

Synthesis and catalytic study of nano CeO₂ compound

A

Thesis

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CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and catalytic study of nano CeO₂ compound**" which is submitted by Punit Kumar Sharma (Regd. No. 901802002) in fulfilment of the requirement for the degree of Doctor of Philosophy in School of Physics and Materials Science, Thapar Institute of Engineering & Technology, Patiala (Punjab), India is an authentic record of my own work carried out under the supervision of Dr. O.P. Pandey. The matter embodied in this thesis has not been submitted in part or full to any other institute/university for the award of any degree.



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This is to certify that the above statement made by the candidate is true to the best of my knowledge.



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INDEX

Contents	Page no.
Certificate	i
Acknowledgement	ii
List of publications	viii
List Conferences and Seminar	viii
List of figures	x
List of tables	xv
Abstract	xvii

Chapter 1	Introduction	
	Overview	1
1.1	Background	2
1.2	Need of waste water treatment	2
1.3	Photocatalysis	4
1.4	Mechanism	4
1.5	Heterogeneous Photocatalysis	7
1.6	Metal oxides	7
1.7	Use of surfactants and capping agent	8
1.7.1	Electrostatic stabilization	9
1.7.2	Steric stabilization	9
1.8	CeO ₂ and its properties over other oxides	10
	References	12
Chapter 2	Literature Review	
	Overview	17
2.0	Synthesis methods	18
2.1	Photocatalysis with CeO ₂ nanoparticles	18
2.2	Factors influencing the photocatalytic activity	23
2.2.1	Effect of solvent	23
2.2.2	Effect of calcination temperature on photocatalytic activity	24
2.2.3	Effect of capping agent	24
2.2.4	Effect of doping on O-vacancies	25

2.2.5	Effect of heterostructures	27
2.2.6	Effect of photocatalyst and dye dosage on the photocatalytic activity	29
2.2.7	Effect of pH on the photocatalytic activity	29
2.2.8	Effect of cationic and anionic dye	30
2.3	Plan of work	30
	References	32
Chapter 3	Methodology	
	Overview	39
3.1	Precursors	40
3.1.1	Raw Materials	40
3.1.2	Characterization Techniques	40
3.1.3	Apparatus used for photocatalytic study	41
	References	44
Chapter 4	Results and discussion-I	
	Overview	45
4.1	Introduction	46
4.2	Synthesis of CeO ₂ NPs	46
4.3	Effect of calcination temperature, capping agent and role of solvent	47
4.3.1	XRD analysis	47
4.3.2	FTIR studies	49
4.3.3	UV analysis	51
4.3.4	TEM analysis	54
4.3.5	Raman analysis	56
4.3.6	BET Analysis	58
4.3.7	Photodegradation of dye	59
4.3.7.1	Effect of Calcination	59
4.3.7.2	Effect of solvent and capping agent	60
4.3.8	Kinetics of photodegradation of dye	61
4.3.9	Effect of H ₂ O ₂ on photocatalysis	64
4.3.10	Adsorption study	66
4.3.11	Degradation mechanism	67

	References	69
Chapter 5	Results and discussion-II	
	Overview	75
5.1	Introduction	76
5.2	Synthesis of Zn-doped and (Y, Zn) co-doped CeO ₂ NPs	77
5.3	Effect of doping and co-doping	78
5.3.1	XRD analysis	78
5.3.2	FTIR analysis	80
5.3.3	UV analysis	82
5.3.4	TEM and EDX analysis	86
5.3.5	Raman analysis	87
5.3.6	Photodegradation of dye	91
5.3.7	Kinetics of photodegradation of dye	93
5.3.8	Degradation mechanism	96
	References	97
Chapter 6	Results and discussion-III	
	Overview	103
6.1	Introduction	104
6.2	Synthesis of CdS heterostructures with Zn-doped and (Y, Zn) co-doped CeO ₂ NPs	104
6.3	Effect of CdS heterostructures on CeO ₂	106
6.3.1	XRD analysis	106
6.3.2	FTIR analysis	108
6.3.3	UV analysis	110
6.3.4	TEM analysis	114
6.3.5	EDS analysis	116
6.3.6	Raman analysis	118
6.3.7	PL spectroscopy	121
6.3.8	XPS analysis	122
6.3.9	Photodegradation of dye	123
6.3.10	Effect of dye concentration	126
6.3.11	Kinetics of photodegradation of dye	127
6.3.12	Degradation Mechanism	130

	References	132
Chapter 7	Results and discussion-IV	
	Overview	139
7.1	Introduction	140
7.2	Experimental details	140
7.3	Effect of $(\text{Zn}_{0.003-x}\text{Cd}_x)\text{S}_{0.003}$ heterostructures on CeO_2	142
7.3.1	XRD analysis	142
7.3.2	FTIR analysis	143
7.3.3	UV analysis	146
7.3.4	Raman Analysis	148
7.3.5	TEM, EDS analysis	150
7.3.6	PL spectra	151
7.3.7	Photodegradation of CV dye	153
7.3.8	Kinetics of photodegradation of dye	158
7.3.9	Effect of various parameters on catalytic activity of synthesized samples	160
7.3.9.1	Effect of dye concentration	160
7.3.9.2	Effect of catalyst concentration	160
7.3.9.3	Effect of different ions	161
7.3.9.4	Effect of pH on photocatalyst.	161
7.3.10	Degradation mechanism	162
	References	164
Chapter 8	Conclusions and Future Scopes	
	Overview	173
8.1	Conclusions	174
8.2	Future Scope	176
	Annexure A	179
	Annexure B	183
	Annexure C	187
	Annexure D	190

LIST OF PUBLICATIONS

1. **Punit Kumar Sharma** and O.P. Pandey, “*Effect of processing parameters on structural and optical properties of CeO₂ nanoparticles for the removal of crystal violet dye*”, **Journal of Sol-Gel Science and Technology** **99**, 75-91 (2021).
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4. **Punit Kumar Sharma** and O.P. Pandey, “*Synthesis and catalytic study of CeO₂ heterostructures with (Zn_{0.003-x}Cd_x) S_{0.003} for the removal of crystal violet dye*”, **Physica B** **631**, 413702 (2022).

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LIST OF FIGURES

Chapter 1

1.1	Different treatment processes used in industries.	4
1.2	Schematic diagram of various steps occurring in photocatalytic process.	5
1.3	Proposed mechanism of synthesized hetero junction of CeO ₂ -CdS.	6
1.4	Proposed mechanism of photosensitization of semiconductor by dye.	6
1.5	Growth mechanism of nanoparticles.	8
1.6	Showing colloidal particles with existing set of charges. It shows the electrostatic forces on the existing system.	9
1.7	Schematic representation of steric stabilization of metal colloid particles (a) Entropic effect and (b) Osmotic effect.	10

Chapter 3

3.1	The photochemical reactor setup to study photocatalysis	42
3.2	UV-visible absorption spectra of CV dye.	43

Chapter 4

4.1	XRD patterns of CeO ₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped), and (d) ethanol (capped).	48
4.2	FTIR spectra of CeO ₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	50
4.3	UV-absorption spectra of CeO ₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	51
4.4	Tauc's plots of synthesized CeO ₂ samples in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	52
4.5	(a) TEM and (b) HRTEM image of E600.	54
4.6	(a) TEM and (b) HRTEM image of WT0.	54
4.7	(a) TEM and (b) HRTEM image of ET300.	54
4.8	Raman spectra of CeO ₂ samples synthesized in (a) water medium and (b) ethanol medium.	56
4.9	N ₂ adsorption-desorption isotherms of (a) WT0 and (b) ET0 and inset of figures having pore size distribution.	58
4.10	Degradation of crystal violet dye by CeO ₂ samples synthesized in	59

	(a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	
4.11	Pseudo first order kinetics of CeO ₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	62
4.12	Pseudo second order kinetics of samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	63
4.13	(a) Degradation of CV dye in the presence of catalyst and H ₂ O ₂ and (b) photo-oxidation of CV dye in the presence of H ₂ O ₂ only.	64
4.14	Adsorption study of crystal violet dye by CeO ₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).	66
4.15	Shows the degradation mechanism for (a) synthesized CeO ₂ compound and (b) synthesized mechanism with H ₂ O ₂ .	67

Chapter 5

5.1	XRD patterns of (a) Y-doped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ samples inset of all figures showing the shifting in the peak corresponding to (111) plane.	78
5.2	FTIR spectra of (a) Y-doped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ samples.	80
5.3	Absorbance spectra of (a) Y-doped CeO ₂ , (b) Zn-doped CeO ₂ and (c) (Y, Zn)-co-doped CeO ₂ samples.	82
5.4	Tauc's plot of (a) Y-doped CeO ₂ , (b) Zn-doped CeO ₂ and (c) (Y, Zn) co-doped CeO ₂ .	83
5.5	(a) TEM and (b) HRTEM image of 8%Y (c) TEM and (d) HRTEM image of 4%Zn4%Y.	86
5.6	EDX spectra of 4-4-ZYDC.	87
5.7	Raman spectra of (a) Y-doped CeO ₂ , (b) Zn-doped CeO ₂ and (c) (Y, Zn) co-doped CeO ₂ .	88
5.8	Percentage degradation of CV dye with the help of (a) Y-doped CeO ₂ , (b) Zn-doped CeO ₂ , (c) (Y, Zn) co-doped CeO ₂ .	91
5.9	Pseudo first order kinetics of CV dye using synthesized (a) Y-doped CeO ₂ , (b) Zn-doped CeO ₂ and (c) (Y, Zn) co-doped CeO ₂ .	94
5.10	Pseudo second order kinetics of CV dye with the help of (a) Y-doped CeO ₂ , (b) Zn-doped CeO ₂ , (c) (Y, Zn) co-doped CeO ₂ .	95

5.11	Degradation mechanism for doped CeO ₂ sample.	96
------	--	----

Chapter 6

6.1	XRD patterns of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ .	106
6.2	FTIR spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ .	108
6.3	UV-Reflectance spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO ₂ .	110
6.4	UV-absorbance spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO ₂ .	111
6.5	Tauc's plot of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ .	112
6.6	(a) TEM and (b) HRTEM image of ZCCDS-1:1.	114
6.7	(a) TEM image (b) HRTEM image, (c) mapping of S, (d) Ce, (e) O, (f) Zn, (g) Y and (h) Cd of ZYCCDS-1:1.	116
6.8	(a, b): EDS spectra of ZCCDS-1:1 at different locations.	117
6.9	Raman spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ .	118
6.10	PL spectra of CdS heterostructures synthesized using (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ .	121
6.11	XPS HR spectra of (a) Zn 2p (b) Cd 3d (c) O 1s (d) Y 3d (e) Ce 3d and (f) S 2p of ZYCCDS-1:1 sample.	122
6.12	Degradation of crystal violet dye by CdS heterostructures with (a) undoped, (b) Zn-doped, (c) (Y, Zn) co-doped CeO ₂ (d) leaching properties of Cd ion in photocatalysis.	124
6.13	Shows the effect of dye concentration for CV dye.	126
6.14	First order kinetics of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO ₂ .	127
6.15	Second order kinetics of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO ₂ .	128
6.16	Degradation mechanism of CdS heterostructure with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO ₂ .	130

6.17	Showing the band gap calculations for synthesized undoped, Zn-doped, (Y, Zn) co-doped CeO ₂ and CdS NPs.	131
-------------	---	-----

Chapter 7

7.1	XRD pattern of synthesized samples.	142
7.2	FTIR spectra of synthesized samples.	144
7.3	Showing the (a) UV-Reflectance spectra, (b) UV-absorbance spectra and (c) Tauc's plot of synthesized samples.	146
7.4	Raman spectra of synthesized samples.	148
7.5	Showing TEM and HRTEM image of CZ-22.	150
7.6	Mapping of CZ-22 sample (a) zinc (Zn), (b) oxygen (O), (c) cerium (Ce), (d) cadmium (Cd) and (e) sulphur (S).	151
7.7	Showing the PL spectra of synthesized samples.	151
7.8	Showing the photodegradation of synthesized samples under UV-visible illumination.	153
7.9	Shows the comparison of photolysis and % degradation of synthesized samples under 2h of UV-illumination irradiation of light.	154
7.10	(a) Shows the FTIR spectra of crystal violet dye before and after degradation and (b) FTIR spectra of CZ-22 catalyst.	155
7.11	LC-MS spectra of CV dye after complete degradation under UV-visible illumination.	156
7.12	(a) First order kinetics (b) second order kinetics of synthesized samples.	158
7.13	Effect of (a) dye concentration, (b) catalyst amount, (c) various of cations and (d) pH variation of dye solution.	160
7.14	Showing the degradation mechanism of CV dye.	162

Annexure A

A1	Spectral variation of optical thickness of CV degraded with (a) W0 (b) W300 and (c) W600.	179
A2	Spectral variation of optical thickness of CV degraded with (a) E0, (b) E300 and (c) E600.	180
A3	Spectral variation of optical thickness of CV degraded with (a)	181

WT0, (b) WT300 and (c) WT600.

A4	Spectral variation of optical thickness of CV degraded with (a) ET0, (b) E3T00 and (c) E6T00.	182
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Annexure B

B1	Spectral variation of optical thickness of CV degraded with (a) 2%Y, (b) 4%Y, (c) 6%Y, (d) 8%Y and (e) 10%Y.	183
B2	Spectral variation of optical thickness of CV degraded with (a) 2%Zn, (b) 4%Zn, (c) 6%Zn, (d) 8%Zn and (e) 10%Zn.	184
B3	Spectral variation of optical thickness of CV degraded with (a) 6%Zn2%Y, (b) 4%Zn4%Y and (c) 2%Zn6%Y.	185
B4	Spectral variation of optical thickness of CV degraded with 4%Zn4%Y as an effect of catalyst concentration (a) 1 mg, (b) 3 mg, (c) 5 mg, and (d) 7 mg.	186

Annexure C

C1	Spectral variation of optical thickness of CV degraded with (a) CCDS-2:1, (b) CCDS-1:1 and (c) CCDS-1:2.	187
C2	Spectral variation of optical thickness of CV degraded with (a) ZCCDS-2:1, (b) ZCCDS-1:1 and (c) ZCCDS-1:2.	188
C3	Spectral variation of optical thickness of CV degraded with (a) ZYCCDS-2:1, (b) ZYCCDS-1:1 and (c) ZYCCDS-1:2	189

Annexure D

D1	Spectral variation of optical thickness of CV degraded with (a) CZ-04, (b) CZ-13 and (c) CZ-22 and (d) CZ-31.	190
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LIST OF TABLES

Chapter 1

1.1	Amount of metal ion present in water sample of Kabini river.	3
1.2	Shows the amount of pollutants present in the Sutlej river water.	3
1.3	Shows the amount of pollutants present in Beas river water.	3

Chapter 2

2.1	The photocatalytic studies of synthesized CeO ₂ NPs by different researchers and their outcomes.	18
-----	---	----

Chapter 4

4.1	Details of samples along with their preparation conditions.	47
4.2	Band position of each vibration.	51
4.3	Calculated bandgap values and extinction coefficient of CV dye when degraded with synthesized samples.	53
4.4	Measured peak absorption edge of synthesized CeO ₂ samples	61
4.5	Rate constant for first and second-order kinetics and corresponding R ² value.	64
4.6	Rate constant for first and second-order kinetics and corresponding R ² values in the presence of H ₂ O ₂ .	66

Chapter 5

5.1	Calculated crystallite size from XRD.	79
5.2	Band position of different vibrations.	81
5.3	Calculated band gap values and extinction coefficient of CV dye when degraded with Y, Zn doped and co-doped CeO ₂ samples.	85
5.4	Calculated extinction coefficient at different catalyst concentration.	93
5.5	Rate constant for first and second order kinetics and corresponding R ² values	96

Chapter 6

6.1	Details of samples along with their preparation conditions.	105
6.2	The calculated crystallite size of samples.	108
6.3	Peak assignments for all samples with different bonds.	109
6.4	Calculated bandgap values and extinction coefficient of CV dye degraded with synthesized samples.	114

6.5	Elemental composition of ZCCDS-1:1.	117
6.6	Position of F _{2g} peak (Raman active spectra) and relative peak area ratio.	120
6.7	Showing the rate constant for first and second order and their respective R ² value.	129
6.8	Calculated valence and conduction band edge.	130

Chapter 7

7.1	Details of samples along with their preparation conditions.	141
7.2	Variation in crystallite size of the synthesized samples.	143
7.3	Peak assignment to different bonds in all the synthesized samples.	145
7.4	Calculated bandgap of synthesized samples and extinction coefficient of CV dye when degraded with synthesized samples.	148
7.5	The degraded intermediates of CV dye under UV-visible illumination.	156
7.6	Calculated rate constant for first and second order kinetics with their corresponding R ² values.	159
7.7	Calculated valence and conduction band edge.	162

Annexure

A1	Shows the sample spectra labelling	179
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ABSTRACT

CeO₂ is a stable compound having wide band gap. Considering its high temperature stability, CeO₂ samples were synthesized in water and ethanol medium. Thioglycerol (TG) was used as capping agent. The Zn-doped and (Y, Zn) co-doped CeO₂ nanoparticles (NPs) were also synthesized to reduce the band gap and also to generate the oxygen vacancies. Further, their heterostructures were synthesized with CdS and ZnS. It was observed that CeO₂ NPs synthesized in ethanol as reaction medium with TG as capping agent showed enhanced catalytic activity as compared to samples synthesized in water medium. The synthesized samples calcined at 300 °C have shown large catalytic activity. Moreover, doped and co-doped CeO₂ NPs have shown many fold degradation efficiency towards CV dye as compared to bare CeO₂ NPs. The 8% Zn-doped CeO₂ NPs have shown 100 % dye degradation in 5h of UV-visible irradiation which is higher than bare CeO₂ samples (100 % dye removal in 7h). While, (Y, Zn) co-doped CeO₂ samples have shown 100 % dye degradation in 3 h of UV-visible irradiation. Further, the CdS and ZnS heterostructures were synthesized with Zn-doped and (Y, Zn) co-doped CeO₂ NPs. It was found that CdS heterostructures have shown enhanced catalytic activity with Zn-doped CeO₂ NPs. Moreover, the synthesized heterostructures degraded the CV dye in 2h of UV-visible irradiation. Further, the leaching properties of CeO₂ heterostructures synthesized with CdS have been studied. No leaching of Cd atoms in the dye solution was observed which shows that the synthesized heterostructures are UV-visible resistible. The photocatalytic activity of synthesized compound was also studied with variation in catalyst concentration. The catalytic activity is found to increase with the amount of catalyst dosage upto 3 mg in 100 ml of dye solution. The optical thickness of synthesized CeO₂ NPs has been calculated to check its relation with observed photocatalytic results. The optical thickness is found to increase with catalyst dosage. It was found that at optimum value of optical thickness, the rate of conversion is maximum. Beyond this value, the rate of conversion is found to decrease. The results indicated that oxygen vacancies play vital role in deciding the catalytic activity of the synthesized compound as no corelationship was observed for optical thickness and degradation rate.

The work shows that CeO₂-based photocatalyst can play an important role for degradation of pollutants because of its non-toxicity and formation of formation of oxygen vacancy due to transformation of Ce⁴⁺ to Ce³⁺. It is observed that the formation of Ce³⁺ by creation of O-vacancies plays important role as Ce in CeO₂ has stable states of both Ce⁴⁺ and Ce³⁺ ions.

CHAPTER 1

INTRODUCTION

Overview

This chapter presents the application of nanomaterials to remove the pollutants from waste water. The extensive discharge of waste water into the natural water resources contaminates the water sources. This discharge also depletes the dissolved oxygen in natural water resources. There are many techniques which are used for the treatment for waste water. Among various techniques, semiconductor photocatalysis technique is more useful due to non-toxic nature of semiconductors. Role of different semiconductors to degrade these pollutants has been discussed in detail in this chapter. Various methods to increase the photocatalytic activity has been presented. This include the use of dopants, attachment of second semiconductor to modify the band gap and also the influence of different medium to synthesize the nanoparticles has been described in this chapter.

1. Introduction

1.1 Background

The increasing standard of the society has led to growth of many industrial sectors. These industries consume lot of water for the processing of their products. In turn they produce lot of waste water which release organic effluents in the natural water resources. Many of these industries release organic effluents in the natural water resources without any treatment. In these waste water the organic pollutants such as benzene compounds and organic dyes are discharged which are highly toxic. Nearly, 1-20 % of these dyes are released by textile industries during dying process. These organic pollutants are very harmful to human health. Moreover, aquatic life is also influenced by these effluents as the dyes discharged deplete the dissolved oxygen level in the water. Since last few years, efforts are being made to degrade these dyes using different semiconductor nanomaterials. Different types of semiconductors have been tried to increase the photocatalytic properties to degrade varieties of dyes [1–3]. Some of these like ZnO, TiO₂, ZnS and MnO₂ are used for the purpose of photocatalysis [4]. Among these NPs, TiO₂ has shown better efficiency and is well-known compound for photocatalysis. CeO₂ is high temperature stable compound having band gap of 3.2 eV [5]. This can be used as photocatalyst with modification in its band gap. But, very little work is reported on CeO₂ as photocatalyst. Thus, CeO₂ is chosen to study the photocatalytic activity because CeO₂ can absorb larger fraction of solar spectrum as compared to TiO₂ and its photoinduced charge carriers have longer lifetime [6].

1.2 Need of Waste water treatment

In the recent years the contaminations of water due to organic dyes and toxic organic compounds have increased to alarming level. According to National Environment Research Institute, India (NERRI), most of the Indian rivers are polluted and need a powerful pollution treatment [7]. The government of India is also serious to reduce the water pollution in India. Renovation and restoration of water, National Lake Conservation plan, National Water Mission, Rain water Harvesting, Sewage treatment and many more policies are deployed which are very useful to treat the contaminated water. The Kabini river data as given below shows presence of heavy metal concentration in water. The metal concentration has been determined from atomic absorption spectroscopy [8]. Table 1.1 shows the presence of different elements of Kabini River which is one the tributaries of the river Cauvery in the southern India. Table 1.2 depicts the pollutant level in the Sutlej river water.

Table 1.1 Amount of metal ion present in water sample of Kabini river.

Kabini River	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)	Mn (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)
	21.80	27.44	63.55	53.95	21.71	87.96	55.82	21.24	2.41

The locations for the measurement of pollutants were Rampur, Ludhiana and Amritsar for Sutlej River. Four samples (S1-S4) were collected in different temperature conditions [7,9]. Similarly, Beas river also contains pollutants which has been cited in different publications and shown in table 1.3 [10].

Table 1.2: shows the amount of pollutants present in the Sutlej river water.

Sample	TDS (mg/L)	turbidity (NTU)	total alkalinity (mg/L)	total hardness	dissolved oxygen	COD (mg/L)	phosphate (mg/L)	Nitrate (mg/L)	Chloride (mg/L)
S1	231.21	15.61	115.46	102.41	8.97	17.51	0.114	0.64	26.52
S2	402.60	39.52	205.86	170.42	3.81	243.95	1.298	2.70	40.92
S3	244.22	22.41	128.54	126.73	8.01	46.22	0.271	1.26	28.47
S4	389.93	35.00	160.14	140.72	5.30	107.49	0.690	2.14	33.53

Table 1.3: shows the amount of pollutants present in Beas river water.

Pollution index of individual metals	Zn	Co	Cu	Cd	Cr	Mn	Ni
Pre-monsoon season	0.0005	0.0010	0.0011	0.0110	0.0008	0.0027	0.0137
Pre-monsoon season	0.0006	0.0011	0.0009	0.0082	0.0007	0.0023	0.0347
Winter Season	0.0006	0.0012	0.0009	0.0099	0.8808	0.0010	0.0061

The synthetic dyes are used widely for dyeing clothes, leather and also for plastic products [11]. This has led to decrease in drinkable water resources as ground water is mostly contaminated. Thus, purification of water is the need of the era. There are many processes which are being used for purification of waste water. These include activated carbon, oxidation, activated sludge, nanofiltration and adsorption. However, from the last 2 decades the photocatalysis technique has been proved very effective for purification of the industrial waste water. These processes are categorized in different sectors as given below in Fig. 1.1.

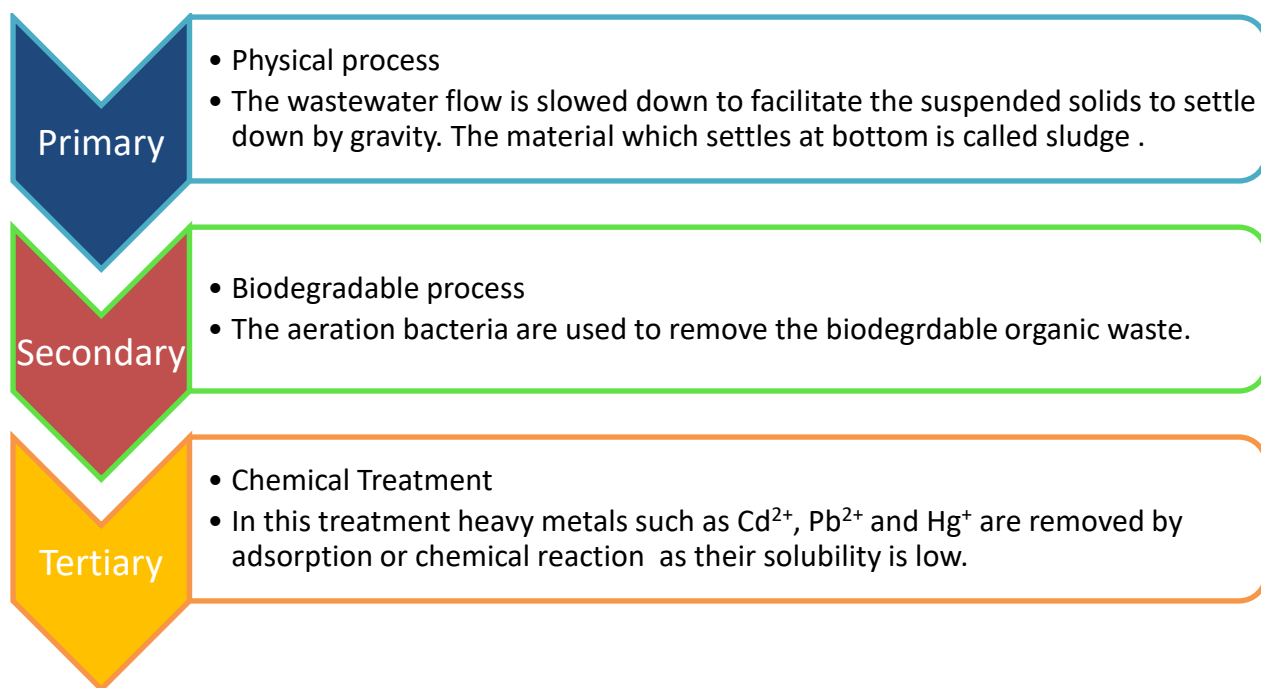


Fig. 1.1: Different treatment processes used in industries.

1.3 Photocatalysis

In order to reduce pollutants in discharged water, researchers have developed various techniques to reduce the contaminants such as adsorption [12], chemical precipitation, coagulation and flocculation [13]. Among several treatment methods, advanced oxidation process (AOP) is highly useful. This is on the basis of photocatalysis where the generation of hydroxyl radicals occurs and these facilitate the oxidation of the dyes to convert them into CO_2 , H_2O and other byproducts which are non-toxic [1]. The photocatalysis is considered as a green advanced process which occurs in the presence of light and catalyst. In the dye degradation process, the large molecules of dye are broken down into smaller molecules. Finally, these smaller molecules are converted to CO_2 , water and other mineral products.

The photocatalysis is divided into two categories (1) homogeneous and (2) heterogeneous catalysis. Homogeneous photocatalysis is a process in which both the catalyst and reactant are in the same phase. The phase can be gas or liquid. Heterogeneous photocatalysis is a process in which catalyst and organic pollutants both are in different states. This process has been used widely by researchers to degrade different types of dyes using different semiconductors [14].

1.4 Mechanism

When the photon of energy larger than the band gap of semiconductor materials falls on the surface of catalyst, the electrons are excited up to conduction band level [15]. Further, the electron in the conduction band performs the photo-reduction. Moreover, the holes in the

valence band perform photo-oxidation. Secondly, the VB and CB edge potential also are important factors to decide the photocatalytic activity of synthesized catalyst because the VB and CB of synthesized compound generates radicals for redox reactions. Thus, CB and VB of synthesized catalyst are important for degradation of dye molecules. Fig. 1.2 demonstrates the generation of charge carriers during photocatalytic process.

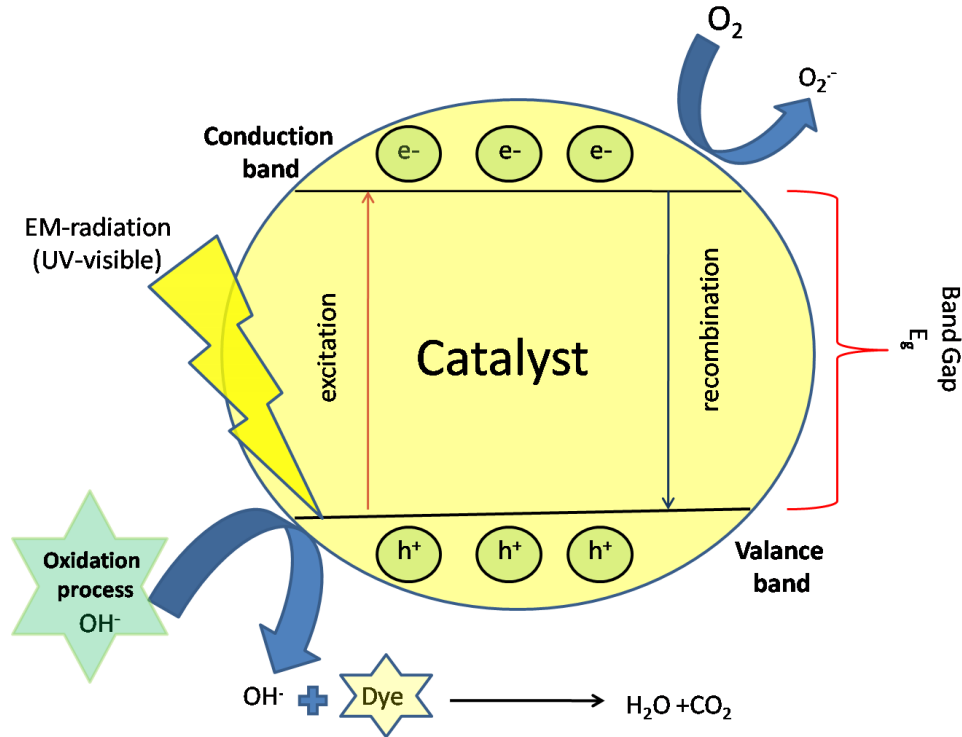


Fig. 1.2: Schematic diagram of various steps occurring in photocatalytic process.



The modifications in the generation of charge carriers can be done by incorporating the dopant ion in the host lattice or by attachment of other material to the primary material referred as heterostructures. In synthesized heterostructures, there are two or more conduction and valence band edge levels. The edge levels of other semiconductor act as acceptor for excitons excited in primary semiconductor. The electrons generated in first material goes to

conduction band of second material which has less negative potential. Similarly, the holes generated in VB of first component are transferred to VB of second component which have more negative potential. Also, formation of interface between two different materials increases the efficiency of synthesized photocatalyst. The charge transfer between different components of synthesized heterostructures increases the efficiency of synthesized heterostructures. Fig. 1.3 shows the proposed mechanism for synthesized CeO_2 -CdS heterojunction.

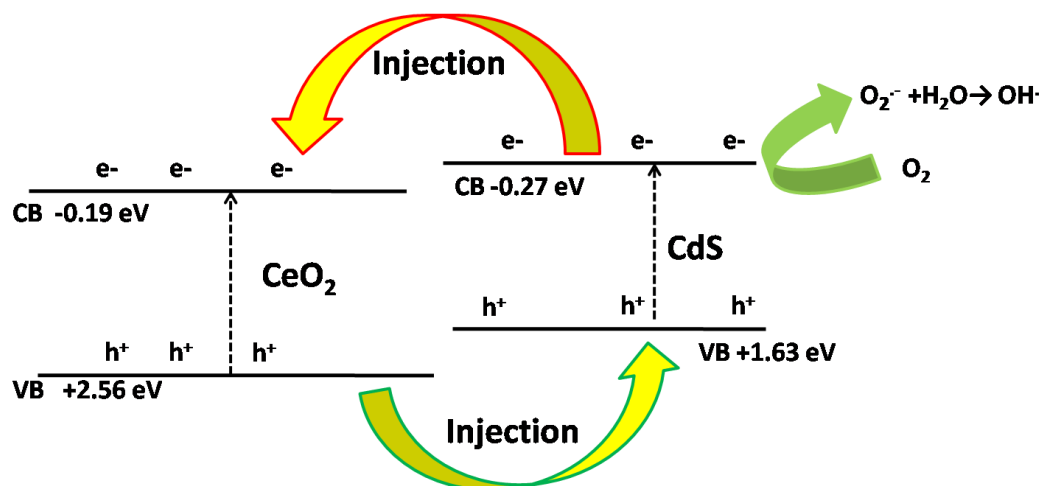


Fig. 1.3: Proposed mechanism of synthesized hetero junction of CeO_2 -CdS [16].

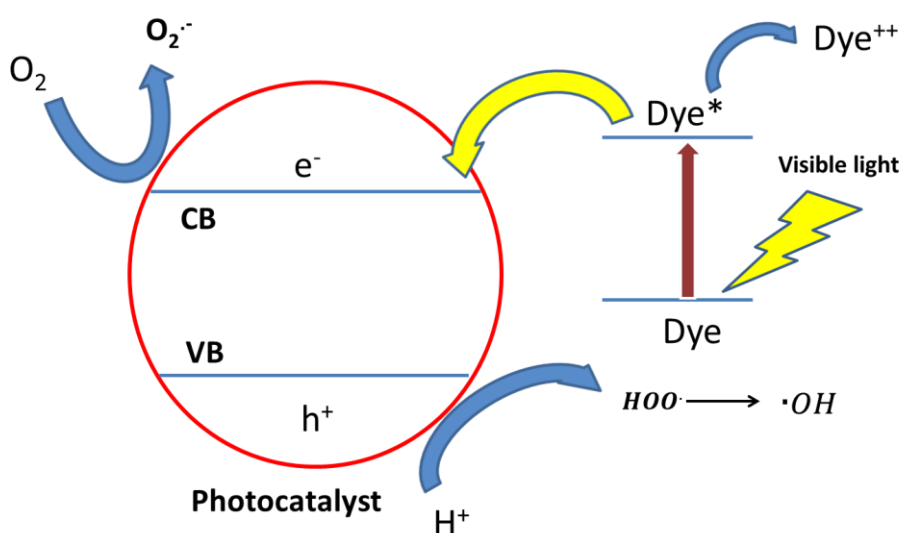


Fig. 1.4 : Proposed mechanism of photosensitization of semiconductor by dye [17].

Another interesting photosensitization process observed is also shown in Fig. 1.4. In this process the initial excitation of dye molecules rather than photocatalyst occurs. This makes the difference between the photodegradation of the dye pollutants under visible light irradiation and that under UV radiation. Here, it can be observed that electron generated in

the conduction band of dye molecule (more negative potential) is transferred to less negative potential of semiconductor. This is how the dye sensitization process of semiconductors by dye molecules happens.

1.5 Heterogeneous photocatalysis

The photocatalysis field expanded rapidly within the last two decades. It has undergone various developments related to energy and environment [18,19]. Semiconductors possess a wide band gap where energy levels are not available to promote the recombination of charge carriers. Once the excitation has taken place by absorbing the EM radiations falling on the surface of catalyst, there is sufficient lifetime for charge carriers to perform oxidation-reduction of adsorbed species. The charge transfer from the semiconductor to the adsorbed species occurs after making contact and reaction is exothermic in nature. This process is known as heterogeneous photocatalysis. The generation of radicals is primary requirement before proceeding for heterogeneous photocatalysis. However, metals have merged VB and CB because of which there is no possibility of separation of charge carriers to perform redox reaction. Thus, semiconductor photocatalysis has been used by researchers for removal of organic pollutants.

Semiconductors are of two types. These are (i) Direct band gap and (ii) Indirect band gap semiconductors. Direct band gap means that the minimum of conduction band lies directly above the maximum of valence band gap. Thus, excitation of electron requires no momentum transfer from valence to conduction band [20]. While, in the indirect bandgap semiconductor, momentum transfer is required as conduction band minima does not lie above the valence band maxima. Thus, electron has to transfer momentum when excited from valence band to conduction band. This configuration of band gap directly affects the activity of catalyst. These types of composites enhance the catalytic activity of nanomaterials by inhibiting the charge carrier recombination.

The high charge recombination is the main disadvantage in the direct band semiconductor [20]. Thus, modifications are required to reduce recombination of charge carriers.

1.6 Metal Oxides

Metal oxides based photocatalyst are used for the treatment of waste water since last two decades and has shown large applications. As compared to bulk metal oxides, the nanosized materials have shown enhanced degradation efficiency because of quantum confinement effect. The performance of these nano metal oxides depends upon their shape and size which can be controlled by different synthesis parameters. Thus, metal oxide nanomaterials have

gained much popularity. The nanomaterials can be produced with different shapes and sizes exhibiting variation in their physical and chemical properties.

There are various methods to produce nanoparticles with different shapes and size such as hydrothermal, sol-gel, chemical precipitation, thermal decomposition, solvothermal and chemical bath deposition [21]. However, some of these methods require high pressure and temperature [22]. These techniques also add complexities to experiments. Moreover, special design of apparatus is also required for the synthesis.

Among all these methods, co-precipitation method is most suitable for the synthesis of nanomaterials as this method is simple, reproducible, and economical leading to large scale production [23]. When the synthesis of these nanoparticles is done by chemical route, nucleation of solid particles occurs. However, in due course of time these nucleated particles grow in size. This growth of nanoparticles should be controlled otherwise due to Vander Walls interactions and Ostwald ripening their size become very large. The growth of NPs is shown in Fig. 1.5.

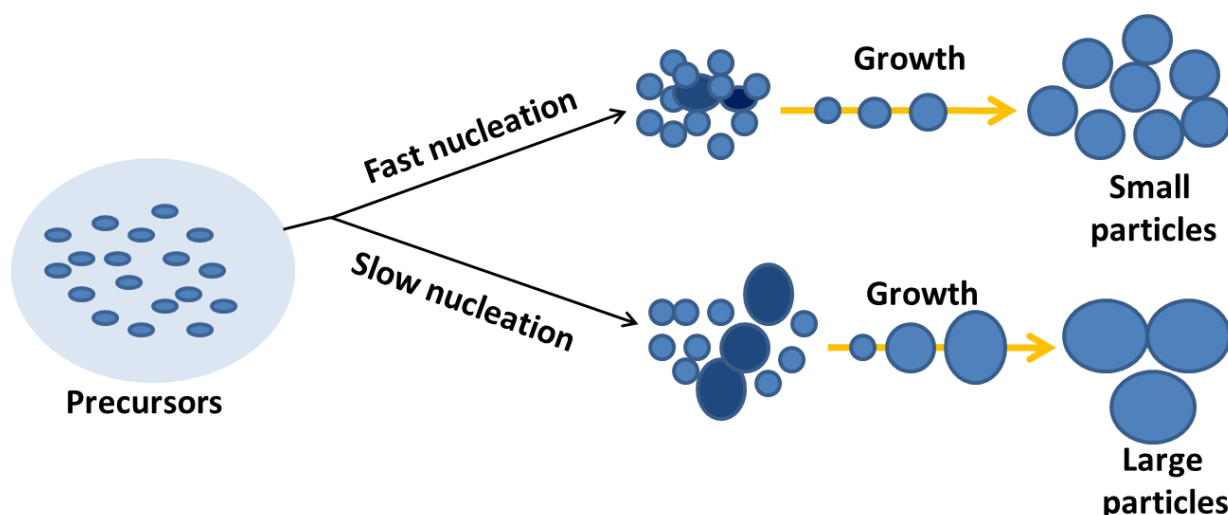


Fig. 1.5: Growth mechanism of nanoparticles.

1.7 Use of surfactant and capping agent

The synthesized nanoparticles have higher tendency to agglomerate. This occurs because of Vander Waals interactions. Thus, modification in the synthesis parameter is required to stop agglomeration. For it capping agent are added during the synthesis. These capping agents are adsorbed on the particle surface and provide repulsive forces and thus balance the attraction forces between the synthesized nanoparticles as shown in Fig. 1.6 and 1.7.

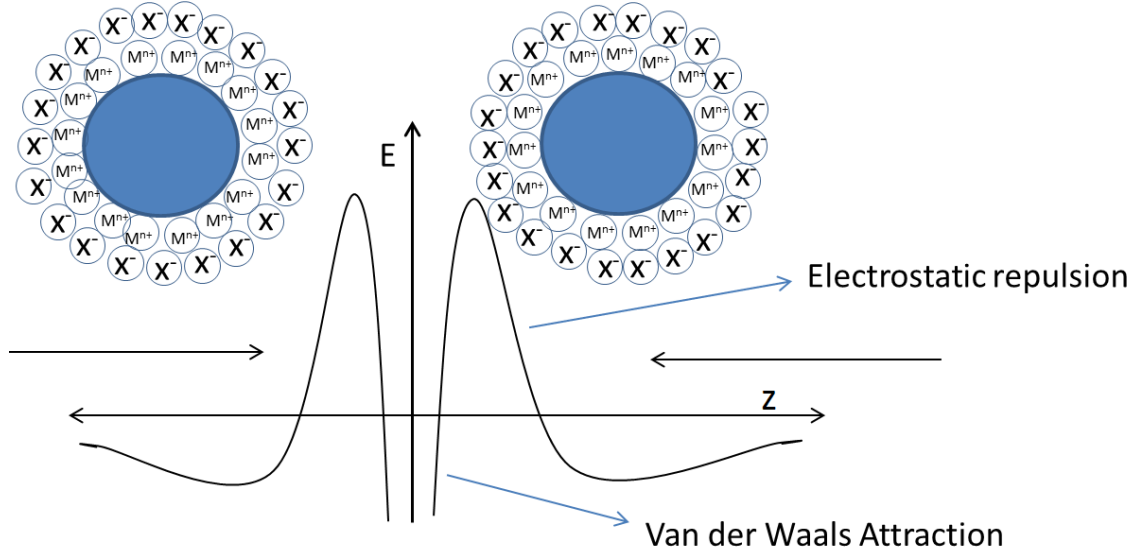


Fig. 1.6: Showing colloidal particles with existing set of charges. It shows the electrostatic forces on the existing system.

1.7.1 Electrostatic Stabilization

In general, electrostatic and steric forces are responsible to prevent agglomeration of NPs. Electrostatic stabilization requires the stabilization of electrical double layer. It arises from ions adsorbed on the surface and surrounding ions in that particular medium [24]. This causes coulombic repulsion between the particles and provide stable arrangement of the colloidal NPs. The coulomb's law states that every charge has electric potential and it is compensated by opposite charge in its proximity. Here each negatively charged ion is surrounded by positive charges and also negative charged particles with positive charges. This is called electric double layer [25]. The electrostatic stabilization of colloidal particles is shown in Fig. 1.6. This double layer causes coulombic repulsion among the charged particles when they approach each other. It causes exponential decay with interparticle distance z as described below.

$$\Psi = \Psi^0 e^{-k/z} \quad (1.8)$$

1.7.2 Steric Stabilization

The surfactants help to have colloidal dispersions. In most of the cases it is done by addition of polymers. These surfactants form a protecting layer around the particles. This prevents flocculation. The vander waals forces influence the force of attraction and repulsion among the particles. Thus steric stabilization is provided [25–27]. This stabilization is shown in Fig. 1.7.

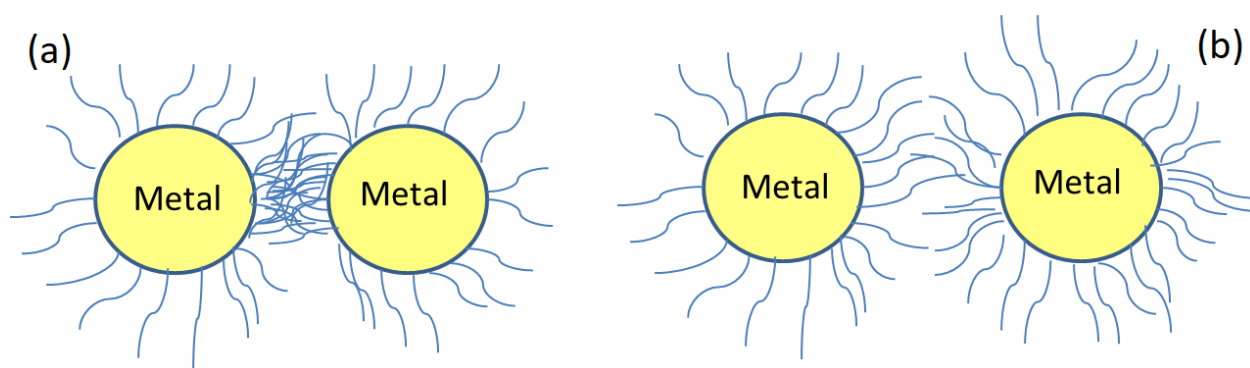


Fig. 1.7: Schematic representation of steric stabilization of colloidal particles. It shows (a) Entropic effect and (b) Osmotic effect.

Because of dimensional variation of polymers the nature of attractive forces between the colloidal particles may vary. This causes volumetric restriction and also osmotic diffusion effect to make the system stable.

As shown in Fig. 1.7 (a), first it restrict the motion of adsorbed molecule. This decreases the configurational entropy. Secondly, the adsorbed polymer layer of NPs approach each other. As a result the compressive force lead to increased local density of polymeric chains in the overlapped region. This causes strong repulsion. As a result there is an increase in osmotic pressure in the region. This type of repulsion is called osmotic repulsion (Fig. 1.7 (b)).

1.8 CeO₂ and its properties compared with other oxides

CeO₂ also known as ceria is a rare earth metal oxide. CeO₂ is a strong oxidizing agent with wide band gap and attracted much attention due to its high catalytic activity. The low cost with environmental friendly nature makes it more useful [28]. As CeO₂ has large surface to volume ratio which allows CeO₂ to absorb only UV-rays present in the solar spectrum [18]. The CeO₂ as a catalyst is better than TiO₂ because it has higher range of absorption of radiations which allows CeO₂ to generate more charge carriers for the same amount of light falling on the catalyst [29]. It is observed that CeO₂ has exceptional properties like mechanical strength, electronic conductivity and oxygen storage capacity [30,31]. The higher concentration of O-vacancies formation is due to its redox chemistry by making transformation from Ce⁴⁺ to Ce³⁺ [14, 15]. The Ce⁴⁺ oxidation state has electronic configuration of [Xe]4f⁰ being more stable state as empty than [Xe]4f¹ for Ce³⁺ [34]. Thus, there is possibility of formation of two oxides cerium oxide (CeO₂) and cerium sesquioxide (Ce₂O₃). However, CeO₂ is used due to higher stability than Ce₂O₃. CeO₂ is one of the high refractory oxides and has the fluorite structure with Fm3m space group. It is stable compound

up to its melting point of 2700 °C [35]. The fluorite structure consists of face centered cubic (FCC) unit cell. Here the anions and cations occupy octahedral sites. It has pale yellow color because of charge transfer between Ce (IV) and O (II) [36]. CeO₂ NPs has wide band gap of 3.2 eV. It is used in many applications. Among these its major application is in solid oxide fuel cells (SOFC) at higher temperature [16]. The basic use of CeO₂ is for the fabrication of sensors, drug delivery carriers, catalysis, and anti-plastic ointments. It is found that CeO₂ remains in its fluorite structure even after the loss of considerable amount of oxygen via formation of O-vacancies. Also, it has been observed that CeO_{2-x} can be reoxidized after getting exposure to oxidizing environment [37]. Thus, CeO₂ can release and store oxygen via interchanging its ionic state Ce³⁺/Ce⁴⁺ [38,39]. In the redox reactions, there is need to separate the charge carriers (e⁻, h⁺) to perform redox reactions. Thus, large band gap offers excellent driving force to induce redox reactions. However, it is also observed that wide band gap of CeO₂ reduces its catalytic activity and thus the application of CeO₂ is limited to its UV region only. It indicates that CeO₂ can absorb the light which is only 5 % of solar spectrum [40]. Thus, applications of CeO₂ are restricted.

For the reduction of the band gap of CeO₂, different elements have been doped to CeO₂ to increase the absorption spectra limit of CeO₂ [41]. Also, heterostructures of various semiconductors such as ZnO, TiO₂, CdS and ZnS etc. were synthesized with CeO₂ to increase its efficiency of higher spectral range of light falling on the surface of synthesized sample [42–45].

The CeO₂ has been synthesized due to its non-toxicity and high photosensitivity. Since photocatalytic reactions are redox reactions so, large band gap offers better separation of charge carriers which offers excellent driving force to perform redox reactions. However, UV-visible light also has visible light radiations in it. Thus, low energy photons could not generate charge carriers in undoped CeO₂ samples. The (Y, Zn) co-doping induces oxygen vacancies below the conduction band and reduces the band gap. Hence, low energy photons also induces charge carriers in redox reactions. Further, it has been observed that doped and co-doped CeO₂ samples shows enhanced catalytic activity towards CV dye due to reduced band gap and optimum O-vacancies.

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CHAPTER 2

LITERATURE REVIEW

Overview

This chapter describes the details of literature review on CeO₂ nanoparticles (NPs) and their properties. Different synthesis parameters adopted to enhance the catalytic properties has been presented in this chapter. This includes doping and synthesis of heterostructures which are used for enhancing the catalytic activity of synthesized compounds. Different parameters which affect the photocatalytic activity of synthesized material has been discussed. Among these, oxygen vacancies, surface area, hydroxyl groups and formation of other impurity band edge levels are critical. These occurs because of introduction of other material which inhibits the recombination of photo-generated charge carriers which has been described and discussed in detail. Further, the effect of capping agent on the catalytic activity of synthesized nanoparticles has also been discussed.

2.0 Synthesis methods

Synthesis of CeO_2 is critical as the procedures adopted for its synthesis influences the properties. The shape, size and morphology of the CeO_2 nanoparticles affect the properties. Thus, it is necessary to examine the synthesis method adopted by various researchers. As per available literature, CeO_2 has been synthesized by sol-gel method, hydrothermal or solvothermal, thermal decomposition, and also by combustion synthesis [1,2]. Some of these methods, however, require high pressure specially the designing of different types of apparatus. This also adds to the experimental complexities, high cost which could not meet the requirements on the industrial scale [3].

Among these, sol-gel and co-precipitation methods are simpler one. In this work, co-precipitation synthesis route was adopted because this method is simple, facile, reproducible, and economical with large scale production [4].

2.1 Photocatalysis with CeO_2 nanoparticles

In the year 2000, it was reported for the first time that CeO_2 is the better candidate for the decomposition of water to produce the oxygen in aqueous suspension [5]. It was also observed that the yield of O_2 depends upon the duration of light irradiation and the amount of CeO_2 present in the system. This experiment confirmed that CeO_2 is a promising candidate for photocatalytic reactions [6]. In 2002, Coronado et al. [7] reported that the irradiation on CeO_2 sample produces the superoxide radicals which are useful for the oxidation of organic pollutant such as toluene. Moreover, CeO_2 has large specific surface area which also helps to adsorb the dye molecules and is helpful for the degradation of the dye molecules.

The photocatalytic performance explored by different research groups for the undoped, doped and synthesized heterostructures are compared in table 2.1.

Table 2.1: The photocatalytic studies of synthesized CeO_2 NPs by different researchers and their outcomes.

Author's Name (Year) [Reference]	System	Synthesis Method	Organic pollutant degraded	Outcomes
Saravanan et al. (2012) [8]	ZnO/ CeO_2 heterojunction	Thermal decomposition method	Methylene Blue dye	The specific surface area of ZnO/CeO_2 is found higher than ZnO.

				Also, the photocatalytic activity of ZnO/CeO₂ is more than ZnO.
Sifontes et al. (2013) [9]	CeO ₂ nanoparticles	Thermal treatment	Congo red	- The congo red degradation rate is found to increase with illumination time. - The percentage degradation of congo red dye is 62, 71 and 91 % by CeO₂ NPs calcined at 350, 650 and 960 °C, respectively after 24 h of UV-illumination.
Channei et al. (2014) [10]	Fe doped CeO ₂ nanoparticles	Homogeneous precipitation method	Methyl orange (MO)	- Fe doped CeO₂ NPs have shown enhanced photocatalytic activity. 1.5 mol% Fe doping was found to be optimum to achieve higher catalytic activity in 120 minutes.
Hao et al. (2014) [11]	Fe ³⁺ doped CeO ₂	Hydrothermal Method	Rhodamine Blue dye	The BET surface area of Fe³⁺-doped

				CeO ₂ is more than pure CeO ₂ which enhances the photocatalytic activity of doped CeO ₂ samples.
Mandal et al. (2015) [12]	Sm ³⁺ doped CeO ₂ nano powder	Microwave heating route	Acid orange 7	Sm³⁺ doped CeO₂ calcined at 500 °C has shown higher photocatalytic activity as compared to 600 and 800 °C.
Saravanakumar et al. 2016 [13]	Ag/CeO ₂	Hydrothermal Method	Methylene Blue, Crystal violet and Rhodamine Blue	- Ag/CeO₂ (1:3) has shown higher photocatalytic activity. - The higher content of Ag favor higher recombination of charge carriers.
Aslam et al. (2015) [14]	CeO ₂	Co-precipitation method	Phenol	After 180 minutes of sun light exposure, 98 %, 96 % and 99 % degradation for 2-chlorophenol, 2-bromophenol and 2-nitrophenol, respectively.
Xu et al. (2016) [15]	Yttrium doped CeO ₂	Hydrothermal method	Acetaldehyde	The oxygen vacancies are found to increase

				with the Y doping and also photocatalytic activity is found to increase with doping.
Wen et al. (2017) [16]	Ag ₂ CO ₃ /CeO ₂ heterojunction	In-situ co-precipitation method	Enrofloxacin (EFA)	The loading of Ag₂O on CeO₂ enhanced the photocatalytic activity as loading of Ag₂O on CeO₂ form more active sites, which enhances the photocatalytic activity.
Mittal et al. (2018) [17]	Au and Ag -doped CeO ₂	Co-precipitation method	Rhodamine blue (RhB)	- The photocatalytic activity was found to increase with doping. - Also, the photocatalytic activity decreased at higher doping as oxygen vacancies are generated above optimum level induce the deep traps for photogenerated charge carriers.
Das et al.	ZnO-CeO ₂	Hydrotherma	Methylene	The heterojunction

(2020) [18]	heterojunction	l Method	Blue (MB)	which has 50 wt% CeO₂ has shown enhanced photocatalytic activity. This enhanced photocatalytic activity is due to high visible light adsorption and also due to oxygen vacancies.
Nascimento et al. (2020) [19]	CeO ₂ -TiO ₂ heterojunction	Microwave assisted hydrothermal method (MAH method)	MB dye	It has been observed that adding TiO₂ to CeO₂ generally improves the photocatalytic activity due to improvement in absorption capacity of synthesized catalyst.
Kaur et al. (2021) [20]	CeO ₂ -ZnS heterojunction. CeO ₂ supported Zn _{1-x} Mn _x S (x: 0.025, 0.05, 0.075 and 0.10) catalyst for photoremovable of rhodamine B dye	Hydrothermal method	RhB dye	The enhanced photocatalytic activity is mainly due to enhanced photo absorption and charge separation through synergistic interface.

Khan et al. (2022) [21]	CeO ₂ -MnFe ₂ O ₄ heterostructures	Ultrasound assisted co-precipitation method	MB dye	The CeO₂/MnFe₂O₄-1:1 NCs has shown 86 % efficiency within 150 minutes of visible light illumination.
Sidarai et al. (2022) [22]	ZnO/CeO ₂ nanocomposites	Hydrothermal method	Neutral Red (NR)	Nearly 65 % of dye degradation was found using synthesized nanocomposites.

2.2 Factors influencing the photocatalytic activity

2.2.1 Effect of solvent

Khokhra et al. [23] synthesized ZnO by using ethanol and water as solvent. They reported that photocatalytic activity not solely depends upon oxygen vacancies but also upon specific surface area. They have further checked the morphology of synthesized powders by TEM. It has been observed that ethanol synthesized ZnO showed interwoven nanosheets whereas ZnO synthesized in aqueous medium gives flower-like nanosheets. The flower-like nanostructure results from higher tendency of aggregation. The higher amount of aggregation is due to hydrogen bonding in different synthesis medium. The hydrogen bonding in H₂O medium is higher due to high polarity of water. However, in C₂H₅OH medium, such a hydrogen bonding is relatively weak due to interference of bulky ethyl groups and low polarity of ethanol.

Moreas et al. [24] synthesized ZnO/carbon xerogel composites using ethanol as solvent medium. It has been observed that alcoholic medium has higher values of surface area and pore volume. Since the photocatalytic activity is a surface process, so the synthesized material with higher surface area has shown enhanced photocatalytic activity. It has been observed that $\approx 20\%$ specific surface area increased when the samples are synthesized with ethanol as solvent.

Mendil et al. [25] synthesized ZnS with different ratios of ethylenediamine (EN) and distilled water (W). When the ratio of EN (75 to 100%) has been increased, the phase transformation of ZnS from cubic to WZ (wurtzite) occurred. It has been also observed that when EN

medium has been used, low particle size is obtained. However, water as solvent has shown excellent crystallinity. Moreover, to the best of knowledge from literature survey no such synthesis of CeO₂ has been reported using different solvent parameters.

2.2.2 Effect of calcination temperature on photocatalytic activity

Nadarajan et al. [26] synthesized different metal oxides and calcined them at different temperatures. The surface defects such as oxygen vacancies are generated with calcination temperature. However, it has been observed that specific surface area of synthesized sample is not following a significant trend at higher calcination temperature. It is concluded that high specific surface area could increase the adsorption capacity of catalyst and thus increases the photocatalytic activity.

