Mn-DOPED ZnS QDs: A STUDY ON OPTICAL AND PHOTOLUMINESCENT PROPERTIES

Dissertation Submitted
in Partial Fulfillment of the Requirements for the
Degree of

MASTER OF SCIENCE

in

CHEMISTRY

by

Deepika
(2k22/MSCCHE/08)

Under the Supervision of

Dr. Mohan S. Mehata and Prof. Archna Rani

To the

Department of Applied Chemistry

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India
JUNE, 2024

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

CANDIDATE DECLARATION

I, Deepika (2k22/MSCCHE/08) hereby certify that the work which is being presented in the thesis entitled **"Mn-doped ZnS QDs: A study on optical and photoluminescent properties"** in partial fulfillment of the requirements for the award of the Degree of Master of Science, submitted in the Department of Applied Chemistry, Delhi Technological University is an authentic record of my own work carried out during the period from Aug 2023 to Mar 2024 under the supervision of Dr. Mohan S. Mehata and Prof. Archana Rani.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other institute.

Deepika
(2k22/MSCCHE/08)

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

CERTIFICATE

Certified that Deepika (2k22/MSCCHE/08) has carried out her research work presented in this thesis entitled **"Mn-doped ZnS QDs: A study on optical and photoluminescent properties"** for the award of Master of Science from the Department of Applied Chemistry, Delhi Technological University, Delhi, under our supervision. The thesis embodies results of original work, and studies are carried out by the student herself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

Dr. MOHAN S. MEHATA
Assistant Professor
Department of Applied Physics
Delhi Technological University

Prof. ARCHNA RANI
Professor
Department of Applied Chemistry
Delhi Technological University

Place -New Delhi

Date- 06.06.2024

ACKNOWLEDGEMENTS

The success and outcome of this project required a lot of guidance and assistance from many people and we are extremely fortunate to have got this all along the completion of this project work.

I wish to express my gratitude towards my project supervisors**, Prof. Archna Rani and Dr. Mohan S. Mehata, Department of Applied Chemistry, Delhi Technological University**, who provided us with a golden opportunity to work under their able guidance. Their scholastic and sagacious suggestions help me to complete the project on time.

I wish to thank **Prof. Anil Kumar, Head of the Department of the Applied Chemistry**, **Delhi Technological University** for his constant motivation.

I am thankful for and fortunate enough to get constant encouragement, support, and guidance from all teaching staff of the Department of Applied Chemistry, which helped me in completing our project work. I am also thankful to **Research Scholar Mr. Vinay K. Yadav** for his constant support and motivation.

Finally, yet importantly, I would like to express my heartfelt thanks to my beloved family and friends who have endured my long working hours and whose motivation kept me going.

Deepika

ABSTRACT

This study focuses on the synthesis, characterization and potential applications of manganese (Mn) doped zinc sulfide (ZnS) quantum dots (QDs) via hot injection method, allowing a precise control over the doping concentration. In this facile and reproducible synthesis, 2- Mercaptoethanol is used as capping agent. The synthesis was conducted at 70 °C in an inert environment of N_2 gas. This study's primary goal was to find out how Mn doping affected the structural, optoelectronic, and magnetic characteristics of ZnS QDs, with 1% and 2% doping concentrations in different samples. Synthesis is followed by detailed characterization using several techniques such as X-ray diffractometry (XRD), Transmission electron microscopy (TEM), Photo Luminescence (PL) spectroscopy, and UV-Vis spectroscopy. The ZnS lattice's crystalline structure and the successful integration of Mn ions are verified using XRD examination. TEM images demonstrate the formation of well-dispersed Mn-doped ZnS QDs with controlled particle size. This research provides valuable insights into the synthesis and properties of Mn-doped ZnS quantum dots, giving the ways for their utilization in various technological applications in optoelectronic devices, bioimaging, photocataysts , sensors and various drugs.

Keywords: Zinc Sulfide Quantum dots, Hot injection method, Optoelectronic devices etc.

TABLE OF CONTENTS

S.no	Topic	Page no.
1.	Cover Page	i
2.	Candidate's Declaration	ii
3.	Certificate	iii
4.	Acknowledgment	iv
5.	Abstract	v
6.	Table of Contents	vi-viii
7.	List of Figures	ix
8.	List of Symbols and Abbreviations	x-xi
9.	**CHAPTER 1 INTRODUCTION** 1.1 Nanotechnology 1.2 Literature Review 1.2.1 Quantum Dots 1.2.2 ZnS QDs	1-8

	1.2.3 Methods of Synthesizing ZnS QDs 1.2.3.1Top-down approach 1.2.3.2 Bottom-up approach 1.2.4 Properties of ZnS QDs 1.2.5 Added benefits of ZnS QDs over CdSe QDs 1.2.6 Potential Applications of ZnS QDs	
10.	**CHAPTER 2 SYNTHESIS AND CHARACTERIZATION TECHNIQUES** 2.1 Chemical and Reagents used 2.2 Synthesis of ZnS QDs 2.3 Characterization Techniques 2.3.1 X-Ray Diffractometry (XRD) 2.3.2 Transmission Electron Micrography (TEM) 2.3.3 UV Spectroscopy 2.3.4 Photoluminescence spectra	**9-15**
11.	**CHAPTER 3 RESULTS AND DISCUSSION** 3.1 X-Ray Diffraction (XRD) pattern 3.2 Transmission Electron Micrograph (TEM) 3.3 UV spectroscopy 3.4 Photoluminescence analysis	**16-22**

12.	**CHAPTER 4 APPLICATIONS OF ZnS QDs** 4.1 Applications of QDs in solar cells 4.2 ZnS QDs in QDSSCs 4.3 Challenges and Future perspectives of ZnS QDs in QDSSCs 4.4 Applications beyond QDSSCs	**23-26**
13.	**CONCLUSION**	**27**
14.	**REFERENCES**	**28-34**
15.	**PLAGIARISM REPORT**	**35-38**

LIST OF FIGURES

Figure no.	Title of the figure	Page no.
Fig.2.1	XRD Rigaqu: Model- K-alpha	10
Fig.2.2	HR-TEM Thermo Scientific, Talos	11
Fig.2.3	UV/VIS/NIR: Model- Perkin Elmer LAMBDA 750	12
Fig.2.4	Spectroflourometer: Model- Horiba Scientific Flourolog-3	13
Fig.3.1	XRD pattern of synthesized Mn^{2+} doped ZnS QDs	15
Fig.3.2	(a)TEM of Mn^{2+} doped ZnS QDs at 50nm resolution (b)Particle size distribution of Mn2+ doped ZnS QDs	16
Fig.3.3	(a) UV-vis spectra of Mn^{2+} doped ZnS QDs with corresponding band gap (b) UV-vis spectra with varying doping concentration of Mn^{2+}	17
Fig.3.4	Photoluminescence spectra of ZnS QDs with varying doping concentrations of Mn^{2+}	18

LIST OF SYMBOLS AND ABBREVIATIONS

NPs	Nanoparticles
QDs	Quantum dots
0-D	0- Dimensional
1-D	1- Dimensional
2-D	2-Dimensional
DOS	Density of states
LEDs	Light emitting devices
ZB	Zinc Blende
WZ	Wurtzite
XRD	X-ray diffraction
TEM	Transmission electron micrograph
HR-TEM	High resolution transmission electron micrograph
UV-vis	Ultravoilet-visible

PL	Photoluminescence
JCPDS	Joint committee on powder diffraction standards
FWHM	Full width at half maximum
DSSCs	Dye-sensitized solar cells
QDSSCs	Quantum dots sensitized solar cells
PV	Photovoltaic

CHAPTER 1

INTRODUCTION

1.1. Nanotechnology

Nanotechnology is an advancing scientific field focused on creating and advancing various nanomaterials. It encompasses processes and materials whose components and structures exhibit new and significantly enhanced chemical, physical, and biological qualities, processes, and phenomena at the nanoscale level. It involves developing and utilizing materials made up of components that are at the nanoscale, conventionally 1-100 nm in size. Nowadays scientific community is fascinated with the various fields of nanotechnology. This subcategory of technology examines phenomena at the nanoscale and is focused on fields such as colloidal science, chemistry, physics, biology, and other related fields[1,2].

Nanoscale materials are utilized in various fields, including electronics, magnetism, optoelectronics, healthcare, pharmaceuticals, cosmetics, energy production, environmental protection, catalysts, and materials development. Due to the immense potential of this technology, there has been a global surge in investments for nanotechnology research and advancement [3]. Nanoparticles (NPs) offers unique and capitative properties that are distinct from bulk materials. These properties are superior to those of bulk materials and hold significant promise for applications in electronics, optoelectronics, and photocatalysis.

