [11]. Material scientists have developed nanosized/quantum-sized particles and photocatalysts which can trap solar radiations [20]. The various doping techniques also assist in modifying the band gap energy, extending the absorption spectrum, and trapping of the excited electrons. Metal ion doping also influences the surface morphology, particle shape, size and porosity of the material. Semiconducting nanomaterials are being prepared, characterized and evaluated for their photocatalytic applications [21]. Hence, the critical part is designing intricate material properties employing different compositions and structures. Hence, photocatalysis has opened new research opportunities and grown exponentially over the past few decades.

Another potential application is the light-induced organic reactions carried out over the photocatalysts. After the excitation of the catalyst by light energy, it acts as both an oxidizing and a reducing agent to carry out several organic reactions. The practical utility of such catalysts has been adopted in numerous photocatalytic organic syntheses. Hence, current research also deals with the synthesis of materials, their characterization, and applications in photocatalysis [22,23].

1.2 Types of Photocatalyst

Over many decades, different types of photocatalytic materials have been tried and tested by several scientists. The photocatalyst and light source are the two important components of any conventional photocatalytic reaction. Hence, several research articles have been published on diverse photocatalytic materials. The detoxification of water is the most viable option using a photocatalyst because it is versatile, inexpensive and highly practical. In literature, different types of photocatalysts are reported; mainly classified into homogeneous and heterogeneous [24,25].

The most common examples of heterogeneous photocatalysts employed are metal oxides such as TiO_2 , ZnO , ZrO_2 , V_2O_5 , Fe_2O_3 , WO_3 , and CeO_2 [26]. Other semiconducting material which absorbs light and degrades dye over the surface is $\text{g-C}_3\text{N}_4$. However, these types of catalysts suffer from poor light absorption, rapid recombination and low surface area [27]. H. Heidarpour *et al* produced novel Ag/AgCl photocatalysts inside cross-linked carboxymethyl cellulose beads hydrogels for visible-light-induced photocatalysis [28]. Different metal sulfides are also being employed as photocatalysts. They possess excellent charge migration properties and light-capturing ability; however, they lack physico-chemical stability and undergo photocorrosion [29].

1.3 The basic principle of semiconductor metal oxide-based photocatalysis: A model dye degradation

When a semiconducting metal oxide photocatalyst is illuminated with UV-visible light using an artificial source or natural sunlight, the electrons (e^-) present in the valence band (VB) of the photocatalyst are excited to the conduction band (CB), while the transferred valence electron creates a hole (h^+) in VB. In this process large number of ($\text{e}^- - \text{h}^+$) charge pairs are created, and this stage is known as the excited or ‘photo-excited’ state of the catalyst, and the energy level difference between the VB and CB is known as band gap energy (E_g , eV). The light/photon energy ($h\nu$) equivalent or greater than E_g must be supplied to the photocatalyst for high absorption, excitation, and separation of charge pairs. However, the lifetime of the excited CB electrons is short-lived, and most of them dissipate energy in the form of heat and recombine with holes present in the VB. Few of the CB electrons and VB holes are available for the oxidation or reduction of the molecules at the

catalyst surface. The electrons and holes combine with oxygen and water from aqueous media to produce highly reactive superoxide ($\text{O}_2^{\bullet-}$) and hydroxyl ($\text{OH}^{\bullet}$) radical species. These reactive species are then utilized for redox chemical reactions of the organic chemical molecules to produce fragments or degradants. These degradants can further undergo mineralization to form eco-friendly molecules like water and carbon dioxide [30,31]. In general, the photocatalytic mechanism can be summarized as per the six steps mentioned below and the corresponding electron transfer pathways are depicted in Figure 1.1.

- Photoexcitation: $\text{TiO}_2 + h\nu$ (photon energy) $\rightarrow$ Photocatalyst ($e^-_{\text{CB}} + h^+_{\text{VB}}$).....(1)
- ($e^- - h^+$) recombination: $(e^-_{\text{CB}} + h^+_{\text{VB}}) \rightarrow e^-_{\text{CB}} + \text{heat/light}$ (2)
- Photoexcited e^-_{CB} scavenging: $(\text{O}_2)_{\text{ads}} + e^-_{\text{CB}} \rightarrow \text{O}_2^{\bullet-}$ (3)
- Oxidation of water (H_2O) by h^+_{VB} : $\text{H}_2\text{O} + h^+_{\text{VB}} \rightarrow \text{OH}^{\bullet}$(4)
- Photodegradation by $\text{O}_2^{\bullet-}$: Chemical molecule + $\text{O}_2^{\bullet-} \rightarrow$ Degradants.....(5)
- Photodegradation by $\text{OH}^{\bullet}$: Chemical molecule + $\text{OH}^{\bullet} \rightarrow$ Degradants(6)

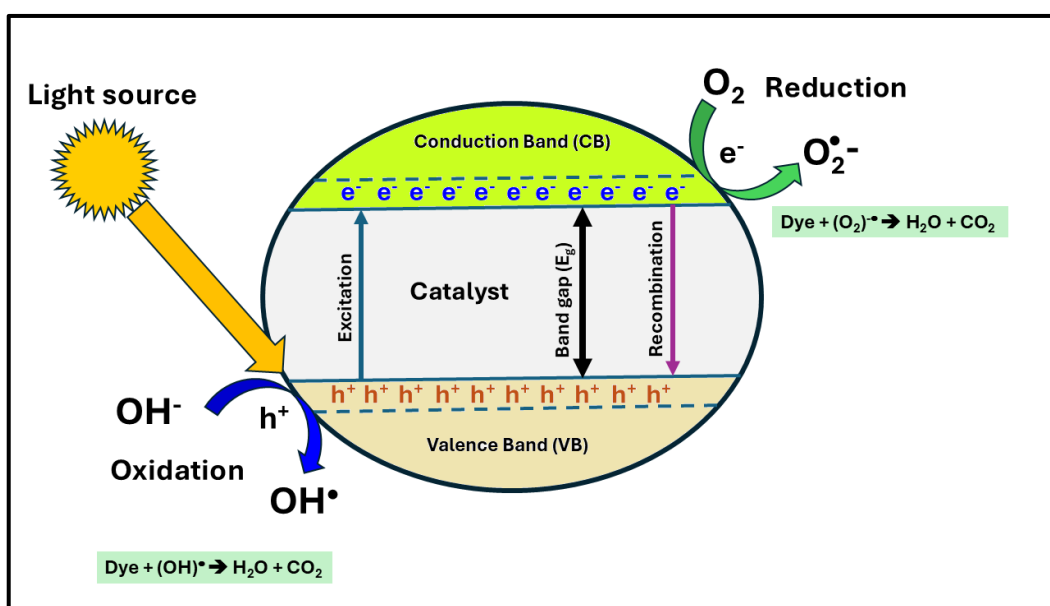


Figure 1.1: Schematic diagram showing the mechanism of model photocatalyst activated by light energy and electron transfer pathways.

1.4 Factors Influencing Photocatalysis

The efficiencies of the nanosized metal oxide-based photocatalyst are mainly influenced by crystal structure, particle size, surface area, surface morphology and light absorption capability. The adsorption of reactants on the surface of the photocatalyst depends on the crystallite structure, crystal facets/ planes and the charge of the dye molecule. Moreover, other environmental conditions that determine the rate of reaction are pH, temperature, concentration of dye and photocatalyst, type of light source or wavelength of radiation used, and the intensity of light energy. Hence, synthesis and modification of photocatalysts by doping certain impurities or hetero-nanostructures composite were crucial in the photocatalytic performance [32].

1.5 ZnO and TiO₂-based Photocatalysts

ZnO and TiO₂ semiconducting metal oxide materials possess exceptional optical properties and display potential for photocatalytic applications [30,33]. Both demonstrate excellent light absorption properties, energy transfer, and attain properties which are distinctively different from those of non-excited materials. The major drawback of these photocatalysts is that they are activated mainly in the UV region of the spectrum. The earth receives $\approx 4\%$ of UV light from the incoming solar spectrum, whereas $\approx 46\%$ of solar light falls in the visible spectrum. Hence, the materials sensitive to visible light are highly beneficial in photocatalysis from their environmental sustainability point of view [34]. Hence, the development of visible light-sensitive materials is a fascinating area of research. Various chemical and physical methods are reported for the synthesis of TiO₂ and ZnO-based nanomaterials, namely, but not limited to, sol-gel, physical/chemical vapour deposition, mechanochemical, hydrothermal, precipitation, precursor, solvothermal, direct metal oxidation, sonochemical, microwave, electrode deposition, and microemulsion [35–40].

Moreover, recent advancements in novel nanomaterials have shown good progress in photocatalytic preparation [41]. The advanced synthesis procedures and techniques assisted in developing new innovative materials. Also, characterization tools facilitated the in-depth correlation between the material structure and properties [42]. Hence, customization of the solid-state properties is possible by adopting a suitable synthesis

procedure. The structure, shape, size, morphology and surface area of photocatalytic materials can have a profound influence on photocatalytic applications.

The light absorption properties of metal oxide materials can be tuned by introducing dopants such as metal ions into host lattice positions. Such catalyst generates mid-gap energy levels, produces active sites, retards the electron-hole recombination rate, and possesses high redox capabilities. These key attributes of photocatalysts could be easily achieved by adopting a suitable synthesis methodology and doping impurities, and band gap engineering [43,44].

Another interesting area is the sunlight-assisted photo redox organic chemistry synthetic reaction [45]. Among synthetic chemists, there is always a quest to perform reactions with an economical, sustainable, and environmentally benign approach. Light absorption by photocatalyst, followed by radical formation, has emerged as a powerful technique for light-assisted catalytic reactions [46]. The development of novel graphene-TiO₂ hybrid photocatalytic materials has been a significant milestone, which showed a fourfold improvement in dye degradation rate compared to the pristine simple TiO₂ material [47]. Since then, graphene with different TiO₂ nanostructures, or the fabrication of multi-walled carbon nanotubes (MWCNT) and TiO₂ nanoparticles, has shown high photoactivity compared to unmodified TiO₂ particles [48]. Over several years, TiO₂ has been an outstanding catalyst support for various light-induced organic transformation or synthesis applications. However, the TiO₂ supported on MWCNT provides additional benefits such as a larger surface area and the formation of active sites. The reactants could be adsorbed over the catalyst and undergo electron transfer reactions to form the final product [49].

1.6 Aim and objective of current research

Aim: To synthesize ZnO and TiO₂-based photoactive materials in the framework of nano-sciences by precursor method, understand the fundamental structure-property relationship employing different characterization techniques and evaluate their possible photocatalytic applications.

Objective: The objective of the thesis titled “SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF PHOTOCATALYTIC NANOMATERIALS” are as follows:

1. To select a suitable preparation strategy for the preparation of novel and modified ZnO and TiO₂-based photocatalysts.
2. To prepare a series of Ce-doped ZnO nanomaterials via the precursor method and investigate the influence of Ce doping on the photocatalytic properties of ZnO.
3. To synthesize different rare earth metal ion doped-ZnO from thermal decomposition of mixed metal (M/Zn)-oxalate/oxalate-hydrazinate precursors, where (M=Nd/Sm/Dy/Ho) and assess the influence of metal ions on the photocatalytic dye degradation.
4. To stabilize the photoactive anatase TiO₂ phase using titanyl-oxy-hydroxide bonded through novel cyclodextrin complex precursor and photocatalytic degradation of dye and drug molecules.
5. To fabricate MWCNT/TiO₂ composite material by novel precursor-layer-coating (PLC) method and understand their synergistic effect, and study the photocatalytic conversion of benzophenone to benzopinacol.
6. To characterize and confirm structural, particle morphology, size, and surface properties of photoactive materials.
7. To understand the interaction of UV-visible light, absorption and band gap energy, and the formation of mid-gap states of modified ZnO and TiO₂ photocatalysts.
8. To explore the multiple applications of the synthesized materials, such as photocatalytic dye degradation for environmental pollution remediations, photocatalytic organic synthesis and photoluminescence.

1.7 Literature review: Photocatalytic nanomaterials

Over several decades, volumes of research papers and works have been dedicated to the development of semiconductor-based photocatalysts. The TiO_2 and ZnO -based photocatalytic materials are being extensively investigated for various applications [50,51]. The current research focuses on the material synthesis via the precursor method, characterization, and evaluation for their potential photocatalytic applications. The rare earth (RE) metal ion-doped ZnO are known to absorb in the UV-visible regions and has been studied by several researchers [52]. The Ce, Nd, Sm, Ho and Dy dopants can create mid-gap levels that act as an electron sink, facilitate electron-hole transfer, and slow down the recombination process in the bulk ZnO lattice. Metal ion doped- ZnO materials usually show a band gap reduction and a red shift in the light absorption edge, thereby enhancing the photocatalytic efficiency [53]. The doping can be achieved through the selection of suitable methods of synthesis. The common methods employed were sol-gel, precursor, combustion and chemical vapour deposition techniques [54–56]. The bulk charge recombination in photocatalysts can be retarded when the particle size is in nanometer range. In nanosized materials, the number of grain boundaries is reduced, hence, the recombination rate is reduced [57]. Anatase TiO_2 exhibits the best catalytic performance with high dye degradation efficiency. However, it is less stable at higher temperatures, and the catalytic process should be restricted below 600 °C. The anatase TiO_2 can be used in fixed-bed photoreactors or slurry form [58]. Furthermore, TiO_2 particles impregnated on carbon nanotubes are promising and versatile materials for light energy trapping, such as photovoltaics and photocatalytic applications [59]. To understand the relationship between the structure and photocatalytic properties, the materials were systematically characterized by various instrumental techniques [60].

1.7.1 Cerium-doped zinc oxide nanomaterials for photocatalytic degradation of methylene blue and textile dye

In photocatalysis, ZnO has been a prospective material for several applications [61]. The ZnO nanomaterials have been strongly fostered because of their high stability and UV-visible light absorption ability. The high surface area, reduced band gap energy (E_g), and optimal dopant concentration were the key factors for enhancing the

photocatalytic activity [62–64]. These properties were achieved by adopting a suitable synthesis method and doping certain metal or non-metal ions into the host ZnO lattice [65]. The intentional addition of a small amount of metal ion impurities in ZnO generated mid-band gap energy level that improved electronic transitions from the VB to CB. In ZnO, varied impurities were reported, such as n-type, p-type, co-doping and defect engineering, which resulted in modified E_g and electronic transitions. Dopants such as Al^{3+} , Ga^{3+} , In^{3+} and Sc^{3+} produced n-type ZnO and introduced shallow donor levels close to CB. Such doping facilitated electronic transitions to the CB and improved the n-type conductivity in the catalyst [66–69]. The p-type ZnO was produced when the Zn^{2+} ions were replaced by N, As, and P as dopants. These types of dopants formed shallow acceptor levels and altered the electronic properties and light absorption capacity [70]. In co-doped ZnO materials, double elements (metal/metal or non-metal/metal) were substituted in Zn^{2+} ion sites. The co-doped ZnO improved the charge separation and shifted the band edge towards the visible region. Also, the surface area and morphology of ZnO modified compared to pure ZnO [71]. Further, the synthesis and post-annealing treatments introduced the intrinsic defects (Zn_i) and oxygen vacancies (V_o) in ZnO. The Zn_i created a mid-gap energy level just below the conduction band, while V_o created energy levels above the valence band of ZnO. The introduction of Zn_i and V_o defects in ZnO also generated deep energy levels [72,73]. These mid-gap energy levels produced a large number of (e^-h^+) pairs, which promotes the organic dye degradation activity [74,75]. Thus, despite substantial research work carried out on ZnO photocatalysts by different scientific groups, there is a vast scope to achieve higher photosensitivity, retard the rate of (e^-h^+) pair recombination, and in turn improve the photocatalytic efficiency for a specific application. Hence, metal/non-metal ion doping in the ZnO lattice has been considered as the most promising strategy for tailoring the E_g and improving the photoactivity [76].

The light absorption properties of ZnO are normally modified by band gap engineering. Metal and non-metal ion dopants such as Ga, N, Ag, Fe, S, Co, and Ln were incorporated into the ZnO lattice, which altered the E_g and electron charge mobilities [68,77–80]. Mostly rare earth metal ion-doped ZnO materials have been fabricated either using lengthy, expensive or cumbersome procedures, namely sol-gel, laser ablation, chemical vapour deposition, spray pyrolysis, electrochemical synthesis, sputter deposition, and electrodeposition [81]. The ZnO modified with g- C_3N_4 showed improved results for environmental pollution control applications [82]. In one of the research papers, mentioned

that when carbon dots were embedded in ZnO nanostructures, a dramatic increase in pollutant photodegradation efficiency in sunlight [83]. The nanocomposites consisting of graphene oxide/ZnO with embedded metal nanoparticles also showed high performance in chemical molecule photodegradation [84]. C. J. Silva *et al* investigated ZnO impregnated with gold atoms prepared via the chemical vapour deposition (CVD) method. They characterized the catalysts by XRD, spectroscopy, and surface / microstructural analysis and noted that the catalyst became photoactive for phenol oxidation in the solar spectrum [85]. The synthesis influences the structure, morphology, particle size distribution, and optical and photocatalytic properties of the prepared nanomaterials. V. Borker *et al* reported the synthesis of gamma-iron oxide nanomaterials via the thermal decomposition of oxalate and oxalate-hydrazine precursors, stabilising the phase formation and stabilising the spinel structures by controlling the atmosphere during synthesis [86,87]. R.L. Fomekong *et al* obtained $\text{Ni}_{1-x}\text{Zn}_x\text{O}/\text{ZnO}$ nanocomposites on pyrolysis of nickel-zinc-malonate precursor and characterized by XRD, SEM/TEM and XPS [88]. Verenkar *et al* prepared nanosized NiMn_2O_4 via thermal decomposition of nickel-manganese-succinato-hydrazinate precursors [89]. Jianguo Pan *et al* reported the synthesis of zinc-succinate crystals [90]. In another reported work, ZnO became an efficient visible-light-sensitive photocatalyst on doping with Ce^{4+} metal ions [91]. Further, R. Kumar *et al* fabricated Ce-doped ZnO nanoparticles for superior photocatalytic degradation of Direct Red-23 dye [92]. Also, M. Ahmed *et al* reported the enhanced photocatalytic activity of Ce-doped ZnO nanopowders synthesized by the combustion method. They varied the Ce concentration (0.5 wt.% – 10.0 wt.%) in ZnO and studied the trend in photoactivity [93]. Chuanhui Xia *et al* introduced Ce ions in ZnO nanorod arrays on zinc foils through a hydrothermal method at 180 °C [94]. More recently, J.R. Mora *et al* investigated the Ce-doped ZnO nanonails synthesized by a thermal evaporation method. The 0, 1, 5 and 10 % CeO_2 was doped in ZnO and compared for their photocatalytic degradation. The 10% CeO_2 -doped sample showed maximum photocatalytic activity, which was owed to the reduced band gap energy (E_g) caused by Ce doping in ZnO [95]. The precursor method of synthesizing nanosized materials via a mixed metal-oxalate complex has been a well-established methodology for producing functional materials. In this context, the main aim was the preparation of Ce-doped ZnO by the succinate precursor method, characterized their critical material properties and evaluated for methylene blue model dye and textile dye degradation in UV-visible light.

1.7.2 Rare earth metal ion-doped zinc oxide nanomaterials for photocatalytic degradation of organic dyes

Rare-earth (RE=Nd/Sm/Dy/Ho) metal ions are suitable dopants to modify the band gap energy (E_g) of ZnO photocatalyst. On RE doping, ZnO photocatalyst showed significant improvement in the activity when compared to pure ZnO. The RE metal ion introduces new mid-gap energy levels and facilitates the electron transfer, separation and subsequent mobilization of the charges, which are beneficial for improving the catalytic efficiency. The light absorption characteristics of ZnO were also enhanced due to the high electron density and variable valency of the 4f energy shells of RE metal ions [96]. In the literature, different preparation methods were reported for RE-doped ZnO photocatalytic materials [97,98].

The synthesis of mixed-metal oxides via metal-carboxylate has been explored for decades by many scientists [99]. Amongst all preparation techniques, the precursor method of preparation is quite simple, inexpensive and capable of forming nanosized ZnO particles. The (RE=Nd/Sm/Dy/Ho) doped ZnO could be co-precipitated as mixed metal-oxalate. Additionally, the mixed metal precursors, on attaching hydrazine molecule, exhibited modified optical properties [100]. In reported literature, A. S. H. Hameed *et al* showed that the solid-state properties of pure ZnO were modified with neodymium (Nd) metal ion doping in ZnO. They prepared Nd-doped ZnO nanoparticles via the co-precipitation method [101]. While T. Indumathi *et al* prepared Nd-doped ZnO nanomaterials by chemical precipitation method and investigated the effect of doping on structural, optical, morphological and surface-chemical state for antimicrobial and anticancer activities [102]. Also, S. Kumar *et al* in their research paper reported the chemical precipitation method for the synthesis of Nd-doped ZnO and investigated their multifunctional properties [103]. Further, Nd-doped ZnO nanostructures with variable concentrations of Nd were synthesized by the electrospinning–calcination method as reported by P. Pascariu *et al*. They noted that the photocatalytic methylene blue degradation efficiencies improved in the case of 0.1 % Nd doped ZnO [104].

H. Eskandarloo *et al* reported ultrasonic-assisted degradation of phenazopyridine on Sm-doped ZnO nanoparticles and inorganic oxidants [105]. D. R. Kumar *et al* prepared vertically aligned, Sm-doped ZnO nanorod arrays by vapour transport process. The materials were characterized by FESEM, XRD, PL, Raman spectroscopy and XPS. The

photocatalytic degradation activities for MB dye were enhanced under natural sunlight irradiation. They noted that the photocatalytic activity ranged from 83.02 to 97.3 % as Sm content increased from 0 to 6% in ZnO. The studies also highlighted the positive effect of Sm-dopant on the visible-light-driven photocatalytic properties of ZnO [106]. M. M. Ba-Abbad synthesized and characterized Sm-doped ZnO nanoparticles via a sol-gel method. They also evaluated the photocatalytic degradation of 2-chlorophenol under sunlight in the presence of ZnO and Sm-doped ZnO nanoparticles. The performance of 0.5 wt % Sm-doped ZnO was highest compared to pure ZnO nanoparticles under the same experimental conditions [107]. M. Faraz *et al* fabricated Sm-doped ZnO nanoparticles (1%, 3%, and 5%) by a gel-combustion route and demonstrated efficient photocatalytic degradation of Malachite green (MG) dye [108]. Additionally, Sukriti *et al* synthesized Sm doped ZnO nanostructures ($\text{Zn}_{1-x}\text{Sm}_x\text{O}$; where $x = 0.00, 0.02, 0.04$ and 0.06) via precipitation method. They characterized the materials and investigated their structural, optical, morphological and photocatalytic properties. The $\text{Zn}_{1-x}\text{Sm}_x\text{O}$, $x = 0.04$ % exhibited maximum photodegradation efficiency (94 %) for methylene blue (MB) under visible light irradiation [109]. Debasrita Dash *et al* prepared Sm doped ZnO nanocolumns using wet chemical method with improved visible light absorption. They reported the degradation of MB and methyl orange (MO) and proposed for remediation of industrial wastewater [110]. A novel Sm-doped spherical-like ZnO hierarchical nanostructure (Sm/ZnO) was synthesized via a facile and surfactant-free chemical solution route. The materials were characterized by XRD, BET, SEM, EDAX, TEM, UV-visible DRS, and PL. The photocatalytic studies revealed that the Sm/ZnO exhibited excellent photocatalytic degradation of 2,4-dichlorophenol compared with the pure ZnO and commercial TiO_2 under visible light irradiation [111].

A. Khataee *et al* investigated Dy-doped ZnO nanoparticles synthesized by the sonochemical method and characterized by XRD, ICP-MS, FTIR, UV-visible DRS, and SEM. The 3% Dy-doped ZnO nanoparticles efficiently degraded C.I. Acid Red 17 solution under visible light irradiation [112]. In another study, G. E. Fidha *et al* reported the physical and photocatalytic activity of Dy-doped ZnO, which was prepared via the spray pyrolysis technique. The highest MB dye degradation activity was obtained for 6%-Dy-doped ZnO material [113]. U. Alam *et al* reported the fabrication of RE-metal ion (RE=La, Nd, Sm and Dy)-doped ZnO nanoparticles using a sol-gel method and compared their photocatalytic activity by degrading the methylene blue (MB) and Rhodamine B (Rh B)

under UV-light irradiation [114]. O. Yayapao *et al* studies Dy-doped ZnO nanostructures (nanorods) for photocatalytic activities. They synthesized materials by a sonochemical method and examined the phase, morphology, optical properties and photocatalytic activities. The photocatalytic activities of performed on MB dye by UV radiation. They reported 3% Dy-doped ZnO material showed the highest photocatalytic activity [115]. Moreover, S. S. Nguanprang *et al* reported the preparation of Dy doped ZnO samples by a tartaric acid-assisted combustion method, characterized and studies its photocatalytic applications. The 5 at.% Dy-doped ZnO nanoparticles showed the maximum photocatalytic activity for MB degradation of 97% within 75 min [116].

In the case of Ho-doped ZnO, S. A. Ayon *et al* reported the synthesis of nanocrystalline photocatalyst via the modified sol-gel method. They prepared $\text{Zn}_{1-x}\text{Ho}_x\text{O}$ ($x = 0.01, 0.03$ and 0.05) and studied their structural and morphological properties. The photocatalytic activity was measured using the degradation of Rhodamine B dye. The doping of Ho^{3+} ions led to a decreased electron-hole recombination rate due to electron trapping by partially filled 4f orbitals, a change in particle morphology and the red shift of the optical band gap, which resulted in the enhanced photocatalytic performance of $\text{Zn}_{0.97}\text{Ho}_{0.03}\text{O}$ nanomaterial [117]. In one of the studies conducted by the K. Narasimharao *et al* group, different rare earth metal ions (Sm, Nd and Ho) oxides were synthesized via organic and inorganic routes. The materials were characterized comprehensively using different solid-state techniques. These materials were evaluated for photocatalytic degradation of crystal violet dye under visible light irradiation. They also mentioned that the materials prepared using the organic route exhibited high photocatalytic efficiencies. Samarium oxide synthesized using an organic route offered the superior photocatalytic activity due to low band gap energy, high surface area, pore volume and presence of surface reactive -OH groups. They also showed that the photocatalysts exhibited excellent recyclability for photocatalytic crystal violet degradation [118]. M. Popa *et al* studied optical properties of Polycrystalline Ho (1, 3, 5 at %) doped ZnO thin films, which were prepared by sol-gel method [119]. A. Phuruangrat *et al* prepared Ho-doped ZnO materials, characterized and studies its photocatalytic properties using MB in UV light [120].

1.7.3 Anatase titanium dioxide nanomaterial for photodegradation of drug and dye molecules

Anatase TiO_2 is a highly active photocatalytic material widely investigated for the catalytic degradation of harmful molecules and detoxification of water [121]. TiO_2 displayed exemplary chemical stability across a wide pH range, superior optical properties, oxidizing abilities and is highly hydrophilic [122]. The preparation of nanosized anatase TiO_2 powders using beta-cyclodextrin (β -CD) has been well comprehended in many research papers [123–126]. Earlier, Anandan *et al* reported that the bonding of β -CD on the surface of TiO_2 particles to form colloids, which provided a microenvironment for the degradation of Niel red dye [127]. Rane *et al* synthesized visible light-sensitive yellow N-doped titanium dioxide from the thermal decomposition of titanyl-oxalate-hydrazine precursor [128]. W. Zhou *et al* studied the TiO_2 - β -CD-MWCNT wires, which they successfully fabricated under solar irradiation [129]. Further, X. Zhang *et al* prepared cyclodextrin-grafted titanium dioxide synthesized through photoinduced self-assembly methods, which showed high photoactivity under visible light irradiation and simulated solar irradiation for photodegradation of Orange II [130]. Additionally, M. A. Kakroudi *et al* showed that the β -CD and commercial nano- TiO_2 P25 could be self-assembled under sunlight irradiation in water, which resulted in deprotonation from a hydroxyl group of the CD molecules on TiO_2 [131]. X. Sun *et al* fabricated β -CD metal-organic framework/titanium dioxide hybrid nanocomposite material for dispersive solid-phase extraction of pesticide residues in honey samples [132]. D. Jia *et al* designed and synthesized a TiO_2 / β -CD double-ring composite, where β -CD vesicles make up the inner ring while the TiO_2 comprises the outer ring [133]. R. Bleta *et al* synthesized mesoporous titania with varied structural and textural characteristics in an aqueous phase via a colloidal self-assembly approach using CD. They also reported the structure-directing properties of CDs [124]. In one of the studies, CDs were utilized for the controlled synthesis of silver (Ag) nanostructures in aqueous solutions. The 10 nm Ag nanoparticles (NP) were produced by the reduction of silver nitrate with sodium borohydride in the presence of α -CDs. The Ag NPs showed hydrophobic interactions with the apolar primary faces of α -CDs. Also, the researchers mentioned the head-to-head hydrogen-bonding interactions between the exposed secondary -OH groups with the neighbouring CDs to form the self-assembly of the Ag NPs into 1-D array [134]. A. D. Vincenzo *et al* in their research paper

reported a significant improvement in photocatalytic activity over graphene oxide-silver nanocomposite photocatalysts prepared via cyclodextrin-based nanosponge materials. They attributed the higher activity to the synergistic effect provided by the supramolecular host abilities of the nanosponge [135]. Also, Kwak *et al* in their patent mentioned the preparation of porous TiO₂ with uniform pore size using CD as and titanium precursor as a template [136]. In another study, D. Bonacchi *et al* devised a novel technique, wherein they synthesized very small metal oxide particles of γ -Fe₂O₃, NiO and CoO magnetic nanoparticles by the addition of NaOH to a ferrous chloride solution in the presence of γ -cyclodextrin [137]. Recently, H. Li *et al* in their review mentioned about the synthesis of mesoporous TiO₂ materials for energy conversion and storage applications. Various templates, including hard, soft, and multi-templating methods were used for the mesoporous material preparation [138].

1.7.4 Multiwalled carbon nanotube/titanium dioxide composite for photocatalytic organic synthesis

A composite material comprising nanosized TiO₂ supported on multi-walled carbon nanotubes (MWCNT) are well-known photocatalyst for various applications [139–141]. The separation of photogenerated charged pairs could be achieved by employing conducting carbon nanomaterials. The TiO₂ supported on carbon nanotubes (CNT) can trap light photon energy, separate charge pairs more efficiently and transfer to CNT for the photocatalytic process. The photocatalytic organic synthesis is also considered to be a green chemistry process. Based on the previously published reports, MWCNT/TiO₂ composites were fabricated by various methods, namely, hydrothermal, molecular grafting, solvothermal, and heterogeneous coagulation. N. Abbas *et al* prepared CNT/ TiO₂ composites by loading 0, 2, 5, 10, 15, and 20% CNT via the sol-gel method employing CNT and TiOCl₂ as precursors [142]. K. Nemeth *et al* coated MWCNT with SiO₂–MgO particles to produce a composite material by the sol-gel method [143]. N. G. Akalework *et al* prepared MWCNT-supported ultrathin TiO₂ films using a modified sol-gel method [144]. Additionally, M. R. Ardani *et al* prepared TiO₂-MWCNT nanocomposites from titanium tetrachloride (TiCl₄) and MWCNT as starting precursors, by adopting an ultrasonic method of synthesis [145]. M. Alsawat *et al* also reported that the TiO₂ nanotubes could be synthesized inside MWCNT by the chemical vapour deposition (CVD)

method for photocatalytic applications [146]. In addition, P-doped TiO₂/MWCNTs thin films were also synthesized by D. R. Sarker *et al* [147]. U. C. Flores *et al* monitored the photocatalytic activity of MWCNT/TiO₂ heterojunction photocatalysts obtained by the microwave-assisted method using titanium butoxide as a precursor [148]. J. Feng *et al* investigated the hydrophilic CNT-hybrid metal oxides (ZnO and TiO₂) membranes prepared by the atomic layer deposition (ALD) method [149]. Besides, L. Tian *et al* also reported that MWCNT, when decorated with TiO₂ particles, produced hybrid nanostructures via solvothermal and sol-gel methods using benzyl alcohol as a surfactant. [150]. Based on published reports, it was evident that the composite materials could significantly improve the performance of the individual materials and displayed a significant influence on the optical, electrical, and photocatalytic properties. In current research, the (MWCNT/TiO₂) composite photocatalytic materials have been fabricated by the novel precursor-layer-coating (PLC) method, characterized and studied for photocatalytic organic synthesis reaction.

Based on the literature survey, ZnO and TiO₂ systems were prepared, and their structure-property relationship was systematically studied. Some of the key drawbacks of TiO₂ and ZnO-based photocatalysts that require attention, along with their potential solutions, are noted below:

- (1) The photocatalytic activity is directly proportional to the number of reactant molecules absorbed on the catalyst surface. ZnO and TiO₂ surfaces are highly hydrophilic due to the hydroxyl groups formed in aqueous media. Consequently, they have poor affinity for hydrophobic organic molecules. The precursor technique can increase the hydrophobicity of the surface. Alternatively, supporting the photocatalyst on a hydrophobic material like CNT can enhance the affinity towards organic reactants on the surface.
- (2) The surface area of photocatalytic materials is a crucial parameter; however, particle aggregation reduces surface area, diminishing the active sites for photocatalytic activities. Nanosized materials with high specific surface areas and mesoporous nature can overcome this limitation.
- (3) Photocatalytic degradation reactions occur at the interface between the photocatalyst surface and pollutant molecule, as a result, the transfer of charge after the separation of electron and hole pairs is vital. Hence, the charge pair recombination rate should be as low as possible to increase the photocatalytic activity. This point can be addressed by doping

certain metal ions and creating mid-gap energy levels, consequently delaying the recombination process.

(4) High doping concentration of a metal ion in a photocatalyst leads to a reduction of photocatalytic activity due to the formation of recombination centres. The appropriate doping concentration of dopants is critical to increase the photocatalytic activity. Hence, a very low concentration of dopants is crucial in photocatalysis.

(5) For organic compound degradation in wastewater, the major practical challenge is to recover the nanosized TiO_2 particles from the treated water efficiently and safely. The TiO_2 nanosized powder can be well dispersed and suspended when fixed on support materials. Hence, the integration of photocatalysts with different support materials can assist in the separation of the catalyst.

(6) Due to the high band energy, the pure TiO_2 and ZnO photocatalyst mainly absorbs UV light, and the sensitivity towards visible light is negligible. Hence, their applicability in sunlight needs to be improved. In this regard, doping certain elements can reduce the band gap energy and improve visible light photoactivity.

1.8 Material characterization techniques

To understand the structure-property relationship and key attributes of the photocatalyst, the prepared material was characterized using multiple techniques as described briefly below [151]:

Infrared spectroscopy: When a molecule absorbs infrared (IR) radiation, it experiences a change in dipole moment and becomes IR active. The spectrum reveals the positions of bands that correspond to the strength, nature of bonds, and the identification of specific functional groups. This information helps in understanding the molecular structures and types of interactions.

Thermal analysis: The TGA-DSC technique is adopted to analyze precursors, identifying components through decomposition or degradation temperatures while recording mass changes and heat flow. This method provides information about the type and quantity of organic ligands in precursors. In DSC, thermal events are identified by observing endothermic or exothermic heat flow thermograms and correlated with TGA mass loss.

X-ray diffraction: XRD analysis reveals the crystalline structure and phase of the material under investigation. The lattice parameters and crystalline grain size are derived from the diffraction data, peak positions and shapes. The material phase and composition are compared with reference patterns from the International Centre for Diffraction Data (ICDD) or the Joint Committee on Powder Diffraction Standards (JCPDS) database, based on the peak positions and intensities.

Microstructural analysis (SEM/TEM/EDAX): SEM are used for the high-resolution imaging of particle surfaces at the nanoscale. The shape, size and morphology of particles are evaluated from the images. A transmission electron microscope (TEM) is utilized for advanced nanoparticle analysis. Detailed information about particle shape, size, morphology and crystallite planes is observed from TEM images. Energy dispersive absorption X-ray spectroscopy (EDAX) is generally a probe coupled with SEM for elemental analysis. When electrons are bombarded on the material surface, the energy released in the form of X-rays due to the energy difference between the electronic shells helps to identify the atoms/elements present in the material under investigation.

Surface area analysis: The surface area, pore size and distribution, and mean pore volume of a nanomaterial are quantified based on the Brunauer–Emmett–Teller (BET) technique. In the BET technique, nitrogen gas is physisorbed on a solid surface and the adsorption and desorption isotherms are recorded, which reveal the surface area in m^2/g , pore size/volume and distribution.

X-ray photoelectron spectroscopy: XPS is a powerful quantitative technique, useful to elucidate the elemental composition, electronic structure, and oxidation(valence) states of elements present in the material based on the binding energy values.

Raman spectroscopy: It is a type of vibrational spectroscopy where the identification and chemical structure of a material can be evaluated from the Raman spectrum and peak positions. The Raman peaks also contain quantitative information about the phases present.

UV-visible light diffuse reflectance spectroscopy: In this technique, the information about the material light absorption ability, absorption edge (λ -edge) and optical band gap energy (E_g) of the material can be calculated.

Photoluminescence: The photoluminescence intensities and peak positions (λ) of emission spectra provide information regarding the state of excited photogenerated electron-hole pairs, the recombination process and the various types of intrinsic defects formed during synthesis in the semiconductor materials.

Liquid chromatography-Mass spectroscopy:

Liquid chromatography with a mass spectrometer detector is employed to separate the various fragments/degradants formed during photocatalysis, and eluent is analysed by Mass Spectrometer (MS) for detection, identification, and molecular mass determination. The quantitative and qualitative analysis of different compounds in solutions can be evaluated.

REFERENCES

1. R. K. Sharma, R. Bandichhor, V. Mishra, S. Sharma, S. Yadav, S. Mehta, B. Arora, P. Rana, S. Dutta, and K. Solanki, *Mater. Adv.* **4**, 1795 (2023).
2. K. R. Zodrow, Q. Li, R. M. Buono, W. Chen, G. Daigger, L. Dueñas-Osorio, M. Elimelech, X. Huang, G. Jiang, J. H. Kim, B. E. Logan, D. L. Sedlak, P. Westerhoff, and P. J. J. Alvarez, *Environ. Sci. Technol.* **51**, 10274 (2017).
3. Y. Zhu, Q. Lin, Y. Zhong, H. A. Tahini, Z. Shao, and H. Wang, *Energy Environ. Sci.* **13**, 3361 (2020).
4. A. M. Sadeq, R. Z. Homod, A. K. Hussein, H. Togun, A. Mahmoodi, H. F. Isleem, A. R. Patil, and A. H. Moghaddam, *Sci. Total Environ.* **939**, 173622 (2024).
5. N. Abas, E. Kalair, A. Kalair, Q. ul Hasan, and N. Khan, *Int. J. Hydrogen Energy* **45**, 20787 (2020).
6. R. Ningthoujam, Y. D. Singh, P. J. Babu, A. Tirkey, S. Pradhan, and M. Sarma, *Chem. Phys. Impact* **4**, 100064 (2022).
7. X. Yang and D. Wang, *ACS Appl. Energy Mater.* **1**, 6657 (2018).
8. J. M. Herrmann, *Top. Catal.* **34**, 49 (2005).
9. T. Tsukamoto, T. Shimada, and S. Takagi, *ACS Omega* **3**, 18563 (2018).
10. D. Lincot, *Comptes Rendus Phys.* **18**, 381 (2017).
11. F. Mohamadpour and A. M. Amani, *RSC Adv.* **14**, 20609 (2024).
12. Rachna, M. Rani, and U. Shanker, *J. Environ. Chem. Eng.* **8**, 104040 (2020).
13. R. Homlok, E. Takács, and L. Wojnárovits, *Chemosphere* **91**, 383 (2013).
14. M. J. Sampaio, Z. Yu, J. C. Lopes, P. B. Tavares, C. G. Silva, L. Liu, and J. L. Faria, *Sci. Rep.* **11**, 1 (2021).
15. L. Ju, P. Liu, Y. Yang, L. Shi, G. Yang, and L. Sun, *J. Energy Chem.* **61**, 228 (2021).
16. S. Samsami, M. Mohamadi, M. H. Sarrafzadeh, E. R. Rene, and M. Firoozbahr, *Process Saf. Environ. Prot.* **143**, 138 (2020).
17. S. Khan, T. Noor, N. Iqbal, and L. Yaqoob, *ACS Omega* **9**, 21751 (2024).

18. M. S. Chavali and M. P. Nikolova, *SN Appl. Sci.* **1**, 1 (2019).
19. D. Barreca and C. Maccato, *CrystEngComm* **25**, 3968 (2023).
20. R. Medhi, M. D. Marquez, and T. R. Lee, *ACS Appl. Nano Mater.* **3**, 6156 (2020).
21. A. Chakraborty, G. H. Debnath, N. R. Saha, D. Chattopadhyay, D. H. Waldeck, and P. Mukherjee, *J. Phys. Chem. C* **120**, 23870 (2016).
22. C. K. Prier, D. A. Rankic, and D. W. C. MacMillan, *Chem. Rev.* **113**, 5322 (2013).
23. H. A. A. Jamjoum, K. Umar, R. Adnan, M. R. Razali, and M. N. Mohamad Ibrahim, *Front. Chem.* **9**, 1 (2021).
24. J. Iyyappan, B. Gaddala, R. Gnanasekaran, M. Gopinath, D. Yuvaraj, and V. Kumar, *Case Stud. Chem. Environ. Eng.* **9**, 100599 (2024).
25. S. B. Beil, S. Bonnet, C. Casadevall, R. J. Detz, F. Eisenreich, S. D. Glover, C. Kerzig, L. Næsborg, S. Pullen, G. Storch, N. Wei, and C. Zeymer, (2024).
26. M. S. H. Abdullah Al Miad, Shassatha Paul Saikat, Md. Kawcher Alam and Newaz Mohammed Bahadura and Samina Ahmed, *Nanoscale Adv.* **6**, 4781 (2024).
27. F. P. D. F. Hern, V. Bernal, L. Giraldo, J. Carlos, E. Alves, C. Martins, J. Morais, Y. Hernandez, T. Cort, and M. A. Mac, *ACS Omega* **8**, 47821 (2023).
28. H. Heidarpour, M. Golizadeh, M. Padervand, A. Karimi, M. Vossoughi, and M. H. Tavakoli, *J. Photochem. Photobiol. A Chem.* **398**, 112559 (2020).
29. F. Wang, F. Huang, F. Yu, X. Kang, Q. Wang, and Y. Liu, *Cell Reports Phys. Sci.* **4**, 101450 (2023).
30. N. Madkhali, C. Prasad, K. Malkappa, H. Y. Choi, V. Govinda, I. Bahadur, and R. A. Abumousa, *Results Eng.* **17**, 100920 (2023).
31. N. Baig, I. Kammakakam, W. Falath, and I. Kammakakam, *Mater. Adv.* **2**, 1821 (2021).
32. A. H. Kamel, H. S. M. Abd-Rabboh, A. Abd El-Fattah, G. Boudghene Stambouli, and L. Adeida, *RSC Adv.* **15**, 6875 (2025).
33. Y. Sun, W. Zhang, Q. Li, H. Liu, and X. Wang, *Adv. Sens. Energy Mater.* **2**, 100069

(2023).

34. A. Joy, M. R. Viswanathan, B. K. Vijayan, C. G. Silva, I. Basheer, S. Sugathan, P. A. Mohamed, A. Solaiappan, and A. Shereef, *RSC Adv.* **14**, 21655 (2024).
35. R. Ghamarpoor, A. Fallah, and M. Jamshidi, *ACS Omega* **9**, 25457 (2024).
36. S. Harish, M. Sabarinathan, A. P. Kristy, J. Archana, M. Navaneethan, H. Ikeda, and Y. Hayakawa, *RSC Adv.* **7**, 26446 (2017).
37. A. Hezam, K. Namratha, D. Ponnammam, Q. A. Drmosh, A. M. N. Saeed, K. K. Sadasivuni, and K. Byrappa, *ACS Omega* **4**, 20595 (2019).
38. B. Endrödi, E. Kecsenovity, K. Rajeshwar, and C. Janáky, *ACS Appl. Energy Mater.* **1**, 851 (2018).
39. K. Mondal and A. Sharma, *RSC Adv.* **6**, 83589 (2016).
40. Y. Wang, Y. He, Q. Lai, and M. Fan, *J. Environ. Sci. (China)* **26**, 2139 (2014).
41. A. O. Ibhadon and P. Fitzpatrick, *Catalysts* **3**, 189 (2013).
42. L. Zhang, J. Ran, S. Z. Qiao, and M. Jaroniec, *Chem. Soc. Rev.* **48**, 5184 (2019).
43. C. Siri Wong, N. Wetchakun, B. Inceesungvorn, and D. Channei, *Prog. Cryst. Growth Charact. Mater.* **58**, 145 (2012).
44. R. Asahi, T. Morikawa, H. Irie, and T. Ohwaki, *Chem. Rev.* **114**, 9824 (2014).
45. A. Dandia, P. Saini, R. Sharma, and V. Parewa, *Curr. Res. Green Sustain. Chem.* **3**, 100031 (2020).
46. M. A. Hassaan, M. A. El-Nemr, M. R. Elkatory, S. Ragab, V. C. Niculescu, and A. El Nemr, *Top. Curr. Chem.* **381**, 1 (2023).
47. N. T. Padmanabhan, N. Thomas, J. Louis, D. Treasa, P. Ganguly, H. John, and S. C. Pillai, *Chemosphere* **271**, 129506 (2021).
48. M. Dahl, Y. Liu, and Y. Yin, *Chem. Rev.* **114**, 9853 (2014).
49. N. B. Trinh, T. A. Nguyen, S. Van Vu, H. G. T. Vo, T. N. H. Lo, I. Park, and K. Q. Vo, *RSC Adv.* **14**, 34037 (2024).
50. J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, and D. W.

- Bahnemann, **114**, 9919 (2014).
51. X. Chen, Z. Wu, D. Liu, and Z. Gao, *Nanoscale Res. Lett.* **12**, 4 (2017).
52. S. G. Kumar and K. S. R. K. Rao, *RSC Adv.* **5**, 3306 (2015).
53. Y. Zhang, A. Apostoluk, C. Theron, T. Cornier, B. Canut, S. Daniele, and B. Masenelli, *Sci. Rep.* **9**, 1 (2019).
54. J. Yang, M. Gao, L. Yang, Y. Zhang, J. Lang, D. Wang, Y. Wang, H. Liu, and H. Fan, *Appl. Surf. Sci.* **255**, 2646 (2008).
55. L. Wang, Z. Ji, J. Lin, and P. Li, *Mater. Sci. Semicond. Process.* **71**, 401 (2017).
56. K. K. Taha, A. Modwi, L. Khezami, and M. Heikal, *Dig. J. Nanomater. Biostructures* **13**, 1213 (2019).
57. M. Y. Qi, M. Conte, M. Anpo, Z. R. Tang, and Y. J. Xu, *Chem. Rev.* **121**, 13051 (2021).
58. T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, and M. Batzill, *Sci. Rep.* **4**, 1 (2015).
59. K. E. Tettey, M. Q. Yee, and D. Lee, *ACS Appl. Mater. Interfaces* **2**, 2646 (2010).
60. A. El Mragui, O. Zegaoui, I. Daou, and J. C. G. Esteves da Silva, *Environ. Sci. Pollut. Res.* **28**, 25130 (2021).
61. F. Güell, A. Galdámez-Martínez, P. R. Martínez-Alanis, A. C. Catto, L. F. da Silva, V. R. Mastelaro, G. Santana, and A. Dutt, *Mater. Adv.* **4**, 3685 (2023).
62. N. Mohaghegh, M. Tasviri, E. Rahimi, and M. R. Gholami, *Mater. Sci. Semicond. Process.* **21**, 167 (2014).
63. S. Anandan, N. Ohashi, and M. Miyauchi, *Appl. Catal. B Environ.* **100**, 502 (2010).
64. M. Baitimirova, J. Andzane, R. Viter, B. Fraisse, O. Graniel, M. Bechelany, J. Watt, D. Peckus, S. Tamulevicius, and D. Erts, *J. Phys. Chem. C* **123**, 31156 (2019).
65. S. Faisal, H. Jan, S. A. Shah, S. Shah, A. Khan, M. T. Akbar, M. Rizwan, F. Jan, Wajidullah, N. Akhtar, A. Khattak, and S. Syed, *ACS Omega* **6**, 9709 (2021).
66. A. H. Ajil, N. M. Ahmed, F. K. Yam, Z. U. Zango, I. A. Wadi, A. M. Binzowaimil, O.

- Aldaghri, K. H. Ibnaouf, and H. Cabrera, *Appl. Sci.* **13**, 11857 (2023).
67. S. C. Dixon, S. Sathasivam, B. A. D. Williamson, D. O. Scanlon, C. J. Carmalt, and I. P. Parkin, *J. Mater. Chem. C* **5**, 7585 (2017).
68. H. S. Alanazi, N. Ahmad, and F. A. Alharthi, *RSC Adv.* **11**, 10194 (2021).
69. F. Khan, S. H. Baek, and J. H. Kim, *J. Alloys Compd.* **709**, 819 (2017).
70. B. Chavillon, L. Cario, A. Renaud, F. Tessier, F. Chevire, M. Boujtita, Y. Pellegrin, E. Blart, A. Smeigh, L. Hammarström, F. Odobel, and S. Jobic, *J. Am. Chem. Soc.* **134**, 464 (2012).
71. F. Khan, S. H. Baek, and J. H. Kim, *J. Alloys Compd.* **682**, 232 (2016).
72. D. Liu, Y. Lv, M. Zhang, Y. Liu, Y. Zhu, R. Zong, and Y. Zhu, *J. Mater. Chem. A* **2**, 15377 (2014).
73. D. Chen, Z. Wang, T. Ren, H. Ding, W. Yao, R. Zong, and Y. Zhu, *J. Phys. Chem. C* **118**, 15300 (2014).
74. L. B. V. S. Garimella, T. K. Dhiman, R. Kumar, A. K. Singh, and P. R. Solanki, *ACS Omega* **5**, 2552 (2020).
75. J. El Ghoul, *Bull. Mater. Sci.* **39**, 7 (2016).
76. P. Singh, R. Kumar, and R. K. Singh, *Ind. Eng. Chem. Res.* **58**, 17130 (2019).
77. R. Georgekutty, M. K. Seery, and S. C. Pillai, *J. Phys. Chem. C* **112**, 13563 (2008).
78. J. B. M. Goodall, D. Illsley, R. Lines, N. M. Makwana, and J. A. Darr, *ACS Comb. Sci.* **17**, 100 (2015).
79. E. Cerrato, C. Gionco, I. Berruti, F. Sordello, P. Calza, and M. C. Paganini, *J. Solid State Chem.* **264**, 42 (2018).
80. M. Adeel, M. Saeed, I. Khan, M. Muneer, and N. Akram, *ACS Omega* **6**, 1426 (2021).
81. C. B. Ong, L. Y. Ng, and A. W. Mohammad, *Renew. Sustain. Energy Rev.* **81**, 536 (2018).
82. D. R. Paul, S. Gautam, P. Panchal, S. P. Nehra, P. Choudhary, and A. Sharma, *ACS Omega* **5**, 3828 (2020).

-
83. M. T. Efa and T. Imae, *J. Taiwan Inst. Chem. Eng.* **92**, 112 (2018).
84. N. A. F. Al-Rawashdeh, O. Allabadi, and M. T. Aljarrah, *ACS Omega* **5**, 28046 (2020).
85. C. G. Silva, M. J. Sampaio, S. A. C. Carabineiro, J. W. L. Oliveira, D. L. Baptista, R. Bacsá, B. F. Machado, P. Serp, J. L. Figueiredo, A. M. T. Silva, and J. L. Faria, *J. Catal.* **316**, 182 (2014).
86. V. Borker, K. S. Rane, and V. N. Kamat Dalal, *J. Mater. Sci. Mater. Electron.* **4**, 241 (1993).
87. V. Moye, K. S. Rane, and V. N. K. Dalal, *J. Mater. Sci. Mater. Electron.* **1**, 212 (1990).
88. R. Lontio Fomekong, P. Kenfack Tsobnang, D. Magnin, S. Hermans, A. Delcorte, and J. Lambi Ngolui, *J. Solid State Chem.* **230**, 381 (2015).
89. R. A. Porob, S. Z. Khan, S. C. Mojumdar, and V. M. S. Verenkar, *J. Therm. Anal. Calorim.* **86**, 605 (2006).
90. J. Pan, G. Zhang, Y. Zheng, J. Lin, and W. Xu, *J. Cryst. Growth* **308**, 89 (2007).
91. T. K. Pathak, E. Coetsee-hugo, H. C. Swart, C. W. Swart, and R. E. Kroon, *Mater. Sci. Eng. B* **261**, 114780 (2020).
92. R. Kumar, A. Umar, G. Kumar, M. S. Akhtar, Y. Wang, and S. H. Kim, *Ceram. Int.* **41**, 7773 (2015).
93. M. Ahmad, E. Ahmed, F. Zafar, N. R. Khalid, N. A. Niaz, A. Hafeez, M. Ikram, M. A. Khan, and Z. Hong, *J. Rare Earths* **33**, 255 (2015).
94. C. Xia, C. Hu, and P. Zhou, *J. Exp. Nanosci.* **8**, 69 (2013).
95. J. R. Mora, G. Flores-Carrasco, H. Juárez, M. Pacio, M. de la L. Olvera, and M. E. Rabanal, *Opt. Mater. (Amst.)* **157**, 116156 (2024).
96. F. Sordello, I. Berruti, C. Gionco, M. C. Paganini, P. Calza, and C. Minero, *Appl. Catal. B Environ.* **245**, 159 (2019).
97. S. Ji, L. Yin, G. Liu, L. Zhang, and C. Ye, *J. Phys. Chem. C* **113**, 16439 (2009).
98. D. Daksh and Y. K. Agrawal, *Rev. Nanosci. Nanotechnol.* **5**, 1 (2016).

-
99. C. N. R. Rao, S. Natarajan, and R. Vaidhyanathan, *Angew. Chemie - Int. Ed.* **43**, 1466 (2004).
100. X. Y. Fei, T. Z. Liu, H. Zhang, X. M. Xu, and S. W. Duo, *Adv. Mater. Res.* **1015**, 684 (2014).
101. A. S. H. Hameed, C. Karthikeyan, A. P. Ahamed, N. Thajuddin, N. S. Alharbi, S. A. Alharbi, and G. Ravi, *Sci. Rep.* **6**, 1 (2016).
102. T. Indumathi, C. Theivarasu, I. Pradeep, M. T. Rani, G. Magesh, C. S. Rahale, and E. R. Kumar, *Surfaces and Interfaces* **23**, 101000 (2021).
103. S. Kumar and P. D. Sahare, *J. Rare Earths* **30**, 761 (2012).
104. P. Pascariu, C. Cojocaru, P. Samoila, and C. Romanitan, *Int. J. Mol. Sci.* **24**, (2023).
105. H. Eskandarloo, A. Badiei, M. A. Behnajady, and G. Mohammadi, *Ultrason. Sonochem.* **28**, 169 (2016).
106. D. R. Kumar, K. S. Ranjith, and R. T. R. Kumar, *Opt. - Int. J. Light Electron Opt.* **154**, 115 (2018).
107. M. M. Ba-Abbad, M. S. Takriff, A. Benamor, M. S. Nasser, E. Mahmoudi, and A. W. Mohammad, *J. Sol-Gel Sci. Technol.* **85**, 178 (2018).
108. M. Faraz, F. K. Naqvi, M. Shakir, and N. Khare, *New J. Chem.* **42**, 2295 (2018).
109. P. Chand and V. Singh, *J. Rare Earths* **38**, 29 (2020).
110. D. Dash, N. R. Panda, and D. Sahu, *Nano Express* **2**, 010007 (2021).
111. J. C. Sin, S. M. Lam, K. T. Lee, and A. R. Mohamed, *J. Colloid Interface Sci.* **401**, 40 (2013).
112. A. Khataee, R. D. C. Soltani, Y. Hanifehpour, M. Safarpour, H. Gholipour Ranjbar, and S. W. Joo, *Ind. Eng. Chem. Res.* **53**, 1924 (2014).
113. G. El Fidha, N. Bitri, F. Chaabouni, S. Acosta, F. Güell, C. Bittencourt, J. Casanova-Chafer, and E. Llobet, *RSC Adv.* **11**, 24917 (2021).
114. U. Alam, A. Khan, D. Ali, D. Bahnemann, and M. Muneer, *RSC Adv.* **8**, 17582 (2018).

-
115. O. Yayapao, T. Thongtem, A. Phuruangrat, and S. Thongtem, *J. Alloys Compd.* **576**, 72 (2013).
116. S. Sa-nguanprang, A. Phuruangrat, T. Thongtem, and S. Thongtem, *Inorg. Chem. Commun.* **117**, 107944 (2020).
117. S. A. Ayon, M. M. Billah, S. S. Nishat, and A. Kabir, *J. Alloys Compd.* **856**, 158217 (2021).
118. K. Narasimharao and T. T. Ali, *J. Mater. Res. Technol.* **9**, 1819 (2020).
119. M. Popa, L. C. Pop, G. Schmerber, C. Bouillet, and O. Ersen, *Appl. Surf. Sci.* **562**, (2021).
120. A. Phuruangrat, O. Yayapao, T. Thongtem, and S. Thongtem, *Superlattices Microstruct.* **67**, 118 (2014).
121. S. Y. TEE, J. Kong, J. J. Koh, C. P. Teng, X. Z. Wang, X. Wang, S. L. Teo, W. Thitsartarn, M.-Y. Han, and Z. W. Seh, *Nanoscale* 18165 (2024).
122. S. G. Kumar and L. G. Devi, *J. Phys. Chem. A* **115**, 13211 (2011).
123. P. Velusamy, S. Pitchaimuthu, S. Rajalakshmi, and N. Kannan, *J. Adv. Res.* **5**, 19 (2014).
124. R. Bleta, A. Lannoy, C. Machut, E. Monflier, and A. Ponchel, *Langmuir* **30**, 11812 (2014).
125. S. Mourdikoudis, R. M. Pallares, and N. T. K. Thanh, *Nanoscale* **10**, 12871 (2018).
126. R. Bleta, A. Ponchel, and E. Monflier, *Environ. Chem. Lett.* **16**, 1393 (2018).
127. S. Anandan and M. Yoon, *Catal. Commun.* **5**, 271 (2004).
128. K. S. Rane, R. Mhalsiker, S. Yin, T. Sato, K. Cho, E. Dunbar, and P. Biswas, *J. Solid State Chem.* **179**, 3033 (2006).
129. W. Zhou, K. Pan, L. Zhang, C. Tian, and H. Fu, *Phys. Chem. Chem. Phys.* **11**, 1713 (2009).
130. X. Zhang, F. Wu, and N. Deng, *J. Hazard. Mater.* **185**, 117 (2011).
131. M. . Kakroudi, F. Kazemi, and B. Kaboudin, *RSC Adv.* **4**, 52762 (2014).

-
132. X. Sun, Z. Fu, T. Jiang, F. Ning, Y. Cheng, T. Fu, M. Zhu, H. Zhang, M. Zhang, and P. Hu, *J. Chromatogr. A* **1663**, (2022).
133. D. Jia, Y. L. Wang, and H. G. Yang, *ChemistrySelect* **2**, 11231 (2017).
134. C. H. Bernard Ng, J. Yang, and W. Y. Fan, *J. Phys. Chem. C* **112**, 4141 (2008).
135. A. Di Vincenzo, D. Chillura, E. Piacenza, P. Conte, A. Pettignano, G. Lazzara, and P. Lo, **15**, 100407 (2023).
136. S. Y. Kwak and J. W. Chung, *US Pat. No. US 2010/0092376 A1* **1**, 1 (2010).
137. D. Bonacchi, A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, and A. Falqui, *J. Phys. Chem. Solids* **65**, 719 (2004).
138. H. Li, W. Zhang, D. Liu, and W. Li, *Emergent Mater.* **3**, 315 (2020).
139. Y. Yao, G. Li, S. Ciston, and R. M. Lueptow, *Environmetal Sci. Technol.* **42**, 4952 (2008).
140. J. Wang, Y. Lin, M. Pinault, A. Filoramo, M. Fabert, B. Ratier, J. Bouclé, and N. Herlin-Boime, *ACS Appl. Mater. Interfaces* **7**, 51 (2015).
141. H. Yu, X. Quan, S. Chen, and H. Zhao, *J. Phys. Chem. C* **111**, 12987 (2007).
142. N. Abbas, G. N. Shao, M. S. Haider, S. M. Imran, S. S. Park, S. J. Jeon, and H. T. Kim, *Mater. Sci. Eng. C* **68**, 780 (2016).
143. K. Nemeth, N. Varro, B. Reti, P. Berki, B. Adam, K. Belina, and K. Hernadi, *Sci. Rep.* **9**, 1 (2019).
144. N. G. Akalework, C. J. Pan, W. N. Su, J. Rick, M. C. Tsai, J. F. Lee, J. M. Lin, L. D. Tsai, and B. J. Hwang, *J. Mater. Chem.* **22**, 20977 (2012).
145. M. R. Ardani, A. L. Pang, U. Pal, M. A. S. M. Haniff, A. G. Ismail, A. A. Hamzah, W. A. Khanday, and M. Ahmadipour, *Diam. Relat. Mater.* **137**, 110066 (2023).
146. M. Alsawat, T. Altalhi, K. Gulati, A. Santos, and D. Losic, *ACS Appl. Mater. Interfaces* **7**, 28361 (2015).
147. D. R. Sarker, M. N. Uddin, M. Elias, Z. Rahman, R. K. Paul, I. A. Siddiquey, M. A. Hasnat, R. Karim, M. A. Arafath, and J. Uddin, *Clean. Eng. Technol.* **6**, 100364 (2022).

148. U. Caudillo-Flores, J. Lara-Romero, J. Zárate-Medina, M. J. Muñoz-Batista, R. Huirache-Acuña, E. M. Rivera-Muñoz, and J. A. Cortés, *Catal. Today* **266**, 102 (2016).
149. J. Feng, S. Xiong, and Y. Wang, *Compos. Commun.* **12**, 39 (2019).
150. L. Tian, L. Ye, K. Deng, and L. Zan, *J. Solid State Chem.* **184**, 1465 (2011).
151. U. Caudillo-Flores, I. Barba-Nieto, M. J. Muñoz-Batista, A. Kubacka, and M. Fernández-García, *Top. Curr. Chem.* **377**, 1 (2019).

Chapter-2:

Synthesis of cerium-doped zinc oxide nanomaterials, characterization and photocatalytic degradation studies of methylene blue and textile industry Red CL 5B dye

2.1 Introduction

Effluents from textile and other industries contain high concentrations of pigments, dyes, and other harmful chemicals [1]. It is essential to decompose these pollutants before they are released into the environment. However, the main constraints in the degradation of these chemicals are their high chemical stability, large volume, and resistance to natural biodegradation processes. Physical and chemical water treatment methods are lengthy, cumbersome, uneconomical, and impractical to implement on a large scale [2].