Sifontes et al. [27] synthesized CeO₂ and calcined the as-prepared CeO₂ at 350, 650 and 960 °C. Specific surface area and crystallinity are two contradictory factors. The amorphous semiconductor has high surface area and is generally associated with large amount of crystal defects or weak crystallization. However large defects and weak crystallization favors the fast recombination of photogenerated charge carriers. Thus, it causes the poor photocatalytic activity. This illustrates that large surface area is not the only decisive factor to decide the photocatalytic activity.

Also, calcination breaks the metal-oxide bonds and converts the Ce⁴⁺ to Ce³⁺. The higher calcination temperature leads to the breaking of some of the Ce-O bonds and after structural relaxation, creation of oxygen vacancies takes place [28]. Further, it has been also observed that calcination increases the particle size of synthesized NPs and maximum absorption peaks shifts toward the higher wavelength [29,30]. Thus, higher shifting of wavelength illustrates that synthesized sample can absorb more visible range region. The increase in the size of synthesized NPs reduces the energy band gap and vice versa [31].

2.2.3 Effect of capping agent

The capping agent also plays vital role to increase the catalytic activity of synthesized sample. The capping agent hinders the crystallites coagulation, thus enhances the exposed surface area of nanoparticles and provides better adsorption of dye molecules on the surface of the catalyst. Further, surface passivation by capping agent leads to better charge transfer from catalyst's surface to adsorbed dye molecule. It also provides better generation of excitons and a delayed recombination when thioglycerol (TG) is used [32,33]. Also, thiols prevents the radiative recombination of excited carriers as they have the ability to trap the photo-induced charge carriers [34]. The capping agent also affects the crystallite size as it is observed that 1-thioglycerol inhibits the growth of nanoparticles and reduces the particle size

[35]. Also, when the particle size reduces, the valence band edge shifts downwards [36]. Thus, emitted photon has comparatively higher energy because band gap of synthesized nano material increases. The band gap increases with decrease in particle size due to quantum confinement [17,61].

2.2.4 Effect of doping on O-vacancies

Generally doping of foreign element is done to reduce the band gap of host material. The reduced band gap enhances the visible light absorption for the synthesized semiconductor and thus generation of charge carriers takes place even for low energy photons. The dopants create their own impurity level near the position of CB and VB edge of host material and alter the edge position (VB and CB) of host materials and thus, modify the band gap of synthesized material. Moreover, these impurity levels help to increase the photocatalytic activity via capturing the e^-/h^+ generated in the parent material [37]. The charge carrier separation and absorption capacity is enhanced by dopant ions. It has been observed that localized Ce3d levels will shift to lower energy level with increasing atomic number of dopants [38,39].

According to Kroger-Vink notation, oxygen vacancies can be generated in CeO₂ via addition of external element [40–42]. The formation of O-vacancy leads to reduction of Ce⁴⁺ state to Ce³⁺. When the chosen dopants are much smaller than the host lattice cations, the dopants are free to move off the lattice and leads to distortion in CeO₂ lattice [43]. Critical ionic radii is the ionic radii of dopant which will cause neither expansion nor contraction to lattice. For example, the doping of Sm, Nd, Pd and La in CeO₂ makes harder to remove the oxygen ions from the lattice. The Al and Ga as dopant ions in the host lattice site, leads to distortion in the CeO₂ lattice. Doping of trivalent ion in the host lattice creates distortion in the local symmetry of oxygen ions around the Ce ions in the host lattice [44]. The distortion in the lattice is mainly due to ionic radii of dopant and host ions. Mittal et al. [17] confirmed that when the size of dopant is larger than host ion lattice, the doping causes distortion in the lattice. Thus, amount of dopant should be low. Hence, generation of oxygen vacancies mainly depends upon the type of dopant, charge state and amount of doping concentration. Addition of M⁺ in nanocerium results in the reduction of Ce⁴⁺ to Ce³⁺ that leads to formation of some new networks (Ce⁴⁺ – O – Ce³⁺ & Ce⁴⁺ – O – M⁺) which are responsible for formation of defects in the host lattice [44,45].

Ma et al. [46] synthesized Mg²⁺ (0.72 Å) doped CeO₂ i.e. Ce_{1-x}Mg_xO₂. It has been observed that when x > 0.04, the Mg²⁺ ions start to occupy the interstitial sites. This observation shows

that higher amount of doping distorts the CeO₂ lattice. Thus, it is concluded that amount of doping should be optimized.

Nurhasanah et al. [47] synthesized Zn²⁺ (0-20 mol %) - doped CeO₂ nanoparticles. The band gap reduced by incorporation of Zn into CeO₂ lattice which is due to formation of O-vacancies caused by conversion of Ce⁴⁺ to Ce³⁺. Thus, doping of foreign element enhances the O-vacancies and is helpful to enhance the photocatalytic activity of synthesized catalyst.

Chahal et al. [48] found that O-vacancies are increased with the doping of Sm³⁺ into the CeO₂ lattice and are increased up to 6 % doping. However, increasing the doping concentration beyond 8%, the O-vacancies further decreased which is due to occupancy of Sm ions in the interstitial sites or surface rather than Ce⁴⁺ sites. Thus, it can be concluded that O-vacancies not always follow increasing pattern with the increasing amount of doping. It only depends upon the amount of doping and dopant size in the host lattice.

Chennai et al. [49] synthesized Fe³⁺-doped CeO₂ and found that O-vacancies increased with increasing Fe doping level. The Ce⁴⁺/Ce³⁺ and Fe³⁺/Fe²⁺ form redox couples and due to this the formation of O-vacancies has increased. It is also observed that surface contains some of the Ce³⁺ species associated with the oxygen vacancies while the bulk volume predominantly consists of Ce⁴⁺ species.

The tetravalent elements including Zr⁴⁺, Hf⁴⁺, Si⁴⁺, Tb⁴⁺, Pr⁴⁺, Ti⁴⁺ and Sn⁴⁺ have smaller ionic radii than Ce⁴⁺. It is observed that doping of smaller atom in the host lattice breaks the bond i.e. weaken the interaction between metal and oxygen and thus makes the oxygen atoms easier to remove [50]. These doping can be classified into two categories; one is reducible elements and others are non-reducible elements. As the cationic radii of Zr⁴⁺ is lower than Ce⁴⁺ and Ce³⁺, the doping of Zr⁴⁺ into CeO₂ compensate the volume expansion created due to reduction of Ce⁴⁺ to Ce³⁺. Thus, it is reducible element as it reduces Ce⁴⁺ to Ce³⁺. The doping of smaller cations can create longer metal-oxide bonds. This will weaken the interaction between metal and oxygen and thus oxygen atoms are easier to remove and O-vacancies are easily created. More number of O-vacancies are also created due to change in lattice parameters.

Similarly, the doping of Pr and Tb into the CeO₂ not only induces the intrinsic O-vacancies, but also induces the extrinsic O-vacancies, thus, enhancing the dynamic oxygen storage capacity because surface O-vacancies are more helpful to promote catalytic activity. It is known that the migration of O-vacancies from bulk to the surface is very slow. However, doping of Pr help to migrate the O-vacancies from bulk to surface. Addition Pr help to create

more anionic vacancies associated with $\text{Pr}^{4+}/\text{Pr}^{3+}$ ($\text{Ce}^{4+}/\text{Ce}^{3+}$) and thus enables to create the bulk O-vacancies.

Mordekovitz et al. [51] synthesized nano- $\text{Ce}_{1-x}\text{Ti}_x\text{O}_2$ ($x \leq 0.12$) and $\text{Ce}_{1-x}\text{Ti}_x\text{Ca}_{0.05}\text{O}_{1.95}$ powders. It has been observed that doping of Ti limits the Ce reducibility in CeO_2 which limits the formation of O-vacancies. This is because Ti cation moved off from its initial site due to large size mismatch and creates lattice distortion and thus, Ti as dopant limits the Ce reducibility.

Rehman et al. [52] observed an increase in O-vacancies as a result of doping of transition metal (Gd) in CeO_2 (GDC). A divalent TM doping in CeO_2 generates one oxygen vacancy for every TM^{2+} -cation doping. The aliovalent TM-cation doping in CeO_2 enhances the oxygen vacancy content of GDC. However, they have observed the generation of variable amount of O-vacancies with the same amount of doping of transition metal ion. The variable amount of generation of O-vacancies for same amount of doping is attributed to variable oxidation states and the location of the transition metals in the ceria lattice.

Chanu et al. [53] synthesized (undoped, V, Nb and Ta)-doped CeO_2 samples. They reported the presence of Ce^{3+} in undoped (24.81 %), Nb-doped CeO_2 (32.6 %) and Tb-doped CeO_2 (31.0 7%) samples. The existence of multiple oxidation state in Vanadium might be the reason for the compensation of Ce^{3+} . Thus, lower amount of Ce^{3+} exists in V-doped CeO_2 than Nb and Ta-doped CeO_2 . Also, the existence of O-vacancies due to creation of Ce^{3+} by introduction of other dopants modify the optical properties i.e. changes the valence band edge (VBE) and conduction band edge (CBE) which delayed the recombination of charge carriers and enhances the photocatalytic activity.

Thus, from above discussion it can be concluded that the selection of particular dopant and amount of doping should be optimized carefully.

2.2.5 Effect of heterostructures

Hu et al. [54] synthesized $\text{Cu}_2\text{O}/\text{CeO}_2$ heterojunction. When p-type Cu_2O is loaded on n-type CeO_2 semiconductor surface, it makes favorable for separation of photo-generated charge carriers. The conduction band and valence band of Cu_2O has more negative potential than CB and VB of CeO_2 , respectively. Thus, the position of CB and VB of Cu_2O makes electron-hole pair separation more efficient and delays the charge recombination process. Therefore, this combination enhances the catalytic activity of synthesized heterostructures.

Saravan et al. [8] synthesized ZnO/CeO_2 nanocomposite materials and found that BET specific surface area of ZnO/CeO_2 is higher than ZnO . The particle size of synthesized heterostructures is also found lower than ZnO . The higher specific area enhances the catalytic

activity due to more active sites and better absorption capacity of UV-light photons that falls on the synthesized heterostructures. Thus, the higher surface area is beneficial for higher catalytic activity of synthesized material.

Issarapanacheewin et al. [55] synthesized $\text{CeO}_2/\text{BiWO}_6$ nanocomposite. They observed a decrease in specific surface area for the synthesized nanocomposite. However, the catalytic activity of $\text{CeO}_2/\text{BiWO}_6$ is found to be more than CeO_2 despite of lesser specific surface area. They have found that CB of CeO_2 is more negative than CB of $\text{CeO}_2/\text{BiWO}_6$, thus electrons migrate from the CB of CeO_2 to the CB of Bi_2WO_6 and perform photo-reduction. On the other hand, holes generated in Bi_2WO_6 migrate to VB of CeO_2 and perform the oxidation. This observation suggests that the alignment of CB and VB edge is more preferred for good photocatalytic activity rather than specific surface area for the synthesized heterostructures.

Lu et al. [56] synthesized N-doped $\text{CeO}_2\text{-TiO}_2$ nano-sheets. The concentration of Ce^{3+} has been checked by XPS analysis. The concentration of Ce^{3+} is found to be more for synthesized $\text{CeO}_2\text{-TiO}_2$ than CeO_2 . This observation shows that formation of heterostructures enhances the formation of O-vacancies. Also, the specific surface area has been checked from BET analysis. The BET analysis also shows that specific surface area increased for synthesized heterostructures. Further, PL results also show a decrease in recombination of charge carriers because photogenerated charge carriers uses the band edge levels of other material. Hence, combining the two materials control the quenching of charge carriers. Thus, the heterostructure provide a good photocatalytic effect.

Shen et al. [57] synthesized $\text{CeO}_2/\text{Co}_3\text{O}_4$ (p-n) and successfully used it as a visible light active catalyst. They have found that by combining a p-type and n-type semiconductor enhances the light-absorption efficiency. Also, TEM analysis shows distinct phase of both catalysts. Distinct phase of both the materials contribute to the separation of the photo-generated charge carriers. This improves the charge transfer efficiency. The above observation shows that the synthesized material can be used as photocatalyst.

Li et al. [58] synthesized $\text{CeO}_2@\text{CdS}$ heterostructures and they observed enhanced catalytic activity. The synthesized hetero junctions have type-II band alignment. The CB of CeO_2 is more positive than that of CdS and VB of CeO_2 is also more positive than CdS. Thus, it makes easy pathway for charge to transfer. Further, they have checked the recombination of charge carriers via using PL spectroscopy. It is observed that type-II band alignment reduced the charge carrier recombination that results in the quenching effect of PL intensity. Hence above results show the path way for the synthesis of good photocatalyst.

The formation of heterostructures has been confirmed by various characterization techniques such as XRD, FTIR and Raman analysis [37]. Also due to formation of heterostructures it has been observed that visible-light absorption capacity gets enhanced which increases the photocatalytic activity of the synthesized samples.

2.2.6 Effect of photocatalyst and dye dosage on the photocatalytic activity

All the above discussion is based on the synthesis parameters such as doping, co-doping, heterojunction and synthesis medium which either generates O-vacancies or increase the specific surface area. These synthesis parameters increase the photocatalytic activity of synthesized catalyst. However, after synthesis of photo-catalyst it is also necessary to optimize the optimum amount of catalyst required to degrade the dye.

Kristianto and Saleh [59] synthesized $\text{CeO}_2/\text{ZrO}_2$ with different ratios of $\text{CeO}_2:\text{ZrO}_2$. The catalyst dosage has been optimized. It has been observed that catalytic activity increased with the catalyst dosage. The increase in catalytic activity is attributed to more active sites and hydroxyl groups that are present on the catalyst surface. However, beyond an optimum amount of catalyst dosage, it led to decrease in photocatalytic activity. This observation is attributed to aggregation of NPs catalyst and inhibits the production of charge carriers. Further, it might be also due to high amount of catalyst which may block the absorbance of UV light due to increase in opacity of the suspension. This increases photon scattering and ultimately decreases the catalytic activity of synthesized catalyst [59,60].

Shanavas et al. [39] synthesized Pb-doped CeO_2 with different doping concentration of Pb. The degradation efficiency of synthesized catalyst has been checked by optimizing the dye concentration. The dye concentration was taken in between 10 mg/L to 50 mg/L. It is observed that dye degradation efficiency was decreased with increase of dye concentration. This is attributed to insufficient amount of active species for the degradation of higher amount of dye concentration. The penetration of light also plays an important role for deciding the catalytic activity of catalyst. However, when more dye molecules are present in the solution then dye molecules screens the incident light source reaching the surface of catalyst. Thus, reduces the generation of charge carriers.

2.2.7 Effect of pH on the photocatalytic activity

The zeta potential is the potential difference between the dispersion medium and layer of the fluid attached to the dispersed particle. Zeta potential is the measure of the magnitude of the electrostatic or charge repulsion or attraction between the particles. It is one of the main parameter which affects the stability of the solution.

The pH variation during the synthesis of nanoparticles affects the zeta potential of nanoparticles. It is found from the literature that zeta potential of synthesized CeO₂ NPs is -35 mV at the pH of 8.0. The zeta potential of CeO₂ NPs is -43.2 mV when the particle is synthesized at pH of 12 [62]. Thus, negative charge is increased with the increase in pH. The point of zero charge of CeO₂ is 7.9 (isoelectric point). Thus, if the pH of synthesized sample is greater than PZC of CeO₂, the surface of CeO₂ becomes negative. Hence, the cationic dyes shows great affinity towards catalyst. The pH of various dye concentration (1 ppm-10 ppm) has also been measured. The pH of dye solution (CV) is found to vary between 6.2-6.36 which shows very small variation in pH with change in concentration. This pH study shows a stronger interaction between dye molecules and catalyst. Hence, dye molecules adsorbed on the surface of catalyst undergo higher degradation.

2.2.8 Effect of cationic and anionic dye

The dyes can be classified into two types (i) cationic dye and (ii) anionic dye. The cationic dyes are mostly used in silk, wool and nylon dyeing [63]. Cationic dyes include methylene blue (MB), methyl violet (MV) and crystal violet (CV). Similarly, anionic dyes are sunset yellow, methyl orange (MO) [64]. The point of zero charge (PZC) of CeO₂ is 7.9 [65]. Thus, CeO₂ NPs shows higher affinity towards anionic dye when the CeO₂ is synthesized below pH of 7.9. However, when the samples are synthesized at the pH more than of 7.9, it shows more affinity towards cationic dyes because of negative charge of catalyst surface [17,66]. Thus, CeO₂ makes good electrostatic interaction and allows higher interfacial charge transfer for redox reactions.

2.3. Plan of work

Based on the literature survey, we get an insight on various synthesis parameters and doping conditions. CeO₂ has been synthesized with many modifications such as change in dopant concentration and at different pH. Apart from this, many composites were synthesized to enhance the photocatalytic activity. However, the photocatalytic efficiency of synthesized compound can be improved further by modifications in synthesis parameters. The photocatalytic degradation of dye needs high specific surface area, O-vacancies and presence of hydroxyl groups on the surface of synthesized catalyst as discussed in above sections. Chahal et al. [44] synthesized yttrium (Y)-doped CeO₂ and degraded the rose Bengal dye (anionic dye). However, they have not checked its catalytic activity towards cationic dye (crystal violet dye). Also, the efficiency of Y-doped CeO₂ can be increased more by making use of co-dopants. Further, to the best of knowledge from literature survey, the synthesis of

heterostructures with doped and co-doped CeO_2 has not been reported so far. The above mentioned work can be taken by optimizing the synthesis parameters.

Thus, considering the gaps as mentioned in above studies, the main objectives chosen for the present work is as follows:

1. To synthesize the CeO_2 nanoparticles by using co-precipitation method and optimize the synthesis parameters such as solvent, calcination temperature and capping agent.
2. To understand the effect of doping (Y) or (Y, Zn) co-doping on structural and optical properties on CeO_2 nanoparticles and its heterostructures with CdS and ZnS.
3. To study the photocatalytic properties using techniques PL, UV-visible spectroscopy.
4. To study the morphological studies for structural and size measurement using XRD, SEM, TEM, Raman etc.
5. To study the photocatalytic activity of synthesized samples.

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CHAPTER 3

METHODOLOGY

Overview

Synthesis of undoped and doped CeO₂ nanoparticles has been done to degrade crystal violet dye. The heterostructures of CeO₂ with CdS and ZnS has been also prepared and characterized. In order to avoid ambiguity their preparation techniques has been described in the respective results and discussion section. Many characterization techniques such as X-ray diffraction (XRD), UV-visible spectroscopy, transmission electron microscopy (TEM), Raman and FTIR have been used and described in this chapter. Further, the photocatalytic efficiency of synthesized samples has been done using UV spectrophotometer. The photochemical reactor set-up and the photocatalytic experimental procedure has also been presented in this chapter.

3.1 Precursors

3.1.1. Raw Materials

The raw materials used for the synthesis of various undoped, doped and heterostructures were cerium nitrate hexahydrate $[(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})]$ (99.9%, Sigma Aldrich), yttrium nitrate hexahydrate $[(\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})]$ (99.9 %, Sigma Aldrich), Zinc nitrate hexahydrate $[(\text{Zn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})]$ (99.9 %, Sigma Aldrich), 1-Thioglycerol (1-TG) (sigma Aldrich), ethanol (99.9% pure, Loba Chemie Pvt. Limited), cadmium acetate $[(\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O})]$ (Loba Chemie Pvt. Limited, purity 98%), zinc acetate $[(\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O})]$ (s d Fine chem. Limited, 99.5 %), sodium sulphide (s d fine chem. Limited). The chemicals were used as such as in received form. Undoped and doped CeO_2 nanoparticles have been synthesized. Moreover, heterostructures of CeO_2 with CdS and ZnS has also been developed. The synthesis process adopted has been described in the respective results and discussed to have a better understanding.

3.1.2. Characterization Techniques

The synthesized samples were characterized by X-ray diffraction (XRD) technique using Panalytical Xpert Pro MPD diffractometer with Cu ($K\alpha$) radiations having Ni filter to check the phase formation of synthesized samples. The X-ray diffraction machine X'Pert Pro XRD is equipped with x'Celerator solid state detector. Transmission electron microscopy (TEM) – JEOL-2100F has been used to study the morphology and particle size of synthesized samples. The working voltage of TEM is 80 to 200 kV. Further, Fourier transformed infrared spectroscopy (FTIR) spectra was recorded using Spectrum 400 FT-IR/FIR Spectrometer at room temperature between $400\text{--}4000\text{ cm}^{-1}$ using KBr pellet technique to identify the functional groups attached to the surface of CeO_2 . The FTIR has resolution of 1 cm^{-1} and scan range of $4000\text{ to }250\text{ cm}^{-1}$. The UV-visible analysis was done using UV-visible spectrophotometer (Hitachi U-3900H double beam spectrophotometer) by observing absorbance spectra in the range 200-800 nm. Raman spectra was recorded on Varian FT-Raman with 532 nm equipped with SSD laser operating on single phase voltage 230 V to understand the structural features of the prepared samples. The Cary Eclipse fluorescence spectrophotometer (G9800A) was used to obtain emission spectra (with $\lambda_{\text{exc}}=250\text{ nm}$) of the synthesized samples. The composition and various chemical states of elements has been confirmed from XPS by Thermo fisher ESCALAB XI+.

3.1.3. Apparatus used for photocatalytic study

To understand the photocatalytic activity of synthesized samples, mercury lamp (125 W; wavelength 300-400 nm and intensity= $\sim 110 \text{ W/m}^2$) was used. For photo-catalytic studies, a specially designed 3-jacket reactor was used as shown in Fig. 3.1. The outermost jacket was used for the dye solution and catalyst. The whole system was put on the magnetic stirrer in which the temperature and revolution per minute (rpm) can be varied. To check the degradation efficiency of synthesized CeO_2 catalyst and its heterostructures with CdS and ZnS, crystal violet (CV) dye (peak absorbance wavelength i.e. $\lambda_{\text{max}}=591 \text{ nm}$), a cationic dye was selected for this purpose. 1 mg/L dye solution was chosen to perform the photocatalytic experiments. First, the 3 mg of synthesized catalyst was added to 100 ml of dye solution (1 mg/L) and then the mixture was first placed in the dark for 2h so that adsorption-desorption equilibrium was established (saturation of adsorption of dye molecules on the catalyst surface). Various experiments were performed with different catalyst concentration. However, 3 mg of catalyst in 100 ml of dye solution (1mg/L) give enhanced photocatalytic degradation. Fig. 3.2 shows the absorption spectra of CV dye. The degradation of dye was performed under the UV-visible light after the completion of adsorption-desorption process. The UV-visible light is distributed uniformly in the photocatalytic chamber reactor. The intensity of lamp measured was 3500 lux. The 4 ml of sample was collected after different intervals of time and centrifuged at 4500 RPM to remove the catalyst. After each interval, 4 ml of sample was extracted with sonication. Thus, distribution of catalyst amount in solution is invariant and does not affect the measured reaction kinetics. The UV-visible spectrophotometer was used to measure the change in the concentration of dye (CV) which can be expressed as follows;

$$\% \text{ change in concentration} = \frac{C_o - C_t}{C_o} \times 100.$$

Where, C_o and C_t are the concentration of CV dye at $t=0$ and t h, respectively. The wavelength for CV dye selected is 591 nm to check the C_o and C_t after different intervals of time.

Further, the value of pseudo first (k_1) and second order (k_2) has been studied and calculated as given in the following equation:

$$\text{First order} \quad -\ln\left(\frac{C}{C_o}\right) = k_1 t \quad (3.1)$$

$$\text{Second order} \quad \frac{t}{C} = \frac{1}{k_2 C_o^2} + \frac{t}{C_o} \quad (3.2)$$

The kinetics was studied to establish the mechanism of photochemical reaction i.e. whether the reaction is taking place from physical adsorption or chemical adsorption. The pseudo first order kinetics describes the adsorption of dye molecules through physical bond i.e. hydrogen bond formation between catalyst and dye molecules which is referred as physisorption [1–3]. The formation of chemical bond through O-species present on the surface of catalyst can be referred to as chemisorption, pseudo second-order kinetic model.

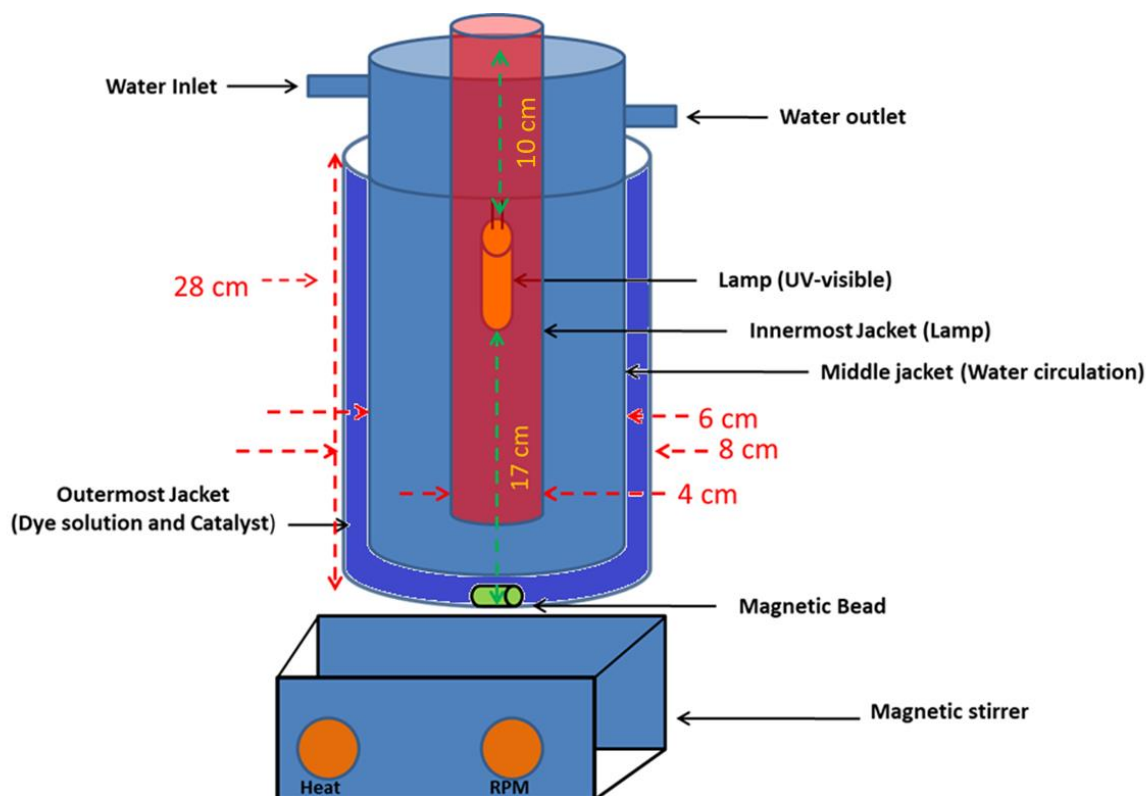


Fig. 3.1: The photochemical reactor setup to study photocatalysis.

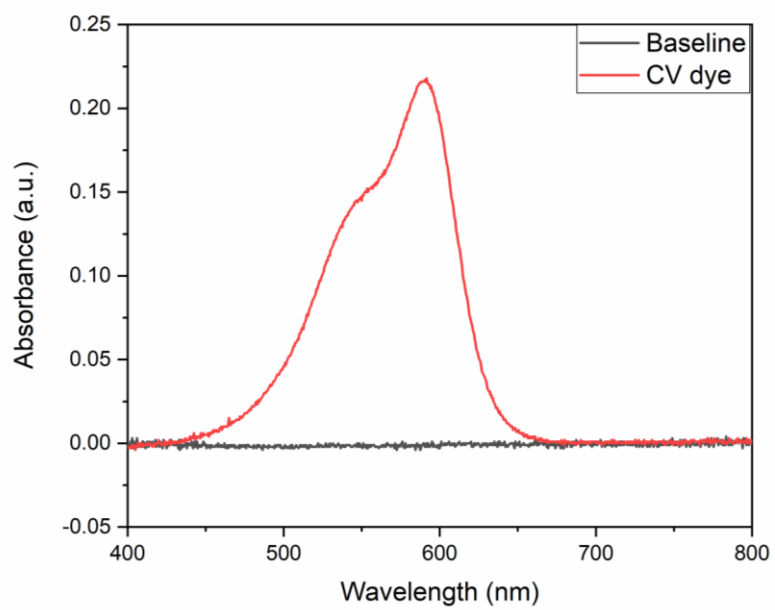


Fig. 3.2: UV-visible absorption spectra of CV dye.

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Effect of processing parameters on structural and optical properties of CeO₂ nanoparticles for the removal of crystal violet dye

Overview

The present chapter reports the synthesis of CeO₂ nanoparticles (NPs) via chemical route by optimizing synthesis parameters such as solvent, capping agent, and calcination temperature. The prepared samples were characterized via XRD, TEM, FTIR, Raman spectroscopy, and UV-visible spectroscopy for structural, morphological, and optical studies. The XRD results confirmed the formation of cubic fluorite structured CeO₂ with an average crystallite size ~5-11 nm. The enhancement in crystallite size was observed along with agglomerated irregular spherical shaped NPs after calcination at higher temperatures. The use of capping agent (thioglycerol; TG) led to the reduced aggregation of NPs. With the help of UV-visible spectroscopy, a redshift was observed in the maximum absorbance peak as an effect of calcination. The NPs synthesized in ethanol as solvent exhibited better degradation efficiency for crystal violet dye than the NPs synthesized in water medium. It was observed that (TG) capped samples exhibited more photocatalytic activity towards the degradation of crystal violet dye than uncapped samples due to less agglomeration of particles. Further, in the presence of the optimum amount of H₂O₂ the catalytic activity was achieved upto 97% within 90 minutes only.

4.1 Introduction

As discussed in chapter one, CeO_2 is a non-toxic promising photocatalyst for the degradation of water pollutants. It has been extensively used in many catalytic applications due to its unique redox chemistry by changing Ce^{4+} to Ce^{3+} state. Also, higher oxygen vacancies are associated with the conversion of Ce^{4+} to Ce^{3+} which enables it to store electrons which are essential for photoreduction [1–3].

Furthermore, the catalytic efficiency of these metal oxides depends on many factors such as morphology, size, and extent of agglomeration during synthesis. One of the major causes of the lower photocatalytic activity is the relatively low efficiency of the generation of radicals by catalyst due to the lower surface to volume ratio. Also, photocatalytic activity is reduced due to the agglomeration of nanoparticles (NPs) which may block the separation of photoinduced carriers [4]. Thus, the synthesis parameters needs an optimization to get enhanced catalytic activity.

Ollis et al. [5] discussed the photocatalysis rate versus illumination intensity. The photocatalytic degradation rate is divided on the basis of light intensities used for photodegradation.

- a. At low intensities ($0\text{--}20 \text{ mW/cm}^2$), the rate reaction is proportional to light intensity (first order).
- b. At high intensities (25 mW/cm^2), the rate of reaction is directly proportional to the square root of light intensity (half order).
- c. At higher light intensities, the rate of photocatalytic degradation is independent of light intensities (Zero order).

4.2 Synthesis of CeO_2 NPs

For it, 0.3 M of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 ml of ethanol or distilled water (D.W.) as a solvent medium. For the preparation of capped samples, 1% thioglycerol (TG) with respect to $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution was added after the addition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to avoid the agglomeration [6]. To this solution, ammonia (precipitating agent) was added drop-wise until $\text{pH } 7.5$ was obtained followed by overnight aging. Finally, the precipitates were washed several times with water and ethanol. Thereafter, the precipitates were dried at 80°C for 24h and calcined at 300 and 600°C for 2h . The details of samples such as sample labels and synthesis conditions are given in table 4.1.

Table 4.1: Details of samples along with their synthesis conditions.

Sample Ids	Solvent	Temperature (°C)	Capping agent (TG)	Crystallite size (nm)	Specific surface area (m ² /g)
W0	Water	-	-	6.15±0.40	
W300	Water	300		6.14±0.33	
W600	Water	600		11.15±0.41	
WT0	Water	-	1%	10.02±0.50	96
WT300	Water	300		7.57±0.39	
WT600	Water	600		11.32±0.42	
E0	Ethanol	-	-	8.31±0.57	
E300	Ethanol	300		8.34±0.52	
E600	Ethanol	600		9.48±0.49	
ET0	Ethanol	-	1%	5.92±0.37	100
ET300	Ethanol	300		5.83±0.29	
ET600	Ethanol	600		11.01±0.78	

4.3 Effect of calcination temperature, capping agent and role of solvent

4.3.1 XRD analysis

Fig. 4.1 (a-d) shows the XRD patterns of the as-prepared samples in which the diffraction peaks at (2θ) values of 28.63, 33.26, 47.64, 56.24, and 76.50° corresponding to (111), (200), (220), (311) and (331) planes, respectively are observed. These peaks are well-matched with ICDD card 03-065-5923 corresponding to CeO₂ NPs [3]. The crystallite size (D) is calculated using Scherrer formula i.e., $\frac{0.9\lambda}{\beta \cos\theta}$, where β is full width half maxima (FWHM; $\beta = \sqrt{\beta_{observed}^2 - \beta_{instrumental}^2}$), λ=wavelength of incident X-rays (0.154 nm). The calculated values of the crystallite size are given in Table 4.1. The crystallite sizes are in the range of 5-11 nm.

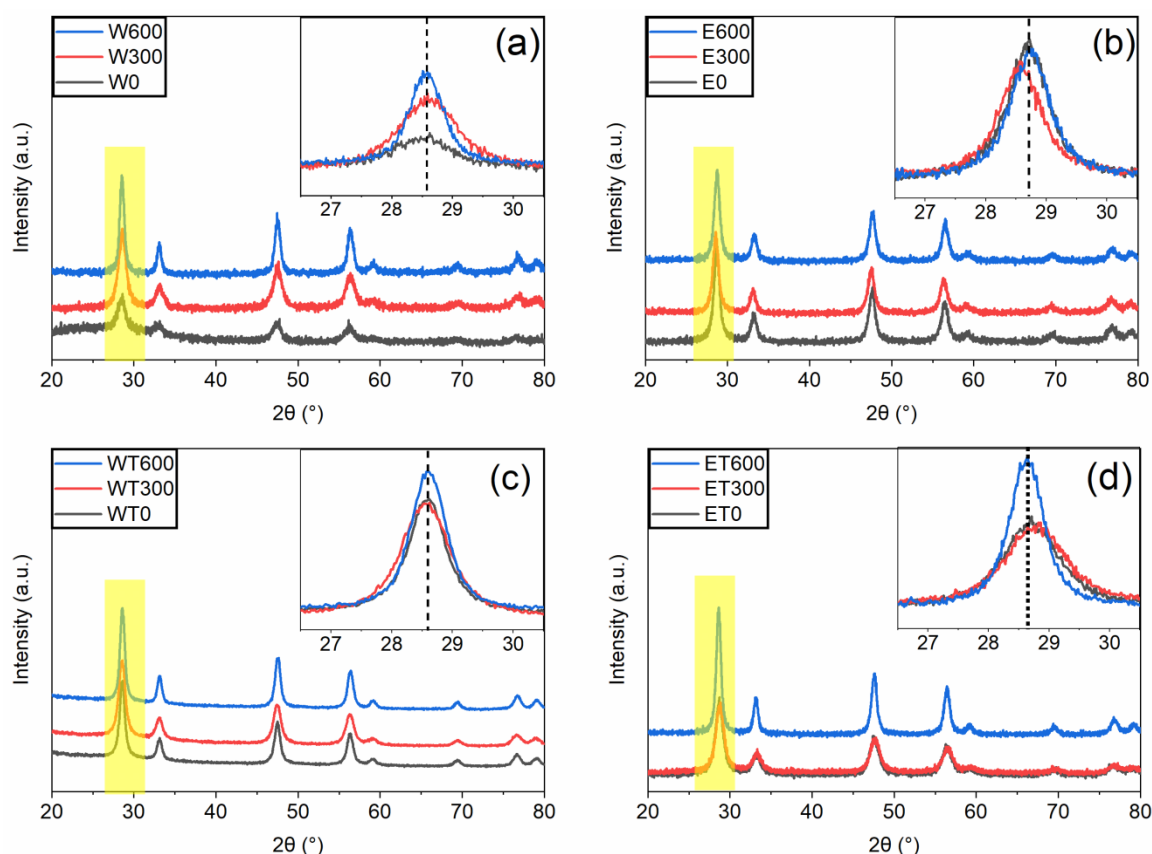


Fig. 4.1: XRD patterns of CeO₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped), and (d) ethanol (capped).

Fig. 4.1 (a, b) represents the XRD patterns of the samples prepared in water and ethanol as solvent medium without using capping agent. It is observed that the intensity of the XRD peaks increases with increase in the calcination temperature. The increase in the peak intensity reflects the enhanced crystalline nature with increasing calcination temperature. Also, the average crystallite size increased with increase in the calcination temperature. The increase in crystallite size is attributed to coalesce of many crystallites to form larger grains [7–9]. Fig. 4.1 (c-d) represents the XRD patterns of the CeO₂ NPs synthesized using water and ethanol as reaction medium, and capping agent, respectively. It is observed that the crystallite size of samples initially decreased (i.e. calcination at 300 °C) and then increased with increasing calcination temperature (600 °C) (Table 4.1). This observation indicates the restricted crystalline growth of synthesized CeO₂ NPs at 300 °C. The plausible reason for decrease in crystallite size is that initially TG might be adsorbed on nucleated CeO₂ NPs and inhibits their growth [10]. However, when calcined at 300 °C, the crystallite size decreases. This is because of presence of Ce³⁺ and Ce⁴⁺ ions both in the calcined mass [3,11,12]. The presence of Ce³⁺ gives amorphous nature in the sample causing crystallite size to decrease. The presence of high intensity peak for WT300 at 600 cm⁻¹ is observed in Raman spectra

which correspond to Ce^{3+} (section 4.2.5). Moreover, when calcined at 600 °C, the Ce^{3+} oxidized to Ce^{4+} and lead to fully crystalline normal lattice at higher temperature [13,14]. It is also reported that, at higher calcination temperature, the capping agent decomposes and its capping property is lost [15]. Thus, crystallite size is found to increase again with further increase in calcination temperature where coalesce of many crystallites occur to form larger crystallites due to transformation of Ce^{3+} to Ce^{4+} . Thus, it is concluded that recrystallization takes place when the heat treatment is given for TG capped synthesized NPs above the optimum calcination temperature. A small peak shifting is also observed in the XRD patterns after heat treatment as shown in insets of Fig. 4.1 (a-d). In Fig. 4.1 (a), XRD peak does not show any significant change in peak position. In Fig. 4.1 (b), XRD peak at 28.71° for E0 shifts to 28.57° for E300 and then again shifts to 28.74° for E600. In Fig. 4.1 (c), XRD peak at 28.61° for WT0 shifts to 28.56° for WT300 and then again shifts to 28.59° to WT600. In Fig. 4.1 (d), XRD peak at 28.70° for ET0 shifts to 28.75° for ET300 and then again shifts to 28.65° for ET600. The higher 2θ shifts attribute to the reduction in inter planar spacing. The rearrangement of the atom periodicity during heat treatment also leads to this 2θ shifting [16]. Also, the conversion of Ce^{4+} to Ce^{3+} , results in lattice expansion and leads to lower 2θ shifting in XRD peak [17]. Zhou and Huebner [12] suggested that small particle size gives expansion to CeO_2 lattice as higher concentration of Ce^{3+} are present in finer particles. Thus, an XRD peak shifts (expansion and contraction of lattice) is the combined result of particle size and lattice spacing.

4.3.2 FTIR studies

FTIR spectroscopy is used to study the vibrational motion of atomic/molecular bonds related to different functional groups present in the samples synthesized under different conditions as shown in fig. 4.2 (a-d) [18]. All the spectra consisted of vibration band around 500 cm^{-1} , which is attributed to Ce-O stretching mode and confirming the formation of CeO_2 [18,19]. The effect of calcination and capping agent (TG) is also observed in fig. 4.2 (a-d), in which the band at 500 cm^{-1} is shifted to higher wavenumber after calcination at 300 and 600 °C, depicting the reduced bond length. This peak is not showing any significant pattern of shifting as an effect of solvent and capping agent. The peaks around 1388 and 1629 cm^{-1} are attributed to the physically adsorbed water from atmosphere [18]. The peaks at 1065 and 1388 cm^{-1} have become more intense after calcination at 300 °C than uncalcined samples which might be the intrinsic hygroscopic nature of CeO_2 [20,21].

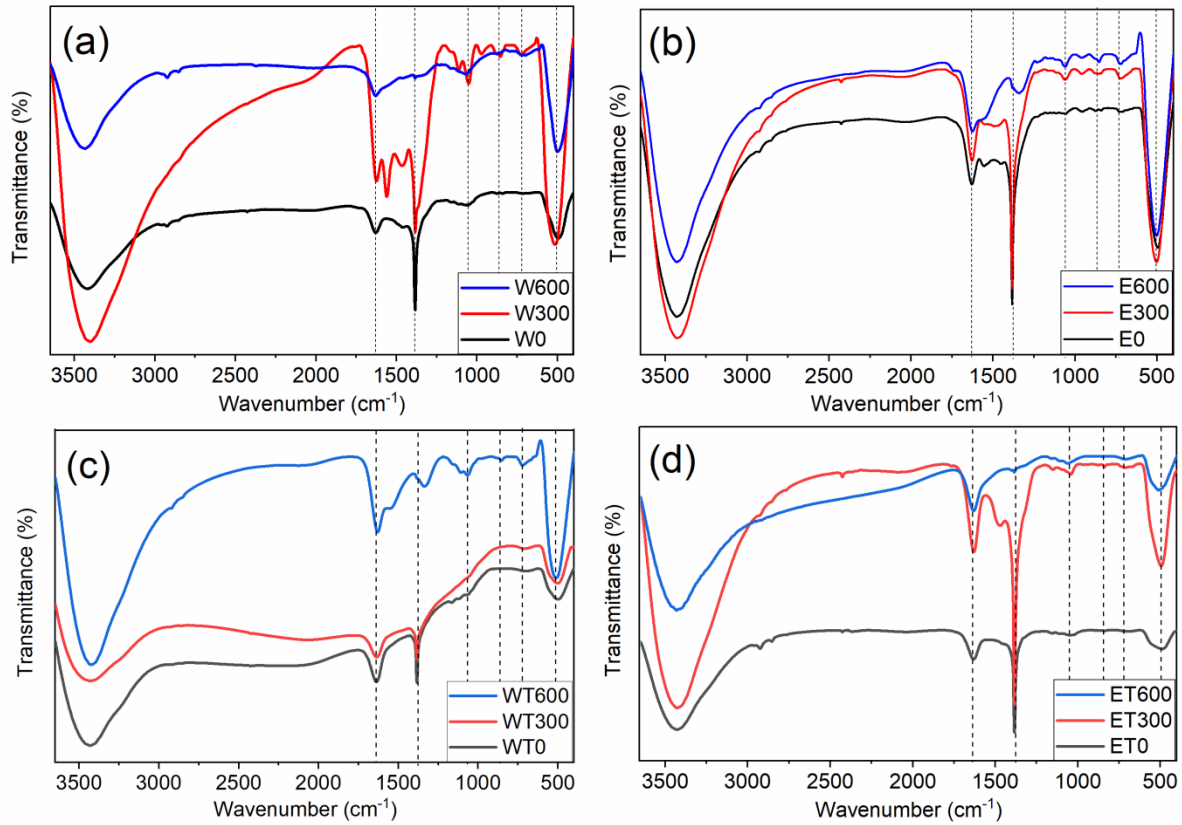


Fig. 4.2: FTIR spectra of CeO₂ samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

The small band around 725 and 840 cm⁻¹ are associated to Ce-O-Ce bridging oxygen which are originated after calcination [21]. The absence of S-H vibration at 2555 cm⁻¹ in the capped samples may infer the de-protonation of TG molecule and attachment with CeO₂ [6]. The peak present around 3300-3450 cm⁻¹ is attributed to the surface hydroxyl group which in turn plays a vital role in the photocatalytic reaction to provide dye sensitization [22–24]. Also, this band shifts to higher wavenumber when the sample is synthesized using ethanol as solvent and TG as capping agent. This indicates that the hydroxyl group has become more active when the synthesized parameters are changed [25]. The various band positions and their modes of vibrations are summarized in table 4.2.

Table 4.2: Band position of each vibration.

Band Position (cm^{-1})	Vibration mode	Reference
500	Ce-O stretching	[18,19]
840, 725	Ce-O-Ce bridging oxygen	[21]
1065	Due to hygroscopic nature of CeO_2	[20,21]
1629, 1388	Physically adsorbed water	[18]
3300-3450	Hydroxyl group	[22]
2555	S-H group from Thioglycerol	[6]

4.3.3 UV analysis

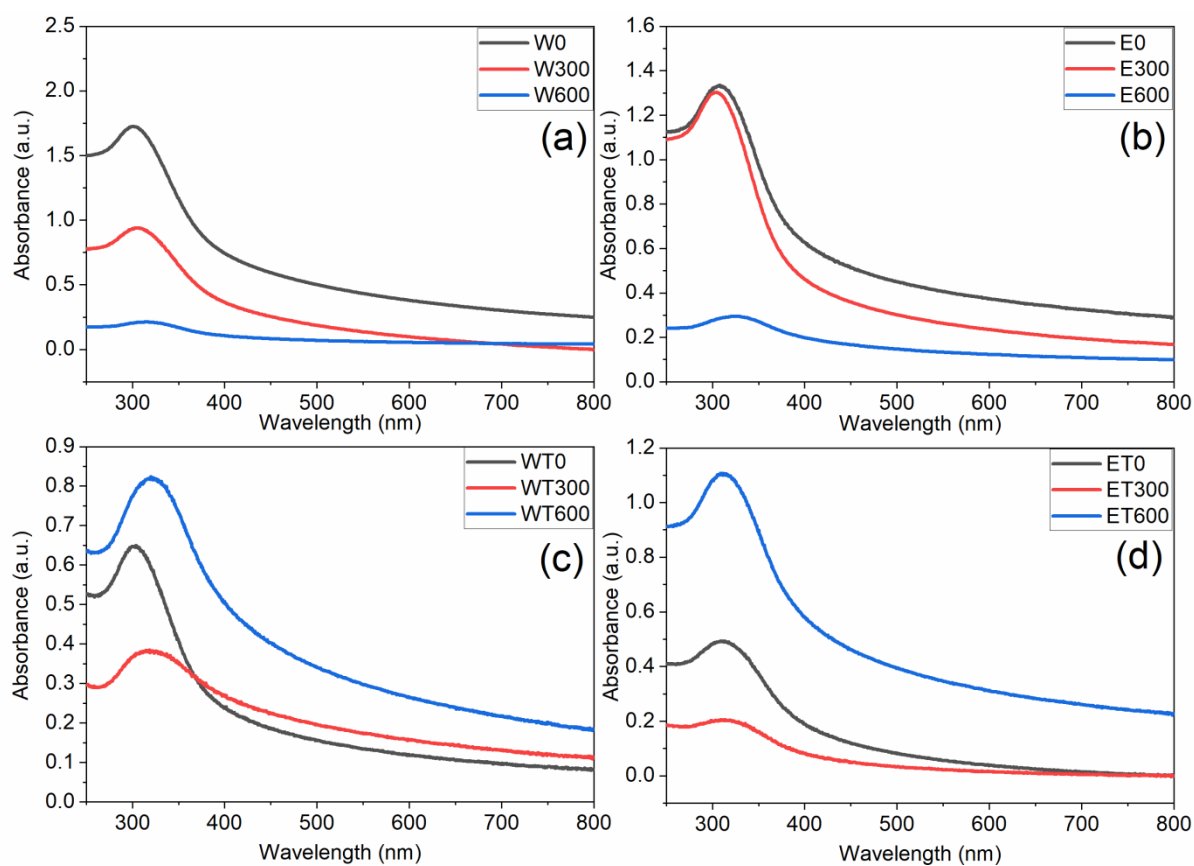


Fig. 4.3: UV-absorption spectra of CeO_2 samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

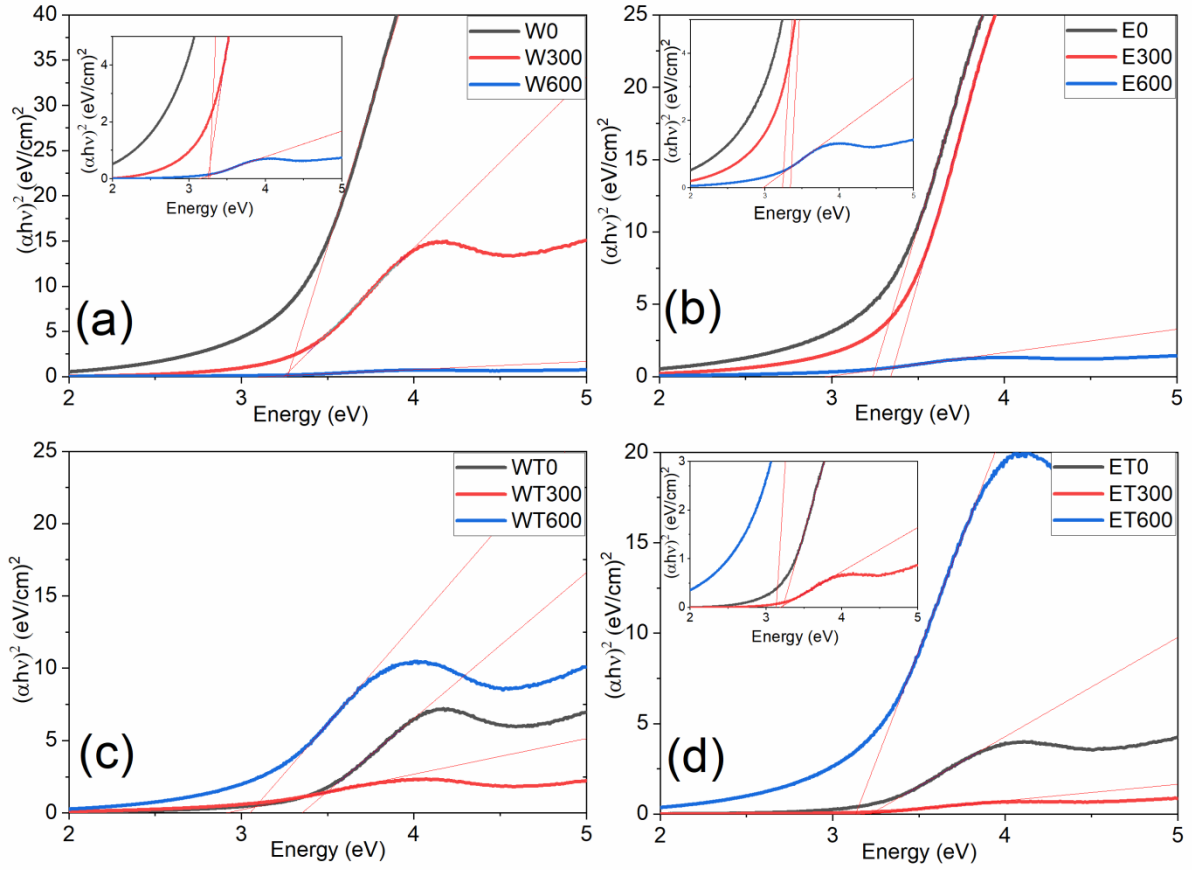


Fig. 4.4: Tauc's plots of synthesized CeO_2 samples in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

Fig. 4.3 (a-d) shows the absorption spectra of synthesized samples recorded in the range 200–800 nm. The absorbance of all the synthesized samples is observed in between 290 to 350 nm. In fig. 4.3 (a-c), the absorption peak shifts to higher wavelength after calcination [26]. The red shift of maximum absorbance may be related to the conversion of Ce^{4+} to Ce^{3+} as higher calcination leads to the breaking of some of Ce-O bonds and after structural relaxation creates oxygen vacancies [27]. The shifting of maximum absorbance after calcination can be explained as a consequence of quantum confinement originated by diminishing the particle size of CeO_2 and also due the charge transfer between Ce^{4+} (4f) and O^{2-} (2p) [18,28]. However, small peak shifting towards higher wavelength after calcination is observed as shown in fig. 4.3 (d), which might be due to low charge transfer between Ce (4f) and O (2p). The maximum absorbance peak shifting does not show any significant correlation as an effect of solvent and capping agent. The variation in lattice defects and particle size leads to the maximum absorbance peak [29,30].

In order to determine the optical bandgap (E_g) from the absorption spectra, Tauc's equation is used. According to this equation; $(\alpha h\nu) = A(h\nu - E_g)^n$, where E_g is the bandgap, α is

the absorption coefficient, and $n=1/2, 2, 3/2$, and 3 correspond to direct, indirect, forbidden direct and forbidden indirect transitions, respectively [31,32]. The plots of $(\alpha h\nu)^2$ vs $h\nu$ for direct transition is plotted to calculate the bandgap of CeO_2 samples as shown in fig. 4.4 (a-d). The bandgap is calculated by extrapolating the straight-line portion of $(\alpha h\nu)^2$ to the x-axis where $(\alpha h\nu)^2$ is 0. The direct bandgap values are given in table 4.3.

Fig. 4.4 (a) and 4.4 (d) shows the decrement of bandgap after calcination of the as-prepared sample due to the broadening of both the energy levels i.e. HOMO (highest occupied molecular orbit in the valence band) and LUMO (lowest unoccupied molecular orbit in the conduction band [18]. However, in fig. 4.4 (b) and 4.4 (c) no significant narrowing of the bandgap is observed as a result of calcination. Here, the decrement of particle size within nano-regime leads to increase in the optical bandgap due to quantum confinement effect [33]. No significant correlation of bandgap with calcination temperature is observed in the synthesized samples. The red shifting of bandgap may be due to interfacial charge-transfer between the valence band and to the oxygen vacancies related defects which are present below the $\text{Ce}4f$ band [34–36]. Also, it is observed that bandgap value increases or decreases as an effect of solvent and capping agent. Hence, the variations in the bandgap values are the combined effect of the quantum confinement, presence of oxygen vacancies and lattice disorders in the samples [3,29,30]. The extinction coefficient of CV dye was calculated when degraded with different catalyst by using following formula:

$$\text{Optical thickness} = \epsilon cl \quad (4.1)$$

Where, ϵ and c are the extinction coefficient and the molar concentration of dye solution and l is the length of cuvette used. As expected that the variation of extinction coefficient is in line with the variation in optical thickness that has been given in appendix A.

Table 4.3: Calculated bandgap values and extinction coefficient of CV dye when degraded with synthesized samples.

Sample Id	Band Gap (eV)	Extinction coefficient of CV dye at different time intervals $\times 10^{-8}$ ($\text{M}^{-1}\text{cm}^{-1}$)								
		0HA	2HA	1HD	2HD	3HD	4HD	5HD	6HD	7HD
W0	3.24	11.83	5.30	4.24	3.63	2.24	1.59	1.59	1.59	1.59
W300	3.22	11.02	5.55	4.28	3.14	2.61	1.87	1.24	1.24	1.24
W600	3.13	11.42	1.26	1.14	0.89	0.69	0.36	0.24	0.08	0.08
E0	3.23	10.93	7.22	6.00	4.44	3.55	2.65	2.00	1.59	1.46
E300	3.34	11.10	7.26	6.04	4.49	2.89	2.36	1.79	1.59	1.46
E600	2.97	11.18	6.00	4.16	3.42	2.85	1.30	1.14	0.61	0.61
WT0	3.35	10.73	6.04	4.77	4.00	3.18	1.87	1.63	1.06	0.89
WT300	2.91	10.77	4.32	3.26	2.04	1.46	0.93	0.57	0.36	0.28
WT600	3.04	10.77	2.49	1.46	1.02	0.61	0.36	0.24	0.20	0.20

ET0	3.22	10.77	3.14	1.83	1.22	0.81	0.40	0.24	0.12	0.04
ET300	3.18	10.77	2.89	1.59	0.98	0.61	0.24	0.08	0.04	0
ET600	3.13	10.77	2.93	1.75	1.22	0.81	0.53	0.40	0.28	0.12

4.3.4 TEM analysis:

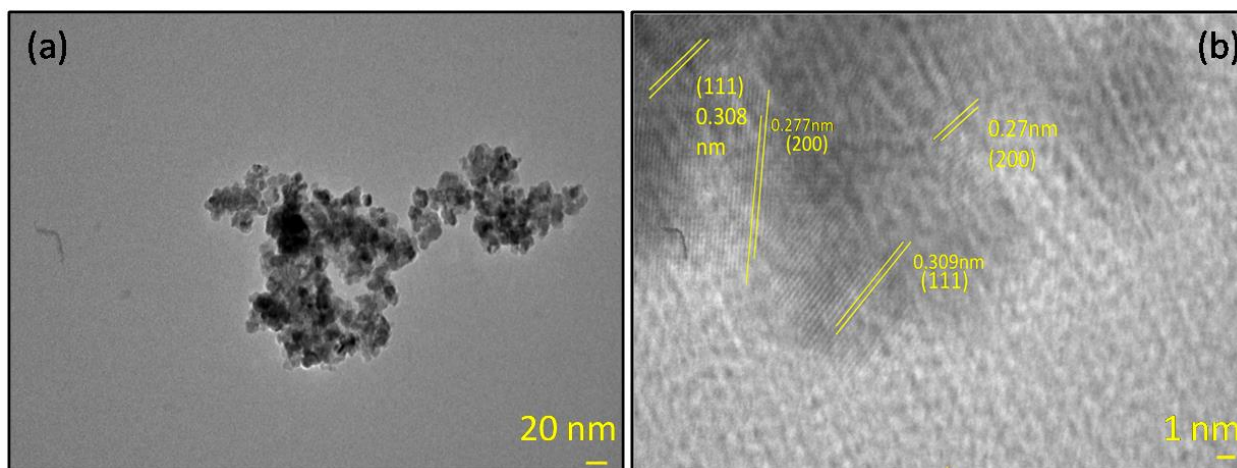


Fig 4.5: (a) TEM and (b) HRTEM image of E600.