Many years have passed since the inception of research materials with reduced dimensionality featuring precisely controlled structures, evident in nanoparticles, nanotubes, nanofilms, nanosheets, and nanoporous materials. These advancements have yielded numerous valuable innovations in science and technology. Among them, Quantum dots, also known as QDs, are semiconductor materials that have attracted significant attention because of their distinctive optical properties and confined size [4] . QDs were first discovered in the 1980s by Russian physicist Alexei Ekimov [5]. Quantum dots are also referred as “artificial atoms”. A quantum dot (QD) is a

crystalline nanoparticle that has dimensions small enough to induce the effect of quantum confinement (QC). Their sizes range from in diameter1 to 10 nm, typically composed of combinations of elements from various groups of the periodic table which generally include groups II and VI (such as CdS,CdSe, ZnS, ZnSe, and CdTe,), groups IV and VI (like PbSe and PbS), and groups VI and V (including GaAs, InAs, GaAs, GaA and GaN) [6,7].

There exist various methods for categorizing nanomaterials. The reduced dimension or order of particle confinement in the system is typically used to classify nanomaterials and structure. Low-dimensional structured materials include those of 0-dimensional (0-D); when they are uniform, 1-dimensional (1-D); when they are elongated, and 2-dimensional (2-D); when they are planar, materials madeup of ultra-fine particles. 0-D materials, such as nanoclusters, nanoparticles and quantum dots ; 1-D materials, such as nanorods, nanowires and nanotubes,; and 2-D materials, which are the extension of the two spatial coordinates, such as superlattices and nanofilms, are examples of low-dimensional structured materials. The greater surface area and confinement effect of low-dimensional QDs make them superior than bulk materials. Researchers have been interested in advanced low-dimensional QDs because of their distinctive characteristics, which include a high electron-hole pair (e-h) separation efficiency, a large surface to volume ratio, and other irregular surface qualities[6-8].

1.2. Literature Review

1.2.1. Quantum Dots

In contrast to bulk materials, quantum dots (QDs) are zero dimensional (0-D) structures. For non-aggregated QDs, the density of states (DOS) displays discrete quantized energies due to the limited number of electrons. In terms of physical dimensions QDs are particles which are lower than the exciton Bohr radius[9, 10]. There are two types of semiconductor quantum dots that are commonly found. A surface is used to grow or pattern epitaxial quantum dots. Colloidal quantum dots are produced in solution by growing precursors. The phenomenon of quantum confinement results in unique electronic nanotubes, characteristics that are absent in

discrete atoms, bulk solids and discrete atoms. Once the nanocrystal is small enough to confine the electron or hole, the electrical and optical properties start to change. Their size-dependent and controllable fluorescence emission, excellent electrical properties, high brightness, and high surface- to-volume ratios are just a few of their intriguing features. In comparison to commercially available dyes, they are also more stable against chemical degradation and photobleaching. Furthermore, they demonstrate a high level of biocompatibility, quantum yields, symmetric fluorescence spectra, broad and narrow absorption, and high molar extinction coefficients.

Until now, biological chromophores have been made from a variety of elements of groups II-IV of highly fluorescent QDs, such as CdSe and CdS, with tunable wavelength emission. But because Cd is a highly toxic heavy metal that poses serious dangers to human health and the environment, using CdSe QDs is hazardous. For biological applications, non-toxic or less-toxic QDs that can substitute Cd-based QDs are therefore needed. Current studies are focused on utilizing the distinctive optical characteristics of QDs in various devices such as biological markers, solar cells and light-emitting devices (LEDs) [9-11].

1.2.2. ZnS QDs

Zinc sulfide (ZnS) is the semiconducting materials that have been found since ancient times. [12]. It has a direct tunable and wide band gap of 3.66 eV and has immense interest among researchers because of its potentially versatile applications, such as optical coating, photoconductors, optical sensors, infrared windows, sensors, lasers and LEDs. These are considered to be safe for biological and medical purposes[13-15] .

Zinc Sulfide (ZnS) is found in two main forms: Wurtzite (WZ) and Zinc Blend (ZB) structures. The former is a stable at low temperatures, while the latter polymorph emerges at higher temperatures[12]. It is commonly used as a shell material in core-shell quantum dots (such as CdSe/ZnS) to passivate the surface of the core material.. The ZnS shell enhances the quantum yield and stability of the core material by protecting it from oxidation and other environmental effects (also comparatively less

or not toxic than CdSe). CdSe and core-multi-shell structured QDs are commonly utilized due to the quantum confinement effect on electrons and their ability to emit light across the entire visible spectrum[16]. It has the capability of being incorporated into various conductive polymer matrices, including polyaniline, polythiophene, polysulphone, and poly (3,4-ethylenedioxythiophene).

Owing to the quantum confinement phenomenon, it shows strong photoluminescence, which raises the bandgap due to decreasing particle size that shifts the emission to higher energies (indicating blue shift). Although colloidal ZnS produce good yield of product but still to increase the yield passivation with organic ligands or core-shell structures (e.g., ZnS overcoated with another semiconductor) is done.

1.2.3. Methods of Synthesizing ZnS quantum dots

Synthesis of QDs can be done through various approaches or methods. Mainly we deal with the two: Top-down approach and Bottom-up approach[9], [17]. Selecting the right synthesis technique can be extremely important for identifying and describing ZnS QD characteristics.

1.2.3.1. Top-down routes

Top-down routes involves breaking or cleaving large bulk materials into nanoscale quantum dots with the use of physical reactions through electron beams or lasers. Structural imperfections are caused during these processes due to incorporation of impurities[9], [18]. The top down approaches involve following techniques:

* Electrochemical etching,
* Laser ablation,
* Electron beam lithography,
* Liquid-phase exfoliation techniques etc.

1.2.3.2 Bottom-up routes

Bottom-up routes are important techniques in fabrication of ZnS quantum dots. These are irreversible chemical reactions building nanoparticles from bottom, from atom to atom, molecule to molecule. Segregation of atoms or molecules results in formation of desired ZnS quantum dots with the use of precursors. It involves wet chemical and vapour phase methods of synthesis which include [9]:

* Microwave irradiation,
* Hydrothermal/solvothermal,
* Pyrolysis,
* Soft template

1.2.4. Properties of ZnS quantum dots

ZnS exhibits unique optical, electronic, physical and chemical properties due to its nanoscale size and quantum confinement effects which makes them useful for various applications.

1. **Optical Properties**

a) **Quantum confinement effects:** The emission and absorption spectra shows a blue shift when the ZnS quantum dot's size decreases due to a rise in the bandgap energy.

b) **Photoluminescence:** Zinc sulfide quantum dots exhibits strong photoluminescence, emitting light typically in the blue to ultraviolet spectrum. The quantum yield of photoluminescence can be enhanced by surface passivation thus reducing non-radiative recombination.

2. **Electronic properties**

a) **Wide Bandgap:** ZnS has a direct wide band gap (approximately 3.66eV at room temperature) making it appropriate for processes that require high energy photons.

b) **High Dielectric constant:** Large dielectric constant of ZnS increases the charge separation efficiency which can prove useful in photovoltaic and photocatalytic applications.

3. Chemical Properties

a) **Stability:** ZnS QDs exhibit higher stability in regular conditions than the other semiconductor QDs such as CdSe. They can be further enhanced with appropriate surface coatings or passivation layer.

b) **Surface chemistry:** The surface of ZnS quantum dots can be modified by different functionalization with ligands and helps them in better dispersion in different solvents and compatibility with other chemical environments. This also allows for a better bio-conjugation process, which can be suitable for biological imaging applications

c) **Reactivity:** ZnS quantum dots have the potential to participate in chemical reactions to form the core–shell structure or can encapsulate other elements for tailoring optical and electronic properties.

4. Physical Properties

a) Size and Shape: Zinc sulfide quantum dots are generally spherical in shape and range in size between 2 to 10 nanometers. By controlling the exact size and the structure one can generate during the synthesis, specific properties can be tuned.

b) Surface area: It is understood that ZnS QDs possess a high surface-to-volume ratio, which enhances the reactivity and interaction with the surrounding environments—these advantages beneficial for sensing applications.

1.2.5. Added Benefits of ZnS Quantum Dots over CdSe Quantum Dots

a) Cost effective and simpler synthesis

b) High photostability

c) Low toxicity,

d) Good biocompatibility, and

e) Wide bandgap

1.2.6. Potential Applications of ZnS QDs-

• Optoelectronics

ZnS QDs have large bandgap energy and high efficiency in charge separation; hence, they can be used in solar cells and photodetectors.

Tunable emission wavelength allows them to be used in LED applications.

• Biological Imaging

ZnS quantum dots can be conjugated with biomolecules for fluorescence imaging and labeling due to their bright and stable photoluminescence.

• Sensing

ZnS quantum dots have high surface area and reactivity, allowing them to be effective chemical and biological sensors.

These QDs are used in gas and biosensors for the detection of particular molecules.

• Catalysis

ZnS QDs have wide bandgap, and their stability is well under the ultraviolet light; this aspect permits their usage in photocatalysis for environmental remediation and water splitting.

