

Tuning of Photophysical Properties of ZnCdS Quantum Dots by Varying the Concentration of Capping Ligand



A dissertation submitted to the department of Chemistry,
Quaid-i-Azam University, Islamabad, in the partial fulfillment of the
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In

Physical Chemistry

By

Noor ul Ain

Department of Chemistry,
Quaid-i-Azam University, Islamabad

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*IN THE NAME OF ALLAH,
THE MOST BENEFICENT, THE MOST MERCIFUL*

“He grants wisdom to whom He pleases; and he to whom wisdom is granted receives indeed a benefit overflowing; but none will grasp the Message but men of understanding”.

(Quran, 2:269)

DEDICATION

Wholeheartedly dedicated to my beloved parents

Mr. and Mrs. Karamat Hussain

and caring brothers,

Tauqir Waqas and Sohail Khayam,

their constant source of motivation, trust and encouragement, gave me

strength and support throughout my educational career.

DECLARATION

I hereby declare that this dissertation entitled “**Tuning of Photophysical Properties of ZnCdS QDs by Varying the Concentration of Capping Ligand**” was composed by myself under the kind supervision of **Dr. Azhar Iqbal**. The work contained herein is my own except where explicitly stated otherwise in the text, further, I declare that this work has not been submitted for any other degree or professional qualification except as specified. A dissertation submitted to the Department of Chemistry, Quaid-i-Azam University Islamabad, in partial fulfillment of the requirements for the degree of **Master of Philosophy in Physical Chemistry**.

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Abstract

Quantum dots (QDs) are zero-dimensional luminescent semiconducting nanocrystals having diameter ranges from 1-10 nm which lead to show distinct optical and electronic properties that include narrow band emission spectra, large absorption coefficient and tunable bandgap energies. This thesis reports tuning of photophysical properties of ternary alloyed ZnCdS QDs by varying the concentration of capping ligand mercaptoacetic acid (MAA). The MAA capped ZnCdS QDs are synthesized via a colloidal method that is the most accessible and inexpensive way. Ternary ZnCdS QDs also known as blue emitters having wide bandgap energy, composition tunable bandgap and size-tunable fluorescence emission. Herein, tuning of photophysical properties of ZnCdS QDs is achieved via increasing the concentration of MAA that results in the decrease in the particle size. Fourier-transform infrared (FTIR) analysis confirmed the successful capping of QD surface with MAA. X-rays diffraction (XRD) pattern revealed that ZnCdS QDs have been synthesized in the cubic phase. A blue shift in absorption wavelength was observed in UV-VIS absorption and PL emission spectra with increasing concentration of MAA. Moreover, this blue shift in wavelength was associated with an increase in bandgap energy which confirmed a strong quantum confinement effect. The size tunable ZnCdS QDs find many applications in the optoelectronic field, for example photovoltaic devices, light emitting diodes (LEDs) and sensors. Moreover, ZnCdS QDs are eco-friendly so they are used in wastewater treatment and in nanomedicines for bioimaging and bio-marking.

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Abbreviations

Abbreviation	Description
CB	Conduction band
DOS	Density of states
EL	Electroluminescence
EN	Engineered Nanomaterials
FT-IR	Fourier-transform infrared
GMR	Giant magnetoresistance
LED'S	Light-emitting diodes
MAA	Mercaptoacetic acid
NMs	Nanomaterials
PL	Photoluminescence
QY	Quantum yield
SSPL	Steady-state photoluminescence
TCSPC	Time-correlated single-photon counting.
TGA	Thioglycolic acid
TOPO	Tri-n-octyl phosphene oxide
TRPL	Time-resolved photoluminescence
VB	Valance band
XRD	X-Ray Diffraction

Chapter 1
INTRODUCTION

1.1 Nanotechnology

As time goes on, the scientific spacecraft flew from imagination to existence and nanotechnology is one of that imagination which come into existence by an innovative breakthrough of Richard Feynman “ There is plenty of room at the bottom”. Nanotechnology was first defined by Norio Taniguchi in 1974,¹ since then it is used to manipulate the application and properties of materials at the nanoscale.