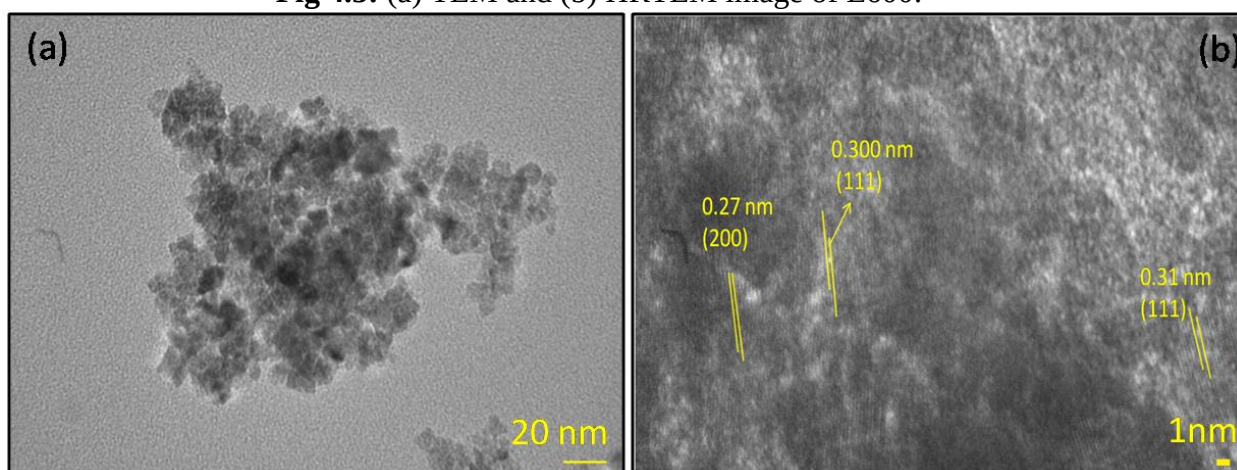


Fig 4.6: (a) TEM and (b) HRTEM image of WT0.

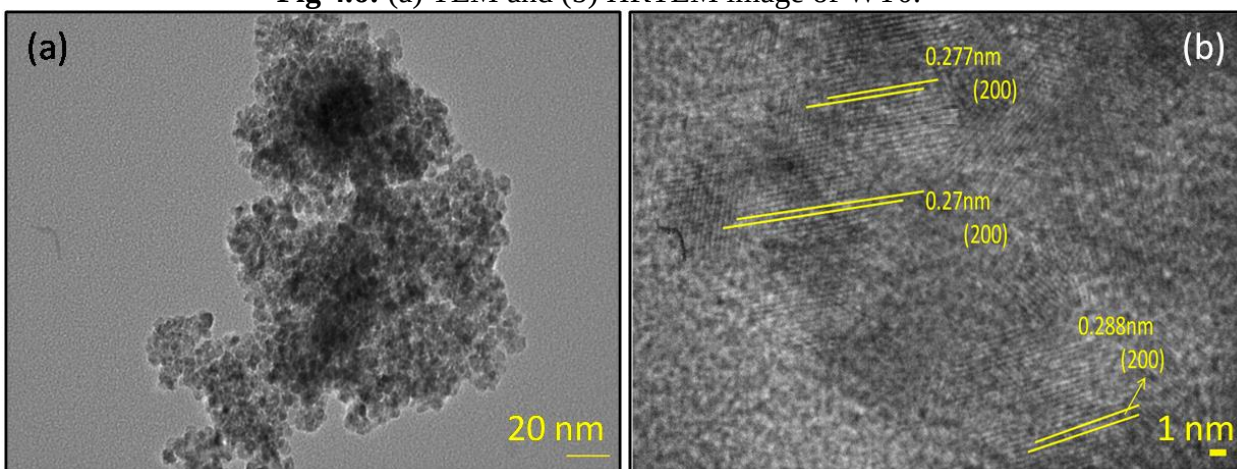


Fig. 4.7: (a) TEM and (b) HRTEM image of ET300.

To explore the morphological features of CeO_2 , TEM studies was done for the selected samples which have shown better photocatalytic activity. Fig. 4.5-4.7 represents the TEM and HRTEM micrograph for E600, WT0, and ET300, respectively. Fig. 4.5 (a) and 4.6 (a) shows the agglomerated particles where proper symmetry of particles cannot be determined. In Fig. 4.7 (a), particles seems to be agglomerated but are in spherical shape. However, it is expected that the capping agent may cover the CeO_2 particles and particles do not coalesce to form large aggregate [6]. The agglomeration of NPs occurs to minimize the surface energy and allows the growth of crystallite [37,38]. Since the FTIR results demonstrated the de-protonation of the capping agent, this might be the reason for the observed agglomeration of NPs.

The particle size was calculated using *ImageJ* software. The calculated values of particle size for the samples E600, WT0, and ET300 were found 9.92, 8.59, and 4.92 nm, respectively. The samples synthesized in ethanol medium using capping agent have the smallest particle size i.e. 4.92 nm. It shows that samples prepared using the capping agent in ethanol medium controls the growth and resist to coalesce followed by the formation of bigger size aggregates. This observation is due to combined effect of ethanol (low polarity and weak hydrogen bonding than water) and capping agent [39]. Thus, in order to achieve smaller size particles, the ethanol solvent with capping agent is better one rather than water as solvent with capping agent.

The fringe width calculated from *ImageJ* software as shown in fig. 4.5 (b), 4.6 (b) and 4.7 (b) are found to be nearly 0.277 nm and 0.31 nm, respectively. The calculated fringe width is well-matched with XRD ICDD card. The fringe width values corresponding to the (111) and (222) planes are 0.31 and 0.277 nm which confirms the cubic fluorite structure of synthesized CeO_2 samples. The distinct lattice planes in HRTEM images shown in fig. 4.5 (b) and 4.7 (b) corresponds to the higher amount of crystallinity in the samples.

4.3.5 Raman analysis:

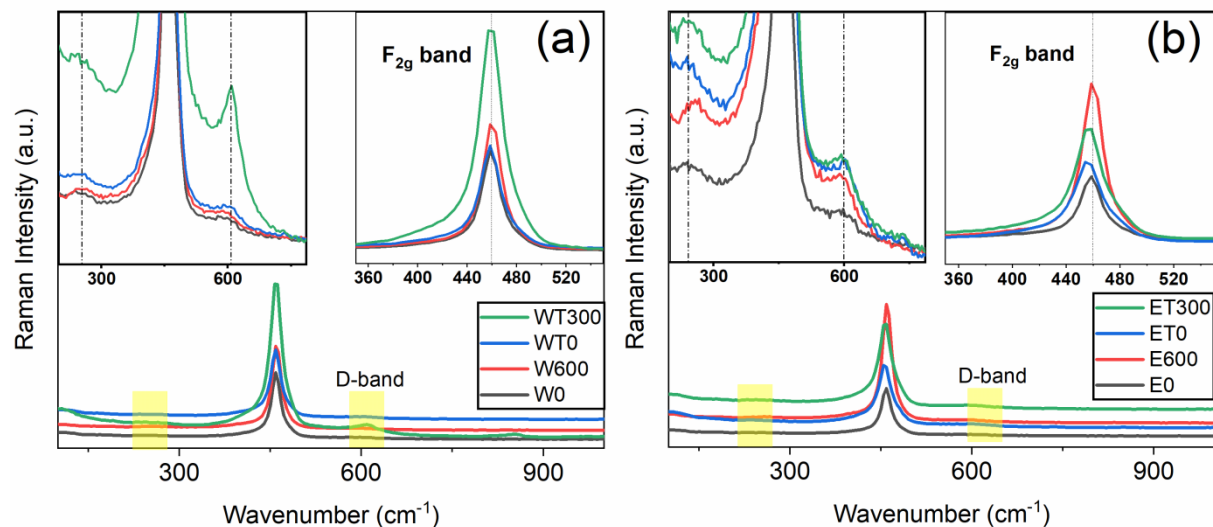


Fig. 4.8: Raman spectra of CeO₂ samples synthesized in (a) water medium and (b) ethanol medium.

Fig. 4.8 (a, b) shows the Raman spectra of CeO₂ NPs. The cubic structure of CeO₂ is also confirmed by Raman spectra. Raman spectra consist of intense peaks around 454 cm⁻¹. This band is attributed to Ce-O₈ vibrational unit [28]. This peak is associated with the F_{2g} Raman vibrational mode of the crystalline cubic fluorite type structure of CeO₂ with Fm3m space group and originated from the tension vibration of the oxygen atoms that surround the cerium [40]. As only O-atoms move so this vibrational mode is nearly independent of cation mass [41]. This stretching helps to maintain the structural symmetry of CeO₂ fluorite structure [42]. This Ce-O₈ vibrational mode is very sensitive to any type of disorder and any change in synthesis parameter. In fig. 4.8 (a), F_{2g} mode intensity almost remains the same when the sample is calcined at 600 °C, but intensity increases when the sample is synthesized using the capping agent. In fig. 4.8 (b), the peak intensity increases for the samples synthesized using capping agent and calcined as well.

The F_{2g} band intensity is found to increase when the sample is synthesized using ethanol as solvent except for the intensity of WT0 which is more than ET0. Hence, the non-uniform intensity variation of this peak is due to the non-uniform variation of particle size which causes strain in lattice leading to expansion or contraction of lattice [18,43]. This F_{2g} band is found to be slightly shifted (red shift) for ET0 and ET300 which may be due to particle size variation [18]. Red shift is due to the conversion of Ce⁴⁺ to Ce³⁺ oxidation state with a localized 4f state electron as lattice relaxation takes place after shifting [42]. This indicates the presence of Ce₂O₃ in the powder samples which is beyond the detection limit of

XRD. Moreover, Ce_2O_3 is in amorphous form. Hence, F_{2g} peak gives information about the reduction of Ce state and informs about Fluorite-type structure of CeO_2 .

In fig. 4.8 (a, b), there is a very less intense peak around 600 cm^{-1} , which is induced due to the creation of oxygen vacancies to maintain the charge imbalance between Ce^{4+} and Ce^{3+} [43]. The low intensity of this peak indicates that only a few oxygen vacancies are present in the CeO_2 lattice [43]. This peak becomes more intense when the sample is calcined at higher temperature and synthesized with the help of capping agent. The oxygen vacancies at higher calcination temperatures are induced due to thermal stress caused by rapid change in the calcination process [44]. This peak at 600 cm^{-1} becomes more intense when the sample is synthesized using the capping agent. The increased intensity illustrates that there is an increase in oxygen vacancies when the synthesis parameters are changed. However, this peak is not following a specific trend of increasing intensity with change in the solvent. Whenever an oxygen vacancy is created, the strain parameter increases due to size difference of Ce^{3+} and Ce^{4+} and this contributes to both in XRD and Raman intensity peaks [43]. Moreover, WT300 has shown significantly large intensity of the D-band, which might be due to the creation of O-vacancies and the conversion of Ce^{4+} to Ce^{3+} during the calcination at $300\text{ }^\circ\text{C}$. This proves that Raman spectroscopy is very sensitive for detecting small or nano-crystalline structures. These oxygen vacancies help to trap the photoexcited electrons and decrease the recombination rate of the excited electrons [3,45]. These oxygen vacancies help in the enhancement of the photocatalytic activity of CeO_2 NPs.

The band near 250 cm^{-1} due to the Ce-OH stretching is related to the subsurface oxygen vacancies which are present below the surface of CeO_2 NPs. In fig. 4.8 (b), there is a very small redshift in this peak for ET300 sample, which might be due to strain-induced by these vacancies [46]. This mode has a very low intensity for E0 and ET0, which indicates low amount of subsurface oxygen vacancies. However, very small increase in the intensity is observed for E600 and ET300, which indicates the increased subsurface vacancies after calcination due to strain-induced in lattice after heat treatment. These subsurface oxygen vacancies play a vital role in photocatalytic activity by enabling the process of stabilizing the formation of linear cluster of oxygen vacancies on the strongly reduced surface [47]. Hence, the asymmetry in the peak intensity and shifting in Raman peak come from the combined result of all the particles formed and strain induced due to oxygen vacancies.

4.3.6 BET Analysis

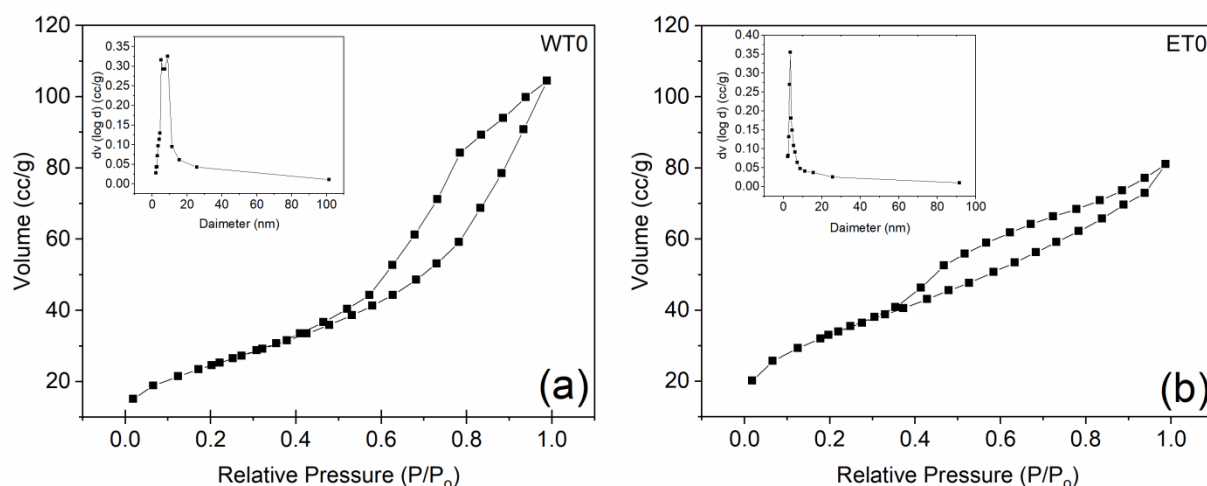


Fig. 4.9: N_2 adsorption-desorption isotherms of (a) WT0 and (b) ET0 and inset of figures having pore size distribution.

The specific surface area, pore volume, and size distribution are studied by BET technique in nitrogen adsorption and desorption environment, as shown in Fig. 4.9 (a-b). The porosity of the material is measured by Barret-Joyner-Halenda (BJH) pore size distribution [48]. Fig. 4.9 (a-b) represents the adsorption-desorption isotherms of WT0 and ET0, respectively. The adsorption-desorption isotherms demonstrated for the type IV curves [49]. This type of curve is typically a feature of porous material. Moraes et. al [50] suggested that the synthesis in alcoholic medium provides increased surface area ($\sim 26\%$). However, in the present case, BET surface area is found to increase by $\sim 4\%$ for sample synthesized with capping agent and ethanol as reaction medium ($100 \text{ m}^2/\text{g}$) than sample synthesized with water as reaction medium ($96 \text{ m}^2/\text{g}$). Although, the pore volume and pore diameter are found to decrease for sample synthesized in ethanol as solvent, the large surface area provides more active sites, which are helpful for degradation of dye molecules.

4.3.7 Photodegradation of dye

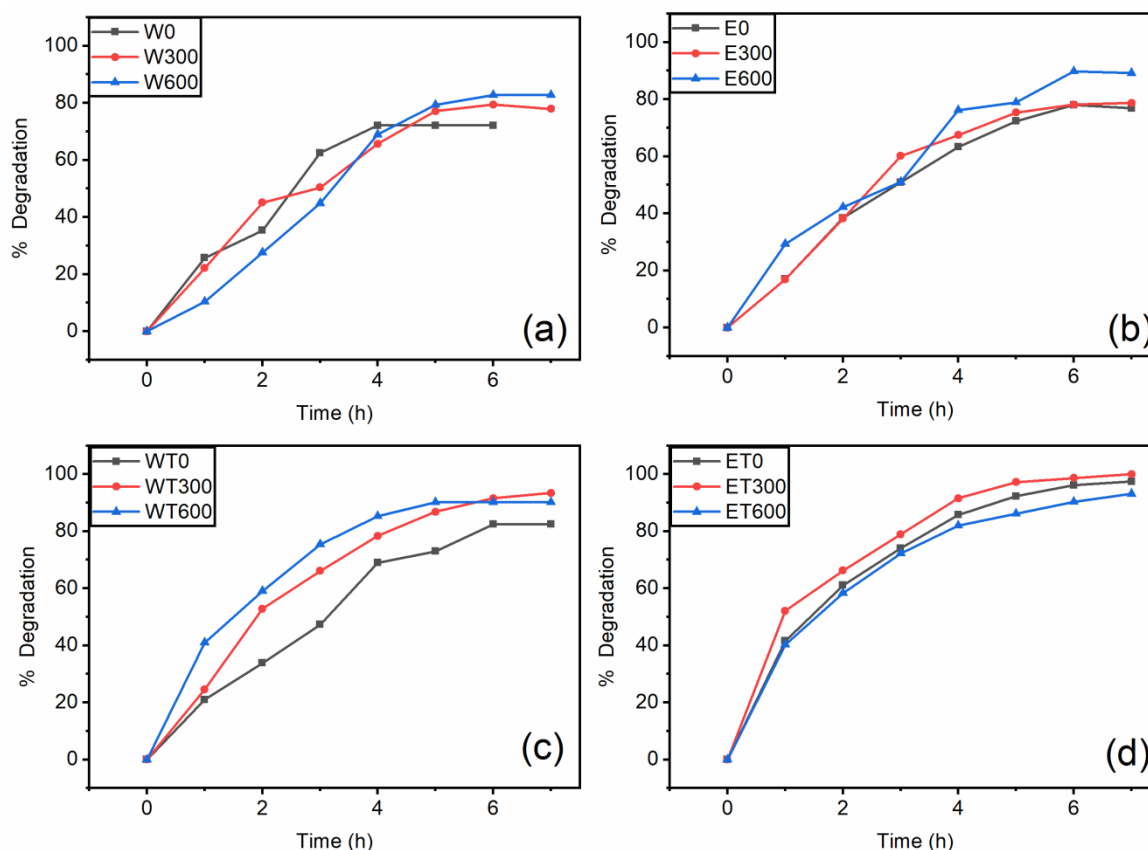


Fig. 4.10: Degradation of crystal violet dye by CeO_2 samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

4.3.7.1 Effect of Calcination

Fig. 4.10 represents the effect of different synthesis parameters on the photocatalytic removal of crystal violet dye in the presence of synthesized CeO_2 under UV-visible irradiation. As an effect of calcination on the photodegradation of CV dye, enhanced degradation efficiency is observed with increased calcination temperature i.e. 300 and 600 °C as compared to uncalcined CeO_2 sample. The 0, 300 and 600 defines uncalcined, calcined at 300 and calcined at 600 °C, respectively. The lower efficiency of uncalcined samples may be associated to fast recombination of excitons due to some surface defects which act as a recombination center for photoexcited electrons [51]. Also, the reduced bandgap as discussed earlier in the UV section for calcined samples allows the low energy photons to excite electrons from the valence band to the conduction band resulting in the enhanced density of excitons exhibiting the higher photocatalytic activity [52]. Thus, calcination enhances the light absorption efficiency of synthesized sample as it forms additional layer in between the valence and conduction band. Table 4.4 also shows red shift in the absorption edge of synthesized samples as an effect of calcination. However, ET300 sample exhibit higher

degradation efficiency than ET600, which is associated to the higher concentration of hydroxyl groups on the surface of the CeO₂ particles as observed in FTIR results also (Fig. 4.2(d)). Jun et al. [22] and Munawaroh et al. [23] discussed the direct co-relationship of hydroxyl groups towards better photocatalytic efficiency of the system providing more trap centers for photo-generated holes. Moreover, the presence of O-defects inside CeO₂ lattice also contributes towards better photocatalytic efficiency by delaying the recombination of excitons as it has been confirmed from Raman results showing increased O-defects, when the samples are calcined at higher temperature. Gharibshahi et al. [15] claimed that the capping agent slowly released its capping property at higher calcination temperature, which might be the possible reason for enhanced efficiency of ET300 and WT300 than ET600 and WT600, respectively.

4.3.7.2 Effect of solvent and capping agent

Comparing the results from fig. 4.10 (a, c) and 4.10 (b, d), the photocatalytic efficiency is found to be higher for the CeO₂ samples which are synthesized in ethanol as solvent. Moraes et. al [50] suggested that the synthesis in alcoholic medium provides increased surface area (~ 26%) in the samples. In the present study, ~ 4% increment is observed in TG capped sample synthesized in ethanol medium. As an effect of capping agent, red shift is observed for samples synthesized using water as reaction medium. No particular trend has been observed for samples synthesized using ethanol as reaction medium.

By comparing the results of fig. 4.10 (a, c) and 4.10 (b, d), the photocatalytic efficiency is found to increase for the capped CeO₂ samples than uncapped samples. This is related to many factors. First of all, the ability of capping agent hinders the coagulation of crystallites, which in turn enhances the exposed surface area of nanoparticles and provides better adsorption of dye molecules on the surface of the catalyst. Further, surface passivation by TG molecule leads to better charge transfer from catalyst's surface to adsorbed dye molecule along with the better generation of excitons and delayed recombination [53,54]. Moreover, Raman results also suggested the higher concentration of O-defects i.e. vacancies in capped CeO₂ sample as compared to uncapped samples.

The geometry of the photocatalytic reactor also influences the reaction kinetics. The inappropriate photoreactor design leads to increase in energy consumption, inappropriate flow rate and uneven photon distribution. Sometimes, it also leads to catalyst deactivation which directly affects the photocatalyst efficiency [55].

While designing the reactor care should be taken to avoid turbulence which might damage the surfaces of catalyst. It is found that high amount of phenol has been completely removed in

cylindrical reactor with low intensity UV sources (40 W). However, size of reactor also plays important role. It is reported that rectangular micro reactors completely removed the salicylic acid and MB dye using 5 W UV light source [55]. Comparing the cylindrical reactors, the efficiency in rectangular reactor is low. Thus, designing of reactor directly affects the rate kinetics of photocatalytic reactions. Hence, various parameters control the rate constant. It also depends upon temperature of reaction. Moreover, temperature varies when reaction geometry changes. The change in temperature directly affects the photogenerated charge carriers. Chen and Hsu [56] optimized the reaction temperature. They found that 0-50 °C, the rate increases with temperature. When the temperature is more than 70 °C, the reaction rate decreases.

By considering the above observations, the photocatalytic reactions were performed in the cylindrical reactor by maintaining the constant temperature of reaction.

Table 4.4: Measured peak absorption edge for synthesized CeO₂ samples.

Sample Id	Absorption edge (nm)	Sample Id	Absorption edge (nm)	Sample Id	Absorption edge (nm)	Sample Id	Absorption edge (nm)
W0	300	WT0	302	E0	302	ET0	312
W300	305	WT300	314	E300	314	ET300	312
W600	314	WT600	321	E600	321	ET600	310

4.3.8 Kinetics of photodegradation of dye:

The photochemical reaction kinetics are determined by pseudo first and second-order models. The photocatalytic decomposition of an organic molecule is a very complex process involving different chemical reactions taking place at the same time. Here, pseudo first-order kinetic model describes the adsorption of dye molecule through physical bond i.e. hydrogen bond formation between catalyst and dye molecule which is referred as physisorption. The formation of chemical bond through O-species present on the surface of catalyst can be referred to as chemisorption referred as pseudo second-order kinetic model [57]. Both kinetic models can also be represented in the following equations:

$$\text{First order} - \ln\left(\frac{C}{C_0}\right) = k_1 t \quad (4.2)$$

$$\text{Second order} \frac{t}{C} = \frac{1}{k_2 C_0^2} + \frac{t}{C_0} \quad (4.3)$$

where C_0 , C are the initial concentration, concentration after time t ; k_1 and k_2 are rate constants for first and second order kinetic models, respectively [58].

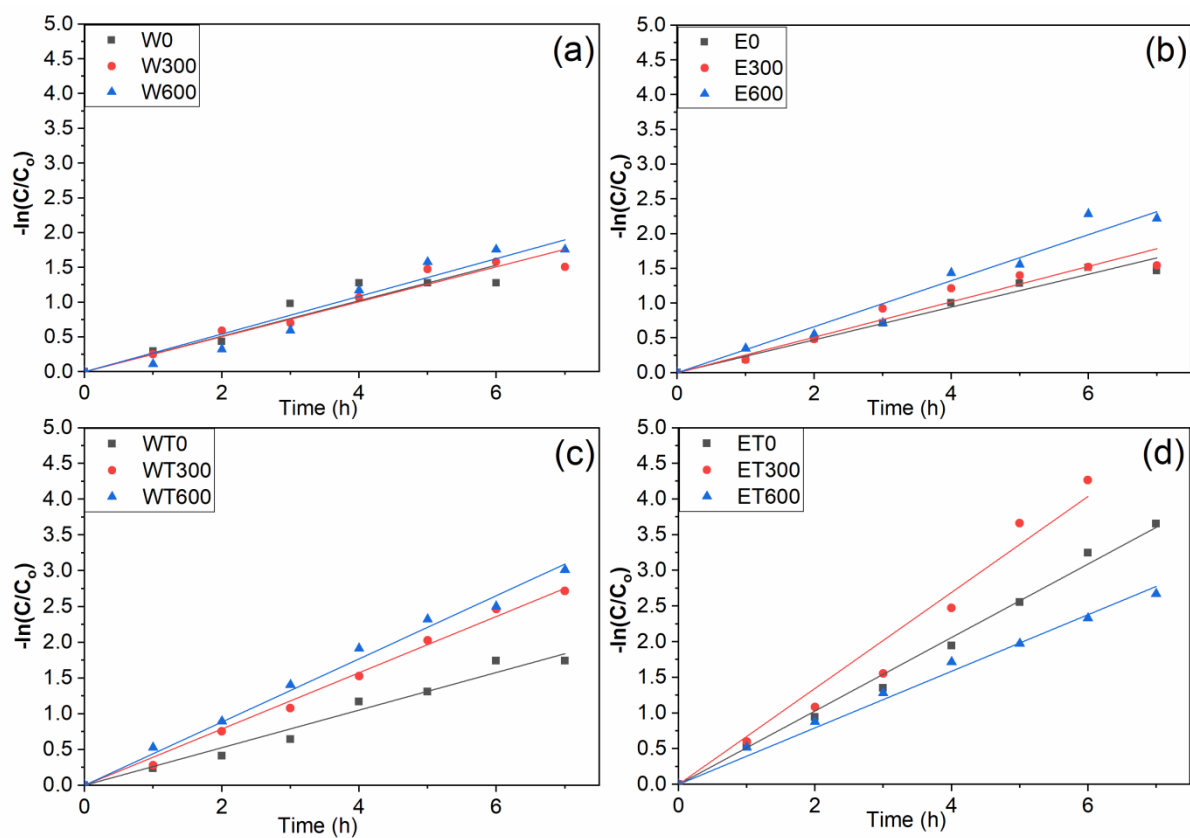


Fig. 4.11: Pseudo first order kinetics of CeO_2 samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

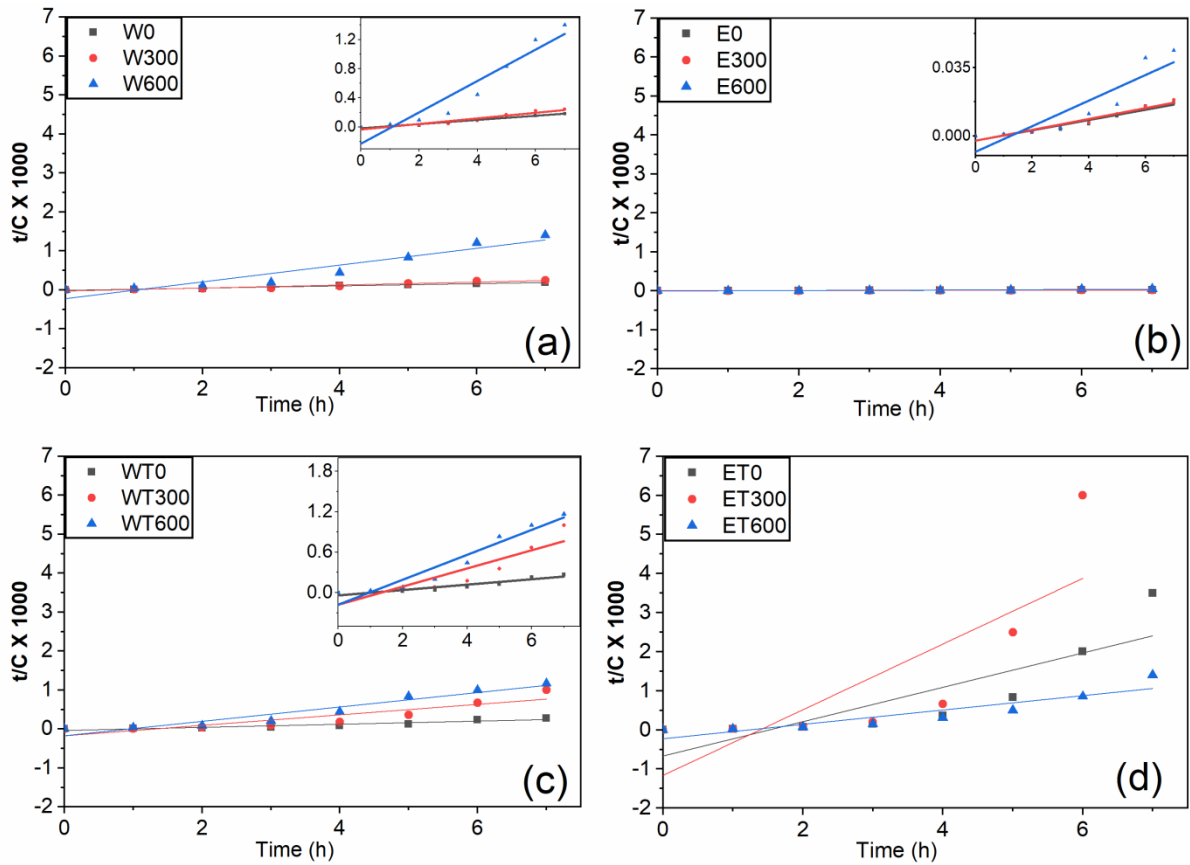


Fig. 4.12: Pseudo second order kinetics of samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

Both of models are implemented by plotting $-\ln(\frac{C}{C_0})$ vs. t and t/C vs t in which regression coefficients (i.e. R^2) determine the quality of fitting and k_x represents the rate constant as shown in Fig. 4.11, 4.12 [58,59]. The various parameters related to first and second-order kinetics are given in table 4.5. The R^2 value is found to be more than 0.95 for first-order kinetics. However, the rate constant value k_2 is found to be more than k_1 , but has low value of regression coefficients R^2 . Hence, all the synthesized samples follow the first-order kinetics. The rate constant k_1 for capped samples prepared in ethanol solvent is found to be more than uncapped samples, which may be due to more oxygen vacancies and more hydroxyl groups that promote the photocatalytic activity [3,22,50]. The rate constant k_1 is found to be more for ET0 than WT0 as higher specific surface area (confirmed from BET analysis) provides more active sites for the generation of charge carriers. The rate constant k_1 is found to be increased for the calcined samples, except for ET600 which is due to the low number of hydroxyl groups attached to the surface of ET600 as observed from FTIR results. Bayu et al. [60] claimed that increased crystallite size promotes catalytic activity due to improved absorbance capacity. The rate constant k_1 for ET300 is found to be more than all other synthesized

samples despite of lower crystallite size (Table 4.1). Thus, increased crystallite size is not a specific parameter for enhanced photocatalytic activity. This indicates that oxygen vacancies, specific surface area, and hydroxyl groups all play an important role in photocatalytic activity.

Table 4.5: Rate constant for first and second-order kinetics and corresponding R^2 value.

Sample Id	k_1 (h^{-1})	R^2	k_2 (h^{-1})	R^2	Sample Id	k_1 (h^{-1})	R^2	k_2 (h^{-1})	R^2	Sample Id	k_1 (h^{-1})	R^2	k_2 (h^{-1})	R^2
W0	0.256	0.96	50.177	0.97	W300	0.251	0.98	43.706	0.92	W600	0.271	0.98	202.796	0.89
E0	0.236	0.99	29.357	0.92	E300	0.255	0.98	32.379	0.94	E600	0.331	0.98	53.135	0.80
WT0	0.263	0.99	37.607	0.88	WT300	0.393	0.99	100.949	0.79	WT600	0.442	0.99	191.923	0.92
ET0	0.514	0.99	287.789	0.68	ET300	0.672	0.99	605.232	0.59	ET600	0.396	0.99	146.841	0.80

4.3.9 Effect of H_2O_2 on photocatalysis

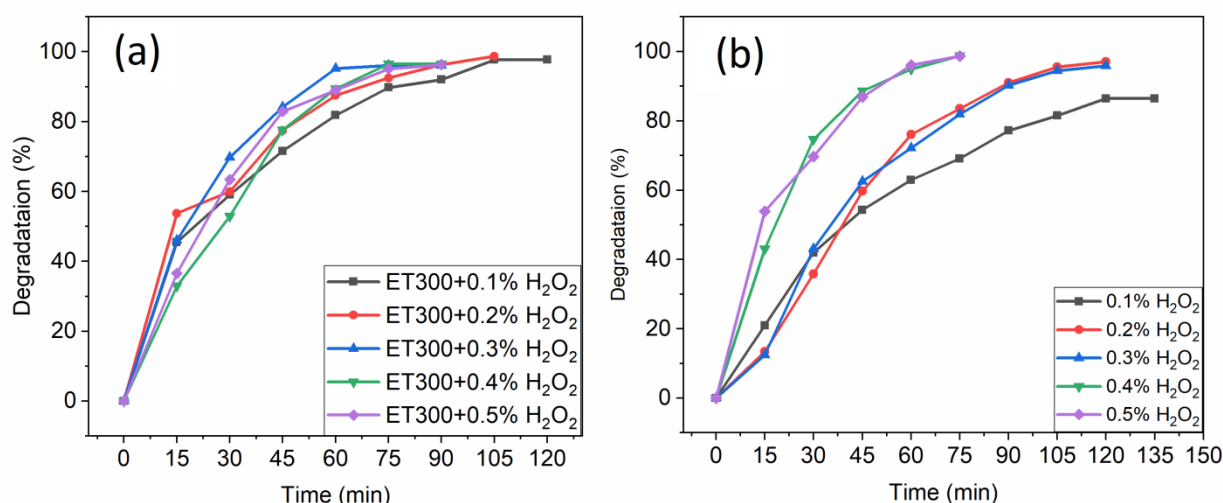


Fig. 4.13: (a) Degradation of CV dye in the presence of catalyst and H_2O_2 and (b) photo-oxidation of CV dye in the presence of H_2O_2 only.

Fig. 4.13 (a, b) shows the effect of H_2O_2 on photo-oxidation and photocatalysis i.e. in the presence of UV-visible light without catalyst and in the presence of a catalyst. It is found that photocatalytic activity increased in the presence of H_2O_2 . Mittal et al. [52] also claimed that H_2O_2 is a better electron acceptor than oxygen. This reduces the chances of recombination of electron-hole pair. So by the addition of H_2O_2 , the photocatalytic activity is increased. The proposed reaction mechanism is [61]:



Moreover, it is also observed that the addition of H_2O_2 above optimum level (i.e. 0.3%) exhibits reverse effect i.e. the photocatalytic activity is less than photooxidation. Pouretedal and Kadakhodaie [62] have suggested that hydrogen peroxide promotes degradation mechanism in two ways; firstly it adsorbs onto the catalyst surface and inhibits the electron-hole recombination. Second, after adsorption on the catalyst surface, it accepts the photogenerated electrons from the conduction band and promotes charge separation. However, at higher concentration of H_2O_2 molecules scavenge the valuable $OH^\cdot$ and form a oxidant $\cdot OH_2$. These $\cdot OH_2$ radicals are less reactive than $OH^\cdot$ radicals. Thus, at higher concentration of hydrogen peroxide in the presence of catalyst reduces the photocatalytic activity. It can be observed that the rate of degradation is faster in 15 minutes and it becomes slower in the remaining time period. This observation can be explained on the basis of the fact that initially, only CV dye is the key recipient of the hydroxyl radicals ($OH^\cdot$) to undergo the oxidative reaction. However, in the later stage, smaller molecule fragments also receive those radicals for oxidation. This causes less number of radicals that are available for CV resulting in slower degradation of CV dye [61]. The mechanism is illustrated by the following equations:



So based on the above studies, it can be concluded that only a optimum amount of H_2O_2 will give good catalytic activity. The studies also show that hydroxyl radicals are very important to increase the photocatalytic activity as they act as acceptor for photoexcited electrons.

Table 4.5 shows the calculated values for first and second-order kinetics. The R^2 value for first-order kinetics is greater than 0.95, which shows that reaction is following first-order kinetics rather than second-order. The value of rate constant k_2 is found to be larger than rate constant k_1 , but has low value of regression coefficients R^2 . Hence, the reaction follows first-order kinetics. As it can be observed from table 4.6 that the rate constant value for k_1 increases up to 0.3% concentration of H_2O_2 in the presence of ET300 and then decrease because more number of H_2O_2 molecules in the presence of catalyst act as scavenge for $OH^\cdot$. However, in the absence of catalyst, it can be seen that k_1 value increases with increased concentration of H_2O_2 which shows that higher amount of H_2O_2 in the presence of catalyst acts as trapping center for photoexcited electrons. So, a conclusive statement can be given that only an optimum amount of H_2O_2 in the presence of catalyst gives enhanced activity.

Table 4.6: Rate constant for first and second-order kinetics and corresponding R^2 values in the presence of H_2O_2 .

Sample Id	k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2	Sample Id	k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2
ET300+0.1% H_2O_2	0.0315	0.98	17.50	0.64	0.1% H_2O_2	0.0153	0.99	4.235	0.90
ET300+0.2% H_2O_2	0.0375	0.99	30.45	0.46	0.2% H_2O_2	0.0271	0.98	15.32	0.65
ET300+0.3% H_2O_2	0.0442	0.98	22.81	0.75	0.3% H_2O_2	0.0253	0.99	11.37	0.70
ET300+0.4% H_2O_2	0.0382	0.99	19.07	0.73	0.4% H_2O_2	0.0529	0.99	46.13	0.48
ET300+0.5% H_2O_2	0.0377	0.99	17.65	0.74	0.5% H_2O_2	0.0531	0.99	55.46	0.72

4.3.10 Adsorption study

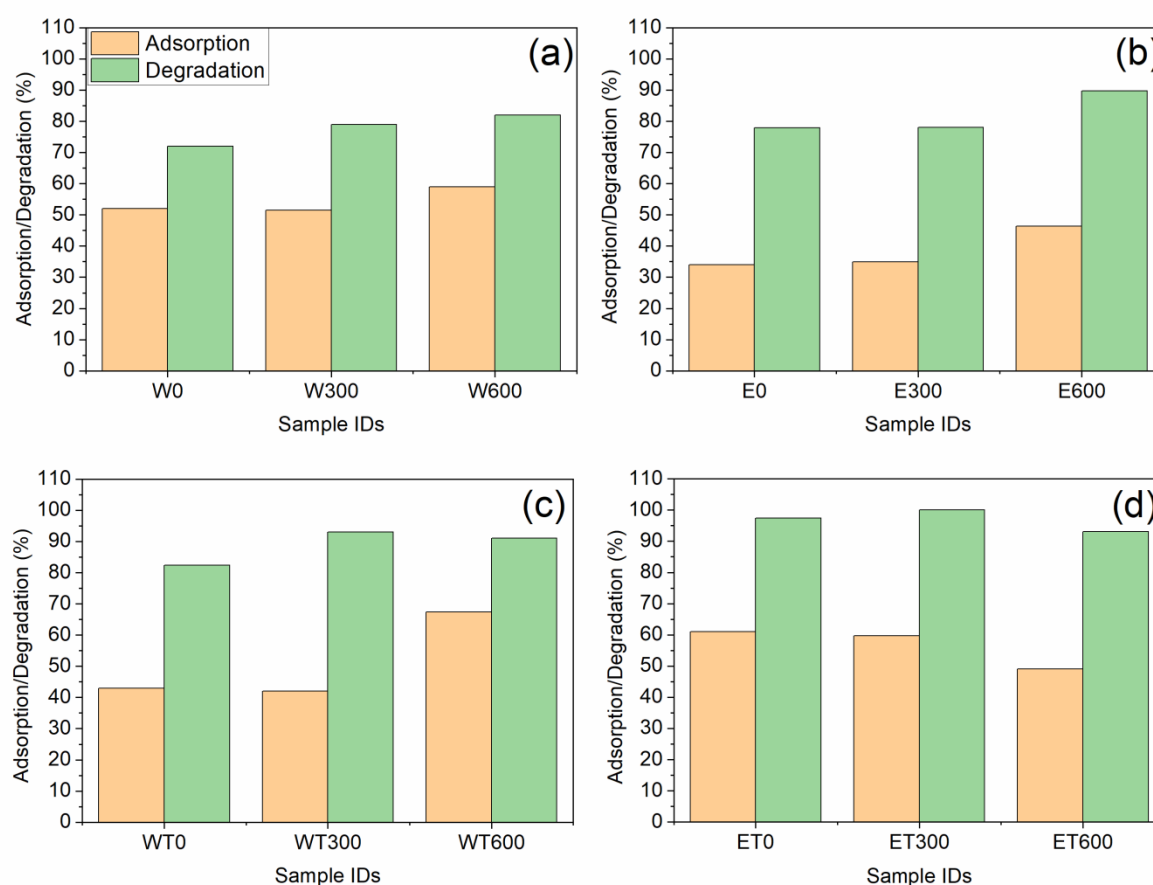


Fig. 4.14: Adsorption study of crystal violet dye by CeO_2 samples synthesized in (a) water, (b) ethanol, (c) water (capped) and (d) ethanol (capped).

Fig. 4.14 shows the adsorption and degradation study of crystal violet dye by synthesized CeO_2 samples. The absorbance of dye molecules for the samples synthesized in ethanol as a solvent is found to be less than the samples synthesized in water as a solvent for uncapped samples. However, the absorbance value for samples synthesized in water as a solvent with capping agent is found to be less than samples synthesized in ethanol as a solvent with a capping agent. The more adsorption of dye molecules determines the possibilities of contact between the active surface of catalyst and dyes [63]. This contact provides the interfacial charge transfer between the active site of catalyst and dye molecules resulting in the spontaneous reaction. However, the samples synthesized with capping agent and water as reaction medium show better degradation efficiency with low adsorption. Chen et al. [64] observed that when more dye molecules are adsorbed on the catalyst surface, the adsorption of photons was decreased by the photocatalyst. Thus, from the above results it is observed that adsorption of dye molecules is an important factor but, cannot be solely deciding factor for the photocatalytic activity.

4.3.11 Degradation mechanism

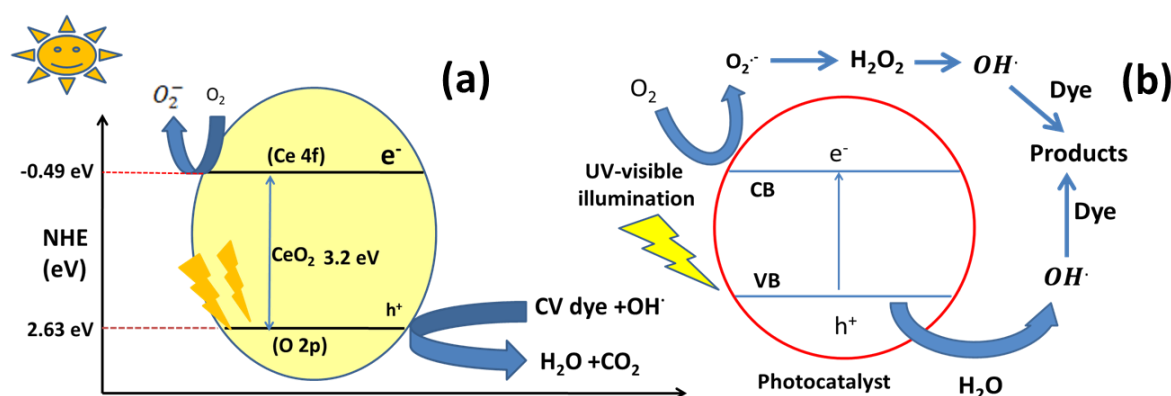


Fig. 4.15: Shows the degradation mechanism for (a) synthesized CeO_2 compound and (b) synthesized mechanism with H_2O_2 .

Based on above observations a detailed mechanism responsible for photocatalytic efficiency is discussed for the synthesized CeO_2 NPs (Fig, 4.15 (a)). The band gap of synthesized CeO_2 is 3.2 eV. Whenever a light falls on semiconductor greater than its band gap, the following reactions (4.7-4.10) take place. The reactions described below represent the mechanism of photocatalysis [65].





If solution containing catalyst is irradiated by UV-visible light, electrons from the valence band (O_{2p}) are excited to the conduction band (Ce_{4f}). The excited photoelectron scavenge by dissolved oxygen in the water to form superoxide anions ($O_2^{\cdot -}$) and holes are scavenged by water molecules from dye solution to form hydroxyl radicals ($OH^{\cdot}$). These radicals are oxidative species and degrades the CV dye.

The degradation of CV dye CeO_2 NPs with H_2O_2 is shown in Fig. 4.15 (b). All the proposed reaction has been discussed in section 4.3.9.

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Effect of doping and co-doping on photocatalytic activity of CeO₂ nanoparticles

Overview

In the present chapter effect of Yttrium (Y) and Zinc (Zn) doping and co-doping on the structural and optical properties of CeO₂ nanoparticles to evaluate its photocatalytic activity for the removal of crystal violet dye is presented. A series of Y (2-10 mol %) and Zn (2-10 mol %) doped CeO₂ are synthesized via co-precipitation route. The synthesized samples were characterized via XRD, TEM, EDX, FTIR and Raman spectroscopy. The presence of different functional groups are studied via FTIR and Raman spectroscopy. XRD results confirmed the formation of cubic fluorite structured of CeO₂ with average crystallite size in the range 3-7 nm. Y doping in CeO₂ resulted an increase in the crystallite size, whereas Zn led to decrease in the crystallite size. The photocatalytic activity is studied via UV-visible spectroscopy technique by examining the absorbance spectra. Among the various samples, 8 mol % Y-doped CeO₂ exhibited 100% degradation efficiency within 7h, while 8% Zn-doped CeO₂ exhibited 100% degradation efficiency towards crystal violet (CV) dye within 5h under UV-visible illumination. In case of Y, Zn co-doped CeO₂ samples, 100% degradation efficiency towards CV dye was achieved within 3h under UV-visible light. The present study shows that the metal ion co-doping can lead to enhancement in the degradation efficiency by several folds as compared to doped samples.

5.1 Introduction

The semiconductor catalyst generates e^-/h^+ pairs due to better absorption efficiency towards the UV-visible light [1]. CeO_2 has received attention due to its non-toxic nature and easy availability [2]. CeO_2 is a cubic fluorite-type semiconductor and maintains its fluorite type structure up to 2700 °C. Further, CeO_2 absorbs large fraction of solar spectrum than TiO_2 which makes CeO_2 a good photocatalyst than TiO_2 [3]. However, the efficiency of CeO_2 is less due to low amount of O-vacancies, which can be enhanced by modifying some synthesis parameters. In the recent years, doped and co-doped CeO_2 has attracted large attention for the decomposition of these pollutants through photocatalysis [4–6]. These dopants or co-dopants introduce new energy levels by creating O-vacancies, which act as trapping centers for excited electrons and also lead to red shift in the absorption bands due to transition from O (2p) (valence band of CeO_2) to the lower energy unoccupied orbitals of the dopants which exist below conduction band of CeO_2 [7–9]. Thus, the important concern to improve the photocatalytic activity under UV light is the variation in the concentration of O-vacancies of photocatalytic material [7,10]. The reduction of Ce^{4+} to Ce^{3+} ions takes place upon doping the metal ion (M^+) in CeO_2 . Further, doping of metal ion is responsible for the formation of new networks (Ce^{4+} -O- Ce^{3+} and Ce^{4+} -O- M^+), which induces new defects in the host lattice [11]. Whenever CeO_2 is doped with any metal ion, an improvement in photocatalytic efficiency is observed [11–13]. Mittal et. al [14] doped CeO_2 with silver (Ag) and gold (Au) and found that 2% - Ag doped CeO_2 exhibited 97.7% efficiency in 4 h, while 0.4 % Au-doped had 94.1% efficiency in 2.5 h for RhB dye, which was better than the undoped CeO_2 . Chanu et. al [15] synthesized V, Nb and Ta doped CeO_2 and found that Nb-doped CeO_2 exhibits better catalytic performance with nearly 96.8 % removal of methylene blue (MB) dye.

The ionic radii of Y^{3+} and Zn^{2+} is 102 pm and 74 pm, respectively. In the present study, the effect of both dopants Y^{3+} and Zn^{2+} on the structural and optical properties has been studied. Also, the effect of both dopants as well as co-dopants has been studied. Y^{3+} (102 pm) has larger ionic radii than Ce^{4+} (97 pm) and Zn^{2+} (74 pm) [11,14,16]. The Y^{3+} has been chosen as it has same charge as of Ce^{3+} . Thus, it helps to convert Ce^{4+} to Ce^{3+} and forms O-vacancies which are helpful for enhanced photocatalytic activity. The Zn^{2+} as dopant also replaces Ce^{4+} and creates an O-vacancy as photocatalytic reaction is redox reaction. Thus, presence of O-defects inside CeO_2 lattice also contributes towards better photocatalytic efficiency by delaying the recombination of excitons. The doping of Zn has been done in CeO_2 lattice to induce the O-vacancies as Zn^{2+} is divalent and Ce^{4+} in CeO_2 lattice is tetravalent. Thus, doping of divalent in CeO_2 induces an O-vacancy. Also, doping of metal ion is responsible

for the formation of new networks ($\text{Ce}^{4+}\text{-O-Ce}^{3+}$ and $\text{Ce}^{4+}\text{-O-M}^+$), which induces new defects in the host lattice [8]. The photocatalytic reactions are based on oxidation (due to holes) and reduction (due to electrons)). Thus, presence of O-defects inside CeO_2 lattice also contributes towards better photocatalytic efficiency by delaying the recombination of excitons (electrons and holes).

5.2 Synthesis of Zn-doped and (Y, Zn) co-doped CeO_2 NPs

The doped and co-doped samples are synthesized by co-precipitation method. In a typical procedure stoichiometric amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are dissolved in 30 ml of ethanol medium under vigorous stirring. For doped samples concentration of Y and Zn was varied from 2 to 10 mol%. While for co-doped samples the concentration was varied from 2 to 6 mol%. The concentration of mother solution was maintained at 0.3 M. To this solution, known amount of 1-thioglycerol (TG) was added as capping agent. After stirring for half an hour, 25 wt% ammonia solution was added dropwise into the solution to maintain pH 7-7.5. The samples were stirred for 1 h at room temperature after complete addition of ammonia. The samples were aged for 24h. The samples were further filtered using whatman filter paper and washed several times. Finally the sample was dried at 80 °C for overnight in electrical oven. The as-prepared precursor was further calcined at 300° C for 2h in a muffle furnace. The concentration of Y and Zn ions varied from 2 to 10 mol % in the host lattice. While for co-doped samples the concentration of Y and Zn ions was varied from 2 to 6 mol % in the host lattice. The obtained oxides were crushed in a mortar and pestle to get fine powders and then used for further analysis.

5.3 Effect of doping and co-doping

5.3.1 XRD analysis:

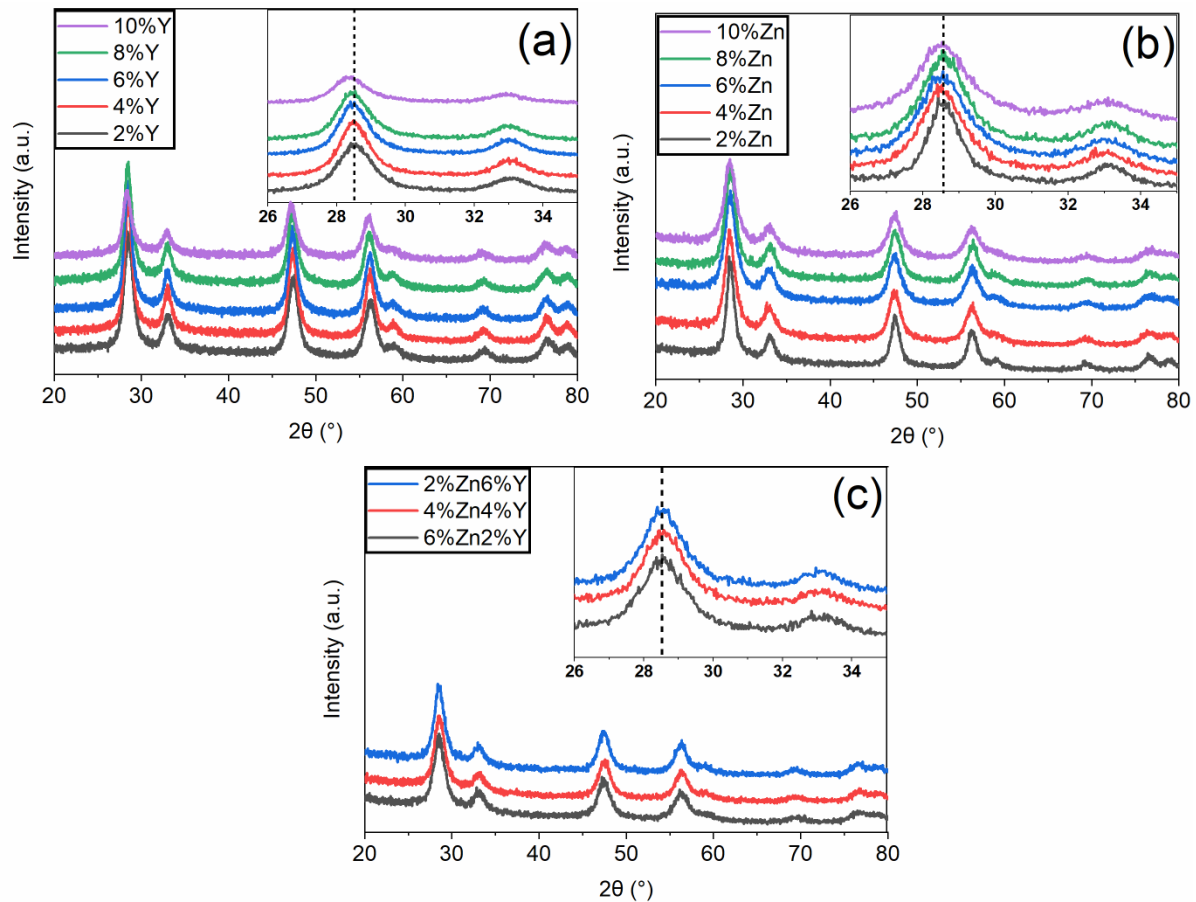


Fig. 5.1: XRD patterns of (a) Y-doped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO_2 samples inset of all figures showing the shifting in the peak corresponding to (111) plane.

Fig. 5.1 (a-c) represents the XRD pattern of Y, Zn doped and (Y, Zn) co-doped CeO_2 samples, respectively. All the XRD patterns are well matched with the standard International Centre for Diffraction Data (ICDD) card no. 00-000-0593 corresponding to the fluorite structure of CeO_2 with fm-3m space group symmetry. The main peaks are found around 28.53 , 33.02 , 47.43 , 58.76 and 76.69° corresponding to (111), (200), (220), (311) and (331) planes, respectively. No peak corresponding to initial precursors or mixed phases are found, representing the formation of pure phase CeO_2 . It can be observed from Fig. 5.1 (a), that peak shifting towards lower angle with incorporation of Y^{3+} ions on Ce^{4+} ions sites has taken place [11]. The shift in the peaks to lower 2θ values attributes to expansion of CeO_2 crystal lattice due to substitution by larger Y^{3+} (102 pm) on Ce^{4+} (97 pm) site [7,11]. However, in case of Zn doped samples, slight shift in the peak is observed towards the higher angle. This is due to lattice contraction with increase in Zn concentration. Also, the reduced intensity with Zn-doping shows low crystalline nature at higher Zn doping of CeO_2 NPs. The lattice contraction

might have caused with the substitution of smaller Zn^{2+} (74pm) size dopant at Ce^{4+} (97 pm) site [14,16]. Although, no significant shifting is observed with increasing concentration, but peak corresponding to (311) plane and peaks after this at higher 2θ disappeared. The disappearing of these peaks shows restricted growth of CeO_2 phase due to higher doping of Zn. It has been found that there is only small change in broadening and peak position which confirmed the incorporation of Zn in CeO_2 lattice. For (Y, Zn) co-doped samples, no significant shifting in peaks is observed. The insignificant shifting of 2θ peaks shows no significant change in crystal lattice after incorporation of (Y, Zn) co-dopants simultaneously in CeO_2 lattice. Since Y^{3+} leads to expansion and Zn^{2+} leads to contraction so presence of both ions in the lattice compensate both phenomenon so there is no significant change in the lattice parameters.

Table 5.1: Calculated crystallite size from XRD.

Sample Id	2%Y	4%Y	6%Y	8%Y	10% Y	2%Zn	4%Zn	6%Zn	8%Zn	10%Zn	6%Zn 2%Y	4%Zn 4%Y	2%Zn 6%Y
Crystallite Size (nm)	5.75± 0.35	5.74± 0.52	6.25± 0.63	6.17± 0.37	5.46± 0.37	5.95± 0.62	4.55± 0.37	4.20± 0.33	4.60± 0.34	3.79±0. 44	4.13± 0.45	4.57± 0.41	4.85± 0.40

Further, average crystallite size (D) is calculated using Scherrer criteria [17],

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (5.1)$$

Where, λ is the wavelength of incident X-rays (0.154 nm), θ is the bragg angle and β is full width at half maxima (FWHM) and calculated by following equation,

$$\beta = \sqrt{(\beta_{observed}^2 - \beta_{instrumental}^2)} \quad (5.2)$$

The calculated values of average crystallite size are tabulated in the table 5.1. It is observed that Y^{3+} as dopant, the crystallite size increases in the beginning up to 6% doping then decreases due to lattice expansion [11]. The increase in crystallite size might be due to incorporation of Y^{3+} (102 pm) on Ce^{4+} (97 pm) site [7,11]. However, there was decrease in crystallite size for 8%Y and 10%Y which might be due to higher doping of Y that restricts the crystallite growth. For Zn^{2+} as dopant, the crystallite size is found to decrease with doping except for 8%Zn. The decrease in crystallite size might be due to lattice contraction and also higher doping restricts the crystallite growth of CeO_2 [11,18]. However, for 8%Zn, there is an increase in crystallite size. This might be due to formation of interstitial cation which makes expansion in the lattice [19,20]. For co-doped CeO_2 samples, crystallite size is found to increase with increase in concentration of Y, while it decreases with increase in

concentration of Zn due to restricted growth of CeO₂. Hence, it is concluded that higher doping of Y and Zn restricts the growth of CeO₂.