1.3. Challenges of study

For applications in solid-state lighting and displays, colloidal quantum dots (QDs) offer significant potential as light emitters in light-emitting diodes (LEDs) but these applications require low-cost solution process capabilities, high quantum efficiency, high color purity as well as an easily tunable emission wavelength[11], [19]. The development and application of ZnS quantum dots (QDs) face several challenges.

• Uniform size distribution becomes critical in synthesizing colloidal QDs because achieving precise control over the size and shape of ZnS QDs during fabrication is difficult. Variations can lead to inconsistent optical and electronic properties.

• Surface defects and dangling bonds can act as non-radiative recombination centers, reducing the photoluminescence efficiency. Eliminating these defects requires effective passivation techniques, which can be complex and costly.

• The properties of these dots can be affected by surroundings such as pH, temperature, light, and exposure to air and its quality may deteriorate.

• The synthesis and disposal of ZnS QDs must be managed to minimize environmental impact and toxicity. Developing eco-friendly synthesis methods and ensuring safe disposal are important. Potential release of nanoparticles into the environment poses ecological threats, requiring careful management with regulation.

• Surface defects and non-radiative recombination pathways are major challenges in the development of high-efficiency ZnS QDs. Research is still going to develop better passivation techniques and core-shell structures to mitigate this. Modifications, such as doping with transition metals or coupling with other semiconductors are performed to reduce this issue to some extent[17-20]

1.4. Aim of Study

• Chemical fabrication of Mn- doped ZnS Quantum Dots.

• Analyzing fabricated QDs through various characterization techniques.

• Reviewing potential application of developed QDs in solar cells.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION TECHNIQUES

2.1 Chemicals used

The chemicals and reagents used were all of the ultra-pure grade. Zinc acetate dehydrate ($Zn(CH_3CO_2)_2.2H_2O$, molecular weight 219.49 g/mol) and Thiourea (CH_4N_2S, molecular weight 76.12 g/mol) were used as main precursors for the reaction. Manganese acetate tetrahydrate ($C_4H_{14}MnO_8$) was employed as dopant, 2-mercaptoethanol for capping and sodium hydroxide (NaOH, molecular weight 40 g/mol) for pH stabilization.

2.2 Synthesis of ZnS QDs

ZnS QDs capped with 2-mercaptoethanol were prepared using a hot injection method modified from existing literature[22-24]. Zinc and sulfur precursors, such as $Zn(CH_3CO_2)_2.2H_2O$ and CH_4N_2S were first dissolved in deionized water to prepare a fixed equimolar ratio of these two. In 30 mL of DI, 0.6548 g of $Zn(CH_3CO_2)_2.2H_2O$ was dissolved and in 10 mL of DI water,0.0761 g of CH_4N_2S was dissolved. Each of the precursors was then kept on a magnetic stirrer for 30 minutes to be completely dissolved. Dopant Mn^{2+} was added to zinc precursor solution after dissolution and pH was maintained at 10.5. Transferred this solution to a three neck flask and which then placed on a magnetic stirrer (with constant stirring rate) with passage of N_2 gas continuously. After that the second solution containing sulfur precursor was added drop by drop into three neck flask and temperature was maintained at 80°C. After 30 minutes 2- mercaptoethanol was added and quit the reaction for another 30 minutes. A milky-coloured solution appeared on completion of the reaction. Stopped the gas flow and centrifuged the solution to get pure QDs.

2.3 Characterization Tools-

2.3.1 X-Ray diffractometry (XRD)

XRD is a widely employed characterization tool in material science and technology. It is a non-destructive technique that is employed to analyze a wide range of materials including semiconductor nanoparticles, polymers, minerals, fluids, catalysts etc. X-ray photons are elastically scattered by atoms organized in a regular lattice structure during the process of X-ray diffraction. This instrument or method works by diffracting an x-ray beam via crystal slits in all directions to identify the atomic or molecular structure of crystal. Both qualitative and quantitative analysis can be done with it. The data used in qualitative analysis comprises crystallite size and orientation, phase composition, and phase type identification. On the contrary, the lattice constant, peak intensity, and two theta angels are included in the quantitative analysis data.

The orientation of crystal lattice is represented with the use of miller indices, which are a set of three integers hkl. Each crystal lattice have a unique set of hkl value that are to be compared with standard reference patterns from International Centre for Diffraction Data (ICDD),earlier known as Joint Committee on Powder Diffraction Standards (JCPDS) .

Based on how the atoms are arranged internally, the solid-state compounds are generally divided into three types: amorphous, single-crystalline, and polycrystalline materials. Information regarding atom positions, arrangements within each unit cell, and the spacing between atomic planes are provided by diffraction patterns[25-30].

To calculate the size of crystal (crystallite size) XRD can be employed by using Scherrer's equation[31].

According to Debye Scherrer's equation,

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D represents crystallite size, K is the Scherrer constant (value= 0.9), λ represents the wavelength of the X-rays used (0.15406 nm), β represents the Full Width at Half Maximum (FWHM, radians), and θ represents the peak position (radians).

Figure 2.1 XRD Rigaqu: Model – K-alpha

2.3.2 Transmission Electron Microscopy (TEM)

This instrument or method is used for the microstructural analysis of nanomaterials employing electrons as illuminating source. The collection of transmitted electrons via sample is the main approach used by TEM. It provides high precision and high spatial lateral resolution of order of angstrom. This technique can thoroughly characterize any material provided. A thin and narrow grid holding a specimen is subjected to high energy electron beam, which in result provides with the crystallographic and

microstructure information (morphological, electrical, structural, and chemical properties at the nanoscale level). Condenser lenses and the condenser aperture are used to focus the electron stream from the electron gun (tungsten filament, LaB6, or field emission) into tiny, narrow, parallel electron beam. A portion of the electron beam is transferred when the beam hits the prepared specimen. The objective lens focuses the transmitted portion to produce the image. The intermediate and projection lenses carry the image down the column, enlarging it as it passes through each lens.

Figure 2.2 HR-TEM Thermo Scientific, Talos

It finds useful applications in various fields including material sciences, geology, environmental science, biological science etc.[32-34]. Nanotechnology is probably benefitted the most with advancements in TEM.

2.3.3 UV-vis spectroscopy

UV-Visible spectroscopy is a rapid, inexpensive analytical method involving the absorption of ultraviolet or visible light by chemical substance. In this absorption of light takes place in ultraviolet region of electromagnetic spectrum (200-800nm). When molecules absorb these UV radiations, electrons in molecule gets promoted from a lower energy state (i.e. ground state) to higher energy state (i.e. excited state). The obtained absorption spectra gives valuable information about amount of light absorbed at each wavelength. Mainly liquid samples are analyzed through this technique. For those liquid samples, ethanol or water are used as reference solvents as they show no absorption in this region.

The sample's concentration must be in a range where Beer Lambert law is applicable[35].

Beer Lambert law states that:

$$\boldsymbol{A = \varepsilon c l}$$

Where A represents absorbance, ε represents molar absorptivity, c represents concentration, and l represents path length.

It is an important technique in analytical chemistry due to its ease of use and various applications in structural elucidation of organic compounds, pharmaceuticals, impurity detection, drug discovery, DNA and RNA detection, functional group detection etc.[36,37].

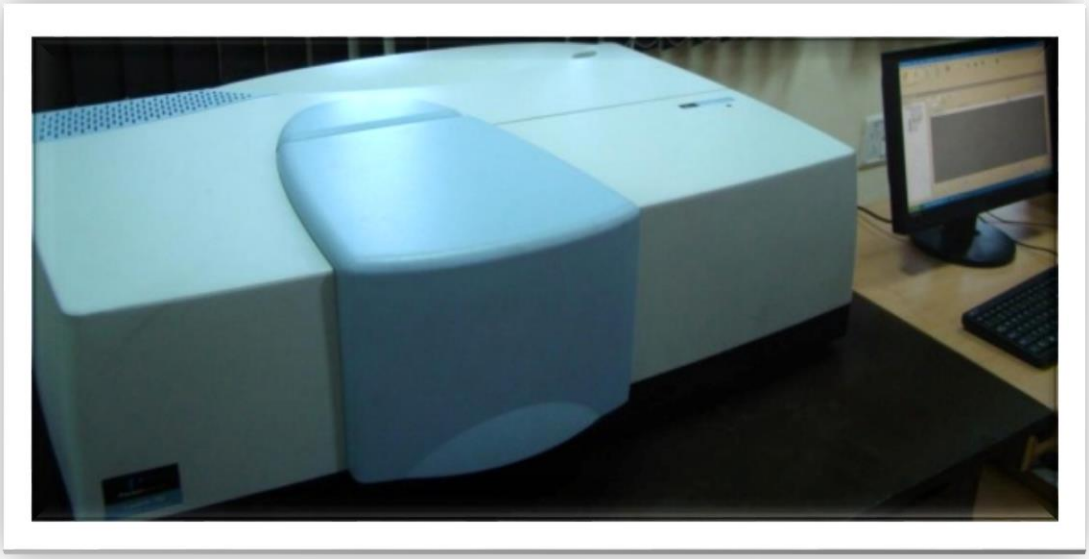

Figure 2.3. UV/VIS/NIR spectrometer: Model- Perkin Elmer LAMBDA-750.