Various research groups have developed effective strategies for the disintegration of harmful organic molecules [3]. These molecules can be broken down into smaller, eco-friendly molecules such as carbon dioxide, water, nitrates, and sulfates through photocatalytic mineralization techniques using metal oxides and light [4]. The performance of a photocatalyst is directly influenced by its ability to trap UV-visible light energy, facilitate high charge transfer, slow down the rate of charge recombination process, and generate highly reactive species for redox reactions. These properties significantly influence the photocatalytic degradation of toxic molecules [5]. Despite several advantages, pure bulk microcrystalline ZnO has disadvantages compared to nanosized materials. Therefore, controlled doping of metal ion impurities, nanosized material, high specific surface area, and morphology are desirable attributes for a high-performing photocatalyst [6].

ZnO has a hexagonal wurtzite crystal structure and a wide band gap of 3.3 eV, which can be easily activated by UV-visible light irradiation. The band gap energy represents the difference between the lowest unoccupied molecular orbital (conduction band (CB) and the highest occupied molecular orbital, the valence band (VB) [7]. In this context, three main processes are involved: first, the absorption of light with photon energy greater than the band gap energy, leading to the generation of electron-hole pairs; second, the separation and transfer of electrons (e^-) and holes (h^+) and transfer to the catalyst surface; and third, the photo-redox reaction at the interface, producing highly reactive species [8]. If the catalyst is designed to absorb solar energy, such technology becomes cleaner, more sustainable, and economical [9]. However, altering the band gap energy (E_g) of the catalyst is quite challenging. A high band gap hinders the absorption of visible light, preventing the generation of sufficient photoelectrons. The number of electron-hole (e^-h^+) pairs generated depends on the

type and quantity of impurities doped into the photocatalyst. It is well known that impurities act as electron traps, inhibit the fast recombination of charge carriers, and facilitate the photodegradation mechanism [10].

Doping cerium (Ce) into the lattice sites of zinc oxide (ZnO) creates new mid-gap energy levels within the band gap close to the conduction band (CB) [11]. These localized electronic energy levels act as electron traps for low-energy transitions, enabling Ce-doped ZnO to absorb visible light. The incorporation of Ce^{3+} ions into ZnO enhances UV light absorption and shifts the absorption edge of ZnO towards the visible region of the spectrum [12]. This improvement in light absorption can be attributed to the mixing of Ce and ZnO orbitals, the overlap of impurity levels with the CB of ZnO, and the increased electron density in the CB and mid-gap impurity levels. In this chapter, the optical and electronic properties of Ce-doped ZnO were studied and the key insights about the dye degradation activity were evaluated. The performance of Ce-doped ZnO largely depended on the fabrication strategies, morphology, shape, size, surface area, and light absorption capability.

2.2 Experimental

2.2.1 Preparation of $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ nanomaterials

The chemicals were of high-purity analytical grade and used as received. Zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, cerium nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) purchased from Merck, the purity >99%. Double-distilled water was used as a solvent for the preparation of solutions. Zinc nitrate and succinic acid were appropriately weighed and dissolved separately in distilled water to achieve equimolar (0.1 M) concentration solutions. The equal volume of zinc nitrate and succinic acid solution was mixed with constant stirring. The solution was adjusted to $\sim\text{pH}7$ using dilute ammonium hydroxide (1:1) and stirred continuously for 60 min. The white zinc-succinate precipitate was obtained. The precipitate was filtered, washed with ample distilled water and finally with ethanol. The precursor was air-dried to obtain a free-flowing powder. On similar lines, a series of $\text{Ce}_x\text{Zn}_{(1-x)}$ -succinate precursors were prepared by mixing a stoichiometric quantity of zinc nitrate with varying concentrations of cerium nitrate solution; (where $x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$, and 0.07 moles) and co-precipitated as per the procedure mentioned

above. Further, the precursors were decomposed in a muffle furnace at 800 °C for 5 h in the air to obtain the Ce-doped ZnO, ($\text{Ce}_x\text{Zn}_{1-x}\text{O}$) photocatalyst. The chemical compositions of the precursors were established based on isothermal weight loss and chemical analysis. The chemical composition for $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ (where $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, \text{ and } 0.07$, moles) and their respective codes are presented in Table 2.1.

2.3 Characterization techniques

The vibrational infra-red (IR) spectra were recorded in the wavenumber range of 4000–400 cm^{-1} on a Shimadzu IR Affinity-1S, Japan. The attenuated total reflection (ATR) diamond accessory was employed for sample analysis. The simultaneous thermogravimetric analyser-Differential Scanning Calorimeter (TGA-DSC) thermal profiles of precursors were recorded on the Setaram 1600 instrument. About 10 mg of precursor was taken in an alumina (Al_2O_3) crucible (70 μl) and heated at a controlled rate of 10 °C/min in air. The sample was scanned in the temperature range of 30 – 800 °C. The % mass loss (TGA) and heat flux (DSC) graphs were plotted against the dynamic temperature range. The X-ray diffraction (XRD) studies were carried out using Rigaku XRD equipment. The X-ray source was a Cu target anode with $K_{\alpha 1}$ ($\lambda = 1.5418 \text{ \AA}$) used for the scanning sample. The set parameters for the XRD run were: scanning range 2-theta angle from 20 to 80°, step size = 0.02°, data acquisition time of 1 sec/step, and 0.6 ° divergent slit. The semiconductor-type detector was used for the collection of reflected X-rays. The XRD patterns of the synthesized materials ($\text{Ce}_x\text{Zn}_{1-x}\text{O}$) were compared with the standard ZnO, hexagonal wurtzite structure diffractogram database JCPDS (Joint Committee on Powder Diffraction Standards cards). The particle morphology, size, and topography images of the material were captured on a Zeiss EVO-18 scanning electron microscope (SEM). The accelerating voltage of the electron was set to 20.0 kV. The Oxford Energy-dispersive X-ray spectroscopy (EDS) probe was employed for elemental composition analysis. The detailed particle/crystallite size, lattice structure/fringes, and surface morphology images were captured on a JEOL JEM2100F high-resolution transmission electron microscope (HRTEM). The accelerating voltage of the instrument was fixed at 120 kV. The X-ray photoelectron spectroscopy (XPS) analysis was done using PHI 5000 versa probe II

FEI, with a pass setting of 23.5 eV, 0.025 eV/0.05 eV step, 50 ms time/step, and 10 cycles, source Al K α -1486 eV. The powder surface characteristics were studied by N₂-gas adsorption-desorption isotherms. The specific surface area of powder materials was evaluated by the Brunauer-Emmett-Teller (BET) method using the Belsorp-2, Japan instrument at liquid nitrogen temperature. A multipoint adsorption curve was used for calculating the specific surface area in (m²/gm). The average pore size (nm) and total pore volume (cm³/g) values were also derived from the measurements. The optical light absorption properties and band gap energy (E_g) of materials were examined on the Shimadzu UV2600 UV-visible spectrophotometer. The UV-visible absorbance spectra were recorded in diffuse reflectance spectroscopy (DRS) mode in the wavelength range (λ = 200 to 450 nm). The absorption spectra of materials were transformed into Kubelka-Munk plots, and then the Tauc plot absorption edge was determined by intersecting the extended plot on the X-axis energy (eV) scale. Room temperature-Photoluminescence (RT-PL) emission spectra were recorded on a Fluorolog-3 spectrometer (Horiba Jobin Yvon, Germany) equipped with a xenon lamp (450 W). The excitation wavelength of λ_{exc} = 325 nm was used with a long-pass filter KV58. The emission slits of the monochromator were set to a 1 nm bandpass.

2.4 Photocatalytic organic dye degradation studies

The model organic dye molecule-Methylene blue (MB), was subjected to photocatalytic degradation in the presence of Ce_xZn_{1-x}O materials. The reactor set-up used for the photocatalytic dye degradation studies was procured from Lelesil Scientific, India. The reactor consisted of a 250 mL three-necked cylindrical quartz glass vessel with a water-cooled jacket. The temperature of the reaction vessel was maintained at 25 $\pm$ 2 °C during the entire study. The 450 W medium-pressure Mercury (Hg) lamp with an emission wavelength range (λ = 250 to 450 nm) was used as a light source for activation of the photocatalyst. The reaction mixture was continuously stirred with an inbuilt magnetic stirrer. 200 mL of MB dye solution (10 ppm) and 40 mg of Ce_xZn_{1-x}O photocatalyst were added to the reaction vessel. Initially, the content was stirred in the dark for 30 min to achieve dispersion and adsorption equilibrium with the catalyst surface. The equilibrated solution was then illuminated with a tubular mercury lamp UV source installed in the middle of the reactor. The schematic diagram

of the reactor set-up employed for MB-dye degradation studies is presented in Figure 2.1

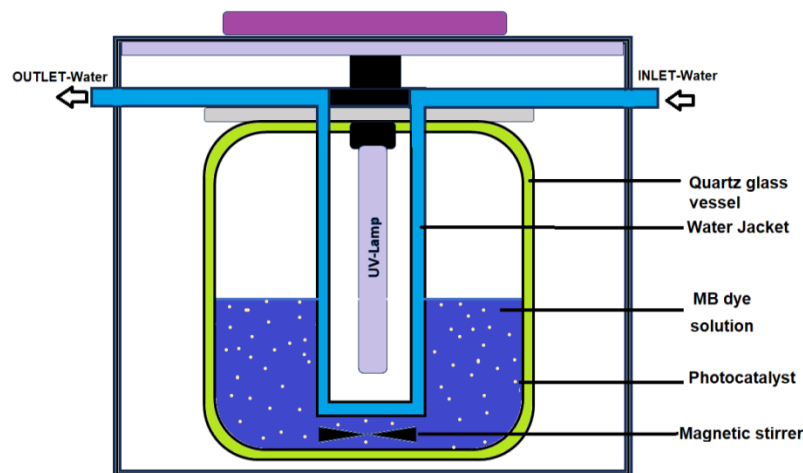


Figure 2.1: Schematic diagram of the reactor set-up for photocatalytic degradation of dye molecules.

After every 20-minute illumination time interval, 3 mL aliquot of dye solution was withdrawn from the reaction vessel using a syringe and filtered to obtain a clear solution. Further, the absorbance spectra of the withdrawn solution were recorded on a Shimadzu UV2600 UV-visible spectrophotometer in the wavelength range of 200 to 800 nm. The absorbance values of the MB solution were measured at the $\lambda_{\text{max}} = 665$ nm to monitor the change in concentration. The % degradation efficiency of the photocatalyst was evaluated by considering equation 1.

$$\% \text{ Degradation} = \{(C_o - C_t)/C_o\} * 100 \quad (1)$$

Where C_o and C_t are the concentration of MB at the initial (o) and at the time (t) min, respectively. The percent degradation profiles of each photocatalyst were recorded against time in minutes to assess the efficiency of the photocatalyst. The rate constant (k) values for each photocatalyst were also established based on the chemical kinetic rate equation. The comparative photocatalytic efficiency of all materials in UV light was studied by exposing the dye solution for 120 min [13]. The % dye degradation studies were also carried out in natural sunlight during midday. The sunlight intensity (I) was measured using a Lux meter: I-value = 1190 x 100 Lux. All other experimental conditions/parameters were kept constant, as in UV-light degradation studies. The % degradation efficiencies in UV and sunlight were compared for all prepared photocatalysts.

2.5 Textile Industry Red CL-5B dye degradation studies

The applicative photocatalytic degradation studies were also carried out on the textile industry Red CL-5B dye. The heterogeneous mixture of photocatalyst $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ plus dye solution was irradiated with UV and sunlight separately, and then the difference in concentration was measured using the UV-visible spectrophotometer. The absorption spectra of the dye solution were scanned in the range of 200 to 800 nm after definite time intervals (0, 10, 20, 30 and 40 min) using a UV-visible spectrophotometer. About 100 mg of catalyst was transferred to the photoreactor vessel containing 100 mL of aqueous Red CL-5B dye solution (25 ppm). The (dye solution + photocatalyst) mixture was irradiated with 450 W, UV light source ($250 \leq \lambda \leq 400$ nm) and natural sunlight (Lux meter I-value = 1190×100 Lux). The absorbance values at the visible absorption maxima were noted for all the prepared materials. The diminished red colour change was the first evidence of the photodegradation of Red CL-5B dye. The visible absorption maxima at $\lambda_{\text{max}} = 541$ nm were monitored at fixed time intervals and then the % dye degradation was based on the change in initial concentration as per equation 1.

2.6 Results and Discussions

2.6.1 Chemical composition of oxides and codes

The chemical composition of the precursor was established based on chemical analysis, isothermal weight loss, and thermal analysis data. The proposed generic formula for all the precursors was $[\text{Ce}_x\text{Zn}_{1-x}(\text{C}_4\text{H}_4\text{O}_4) \cdot \text{H}_2\text{O}]$, where $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$, and 0.07 . The precursors were heated at 800°C for 5 h in the air to yield respective oxide materials. The fine powders were collected and stored at room temperature for structural characterization and photocatalytic application. The general chemical composition of the metal oxide series was established as $\text{Ce}_x\text{Zn}_{1-x}\text{O}$, where $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$, and 0.07 . The oxide materials obtained from their respective precursors were denoted as CZ0, CZ1, CZ2, CZ3, CZ4, CZ5, CZ6, and CZ7, and mentioned in Table 2.1.

2.6.2 IR studies

The characteristic vibrational absorption bands of synthesized cerium-zinc-succinate precursor and $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials were examined by infrared (IR) spectroscopy. Figure 2.2 (a,b) shows the representative IR spectra of cerium-zinc-succinate precursors and their corresponding $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials (CZ0, CZ3 & CZ7), respectively. The broad doublet bands centered at ~ 3474 and ~ 3375 cm^{-1} were attributed to -O-H bending vibrations of hydrogen-bonded hydroxyl groups of water molecules present in the precursor[14]. The dual strong intensity vibrational bands positioned at ~ 1533 and ~ 1390 cm^{-1} were assigned to the asymmetric and symmetric stretching bonds of the carbonyl group (-C=O) of the Zn-succinate moiety, respectively. The medium intensity bands at ~ 1220 and ~ 1026 cm^{-1} were assigned to -C-C- asymmetric and symmetric bending modes of the succinate ligand, respectively. A weak-intensity shoulder band at ~ 705 cm^{-1} was assigned to the wagging of the -C-H bond of the $-\text{CH}_2-$ group of succinate ligands [15]. Based on the IR band position, it was confirmed that the zinc/cerium-succinate monohydrate precursor was formed.

The typical IR spectra of $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials showed distinct strong and broad Zn-O stretching bands in the range of ~ 600 – 430 cm^{-1} . A noticeable variation in the Zn-O band position and shape could be seen with the increase in Ce^{4+} ion doping concentration in ZnO. The Zn-O band intensity decreased, and a slight shift in band position was observed with dopant addition. Such observation was attributed to the perturbation caused by the Ce^{4+} ion doped in the ZnO crystal lattice positions [16].

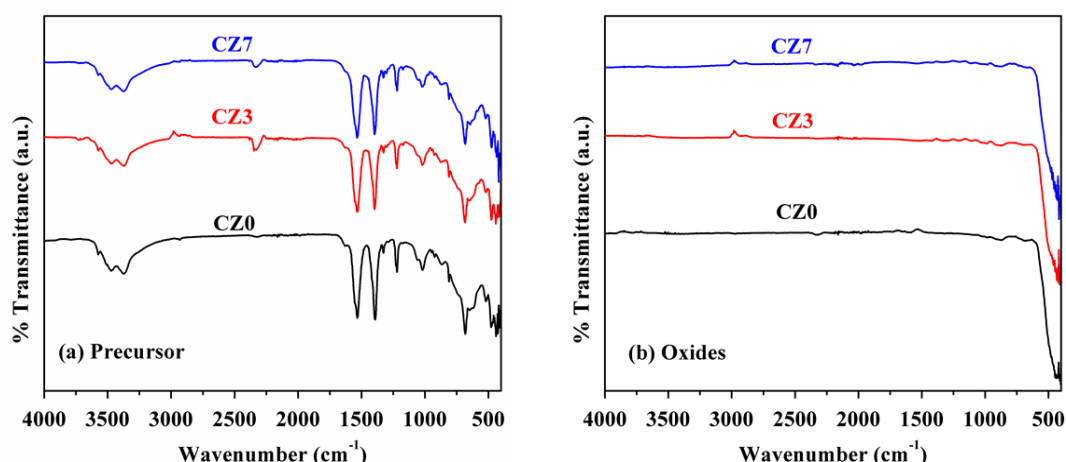


Figure 2.2: Infrared spectra of samples CZ0, CZ3, and CZ5 (a) cerium-zinc-succinate precursor (b) Ce/Zn-oxide.

2.6.3 Thermal analysis of precursor

To determine the decomposition temperature and pathway, thermal analysis was performed on the precursor. The combined TGA-DSC profiles of the CZ5 precursor in the temperature range 30 to 800 °C are shown in Figure 2.3. The TGA thermogram showed 10% mass loss from 30 to 150 °C, which was assigned to the loss of crystalline water to form an anhydrous precursor. The dehydration event was complimented by an endothermic peak in the DSC graph, seen at 102 °C. Further, as the temperature was ramped from 150 to 500 °C, a multi-step mass loss of ~39% was observed in the TGA thermogram. This event was attributed to the oxidative decomposition of anhydrous cerium-zinc-succinate precursor [17]. The corresponding DSC events exhibited multiple peaks; an endotherm at 185 °C, an exotherm at 325 °C, followed by another endothermic peak at 454 °C. Finally, a minor TGA step in the range of 700 to 800 °C, accompanied by a small DSC endothermic peak at 750 °C, was due to the oxidation of carbonaceous matter to form cerium-zinc-oxide material. The observed total mass loss was ~58 % (30 °C – 800 °C), which was equivalent to the theoretical total mass loss of the precursor; hence, based on TGA-DSC data, a general chemical formula of the precursor was proposed as $[\text{Ce}_x(\text{Zn}_{1-x})(\text{C}_4\text{H}_4\text{O}_4)\cdot\text{H}_2\text{O}]$. All precursors showed similar TGA-DSC profiles with nearly the same mass loss and thermal events as observed for the CZ5 precursor. The general chemical formula of oxide materials was considered as $\text{Ce}_x\text{Zn}_{1-x}\text{O}$. Based on thermal analysis data, 800 °C was considered the annealing temperature for material synthesis.

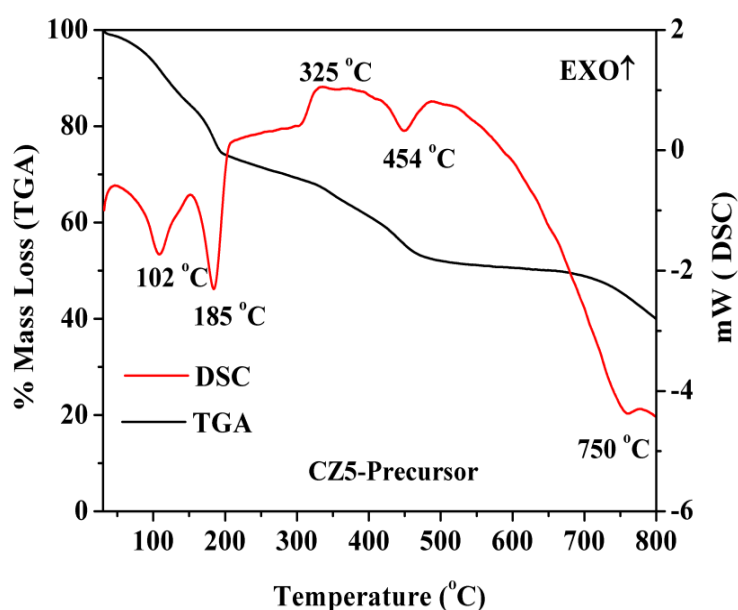


Figure 2.3: TGA-DSC thermograms of cerium-zinc-succinate precursor.

2.6.4 X-ray diffraction studies

The crystalline structure of the synthesized cerium-doped zinc oxide powder materials was investigated using X-ray diffraction (XRD) analysis. Figure 2.4 shows the XRD diffraction patterns of all synthesized materials, $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, \text{ and } 0.07$). The diffractograms of pure ZnO (CZ0) and Ce-doped ZnO (CZ1 to CZ7) materials were comparable with respect to the peak position/reflection. However, on close examination, there was a slight reduction in peak intensities in the case of Ce-doped samples. The major peak positions ($^{\circ}2\theta$) and the miller indices (hkl) values of samples were marked as 31.8° (100), 34.5° (002), 36.4° (101), 47.4° (102), 56.7° (110), 62.9° (103), 66.0° (200), 68.4° (112), and 69.0° (201). These values corresponded to the standard hexagonal wurtzite ZnO crystal system (JCPDS card number: 36-1451). The diffractograms of $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials were devoid of any CeO_2 impurity peaks, hence inferred that the doped Ce^{4+} ions were incorporated into the Zn lattice sites of ZnO. In the literature, it was mentioned that the Ce dopants can be substituted into the Zn lattice positions and the solubility of CeO_2 in ZnO yielded in solid solution [18]. The method of synthesis also influences the introduction of impurity metal ions in the host crystal lattice. The doping of Ce metal ion can create mid-gap energy states, retards ($e^- - h^+$) pair recombination rate and also extends the absorption edge towards the visible region. Ce doping in ZnO can contribute to enhanced photoactivity, such as degradation and mineralization of organic dye molecules.

In samples CZ0 to CZ7, the hexagonal wurtzite structure was conserved, although the Ce^{4+} content was increased from 0.00 to 0.07 moles. However, on close examination slight shift in peak position towards the lower $^{\circ}2\theta$ values could be seen, as shown in the inset picture in Figure 2.4. The gradual downshift in peak position from its reference $36.4^{\circ}2\theta$ corresponded to 0.0, 0.3, 0.5, and 0.7 moles of Ce in ZnO could be attributed to the minor crystal structure distortions. Furthermore, the calculated lattice parameters a and c values varied as the Ce content increased in ZnO. These distortions in crystal lattice parameters were attributed to the difference in the ionic size of the Ce^{4+} ion with that of Zn^{2+} [19]. The disparity in ionic radius of $r_{\text{Zn}^{2+}} 0.88 \text{ \AA}$ and $r_{\text{Ce}^{4+}} 1.01 \text{ \AA}$, caused minor distortions in lattice parameters a and c values and shift of peak positions. The inset picture also indicated minor differences in peak shape and height, which could be associated with the crystallite size within the synthesized sample. When Zn^{2+} ions were replaced by Ce^{4+} in

ZnO lattice, in order to maintain the charge neutrality, the extra positive charges were neutralized by creation of oxygen vacancies (V_O) leaving behind 2 electrons in ZnO and resulted into $ZnO_{1-\delta}$. The loss of O_2 from the ZnO counterbalanced the extra positive charges by Ce^{4+} ions. Hence, oxygen vacancies increased while ZnO became more oxygen deficient [20].

The average crystallite size of the oxide materials was calculated based on Scherrer equation 2 [21],

$$D_p = (K\lambda) / (\beta \cos\theta) \quad (2)$$

where D_p is the average crystallite size in nm, K is the constant factor with a value of 0.9, λ is the X-ray wavelength used, β is the full width of the peak at half maximum, and θ is the diffraction angle in radians. The calculated crystallite size indicated that all materials were nanosized with an average diameter ranging from 38 nm (CZ0) to 28 nm (CZ7). The crystallite size gradually reduced as the Ce doping concentration (moles) increased in ZnO [22]. The $Ce_xZn_{1-x}O$ composition, material codes, Ce substituted in ZnO, calculated lattice parameters (a and c in Å), and average crystallite size (nm) estimated from XRD data are compiled in Table 2.1.

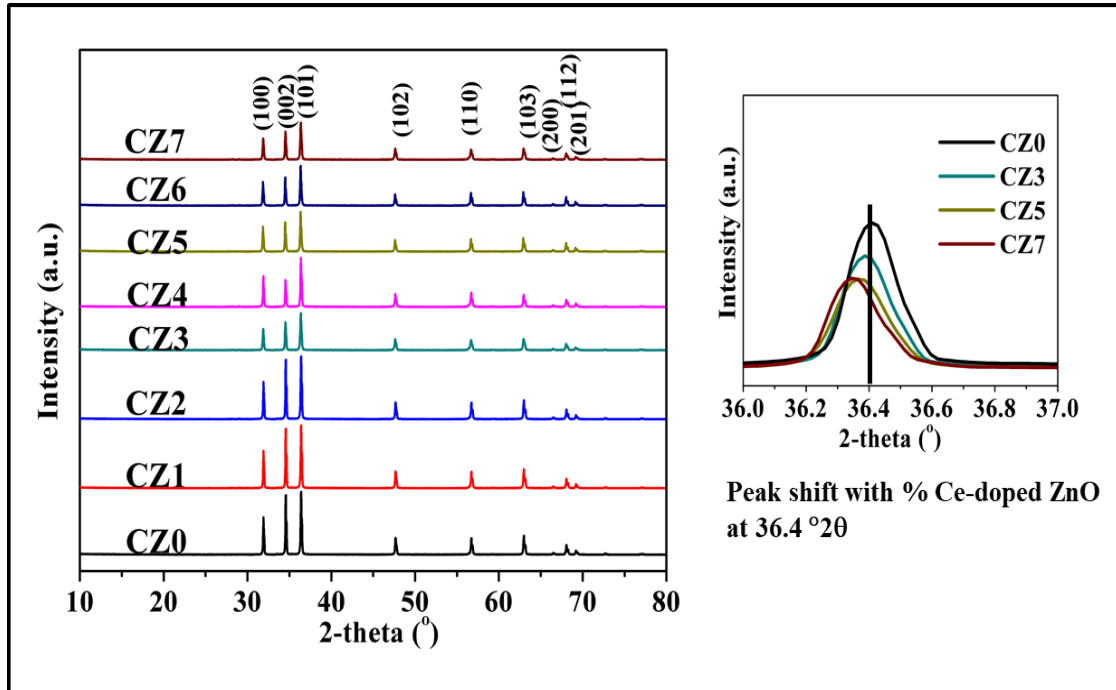


Figure 2.4: XRD patterns of CZ0, CZ1, CZ2, CZ3, CZ4, CZ5, CZ6 and CZ7 materials. Inset picture: Observed shift in peak position for samples CZ0, CZ3, CZ5 and CZ7.

2.6.5 Nitrogen adsorption-desorption studies

The nitrogen (N_2) gas adsorption-desorption data of undoped ZnO (CZ0) and Ce-doped ZnO material (CZ7) were compared. The adsorption-desorption isotherms for both materials are shown in Figure 2.5(a,b). Materials exhibited type-IV isotherms, however, the hysteresis loop of CZ7 was slightly larger compared to CZ0 material. This suggested that Ce-doped ZnO materials become extra porous or with irregular surface characteristics. The hysteresis loop appeared at a relatively higher partial pressure range ($p/p_0 = 0.80$ to 1.00), suggesting that the materials were mesoporous. Such surface characteristics could be attributed to the precursor method of synthesis [23]. The surface properties, such as BET-specific surface area, average pore size and mean pore volume values, are compiled in Table 2.1. From the data, it was clear that the incorporation of Ce-dopant resulted in a slight reduction in the surface area of the prepared materials. However, there was a slight increasing trend in surface area with Ce-doping, which may contribute to the enhanced photoactivity of materials. The BET surface area and crystallite size by XRD showed a good correlation, whereas smaller crystallite-sized materials showed higher surface area values

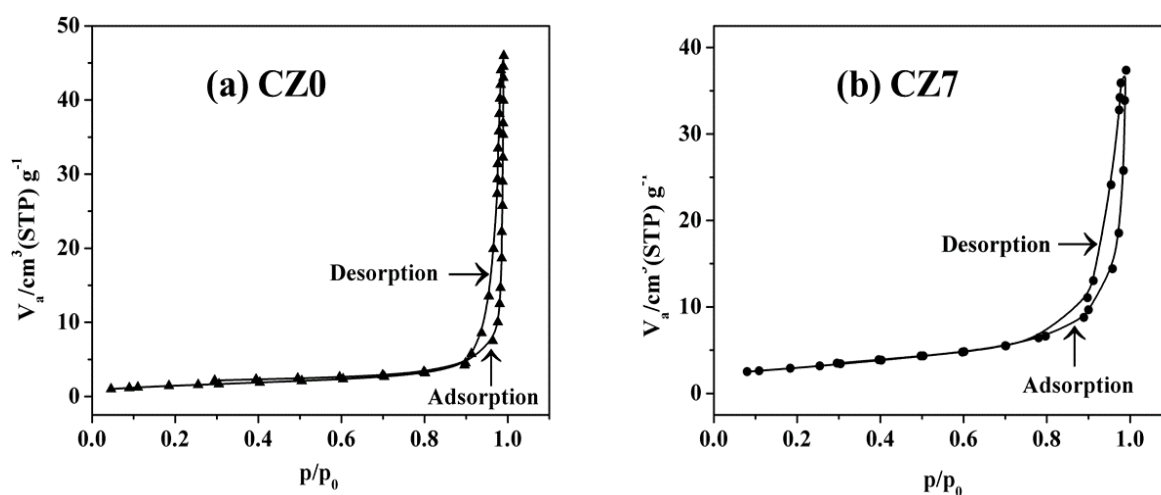


Figure 2.5: Adsorption/desorption isotherms for (a) CZ0, and (b) CZ7.

Table 2.1: Chemical composition of material, material code, moles of Ce doped in ZnO, average crystallite size estimated from XRD-Scherrer formula, calculated lattice parameters (a, c), and BET-specific surface area.

Chemical composition	Material Code	Moles of Ce in ZnO	Average Crystallite Size (nm) – XRD	Lattice parameter		BET-specific surface area (m ² /gm)
				a (Å)	c (Å)	
ZnO	CZ0	0.00	38	3.2556	5.2542	5.25
Ce _{0.01} Zn _{0.99} O	CZ1	0.01	38	3.2556	5.2543	9.66
Ce _{0.02} Zn _{0.98} O	CZ2	0.02	35	3.2559	5.2546	9.49
Ce _{0.03} Zn _{0.97} O	CZ3	0.03	34	3.2565	5.2548	9.20
Ce _{0.04} Zn _{0.96} O	CZ4	0.04	33	3.2566	5.2545	10.38
Ce _{0.05} Zn _{0.95} O	CZ5	0.05	33	3.2568	5.2553	10.41
Ce _{0.06} Zn _{0.94} O	CZ6	0.06	30	3.2571	5.2555	10.10
Ce _{0.07} Zn _{0.93} O	CZ7	0.07	28	3.2573	5.2557	11.58

2.6.6 X-ray photoelectron spectroscopy studies

The X-ray photoelectron spectroscopy (XPS) studies were performed to determine the chemical composition, valence states of bonding elements, and type of chemical bonding involved in Ce_xZn_{1-x}O materials. Figure 2.6a represents the wide energy (0 –1200 eV) survey spectra of representative Ce_{0.05}Zn_{0.95}O (CZ5) material. The binding energies (BE) of components were corrected with respect to graphitic carbon, C 1s peak (BE = 284.6 eV). From the survey scan it can be seen that the photoemission peaks originated from zinc (Zn 2p), oxygen (O 1s), and cerium (Ce 3d) components present in the material under investigation. Figure 2.6b shows the high-resolution XPS spectra of Zn 2p with characteristic doublet peaks centred at BEs 1044.10 eV and 1021.20 eV. These dual signals were assigned to core-level photoelectron peaks of Zn 2p_{1/2} and Zn 2p_{3/2}, respectively. The difference of 22.9 eV between the two peaks indicated the existence of a Zn²⁺ oxidation state in the wurtzite lattice, and the formation of a Zn-O bond in the material [24]. Figure 2.6c depicts the Gaussian deconvoluted O 1s peak, which resolved into two peaks, positioned at BEs 531.98 eV(high) and 529.52 eV(low). These peaks were typically assigned to chemisorbed surface hydroxyl oxygen (OH⁻) and lattice O²⁻ ions of ZnO, respectively [25]. The percentage of hydroxyl oxygen (OH⁻) and lattice O²⁻ were about 27% and 73%, respectively. Figure 2.6d shows the deconvoluted Ce 3d spectrum resolved

into five low-intensity peaks located at 882.34, 887.86, 898.86, 904.50, and 916.12 eV, which were characteristic peaks of doped Ce^{4+} ion of CZ5 material. Hence, the presence of Ce^{4+} ions was confirmed in Ce-doped ZnO materials [26]. The XPS studies showed a good agreement with chemical composition and XRD data. There were no peaks due to metallic Zn or CeO_2 impurities detected in the XPS spectra. Hence, proved that the Zn^{2+} ions were replaced by the Ce^{4+} in the ZnO crystal lattice to form single-phase $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials.

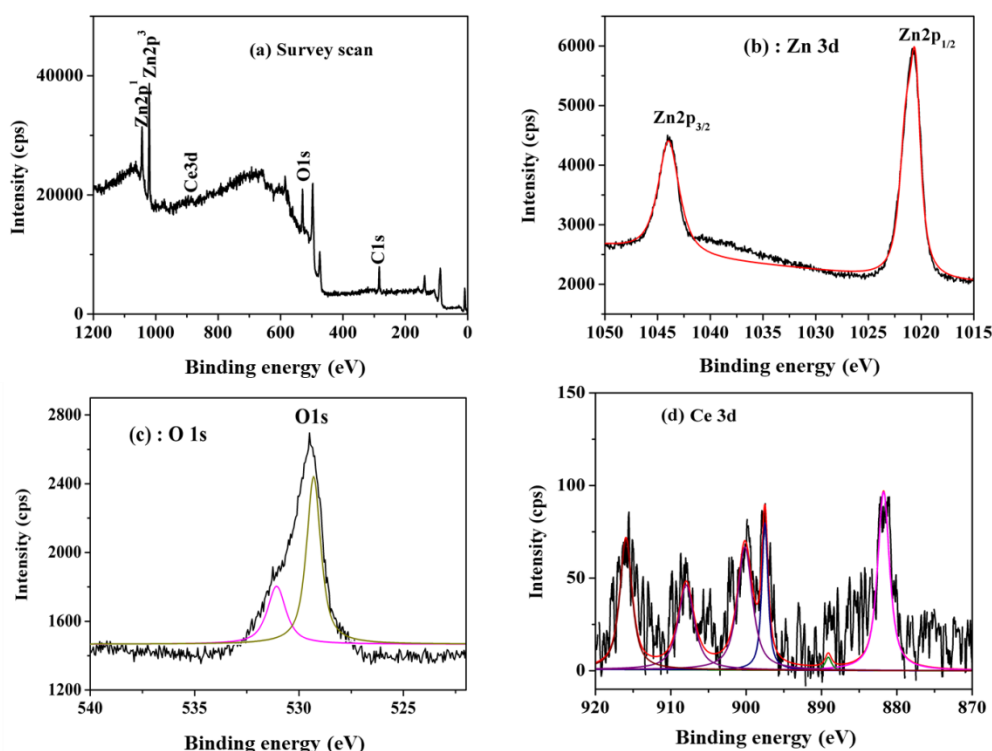


Figure 2.6: XPS spectra of CZ5 (a) Survey spectrum (b) Zn 2p (c) O1s and (d) Ce 3d.

2.6.7 UV-visible DRS: Light absorption and band gap

The development of high-performance photocatalysts depends upon the material band gap energy (E_g), which was generally modified by doping metal ions into the host lattice sites. In ZnO, the valence band (VB) contains electrons and is separated from the empty conduction band (CB) by band gap energy ($E_g \approx 3.32$ eV). To understand the implication of Ce^{4+} ion doping on the band gap and light absorption properties of ZnO, the synthesized materials were investigated by UV-visible diffuse reflectance spectroscopy (DRS). Figure 2.7a shows the plots of absorbance versus wavelength (nm) of $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ (CZ0 to CZ7) materials. From the profiles, it was understood that all materials showed major absorbance

in the UV region. The absorption edge of pure ZnO cuts in the UV region (<372 nm), whereas the Ce-doped ZnO curves displayed a gradual shift in absorption edge towards the visible region (> 372 nm). The absorption edge progressively shifted towards the longer wavelength (red shift) as the Ce content increased in ZnO. Also, light absorbance capability improved noticeably for Ce-doped ZnO. Thus, $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials showed a positive influence on the UV-visible light absorption property. This type of absorption by materials can lead to higher electronic transitions, which is a fundamental requirement for tapping UV-visible light energy (sunlight) and its photocatalytic applications. The band gap energy (E_g) of the materials was calculated using Tauc equation[27],

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (3)$$

Where α is the absorption coefficient, $n = 1/2$ (direct allowed transitions), $h\nu$ is the photon energy, A is a proportionality constant, and E_g represents the band gap energy of the material. The Tauc plots, shown in Figure 2.7b, assisted in calculating the E_g of materials by extrapolating the rising linear part of the curves to the photon energy on the x-axis. The pure ZnO (CZ0) absorption edge intersected in the UV region (378 nm) which corresponded to $E_g = 3.211$ eV. This value was smaller compared to the reported intrinsic E_g (3.32 eV). Such variation can be attributed to the route of material synthesis. A similar type of observation was also reported earlier for differences in E_g values depending on the synthetic strategy [28]. Likewise, the direct band gaps energy values were calculated for each Ce-doped material (CZ1 to CZ7) and recorded as follows: 3.196, 3.190, 3.188, 3.186, 3.182, 3.181, 3.170 eV respectively.

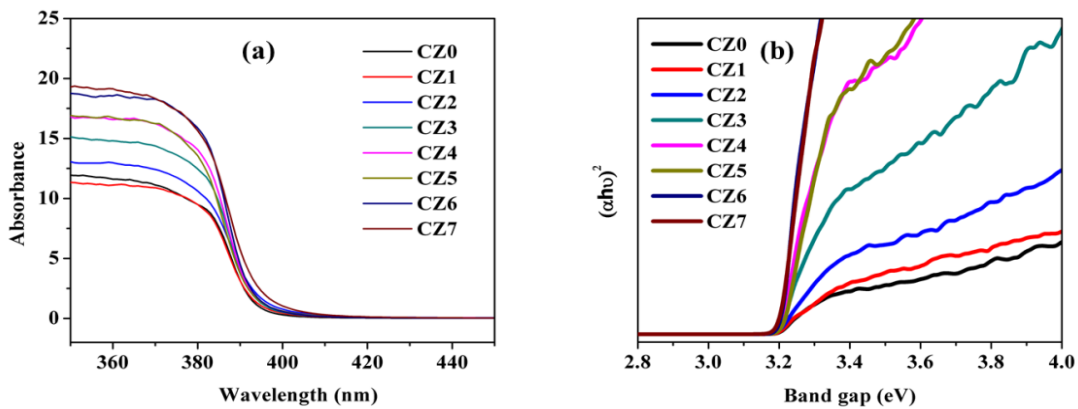


Figure 2.7: (a) UV-visible absorption spectra for samples CZ0 to CZ7 (b) Tauc plots for samples CZ0 to CZ7.

Hence, concluded the band gap reduced as Ce-content progressively increased in ZnO. The shrinkage in the band gap was attributed to the number of mid-gap energy levels formed by

Ce-doping in ZnO. The lowered E_g can induce efficient electronic transfer from VB to newly created energy levels below CB. It is noteworthy to mention here that the intrinsic E_g of ZnO, ~ 3.32 eV, was reduced to 3.170 eV (CZ7 sample). Generally, ZnO shows a strong absorption in the UV region; however, herein synthesized materials showed a red shift in absorption edge with reduced E_g which can significantly contribute to superior photocatalytic activity [29].

2.6.8 Photoluminescence: Spectral emission analysis

To understand the light absorption-emission properties of the synthesized materials, photoluminescence (PL) studies were carried out at room temperature. The samples were irradiated with laser light of wavelength, $\lambda_{exc} = 325$ nm. Figure 2.8a represents the PL spectral intensities plotted against the emitted wavelength and the corresponding energy (eV) for all materials is shown in Figure 2.8b. The spectra primarily consisted of two broad bands, the first high-intensity sharp band in UV, while the second low-intensity broadband with multiple peaks in the visible region. The UV region peak indicated the rapid recombination of excited electrons or the band edge emission of ZnO and Ce-activated atomic levels. The secondary broad visible emission band were mainly due to the radiative recombination process through point defects in the ZnO lattice, such as oxygen vacancy, zinc vacancy, oxygen interstitial, zinc interstitial and anti-site defects, as reported by many researchers [29]. The UV emission peak of pure ZnO was centered at 394 nm, while Ce-doped ZnO materials exhibited a marginal redshift in peak position [30]. The extent of peak shift was proportional to %Ce doped in ZnO. The PL intensity of undoped ZnO was higher compared to the Ce-doped ZnO. The reduced intensities specified the incorporation of Ce in ZnO to form impurity centres. The PL band in the visible range, 450–550 nm mainly associated with (e^-h^+) pair recombination due to oxygen vacancy sites or other intrinsic defect deep levels. As the %Ce in ZnO increased, the PL intensities decreased. The high PL intensity peaks represented a faster (e^-h^+) recombination process, and, on the contrary, low-intensity broader peaks revealed better (e^-h^+) charge separation [19]. Hence, the Ce-doped sample displayed retardation in charge recombination rate, and such a phenomenon is directly associated with improved photocatalytic efficiencies of the materials. The Ce^{4+} ions occupy the substitution position of Zn^{2+} ions; as a result, cationic vacancies were created locally due to their different ionic states, thus inducing defects in

the ZnO. Thus, Ce doping resulted in defect centers of ZnO which could contribute to the photocatalytic efficiency of $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials.

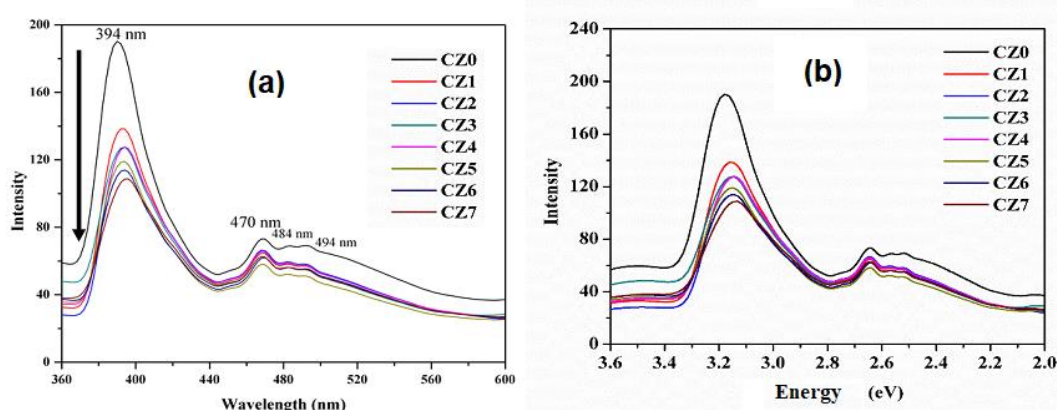


Figure 2.8: (a) PL intensity versus wavelength (b) PL intensity versus energy (eV) of samples CZ0 to CZ7.

2.6.9 Microstructural studies: SEM/HRTEM/EDAX

The SEM images of pure ZnO (CZ0) and $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ (CZ5) materials are presented in Figure 2.9(a,b), respectively. The effect of Ce-dopant on the particle morphology was compared with pure ZnO. The images revealed that both materials were highly agglomerated with spherical to oblong-shaped particles. However, the pure ZnO material showed uneven particle size distribution when compared to Ce-doped ZnO (CZ5). This observation was supported by surface analysis data, where a higher BET surface area was observed for Ce-doped ZnO. The high surface areas are directly proportional to the number of adsorbed dye molecules on the catalyst surface leading to improved photocatalytic activity. The formation of nanosized and uniform particle morphology could be attributed to the thermal decomposition of the precursor and doping of Ce in ZnO.

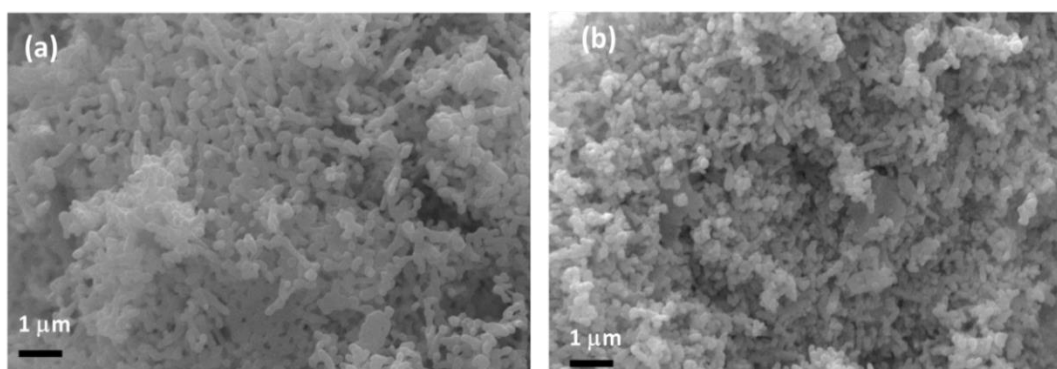


Figure 2.9: SEM images of (a) CZ0 and (b) CZ5 materials.

The high-resolution transmission electron microscopy (HR-TEM) images of pure ZnO and $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ samples are depicted in Figure 2.10(a,b), respectively. The micrographs revealed particle sizes in the nanometer range. The Ce-doped ZnO material showed slightly smaller particles in the range of ~30 to 55 nm, while the pure ZnO particle size range was ~45 to 70 nm. The appearance-wise CZ0 crystallites were slightly longer compared to CZ5 and the shapes were hexagonal to spherical. The crystallite size measured from TEM and Scherrer's method (XRD) was analogous. The ultra-high resolution TEM images showed distinct crystal lattice fringes or planes, which indicated that the materials were highly crystalline. The interplanar lattice plane spacing (d) was found to be ~ 0.280 nm, which corresponded to the (100) plane of the ZnO wurtzite hexagonal structure [31]. No impurity phases were detected in HR-TEM images.

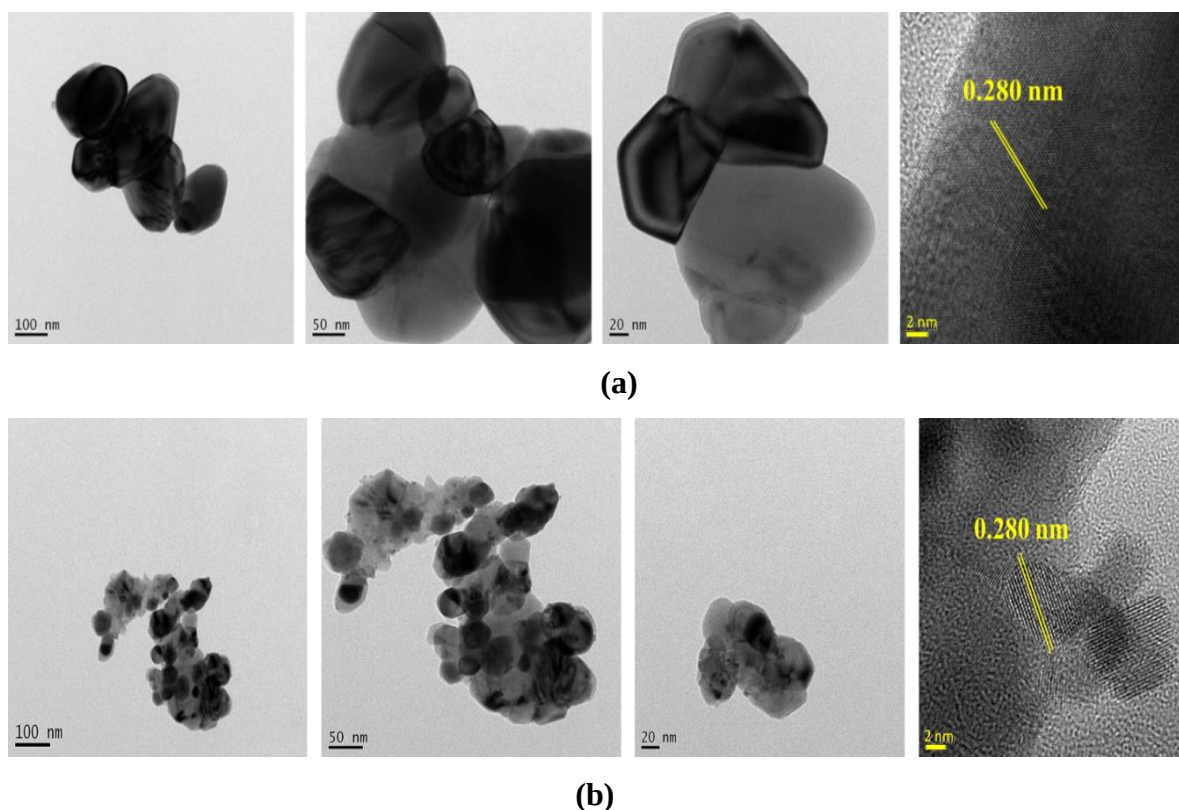


Figure 2.10: HR-TEM images of (a) CZ0 and (b) CZ5 materials.

The particle size distribution of CZ0 and CZ5 powder materials was measured using HRTEM images and presented in the form of a bar graph (histogram). Figure 2.11(a,b) shows the particle size distribution in nanometers (nm) plotted against the number of particles (%) for CZ0 and CZ5 samples. The average particle diameters of CZ0 and CZ5 were 60 and 45 nm, respectively. The particle size of CZ0 spanned from 45 to 75 nm,

while CZ5 particles ranged from 30 to 55 nm. Thus, it could be concluded that with the introduction of Ce in the ZnO lattice, the particle size decreased.

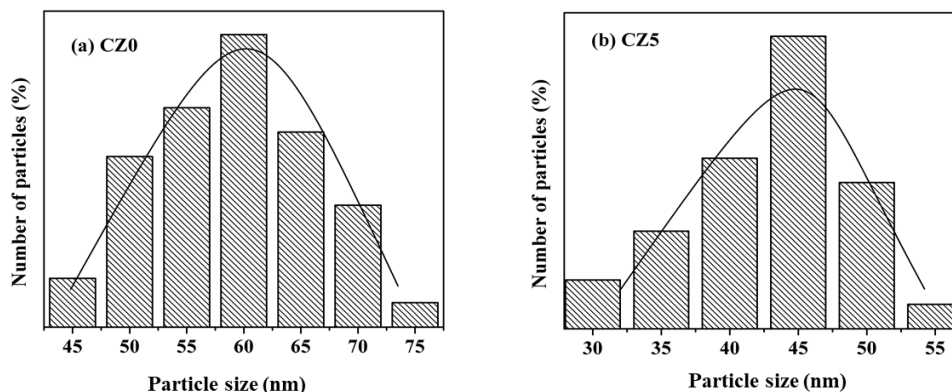


Figure 2.11: Particle size distribution of (a) CZ0 and (b) CZ5 materials.

The EDAX analysis provided evidence of the elemental composition of $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$. Figure 2.12 shows the elemental mapping spectrum of the CZ5 sample. The EDAX peaks resembled the investigated elements: Ce, Zn, and O in proportionate intensity. Both XPS and EDAX data supported the material chemical composition as $\text{Ce}_x\text{Zn}_{1-x}\text{O}$.

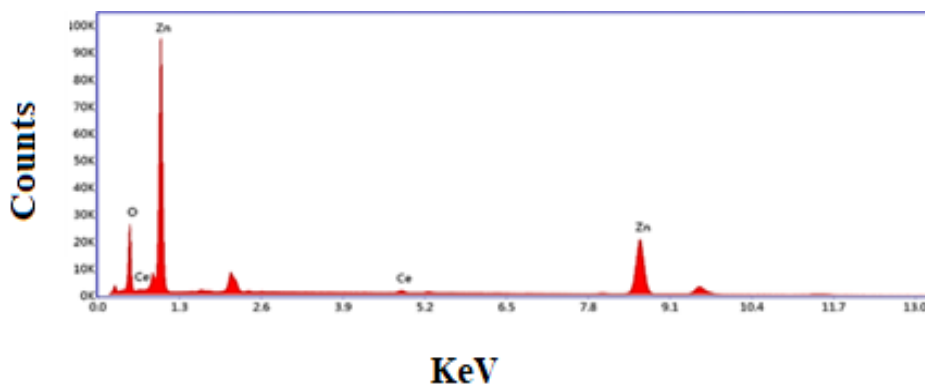


Figure 2.12: EDAX spectrum of CZ5 material.

2.7 Photocatalytic studies

2.7.1 Photocatalytic degradation of methylene blue dye

The photocatalytic activities of synthesized materials, CZ0, CZ1, CZ2, CZ3, CZ4, CZ5, CZ6, and CZ7 were evaluated by measuring the change in concentration of MB dye on exposure to UV and visible light (direct sunlight) with time. The model MB dye solution showed typical two strong absorption peaks, first in UV ($\lambda_{\max} = 292$ nm) and the second in the visible region ($\lambda_{\max} = 665$ nm). The % degradation efficiency of MB dye was calculated by monitoring the peak absorption maxima at $\lambda_{\max} = 665$ nm at each time interval, as depicted in Figure 2.13a. The competitive photocatalytic efficiency for all samples was evaluated at the end of the 120-minute time point.

Figure 2.13b represents the full range absorbance spectra of MB dye measured at time intervals of 0, 20, 40, 60, 80, 100 and 120 min for the representative sample-CZ5. The time-dependent spectral profiles of MB indicated that the absorbance peak intensities for both peaks in UV and visible regions gradually decreased with time. This proved that the parent dye molecule was fragmented by the photocatalyst on irradiation with light without generating any new impurity peaks.

The calculated % degradation efficiency values in UV light at the end of 120 min followed the trend as given: CZ0 (62%) < CZ1(75%) < CZ2(78%) < CZ3(85%) < CZ4(92%) < CZ5(98%) > CZ6(96%) > CZ7(92%). On similar lines, the trend in % degradation efficiency values in sunlight were as follows: CZ0 (45%), CZ1(48 %), CZ2(51 %), CZ3(52%), CZ4(60%), CZ5(65%), CZ6(60%), and CZ7(59%). The comparative % degradation efficiencies in UV and sunlight are depicted in a bar graph in Figure 2.13c. The photocatalytic activity progressively increased with %Ce doping in ZnO. The highest degradation efficiency was observed for $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$, (CZ5 = 98%), whereas pure ZnO, showed the least activity (CZ0 = 62%). The study also revealed that beyond 0.05 mole Ce in ZnO level, a downward trend in efficiency was observed in UV and sunlight. The probable reason for such observation could be attributed to the increased recombination rate of the photogenerated (e-h^+) pairs, leading to decreased photocatalytic activity. Hence, the samples CZ6 and CZ7 notably showed a lower photocatalytic activity. Hence, current studies indicated that 0.05 mole Ce in ZnO proved to be the most optimal doping amount for enhancing the photocatalytic activity of ZnO in both UV and sunlight.

The photodegradation efficiency of the synthesized photocatalyst was evaluated quantitatively by adopting the model proposed by the Langmuir–Hinshelwood kinetic equation: $\ln(C_0/C_t) = kt$; where C_0 and C_t are initial and final MB concentration, k is the rate constant and t is time in min [32]. Figure 2.13d shows the data fitted in a graph of (C_0/C_t) versus time (t) in min, which resulted in a straight line with rate constant values (k). The rate equation certainly indicated that the photodegradation reaction proceeded via pseudo-first-order kinetics. From k values, it was evident that the reaction rate improved from CZ0($k=0.00470 \text{ min}^{-1}$) through CZ5($k=0.03579 \text{ min}^{-1}$) and then decreased for CZ6($k=0.02806 \text{ min}^{-1}$) and CZ7($k=0.02143 \text{ min}^{-1}$) samples. Based on rate constant values, it was demonstrated that the degradation efficiency of CZ5 was improved 8-times compared to pure ZnO. Thus, it was established that Ce(0.05) in ZnO level was the most optimal concentration for the generation of the highest (e^-h^+) pairs during the photocatalytic reaction and with the lowest recombination rate. Hence, Ce^{4+} ions created mid-gap energy levels within the ZnO band gap which facilitates the generation of a large number of (e^-h^+) pairs with optimum charge separation [33].

From the above photocatalytic studies, it can be inferred that the three main factors that influenced the photocatalytic activity in the case of Ce-doped ZnO materials were: (i) improved visible-light absorption capability, (ii) retardation in recombination rate of photogenerated charge carriers by the Ce doping, and (iii) Nanoparticle morphology. The E_g was reduced by mid-gap energy levels formed below the conduction band (CB) by Ce-doping. Therefore, band gap engineering could be the main factor responsible for higher photocatalytic activity in Ce-doped ZnO compared to pure ZnO.

Furthermore, to evaluate the mineralization effect on the organic molecule by the catalyst, the total organic carbon (TOC) content of the dye solution was measured before (TOC_i) and after (TOC_t) the photoactivity. The TOC analysis was carried out using the Shimadzu TOC analyser (TOC-LCPH), Japan. The mineralization was calculated based on the % TOC reduced at 120 min of photoactivity using the equation given below [34]:

$$\%TOC \text{ (Mineralization)} = [(TOC_i - TOC_t)/TOC_i] \times 100 \quad (4)$$

The experimental % mineralization values for MB and Red CL-5B dye were found to be 28% and 33%, respectively. This signified that the photocatalyst not only degraded the molecule but also mineralized it into more eco-friendly molecules such as CO_2 and water.

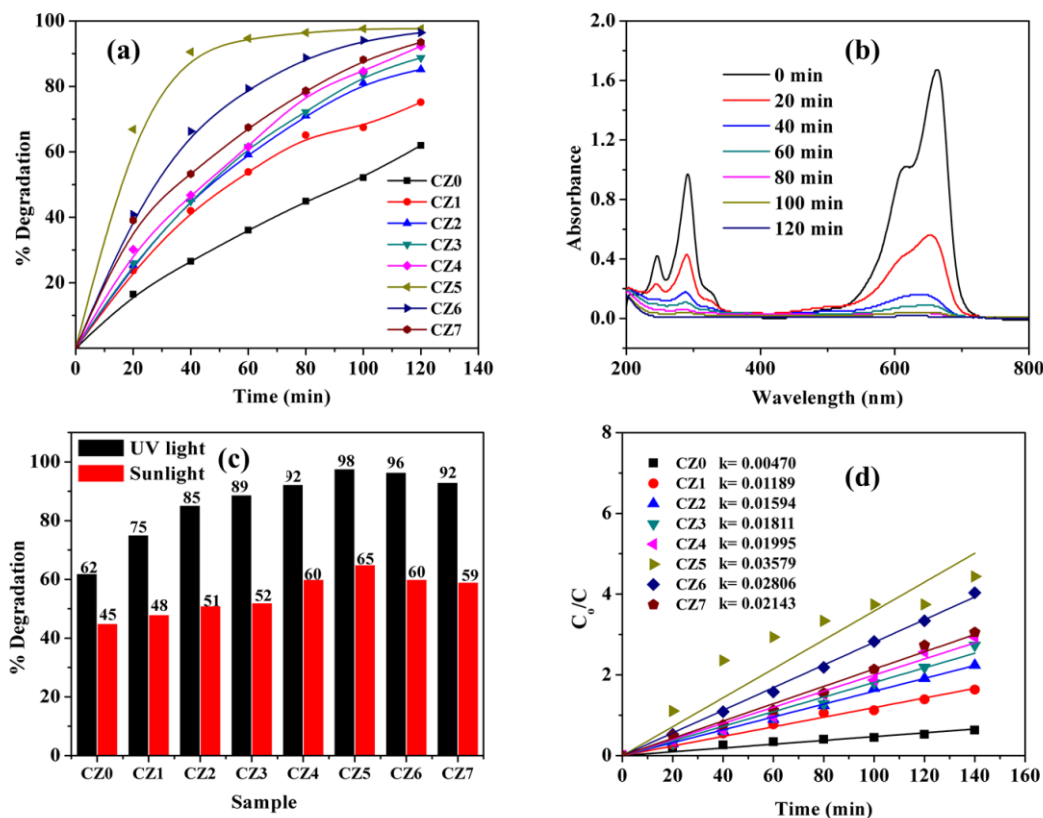


Figure 2.13: (a) % MB degradation efficiency profiles for photocatalysts (CZ0 to CZ7). (b) UV-visible absorbance spectra of MB dye recorded at time points for CZ5. (c) % MB degradation in UV and sunlight at 120 min time point for photocatalyst (CZ0 to CZ7). (d) $\ln(C_0/C_t)$ versus time plot for calculating the rate constant for photocatalyst (CZ0 to CZ7).

2.7.2 pH-dependent photocatalytic methylene blue dye degradation studies

To understand the effect of pH on the dye degradation over the photocatalyst, various MB solutions were prepared at pH values of 1.5, 3.5, 5.5, 8.5, 10.0 and 11.0. The photocatalytic degradation experiments were performed on the above-mentioned pH-adjusted MB dye solution, keeping all other conditions constant as mentioned in the experimental section. The variation in the % degradation against time interval for each solution was recorded and plotted as shown in Figure 2.14. From the profiles, the trend in MB degradation was noted as: pH 11.0 > pH 10.0 > pH 8.5 $\approx$ pH 5.5 > pH 3.5 > pH 1.5. Hence, from the pH-dependent profiles, the nature of the electrostatic forces between MB dye and the surface of the photocatalyst can be ascertained. In the acidic pH range (H^+), the

electrostatic repulsion was dominant between MB dye and the surface of the Ce/ZnO photocatalyst. Hence, there observed lower MB dye degradation activity. However, in the case of basic pH (OH^-), the electrostatic attraction promoted the adsorption of MB dye on the catalyst surface [35]. In the mid pH range 5.5 to 8.5, the degradation profiles showed fairly good photoactivity, which is beneficial for treating effluents close to neutral pH. The initial readings of aqueous MB and Red CL-5B dye solutions were found to be pH 5.5 and pH 5.7, respectively.

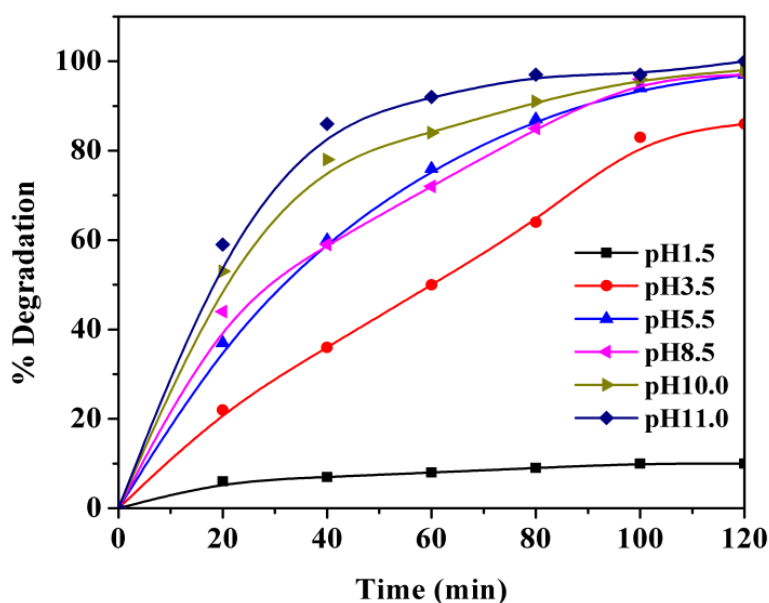


Figure 2.14: pH-dependent % degradation profiles of MB dye.

2.7.3 Photocatalytic degradation of textile industry Red CL-5B dye

To assess the potential application of the synthesized $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ photocatalyst, the % degradation of textile industry Red CL-5B dye was evaluated in the UV and natural sunlight.