Breakthroughs in almost every field of science and nanotechnology in nanoscience have made life in this era easier. Nanoscience and nanotechnology represent an expanding field of research, due to the arrangement of its atoms in the range of 1-100 nm, involving structures, devices and systems with novel properties and functions.²

The prefix "nano" refers to the Greek prefix, meaning "dwarf" or something negligible, representing one billionth of a meter (10^{-9} m). Nanotechnology and nanoscience differ as Nanoscience is the study of structures and molecules on the nanometer scale ranging from 1 to 100 nm. The technology that is used in practical applications such as equipment etc.

1.1.1 The progress of nanoscience and nanotechnology

The development of nanoscience and nanotechnology in different scientific fields has broadened in many directions for example in Physics from microscopic to nanometer by using different microscopes and even smaller things can be observed, in Chemistry from microscopic bulk substances to small size quantum dots, in the field of computer science, a room-sized computer can be transplanted into a portable thin notebook computer, and in biological science the behavior of the cell nucleus can be observed in-depth, to study nano-level complex biological molecules. A summary of all these developments in different scientific fields is overviewed as below in Figure 1.1.

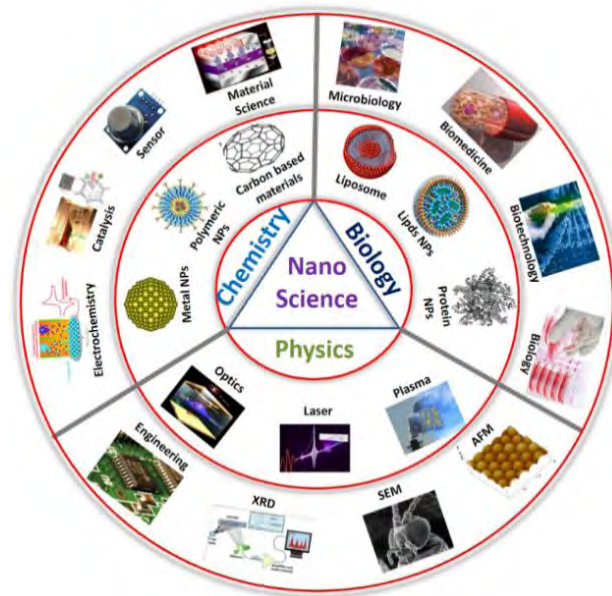


Fig.1.1 Applications of nanoscience and nanotechnology in various fields. ³

1.1.2 Advancement in nanotechnology

Within no time, nanotechnology, and nanoscience gained so much importance in industrial and medical applications. Many medical devices have been invented at the nanoscale like diagnostic biosensors, drug delivery systems and imaging probes. For the food industry, Nanomaterials (NMs) have been used to greatly improve production, packaging, shelf life and nutritional bioavailability. Zinc oxide nanostructure show antimicrobial activity, that fight against foodborne bacteria, and there are abundant other NMs that work for diagnostic purposes such as food sensors to identify food quality and food safety. ⁴

NMs are more advance in building new generation solar cells, hydrogen fuel cells and reliable hydrogen storage systems that can deliver clean energy to countries still dependent on conventional and non-renewable fuels. In the vast area of biomedicine and more specifically in cancer therapeutics, nanotechnology has remarkable advances because of its novel approach to find solutions and ideas to overcome the problems and limitations that were offered by traditional chemotherapy and radiotherapy approaches.

The development in different branches of science that is chemistry, physics, and biology, gives us NMs with peculiar properties. These NMs are used to enhance the

treatment of numerous tumors, this will be achievable because of their inherent cytotoxic activity and their ability to act as nanocarriers to provide therapeutic molecules for example drugs, proteins, nucleic acids, or immune agents. These novel biomedical applications have been used in various clinical assessments and this may also help for the advancement in the field of cancer therapies.⁵

1.2 Nanomaterials (NMs)

NMs refer to materials whose size of a single component in at least one dimension is ranging from 1-100 nm. The composition, fabrication, and exploitation of functional structures with at least one feature size measured in nanometers are called NMs. In different areas of science, engineering and technology, NMs play a vital role which leads the way for nanotechnology induction. These NMs demonstrate drastic variation in their physical, chemical, and biological properties due to their diminished size and shape.⁶