5.3.2 FTIR analysis:

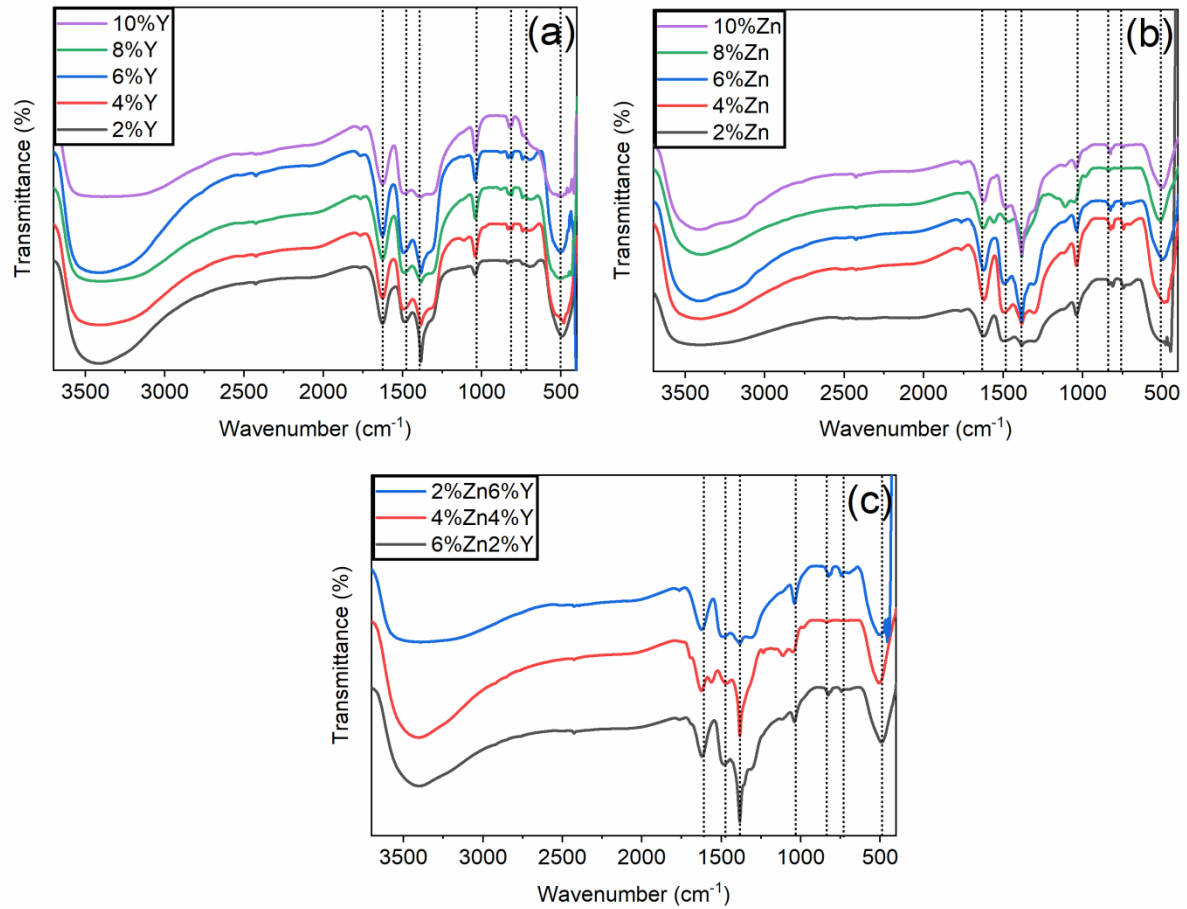


Fig. 5.2: FTIR spectra of (a) Y-doped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO₂ samples.

Fig. 5.2 (a-c) represents the FTIR spectra of Y, Zn doped and co-doped CeO₂ samples in the range 450 to 3750 cm⁻¹. FTIR spectroscopy is used to determine the vibrational motion of atomic/molecular bonds related to different functional groups present on the surface of synthesized samples with various doping concentration. Fig. 5.2 (a) represents the FTIR spectra for synthesized Y-doped CeO₂. The peak around 500 cm⁻¹ is attributed to Ce-O (M-O) stretching mode and confirmed the formation of CeO₂ [21,22]. There is no extra peak or splitting of peak related to Y-O. It is also confirmed from XRD results that there is no phase separation of Y related impurity. This peak shifts from 492 to 505 cm⁻¹ for 2%Y to 10%Y samples. The shifting of this peak to higher wavenumber depicts the shortening of bond length. This might be due to introduction of dopant and distortion produced in the lattice because of ionic radii difference [11]. All these factors are responsible for making the bond more active when doping concentration is increased. The peak at 3300-3450 cm⁻¹ is attributed

to surface hydroxyl group or from Ce-OH group, which are very helpful in terms of photocatalytic activity to provide dye sensitization [11,23–26]. This peak shifts from 3424 to 3378 cm^{-1} for 2%Y to 10%Y sample, depicting the increased bond length. The photogenerated holes directly react with CV dye or interact with surface bound H_2O or OH^- to produce the $\text{OH}^\cdot$ - radicals species, which is a strong oxidant for the mineralization of CV dye [27]. Fig. 5.2 (b) represents the FTIR spectra of Zn-doped CeO_2 . The M-O peak shifts from 495 to 504 cm^{-1} for 2%Zn to 10%Zn sample. The peak at 3401 cm^{-1} for 2%Zn shifts to 3420 cm^{-1} for 10%Zn sample, representing that bond length is decreased after introduction of Zn. Fig. 5.2 (c) represents the FTIR spectra for (Y, Zn) co-doped CeO_2 samples. The M-O peak for 6%Zn2%Y existing at 492 cm^{-1} shift to 506 cm^{-1} for 2%Zn6%Y depicting the shortening of M-O bond. The peak at 3402 cm^{-1} for 6%Zn2%Y compound shifts to 3396 cm^{-1} for 2%Zn6%Y. The peak at 1388 and 1629 cm^{-1} are attributed to adsorbed water from the atmosphere [21]. The peaks at 1388 and 1065 cm^{-1} might be due to hygroscopic nature of CeO_2 [28,29]. The intensity of these peaks reduces as an effect of doping. The small vibrations at 741 and 840 cm^{-1} are associated to Ce-O-Ce bridging oxygen (BO's) and becomes more intense with the increasing doping concentration, which proves that these bands become more active after doping [29]. The absence of S-H peak for TG at 2555 cm^{-1} is due to de-protonation of TG molecule and its attachment with Ce-atom [30]. The bond (O-H) strength is affected by introduction of dopants as dopants reduces the contribution of oxygen ions in the host lattice as discussed above [11]. The reduction in the intensity of the peaks has also been observed on doping which is due to increase in O-vacancies in the host matrix. The various band positions in FTIR corresponding to different functional groups are given in table 5.2.

Table 5.2: Band position of different vibrations.

Band position (cm^{-1})	Vibration mode	Reference
500	Ce-O stretching	[21,22]
840, 741	Ce-O-Ce bridging oxygen	[29]
1629	Physically adsorbed water	[21]
1065,1388	Intrinsic hygroscopic nature	[21,28,31]
3300-3450	Hydroxyl group	[23–25]
2555	S-H group from Thioglycerol	[30]

5.3.3 UV analysis

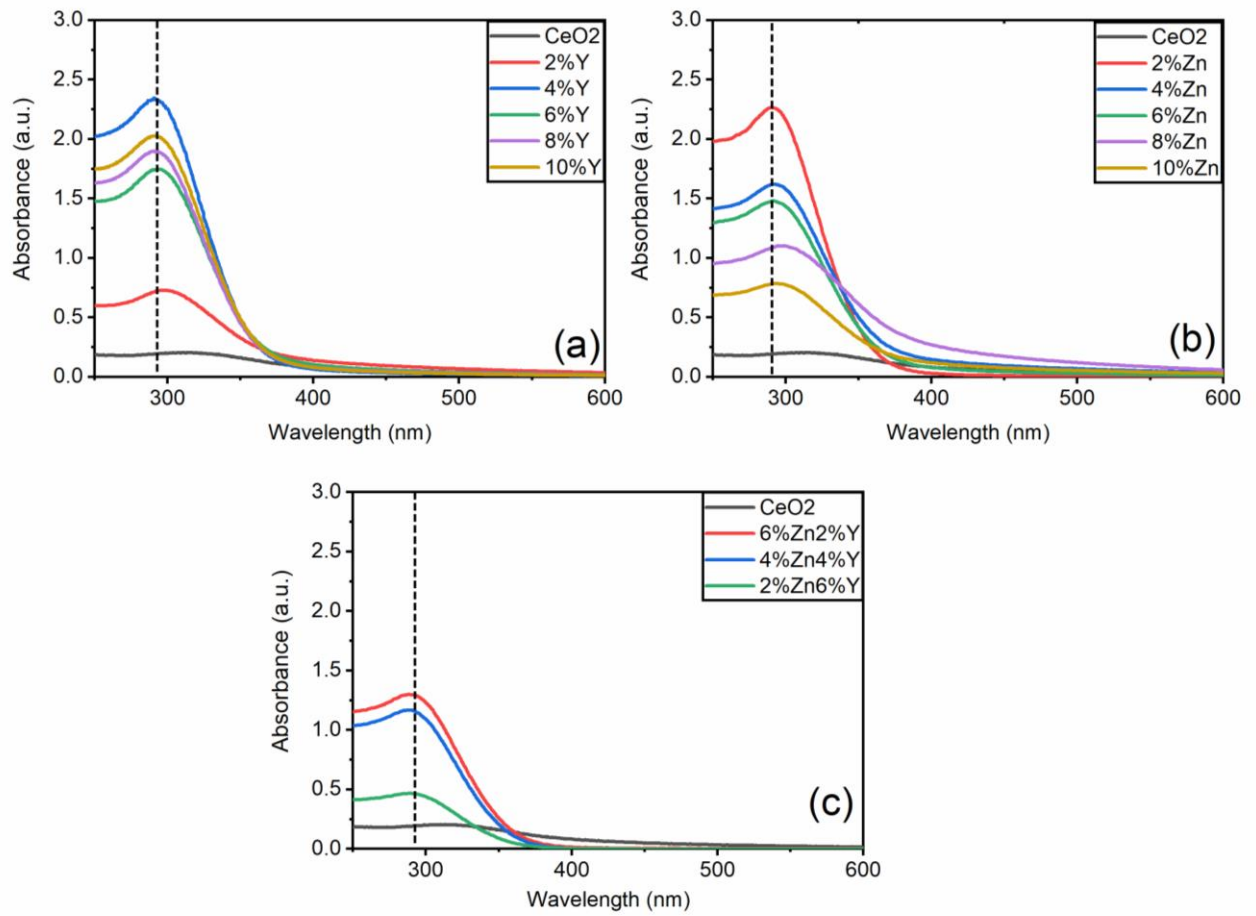


Fig. 5.3: Absorbance spectra of (a) Y-doped CeO₂, (b) Zn-doped CeO₂ and (c) (Y, Zn)-co-doped CeO₂ samples.

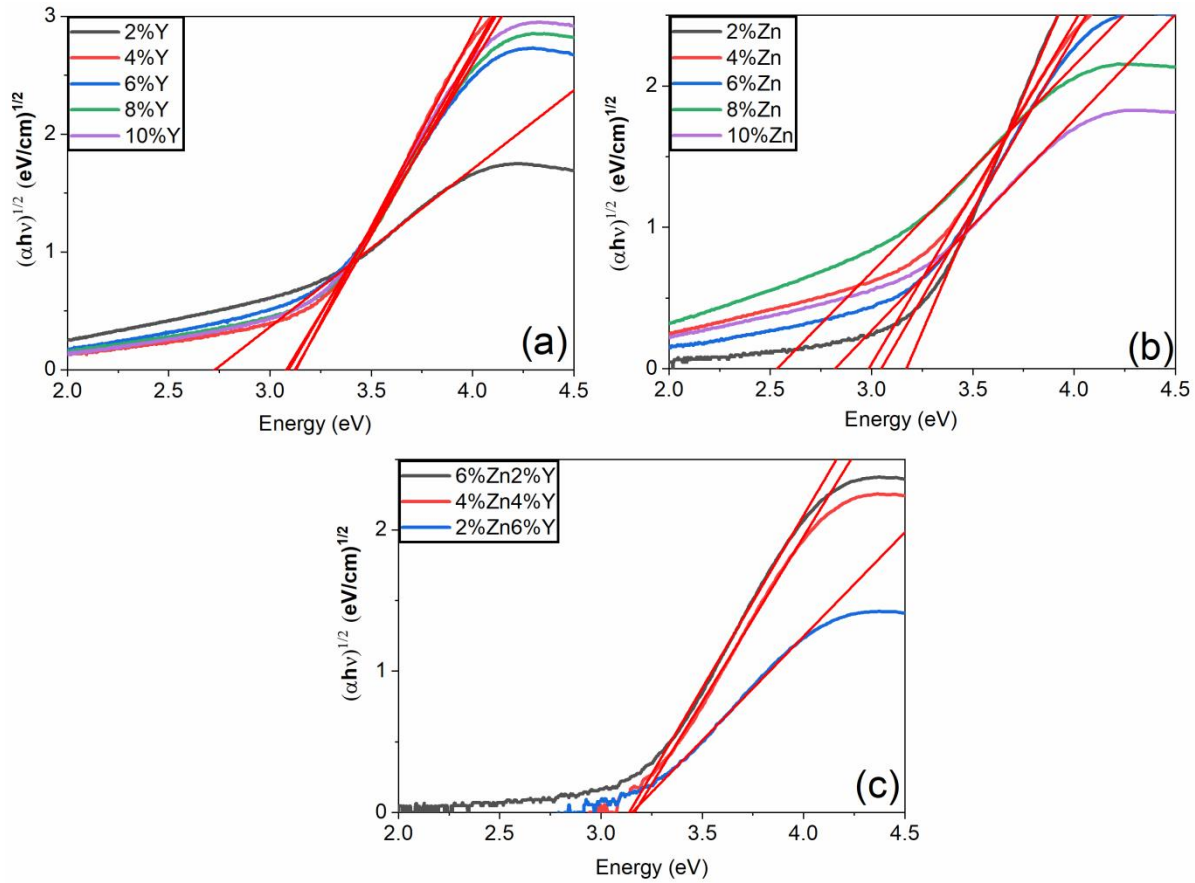


Fig. 5.4: Tauc's plot of (a) Y-doped CeO_2 , (b) Zn-doped CeO_2 and (c) (Y, Zn) co-doped CeO_2 .

Fig. 5.3 (a-c) represents the absorbance spectra of Y, Zn doped and (Y, Zn) co-doped CeO_2 samples, respectively recorded in the range 200-800 nm. The absorption peak of all the samples is found in between 280-350 nm. It can be seen from Fig. 5.3 (a) that the absorption peak for 2%Y existing at 297 nm shifts to 291 nm for 4%Y. It further shows red shift for 6%Y where peak is observed at 294 nm. This main absorbance peak for 8%Y and 10%Y again shifts to 290 nm. So, this peak is not following any pattern of red or blue shifting as an effect of Y-doping in CeO_2 . Fig. 5.3 (b) represents the absorption spectra for Zn-doped CeO_2 samples. The absorbance peak is observed at 291 nm for 2%Zn, which shifts to 293 nm for 4%Zn. Further in case of 8%Zn, it appears at 297 nm and shifts to 292 nm for 10%Zn. Hence, blue and red shifts are observed with different doping concentration of Zn. The blue shifting in the maximum absorbance peak might be due to suppression of Ce^{3+} at higher concentration of doping. Also, the quantum confinement originated by decreasing particle size of CeO_2 for Y or Zn as dopant leads to blue shift whereas red shift may be related to conversion of Ce^{4+} to Ce^{3+} [14,21,32,33]. Fig. 5.3 (c) represents the absorption spectra for (Y, Zn) co-doped CeO_2 samples. The maximum absorbance peak for (Y, Zn) co-doped samples does not show any

significant shift. The insignificant blue or red shift in the peak might be due to low charge transfer between Ce (4f) and O (2p) [21,32]. For nanocrystals, the wave functions of electrons and holes are confined to the particle volume. If the particle size becomes comparable to or smaller than the de Broglie wavelength of the charge carriers, the confinement increases the energy sufficient enough to create an electron/hole pair. This results in blue shift in the absorption peak [34]. Thus, it can be concluded that the shift of maximum absorbance of peak is due to quantum confinement which is produced by reducing the particle size of CeO₂ and due to charge transfer between Ce (4f) and O (2p).

The band gap of the doped and co-doped CeO₂ samples is determined by Tauc's equation. According to this equation, $(\alpha h\nu) = A(h\nu - E_g)^n$, where E_g is the band gap, α is the absorption coefficient corresponding to wavelength, and $n=1/2, 2, 3/2$ and 3 corresponds to allowed direct, allowed indirect, forbidden direct and forbidden indirect, respectively [35]. Fig. 5.4 (a-c) represents the Tauc's plots for indirect transition for Y, Zn-doped and co-doped CeO₂ samples. A graph of $(\alpha h\nu)^{1/2}$ vs $h\nu$ is plotted to determine the indirect band gap for all the samples. The band gap is calculated by extrapolating the straight-line portion of $(\alpha h\nu)^{1/2}$ to the x-axis where, $(\alpha h\nu)^{1/2}$ is 0 [14,36]. The indirect band gap is calculated for all samples as given in table 5.3.

It is observed from table 5.3 that band gap does not follow any significant pattern of increase or decrease with increase in Y, Zn-doping and co-doping concentrations. The blue shift in the band gap is due to quantum confinement or might be due to reduced O-vacancies as dopants might suppress the creation of Ce³⁺ [7,37,38]. The red shift in band gap is due to transformation of Ce⁴⁺ to Ce³⁺ [14]. The 8%Zn shows higher red-shift in band gap, which is because of more O-vacancies created due to conversion of Ce⁴⁺ to Ce³⁺. The higher charge transfer between valence band (O2p) and the oxygen vacancies related defects which are present below conduction band (Ce4f) at 8% Zn-doped CeO₂ also lead to red shift [14]. There is no significant correlation of band gap with increasing doping co-dopant (Y, Zn) concentration. The irregular variations in the band gap might also be related to formation of new impurity levels in between conduction and valence band of doped CeO₂ with different doping concentration of Y and Zn [39]. The changes in the optical band gap is correlated with reduction of structural defects or localized states inside the band gap which decreases the intermediary energy levels in crystal structure [40].

The band gap variation can also be defined on the basis of Burstein-Moss (BM) effect [41]. This effect suggests that, above the Mott critical density, the increased number of free electron concentration leads to fill 4f level partially, which in turn blocks the lowest states

and leads to increase in the band gap. Similarly, red shift in the band gap for 6%Y and 8%Zn might be due to high 6% Y and 8% Zn doping concentration which is not sufficiently enough to cross the Mott critical density concentration for BM effect, leading to decrease in the band gap energy. Hence, the band gap variation is due to the combined effects of quantum confinement, oxygen vacancies created and charge carrier concentration. The extinction coefficient of CV dye using different catalyst was calculated. The formula used for calculating it is as follows:

$$\text{Optical thickness} = \epsilon cl \quad (5.3)$$

Where, ϵ and c are the extinction coefficient and molar concentration of dye solution and l is the length of cuvette used. The variation of extinction coefficient is in tune with the variation in optical thickness as given in appendix B.

Table 5.3: Calculated band gap values and extinction coefficient of CV dye when degraded with Y, Zn doped and co-doped CeO₂ samples.

Sample ID	Band gap (eV)	Extinction coefficient of CV dye at different time intervals $\times 10^{-8}$ (M ⁻¹ cm ⁻¹)								
		0HA	2HA	1HD	2HD	3HD	4HD	5HD	6HD	7HD
2%Y	2.72	8.65	5.57	4.20	3.42	2.32	1.34	1.10	0.61	0.53
4%Y	3.12	8.81	3.18	2.12	1.91	1.38	1.10	0.77	0.49	0.12
6%Y	3.02	8.20	5.87	4.00	3.79	3.75	3.55	3.10	2.65	2.36
8%Y	3.12	8.49	3.14	2.89	2.32	1.79	1.02	0.61	0.28	0.08
10%Y	3.09	8.53	3.22	2.57	2.12	1.75	0.77	0.53	0.36	0.32
2%Zn	3.17	8.44	3.95	2.73	1.91	1.55	1.06	0.81	0.61	0.057
4%Zn	2.98	8.04	5.02	3.38	2.53	1.59	1.06	0.69	0.65	0.53
6%Zn	3.04	9.18	4.08	2.49	1.63	1.06	0.49	0.28	0.20	0.20
8%Zn	2.53	8.08	3.91	2.53	1.30	0.81	0.53	0.04	0.04	0.04
10%Zn	2.81	8.44	4.49	3.51	2.28	1.51	0.85	0.77	0.40	0.40
6%Zn2%Y	3.13	9.91	5.87	1.83	0.61	0.08	0	0	0	0
4%Zn4%Y	3.16	9.91	2.24	0.40	0	0	0	0	0	0
2%Zn6%Y	3.15	9.91	3.06	1.87	1.22	0.77	0.40	0.27	0.24	0.24

5.3.4 TEM and EDX analysis:

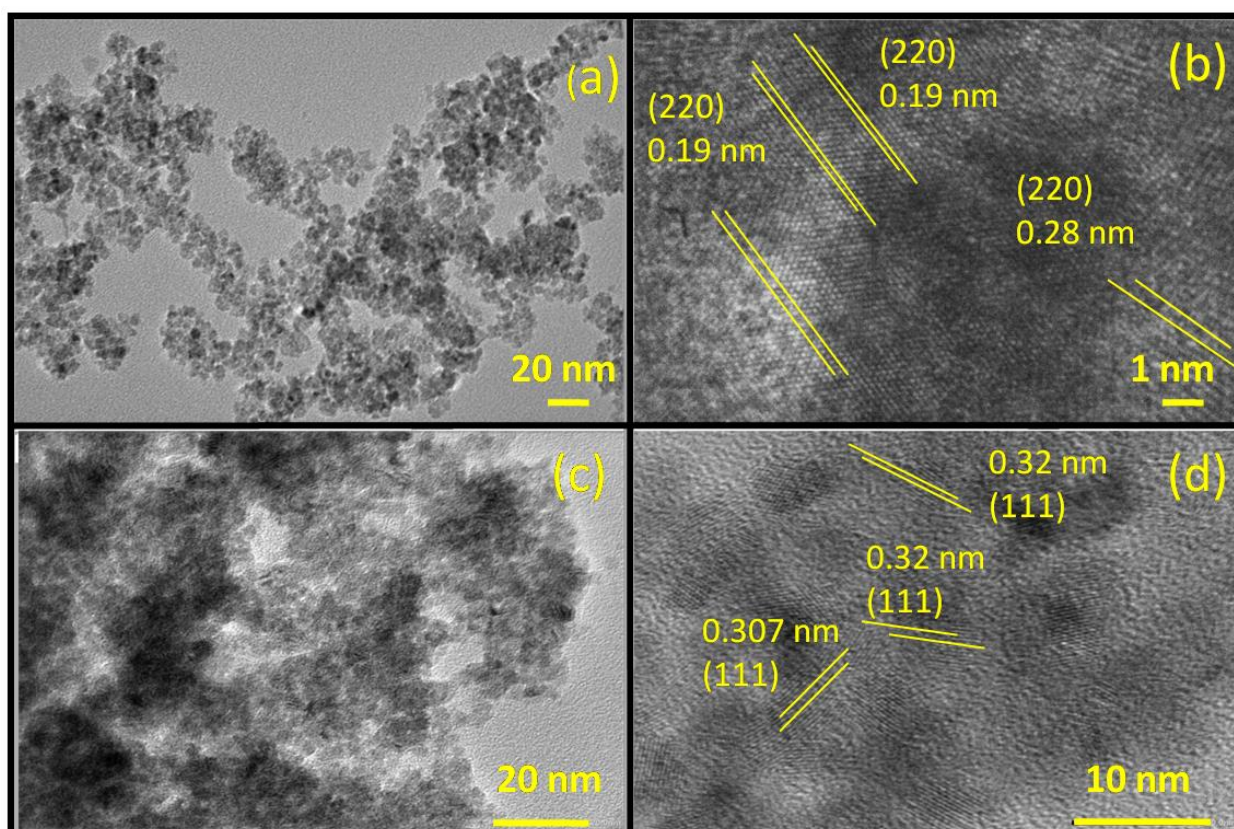


Fig. 5.5: (a) TEM and (b) HRTEM image of 8%Y (c) TEM and (d) HRTEM image of 4%Zn4%Y.

Fig. 5.5 (a, c) represents the TEM images of 8%Y and 4%Zn4%Y samples, respectively. Fig. 5.5 (a, c) shows that particles are randomly distributed with irregular shapes. It might be due to the fact that capping agent might have covered the CeO_2 NPs to avoid the coalesce to form the large aggregates [42]. A small agglomeration in NPs is observed because of electrostatic forces which allows the crystallite to grow [43]. Also, the agglomeration of NPs is more stable from energy point of view [37]. The Van der waals forces might be the reason for this agglomeration causing the NPs to reduce their interfacial energy after formation of large aggregates [34,44]. Also, FTIR results illustrate the de-protonation of capping agent and attachment to atoms, which might be the possible reason for agglomeration.

The particle size is calculated using ImageJ software. The average particle size is found to be 7.8 nm and 5.92 nm for 8%Y and 4%Zn4%Y, respectively. The calculated particle size further confirms the synthesis of NPs and these values are in strong agreement with the XRD results.

The fringe width calculated for sample 8%Y and 4%Zn4%Y are shown in Fig. 5.5 (b, d). The calculated fringe widths values are well matched with XRD ICDD card and the

corresponding planes that has been marked. The plane corresponds to the (111) for fringe width 0.31 nm, (200) for 0.27 nm and (220) for 0.19 nm and the planes reveal the cubic CeO₂ fluorite structure. Here also, no planes related to Y, Zn-related impurity is found. Moreover, it is found that 8%Y has distinct planes than 4%Zn4%Y, which represents that 8%Y has higher amount of crystallinity [45]. This observation also shows that Zn as dopant reduces the crystallinity as discussed in XRD section.

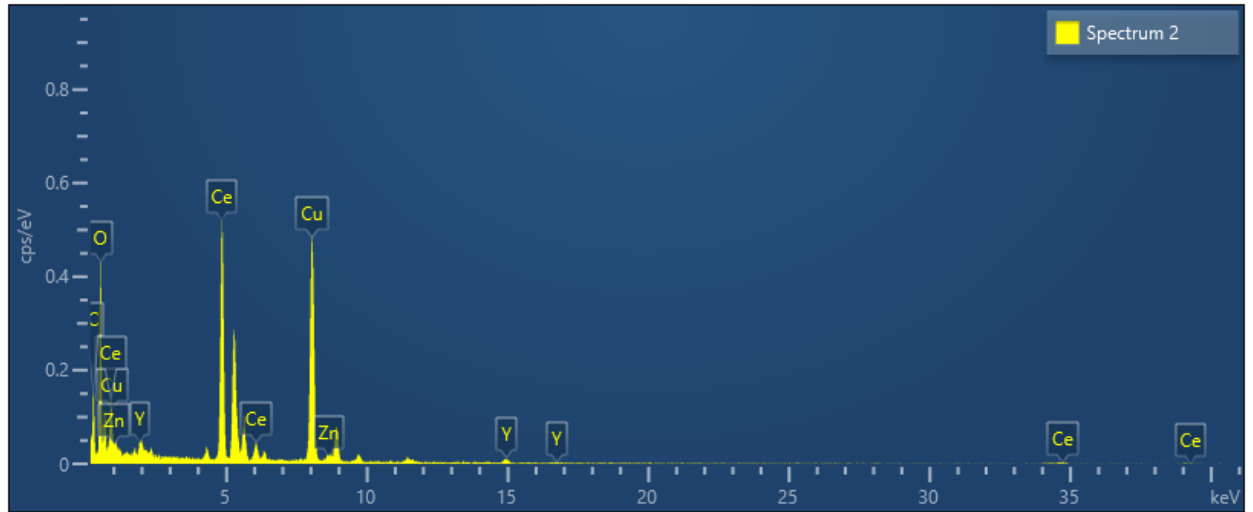


Fig. 5.6: EDX spectra of 4-4-ZYDC.

Fig. 5.6 represents the EDX spectra of 4%Zn4%Y. EDX spectrum shows the presence of Ce, O, Zn and Y elements. No other elements due to initial precursors are formed, which represents the formation of pure 4%Zn4%Y samples. Since carbon coated copper grid was used for EDX measurements so the signals for Cu and C are also observed. The peaks between 5 to 6 KeV is due to Ce element [46]. Different peaks corresponding to same element is due to excitation of atomic energy levels of respective element under incident energy.

5.3.5 Raman analysis:

Fig. 5.7 (a-c) represents the Raman spectra of Y, Zn-doped and (Y, Zn) co-doped CeO₂ samples, respectively. In Fig. 5.7 (a-c), an intense peak around 459.70 cm⁻¹ is observed which is associated with the F_{2g} Raman vibrational mode of crystalline cubic fluorite type structure of pure CeO₂ with fm3m space group. This peak is originated from tensional vibration of oxygen atoms that surround the Ce⁴⁺ ions in the CeO₈ octahedral [7,47,48]. As a result of doping, the local symmetry of O²⁻ ions distorts around Cerium atom in fluorite structure which creates oxygen vacancies in the system. The reason for this distortion is the different ionic radii for Ce and dopants ions. This difference results in the change in the lattice parameters and thereby a change in the crystal structure [11]. The modifications such as peak

shifts and broadening of peak are due to presence of oxygen vacancies, corresponding to a stoichiometry in doped CeO_2 [47].

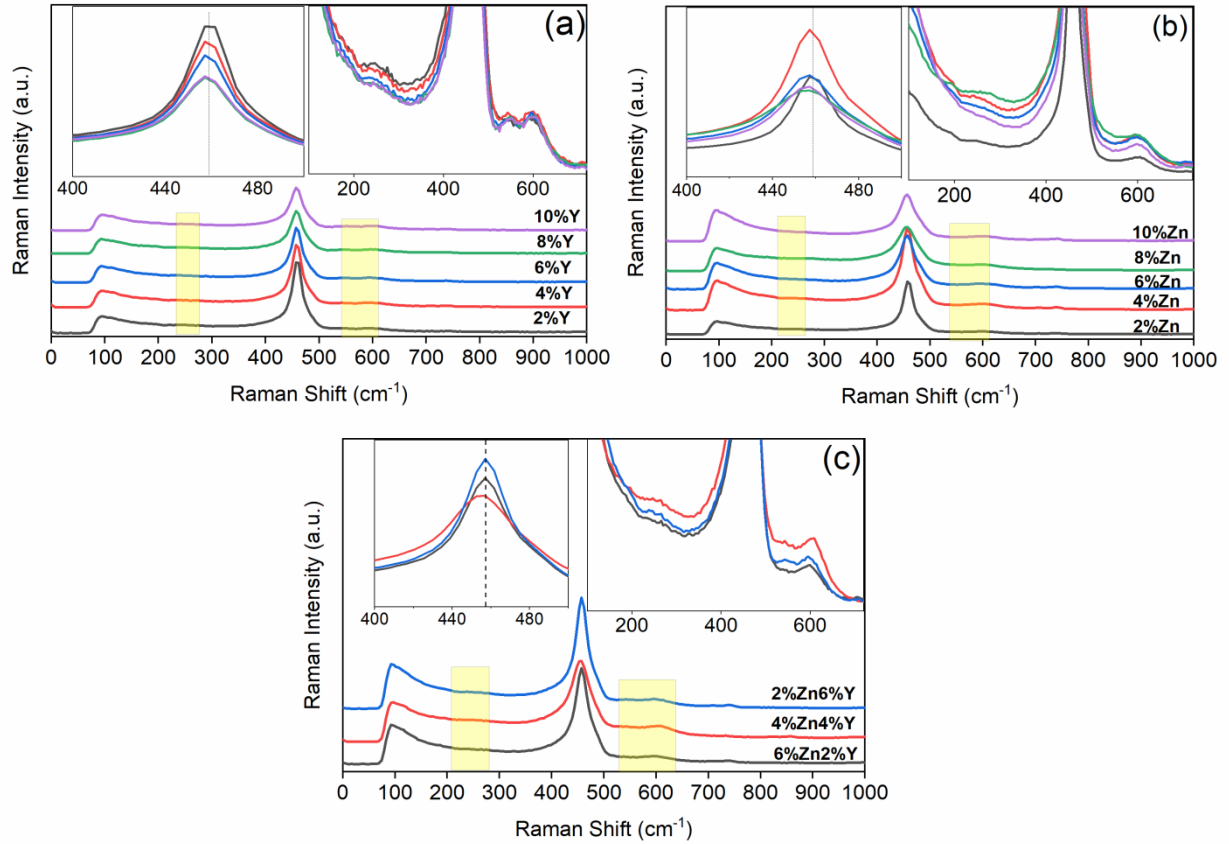


Fig. 5.7: Raman spectra of (a) Y-doped CeO_2 , (b) Zn-doped CeO_2 and (c) (Y, Zn) co-doped CeO_2 .

When the concentration of Y^{3+} ions is increased the peak shows insignificant red shift as shown in Fig. 5.7 (a). This shows that Y doping suppress the formation of Ce^{3+} . In case of Zn doped samples, as shown in Fig. 5.7 (b) a significant red shifting as compared to Y-doping is observed. This confirms that more O-vacancies are created due to conversion of Ce^{4+} to Ce^{3+} as an effect of Zn doping [11]. But, this peak again shifts to higher wavenumber (blue shift) for 10%Zn which represents that higher doping of Zn restricts the formation of Ce^{3+} . These results are in good agreement with UV results. It is observed from UV results that there is an increase in the band gap from 8%Zn to 10%Zn with higher doping of Zn, which suppresses the formation of Ce^{3+} . In Fig. 5.7 (c), for (Y, Zn) co-doped samples, this peak shows more red shifting that indicates creation of more Ce^{3+} [49]. Also, it can be observed that there is non-uniform intensity variation as an effect of doping or co-doping which might be due to particle size variation which resulted strain in the lattice i.e. expansion or contraction of

lattice [21,50]. So, it can be concluded that shifting and intensity variation in the F_{2g} band is due to combined effect of particle size variation and creation of Ce^{3+} due to dopants.

A very less intense peak around 600 cm^{-1} is observed, which is induced due to creation of intrinsic oxygen vacancies (I_{IV}). These O-vacancies are produced due to imbalance between Ce^{4+} and Ce^{3+} [51]. It is expected that for the formation of O-vacancies two electrons should remain unpaired. These electrons might have been transferred to neighboring Ce atoms or are localized at the oxygen vacancy site, giving rise to different valance states of Ce i.e. Ce^{3+} [52].

In Fig. 5.7 (a), peak around 550 cm^{-1} is evolved due to introduction of trivalent impurity and attributed to extrinsic oxygen vacancies (I_{EV}) which has arisen due to substitution of Ce^{4+} with the trivalent Y^{3+} [7]. The low intensity of these peaks (I_{IV} , I_{EV}) illustrates that only a few oxygen vacancies exist [50]. The peak intensity of both intrinsic and extrinsic O-vacancies is found to increase as the Y-concentration in the host lattice increases which confirm the introduction of Y-atoms in the lattice. Soni et al. [41] also reported the similar results with doping of trivalent Sm^{3+} in the CeO_2 . XRD pattern does not show any Y-related impurity introduced in the lattice except shifting of peaks. However, Raman peaks confirms the introduction of Y as a dopant. In Fig. 5.7 (b), there is no such peak induced for extrinsic oxygen vacancies (I_{EV}) for Zn as a dopant. It shows that Zn doping helps to create O-vacancies which is only due to the reduction of Ce^{4+} to Ce^{3+} . The peak intensity is also found to increase with increase in Zn concentration. However, 10%Zn has low intensity which shows that higher doping restricts the formation of Ce^{3+} . The ionic radii of Zn^{2+} (74 pm), which is less than Ce^{4+} (97 pm), might be the possible reason to inhibit the induction of the extrinsic O-vacancies [14,16]. In Fig. 5.7 (c), for (Y, Zn) co-doped samples, there is also no such peak induced for extrinsic O-vacancies (I_{EV}) for 6%Zn2%Y except for 2%Zn6%Y. This observation again shows that Y as dopant introduces extrinsic O-vacancies. These observation shows that Raman technique is a very sensitive to any type of defects, disorder and impurities introduced in the lattice.

The ratio of peak intensity of intrinsic to extrinsic oxygen vacancies i.e. I_{IV}/I_{EV} is found to be more than 1 for 2%Y to 10%Y, but not following significant trend of increase or decrease with the doping concentration. However, for 6%Y, this ratio is extremely higher than other Y-doped samples, which shows high amount of O-vacancies. For Zn-doped samples, this ratio cannot be calculated as there is no such peak induced for extrinsic O-vacancies. For (Y, Zn) co-doped samples, this ratio is found to be more for 6%Zn2%Y and

4%Zn4%Y. So, it is observed that an optimum amount of Y and Zn doping creates maximum amount of O-vacancies due to creation of Ce^{3+} .

Similarly, the ratio of I_{IV}/I_{F2g} is calculated to measure the distortion in lattice due to creation of intrinsic oxygen vacancies. It is found to increase with increase in concentration of Y, which shows increased distortion. For Zn-doped and co-doped samples, the ratio I_{IV}/I_{F2g} does not follow a significant pattern of increase or decrease. However, the ratio for 8%Zn and 4%Zn4%Y is found to be more, which might be due to more number of O-vacancies.

The band near 250 cm^{-1} is attributed to Ce-OH and also related to subsurface oxygen vacancies, which are present below the surface of CeO_2 NPs. The introduction of this band might be due to strain induced by creation of subsurface O-vacancies [48]. In Fig. 5.7 (a), this peak is induced as an effect of Y as dopant, but in Fig. 5.7 (b), this peak is induced only at higher amount of Zn doping, representing that subsurface O-vacancies are absent at low concentration of Zn. The 8%Zn has more intensity which indicates large amount of subsurface O-vacancies. In Fig. 5.7 (c), for (Y, Zn) co-doped samples, this peak has large intensity for 4%Zn4%Y which shows that it has large amount of sub-surface oxygen vacancies. The above results illustrate that doping with large ionic radii induces more strain in the lattice. These subsurface O-vacancies play a vital role in photocatalytic activity by providing chain of linear cluster of O-vacancies on the strongly reduced surface [53].

5.3.6 Photodegradation of dye

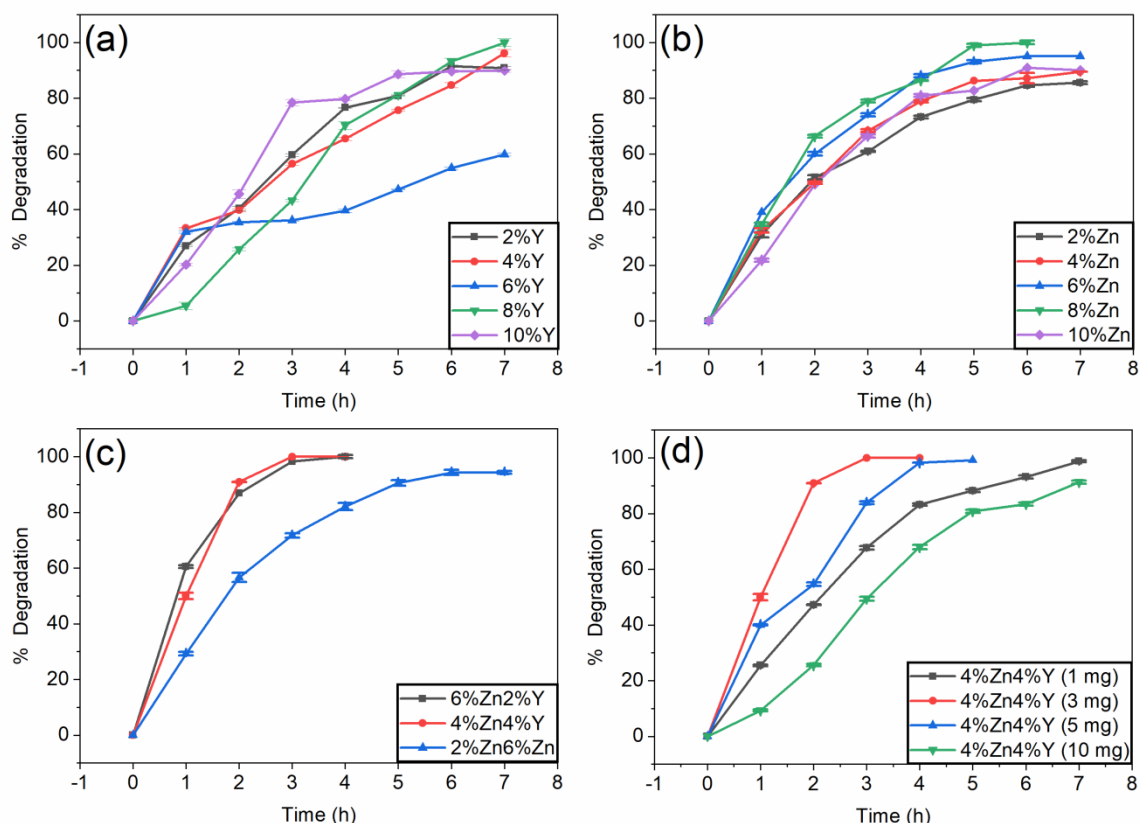


Fig. 5.8: Percentage degradation of CV dye with the help of (a) Y-doped CeO_2 , (b) Zn-doped CeO_2 , (c) (Y, Zn) co-doped CeO_2 and (d) effect of catalyst concentration (3 mg (catalyst dosage), 1 mg/L (CV dye concentration), 110 W/m^2 (light intensity) and $\lambda_{\text{max}} = 591 \text{ nm}$.

Fig. 5.8 (a-c) represents the photocatalytic degradation efficiency for removal of crystal violet dye in the presence of Y, Zn doped and co-doped synthesized CeO_2 under UV-visible irradiation in a self designed photo-reactor. Fig. 5.8 (a, b) represents photocatalytic removal of CV dye by Y and Zn doped CeO_2 samples, respectively. It can be observed from Fig. 5.8 (a), that photocatalytic activity does not follow any significant trend of removal of dye as an effect of Y as dopant. It can be explained from Raman spectra that I_{IV}/I_{EV} is not following any pattern of increase or decrease with increasing concentration of Y. Among all the synthesized samples, 8%Y has shown highest activity due to creation of optimum amount of Ce^{3+} , which resulted in highest photocatalytic activity among all Y-doped samples as has been discussed in Raman section. However, 6%Y shows lower activity although it has higher concentration of O-vacancies due to creation of Ce^{3+} . This is owing to increase in the oxygen vacancies beyond a particular concentration that inhibit the photocatalytic rate. Mittal et al. [14] also demonstrated that O-vacancies above an optimum amount increase the deep traps

which favors the fast electron-hole recombination center and causes the reduction in photocatalytic activity. Higher number of hydroxyl groups attached to surface act as trapping center for photogenerated holes and help to increase the photocatalytic activity [10], [55]. However, in the present case, there is no significant correlation of photocatalytic activity with these hydroxyl groups for Y-doped CeO_2 samples. Thus, it can be concluded that for Y-doped CeO_2 , O-vacancies are more important for photocatalytic activity. Fig. 5.7 (b) represents the photocatalytic activity for Zn-doped CeO_2 samples. It is observed that photocatalytic efficiency increases with Zn concentration, which is due to increase in O-vacancies with Zn-doping. However, 10%Zn has lower efficiency than 8%Zn which is due to lower amount of O-vacancies than 8%Zn (as discussed in section 5.2.5). So, based on above studies, it can be concluded that only optimum amount of O-vacancies are helpful for exhibiting good photocatalytic activity.

Fig. 5.8 (c) shows the effect of co-doping on photocatalytic activity for the removal of CV dye. It is observed that 6%Zn2%Y and 4%Zn4%Y show very efficient activity (100%) in 3h. Also, the activity of co-doped samples is found to be higher than Y, Zn-doped CeO_2 samples. Here, concentration of O-vacancies is more for co-doped samples (discussed in section 5.2.2 and 5.2.5) and these O-vacancies act as trapping centers for photogenerated electrons [14,55]. Among all the co-doped samples, 2%Zn6%Y exhibits the lower photocatalytic activity i.e. 94 %. As, observed from the Raman result, that extrinsic vacancies are also induced for 2%Zn6%Y, which may act as recombination center for photo excited charge carriers. It has been observed that Y-doped samples have shown 100 % degradation efficiency in 7h and Zn-doped samples have shown 100 % efficiency in 5h of UV-visible illumination of light. However, (Y, Zn) co-doped samples have shown 100 % removal of dye in 3h of UV-visible illumination. Thus, for achieving good photocatalytic activity under UV-visible illumination with low energy consumption (Y, Zn) co-doped samples are preferred.

Moreover, the catalytic activity of bare CeO_2 , Y_2O_3 and ZnO has been checked. The CeO_2 catalytic activity is found to be 76 % in 3h of UV-visible illumination and 97 % in 7h of UV-visible illumination. For Y_2O_3 , CV dye degradation was found to be 4.6 % in 3h and 7.07 % in 7h of UV-visible illumination. However, ZnO degrades 32.06 in 3h of UV-visible illumination and 63 % in 7h of UV-visible illumination. Hence, it shows Zn-doping and (Y, Zn) co-doping enhances the photocatalytic activity.

Thus, it can be concluded from the photocatalytic results for doped and co-doped samples that O-vacancies play an important role for photocatalytic efficiency. In literature, it is

reported that hydroxyl groups increase the photocatalytic efficiency. But in the present case, the oxygen vacancies solely are playing a vital role in photocatalytic activity.

The effect of the catalyst concentration is also studied. Fig. 5.8 (d) represents the effect of catalyst concentration on the photocatalytic activity. The photocatalytic activity of 4%Zn4%Y has been optimized by using different catalyst concentration. It has been found that photocatalytic activity increases for catalyst amount of 3 mg and then decreases with increased amount of catalyst. This observation can be explained on the basis of the excess amount of catalyst that leads to aggregation of particles. This aggregation may inhibit the production of charge carriers. Further, high amount of catalyst may block the absorbance of UV light due to increase in opacity of the suspension. This increases the light scattering and infiltration depth of the photons is diminished, thus leading to less photocatalyst activity [56]. So, reduction in the generation of hydroxyl radicals occurs which results in low photocatalytic activity [57]. Puma and Brucato [30] discovered that conversion of organic pollutants is maximum at optimum value of optical thickness (i.e. optimum value of catalyst particles). Beyond this optical thickness value, rate of conversion starts to decrease. Now, from the present results it is evident that % efficiency increased up to optimum value of catalyst particles. This might be due to fact that with increase in catalyst concentration, the scattering is more as of photons compare to their absorbance on the catalyst surface. Table 5.4 shows the extinction coefficient calculations at different catalyst concentration.

Table 5.4: Calculated extinction coefficient at different catalyst concentration.

Catalyst amount	Extinction coefficient of CV dye at different time intervals $\times 10^{-8} \text{ (M}^{-1}\text{cm}^{-1}\text{)}$								
	0HA	2HA	1HD	2HD	3HD	4HD	5HD	6HD	7HD
1 mg	9.91	2.49	6.57	4.89	3.46	2.12	1.10	0.77	0.44
3 mg	9.91	2.24	0.40	0	0	0	0	0	0
5 mg	9.91	4.81	2.93	2.16	0.77	0.08	0.04	0.04	0.04
7 mg	9.91	7.02	6.36	5.22	3.55	2.24	1.34	0.81	0.61

5.3.7 Kinetics of photodegradation of dye

The photochemical reaction kinetics are determined by pseudo first and second-order model. The photocatalytic decomposition of an organic molecule is very complex process, which includes different chemical reactions at a same time. Here, pseudo first order kinetic model describes the adsorption of dye molecule through physical bond i.e., hydrogen bond

formation between catalyst and dye molecule, which is referred as physisorption. While, the formation of chemical bond through O-species is present on the surface of catalyst which can be referred as chemisorptions and hence can be represented by pseudo second order kinetic model [59]. Both kinetic models can also be represented by following equations:

$$\text{First order} \quad -\ln\left(\frac{C}{C_0}\right) = k_1 t \quad (5.4)$$

$$\text{Second order} \quad \frac{t}{C} = \frac{1}{k_2 C_0^2} + \frac{t}{C_0} \quad (5.5)$$

where C_0 is the initial concentration, C is concentration at after time t , k_1 and k_2 are the rate constants for both kinetic models, respectively [60].

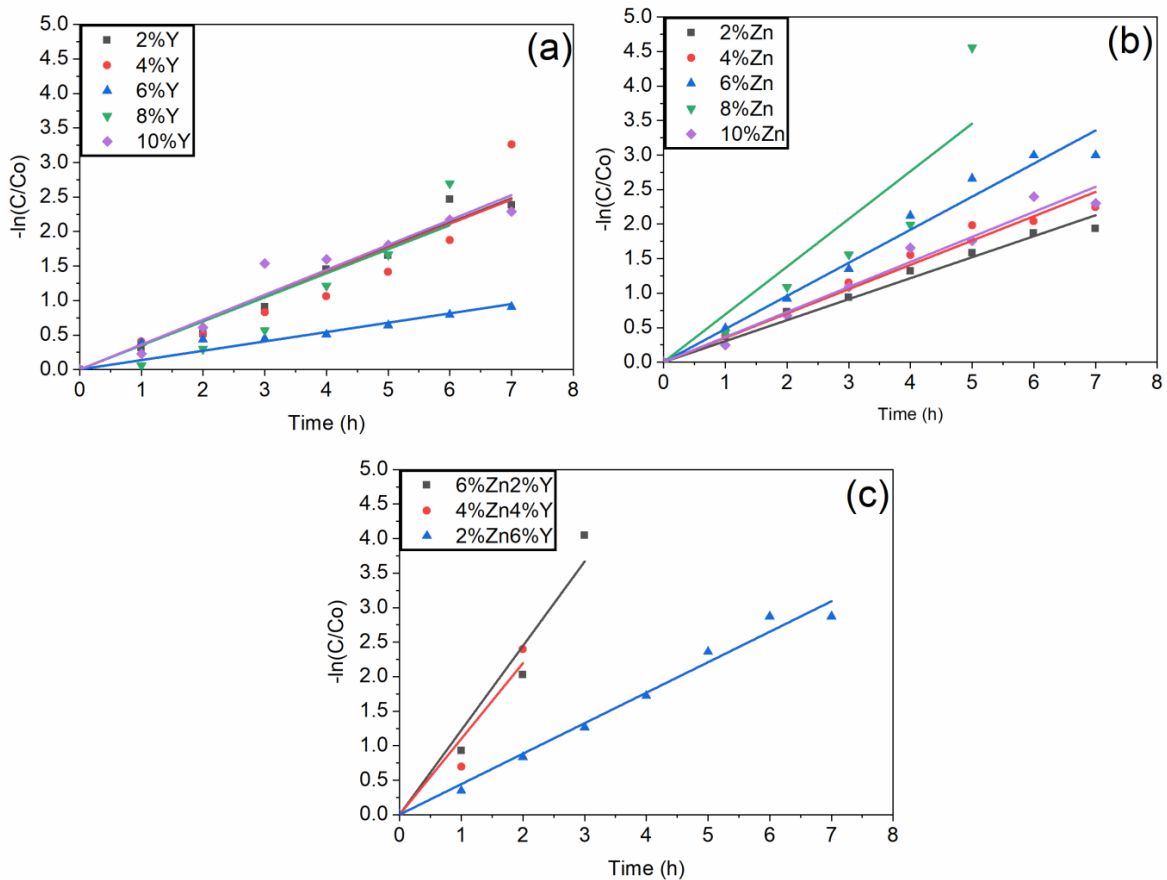


Fig. 5.9: Pseudo first order kinetics of CV dye using synthesized (a) Y-doped CeO_2 , (b) Zn-doped CeO_2 and (c) (Y, Zn) co-doped CeO_2 .

Both of models are implemented by plotting $-\ln\left(\frac{C}{C_0}\right)$ vs. t and t/C vs. t , in which regression coefficients (i.e. R^2) determine the quality of fitting and k_x represents the rate constant as shown in Fig. 5.9 and Fig. 5.10 [60,61]. The various parameters calculated for first and second order kinetics are summarized in table 5.5. Fig. 5.10 (a-c) represents the rate constant for first order kinetics of Y, Zn and (Y, Zn) co-doped CeO_2 samples, respectively. In Fig. 5.10 (a), rate constant is found to increase with increasing Y concentration, except 6%Y. As

discussed in Raman section, O-vacancies are found to increase for 6%Y, which act as recombination center for photo excited charge carriers. Similarly, in Fig. 5.10 (b), it is observed that rate constant k_1 is found to increase with increase in Zn-concentration except for 10%Zn. The 10%Zn has low amount O-vacancies as discussed earlier. The rate constant k_1 for (Y, Zn) co-doped samples is found to be more than doped samples, which is due to optimum amount of O-vacancies [14,23,62].

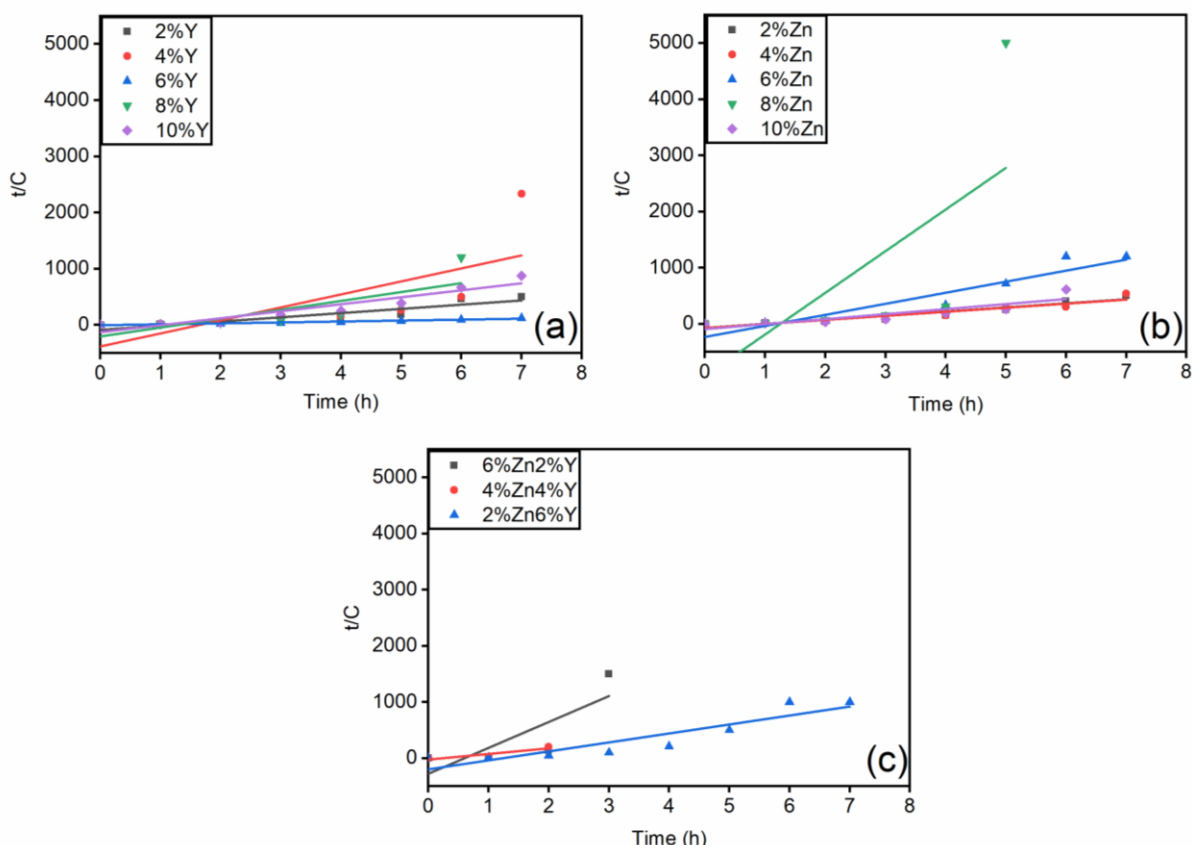


Fig. 5.10: Pseudo second order kinetics of CV dye with the help of (a) Y-doped CeO_2 , (b) Zn-doped CeO_2 , (c) (Y, Zn) co-doped CeO_2 .

The R^2 value is found to be more than 0.90 for first order kinetics. However, rate constant k_2 is found to be more than k_1 , but have low value of regression coefficients R^2 . Hence, it can be concluded that synthesized samples follow first order kinetics. The increase in crystallinity promotes the catalytic activity [63]. But in present case, there is no significant correlation of photocatalytic activity with the crystalline size. Thus, oxygen vacancies solely plays a vital role for enhancing the catalytic activity. Also, based on above studies it can be concluded that oxygen vacancies are more important than hydroxyl groups in photocatalytic activity.

Table 5.5: Rate constant for first and second order kinetics and corresponding R^2 values.