Photocatalytic activity in UV light: The bar graph shown in Figure 2.15a illustrates the extent of dye degradation with time in UV light at 40 min time point. The concentration of the Red CL-5B dye solution was monitored in the absence of catalyst as a blank run (black bar) and in the presence of ZnO (red bar), $\text{Ce}_{0.03}\text{Zn}_{0.97}\text{O}$ (blue bar) and $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ (green bar), respectively. The blank run without a catalyst showed 2% dye degradation, probably due to the photolysis of the dye molecule. In the case of ZnO, the photoactivity reached nearly 50%. As far as Ce-doped ZnO was concerned, it was imperative to note that the %

dye degradation activity was influenced by the addition of Ce in ZnO. The % degradation efficiency improved drastically, the $\text{Ce}_{0.03}\text{Zn}_{0.97}\text{O}$ showed 80%, while $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ achieved a maximum value of 100%. The results indicated that photoactivity was sensitive to the amount of Ce added to ZnO. Here, Ce acts as electron traps thus preventing a rapid (e^-h^+) pair recombination process, thus facilitating photodegradation of Red CL-5B dye.

Photocatalytic activity in sunlight: Figure 2.15b indicates the performance of the pure ZnO, $\text{Ce}_{0.03}\text{Zn}_{0.97}\text{O}$ and $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ catalysts in terms of % Red CL-5B dye degraded at 40 min time point in direct sunlight. The blank run without catalyst (black bar), ZnO (red bar), $\text{Ce}_{0.03}\text{Zn}_{0.97}\text{O}$ (blue bar) and $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ (green bar) are shown for comparative purposes. The trend in photocatalytic activity in sunlight was analogous to UV light but with slightly lower efficiency. The blank sample showed negligible activity and can be overlooked, while pure ZnO, $\text{Ce}_{0.03}\text{Zn}_{0.97}\text{O}$ and $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ photocatalysts displayed 35%, 65% and 87% degradation efficiency, respectively. Hence, the destruction of the Red CL-5B dye molecule in natural sunlight was also advocated by Ce-doping in ZnO. Hence, the efficiency of photocatalysts critically depends on the concentration of the Ce introduced into the ZnO lattice. From the above study, it was proved that prepared materials were photosensitive to UV-visible light and can be a promising catalyst to degrade Red CL-5B dye.

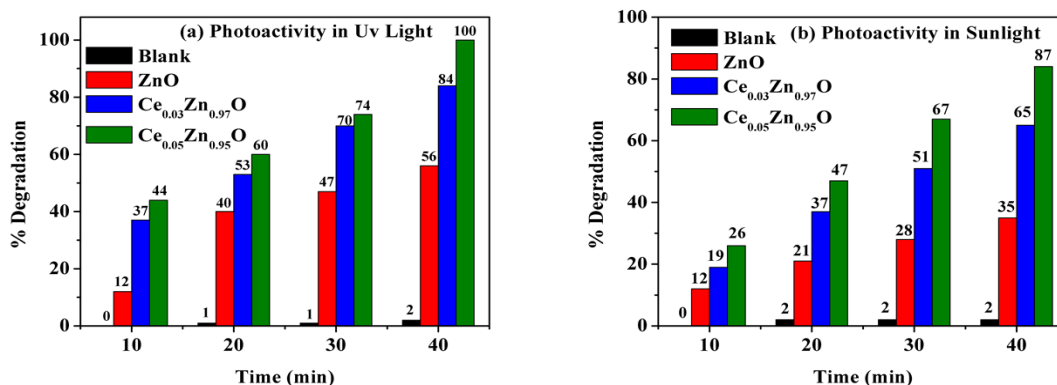


Figure 2.15: % Degradation of Red CL-5B dye for Blank, CZ0, CZ3 and CZ5 materials in (a) UV light and (b) Sunlight.

A comparison of the MB dye degradation efficiencies reported in the literature for various Ce-doped ZnO materials is compiled in table 2.2. The performance of the new Ce-doped ZnO (CZ5) material synthesized in this study was compared with the previously reported data. From Table 2.2, it was observed that the CZ5 catalyst showed better

efficiency compared to other reported catalysts. The Ce(0.05)-doped in ZnO showed excellent efficiency for MB as well as Red-CL 5B dye degradation. The faster dye degradation was mainly attributed to higher photon energy of UV light compared to sunlight. The production of electron-hole pair was directly proportional to the incident energy on the surface of photocatalyst. Hence, the reactive species formed by UV light were comparatively higher than in sunlight resulted in higher efficiency in UV than in sunlight[36].

Table 2.2: Comparative photodegradation efficiencies of reported Ce-doped ZnO with that of CZ5 material.

Catalyst	Dye concentration/ volume(ml)	Type of irradiation	Catalyst dose	MB degradation efficiency (%)	Completion Time (mins)	Reference
1% Ce-doped ZnO	MB(10 ppm)/100ml	UV(250 W)	40 mg	96.11	140	[37]
5mol % Ce doped ZnO	MB(2×10^{-5} M)/ 100 ml	UV (8 W)	0.15 g	65.8%	300	[19]
0.06% Ce-doped ZnO	MB(20 ppm)/ 100 ml	Visible (300 W)	0.2 g/L	94.11	60	[38]
0.075mol % Ce-doped ZnO	MB(1 ppm)/100 ml	sunlight	0.2 g	94.33	120	[21]
0.03% Ce-doped ZnO	MB(0.25 mM)/ 200 ml	sunlight	1 g	92.62	120	[39]
Ce _{0.05} Zn _{0.95} O	MB(10 ppm)/ 200 ml	UV(450 W)	40 mg	98	120	Present study

2.7.4 Recyclability of photocatalyst

The recyclability as well as the conservation of catalytic properties are important parameters for the long-term use of photocatalysts. The performance of the catalyst usually decreases because of photo-corrosion within repeated experiments. The reusability test was demonstrated by repeated photocatalytic dye degradation experiments using the same Ce_{0.05}Zn_{0.95}O catalyst. The concentration and volume of Red CL-5B dye solution used in the experiment were kept constant, that is 100 mg of catalyst in 100 mL of dye solution. Other experimental conditions were identical as mentioned in section 2.4. The catalyst was recovered by filtration, washed with water, ethanol, air dried and then reused for subsequent photocatalytic reaction. The dye concentration was measured at 0, 10, 20, 40

and 50 min time intervals using a UV-visible spectrophotometer. The four consecutive cycles were performed on the same catalyst after recovery. The % dye degraded at different time points (0, 10, 20, 30, 40, and 50 min) for four cycles using the same CZ5 catalyst is depicted in the bar graph shown in Figure 2.16a. The first cycle showed the highest degradation efficiency, and thereafter the second cycle exhibited slightly lower activity at initial time points 0 to 40 min compared to the first cycle; however, at the final 50 min time point, the % dye degradation values remained identical, that is, 100%. A similar trend was also observed for the third and fourth cycles. These results proved that, although the kinetic rate of the reaction reduced slightly, the final degradation efficiency remained the same. Hence, from these studies, it could be established that the catalyst reusability was reasonably good, showing equivalent efficiency, stability, and reusability over four 4-cycles. The stability of the photocatalyst was evaluated by recording field emission SEM images of the CZ5 photocatalyst at the initial and the end of the 4th-cycle stage, shown in Figure 2.16(b,c). On close comparison, the SEM images do not show any variations in photocatalyst morphology or multiphase formation. Hence, the catalyst demonstrated reasonably good reusability properties.

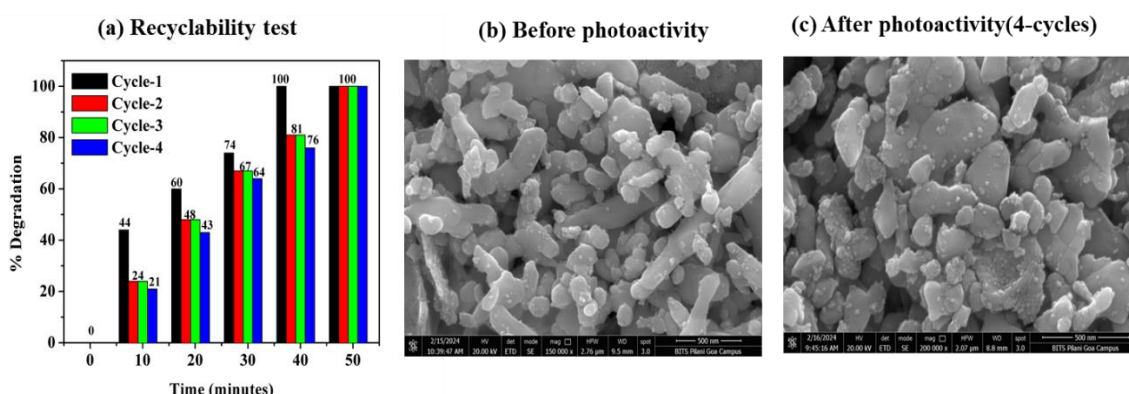


Figure 2.16: (a) % Degradation of Red CL-5B dye for 4 cycles at time points 0, 10, 20, 30, 40 and 50 min. (b) FESEM of catalyst CZ5 before photoactivity (c) FESEM of catalyst CZ5 after 4th photoactivity cycle.

2.7.5 Reactive species trapping experiment

The reactive species generated by the photocatalyst during the photoreaction were determined by various experiments performed in the presence of trapping agents. The charge scavengers such as para-Benzoquinone (BZQ), ethylenediaminetetraacetic acid disodium (EDTA-2Na), and isopropanol (IPA) were employed to trap the reactive species, namely, superoxide (O_2^-) radicals, holes (h^+), and hydroxyl radicals ($\text{OH}^\cdot$), respectively

[40]. The % MB degradation in the presence of various scavengers was compared with the scavenger-free condition over the CZ5 photocatalyst. The comparative % degradation efficiency of the catalyst with and without trapping agents is presented in Figure 2.17. The experimental % degradation efficiency values recorded were 86%, 15% and 20% for photoreactions in the presence of BZQ, EDTA-2Na and IPA % respectively, while the CZ5 material alone, showed maximum 98% photodegradation. From these values, it could be inferred that the holes (h^+), hydroxyl ($\cdot OH$) and superoxide ($\cdot O_2^-$) radicals were responsible for the photocatalytic dye degradation of dyes. Hence, reactive species trapping experiments pointed out that the most dominant reactive species involved in the MB and Red CL-5B dye degradation were ($\cdot OH$), (h^+) and ($\cdot O_2^-$) radicals.

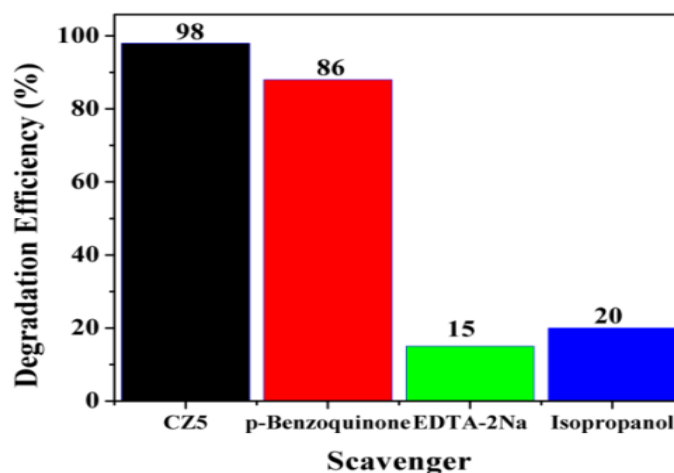


Figure 2.17: Trapping of charged species by scavengers

2.8 Proposed mechanism for photocatalytic dye degradation

The plausible dye degradation mechanism in the presence of light and the photocatalyst has been proposed for both MB and Red CL-5B dyes. Figure 2.18 depicts the general scheme showing the photoexcitation of Ce-doped ZnO under irradiated light, followed by the redox reactions. On light irradiation, the photocatalyst absorbs photon energy ($h\nu$) and activates the valence band (VB) electrons (e^-) to the conduction band (CB), leaving behind holes (h^+), generating electron-hole ($e^- - h^+$) pairs. Generally, excited CB electrons rapidly recombine, thus reducing the photocatalytic performance of the catalyst. However, here the doped ' Ce^{4+} ' ions act as a trap by creating mid-gap energy levels for the excited electrons below the CB of ZnO, thus quenching the ($e^- - h^+$)

recombination process. These mid-gap levels are responsible for generating numerous (e^- - h^+) pairs, thus increasing the photocatalytic reaction rate. From the reactive species trapping experiment, it was evident that the principal reactive species generated by the photocatalysts were hydroxyl ($\cdot\text{OH}$), holes (h^+) and superoxide ($\cdot\text{O}_2^-$) radicals. This suggests that the (h^+) generated in VB of ZnO reacts with water (H_2O) to produce highly reactive hydroxyl ($\cdot\text{OH}$) radicals and $\cdot\text{OH}$ species. The ($\cdot\text{OH}$) acted as a strong oxidizing agent for dye molecules, producing several smaller fragments. Further, these small fragments mineralize to CO_2 and H_2O . The photocatalyst CZ5 exhibited superior photocatalytic activity, but as the doping concentration increased, the photocatalytic activity decreased because excess Ce acts as a recombination center rather than electron-trap sites in bulk ZnO. The proposed mechanism holds good for both MB and Red CL-5B aqueous dye solutions in the presence of UV-visible light and Ce-doped photocatalyst.

Reaction Mechanism steps:

- $[\text{Ce}_x\text{Zn}_{1-x}\text{O}] + (h\nu) \rightarrow e^- (\text{CB}) + h^+ (\text{VB})$
- $\text{Ce}^{4+} + e^- (\text{CB}) \rightarrow \text{Ce}^{3+}$
- $\text{O}_2 + \text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + (\cdot\text{O}_2^-)$ (superoxide radicals)
- $(\cdot\text{O}_2^-) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot\text{HO}^*$
- $h^+ (\text{VB}) + \text{H}_2\text{O} (\text{adsorbed}) \rightarrow \text{H}^+ + \cdot\text{HO}^*$
- $h^+ (\text{VB}) + \text{OH}^- (\text{adsorbed}) \rightarrow \cdot\text{HO}^*$ (hydroxyl radicals)
- $\cdot\text{HO}^* (\text{adsorbed}) + \text{MB/Red CL-5B} \rightarrow \text{MB}^{+\cdot} / \text{Red CL-5B}^{+\cdot}$
- $\text{MB}^{+\cdot} / \text{Red CL-5B}^{+\cdot} \text{ mineralization} \rightarrow \text{H}_2\text{O} + \text{CO}_2 \uparrow$

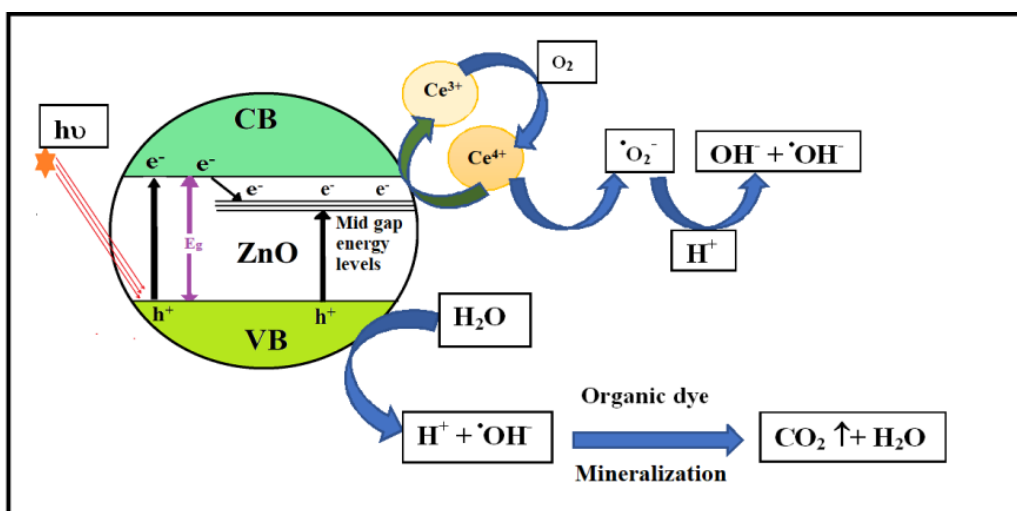


Figure 2.18: Schematic diagram depicting the mechanism of methylene blue and Red CL-5B dye degradation in the presence of light on Ce-doped ZnO photocatalyst.

2.9 Conclusions

In the current study, photosensitive $\text{Ce}_x\text{Zn}_{1-x}\text{O}$, (where $x=0.01, 0.02, 0.03, 0.04, 0.05, 0.06$, and 0.07 moles) materials were conveniently synthesized by employing a simple and cost-effective precursor method. The crystalline phase of nanomaterials, confirmed by XRD, was a hexagonal wurtzite ZnO structure. The microstructural particle images of SEM/HR-TEM indicated that the particles were spherical to oblong-shaped and sizes ranged from 30 to 55 nm with an average diameter of 45 nm. The undoped ZnO materials showed a higher range of particle size with a mean diameter of 60 nm. The particle size reduced significantly with Ce-doping in ZnO. There was a marginal effect of Ce-doping on the surface properties of the nanomaterials produced by the current method of synthesis. The EDS and XPS analysis confirmed the elemental composition with oxidation states as Zn^{2+} , O^{2-} , and Ce^{4+} and chemical bond formation in $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ materials. The Ce^{4+} ions doped in ZnO were incorporated into the lattice position, which was proved from XPS, EDS and XRD data. The Ce^{4+} were responsible for the generated mid-gap energy levels in ZnO, which consequently improved the UV-visible light absorption properties. With increased Ce-concentration in ZnO, the band gap energy (E_g) gradually reduced. The band gap of pure ZnO and $\text{Ce}_{0.07}\text{Zn}_{0.93}\text{O}$ were lowered to 3.211 and 3.170 eV, respectively, compared to the reported intrinsic band gap of ~ 3.32 eV. As a result, a gradual redshift in the absorption edge was noticed in Ce-doped ZnO. The PL emission spectra of materials also supported the fact that the fast electron exchange with a high ($e^- - h^+$) charge recombination rate retarded as the Ce-dopant concentration was increased in ZnO. These phenomena proved that the mid-gap energy levels created within the band gap acted as an electron trap; hence, a greater number of electrons were excited to the conduction band that participated in the redox reactions with dye molecules. The photocatalytic dye degradation efficiencies of materials evaluated in the presence of UV and direct sunlight showed promising results. The maximum efficiency of 98% for MB and 100% for Red-CL 5B dye was recorded for $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$. The degradation efficiency of $\text{Ce}_{0.05}\text{Zn}_{0.95}\text{O}$ was enhanced 8-fold compared to pure ZnO, calculated from the rate constant value. However, when Ce content in ZnO increased beyond 0.05 Ce moles, a negative impact was seen on photodegradation efficiency, which could be attributed to the formation of excess recombination centres. Hence, our studies indicated that the optimal doping concentration was 0.05 moles in ZnO for efficient dye degradation in UV-visible

light. The reactive species trapping experiment indicated that the photocatalyst generated hydroxyl ($\cdot\text{OH}$), holes (h^+) and superoxide ($\cdot\text{O}_2^-$) radicals during the photodegradation reaction. These reactive radicals conveniently aided in the mineralization of MB and Red CL-5B dye molecules. The mineralization efficiency calculated based on TOC was 28% and 33% for MB and textile industry Red CL-5B dyes, respectively. The prepared Ce-doped ZnO photocatalyst exhibited excellent stability and reusability properties over a 4-cycles. These materials can be effectively utilized in an industrial effluent treatment plant, wherein the harmful organic molecules could be fragmented by natural sunlight.

REFERENCES

1. D. A. Yaseen and M. Scholz, *International Journal of Environmental Science and Technology* **16**, 1193 (2019).
2. A. Azanaw, B. Birlie, B. Teshome, and M. Jemberie, *Case Studies in Chemical and Environmental Engineering* **6**, 100230 (2022).
3. S. S. Shinde, P. S. Shinde, C. H. Bhosale, and K. Y. Rajpure, *Journal of Photochemistry and Photobiology B: Biology* **104**, 425 (2011).
4. G. Kale, S. Arbuj, U. Kawade, S. Rane, J. Ambekar, and B. Kale, *Materials Chemistry Frontiers* **2**, 163 (2018).
5. M. C. Uribe-López, M. C. Hidalgo-López, R. López-González, D. M. Frías-Márquez, G. Núñez-Nogueira, D. Hernández-Castillo, and M. A. Alvarez-Lemus, *Journal of Photochemistry and Photobiology A: Chemistry* **404**, (2021).
6. M. Adeel, M. Saeed, I. Khan, M. Muneer, and N. Akram, *ACS Omega* **6**, 1426 (2021).
7. F. Gull, R. Riaz, K. Ansari, and H. Atiq, *Scientific Reports* **14**, 1 (2024).
8. P. L. Meena, A. K. Surela, L. K. Chhachhia, J. Meena, and R. Meena, *Nanoscale Advances* **7**, 1335 (2025).
9. N. S. Ferreira, J. M. Sasaki, R. S. Silva, J. M. Attah-Baah, and M. A. Macêdo, *Inorganic Chemistry* **60**, 4475 (2021).
10. R. Medhi, M. D. Marquez, and T. R. Lee, *ACS Applied Nano Materials* **3**, 6156 (2020).
11. R. Al Abri, F. Al Marzouqi, A. T. Kuvarega, M. A. Meetani, S. M. Z. Al Kindy, S. Karthikeyan, Y. Kim, and R. Selvaraj, *Journal of Photochemistry and Photobiology A: Chemistry* **384**, 112065 (2019).
12. Y. Liang, N. Guo, L. Li, R. Li, G. Ji, and S. Gan, *RSC Advances* **5**, 59887 (2015).
13. A. H. Ajil, N. M. Ahmed, F. K. Yam, Z. U. Zango, I. A. Wadi, A. M. Binzowaimil, O. Aldaghri, K. H. Ibnaouf, and H. Cabrera, *Applied Sciences* **13**, 11857 (2023).
14. K. I. Hadjiivanov, D. A. Panayotov, M. Y. Mihaylov, E. Z. Ivanova, K. K. Chakarova, S. M. Andonova, and N. L. Drenchev, *Chemical Reviews* **121**, 1286 (2021).
15. N. Rahahlia, B. Benmerad, A. Guehria-Laïdoudi, S. Dahaoui, and C. Lecomte, *Journal of Molecular Structure* **833**, 42 (2007).
16. O. Bechambi, A. Touati, S. Sayadi, and W. Najjar, *Materials Science in Semiconductor Processing* **39**, 807 (2015).
17. V. Borker, K. S. Rane, and V. N. Kamat Dalal, *Journal of Materials Science: Materials in Electronics* **4**, 241 (1993).
18. G. Li, X. Lu, W. Zhao, C. Su, and Y. Tong, *Crystal Growth & Design* **8**, 1276 (2008).
19. T. K. Pathak, E. Coetsee-hugo, H. C. Swart, C. W. Swart, and R. E. Kroon, *Materials Science & Engineering B* **261**, 114780 (2020).
20. V. Gurylev and T. P. Perng, *Journal of the European Ceramic Society* **41**, 4977 (2021).

21. N. Kannadasan, N. Shanmugam, S. Cholan, K. Sathishkumar, G. Viruthagiri, and R. Poonguzhali, *Materials Characterization* **97**, 37 (2014).
22. S. Anandan and M. Miyauchi, *Physical Chemistry Chemical Physics* **13**, 14937 (2011).
23. C. Zhou, Y. Wang, L. Du, H. Yao, J. Wang, and G. Luo, *Industrial and Engineering Chemistry Research* **55**, 11943 (2016).
24. C. Xia, C. Hu, and P. Zhou, *Journal of Experimental Nanoscience* **8**, 69 (2013).
25. R. Al-Gaashani, S. Radiman, A. R. Daud, N. Tabet, and Y. Al-Douri, *Ceramics International* **39**, 2283 (2013).
26. T. V. H. Luu, Q. B. Nguyen, N. N. Dao, M. D. Luu, V. D. Doan, N. C. Pham, T. L. Duong, and N. N. Pham, *RSC Advances* **11**, 36078 (2021).
27. C. C. Naik and M. Fernando, *Journal of Materials Science: Materials in Electronics* **33**, 4330 (2022).
28. K. Davis, R. Yarbrough, M. Froeschle, J. White, and H. Rathnayake, *RSC Advances* **9**, 14638 (2019).
29. L. Kumar Jangir, Y. Kumari, A. Kumar, M. Kumar, and K. Awasthi, *Materials Chemistry Frontiers* **1**, 1413 (2017).
30. I. Ahmad, M. S. Akhtar, M. F. Manzoor, M. Wajid, M. Noman, E. Ahmed, M. Ahmad, W. Q. Khan, and A. M. Rana, *Journal of Rare Earths* **39**, 440 (2021).
31. B. Abebe, D. Tsegaye, C. Sori, R. C. kuppe Renuka Prasad, and H. C. A. Murthy, *ACS Omega* **8**, 9597 (2023).
32. I. M. P. Silva, G. Byzynski, C. Ribeiro, and E. Longo, *Journal of Molecular Catalysis A: Chemical* **417**, 89 (2016).
33. S. Anandan, N. Ohashi, and M. Miyauchi, *Applied Catalysis B: Environmental* **100**, 502 (2010).
34. Z. Kalaycioğlu, B. Özüğür Uysal, Ö. Pekcan, and F. B. Erim, *ACS Omega* **8**, 13004 (2023).
35. D. R. Paul, S. Gautam, P. Panchal, S. P. Nehra, P. Choudhary, and A. Sharma, *ACS Omega* **5**, 3828 (2020).
36. C. G. Silva, M. J. Sampaio, S. A. C. Carabineiro, J. W. L. Oliveira, D. L. Baptista, R. Bacsá, B. F. Machado, P. Serp, J. L. Figueiredo, A. M. T. Silva, and J. L. Faria, *Journal of Catalysis* **316**, 182 (2014).
37. L. Wang, Z. Ji, J. Lin, and P. Li, *Materials Science in Semiconductor Processing* **71**, 401 (2017).
38. Sukriti, P. Chand, V. Singh, and D. Kumar, *Vacuum* **178**, 109364 (2020).
39. S. Karidas, B. K. Veena, N. Pujari, P. Krishna, and V. Chunduru, *Sadhana - Academy Proceedings in Engineering Sciences* **45**, 1 (2020).
40. U. Alam, A. Khan, D. Ali, D. Bahnemann, and M. Muneer, *RSC Advances* **8**, 17582 (2018).

Chapter-3:

Synthesis of rare-earth metal ion (Nd/Sm/Dy/Ho)-doped zinc oxide nanomaterials, characterization and photocatalytic degradation of Rhodamine B and Red CL 5B dye

3.1 Introduction

Global environmental issues are worsening year on year; hence, there is an urgent necessity to reduce harmful chemicals through innovative materials and processes. Substantial research has been devoted to materials for advanced oxidation processes. Purifying water using a photocatalyst in the presence of light is a benign and promising strategy [1]. Pure and rare-earth metal ion-doped zinc oxide (ZnO) photocatalytic nanomaterials are widely investigated for destroying chemicals and environmental pollution control measures. The light absorption and band gap restructure of the material are being widely explored by several research groups [2].

ZnO is an n-type semiconducting material with a wide band gap (~ 3.37 eV) demonstrating excellent light absorption properties, particularly in the UV region. Owing to its good physico-chemical stability and bio-compatibility attributes, ZnO is a suitable candidate for photocatalysis processes [3]. However, certain limitations associated with ZnO photocatalysts, such as (i) requiring high activation energy (b) mainly sensitive to UV light and inactive in the visible range, and (c) rapid charge recombination. Hence, to overcome these drawbacks and achieve superior UV-visible light absorption capability, improve the charge separation and narrow down the band gap, the ZnO is often doped or co-doped with metal and non-metal ions. The type and amount of dopant affect the band gap and spectral absorption range of ZnO [4]. Herein, certain rare earth metal ions were doped in the ZnO matrix, which modified the electronic energy level band structure. This resulted in a higher number of electron-hole migrations at the surface of the photocatalyst. In this context, there is a huge scope for nanomaterial synthesis, its characterization and an understanding of the fundamental principles behind the enhanced photocatalytic efficiencies of ZnO. The development of novel photocatalysts and exploring newer reactions at the ZnO surface have been pursued by different scientific groups [5].

The ideal and good photocatalyst should satisfy at least these three main criteria: first, efficient light absorption (preferably in the visible range), second, high photocatalytic efficiency, and lastly, resistance to photo-corrosion. Hence, it is imperative to strike a balance and optimize these three conditions to realize the highest photocatalytic efficiency. The current chapter describes the material preparation, characterization and the photocatalytic degradation studies using organic dyes. The correlation between structure,

morphology and optical properties of materials and their application for environmental pollution remediation [6].

Based on the available literature, the metal ion doped ZnO has been fabricated using lengthy, expensive or cumbersome procedures, namely sol-gel, laser ablation, chemical vapour deposition, spray pyrolysis, electrochemical synthesis, sputter deposition, and electrodeposition [7–13]. In the current work, a metal-organic framework, that is, metal-oxalate complexes, was initially prepared and then decomposed thermally to obtain the intended functional materials [14]. The simple metal-oxalate and hydrazine-modified metal-oxalate precursors assisted in tuning the properties of nanomaterials [15]. The benefits of hydrazinated precursors include smaller particle size, high surface area and single-phase formation of mixed-metal oxides. The exothermic thermal decomposition of hydrazinated precursor also facilitated metal ion doping into the host lattice [16]. Consequently, the doped nanomaterial band gap energy was altered. The binding of hydrazine molecules to the precursor and controlled heat treatment are the two critical steps in material synthesis. It has been proved that the hydrazination of the precursor can modify the microstructure and tailor the inherent properties of the materials required for specific applications [17]. Doping of rare-earth (RE) metal ions (M^{3+}) in ZnO can extend the light absorption towards the visible region, introduce new energy levels within the band gap, reduce the recombination rate, and thereby enhance photocatalytic activity.

The valence band (VB) electrons of ZnO can be easily excited to the conduction band (CB) on UV light irradiation. However, the activated CB electrons rapidly recombine back with the VB holes, dissipating the energy in the form of heat or light. The fast recombination process is detrimental to photocatalytic applications [18]. Therefore, the photoexcited electrons can be effectively channelized by introducing mid-gap energy levels and then utilized for various surface reactions [19]. The incorporation of optimal concentration of M^{3+} ions in the ZnO lattice is crucial for modifying the energy levels and photocatalytic applications. The M^{3+} creates a mid-gap energy level and traps the electrons and retards the recombination process in ZnO, which is crucial in enhancing the charge separation. Some researchers noted that higher doping concentration levels can retard the photocatalytic activities, this is because at higher concentrations dopants can act as a recombination centre, thus accelerating the charge recombination rate [20]. The RE metal ions with partially filled 4f-orbitals lie just below the conduction band. It enhances the

electron excitation of ZnO by creating mid-gap energy levels. Hence, the type of dopant and concentration are of high practical significance in photocatalysis [21].

This chapter describes the synthesis of Nd/Sm/Ho/Dy-doped ZnO materials, characterization and comparison of the photocatalytic activities. The effect of hydrazine on the solid-state properties was also compared with the materials derived from their counterpart oxalate precursors. The optical properties of the materials doped with 0.05 and 0.1 moles of M^{3+} in ZnO were investigated. The M/Zn-oxide materials were comprehensively characterized and investigated for their structural and optical properties.

3.2 Experimental: Materials and Methods

3.2.1 Materials

Zinc nitrate was purchased from Loba Chemie (AR grade) and used directly for the materials synthesis. The nitrate salts solution of Neodymium (Nd), Samarium (Sm), Dysprosium (Dy), and Holmium (Ho), respectively, were used as dopant sources. Oxalic acid ($C_2H_2O_4$), AR grade, and Hydrazine hydrate were purchased from Loba Chemie (purity >99%) for the preparation of hydrazinated precursors.

The detailed experimental procedure for the synthesis of materials ($M_xZn_{1-x}O$, $M = Nd/Sm/Dy/Ho$ and $x = 0.05$ and 0.1 moles) via M/Zn-oxalate and M/Zn-oxalate-hydrazinate precursors are described below:

3.2.2 Preparation of $M_xZn_{1-x}O$ materials from M^{3+} /Zn-oxalate precursor

Synthesis of $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$ nanomaterials via ($M^{3+}=Nd/Sm/Dy/Ho$)/Zn-oxalate precursor

The $M_xZn_{1-x}O$ ($x = 0.05$ and 0.1 moles) materials were prepared by mixing a stoichiometric amount of metal ions and then co-precipitated by adding oxalate ions. Initially, mixed 0.1 molar aqueous zinc-nitrate (Zn^{2+}) with 0.05 and 0.1 millimolar concentration of metal-nitrate (M^{3+}) solutions separately. To this mixture, an equal volume of 0.1 molar aqueous solution of oxalic acid was added slowly with continuous stirring to precipitate M^{3+} /Zn-oxalate precursor. The precipitate was filtered, washed with water, ethanol and then air dried. Finally, the dried precipitate (precursor) was thermally decomposed in air at ~ 700 °C for 5 h to produce $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$

nanomaterials. The M^{3+} /Zn-oxalate precursors of $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$ materials were denoted as MZOx1 and MZOx2, respectively. The prepared nanomaterial $M_xZn_{1-x}O$ ($x = 0.05$ and 0.1) were assigned codes as mentioned in table 3.1.

3.2.3 Preparation of hydrazinated $M_xZn_{1-x}O$ materials from M^{3+} /Zn-oxalate hydrazinate precursor

Synthesis of $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$ nanomaterials via ($M^{3+}=Nd/Sm/Dy/Ho$)/Zn-hydrazinate-oxalate precursor

For the preparation of hydrazinated $M_xZn_{1-x}O$ materials, the MZOx1 and MZOx2 precursors were modified by attaching hydrazine molecules. The hydrazination of precursors was achieved by equilibrating the above-prepared MZOx1 and MZOx2 precursor powders with hydrazine hydrate vapours in a closed vessel for seven days. The exposed MZOx1 and MZOx2 precursors were converted into hydrazinate–M/Zn-oxalate precursors. The hydrazinated precursors were thermally decomposed in air at ~ 700 °C for 5 h, which produced the hydrazinated $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$ materials. The hydrazinated precursors of $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$ were denoted with codes as MZOxHz1 and MZOxHz2, respectively. The hydrazinated oxide materials, $M_{0.05}Zn_{0.95}O$ and $M_{0.1}Zn_{0.9}O$, were assigned codes MZOH1 and MZOH2, respectively. The schematic diagram for the synthesis of $M_xZn_{1-x}O$ ($x = 0.05$ and 0.1) materials via oxalate and hydrazine-oxalate precursors is depicted in Figure 3.1. The prepared oxide nanomaterials via both schemes were assigned codes and presented in table 3.1

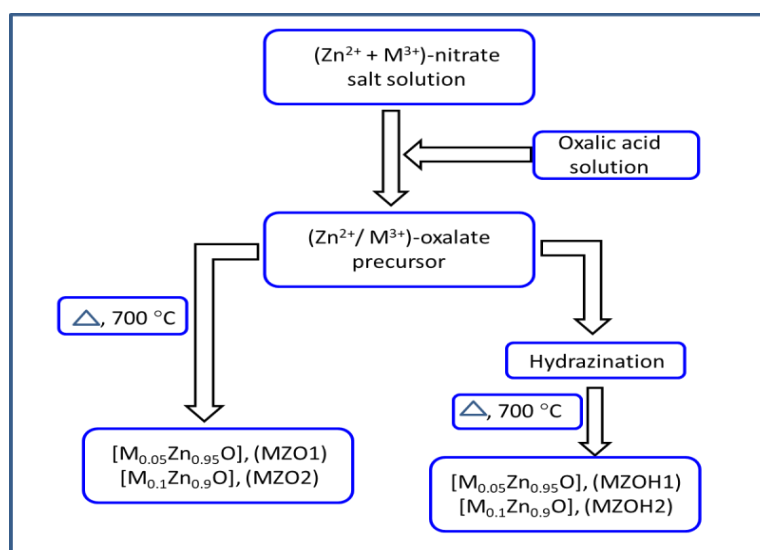


Figure 3.1: Synthesis scheme for $M_xZn_{1-x}O$ ($x=0.05, 0.1$) via M/Zn-oxalate (MZOx1 and MZOx2) and hydrazine-M/Zn-oxalate (MZOxHz1 and MZOxHz2) precursors.

Table 3.1: Compilation of synthesized material compositions and their codes

Sample	Oxalate		Oxalate-hydrazinate	
	x = 0.05	x = 0.1	x = 0.05	x = 0.1
Nd_xZn_{1-x}O	NZO1	NZO2	NZOH1	NZOH2
Sm_xZn_{1-x}O	SZO1	SZO2	SZOH1	SZOH2
Dy_xZn_{1-x}O	DZO1	DZO2	DZOH1	DZOH2
Ho_xZn_{1-x}O	HZO1	HZO2	HZOH1	HZOH2

3.3 Characterization techniques

The precursors and their decomposed products, [M_xZn_{1-x}O (M = Nd/Sm/Dy/Ho; x = 0.05 and 0.1 moles)], were systematically characterized by various analytical techniques. The infrared (IR) spectra were recorded using the Shimadzu IR prestige instrument in the range of 4000 – 400 cm⁻¹. The precursor thermal decomposition profiles were recorded on a Netzsch thermal analyzer. The simultaneous Thermogravimetric Analyzer (TGA) and Differential Thermal Analyzer (DTA) thermograms were recorded in the dynamic temperature mode, ranging from 25 to 800 °C at a heating rate of 10 °C/min in air. The phase identification was performed on a Rigaku Powder X-ray diffractometer (XRD). The X-ray source was a copper X-ray tube with Cu-Kα₁ radiation (λ_{α₁}=1.5418 Å). The scanning range was set from 10 to 80 °2-theta, step time of 0.1 sec, step size of 0.01° and divergent slit of 0.3°. The microstructural images of materials were captured on JSM-IT300LV (JEOL) scanning electron microscopy (SEM). The SEM was equipped with an Oxford EDAX probe to identify the elemental composition. The high-resolution transmission electron microscopy (HR-TEM) images were obtained from the JEOL JEM2100F instrument. The accelerating voltage of 120 kV was set during the measurements. The X-ray photoelectron spectroscopic analysis was performed on a PHI5000 Versa Probe II FEI. The binding energies (BE) of the elements were calculated based on the C 1s spectral component as the reference peak at 284.8 eV. The nitrogen gas adsorption-desorption studies were carried out using the Belsorp-II Japan instrument. Before measurement, the samples were degassed and activated at 250 °C for 3 h. Nitrogen

(N₂) gas was used as an adsorptive probe for the adsorption-desorption isotherm measurements. The specific surface area and pore volume of the powder sample were estimated based on the Brunauer-Emmett-Teller (BET) equation and Barret-Joyner-Halenda (BJH) plots. Raman spectra were recorded on a Horiba LabRAM HR evolution Raman microscope in the range 100 to 1200 cm⁻¹ using a laser with an excitation wavelength of 532 nm and equipped with a CCD camera as the detector.

3.4 UV-visible DRS studies: Light absorption and band gap

Diffuse reflectance spectroscopy (DRS) was performed on the Shimadzu UV2500 instrument in the UV-visible range (250 – 500 nm). The optical properties of M-doped ZnO materials were analyzed based on the absorption spectra and further used in the calculation of band gap energy (E_g). The Tauc equation provides a relation between the band gap (E_g) and the light energy photon as given in equation 1:

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (1)$$

Where, α is the absorption coefficient, h is Planck's constant, ν is the frequency of incident light, A is a constant, and n is the constant for the type of optical transition, with values $n = 1/2$ for permitted direct transitions in the current ZnO sample. The DRS spectra were converted into the Kubelka-Munk function. The y-axis values were converted into quantity $(F(R_\infty))$, which was proportional to the absorption coefficient and the values of α is substituted with $F(R_\infty)$. Hence, the Tauc equation can be represented in equation 2.

$$(h\nu F(R_\infty))^2 = A(h\nu - E_g) \quad (2)$$

The $(h\nu F(R_\infty))^2$ function values were plotted against the energy of the photon ($h\nu$) in electron volts (eV). The E_g can be obtained by extending the linear portion of the graph, intersecting the energy (eV) value on the x-axis [22].

The relationship of E_g with respect to the absorption edge at the wavelength (λ) is also expressed as per equation 3 [23]

$$E_g = 1239.8/\lambda(\text{nm}) \quad (3)$$

3.5 Photoluminescence studies

The information regarding the newly formed band gap energy levels and electronic transitions and the lifetime of the separated charged species can be well understood by photoluminescence (PL) analysis. The PL emission spectra for $M_xZn_{1-x}O$ materials were recorded at room temperature (RT) after excitation with the laser light of wavelength $\lambda_{exc} = 252$ nm. The equipment on which RT-PL studies were performed was a spectrofluorometer (FP8200, Jasco Japan) equipped with a xenon laser as the excitation source. The pulse duration of 10 ns, power of 2.88 mW, and 3 mm of spot size were set during the measurement. The emitted light was collected using a collimating lens assembled with an optical fibre. PL emission spectra were recorded in the range of 340 – 540 nm and the emission maxima were noted for each material. The peak intensities were recorded as a function of emission wavelength (nm). The PL intensities directly indicated the nature of the recombination process, which is crucial in photocatalysis [24]. The microstructural defects, such as oxygen vacancies and interstitial sites, resulted in various radiative transitions of excited electrons and holes. The preparation method and annealing temperature influence the oxygen vacancies, thus impacting the PL emission intensities.

3.6 Photocatalytic studies: Rhodamine B and Red CL 5B dye degradation

The photocatalytic activity of the synthesized $M_xZn_{1-x}O$ nanomaterials was evaluated using Rhodamine B (Rh-B) as a model dye. The typical experimental set-up consisted of a 250 mL quartz glass reactor jacketed by circulating water maintained at 25 °C. The reactor solution was illuminated from the centre using a tubular medium-pressure Hg lamp, emitting UV light (λ range: 200 to 400 nm). Weighed and transferred 100 mg of photocatalyst and 100 mL of dye solution (10 ppm) into the quartz reactor vessel. Initially, the solution was stirred in the dark for 30 min to achieve surface adsorption equilibrium. The UV lamp was switched on, and the catalyst dispersed in the dye solution was activated. At a definite time interval of 0, 20, 40, 60, 80, 100, 120, 140, 160 and 180 min, 2 mL of an aliquot was withdrawn using the syringe, filtered and the UV spectrum of the clear solution was recorded using a Shimadzu UV-Visible spectrophotometer. The scanning range was set between 200 to 800 nm and the absorbance data points were collected at different time intervals. The absorbance of Rhodamine B (Rh B) was noted at

$\lambda_{\max} = 554 \text{ nm}$. Also, Rh B dye degradation studies were carried out in the presence of sunlight, keeping all other parameters constant. The percentage (%) dye degradation efficiency by the photocatalyst was calculated based on the formula given in equation 4.

$$\% \text{ Degradation Efficiency} = (C_0 - C_t) / C_0 * 100 \quad (4)$$

The C_0 = Absorbance at '0' min and C_t = Absorbance at 't' min. The % degradation efficiency was plotted against the time points.

On similar lines, a textile industry Red CL 5B dye was considered for degradation studies. The initial concentration was 25 ppm and the 2mL of sample aliquot was withdrawn at a regular time interval of 0, 10, 20, 30 and 40 min. Other experimental conditions were kept constant as mentioned for Rh B dye degradation studies.

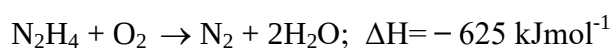
3.7 LC-MS studies: Identification of Rhodamine B degradants

To understand the degradants formed during the photocatalysis process, the aliquots were analysed by liquid chromatography coupled with mass spectrometry (LC-MS) technique. The LC-MS studies were performed on the Agilent LC-MS 6460 instrument. The important parameters which were set during the analysis were: spray voltage: $\pm 1 \text{ kV}$, capillary temperature 300°C . For LC, the mobile phase was premixed water and acetonitrile was used to elute the degradants. The flow rate of 0.5 mL/min and the C18 analytical column were used to separate the impurities. The final time point degraded solution was injected into the LC-MS system and the retention time by LC of the degradants and analyzed its m/z was analysed using MS. The degradants were identified based on the molecular mass. The Orbitrap analyzer was employed to scan the molecular mass of the degradant in the range of $50\text{--}500 \text{ m/z}$ with a mass resolution of 60,000.

3.8 Results and Discussion

3.8.1. Modification of precursors by hydrazine and its influence on material properties

The photocatalytic properties of material are profoundly influenced by its crystal structure, shape, size, morphology, surface area, composition, dopants and defects. Hence, the selection of a suitable synthetic strategy is of prime importance in obtaining their functional properties. In the literature, there are several reports on the use and integration of the hydrazine molecule to modify the metal-oxalate precursors. When the hydrazine was attached to native metal-organic precursors like M/Zn-oxalate, the material properties could be modified significantly [25]. It is well known that hydrazinated precursors decompose at lower temperatures exothermically and produce nanosized metal oxide materials [15]. In the current study, the rare earth (RE) metal-doped ZnO nanomaterials were conveniently prepared via oxalate-M/Zn and hydrazinated precursor methods. The critical properties of $M_xZn_{1-x}O$ ($M=Nd, Sm, Dy, Ho$) nanomaterials derived from both precursors were characterized and compared. The hydrazinated oxalate-M/Zn-precursors displayed exothermic decomposition when compared to their counterpart simple M/Zn-oxalate precursors. The liberated hydrazine from the precursors reacted with the oxygen from the air and produced enormous heat energy and released large volumes of gases. Such reactions were beneficial for the production of $M_xZn_{1-x}O$ nanopowders. Some researchers believed that the exothermic decomposition processes were beneficial in the production of nanomaterials with superior surface characteristics [26]. Moreover, the hydrazination of the precursor mostly results in single-phase doped ZnO materials. Materials prepared from hydrazinated precursors showed a single phase with improved microstructural and functional properties. In case of hydrazinated-metal oxalate precursors, during the decomposition step, the immediate contacts between the particles were restricted by metal-organic molecules, which facilitated the disintegration of particles and hence resulted in nanosized materials. At high temperatures, the liberated hydrazine molecule chemically reacted with oxygen as given in the reaction below:



Thus, the liberated heat energy was high enough to oxidatively decompose the precursor [16]. Here, N_2 gases and H_2O vapour created a micro-atmosphere around the particles,

which had a positive impact on the material dispersion, micro-structure and particle size. The oxalate and hydrazine content of the precursors were chemically analysed using standard procedures. Hence, the optical properties could be modified by binding hydrazine to the native oxalate precursor. The improved optical properties of $M_xZn_{1-x}O$ materials were tested for photoluminescence (PL) and photocatalytic dye degradation activities in UV-visible range.

3.8.2 IR studies

To ascertain the formation of precursors, the IR studies were performed on all the synthesized M/Zn-oxalate and hydrazinated M/Zn-oxalate precursors. The bond formed between the metal ion and the organic complexing agent were identified and noted. Also, the metal-oxygen bonds were confirmed based on the IR band positions. The presence of oxalate functional groups, hydrazine and Zn-O bonds were confirmed from the characteristic vibrational band positions. The representative IR spectra of Nd/Zn-oxalate, hydrazinated precursors and their respective metal-oxide materials are presented in Figure 3.2. The observed IR data of the all precursors (MZOx1, MZOx2, MZOxHz1, MZOxHz2,) and their corresponding $M_xZn_{1-x}O$ materials (MZO1, MZO2, MZOH1 and MZOH2) are reported in table-3.2. The assigned IR band position (wavenumber, cm^{-1}), bond strength, type of chemical bonding and the functional group present in all M/Zn-oxalate, hydrazine-M/Zn-oxalate precursors and $M_xZn_{1-x}O$ are compiled in table 3.2. The IR studies it can be stated that the formation of oxalate and hydrazination of M/Zn-oxalate precursors were successful. The typical metal-oxygen bond was also identified in all the $M_xZn_{1-x}O$ materials in the range of 650 to 400 cm^{-1} [27].

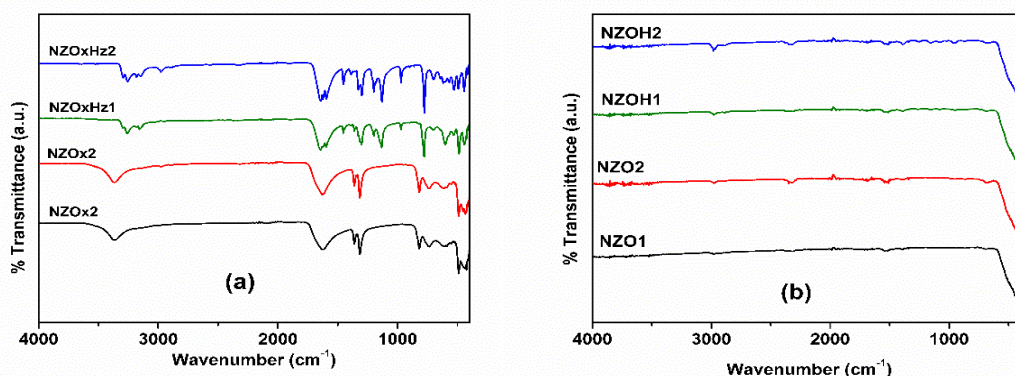


Figure 3.2: IR spectra (a) Precursors: NZOx1, NZOx2, NZOxHz1, and NZOxHz2 and (b) Nd/Zn-oxides: NZO1, NZO2, NZOH1 and NZOH2.

Table 3.2: Compilation of IR bands of precursor and their $M_xZn_{1-x}O$ material.

IR band position (cm^{-1})	Bond strength	Type of Chemical Bond	Assigned to Functional group/ bond
Precursors-M/Zn-oxalate and hydrazine-M/Zn-oxalate			
3350	strong	-O-H stretching	water of crystallization
3250	strong	-N-H stretching	hydrazine
1638	strong	-O-C-O asymmetric stretching	oxalate
1311	medium	-O-C-O symmetric stretching	oxalate
1195	medium	-NH ₂ bending	hydrazine
1128	medium	-NH ₂ bending	hydrazine
970	medium	-N-N- bending	bridging hydrazine
816	medium	(O-C-O) bending	oxalate
775	medium	(O-C-O) bending	oxalate
727	medium	O-Zn-O stretching	Zn-oxalate
Oxide materials - $M_xZn_{1-x}O$			
486-435	medium	Zn-O stretching	Zn-O

3.8.3 Thermal analysis of precursor

Figure 3.3 (a, b) depicts the typical TGA/DTA thermal profiles of $MZOx_2$ (Nd/Zn-oxalate) and $MZOxHz_2$ (Nd/Zn-oxalate-hydrazinate) precursors. In the case of $NZOx_2$ precursor, the TGA graphs indicated a dual-step decomposition pattern with a total mass loss $\sim 60\%$ to form a stable oxide material. The complementary DTA graph indicated two large endotherms centered at $\sim 170^\circ\text{C}$ and $\sim 410^\circ\text{C}$ attributed to decarboxylation followed by oxidative decomposition of the precursor to form Nd/Zn-oxide. Interestingly, when compared with the $NZOxHz_2$ precursor, the TGA/DTA graphs showed different profiles. As the temperature was ramped from room temperature to 200°C , an endotherm appeared at $\sim 170^\circ\text{C}$ in the DTA, which was assigned to the decarboxylation of $NZOxHz_2$,

accompanied by a mass loss step in the TGA curve. Further, as the temperatures were elevated to 700 °C, the DTA graph showed multiple exothermic peaks at ~ 250 °C, 330 °C, 410 °C and 600 °C assigned to the oxidative thermal decomposition of the precursor to yield stable oxide material. The TGA thermogram showed a total mass loss of ~70 % with a flat baseline above 700 °C. Hence, all materials were annealed at 700 °C in air for 5 h and then subjected to instrumental characterization. Similar thermal events were reported in the literature for hydrazine metal oxalate precursors [16]. From TGA/DTA plots, it was evident that hydrazination of M/Zn-oxalate precursor induced exothermic and combustible thermal events, which could modify the solid-state properties of $M_xZn_{1-x}O$ materials.

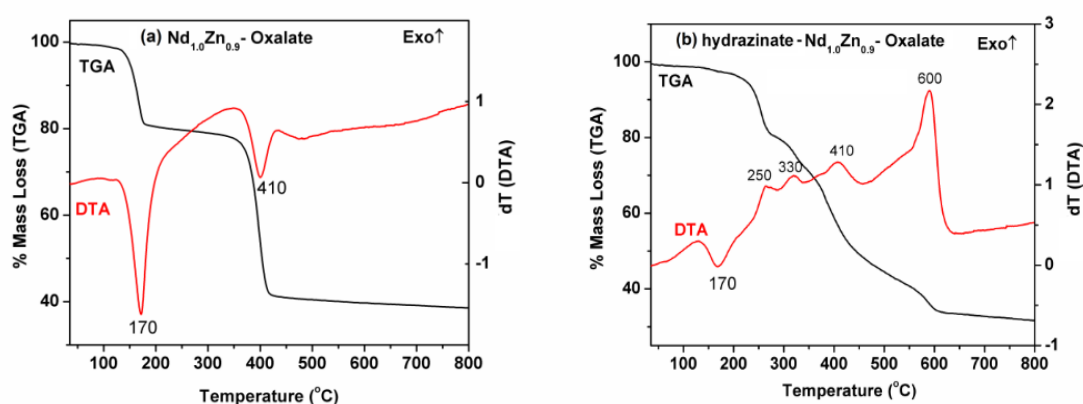


Figure 3.3: TGA – DTA thermograms of (a) NZOx2 (b) NZOxHz2 precursor.

3.8.4 X-ray diffraction studies

The crystal structure is crucial as it affects the band gap of photocatalytic materials [7]. The phase identification, crystal planes and crystallite size of $M_xZn_{1-x}O$, where $M=Nd, Sm, Ho, Dy$ and $x=0.05$ and 0.1 , were investigated by powder X-ray diffraction (XRD). Figure 3.4(a,b,c,d) depicts the XRD patterns of $M_xZn_{1-x}O$ materials. From the diffractograms, it was confirmed that all materials depicted sharp and highly crystalline peaks/reflections corresponding to the hexagonal wurtzite ZnO structure with a $P6_3mc$ space group. The major peaks were assigned with ($^{\circ}2$ -theta) and crystal planes indexed (hkl) values as 31.8° (100), 34.5° (002), 36.4° (101), 47.4° (102), 56.7° (110), 62.9° (103), 66.0° (200), 68.4° (112), 69.0° (201). The diffraction data conformed to JCPDS # 036-1451. There were no impurity peaks (phase) observed due to metal or oxides of dopants ($M=Nd, Sm, Ho, Dy$) in all materials. Hence, it can be stated that the M^{3+} ions were

successfully doped and uniformly distributed within the Zn^{2+} lattice sites. Thus, the incorporation of dopants was considered to be the most crucial for photocatalysis as it alters the band gap energy structure, thus affecting the optical properties of the material.

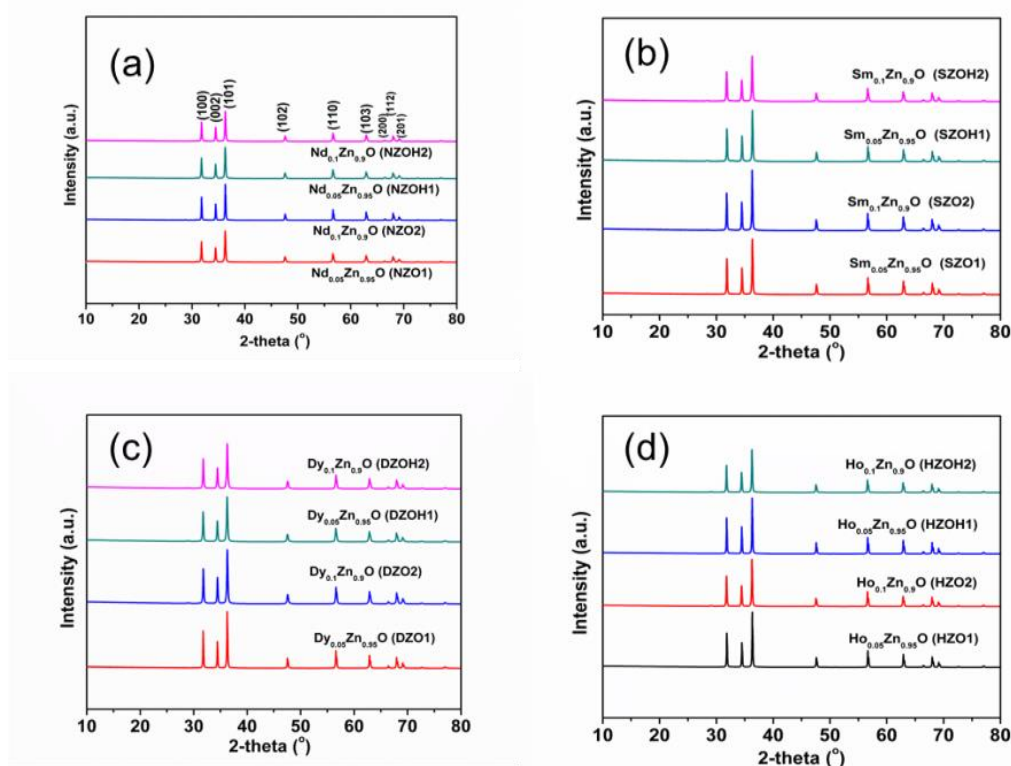
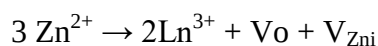


Figure 3.4: XRD patterns of (a) $\text{Nd}_x\text{Zn}_{1-x}\text{O}$ (b) $\text{Sm}_x\text{Zn}_{1-x}\text{O}$ (c) $\text{Dy}_x\text{Zn}_{1-x}\text{O}$ (d) $\text{Ho}_x\text{Zn}_{1-x}\text{O}$, where $x=0.05$ and 0.1 prepared from oxalate and oxalate-hydrazinate precursors.

Furthermore, on close examination, at a higher doping level of 0.1 of M^{3+} in ZnO , a noticeable XRD peak shift at 2-theta : 31.8° (100), 34.5° (002), 36.4° (101) could be seen; shown in inset picture of Figure 3.5 for one of the representative $\text{Nd}_x\text{Zn}_{1-x}\text{O}$ material. When Zn^{2+} were replaced by M^{3+} ions in the lattice sites, which resulted in minor variations in the a and c lattice parameter values of host ZnO . These minor distortions were attributed to the difference in ionic sizes between Zn^{2+} and M^{3+} . As the atomic radii of the dopants, Nd^{3+} ($1.11 \text{ \AA}$), Sm^{3+} ($1.06 \text{ \AA}$), Dy^{3+} ($0.910 \text{ \AA}$), and Ho^{3+} ($0.89 \text{ \AA}$) were comparatively higher than Zn^{2+} ($0.88 \text{ \AA}$), an expansion of the hexagonal wurtzite unit cell along c -axes was anticipated [28]. Additionally, defects such as interstitial zinc (Zn_i) or oxygen vacancies (V_O) in the lattice were also expected to form within the ZnO crystal system in order to conserve the electrical neutrality and local crystal structure equilibrium [29]. The mechanism of defect or vacancy formation is based on the following equation:



Moreover, on a detailed examination of the diffraction patterns, although the peak shapes of all materials were identical, there were minor disparities in peak intensities between the materials prepared from the two different routes. The materials obtained from hydrazinted precursors displayed slightly reduced intensity and broadened peak shapes compared to materials obtained from simple oxalate precursors. Hence, the effect of the hydrazine could be seen on the crystallite size of the $M_xZn_{1-x}O$ nanomaterials. Hence, the crystallite sizes of all the materials were evaluated using Scherrer equation 5,

$$D_{avg} = (0.94\lambda/\beta\cos\theta) \quad (5)$$

where D_{avg} is the average crystallite size (nm), λ is the wavelength of the X-ray used for analysis (Cu $K_{\alpha 1}$ = 1.5418 Å), β is the full width at half maximum (fwhm) of peak intensity (radians), and θ is the diffraction angle [30]. The average crystallite size values of $M_xZn_{1-x}O$ were slightly reduced for materials produced from the hydrazinate precursor compared to materials obtained from oxalate-precursor. The variation in crystallite size could be explained based on the exothermic decomposition of hydrazinated precursors. Considering the influence of the hydrazinated method of preparation and doping M^{3+} on the crystallite size, other parameters such as crystal strain and dislocation densities were also calculated and compared. The strain (ϵ) and dislocation densities (δ) values were calculated using the following equations 6 and 7.

$$\text{Strain } (\epsilon) = \beta / 4\tan\theta \quad (6)$$

$$\text{Dislocation density } (\delta) = (1/D^2), \text{ where } D_{avg} \text{ is the average crystallite size (nm)} \quad (7)$$

Here, it is worth mentioning that the strain and dislocation density values of MZOH1 and MZOH2 were much higher compared to MZO1 and MZO2 nanomaterials.

Table 3.3 presents the compilation of material composition, assigned codes, calculated lattice parameters a and c , Scherrer average crystallite size, strain and dislocation density values.

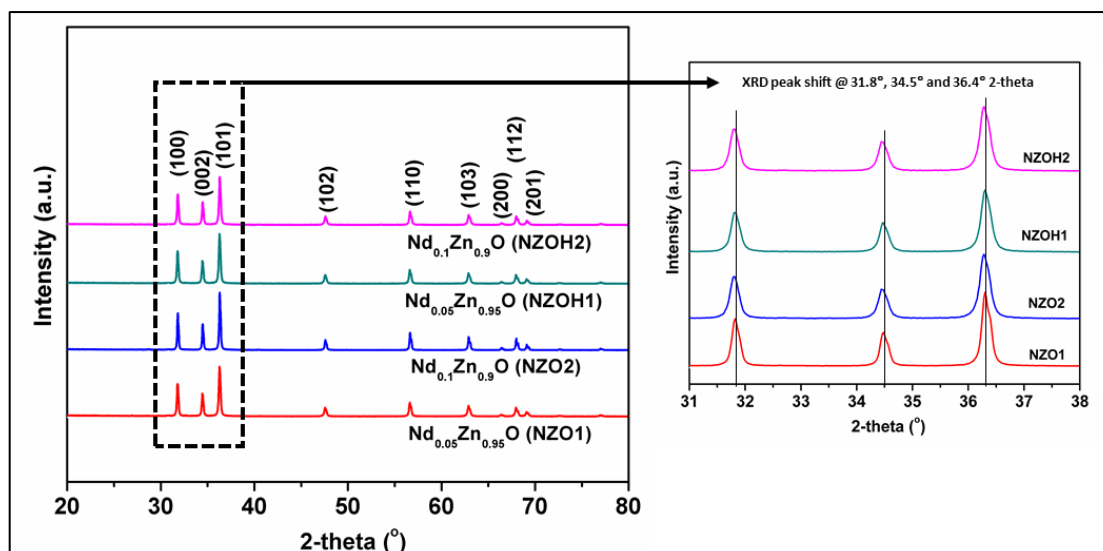


Figure 3.5: XRD patterns of NZO1, NZO2, NZOH1 and NZOH2 with an inset picture showing the peak shift effect due to Nd^{3+} doping in ZnO.

Table 3.3: Compilation of material composition, assigned codes, observed lattice parameters a and c , Scherrer average crystallite size (D_{avg}), strain (ϵ) and dislocation density (δ).