2.3.4 Photoluminescence spectroscopy (PL)

Photoluminescence (PL) spectroscopy is a non-destructive quantum mechanical process that examines light after its emission by a material after it has absorbed photons. It is also defined as a radiative emission process which occurs through optical (photon) absorption and is categorized as a non-contact process. When a material absorbs a photon, it transfers energy to an electron in its ground state, where it gets quickly excited to an excited state within femtoseconds (1 femtosecond = 10^{-15} sec). These excited electrons return to their ground state after a short while, releasing energy in the form of photon, transitions are although quantized. Those emitted photons are collected and analyzed to reveal information about electronic structure, defects and optical properties of specimen[38, 39].

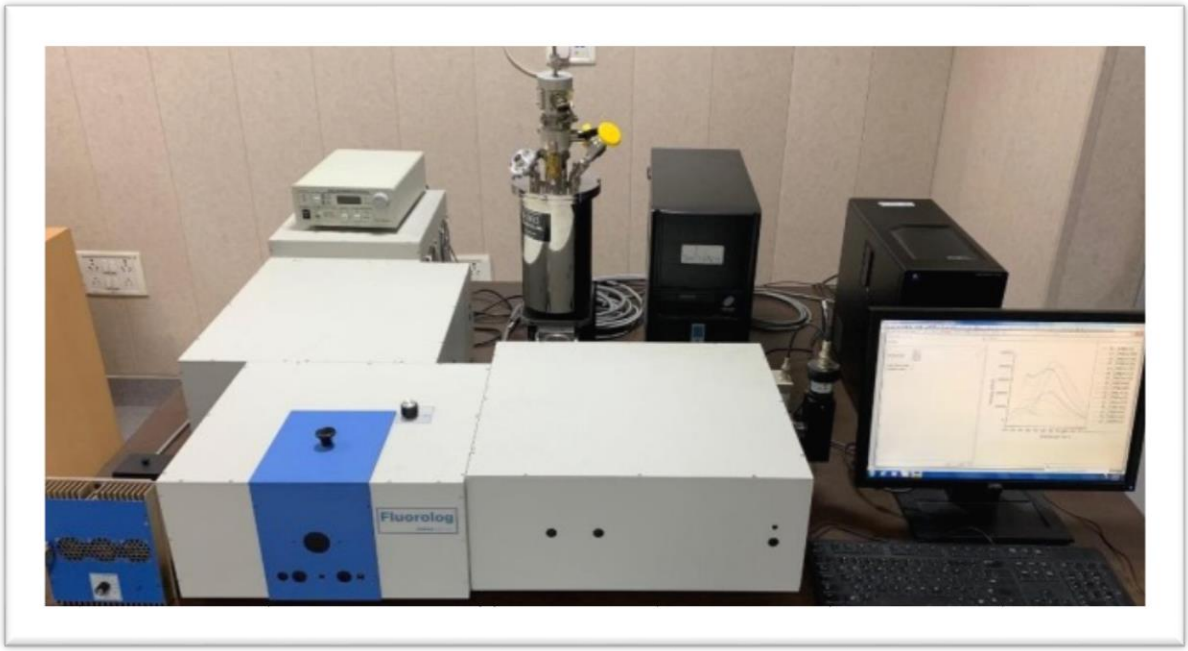

Figure 2.4. Spectrofluorometer: Model- Horiba Scientific Flouorolog-3

It is a leading technique to reveal information like mono-dispersibilty, quantum yield, quenching etc. It is a sensitive optical method for characterizing specimens in material science, biological science, nanomaterials, medicines etc. This method is frequently used to help elucidate the surface band structures and active sites of semiconductors and photocatalysts. Helpful in exploring molecular photochemistry, 2D- transition metal dichalcogenides, bioanalysis on QDs etc.[40-42].

CHAPTER 3

RESULTS AND DISCUSSION

3.1. X-ray diffractometry (XRD)

XRD study of Mn^{2+} doped ZnS QDs was taken on XRD Rigaqu: Model K-alpha using Cu Kα radiation (k = 1.5406 A˚) and 2θ value ranging from 20° to 60°. The drop cast method was used to deposit the sample over a glass cover slide. As previously discussed in literature, ZnS exists in two forms: Zinc blende and wurtzite. And at low-temperature synthesis conditions, cubic zinc blende is commonly formed. The obtained XRD pattern is shown in Figure 3.1, which shows two strong diffraction peaks at angles 2θ= 28.30° and 47.36° with diffracting planes 111 and 220 respectively, that match with **JCPDS card no: (80-0020).** One characteristic peak found missing or less intense at 57.3° became indistinguishable from the noise due to low concentrations or low crystallinity of the sample and long range order for some indices is lost [43] . The pattern indicates that there is no effect of incorporation of Mn on ZnS crystal structure.

The average crystalline size of fabricated QDs was calculated using Debye-Scherrer formula,

$$D = \frac{K\lambda}{\beta \cos\theta}$$

The value for average crystallite size D = 9.1nm.

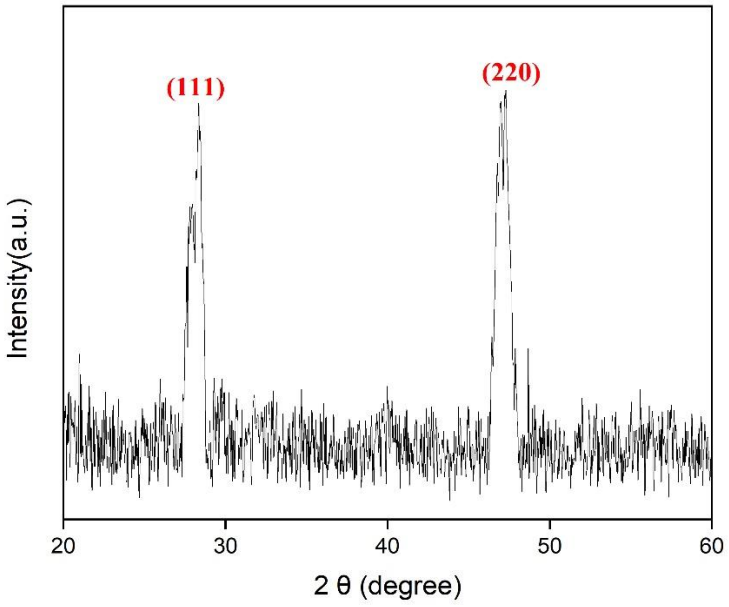

Figure 3.1. XRD pattern of synthesized Mn^{2+}doped ZnS quantum dots

3.2. Transmission Electron Micrograph (TEM)

Fig. 3.2 (a, b) depicts the TEM images of Mn^{2+} doped ZnS QDs with agglomerated particles. Smaller grain sizes cause particles to agglomerate more readily since they have bigger surface areas. The agglomeration can be attributed to solvent evaporation techniques employed during TEM analysis. Figure 3.2 (a) shows TEM images at 50 nm magnification. There is a range of particle size with spherical but agglomerated particles having average particle size of 46nm.