Sample ID	$k_1 (h^{-1})$	R^2	$k_2 (h^{-1})$	R^2
2% Y	0.354	0.98	60.253	0.80
4% Y	0.357	0.93	138.860	0.44
6% Y	0.135	0.95	28.520	0.94
8% Y	0.348	0.91	119.325	0.56
10% Y	0.360	0.98	115.673	0.89
2% Zn	0.303	0.99	70.763	0.89
4% Zn	0.352	0.98	67.829	0.85
6% Zn	0.479	0.99	164.742	0.84
8% Zn	0.691	0.90	590.554	0.35
10% Zn	0.362	0.98	82.258	0.73
6% Zn2% Y	1.23	0.98	765.440	0.51
4% Zn4% Y	1.10	0.96	366.659	0.63
2% Zn6% Y	0.441	0.96	127.190	0.81

5.3.8 Degradation mechanism

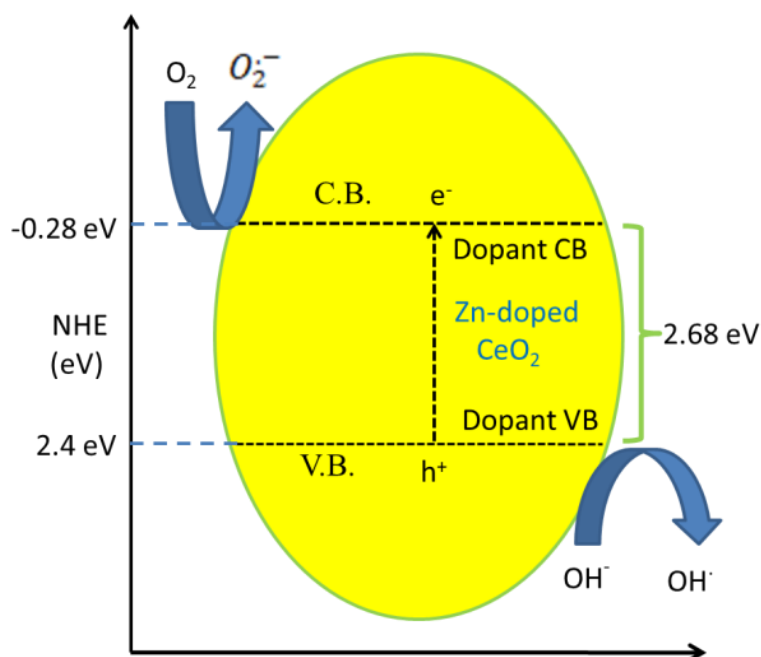


Fig. 5.11: Degradation mechanism for doped CeO_2 sample.

Fig. 5.11 shows the degradation mechanism for doped CeO_2 sample. Based on above observations a detailed mechanism responsible for photocatalytic efficiency is discussed. Whenever a light falls on semiconductor greater than its band gap, the following reactions (5.5-5.8) take place. The reactions described below represent the mechanism of photocatalysis [64].



If solution containing catalyst is irradiated by UV-visible light, electrons from the valence band (O_{2p}) are excited to the conduction band (Ce_{4f}). The excited photoelectron scavenge by dissolved oxygen in the water to form superoxide anions (O_2^-) and holes are scavenged by water molecules from dye solution to form hydroxyl radicals ($\text{OH}^\cdot$). These radicals are oxidative species and degrades the CV dye.

Thus, it can be concluded that co-doping of Y and Zn has improved the photocatalytic activity by many fold due to presence of optimum amount of O-vacancies.

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Photocatalytic studies of Zn-doped and (Y, Zn) co-doped CeO₂/CdS heterostructures for the removal of crystal violet dye**Overview**

The present chapter describes the synthesis of Zn-doped and (Y, Zn) co-doped CeO₂ and CdS heterostructures via co-precipitation route using different molar concentration of sodium sulphide. The synthesized samples were characterized by XRD, TEM, and EDS to study their structural, morphological, and elemental composition, respectively. XRD results confirmed the cubic phase for CeO₂ and wurtzite structure for CdS with average crystallite size in the range of 3-5 nm. The crystallite size of CdS heterostructures with (Y, Zn) co-doped CeO₂ sample is found to be slightly larger than Zn-doped CeO₂. The different modes of vibrations are observed in Raman spectra. The absorbance spectra and calculated bandgap exhibited the formation of UV-visible active compound. TEM image depicted the formation of agglomerated nanoparticles (NPs) having irregular shapes. The PL spectra exhibited the charge recombination in synthesized samples. The photocatalytic activity was studied via UV-visible spectroscopy technique by examining the absorbance spectra using crystal violet (CV) dye. The present chapter elucidates the photocatalytic activity of CdS heterostructures synthesized with undoped, Zn-doped and (Y, Zn) co-doped CeO₂ samples. Among the various synthesized samples, CdS heterostructures which were synthesized using Zn-doped CeO₂ exhibited the quick removal of CV dye within 2h under UV-visible illumination. The role of oxygen vacancies in accelerating the photocatalytic activity of CdS heterostructures with doped and co-doped CeO₂ NPs, Zn-doped and (Y, Zn) co-doped CeO₂/CdS heterostructures for the removal of crystal violet dye has been studied in detail.

6.1 Introduction

The wide band gap of CeO_2 inhibits the visible absorbance activity [1]. In order to facilitate the absorbance of visible light for generating the photo induced charge carriers for photocatalysis, heterostructures of different components are prepared. In photocatalysis, multiphase heterojunction improve the charge separation of photogenerated holes and electrons [2].

Sulfides have shown very good visible absorbance because of narrow bandgaps with slightly negative potential of conduction band. Compared to other semiconductors (TiO_2 , ZnO) with large bandgap, semiconductors which have narrow bandgap can also be excited with visible light radiation [3], [4]. CdS is very good photocatalyst due to its visible absorbance and suitable conduction band edge with band gap of 2.40 eV [1], [5]. The conduction band edges of CdS and CeO_2 are such that photogenerated electrons are thermodynamically transferred from CeO_2 to CdS by which CB edge of CdS acts as trapping center for photo excited electrons.

The photocorrosion is also observed in CdS as photocatalyst. This phenomenon arises when (i) sulphur ions are attacked by photogenerated holes and sulphur gets oxidized into elemental sulphur and (ii) photogenerated hole lead to anodic corrosion under irradiation (iii) defects created on the CdS surface during photocatalysis facilitate redox reactions on the surface under aerobic conditions. During photocorrosion, Cd^{2+} ions are leached into the solution. It can be prevented by using carbon materials which makes them UV-visible resistible, superior chemical stable and excellent light response [6], [7]. The coating of other material reduces the leaching of Cd^{2+} into solution.

In the present chapter, undoped, doped and co-doped CeO_2/CdS heterostructures have been successfully synthesized by co-precipitation method by using different molar ratio of sulphide ions. The photocatalytic properties of these compounds to degrade CV dye has been studied.

6.2 Synthesis of CdS heterostructures with Zn-doped and (Y, Zn) co-doped CeO_2 NPs

For the synthesis of CeO_2 , 0.3 M of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 ml of ethanol. In order to synthesize doped (8 mol% Zn) and co-doped (4 mol % Y, 4 mol % Zn) CeO_2 nanoparticles (NPs), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 30 ml of ethanol. The concentration of mother solution was maintained at 0.3 M. For the preparation of capped samples, known amount of thioglycerol (TG) was added into mother solution after the addition of metal nitrate salts to avoid the agglomeration [8]. Ammonia as a precipitating agent was added drop wise to the above solution until pH 7.5 was attained followed by

overnight aging. Finally, the precipitates were filtered and washed several times with water and ethanol. The precipitates of synthesized sample were dried at 80 °C for 24h. Thereafter, the dried precipitates were calcined at 300 °C for 2h.

For the preparation of CeO₂/CdS heterostructures, 0.5 g of already prepared CeO₂ was dissolved in 30 ml of ethanol. To the above CeO₂ NPs solution, 1% of 1-TG (thioglycerol) was added as a capping agent with respect to CeO₂ solution. The solution color immediately changed after the addition of 1-TG due to variation in sulphur vacancies in the precipitates [9]. The solution of known molarity of (CH₃COO)₂Cd.2H₂O and Na₂S was prepared. Firstly, the solution of (CH₃COO)₂Cd.2H₂O was added dropwise to the solution of CeO₂ NPs. Then, after half an hour of stirring, prepared solution of Na₂S was added drop wise to this solution. The solution turned to dark yellow with the addition of Na₂S solution. The solution was stirred continuously for 1h after the complete addition of Na₂S solution. The samples were aged for 24h. Further, the samples were filtered using Whatman filter paper and washed first with water then ethanol several times to remove the excessive S²⁻ ions from the precipitates [10]. Thereafter, precipitates were dried at 80 °C for 24h and then calcined at 300 °C for 2h in a muffle furnace. The synthesis conditions along with sample Ids are given in table 6.1.

Table 6.1: Details of samples along with their preparation conditions.

Samples Ids	Already prepared CeO ₂ taken	Cadmium acetate amount	Sodium sulfide amount
CCDS-2:1	CeO ₂	0.1 M	0.05 M
CCDS-1:1		0.1 M	0.1 M
CCDS-1:2		0.1 M	0.2 M
ZCCDS-2:1	CeO ₂ : 8 mol% Zn	0.1 M	0.05 M
ZCCDS-1:1		0.1 M	0.1 M
ZCCDS-1:2		0.1 M	0.2 M
ZYCCDS-2:1	CeO ₂ : 4 mol % Zn and 4 mol % Y	0.1 M	0.05 M
ZYCCDS-1:1		0.1 M	0.1 M
ZYCCDS-1:2		0.1 M	0.2 M

6.3 Effect of CdS heterostructures on CeO₂

6.3.1 XRD analysis

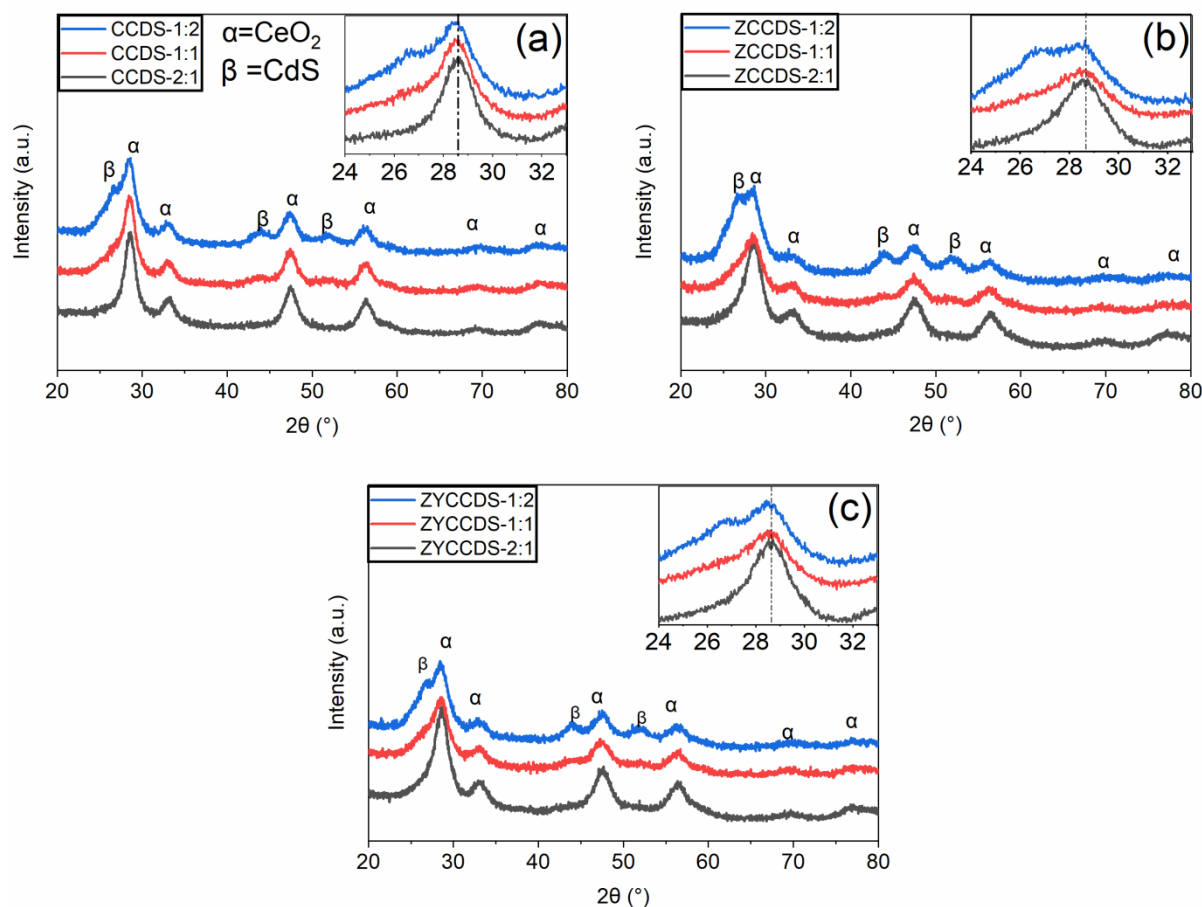


Fig. 6.1: XRD patterns of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO₂.

X-ray diffraction patterns of the synthesized CdS heterostructures with CeO₂, Zn-doped CeO₂ and (Y, Zn) co-doped CeO₂ are shown in Fig. 6.1 (a-c), respectively. XRD patterns are well matched with the standard International centre for diffraction data (ICDD) card no. 00-004-0593 for CeO₂ and 01-080-0006 for CdS, respectively. In Fig. 6.1 (a), it is noted that the peaks around 28.56°, 33.18°, 47.39°, 56.22°, 59.04°, 69.19°, 76.77° and 78.84° for CCDS-2:1 correspond to (111), (200), (220), (311), (222), (400), (331) and (420) planes, respectively which are related to CeO₂. The peaks around 26.50°, 43.83° and 51.50° correspond to (002), (110) and (200) plane of CdS, respectively. The increased peak intensity at 26.50°, 43.83° and 51.50° for CCDS-1:2, ZCCDS-1:2 and ZYCCDS-1:2 shows the formation of CdS. This observation confirmed the formation of mixed phase of CeO₂ and CdS. In the synthesized CeO₂/CdS heterostructures, there are strong characteristic peaks which correspond to CeO₂ phase suggests that synthesized sample is largely made up of CeO₂ and has higher crystallinity of CeO₂. However, relatively weak characteristic peaks corresponding to CdS

phase are due to low content of CdS than CeO₂. In Fig. 6.1 (a), peak around 28.60° for CCDS-2:1 shifts to lower 2θ angle 28.40° for CCDS-1:2. In Fig. 6.1 (b), peak at 28.60° for ZCCDS-2:1 shifts to 28.45° for ZCCDS-1:2. In Fig. 6.1 (c) also, peak around 28.60° for ZYCCDS-2:1 shifts to 28.45° for ZYCCDS-1:2. The shifting of this 2θ value to lower side indicates increase in d spacing and expansion of lattice. The shifting of this 2θ peak is attributed to interaction between CeO₂ and CdS [11]–[13]. The lower angle shifting might also be due to reversible conversion of Ce⁴⁺ to Ce³⁺, resulting in lattice expansion and leads to increase in d spacing [12]. The presence of small particles in the synthesized sample also contribute expansion to CeO₂ lattice because of higher concentration of Ce³⁺ having small particle size [14]. Thus, a peak shifting is integrated result of interaction between semiconductor, particle size variation and presence of Ce³⁺ in the crystal lattice.

Further, crystallite size was calculated by Scherer formula, i.e. $D = \frac{0.9\lambda}{\beta \cos \theta}$ [15], [16], where β is full width at half maxima (FWHM); $\beta = \sqrt{\beta_{observed}^2 - \beta_{instrumental}^2}$, λ=wavelength of incident X-ray (0.154 nm), D corresponds to average crystallite size. The calculated values of average crystallite size are given in table 6.2. The increased intensity of peak related to (002) plane of CdS shows the growth of CdS for CCDS-1:2, ZCCDS-1:2 and ZYCCDS-1:2. It is also observed that FWHM (β) value for CeO₂ peak which is related to (111) plane (2θ=28.60°) increases. The overall crystallite size is found to increase for CCDS-1:2, ZCCDS-1:2 and ZYCCDS-1:2. In Fig. 6.1 (b), FWHM (β) value for CdS heterostructures synthesized with Zn-doped CeO₂ samples is found to be more than undoped (Fig. 6.1 (a)) and (Y, Zn) co-doped CeO₂ (Fig. 6.1 (c)) samples showing restricted growth of synthesized heterostructures. The lower crystallite size for samples synthesized with Zn-doped CeO₂ might be due to lower ionic radii of Zn²⁺ than Ce⁴⁺ which creates distortion in the lattice [17]. The decrease in the crystallinity is due to periodicity alteration by Zn doping [18]. In Fig. 6.1 (c), the crystallite size of CdS heterostructures synthesized with (Y, Zn) co-doped CeO₂ samples is found to be more than Zn-doped CeO₂ samples (Fig. 6.1 (b)). The size of Y³⁺ (102 pm) is more than Zn²⁺ (74 pm) and Ce⁴⁺ (97 pm) [19]–[22]. Thus, doping of small ion (Zn²⁺) contracts the lattice and restricts the growth of CeO₂. However, when CdS samples are synthesized with (Y, Zn) co-doped CeO₂ (4 mol %Y, 4 mol % Zn), the increase in doping of large ion (Y³⁺) makes expansion in lattice. The doping of 4 mol % Y³⁺ (102 pm) and 4 mol % Zn²⁺ (74 pm) allows both expansion and contraction of the CeO₂ lattice. Thus, crystallite size

of CdS heterostructures synthesized with (Y, Zn) co-doped CeO₂ sample is slightly larger than Zn-doped CeO₂.

Table 6.2: The calculated crystallite size of samples.

Sample ID	Crystallite Size (nm)	Sample ID	Crystallite Size (nm)	Sample ID	Crystallite Size (nm)
CCDS-2:1	4.08±0.48	ZCCDS-2:1	3.05±0.27	ZYCCDS-2:1	3.45±0.58
CCDS-1:1	4.79±0.59	ZCCDS-1:1	3.33±0.67	ZYCCDS-1:1	3.60±0.64
CCDS-1:2	5.25±0.63	ZCCDS-1:2	3.80±0.58	ZYCCDS-1:2	3.95±0.50

6.3.2 FTIR analysis:

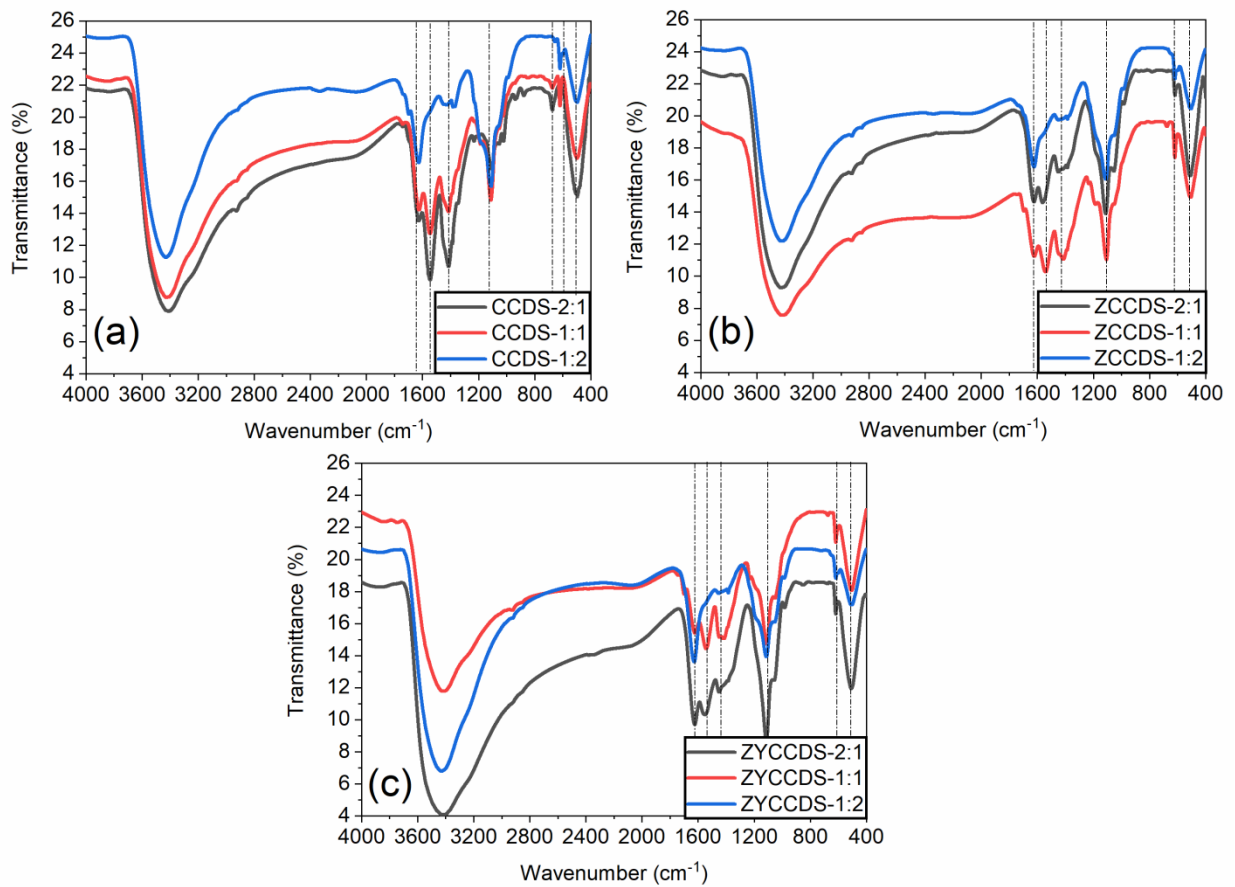


Fig. 6.2: FTIR spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO₂.

Fig. 6.2 (a-c) represents the FTIR spectra of synthesized CdS heterostructures with CeO₂, Zn-doped CeO₂ and (Y, Zn) co-doped CeO₂, respectively. The peak present at 500 cm⁻¹ corresponds to Ce-O (M-O) stretching mode and confirmed CeO₂ formation [23], [24]. In Fig. 6.2 (a), M-O peak at 499 cm⁻¹ for CCDS-2:1 shifts to 500 cm⁻¹ for CCDS-1:2. In Fig. 6.2 (c), M-O peak at 507 cm⁻¹ for ZYCCDS-2:1 shifts to 503 cm⁻¹ for ZYCCDS-1:1 and then

again shifts to 506 cm^{-1} for ZYCCDS-1:2. However, in Fig. 6.2 (b), this peak does not show any significant shifting. The higher and lower shifts are attributed to change in bond length as the bond length is inversely proportional to wavenumber [25]. The lower shift depicted the increase in bond length while the higher shift is due to shortening of bond length [26]. The change in bond length might be due to interaction of synthesized heterostructures as discussed in XRD section. The presence of peak around $3300\text{--}3450\text{ cm}^{-1}$ corresponds to surface hydroxyl groups or from M (metal)-OH groups including the --OH groups of 1-TG, which are very helpful for photocatalytic activity [22], [27]–[30]. The area of this peak is calculated using Origin software for better understanding of the role of hydroxyl groups in photocatalytic activity. The order of area is found to $\text{ZYCCDS-1:1} > \text{CCDS-2:1} > \text{ZYCCDS-1:2} > \text{CCDS-1:1} > \text{ZCCDS-2:1} > \text{CCDS-1:2} > \text{ZCCDS-1:2} > \text{ZCCDS-1:1}$. The peaks around 618 and 673 cm^{-1} are attributed to Cd-S stretching vibrations [31], [32]. The presence of these peaks signifies the presence of CdS in the synthesized heterostructures. The peak at 1050 cm^{-1} might be due to intrinsic hygroscopic nature of CeO_2 [33], [34]. The peaks around $1550\text{--}1560\text{ cm}^{-1}$ and 1430 cm^{-1} (symmetric and antisymmetric respectively) are due to presence of acetate group on the surface of synthesized sample [32], [35], [36]. The peak intensity also becomes less for CCDS-1:1, ZCCDS-1:1 and ZYCCDS-1:1 and disappears for CCDS-1:2, ZCCDS-1:2 and ZYCCDS-1:2. This might be due to more Na_2S added to solution as more S^{2-} combined with Cd^{2+} ions and forms CdS and hence reduces the acetate group peak intensity. The peak at 1630 cm^{-1} is attributed to adsorbed water from the atmosphere [23]. The absence of peak for TG at 2555 cm^{-1} is due to of TG molecule de-protonation and attachment to metal-atom [8]. Thus, FTIR results confirmed the presence of both CeO_2 and CdS formation in the synthesized sample. The different bands and functional groups are given in table 6.3.

Table 6.3: Peak assignments for all samples with different bonds.

Wavenumber (cm^{-1})	Functional group and type of vibration	References
500	Ce-O	[23], [24]
3300-3450	Hydroxyl group	[22], [27]–[30]
618, 673	Cd-S stretching	[31], [32]
1050	Intrinsic hygroscopic nature	[33], [34]
1550-1560	Symmetric stretching of acetate group	[32], [35], [36]

1430	Antisymmetric stretching of acetate group	[32], [35], [36]
1630	Adsorbed water from atmosphere	[23]
2555	S-H group from 1-TG	[8]

6.3.3 UV analysis:

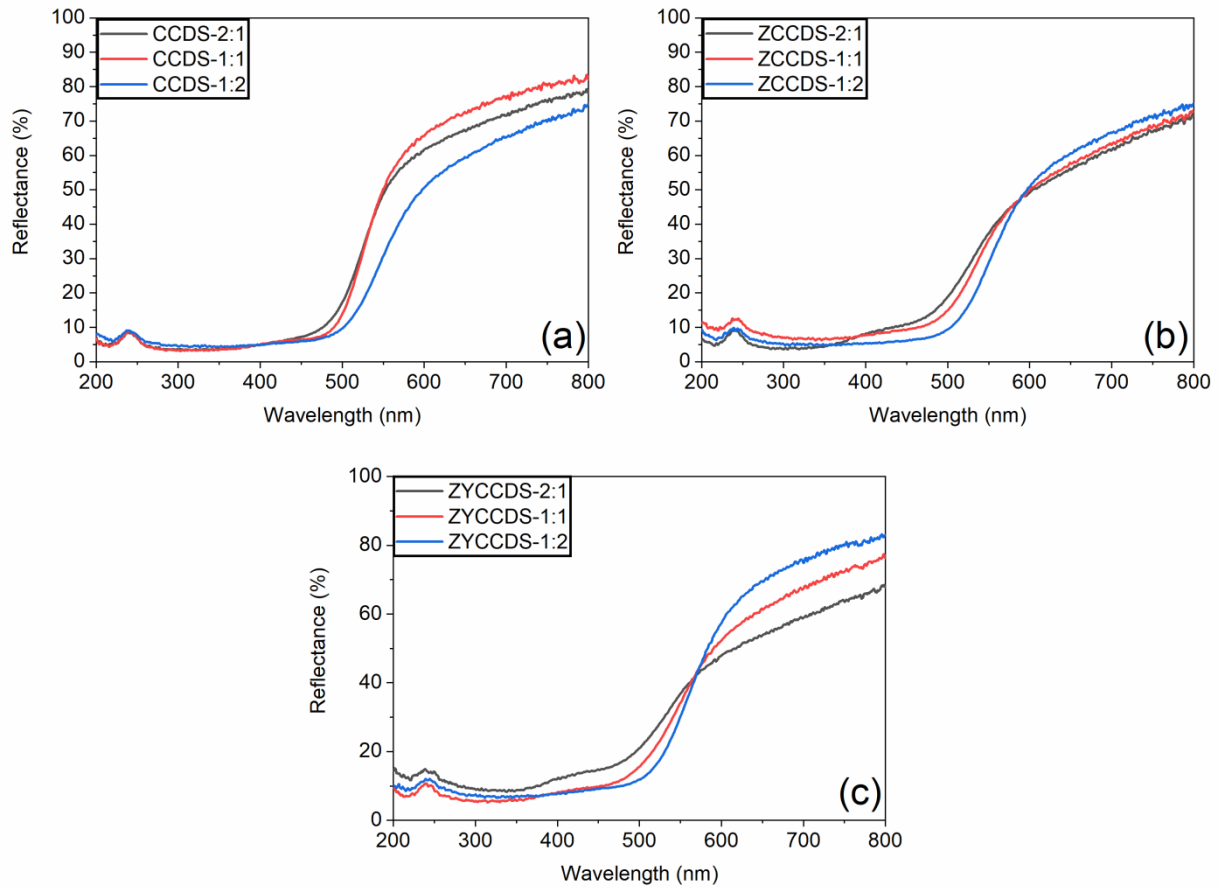


Fig. 6.3: UV-Reflectance spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO_2 .

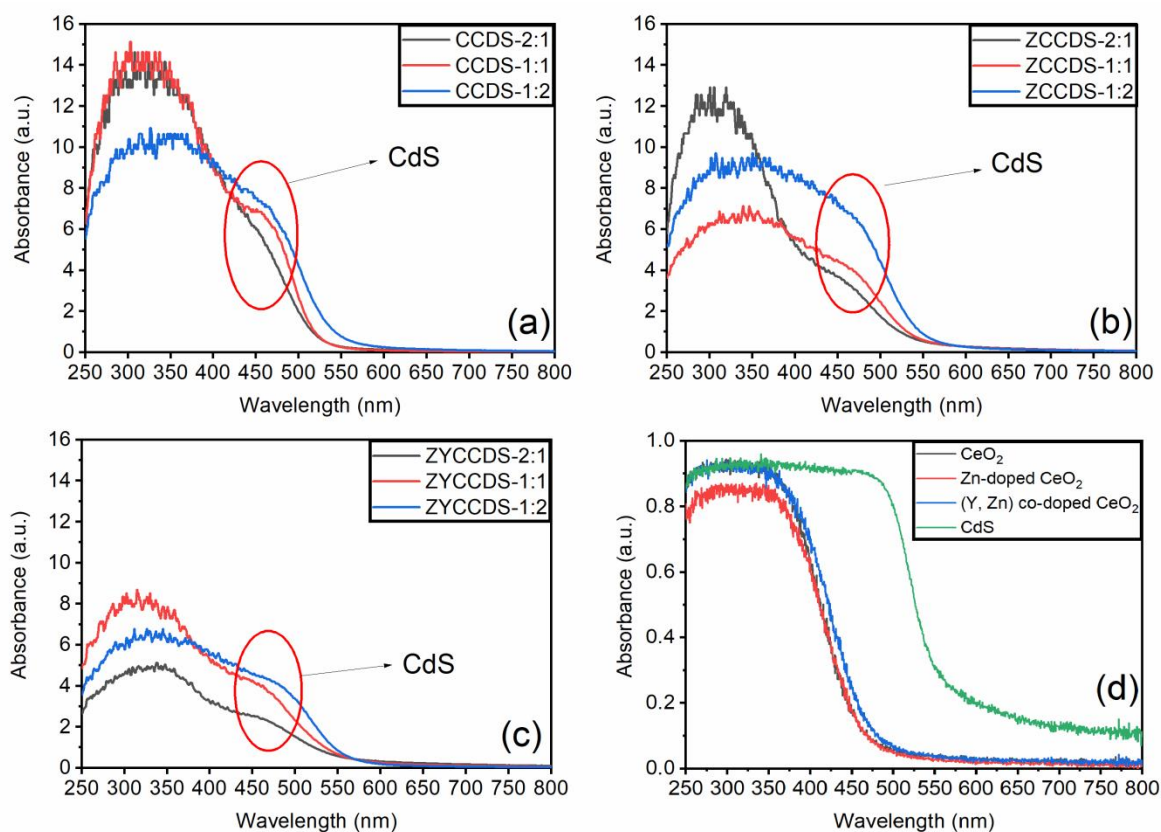


Fig. 6.4: UV-absorbance spectra of CdS heterostructures with (a) undoped, (b) Zn-doped, (c) co (Y, Zn)-doped CeO₂ and (d) UV-absorbance spectra for undoped and doped CeO₂.

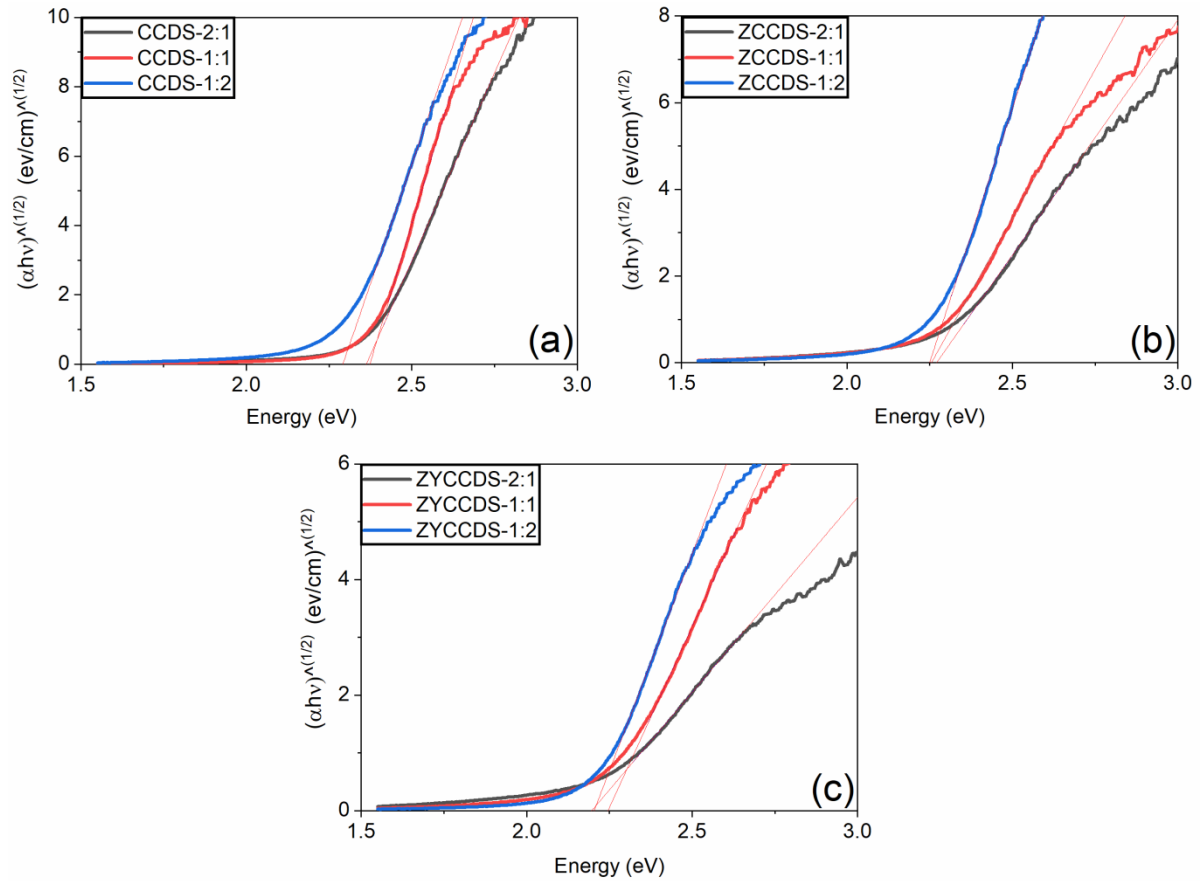


Fig. 6.5: Tauc's plot of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO₂.

UV-vis diffused reflectance spectra were taken to study the optical properties of the synthesized samples [37]. Fig. 6.3 (a-c) shows the reflectance spectra of synthesized CdS heterostructures with undoped CeO₂, Zn-doped CeO₂ and (Y, Zn) co-doped CeO₂ samples, respectively. The Kubelka-Munk function is used to convert diffuse reflectance spectra into absorption spectra [38]. Fig. 6.4 (a-c) shows the absorption spectra of CdS heterostructures with undoped, Zn-doped and (Y, Zn) co-doped CeO₂ samples, respectively. The absorption spectra consist of two peaks, one in UV-region and other in visible region. The absorption peak in UV-region is due to CeO₂ because of its wide band gap, while absorption peak in the visible region is due to CdS because of its narrow band gap ranging from 1.9 eV to 2.5 eV [39]. The absorption peak in the UV-region is attributed to the charge transfer between O²⁻ (2p) to Ce⁴⁺ (4f), while the peak in the visible range arises due to electronic transition from S²⁻ (3p) to Cd²⁺ (4d) [40], [41]. Thus, the formation of heterostructures is also confirmed from UV-visible absorption spectra.

As shown in Fig. 6.4 (a), absorption peak at 317 nm for CCDS-2:1 shifts to 332 nm for CCDS 1:2. In Fig. 6.4 (b), the absorption peak at 310 nm for ZCCDS- 2:1 shifts to 342 nm

and 343 nm for ZCCDS-1:1 and ZCCDS-1:2, respectively. However, as observed from Fig. 6.4 (c), the absorption peak at 337 nm observed for ZYCCDS-2:1 shifts to 315 nm and 328 nm for ZYCCDS-1:1 and for ZYCCDS-1:2, respectively. It is observed that maximum absorbance showing red shift is for CCDS-1:2 and ZCCDS-1:2. The energy gradient on the interface has been provided by synthesized CdS heterostructures with CeO₂ which causes shift in absorbance peak [38], [40]. The low charge transfer and low energy gradient between CeO₂ and CdS is also responsible for blue shifting.

Tauc's equation; $(\alpha h\nu) = A(h\nu - E_g)^n$, where E_g is the band gap of compound, α is the absorption coefficient which is extracted from %R value from reflectance spectra and $n=1/2, 2, 3/2$ and 3 correspond to direct, indirect, forbidden direct and forbidden indirect transitions, respectively has been used to determine the band gap of synthesized samples [42]. Fig. 6.5 (a-c) shows indirect value using tauc's plot [19]. The indirect value of band gap is calculated by extrapolation of straight-line portion of $(\alpha h\nu)^{1/2}$ to the x-axis where $(\alpha h\nu)^{1/2}$ is 0. The indirect band gap has been calculated for all samples and is shown in table 6.4.

Fig. 6.5 (a-c) shows the calculated band gap of CdS heterostructures with undoped CeO₂, Zn-doped CeO₂ and (Y, Zn) co-doped CeO₂ samples. The calculated band gaps are found in the range of 2.19 eV to 2.36 eV. It is observed that reduced band gap heterostructures of CeO₂ and CdS leads to increase the visible absorbance efficiency [43]. In Fig. 6.5 (a, c), it is observed that band gap value first increases for CCDS-1:1 and ZYCCDS-1:1 and then decreases for CCDS-1:2 and ZYCCDS-1:2. However, in Fig. 6.5 (b), band gap value is found to decrease for ZCCDS-1:1 and ZCCDS-1:2. The red-shift in the band gap value is due to the fact that synthesized CdS heterostructure with CeO₂ creates an intermediate impurity band level below the minima of conduction band (Ce4f) of CeO₂ [11]. This may be due to induced O-vacancies [40], [44]. The O-vacancies which are created due to presence of Ce³⁺ makes red shift in the band gap [19]. In these heterostructures, the size effect and also quantum confinement allow further delocalization of the electronic wave function causing blue shift in the band gap [45]. Moreover, decrease in Ce³⁺ concentration also makes blue shift in the band gap value [19]. Thus, the red or blue shift in the band gap is due to cumulative effect of lattice defect and quantum confinement [46], [47]. The extinction coefficient of CV dye was calculated after degradation with different catalyst by using following formula:

$$\text{Optical thickness} = \epsilon cl \quad (6.1)$$

Where, ϵ and c are the extinction coefficient and the molar concentration of dye solution and l is the length of cuvette used. As expected that the variation of extinction coefficient is in line with the variation in optical thickness as given in appendix C.

Table 6.4: Calculated bandgap values and extinction coefficient of CV dye degraded with synthesized samples.

Sample Id	Band gap (eV)	Extinction coefficient of CV dye at different time intervals $\times 10^{-8}$ ($M^{-1}cm^{-1}$)							
		0H	2HA	0.5HD	1HD	1.5HD	2HD	2.5HD	3HD
CCDS-2:1	2.36	12.61	4.53	3.02	2.08	0.98	0.28	0.16	0.12
CCDS-1:1	2.37	12.61	4.44	2.65	1.63	0.77	0.28	0.040	0.040
CCDS-1:2	2.29	12.61	4.20	2.12	1.63	1.02	0.65	0.49	0.03
ZCCDS-2:1	2.27	12.61	3.34	2.04	1.42	0.69	0.44	0.28	0.12
ZCCDS-1:1	2.25	12.61	4.24	1.67	0.89	0.32	0.16	0	0
ZCCDS-1:2	2.24	12.61	3.02	0.93	0.65	0.24	0	0	0
ZYCCDS-2:1	2.19	12.61	3.51	2.61	1.51	0.85	0.40	0.16	0.16
ZYCCDS-1:1	2.24	12.61	4.24	2.32	1.51	1.10	0.77	0.53	0.53
ZYCCDS-1:2	2.20	12.61	3.26	1.06	0.73	0.24	0.16	0.12	0.12

6.3.4 TEM analysis:

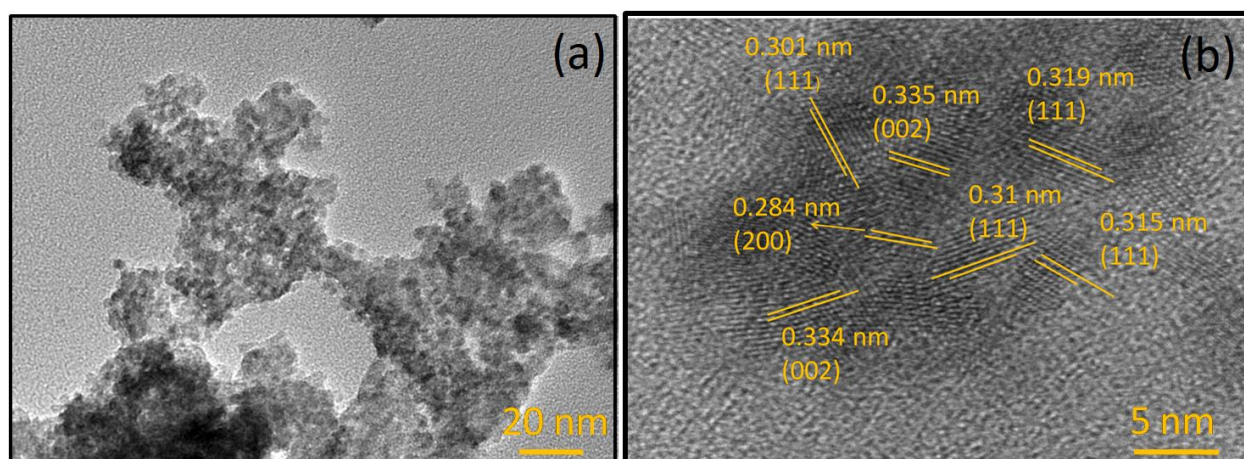


Fig. 6.6: (a) TEM and (b) HRTEM image of ZCCDS-1:1.

Fig. 6.6 (a) shows the TEM image and (b) HRTEM showing lattice fringes of ZCCDS-1:1 sample. Fig. 6.7 (a) represents TEM image of ZYCCDS-1:1 sample and Fig. 6.7 (b) represents HRTEM image of the same. The morphological results reveal agglomerated particles in both samples. Fig. 6.6 (a) shows that the particles are agglomerated with no proper symmetry. However, Fig. 6.7 (a) shows that most of the particles are spherical. The capping agent cover the NPs and prevents them from coalesce [8]. The agglomeration of NPs is because NPs become more stable by minimizing the surface area and allow crystallite to grow [50], [51]. The average particle size is calculated using *ImageJ* software and found to be 3.7 nm and 4.2 nm for ZCCDS-1:1 and ZYCCDS-1:1, respectively. The crystallite size calculated from XRD analysis is 3.33 nm and 3.6 nm for ZCCDS-1:1 and ZYCCDS-1:1, respectively which is comparable to particle size calculated from TEM analysis. The small variation in crystallite size and particle size is because of the agglomeration observed in the

sample. The fringe width was measured using *ImageJ* software [52]. The d-spacing has been calculated at different locations and found to be 0.301 nm, 0.319 nm, 0.315 nm, 0.284 nm and 0.335 nm. The calculated fringe width values are matched with XRD ICDD cards. The plane corresponding to fringe width of 0.31 nm and 0.284 nm are for (111) and (222) planes of CeO₂, card no. 00-004-0593, respectively. Hence, it confirmed the formation of cubic fluorite structure of synthesized CeO₂ samples. The 0.335 nm fringe width corresponds to (002) plane of wurtzite of CdS card no. 01-080-0006. In the XRD spectrum, less intensity peak is observed at 26.45° which is related to (002) plane of Wurtzite CdS. However, in HRTEM the fringes which correspond to (002) plane of CdS phase are clearly visible. These clear and distinct fringes exhibit crystalline nature of both CeO₂ and CdS [38]. Thus, formation of mixed phase has been confirmed from above analysis.

The presence of different elements has been monitored by elemental profile. Fig. 6.7 (c-h) shows the elemental mapping profile of S, Ce, O, Zn, Y and Cd, respectively for ZYCCDS-1:1. The elemental mapping reveals fine distribution of all the elements for the synthesized sample. This depicts no segregation of elements in the synthesized nanoparticles.

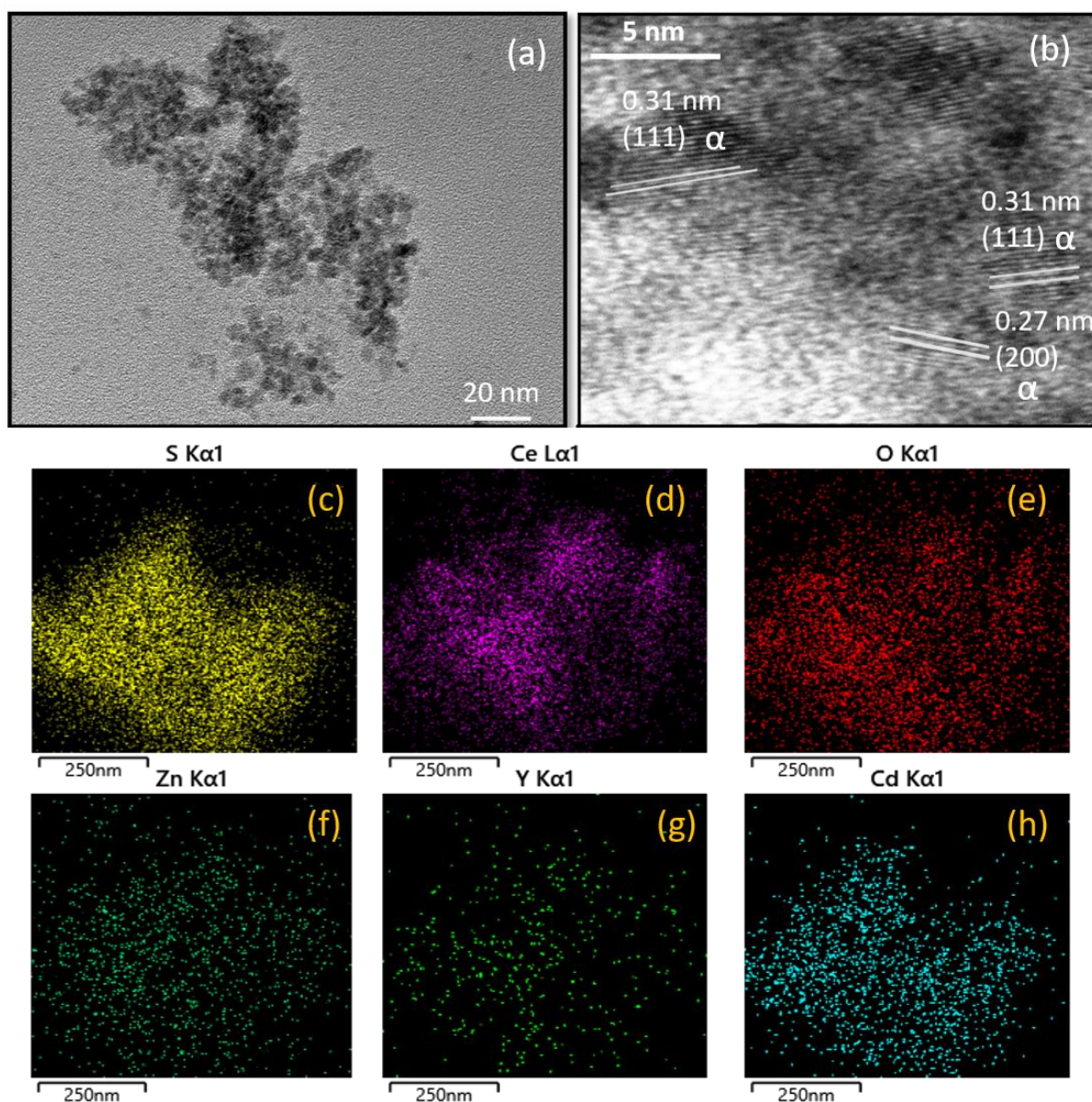


Fig. 6.7: (a) TEM image (b) HRTEM image, (c) mapping of S, (d) Ce, (e) O, (f) Zn, (g) Y and (h) Cd of ZYCCDS-1:1.

6.3.5 EDS analysis

Fig. 6.8 (a, b) shows the EDS spectra of ZCCDS-1:1 at different areas. It shows the presence of peaks corresponding to Ce, Cd, Zn, O and S elements. Thus, presence of all elements have been also confirmed from EDS analysis. No other impurity elements are detected. Hence, Zn-doped CeO_2 is co-anchored with the CdS nanostructures, which is consistent with the XRD results. The elemental analysis of ZCCDS-1:1 done at two different areas is given in table 6.5.

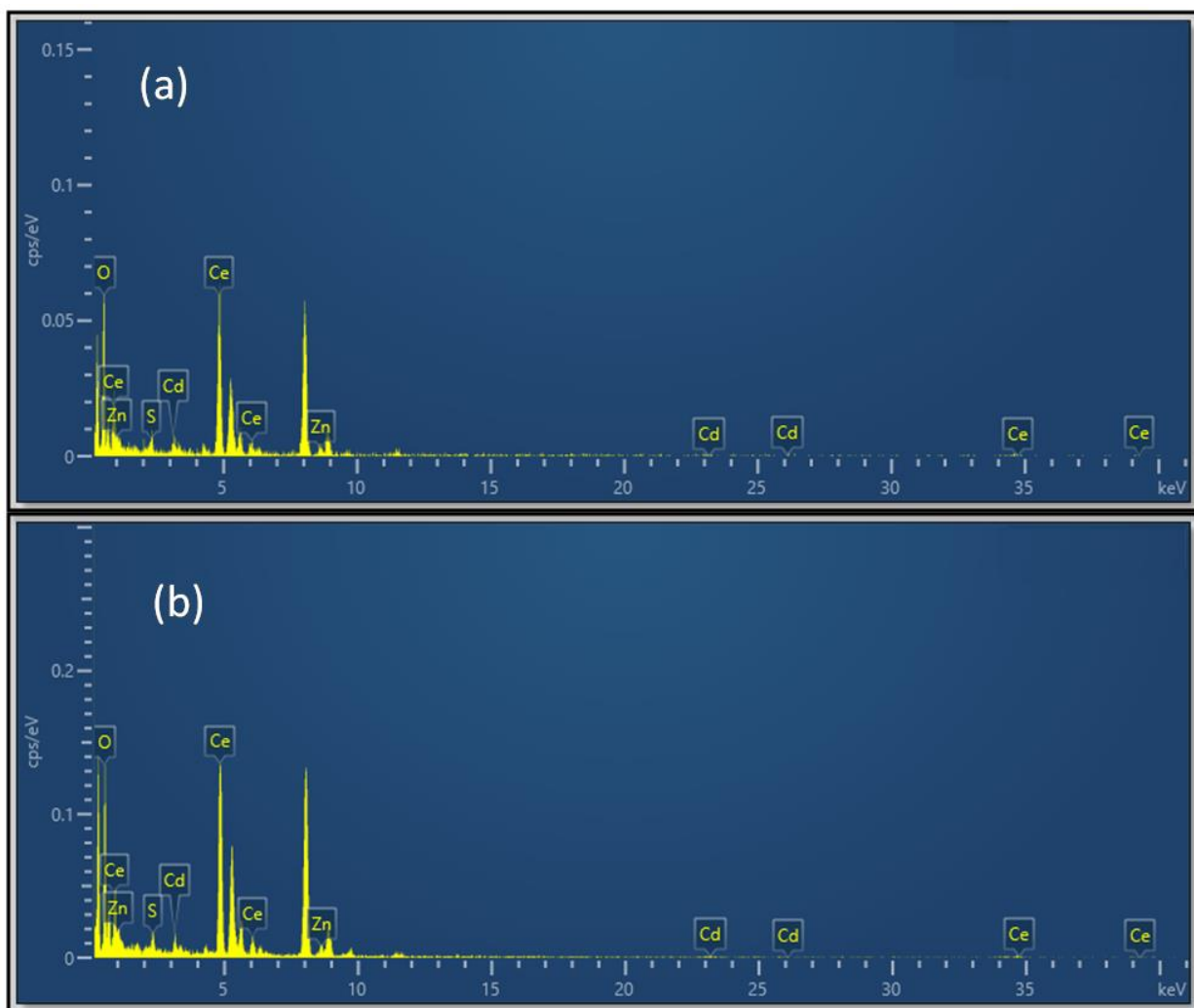


Fig. 6.8: (a, b): EDS spectra of ZCCDS-1:1 at different locations.

Table 6.5: Elemental composition of ZCCDS-1:1.

Elemental composition for spectra in Fig. 6.8			
Element	6.8 (a) Wt %	6.8 (b) Wt%	Average Wt%
O	21.65	20.06	20.85
S	1.68	1.31	1.49
Zn	1.76	0.56	1.16
Cd	4.51	2.81	3.66
Ce	70.4	75.26	72.83

6.3.6 Raman analysis

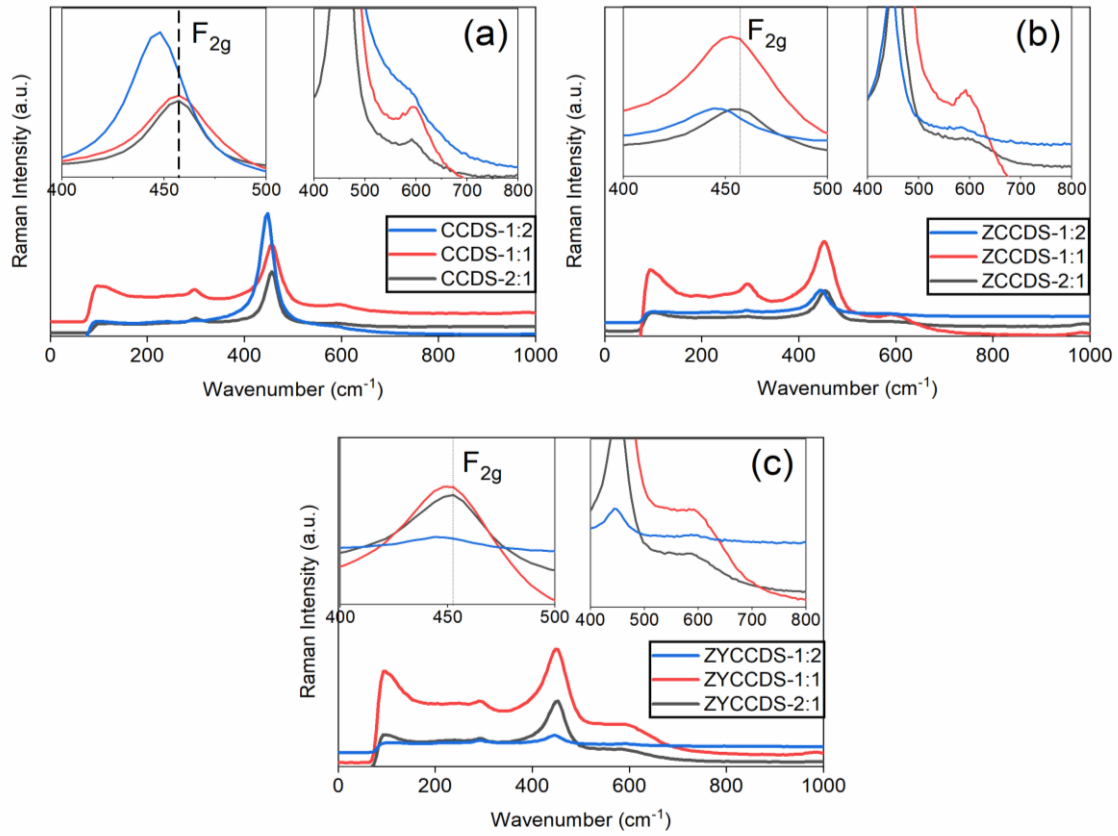


Fig. 6.9: (a) Raman spectra of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO₂.

Fig. 6.9 (a-c) shows the Raman spectra of synthesized CdS heterostructures with undoped CeO₂, Zn-doped CeO₂ and (Y, Zn) co-doped CeO₂ samples, respectively. All the given spectra consist of intensive peak around 450 cm⁻¹, corresponds to Ce-O₈ vibrational unit [53] [23]. This peak corresponds to F_{2g} Raman vibrational mode of CeO₂ which have cubic fluorite type structure with fm3m space group and originated from the tensional vibrational motion of the O-atoms that surrounds the cerium. It can be viewed as symmetrical stretching vibration of O-atoms around cerium ions which is independent of cation mass [21], [54]. The stretching around Ce ions helps to maintain the fluorite structure. Whenever there is change in any synthesis parameter, variation in Ce-O₈ vibrational mode is observed. The broadening and asymmetry of peak of Raman active mode depicts the presence of oxygen vacancy (whether extrinsic or intrinsic) [55]. The non-uniform particle size variation will cause strain in the lattice leading to variation in F_{2g} Raman mode [23], [56]. In Fig. 6.9 (a), peak (Ce-O₈) existing at 457 cm⁻¹ for CCDS-2:1 shifts to 445 cm⁻¹ for CCDS-1:2. In Fig. 6.9 (b), peak (Ce-O₈) at 456 cm⁻¹ for ZCCDS-2:1 shifts to 443 cm⁻¹ for ZCCDS-1:2. However, in Fig. 6.9 (c), peak (Ce-O₈) at 452 cm⁻¹ for ZYCCDS-2:1 shifts to 445 cm⁻¹ for ZYCCDS-1:2. Thus, this

band shows red shift with the formation of CdS phase as has been confirmed from XRD analysis. This red shift in F_{2g} band is due to the transformation of Ce^{4+} to Ce^{3+} oxidation state with the localized 4f state electron as lattice relaxation takes place after shifting [22], [44], [57]. Thus, it is concluded that CdS heterostructures which are synthesized with Zn-doped CeO_2 samples have shown large red shift which is due to creation of more O-vacancies for CdS heterostructures synthesized using Zn-doped CeO_2 . The more red shifting is also due to strain in the lattice as is also observed in XRD. The samples synthesized with Zn-doped CeO_2 have lower crystallite size which might be due to creation of Ce^{3+} . The higher content of Ce^{3+} may lead to amorphous nature of Ce_2O_3 [22]. Thus, Raman and XRD results are related to each other. Hence, F_{2g} peak gives the information of the ionic state of Ce having fluorite-type structure of CeO_2 .