Material composition	Material Code	Lattice parameter		Crystallite size D_{avg} (nm)	Strain (ϵ)	Dislocation density (δ) (line $\times 10^{14}$) (m^{-2})
		a (Å)	c (Å)			
$\text{Nd}_{0.05}\text{Zn}_{0.95}\text{O}$	NZO1	3.2537	5.2546	43	0.00265	5.40
$\text{Nd}_{0.1}\text{Zn}_{0.9}\text{O}$	NZO2	3.2533	5.2548	38	0.00305	6.92
$\text{Nd}_{0.05}\text{Zn}_{0.95}\text{O}$	NZOH1	3.2538	5.2545	28	0.00413	12.75
$\text{Nd}_{0.1}\text{Zn}_{0.9}\text{O}$	NZOH2	3.2529	5.2553	26	0.00445	14.79
$\text{Sm}_{0.05}\text{Zn}_{0.95}\text{O}$	SZO1	3.2538	5.2548	41	0.00268	5.95
$\text{Sm}_{0.1}\text{Zn}_{0.9}\text{O}$	SZO2	3.2534	5.2550	35	0.00311	8.16
$\text{Sm}_{0.05}\text{Zn}_{0.95}\text{O}$	SZOH1	3.2537	5.2547	27	0.00418	13.72
$\text{Sm}_{0.1}\text{Zn}_{0.9}\text{O}$	SZOH2	3.2530	5.2555	26	0.00455	14.79
$\text{Dy}_{0.05}\text{Zn}_{0.95}\text{O}$	DZO1	3.2540	5.2551	40	0.00272	6.25
$\text{Dy}_{0.1}\text{Zn}_{0.9}\text{O}$	DZO2	3.2535	5.2553	37	0.00341	7.30
$\text{Dy}_{0.05}\text{Zn}_{0.95}\text{O}$	DZOH1	3.2538	5.2549	29	0.00425	11.89
$\text{Dy}_{0.1}\text{Zn}_{0.9}\text{O}$	DZOH2	3.2531	5.2554	25	0.00459	16.00
$\text{Ho}_{0.05}\text{Zn}_{0.95}\text{O}$	HZO1	3.2539	5.2549	40	0.00278	6.25
$\text{Ho}_{0.1}\text{Zn}_{0.9}\text{O}$	HZO2	3.2536	5.2553	37	0.00319	7.30
$\text{Ho}_{0.05}\text{Zn}_{0.95}\text{O}$	HZOH1	3.2539	5.2549	26	0.00428	14.79
$\text{Ho}_{0.1}\text{Zn}_{0.9}\text{O}$	HZOH2	3.2531	5.2555	25	0.00458	16.00

3.8.5 Nitrogen adsorption-desorption studies

The material surface properties, such as the specific surface area, pore volume, and mean pore diameter, were studied from nitrogen gas adsorption-desorption isotherms. These particle attributes are important in photocatalysis as the activity directly depends on the number of reacting molecules adsorbed over the surface area. The pore size and pore volume also impact the performance of the photocatalysis. The $M_xZn_{1-x}O$ materials specific surface area, pore size distribution, and total pore volume were evaluated and compared. Figure 3.6 (a, b) represent the BET adsorption-desorption isotherms along with BJH plots for representative samples NZO2 and NZOH2. The specific surface area (m^2/g), total pore volume (cm^3/g), and mean pore size (nm) values for all $M_xZn_{1-x}O$ materials prepared via oxalate and oxalate-hydrazinate methods are compiled in Table 3.4.

As per the International Union of Pure and Applied Chemistry (IUPAC), adsorption isotherms of both samples showed typical type-IV(a) isotherms, with a small hysteresis loop appearing at a higher relative partial pressure (p/p_0) range of 0.8 – 1.0, which signified mesoporous (2 to 50 nm) materials. The hysteresis loop for MZOH2 was slightly larger compared to MZO2, which indicated that the materials obtained from the hydrazinated precursors were slightly extra mesoporous with larger pores. From the compiled data, it could be noted that the BET surface area of MZOH1 and MZOH2 materials were slightly higher values of 4.67 and 5.21 m^2/g , respectively. While the materials obtained via conventional oxalate precursor MZO1 and MZO2 had slightly lower values of 3.21 and 3.56 m^2/g , respectively. The total pore volume and mean pore diameter values also improved with M^{3+} doping levels and exothermic decomposition of hydrazinated precursors [4]. The surface distortions increased with the dopant concentration and the hydrazine method of synthesis. The BJH pore size distribution and the pore diameters were less than 50 nm, conforming to mesoporous materials. Hence, it can be stated that the MZOH1 and MZOH2 particles displayed well-dispersed mesoporous structures.

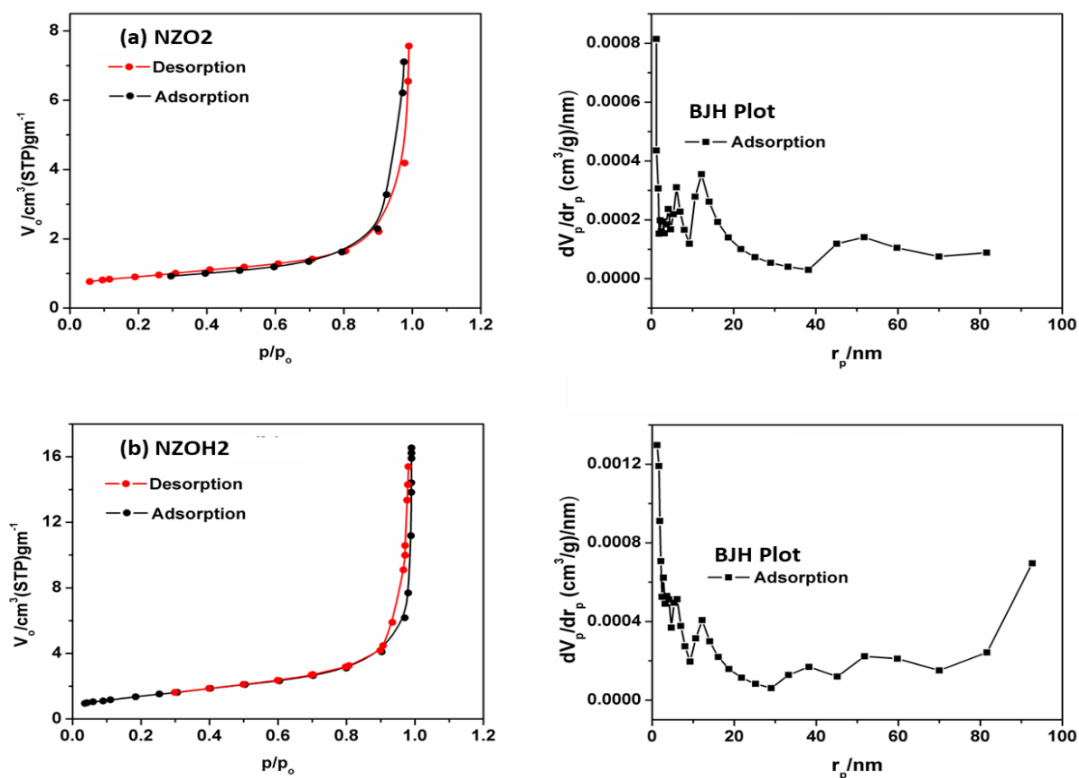


Figure 3.6: BET adsorption-desorption isotherms along with BJH plots for (a) NZO2 and (b) NZOH2.

Table 3.4: Material code, surface area, total pore volume and mean pore diameter values.

Material code	BET Specific surface area(m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter(nm)
ZnO	1.92	0.019365	40.39
SZO2	3.48	0.018159	20.87
HZO2	3.34	0.017024	18.36
DZO2	3.72	0.012801	13.78
NZO1	3.56	0.016416	18.45
NZO2	3.21	0.011698	14.56
NZOH1	4.67	0.014957	12.81
NZOH2	5.21	0.025295	19.41

3.8.6 Microstructural studies: SEM/TEM/EDAX/SAED

The surface morphology of the as-prepared materials by two different precursors, oxalate and oxalate-hydrazinate and doping with different metal ions was investigated by scanning electron microscopy (SEM). Figure 3.7(a,b) present the SEM images of NZO2 and NZOH2 materials, respectively. The SEM images indicated the formation of spherical-shaped nanoparticles with smooth surfaces. The particles showed cohesiveness and agglomerated to form bigger clusters. However, on close comparison, some variations in surface morphologies between the two samples. The particles of NZOH2 were slightly smaller than NZO2 with distinct grain boundaries. Hence, it can be stated that the materials synthesized via hydrazine-Nd/Zn-oxalate precursor displayed improved particle morphology and a smaller size. Such types of materials are suitable for photocatalytic activities.

In literature, it was mentioned that the precursor method of synthesis produced microstructural effects on the surface of particles, which could be beneficial for photocatalytic performance [31]. The micropores generally depend on the method of synthesis adopted and it is worth mentioning that the hydrazine method of synthesis could induce mesoporous nature in the materials, which was well supported by the surface analysis data.

On similar lines, SEM images of all samples ($M_xZn_{1-x}O$) were recorded and presented in Figure 3.8. The $M_xZn_{1-x}O$ materials exhibited similar shape, size and morphology to that of Nd-doped ZnO.

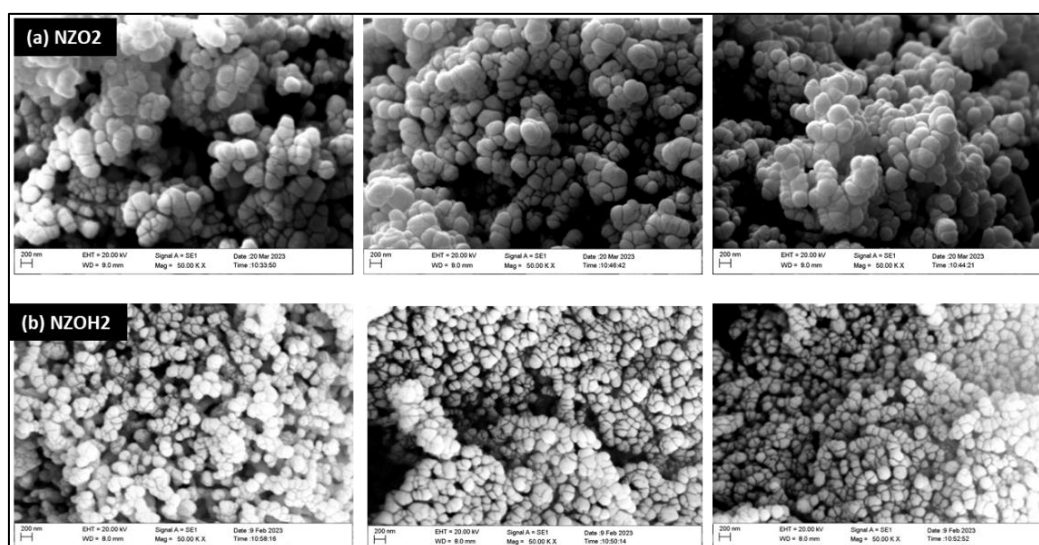


Figure 3.7: SEM images of (a) NZO2 (b) NZOH2

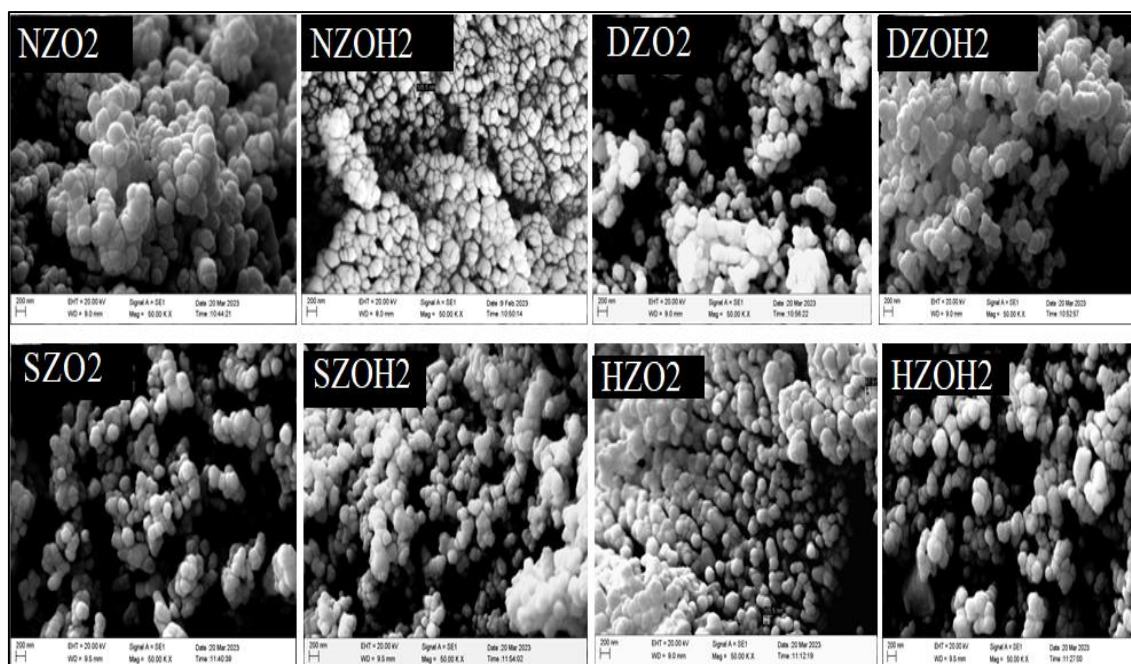


Figure 3.8: SEM images of $M_xZn_{1-x}O$, ($M=Nd/Sm/Dy/Ho$, $x = 0.1$)

Figure 3.9(a,b) shows the detailed HR-TEM micrographs of $Nd_xZn_{1-x}O$ nanomaterial (NZO2 and NZOH2) powders. The images showed that the materials were made up of tiny crystallite nano-aggregates. The crystallite size ranged from 30 – 90 nm (average size 60 nm) for NZO2, while that of NZOH2 spanned between 10 – 70 nm (average size 40 nm). The particles of NZO2 were non-uniform, irregular to squarish-shaped crystallites, integrated with other particles. On comparing, the particles prepared from hydrazinated precursors (NZOH2) showed uniform spherically shaped nano-crystallites. The ultra-high magnified images of both oxide materials revealed highly crystalline structures with well-aligned lattice plane fringes. The inter-planar spacing measured for both materials was ~ 0.281 nm, which corresponded to the (100) crystal plane of the hexagonal wurtzite ZnO structure [32]. Similar explanation is valid for other nanomaterials examples: NZO2, SZO2 and DZO2 and the HR-TEM images are shown in Figure 3.10.

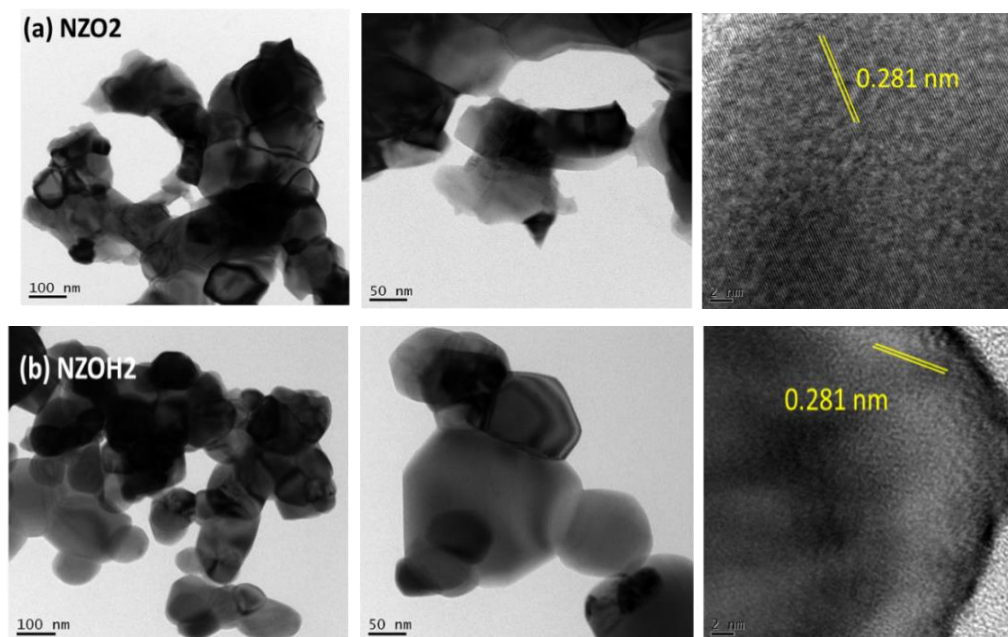


Figure 3.9: TEM images (a) NZO₂ and (b) NZOH₂

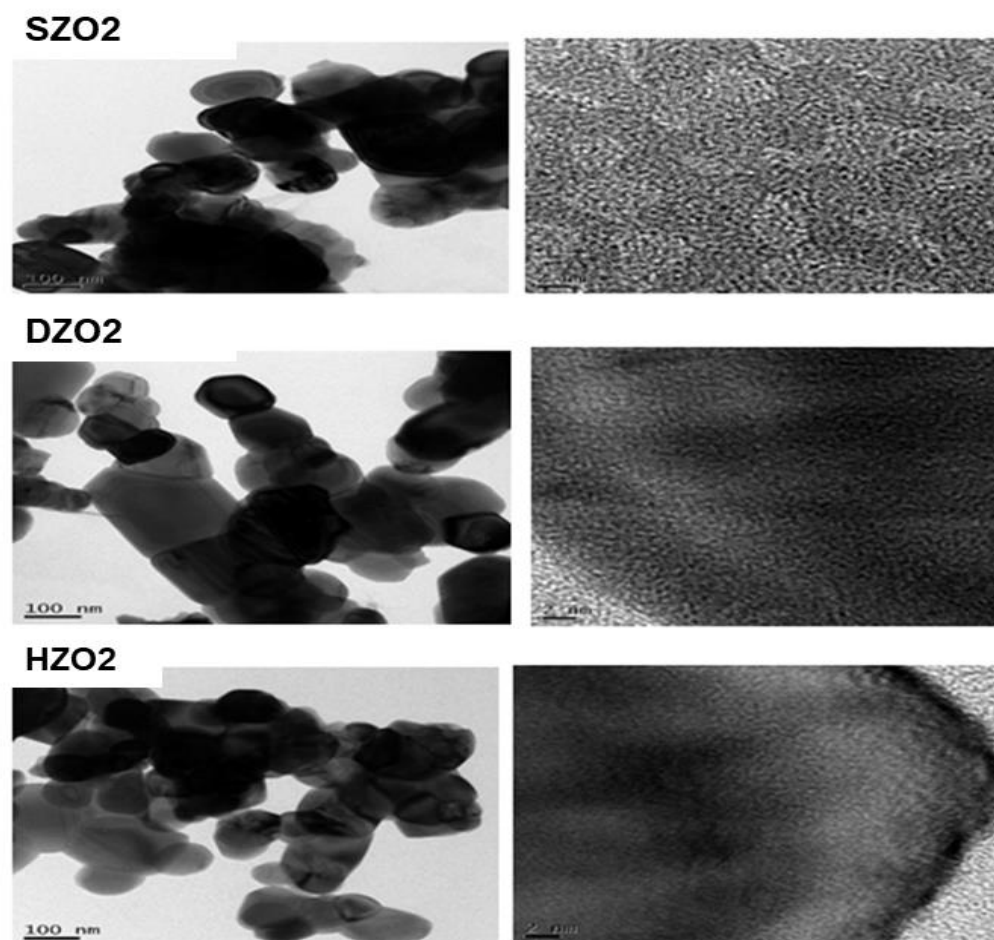


Figure 3.10: TEM images (a) SZO₂ (b) DZO₂ and (c) HZO₂

The particle size distribution histograms were also plotted based on TEM images, shown in Figure 3.11(a,b). The average particle size estimated for NZO₂ and NZOH₂ was ~60 nm and ~40 nm, respectively, with a fairly narrow distribution [33].

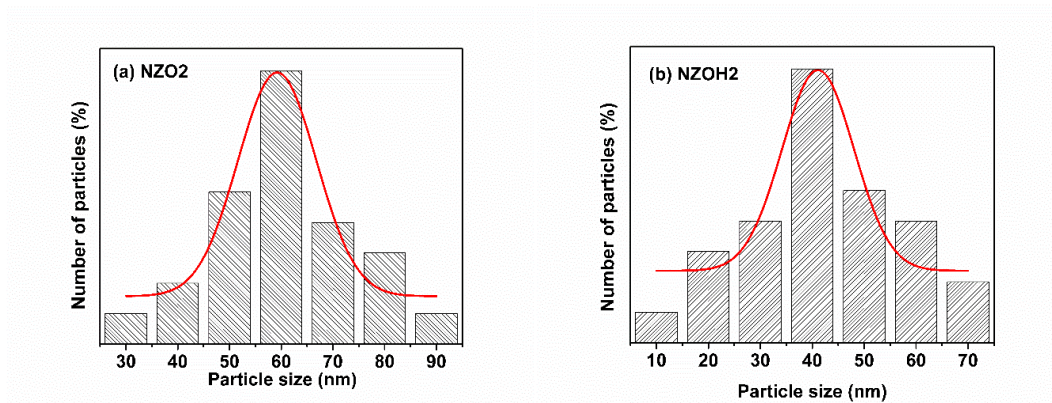


Figure 3.11: Particle size distribution of (a) NZO₂ and (b) NZOH₂.

The selected area electron diffraction (SAED) patterns of NZO₂ and NZOH₂ were captured from the TEM under dark field diffraction mode. The SAED patterns shown in Figure 3.12 (a,b) were indexed to the (hkl) values and revealed wurtzite nano-crystalline structure for both materials. On close examination, the NZOH₂ nanomaterial exhibited well-aligned crystal growth with uniform lattice spacing. The SAED patterns for the NZO₂ exhibited weak crystalline diffractions pertaining to first, second, and third-order facets of the nanocrystal diffraction planes [7].

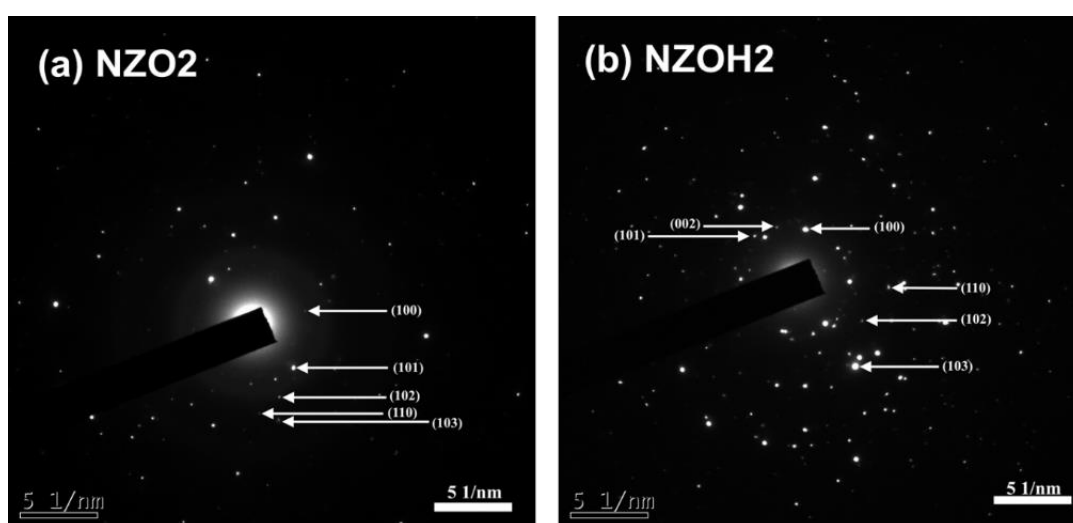


Figure 3.12: SAED patterns of (a) NZO₂ and (b) NZOH₂

The EDAX spectra of the $M_{0.1}Zn_{0.9}O$ samples are presented in Figure 3.13(a,b,c,d), respectively. Considering the X-ray emission energy positions, the expected Zn, O and M elements peaks were identified and marked. The mapped elemental composition was in line with the XPS data, which proved the incorporation of M in the ZnO lattice. The prominent peak at respective BE (keV) of the elements confirmed the Zn, O and the dopant (M) element in the material under investigation [34]. The low-intensity multiple peaks originating from the M-dopants in ZnO were also identified. Table 3.5 presents the compiled data of EDAX analysis, showing the elemental composition and their approximate atomic and weight percentages.

Table 3.5: Elemental composition by EDAX showing the weight (%) and atomic (%) for $M_xZn_{1-x}O$ samples.

Sample	Element	Weight (%)	Atomic (%)
NZO2	Zn	88.62	66.70
	O	10.76	33.09
	Nd	0.62	0.21
SZO2	Zn	8.13	64.64
	O	11.52	34.93
	Sm	1.35	0.44
DZO2	Zn	92.24	76.63
	O	6.79	23.05
	Dy	0.97	0.32
HZO2	Zn	88.55	67.35
	O	10.40	32.33
	Ho	1.05	0.32

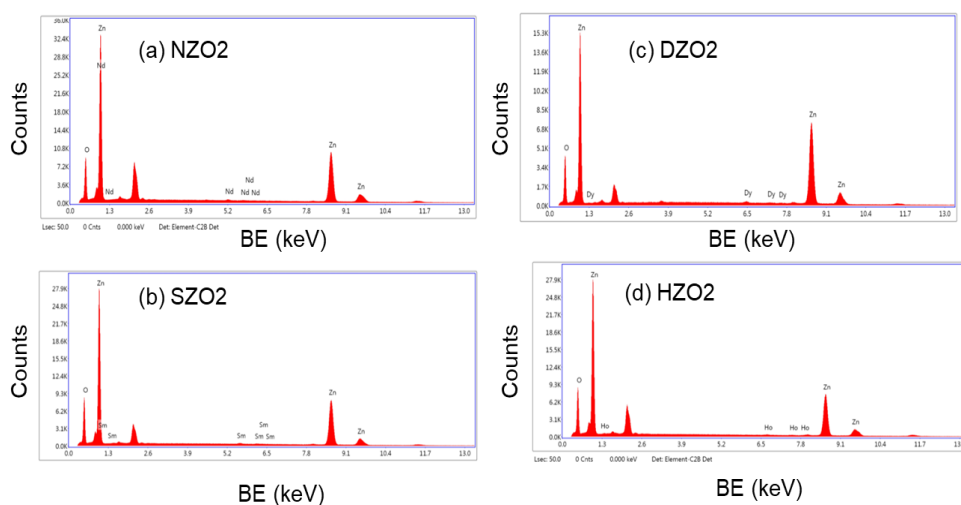


Figure 3.13: EDAX spectra of (a) NZO2 (b) SZO2 (c) DZO2 and (d) HZO2

3.8.7 X-ray photoelectron spectroscopy studies

The elemental identification, chemical bonding and oxidation states of the present in $M_xZn_{1-x}O$ material were investigated by X-ray photoelectron spectroscopy (XPS). Figure 3.14(a,b,c,d) shows the XPS survey scan of $M_xZn_{1-x}O$ ($M=Sm, Nd, Ho, Dy$), which identified the elemental composition peaks (Zn, O and Sm/Nd/Ho/Dy) present in the material. Figure 3.15a represents the survey scan of NZOH2 material, which clearly shows elemental peaks of Nd, Zn, and O along with the C peak as a reference. The high-resolution XPS spectrum of the Zn 2p is depicted in Figure 3.15b. The characteristic deconvoluted dual peaks with binding energy (BE) 1022 eV and 1045 eV were assigned to Zn 2p_{1/2} and Zn 2p_{3/2}, respectively, with a splitting difference of 23 eV, which confirmed the Zn²⁺ ions of ZnO [35]. Figure 3.15c shows the O 1s peak fitted by Lorentzian-Gaussian resolved into two types of O peaks centered at ~530 eV and ~532 eV. These peaks were assigned to O²⁻(lattice) and O²⁻(oxygen vacancies) respectively present in Zn-O bonds of ZnO [36]. The presence of two peaks corroborated the existence of different kinds of O²⁻ states in the NZOH2. This proved that the V_O were present on the surface of the material. It was interesting to note that the surface oxygen-deficient contents were higher than usual, which may be attributed to the hydrazination effect. The oxygen-deficient materials are known to influence the visible PL emission light. Figure 3.15d shows the deconvoluted high-resolution XPS spectra peaks for Nd 3d, which resolved into two peaks corresponding to Nd_{3/5} and Nd_{3/2} positioned at BE, 1005 eV and 989 eV, respectively. These values were in agreement with the reported values for the Nd³⁺ ion in ZnO [37]. Hence, doping of RE metal ions in the ZnO was confirmed by XPS analysis.

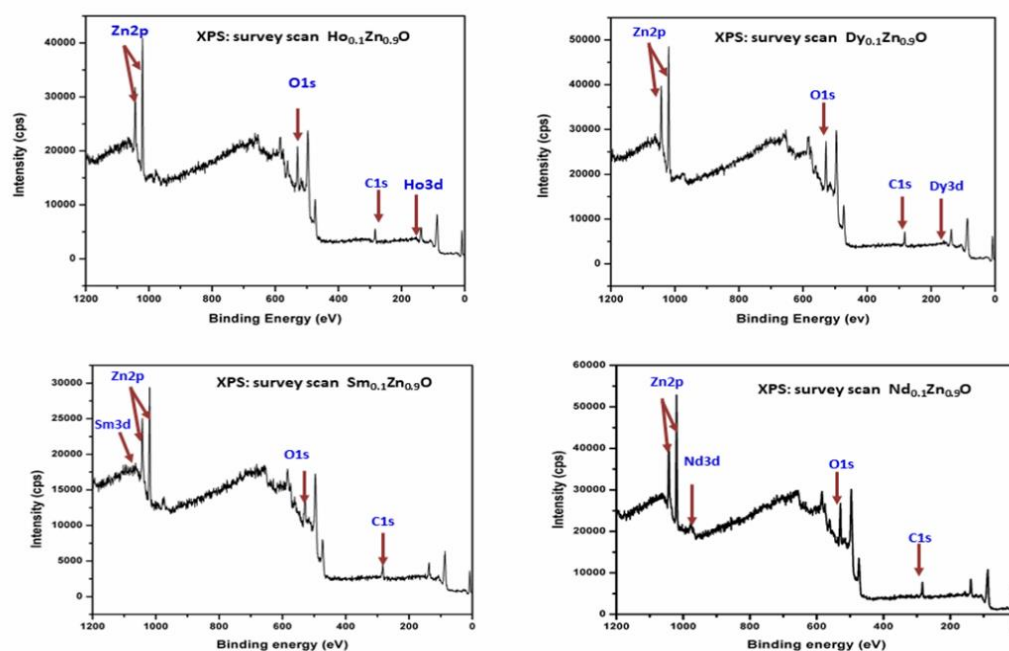


Figure 3.14: XPS Survey scan of $M_xZn_{1-x}O$ samples

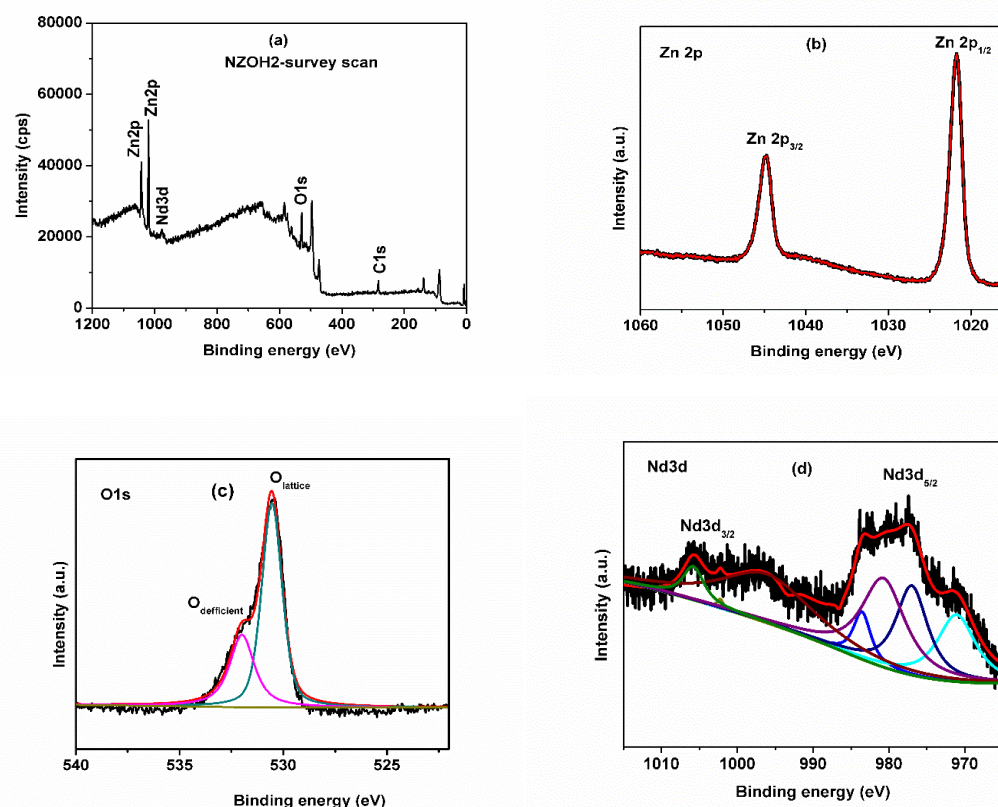


Figure 3.15: XPS spectra of NZOH2 (a) Survey scan (b) HR-XPS: Zn 2p (c) O 1s (d) Nd 3d.

3.8.8 Raman studies

Phase identification and purity of the materials were established by Raman spectroscopic analysis. The overlaid Raman spectra of NZO2, SZO2, DZO2 and HZO2 are displayed in Figure 3.16. All spectra showed prominent six bands assigned to the first-order optical modes of ZnO belonging to the hexagonal wurtzite structure with space group C_{6v}^4 . The typical six peaks of ZnO were observed; E(low)2, E(high)2, A(TO)1, A(LO)1, E(TO)1, and E1(LO) with no additional M_2O_3 impurity peaks, which proved that there is no secondary phase in the materials. There existed a fairly good correlation between the Raman and XRD data for all materials. The two major peaks intensities at 103.81 cm^{-1} and 440.74 cm^{-1} were attributed to E(low)2 and E(high)2, while three low-intensity broad peaks at 384.29 , 417.85 and 587 cm^{-1} were associated with A(TO)1, E(TO)1, and E(LO)1 respectively [38]. The E(low)2, and E(high)2 were assigned to the vibration of O and Zn atoms in ZnO. The sharp and intense peaks indicated highly crystalline materials. These peak intensities decreased with an increase in M^{3+} doping concentration in ZnO. Other weak intensity peaks in the spectra were due to second-order optical modes caused by the multi-phonon effect. The broadband at $540\text{--}670\text{ cm}^{-1}$ was attributed to the intrinsic defects present in ZnO. The introduction of M^{3+} in Zn^{2+} positions can cause crystal lattice strains and contribute to modified energy levels in $M_xZn_{1-x}O$ nanomaterials.

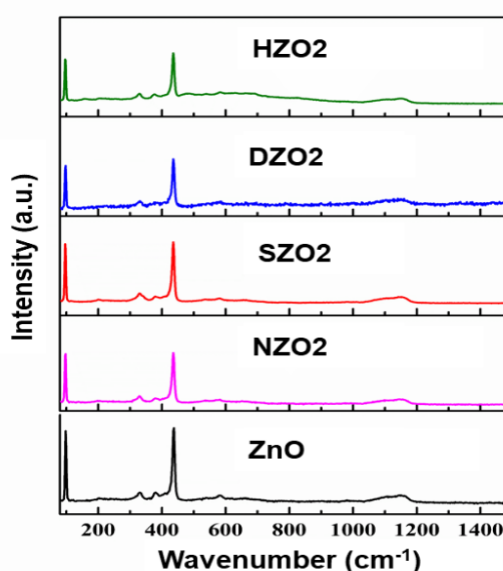


Figure 3.16: Raman spectra of ZnO, NZO2, SZO2, DZO2 and HZO2 materials.

To summarise the characterization data, XRD confirmed that the M^{3+} doped ZnO materials synthesized by the hydrazine method were of a pure crystalline phase. The surface analysis revealed that the materials were mesoporous. The smooth, spherical, narrow particle size distribution of nanomaterials was attributed to the exothermic thermal decomposition of the hydrazinated precursor. The EDAX, XPS and Raman confirmed the doping of M^{3+} caused oxygen vacancies (V_O) in ZnO.

3.8.9 UV-visible light absorption and band gap energy

The light absorption and band gap energies of $M_xZn_{1-x}O$ materials prepared by oxalate and oxalate-hydrazinate precursors were evaluated using UV-visible diffuse reflectance spectroscopy (DRS). Figure 3.17(a,b,c,d) presents the absorption spectra of all samples in the range of 250 to 500 nm. The materials showed absorbance in the UV range of 250 to 370 nm, attributed to the typical intrinsic band gap absorption of ZnO. On activation by light energy, the electrons from the VB are excited to the CB (transition: $O2p$ to $Zn3d$)[39]. The samples NZOH1 and NZOH2 displayed marginal improvement in visible light absorption capability compared to NZO1 and NZO2 samples. The minor noticeable improvement in visible light absorption by the materials could be attributed to the small addition of Nd^{3+} dopant and hydrazine-based synthesis. Another probable reason could be attributed to the nature and concentration of crystal defects introduced into the ZnO. Therefore, we report that the hydrazine precursor method can induce a red band-edge shift in ZnO. The Nd^{3+} ion doping introduced new energy levels below the CB of ZnO [40]. While zinc and V_O are believed to generate energy levels above the valence band of ZnO. Such intricate deep levels play a crucial role in defining the electronic transitions and band gap energy.

The material band gap energies (E_g) were estimated using the band gap equation 3. The E_g values for MZO1, MZO2, MZOH1, and MZOH2 are compiled in Table 3.6. These values indicated that the E_g was reduced with the M^{3+} doping concentration level. Moreover, E_g was reduced to a greater extent with the hydrazination method of fabrication. Such reduced E_g can facilitate a large number of band-to-band electronic transitions (VB $\rightarrow$ CB), resulting in several electron-hole pairs. This could be better explained based on the crystallite size, morphology, and defect concentration. The PL study is an efficient way to investigate the defects and emission characteristics of the materials.

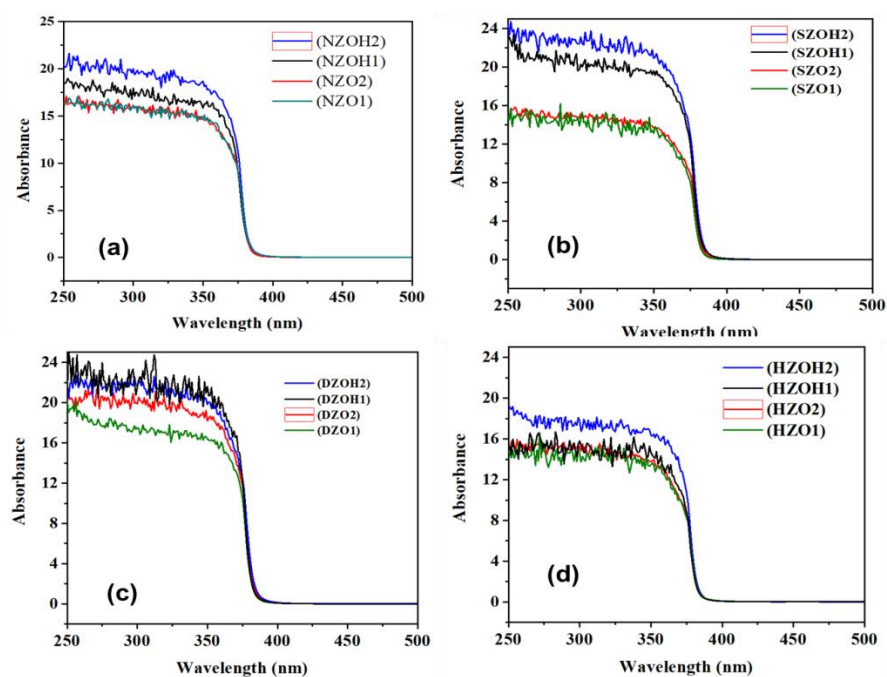


Figure 3.17: UV-visible absorption spectra of $M_xZn_{1-x}O$ where [M = (a) Nd (b) Sm (c) Dy (d) Ho and $x = 0.05$ and 0.1] materials.

Table 3.6: Compilation of band gap values of $M_xZn_{1-x}O$ materials

Sample	Synthesized from Oxalate		Synthesized from Oxalate hydrazinate	
	X=0.05	X=0.1	X=0.05	X=0.1
$Nd_xZn_{1-x}O$	NZO1	NZO2	NZOH1	NZOH2
	3.289	3.280	3.271	3.263
$Sm_xZn_{1-x}O$	SZO1	SZO2	SZOH1	SZOH2
	3.280	3.271	3.263	3.254
$Dy_xZn_{1-x}O$	DZO1	DZO2	DZOH1	DZOH2
	3.289	3.289	3.271	3.263
$Ho_xZn_{1-x}O$	HZO1	HZO2	HZOH1	HZOH2
	3.271	3.263	3.254	3.246

Figure 3.18 presents the trend in band gap energy values for all the $M_xZn_{1-x}O$ materials. With the increase in M^{3+} dopant concentration, 0.05 to 0.1 moles, the band gap values decrease slightly for both oxalate and oxalate hydrazinate precursor samples. This suggested that the band gap was inversely proportional to M^{3+} concentration for all $M_xZn_{1-x}O$ samples. With a larger number of dopants, the mid-gap energy levels increased, hence the E_g narrowed down. When comparing oxalate and oxalate hydrazinate samples, the E_g values consistently showed lower values for materials prepared via oxalate hydrazinate samples. This could be attributed to the extra defect levels formed during the decomposition of hydrazinated precursors. It was also noted that in the sample with different dopants, the band gap values increased and showed the trend as: $Ho_xZn_{1-x}O < Sm_xZn_{1-x}O < Nd_xZn_{1-x}O < Dy_xZn_{1-x}O$.

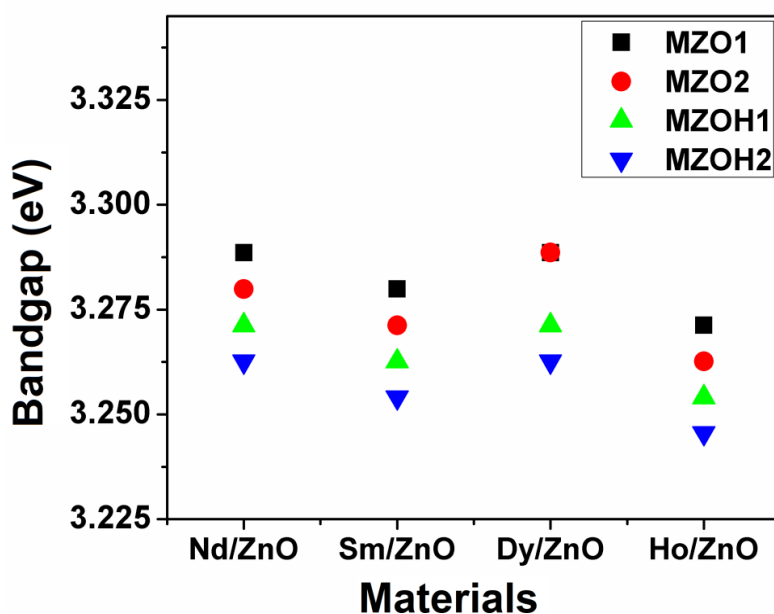


Figure 3.18: Comparative bandgap (E_g) of $M_xZn_{1-x}O$ materials.

3.9 Photoluminescence studies

The room-temperature photoluminescence (RT-PL) emission spectra of $M_xZn_{1-x}O$, ($x=0.05$ and 0.1) nanomaterials were recorded after activation with laser light of wavelength, $\lambda_{exc} = 298$ nm (Energy = 5.28 eV). Figure 3.19 represents the emission intensities plotted on the y-axis against the emitted wavelength on the x-axis for all materials. In general, the spectra showed two bands, the first broad emission band

extending from UV to the near visible region, ranging from 370 – 430 nm. This band had lower intensities and was associated with near-band-edge (NBE) emission of ZnO. The NBE was attributed to the rapid electronic recombination of electron-hole pairs with the release of energy in the form of UV light. The second broad emission band, with relatively higher intensities than NBE, was attributed to the deep-level-emission (DLE) effect [41]. The DLE emission band consisted of the four main emission peaks centred at $\lambda = 445$ nm (2.79 eV)-violet colour (weak), 468 nm (2.65 eV)-blue colour (strong), 483 nm (2.57 eV)-Green colour (weak) and 495 nm (2.51 eV)-green colour (weaker). These lines appeared in the visible region mostly due to an interstitial oxygen defect (V_O). The origin of V_O in the samples was most likely formed during the synthesis process. Hydrazine-based materials exhibited higher PL emission, which may have generated a large amount of V_O . The visible range PL intensities warranted special attention because they provided vital information regarding the band gap, electronic configuration and electronic mobility within the material. It has been reported that such alterations in electronic levels of ZnO are crucial and beneficial in photosensors, photocatalysis, photoelectrochemical water splitting hydrogen production, degradation of harmful chemicals, etc. [42].

Several types of imperfections are introduced in ZnO due to the doping of M^{3+} ions in the fabricated materials. Among various imperfections, structural defects such as V_O and V_{Zn} in the ZnO lattice were of prime importance [43]. Thus, doping M^{3+} in ZnO resulted in higher defect concentration and was directly proportional to the level of doping. The probable reason for defect formation in ZnO could be connected to the distortions or stress caused by doping M^{3+} ions with different ionic radii and local charges in the host ZnO crystal structure.

The origin of the second visible broad band is attributed to the structural defects or/impurities, caused by M^{3+} impurity ions incorporated in ZnO. The DLE imparts violet-blue luminescence colour in the range 440-468 nm (2.81-2.65 eV) plausibly due to the transition of trapped electrons in the V_{Zn} and Zn_i to the valence band. The green luminescence band, ranging from 475-500 nm (2.61-2.48 eV) originates probably due to the radiative recombination of electrons from the M^{3+} energy levels to the holes in the valence band or deep-level energy levels created by V_{Zn} and V_O . The weaker green band at 490 nm (~ 2.51 eV) is attributed to Zn vacancies; however, the possibility of the origin of green-band emission due to V_O cannot be ruled out. The M^{3+} acts as an electron trap and thus reduces the recombination of photogenerated electron-hole pairs. This observation

was corroborated by the enhancement of PL intensities in the case of higher doping concentrations of M^{3+} in ZnO. The electrons from the host ZnO were transferred to M^{3+} energy levels, which enhanced visible light PL emission intensity. The M^{3+} acted as an activator, thus improving visible PL spectra [44]. This hypothesis was proved by the lower PL intensity in the case of $M_{0.05}Zn_{0.95}O$ compared to $M_{0.1}Zn_{0.9}O$, although the spectral pattern remains identical. This was experimentally proven by the UV-visible DRS studies, where absorbance was directly proportional to the M^{3+} concentration in ZnO. There was a corresponding energy transfer between the CB of ZnO and M^{3+} mid-gap energy levels. Hence, the larger the number of Zn ions replaced by Nd in the ZnO, the more intense the PL emission. Also, hydrazinated samples MZOH1 and MZOH2 showed enhanced PL emission intensities compared to their un-hydrazinated counterparts, MZO1 and MZO2; the reason for such observation can be linked to defect-related emissions.

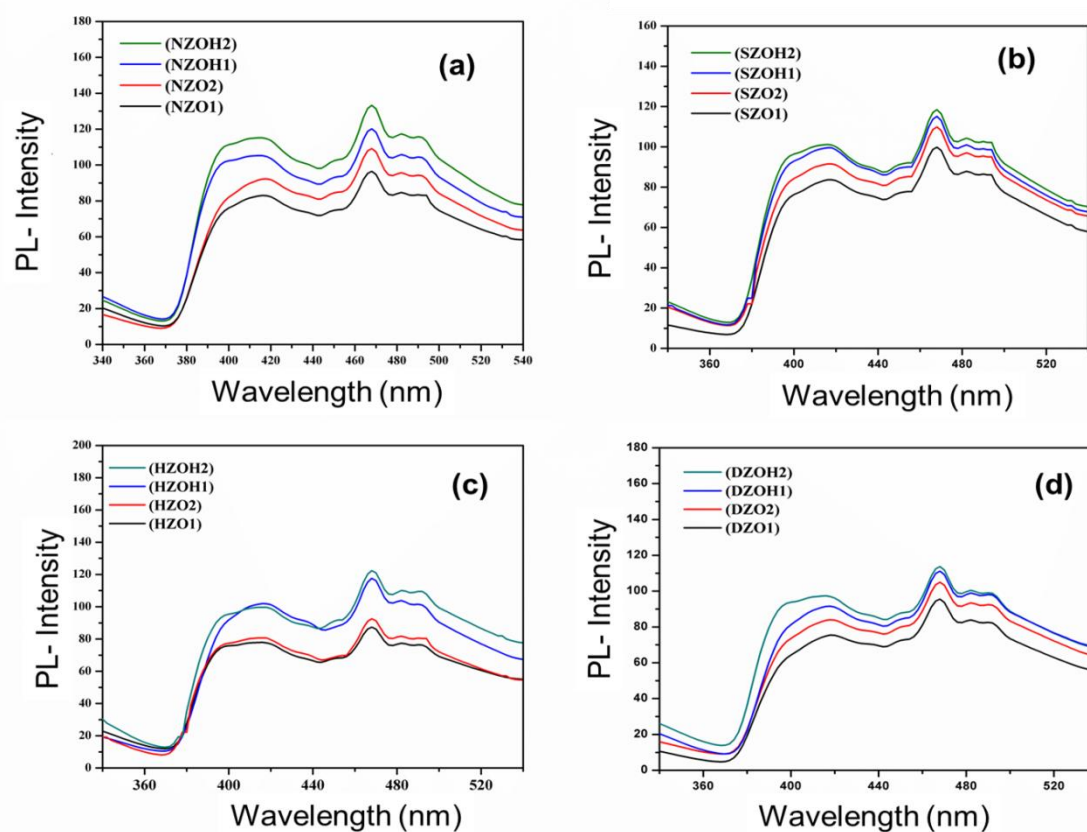


Figure 3.19(a,b,c,d): PL emission spectra for MZO1, MZO2, MZOH1 and MZOH2 materials

Figure 3.20(a,b) depicts the detailed analysis of the PL spectra of NZO1, NZO2, NZOH1 and NZOH2 samples at ~ 468 nm, which is responsible for the blue colour

emissions. Figure 3.20c presents the observed trend in blue-PL emission intensities as follows: NZO1 < NZO2 < NZOH1 < NZOH2. The blue lines revealed the evolution of V_O due to V_{Zn} , when Zn^{2+} ions were replaced by Nd^{3+} in the ZnO lattice. The blue-PL intensity of hydrazinated nanomaterials was comparatively higher than the un-hydrazinated nanomaterials. The probable reason for such enhanced PL intensity could be associated with the uniform particle shape, reduced particle size, superior morphology and a large number of V_O in materials. The TEM images also confirmed that the NZOH1 and NZOH2 had better control of the shape, size and morphology. The blue-peak intensity of NZOH2 was almost 1.5 times higher compared to NZO2. The blue emission peak width of the synthesized materials, calculated based on full width at half maxima, showed a much sharper peak of ~ 15 nm [45]. The sharper band widths depend on the synthesis process and indicate superior optical properties of crystalline solids [46]. The enhanced blue emission with higher Nd^{3+} doping concentration and hydrazinated method of synthesis implied a high degree of crystallinity and uniform particle size of the nanomaterials with a higher number of V_O .

Figure 3.20d depicts the proposed mechanism, which can provide more insights regarding the various transitions / PL emissions involved in the samples. It is well known that the UV emission was mostly assigned to the band-to-band rapid electronic recombination of electron-hole pairs. The violet-blue band with the highest intensity were assigned to various transitions from the conduction band of ZnO and Nd^{3+} shallow impurity levels to the valence band and the deep V_{Zn} level. The green PL peaks were attributed to transitions from the CB and Nd^{3+} level or zinc interstitial levels Zn_i to V_O .

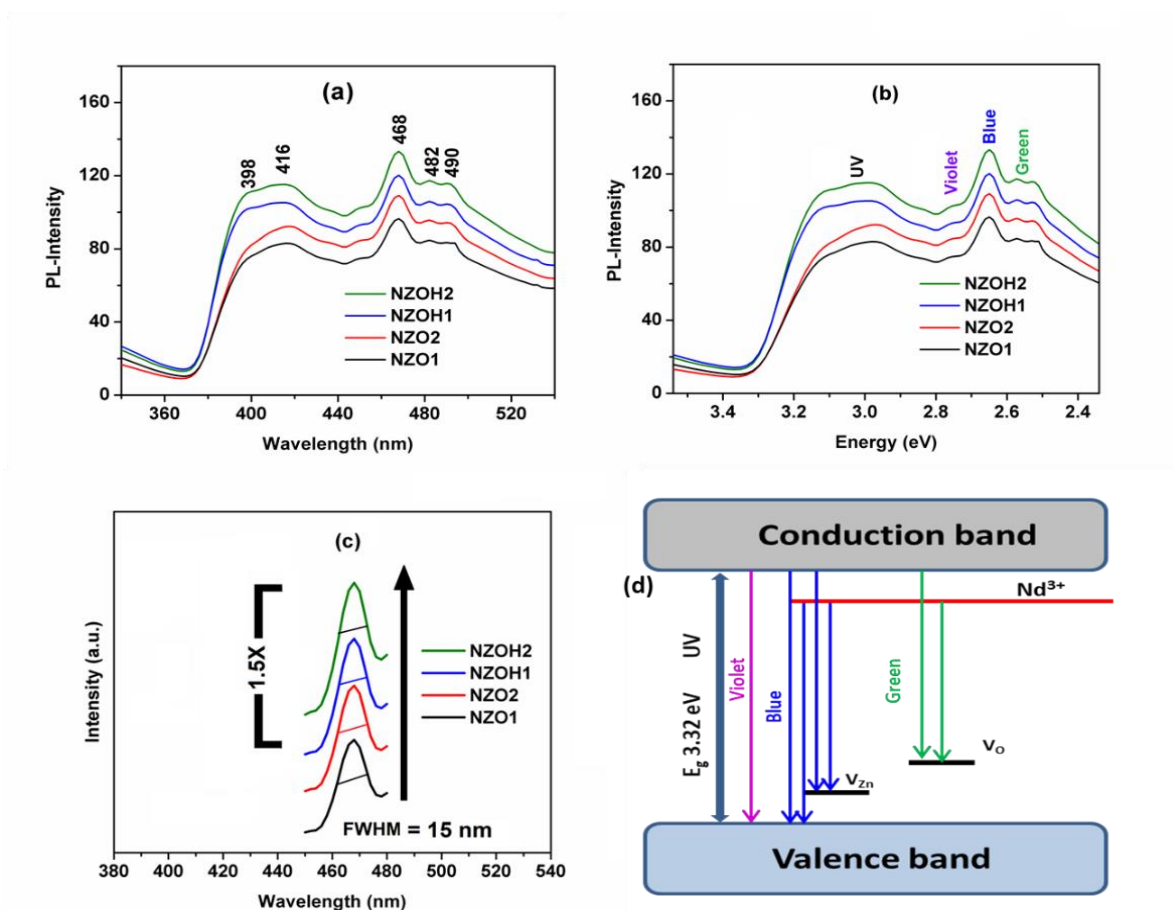


Figure 3.20: PL emission spectra of NZO1, NZO2, NZOH1 and NZOH2 (a) PL-intensity versus emitted wavelength (b) PL-intensity versus energy (c) FWHM of blue PL peak at $\lambda=468$ nm (d) Mechanism showing various electronic transitions in $M_xZn_{1-x}O$.

The oxides obtained from hydrazinated oxalate precursor showed approximately 1.5 times higher blue PL intensities compared to oxides from oxalate precursors. Table 3.7 shows the compilation of various doped ZnO systems and their blue-light emission sources. When compared with reported literature, the current material presents the following advantages over others (1) Simple and inexpensive method of synthesis of Nd-doped ZnO materials. (2) Nanosized narrow particle distribution (3) High-intensity blue-PL emission at room temperature, and finally (4) Blue-emitted light possessed narrow bandwidth of ~ 15 nm.

Table 3.7: Compilation of PL emissions due to different elements doped ZnO.

Blue-Green Emission-Peak	Peak position (nm)	Dopant added in ZnO	PL emission due to	Reference
Blue	450	Cu ⁺	Zn _i	[47]
Blue	438-462	Gd/Nd/Sm	V _{Zn} , V _o , Zn _i , O _i , Zn(O _{Zn})	[48]
Blue	430	Nd ³⁺	Zn _i	[8]
Blue	493	Tb ³⁺	V _O , V _{Zn} , Tb ³⁺ , Zn _i	[49]
Blue	492	Ni ²⁺	V _O , V _{Zn} , O _i , Zn _i , Ni ²⁺	[50]
Blue	465 (FWHM ~15 nm)	Nd ³⁺	V _O , V _{Zn} , Nd ³⁺ , Zn _i	Current study

3.10 Dielectric studies

The dielectric constant (ϵ) values of NZO2 and NZOH2 were plotted as a function of the log frequency scale in MHz at room temperature, as depicted in Figure 3.21. The nanomaterial powders were compacted into a disc form (1 cm diameter and 0.3 cm thickness) and then loaded without sintering into a dual-probe dielectric measuring device. The dielectric constant (ϵ) value was calculated using the equation 8 [51],

$$\epsilon = Cl / \epsilon_0 A \quad (8)$$

Where C is the capacitance, l is the thickness, A is the area of the cross-section of the pellet, and ϵ_0 is the dielectric relaxation of the sample. From the plots, it was evident that, as the frequency values were raised from 1 to 3 MHz, both materials showed a rapid decrease in ϵ value. At higher frequencies between 3 to 10 MHz, the ϵ was independent of changes in frequency and remained constant. Such dielectric behaviour was due to space charge polarization of the material, which can be explained based on the Maxwell–Weigner model [52]. According to this model, it is assumed that the dielectric medium consisted of well-conducting grains and poorly conducting grain boundaries. The NZOH2 material showed slightly lower ϵ values when compared to values of NZOH at ~ 1 MHz frequency. The explanation for this observation could be linked to the difference in morphology of particles in both samples. Since the particles of NZOH2 were spherical, hence demonstrated better particle packing and contact, compared to the NZO2 sample,

which had irregular shapes and had poor packing and contact between the particles. Also, the lowering of dielectric constant values caused by various defects formed during the synthesis of NZOH2 material cannot be ruled out.

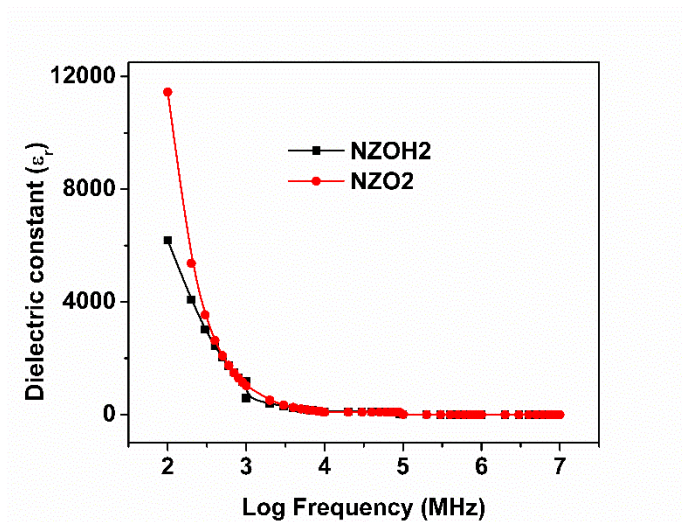


Figure 3.21: Comparative dielectric constant plots of NZO2 and NZOH2 samples

3.11 Electrical conductivity

The direct current (DC) electrical conductivity of NZO2 and NZOH2 was measured using a standard two-electrode system connected to a Keithley multimeter. The unsintered samples were compressed into a disc (diameter = 0.5 cm and thickness (l) = 0.3 cm) and then loaded into the measuring system. The probe was connected using a platinum wire with the current measuring device. The probe was inserted into the furnace, heated from 50 °C to 500 °C and the current was recorded. The conductivity values of the material were calculated and plotted against the temperature (°C). Figure 3.22 shows the conductivity plots of NZO2 and NZOH2 samples, which displayed an increasing trend with a rise in temperature from 50 °C to 200 °C and then decreased from 200 °C to 500 °C. Such a trend was observed for temperature-dependent semiconducting materials [57]. The NZOH2 exhibited slightly lower conductivity compared to that of NZO2, which was attributed to the additional defects produced by the hydrazinated precursor. The combined effect of Nd^{3+} and defects (V_O , V_Zn , Zn_i) in the ZnO host lattice was responsible for such behaviour. Therefore, doping increases the imperfections which facilitate the formation of grain boundary defect barriers, leading to blockage in the flow of charge carriers. This in turn, decreases the conductivity of the system on doping. A similar observation was also

reported by other researchers, wherein with increased metal ion dopant concentration (Er) in ZnO, the resistivity in Er-doped ZnO nanocrystalline film increases as compared to pure ZnO. Such a rise in resistivity was attributed to the reduced charge carrier concentration caused by V_O and impurity scattering effects due to excess metal ion dopants in ZnO [42].

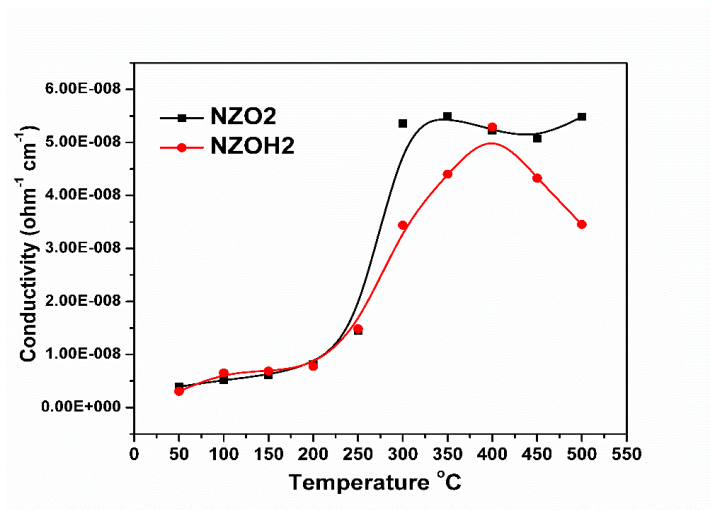


Figure 3.22: Conductivity recorded against the temperature scale (°C) for NZO2 and NZOH2 samples.

3.12 Correlation between structural and charge separation in photocatalyst

Characterization data indicated that the M^{3+} ions (0.05 and 0.1) were successfully incorporated into the ZnO lattice positions. The elemental states of materials were M^{3+} , Zn^{2+} and O^{2-} , additionally, possibilities of oxygen species (O^{2-}), and interstitial zinc (Zn_i) could be generated within the materials. The decreased electrical resistivity and dielectric constant values supported the fact of the high amount of V_O and other intrinsic defects produced in ZnO nanomaterials, which could be associated with the hydrazine method of synthesis. These impurities altered the optical properties and in turn, affected the photocatalytic activities. The literature reports also supported the observation higher intensity of blue PL lines was caused by V_O , V_{zn} , O_i and Zn_i [53]. The V_O in NZOH2 was believed to be formed during the exothermic decomposition of hydrazine-bonded Nd/Zn-oxalate precursor. We infer that both Zn and O vacancies enhance the PL intensities in the visible region.