NMs are bedrocks of nanoscience and nanotechnology. Nanoscience and nanotechnology primarily cope with synthesis and characterization techniques, they mostly use nanostructured materials. These materials are categorized by a minimum of one dimension lies in the nanoscale (1-100) nm range. Nanostructures work as a bridge between molecules and bulk materials. The nanostructures encompass clusters, quantum dots, nanocrystals, nanowires, nanotubes, arrays, assemblies, and superlattices. The chemical and physical properties of NMs show remarkable variations from that of bulk materials containing the same structures. Proper control of properties and reactivity of nanostructures gives on to new devices and technologies.⁷

Several NMs are naturally occurring, but particularly eye-catching are engineered nanomaterials (EN), which are devised and used in many industrial goods and activities. In medicine for drug delivery, imaging, and diagnosis these engineered NMs can be used. They can also be used in electronics, stain-resistant clothing, sunscreens, cosmetics, tires, and sporting goods. Nanoparticles are quite familiar material in many distinct conditions, and they can almost pass over without being discovered unless one pays attention to their presence. Natural nanoparticles can be found in fine ocean spray, volcanic ash, fine sand, and dust, in fact in biological matter.⁸

1.2.1 Classification of NMs

Nanostructured materials⁹ grasp so much interest because they create linkage between molecules and bulk materials and give away to utter new inventions and applications more specifically in electronics, optoelectronics and biological field. When the optical and electronic properties of a solid show obvious changes, and variation in particle size is less than 100 nm, it can be termed as a nanostructure and classified as (1) 2-dimensional i.e., quantum wells and thin film, (2) 1-dimensional i.e., quantum wires, or (3) 0-dimensional i.e., quantum dots (QDs). For non-agglomerated zero-dimensional structures, a finite number of electrons leads to discrete quantized energy in the density of states (DOS).¹⁰

1.2.1.1 Zero-dimensional NMs

When all external dimensions of NMs are in the nanoscale range (1-100) nm is categorized as zero-dimensional. This encompasses QDs, a semiconductor nanocrystal with a size less than 10 nm, which can be used in the field of electronics to confine electrons and holes.¹¹ Examples of zero-dimensional QDs are dendrimers, hollow spheres, fullerenes, heterogeneous particle arrays, core-shell QDs and nano lenses.

1.2.1.2 One-dimensional NMs

When two out of three dimensions are at the nanoscale range and one dimension generally lies in the microscale range that is categorized as one-dimensional NMs. This involves nanotubes, nanorods, nanofibers and nanowires. Mostly inorganic materials for example carbon, silica, titania, zirconium dioxide, aluminum oxide, titanium nitride or platinum are used to produce nanofibers.¹² For decades, One-dimensional membranes have been widely used in the fields of electronics and chemical engineering. The production of single-layer films has become very common in the field of solar cells and catalysis.¹³

1.2.1.3 Two-dimensional NMs

Two-dimensional materials have two dimensions outside the nanoscale range. These materials are intensely thin with a high degree of anisotropy and chemical functionality. Two-dimensional nanomaterials include thin films, nanocoating, and nanoplates. The film is composed of ceramic or metal coating with atomic layer thickness.¹⁴ Thin films have many applications in physics and electronics, in manufacturing

electronic components with insulating or conductive surfaces or change the light reflectivity of the surface.

1.2.1.4 Three-dimensional NMs

Three-dimensional NMs have all the dimensions that are not confined to nanoscale and are described as bulk materials. Nanocomposites and nanostructured materials fall in this category. Three-dimensional NMs have superior properties such as high specific surface area owing to their quantum size effect which distinguishes them from their bulk counterparts. Considerable attention has been paid to synthesize three-dimensional NMs with controlled morphology and structure.

Classification of nanomaterials based on dimensionality along with their example is shown in Figure 1.2.