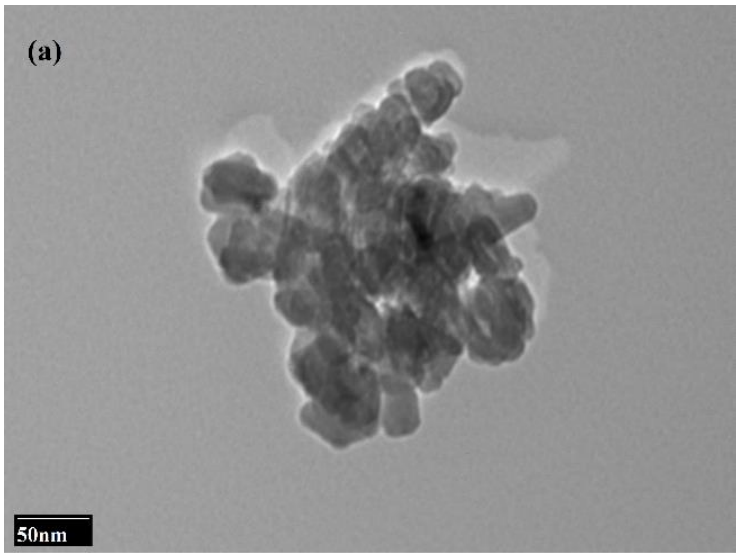

Figure 3.2(a) TEM of Mn^{2+} doped ZnS QDs at 50nm resolution

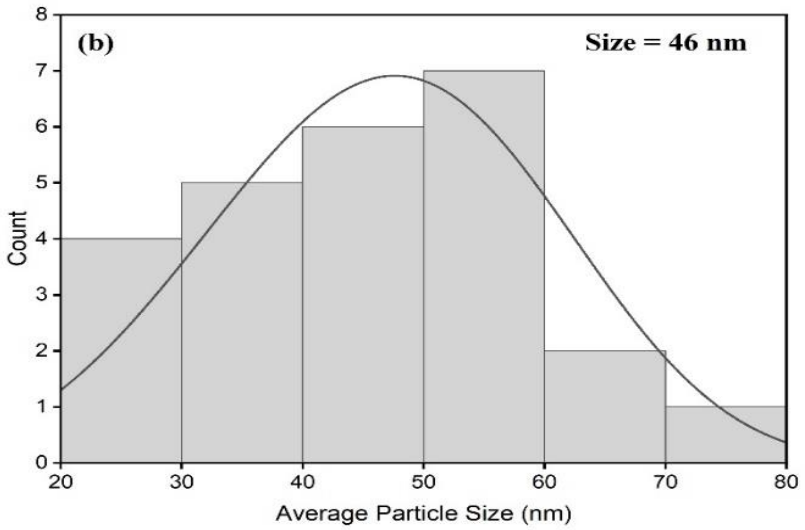

Figure 3.2. (b) Particle size distribution of Mn^{2+}doped ZnS QDs

3.3. UV-visible Spectroscopy

UV-visible spectroscopy was used to investigate the optical characteristics of the synthesized quantum dots. Using a Perkin Elmer LAMBDA-750, the absorption spectra was captured. UV/vis spectrometer from 200-800nm at room temperature. The obtained spectra is depicted in Fig.3.3 (a) with absorption peak at 280nm. The band gap of a quantum dot depends on its size which is an inverse function derived from Schrodinger's equation. Thus reduction in particle size indicates that corresponding band gap has increased.

Band gap is calculated using Tauc's relationship,

$$(\alpha h\nu)^{\frac{1}{n}} = A\,(h\nu - Eg)$$

where, A is a constant, Eg represents the bandgap energy of the material and exponent n depends on the type of transition[44].

The synthesized QDs has a direct band gap temperament which was acquired from $(\alpha h\nu)^2$ Vs hν graph. The band gap value = 4.1 eV which showed some increment in band gap value from exiting literature due to size reduction with doping[45].

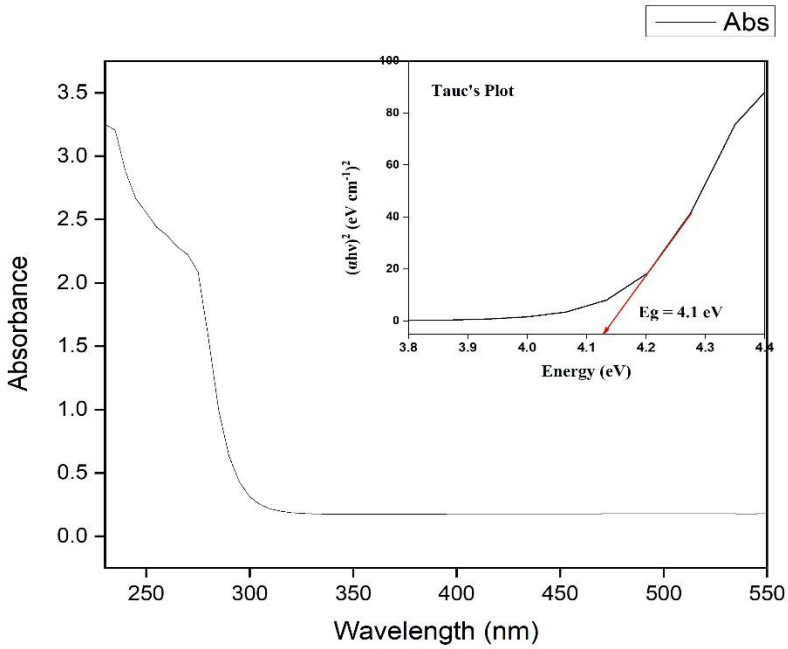

Figure 3.3(a)UV-vis spectra of Mn-doped ZnS Quantum dots with corresponding band gap

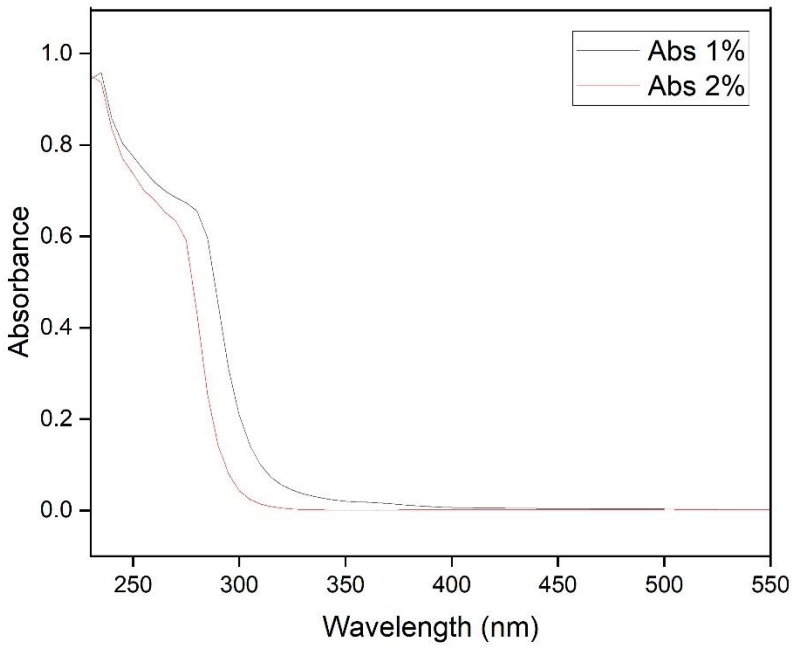

Figure 3.3(b) UV-vis spectra with varying doping concentration of Mn^{2+}

The impact of doping on ZnS quantum dots capped with 2-mercaptoethanol was investigated by varying doping concentrations precisely. It was noted that the introduction of transition metal dopants led to a slight blue shift, which means the maximum absorption wavelength shifted to a shorter wavelength when the concentration of dopant is increased from 1% to 2%. This shift towards shorter wavelengths indicates a decrease in particle size. The blue shift that is noticed rises when ZnS QDs' particle and crystallite sizes decrease. Therefore, incorporating transition metals into ZnS nanocrystals results in further particle size reduction[22].

3.4. Photoluminescence (PL) analysis

As shown in Figure 3.4, PL spectra for two different concentrations of Mn^{2+} were taken. In spectra the peak positions are shifted towards a lower wavelength on increasing doping concentration from 1% to 2%. At lower doping levels, adding Mn can potentially boost the PL intensity by enhancing the separation of charge carriers or minimizing defect states. Mn^{2+} serves as a luminescent center, aiding in the radiative recombination of electron-hole pairs[46].

The PL spectra with 1% doping depict a small peak or band at 340nm and a broad emission band at 422nm when excited at 310nm, indicating water Raman and trap-states emission respectively. Trap states result from point defects, like Schottky (vacancies) and Frenkel (interstitial) defects. In our study Schottky defects dominate over Frenkel indicating recombination of electron-hole pairs from zinc and sulfur.

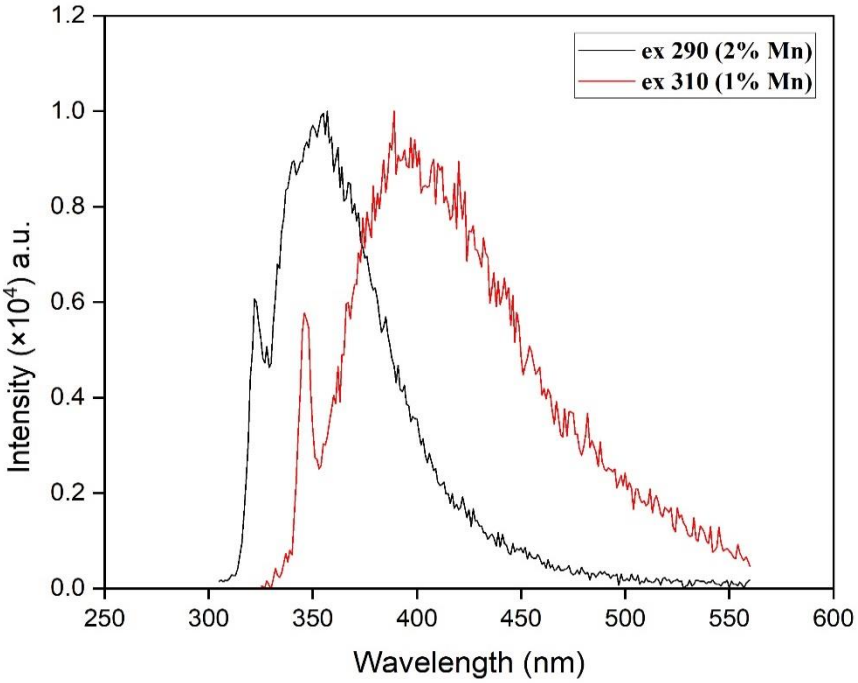

Figure 3.4. Photoluminescence spectra of ZnS QDs with varying doping concentration of Mn and excitation wavelenghts

CHAPTER 4

APPLICATIONS OF ZnS QDs

4.1. Applicatons of ZnS QDs in solar cells

Solar cells could be broadly categorized into 3 categories in terms of timeline and their development:

(a) First-generation solar cells, composed of thin silicon wafers, convert solar radiation into electrical energy. It is oldest and most popular technology due to its good efficiency. But their efficiency decreases at high temperature[47]. The indirect electronic band gap of crystalline silicon proves as one of its disadvantages, as it results in a comparatively weak absorption of long wavelength sunlight.