Interestingly, it was observed that materials prepared with the hydrazinate method showed enhanced PL emission band intensities compared to their counterpart prepared

using oxalate precursors. Hence, hydrazinated materials showed better PL emissions compared to unhydrazinated ones. This could be explained based on the electron-hole pair recombination rate, which increased with hydrazination, thus emitting stronger PL effects. The rate of recombination may be associated with the generation of the number of deep energy levels formed due to V_{Zn} and V_o , thus accelerating the electron-hole pair recombination. Consequently, the PL intensities of hydrazinated materials increased. In this case, the unhydrazinated M-doped ZnO could be a good photocatalyst compared to hydrazinated materials.

3.13 Photocatalytic degradation activity of Rhodamine B and Red CL-5B dye

One of the potential strategies employed for the removal of harmful organic molecules and dyes from water is the degradation over photoactive inorganic materials. The poor surface reaction kinetics can be improved by doping with metal ions. The increased charge mobility and reactive species formation can enhance the degradation performance. This section describes the photocatalytic activities of the prepared materials using Rhodamine B (model dye) and Red CL-5B dye (textile industrial dye).

3.13.1 Effect of catalyst quantity

Catalyst loading is one of the important parameters which can have a profound impact on the photocatalytic activity. The overall rate of dye degradation is significantly altered by the concentration of catalyst during the photocatalytic reaction. The number of active sites and the charge species generated are directly proportional to the amount of photocatalyst present in the reaction vessel. However, catalyst concentration above a certain optimum level can have a negative impact on the rate of reaction. Initially, the rate of degradation linearly rises with catalyst loading upto certain appropriate amount called the 'threshold limit', beyond the threshold limit, the rate may start decreasing, the reason could be, at higher concentrations agglomeration of catalyst particles can occur and also the light scattering effect increases with the rise in turbidity. Another reason could be decreases in light penetration, hence hampers the photoexcitation of the catalyst surface.

Figure 3.23 displays the graphs of % degradation versus time interval for different amounts of catalyst used for the photodegradation activity. In this study, a varying amount

of SZO2 photocatalyst was weighed and added to the reaction vessel. All other experimental parameters were kept constant. Weighed and transferred 80, 90, 100, 110 and 120 mg of photocatalyst and performed degradation studies. The % degradation activity profiles were plotted against the different time intervals. From the graphs, it was obvious that initially the rate increased and then decreased with photocatalyst loading. The observed trend in rate of reaction was $80 \text{ mg} < 90 \text{ mg} < 100 \text{ mg} > 110 \text{ mg} > 120 \text{ mg}$. Hence, from the trend, it was confirmed that 100 mg of catalyst was the optimum quantity (threshold limit) of photocatalyst required to achieve the highest degradation efficiency.

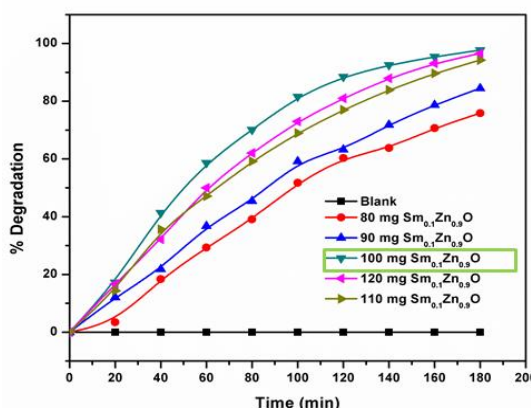


Figure 3.23: Effect of catalyst concentration on the % degradation efficiency

The higher catalyst loading decreases the rate of reaction than such issues can be tackled by coating or supporting the photocatalyst on the surface of glass tubings through which the dye solution could be passed continuously and exposed to light energy. Alternately, the photocatalyst can be coated on to a suitable substrate to form thin film over which dye solution can be passed and exposed to UV or sunlight for degradation activity [54].

3.13.2 Effect of pH

The pH of the dye solution also impacts the photocatalytic activity. In an acidic environment, the ZnO is positively charged and therefore adsorbs negatively charged organic dye molecules on its surface. In such cases, the photoactivity increases in acidic conditions as compared to basic conditions. From Figure 3.24, it was evident that the pH 10 (basic) showed maximum photoactivity, while the least activity was noted at neutral ~pH 6. The acidic pH2 also showed lower activity, however, increased with the rise in pH

values upto pH10. The trend in degradation efficiency was $\text{pH}6 < \text{pH}2 < \text{pH}4 < \text{pH}8 < \text{pH}10$. The actual pH observed for the Rh B solution was weakly acidic, pH 4.5. Although pH10 showed maximum efficiency, due to its high alkalinity, therefore not environmentally feasible to adopt, and hence not recommended for degradation studies. Hence, all the studies were carried out at as such pH 4.5 and all other parameters were kept constant.

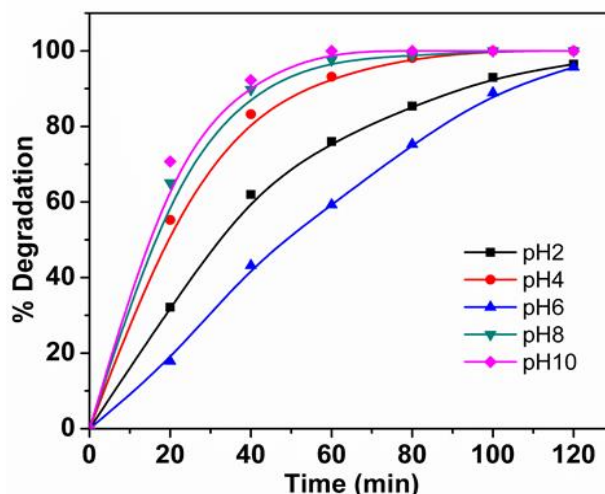


Figure 3.24: Effect of pH on the % degradation efficiency of catalyst.

3.13.3 Effect of $\text{M}_x\text{Zn}_{1-x}\text{O}$ catalyst

Different types of photocatalysts are generally applied to check the performance of the dye degradation. The catalyst that exhibits the highest activity is mostly preferred and suitable for photocatalysis processes. Figure 3.25 shows the influence of different photocatalysts on the degradation of Rh B dye on the illumination of UV light. The % degradation profiles against time intervals for all synthesized $\text{M}_x\text{Zn}_{1-x}\text{O}$ photocatalysts were plotted and compared. From the profiles, it was evident that the highest catalytic activity was exhibited by $\text{Ho}_x\text{Zn}_{1-x}\text{O}$, followed by $\text{Sm}_x\text{Zn}_{1-x}\text{O}$, $\text{Dy}_x\text{Zn}_{1-x}\text{O}$, and least by $\text{Nd}_x\text{Zn}_{1-x}\text{O}$. For comparative purposes, the minimum activity was demonstrated by pure ZnO. The blank experiment without a photocatalyst showed negligible degradation in UV light. This trend was attributed to the formation of mid-gap energy levels due to metal ion doping in ZnO. The main reasons for the different % efficiency could be linked to the type of metal ion doped in ZnO, which could be assigned to the efficient (e^- - h^+) charge separation by M^{3+} ions. Dy and Nd ions acted as a recombination center for electrons and

holes, which resulted in the charge carriers recombining before they reached the surface of the photocatalyst. Therefore, the photocatalytic activity was retarded with doping of certain metal ions.

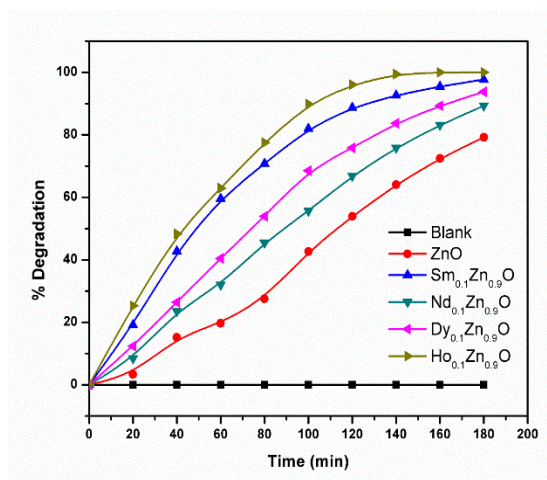


Figure 3.25: Effect of type of catalyst (MZO2) on the % degradation efficiency

3.13.4 Photocatalytic degradation studies of textile industry Red CL 5B dye

Ho (0.1 moles) doped ZnO was the most active material for the degradation of model Rh B dye under UV-visible light compared to other materials, mainly due to the efficient electron trapping by Ho³⁺ ions and smaller crystallite size. The % degradation in UV and sunlight for Red CL 5B dye was evaluated and plotted as shown in Figure 3.26(a,b). The % degradation reached 100 % in just 20 min in UV light, while the same in sunlight was achieved after 80 min. This indicated the reaction rate was almost 4 times faster in UV light compared to sunlight. The higher photon energy of UV light was responsible for improved degradation efficiency than compared to sunlight.

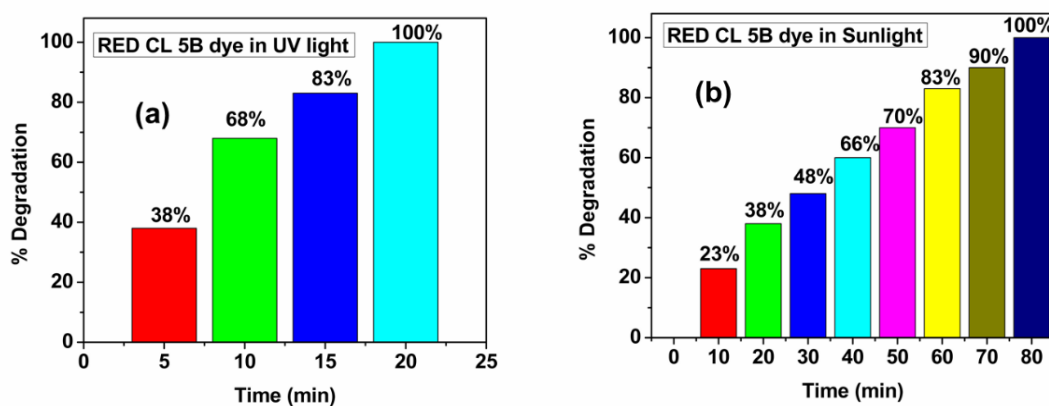


Figure 3.26: Percentage degradation efficiency of Red CL 5B dye in (a) UV light (b) sunlight.

3.14 Reactive species trapping experiment

The charge-trapping experiments were carried out to identify the reactive species generated by the photocatalyst on illumination with UV light. In the current study, a definite amount of charge-trapping agent (scavenger) was added to the reactor during the photocatalytic Rh B dye degradation. The catalyst selected was HZO2, and other experimental conditions were kept constant during the study. The photocatalytic activity was measured in the presence of individual scavengers, and the observed efficiency was noted as 50 % with 2Na-EDTA, 68 % with isopropanol (IPA), 11 % with para-benzoquinone (BZQ), while without scavengers, the efficiency was 90%(HZO2). Figure 3.27 shows the extent of photocatalytic % degradation efficiency against specific scavengers. In the presence of EDTA, IPA and BZQ, the photoactivity decreased drastically, hence confirming that the h^+ , $(OH^\bullet)$ and $(O_2^\bullet)$ radicals were major reactive species generated by photocatalysts. These reactive species were responsible for the destruction of pollutants in aqueous solution.

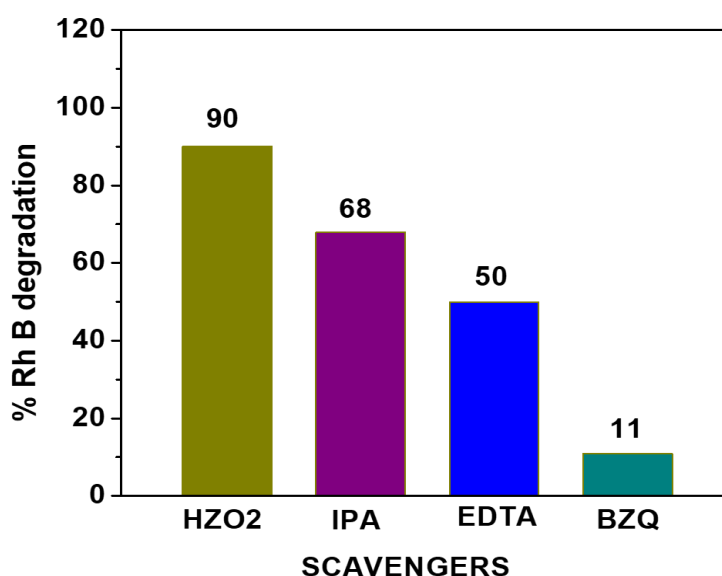
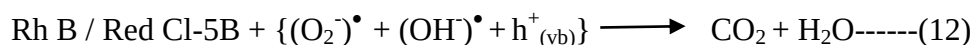
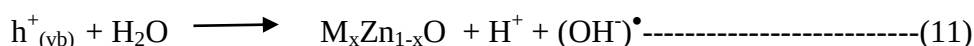
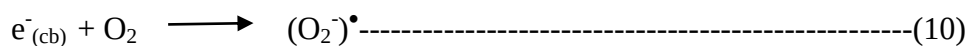
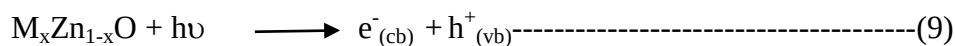


Figure 3.27: Trapping of charged species.

3.15 Proposed mechanism for photocatalytic degradation of dyes

The plausible reaction mechanism has been proposed for the photocatalysis process as follows (equation 9-12):



The plausible explanation for the observed enhanced efficiency in the dye degradation could be associated with the introduced new mid-gap energy levels by the dopants in ZnO. The 4f energy levels of M^{3+} were introduced within the ZnO E_g , below CB as charge-trapping sites, shown in the schematic diagram, Figure 3.28. The M^{3+} ions acted as an electron trap and reduced to M^{2+} ions and later transferred for reaction with the adsorbed oxygen, which generated superoxide radicals and restored them to their original M^{3+} state. Whereas the holes from the CB reacted with water and resulted in hydroxyl radicals. This type of mechanism was favoured because the dopant concentration was very low, and shallow trap states were incorporated within the ZnO band gap (E_g). The effect of dopant content on the photoactivity largely depended on the preparation methodology. Other factors which could intricately influence the performance of photocatalysts were particle size, surface area, surface hydroxyl groups, electron configuration of the dopant, defect states. In the current study, the charge separation and type of reactive species formed by the photocatalyst also supported the high efficiency of $M_xZn_{1-x}O$ nanomaterials.

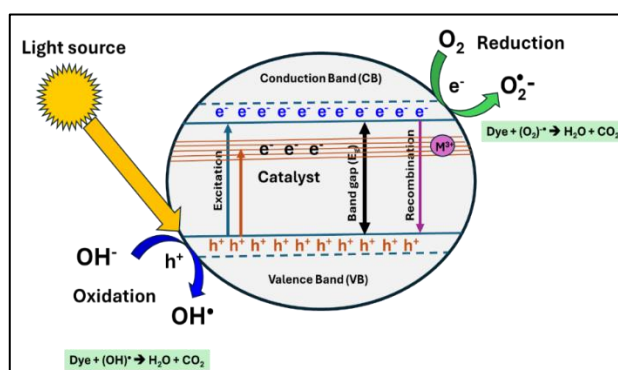


Figure 3.28: Schematic diagram showing the photocatalytic process, charge mobility, formation of reactive species and degradation of dye molecule over the photocatalyst.

3.16 LC-MS studies: Identification of Rhodamine B (Rh B) degradants

To investigate the photocatalytic degradation process of Rh B catalyzed by the $M_xZn_{1-x}O$ photocatalyst, the final time point degraded aliquot of Rh B was analyzed by the LC-MS system. Figure 3.29(a-e) shows the LC-MS data for the Rh B solution initial and final degradation time point solutions. Initially, before UV-light irradiation, the sample mainly showed a single peak at the retention time of 2 min in the LC chromatogram presented in Figure 3.29a, and the corresponding mass spectra showed a single peak due to Rh B with m/z of 443.40 that was attributed to the original undegraded Rh B molecule, shown in Figure 3.29b.

Further, the analysis of after after-degradation solution of Rh B was carried out, where the chromatogram showed multiple peaks between 0.5 to 1.2 retention time, shown in Figure 3.29c. In MS, spectrum showed a single highest intensity main degradant peak with m/z 415.30, presented in Figure 3.29d. Based on the literature survey, the m/z 415.30 corresponded to the mass spectra and chemical structures of the possible intermediate (E)-N-(6-amino-9-(2-(ethoxycarbonyl)phenyl)-2,7-dimethyl-3H-xanthen-3-ylidene)-ethanaminium as the main Rh B degradant of Rh B dye molecule. This degradant formed when Rh B was attacked by $(OH)^{\bullet}$ radical and de-ethylated to form the degradant with m/z 415. Besides the above major intermediate, a large number of small other degradants, like 8-Phenyl-3H-dicyclopenta [b, e] pyran-2,6-diylum ($m/z = 232$), adipic acid ($m/z = 146$) and maleic acid ($m/z = 117$) were also seen in MS spectra; as shown in Figure 3.29(e) [55,56]. Thus, LC-MS studies indicated that the peak due to Rh B (m/z 415.30) disappeared after 50 min degradation time point, which confirmed the complete oxidation of the Rh B molecule. The degradation of Rh B was also indicated by the decolourization of the original orange dye solution. Ultimately, it can be inferred that the Rh B was mineralized into non-polluting water and carbon dioxide molecules.

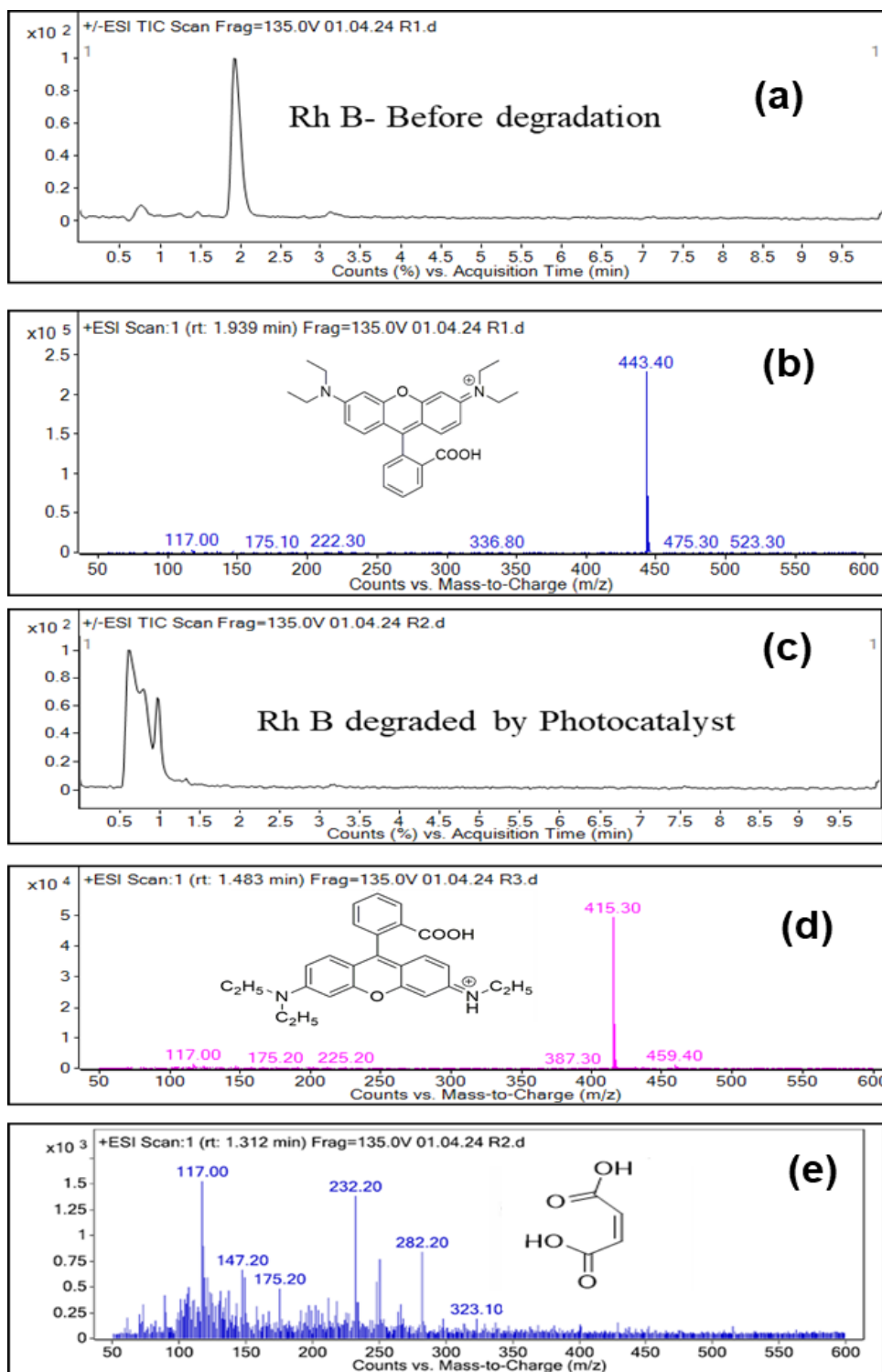


Figure 3.29: LC-MS spectrum of Rh B solution (a) Chromatogram before degradation of Rh B solution, (b) MS of Rh B before degradation, (c) Chromatogram of Rh B after degradation, (d) MS spectrum of degradant-1 with $m/z=415$ and (e) MS spectrum of degradant-2 with $m/z=117$.

3.17 Recyclability of photocatalyst

From a practical applicability point of view, the stability and recyclability of photocatalysts are very important factors. Herein, the stability of the photocatalyst was evaluated by evaluating the photocatalytic degradation efficiency using Rh B dye solution over the $\text{Ho}_{0.1}\text{Zn}_{0.9}\text{O}$ photocatalyst. The % degradation efficiency of Rh B for $\text{Ho}_{0.1}\text{Zn}_{0.9}\text{O}$ catalyst was measured and plotted against 3-cycles. From the bar graph shown in Figure 3.30, it was demonstrated that the degradation efficiency remained constant (~98 %) at the end of the final time point (20 min) over 3-cycles [57]. This indicated that the photocatalyst displayed reasonably good stability with negligible photocorrosion effect.

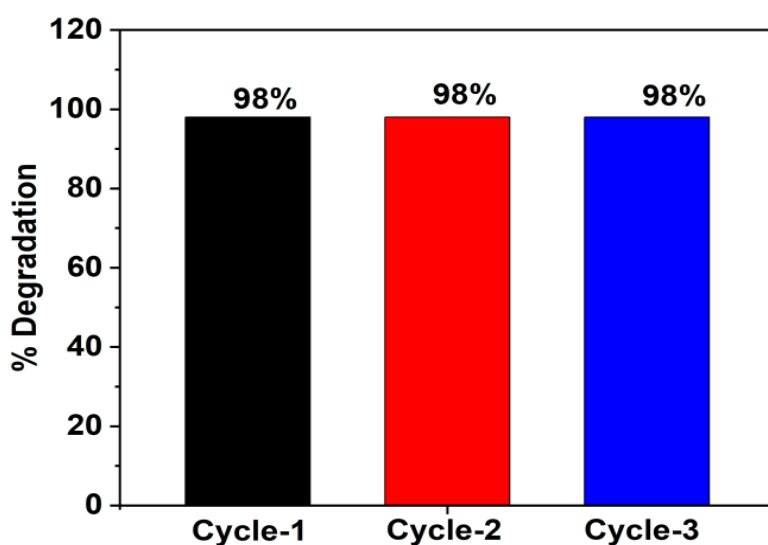


Figure 3.30: Recyclability test of photocatalyst.

3.18 Conclusions

The $M_xZn_{1-x}O$ ($M = Nd, Sm, Dy, \text{ and } Ho$ and $x = 0.05$ and 0.1) nanomaterials were successfully synthesized from M/Zn -oxalate and hydrazinate precursors. The use of hydrazine in the precursors seamlessly altered the particle microstructure, morphology and light absorption properties of nanomaterials. All materials crystallized into a hexagonal wurtzite ZnO structure with particle sizes ranging from 10 to 70 nm. The nanoparticles were uniform, crystalline and spherically shaped. The examined chemical composition, oxidation states and bonding of elements provided strong evidence of $M_xZn_{1-x}O$ material formation. The marginal band gap reduction of ZnO was due to low M^{3+} doping concentration, which improved the UV-visible light absorption. The PL emission proved the formation of mid-gap energy levels due to M^{3+} doping and hydrazination of precursors. The improvement in PL emissions was attributed to dopant concentration and the effect of precursor hydrazination. The blue emission band $\lambda = 468$ nm (~ 2.65 eV) was emitted due to the extra intrinsic ZnO defects such as oxygen vacancy (V_O), zinc vacancy (V_{Zn}), and interstitial zinc (Zn_i) caused by hydrazinated precursor. The PL emission in visible regions with weak-violet, strong-blue, and intermediate-green band emissions was also attributed to various electronic transitions. The $M_xZn_{1-x}O$ materials prepared from hydrazinated precursors demonstrated enhanced blue-light PL emission with a narrow bandwidth of 15 nm. Hence, the effects of hydrazinated precursor resulted in superior microstructure, defects and visible light PL emissions $M_xZn_{1-x}O$ materials. The EDAX confirmed the elemental composition of materials as Zn, O and $M = Nd, Sm, Dy, \text{ and } Ho$. XPS also established the oxidation states of elements and dopants in synthesized materials. The oxidation states were Zn^{2+} , O^{2-} and M^{3+} in $M_xZn_{1-x}O$ ($M = Nd, Sm, Dy, \text{ and } Ho$). TEM showed highly crystalline material with spherical-shaped crystallites with a crystal lattice fringes spacing ~ 0.28 Å, corresponding to the (100) plane of ZnO . BET surface area of pure ZnO was ~ 1.92 m²/g, whereas Nd/Sm/Dy/Ho doped ZnO showed slightly higher surface area of ~ 5 m²/g with a mesoporous nature. The band gap of ZnO was modified with M^{3+} doping and showed higher UV-visible light absorption capability due to the introduction of mid-gap energy levels. However, there was a marginal reduction in the band gap energy ($E_g = \sim 3.27$ eV). The comparative RT-PL intensity showed an enhanced effect with an increase in dopant concentration and hydrazination of precursors, probably due to the effective transfer of CB electrons to the newly created impurity energy levels.

The photocatalytic dye degradation efficiencies of materials evaluated in the presence of UV and direct sunlight showed promising results for Rhodamine B Dye, and Red CL5B dye. The degradation efficiency followed the trend: $\text{Ho}_x\text{Zn}_{1-x}\text{O} > \text{Sm}_x\text{Zn}_{1-x}\text{O} > \text{Dy}_x\text{Zn}_{1-x}\text{O} > \text{Nd}_x\text{Zn}_{1-x}\text{O}$. The catalyst concentration on dye degradation efficiency showed a direct correlation; 100mg of catalyst exhibits maximum degradation efficiency. The mid-gap energy levels acted as an electron trap; hence large number of electrons were excited to the conduction band that participated in the redox reactions with dye molecules. The photocatalytic dye degradation efficiencies of materials evaluated in the presence of UV and direct sunlight showed promising results. The reactive species generated were hydroxyl ($\text{OH}^\bullet$), holes (h^+) and superoxide ($\text{O}_2^\bullet$) radicals for degradation of Rh B and textile industry Red CL-5B dyes. The LC-MS studies confirmed that the Rh B was completely fragmented into several smaller degradants and ultimately mineralized larger molecular fragments into non-polluting water and carbon dioxide molecules. The photocatalyst exhibited excellent stability and reusability properties over 3-cycles. These materials can be effectively utilized in an industrial effluent treatment plant, wherein the harmful organic molecules could be fragmented in the presence of UV or natural sunlight.

REFERENCES

1. B. Abebe, N. K. Gupta, and D. Tsegaye, RSC Advances **14**, 17338 (2024).
2. T. Viet, H. Luu, B. Nguyen, N. Dao, and D. Luu, : : RSC Adv **11**, 36078 (2021).
3. Y. Sun, W. Zhang, Q. Li, H. Liu, and X. Wang, Advanced Sensor and Energy Materials **2**, 100069 (2023).
4. W. Raza, S. M. Faisal, M. Owais, D. Bahnemann, and M. Muneer, RSC Advances **6**, 78335 (2016).
5. S. Khan, T. Noor, N. Iqbal, and L. Yaqoob, ACS Omega **9**, 21751 (2024).
6. S. S. Shinde, P. S. Shinde, C. H. Bhosale, and K. Y. Rajpure, Journal of Photochemistry and Photobiology B: Biology **104**, 425 (2011).
7. K. Davis, R. Yarbrough, M. Froeschle, J. White, and H. Rathnayake, RSC Advances **9**, 14638 (2019).
8. N. Tarasenko, V. Kornev, A. Ramanenka, R. Li, and N. Tarasenko, Heliyon **8**, 09554 (2022).
9. M. Ahmad, H. Sun, and J. Zhu, ACS Applied Materials and Interfaces **3**, 1299 (2011).
10. A. Rohini Devi, A. Jegatha Christy, K. Deva Arun Kumar, S. Valanarasu, M. S. Hamdy, K. S. Al-Namshah, A. M. Alhanash, D. Vikraman, and H. S. Kim, Journal of Materials Science: Materials in Electronics **30**, 7257 (2019).
11. A. Khataee, B. Vahid, S. Saadi, and S. W. Joo, Ultrasonics Sonochemistry **29**, 146 (2016).
12. H. Zhou, C. Wang, Y. Lai, J. Yu, and S. Cheng, Applied Physics A: Materials Science and Processing **127**, 1 (2021).
13. P. Cao and Y. Bai, Xiyou Jinshu Cailiao Yu Gongcheng/Rare Metal Materials and Engineering **45**, 1419 (2016).
14. V. Moye, K. S. Rane, and V. N. K. Dalal, Journal of Materials Science: Materials in Electronics **1**, 212 (1990).
15. V. Borker, K. S. Rane, and V. N. Kamat Dalal, Journal of Materials Science: Materials in Electronics **4**, 241 (1993).
16. K. S. Rane, H. Uskaikar, R. Pednekar, and R. Mhalsikar, Journal of Thermal Analysis and Calorimetry **90**, 627 (2007).
17. R. A. Porob, S. Z. Khan, S. C. Mojumdar, and V. M. S. Verenkar, Journal of Thermal Analysis and Calorimetry **86**, 605 (2006).
18. F. Mohamadpour and A. M. Amani, RSC Advances **14**, 20609 (2024).
19. V. Batra, I. Kaur, D. Pathania, and V. Chaudhary, Applied Surface Science Advances **11**, 100314 (2022).

20. P. Pascariu, C. Cojocaru, N. Olaru, P. Samoila, A. Airinei, M. Ignat, L. Sacarescu, and D. Timpu, *Journal of Environmental Management* **239**, 225 (2019).
21. D. Sarkar, S. Ganguli, T. Samanta, and V. Mahalingam, *Langmuir* **35**, 6211 (2019).
22. N. Kamarulzaman, M. F. Kasim, and R. Rusdi, *Nanoscale Research Letters* **10**, (2015).
23. M. S. Geetha, H. Nagabhushana, and H. N. Shivananjaiah, *Journal of Science: Advanced Materials and Devices* **1**, 301 (2016).
24. H. S. Alanazi, N. Ahmad, and F. A. Alharthi, *RSC Advances* **11**, 10194 (2021).
25. K. S. Rane, V. M. S. Verenkar, R. M. Pednekar, and P. Y. Sawant, *Journal of Materials Science: Materials in Electronics* **10**, 121 (1999).
26. U. B. Gawas and V. M. S. Verenkar, *Thermochimica Acta* **556**, 41 (2013).
27. M. Shamsipur, M. Roushani, and S. M. Pourmortazavi, *Materials Research Bulletin* **48**, 1275 (2013).
28. Z. Nazir, M. Sahar, S. Riaz, S. Naseem, and Z. Saddiqe, *Optical Materials* **108**, 110457 (2020).
29. V. Gurylev and T. P. Perng, *Journal of the European Ceramic Society* **41**, 4977 (2021).
30. B. Poornaprakash, U. Chalapathi, S. V. P. Vattikuti, A. Balakrishna, H. C. Swart, Y. Suh, and S. H. Park, *Journal of Materials Science: Materials in Electronics* **29**, 20650 (2018).
31. S. Thakur and S. K. Mandal, *ACS Omega* **5**, 16670 (2020).
32. T. M. Hammad, J. K. Salem, and R. G. Harrison, *Applied Nanoscience (Switzerland)* **3**, 133 (2013).
33. N. M. Hosny, I. Gomaa, M. G. Elmahgary, and M. A. Ibrahim, *Scientific Reports* **13**, 1 (2023).
34. K. V. Chandekar, M. Shkir, B. M. Al-Shehri, S. AlFaify, R. G. Halor, A. Khan, K. S. Al-Namshah, and M. S. Hamdy, *Materials Characterization* **165**, 110387 (2020).
35. T. Indumathi, C. Theivarasu, I. Pradeep, M. T. Rani, G. Magesh, C. S. Rahale, and E. R. Kumar, *Surfaces and Interfaces* **23**, 101000 (2021).
36. M. Mhalsekar and V. Borker, *Journal of Materials Science: Materials in Electronics* **35**, 1 (2024).
37. G. Vijayaprasath, R. Murugan, T. Mahalingam, Y. Hayakawa, and G. Ravi, *Ceramics International* **41**, 10607 (2015).
38. S. Chauhan, M. Kumar, S. Chhoker, S. C. Katyal, and V. P. S. Awana, *Journal of Materials Science: Materials in Electronics* **24**, 5102 (2013).
39. A. K. Zak, M. E. Abrishami, W. H. A. Majid, R. Yousefi, and S. M. Hosseini, *Ceramics International* **37**, 393 (2011).
40. J. B. M. Goodall, D. Illsley, R. Lines, N. M. Makwana, and J. A. Darr, *ACS Combinatorial*

Science **17**, 100 (2015).

41. Y. Liu, W. Luo, R. Li, G. Liu, M. R. Antonio, and X. Chen, *Journal of Physical Chemistry C* **112**, 686 (2008).

42. X. Mo, Z. Li, C. Liu, X. Tao, Y. Zhou, H. Long, H. Wang, and Y. Ouyang, *Journal of Luminescence* **213**, 127 (2019).

43. Y. Sun, W. Chen, S. Liu, S. Yan, S. Zhang, L. Huang, and Z. Zheng, *Journal of Solid State Chemistry* **301**, (2021).

44. V. Kumar, O. M. Ntwaeaborwa, T. Soga, V. Dutta, and H. C. Swart, *ACS Photonics* **4**, 2613 (2017).

45. Y. Kondo, K. Yoshiura, S. Kitera, H. Nishi, S. Oda, H. Gotoh, Y. Sasada, M. Yanai, and T. Hatakeyama, *Nature Photonics* **13**, 678 (2019).

46. S. Ida, C. Ogata, U. Unal, K. Izawa, T. Inoue, O. Altuntasoglu, and Y. Matsumoto, *Journal of the American Chemical Society* **129**, 8956 (2007).

47. J. Lv, C. Li, and Z. Chai, *Journal of Luminescence* **208**, 225 (2019).

48. K. Kasirajan, L. Bruno Chandrasekar, S. Maheswari, M. Karunakaran, and P. Shunmuga Sundaram, *Optical Materials* **121**, 111554 (2021).

49. M. Shkir, K. V. Chandekar, B. M. Alshehri, A. Khan, S. AlFaify, and M. S. Hamdy, *Applied Nanoscience (Switzerland)* **10**, 1811 (2020).

50. L. Suganya, K. S. Balamurugan, A. Sivakami, P. Sakthivel, N. Asthana, and B. Sundaresan, *Topics in Catalysis* **67**, 3 (2024).

51. K. Saravanakumar, P. Sakthivel, and R. K. Sankaranarayanan, *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* **267**, 120487 (2022).

52. C. J. Raj, G. Paramesh, B. S. Prakash, K. R. S. P. Meher, and K. B. R. Varma, *Materials Research Bulletin* **74**, 1 (2016).

53. R. Khokhra, B. Bharti, H. N. Lee, and R. Kumar, *Scientific Reports* **7**, 1 (2017).

54. C.S Gopinath, and N.Nalajala, *Journal of Materials Chemistry A* **9**, 1353 (2021).

55. A. V. Mohod, M. Momotko, N. S. Shah, M. Marchel, M. Imran, L. Kong, and G. Boczka, *Water Resources and Industry* **30**, 100220 (2023).

56. A. Rebekah, R. Maddipatla, C. Loka, S. Sahoo, and K. S. Lee, *Applied Surface Science Advances* **19**, 100576 (2024).

57. S. A. Mousa, D. A. Wissa, H. H. Hassan, A. A. Ebnalwaled, and S. A. Khairy, *Scientific Reports* **14**, 16713 (2024).

Chapter-4:

Synthesis of anatase titanium dioxide nanomaterial, characterization and photocatalytic degradation studies

4.1 Introduction

Nanostructured titanium dioxide (TiO_2) materials are in high demand due to their excellent functional properties and applications in photocatalysis, environmental pollution remediation, and sustainable energy production [1]. The nanosized TiO_2 materials are mainly synthesized via wet-chemistry bottom-up approaches. Out of these, the precursor and sol-gel techniques are the most commonly applied for synthesis because they allow easy modification of the particle and microstructural properties of TiO_2 materials [2]. Hence, a suitable metalo-organic precursor could be precipitated out and then calcined to acquire the desired phase, shape, size, and surface morphology of TiO_2 material [3].

The commonly adopted methods for the synthesis TiO_2 nanomaterials include sol-gel, chemical / physical vapour deposition, hydrothermal, laser ablation, hard/soft template, direct oxidation, non-hydrolytic sol-gel, reverse microemulsion, sonochemical electrodeposition and ionic liquid and microwave, etc. [4,5]. However, the aforementioned methods face some drawbacks, such as lengthy, cumbersome procedures, expensive, high energy consumption, unscalable, and pollution concerns. Moreover, TiO_2 exhibits polymorphism, and the most common polymorphs found in nature are anatase, rutile, brookite and $\text{TiO}_2\text{-B}$ [6]. Amongst all polymorphs, anatase is the most active for catalytic applications and has been widely investigated by many researchers. The high activity was assigned to the (101) crystal plane of anatase [7]. Although the thermodynamically stable rutile phase possessed a narrow band gap energy of ~ 3.0 eV, it exhibits the lowest catalytic activity compared to anatase and brookite. While the metastable brookite is highly susceptible to phase transformations, either to anatase or rutile structure, when heated at high temperatures [8]. Hence, in the current work, the important TiO_2 material attributes like phase, shape, size, morphology and surface area were improved through beta-cyclodextrin-based precursors. The synthesized TiO_2 nanomaterials were investigated for their structure-property relationship. The proposed beta-cyclodextrin precursor offers an alternate, cost-effective, eco-friendly, and reproducible process to fabricate the TiO_2 photocatalyst.

The beta-cyclodextrin (β -CD) is a white crystalline solid powder, sparingly soluble in water (solubility ≈ 18 mg/ml at 25°C), with a cyclic ring structure molecule. The presence of external hydrophilic and internal hydrophobic ring character in the β -CD resulted in the cavity

formation, which has been extensively utilized by cosmetic and pharmaceutical industries as a carrier molecule [9]. The presence of multiple hydroxyl groups in β -CD were beneficial in the hydrogen bond formation with the drug molecule and thereby acted as a vehicle for drug molecules [10]. Therefore, the host-guest chemistry of β -CD could be very well exploited for the preparation of nano-photoactive TiO_2 materials. Here, β -CD acts as a binding agent and triggers the precipitation of the precursor. The precursor was decomposed by heating to eliminate water and the β -CD to produce nanosized TiO_2 powders. The presence of β -CD prevented the TiO_2 particles from agglomeration and controlled the surface morphology. The current β -CD-based precursors offer several advantages, such as inexpensive and biocompatible synthesis. The current preparation method could be easily scaled up for bulk TiO_2 production.

Additionally, facet engineering is also an effective technique to improve photoactivity. During the synthesis of material, a particular plane, for example, (101) of anatase TiO_2 was fabricated and utilized for catalysis [11]. The β -CD concentration can facilitate the formation of anatase TiO_2 with the (101) crystal plane. The large percentage of (101) facets are responsible for high photoactivity in anatase compared to other polymorphs [12].

The current work also describes the characterization and photodegradation studies of drug and dye molecules on TiO_2 photocatalyst under irradiation with UV-visible light. Pharmaceutical industries encounter the challenging task of eliminating drug molecules from their effluents. These molecules are detrimental to the environment, aquatic organisms and human health, thus posing serious pollution issues [13]. Wastewater discharges from these industries contain high concentrations of organic and coloured compounds. These toxic molecules are categorized broadly as carcinogens (cancer-causing agents), mutagens (change the genetic materials) and reprotoxic (harmful to the reproductive system) substances. These obnoxious compounds make their way into our delicate ecosystem. Hence, effluent treatment facilities may not be effective enough to destroy these chemically stable molecules and therefore cause grave air, soil, and water pollution. Complete degradation of drug molecules by effluent treatment plants is a daunting task, hence, photocatalytic disintegration can be a promising approach for mineralization of molecules. The photocatalytic degradation efficiencies of the prepared materials were evaluated using Rhodamine B as a model dye and paracetamol drug molecule in Uv-visible light.

4.2 Materials and Methods

4.2.1 Chemicals

The chemicals were of analytical grade and used as received from the supplier. The Titanium (IV) isopropoxide was supplied by SRL, India (extra pure 27.8 to 28.6 % TiO_2), beta-cyclodextrin (Pharmaceutical excipient grade), and isopropanol from Loba Chemie, India, were used in the preparation of materials.

4.2.2 Preparation of TiO_2 nanomaterial via β -CD-based precursor method

The chemical synthesis offers several advantages, such as cost-effectiveness, low energy consumption, simplicity, and better control over particle morphology. The nanosized anatase TiO_2 materials were fabricated using the β -CD-modified precursor method. Initially, the titanium isopropoxide and isopropanol (1:1) mixture solution was prepared and then added dropwise to the aqueous 1% β -CD solution (250 mL) to form the precipitate of β -CD-titanyl oxyhydroxide. The precipitate was stirred for 1 h, filtered through a Buchner funnel, washed with water and then dried in an oven at 60 °C for 12 h. The dried precursor was ground to a fine powder and calcined at 450 °C for 5 h in air. The nanosized TiO_2 powder material was denoted as 1DT. Similarly, the above procedure was followed for 2% and 3% β -CD concentration, and the materials were assigned codes as 2DT and 3DT, respectively. TiO_2 material without β -CD was also prepared and assigned code TH for comparative purposes. The schematic diagram depicting the synthesis of TiO_2 via β -CD precursor is depicted in Figure 4.1.

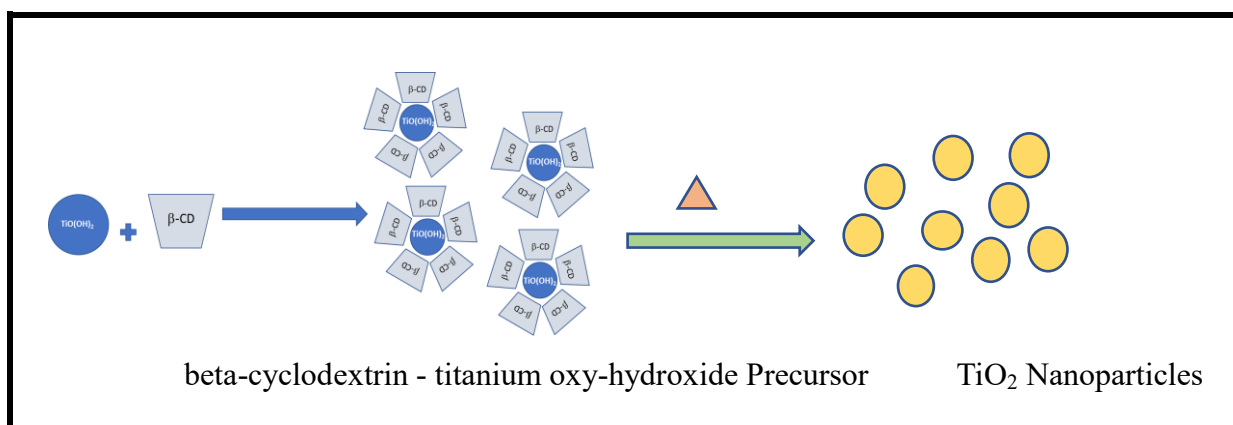


Figure 4.1: The schematic diagram depicting the synthesis of TiO_2 using β -CD

4.3 Characterization techniques

The IR spectra of precursor and TiO₂ materials were recorded on a Shimadzu, IR-prestige instrument. The precursor thermal decomposition profiles were studied on the Netzsch TGA-DTA instrument. The phase identification was performed using a Rigaku SmartLab powder X-ray diffractometer (XRD) in the 2-theta range of 20 – 80°. The Rietveld XRD analysis was performed on the Bruker D8-Advance instrument. The field emission-scanning electron microscopy (FE-SEM) and energy-dispersive absorption X-ray spectroscopy (EDAX) were performed on (FEI Quanta 400 FEG SEM equipped with Genesis X4M. The transmission electron microscopy (TEM) images of materials were captured on a JEOL JEM 1400 TEM microscope, operating at an accelerating voltage of 120 kV. The Raman spectra were acquired at room temperature on a Bruker Lab Raman spectrometer equipped with a charge-coupled device (CCD) camera and a He–Ne laser with an excitation wavelength $\lambda = 632$ nm and 20 mW power. Surface property measurements were investigated on Belsorb instrument. The UV-visible diffuse reflectance spectroscopy (DRS) spectra were recorded on a Shimadzu UV-probe spectrophotometer. Room temperature photoluminescence (RT-PL) emission spectra were recorded spectrofluorometer (FP8200, Jasco Japan) equipped with a xenon lamp (450 W) and excitation wavelength of $\lambda_{\text{exc}} = 291$ nm.

The degradants formed during the photocatalysis process were analysed by liquid chromatography coupled with mass spectrometry (LC-MS) technique, using an Agilent LC-MS 6460 instrument. The parameters set during the analysis were: spray voltage: ± 1 kV, capillary temperature 300 °C. For LC, the mobile phase was premixed water and acetonitrile was used to elute the degradants. The flow rate of 0.5 mL/min and the C18 analytical column were used for the separation of impurities. The Orbitrap analyzer was employed to scan the molecular mass of the degradant in the range of 50–500 m/z. The final time point degraded solution was injected into the LC-MS system, and the retention time by LC of the degradants and their m/z was analysed using MS. The degradants were identified based on the molecular mass.

4.4 Photocatalytic degradation of Paracetamol drug molecule

The paracetamol drug molecule degradation studies were performed using the catalyst under UV light irradiation. The change in the initial concentration of paracetamol was recorded at different time intervals by capturing the absorbance values at $\lambda_{\text{max}} = 243 \text{ nm}$. About 100 mg of catalyst was suspended in 100 mL of paracetamol solution (25 ppm). The solution was initially equilibrated with the photocatalyst for 30 min in the dark. Then the vessel was placed in the photocatalytic reactor and irradiated with a UV lamp ($\lambda = 250 \text{ nm}$ to 450 nm). The absorbance spectra of the paracetamol solution were recorded in the range $200 - 400 \text{ nm}$ at 0, 20, 40, 60, 80, 100 and 120 min time points. The degradation efficiency of the catalyst was calculated using equation 1.

$$\% \text{ Degradation Efficiency} = (C_0 - C_t) / C_0 * 100 \dots \dots \dots (1)$$

The change in concentration or % degradation efficiency was plotted against the time points and determined the performance of the photocatalyst.

Further, to understand the fragmentation pattern of paracetamol molecules by photocatalyst, liquid chromatography coupled with mass spectrometry (LC-MS) studies were performed on the paracetamol solution before and after degradation. The LC peak position (retention time) and m/z values were matched with the chemical formula of the degradant. The LC-MS studies were performed on the Agilent LC-MS 6460 instrument.

4.5 Photocatalytic degradation of Rhodamine B dye molecule

The synthesized mesoporous TiO_2 nanomaterials were tested for photocatalytic activity using Rh B dye solution. Photocatalytic reactions were carried out under UV light and with TiO_2 materials. The blank run was carried out without light and a catalyst and showed no significant decrease in the Rh B dye concentration. The efficiency of photocatalytic degradation of Rh B solution was monitored by measuring the absorbance of the dye solution at different time intervals using UV-visible spectrophotometry. The UV light (Hg lamp; $\lambda = 250 \text{ nm}$ to 450 nm) source was used to illuminate dye degradation experiments (in 100 mL of

10 ppm) using a double-walled water-cooled photoreactor. For photocatalysis studies, 100 mg of photocatalyst was dispersed in 100 mL of appropriate Rh B dye concentration. The absorbance versus time (0, 20, 40, 60, 80, 100 and 120 min) was recorded and degradation kinetics were calculated based on the kinetic rate equation. The Rh B maximum absorption wavelength, $\lambda_{\text{max}} = 554 \text{ nm}$, was monitored for the change in concentration with time using a UV-visible spectrophotometer. The molecular structure of the Rh B dye is displayed in Figure 4.2. The schematic diagram of the photocatalytic reactor used for degradation activity is shown in Figure 4.3.

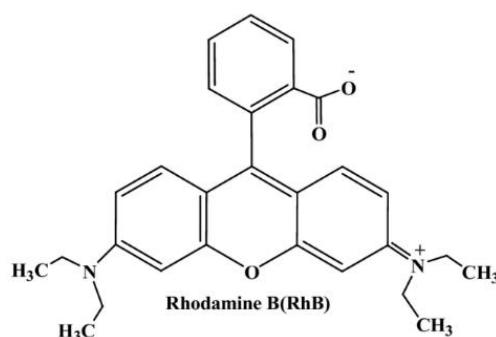


Figure 4.2: Molecular structure of Rhodamine B dye molecule

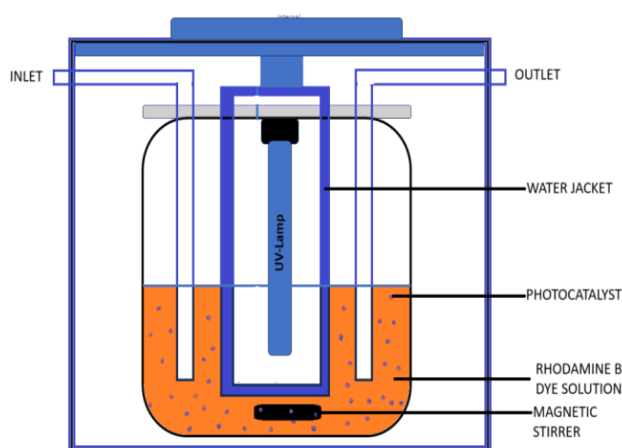


Figure 4.3: Schematic diagram of the photocatalytic reactor used for dye/drug degradation activity

4.6 Results and discussion

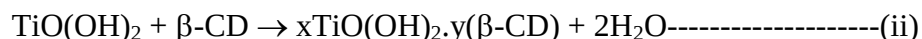
4.6.1 Possible mechanism for the formation of nanosized TiO₂

The plausible reaction mechanism has been proposed for the synthesis of nanosized TiO₂ particles employing the β -CD molecule. β -CD played an important role in the formation of TiO₂ nanoparticles due to its complexation with the titanyl oxyhydroxide. The precipitation occurred when the β -CD was bonded with titanyl oxyhydroxide. The hydrogen bonding between titanyl oxyhydroxide and -OH groups of β -CD resulted in self-assembly clusters, which were then calcined to TiO₂ nanoparticles [14]. The water of hydration and β -CD were eliminated during the thermal decomposition process, leaving behind mesoporous TiO₂ nanoparticles as illustrated in Figure 4.1. The probable reactions involved in the formation of anatase TiO₂ nanomaterials are presented below:

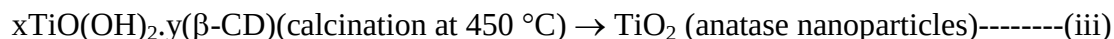
(1) Hydrolysis of TiP



(2) Complexation of TiO(OH)₂ + β -CD



(3) Crystallization of TiO₂ via calcination



In step (i), the titanyl isopropoxide was hydrolyzed by an aqueous β -CD solution to form titanyl oxyhydroxide. In the stage (ii), titanyl oxyhydroxide was bonded to β -CD to form $x\text{TiO}(\text{OH})_2.y(\beta\text{-CD})$, where x = water molecules and y = number of β -CD. In step (iii), the TiO₂ nanoparticles were formed when the precipitate was heated at $\sim 450^\circ\text{C}$ to form the crystalline anatase TiO₂ nanoparticles. The interaction and concentration of titanyl oxyhydroxide and β -CD were the two main factors responsible for the control of nanoparticle properties. Hence, the goal in this preparation was to adopt an easy, scalable and rapid method for stable and pure phase TiO₂ nanomaterials.

4.6.2 IR and thermal analysis of precursor

Beta-cyclodextrin (β -CD) is a natural cyclic oligosaccharide with a hollow, truncated cone-shaped structure capable of forming a complex with titanyl oxyhydroxide [15]. Figure 4.4a depicts the glycosidic hydroxyl (-OH) groups of the β -CD molecule effectively bonded through hydrogen bonding to $\text{TiO}(\text{OH})_2$. The formation of precursor clusters was attributed to the chelation of β -CD to the titanyl-oxyhydroxide [$\text{TiO}(\text{OH})_2$], which was confirmed by infrared spectroscopy (IR) and thermal analysis. The IR spectra of cyclodextrin-titanyl-oxyhydroxide precursor (p-2DT) were compared against the pure β -CD and titanyl oxyhydroxide (p-TH) as depicted in Figure 4.4b. The complexed precursor was identified by comparing the characteristic vibrational band positions. In p-2DT, the H-bond formed between the -O-H groups of β -CD with [$\text{TiO}(\text{OH})_2$] was ascertained by the presence of a strong and broad -O-H stretching vibration band centered at $\sim 3300 \text{ cm}^{-1}$ [16]. The band positioned at $\sim 2880 \text{ cm}^{-1}$ and $\sim 2925 \text{ cm}^{-1}$ were attributed to vibrational bands $-\text{CH}_2-$ and $-\text{CH}-$ of native β -CD in p-2DT. Hence, IR spectroscopy indicated the formation of many H-bond interactions in the precursor. Additionally, the presence of bands at ~ 1380 (strong) and $\sim 1460 \text{ cm}^{-1}$ (weak) were attributed to the C-H deformation and scissoring vibration, respectively [17]. Figure 4.4c shows the IR spectra of final annealed TiO_2 materials, derived from 1%, 2% and 3% β -CD precursors. They were assigned codes 1DT, 2DT and 3DT (obtained via β -CD precursors) and TH (without β -CD), respectively. The TiO_2 materials exhibited a strong intensity band between $850 - 450 \text{ cm}^{-1}$, which was assigned to the characteristic Ti-O stretching band. The absence of β -CD peaks in oxide materials indicated that the materials were devoid of any residual organic impurities. The β -CD was decomposed into CO_2 gas, thus eliminated during the annealing stage.

Additional information about the thermal decomposition of β -CD-titanyl-oxyhydroxide precursor was obtained from simultaneous thermogravimetric and differential thermal analysis (TGA-DTA). Figure 4.4d represents the TGA-DTA profiles of precursor (2DT) recorded from 30°C to 800°C temperature. The TGA graph showed a gradual mass loss of $\sim 35\%$ in the temperature range of 30 to 450°C due to dehydration and decomposition of β -CD to form the TiO_2 material. The endothermic peak at $\sim 100^\circ\text{C}$ was attributed to the

loss of water molecules, followed by a broad exotherm assigned to the decomposition of β -CD [18]. The flat baseline beyond 450 °C in TGA indicated the formation of stable TiO_2 material. Hence, materials were annealed in air at 450 °C for 5 hr. During the thermal decomposition of TiO_2 precursors, the β -CD assisted in the formation of the mesoporous anatase structure. Such materials facilitated the adsorption of degradant molecules in the mesopores. Consequently, the photocatalytic activity of TiO_2 was expected to increase with β -CD concentration.

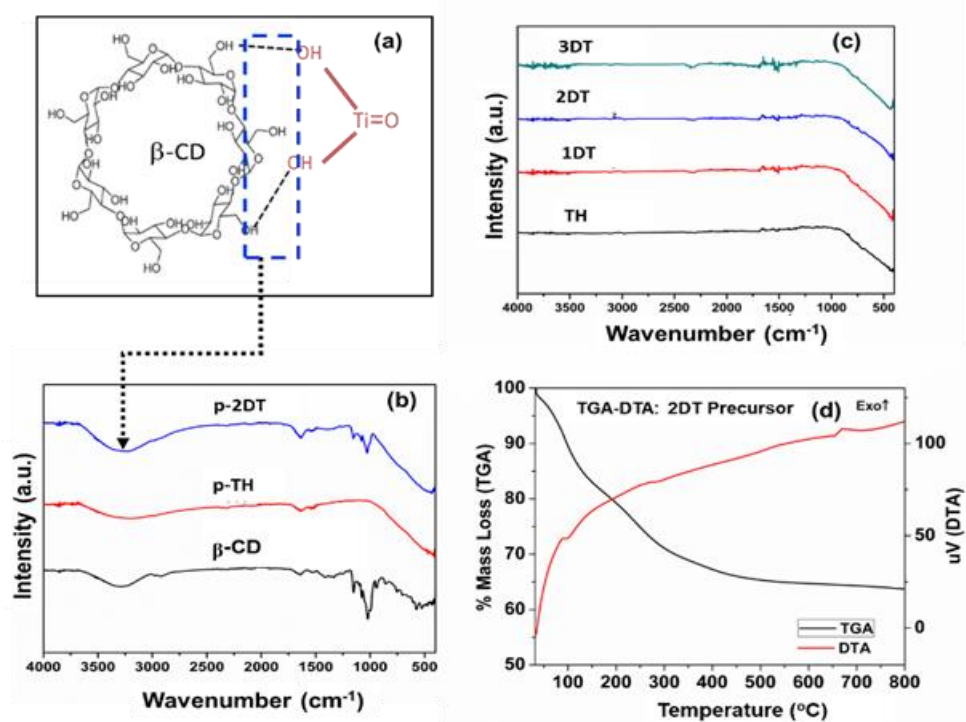


Figure 4.4 (a) Hydrogen bonded β -CD and $\text{TiO}(\text{OH})_2$ (b) FTIR of precursor (c) FTIR spectra of annealed TiO_2 samples; TH, 1DT, 2DT and 3DT (d) TGA-DTA profiles of 2DT precursor.

4.6.3 XRD phase analysis

The phase identification and thermal stability of TiO_2 material were studied by XRD analysis. The materials with β -CD were compared with those prepared by the simple hydrolysis method. In Figure 4.5a, the XRD patterns of 1DT, 2DT, 3DT revealed anatase (A) phase, while TH exhibited anatase + brookite (A+B). While sample TH, synthesized by a simple hydrolysis method (without β -CD) and lacked structure-directing property. When the

TH sample was heated at 450 °C, 500 °C and 600 °C, the (A+B)-TiO₂ transformed into anatase(A) and rutile(R) phases, as shown in Figure 4.5b. Hence, it can be stated that the materials derived from simple titanyl-oxyhydroxide precursors produced mixed phases (A+B/R), therefore requiring a structure-directing agent. On the contrary, TiO₂ materials prepared via β -CD precursor yielded a pure anatase TiO₂ phase, shown in Figure 4.5c. The representative sample 2DT exhibited sharp diffraction peaks at 2θ : 25.4°, 37.8°, 48.1°, 53.9°, 55.2°, 68.9°, 70.4°, 75.1°, which corresponded to (101), (004), (200), (105), (211), (116), (220) and (215) crystallographic planes of anatase-TiO₂. The crystal structure of 2DT conformed to the tetragonal anatase TiO₂ with space group (I41/amd) and matched well with the JCPDS card No: 21-1272 [19].

The formation of pure anatase-TiO₂ was attributed to the structure-directing property and chemical interaction (H-bonds) of β -CD with TiO₂ during the crystallization process. The probable reason for such a phenomenon could be attributed to the binding of titanium oxyhydroxide and the multi-chelating property of β -CD, thus assists in the fabrication of a single anatase polymorph. Moreover, the temperature-dependent XRD studies carried out on the 2DT material displayed promising results concerning phase composition and stability. The XRD patterns of 2DT annealed at different temperatures are shown in Figure 4.5c, which revealed mixed phases (A + R) only at ~600 °C, while at 450 °C and 500 °C anatase phase was found to be intact or stable. Hence, it was noteworthy to mention that the β -CD demonstrated structure directing as well as phase stabilization effect on TiO₂. The material was highly crystalline and presented an intense peak at 25.4° corresponding to the (101) crystal plane. The high catalytic activity in the case of anatase-TiO₂ was associated with this (101) crystal plane of TiO₂ [20].

The crystallite sizes of the materials were derived from the XRD diffraction peak analysis. With an increase in concentration of β -CD, the XRD peak intensity and width were seen to be broadened. This indicated a change in the degree of crystallinity and the mean crystallite size. The average crystallite sizes (D_{avg}) were estimated using the Scherrer formula using equation 2.

$$D = k\lambda/(\beta \cos \theta) \dots \dots \dots (2)$$

where λ = X-ray wavelength in nm (1.5418 Å), β is the half-width of the highest intensity (110) peak, θ is the Bragg diffraction angle in radians, and $k = 0.9$ is a correction factor. There

was a marginal reduction in crystallite size values between the materials with the addition of β -CD. Table 4.1 presents the compilation of the material codes, the phases formed at different annealing temperatures and the average crystallite sizes of the materials.