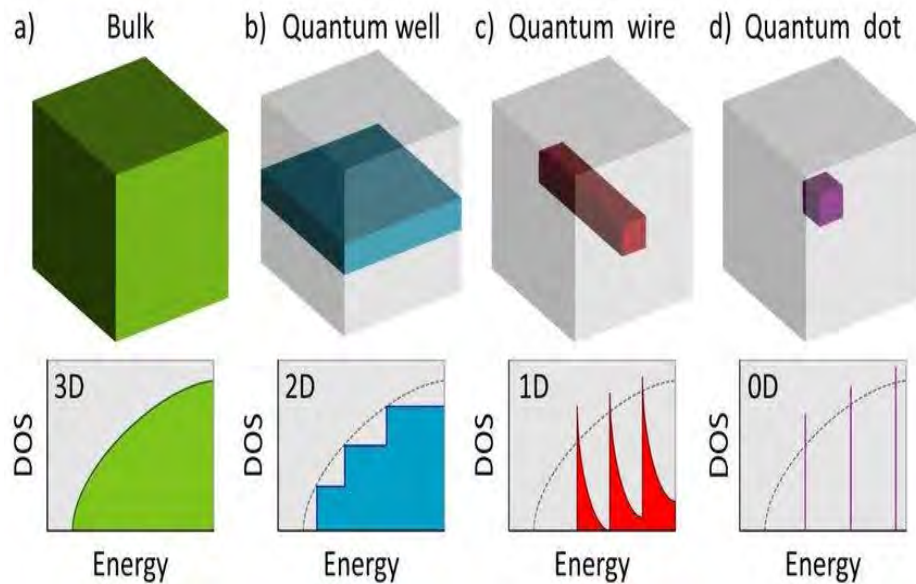


Fig.1.2 Dimensions and density of states of NMs.¹⁵

1.3 Quantum dots (QDs)

Luminescent semiconductor materials with diameters in the range of 1 to 10 nm¹⁶ are composed of the number of atoms of II-VI group elements i.e., CdSe, CdTe and ZnO, III-V group elements i.e., InP and InAs, IV-VI Group element i.e., PbS. QDs are often artificial in nature and they show distinct optical and electronic properties that are narrow emission spectra, continuous and wide absorption spectra, and high photostability.¹⁷ These exceptional optical and electronic properties which are size and shape-dependent differ

them from bulk materials which leads to a 3-dimensional quantum confinement effect which is the strongest confinement of electron and hole between valance band (VB) and conduction band (CB).^{18, 19}QDs having lots of crystal lattice structures which under pressure transformed into thin films. Later, due to stress, the subsequent flat films incline to separate into dots which is three-dimensional.²⁰QDs are one of the earliest nanotechnology fusions with biological sciences²¹ and having wide applications in clinical products and commercial consumers. ²² Some photophysical properties of QDs are listed in the Table 1.1.

Table 1.1. Photophysical properties of quantum dots

S. No	Photophysical properties	Description
1	Size	1-10nm range ²³
2	Highly tunable	By tuning, the characteristic wavelengths of emitted light, the variable core sizes give off different colors and exhibit different optoelectronic properties. ²⁴
3	Excitable	Emit light of different wavelengths when excite to higher energy level. ²⁵
4	Configuration	Confined in 3-dimensions ²⁶
5	Quantum Confinement effect	Observed when the size of the particle is too small \approx Bohr exciton radius.

1.4 Types of quantum dots (QDs)

QDs semiconductors having nanometer range made up of many atoms of group II-VI elements, group III-V elements and group IV-VI elements and having dimensions smaller than Bohr exciton radius. ²⁷

Based on structure and composition, quantum dots are divided into three types.

1.4.1 Type I (Core-typed QDs)

QDs that made up of single material with intermural uniform structures with tunable opto /electro luminescence for instance Metal chalcogenides.²⁸

1.4.2 Type II (Core-shell QDs)

Core-shell QDs are composed of core type material encapsulated in a second semiconductor which have high bandgap energy, and they show enhanced optoelectronic properties. Core-shell QDs also called Core-shell semiconductor nanoclusters which have flexible photophysical characteristics for example ZnO QDs (ZnO/Zn(OH) core-shell structure).²⁹

1.4.3 Type III (Alloyed QDs)

Multicomponent dots offer an alternative method to tune properties without changing crystallite size. Alloyed semiconductor QDs formed by alloying together two semiconductors with different bandgap energies exhibited interesting properties distinct not only from the properties of their bulk counterparts but also from those of their parent semiconductors for example alloyed quantum dots of the compositions $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$.³⁰