(b) Second generation solar cells include thin-film solar cells fabricated on glass material and made up of materials like copper indium gallium selenide (CIGS), cadmium telluride (CdTe). They are low-end to produce than Si solar cells and can be made flexible, but generally they have low efficiency[48].

(c) Third-generation solar cells are a group of modern innovations that perovskite solar cells, quantum dots sensitized solar cells (QDSSCs), include organic photovoltaics, dye-sensitized solar cells (DSSCs), and other semiconducting-based solution-processed PV technologies. They have the ability to convert power efficiently at a high rate while keeping production costs low[50,51].

Typically, the materials used to make solar cells are made up of several nanostructured components. Light harvesting and the conversion of light into electricity are two uses for the active material. The passive substance is employed to either retard the recombination of charge carriers or improve charge activity, which helps with photo-charge carrier separation and transportation. The electrode serves as a means of

collecting charge carriers. This concept has led to the investigation and design of numerous solar cell configurations to achieve maximum efficiency[51].

4.2. ZnS QDs in QDSSCs

ZnS nanostructure is being widely employed in advanced including organic–inorganic hybrid solar cells, dye-sensitized solar cells (DSSCs), quantum dot-sensitized solar cells (QDSCs), solar cell technologies, and thin film solar cells based on Cu(InGa)Se2 (CIGS). QDSCs and DSSCs have made considerable use of wide band gap semiconductors including ZnO, SnO_2, and TiO_2 as their anode materials.[14].

ZnS quantum dots find its potential applications in a number of displines owing to their unique optoelectronic properties like size dependent wide-tunable bandgap, high molar extinction coefficient, strong photoluminescence, broad absorption spectrum, and emission profile. It has attracted wide application as photosensitizer in developing QDs-sensitized solar cells (QDSSCs) with enhanced efficiency in solar cells. The low-cost, solution-processable quantum dot solar cells (QDSCs) use QDs as photosensitizers in their photovoltaic devices. Due to its wide bandgap it becomes difficult for ZnS QDs to absorb sunlight in infrared and visible regions[52]. But this issue has been resolved with advancement in research and it was found that doping ZnS QDs with manganese can introduce intermediate energy levels which enhances absorption capability across a broader spectrum of sunlight including infrared and visible regions. QDSSCs provide a prominent alternative to traditional dye-sensitized solar cells due to higher efficiency and tunable properties[52].

ZnS QDs exhibit a wide bandgap of 3.66eV in bulk form[53], which can be tuned to produce quantum confinement effects. Owning to its size-dependent tunability, ZnS QDs can absorb a wide range of solar radiation, which increases the efficiency of solar cells. It exhibits strong photoluminescence, which is useful for applications involving light harvesting. Their energy levels can be favorably aligned with conduction band of semiconductors like TiO_2 or ZnO used in QDSSCs. ZnS has a conduction band that is positioned higher than TiO2 and facilitates efficient electron injection. The

management of charge carrier dynamics, electron mobility and recombination rates are essential factors for optimization of QDSSCs performance[54,55].

Surface modifications and passivation are done for enhancing stability and performance. For this techniques such as ligand exchange, coating with organic molecules, or inorganic shells (like ZnO, TiO_2) are employed and it can significantly reduce surface defects and improve charge separation. The integration of ZnS QDs in QDSSCs can be performed through adsorption of ZnS QDs onto semiconductor surface via chemical linking, using linker molecules, or electrostatic assembly or by creating multi-layered structures of ZnS QDs[56].

A typical QDSSC consist of following parts:

* **Photoanode-** Composed of mesoporous TiO_2 or ZnO layer sensitized with ZnS QDs

* **Electrolyte-** Iodide/triiodide or polysulfide solutions are commonly used elctrolytes, which facilitate charge transport and regeneration of sensitizer.

* **Counter Electrode-** Made up of Platinum or carbon based materials which can catalyze the reduction of redox reaction occurring in the electrolyte[57].

ZnS QDs based QDSSCs demonstrate good stability and longevity under environmental conditions, but long-term performance can get affected by some factors such as light and thermal stress. Degradation can be done through photo-oxidation and electrolyte corrosion which can be mitigated by surface passivation and encapsulation techniques.

4.3. Challenges and Future perspectives of ZnS QDs in QDSSCs

* High charge recombination rates limit the efficiency of ZnS QDs based QDSSCs which can be improved by improving charge separation and transport.

* Device performance can be reduced when surface defects starts acting as recombination centers.

* For enhancing device performance ZnS QDs can be combined with other materials such as perovskites that enhances performance through synergistic effects.

* For improving efficiency and stability of device novel electrolytes and hybrid electrolytes should be employed.

* Future research should focus on innovative synthesis techniques, hybrid material systems, and optimized device architectures to fully attain the potential of ZnS QDs in solar energy conversion[58].

4.4. Applications beyond QDSSCs

ZnS QDs have potential applications beyond QDSSCs, including:

* **Light-Emitting Diodes (LEDs)**[59]**:** Exploiting their photoluminescent properties for efficient lighting.

* **Photodetectors**[60,61]**:** Utilizing their size-tunable absorption properties for sensitive photodetection.

* **Biological Imaging**[62,63]**:** Leveraging their non-toxicity and optical properties for bioimaging applications.

CONCLUSION

The fabrication of Mn^{2+} doped ZnS QDs employing a hot injection method was achieved. It included rapid nucleation, which resulted in the creation of controlled and uniform-sized nanoparticles. The doping was effectively accomplished using a nucleation method with two different doping concentrations. The TEM data showed an average particle size of 46nm with spherical but agglomerated particles. The synthesized material had significant optical characteristics, including a small band or peak at 340nm and a broad emission band at 422nm. Absorption spectra showed an absorption peak at 280nm with a bandgap of 4.1eV, which can be tuned by varying nanoparticle size. XRD results reveal two strong diffraction peaks at angles 2θ = 28.30° and 47.36° with diffracting planes 111 and 220, respectively while one significant peak at 57.3° was found less intense. In conclusion, the fabrication and characterization of Mn-doped ZnS QDs have revealed significant details and enhancement in its optical, structure, morphological and positioning properties. The investigation into ZnS QDs based QDSSCs revealed improvements in photovoltaic performance when shifting to this advanced form of solar cells as compared to others like Si based solar cells, organic–inorganic hybrid solar cells, dye-sensitized solar cells (DSSCs), etc. Despite certain limits in stability and scalability, the results highlight the ability of ZnS QDs as efficient sensitizers in solar cells. Future studies should aim to address these issues by investigating advanced synthesis and co-doping strategies. This study offers the foundations for the development of more efficient and low-end solar energy solutions.

REFERENCES

[1] H. Saba, "A Review on Nanoparticles : Their Synthesis and Types," *Res. J. Recent Sci. Res . J . Recent . Sci . Uttar Pradesh (Lucknow Campus)*, vol. 4, no. February, pp. 1–3, 2014.

[2] M. Nasrollahzadeh, S. M. Sajadi, M. Sajjadi, and Z. Issaabadi, *An Introduction to Nanotechnology*, 1st ed., vol. 28. Elsevier Ltd., 2019. doi: 10.1016/B978-0-12-813586-0.00001-8.

[3] C. Y. Wu, "Nanoparticles and the environment," *J. Air Waste Manag. Assoc.*, vol. 55, no. 6, pp. 708–746, 2005, doi: 10.1080/10473289.2005.10464656.

[4] S. Kargozar, S. J. Hoseini, P. B. Milan, S. Hooshmand, H. W. Kim, and M. Mozafari, "Quantum Dots: A Review from Concept to Clinic," *Biotechnol. J.*, vol. 15, no. 12, pp. 1–18, 2020, doi: 10.1002/biot.202000117.

[5] M. Pohanka, "Quantum Dots in the Therapy: Current Trends and Perspectives.," *Mini Rev. Med. Chem.*, vol. 17, no. 8, pp. 650–656, 2017, doi: 10.2174/1389557517666170120153342.