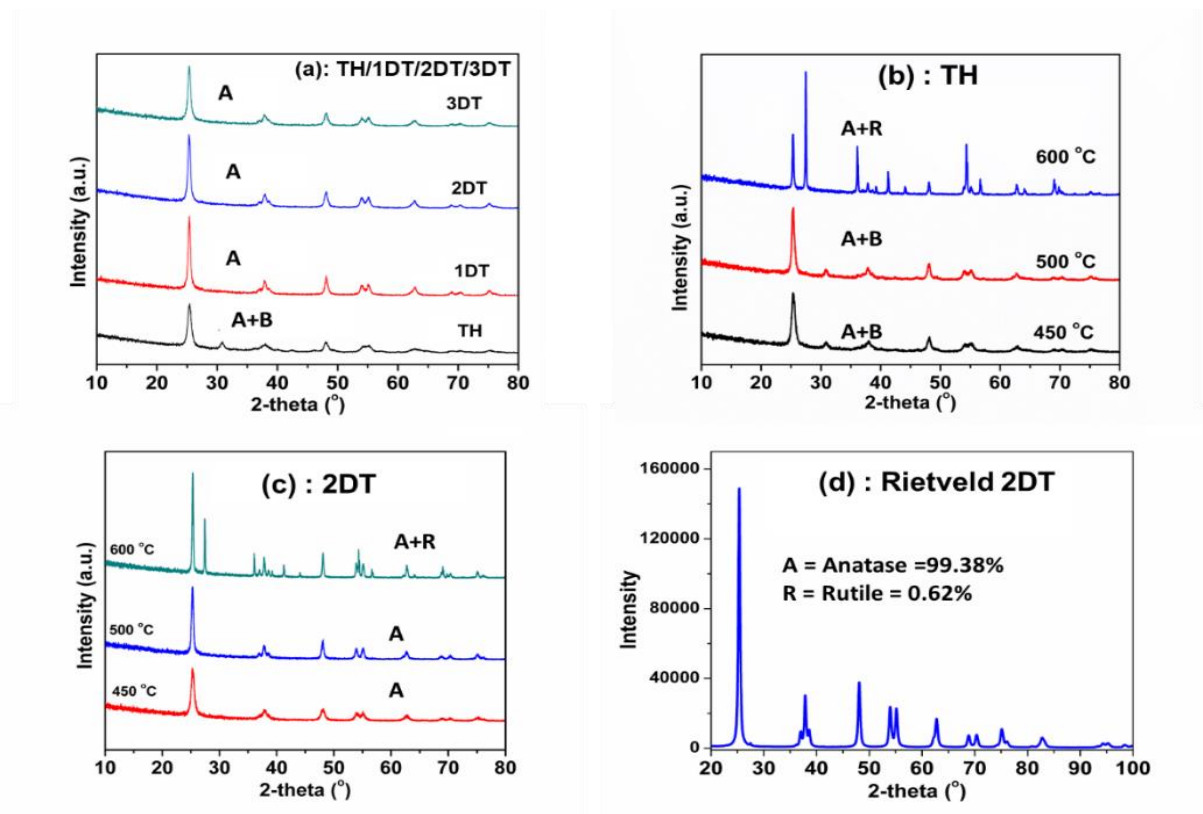


Figure 4.5: XRD diffraction patterns of (a) TH,1DT, 2DT, and 3DT (b) Sample TH annealed at 450, 500, and 600 °C (c) Sample 2DT annealed at 450, 500, and 600 °C (d) Rietveld analysis of 2DT.

Table 4.1: Comparative data of TH, 1DT, 2DT and 3DT materials phases formed at different annealed temperatures and their crystallite sizes.

Material/ Precursors	Material Code	Scherrer average crystallite sizes (nm)	TiO ₂ Phase		
			450 °C	500 °C	600 °C
Titanyl oxy-hydroxide	TH	33	A+B	A+B	A+B+R
Cyclodextrin- Titanyl oxy-hydroxide	1DT	30	A	A	A+R
	2DT	27	A	A	A+R
	3DT	24	A	A	A+R

Additionally, Rietveld XRD analysis was performed on 2DT sample (annealed at 550 °C) to investigate the detailed crystal structure, and the XRD pattern is shown in Figure 4.5d. The detailed Rietveld diffractogram showing the best fits for 2DT sample is presented in Figure 4.6. The vertical bars in the diffractogram indicate the reflections for anatase (red-solid line) and rutile (blue-solid line). The powder patterns were identified/indexed for anatase and rutile phases as per the JCPDS cards # 21-1272 and #21-1276, respectively. The crystal structure analysis was performed on the Rietveld data using Bruker Topaz analysis software. The crystal refinement, whole pattern fitting, qualitative-quantitative phase analysis, structural determination and microstructure analysis were performed on sample data. The structural model of TiO₂ anatase phase was chosen as a tetragonal crystal system.

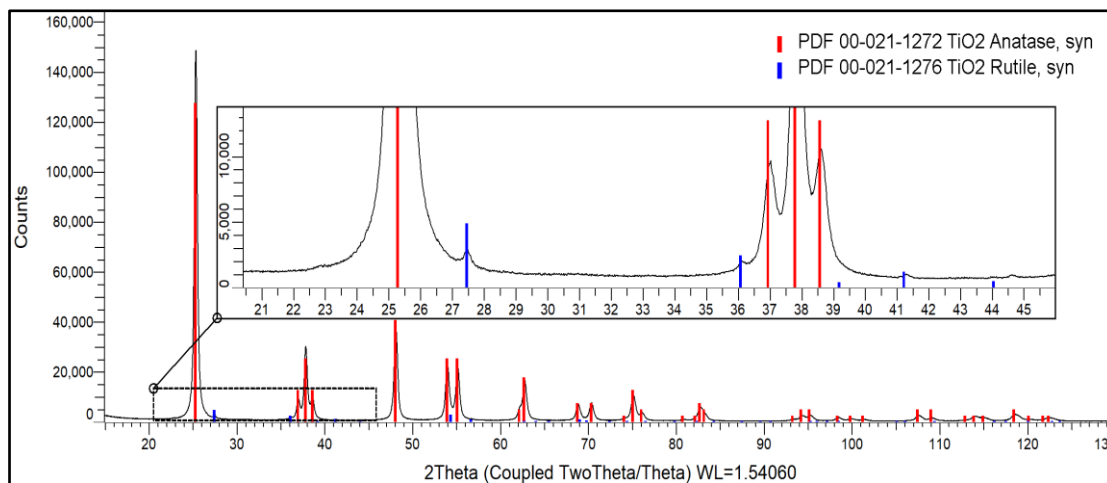


Figure 4.6: Detailed Rietveld XRD pattern of sample 2DT.

The Rietveld XRD pattern indicated high-intensity, sharp crystalline peaks of TiO₂. The quantitative crystalline phase purity of 2DT material was determined, which indicated 99.38 %-anatase and 0.32 %-rutile phase. This indicated that the materials majorly existed in anatase form and the phase transition temperature (anatase to rutile) was ≈ 550 °C. Other important crystallographic data from Rietveld analysis are compiled in Table 4.2. The crystallite sizes of TiO₂ particles were estimated to be about ~ 40 nm, while crystal strain and density values were 0.083 and 3.89099 g/cm³, respectively. The lattice parameters of the crystal unit were $a = b = 3.78507$ Å and $c = 9.51278$ Å, and the cell volume was 136.287 Å³ [21]. From the

XRD studies, it was revealed that the β -CD played a pivotal role in the crystallization and stabilization of pure anatase-TiO₂ material during the synthesis process.

Table 4.2: Rietveld analysis data for sample 2DT.

R-Values							
Rexp : 1.96		Rwp : 5.61		Rp:4.4		GOF : 2.86	
Rexp` : 1.71		Rwp` : 4.89		Rp`:3.9		DW : 0.27	
Quantitative Analysis - Rietveld							
Phase 1 : Anatase				99.38 %			
Phase 2 : Rutile				0.62 %			
Parameter				Structure1		Structure 2	
Phase name				Anatase		Rutile	
R-Bragg				3.334		4.599	
Space group				141		136	
Scale				0.08062		0.00218	
Cell Mass				319.35		160	
Cell Volume (Å^3)				136.287		62.44	
Wt% - Rietveld				99.38		0.62	
Double-Voigt-Approach							
Cry size Lorentzian				40.2		61	
Cry size Gaussian				43.4		39	
k: 1 LVol-IB (nm)				18.64		55	
k: 0.89 LVol-FWHM(nm)				22.75		527.8	
Strain							
Strain L				0.08300		4.2481	
Crystal Linear Absorption Coeff.(1/cm)				483.572		527.8	
Crystal Density (g/cm^3)				3.89099		4.2481	
Preferred Orientation (Dir 1 :10 1)				1.000		1	
Lattice parameters							
a (Å)				3.78507		4.5934	
c (Å)				9.51278		2.9593	
Anatase							
Site	Np	x	y	Z	Atom	Occ	Beq
Ti 1	4	00.00	0.00	0.000	Ti ⁺⁴	1	1.146
O 1	8	00.00	0.00	0.792	O ⁻²	0.9991	1.304

4.6.4 BET Surface analysis

The surface properties of the synthesized TiO_2 powders were investigated by N_2 adsorption-desorption isotherm [22]. Figure 4.7(a-d) shows the Hysteresis loop recorded for all TiO_2 samples, which indicates the monolayer-multilayer reversible type IV isotherms. The small hysteresis loop formed at a relatively higher-partial pressure range of $p/p_0 = 0.70 - 0.90$ indicated the mesoporous nature of the material. The TH sample displayed a typical H2(b) type of hysteresis with capillary condensation at the higher p/p_0 segment in the mesopores (size: 2 – 50 nm) formed on the particle surface, shown in Figure 4.7a. While samples 1DT, 2DT and 3DT exhibited hysteresis closely resembling the H3 type, as shown in Figure 4.7(b,c,d). The BET-specific surface area of samples TH, 1DT, 2DT and 3DT are tabulated in Table 4.3. The BET-specific surface area recorded was a slightly lower value of 31 to 27 m^2/g compared to TH with 46.8 m^2/g , which was attributed to the lower number of pores formed on the surface. Secondly, sample TH existed in mixed-phase (A+B), whereas samples 1DT, 2DT and 3DT were in anatase (A) form.

Figure 4.8(a-d) shows the BJH plot for the pore size distribution for all materials. The 1DT, 2DT and 3DT materials had diameters ranging from 2–30 nm with maximum pore sizes between 10 – 15 nm. The mean pore diameter estimated from the BJH plots was 13.5 nm for these materials. The BJH plot, shown in Figure 4.8c for the pore diameter, exhibited a slightly wider range for sample 2DT compared to TH. Sample 1DT and 3DT also showed similar pore size distribution trends, shown in Figure 4.8b and d. The surface area, pore volume, and mean pore diameter for the materials are compiled in Table 4.3. With the increasing amount of β -CD added during synthesis, the BET surface area, pore volume decreased, while the pore diameter increased. The BJH plot indicated major diameter pores formed with the addition of higher level of β -CD added during the synthesis process.

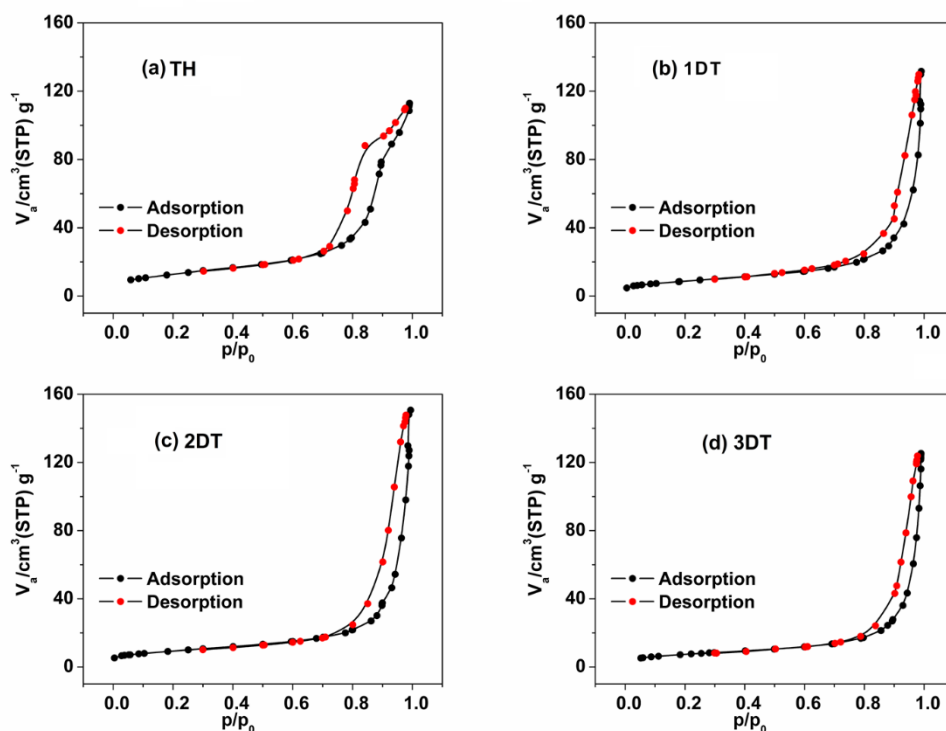


Figure 4.7: BET adsorption-desorption isotherms for (a) TH (b) 1DT (c) 2DT and (d) 3DT

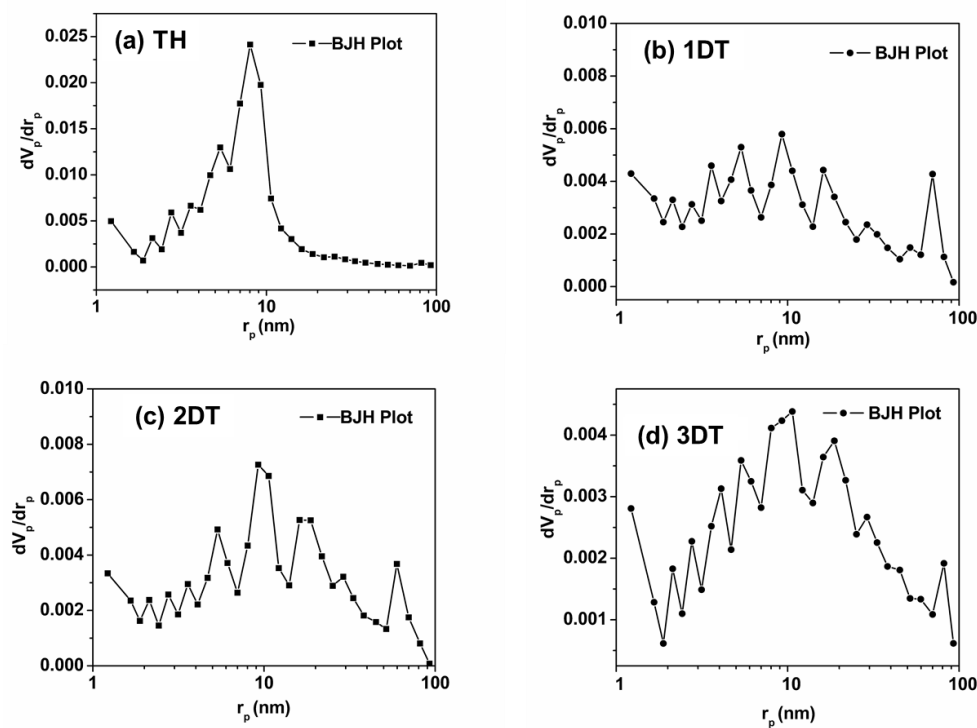


Figure 4.8: BJH plots for pore size distribution for (a) TH (b) 1DT (c) 2DT and (d) 3DT

Table 4.3: Sample codes, BET-specific surface area, total pore volume, and mean pore diameter.

Sample code	Specific surface area (m ² /g)	Total Pore volume (cm ³ /g)	Mean pore diameter (nm)	Phase
TH	46.828	0.1738	14.842	~70%-Anatase + ~30%-Brookite
1DT	31.329	0.2024	25.846	~100%-Anatase
2DT	33.132	0.2303	27.799	~100%-Anatase
3DT	26.704	0.1935	28.991	~100%-Anatase

From the adsorption-desorption isotherms, it was evident that all the materials displayed a similar type of hysteresis; however, the material prepared via β -CD displayed higher capillary condensation and slightly shifted to higher partial pressure, which was attributed to an increased pore size with increasing concentration of β -CD. The trend in specific surface area values for samples TH, 1DT, 2DT and 3DT were $46.828 > 31.329 < 33.132 > 26.704$ m²/g, respectively. Figure 4.9(a,b,c) displays the graphical representation of trends observed for surface area, total pore volume, and mean pore diameter for all samples. Thus, as the concentration of β -CD increased from 0 to 3%, the surface area and mean pore diameter increased proportionately; however, the total pore volume decreased for 3DT sample. These results indicated that the pore volume of materials increased upto 2% CD and then decreased with the addition of 3% β -CD during the synthesis. The probable reason for such observation can be explained based on a cooperative mechanism. In this, β -CD molecules consist of large molecules with an open cavity and with several polar groups (-OH), forming a cone-shaped soft template. During the precipitation, these polar groups tend to aggregate with a micron size. At low β -CD concentration, smaller aggregates with lower diameter particles were formed, and hence the pore size was smaller. Finally, the formation of the mesoporous titania formed after decomposition of β -CD, which increased and then decreased with the concentration of β -CD.

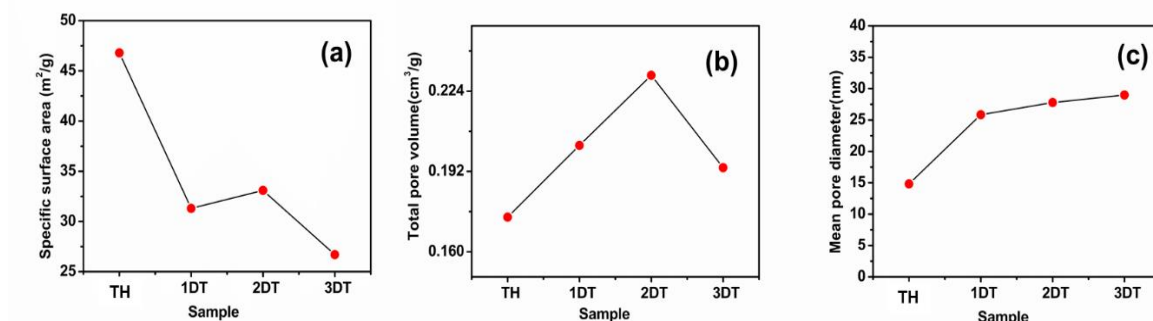


Figure 4.9: Observed trends for (a) surface area, (b) total pore volume and (c) mean pore diameter for samples TH, 1DT, 2DT and 3DT.

4.6.5 X-ray photoelectron spectroscopy studies

X-ray photoelectron spectroscopy (XPS) was employed to gain insights about the surface composition and chemical states of the synthesized TiO_2 materials. Figure 4.10(a,b,c) represents the wide energy survey scan and high-resolution XPS spectra of Ti and O of the 2DT sample. The survey scan showed characteristic dual peaks with binding energies at ~ 460 and ~ 580 eV assigned to Ti 3d and O 2s [23]. A peak at ~ 284 eV was also seen, which was attributed to the standard C peak originating from the carbon used for calibration of the instrument. The Gaussian deconvoluted O1s XPS spectra resolved into two peaks corresponding to Ti-O and surface-adsorbed Ti-OH groups, shown in Figure 4.10b. The Ti 3d peak, when deconvoluted, resolved into two peaks located at BE 458.78 eV and 464.45 eV, which were assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, as shown in Figure 4.10c. Hence, the difference of 5.72 eV indicated that the Ti was in (IV) valence state (Ti^{4+}) and bonded via the -Ti-O bond. There was no peak due to Ti^{3+} , hence absent in the TiO_2 material.

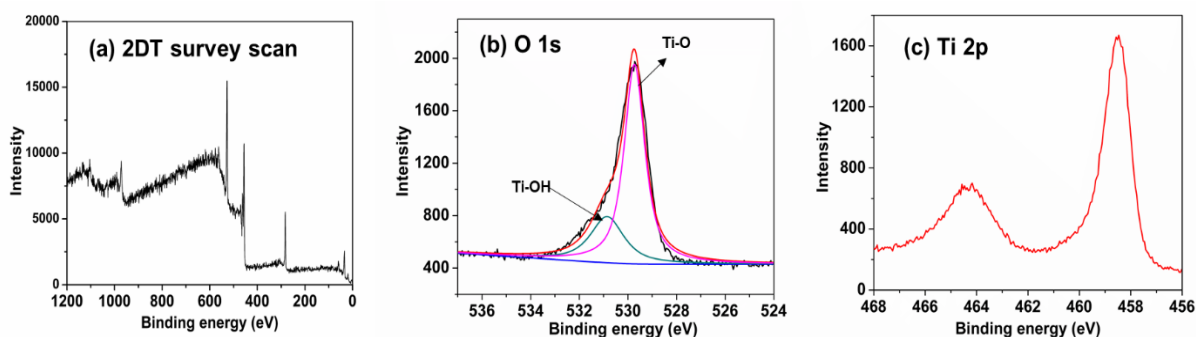


Figure 4.10: XPS of 2DT (a) Survey scan (b) O 1s (c) Ti 2p

4.6.6 Raman analysis

Raman spectroscopy was employed to study the phases of the TiO_2 materials. Figure 4.11a shows the stacked Raman spectra of all synthesized TiO_2 materials. The samples 1DT, 2DT, and 3DT materials showed similar spectral patterns due to the anatase phase. The six Raman bands were expected because anatase possessed D4h symmetry with the space group of (I41/amd) and two formula units per primitive unit cell. Hence, based on the group theory analysis, anatase exhibited six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$). Figure 4.11b shows the enlarged section of Raman spectra (80 to 700 cm^{-1}). The six first-order Raman spectrum allowed bands were marked at 137 cm^{-1} (E_g), 195 cm^{-1} (E_g), 395 cm^{-1} (B_{1g}), 512 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}), and 631 cm^{-1} (E_g), which confirmed the presence of anatase(A) phase. On the contrary, in Figure 4.11a, the sample TH showed multiple peaks indicating a mixture of (anatase + brookite) TiO_2 phases. As per group theory, brookite has lower symmetry and larger unit lattice cells, as a result expected to show 36 Raman active modes ($9A_{1g} + 9B_{1g} + 9B_{2g} + 9B_{3g}$) [24]. Hence, for sample TH, the Raman band positions were not marked due to complicated spectra arising from mixed (A+B) TiO_2 phases. There was a good agreement between the XRD and Raman data. From Raman spectra, it was inferred that the 2DT sample showed high peak intensities in the lower region of the spectra due to the crystalline anatase phase.

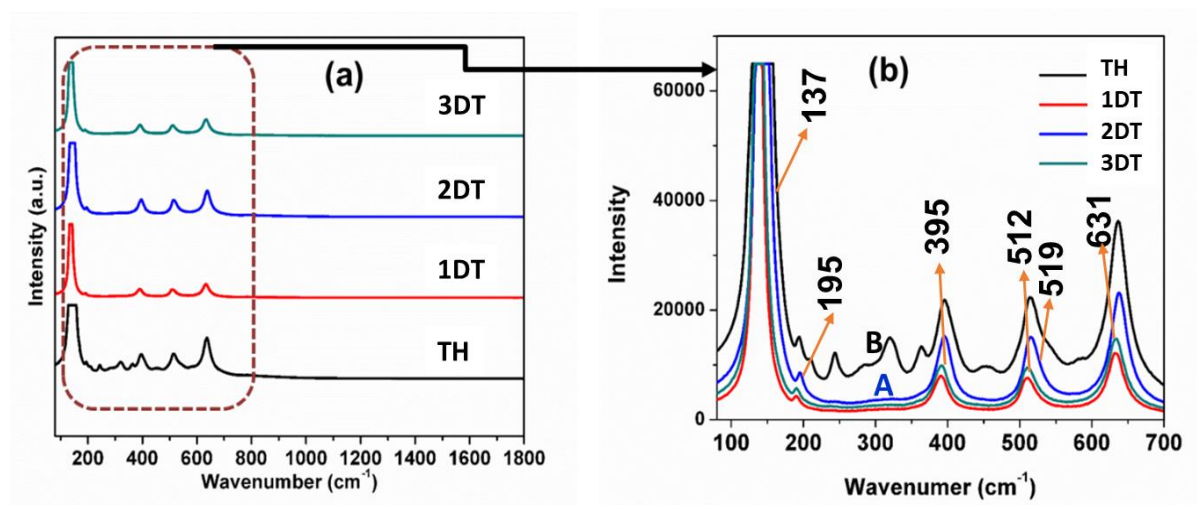


Figure 4.11: (a) Raman spectra (b) Enlarged Raman spectra of TH, 1DT, 2DT and 3DT

4.6.7 Microstructural analysis (SEM/TEM/EDAX/PSD)

The particle morphology and microstructural features of the TiO_2 material were modified by varying β -CD concentrations and then investigated by FE-SEM. The nanosized TiO_2 particles aggregated to form a nano-cluster. Figure 4.12a represents a sample TH produced by the simple hydrolysis of TiP, which showed particles with irregular shape and size, no defined geometry, and an agglomeration effect. While TiO_2 prepared using β -CD (2DT) showed a profound influence on the nanomaterial morphology and size. The particle sizes of the 2DT sample ranged from 15 to 45 nm with an average diameter of 32 nm. The particle shape, size, and morphology were relatively uniform compared to TH [25]. The FE-SEM images of sample TH and 2DT are compared as shown in Figure 4.12(a,b), showing the formation of nanomaterials.

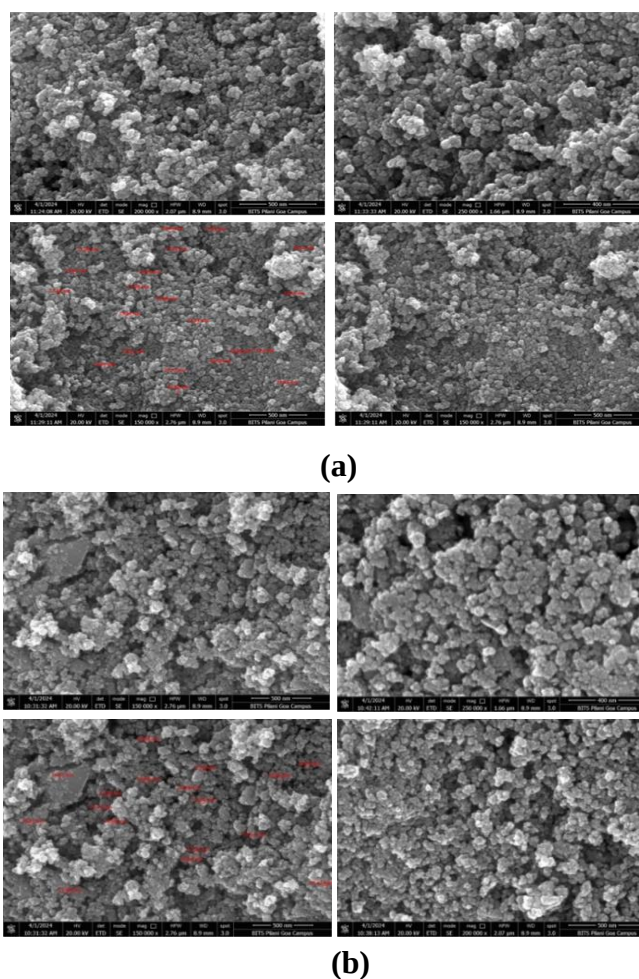


Figure 4.12: FE-SEM images of (a) TH and (b) 2DT

Based on the FE-SEM images, the particle size distribution (PSD) measurements were performed on the materials. Figure 4.13(a,b) shows the comparative PSD histogram for samples TH(a) and 2DT(b), where the % number of particles was plotted against their size on a nanometer scale. The average/ mean particle size for both materials was compared; the mean particle size for TH and 2DT was 32 nm and 28 nm, respectively. The sample 2DT showed lower and narrower PSD compared to TH, which could be attributed to the disintegration of particles to fine powder during the thermal decomposition of the organic-CD moiety.

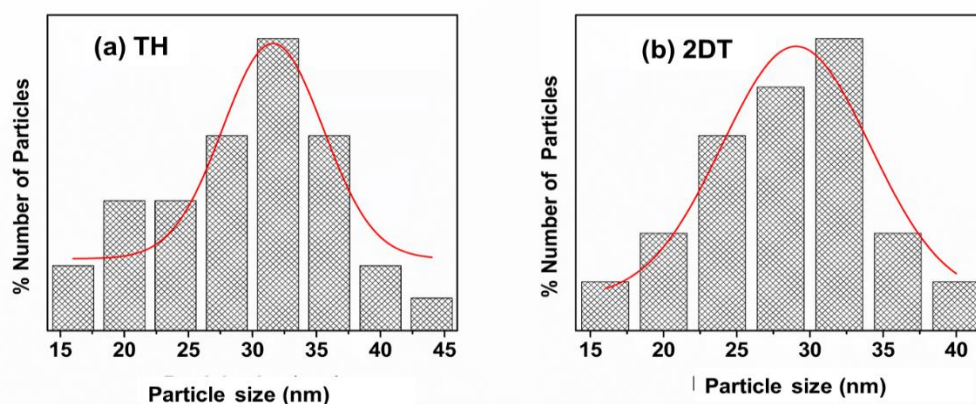


Figure 4.13: Particle size distribution of (a) TH and (b) 2DT.

The EDAX spectral signals originating from titanium and oxygen are shown in Figure 4.14. The EDAX elemental mapping confirmed the titanium (Ti) and oxygen (O) peaks, hence, the purity of TiO_2 nanomaterials was validated. The atomic weight percentage of the 2DT sample is also depicted in the inset table and found to be proportional to the expected atomic concentration. This study confirmed that the material was purely TiO_2 .

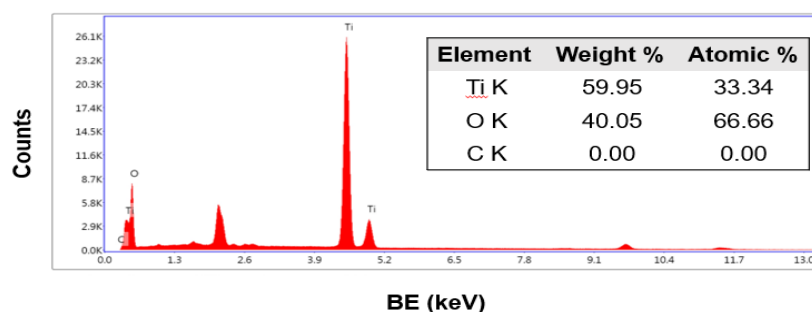


Figure 4.14: EDAX of 2DT sample

High-resolution TEM images were captured to investigate the in-depth morphology of the sample TH and 2DT materials. The introduction of β -CD resulted in narrow PSD, mesoporous materials with uniform particle size and geometry. Hence, it can be concluded that the particle characteristics of nanocrystals of TiO_2 could be controlled by adding a definite quantity of β -CD during the synthesis process. The TH sample showed the spherical to irregular-shaped TiO_2 particles shown in Figure 4.15(a-d). The selected area electron diffraction (SAED) pattern of TH indicated anatase + brookite TiO_2 , shown in Figure 4.15e. The high-resolution TEM images of TH sample are displayed in Figure 4.15(f,g), which indicated crystalline material with a crystal fringe spacing of 0.35 nm.

The TEM images of 2DT sample are shown in Figure 4.16(a-d), displaying spherical to hexagonal-shaped anatase TiO_2 particles. The particles showed translucent images, which indicated nanoparticles. The HR-TEM images of 2DT also showed well-aligned crystal lattice fringes, depicted in Figure 4.16(f,g). This indicated that the material was highly crystalline in nature [26]. The fringe spacing (lattice planes) was ~ 0.35 nm, complying with the interplanar spacing of (101) planes of anatase TiO_2 (JCPDS 12–1272). The SAED pattern revealed a well-defined ring pattern conforming to the crystalline material. The SAED ring patterns were captured, marked, indexed to anatase crystal lattice planes as presented in Figure 4.16e [27].

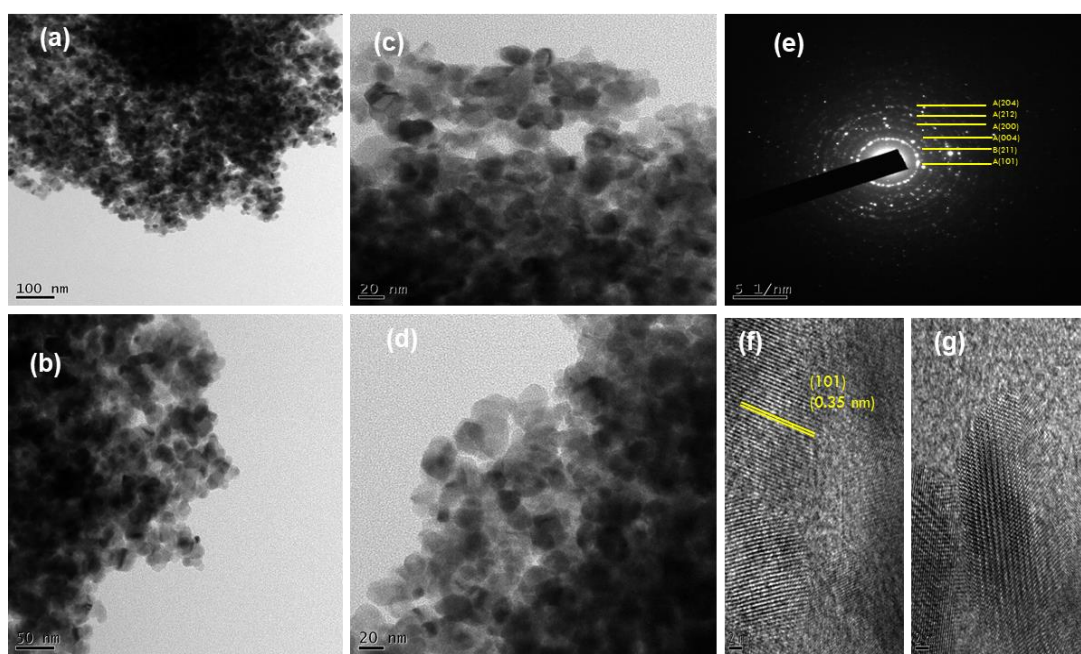


Figure 4.15 (a-d) TEM images (e) SAED and (f,g) HR-TEM images of TH.

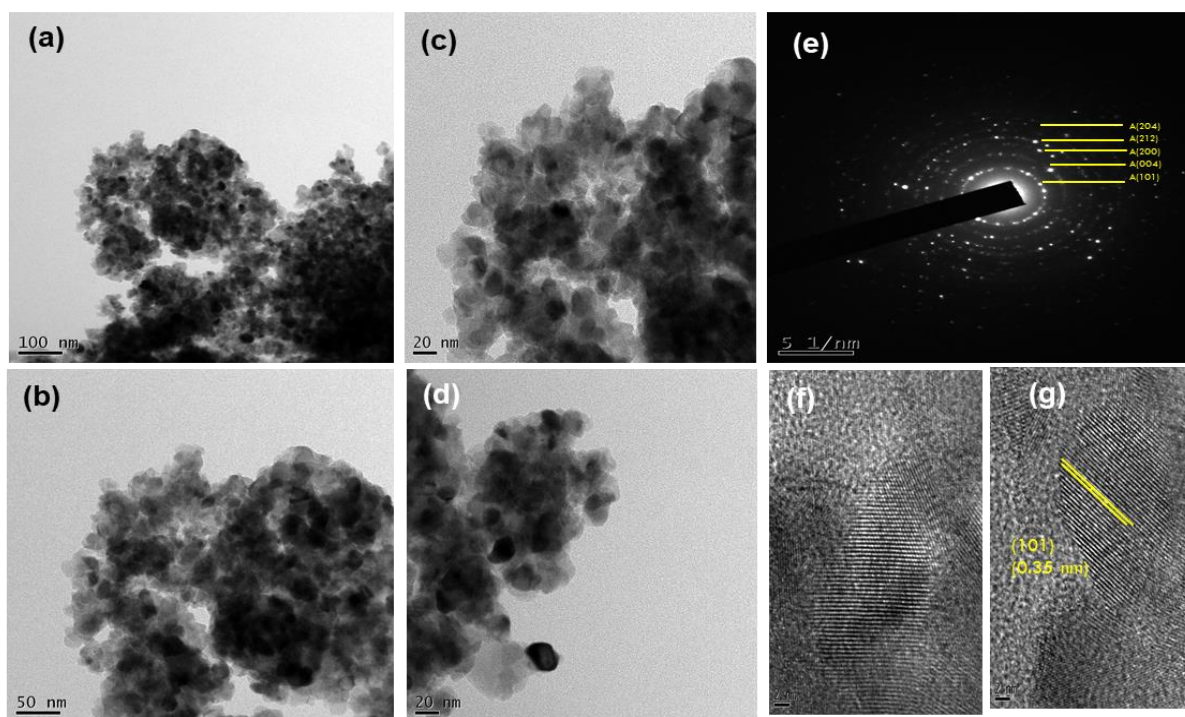


Figure 4.16: (a-d) TEM images (e) SAED and (f,g) HR-TEM images of 2DT.

4.6.8 UV-visible absorption studies and band gap

The UV-visible DRS spectra of the photocatalytic materials were recorded in the range of 200 to 800 nm. The UV-visible light absorption ability and the band gap energy of the material (TH, 1DT, 2DT, and 3DT) were investigated. Figure 4.17a shows the UV-visible DRS absorption spectra of the above-mentioned samples. All samples showed rapid light absorptions below 400 nm (UV region) due to band-to-band electron transition from VB to CB. The absorption sharply increases between 350 to 390 nm due to the band gap energy of the TiO₂ material. On close examination, a marginal blue shift was observed in the case of samples prepared from the β -CD precursor for 1DT, 2DT, and 3DT compared to the TH.

The Kubelka–Munk function was applied to the absorption spectrum to estimate the band gap (E_g) of TiO₂ materials. The absorption part of the material and the band gap energy (E_g) were related by the Tauc equation 3.

$$\alpha h\nu = B (h\nu - E_g)^n \dots \dots \dots (3)$$

where, α was the absorption coefficient, due to inter-band electron transitions near the band gap, ($h\nu$) was the photon energy, B was a constant and E_g was the optical band gap, while the

parameter ‘n’ was a type of electron transition and had value $n = 1/2$ for direct allowed transitions. The linear portion of the $(\alpha h\nu)^2$ versus $(h\nu)$ plots was extrapolated on the x-axis to calculate the band gap energies (E_g). The Tauc plots were plotted, and the band gap energy (eV) was marked, as shown in Figure 4.17b. The samples 1DT, 2DT, and 3DT showed a slightly higher band gap (≈ 3.52 eV) compared to TH (≈ 3.36 eV), which was attributed to the reduced particle size. The band gap energy is inversely proportional to the particle size, hence, E_g increased as the average particle size (d, nm) decreased, and this phenomenon in literature was reported as a ‘quantization effect’ [28]. Alternatively, the E_g of nanocrystalline TiO_2 with particle diameters can be calculated and compared with the Tauc band gap values. The relation between the band gap (E_g) as a function of particle size (d) was expressed as per equation 4 [29]

$$E_g = 3.2 + (0.0186)/(1 - 0.236d + 0.019d^2) \dots \dots \dots (4)$$

The band gap energy (E_g) were calculated considering the average particle size obtained from the XRD Scherrer formula and compared with Tauc E_g values. The E_g showed a decreasing trend as the particle size was reduced, which is in line with quantized nanomaterials. The sample code, particle size (Scherrer), calculated band gap energy from UV-visible DRS (Tauc method), and particle size are compiled in Table 4.4.

Table 4.4: Compilation of particle size (Scherrer), calculated band gap energy from UV-visible DRS (Tauc method) and based on particle size using equation 4

Sample code	Particle size from Scherrer equation (nm)	Band gap (UV-Vis DRS absorption edge) (E_g , eV)	Band gap based on particle size (E_g , eV)
TH	33	3.366	3.2013
1DT	30	3.521	3.2017
2DT	27	3.521	3.2022
3DT	24	3.521	3.2186

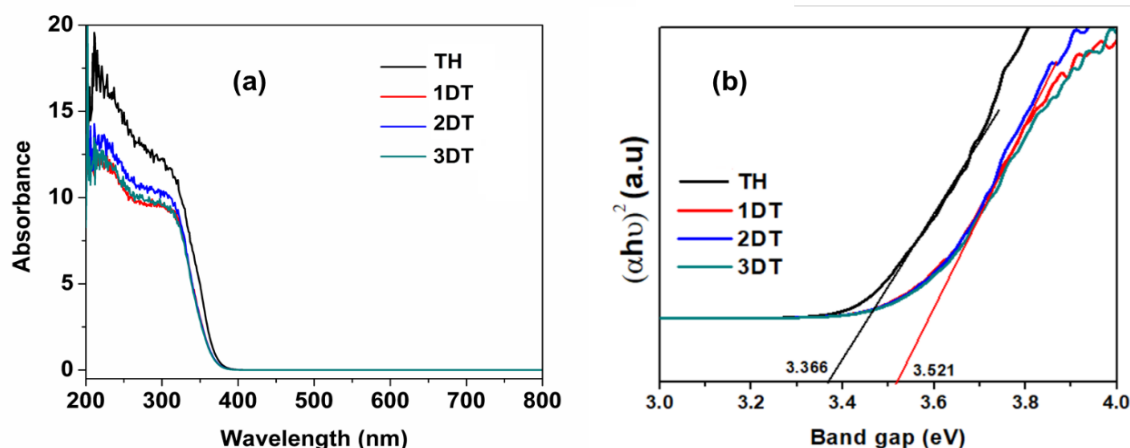


Figure 4.17: (a) Diffuse Reflectance UV–visible absorption spectra and (b) Band gap based on Tauc plots for TiO₂ samples: TH, 1DT, 2DT and 3DT.

4.6.9 Photoluminescence studies

The fate of excited electrons (e^-) in VB and the generated holes (h^+) in CB upon irradiation of light was investigated by room-temperature photoluminescence (RT-PL) studies. Most of the charge pairs ($e^- - h^+$) on recombination released energy in the form of emission radiation. There exists a relation between the PL emission intensities and ($e^- - h^+$) pair recombination rate. The higher the emission intensities, the faster the rate of recombination [30]. In PL, a high-energy UV light source ($\lambda=291$ nm) was used for the excitation of the sample, and the emission spectra of TiO₂ nanomaterials were recorded as shown in Figure 4.18. From the PL emission spectra, it was understood that sample TH exhibited the highest emission peak intensity at $\lambda_{\max}=390$ nm (3.2 eV), which was attributed to the band-to-band transition (band gap). However, the relative intensities of samples 1DT, 2DT, and 3DT were progressively reduced with the % β -CD used in the synthesis, hence, the recombination rate retarded. The observed trend in PL emission intensities for the samples was: TH > 1DT > 2DT > 3DT, however, the extent of PL intensity reduction was nominal. These small variations can be attributed to minor surface variations caused by the β -CD. Moreover, all materials exhibited a second emission band with multiple peaks in the visible region, which was attributed to the intrinsic defects formed in the samples. The decreasing trend in PL emission intensity of the second peak indicated fewer imperfections formed during

the synthesis. The second emission band ranged from 450–500 nm, which was mainly assigned to oxygen vacancies on the catalyst surface. The small peaks at ~480 and ~490 were ascribed to shallow traps formed above the conduction band [31]. Based on PL graphs, it can be stated that the charge recombination rate was inversely proportional to the β -CD concentration used during the synthesis, which could be beneficial for higher photocatalytic efficiencies.

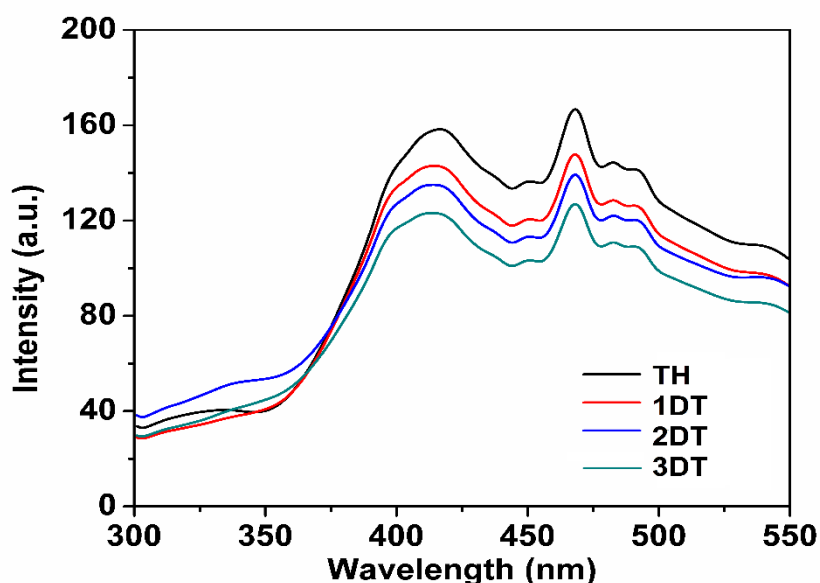


Figure 4.18: PL spectra of TiO₂ samples: TH, 1DT, 2DT and 3DT

4.7 Photodegradation of Rhodamine B (Rh B) model dye molecule

The photocatalytic performance of the TiO₂ materials (TH, 1DT, 2DT and 3DT) were examined using a model Rhodamine B (Rh B) dye molecule as described in section 4.5. The photocatalyst powder was suspended in an aqueous Rh B solution and irradiated with UV light. The Rh B peak position at absorption maxima, $\lambda_{\text{max}} = 554$ nm, in the visible region was monitored at different time intervals (0 to 120 min) in UV light. The absorption maxima or the orange colouration decreased with time on exposure to UV light. Figure 4.19a presents the photo degradation profiles of all the materials in UV light. The 2DT catalyst showed the highest degradation efficiency of 96% at the final time point of 120 min. While the catalysts

1DT and 3DT showed 30 % and 60% degradation efficiency at the same time point, respectively. The photocatalyst TH displayed slightly lower efficiency compared to 2DT [32]. The reason could be attributed to the presence of mixed phases(A+B) of TH, hence the data is for an indicative purpose only.

Figure 4.19b displays the kinetic plots, $\ln(C_0/C)$ on the y-axis versus timescale on the x-axis, which revealed a positive slope with straight lines fitting to the Langmuir-Hinshelwood kinetic model.

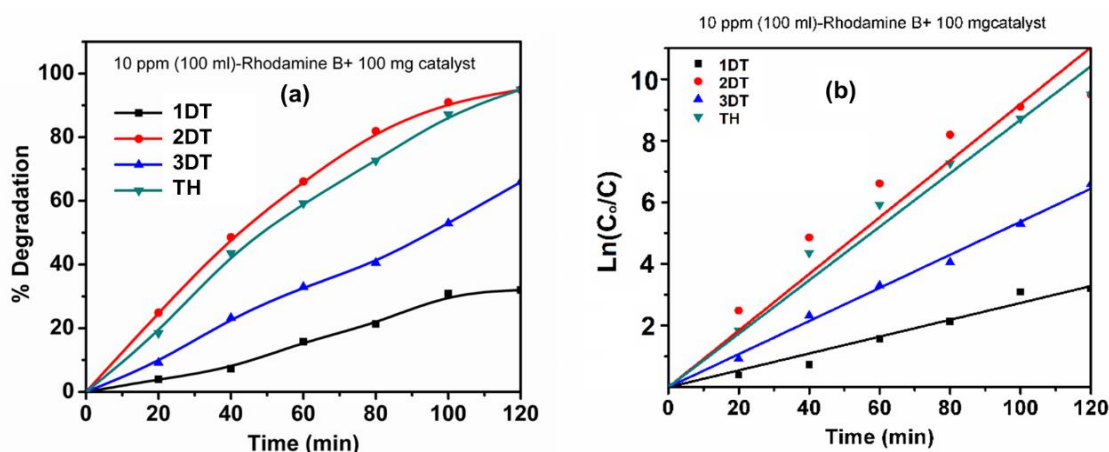


Figure 4.19: % Photocatalytic degradation of Rhodamine B (a) In UV light and (b) Kinetic plots.

The lines followed the pseudo-first-order kinetics during the degradation of Rh B dye, and the equation of a straight line could be stated as $\ln(C_0/C) = \alpha kt$, where 'k' is the rate constant for degradation [33]. The rate constant value 'k' obtained from the straight-line equation was 0.29294, 0.80408 and 0.54054 min^{-1} for 1DT, 2DT and 3DT, respectively. On comparing the 'k' values, the degradation rate for Rh B exhibited by each catalyst followed the trend as: 2DT > 3DT > 1DT. This suggested that 2DT displayed the best performance, while 1DT and 3DT showed intermediate photodegradation activities [34]. The rate constant value for sample TH is not considered due to mixed phases. This proved that the 2DT photocatalyst was considered the most active catalyst for the degradation of organic dyes. The probable reason for the high photodegradation efficiency could be linked to favourable surface properties of 2DT material, such as high surface area, porous morphology, and lower electron-hole recombination rate and linked to the optimal β -CD concentration used during materials synthesis.

4.8 Application of Photocatalyst: Photodegradation of Paracetamol molecule

Paracetamol (4-hydroxyacetanilide, acetaminophen or N-acetyl-p-aminophenol, chemical formula: $C_8H_9NO_2$, molecular mass = 151) is a well-known antipyretic, analgesic, and non-steroidal anti-inflammatory drug molecule, widely used by humans worldwide. The annual global production of paracetamol is about 200 kilo tons per year [35]. In the recent past, environmental and potable water contamination by paracetamol has been a matter of grave concern [36]. Hence, paracetamol and its metabolites or residues are considered to be “compounds of emerging concern” as they create a negative impact on human health and the environment [37]. The main contributors to paracetamol pollution are pharmaceutical industries, human sewage and hospital waste effluents. Moreover, paracetamol is a comparatively stable molecule and difficult to eliminate by conventional effluent treatment plants [38]. Hence, the paracetamol molecule is retained in the environment for a long time without getting degraded and might cause damage to human health and the environment [39]. In this regard, the degradation of paracetamol using photocatalysts (TiO_2) and light has been investigated by different scientific groups [40]. In the current study, the photocatalytic oxidation process was adopted, where the anatase- TiO_2 was activated by light that produced reactive species, which then reacted with paracetamol to break down into smaller fragments.

The paracetamol molecule degradation in the presence of 2DT photocatalyst was carried out as a function of time under UV-light irradiation. The competitive degradation efficiency of 2DT in UV and sunlight at each time point is presented in Figure 4.20. Since 1DT and 3DT samples indicated comparatively lesser activity than 2DT, hence not considered in the study. The 2DT photocatalyst exhibited higher activity in UV light compared to sunlight due to better charge separation and migration of charges at the surface of the photocatalyst. Photogenerated holes in the VB and electrons in the CB generate charged reactive species useful for the degradation of paracetamol. The $(OH)^{\cdot -}$ was formed due to the interaction of solvent molecules with the catalyst surface and light. The adsorbed water molecules were dissociated on the surface of the metal oxide to form proton (H^+) and hydroxyl ($OH^{\cdot -}$) species. The H^+ protons reacted with oxygen molecules and electrons in the conduction band to produce hydrogen peroxide, while the $OH^{\cdot -}$ species reacted with photogenerated holes to

generate $(OH)^{\bullet}$ radical. These $(OH)^{\bullet}$ radicals were responsible for the decomposition of paracetamol into smaller fragments and finally into water and carbon dioxide.

The proposed mechanism for the degradation of paracetamol molecules over the TiO_2 surface on irradiation with light is as follows:

- $TiO_2 + h\nu \rightarrow TiO_2(e^-_{CB} + h^+_{VB})$(i)
- $(O_2)_{ads} + e^-_{CB} \rightarrow O_2^{\bullet-}$ (ii)
- $H_2O + h^+_{VB} \rightarrow OH^{\bullet}$(iii)
- $Paracetamol + h^+ \rightarrow Degradants$(iv)
- $Paracetamol + O_2^{\bullet-} \rightarrow Degradants$(v)
- $Paracetamol + OH^{\bullet} \rightarrow Degradants$ (vi)

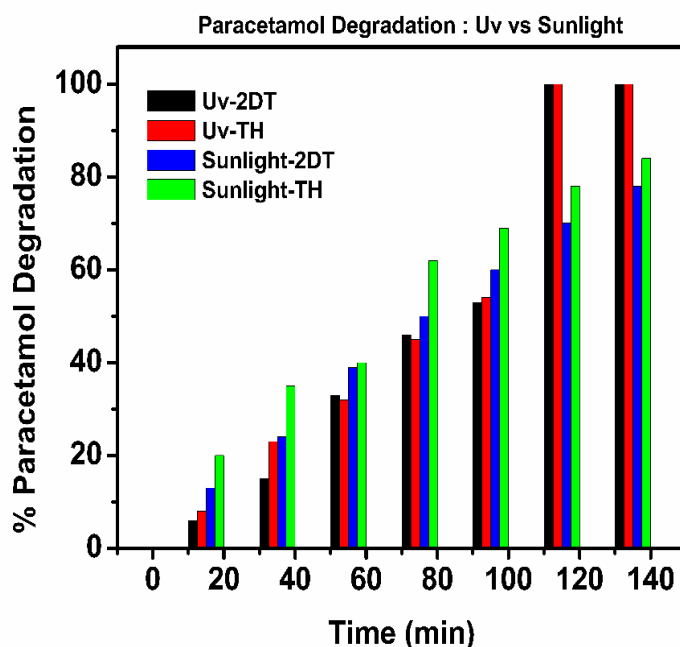


Figure 4.20: Photocatalytic degradation activity of paracetamol over TH and 2DT in UV and sunlight.

4.8.1 Effect of types of catalyst

The effect of the catalyst was demonstrated on the as-prepared photocatalysts: 1DT, 2DT and 3DT by degrading the paracetamol solution. Figure 4.21 displays the paracetamol degradation profiles for 1DT, 2DT and 3DT materials. From the graphs, it was evident that the 2DT material displayed maximum efficiency compared to the 1DT and 3DT. The trend was similar to the Rh B dye degradation activity. The higher degradation could be attributed to the higher adsorption of the drug molecule on the material surface. This also indicated that the use of different β -CD concentrations was critical in modifying the surface morphology. The interaction between inorganic titanyl oxyhydroxide and organic β -CD molecule played a crucial role in altering the TiO_2 material structural properties. Another reason for higher efficiency of DT could be linked to superior surface properties.

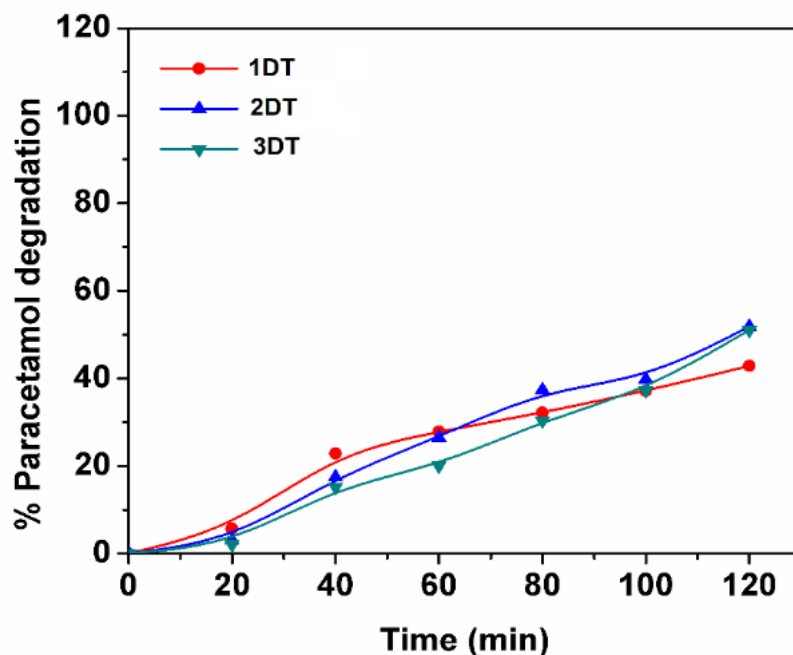


Figure 4.21: Effect of types of catalyst (1DT, 2DT and 3DT) on photocatalytic activity

4.8.2 Effect of concentration of catalyst

The rate of degradation was directly proportional to the amount of photocatalyst added to the reaction vessel during the photocatalytic degradation studies. The number of reactive species generated depended on the quantity of photocatalysts exposed to light. The degradation profiles shown in Figure 4.22 were in line with the above assumption, and the rate of degradation initially increased with the loading of catalyst from 60 mg, 80 mg and 100 mg and then decreased for 120 mg. The reason for such a trend could be explained as follows: (i) at higher concentrations, the agglomeration of catalyst particles may have occurred, and (ii) the light scattering effect dominated at higher dosing. Hence, a decrease in activity can be attributed to the reduction in light penetration at higher photocatalyst concentrations, thus hampering the photoexcitation of the catalyst surface. The study demonstrated that 100 mg of photocatalyst was the optimal concentration for the highest degradation efficiency.

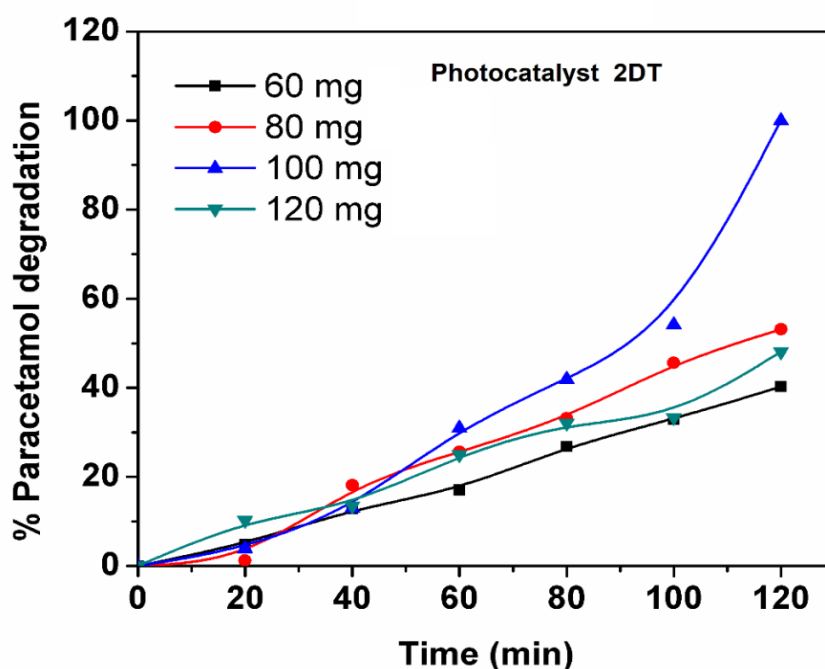


Figure 4.22 Effect of concentration of photocatalyst (2DT) (60 mg, 80 mg, 100 mg and 120 mg) on photocatalytic activity.

4.8.3 Effect of pH of paracetamol solution

The effect of the pH on the degradation efficiency of the paracetamol solution was evaluated experimentally. It is well-known that the TiO_2 material displays good stability across a wide pH range. The pH of paracetamol solution was deliberately varied from acidic to neutral to basic conditions. The photoactivity was measured across the pH range, keeping all other experimental conditions constant. Figure 4.23 shows the % degradation profiles for paracetamol at pH2, pH4, pH7, pH8 and pH10. On the acidic side (pH2 to pH4) and also on the basic side (pH10) showed minimal photoactivity. The degradation efficiency was highest when the pH of the solution was adjusted between 7 to 8, which was close to neutral pH. The enhancement of activity near neutral pH is more practical compared to acidic or basic conditions. Hence, to achieve maximum paracetamol degradation efficiency, the pH of the solution should be close to neutral. The pH has a profound impact on the photocatalytic dye degradation activity. The optimal operating pH conditions vary for different organic dye degradation activity depending on the type of charge they carry. Some dye shows higher degradation in acidic pH. In an acidic condition, the ZnO surface is positively charged. Hence, negatively charged molecules adsorb over the catalyst surface; as a consequence dye degradation is higher. In alkaline conditions, the negatively charged molecules do not get adsorb over the surface due to coulombic repulsion resulting in lowering of dye degradation. The pH condition can also influence the type of reactive species formed and the pathway of photocatalytic degradation also get modified depending on the type of organic compounds. So, optimal pH conditions is a very important parameter which needs to be evaluated during the photocatalytic dye degradation studies [41].

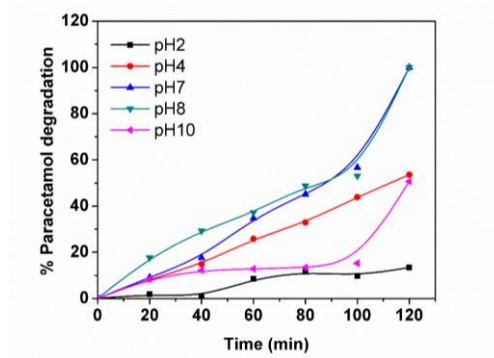


Figure 4.23: Effect of pH of paracetamol solution (pH2, pH4, pH7, pH8, pH10) on photocatalytic activity.

4.9 Reactive species trapping experiment

The charge-trapping experiments were performed to understand the type of reactive species generated by the catalyst on exposure to UV light. A known quantity of charge scavengers/agents were added during the paracetamol photocatalytic degradation activity. Isopropyl alcohol (IPA), sodium salt (EDTA-2Na), and para-benzoquinone (p-BZQ) were added to trap hydroxyl radicals ($\text{OH}^\bullet$), holes (h^+), superoxide $^\bullet(\text{O}_2)^-$ radicals, respectively and compared against the pure 2DT photocatalytic activity (without scavenger). Figure 4.24 shows the % photocatalytic degradation values plotted against each charge scavenger. From the bar graph, it was evident that in the absence of a charge scavenger, the 2DT catalyst exhibited the highest photoactivity of $\sim 100\%$ after a definite time interval. While in the presence of p-BZQ, EDTA, and IPA trapping agents, the activity dropped to 20 %, 42 % and 46%, respectively. Hence, it can be stated that the $^\bullet(\text{O}_2)^-$, (h^+), and ($\text{OH}^\bullet$) were the major reactive species generated and involved in the degradation of the paracetamol molecule over the TiO_2 photocatalyst [42]. This was in agreement with the proposed mechanism for degradation of paracetamol molecules over TiO_2 catalyst surface in the presence of light energy.

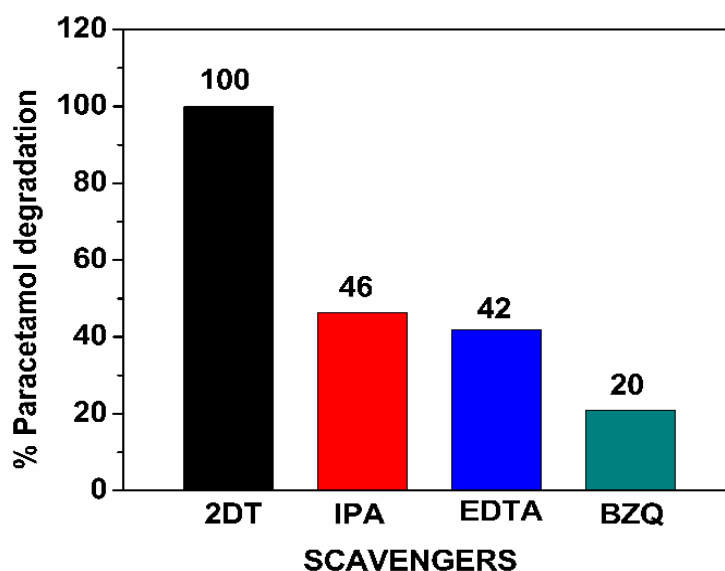


Figure 4.24: Reactive species trapping experiment.

4.10 Liquid chromatography-Mass spectrometry (LC-MS) studies: Identification of Paracetamol drug molecule degradants

Additionally, to identify the degradants formed by the photocatalyst, the final time point (50 min) of the degraded paracetamol solution was analyzed by LC-MS. Based on molecular mass (m/z) spectra, the fragments of paracetamol were identified and reported [43]. Initially, as such pure paracetamol solution (before degradation) was injected into the liquid chromatograph (LC). The obtained chromatogram showed a single main peak eluting at a retention time of 0.694 min due to paracetamol, as seen in Figure 4.25a. At the same retention time, the peak was analyzed by the mass spectrometer (MS), which showed a major intensity peak with $m/z = 150.2$, attributed to native paracetamol molecule in the solution, displayed in Figure 4.25b. This confirmed that the paracetamol molecule was present in an undegraded state in the initial solution. Later, the same solution was subjected to photocatalytic degradation over 2DT and irradiated with UV light.