1.5 Characteristics of QDs

1.5.1 Quantum confinement

The most extensive property of QDs is the quantum confinement effect, which can modify the density of states (DOS) near the edge of the band. In between the continuous bulk materials and discrete atomic particles there lies QDs. When the size is small enough that the spacing between the energy levels of nanocrystals excels kT (where k is Boltzmann's constant and T is temperature), quantum confinement effects will be observed. Energy level greater than kT limits the mobility of electrons and holes in the crystal. Among various unique properties of QDs that are size-dependent, two properties have great importance. First, Quantum confinement effect³¹, which is the blue shift i.e., increase of bandgap energy with the decrease in particle size. In the quantum confinement effect, the energy gap can be tuned by varying the size of particles. Second, Due to small-sized particles comparable to bulk material, well separated and discrete energy states are observed in QDs. This causes the electronic state of every energy level to show atomic-like wave functions. The systematic illustration of quantum confinement effect in Figure 1.3 shows QDs lie between bulk and atomic materials.

QDs exhibit exclusive optical and electronic properties because of quantum confinement effect which has the potential to increase the efficiency of power conversion in solar cells.

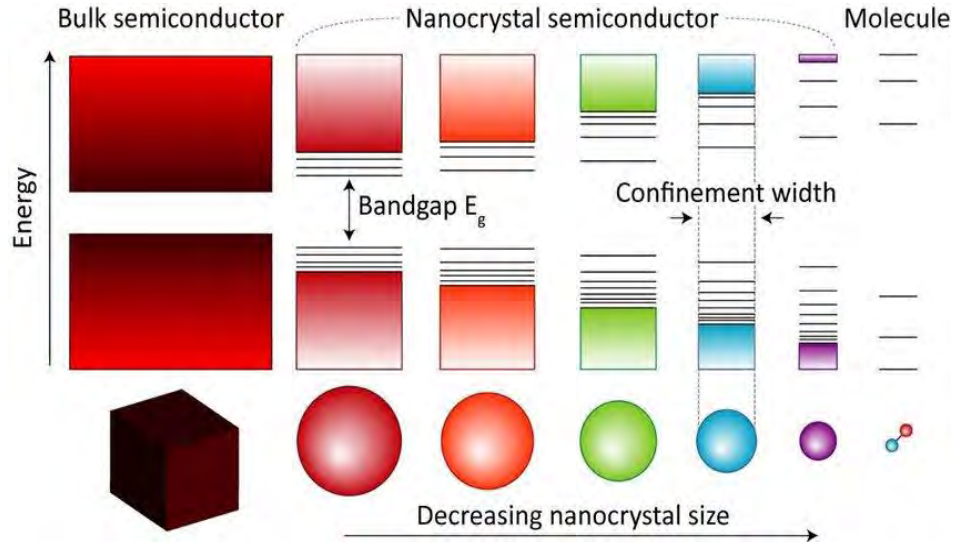


Fig.1.3 Quantum confinement effect of quantum dots.¹⁵

1.5.2 Bandgap

The energy needed to generate an electron and hole having kinetic energy equal to zero (i.e., at rest) is called bandgap energy. That distance should be enough that their Coulombic interaction is minimum but when one reaches the other, an electron-hole pair is generated known as an exciton whose energy is slightly smaller than bandgap energy. Bohr exciton radius (r_B) is the distance between electron and a hole.³² Expression of Bohr exciton radius is as in equation 1.1.

$$r_B = \frac{\hbar^2 \epsilon}{e^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (1.1)$$

ϵ , \hbar , and e are the optical dielectric constant, reduced *Planck's* constant and the charge of an electron, respectively.

There are 2 types of band gap.

1.5.2.1 Direct bandgap

In Brillouin zone, the minima in the conduction band and the maxima in the valence band are categorized by crystal momentum known as k-vector. When k-vector is same this

would be a direct bandgap, electron emit the photon directly because the crystal momentum of both electrons and holes in conduction and valance band is the same.