[6] Y. Hada and M. Eto, "Electronic states in silicon quantum dots: Multivalley artificial atoms," no. March, p. 1, 2003, doi: 10.1103/PhysRevB.68.155322.

[7] J. P. Connerade and J. Connerade, "A Review of Quantum Confinement," vol. 1, 2009, doi: 10.1063/1.3275682.

[8] H. Xu, H. Wang, Y. Shen, Y. Lin, and C. Nan, "Low-dimensional nanostructured photocatalysts," vol. 4, no. 3, pp. 159–182, 2015, doi: 10.1007/s40145-015-0159-8.

[9] D. Bera, L. Qian, T. K. Tseng, and P. H. Holloway, "Quantum dots and their multimodal applications: A review," *Materials (Basel).*, vol. 3, no. 4, pp. 2260–2345, 2010, doi: 10.3390/ma3042260.

[10] W. C. W. Chan, D. J. Maxwell, X. Gao, R. E. Bailey, M. Han, and S. Nie,

"2002-high throughput drug and disease screening Quantum dots," pp. 9–11.

[11] T. Jamieson, R. Bakhshi, D. Petrova, R. Pocock, M. Imani, and A. M. Seifalian, "Biological applications of quantum dots," vol. 28, pp. 4717–4732, 2007, doi: 10.1016/j.biomaterials.2007.07.014.

[12] X. Fang *et al.*, "Progress in Materials Science ZnS nanostructures : From synthesis to applications," *Prog. Mater. Sci.*, vol. 56, no. 2, pp. 175–287, 2011, doi: 10.1016/j.pmatsci.2010.10.001.

[13] R. Li, L. Tang, Q. Zhao, K. S. Teng, and S. P. Lau, "Facile synthesis of ZnS quantum dots at room temperature for ultra-violet photodetector applications," *Chem. Phys. Lett.*, vol. 742, 2020, doi: 10.1016/j.cplett.2020.137127.

[14] S. Ummartyotin and Y. Infahsaeng, "A comprehensive review on ZnS: From synthesis to an approach on solar cell," *Renew. Sustain. Energy Rev.*, vol. 55, pp. 17–24, 2016, doi: 10.1016/j.rser.2015.10.120.

[15] H. Labiadh and S. Hidouri, "ZnS quantum dots and their derivatives: Overview on identity, synthesis and challenge into surface modifications for restricted applications ZnS quantum dots and their derivatives," *J. King Saud Univ. - Sci.*, vol. 29, no. 4, pp. 444–450, 2017, doi: 10.1016/j.jksus.2016.12.001.

[16] R. K. Ratnesh and M. S. Mehata, "Synthesis and optical properties of core-multi-shell CdSe/CdS/ZnS quantum dots: Surface modifications," *Opt. Mater. (Amst).*, vol. 64, pp. 250–256, 2017, doi: 10.1016/j.optmat.2016.11.043.

[17] A. Valizadeh, H. Mikaeili, M. Samiei, S. M. Farkhani, and N. Zarghami, "Quantum dots : synthesis , bioapplications , and toxicity," pp. 19–21, 2012.

[18] R. Eview, "M ETHODS OF P REPARATION OF N ANOPARTICLES – A," vol. 7, no. 4, pp. 1806–1811, 2015.

[19] D. V Talapin, J. Lee, M. V Kovalenko, and E. V Shevchenko, "Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications," pp. 389–458, 2010.

[20] A. M. Derfus, W. C. W. Chan, and S. N. Bhatia, “Probing the Cytotoxicity of Semiconductor Quantum Dots,” 2004.

[21] M. V Kovalenko, “Colloidal Nanocrystals with Molecular,” vol. 1417, no. 2009, 2012, doi: 10.1126/science.1170524.

[22] S. Pradeep, S. Raghuram, M. G. Chaudhury, and S. Mazumder, “ZnS Quantum Dots for Photocatalytic Applications : Effect of 2-Mercaptoethanol and Chitosan as Capping Agents,” vol. 17, no. 2, pp. 1125–1132, 2017, doi: 10.1166/jnn.2017.12599.

[23] C. Zhou, J. Song, L. Zhou, L. Zhong, J. Liu, and Y. Qi, “Greener synthesis and optimization of highly photoluminescence Mn 2 þ -doped ZnS quantum dots,” *J. Lumin.*, vol. 158, pp. 176–180, 2015, doi: 10.1016/j.jlumin.2014.09.053.

[24] S. Tomar, S. Gupta, S. Mukherjee, A. Singh, S. Kumar, and R. K. Choubey, “Manganese-Doped ZnS QDs : an Investigation into the Optimal Amount of Doping,” vol. 54, no. 11, pp. 1450–1458, 2020, doi: 10.1134/S106378262011024X.

[25] R. J. Kirkpatrick, *Handbook of Analytical Techniques in Concrete Science and Technology*. 2001. [Online]. Available: http://www.sciencedirect.com/science/article/pii/B9780815514374500096

[26] A. Ali, Y. W. Chiang, and R. M. Santos, “X-Ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions,” *Minerals*, vol. 12, no. 2, 2022, doi: 10.3390/min12020205.

[27] J. Epp, *X-Ray Diffraction (XRD) Techniques for Materials Characterization*. Elsevier Ltd, 2016. doi: 10.1016/B978-0-08-100040-3.00004-3.

[28] A. A. Bunaciu, E. gabriela Udriştioiu, and H. Y. Aboul-Enein, “X-Ray Diffraction: Instrumentation and Applications,” *Crit. Rev. Anal. Chem.*, vol. 45, no. 4, pp. 289–299, 2015, doi: 10.1080/10408347.2014.949616.

[29] A. Monshi, M. R. Foroughi, and M. R. Monshi, “Modified Scherrer Equation

to Estimate More Accurately Nano-Crystallite Size Using XRD," *World J. Nano Sci. Eng.*, vol. 02, no. 03, pp. 154–160, 2012, doi: 10.4236/wjnse.2012.23020.

[30] X. Zhou *et al.*, "XRD-based quantitative analysis of clay minerals using reference intensity ratios, mineral intensity factors, Rietveld, and full pattern summation methods: A critical review," *Solid Earth Sci.*, vol. 3, no. 1, pp. 16–29, 2018, doi: 10.1016/j.sesci.2017.12.002.

[31] S. Fatimah, R. Ragadhita, D. F. Al Husaeni, and A. B. D. Nandiyanto, "How to Calculate Crystallite Size from X-Ray Diffraction (XRD) using Scherrer Method," *ASEAN J. Sci. Eng.*, vol. 2, no. 1, pp. 65–76, 2022, doi: 10.17509/ajse.v2i1.37647.

[32] W. Wan, J. Su, X. D. Zou, and T. Willhammar, "Transmission electron microscopy as an important tool for characterization of zeolite structures," *Inorg. Chem. Front.*, vol. 5, no. 11, pp. 2836–2855, 2018, doi: 10.1039/c8qi00806j.

[33] B. Kwiecińska, S. Pusz, and B. J. Valentine, "Application of electron microscopy TEM and SEM for analysis of coals, organic-rich shales and carbonaceous matter," *Int. J. Coal Geol.*, vol. 211, no. May, p. 103203, 2019, doi: 10.1016/j.coal.2019.05.010.

[34] Y. Javed, K. Ali, K. Akhtar, J. M. I. Hussain, G. Ahmad, and T. Arif, *TEM for atomic-scale study: Fundamental, instrumentation, and applications in nanotechnology*. 2018. doi: 10.1007/978-3-319-92955-2_5.

[35] A. Mandru, J. Mane, and R. Mandapati, "R EVIEW A RTICLE A Review on UV-visible spectroscopy," 2023, doi: 10.5281/zenodo.10232708.

[36] P. R. Prajapati, D. N. Rathod, and V. S. Modi, "Chemometrics and its Applications in UV Spectrophotometry," vol. 3, no. 1, pp. 43–48, 2016, doi: 10.5958/2394-2797.2016.00005.8.

[37] K. Wang, D. Sun, H. Pu, and Q. Wei, "Principles and applications of spectroscopic techniques for evaluating food protein conformational changes:

A review," *Trends Food Sci. Technol.*, 2017, doi: 10.1016/j.tifs.2017.06.015.

[38] M. Matsuoka, M. Saito, and M. Anpo, "Photoluminescence Spectroscopy," *Charact. Solid Mater. Heterog. Catal. From Struct. to Surf. React. Vol. 1&2*, vol. 1, pp. 149–184, 2012, doi: 10.1002/9783527645329.ch4.

[39] G. D. Gilliland, *Photoluminescence spectroscopy of crystalline semiconductors*, vol. 18, no. 3–6. 1997. doi: 10.1016/s0927-796x(97)80003-4.

[40] T. H. Gfroerer, "Photoluminescence in Analysis of Surfaces and Interfaces," *Encycl. Anal. Chem.*, pp. 9209–9231, 2000, doi: 10.1002/9780470027318.a2510.