Fig. 6.9 exhibits a low intensity peak (I_{IV}) around 600 cm^{-1} (D-band) that can be related to presence of O-vacancies near the surface of CeO_2 due to creation of Ce^{3+} caused by charge imbalance between Ce^{3+} and Ce^{4+} ions in CeO_2 [5]. The charge separation is caused by these oxygen vacancies as they act as electron acceptor for photogenerated electrons [19].

The peaks observed near 300 cm^{-1} and 600 cm^{-1} correspond to 1LO (longitudinal optical) and 2LO optical phonons, respectively for hexagonal CdS NPs [31]. The 1LO and 2LO peaks are the results of phonon vibrations [58]. In Fig. 6.9 (a-c), peak intensity of 1-LO mode is found to be more for CCDS-1:1, ZCCDS-1:1 and ZYCCDS-1:1 than CCDS-1:2, ZCCDS-1:2 and ZYCCDS-1:2 samples, respectively. The low intensity and broadening of the 1-LO peaks is related to scattering loss due to defects at the junction of heterostructures. The breakdown in long range translational order by smaller crystallite size also cause the reduced intensity for the synthesized CeO_2 /CdS heterostructures [59]. The above results confirmed the formation of fluorite CeO_2 structure and hexagonal phase of CdS in the synthesized heterostructures and also the formation of O-vacancies. Thus, formation of heterostructures is also confirmed from Raman results.

The relative ratio of areas are calculated for peaks present at F_{2g} (454 cm^{-1}) and in between $550\text{ to }600\text{ cm}^{-1}$, which show the relative concentration of O-vacancies [52], [60]. The area between $550\text{ to }600\text{ cm}^{-1}$ is a combined result of intrinsic (created due to presence of Ce^{3+}) and extrinsic O-vacancies (created due to introduction of dopants) [21]. This ratio tells about how much O-vacancies (intrinsic and extrinsic) are present in the CdS heterostructures synthesized with different dopants in CeO_2 .

The calculated value of peak area ratios ($A_O/A_{F_{2g}}$) is given in Table 6.6. In Fig. 6.9 (a-b), this ratio is found to increase with the formation and growth of CdS. However, in Fig. 6.9 (c), this

ratio is found to decrease with the CdS growth. The more O-vacancies lead to the formation of new networks and makes the pathway easy for charge transfer [22], [53], [61]. From, these analyses, it is apparent that ZCCDS-1:2 might be a useful compound for potential application in dye degradation. It is also observed that ZCCDS-1:2 has more O-vacancies concentration (15.03%) and ZCCDS-1:1 has less O-vacancies (14.38 %). Also, ZCCDS-1:2 has shown more red shift of F_{2g} band than ZCCDS-1:1 which is due to creation of more Ce^{3+} . It is also possible that peak induced near 600 cm^{-1} is due to 2-LO mode of CdS NPs as observed in Raman spectra. The higher number of O-vacancies created for ZCCDS-1:2 sample is attributed to many factors as discussed above. Apparently, it seems that ZCCDS-1:2 sample may provide higher degradation but it may also provide recombination center for photo-generated charge carrier [19].

Table 6.6: Position of F_{2g} peak (Raman active spectra) and relative peak area ratio.

Sample Id	F_{2g} peak position	$A_O/A_{F_{2g}}$	Oxygen vacancies (%)
CCDS-2:1	457	0.068	6.8
CCDS-1:1	457	0.099	9.9
CCDS-1:2	446	0.1305	13.05
ZCCDS-2:1	456	0.045	4.5
ZCCDS-1:1	452	0.1438	14.38
ZCCDS-1:2	442	0.1503	15.03
ZYCCDS-2:1	452	0.1363	13.63
ZYCCDS-1:1	450	0.115	11.5
ZYCCDS-1:2	441	0.099	9.9

6.3.7 PL spectroscopy

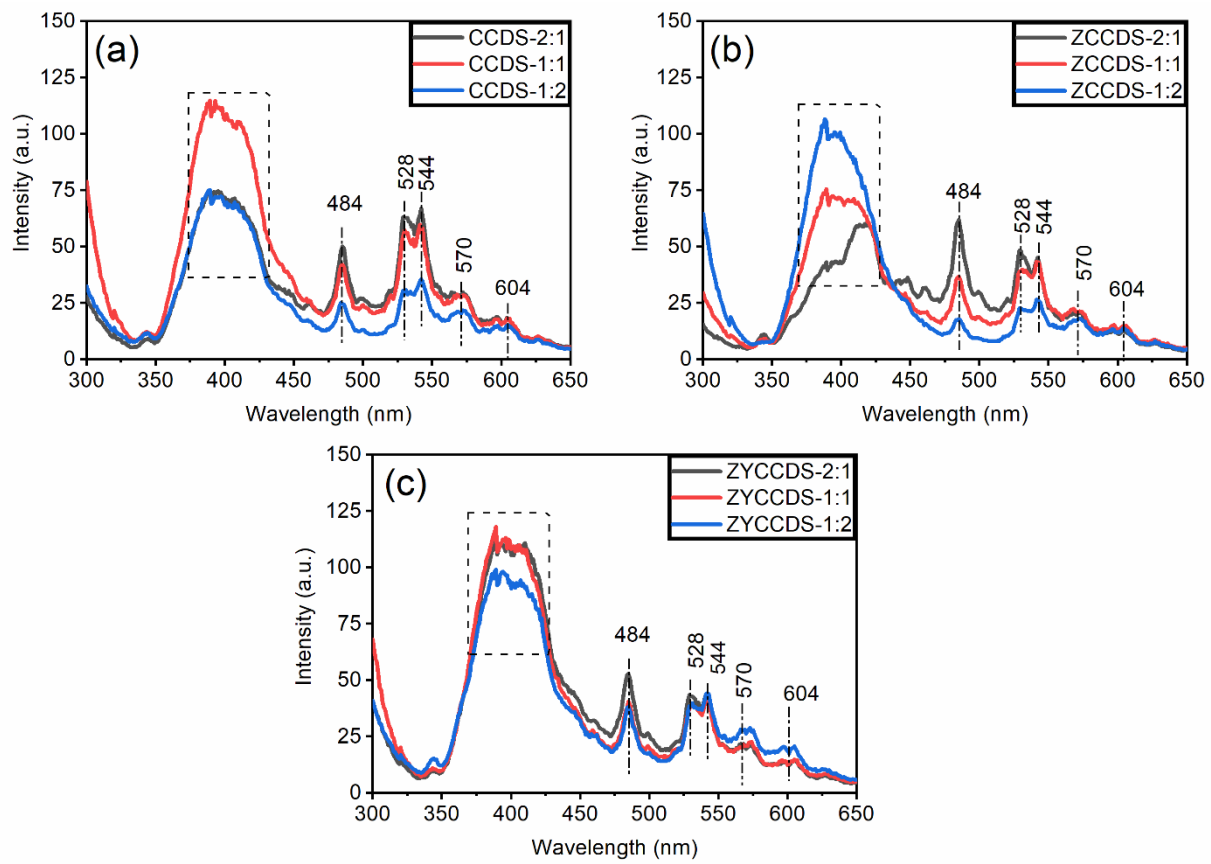


Fig. 6.10: PL spectra of CdS heterostructures synthesized using (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO_2 .

Fig. 6.10 (a-c) shows the PL spectra of synthesized CdS heterostructures with undoped, Zn-doped and (Y, Zn) co-doped CeO_2 , respectively at excitation wavelength of $\lambda_{\text{exc}}=250$ nm. The spectra consist of broad band in between 385 nm and 415 nm, originating from the defect states existing between Ce_{4f} and O_{2p} state and the O-vacancies which exists just below the conduction band Ce_{4f} [56], [62]–[64]. The broadening of peak is due to presence of impurity centers in the material as all the atoms do not emit the same spectra [56]. The peak intensity variation might be due to non-radiative transition. The peak at 484 nm is due to charge transfer from Ce_{4f} energy band level to O_{2p} energy band level [24]. The intensity of peak present at 484 nm decreases with the growth of CdS phase. This observation shows that the growth of CdS phase is inhibiting the charge recombination and also lower the recombination rates in O_{2p} and Ce_{4f} [65]. This variation in peak intensity might be plausible due to vacancy related defects or also due to transfer of photogenerated carriers between different semiconductors [66], [67]. The PL intensity is the result of recombination of charge carriers. Thus, lower PL intensity is due to decrease in the recombination rate [68]. The synergetic

effect between semiconductors of synthesized heterostructures also affects the PL intensity (luminescence quenching) [69]. The peaks present at 528 and 540 nm are due to the excitons or free charge carriers and trapped charge carriers at surface for CdS [32], [70], [71]. The recombination of holes formed in S1s band with electrons in Cd 4d (or 5s) band is observed from peak present at 570 nm [38]. In Fig. 6.10 (a-b), the reduced intensity of these peaks suggest the attachment of CdS with CeO₂ which favors the lower recombination of charge carriers. However, in Fig. 6.10 (c), peak intensity increases for ZYCCDS-1:2 which might be due to the high recombination of electrons Cd 4d (or 5s) with the holes (S 1s). The small peaks near 595 and 604 nm are assigned to recombination via surface defects [70], [72]. The high emission peak intensity is due to large probability of recombination in CdS. Thus, presence of CeO₂ and CdS is confirmed from PL emission spectra. Hence, formation of heterostructures is also confirmed from PL emission spectra.

6.3.8 XPS analysis

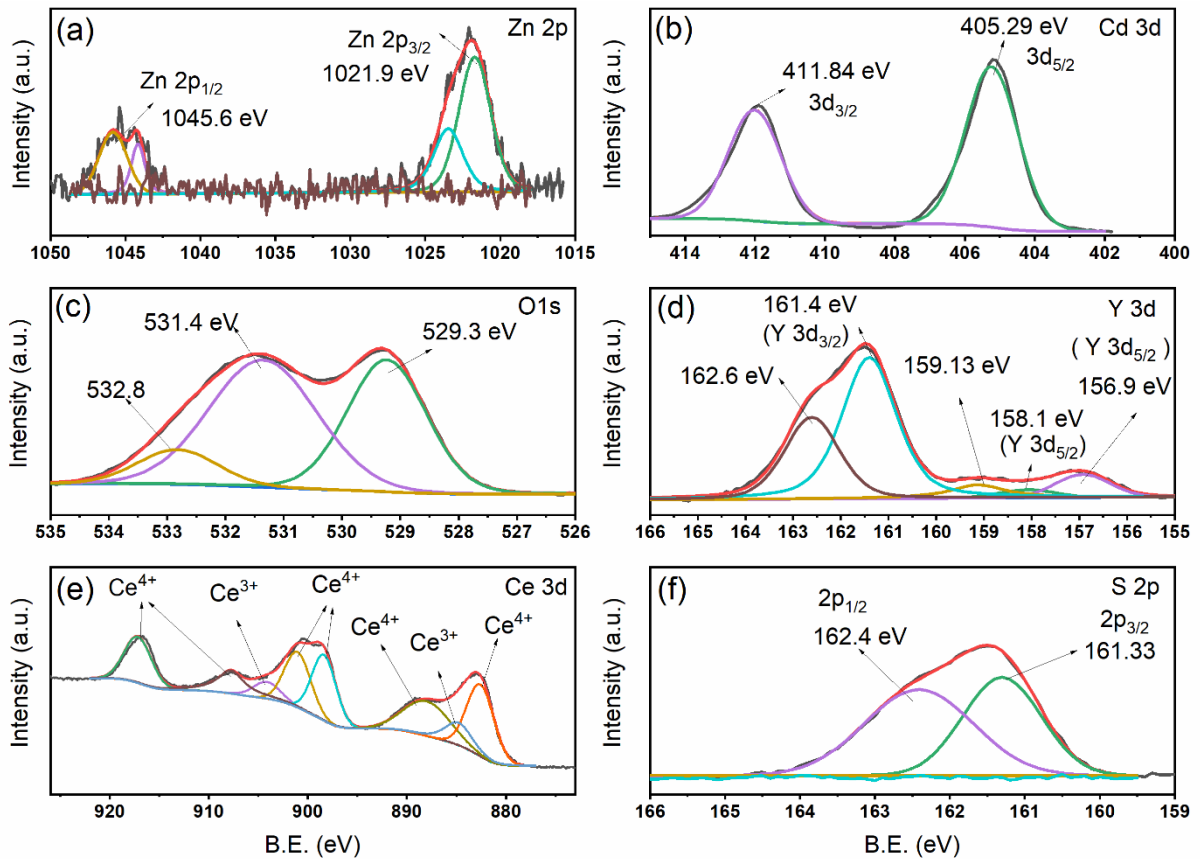


Fig. 6.11: XPS HR spectra of (a) Zn 2p (b) Cd 3d (c) O 1s (d) Y 3d (e) Ce 3d and (f) S 2p of ZYCCDS-1:1 sample.

The composition and various chemical states of elements has been confirmed from XPS [73], [74]. The corresponding HR spectra of sample ZYCCDS-1:1 for different elements are

shown in Fig. 6.11 (a-f). The various spectra of elements (Zn 2p, Cd 3d, O 1s, Y 3d, Ce 3d and S 2p) are shown in Fig. 6.11 (a-f), respectively.

The Ce 3d spectrum is composed of Ce^{3+} and Ce^{4+} . Further, Ce^{3+} concentration has been calculated from the formula: $Ce^{3+}/(Ce^{3+} + Ce^{4+}) = \text{area of } Ce^{3+} \text{ curves}/(\text{total area of } Ce^{4+} \text{ and } Ce^{3+})$. The concentration of Ce^{3+} as calculated is 11.84 %.

The O 1s electron spectrum of ZYCCDS-1:1 is shown in Fig. 6.11 (c). The peak around 529.3 eV is due $Ce^{4+}-O^{2-}$ lattice oxygen and the peak around 531.4 eV is attributed to lattice $Ce^{3+}-O^{2-}$. The surface hydroxyl groups or defect oxides are seen from peak present at 532.8 eV [9]. The Zn 2p spectra consist of two peaks i.e. at 1021.9 eV (Zn 2p_{3/2}) and at 1045.6 eV (Zn 2p_{1/2}). These peaks suggests the presence of Zn^{2+} in the synthesized sample [76]. The Cd 3d spectra (Fig. 6.11 (b)) consist of two peaks present at 405.29 eV (Cd 3d_{5/2}) and 411.84 eV (Cd 3d_{3/2}). The presence of Cd^{2+} on the surface of synthesized material has also been confirmed from splitting energy of 6.55 eV [65]. The peak present at 161.33 eV (S 2p_{3/2}) and 162.4 eV (S 2p_{1/2}) are the characteristics of S^{2-} of CdS NPs. The peaks present at (405 and 411 eV) and (161-163 eV) on deconvolution further confirm the presence of Cd-S bond in the synthesized compound. The peak present at 156.9 eV, 158.1 eV and 159.13 (Y 3d_{5/2}) shows the presence of Yttrium in the synthesized sample [77]. However, peak present at 161.4eV is due to Y 3d_{3/2} [78]. Thus, presence of various elements has been confirmed from the XPS HR-spectra.

6.3.9 Photodegradation of dye

The percentage degradation for all the synthesized samples has been calculated using peak absorption value at 591 nm for CV dye. The corresponding graphs showing % degradation are given in Fig. 6.12.

Fig. 6.12 (a-c) represents the photocatalytic activity of CdS heterostructures with undoped, Zn-doped and (Y, Zn) co-doped CeO₂ samples, respectively for the removal of CV dye. In Fig. 6.12 (a), photocatalytic activity of CCDS-1:1 is found to be more than CCDS-2:1 and CCDS-1:2. In Fig. 6.12 (b), photocatalytic activity of ZCCDS-1:1 and ZCCDS-1:2 are observed to be more than ZCCDS-2:1. This is due to creation of O-vacancies which are generated because of formation of Ce^{3+} as F_{2g} peak shows more red shift (from Raman section 6.3.6). This observation shows that O-vacancies are generated above optimum level for CCDS-1:2 and ZCCDS-1:2. Mittal *et al.* [19] observed that O-vacancies above optimum level act as recombination center for photo excited electrons.

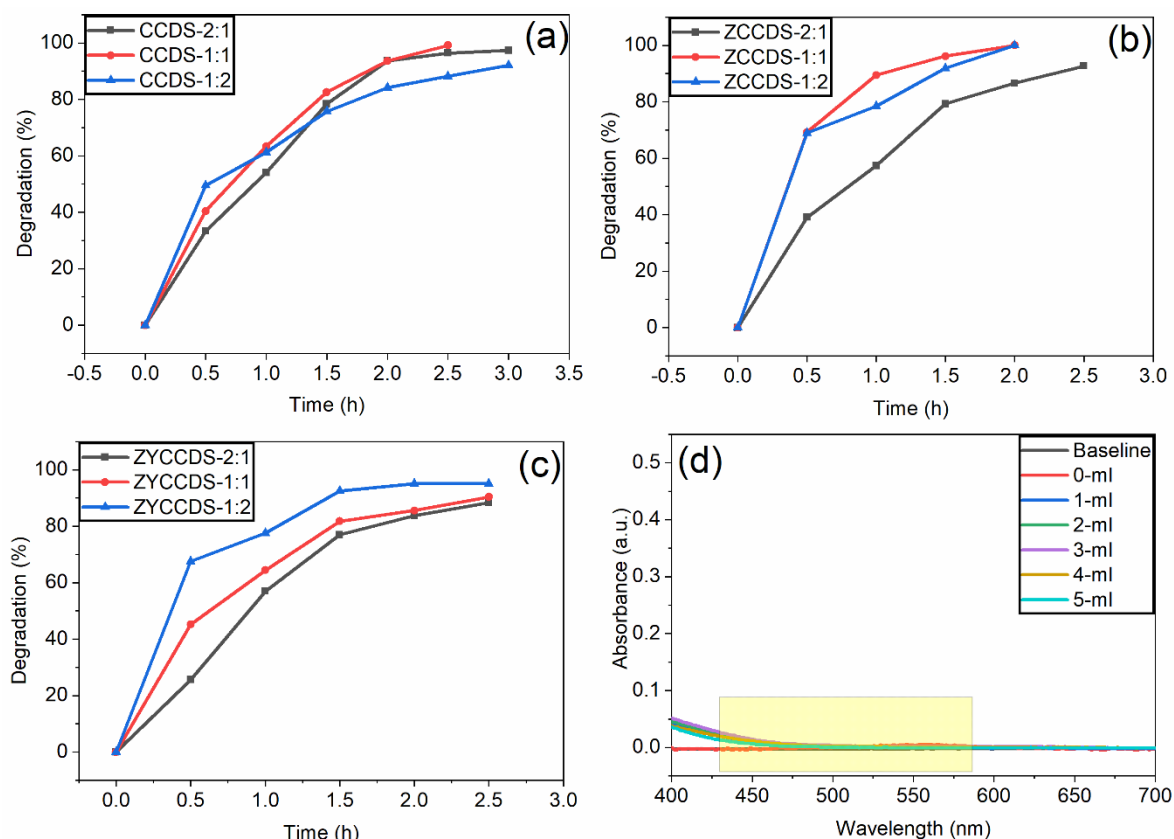


Fig. 6.12: Degradation of crystal violet dye by CdS heterostructures with (a) undoped, (b) Zn-doped, (c) (Y, Zn) co-doped CeO_2 (3 mg (catalyst dosage), 1mg/L (CV dye concentration), 110 W/m^2 (light intensity) and $\lambda_{\text{max}} = 591 \text{ nm}$ (d) leaching properties of Cd ion in photocatalysis.

Hence increased concentration of Ce^{3+} beyond an optimum level acts as deep trap which favors the fast recombination of charge carriers resulting in decreased photocatalytic activity. Also, it has been observed that the ratio A_O/A_{F2g} of O-vacancies for CCDS-1:2 and ZCCDS-1:2 is found to be more than CCDS-1:1 and ZCCDS-1:1, respectively which shows that total amount of O-vacancies (extrinsic and intrinsic) increases. This might be the reason for decrease in photocatalytic activity. As shown in Fig. 6.12 (c), the photocatalytic activity of ZYCCDS-1:2 is more than ZYCCDS-1:1. The calculated area ratio of A_O/A_{F2g} of ZYCCDS-1:2 is found to be less than ZYCCDS-2:1 and ZYCCDS-1:1. This is due to same reason as mentioned above that optimum amount of O-vacancies is helpful to enhance the catalytic activity. Further, the intensity of peak present at 484 nm starts to decrease with the growth of CdS (Fig. 6.10). This observation suggests the decrease in recombination of charge carriers for synthesized heterostructures. The hydroxyl group intensity (as confirmed from FTIR spectra) is found to be more for ZYCCDS-1:2 than ZYCCDS-1:1, which is very helpful for photocatalytic activity to provide dye sensitization [22], [27]–[30]. However, in Fig. 6.12 (b), photocatalytic activity of ZCCDS-1:2 is less than ZCCDS-1:1 despite of higher concentration

of hydroxyl groups (section 6.3.2). Thus, it is concluded that optimum amount of O-vacancies created due to conversion of Ce^{4+} to Ce^{3+} are more important for the enhancement in photocatalytic activity. The O-vacancies are important as they act as charge trapping center for photogenerated charge carriers but the higher amount of oxygen vacancies act as sink to photogenerated charge carriers [19], [79]. The increased number of oxygen vacancies above optimum level favors deep traps which limits the electron mobility due to charge recombination and decreases the photocatalytic activity [80]. For sample containing low amount of O-vacancies, shows their recombination with valence band holes. Thus, optimum amount of O-vacancies is useful for enhanced photocatalytic activity.

It is also observed that CdS heterostructures synthesized with Zn-doped CeO_2 (Fig. 6.12 (b)) have shown enhanced photocatalytic activity than other heterostructures which are synthesized with undoped CeO_2 (Fig. 6.12 (a)) and (Y, Zn) co-doped CeO_2 (Fig. 6.12 (c)). This observation is also based on O-vacancies as Zn-doped CeO_2 have optimum amount of O-vacancies (confirmed from Raman spectra) and stops the recombination of photoexcited charge carriers.

Moreover, the catalytic activity of Zn-doped CeO_2 , bare Y_2O_3 and ZnO has been also checked. The Zn-doped CeO_2 catalytic activity is found to be 77 % in 3h of UV-visible illumination and 98 % in 5h of UV-visible illumination. For Y_2O_3 , CV dye degradation was found to be 4.6 % in 3h and 7.07 % in 7h of UV-visible illumination. However, ZnO degrades 32.06 % in 3h of UV-illumination and 63 % in 7h of UV-illumination. Hence, heterostructures synthesized with CdS NPs enhances the catalytic activity. The above studies indicate that the optimum amount of O-vacancies, recombination of charge carriers and hydroxyl groups are helpful for enhanced photocatalytic activity.

Further, the leaching properties of Cd ion are studied using atomic absorption spectroscopy (AAS). After irradiation the sample for 2h under UV-visible illumination, the concentration of Cd^{2+} in the supernatant solution is less than 1 ppm. Moreover, the supernatants are also checked by addition of Na_2S solution (0.1 M). No change in color has been observed. Also, the solution after addition of Na_2S has been checked by UV-absorption spectroscopy (Fig. 6.12 (d)). A less intense peak is observed in the visible range which shows negligible leaching of Cd during photocatalysis. Further, with different amount of Na_2S solution (0.1 ml-0.5 ml), no change in absorbance occurs which shows that formation of CdS NPs has not occurred. This observation shows that the presence of cadmium ion is very less, indicating strong light resistance.

6.3.10 Effect of dye concentration

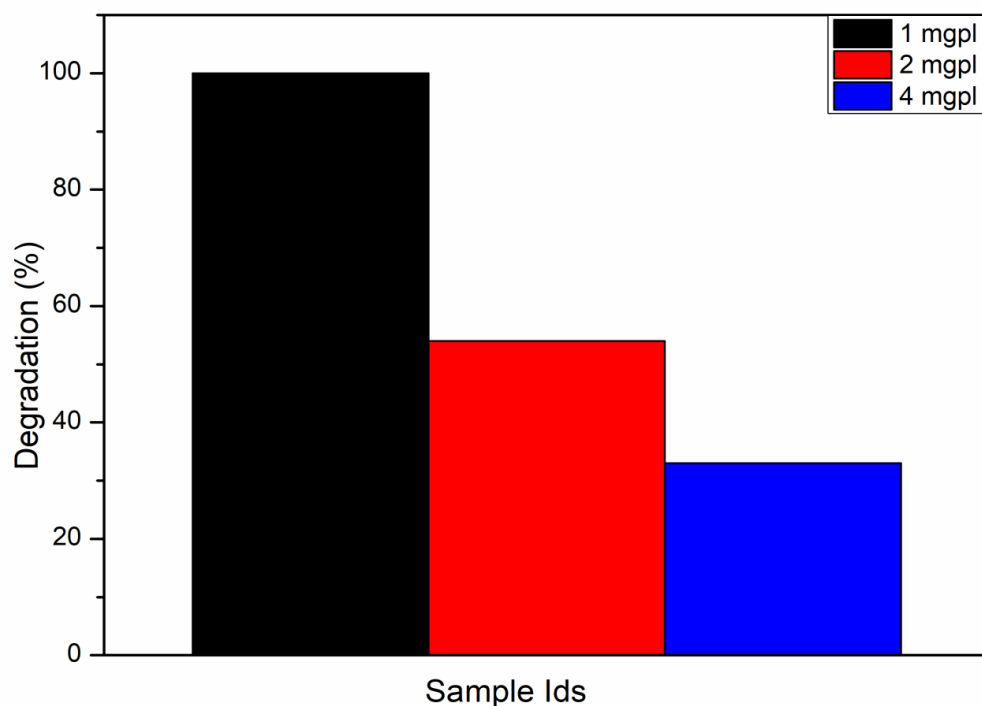


Fig. 6.13: shows the effect of dye concentration for CV dye.

Fig. 6.13 shows the effect of dye concentration on the efficiency of catalyst. The sample ZCCDS-1:1 has been added to the dye solution to check the efficiency of catalyst. The effect of different concentration of CV dye (1 mg/L, 2 mg/L and 4 mg/L) has been studied by synthesized catalyst in which same amount (3 mg) of catalyst is taken for all the reaction. It has been observed that degradation efficiency got reduced when the dye concentration is increased. This is because of the fact that when the concentration of dye is increased, more number of dye molecules cover the surface of catalyst. This decreases the penetration depth of UV light which falls on the surface of dye first and then on the surface of catalyst. Hence reduces the probability of generation of charge carriers for the synthesized catalyst.

Ollis et al. [81] discussed the photocatalysis rate versus illumination intensity. The photocatalytic degradation rate depends upon the light intensities used for photodegradation.

- At low intensities ($0-20 \text{ mW/cm}^2$), the rate reaction is proportional to light intensity (first order).
- At high intensities (25 mW/cm^2), the rate of reaction is directly proportional to the square root of light intensity (half order).
- At higher light intensities, the rate of photocatalytic degradation is independent of light intensities (Zero order).

6.3.11 Kinetics of photodegradation of dye

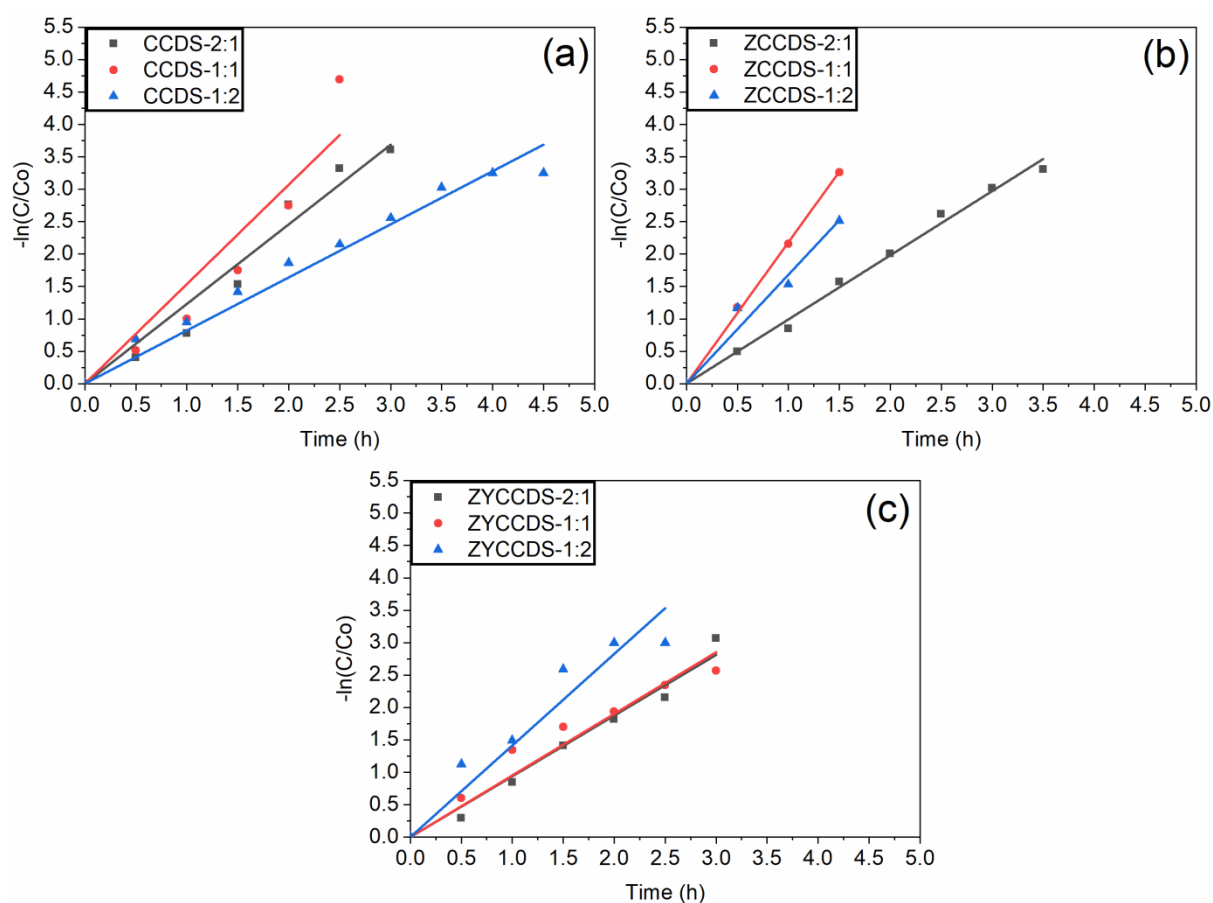


Fig. 6.14: First order kinetics of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO₂.

The rate constant of photocatalytic degradation for crystal violet dye has been studied to understand the efficiency of synthesized CeO₂/CdS heterostructures [82]. The photochemical decomposition of an organic molecule on the surface of CeO₂ NPs is determined by first and the second order kinetic model [15]. The first and the second order kinetics shows that the reaction is taking place through physical adsorption or chemical attachment of dye, respectively [83]. The first and second order kinetics are represented by following equation:

First order
$$-\ln\left(\frac{C}{C_0}\right) = k_1 t \quad (6.2)$$

Second order
$$\frac{t}{C} = \frac{1}{k_2 C_0^2} + \frac{t}{C_0} \quad (6.3)$$

Here, k_1 and k_2 are first and second order rate constant, respectively. The C_0 , C are the concentration at time $t=0$ and after time t , respectively [84]. The graphs $-\ln(C/C_0)$ vs irradiation time (t) are plotted for first order kinetics. For second order kinetics it is t/C and t .

The calculated regression coefficients (i.e. R^2) indicate the quality of fitting and k_x represents the rate constant, as shown in Fig. 6.14 and 6.15 [85].

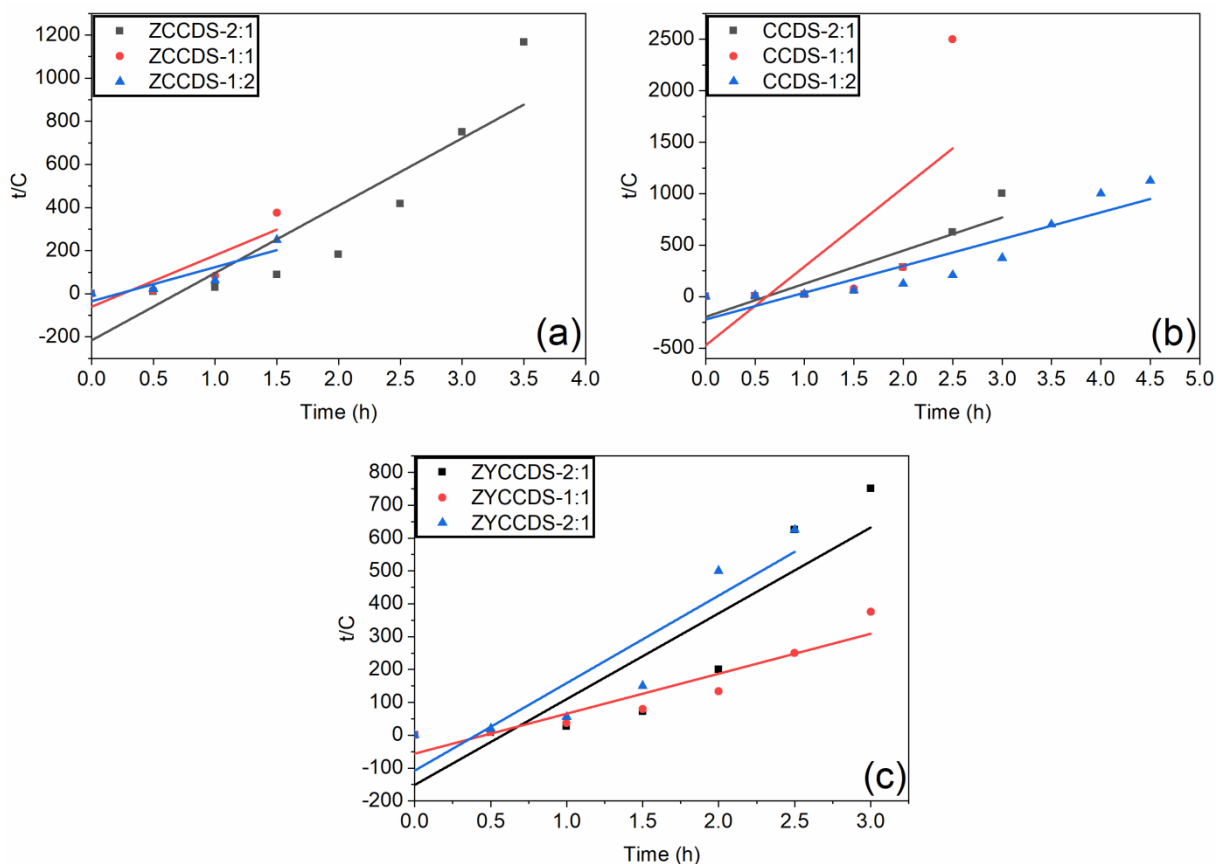


Fig. 6.15: Second order kinetics of CdS heterostructures with (a) undoped, (b) Zn-doped and (c) co (Y, Zn)-doped CeO_2 .

The calculated parameters for first and second order kinetics are given in table 6.7. Fig. 6.14 (a-c) represents the rate constant for first order kinetics of synthesized heterostructures with undoped CeO_2 , Zn-doped CeO_2 and (Y, Zn) co-doped CeO_2 samples, respectively. In Fig. 6.14 (a), the rate constant k_1 of CCDS-1:1 is found to be more than CCDS-2:1 and CCDS-1:2. In Fig. 6.14 (b), the rate constant k_1 of ZCCDS-1:1 is found to be more than ZCCDS-2:1 and ZCCDS-1:2. This variation is due to O-vacancies, as has been discussed in section 6.3.6. The O-vacancies which act as trapping center for photo excited electrons inhibit the recombination of charge carriers [19]. However, in Fig. 6.14 (c), it is observed that rate constant k_1 is found to be more for ZYCCDS-1:2 than ZYCCDS-1:1 and ZYCCDS-2:1. Here, hydroxyl groups attached to the sample surface plays key role in deciding the photocatalytic activity of synthesized samples. The hydroxyl groups attached to the surface of ZYCCDS-1:2 is found to be more than ZYCCDS-1:1 and ZYCCDS-2:1 (FTIR section) which provides dye sensitization [28]. The value of R^2 is more than 0.94 for first order

kinetics. However, it is also observed that rate constant k_2 is larger than k_1 , but have low regression coefficients R^2 . Hence, it is concluded that synthesized samples follow first order kinetics. It is a fact that increased crystallinity promotes the enhanced catalytic activity [86]. In the present case, it is observed that catalytic activity is also increased with crystallinity. However, in Fig. 6.14 (a, b), catalytic activity decreased for CCDS-1:2 and ZCCDS-1:2 despite of larger crystallite size. The calculated crystallite size for heterostructures synthesized with the Zn-doped CeO_2 samples is low. Also, the calculated rate constant k_1 for CdS heterostructures synthesized with Zn-doped CeO_2 samples (Fig. 6.14 (b)) have larger value despite of lower crystallinity. This observation shows that catalytic activity is not following any trend with crystallite size. Thus, crystallinity is not solely affecting the catalytic activity. However, optimum amount of O-vacancies is also more important for enhancing the catalytic activity of the synthesized heterostructures. The hydroxyl groups are also important, but O-vacancies are more important for deciding the catalytic activity of synthesized samples.

Table 6.7: Showing the rate constant for first and second order and their respective R^2 value.

Sample Id	k_1	R^2	k_2	R^2
CCDS-2:1	1.228	0.98	525.67	0.76
CCDS-1:1	1.534	0.94	1236.32	0.40
CCDS-1:2	0.819	0.99	304.12	0.83
ZCCDS-2:1	0.99	0.99	450.80	0.78
ZCCDS-1:1	2.182	0.99	941.81	0.66
ZCCDS-1:2	1.681	0.98	713.46	0.70
ZYCCDS-2:1	0.937	0.99	326.52	0.61
ZYCCDS-1:1	0.95	0.98	261.16	0.86
ZYCCDS-1:2	1.412	0.97	746.22	0.78

6.3.12 Degradation Mechanism

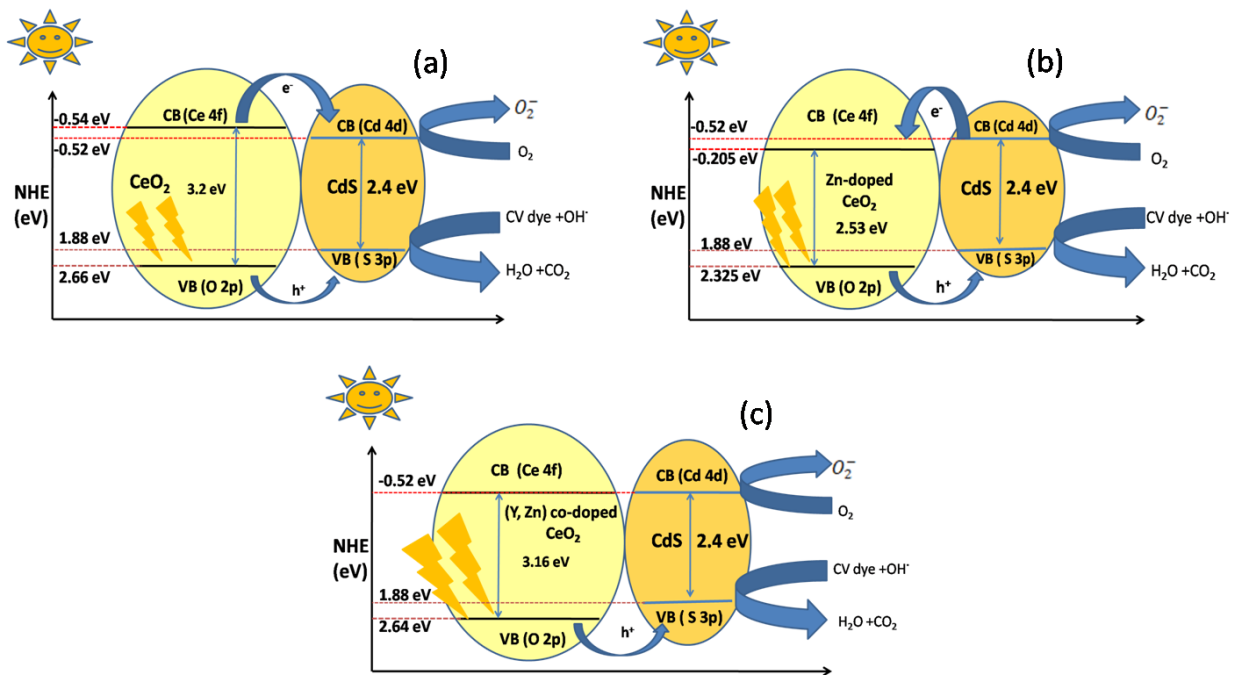


Fig. 6.16: Degradation mechanism of CdS heterostructure with (a) undoped, (b) Zn-doped and (c) (Y, Zn) co-doped CeO₂.

The band gap values of the synthesized samples are used to calculate the valence band (VB) and conduction band (CB) potential and the following relations are used for the calculations [19].

$$E_{CB} = \chi - E^C - 0.5E_g \quad (6.4)$$

$$E_{VB} = E_g - E_{CB} \quad (6.5)$$

Here χ is the absolute electro negativity of the CeO₂ (5.56 eV) and CdS (5.18 eV), E^C denotes the energy of free electron on the hydrogen scale (NHE, 4.5 eV), and E_g is the band gap of CeO₂ and CdS. The calculated values are given in table 6.8.

Table 6.8: Calculated valence and conduction band edge.

Semiconductor	CB edge (eV)	VB edge (eV)	Semiconductor	CB edge (eV)	VB edge (eV)	Semiconductor	CB edge (eV)	VB edge (eV)
CeO ₂	-0.54	2.66	Zn-doped CeO ₂	-0.205	2.325	(Y, Zn) co-doped CeO ₂	-0.52	2.64
CdS	-0.52	1.88	CdS	-0.52	1.88	CdS	-0.52	1.88

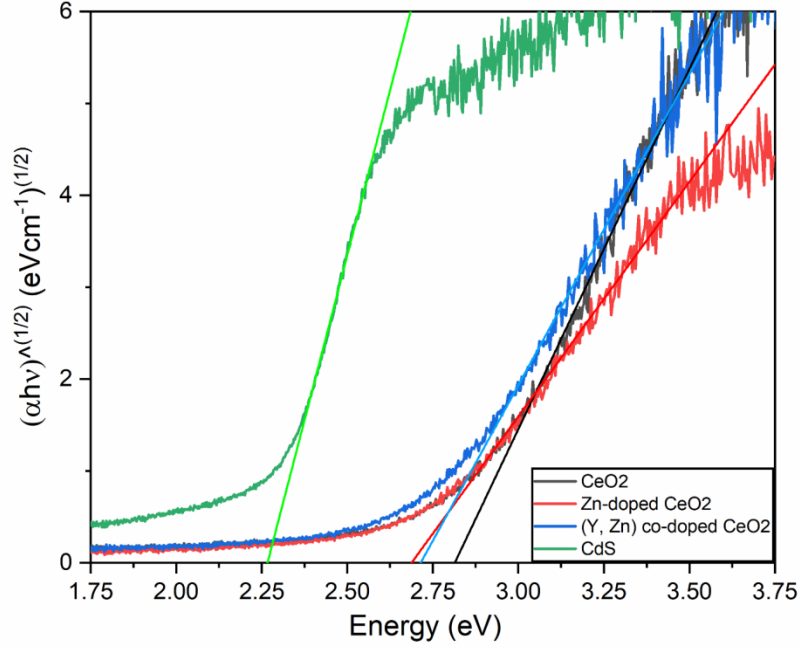


Fig. 6.17: Showing the band gap calculations for synthesized undoped, Zn-doped, (Y, Zn) co-doped CeO₂ and CdS NPs.

From the degradation mechanism shown in Fig. 6.16, it can be concluded that enhanced photocatalytic activity is due to their band gap edge alignment. In Fig. 6.16 (a-c), CdS heterostructures synthesized with undoped, Zn-doped and (Y, Zn) co-doped CeO₂ are of type-II heterojunctions as calculated from equations (6.3) and (6.4) and shown in Fig. 6.16 [38], [87]. The calculated band gaps of synthesized CeO₂, Zn-doped CeO₂, (Y, Zn) co-doped CeO₂ and CdS are 2.81 eV, 2.68 eV, 2.71 eV and 2.26 eV, respectively (Fig. 6.17). In Fig. 6.16 (a-c), CB of CeO₂ is less negative than CB of CdS. Thus, the transfer of electrons from CB of CdS is thermodynamically possible to CB of CeO₂. Hence, CB of CeO₂ acts as trapping center for the photo excited electrons generated in CB of CdS and inhibits the recombination of electrons and holes. On the other hand, VB of CdS is accepting the holes generated in CeO₂ valence band and is performing the photo-oxidation. The CB of CeO₂ acts as trapping center for photogenerated electrons which are generated in the CB of CdS and hence reducing the probability of recombination of charge carriers. On the other hand, VB of CdS acts as holes acceptor due to less positive potential of VB of CeO₂.

It is observed in photodegradation section (section 6.3.9), that heterostructures synthesized with Zn-doped CeO₂ have shown more catalytic activity than undoped and (Y, Zn) co-doped CeO₂ samples. The increase in photocatalytic activity is due to formation of intimate interfacial contact between semiconductor heterojunction. Thus, coupling of semiconductors improve the charge separation and exhibits enhanced photocatalytic activity [88].

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Synthesis and catalytic study of CeO₂ heterostructures with (Zn_{0.003x}Cd_x)S_{0.003} for the removal of crystal violet dye

Overview

In the present chapter different CeO₂ heterostructures were synthesized with (Zn_{0.003-x}Cd_x)S_{0.003} via co-precipitation method by varying the concentration of zinc (Zn) and cadmium (Cd). The synthesized heterostructures were characterized by XRD, TEM, FTIR, PL, UV-visible and Raman spectroscopy. XRD results confirmed the formation of NPs with average crystallite size of 3-5 nm. TEM micrographs depicted the formation of agglomerated non-symmetrical NPs. EDS spectra gives confirmation for the presence of all the elements in synthesized material. FTIR, PL and Raman spectroscopy confirmed the presence of ZnS and CdS in synthesized heterostructures with CeO₂ NPs. The photocatalytic activity has been monitored by the UV-visible spectrophotometer. The crystal violet (CV) dye was used to check the photocatalytic activity of the synthesized heterostructures. It was observed that the heterostructures of CeO₂ with (Cd_{0.0015}Zn_{0.0015})S_{0.003} has shown enhanced catalytic activity and large rate constant than all other synthesized samples.

7.1 Introduction

The requirement of fresh and clean water is basic need of society and its requirement is increasing continuously [1]. Also for the growth of modern society, we need to solve the numerous problems caused by the environmental pollution [2]. The photocatalysts which are mainly used for removal of organic pollutants from waste water are ZnO, TiO₂, AgVO₃, CdS/Cu₂O, CdS/TiO₂, CdS/C etc. [3,4]. The rare earth metal oxides are popular for their unique optical and catalytic properties [4]. CeO₂ get attention due to formation of oxygen vacancies by formation of Ce³⁺ in valence state of Ce⁴⁺/Ce³⁺. Moreover, the relatively longer lifetime span of photo-generated electron-hole pairs for CeO₂ than TiO₂ makes CeO₂ more preferable over TiO₂. However, due to higher band gap range 2.9-3.2 eV, efficiency of CeO₂ is limited. The major disadvantage of wide band semiconductors is the easy recombination of photogenerated charge carriers [5].

Nanoparticles of metal sulfides has been considered as one of the most attractive and suitable compound for enhancing the photocatalytic activity because of suitable conduction and valence band position [6]. Among various metal sulphides, ZnS and CdS have been studied widely in photocatalytic applications as they have the ability to generate charge carriers under the UV-visible light.

7.2 Experimental details

For the synthesis of Zn-doped CeO₂ NPs, 0.00828 moles of Ce(NO₃)₃.6H₂O and 0.00072 moles of Zn(NO₃)₂.6H₂O were dissolved in 30 ml of ethanol as solvent medium. The doping concentration of Zinc (Zn) was taken 8 mol % in the CeO₂ host lattice. To this solution, 1 % of thioglycerol (1-TG) with respect to atomic weight after the addition of metal nitrate salts was added to avoid the agglomeration [7]. Afterwards, ammonia was added dropwise as a precipitating agent until the pH 7.5 was obtained. The solution was further stirred for an hour. After stirring, the solution was kept for overnight aging. Finally, the precipitates were filtered out and washed several times with water and ethanol to remove the traces of any adhere impurities. Thereafter, the precipitates were dried at 80 °C for 24 h and then calcined at 300 °C for 2h. The reduction of Ce⁴⁺ to Ce³⁺ ions takes place upon doping the metal ion (M⁺) in CeO₂. The doping of Zn has been done in CeO₂ lattice to induce the O-vacancies as Zn²⁺ is divalent and Ce⁴⁺ in CeO₂ lattice is tetravalent. Thus, the doping of divalent ion in CeO₂ induces an O-vacancy. Also, doping of metal ion is responsible for the formation of new networks (Ce⁴⁺-O-Ce³⁺ and Ce⁴⁺-O-M⁺), which induces new defects in the host lattice [8].

For the preparation of CeO₂/ZnS/CdS heterostructures, 0.5 g of already prepared Zn-doped CeO₂ was added to 30 ml of ethanol solvent followed by sonication. To this solution, 1% of

1-TG with respect to solution was added as capping agent. The solution color immediately changed after the addition of 1-TG due to variation in sulphur vacancies in the precipitates [9]. In another beaker, 30 ml solution containing of 0.00075 moles of cadmium and 0.00225 moles of Zinc acetate were prepared in ethanol as solvent (e.g. CZ-13). Here, the acetate salts were used because it is reported that acetate salts help to provide spherical morphology [10]. However, for nitrate salts the morphology of synthesized nanoparticles are of flower type [10]. Moreover, spherical morphology provides more specific surface area as has been reported by Kajbafvala et al. [11]. Solution of Na₂S of known molarity was also prepared. The solution of Cadmium and Zinc acetate was added dropwise in the solution containing CeO₂ NPs. Then, after 1 hour of continuous stirring of above solution, the prepared 30 ml solution of 0.1 M (0.003 moles) Na₂S was added drop wise to this solution. The solution was continuously stirred for 1h after the complete addition of Na₂S solution. After that the solution was aged for 24 h. The samples were filtered using Whatman filter paper and washed several times with ethanol and water. Thereafter, the precipitates were dried at 80 °C for 24h and then calcined at 300 °C for 2h in muffle furnace. All other samples were synthesized following the aforementioned synthesis procedure. The synthesized samples along with their synthesis parameters and sample IDs are given in Table 7.1.

Table 7.1: Details of samples along with their preparation conditions.

Samples Ids	Already prepared CeO ₂ taken	Cadmium acetate molar concentration taken	Zinc acetate molar concentration taken	Sodium sulfide amount molar concentration taken	Sample description
CZ-04	Zn-doped CeO ₂	0.0M	0.1M	0.1M	CeO ₂ (Cd ₀ Zn _{0.1} S)
CZ-13	Zn-doped CeO ₂	0.025M	0.075M	0.1M	CeO ₂ (Cd _{0.025} Zn _{0.075})S
CZ-22	Zn-doped CeO ₂	0.05M	0.05M	0.1M	CeO ₂ (Cd _{0.05} Zn _{0.05})S
CZ-31	Zn-doped CeO ₂	0.075M	0.025M	0.1M	CeO ₂ (Cd _{0.075} Zn _{0.025})S

7.3 Effect of $(\text{Zn}_{0.003-x}\text{Cd}_x)\text{S}_{0.003}$ heterostructures on CeO_2

7.3.1 XRD analysis

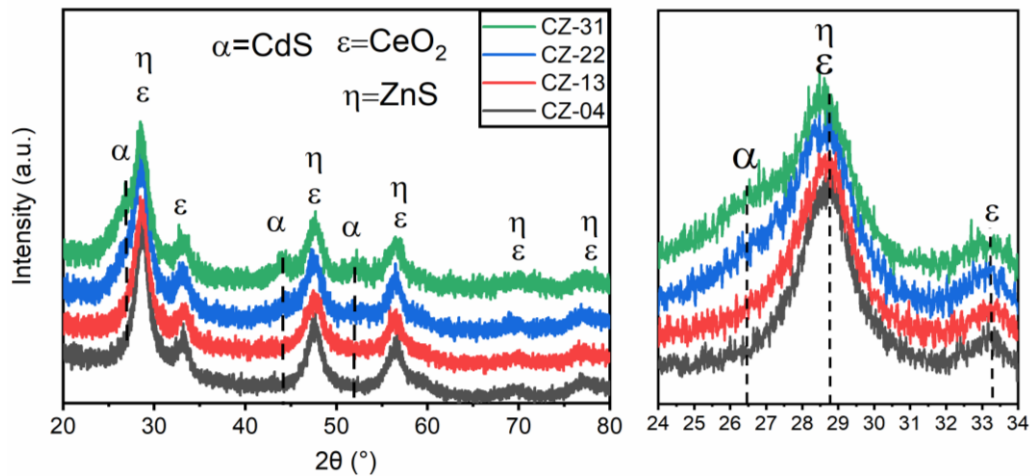


Fig. 7.1: XRD pattern of synthesized samples.

The results of XRD pattern of synthesized CeO_2 heterostructures with ZnS , $\text{Cd}_{0.025}\text{Zn}_{0.075}\text{S}$, $\text{Cd}_{0.05}\text{Zn}_{0.05}\text{S}$, and $\text{Cd}_{0.075}\text{Zn}_{0.025}\text{S}$ having samples Ids CZ-04, CZ-13, CZ-22 and CZ-31, respectively are shown in Fig. 7.1. The XRD patterns are well matched with standard International Centre for Diffraction Data (ICDD) card no. 00-043-1002 for CeO_2 , 01-080-0006 for CdS and 03-065-5476 for ZnS , respectively. It is found that peaks present at 28.75° , 33.13° , 47.65° , 56.56° , 69.76° and 76.99° for CZ-04 corresponds to (111), (200), (220), (311), (400) and (331) planes for CeO_2 , respectively. However, the peaks appearing at 26.84° , 44.05° and 52.08° are due to presence of CdS in the synthesized samples and correspond to (002), (110) and (200) planes, respectively. Although, the presence of ZnS is not confirmed from the XRD diffraction pattern of synthesized samples as X-ray peaks of CeO_2 and ZnS coincides. However, it is also observed that the peak intensity of (111) plane for CZ-04 reduced for CZ-13, CZ-22 and CZ-31. This might be due to formation of CdS phase which reduces the crystallinity of CeO_2 and ZnS . The XRD peak present at 28.75° for CZ-04 shifted to 28.57° which might be due to strong interaction between the CeO_2 , CdS and ZnS [12,13]. This might also be due to reversible conversion of Ce^{4+} to Ce^{3+} , resulting in lattice expansion and leads to increase in d spacing [12]. Also, stacking faults causes stress in crystal lattice and this stress is responsible for this 2θ shifts towards lower side [14]. These stacking faults might be due to interaction between CeO_2 , CdS and ZnS . Zhou and Huebner [15] suggested that small particle size gives expansion to CeO_2 lattice as higher concentration of Ce^{3+} are present in finer particles. Thus, a peak shifting is the integrated results of stacking fault,

interaction between different semiconductors, particle size variation and presence of Ce^{3+} in the crystal lattice.

Further, the crystallite size was calculated by Scherer criteria i.e., $D = \frac{0.9\lambda}{\beta \cos \theta}$ [16,17], where β

is full width half maxima (FWHM; $\beta = \sqrt{(\beta_{\text{observed}}^2 - \beta_{\text{instrumental}}^2)}$, λ =wavelength of

incident X-ray (0.154 nm), D corresponds to average crystallite size calculated from all the peaks represented in Fig. 7.1. The calculated values of average crystallite size are tabulated in

table 7.2. The average crystallite size is found to be 5.71 nm for CZ-04 and it decreases to

4.10 nm for CZ-22. The decrease in crystallite size for CZ-13 and CZ-22 might be due to alternation of periodicity and decrease in crystal symmetry which is caused by stacking fault

due to presence of stress in the lattice [14,18,19]. However, for CZ-31 i.e. for CeO_2

heterostructures synthesized with $\text{Cd}_{0.075}\text{Zn}_{0.025}\text{S}$, the crystallite size again increases and

found to be 4.44 nm. It is also observed that FWHM value of peak corresponding to (111)

plane of CeO_2 is increased for CZ-31 which might be due to alternation of periodicity caused

by stress as interaction between ZnS, CdS and CeO_2 takes place. Thus, again increase in

crystallite size for CZ-31 is due to the growth of CdS as is evident in Fig. 7.1 where the peaks

related to CdS are also induced.

Table 7.2: Variation in crystallite size of the synthesized samples.

Sample Id	Crystallite Size (nm)
CZ-04	5.71±1.29
CZ-13	4.14±0.59
CZ-22	4.10±0.47
CZ-31	4.44±0.33

7.3.2 FTIR analysis:

Fig. 7.2 shows the FTIR spectra of synthesized CeO_2 heterostructures with ZnS,

$\text{Cd}_{0.025}\text{Zn}_{0.075}\text{S}$, $\text{Cd}_{0.05}\text{Zn}_{0.05}\text{S}$, and $\text{Cd}_{0.075}\text{Zn}_{0.025}\text{S}$ with samples Ids CZ-04, CZ-13, CZ-22 and

CZ-31, respectively. FTIR spectroscopy is used to study the vibrational motion of

atomic/molecular bonds related to different functional groups present in the samples

synthesized under different conditions [20]. All spectra have peaks present around 500 cm^{-1}

depicting the presence of Ce-O stretching mode and confirming the formation of CeO_2 in the

synthesized samples [20,21]. The peak present at 494 cm^{-1} for CZ-04 shifted to higher

wavenumber at 497 cm^{-1} for CZ-31 showing the reduced bond length [22].