1.5.2.2 Indirect bandgap

Indirect bandgap having a different k-vector so it's impossible to transfer electrons from conduction band to valance band without altering the momentum of crystals. There will be zero possibility of recombination of electrons and holes in the indirect bandgap. Indirect bandgap is the three-body system because it involves an intermediate state to emit the photon.³³

Figure 1.4 shows the schematic illustration of direct and indirect bandgap in QDs

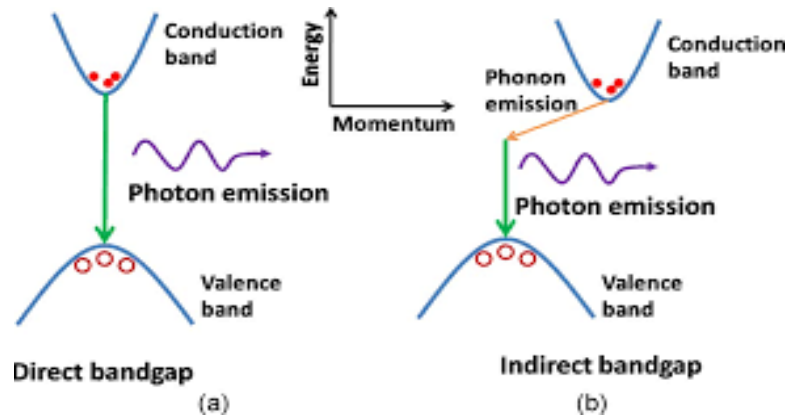


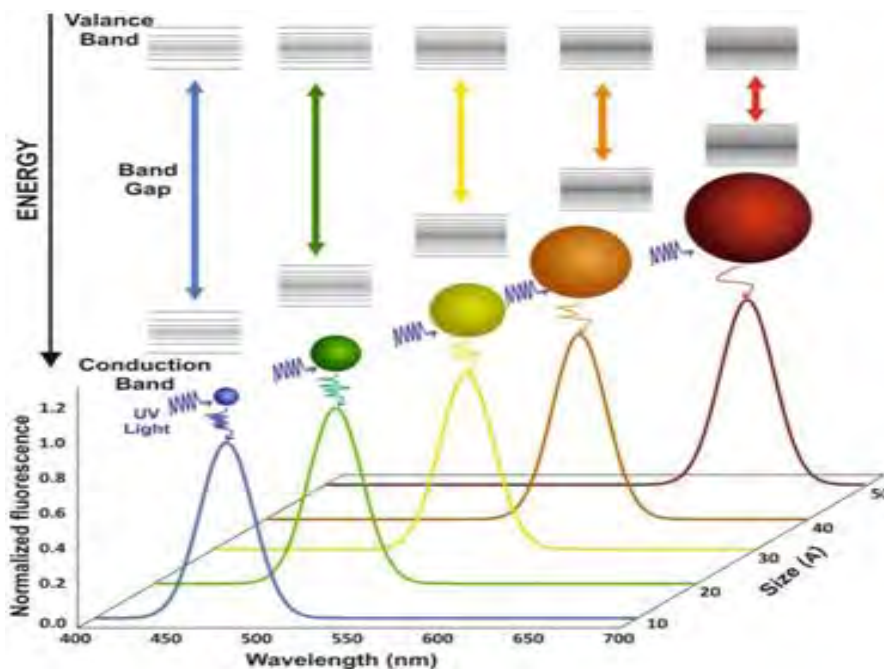
Fig.1.4 Direct and indirect bandgap in quantum dots.³⁴

1.6 Properties of QDs

1.6.1 Optical properties

Luminescent semiconductor nanocrystals show unique optical properties like fluorescence and phosphorescence etc. By absorbing a certain amount of light, electrons jump from the ground state (valence band) to the excited state (conduction band) and generate a hole in the valance band. When excited electron recombines with the hole it releases electromagnetic radiation which is in the range of UV- NIR that phenomenon is known as QDs photoluminescence (PL). There is a large wavelength difference between absorption and emission peaks i.e., large stoke shift because of wide excitation spectra and narrow emission spectra. Moreover, emission wavelength or PL color is different for different nanomaterials or different sizes of same nanomaterials as shown in Figure 1.5.