At the end of 50 min time point, the solution was collected and analyzed by LC-MS. After degradation, the solution showed a distorted peak at a retention time of ~ 0.666 min in the chromatogram due to elution of paracetamol degradants. The peak shape and intensity were completely different compared to the original sample. This indicated that the parent paracetamol molecule was destroyed and converted into smaller multiple fragments. The MS spectra were scanned at the same retention time, as shown in Figure 4.25(c,d,e). The degraded paracetamol solution contained fragmented and disintegrated smaller molecules [38]. The major fragments identified based on m/z values were: Degradant-1: 2, 4-dihydroxyphenol ($m/z = 127.2$) and Degradant-2, which was maleic acid ($m/z = 116.9$), along with unidentified degradants. This suggested that the photocatalyst could disintegrate the paracetamol drug molecules into their smaller fragments and ultimately convert them into carbon dioxide and water.

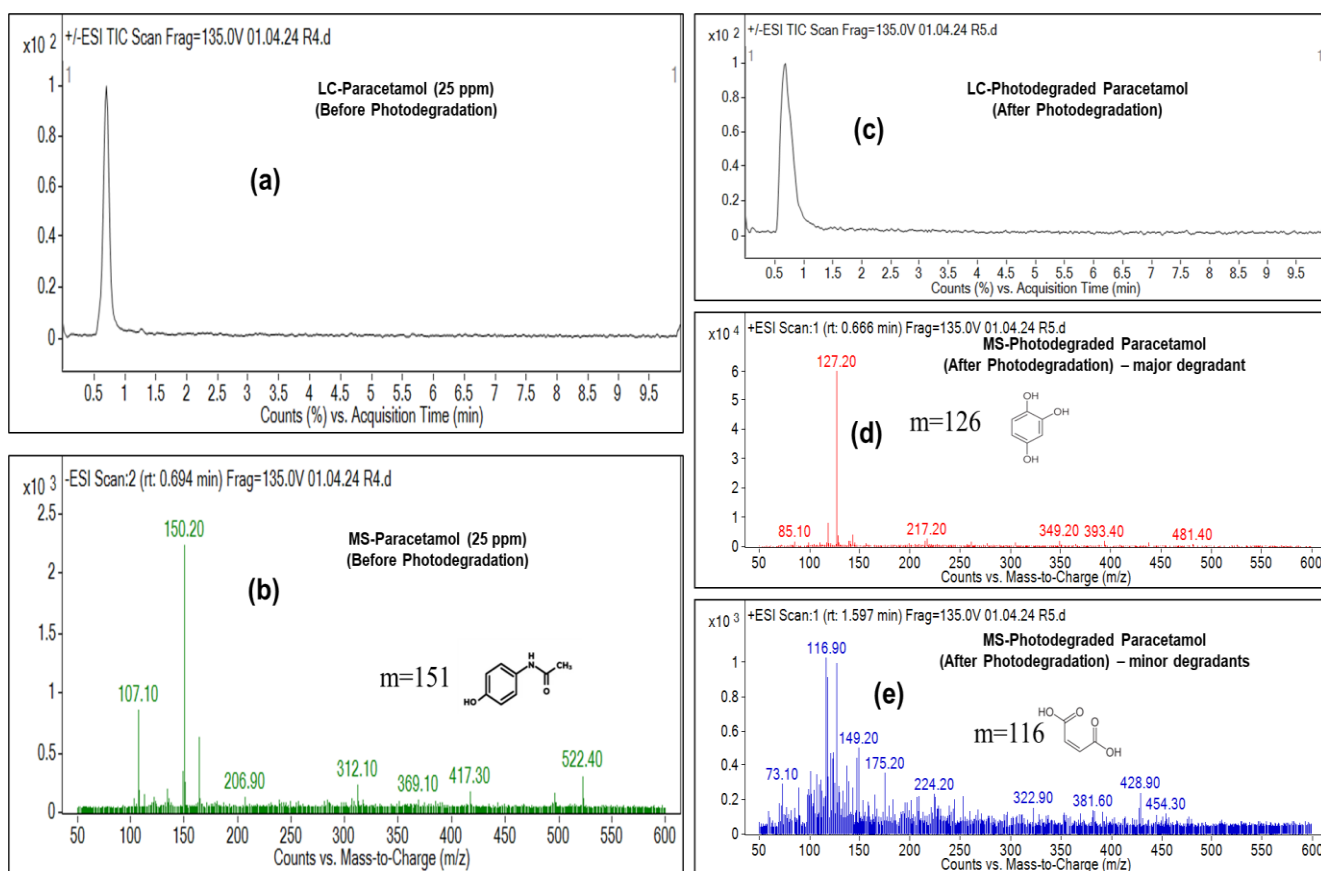


Figure 4.25: LC-MS spectra of paracetamol solution (a) Chromatogram before degradation of paracetamol solution, (b) MS of paracetamol before degradation, (c) Chromatogram after degradation of paracetamol solution, (d) MS spectrum of degradant-1 with $m/z=126$ and (e) MS spectrum of degradant-2 with $m/z=116$.

4.11 Conclusions

The photoactive anatase TiO₂ nanomaterial powders were easily prepared via thermal decomposition of beta-cyclodextrin-titanyl oxyhydroxide precursors. The β -CD displayed the structure-directing property and provided thermal stability to nanosized anatase TiO₂ during the synthesis process. The TiO₂ material properties were tailored with respect to shape, size, morphology and phase by altering the β -CD concentration. The nanomaterial so produced displayed hexagonal to spherical-shaped particles in the nanosized range. The catalytic grade TiO₂ nanoparticles exhibited a high degree of crystallinity with well-defined crystal planes and a narrow particle size distribution range (15 to 35 nm). The fabrication of TiO₂ powders displayed a specific surface area $\sim 35 \text{ m}^2/\text{g}$ and mesoporous characteristics. The band gap of TiO₂ materials showed a small blue shift with a marginal increase in E_g compared to material prepared without β -CD due to the “quantization” effect. The materials synthesized from the β -CD precursors showed a retarded charge pair recombination rate which is of prime importance in photocatalysis process. The XPS, EDAX, and Raman confirmed the anatase phase and chemical purity of the material. Anatase TiO₂ material displayed promising results for the photocatalytic degradation of Rhodamine B (Rh B) dye and paracetamol drug molecule. The degradation rate of Rh B dye was highest when the β -CD concentration was 2% during the preparation. The rate of reaction, determined based on rate constants, displayed a maximum value of 0.804 min^{-1} for the 2DT photocatalyst. LC-MS studies proved that the anatase TiO₂ materials were actively involved in the photodegradation process of the paracetamol drug molecule into smaller fragments. LC-MS studies identified the main fragments of paracetamol as 2, 4-dihydroxyphenol ($m/z = 127.2$) and maleic acid ($m/z = 116.9$) in the degraded solution. The paracetamol original molecular structure was significantly disintegrated into smaller fragments, which was the primary requirement for mineralization of large, harmful molecules. The main highlights of this study were: nanosized catalytic grade anatase TiO₂ powders were conveniently prepared using the β -CD precursors. The method was quite economical and utilized biocompatible, eco-friendly chemicals. The anatase TiO₂ materials displayed efficient degradation of organic chemical molecules (Rh B and paracetamol). These materials could be applied in industrial effluent treatment plants to destroy harmful chemical molecules before they are released into the environment.

REFERENCES

1. S. Reghunath, D. Pinheiro, and S. D. KR, *Applied Surface Science Advances* **3**, 100063 (2021).
2. C. Y. Hsu, Z. H. Mahmoud, S. Abdullaev, F. K. Ali, Y. Ali Naeem, R. Mzahir Mizher, M. Morad Karim, A. S. Abdulwahid, Z. Ahmadi, S. Habibzadeh, and E. Kianfar, *Case Studies in Chemical and Environmental Engineering* **9**, 100626 (2024).
3. A. C. Nkele, U. K. Chime, L. Asogwa, A. C. Nwanya, U. Nwankwo, K. Ukoba, T. C. Jen, M. Maaza, and F. I. Ezema, *Inorganic Chemistry Communications* **112**, 107705 (2020).
4. M. M. Karkare, *International Nano Letters* **4**, 1 (2014).
5. X. Chen and S. S. Mao, *Chemical Reviews* **107**, 2891 (2007).
6. I. Ali, M. Suhail, Z. A. Alothman, and A. Alwarthan, *RSC Advances* **8**, 30125 (2018).
7. M. Zhang, T. Chen, and Y. Wang, *RSC Advances* **7**, 52755 (2017).
8. S. R. Damkale, S. S. Arbuj, G. G. Umarji, S. B. Rane, and B. B. Kale, *RSC Advances* **11**, 7587 (2021).
9. G. Crini, *Chemical Reviews* **114**, 10940 (2014).
10. R. Challa, A. Ahuja, J. Ali, and R. K. Khar, *AAPS PharmSciTech* **6**, 329 (2005).
11. H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, and H. M. Cheng, 4078 (2009).
12. T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, and M. Batzill, *Scientific Reports* **4**, 1 (2015).
13. C. Gadipelly, A. Pérez-González, G. D. Yadav, I. Ortiz, R. Ibáñez, V. K. Rathod, and K. V. Marathe, *Industrial and Engineering Chemistry Research* **53**, 11571 (2014).
14. X. Zhang, Z. Yang, X. Li, N. Deng, and S. Qian, *Chemical Communications* **49**, 825 (2013).
15. R. Bleta, A. Lannoy, C. Machut, E. Monflier, and A. Ponchel, *Langmuir* **30**, 11812 (2014).
16. P. Monreal-Pérez, J. R. Isasi, J. González-Benito, D. Olmos, and G. González-Gaitano, *Nanomaterials* **8**, 1 (2018).
17. P. Velusamy, S. Pitchaimuthu, S. Rajalakshmi, and N. Kannan, *Journal of Advanced Research* **5**, 19 (2014).
18. F. Trotta, M. Zanetti, and G. Camino, *Polymer Degradation and Stability* **69**, 373 (2000).
19. S. R. Gajjela, K. Ananthanarayanan, C. Yap, M. Grätzel, and P. Balaya, *Energy and Environmental Science* **3**, 838 (2010).
20. K. Wang, Y. Zhuo, J. Chen, D. Gao, Y. Ren, C. Wang, and Z. Qi, *RSC Advances* **10**, 43592 (2020).
21. S. Murugesan, R. Thirumurugesan, E. Mohandas, and P. Parameswaran, *Materials Chemistry and Physics* **225**, 320 (2019).
22. Z. Ren, X. Fu, C. Chen, J. Wang, C. Fan, G. Qian, and Z. Wang, *RSC Advances* **4**, 19266

- (2014).
23. L. Wu, J. C. Yu, X. Wang, L. Zhang, and J. Yu, *Journal of Solid State Chemistry* **178**, 321 (2005).
24. F. Tian, Y. Zhang, J. Zhang, and C. Pan, *Journal of Physical Chemistry C* **116**, 7515 (2012).
25. G. He, J. Zhang, Y. Hu, Z. Bai, and C. Wei, *Applied Catalysis B: Environmental* **250**, 301 (2019).
26. M. Pisarek, M. Krawczyk, A. Kosiński, M. Hołdyński, M. Andrzejczuk, J. Krajczewski, K. Bieńkowski, R. Solarska, M. Gurgul, L. Zaraska, and W. Lisowski, *RSC Advances* **11**, 38727 (2021).
27. S. N. Hosseini, X. Chen, P. J. Baesjou, A. Imhof, and A. van Blaaderen, *Applied Sciences (Switzerland)* **12**, (2022).
28. A. K. Mohapatra and J. Nayak, *Optik* **156**, 268 (2018).
29. X. Xue, W. Ji, Z. Mao, H. Mao, Y. Wang, X. Wang, W. Ruan, B. Zhao, and J. R. Lombardi, *Journal of Physical Chemistry C* **116**, 8792 (2012).
30. L. Kernazhitsky, V. Shymanovska, T. Gavrilko, V. Naumov, L. Fedorenko, V. Kshnyakin, and J. Baran, *Journal of Luminescence* **146**, 199 (2014).
31. M. J. Valero-Romero, J. G. Santaclara, L. Oar-Arteta, L. van Koppen, D. Y. Osadchii, J. Gascon, and F. Kapteijn, *Chemical Engineering Journal* **360**, 75 (2019).
32. S. Y. Lee, D. Kang, S. Jeong, H. T. Do, and J. H. Kim, *ACS Omega* **5**, 4233 (2020).
33. X. Zheng, D. Li, X. Li, L. Yu, P. Wang, X. Zhang, J. Fang, Y. Shao, and Y. Zheng, *Physical Chemistry Chemical Physics* **16**, 15299 (2014).
34. Y. Ma and J. N. Yao, *Journal of Photochemistry and Photobiology A: Chemistry* **116**, 167 (1998).
35. J. Park, C. Evans, J. Maier, M. Hatzell, S. France, C. Sievers, and A. S. Bommarius, *ACS Sustainable Chemistry and Engineering* **12**, 16271 (2024).
36. W. Koagouw, Z. Arifin, G. W. J. Olivier, and C. Ciocan, *Marine Pollution Bulletin* **169**, 112558 (2021).
37. F. Hashemzadeh, M. Ariannezhad, and S. H. Derakhshandeh, *Scientific Reports* **14**, 1 (2024).
38. S. Wu, L. Zhang, and J. Chen, *Applied Microbiology and Biotechnology* **96**, 875 (2012).
39. B. Nunes, S. C. Antunes, J. Santos, L. Martins, and B. B. Castro, *Ecotoxicology and Environmental Safety* **107**, 178 (2014).
40. J. Zia and U. Riaz, *ACS Omega* **5**, 16386 (2020).
41. T. Bak, J. Nowotny, M. Rekas, and C. C. Sorrell, *Int.Jr.Hydrog.Energy* **27**, 991 (2010).
42. E. Moctezuma, E. Leyva, C. A. Aguilar, R. A. Luna, and C. Montalvo, *Journal of Hazardous Materials* **243**, 130 (2012).
43. L. Yang, L. E. Yu, and M. B. Ray, *Environmental Science and Technology* **43**, 460 (2009).

Chapter-5:

Synthesis, characterization and application of MWCNT/TiO₂ composite material for the photocatalytic reduction of benzophenone to benzopinacol

5.1 Introduction

The metal oxide (MO) supported on carbon nanotubes (CNT) are an important class of hybrid materials that are being widely investigated for solar cells, catalysis and sensor applications [1,2]. The CNT possess a unique and fascinating structure, morphology, adsorption capability, and electrical properties, which make them an ideal support material for semiconducting MO [3]. The contact between CNT and photosensitive MO heterostructures can generate interactive effects leading to interfacial charge transfer. Hence, homogeneous blending and effective contact at the surfaces are important in producing synergistic cooperative effects between two materials. The fabrication of hybrid MO/CNT composites is mainly achieved through ex-situ and in-situ methods [4]. In the ex-situ approach, the MO particles of the desired shape, size and morphology are first produced and then attached to the surface of CNT either through strong chemical covalent bonding or electrostatic interactions or weak van der Waals forces [5]. On the other hand, in the in-situ method, the bonding of the MO or its precursor to CNT is carried out, wherein the oxide material is grown from solution or precursors as particles, nanowires, or thin films [6].

Titanium dioxide (TiO_2) is a promising photocatalytic material extensively used in catalysis owing to its outstanding physicochemical stability, low cost, light absorption capability, and ability to produce electron-hole (e^-h^+) pairs for number of redox reactions [7]. However, TiO_2 possesses certain limitations which hinder its photocatalytic efficiency, such as rapid recombination of photogenerated (e^-h^+) pairs; consequently, very few, about 10% of electrons, are effectively available for photocatalytic activity. Another reason is the high band gap energy ($E_g \approx 3.32$ eV), which requires high-energy UV radiation to excite the electrons. Moreover, TiO_2 displays lower efficiency in sunlight due to non-absorption in the visible light region [8]. Moreover, isolation and reusability of nanosized TiO_2 particles from the photocatalytic reaction vessel are often the most challenging tasks. The TiO_2 particles tend to agglomerate, which hampers the photoactivity. To overcome all these shortcomings, several alternate preparative methodologies have been reported. Out of these, TiO_2 supported on multi-walled carbon nanotubes (MWCNT) is the most preferred and promising composite material [9]. Here, the main objective of the current study was to prepare MWCNT/ TiO_2 composite material, extend the absorption edge in the UV-visible region, slow down the (e^-

$-h^+$) pair recombination, and increase the mobility of charge, thereby improving the catalytic efficiency of the organic synthesis reaction. When the TiO_2 particles are coated on MWCNT, they are less prone to aggregation and practically feasible to recover the catalyst after usage. The MWCNT/ TiO_2 interface assists in separating the charges and acts like an electron trap, thereby enhancing charge collection and transfer for photocatalytic activity [10]. The use of photoactive anatase or mixed-phase TiO_2 along with MWCNT support can influence the charge separation and enhance the catalytic activity [11]. Depending on the synthetic methodologies, the intrinsic properties of composites, such as specific surface area, electrical conductivity, and optical properties of composites, could be modified and enhance the catalytic activity [12].

Heterogeneous photocatalytic materials are the preferred choice in molecular organic synthesis. The main benefit of using a heterogeneous photocatalyst is its ability to capture the light energy and transfer it to the reacting molecules to obtain the specific product [13]. MWCNT/ TiO_2 nanocomposite, on light irradiation, produces electrons and induces charge separation and transport during the photocatalytic organic synthesis reactions [14][15]. Furthermore, most organic molecules or functional groups absorb high-energy UV light photons and undergo a photodegradation process, which results in multiple products or impurities [16]. In this regard, the photocatalytic organic reactions activated by UV-visible or direct sunlight are more preferred and also contribute to green chemistry approaches [17]. However, the most challenging part is developing a photocatalyst with a reduced band gap, which can trap visible light energy (sunlight) and migration of electrons for the organic synthesis. Hence, conventional catalytic materials involving simple TiO_2 encounter difficulties in harvesting visible light energy due to high band gap energy and, in turn, producing meagre electrons for chemical reactions. The performance of MWCNT/ TiO_2 composite mainly depends on the method of synthesis, and the nano-structural features of TiO_2 and MWCNT, such as shape, size, and high surface area. In the literature, some hybrid composite materials containing MO nanoparticles coated on MWCNT have been synthesized and used as hetero photocatalysts in organic molecule synthesis [18]

In the present work, a photoactive hybrid composite material was designed using a novel precursor-layer-coating method. The TiO_2 precursor was coated onto MWCNT in-situ, aided by a polymeric layer, followed by heat treatment to yield a hybrid composite material,

which comprised nanosized TiO_2 particles coated on the MWCNT surface. The material characterization and application of the hybrid photocatalyst were evaluated by employing an organic synthesis reaction. The photocatalytic activity of pure TiO_2 and the composite materials was compared on irradiation with UV and direct sunlight. The percent photocatalytic conversion (% yield) of benzophenone to benzopinacol was monitored in the presence of the composite as a photocatalyst and light as photon energy after a definite reaction time.

5.2 Materials and Methods

5.2.1. Chemicals

The chemicals used for the preparation of composite materials were of analytical grade. Multi-walled carbon nanotubes (MWCNT) were purchased from Shilpent Chemicals, India, with purity > 98%, 4-8 layers, external diameter: ~20 nm, and length > 1 μm . Titanium isopropoxide (99.97%) procured from Merck, Carbopol 940 [Poly(acrylic acid)] polymer was supplied by Pioneer, India (M.wt. : 40000-50000) and used as such. For the photocatalytic reaction, the analytical grade chemicals, namely benzophenone, isopropanol, and acetone, were directly used without purification.

5.2.2. Preparation of MWCNT/ TiO_2 composite materials

To fabricate MWCNT/ TiO_2 composite materials, the novel precursor-layer-coating (PLC) method was employed, as illustrated in Figure 5.1. In the PLC method, the 2% w/w calculated amount of MWCNT was added to the aqueous carbopol polymer solution (1% w/w) and mixed well for 2 h. In a separate beaker, 30 mL of titanium isopropoxide (TiP) was diluted with an equal volume of isopropanol. The diluted TiP solution was then added dropwise to the beaker containing the 2%-MWCNT-carbopol polymer mixture. The content was continuously stirred for 2 h till a greyish-white precipitate was obtained. The precipitate (precursor) was filtered, dried in an oven at 60 $^\circ\text{C}$ for 15 h and then annealed at 450 $^\circ\text{C}$ for 5 h in the air to produce 2%-MWCNT/ TiO_2 composite material. Similarly, a series of composite materials with 4, 6, 8% MWCNT coated with TiO_2 particles were prepared. The prepared composites were assigned a general chemical formula, $[\text{X}\% \text{-MWCNT}/\text{TiO}_2]$, where $\text{X} = 2, 4,$

6, and 8% w/w. Also, pure bare TiO_2 powder without the MWCNT support was prepared for comparative studies.

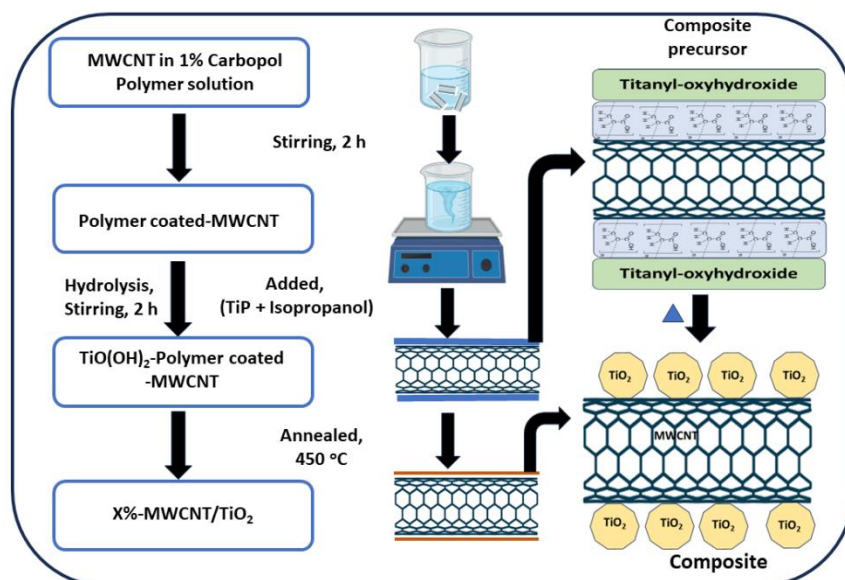


Figure 5.1: Schematic diagram depicting the preparation of MWCNT/TiO₂ composite materials by precursor-layer-coating (PLC) method.

5.3 Characterization techniques

The structure, composition, phase, morphology and optical properties of the composite were investigated by different instrumental techniques. The Fourier transform infrared (FTIR) spectral bands of precursor and composites were recorded on a Shimadzu IR spectrophotometer in the range 4000 to 400 cm^{-1} . The simultaneous thermal analysis (thermogravimetric analyzer-differential scanning calorimeter, TGA-DSC) profiles of the precursor were obtained on a TA-250 instrument. The samples were heated in the dynamic temperature range of 35 °C – 800 °C at a heating rate of 5 °C per minute in the air. The phase identification of composites was investigated using a Rigaku Smart Lab X-ray Diffractometer (XRD) with $\text{Cu K}\alpha_1$ (1.5418 Å) radiation, operated at 40 kV and 30 mA. The average crystallite sizes (D_{avg}) of TiO_2 were estimated using the Scherrer equation 1

$$D_{\text{avg}} = 0.9\lambda / \beta \cos\theta \quad (1)$$

where $\lambda = 1.5418 \text{ \AA}$ is the wavelength of the X-ray used (Cu $k_{\alpha 1}$ -line), θ is Bragg's diffraction angle, and β is the full width at half maximum (FWHM) in radians. The Raman spectroscopy studies were performed on the Horiba Labram instrument, and the sample was excited with a 532 nm laser. The microstructural details of the composites were revealed using FEI Quanta FEG 250, field emission-SEM, coupled with elemental analysis carried out on the Oxford Instruments X-Max-EDAX device. The electron accelerating voltage of 20.0 kV was applied during the analysis. The particle/crystallite size, lattice structure, and morphology images were captured on a Philips CM200 high-resolution transmission electron microscope (HRTEM), with an accelerating voltage of 120 kV. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on JEOL, JPS-9200, with a pass setting of 23.5 eV, 0.025 eV/0.05 eV step, 50 ms time/step, and 10 cycles, source Al K_{α} -1486 eV. The UV-visible light absorption properties were studied on the Shimadzu UV-visible spectrometer. The diffuse reflectance spectroscopy (DRS) spectra were recorded from 300 to 700 nm wavelength range. The band gap of materials was estimated based on the Kubelka-Munk transformation and Tauc plot absorption edge method. The Brunauer-Emmett-Teller (BET) surface area properties of pure and composite powder materials were measured on Belsorp-2, Japan at liquid nitrogen temperature and nitrogen as adsorptive gas. A multipoint sorption curve was employed to calculate the specific surface area in (m^2/g). The average particle size/pore size was derived from the surface analysis. The Photoluminescence (PL) emission spectra in the 300 – 550 nm range were recorded on a spectrofluorometer (FP8200, Jasco Japan). The sample was activated using a 450 W Xenon lamp with excitation wavelength $\lambda_{\text{exc}} = 291 \text{ nm}$. The pulse duration of 10 ns, power of 2.88 mW, and 3 mm of spot size were set during measurement. The emitted light was collected using a collimating lens assembled with an optical fiber.

5.4 Photocatalytic organic reaction experimental set-up

To evaluate the photocatalytic activity of the prepared composite materials, an organic synthetic reaction was carried out in the presence of the composite as a catalyst and irradiated with UV and sunlight separately. The reduction of benzophenone to benzopinacol was employed as a model photocatalytic organic synthetic reaction. Blank reactions without a catalyst and light source were also performed under similar conditions. 2 g (0.011 moles) of

benzophenone and (35 mL-isopropanol + 10 mL-acetone) solvent mixture were added in a quartz glass reactor vessel. Further, 30 mg of the photocatalyst was transferred to the reaction mixture and stirred for 10 min. A tubular 450 W medium-pressure Mercury (Hg) lamp with an emission wavelength range ($\lambda = 250$ to 400 nm) was used as a UV-light source for the photocatalytic reaction. The circulating water jacket was employed to control the reaction temperature of ~ 25 °C. The photoreaction was carried out in the presence of a synthesized photocatalyst with a definite reaction time of 7 h. The schematic diagram of the UV-light photoreactor is shown in Figure 5.2. Similarly, the photocatalytic reactions were performed in direct sunlight (1289 x 100 LUX) for 48 h. At the end of the reaction, the solid benzopinacol (product) and photocatalyst were collected by filtration. The catalyst was separated from the benzopinacol by dissolving it in chloroform, followed by filtration. The pure benzopinacol was recovered by crystallization of the filtrate, oven-dried (80 °C) and weighed. The percent reaction efficiency (% RE) was calculated using equation 2:

$$\% \text{ RE} = (W_e / W_t) * 100, \quad (2)$$

Where W_e and W_t are the experimental and theoretical yields (g) of the benzopinacol product. The portion of the benzopinacol was dissolved in ether, re-crystallized to obtain the pure crystals and then used for characterization. The FTIR, UV-spectroscopy, melting point and ^1H -NMR analysis were recorded for the pure benzopinacol product.

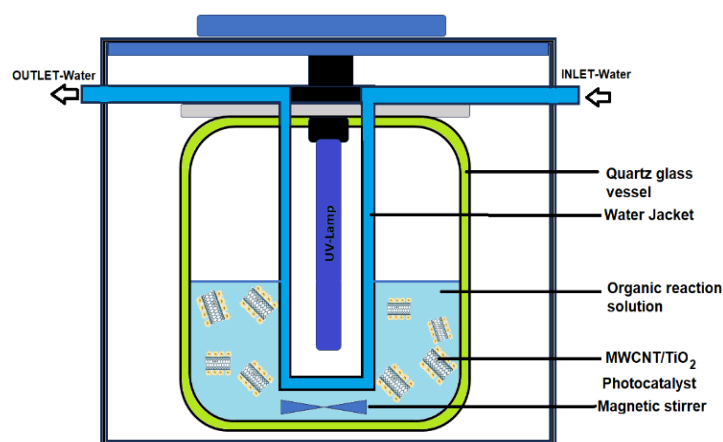


Figure 5.2: Schematic diagram of the reactor used for the photocatalytic conversion of benzophenone to benzopinacol.

5.5 Results and discussion

5.5.1 PLC method of composite preparation

The PLC method of composite preparation consisted of two main steps: (a) in-situ binding of titanyl oxyhydroxide, $[\text{TiO}(\text{OH})_2]$ precursor onto MWCNT via carbopol (poly-acrylic acid) polymer and (b) heat treatment of the coated precursor, $[\text{MWCNT}]-[\text{TiO}(\text{OH})_2]$ at 450 °C for 5 h in air to yield the composite. The carbopol polymer is hydrophilic in nature and water-soluble, capable of forming a high degree of hydrogen bonding with other polar/non-polar molecules. It forms a soft hydrogel-like material with water used as a dispersant and binding agent for hydrophobic MWCNT and titanyl-oxy hydroxide precursor. Due to this unique bonding nature of carbopol, the hydroxyl and carbonyl groups form a large network of hydrogen bonding with the MWCNT and TiO_2 precursor matrix [19]. Additionally, the carbopol polymer is thermally unstable and easily eliminated by annealing at lower temperatures (~ 300 °C) to produce MWCNT/ TiO_2 composite. The synthesized composite materials were assigned with general chemical composition as $X\%-(\text{MWCNT}/\text{TiO}_2)$, where $X = 2, 4, 6$, and 8% w/w, and their corresponding codes were assigned as 2CT, 4CT, 6CT, and 8CT, respectively and presented in Table 5.1. The introduced PLC method could provide a promising alternative in-situ method to coat nanosized TiO_2 particles on the MWCNT surface. It is well known that the in-situ MWCNT/ TiO_2 composites can promote the heterojunction formation, significantly enhance photo-induced free electron transfer from TiO_2 to MWCNT and slow down rapid charge recombination phenomena and facilitate the photocatalytic organic reaction [20].

5.5.2 FTIR studies

Fourier transform Infrared (FTIR) spectroscopic studies were performed to examine the functional groups and intermolecular hydrogen bonding in the precursor. Figure 5.3a represents the IR spectra of the composite precursor (2CT). The sample displayed a broad ($-\text{O}-\text{H}$) stretching band ranging from 3700 to 3200 cm^{-1} due to the multiple ($-\text{O}-\text{H}$) groups of carbopol polymer, titanyl-oxy hydroxide, and water molecules, which were possibly involved in intermolecular hydrogen bonding in the precursor [21]. The strong band $\sim 2320\text{ cm}^{-1}$ could be associated with the ($-\text{O}-\text{H}$) stretching bond of ($-\text{Ti}-\text{OH}$) with hydrogen bonding. The weak

band observed at $\sim 2984\text{ cm}^{-1}$ was attributed to the aliphatic ($-\text{CH}_2$) asymmetric stretching band of MWCNT surface defects [22]. The strong dual sharp bands at $\sim 1697\text{ cm}^{-1}$ and $\sim 1454\text{ cm}^{-1}$ were assigned to asymmetric and symmetric stretching bands of carbonyl ($-\text{C}=\text{O}$) groups of carbopol polymer. The band at $\sim 1608\text{ cm}^{-1}$ was related to the ($-\text{C}=\text{C}-$) stretching bond of MWCNT. The weak intensity $-\text{O}-\text{H}$ bending vibrations overtone band of titanyl-oxy hydroxide and carbopol polymer were seen at $\sim 1640\text{ cm}^{-1}$. The band at $\sim 1545\text{ cm}^{-1}$ was ascribed to the alkene ($\text{C}=\text{C}$) group of MWCNT [23]. The weak band $\sim 1175\text{ cm}^{-1}$ was assigned to the $\text{Ti}-\text{O}-\text{C}$ bond, which indicated the bond formed between TiO_2 and MWCNT [24]. The high-intensity band in the spectral range of 700 to 430 cm^{-1} was assigned to the number stretching band of $\text{Ti}-\text{O}$ and $\text{Ti}-\text{O}-\text{Ti}$ bonds. Based on the FTIR data, it can be strongly stated that the hydroxyl groups of titanyl oxyhydroxide were bonded through hydrogen bonding interaction with the carbopol polymer-coated MWCNT. The noticeable variations in band positions and shape signified a high degree of hydrogen bonding network of the precursor. Hence, it can be inferred that titanyl oxyhydroxide was coated onto MWCNT via carbopol polymer during the synthesis by the PLC method.

Figure 5.3b represents the high temperature-infrared (HT-IR) spectra of the precursor heated at 250 , 350 , 450 , and $550\text{ }^\circ\text{C}$. Also, the IR-band intensities and positions of pure carbopol polymer and titanyl-oxyhydroxide were compared with composite precursors. From the HT-IR spectra, we inferred that the strong band at $\sim 1697\text{ cm}^{-1}$ due to the carbonyl group of carbopol polymer disappeared completely at $\sim 450\text{ }^\circ\text{C}$, which indicated that the carbopol polymer was completely decomposed and eliminated to form MWCNT/ TiO_2 composite material. Thus, $450\text{ }^\circ\text{C}$ was established as the optimal annealing temperature for composite preparation.

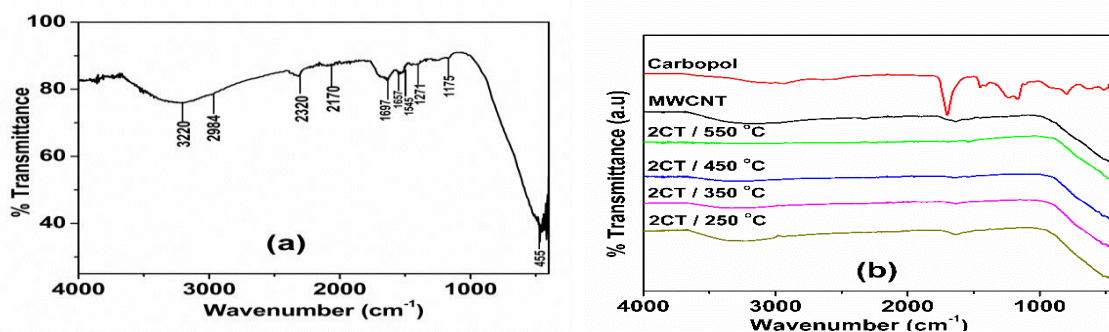


Figure 5.3: IR spectra for (a) synthesized precursor and (b) precursor heated at 250 , 350 , 450 and $550\text{ }^\circ\text{C}$ temperatures, MWCNT and carbopol polymer.

5.5.3 Thermal Analysis (TGA-DSC)

Thermal analysis (TGA-DSC) was performed on the composite precursor to ascertain the annealing temperature, thermal stability, and formation of the composite material. Figure 5.4 shows the TGA-DSC profiles of 2%-MWCNT-titanyl oxy-hydroxide precursor. The initial 15% mass loss observed in the temperature range of 30 to 100 °C in TGA and the corresponding DSC endotherm peak at 85 °C was attributed to the dehydration of the sample. Further, the multiple-step mass loss of ~10% was observed between 100 to 450 °C in the TGA thermogram. These events were complemented by an exotherm at 230 °C, followed by another broad exotherm (350 to 450 °C) associated with the de-hydroxylation of titanyl-oxyhydroxide and decomposition of carbopol polymer to form the 2%-MWCNT-TiO₂ (2CT) composite material. Between 450 to 500 °C, a small step of ~2% mass loss was assigned to the oxidative combustion of MWCNT to carbon dioxide gas [25]. A flat stable baseline in the temperature range of 500 to 800 °C with no mass loss indicated the formation of TiO₂ residue. The total weight loss in the temperature range (30 to 800 °C) observed for the 2CT-precursor was ~27%. Based on the TGA-DSC thermal events, it was demonstrated that 450 °C was the practical and optimum annealing temperature required to produce composites from the precursors.

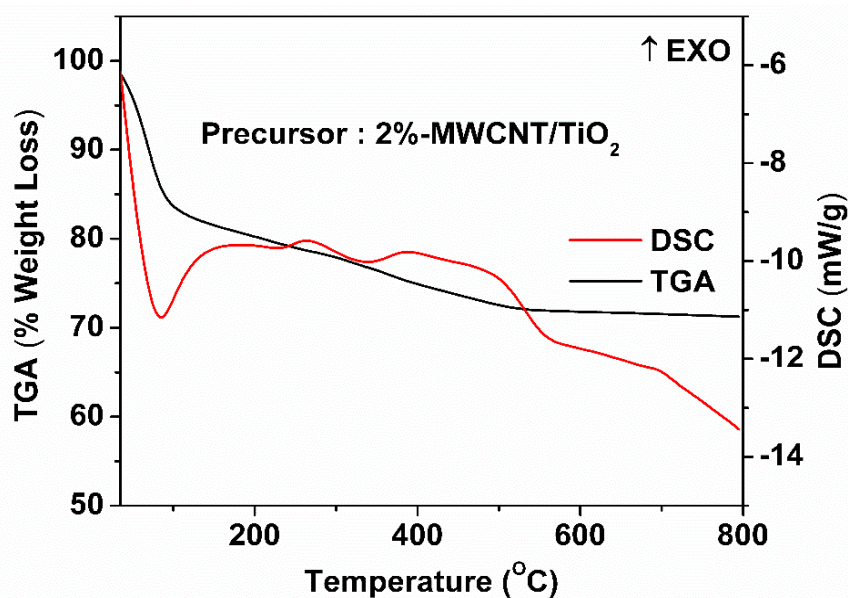


Figure 5.4: TGA-DSC thermogram of 2CT precursor.

5.5.4 X-ray diffraction (XRD) studies

The phase identification of the composites was investigated by powder X-ray diffraction (XRD) technique. Figure 5.5(a-d) shows the XRD patterns of pristine MWCNT, bare TiO₂(T), composite annealed at different temperatures and final composite materials (2CT, 4CT, 6CT and 8CT). The MWCNT support material diffractogram is depicted in Figure 5.5a. The MWCNT exhibited two characteristic crystalline peaks at 2-theta 25.8° and 43.5° which were indexed to (002) and (100) crystal lattice planes, respectively (JCPDS: 41-1487) [26]. Figure 5.5b represents the XRD pattern of bare TiO₂ prepared by annealing titanyl oxy-hydroxide precursor powder at 450 °C. The peak positions matched well with the single tetragonal anatase TiO₂ phase, complying to the standard JCPDS card No. (21-1272). The TiO₂ (hkl) diffraction planes were indexed with (hkl) values: (101), (004), (200), (105), (211), (204), (220) and (215) were assigned with peak positions at 2-theta values: 25.56°, 37.80°, 48.07°, 54.18°, 55.00°, 62.42°, 69.98° and 75.2° respectively [27]. No peaks due to rutile or brookite phases were observed in bare TiO₂. The broad and low-intensity peaks revealed that the TiO₂ particles were in the nanometer range. Based on the Scherrer equation, the estimated average crystallite size (D_{avg}) of TiO₂ was ~20 nm. The high-temperature (HT)-XRD patterns of annealed composite samples at 450, 500 and 600 °C were recorded to identify the phases formed during the heating process. Figure 5.5c depicts the HT-XRD patterns obtained for the representative sample. Surprisingly at 450 °C the composite material showed a mixed TiO₂ phase, major-anatase and minor-brookite along with MWCNT. The %-brookite phases present in the anatase TiO₂ was calculated using equation 3:

$$\%W_b = [(2.721I_b) / (0.886I_a + 2.721I_b)] * 100 \quad (3)$$

Where %W_b is the % weight fraction of the brookite phase, I_a and I_b represent the peak intensity of anatase (101) and brookite (121) planes of the sample. The numeric values, 0.886 and 2.721, are constants for anatase and brookite, respectively [28]. The calculated brookite phase in anatase was found to be approximately 10 %. The HT-XRD studies proved that the precursor was completely transformed into MWCNT/TiO₂ composite material at 450 °C / 5 h in air. At 550 °C the composite TiO₂ retained the same TiO₂ composition that is mixed anatase plus brookite phases along with MWCNT. Interestingly, as the composite was heated to 600 °C, the brookite phase disappeared, however, a mixture of anatase and rutile phases appeared

[29]. The structural modification in TiO_2 is normally attributed to the polymorphism effect. The explanation to the varied crystal structures in bare and composite TiO_2 was mainly attributed to the preparative method and post-annealing procedures. Rutile TiO_2 is a thermodynamically stable structure and is formed at higher temperatures. While anatase and brookite are metastable modified TiO_2 structures typically formed during a wet chemical synthesis method at much lower temperatures ($< 500\text{ }^\circ\text{C}$). Such variations were mainly associated with the surface energy of TiO_2 . Herein, when pure TiO_2 was prepared using the titanyl-oxy hydroxide precursor, the phase identified by XRD was anatase. When composite materials (MWCNT/ TiO_2) were prepared by annealing the precursor, a mixture of anatase ($\sim 90\%$) and brookite($\sim 10\%$) TiO_2 were yielded. This was associated with the structure-directing property of MWCNT during the TiO_2 crystallization process. These types of crystal variations in TiO_2 during the preparation are also reported in the literature [30]. The MWCNT acted as a structure-directing agent, thereby preferably yielding a mixed (anatase + brookite) TiO_2 phase. It is well-known that the anatase TiO_2 , which contains the (101) crystal lattice plane, exhibits the highest catalytic activity [31]. Furthermore, some researchers also mentioned that the mixture of anatase and brookite displayed better catalytic activity compared to individual polymorphs of anatase and rutile TiO_2 [32]. Hence, based on TGA-DSC and XRD data, the annealing temperature for composite preparation was restricted to $450\text{ }^\circ\text{C}$ for 5 h. Finally, Figure 5.5d depicts the XRD patterns of fabricated composite materials with different % MWCNT loadings (2CT, 4CT, 6CT and 8CT). In all composite materials, TiO_2 crystallized into mixed phase, anatase(A) and brookite(B) along with MWCNT [19][33]. The MWCNT peak at 2-theta 26.1° coincided with the highest intensity peak of anatase TiO_2 at 2-theta 25.56° , hence indistinguishable in the XRD pattern [34]. The low-intensity peak at 2-theta 42.8° due to MWCNT could not be detected in the composites. Thus, phase identification, composition and structural information of composites were established from XRD studies. The exact morphology, such as wrapping of the MWCNT surface with nanosized TiO_2 particles in the composites will be discussed later in the microstructural imaging section.

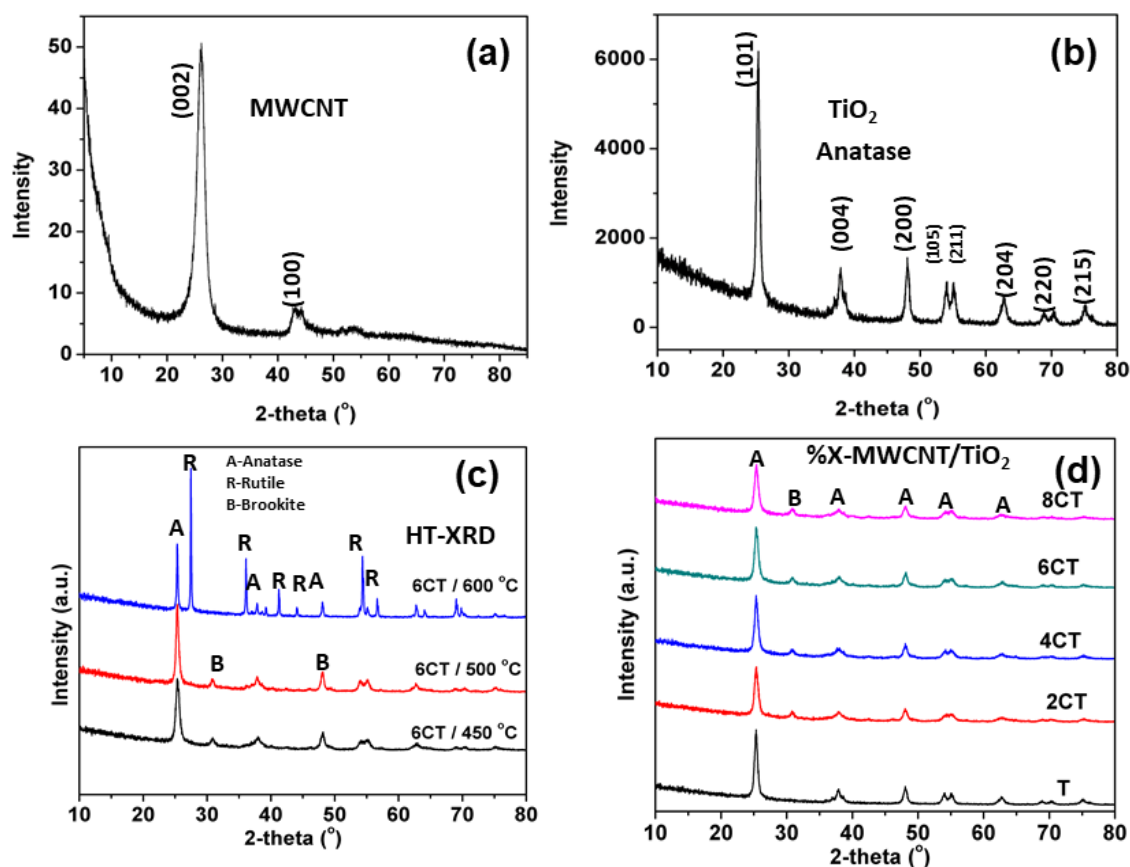


Figure 5.5: XRD diffractograms of (a) MWCNT (b) TiO₂ (c) precursor annealed at different temperatures and (d) Composite materials-2CT, 4CT, 6CT and 8CT.

5.5.5 Surface analysis of composites

The specific surface area, pore volume and mean pore diameter of all the composite materials were investigated by nitrogen gas adsorption/desorption studies. The effect of MWCNT loading on the composite surface area of MWCNT/TiO₂ was evaluated by comparing the isotherms of pure TiO₂ and a representative composite material (8CT). Figure 5.6(a,b) represents the N₂ adsorption/desorption isotherms and its Barrett – Joyner – Halenda (BJH) pore size distribution plots for TiO₂ and 8CT, respectively. Both materials exhibited type-IV adsorption-desorption patterns with H2-type hysteresis. The appearance of the hysteresis loop at higher partial pressure (p/p_0), ranging from 0.7 to 0.9, signified the mesoporous nature of the composite. The hysteresis loop of composite materials appeared much wider compared to pure TiO₂. Such observations could be linked to the coating of

nanosized TiO_2 particles on the MWCNT surface [35]. The surface area, pore volume and mean pore diameter of all composite materials, including bare TiO_2 and MWCNT are compiled in Table 5.1. The BET-specific surface area of pure bare TiO_2 and MWCNT was $90.21 \text{ m}^2/\text{g}$ and $144.97 \text{ m}^2/\text{g}$, respectively. Whereas the composite materials: 2CT, 4CT, 6CT, and 8CT showed an increasing trend in surface area values starting from 83.77, 88.37, 89.11 to $114.39 \text{ m}^2/\text{g}$, respectively. The bare TiO_2 displayed a surface area of $90.21 \text{ m}^2/\text{g}$ compared to MWCNT with $144.97 \text{ m}^2/\text{g}$. The 2CT and 4CT showed slightly lower surface area compared to pure TiO_2 material. This was expected because the % TiO_2 reduced and the % MWCNT content increased progressively in the composites. Hence, when TiO_2 particles were attached to the long-tubular MWCNT surface, the composites experienced the wrapping phenomena [36]. For 2CT and 4CT, the % content of MWCNT was significantly low, hence there was no impact seen on the surface area values. In the 6CT and 8CT samples, as the MWCNT ratios were increased, the surface area value showed an upward trend. The BJH plots shown in the inset Figure 5.6(a,b) indicated that the composite pore size distribution ranged from 5 to 15 nm. The mean pore diameter values of the material hovered $\sim 12 \text{ nm}$. The total pore volume of all composites was found to be $\sim 0.3003 \text{ cm}^3/\text{g}$. There were no significant variations in mean pore diameter and total pore volume across all levels of composite materials. Based on the surface analysis data, the surface area of composite materials improved with MWCNT loading and displayed mesoporous properties.

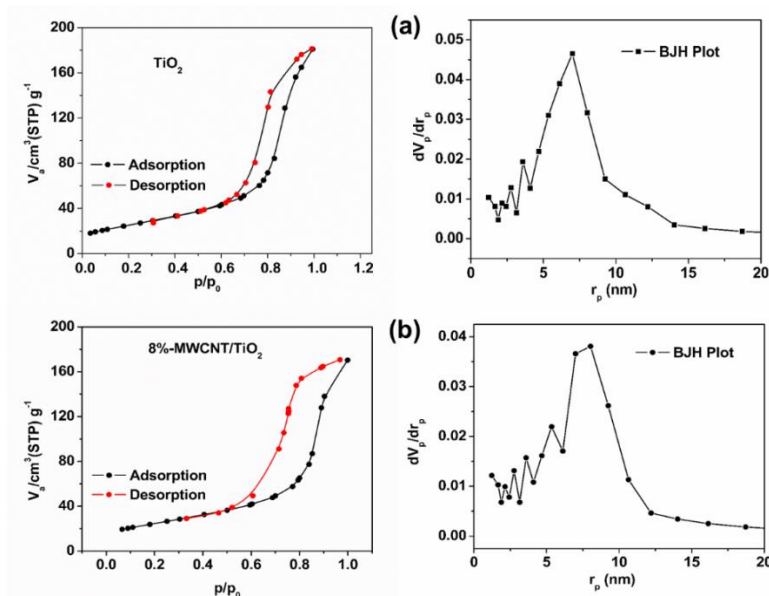


Figure 5.6: Adsorption-desorption isotherms and BJH plots of (a) TiO_2 (b) 8CT.

Table 5.1: Compilation of composite composition, assigned codes, BET-specific surface area, Total pore volume, and Mean pore diameter values.

Composite composition	Material Code	Specific surface area (m^2/g)	Total Pore volume (cm^3/g)	Mean pore diameter (nm)
MWCNT	C	144.97	0.5645	15.57
TiO ₂	T	90.21	0.2778	12.32
2%-MWCNT/TiO ₂	2CT	83.77	0.2735	13.06
4%-MWCNT/TiO ₂	4CT	88.37	0.2590	11.73
6%-MWCNT/TiO ₂	6CT	89.11	0.2557	11.48
8%-MWCNT/TiO ₂	8CT	114.39	0.3864	13.51

5.5.6 Microstructural analysis (SEM/PSD/EDAX/TEM)

The detailed microstructural features of bare TiO₂ and representative composite material (6CT) were examined by FE-SEM/HR-TEM techniques. Figure 5.7(a,b) shows the FE-SEM images of bare TiO₂ and 6CT. From the TiO₂ micrographs, it was revealed that the nanosized, spherically-shaped TiO₂ particles were agglomerated to form nanoclusters. The primary particle size of TiO₂ powder ranged from 10 to 35 nm. Figure 5.8 shows the particle size distribution (PSD) histogram for bare TiO₂. The particle size spanned over the nano-range with an average diameter of ~25 nm. The FE-SEM images for the composite are depicted in Figure 5.7(c,d), which showed elongated tubular-shaped MWCNT coated with a layer of nanosized TiO₂ particles [37]. Few agglomerated TiO₂ particles were also seen within the composite matrix. The TiO₂ particles integrated with the MWCNT resulted in the hybrid hetero-structure composite. Hence, the PLC method enabled the formation of MWCNT-TiO₂ composite materials. The in-situ growth of TiO₂ particles on the surface of MWCNT could generate physical and chemical interactions at the interface.

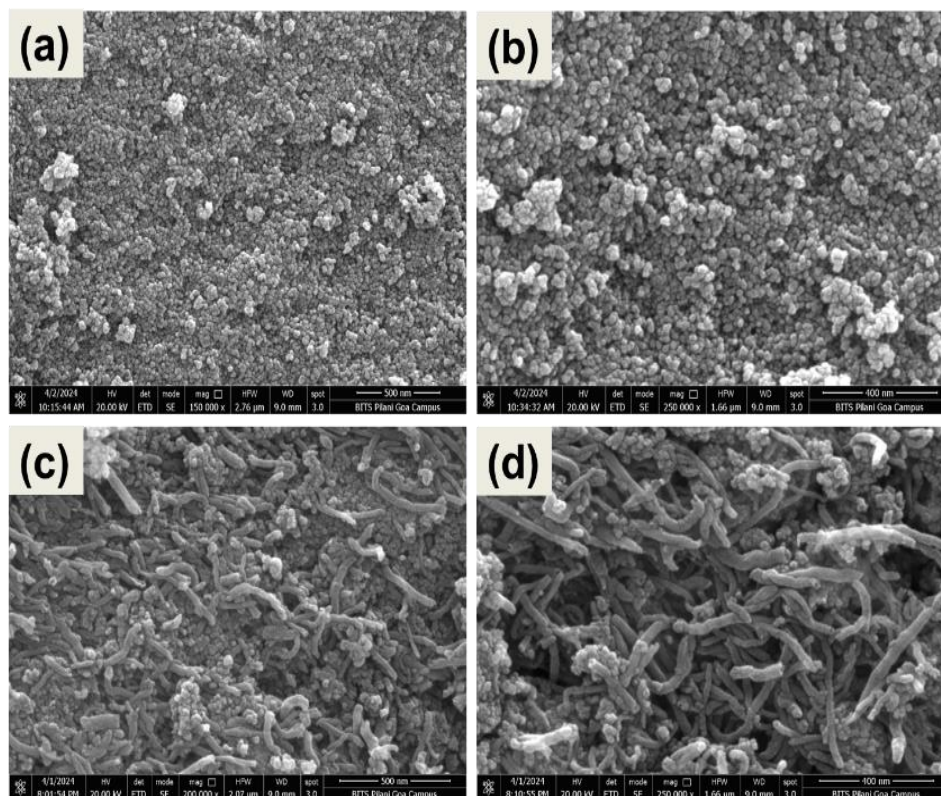


Figure 5.7: FE-SEM images (a,b) TiO₂ and (c,d) 6CT composite material.

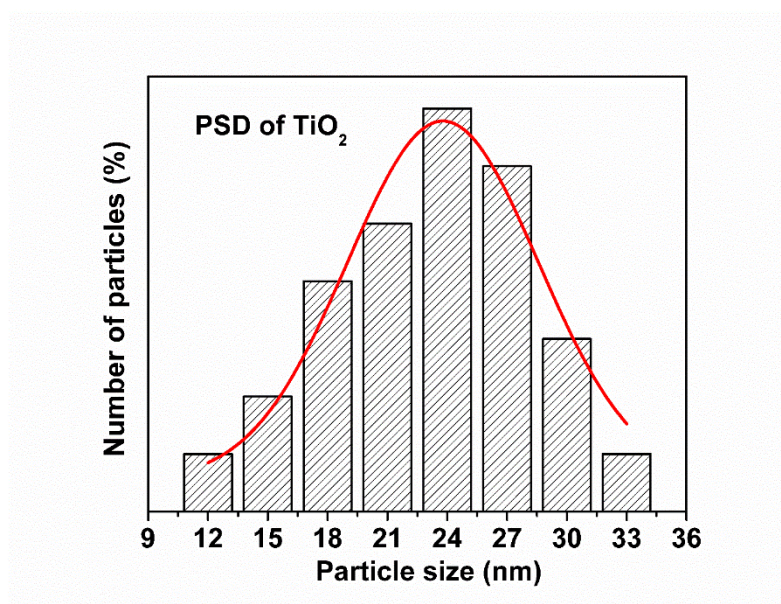


Figure 5.8: Particle size distribution of bare TiO₂ material.

The Energy Dispersive Absorption X-ray (EDAX) tool was used to investigate the elemental or chemical composition of the composite materials. Figure 5.9 represents the EDAX spectra for the 6CT composite material. The binding energy (BE) peak positions (eV) confirmed the presence of C, O, and Ti elements of the representative composite material. The approximate weight percentages are shown in the inset picture of Figure 5.9. The quantitative EDAX analysis indicated that the composite weight % composition consisted of 4.6% C, 39.3% O and 56.1% Ti.

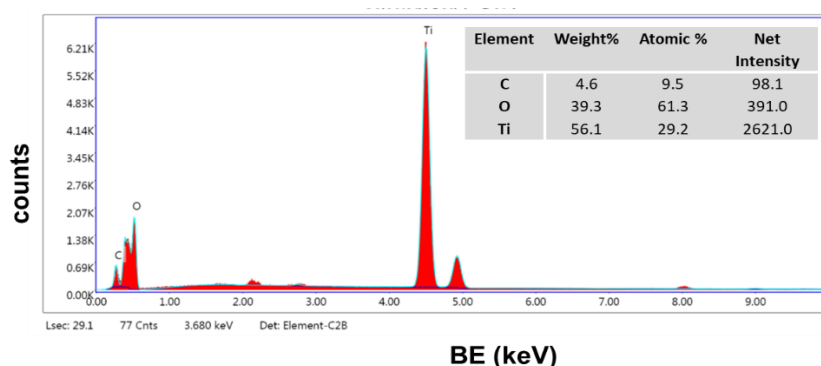


Figure 5.9: EDAX spectrum of 6CT sample showing the presence of C, O and Ti peaks.

The in-depth morphological and microstructural details of the constructed composites were examined by the TEM imaging technique. Figure 5.10 depicts the TEM micrographs for of the 6CT composite samples. Figure 5.10(a–f) depicts the images of the TiO_2 particles attached onto the outer walls of MWCNT which modified the surface morphology. Thus, the PLC method enabled the formation of TiO_2 -MWCNT heterojunctions at the interface. The length of the MWCNT was a few micrometers (μm), while the diameter ranged from 20 to 50 nm. The spherically shaped TiO_2 particles (sizes: 10 to 35 nm) were seen attached to the outer surface of MWCNT. The TEM images confirmed the formation of MWCNT/ TiO_2 heterojunction at the point of contact or interface. These interfaces are directly responsible for modified surface charge interaction in hybrid materials and act as the active sites for catalytic activity [38]. The HR-TEM images are shown in Figure 5.10g, indicating crystalline lattice fringes of (101) anatase TiO_2 plane with a d value of 0.345 nm. According to Figure 5.10h, it was evident that MWCNTs were seen as long multilayered with hollow tubular structures. The long interplanar fringes of MWCNT were also noticeable. Figure 5.10i depicts the selected area electron diffraction (SAED) pattern for MWCNT/ TiO_2 composite material. SAED pattern

indicated that TiO_2 was a nano-crystalline anatase phase, while MWCNT showed two lines due to (200) and (101) lattice phases attributed to nanotubular structures.

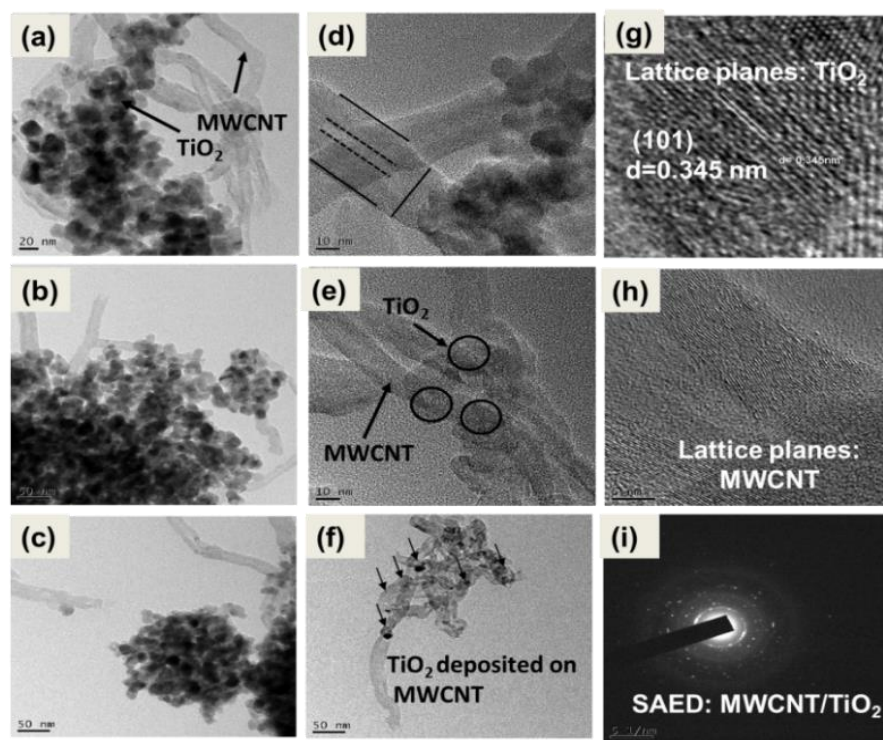


Figure 5.10: HR-TEM images 6CT: (a-f) MWCNT coated with TiO_2 , (g) Lattice fringes of TiO_2 , (h) Lattice fringes of MWCNT and (i) SAED image of composite.

5.5.7 UV-visible DRS light absorption studies

The light absorption capacity and band gap energy of composites were investigated by UV-visible diffuse reflectance spectroscopy (DRS). Figure 5.11a shows the UV-visible absorption spectra of 2CT, 4CT, 6CT, 8CT, and bare $\text{TiO}_2(\text{T})$. From the graphs, it was clear that the visible light absorption of composites improved with the addition of MWCNT in TiO_2 . All composites and TiO_2 showed similar absorption graphs in the UV region, indicated by rapid absorption below 375 nm. However, composites exhibited a marginal shift in absorption edge towards longer wavelengths in the blue region for composites compared to bare TiO_2 [39][18]. The rapid absorption of UV light photons by materials was attributed to the band gap excitation of electrons from the valence band (VB) to the conduction band (CB). The observed blue shift in the absorbance edge with increased % MWCNT loading could be

directly attributed to the number of heterojunctions formed at the MWCNT/TiO₂ interface. Hence, it can be inferred that the physical-chemical interaction between TiO₂ and MWCNT resulted in the band gap reduction in composites. To calculate the E_g of the composite materials, the UV-visible absorption DRS spectra were transformed to the Kubelka–Munk (KM) function $F(R)$. Figure 5.11b shows the Tauc plot of the modified KM function $A(h\nu - E_g)$ versus the energy of the absorbed light $(\alpha h\nu)^n$. The band gap energy (E_g) of all composites and pure TiO₂ was estimated based on the Tauc equation 4 [40]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (4)$$

For the indirect allowed transition type, the n takes the value $1/2$, α is the absorption coefficient, A is the absorbance of the sample, h is the Planck constant, ν is photon frequency. The E_g was obtained by extrapolating the linear portion of plot $(\alpha h\nu)^{1/2}$ against the band gap energy (eV) on the x-axis. The estimated E_g of pure TiO₂ was 3.49 eV, while that of composites, 2CT, 4CT, 6CT, and 8CT, the E_g values were 3.46, 3.45, 3.43, and 3.38 eV, respectively. Thus, it can be stated that the E_g of composites marginally reduced with % MWCNT loading and hence will require lower energy to produce (e^-h^+) pairs and facilitate electron transfer to MWCNT [20]. These minor reductions in E_g could be associated with the heterojunctions formed between TiO₂ and MWCNT.