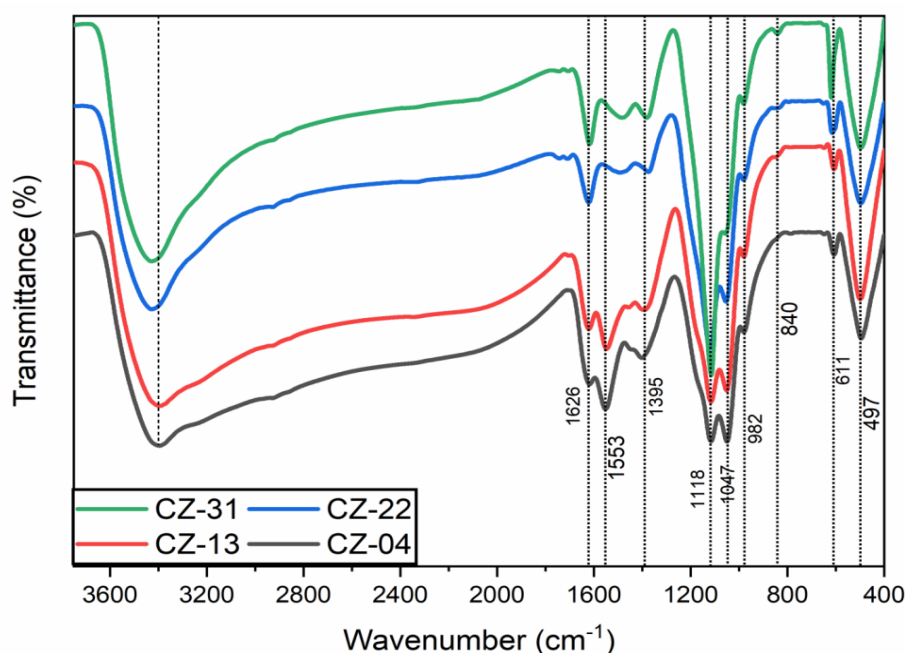


Fig. 7.2: FTIR spectra of synthesized samples.

The higher and lower shifts attributed to change in bond length. The bond length is inversely proportional to wavenumber [23]. The lower shift depicted the increase in bond length while the higher shifts is due to shortening of bond length [22]. The peak present at 611 cm^{-1} is attributed to Cd-S and Zn-S stretching (i.e. corresponds to sulphides) [24–26]. The peak present at 607 cm^{-1} for CZ-04 shifts to 618 cm^{-1} for CZ-31. The higher shifts of the peak might be due to exchange of small size Zn^{2+} ion by large size Cd^{2+} ion during synthesis. The peak present at 840 cm^{-1} is associated to Ce-O-Ce bridging oxygen [27]. The intensity of peak at 980 cm^{-1} does not show any change with variation in concentration of Zn and Cd ions. This peak is due to symmetric stretching mode for SO_4 [28]. The peak present near 1395 cm^{-1} is due to Ce-O-Ce stretching vibration [29,30]. The peak present at 1047 and 1118 cm^{-1} indicates the presence of sulphate ions in bidentate coordinates [28,31]. Thus, from the fingerprint region presence of CeO_2 , ZnS and CdS has been confirmed. The presence of ZnS has not been detected by XRD analysis. However, from FTIR analysis presence of ZnS has been confirmed. The formation of heterostructures is also confirmed. The peak present at 1553 cm^{-1} for CZ-04 and CZ-13 is due to symmetric stretching of acetate group [26,32,33]. However, this peak is absent for CZ-22 and CZ-31. The absence of peak might be because all acetate groups are replaced by sulphide ions. The peak present at 1626 cm^{-1} is due to presence of adsorbed water from the atmosphere [20]. The peak at 3400 cm^{-1} is due to OH groups [8,34–37]. The absence of peak for TG at 2555 cm^{-1} for samples is due to deprotonation of TG molecule and attachment to metal-atom [7]. The peak present at 3398 cm^{-1}

for CZ-04 shifts to 3428 cm^{-1} for CZ-31. The shifting of this peak at higher wavenumber shows that the functional group becomes more active for CZ-31 [38]. The different functional groups and type of vibration are given in table 7.3.

Table 7.3: Peak assignment to different bonds in all the synthesized samples.

Wavenumber (cm^{-1})	Functional group and type of vibration	References
494	Ce-O	[20,21]
611	Corresponding to metal sulphides (Cd-S and Zn-S)	[24–26]
840	Ce-O-Ce metal bridging	[27]
980	Sulphide ions in ZnS crystal	[24,39]
1047	Intrinsic hygroscopic nature of CeO_2	[27,40]
1118	Zn-S and Ce-O-Ce vibration	[41,42]
1395	Ce-O-Ce stretching vibration	[29,30]
1553	Symmetric stretching of acetate group	[26,32,33]
1626	Adsorbed water from atmosphere	[20]
2555	S-H group from 1-TG (thioglycerol)	[7]
3400	Hydroxyl groups	[8,34–37]

7.3.3 UV analysis:

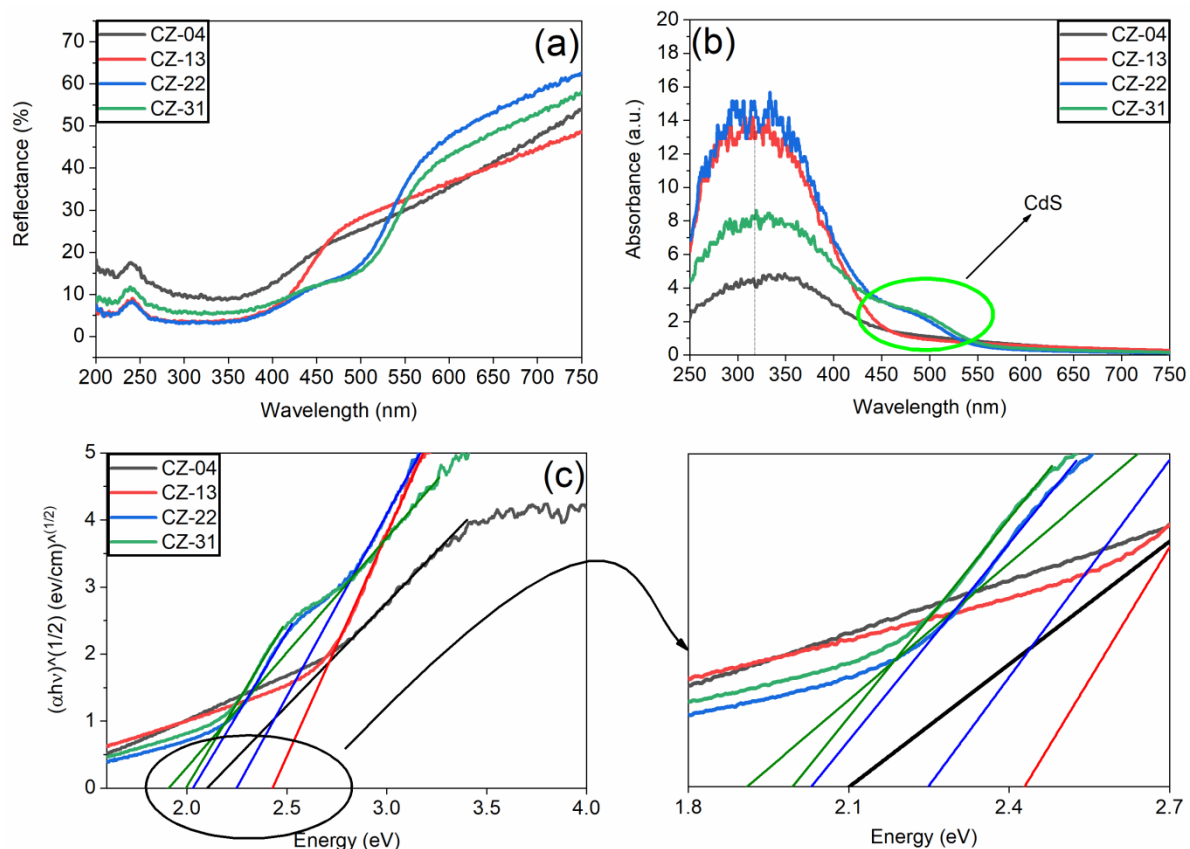


Fig. 7.3: Showing the (a) UV-Reflectance spectra, (b) UV-absorbance spectra and (c) Tauc's plot of synthesized samples.

Fig. 7.3 (a-c) shows the reflectance, absorbance spectra and tauc's plot, respectively for synthesized CeO_2 heterostructures with ZnS , $\text{Cd}_{0.025}\text{Zn}_{0.075}\text{S}$, $\text{Cd}_{0.05}\text{Zn}_{0.05}\text{S}$, and $\text{Cd}_{0.075}\text{Zn}_{0.025}\text{S}$ with samples Ids CZ-04, CZ-13, CZ-22 and CZ-31, respectively. The diffuse reflectance spectra are converted into absorbance spectra using Kubelka-Munk function [4]. The absorbance spectra consist of two peaks one in UV-region and other in visible region. The absorbance peak in UV-region is due to CeO_2 , while the peak in the visible region is due to CdS . Also, the peak in visible region are induced only for samples which have more content of CdS . However, no peak that confirms the presence of ZnS in the synthesized heterostructures is observed. This might be due to fact that the as ZnS has bandgap in UV-range. The band gap of ZnS in 3.66 eV and band gap of CeO_2 is 3.2 eV [43,44]. Thus, this might be the reason for broad hump in the UV-region. Moreover, CeO_2 also has bandgap in UV range, thus generating a broad peak in UV region after overlapping on each other. The absorption peak in the UV-region arises due to the charge transfer between O^{2-} (2p) to Ce^{4+} (4f) while the peak in the visible range arises due to electronic transition from S^{2-} (3p) to Cd^{2+}

(4d) [45,46]. The absorbance peak is not showing any significant shift as the concentration of Zn and Cd varied.

In order to determine the optical band gap from the absorbance spectra, Beer-Lambert law is used. It is $(\alpha h\nu) = A(h\nu - E_g)^n$, where E_g is the band gap of synthesized compound, α is the absorbance coefficient which is calculated from % R value from reflectance spectra and $n=1/2, 2, 3/2$ and 3 corresponds to direct, indirect, forbidden direct and forbidden indirect, respectively. Fig. 7.3 (c) shows the indirect band gap value using Tauc's plot [17]. The indirect value of band gap is calculated from the extrapolation of straight line portion of $(\alpha h\nu)^{1/2}$ to the x-axis where $(\alpha h\nu)^{1/2}$ is 0. The indirect band gap has been calculated for all samples and shown in table 7.4. The calculated band gap of synthesized samples are found in the range of 1.90 and 2.42 eV. The bandgap was first found to increase with increase in cadmium concentration and then decreases. The red shift in the band gap might be due to presence of ZnS and CdS which form intermediate band level below the minimum of conduction band (Ce4f) of CeO₂ that causes red shifts in the band gap [47]. Also, the O-vacancies induced due to creation of Ce³⁺ makes red shifts in the band gap [44,45,48]. The introduction of O-vacancies changes the local atomic structure and the interaction between O and Ce atoms, leading to change in electronic structure of CeO₂ [49]. The red shift in the band gap is also due to interfacial interaction between semiconductors of synthesized heterostructures [45]. In the synthesized heterostructures, the size effect and quantum confinement allows delocalization of the electronic wave function which allows blue shifting in the band gap [50]. Also, the decrease in Ce³⁺ concentration makes blue shifting in the band gap value. Thus, a red or blue shift in the band gap value is the integrated results of O-vacancies, quantum confinement and interfacial interaction that arises due to formation of nanostructures. It is also observed that CZ-22 and CZ-31 exhibits two bandgap values. The multiple band gaps also suggest formation of heterostructures. The color of sample also contributes to change in optical properties [51,52]. It might be due to defect sites below conduction band level which generate multiple band gap and perturbation in the CeO₂ structure due to formation of heterostructures with CdS and ZnS, thus promoting multiple electronic transition in the forbidden gap [53–55]. The extinction coefficient of CV dye was calculated for all catalysts used in the present investigation to degrade the CV dye by using following formula:

$$\text{Optical thickness} = \epsilon cl \quad (7.1)$$

Where, ϵ and c are the extinction coefficient and the molar concentration of dye solution and l is the length of cuvette used. It was observed that the variation of extinction coefficient is in tune with the variation in optical thickness as given in appendix D.

Table 7.4: Calculated bandgap of synthesized samples and extinction coefficient of CV dye when degraded with synthesized samples.

Sample Ids	Band gap (eV)	Extinction coefficient of CV dye at different time intervals $\times 10^{-8}$ ($M^{-1}cm^{-1}$)								
		0H	2HA	0.5HD	1HD	1.5HD	2HD	2.5HD	3HD	3.5HD
CZ-04	2.09	11.95	8.77	5.95	4.24	2.61	1.26	0.49	0.40	0.40
CZ-13	2.42	12.00	6.28	5.67	4.65	3.38	2.28	1.55	1.14	0.93
CZ-22	2.03, 2.24	10.85	5.75	4.04	0.98	0.20	0	0	0	0
CZ-31	1.90,1.99	11.10	6.32	5.55	4.28	3.18	2.40	1.46	0.81	0.24

7.3.4 Raman Analysis:

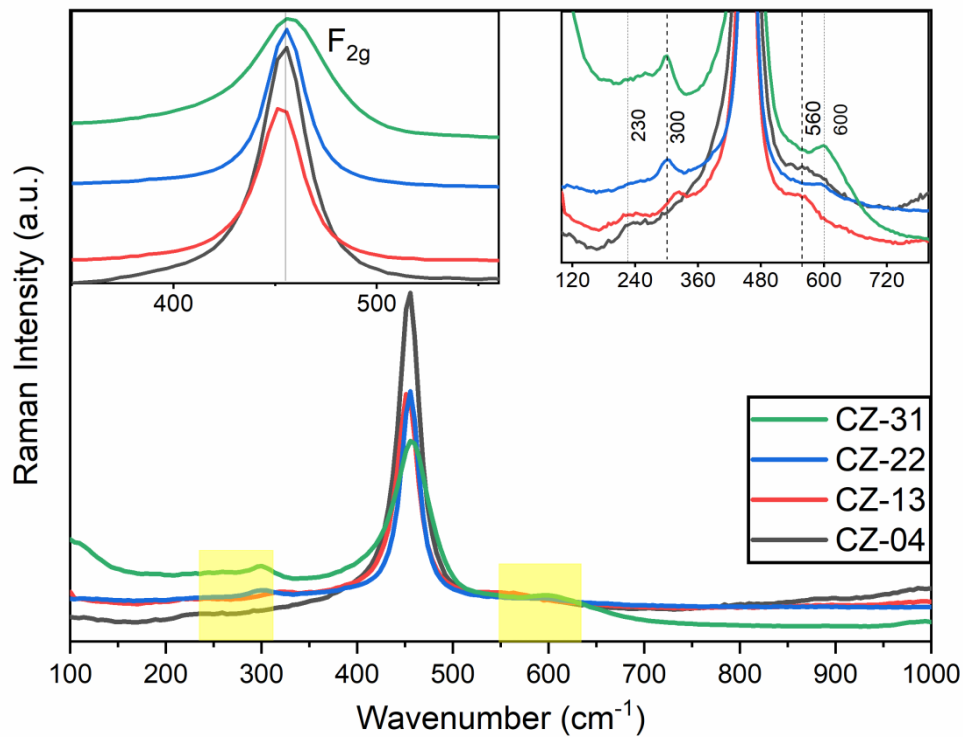


Fig. 7.4: Raman spectra of synthesized samples.

Fig. 7.4 shows the results of Raman spectra for Zn-doped CeO_2 heterostructures with ZnS , $Cd_{0.025}Zn_{0.075}S$, $Cd_{0.05}Zn_{0.05}S$, and $Cd_{0.075}Zn_{0.025}S$ having samples Ids CZ-04, CZ-13, CZ-22 and CZ-31, respectively. Raman spectroscopy is very useful technique to investigate the internal strain and oxygen vacancies in the synthesized sample [56]. The spectra consists of an intense peak situated at 455 cm^{-1} for CZ-04 which is associated to F_{2g} Raman vibrational

mode of crystalline cubic fluorite type structure of pure CeO_2 with $\text{fm}3\text{m}$ space group. This peak is induced from the vibrational motion of oxygen atoms surrounding the Ce atom under tension [20,57,58]. The stretching around Ce ions helps to maintain the fluorite structure. The non-uniform intensity variation in the $\text{F}_{2\text{g}}$ peak is due to the particle size variation in the synthesized sample as non-uniform particle variation causes strain in the lattice leading to non-uniform variation in $\text{F}_{2\text{g}}$ Raman mode [20,56]. The peak broadening or any asymmetry in the $\text{F}_{2\text{g}}$ peak is also due to the presence of oxygen vacancies (extrinsic or intrinsic) [59]. The peak situated at 456 cm^{-1} for CZ-04 shifts to 450 cm^{-1} for CZ-13 and again shifts to 455 cm^{-1} for CZ-22 and then again shifts to 457 cm^{-1} for CZ-31. Thus, the peaks are showing the red or blue shifts with the change in concentration of Zn and Cd in the synthesized heterostructures. The red shift in the $\text{F}_{2\text{g}}$ peak is due to formation of Ce^{4+} to Ce^{3+} oxidation state with the localized 4f state electron as lattice relaxation takes place after shifting of peaks [8,38,48]. The more red shifts for CZ-13 shows existence of higher O-vacancies due to creation of more Ce^{3+} in the synthesized sample. Thus, above results confirm that CZ-13 has more O-vacancies and CZ-31 has low number of O-vacancies due to creation of Ce^{3+} .

Fig. 7.4 shows a low intense peak at 300 and 600 cm^{-1} for CZ-22 and CZ-31 corresponding to 1LO (longitudinal optical) and 2LO optical phonons, respectively which comes from the results of phonon vibrations [25,60]. The increased intensity of these peaks shows the improved crystallinity of CdS in the synthesized heterostructures [61]. These peaks are absent for sample CZ-04 which shows the absence of CdS in the synthesized sample. The CZ-13 has some amount of CdS, but in Raman spectra no peak corresponding to CdS for CZ-13 is observed. The absence of peak might be due to breakdown of long-range translational crystal symmetry caused by smaller crystallite size or less crystallinity of CdS in synthesized NPs [62,63]. Thus, the above results confirm the formation of CdS in the synthesized heterostructures.

In the above Fig. 7.4, there are some low intense peaks situated at 230 cm^{-1} and 560 cm^{-1} for CZ-04 and CZ-13. The peak present at 230 cm^{-1} is due to second order longitudinal acoustic phonon mode in ZnS [64–66]. The peak present at 560 cm^{-1} is due to the 2TO (transverse optical) of ZnS [67]. There is presence of very less intense peak at 315 cm^{-1} for CZ-13 which is due to SO (surface optical phonon mode) phonon mode for ZnS [68,69]. The presence of this peak at 315 cm^{-1} indicates the presence of mixed phase of zinc- blende and wurtzite structure of ZnS [70]. The CZ-13 has some content of CdS. However, the peak at 300 and 600 cm^{-1} are absent for CZ-13 which might be due to the low crystallinity of CdS that causes breakdown of long-range translational order in synthesized sample [62,63]. It is also possible

that Cd ions might be incorporated into ZnS structure due to low content of Cd which gives low intensity peak related to CdS. Abdelouhab et al. [71] synthesized ZnO and found vibrational mode at 267, 335, 379, 404 and at 535 cm^{-1} for Raman spectra of ZnO. Silambarsan et al. [72] synthesized ZnO NPs and they found peaks at 385, 440 and 585 cm^{-1} in the Raman spectra of ZnO. In the present case, the peaks are observed at 230, 300, 455 560 and at 600 cm^{-1} . However, these peaks are also related to CeO_2 , CdS and ZnS as discussed above.

Thus, presence of above bands in the Raman spectra shows the presence of CeO_2 , ZnS and CdS in the synthesized heterostructures.

7.3.5 TEM and EDS analysis:

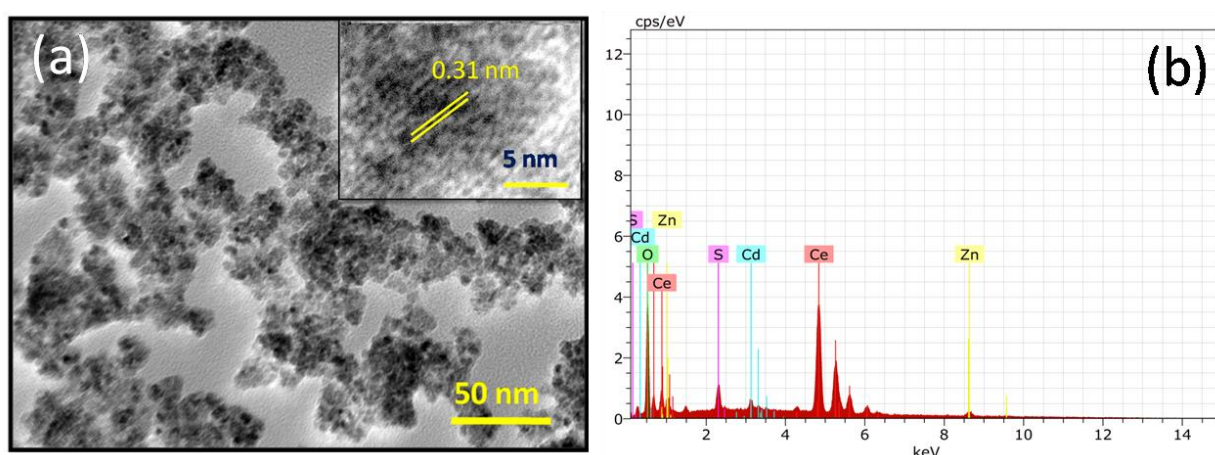


Fig. 7.5: Showing TEM and HRTEM image of CZ-22.

Fig. 7.5 shows the TEM and HRTEM images of CZ-22. The TEM analysis was carried out to calculate the particle size and shape of synthesized sample. The TEM image in Fig. 7.5 shows the non-uniform agglomerated NPs. The agglomeration of NPs is because NPs becomes stable by minimizing the interfacial energy and allows the crystallite to grow [73,74]. The particle size of synthesized NPs was calculated from *ImageJ* software. There is a variation in the calculated particle size from 3 to 8 nm. The calculated particle size again confirms the formation of NPs. Furthermore, HRTEM analysis was carried out to calculate the fringe width. The calculated d-spacing was found to be 0.31 nm for plane of (111) and matched with ICDD XRD score card which confirms the formation of CeO_2 .

Fig. 7.6 shows the elemental mapping of synthesized sample CZ-22. The elemental mapping of CZ-22 has been done to check the presence of different elements. The elemental mapping profile of CZ-22 indicates the uniform distribution of Ce, O, Zn, Cd and S. Further, it has been also confirmed that the S is present in the synthesized sample.

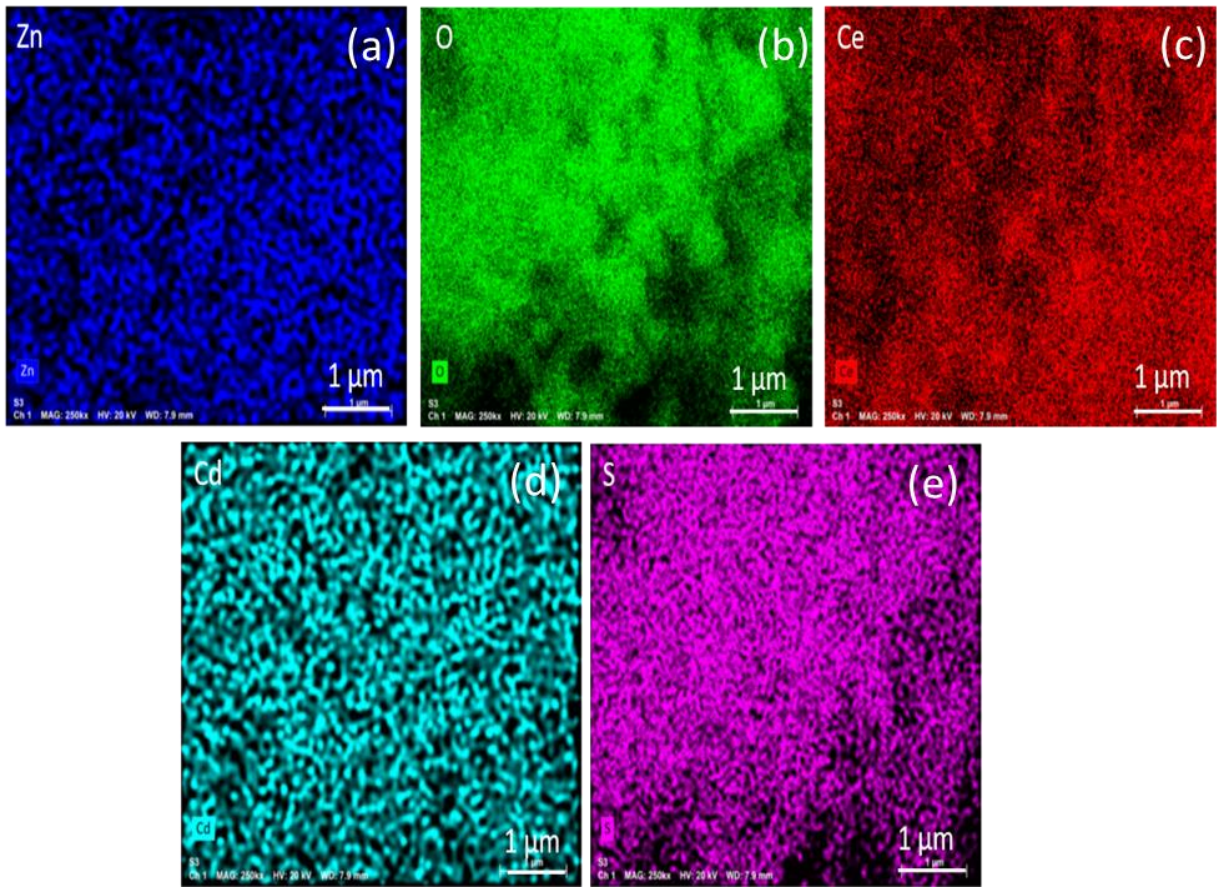


Fig. 7.6: Mapping of CZ-22 sample (a) zinc (Zn), (b) oxygen (O), (c) cerium (Ce), (d) cadmium (Cd) and (e) sulphur (S).

7.3.6 PL spectra

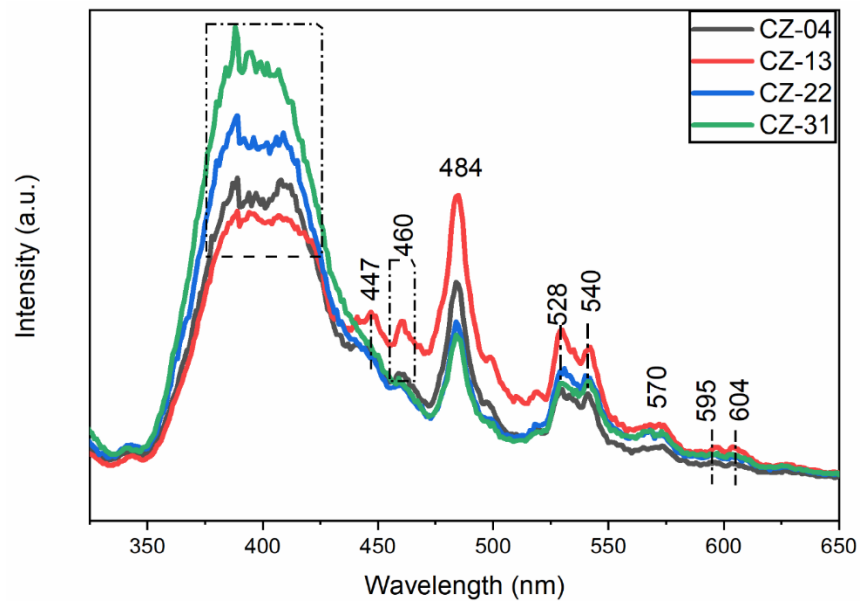


Fig. 7.7: Showing the PL spectra of synthesized samples.

The results of PL measurements of the synthesized CeO_2 heterostructures with $\text{Cd}_0\text{Zn}_{0.003}\text{S}_{0.003}$, $(\text{Cd}_{0.00075}\text{Zn}_{0.00225})\text{S}_{0.003}$, $(\text{Cd}_{0.0015}\text{Zn}_{0.0015})\text{S}_{0.003}$, and $(\text{Cd}_{0.00225}\text{Zn}_{0.00075})\text{S}_{0.003}$ having sample Ids CZ-04, CZ-13, CZ-22 and CZ-31, respectively are shown in Fig. 7.7. To record PL emission spectra of synthesized samples, the excitation wavelength (λ_{exc}) was fixed at 250 nm. The spectra consists of broad band in between 385 nm and 415 nm originating from the defect states that exists between Ce_{4f} and O_{2p} state or the O-vacancies which is just below the conduction band Ce_{4f} [56,75–77]. The broadening of peak might be due to presence of impurity centers in the material because all the atoms do not emit the same spectra [56]. The peak intensity variation might be due to non-radiative transition. The peak intensity for peak situated at 447 nm reduces for CZ-22 and CZ-31 which shows that this peak might be related to interstitial defects in ZnS or defects sites on the surface of ZnS [78,79]. The peak at 460 nm is associated to interstitial Zn atoms [9,79]. The peak present at 484 nm is due to the emission range related to charge transfer from Ce_{4f} energy level to O_{2p} level [21]. The intensity of peak present at 484 nm is also varying with change in concentration of Zn and Cd. This variation of peak intensity might be due to vacancy related defects and might be due to transfer of photogenerated carriers between different semiconductors [80,81]. Phanichphant [82] suggested that PL emission is the result of the recombination of excited electrons and holes. The lower PL intensity indicates the decrease in recombination rate which is due to non-radiative transition. The reduced PL intensity is due to lower recombination rates in O_{2p} from Ce_{4f} [6]. The synergetic effect between semiconductors of synthesized heterostructures also affects the PL intensity (luminescence quenching) [54]. The peak present at 528 nm is due to presence of ZnS self-activated luminescence centers which arises from vacancy states and interstitial defects [80]. The peak present at 540 nm is due to the excitons or free charge carriers and trapped charge carriers at surface defects for CdS [26,83]. The peak present at 570 nm are introduced due to presence of photogenerated holes and oxygen vacancies in ZnS [84]. The peak present at 570 nm might be also due to recombination of holes formed in S 1s band with electrons in Cd 4d (or 5s) band [4]. The small peaks near 595 and 604 nm is assigned to recombination via surface defects [85]. The high emission peak intensity is due to large probability of recombination in CdS. The peak intensity of this peak also increased for CZ-22 which shows that this peak is also due to surface defect emission of CdS [86]. Thus, presence of CeO_2 , ZnS and CdS are confirmed from PL emission spectra. Hence, formation of heterostructures is also confirmed from PL emission spectra.

7.3.7 Photodegradation of CV dye

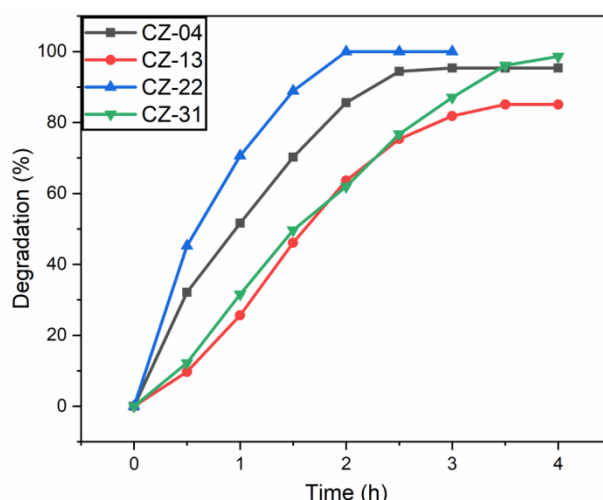


Fig. 7.8: Showing the photodegradation of synthesized samples under UV-visible Illumination (3 mg (catalyst dosage), 1 mg/L (CV dye concentration), 110 W/m² (light intensity) and $\lambda_{\text{max}} = 591$ nm).

The results of photodegradation of CV dye by the synthesized CeO₂ heterostructures with Cd₀Zn_{0.003}S_{0.003}, (Cd_{0.00075}Zn_{0.00225})S_{0.003}, (Cd_{0.0015}Zn_{0.0015})S_{0.003}, and (Cd_{0.00225}Zn_{0.00075})S_{0.003} having sample Ids CZ-04, CZ-13, CZ-22 and CZ-31, respectively are shown in Fig. 7.8. It shows the photocatalytic activity of synthesized samples for the removal of CV dye under UV-visible irradiation in a self-designed photo-reactor. It is observed that CZ-22 shows enhanced photocatalytic activity and degrade CV dye completely within 2h of UV-visible illumination. The enhanced catalytic activity of CZ-22 is due to O-vacancies as they act as trapping center for photo excited electrons (confirmed from Raman spectra). The CZ-04 has shown lower activity than CZ-22 which is due to low amount of O-vacancies as described in Raman section.

It can be seen that CZ-13 has shown less catalytic activity (63 %) in 2h of UV-illumination despite of higher amount of O-vacancies (confirmed from Raman section). Mittal et al. [44] have described the correlation of O-vacancies with photocatalytic activity and suggested that O-vacancies beyond optimum level increase the concentration of deep traps which results in decrease in photocatalytic efficiency. Moreover, the PL intensity for peak situated at 484 nm (emission range related to charge transfer from Ce_{4f} energy level to O_{2p} level of the attribution of oxygen defects) for CZ-13 is more intense than other samples. Phanichphant et al. [82] suggested that PL emission is the result of the recombination of excited electrons and holes. The lower PL intensity indicates the decrease in recombination rate which is due to non-radiative transition. Further, the CZ-22 has shown enhanced photocatalytic activity while the CZ-13 has shown lower activity among all the synthesized samples. This observation can

be explained on the basis of PL results. It has been observed that CZ-13 has large emission intensity of peak present at 484 nm. The large intensity of this peak shows higher recombination of charge transfer from Ce_{4f} to O_{2p} . However, CZ-22 has shown large catalytic activity because of lower PL intensity. The CZ-31 has shown catalytic activity more than CZ-13 but less than CZ-22. However, the PL intensity of CZ-31 and CZ-22 are nearly same. Thus, PL intensity might be helpful for deciding the photocatalytic activity of synthesized samples. However, PL spectroscopy is not a solely technique for deciding the catalytic activity of synthesized samples. Hence, the photocatalytic activity of synthesized samples is the combined results of oxygen vacancies and PL intensity results.

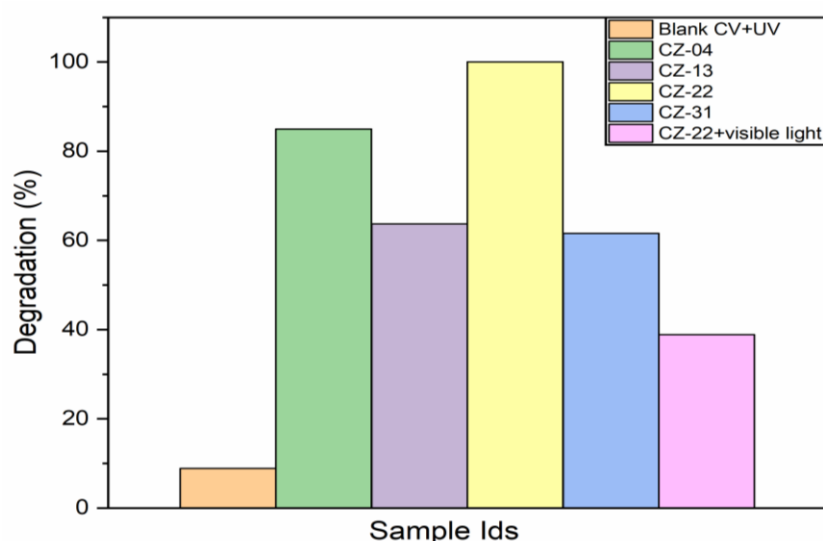


Fig. 7.9: shows the comparison of photolysis and % degradation of synthesized samples under 2h of UV-illumination irradiation of light.

Fig. 7.9 shows the comparison of photolysis and photocatalysis of synthesized samples. The photolysis of CV dye has been also optimized. It has been observed that nearly 8 % of dye degraded under UV-visible light in 2h. However, the CZ-22 has shown 100 % degradation in 2h of UV-visible illumination. The CZ-04 has shown nearly 85 % of degradation for CV dye as shown in Fig. 7.9. Thus, photocatalysis has shown enhanced efficiency as compared to photolysis.

The photocatalytic activity of CZ-22 under visible irradiation has also been optimized and given in Fig. 7.9. Here, CZ-22 has shown 38.88 % removal of CV dye in 2h of visible irradiation. This observation shows that the synthesized catalyst is also visible active compound.

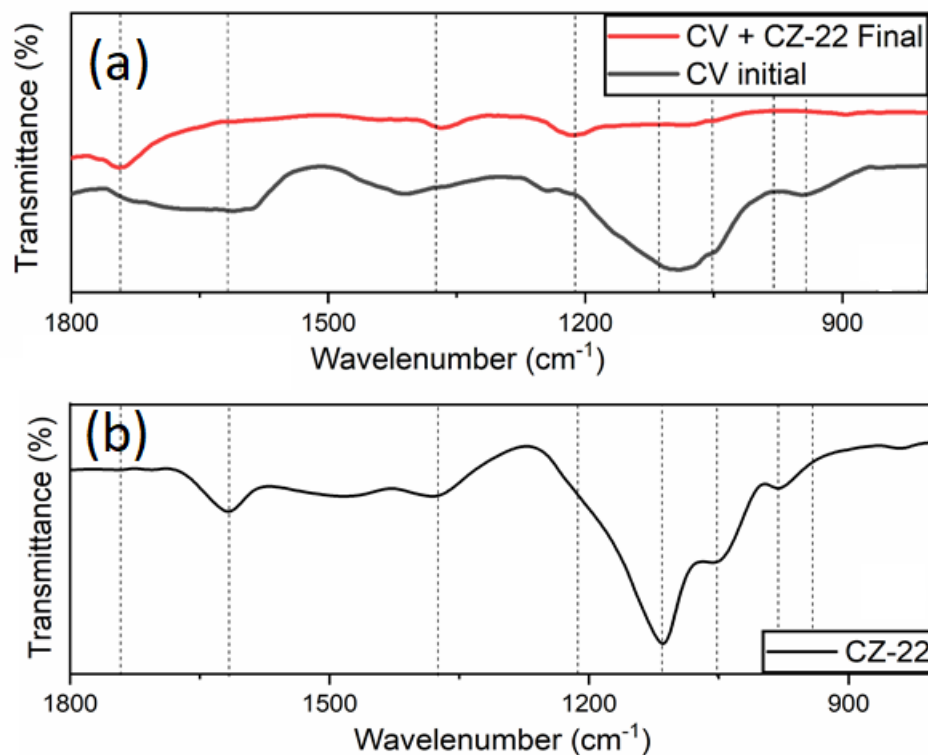


Fig. 7.10: (a) shows the FTIR spectra of crystal violet dye before and after degradation and (b) FTIR spectra of CZ-22 catalyst.

The AT-FTIR of CV dye before and after degradation has been done to optimize the functional groups attached to the surface of dye and is shown in Fig. 7.10. Fig. 7.10 (a) shows the FTIR spectra of CV dye before degradation and also after degradation with catalyst. Fig. 7 (b) shows the FTIR spectra of CZ-22 catalyst. The peak present at 980 cm⁻¹ and 1180 cm⁻¹ (sulphate ions) disappeared after degradation. The peak at 1380 cm⁻¹ (Ce-O-Ce) also disappeared after degradation of crystal violet dye. Thus, it is concluded that functional groups and metal-oxide vibrations got reduced after degradation of dye.

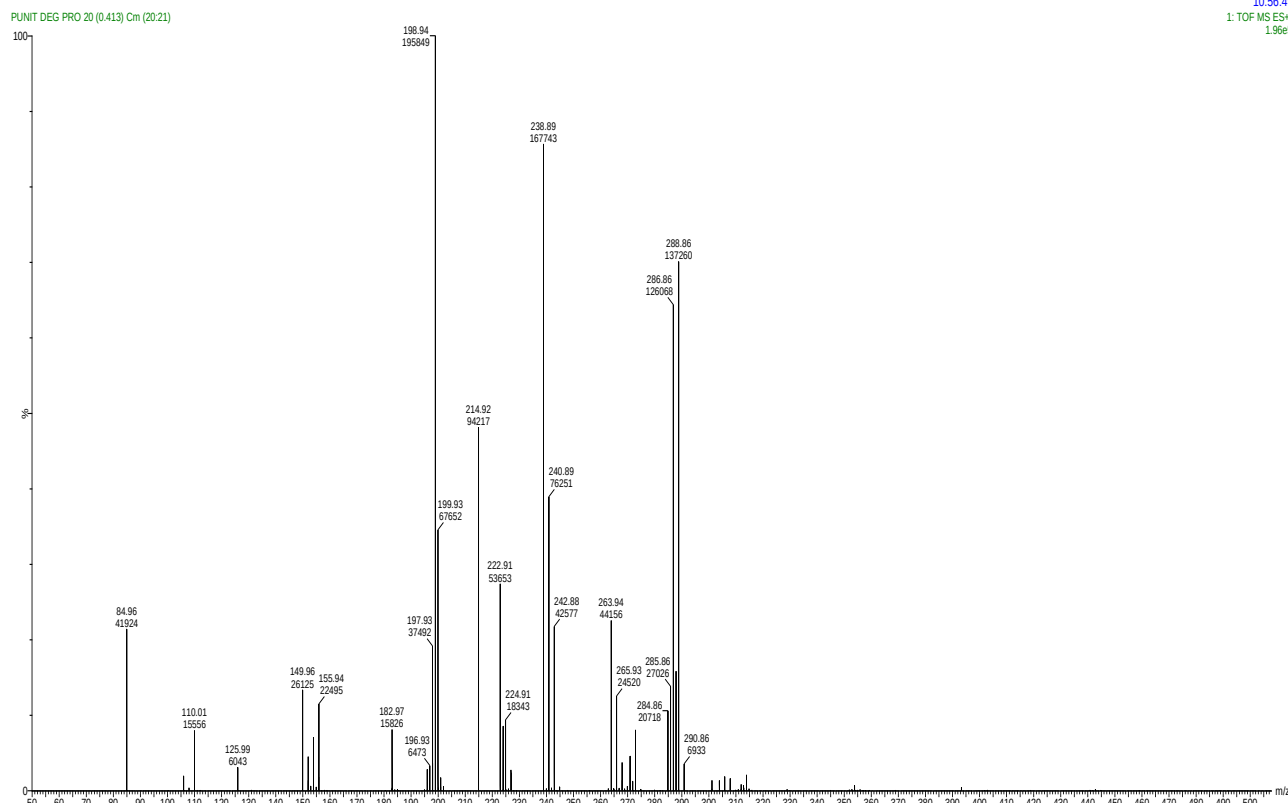


Fig. 7.11: LC-MS spectra of CV dye after complete degradation under UV-visible illumination.

The degradation products and compounds were also analyzed by LC-MS process. Fig. 7.11 shows the LC-MS spectra of CV dye after complete degradation under UV-visible illumination. The product formation has been compared with the literature and are given in table 7.5 [87–92]. The CV dye LC-MS spectra has been given before UV-visible degradation process [93–95].

Table 7.5: The degraded intermediates of CV dye under UV-visible illumination.

MS spectrum (m/z)	Ion Chemical formula (before CV dye degradation)	MS spectrum (m/z)	Intermediates formed after CV dye degradation
236.1	$C_{15}H_{17}N_2O^+$	110.01	4-aminophenol
251.2	$C_{16}H_{15}N_2O^+$	125.99	4-(N-methylamino) phenol
284	$C_{17}H_{38}NO_2^+$	149.96	$C_9H_{10}O_2$
313.2	$C_{20}H_{20}N_3O^+$	214.92	4-4'-Bis-amonobenzophenone
328.3	$C_{22}H_{24}N_3^+$	222.91	4-(N-ethyl-N,N-dimethylamino)-4'-(amino)

			benzophenone
342	$C_{22}H_{26}N_3^+$	224.91	4-(N-methylamoni)-4'-aminobenzophenone
372	$C_{25}H_{30}N_3^+$	240.89	N-methylaminophenyl
		266.93	4-(N, N-dimethylaminophenyl)
		288.86	Pararosaniline

The degradation pathway of CV dye is proposed based on presence of different intermediate products and compared with the related literature.

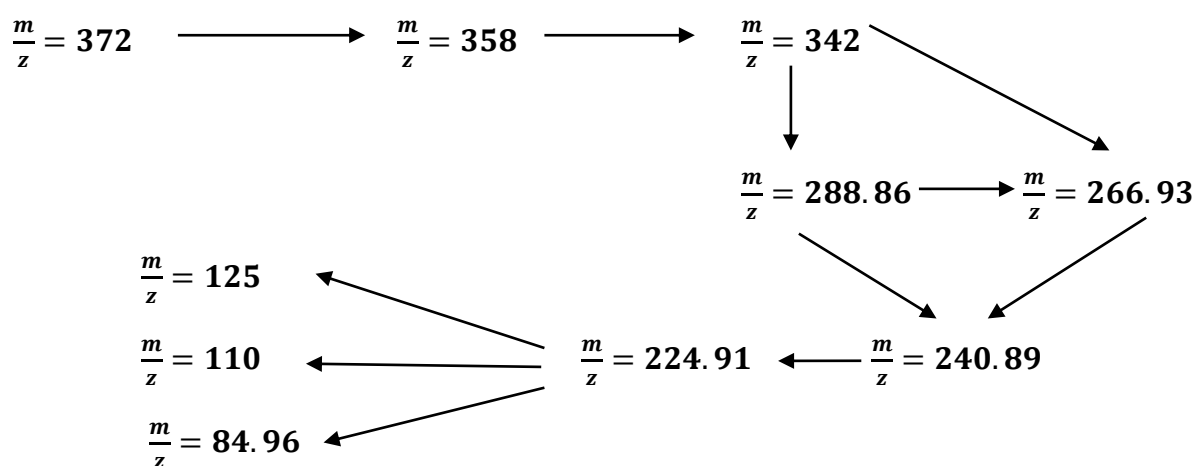


Fig. 7.12: Degradation pathway of CV dye.

The mass spectroscopy results also supported the photodegradation results of CV dye as $\frac{m}{z} = 372$ got converted and reduced to $\frac{m}{z} = 110$ and further it got reduced to $\frac{m}{z} = 84.96$. Thus, mineralization of large $\frac{m}{z}$ has occurred. The mineralization into small products has also been confirmed from the UV-absorption spectra where intensity of peak got reduced after degradation of dye. Thus, degradation of dye has been confirmed. As per literature, when dye converts to CO_2 and H_2O , then intermediates are aniline, phenol, phthalic acid, oxalic acid, acetic acid and formic acid [96]. In the LC-MS results, 4-(N-methylamino) phenol and pararosaniline are obtained. Thus, it is concluded that dye has been converted to CO_2 .

7.3.8 Kinetics of photodegradation of dye

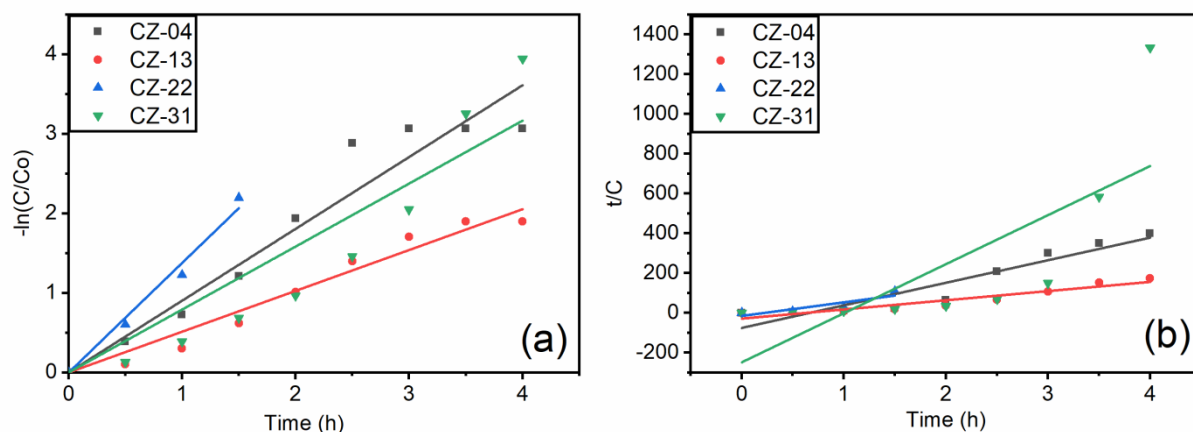


Fig. 7.12: (a) First order kinetics (b) second order kinetics of synthesized samples.

The rate of photocatalytic degradation of crystal violet (CV) dye has been studied to understand the efficiency of synthesized heterostructures [97]. The decomposition of dye is confirmed from first and second order kinetic model [16]. First order kinetics shows that the reaction is taking place through the physical adsorption of dye molecules on the surface of synthesized compound. While, the second order kinetic reaction is taking place through the chemical bonding or chemical attachment of dye molecules through O-vacancies on the surface of the catalyst [98]. The equations for first and second order kinetics are given below:

First order $-\ln\left(\frac{C}{C_0}\right) = k_1 t$ (7.2)

Second order $\frac{t}{C} = \frac{1}{k_2 C_0^2} + \frac{t}{C_0}$ (7.3)

where C_0 , C are the initial concentration, concentration at after time t , k_1 and k_2 are rate constants for first and second order kinetic models, respectively [99,100]. The relationship between $-\ln(C/C_0)$ and irradiation time (t) for first order kinetics and t/C and irradiation time (t) for second order kinetics are plotted in which calculated regression coefficients (i.e. R^2) gives the quality of fitting and k_x represents the rate constant as shown in Fig. 7.12 [1]. The parameters for first and second order kinetics have been calculated and are given in table 7.6. Fig. 7.12 depicts the rate constant for first and second order kinetics for the synthesized samples. The sample CZ-22 has shown higher rate constant k_1 , while CZ-13 has shown low rate constant. The CZ-13 has low rate constant despite of more number of O-vacancies. The O-vacancies above optimum level increases the deep traps and resulted in low rate constant [44]. The CZ-04 and CZ-13 have shown lower rate constant k_1 than CZ-31 and CZ-22 as discussed in above section. This observation can be explained on the basis of PL intensity and

O-vacancies. The PL intensity (section 7.3.6) of CZ-13 is found more than all other synthesized samples which shows higher recombination of charge carriers. The calculated R^2 value for first order kinetics is found to be more than 0.93 for the synthesized samples. However, the calculated rate constant for second order kinetics is more than first order kinetics but with low regression (R^2) constant value. This observation shows that the degradation mechanism is following first order kinetics and reaction is taking place by physical adsorption of dye molecules on catalyst surface. Hence, from the above study it is concluded that O-vacancies and PL intensity of synthesized samples are important factor for the photocatalytic activity of synthesized samples.

The band gap of synthesized samples also play important role for deciding the photocatalytic activity of synthesized samples [101]. The photoexcited electrons generated from low energy photons also takes part in the redox reactions. Thus, band gap also plays an important role for the photocatalytic activity of synthesized samples.

In the present case CZ-13 has large band gap i.e. 2.42 eV and has lower rate constant k_1 . However, CZ-31 has lower band gap but CZ-22 has shown larger rate constant. Thus, band gap is not a solely factor for deciding the catalytic activity of synthesized samples.

Table 7.6: Calculated rate constant for first and second order kinetics with their corresponding R^2 values.

Sample Ids	k_1 (h^{-1})	R^2	k_2 ($\text{mg}^{-1} \text{L h}^{-1}$)	R^2
CZ-04	0.903	0.97	169.565	0.88
CZ-13	0.513	0.98	72.112	0.89
CZ-22	1.377	0.99	294.35	0.70
CZ-31	0.791	0.93	244.73	0.50

7.3.9 Effect of various parameters on catalytic activity of synthesized samples

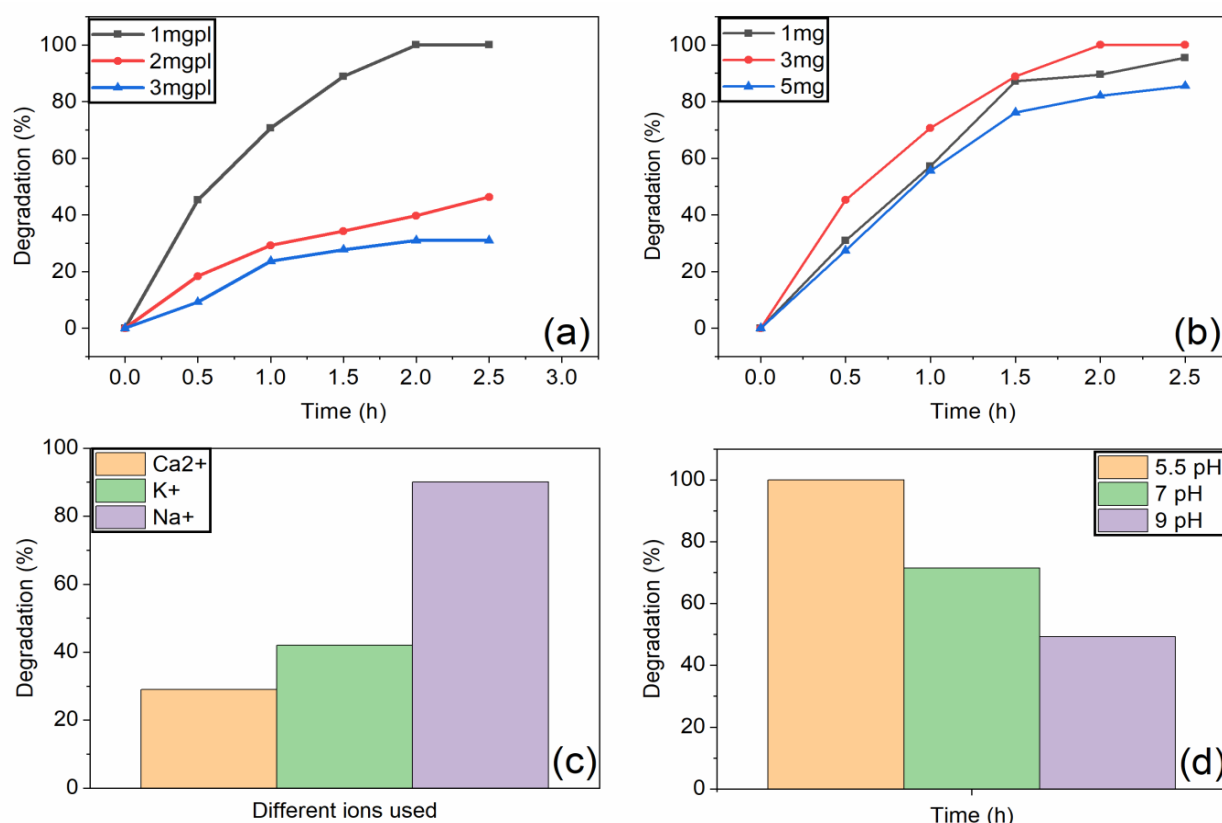


Fig. 7.13: Effect of (a) dye concentration, (b) catalyst amount, (c) various of cations and (d) pH variation of dye solution.

7.3.9.1 Effect of dye concentration

Fig. 7.13 (a) shows the effect of dye concentration on the efficiency of catalyst. The CZ-22 sample has been added to dye solution to check the efficiency. In these reactions the catalyst amount is kept same (3mg) for all the reactions to degrade different concentration of dye solution varying from 1 mg/L to 3 mg/L. It is observed that the degradation efficiency got reduced when the dye concentration is increased. This observation can be explained on the basis of fact that when the concentration of dye is increased, more number of dye molecules cover the surface of the catalyst. This decreases the penetration of UV light which falls on the surface of the dye first followed by catalyst surface and hence decreases the probability of generation of charge carriers for the synthesized photocatalyst.

7.3.9.2 Effect of catalyst concentration

Fig. 7.13 (b) shows the effect of catalyst concentration on efficiency of synthesized catalyst. It has been observed that percentage efficiency of synthesized catalyst decreases above optimum amount (3 mg). The initial enhanced catalytic activity is due to increase in active sites with increase in catalyst concentration. This increases the free radicals ($OH^\cdot$) and (O_2^-)

which further enhances the photodegradation process [102]. However, after a certain catalyst dosage the catalyst nanoparticles tend to agglomerate and block the catalyst active sites. This reduces the generation of hydroxyl radicals which inhibit the photocatalytic activity [103,104]. Puma and Brucato [105] for certain geometrical conditions found that the optimum value of optical thickness (i.e. optimum value of catalyst particles) exist, at which conversion of organic pollutants is maximum. After a certain value of optical thickness, the conversion rate starts to decrease. This might be due to fact that with increase in catalyst concentration, the scattering of photons is more compared to their absorbance on the catalyst surface.

7.3.9.3 Effect of different ions

Fig. 7.13 (c) shows the effect of different ions on photocatalytic activity of synthesized catalyst. In this reaction, first 100 ml (1 mg/l) solution of CV dye has been taken. The prepared solution (1 ml) of 0.1 M for different ions and 3 mg of catalyst has been added to dye solution. The degradation efficiency of catalyst for Na^+ ions is found to be more than Ca^{2+} and K^+ . This observation shows that Ca^{2+} ions suppress the catalytic activity of synthesized ions. It has been observed that more adsorption of dye molecules determines the possible contact between the active surface of catalyst and dyes [106]. This contact provides more possibilities of charge transfer between surface of catalyst and dye molecules. In the present case it has been observed that adsorption capacity of dye molecules for Ca^{2+} ions is 28.98%, for K^+ ions for 42.06 % and for Na^+ ions is 49 %. Thus, adsorption and degradation results are relatable. The above observation also shows that Ca^{2+} ions decrease the adsorption between catalyst and dye molecules.