The smaller the nanomaterials, the bluer its color and the larger its bandgap energy. Other optical properties that QDs have are their high quantum yield (QY), higher molar extinction coefficient, enhanced photostability.³⁵



*Fig.1.5 Optical properties of quantum dots vary with size.*³⁶

1.6.2 Magnetic properties

Nanoparticles exhibit unique magnetic properties like color imaging, magnetic memory with high storage density, ferro-fluid, bioprocessing and refrigeration. As in QDs, there is a large surface area to volume ratio, so more atoms are available for magnetic coupling with its nearby atoms and exhibit different magnetic properties. Usually, the small magnetic nanomaterials contain one domain and show a phenomenon called superparamagnetic whereas the bulk material having multiple domains. The magnetization of nanomaterials due to small size is randomly oriented, so by applying magnetic field particle are aligned in order. Giant magnetoresistance (GMR) that is widely used to store data is found in nanoscale with multilayers.³⁷

1.6.3 Electrical properties

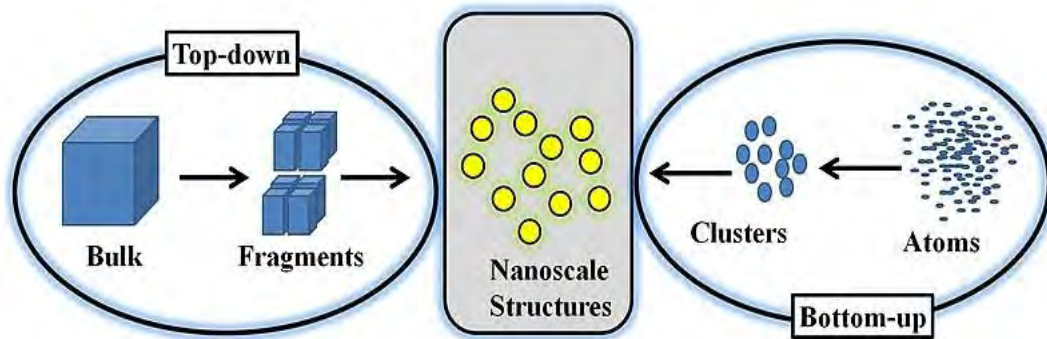
Due to the quantum confinement effect, nanomaterials show unique electronic properties. These electronic properties depend directly on the size of particles. Conduction in semiconductor QDs is highly susceptible to other charged species. A very small amount

of energy is needed by nanomaterials to operate a memory element, switch or transistors because the conduction in QDs is accredited by only a single electron.

Many nanocomposite materials show effective electrical properties. Electronic properties of these materials depend on the shape, size, structure and composition of filler particles. It was noticed that, by altering the composition and size of nanomaterials, the electrical properties can be tuned.³⁷

1.7 Fabrication techniques for quantum dots

Fabrication technologies are the major problems in nanoscience and nanotechnology to investigate unique characteristics and applications of nanomaterials. To fabricate nanomaterials two broad approaches are Top-down and bottom-up approach as shown in Figure 1.6.



*Fig.1.6 Synthetic techniques for nanoscale structure.*³⁸

1.7.1 Top-down approach

The top-down method includes etching away bulk materials into nanoparticles. In this approach etching of bulk materials is done by sputtering, laser ablation, mechanical milling, nanolithography, and thermal decomposition as fabrication techniques with diverse applications. But defects in a surface structure are the main issue in a top-down approach.³⁹

1.7.1.1 Mechanical milling

For the synthesis of nanomaterials of different sizes, mechanical milling is one of the best top-down method amongst others. In the synthesis process, the mechanical grinding method is applied to post-anneal and mill nanoparticles. If wrong conditions are applied, cold welding, fracturing or plastic deformation occur.⁴⁰

1.7.1.2 Nanolithography

The study of manufacturing of nanoscale structure with minimum one-dimensional size between 1 and 100 nm is called nanolithography with different kinds of nanoimprints, such as multiphoton, optical, electron beams, and scanning probe lithography. Generally, in lithography technique ions electrons or photons are focused on light-sensitive materials to get the intended shape or form just like in printing or photographic technique.⁴¹

1.7.1.3 Laser Ablation

Laser ablation synthesis is the most popular process to produce nanomaterials in various solvents. In this technique, a laser beam is required to illuminate the metal that is saturated in liquid solution. The electric field that is generated by a laser beam having high energy enough to eject an electron from bulk material. The material will be converted into plasma comprising atoms, materials, and clusters when laser flux energy is very high. By this technique, growth rate, temperature and pressure can be controlled.⁴²

1.7.2 Bottom-up approach

Building up of nanomaterials by simply adding atom by atom, cluster by cluster or molecule by molecule. It is usually called as self-assembly of atoms or molecules. The bottom-up approach involves the sol-gel method, spinning, chemical vapor deposition, colloidal precipitation, pyrolysis, and biosynthesis. Self-assembly is the basic principle of a bottom-up approach.