[41] M. Tebyetekerwa *et al.*, "Mechanisms and applications of steady-state photoluminescence spectroscopy in two-dimensional transition-metal dichalcogenides," *ACS Nano*, vol. 14, no. 11, pp. 14579–14604, 2020, doi: 10.1021/acsnano.0c08668.

[42] Q. Li, M. Anpo, and X. Wang, "Application of photoluminescence spectroscopy to elucidate photocatalytic reactions at the molecular level," *Res. Chem. Intermed.*, vol. 46, no. 10, pp. 4325–4344, 2020, doi: 10.1007/s11164-020-04209-5.

[43] S. Mahamuni *et al.*, "Thiophenol-capped ZnS quantum dots," *J. Appl. Phys.*, vol. 73, no. 10, pp. 5237–5240, 1993, doi: 10.1063/1.353752.

[44] G. P. Joshi, N. S. Saxena, R. Mangal, A. Mishra, and T. P. Sharma, "Band gap determination of Ni-Zn ferrites," *Bull. Mater. Sci.*, vol. 26, no. 4, pp. 387–389, 2003, doi: 10.1007/BF02711181.

[45] D. K. Bhoi, A. Prof, and M. N. College, "International Journal of Research in all Subjects in Multi Languages A Review on Structural and Optical Performance of ZnS Nanoparticles Synthesized via Chemical Route," vol. 7, pp. 48–53, 2019, [Online]. Available: www.raijmr.com

[46] V. Sharma and M. S. Mehata, "Synthesis of photoactivated highly fluorescent Mn2+-doped ZnSe quantum dots as effective lead sensor in drinking water,"

Mater. Res. Bull., vol. 134, p. 111121, 2021, doi: 10.1016/j.materresbull.2020.111121.

[47] S. Bhattacharya and S. John, "Beyond 30% Conversion Efficiency in Silicon Solar Cells: A Numerical Demonstration," *Sci. Rep.*, vol. 9, no. 1, pp. 1–15, 2019, doi: 10.1038/s41598-019-48981-w.

[48] J. Ramanujam *et al.*, "Flexible CIGS, CdTe and a-Si:H based thin film solar cells: A review," *Prog. Mater. Sci.*, vol. 110, p. 100619, 2020, doi: 10.1016/j.pmatsci.2019.100619.

[49] K. D. G. I. Jayawardena, S. M. Silva, and R. K. Misra, "Solution processed perovskite incorporated tandem photovoltaics: Developments, manufacturing, and challenges," *J. Mater. Chem. C*, vol. 8, no. 31, pp. 10641–10675, 2020, doi: 10.1039/d0tc01440k.

[50] P. Meredith and A. Armin, "Scaling of next generation solution processed organic and perovskite solar cells," *Nat. Commun.*, vol. 9, no. 1, pp. 8–11, 2018, doi: 10.1038/s41467-018-05514-9.

[51] N. Shah *et al.*, "A Review of Third Generation Solar Cells," *Processes*, vol. 11, no. 6, 2023, doi: 10.3390/pr11061852.

[52] S. Horoz *et al.*, "Absorption induced by Mn doping of ZnS for improved sensitized quantum-dot solar cells," *Phys. Rev. Appl.*, vol. 3, no. 2, pp. 1–7, 2015, doi: 10.1103/PhysRevApplied.3.024011.

[53] A. F. Mohammed and W. R. Salah, "Synthesis of ZnS Quantum Dots for QDs-LED hybrid device with different cathode materials," *J. Phys. Conf. Ser.*, vol. 1032, no. 1, 2018, doi: 10.1088/1742-6596/1032/1/012010.

[54] M. Hamada *et al.*, "In Situ Photochemical Surface Passivation of CdSe/ZnS Quantum Dots for Quantitative Light Emission and Enhanced Photocurrent Response in Solar Cells," 2014.

[55] P. N. Kumar, A. Das, A. Kolay, and M. Deepa, "Materials Advances," pp. 2249–2267, 2022, doi: 10.1039/d1ma00851j.

[56] W. Zheng, Y. Zhang, D. Wang, and Q. Wang, “Optimization of the CdS quantum dot sensitized solar cells with ZnS passivation layer,” *J. Mater. Sci. Mater. Electron.*, vol. 29, no. 17, pp. 14796–14802, 2018, doi: 10.1007/s10854-018-9616-9.

[57] H. Kim and H. Kim, “cells : an inclusive review of photoanode ,” no. ii, pp. 4911–4933, 2019, doi: 10.1039/c8tc06476h.

[58] M. Kouhnavard *et al.*, “A review of semiconductor materials as sensitizers for quantum dot-sensitized solar cells,” *Renew. Sustain. Energy Rev.*, vol. 37, pp. 397–407, 2014, doi: 10.1016/j.rser.2014.05.023.

[59] O. Access, “Synthesis of ZnS Quantum Dots for QDs-LED hybrid device with different cathode materials Synthesis of ZnS Quantum Dots for QDs-LED hybrid device with different cathode materials”.

[60] R. Li, L. Tang, Q. Zhao, K. Seng, and S. Ping, “Facile synthesis of ZnS quantum dots at room temperature for ultra-violet photodetector applications,” *Chem. Phys. Lett.*, vol. 742, no. December 2019, p. 137127, 2020, doi: 10.1016/j.cplett.2020.137127.

[61] W. Kuang, X. Liu, Q. Li, Y. Liu, J. Su, and H. Tolner, “Solution-Processed Solar-Blind Ultraviolet Photodetectors Based on ZnS Quantum Dots,” *IEEE Photonics Technol. Lett.*, vol. 30, no. 15, pp. 1384–1387, 2018, doi: 10.1109/LPT.2018.2849345.

[62] J. Selvaraj, A. Mahesh, V. Baskaralingam, A. Dhayalan, and T. Paramasivam, “Organic-to-water dispersible Mn:ZnS–ZnS doped core–shell quantum dots: synthesis, characterization and their application towards optical bioimaging and a turn-off fluorosensor,” 2019, doi: 10.1039/c9nj02222h.

[63] S. Jin, Y. Hu, Z. Gu, L. Liu, and H. Wu, “Application of Quantum Dots in Biological Imaging,” vol. 2011, 2011, doi: 10.1155/2011/834139.

PLAGIARISM REPORT

Similarity Report

PAPER NAME

Deepika thesis - Copy (1).docx

WORD COUNT	CHARACTER COUNT
6822 Words	**40150 Characters**
PAGE COUNT	FILE SIZE
29 Pages	**1.2MB**
SUBMISSION DATE	REPORT DATE
Jun 5, 2024 4:39 PM GMT+5:30	**Jun 5, 2024 4:40 PM GMT+5:30**

7% Overall Similarity

The combined total of all matches, including overlapping sources, for each database.

- 4% Internet database
- 3% Publications database
- Crossref database
- Crossref Posted Content database
- 5% Submitted Works database

Excluded from Similarity Report

- Bibliographic material
- Quoted material
- Cited material
- Small Matches (Less then 10 words)

Similarity Report

7% Overall Similarity

Top sources found in the following databases:

- 4% Internet database
- 3% Publications database
- Crossref database
- Crossref Posted Content database
- 5% Submitted Works database

TOP SOURCES

The sources with the highest number of matches within the submission. Overlapping sources will not be displayed.

1	link.springer.com Internet	<1%
2	Birkbeck College on 2023-03-03 Submitted works	<1%
3	pubs.rsc.org Internet	<1%
4	Chaudhary Charan Singh University, Meerut on 2023-08-16 Submitted works	<1%
5	dspace.dtu.ac.in:8080 Internet	<1%
6	Clemson University on 2014-11-19 Submitted works	<1%
7	Laredo Community College on 2019-10-19 Submitted works	<1%
8	Hao-Min Xu, Huan-Chun Wang, Yang Shen, Yuan-Hua Lin, Ce-Wen Nan.... Crossref	<1%

Similarity Report

9	stax.strath.ac.uk Internet	<1%
10	University of Fort Hare on 2024-06-02 Submitted works	<1%
11	urjc on 2024-06-03 Submitted works	<1%
12	University of Malaya on 2011-10-11 Submitted works	<1%
13	researchgate.net Internet	<1%
14	d.docksci.com Internet	<1%
15	www2.mdpi.com Internet	<1%
16	Amity University on 2020-05-11 Submitted works	<1%
17	B.J. Inkson. "Scanning electron microscopy (SEM) and transmission el... Crossref	<1%
18	Prairie View A&M University on 2016-12-01 Submitted works	<1%
19	SASTRA University on 2019-05-07 Submitted works	<1%
20	University of Sheffield on 2021-01-15 Submitted works	<1%


Similarity Report
21
University of Zululand on 2013-02-26
Submitted works
<1%
22
dspace.univ-msila.dz
Internet
<1%
23
thesis.univ-biskra.dz
Internet
<1%