7.3.9.4 Effect of pH on photocatalyst.

Fig. 7.13 (d) shows the degradation efficiency of synthesized catalyst as an effect of pH of dye solution. The pH of dye solution was varied by addition of NaOH solution. The degradation efficiency has been found to decrease as the pH of solution increased from natural pH (5.5) of dye solution. Also, adsorption can be modulated by varying the pH of the solution. It will facilitate the number of dye molecules adsorbed on the surface of photocatalyst. With increase in pH of dye solution the negative charge of dye solution increases. This will decrease the interaction between dye solution and catalyst surface [101]. Thus, in the present case, higher pH of dye solution is not favorable for higher catalytic activity. The zeta potential of CZ-13 and CZ-22 has been checked. The zeta potential for CZ-13 is -11.5 and for CZ-22 is -9.63. However, rate constant is found more for CZ-22 than CZ-

13. Thus, photocatalytic activity of the synthesized sample is a combined results of O-vacancies, charge present on the surface of catalyst and charge recombination.

7.3.10 Degradation mechanism

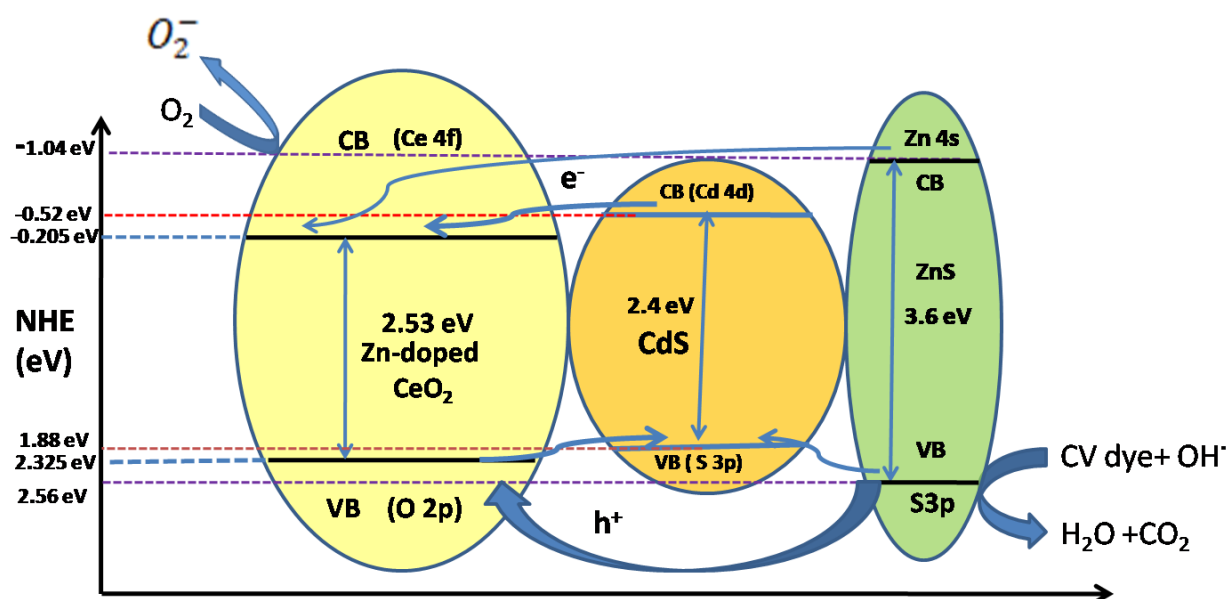


Fig. 7.14: Showing the degradation mechanism of CV dye.

Fig. 7.14 shows the degradation mechanism of synthesized sample. The valence band (VB) and conduction band (CB) potential level are calculated by using following relations [44].

$$E_{CB} = \chi - E^c - 0.5E_g \quad (7.4)$$

$$E_{VB} = E_g - E_{CB} \quad (7.5)$$

Where χ is absolute electro negativity of the CeO_2 (5.56 eV), CdS (5.18 eV) and ZnS (5.26 eV) [107]. E_c refers to the energy of free electron on the hydrogen scale (NHE, 4.5 eV), and E_g is the estimated band gap of CeO_2 , CdS and ZnS . The calculated value of CB and VB are shown in table 7.7.

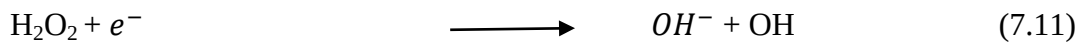
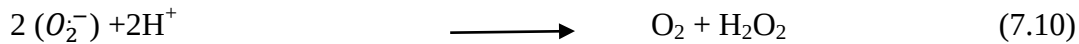
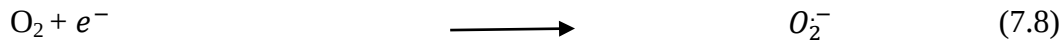
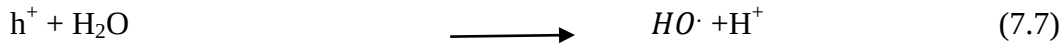
Table 7.7: Calculated valence and conduction band edge.

Semiconductor	CB edge (eV)	VB edge (eV)
CeO_2	-0.205	2.325
CdS	-0.52	1.88
ZnS	-1.04	2.56

From the degradation mechanism shown in Fig. 7.14, it can be concluded that the enhancement of photocatalytic activity is due to the heterostructures. The ZnS-CdS heterostructures are of type-I in which CB and VB of one material (CdS) exists between the

other (ZnS) semiconductor as calculated using eqn. (7.3) and (7.4) and is shown in Fig. 7.14. The CdS-CeO₂ are of type-III heterostructures in which VB and CB of CdS lies above the VB and CB of that of other (CeO₂). The band gap of Zn-doped CeO₂ is 2.53 eV, for CdS is 2.4 eV and for ZnS is 3.6 eV [44,107,108]. As shown in Fig. 7.14, the holes generated in VB of CeO₂ and ZnS are transferred into VB of CdS thermodynamically. It is also observed that the holes generated in VB of ZnS get transferred to VB of Zn-doped CeO₂ and performs photo-oxidation. On the other side, electrons generated in the CB of CeO₂ cannot be energetically transferred to CB of CdS and ZnS due to more negative potential. However, electrons generated in CB of ZnS and CdS are transferred thermodynamically to CB of Zn-doped CeO₂ and performs photoreduction. The modifications in surface hydroxyl groups along with surface O-vacancies occurs when ZnS and CdS are co-anchored with CeO₂ that enhances the photocatalytic activity. These modifications are responsible for enhancement in photocatalytic performance. Thus, enhancement in photocatalytic performance is an integrated result of band edge level, hydroxyl groups and O-vacancies.

The reaction involved for degradation of dye molecules are given below. The given reactions show the role of photogenerated electrons, holes, $HO\cdot$ and $O_2^{\cdot-}$.



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CHAPTER 8

CONCLUSIONS AND FUTURE SCOPE

Overview

In this chapter all the results which are obtained through different experiments to synthesize CeO₂ nanoparticles for the dye degradation has been presented. Various parameters such as effect of capping agent, calcination and nature of solvent to synthesize these nanoparticles are summarized in this chapter. The experimental results for doped and co-doped samples are also summarized. Further, the undoped and doped CeO₂ NPs are used for the synthesis of heterostructures with CdS and ZnS NPs. All the synthesized nanoparticles were used to degrade the CV dye. These synthesized nanoparticles have shown different interdependent parameters to degrade CV dye which has been summarized in this chapter. On the basis of results obtained from the synthesized NPs and their performance to degrade CV dye, suggestions for future work have been given in the chapter.

8.1 Conclusions

The initial objectives of thesis are given below:

On the basis of initial objectives set to carry out the work, experiments were performed. The main objective was to synthesize undoped, doped and hybrid semiconductor composites CeO₂ nanoparticles (NPs) by adopting chemical route and observe their dye degradation properties. From those work following conclusions are drawn.

The CeO₂ NPs have been synthesized in water and ethanol solvent via co-precipitation method. Further, the synthesized NPs have been calcined at different temperatures to check the effect of calcination on their properties. These synthesized NPs were used to degrade CV dye.

It was found that the variation in the synthesis parameters influenced the photocatalytic activity of CeO₂ NPs for the degradation of crystal violet dye under UV-visible illumination. XRD results showed that both the crystallinity and crystallite size increased as an effect of calcination only for samples which were synthesized in water. The CeO₂ NPs synthesized in ethanol medium have shown induced lattice relaxation and coalescence of nanoparticles due to surface functionalization during the growth of nanoparticles. FTIR spectra confirmed the stretching of bonds and different functional groups attached to the surface of CeO₂. TEM micrographs depicted the formation of agglomerated nanoparticles but, the extent of agglomeration was less in the sample calcined using capping agent. Further, the variation in the absorbance spectra revealed the modifications in the electronic structure of CeO₂ with the change in synthesis parameters. Raman spectroscopy confirmed the formation of fluorite structured CeO₂ and also oxygen vacancies by the creation of Ce³⁺. The photo-removal efficiency of TG capped samples have shown 100% degradation which was much higher than uncapped samples (78%) due to more exposed area having less agglomeration and higher concentration of oxygen vacancies on the surface of CeO₂ NPs. Also, the photo-removal efficiency enhanced in the presence of H₂O₂ due to increased hydroxyl groups which acted as electron acceptors and inhibited the recombination rate. The higher concentration of H₂O₂ molecules scavenge the valuable *OH*[•] and form an oxidant [•]OH₂ which are less reactive than *OH*[•].

Further, Y and Zn doped and (Y, Zn) co-doped CeO₂ NPs were successfully synthesized via co-precipitation route. For Y-doped samples, crystallinity and crystallite size were found to increase up to 6 %, no significant enhancement in crystallite size was observed with Zn doping. FTIR spectra confirmed the formation and attachment of different functional groups to the surface of CeO₂. TEM micrographs depicted the formation of agglomerated non-

symmetrical CeO₂ NPs. Further, no significant pattern of red or blue shifting in absorbance peak was observed as an effect of doping and co-doping. The variation in absorbance spectra revealed the modifications in electronic structure of CeO₂ as an effect of dopants and co-dopants. Raman spectroscopy confirmed the formation of fluorite structured CeO₂ and also revealed the formation of O-vacancies due to incorporation of Zn²⁺ and Y³⁺. The degradation efficiency was 100 % for doped samples within 5 h under UV-visible light irradiation. However, the degradation efficiency increased to 100% for (Y, Zn) co-doped samples within 3 h of UV-visible illumination due to presence of O-vacancies on the surface of CeO₂. For photocatalytic degradation efficiency, O-vacancies played a major role. It is concluded from the photocatalytic results that degradation efficiency increases with doping and co-doping of metal ions as compared to bare samples.

The CdS heterostructures were synthesized with Zn-doped and (Y, Zn) co-doped CeO₂ NPs. XRD study reveals that crystallite size increases with the growth of CdS phase as confirmed from XRD results. The formation and attachment of different functional groups to the surface of synthesized heterostructures was confirmed from FTIR spectra. Further, there was reduction in band gap towards visible region showing enhanced efficiency of photocatalyst. The modification in the absorbance spectra depicts the change in the electronic structure of the synthesized heterostructures. TEM micrograph depicts the agglomerated and irregular shape of synthesized NPs. Raman spectroscopy confirmed the formation of fluorite structure of CeO₂ and wurtzite structure of CdS. Raman spectroscopy has also revealed the formations of O-vacancies. The heterostructures which were synthesized using Zn-doped CeO₂ exhibited quick removal for CV dye under UV-visible light illumination due to presence of optimum amount of O-vacancies. For photocatalytic degradation efficiency, O-vacancies, hydroxyl groups and band edge matching played a major role. However, O-vacancies played more vital role for enhancing the photocatalytic activity. It is concluded from photocatalytic results that degradation efficiency get enhanced for heterostructures as compared to bare CeO₂ NPs.

The heterostructures of Zn-doped CeO₂ were successfully synthesized with Cd₀Zn_{0.003}S_{0.003}, (Cd_{0.00075}Zn_{0.00225})S_{0.003}, (Cd_{0.0015}Zn_{0.0015})S_{0.003} and (Cd_{0.00225}Zn_{0.00075})S_{0.003} via co-precipitation method. It has been observed that synthesis parameters highly influenced the photocatalytic activity of synthesized samples for the degradation of crystal violet dye under UV-visible illumination. The crystallite size was in the range of nanometer. The presence of ZnS and CdS in the synthesized heterostructures has been confirmed from FTIR, Raman and PL spectroscopy. The attachment of different functional groups has been confirmed from FTIR spectra. Raman spectroscopy also confirmed the formation of fluorite structure of CeO₂,

wurtzite structure of CdS and ZnS along with presence of O-vacancies by the creation of Ce^{3+} . TEM micrographs depicted the formation of nanoparticles but of irregular shapes. The enhancement in photocatalytic activity was due to creation of optimum amount of O-vacancies by transformation of Ce^{4+} to Ce^{3+} . The sample $(\text{Zn}_{0.0015}\text{Cd}_{0.0015})\text{S}/\text{CeO}_2$ (CZ-22) has shown higher activity due to optimum amount of O-vacancies and more number of hydroxyl groups.

The overall summary of entire work is that the heterostructures with Zn-doped CeO_2 with CdS has shown better efficiency to degrade CV dye within 2h of UV-visible exposure as compared to bare CeO_2 and (Y, Zn) doped CeO_2 .

Sidarai et al. [31] synthesized ZnO/CeO_2 using hydrothermal method and found only 65 % decolorization of Neutral red (NR) for 1 ppm solution with 10^{-5} M of catalyst amount in 100 ml of dye solution. Sekar et al. [27] observed nearly 78.8 % degradation towards CV dye (20 ppm) by bare CeO_2 (20 mg catalyst in 60 ml of dye solution) in 195 minutes. In present study nearly 100 % of decolourization has been observed using bare CeO_2 (3 mg of catalyst dissolved in 100 ml of dye solution) towards CV dye (1 ppm) in 420 minutes (page no. 176, section 8.2). However, CeO_2 heterostructures synthesized with CdS has shown 100 % removal of dye (1 ppm) in 120 minutes of UV-visible illumination. The study shows that the catalysts developed in present study has shown better catalytic property to degrade the dye in less time compared to the work reported in literature so far.

8.2 Future Scope

A detail study has been done to modify the photocatalytic performance of CeO_2 NPs as it has been discussed in previous chapters. However, the photocatalytic activity can be improved further by considering following points.

- The temperature effect on the photocatalytic activity can be optimized as it can increase the generation of more radicals under illumination of UV-visible irradiation.
- In this study, the synthesis of heterostructures of CeO_2 with ZnS and CdS have been done. However, the synthesis of heterostructures with graphene might be more helpful to enhance the photocatalytic activity because graphene can absorb large radiations and increase the photocatalytic activity.
- The CeO_2 heterostructures with C_3N_4 can be synthesized as CeO_2 is UV active compound and C_3N_4 is a visible active compound. Thus, addition of one over another compound might be helpful to reduce the charge carrier recombination.

- CeO₂ based photocatalyst can play very important role for renewable energy production as it has non-toxic nature. Thus, it becomes more important to study its morphological, optical and photocatalytic properties by synthesis of more heterostructures with other metal oxides which can reduce the charge recombination.

Annexure A

Table A1: shows the sample spectra labelling.

Sample Id	Representation
0H	Initial spectra of CV dye
2HA	Spectra of dye after 2 hour adsorption
0.5HD	Spectra of dye after 0.5 hour degradation
1HD	Spectra of dye after 1 hour degradation
1.5HD	Spectra of dye after 1.5 hour degradation
2HD	Spectra of dye after 2 hour degradation
2.5HD	Spectra of dye after 2.5 hour degradation
3HD	Spectra of dye after 3 hour degradation
3.5HD	Spectra of dye after 3.5 hour degradation
4HD	Spectra of dye after 4 hour degradation
5HD	Spectra of dye after 5 hour degradation
6HD	Spectra of dye after 6 hour degradation
7HD	Spectra of dye after 7 hour degradation

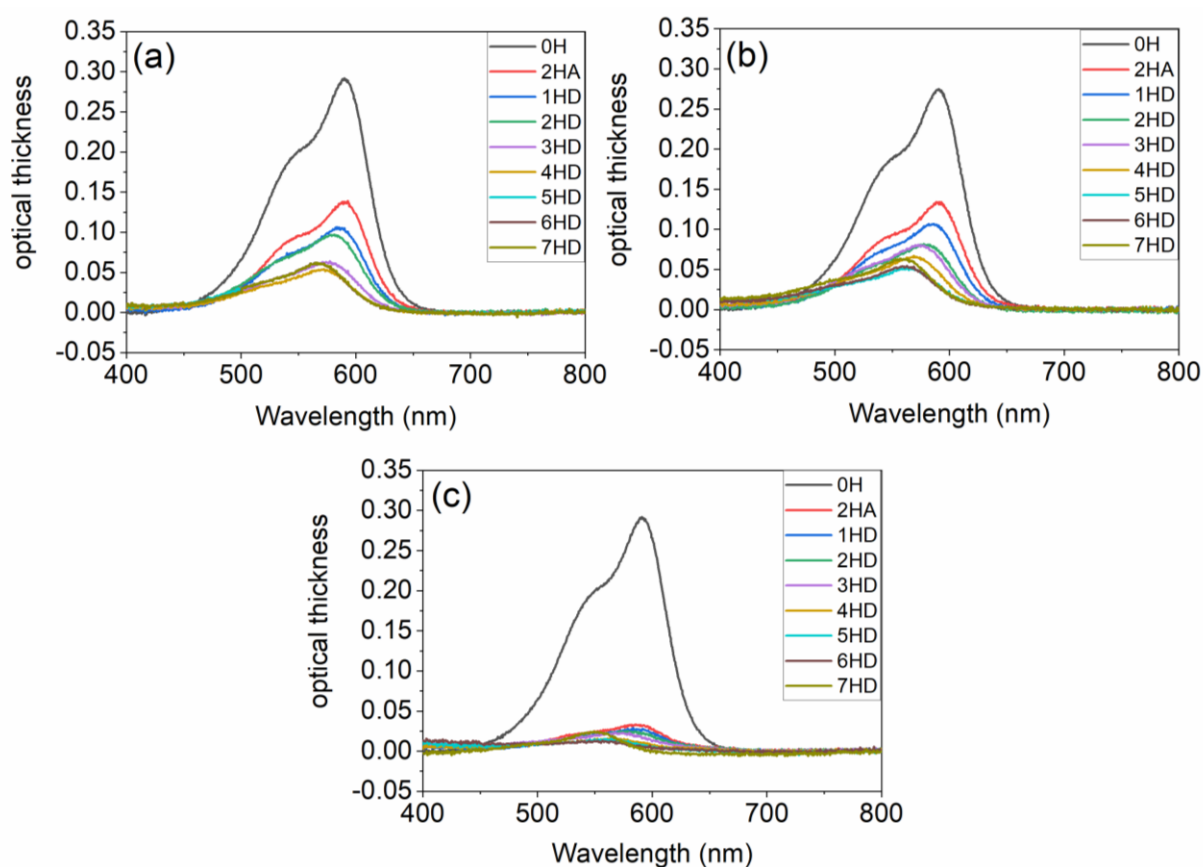


Fig. A1. Spectral variation of optical thickness of CV degraded with (a) W0 (b) W300 and (c) W600.

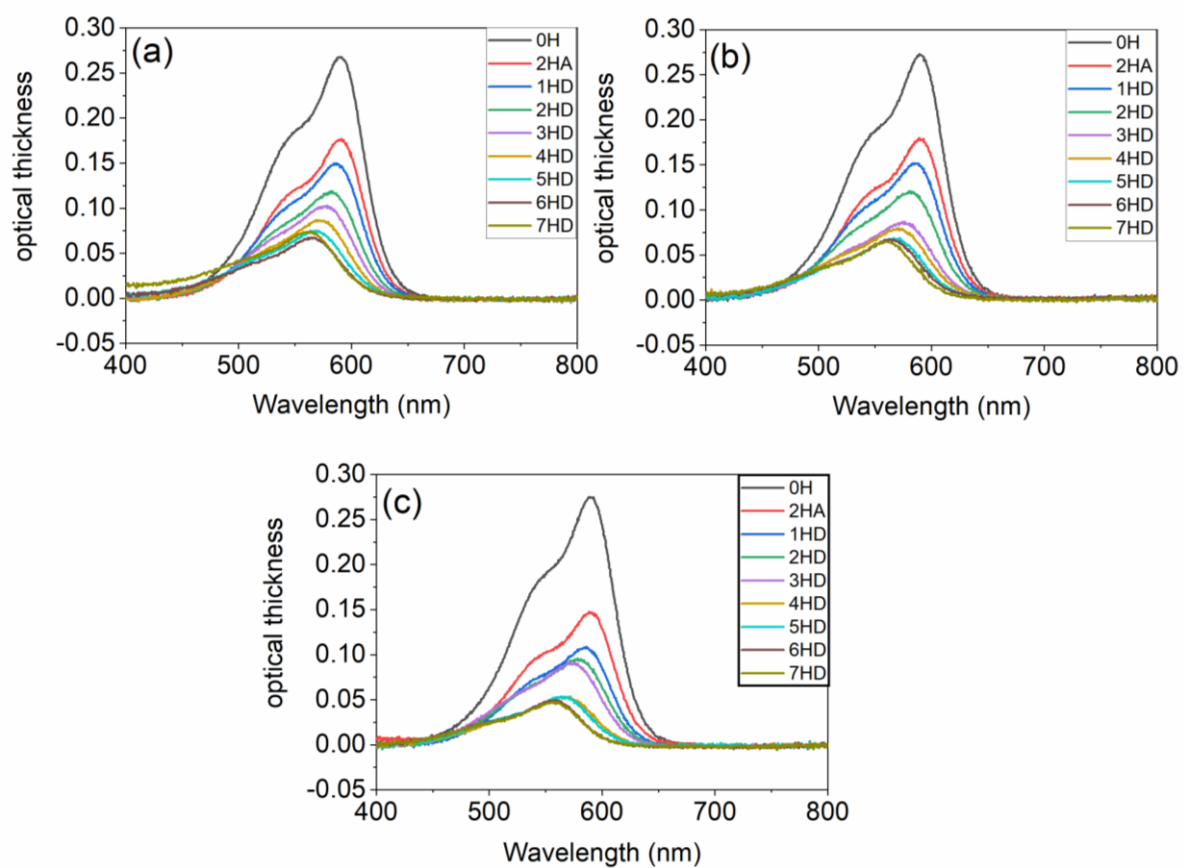


Fig. A2. Spectral variation of optical thickness of CV degraded with (a) E0, (b) E300 and (c) E600.

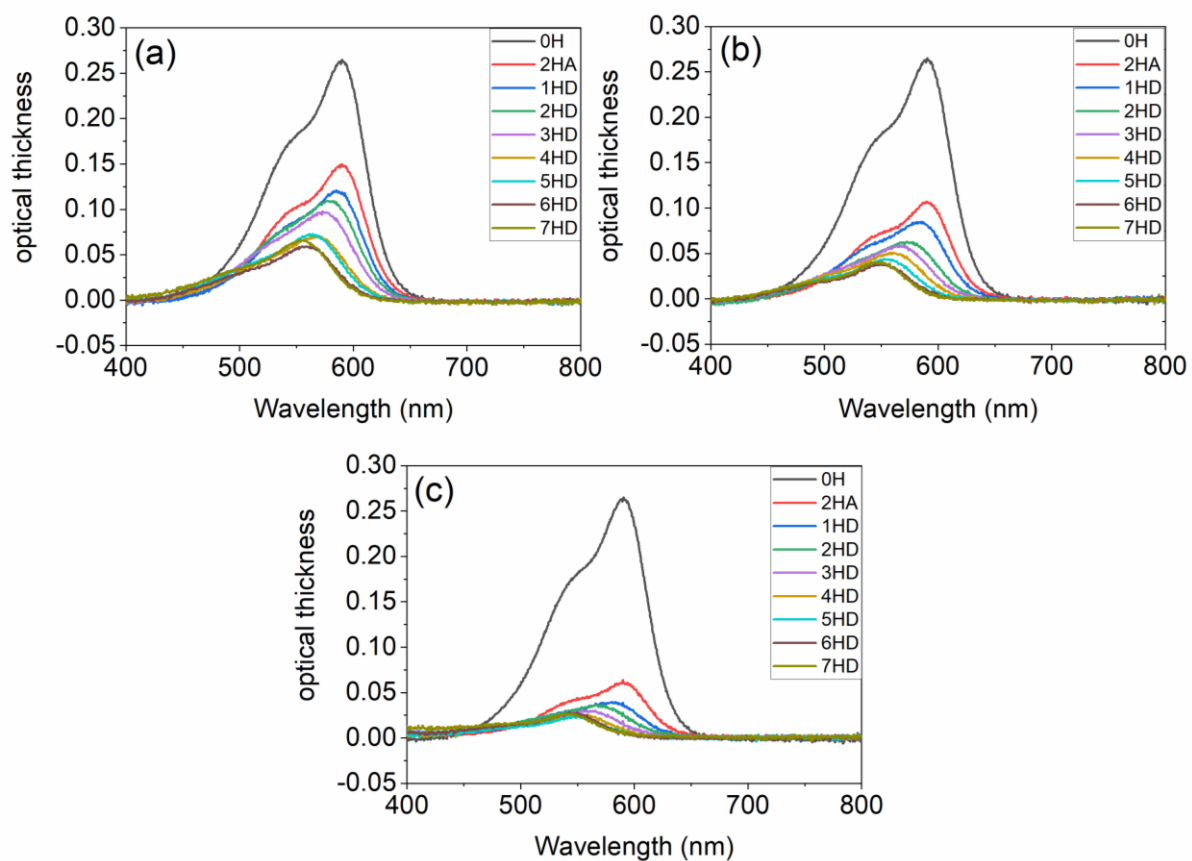


Fig. A3. Spectral variation of optical thickness of CV degraded with (a) WT0, (b) WT300 and (c) WT600.

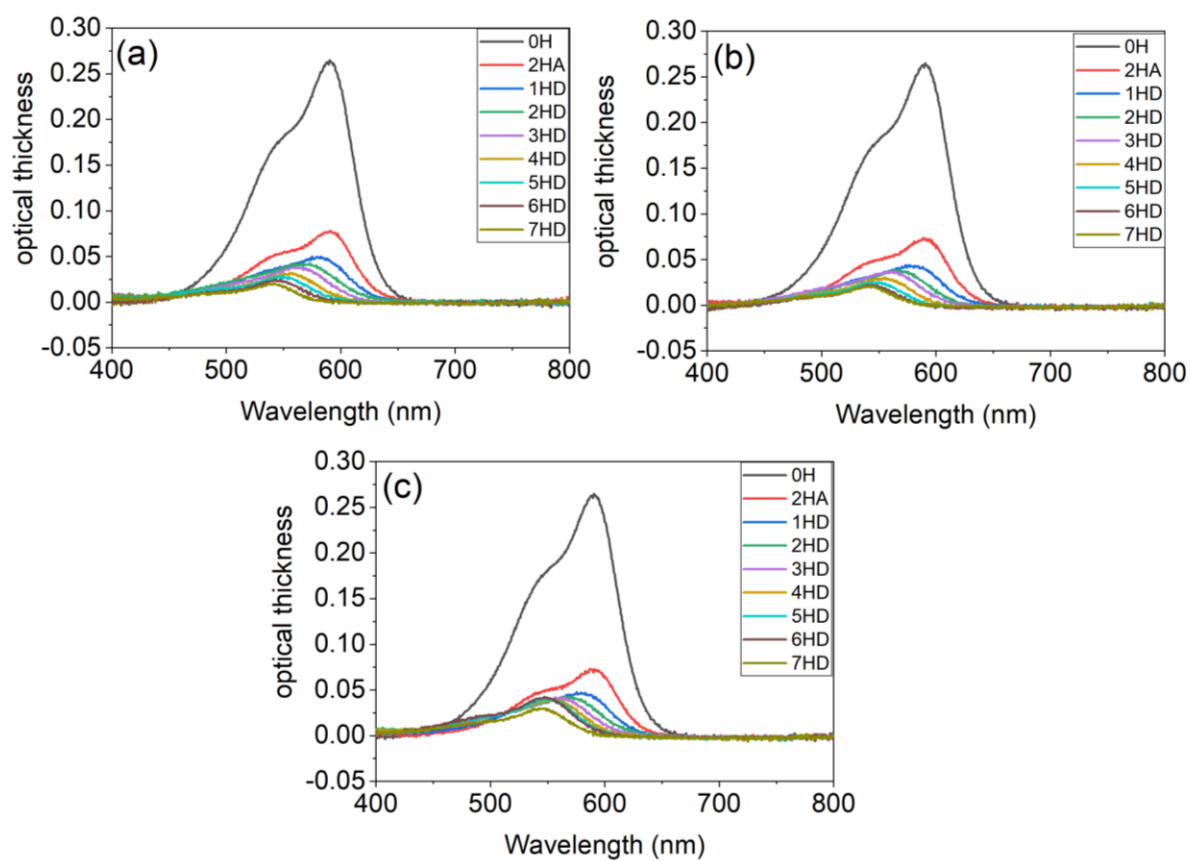


Fig. A4. Spectral variation of optical thickness of CV degraded with (a) ET0, (b) E3T00 and (c) E6T00.

Annexure B

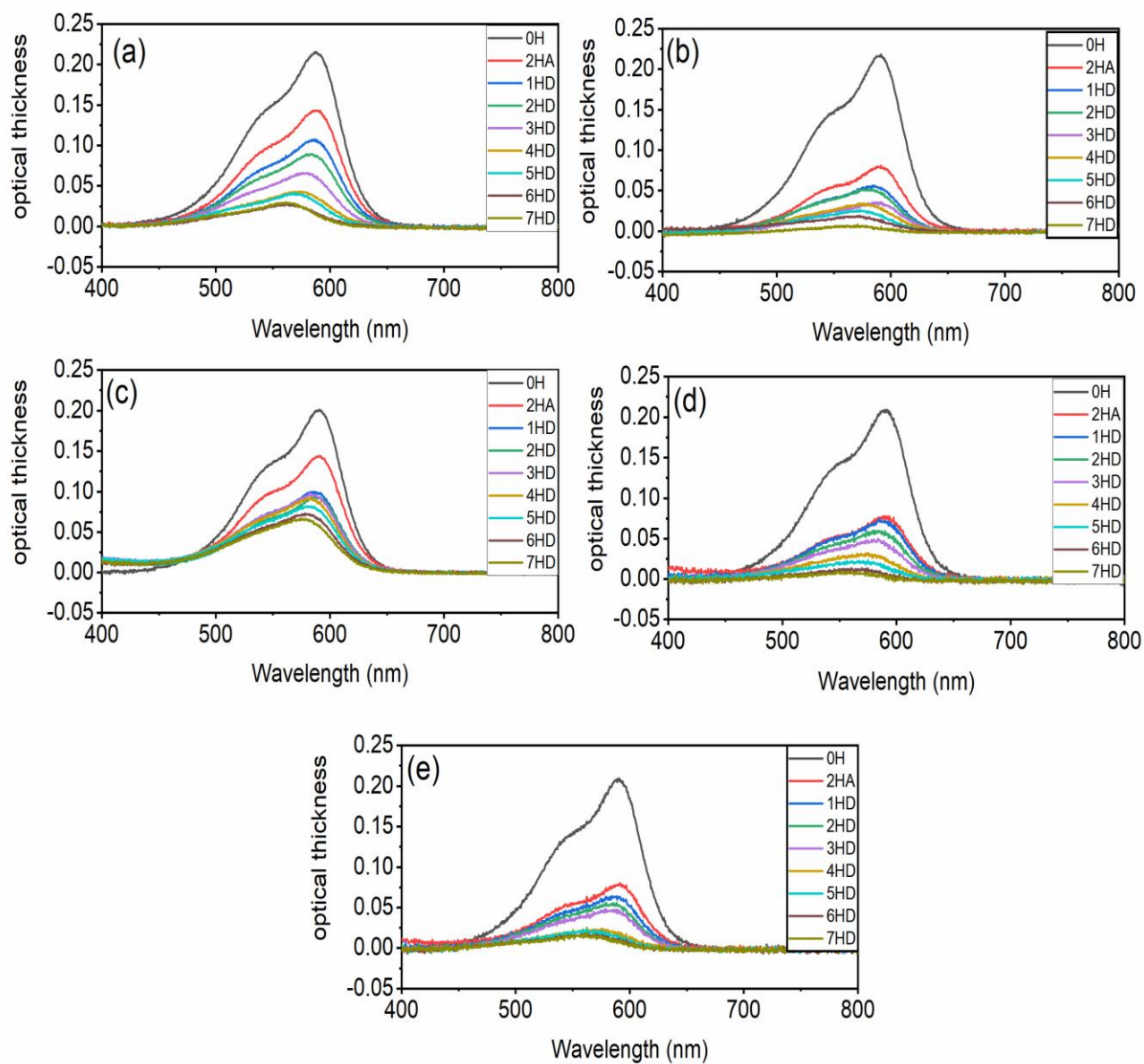


Fig. B1. Spectral variation of optical thickness of CV degraded with (a) 2%Y, (b) 4%Y, (c) 6%Y, (d) 8%Y and (e) 10%Y.

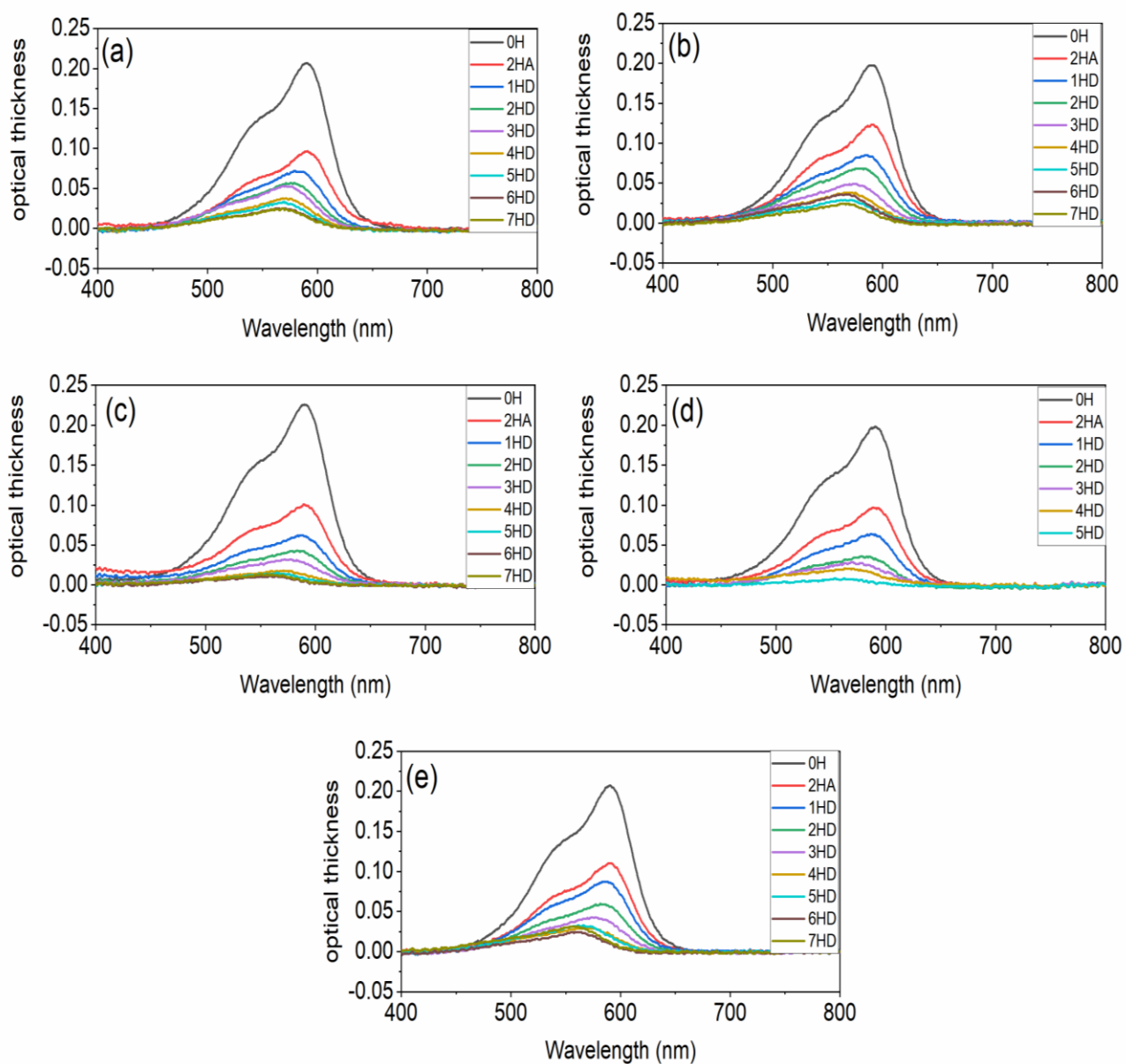


Fig. B2. Spectral variation of optical thickness of CV degraded with (a) 2%Zn, (b) 4%Zn, (c) 6%Zn, (d) 8%Zn and (e) 10%Zn.

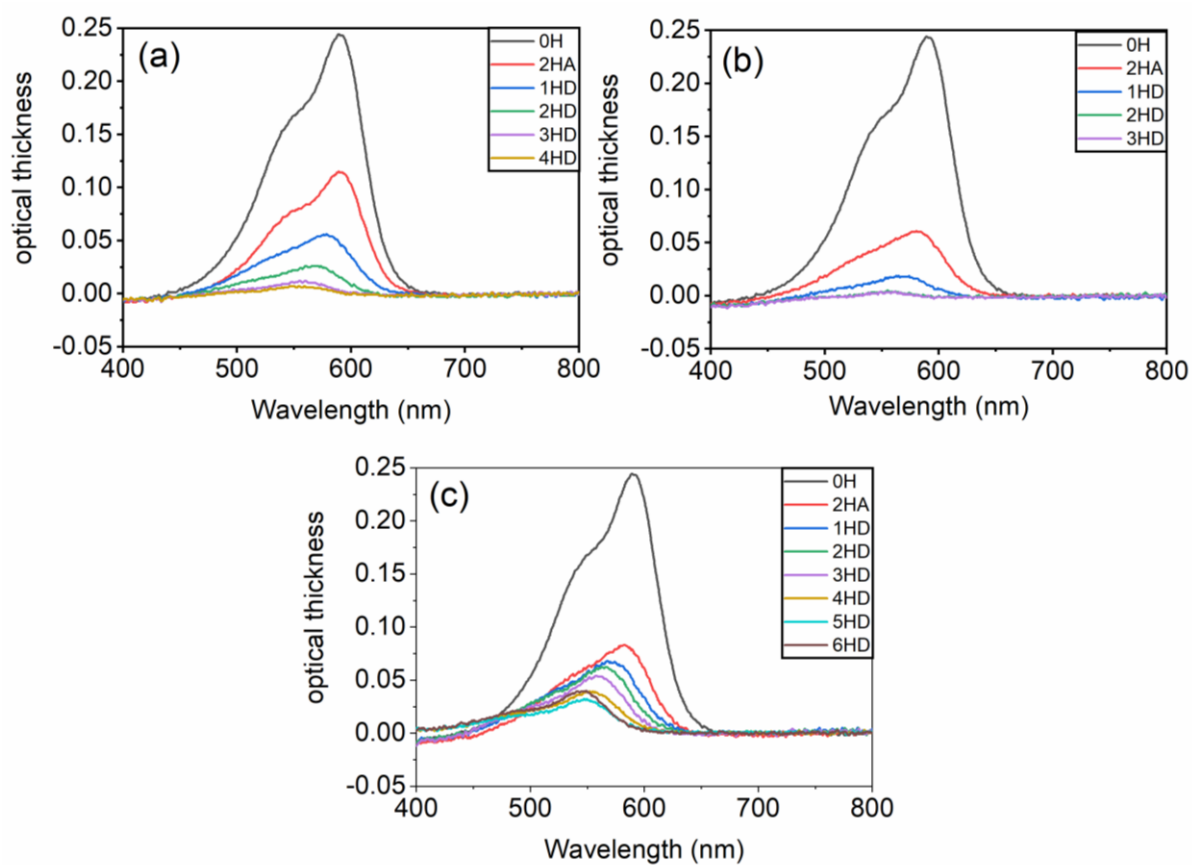


Fig. B3. Spectral variation of optical thickness of CV degraded with (a) 6%Zn2%Y, (b) 4%Zn4%Y and (c) 2%Zn6%Y.

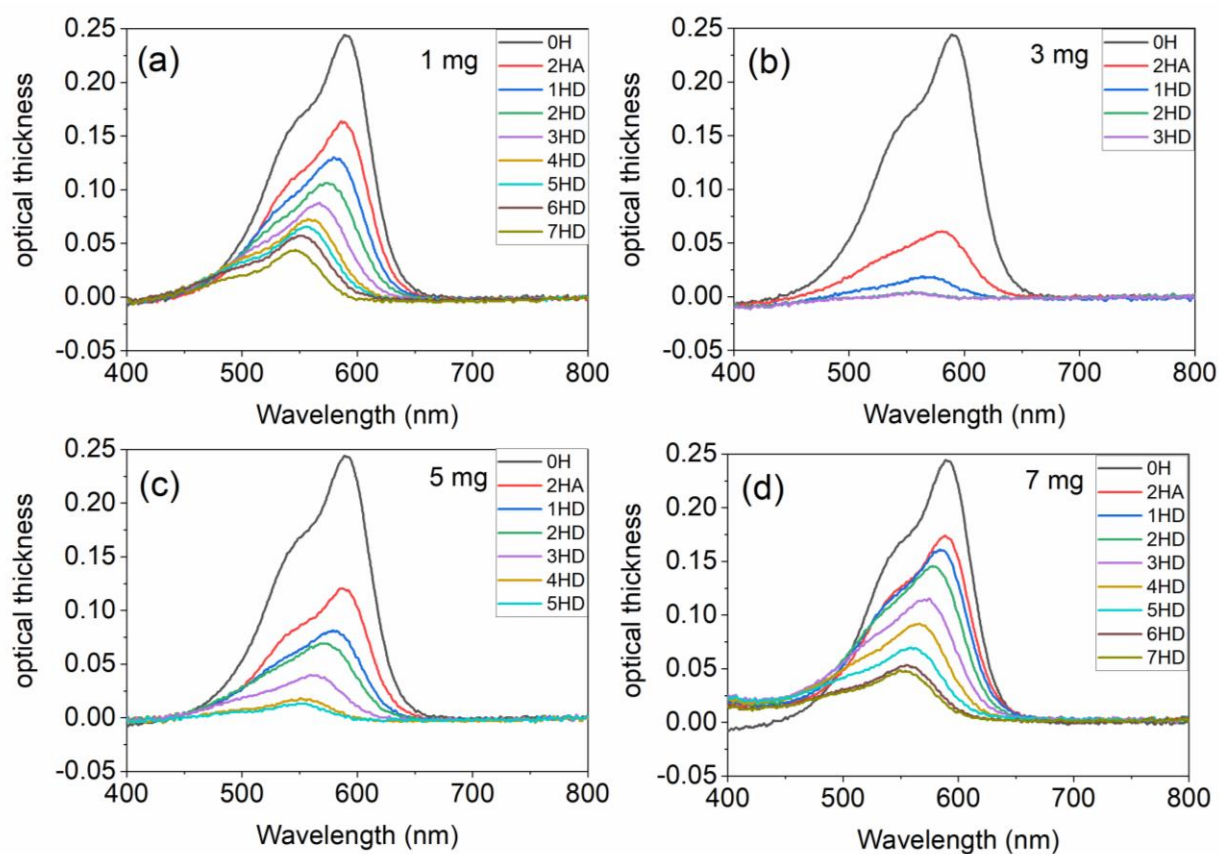


Fig. B4. Spectral variation of optical thickness of CV degraded with 4%Zn4%Y as an effect of catalyst concentration (a) 1 mg, (b) 3 mg, (c) 5 mg, and (d) 7 mg.

Annexure C

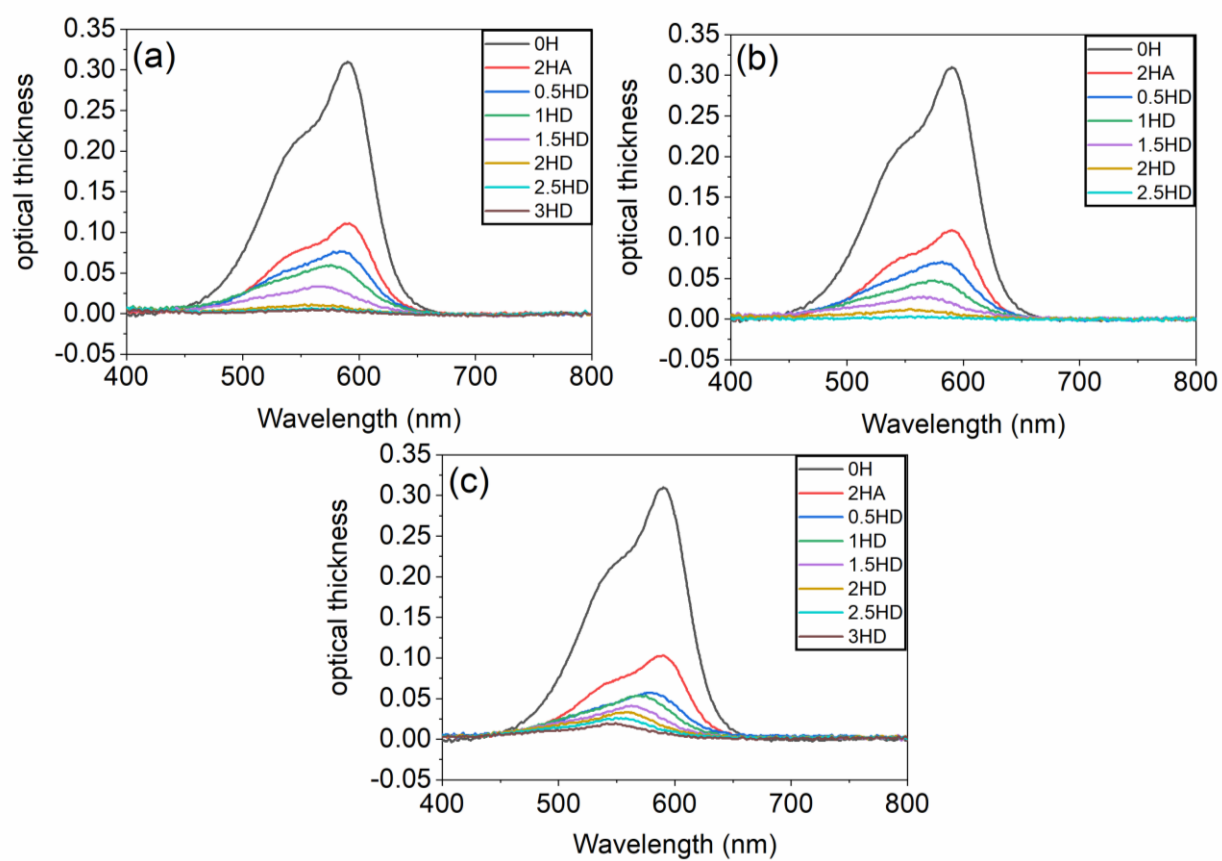


Fig. C1. Spectral variation of optical thickness of CV degraded with (a) CCDS-2:1, (b) CCDS-1:1 and (c) CCDS-1:2.

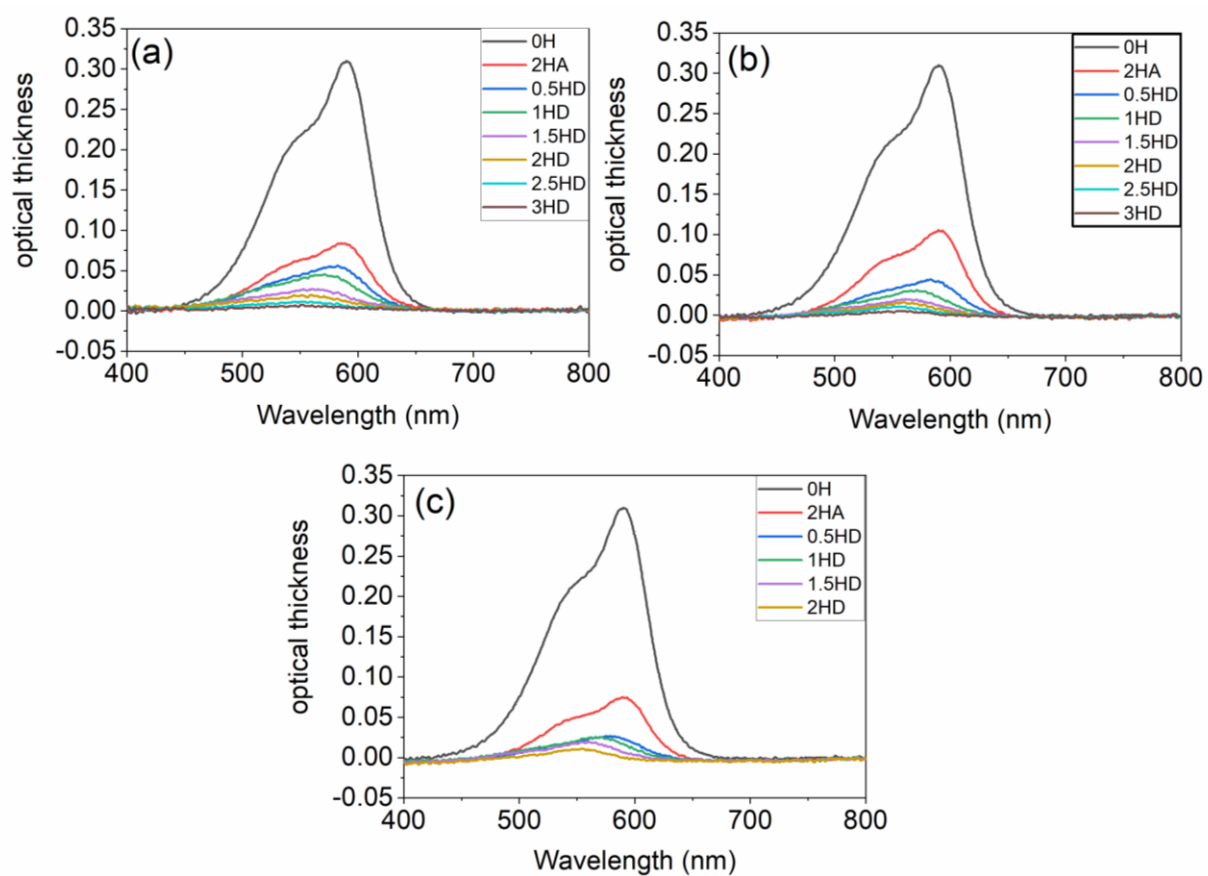


Fig. C2. Spectral variation of optical thickness of CV degraded with (a) ZCCDS-2:1, (b) ZCCDS-1:1 and (c) ZCCDS-1:2.

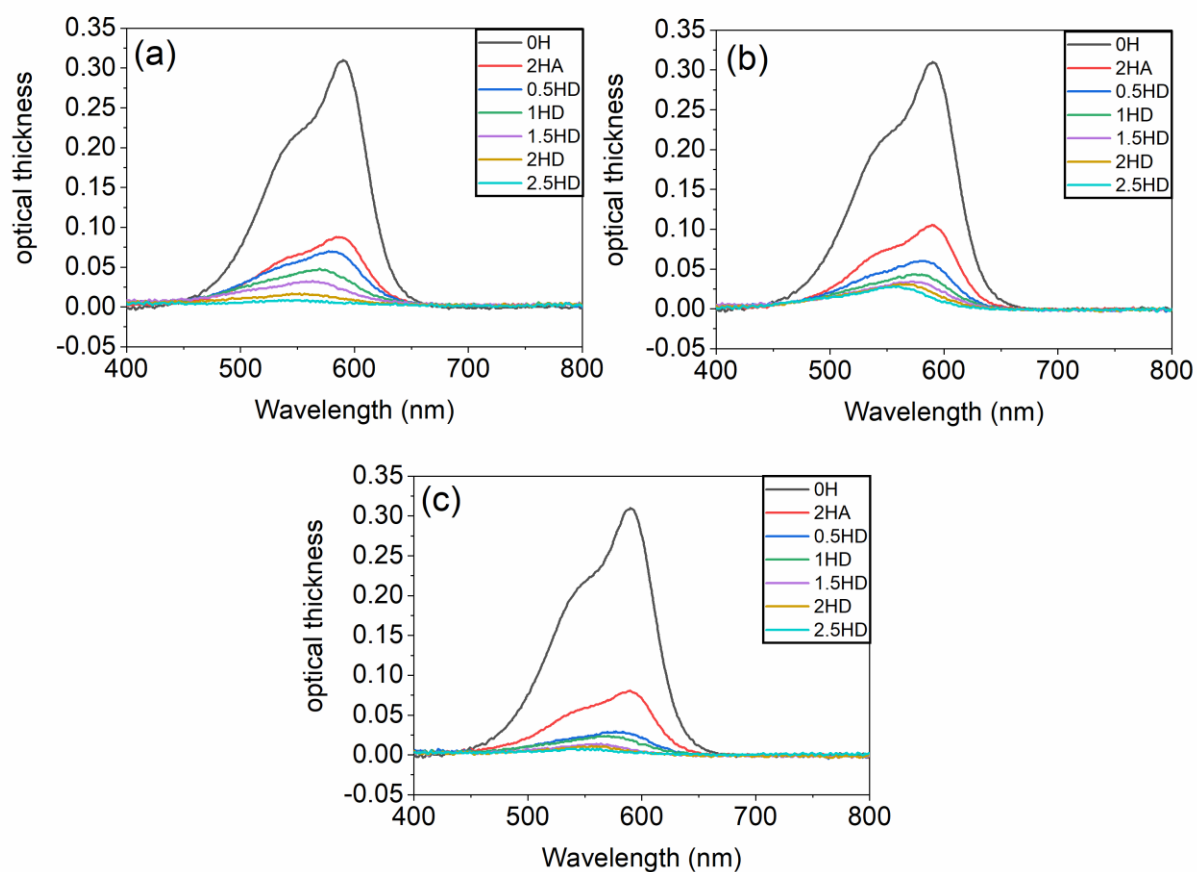


Fig. C3. Spectral variation of optical thickness of CV degraded with (a) ZYCCDS-2:1, (b) ZYCCDS-1:1 and (c) ZYCCDS-1:2.

Annexure D

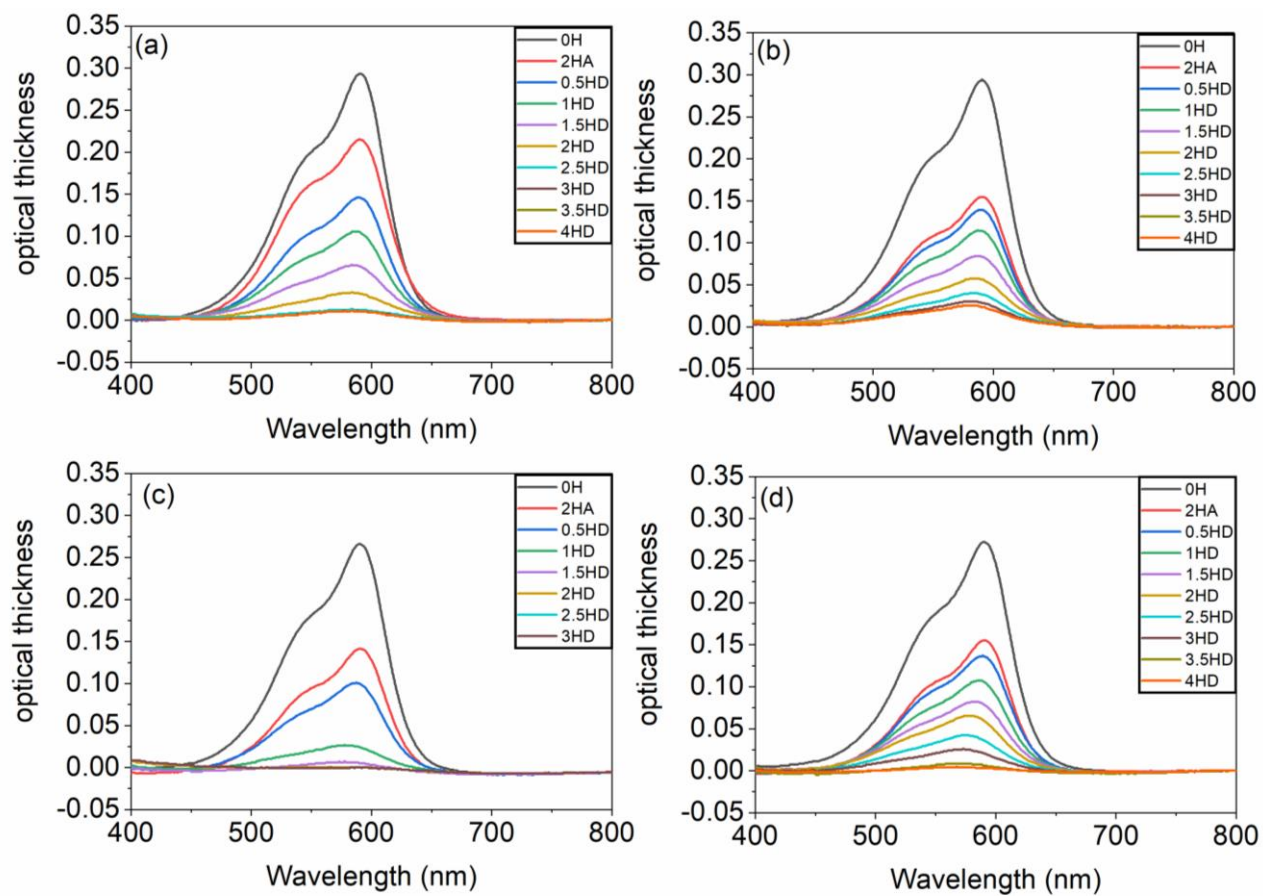


Fig. D1. Spectral variation of optical thickness of CV degraded with (a) CZ-04, (b) CZ-13 and (c) CZ-22 and (d) CZ-31.