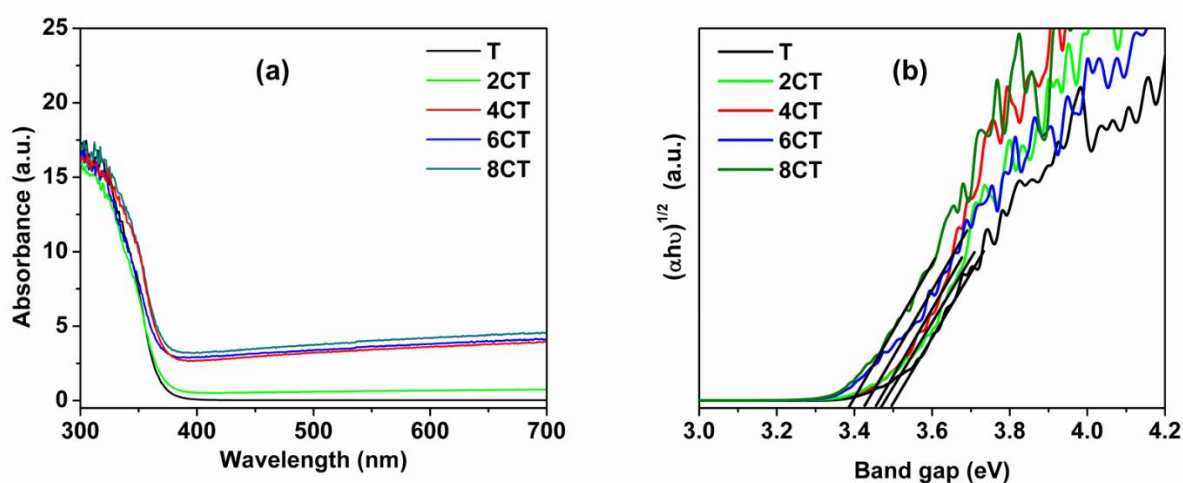


Figure 5.11: (a) UV-visible absorption spectra and (b) Tauc plots of T, 2CT, 4CT, 6CT, and 8CT.

5.5.8 Photoluminescence studies

The electron-hole ($e^- - h^+$) pair charge separation and recombination are often studied by the photoluminescence (PL) technique. Based on PL spectra, one can predict the rate of charge recombination of the trapped electrons in MWCNT/TiO₂ materials. The rapid neutralisation of charge pairs is detrimental to the catalysis process [41]. Figure 5.12 displays the room temperature (RT) PL spectra of TiO₂(T), MWCNT(C), 2CT, 4CT, 6CT and 8CT materials. From the emission spectra, the peak observed at $\lambda_{\text{max}} = 415$ nm showed the highest intensity for bare TiO₂ and lowest for C. Whereas, in the case of composite materials, the PL intensity showed a decreasing trend proportionately with the incremental addition of MWCNT or (%) levels in the materials. This indicated that the radiative ($e^- - h^+$) pair recombination rate of the TiO₂ was significantly retarded after being grafted to the MWCNT surface [42]. This demonstrated that the MWCNT behaved like a sink for the trapped photoexcited electrons in the conduction band of TiO₂. With MWCNT loading, the number of heterojunctions increased proportionately, which caused the free movement of electrons from the TiO₂ to the conducting MWCNT surface. This proved that the number of heterojunctions at the interface was higher for composites compared to bare TiO₂[18]. The two major disadvantages of TiO₂, namely high band gap energy and rapid recombination, were circumvented with the introduction of MWCNT support material. Hence, we inferred that the composite materials fabricated by the PLC method exhibited efficient electronic exchanges at the interface of TiO₂ and MWCNT. On comparing all the samples, 8CT showed the highest electron charge transfer and lowest recombination rate. Consequently, it was assumed that the MWCNTs were decorated with TiO₂ particles via the PLC method, which generated the heterojunctions. Ideally, based on the PL data, the 2CT and 8CT should exhibit the lowest and highest photocatalytic activity, respectively. This hypothesis was experimentally demonstrated and discussed in the photocatalytic activity in the following sections.

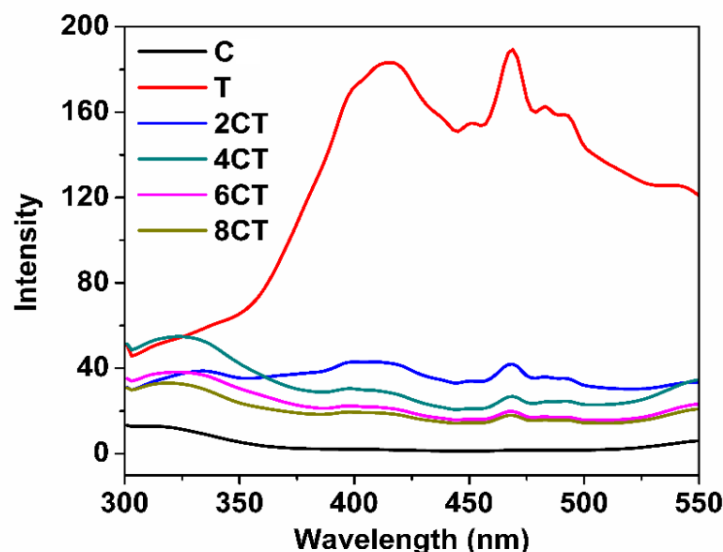


Figure 5.12: PL spectra of bare TiO_2 (T), MWCNT (C) and composites-2CT, 4CT, 6CT and 8CT.

5.5.9 X-ray Photoelectron spectroscopy studies

The identification of elements, oxidation states, and surface interactions in the synthesized composite materials was investigated by X-ray photoelectron spectroscopy (XPS). Figure 5.13(a-d) shows the XPS scan of 2CT, 4CT, 6CT, and 8CT and bare TiO_2 (T). The XPS spectra were calibrated with respect to the C 1s peak at binding energy (BE) 284.8 eV. The survey scan of all samples is stacked in Figure 5.13a. The dual peaks at ~ 459 eV and ~ 465 eV were assigned to Ti, while peaks at ~ 531 eV and ~ 286 eV were associated with O and C, respectively. The C 1s peak intensity amplified proportionately as the % MWCNT increased in the composite. Figure 5.13b displays the high-resolution XPS spectra of Ti 2p of all samples. The XPS spectra exhibited two prominent peaks centered at ~ 459 and ~ 465 eV were assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spin-orbital splitting photoelectrons from TiO_2 . This indicated that the oxidation state of Ti (IV), originated from the TiO_2 material. Figure 5.13c depicts the high-resolution XPS spectra of O 1s, the peak at ~ 531 eV was attributed to the O^{2-} species from the lattice oxygen of anatase TiO_2 particles. Figure 5.13d shows the C 1s peak at 286 eV, ascribed to the C-C bond of MWCNT. Hence, pure TiO_2 and MWCNT showed typical XPS spectra, which confirmed the formation of heterojunctions [43]. The XPS peak width, position, and intensities of MWCNT and nanosized TiO_2 particles showed distinct variations for

composite materials. The peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spin-orbital splitting photoelectrons shifted to higher binding energies and the width at half peak height broadened compared to pristine anatase TiO_2 . The C 1s peak of MWCNT at ~ 286 eV ascribed to a C-C bond was deformed and shifted to higher binding energies due to the bond formation between the MWCNT and TiO_2 . These small but important spectral variations presented direct evidence of heterojunctions formed between the two materials [44]. However, no distinct variations were observed in the O peak of the composite as there was no direct evidence of interaction or bond formation between C and O. Hence, XPS analysis could substantiate the cooperative interaction between TiO_2 and MWCNT at the interface of composite materials fabricated by PLC method.

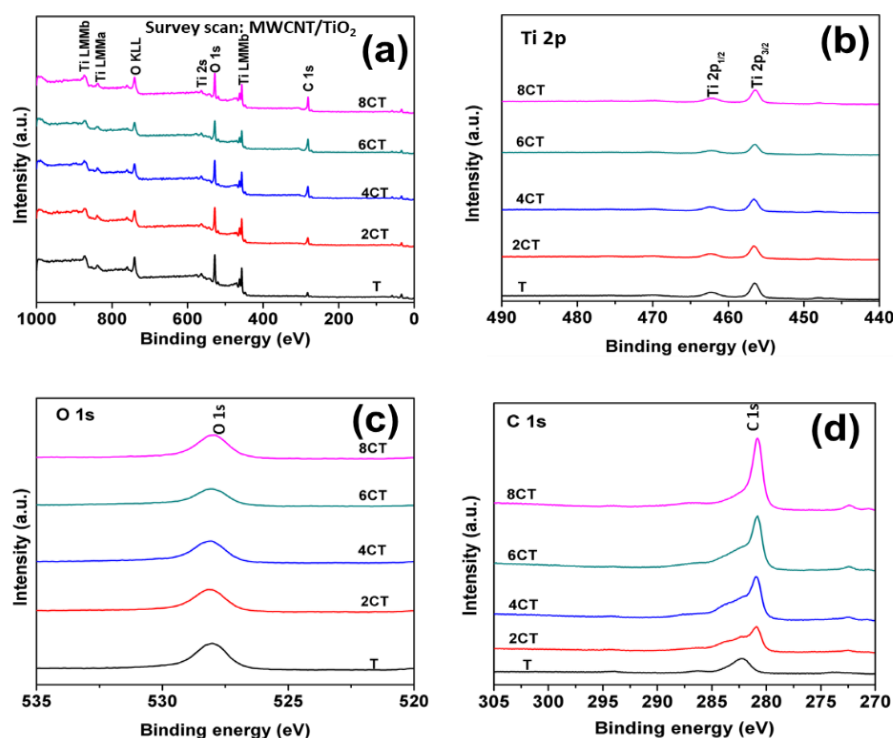


Figure 5.13: XPS of T, 2CT, 4CT, 6CT and 8CT (a) Survey scan (b) Ti 2p, (c) O 1s (d) C 1s

A detailed analysis of bare TiO_2 and MWCNT/ TiO_2 was performed to confirm the valence states and formation of heterojunctions in the composite. Figure 5.14(a-e) shows the high-resolution XPS spectra of Ti, O and C for TiO_2 and 6CT samples. Figure 5.14a displayed two distinct peaks of Ti, attributed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at binding energy (BE) 459.1 and 465.1 eV, which confirmed the Ti^{4+} present in TiO_2 . On similar lines, composite material

exhibited two Ti^{4+} peaks shifted at slightly higher BE. The Ti 2p_{3/2} peak position shifted to 460.5 eV; while the Ti 2p_{1/2} peak shifted to 466.4 eV, shown in Figure 5.14c. This indicated that the chemical environment of TiO_2 was modified by MWCNT bonding in composite materials. Figure 5.14(b,d) shows the O 1s core-level spectra of the TiO_2 and 6CT samples. The deconvoluted O 1s peak exhibited three peaks at BE 531.9, 532.3 and 534.4 eV, assigned to Ti-O, C=O and –OH present in the composite [45]. All three peaks of O 1s were shifted by 1 to 2 eV higher BE when compared with the BE of oxygen in the case of pure TiO_2 , which suggested the implantation of TiO_2 onto the MWCNT surface. The HR-XPS spectra for C 1s are also shown in Figure 5.14e. From the C 1s spectra, it was quite evident the peak was quite distorted in shape. The deconvoluted C 1s peak was resolved into 3 peaks with BE 284.8, 286.1 and 288.0 eV which could be associated with the formation of weak interactions with its counterpart TiO_2 [46]. The compilation of observed HR-XPS spectral BE (eV) for Ti, O and C for bare TiO_2 and 6CT samples are presented in Table 5.2. The SEM/HR-TEM, XRD, and XPS results confirmed the formation of MWCNT- TiO_2 heterojunctions at the interface. Based on the results, it was reasonable to assume that the heterojunctions could have a profound effect on the optical properties of composites compared to pure TiO_2 . The absorption edges moved to a longer wavelength, accompanied by reduced band gap energies with MWCNT loadings. Thus, the MWCNT/ TiO_2 composite could be effectively employed as a photocatalyst for organic molecule synthesis under UV-visible irradiation.

Table 5.2: Compilation of XPS BE (eV) of Ti, O and C for bare TiO_2 and 6CT.

Sample	Ti 2p (eV)	C 1s (eV)	O 1s(eV)
TiO_2	459.1 465.1	----	530.7 531.1 532.5
6CT	460.5 466.4	284.8 286.1 288.0	531.9 532.3 534.4

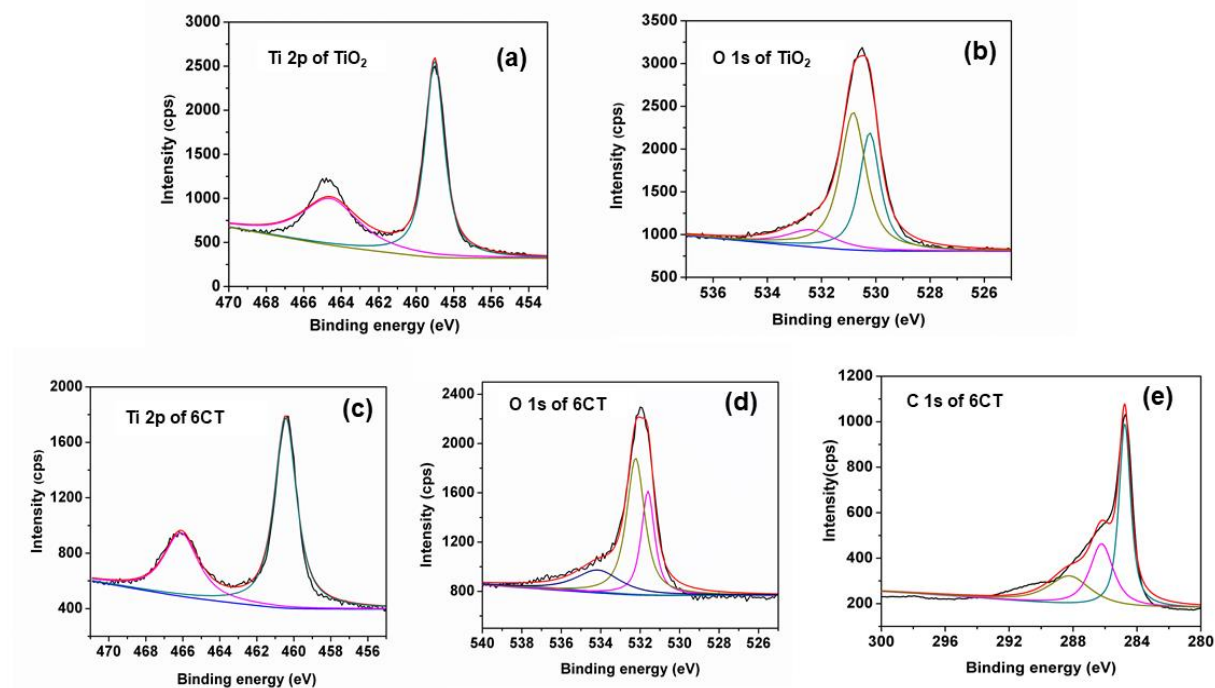


Figure 5.14. High-resolution XPS spectra of bare TiO₂ : (a) Ti (b) O and 6CT : (c) Ti (d) O (e) C

5.5.10 Raman studies

Figure 5.15a presents the Raman spectra of the 2CT, 4CT, 6CT and 8CT, pristine MWCNT and TiO₂ (T). All composite spectra displayed the typical MWCNT dual-band at $\sim 1349\text{ cm}^{-1}$ and $\sim 1570\text{ cm}^{-1}$ attributed to D and G-bands, respectively. The D-band was assigned to the disordered C atoms, while the G-band was assigned to the sp^2 vibration of the C-C bond of MWCNT [47]. Both D and G-bands shifted marginally towards higher wavenumber (cm^{-1}) with the addition of %-MWCNT in the composites, which signified a proportionate rise in the interaction between TiO₂ and MWCNT. Among all the composites, the 8CT sample showed the highest wavenumber shift of ~ 6 and $\sim 12\text{ cm}^{-1}$ for D and G-bands, respectively, compared to pure MWCNT. Figure 5.15b shows the peak shift in D and G-bands of MWCNT present in 2CT, 4CT, 6CT and 8CT in composites. The anatase TiO₂ phase has tetragonal symmetry with six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$) [48]. The spectra with three strong peaks of the anatase TiO₂ phase at $\sim 390\text{ cm}^{-1}$ (B_{1g}), $\sim 511\text{ cm}^{-1}$ ($A_{1g} + B_{1g}$) and

$\sim 626 \text{ cm}^{-1}$ (E_g) attributed to TiO_2 nanoparticles, and these peaks broadened for composite materials. The (E_g) peak of pure TiO_2 was observed at 138 cm^{-1} , whereas the same E_g peak of the composite appeared at a higher wavenumber, 143 cm^{-1} . The vibrational modes of TiO_2 particles were affected by the formation of an interface between the materials which implied the formation of chemical bonds and/or physical interactions. The apparent band broadening and wavenumber shift were due to local interactions and grafting of TiO_2 with MWCNT, which have been reported for TiO_2 supported on MWCNT by other researchers [49]. From the spectra, it can be clearly understood that the possible influence of one component on another post-composite formation. The band intensities of TiO_2 reduced while the G and D-bands of the MWCNT increased proportionately, which could be linked to the progressive increment in MWCNT content in the composites. The inferences drawn from Raman spectroscopy were in agreement with those of TEM, EDAX and XPS.

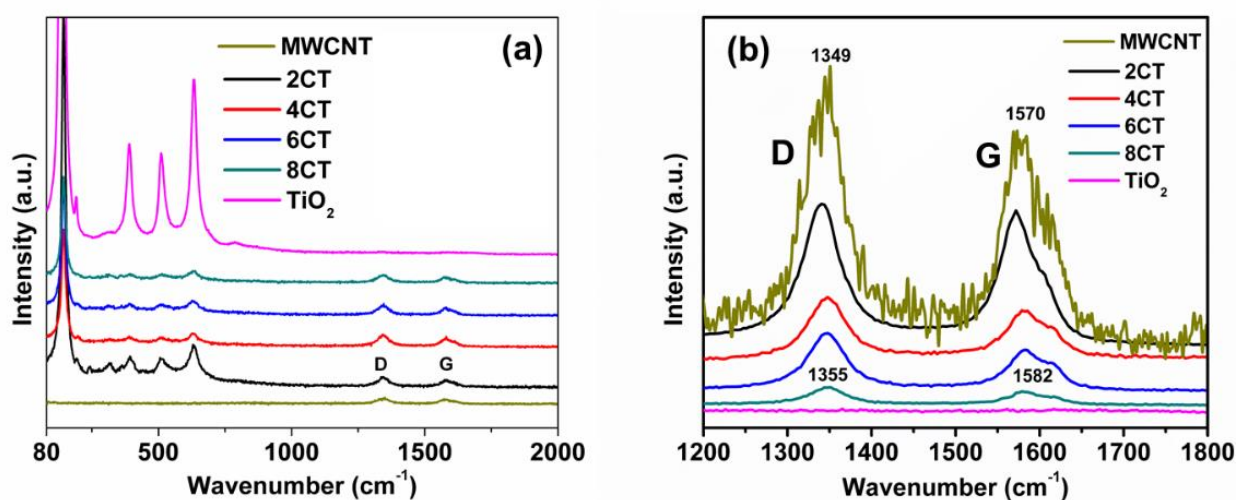


Figure 5.15: Raman spectra of (a) TiO_2 , MWCNT, 2CT, 4CT, 6CT and 8CT; (b) Peak shift in D and G-bands of MWCNT present in 2CT, 4CT, 6CT and 8CT.

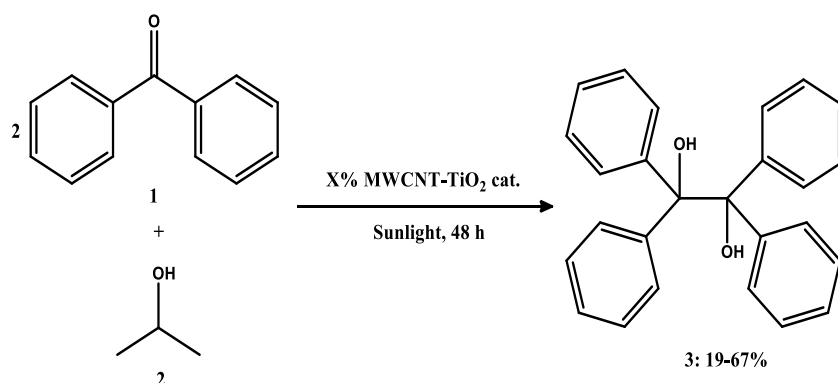
5.6 Photocatalytic activity of X%-MWCNT/TiO₂

5.6.1 Photocatalytic synthesis of Benzopinacol in UV and sunlight

To study the application of the prepared catalyst (MWCNT/TiO₂) in the organic synthetic reaction, a photocatalytic reduction of benzophenone to produce benzopinacol was carried out using MWCNT/TiO₂ as a catalyst under UV and sunlight irradiation. Pinacol is a two-hydroxyl-containing compound, each group attached to the vicinal carbon atom. There are numerous methods in literature available for obtaining these compounds and most commonly they can be synthesized by photo-reduction of benzophenones [50][51]. The benzophenone was reacted with isopropyl alcohol in the presence of the catalyst and the reaction progress was monitored by TLC. On completion of the reaction, the mixture was poured into ice-cold water to obtain a solid. The solid (product) obtained was filtered using a Buckner funnel, washed with cold water and dried. The crude product gained was dissolved in chloroform and the catalyst was separated by filtration. Furthermore, the product was isolated or purified by column chromatography using silica 60-120 mesh as a stationary phase and a combination of ethyl acetate and petroleum ether as a mobile phase. Moreover, the product was analyzed using spectroscopic techniques (FTIR, UV-visible and Nuclear Magnetic Resonance Spectroscopy). The product melting point was also noted [52]. The % reaction efficiency was calculated based on the experimental % weight of the product and compared against the catalyst and reaction time point in UV and sunlight separately. The photocatalytic performance based on the conversion of benzophenone **1** to benzopinacol **3** in the presence of X%-MWCNT/ TiO₂ (X = 2, 4, 6, 8) composite materials and sunlight was evaluated [53].

Initially, the reaction of benzophenone and isopropyl alcohol with a catalyst was performed using a sunlight source (Scheme 1). To observe the selectivity of the catalyst, the reaction was screened for catalyst (2CT, 4CT, 6CT and 8CT) including blank run and in the presence of pure TiO₂ and MWCNT. The % yield for each reaction/material was tabulated in Table 5.3. The product yield was obtained as 45%, 48% and 54% using 2CT, 4CT and 8CT catalysts respectively (Table 5.3, entries 1, 2 and 4). The photoreduction of the substrate was also going smoothly with TiO₂ and MWCNT but product yields were comparatively less (Table 5.3, entries 5 and 6). The reaction product gained 19% yield without a catalyst (Table

5.3, entry 7). Surprisingly, the best results were perceived with the 6CT catalyst, giving 67% yield in 48 h of reaction time (Table 5.3, entry 3).



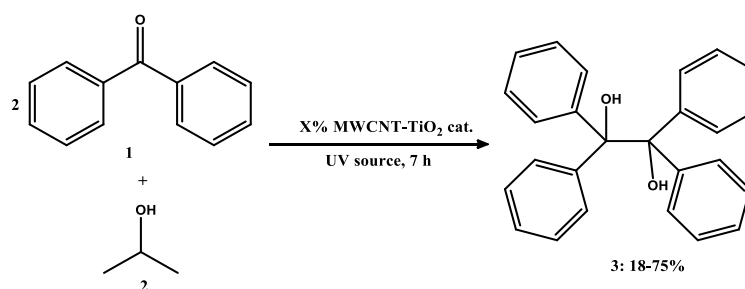
Scheme 1. Synthesis of benzopinacol **3** from benzophenone **1** and isopropyl alcohol **2** in the presence of sunlight and photocatalyst.

Table 5.3: % Yield of benzopinacol from benzophenone in the presence of sunlight and photocatalyst.

Entry	Catalyst	Material Code	Yield (%) of product 3 after 48 h in sunlight
1	2%-MWCNT/TiO ₂	2CT	45
2	4%-MWCNT/TiO ₂	4CT	48
3	6%-MWCNT/TiO ₂	6CT	67
4	8%-MWCNT/TiO ₂	8CT	54
5	TiO ₂	T	42
6	MWCNT	C	40
7	Blank	--	19

Similarly, the reaction was performed in a direct UV source lamp (Scheme 2) and the product was obtained with improved yields as tabulated below in Table 5.3. The reaction delivered product in moderate yields for 2CT (67%), 4CT (69%) and 8CT (53%) of catalyst (Table 5.4, entries 1, 2, and 4). Similar results were seen with 6CT (Table 5.4, entry 3), where the yield was highest upto 75%, and suitable for the high-efficiency reaction. The comparative experimental % yield of benzophenone in UV and sunlight against the catalyst used is represented in Figure 5.16(a,b). The % yield of the product showed a direct correlation with

the % MWCNT loaded with TiO_2 , that is 2CT to 6CT. However, the 8CT sample showed lower efficiency when compared to 6CT, the explanation for the decrease in activity could be linked to the reduction in UV light penetration at higher concentrations of MWCNT in the photocatalyst. On comparing closely, the % yield in UV light was greater than in sunlight. The 6CT catalyst showed 25% and 34% higher efficiency when compared to $\text{TiO}_2(\text{T})$ in sunlight and UV light, respectively. Otherwise, the same reaction takes 4 to 10 days to complete when exposed to sunlight.



Scheme 2. Synthesis of benzopinacol **3** from benzophenone **1** and isopropyl alcohol **2** in UV light and a photocatalyst.

Table 5.4: % Yield of benzopinacol from benzophenone in the presence of UV light and photocatalyst.

Entry	Catalyst	Material Code	Yield (%) of product 3 after 7 h in UV light
1	2%-MWCNT/ TiO_2	2CT	67
2	4%-MWCNT/ TiO_2	4CT	69
3	6%-MWCNT/ TiO_2	6CT	75
4	8%-MWCNT/ TiO_2	8CT	53
5	TiO_2	T	41
6	MWCNT	C	30
7	Blank	--	18

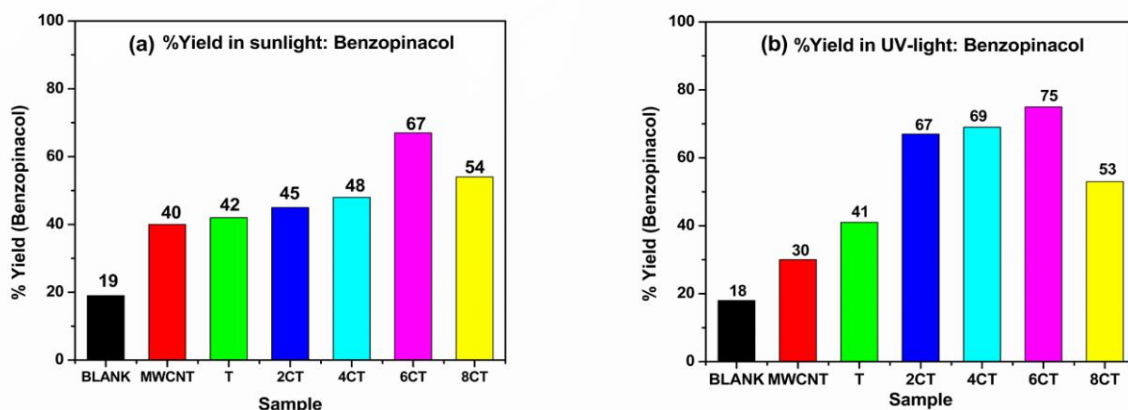


Figure 5.16: Illustrating the reaction product % yield comparison for blank, MWCNT, T, 2CT, 4CT, 6CT and 8CT irradiated with (a) sunlight and (b) UV light.

5.6.2 Proton Chemical Shift Assignment for synthesised benzopinacol

The benzopinacol **3** (product) structure is represented in Figure 5.17. The ^1H NMR was recorded by using CDCl_3 as a deuterated solvent. Figure 5.18 depicts the ^1H NMR spectrum of compound benzopinacol **3** with one singlet signal which was observed at chemical shift δ 3.030 ppm and could be assigned to two protons of the two hydroxy groups attached at C1 and C2 respectively in the structure of product (2H, 2 OH groups, gave singlet in the upfield region of the NMR spectrum). Two multiplets appeared for 20 aromatic protons in the downfield region of the NMR spectrum. One multiplet was observed from δ 7.088-7.197 ppm could be allotted to 12 aromatic protons attached at C10, C11, C12, C15, C16, C17, C20, C21, C22, C25, C26, C27 and while other multiplet from δ 7.263-7.354 ppm corresponded to 8 aromatic protons present at C9, C13, C14, C18, C19, C23, C24, C28 [50].

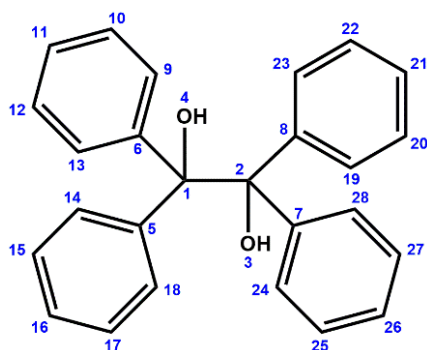


Figure 5.17: Structure of benzopinacol **3**

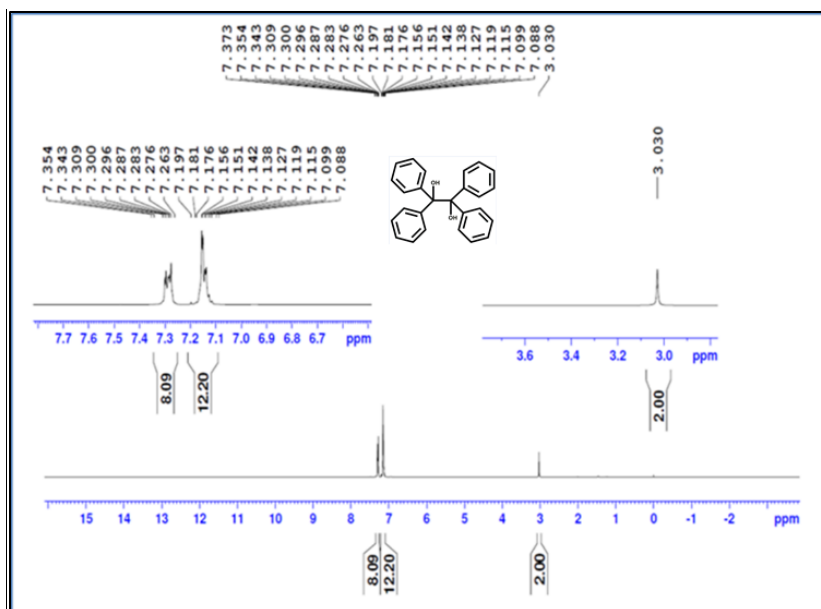
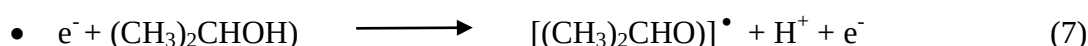
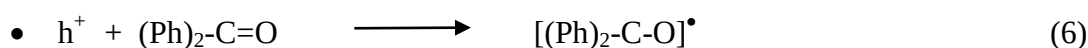
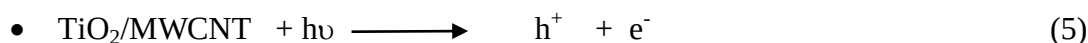


Figure 5.18: ^1H NMR of product benzopinacol 3.

5.7 Reactive species trapping experiment

A series of charge-trapping experiments was performed to gain a broad understanding of the reactive species generated by the catalyst. A specific amount of charge scavenging agent was added to the reaction vessel, involving photocatalytic reduction of benzophenone to benzopinacol. The experimental conditions during the entire study were kept constant. The ethylenediaminetetraacetic acid sodium salt (EDTA-2Na), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and benzoquinone (BZQ) were employed to trap holes (h^+), electrons (e^-), superoxide $\bullet(\text{O}_2)^-$ radicals, respectively [54]. Figure 5.19 presents the photocatalytic reaction efficiency (% RE) plotted against each charge scavenger used during the photocatalytic reaction. From the bar graph, it was evident that in the absence of a charge scavenger, the 6CT catalyst showed the highest photoactivity of 75% at the end of the 7 h reaction time. The addition of BZQ had no adverse effect on the catalyst efficiency and remained at about 72%, nearly equivalent to 6CT. Hence, $\bullet(\text{O}_2)^-$ radicals were neither generated nor involved in the reaction mechanism. However, in the presence of EDTA-2Na, the photoactivity was reduced to 8%, indicating that the (h^+) was involved in the photoactivity. When $\text{K}_2\text{Cr}_2\text{O}_7$ was introduced into the reaction vessel, the 5% efficiency was recorded. Based on the above observation, the (h^+) and (e^-) from

the valence and conduction band played a major role in the photocatalytic reaction mechanism. Herein, the reaction contained isopropanol as a solvent and it is well-established that isopropanol traps $\cdot(\text{OH})^-$ radicals, hence excluded in the charge trapping experiments. Hence, e^- and h^+ were the key reactive species generated by the catalyst on irradiation with UV light, as shown in equation (5). The holes h^+ react with benzophenone to form benzophenone radical as shown in equation (6). The e^- reacts with isopropanol to form an isopropanol radical as shown in equation (7). The overall reaction where benzophenone and isopropanol are converted to benzopincol and acetone, respectively, is shown as per Scheme (3). The proposed generation of charged species is as follows:



The factors responsible for the notable increase in photocatalytic efficiency in presence of X%-MWCNT/ TiO_2 (X = 2, 4, 6, 8) catalytic materials could be attributed to (i) Adsorption of reacting molecules on the surface of composite materials with high specific surface area (ii) Absorption of light by the catalyst (ii) Generation of comparatively large number of reactive electrons (e^-) and holes (h^+) species due to photoexcitation on the catalyst surface (iii) Retardation in the (e^- - h^+) recombination process (iv) Reaction of charged species with the reacting molecules to form the end-product.

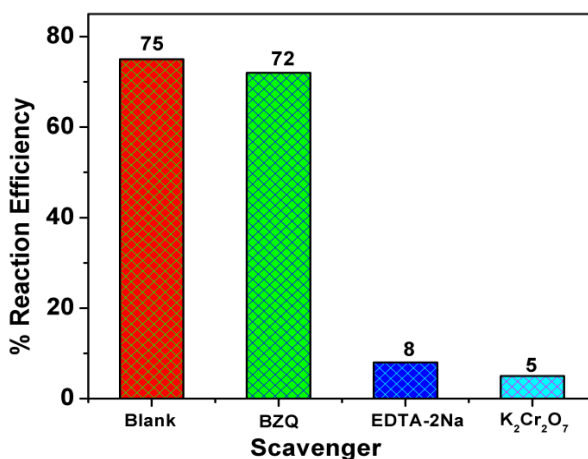
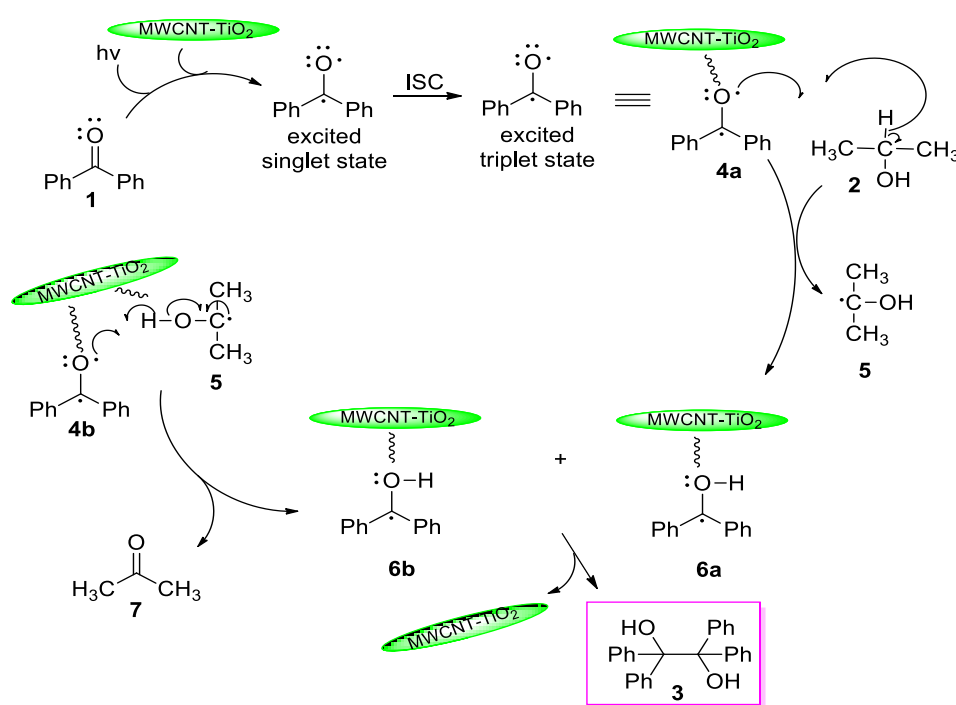


Figure 5.19: The % reaction efficiency without(blank) and with scavenging agents (BZQ, EDTA-2Na and $\text{K}_2\text{Cr}_2\text{O}_7$).

5.8 Proposed Mechanism for the Photocatalytic synthesis of benzopinacol from benzophenone catalyzed by photocatalyst

Based on the available literature reports, a possible mechanism for the synthesis of benzopinacol is described in Scheme 3[55–58]. The mechanism began with the generation of free radicals on benzophenone due to photoexcitation, abstracting of the hydrogen atom from isopropanol, which is driven by UV irradiation and catalyzed by MWCNT/TiO₂. The carbon and oxygen bond of the carbonyl functionality in benzophenone **1** was broken down to generate diradical **4a**. After diradical formation, the oxygen radical immediately combined with the easily removable hydrogen atom from isopropyl alcohol **2** and produced benzhydrol radical **6a** along with newly produced highly reactive propanol radical **5**. The propanol radical stabilized itself by offering a hydrogen atom to the oxygen atom of another benzophenone diradical **4b** and formed acetone **7**, eventually producing another benzhydrol radical **6b**. Finally, both the benzhydrol radicals **6a** and **6b** collided to furnish benzopinacol **3** as a targeted product by the release of a catalyst (Scheme 3) [55].



Scheme 3. The proposed mechanism towards benzopinacol **3** synthesis from benzophenone **1** and isopropanol **2** in the presence of UV-visible light and photocatalyst.

5.9 Plausible role of composite materials for improved photocatalytic activity

Figure 5.20 depicts the schematic diagram for the enhanced photocatalytic activity in the presence of MWCNT/TiO₂ composite. The excellent yield obtained with the addition of a photocatalyst during the reaction could be explained based on the number of free electrons involved during the activity. The valence and conduction bands of TiO₂ are separated by an energy band gap ($E_g = 3.3$ eV). When the MWCNT/TiO₂ composite was illuminated with light, the valence band electrons of TiO₂ were excited into the conduction band, forming electron-hole (e^-h^+) pairs. These formed (e^-h^+) pairs were susceptible to a quick recombination process, hence, only a limited number of these electrons were available for photocatalytic reaction in the case of bare TiO₂, and hence, it displayed lower photocatalytic activity. When the MWCNT was introduced as a support material for TiO₂ nanoparticles, a synergistic effect was created between the two materials, which resulted in improved photocatalytic performance. The high conversion efficiency of the MWCNT/TiO₂ photocatalyst could be associated with the generation of a large number of electrons/hole pairs and their mobility across the heterojunctions. The conducting MWCNT can trap electrons by accepting more photoelectrons, consequently slowing down the recombination rate of photogenerated charge carriers. Here, MWCNT act as an electron trap centre (sink) and retard the (e^-h^+) recombination rate. In pure TiO₂, less than one percent of the excited electrons are reported to be trapped and available for photocatalytic activity. Based on literature reports, the CB of anatase TiO₂ is separated from VB with a band gap of about 3.38 eV [59]. When TiO₂ particles are integrated into the surface of the MWCNT, the CB of MWCNT permits easy transfer of electrons to the TiO₂ surface, allowing charge separation and retarded recombination. The electrons can be freely moved along the MWCNT to TiO₂ CB and then effectively transferred to the reacting molecules to form several radicals. The generated radicals efficiently enhance the photocatalytic reaction to form the benzopinacol.

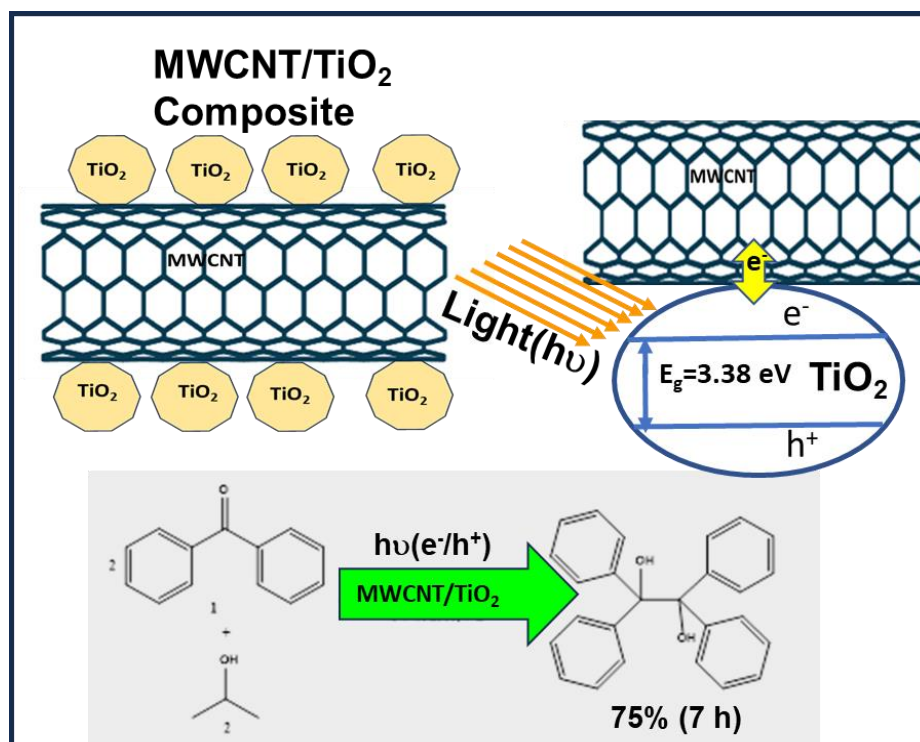


Figure 5.20: Schematic diagram of the proposed model for the electron transfer from TiO₂ to MWCNT composite materials across the heterojunction for enhanced photocatalytic activity.

5.10 Conclusions

Hybrid composites comprising photoactive nanosized TiO_2 material supported on electron-rich tubular MWCNT ($X\text{-MWCNT/TiO}_2$, where $X = 0, 2, 4, 6$, and 8), were successfully synthesized by the novel precursor-layer-coating method. The composite materials were characterized by XRD, IR, SEM-EDAX, HRTEM, BET-surface area, XPS, Raman spectroscopy, and UV-visible DRS, which confirmed the integration of TiO_2 on the surface of MWCNT. The XRD confirmed the mixed anatase ($\sim 90\%$) and brookite ($\sim 10\%$) TiO_2 phases formed on the surface of MWCNT. The detailed microstructural analysis established that the composite consisted of heterostructures. The long tubular micron-sized MWCNT surface onto which the nanosized TiO_2 particles were attached to form heterojunctions. The UV-visible DRS studies indicated that the composite exhibited strong absorbance in the UV region and displayed a shift in absorption edge towards a longer blue wavelength with MWCNT loadings. The band gap energy of composites were reduced and the rate of charge recombination also retarded to a significant extent, probably due to restructuring of the TiO_2 energy levels in composite. The photocatalytic activity of composites was evaluated based on benzopinacol synthesis in the presence of UV and sunlight. The synergistic effect between TiO_2 and MWCNT materials was supported by the dramatic increase in the % yield of benzopinacol product. Amongst all, the 6-MWCNT/TiO_2 photocatalyst showed the highest activity. The 6-MWCNT/TiO_2 photocatalyst displayed 25% and 34% higher efficiencies than pure TiO_2 in sunlight and UV, respectively. The enhanced photocatalytic activity was attributed to the heterojunctions formed at the interface, efficient light absorption, reduced band gap, excellent separation and mobility of charge pairs by the composite material. The proposed mechanism confirmed the electrons and holes as the charged species involved in the photocatalytic benzopinacol synthesis. The current study revealed that the prepared composites could harvest light and facilitated organic synthesis reactions.

REFERENCES

1. S. Mallakpour and E. Khadem, *Chem. Eng. J.* **302**, 344 (2016).
2. C. H. Jung, C. Y. Yoo, J. N. Kim, E. Y. Jeong, J. H. Park, H. C. Choi, M. H. Han, and H. C. Yoon, *Sustain. Energy Fuels* **3**, 431 (2019).
3. S. K. Soni, B. Thomas, and V. R. Kar, *Mater. Today Commun.* **25**, 101546 (2020).
4. A. G. Navrotskaya, D. D. Aleksandrova, E. F. Krivoschapkina, M. Sillanpää, and P. V. Krivoschapkin, *Front. Chem.* **8**, 1 (2020).
5. J. J. Brown, R. A. Hall, P. E. Kladitis, S. M. George, and V. M. Bright, *ACS Nano* **7**, 7812 (2013).
6. M. Kim, J. Park, H. Ju, J. Y. Kim, H. S. Cho, C. H. Kim, B. H. Kim, and S. W. Lee, *Energy Environ. Sci.* **14**, 3053 (2021).
7. J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, and D. W. Bahnemann, *Chem. Rev.* **114**, 9919 (2014).
8. Y. Yang, T. Zhang, L. Le, X. Ruan, P. Fang, C. Pan, R. Xiong, J. Shi, and J. Wei, *Sci. Rep.* **4**, 7045 (2014).
9. A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Béguin, and S. Bonnamy, *Carbon N. Y.* **42**, 1147 (2004).
10. H. Yu, X. Quan, S. Chen, and H. Zhao, *J. Phys. Chem. C* **111**, 12987 (2007).
11. D. Franchi and Z. Amara, *ACS Sustain. Chem. Eng.* **8**, 15405 (2020).
12. M. L. Chen, F. J. Zhang, and W. C. Oh, *Xinxing Tan Cailiao/ New Carbon Mater.* **24**, 159 (2009).
13. D. Friedmann, A. Hakki, H. Kim, W. Choi, and D. Bahnemann, *Green Chem.* **18**, 5391 (2016).
14. J. Fernández-Catalá, Berenguer-Murcia, and D. Cazorla-Amorós, *Mater. Res. Bull.* **134**, 111089 (2021).
15. X. Zhu, Y. Lin, J. San Martin, Y. Sun, D. Zhu, and Y. Yan, *Nat. Commun.* **10**, 1 (2019).
16. Y. Li, Y. Gao, Z. Deng, Y. Cao, T. Wang, Y. Wang, C. Zhang, M. Yuan, and W. Xie, *Nat. Commun.* **14**, 1 (2023).
17. G. E. M. Crisenza and P. Melchiorre, *Nat. Commun.* **11**, 8 (2020).
18. M. M. Gui, S. P. Chai, B. Q. Xu, and A. R. Mohamed, *RSC Adv.* **4**, 24007 (2014).

19. F. Rivadulla, C. Mateo-Mateo, and M. A. Correa-Duarte, *J. Am. Chem. Soc.* **132**, 3751 (2010).
20. A. K. Singh, P. K. Vishwakarma, S. K. Pandey, R. Pratap, R. Giri, and A. Srivastava, *Inorg. Chem. Commun.* **150**, 110540 (2023).
21. S. Chalal, N. Haddadine, N. Bouslah, S. Souilah, A. Benaboura, R. Barille, and A. Haroun, *Open J. Org. Polym. Mater.* **04**, 55 (2014).
22. M. Shaban, A. M. Ashraf, and M. R. Abukhadra, *Sci. Rep.* **8**, 1 (2018).
23. T. Sainsbury and D. Fitzmaurice, *Chem. Mater.* **16**, 3780 (2004).
24. S. Srinithi, V. Balakumar, T. W. Chen, S. M. Chen, M. Akilarasan, B. S. Lou, and J. Yu, *Diam. Relat. Mater.* **138**, 110245 (2023).
25. Z. Li, B. Gao, G. Z. Chen, R. Mokaya, S. Sotiropoulos, and G. Li Puma, *Appl. Catal. B Environ.* **110**, 50 (2011).
26. N. O. Ramoraswi and P. G. Ndungu, *Nanoscale Res. Lett.* **10**, 1 (2015).
27. A. K. Mohapatra and J. Nayak, *Optik (Stuttg.)* **156**, 268 (2018).
28. N. Bouazza, M. Ouzzine, M. A. Lillo-Ródenas, D. Eder, and A. Linares-Solano, *Appl. Catal. B Environ.* **92**, 377 (2009).
29. Y. Uesugi, H. Nagakawa, and M. Nagata, *ACS Omega* **7**, 11946 (2022).
30. K. Bourikas, C. Kordulis, and A. Lycourghiotis, *Chem. Rev.* **114**, 9754 (2014).
31. G. Zerjav, K. Zizek, J. Zavasnik, and A. Pintar, *J. Environ. Chem. Eng.* **10**, 107722 (2022).
32. C. Y. Hsu, Z. H. Mahmoud, S. Abdullaev, F. K. Ali, Y. Ali Naeem, R. Mzahir Mizher, M. Morad Karim, A. S. Abdulwahid, Z. Ahmadi, S. Habibzadeh, and E. Kianfar, *Case Stud. Chem. Environ. Eng.* **9**, 100626 (2024).
33. B. K. Mutuma, G. N. Shao, W. D. Kim, and H. T. Kim, *J. Colloid Interface Sci.* **442**, 1 (2015).
34. S. Kiran, S. K. Naveen Kumar, K. C. Yogananda, and D. Rangappa, *J. Mater. Sci. Mater. Electron.* **29**, 12681 (2018).
35. M. Chen, F. Zhang, and W. Oh, *Bull. Mater. Sci.* **34**, 835 (2011).
36. A. Al Mayyahi, B. M. Everhart, T. B. Shrestha, T. C. Back, and P. B. Amama, *RSC Adv.* **11**, 11702 (2021).
37. J. Li, S. Tang, L. Lu, and H. C. Zeng, *J. Am. Chem. Soc.* **129**, 9401 (2007).
38. L. Tian, L. Ye, K. Deng, and L. Zan, *J. Solid State Chem.* **184**, 1465 (2011).

-
39. M. Božič, I. Ban, S. Hribernik, D. Fakin, and K. Stana Kleinschek, *J. Sol-Gel Sci. Technol.* **83**, 132 (2017).
40. P. Makuła, M. Pacia, and W. Macyk, *J. Phys. Chem. Lett.* **9**, 6814 (2018).
41. Z. Peining, A. S. Nair, P. Shengjie, Y. Shengyuan, and S. Ramakrishna, *ACS Appl. Mater. Interfaces* **4**, 581 (2012).
42. K. Rajasekar, S. Thennarasu, R. Rajesh, R. Abirami, K. Balkis Ameen, and A. Ramasubbu, *Solid State Sci.* **26**, 45 (2013).
43. S. M. Yuen, C. C. M. Ma, C. Y. Chuang, Y. H. Hsiao, C. L. Chiang, and A. di Yu, *Compos. Part A Appl. Sci. Manuf.* **39**, 119 (2008).
44. S. D. Delekar, A. G. Dhodamani, K. V. More, T. D. Dongale, R. K. Kamat, S. F. A. Acquah, N. S. Dalal, and D. K. Panda, *ACS Omega* **3**, 2743 (2018).
45. M. Wang, S. Wang, Z. Li, X. Wang, L. Guo, H. Liu, L. Liao, and W. Zhou, *J. Photochem. Photobiol. A Chem.* **455**, 115754 (2024).
46. M. P. de la Flor, R. Camarillo, F. Martínez, C. Jiménez, R. Quiles, and J. Rincón, *J. Environ. Chem. Eng.* **9**, 106278 (2021).
47. Y. Piao, V. N. Tondare, C. S. Davis, J. M. Gorham, E. J. Petersen, J. W. Gilman, K. Scott, A. E. Vladár, and A. R. Hight Walker, *Compos. Sci. Technol.* **208**, 108753 (2021).
48. D. Vasu, A. Karthi Keyan, S. Sakthinathan, and T. W. Chiu, *Sci. Rep.* **12**, 1 (2022).
49. J. Wang, Y. Lin, M. Pinault, A. Filoramo, M. Fabert, B. Ratier, J. Bouclé, and N. Herlin-Boime, *ACS Appl. Mater. Interfaces* **7**, 51 (2015).
50. K. Volpe and E. E. Podlesny, *J. Chem. Educ.* **97**, 586 (2020).
51. L. D. Elliott, J. P. Knowles, P. J. Koovits, K. G. Maskill, M. J. Ralph, G. Lejeune, L. J. Edwards, R. I. Robinson, I. R. Clemens, B. Cox, D. D. Pascoe, G. Koch, M. Eberle, M. B. Berry, and K. I. Booker-Milburn, *Chem. - A Eur. J.* **20**, 15226 (2014).
52. L. C. P. Lata.C.Potey, D. S. B. K. D. S. B. Kosalge, and R. S. S. R. S. Sarode, *Int. J. Pharm. Drug Anal.* **2**, 55 (2014).
53. S. Reischauer and B. Pieber, *IScience* **24**, 1 (2021).
54. N. B. Trinh, T. A. Nguyen, S. Van Vu, H. G. T. Vo, T. N. H. Lo, I. Park, and K. Q. Vo, *RSC Adv.* **14**, 34037 (2024).
55. Z. W. Xi, L. Yang, D. Y. Wang, C. W. Feng, Y. Qin, Y. M. Shen, C. Pu, and X. Peng, *J. Org. Chem.* **86**, 2474 (2021).

56. J. C. Lopes, M. J. Sampaio, B. Rosa, M. J. Lima, J. L. Faria, and C. G. Silva, J. Photochem. Photobiol. A Chem. **391**, 112350 (2020).
57. E. A. Escobar, M. Á. V. Zapata, S. A. Hernández, S. O. F. Valle, O. R. Berny, V. J. G. Ángeles, and I. C. Reyes, J. Mex. Chem. Soc. **54**, 133 (2010).
58. G. Verma, Chem. Sci. J. **08**, 10 (2017).
59. M. Y. Qi, M. Conte, M. Anpo, Z. R. Tang, and Y. J. Xu, Chem. Rev. **121**, 13051 (2021).

Chapter-6:
Summary and future scope of research work

SUMMARY & FUTURE SCOPE OF RESEARCH WORK

To summarise, current research provided a promising alternative methodology for the preparation of nanosized photocatalytic materials that showed improved photocatalytic properties for specific applications. The degradation of harmful chemicals that were practically difficult or thermodynamically not feasible under normal conditions was accomplished using the prepared photocatalyst. The photocatalytic material systems, such as $\text{Ce}_x\text{Zn}_{1-x}\text{O}$, $\text{M}_x\text{Zn}_{1-x}\text{O}$ ($\text{M}=\text{Nd}/\text{Sm}/\text{Ho}/\text{Dy}$), anatase TiO_2 and $\text{X}\%-\text{MWCNT}/\text{TiO}_2$ prepared in this study were simple, straight-forward, and cost-effective. These photocatalysts exhibited sensitivity towards UV light and, to some extent, natural sunlight. Hence, sunlight trapping can contribute to a green and sustainable way to address environmental pollution issues using solar energy. The nanomaterials could successfully harness the light energy and convert it into a useful chemical reaction process on the photocatalyst surface. The photocatalysts were comprehensively characterized for their chemical, structural and particle properties. The critical photocatalytic properties were optimized by adopting novel synthesis methods and doping of impurities in the host materials. Also, TiO_2 particles were integrated on the surface of MWCNT, which profoundly modified the electronic band gap energy of the heterosystem. The materials were successfully applied for photodegradation studies, wherein the harmful dye molecules were disintegrated into smaller fragments and eventually disintegrated into environmentally friendly species like water and carbon dioxide. The photocatalysts were quite robust enough over multiple cycles. The proposed mechanism provided a guideline and understanding of the role of materials and the charged species generated during photocatalysis processes.

FUTURE SCOPE AND PERSPECTIVES

1. Preparation of new, improved photocatalytic materials

There is an ever-increasing demand for high-efficiency and novel photocatalytic materials, which are important for prospective photocatalytic applications. Indeed, current research work paved the way for the synthesis of newer inorganic materials, such as $\text{Ce}_x\text{Zn}_{1-x}\text{O}$, ($x = 0.00$ to 0.07 moles), $\text{M}_x\text{Zn}_{1-x}\text{O}$ ($\text{M}=\text{Nd}/\text{Sm}/\text{Ho}/\text{Dy}$), anatase TiO_2 and $\text{X}\%-\text{MWCNT}/\text{TiO}_2$ ($\text{X}=2, 4, 6, 8\%$), employing novel precursor method. Secondly, the bandgap of materials was appropriately modified by doping and through heterojunction

formation, which not only improved the light absorption properties of the native materials but also exhibited synergistic effects between the two materials. The synthesised materials were of nanometre scale, hence showing an optimistic effect on the photocatalytic activities. The photocatalytic properties of TiO_2 and ZnO were optimized by band gap engineering. The method of preparation, concentration and type of dopants influenced the photoactivities. The material preparation presented here can be scaled up owing to low-cost, easy and reproducible methods. The $\text{Ce}_x\text{Zn}_{1-x}\text{O}$ demonstrated enhanced activity toward MB and Red CL-5B dye solutions under UV-visible light. On similar lines, $\text{M}_x\text{Zn}_{1-x}\text{O}$ ($\text{M}=\text{Nd}/\text{Sm}/\text{Ho}/\text{Dy}$) exhibited a good photoluminescence effect and photodegradation of Rh B dye with mineralization effect. Pure anatase TiO_2 materials exhibited promising degradation of harmful Rh B dye and new emerging pollutants like paracetamol drug molecule. The MWCNT/ TiO_2 composite material also displayed excellent efficiency for photocatalytic organic synthesis, which is important in the conversion of benzophenone to benzopinacol.

2. Multi-functional applications of the photocatalytic materials.

The synthesized materials could be employed for various other aspects of photocatalysis. Hence, multi-faceted research can be pursued using the prepared catalysts. In particular, the precursor-layer-coating method, where the different materials can be fabricated using alternate metal oxides supported on CNT. Further investigations can be extended to alternative organic synthesis reactions and compounds. The current-voltage characteristics can also be investigated due to heterojunction formation at the interface of TiO_2 and MWCNT to understand the electronic properties.

3. Proposed mechanism

The proposed photocatalytic mechanism provided a fundamental understanding of the route of reactions, the type of reactive species generated by the materials and the role played by the photocatalytic materials in the reported applications. This can be used as a guideline for future research and can be deeply investigated.

4. Kinetic studies and the degradants

The photocatalytic performances or rate of reactions over the materials were realized based on the chemical kinetics and by-products formed during the processes. This information will provide key insights into the rate and nature of reactions occurring on the

surface of the material. Such data will assist scientists to design and fabricate novel and improved photocatalysts in future.

5. Modification of band gap and interaction between the heterostructure in composite materials

The modification of surface electronic properties by doping and integration of materials was well accomplished in current research. At the same time, band gap engineering by doping in host materials influenced the photocatalytic activities. The $\text{TiO}_2/\text{MWCNT}$ composite altered the light absorption and photocatalytic properties when compared to their individual pristine materials. The electronic charge separation and mobility could be studied in-depth for the $\text{MWCNT}/\text{TiO}_2$ system.

In the overall conclusion, the current research work showcased the preparation of newer materials for the multifaceted photocatalytic applications. The materials were systematically characterized, showed improved optical properties and were well-tested for potential photocatalytic applications. The current research work will provide fundamental knowledge and serve as a stepping stone for future researchers in the field of photocatalysis. The current research throws light on the preparation of novel photocatalytic materials in terms of simplicity, cost, reusability, and high photocatalytic degradation efficiency of organic pollutants from wastewater using light energy. Likewise, its applications can be extended across other research arenas comprising catalysis, synthetic organic chemistry, and photo-redox catalysis. Other prospective applications could be artificial photosynthesis, environmental pollution control, hydrogen/clean energy production and water purification. The current research provided the fundamental knowledge to forthcoming researchers in the field of photocatalysis.

7:

List of Publications and Oral Presentations

List of Publications and Oral Presentations

I. Research Paper Publications in peer-reviewed scientific journals

1. **Mhalsekar, M*.**, Borker, V., Synthesis of cerium-doped zinc oxide nanomaterials by precursor method with improved photodegradation activity for Methylene blue and Red CL-5B dye. *J Mater Sci: Mater Electron*, **35**, 1071 (2024). Springer (**Impact factor 2.8**)
2. **Mhalsekar, M*.**, Borker, V., Nd_xZn_{1-x}O nanomaterials: Revealing the effects of hydrazine-based synthesis on the structural, morphology and optical properties., *Journal of Molecular Structure*, 1321, 139816 (2025) Elsevier (**Impact factor 4.0**)
3. **Mhalsekar, M*.**, Borker, V., Kole, P., Synthesis, characterization, and application of MWCNT/TiO₂ composite for photocatalytic reduction of benzophenone to benzopinacol. *Journal of Environmental Chemical Engineering*, **12** 114681 (2024). Elsevier (**Impact factor 7.4**)
4. **Manisha Mhalsekar***, Vrinda Borker, Priyanka Kole, **Manuscript accepted for publication** “Photosensitive anatase-TiO₂ nanomaterial: β-cyclodextrin based synthesis, characterization and photocatalytic degradation of paracetamol” *Journal of Nanoparticle Research*, Springer-nature (**Impact factor 2.6**).

II. Oral paper Presentations at Conferences

1. Paper presentation, “Thermal Analysis of Polymer-based Precursor for Synthesis of MWCNT/TiO₂ Composite Materials”, **Manisha Mhalsekar**, Vrinda Borker, was presented at DAE – BRNS 23rd Symposium on Thermal Analysis ” THERMANS-2022, November 3-5, 2022 at Khalsa College, Amritsar Punjab, India.
2. Paper presentation, “The effect of Hydrazinated precursor on band gap and photoluminescence properties of Nd-doped ZnO nanomaterials”, **Manisha Mhalsekar**, Vrinda Borker was presented ”at International Conference on Advances in Material Science and Chemistry ICAMSC-2023, conducted by Amrita Vishwa Vidhyapeetham, Kerala on 2nd - 4th November 2023.
3. Paper presentation “Facile Thermal Decomposition Of Zinc-succinate Precursor Yielding Nanosized Zinc Oxide Materials”, **Manisha Mhalsekar**, Vrinda Borker* was presented at Nobel Laureate S&T seminar series 11th India-Japan Science and technology co-organised by Sree Chitra Tirunal Institute for Medical Sciences & Technology (Dept. of Science and Technology, Govt. of India) and Indian JSPS Alumni Association (IJAA) on 6-7 December 2021.
4. Paper presentation “A green approach for high-efficiency benzopinacol synthesis using MWCNT/TiO₂ Photocatalyst” **Manisha Mhalsekar**, at the International Conference on Inter-disciplinary studies and Advancement in Chemical Sciences, Nirmalagiri College Kannore, Kerala 29-30th January 2025.