Broadly, the bottom-up approach is classified into two classes depending on the medium in which nanomaterials are formed.

- Gas-phase methods
- Wet chemical methods

1.7.2.1 Wet Chemical methods

For manufacturing and constructing materials at the nanoscale, the chemical method plays a key role because of many advantages. The prime advantage of the chemical method is the versatility in designing and structuring nanomaterials. The second main advantage is the chemical homogeneity while mixing materials at atomic/molecular levels. On the other hand, Chemical methods offer some drawbacks includes toxic precursors or

solvents that are used in the synthesis of nanomaterials and by-products for which need some purification steps to eliminate.⁴³

1.7.2.1.1 Colloidal method

The best, easiest and cheapest wet chemical method to synthesis nanomaterial is the colloidal method. Both organic and inorganic precursors are used in this process, but mostly metal salts are reduced to nanoparticles of QDS. Agglomeration of particles can be adverted by using stabilizing agents. The particle size that is obtained by the colloidal method is in 1-200 nm range, but this size can be controlled by using either stabilizing/capping agent or by changing the concentration of precursors. Colloidal method having high stability, better solubility, absorption, and bioavailability.⁴⁴

1.8 Applications of QDs

Over the decades, QDs based light-emitting diodes (QLEDs) have earned much attention in the research field. Due to the optical and electronic properties of QDs, it is widely used in solar cells, photovoltaics, optical amplifiers, lasers and sensors.⁴⁵ Group III-V semiconductor QDs that is InP, InAs, InGaAlN, GaP and GaAs play a key role in optoelectronic properties. The Auger recombination process is the major issue in the lasing process while using QDs. QDs having many biological applications such as Vivo and in-vitro imaging, magnetic resonance imaging, DNA assays, drug delivery etc.^{46 47} Due to small size, brightness, and stability it would be advantageous to use QD as a marker for plant bioimaging cells or their cell walls. QDs having high photostability and also breaks the restrictions related to photobleaching.⁴⁸ As QDs having a very small size, therefore, they have unique physical properties for example optical and electron transport which are different from those of bulk materials.

1.9 Demerits of QDs

Despite having so many advantages in the field of QDs, they do have some limitations as well for example QDs comprising Cd, In or Pd etc are toxic, costly and a source of environmental pollution. There are some major factors on which toxicity of QDs depend such as size, capping ligands, materials used for preparations, route of administration, a dose of QDs and environmental conditions. Toxicity is the main problem of using QDs in biological applications. The physical size of QDs is largely due to which

they cannot disperse across cell membranes. The transportation process may be hazardous for the cell or may damage it too. In short, QDs are unsuitable for biological applications and prove to be noxious for cells. Their relatively long lifetime may hinder several applications that expect QDs to be biodegraded instantly after the experiment has been done. QDs are extensively used in new light-emitting diodes (LED) known as QD-LEDs. Though, to devise QDs with blue emission light is a challenging task because compared with other colors of light-emitting dots, it needs a smaller size and amplified emission so that the same signals can be detected by the human eye. Furthermore, Surface defects in QDs act as temporary traps which alters the electron-hole recombination this causes the blinking effect and Quantum yield declines. Biocompatible functionalization can be used to minimize the toxicity of QDs hence the mercapto group is used in this regard. Besides, metal-free or carbon-based materials can also be used to prepare QDs with less toxicity.⁴⁹

1.10 Ternary quantum dots

QDs based on metal chalcogenide alloys, mainly belong to group II-VI semiconductors (type MX, M = Cd, Zn, Pb; X = Te, Se, S), have gained much importance in research fields essentially in optoelectronics, QDs lasers, heterojunction solar cells, photodetector, photovoltaics and for bio-sensing and bio labeling due to their tunable optical properties and size-tunable fluorescence emission.⁵⁰ Semiconducting nanocrystals of group II-VI show unique linear and nonlinear properties which are often called optical limiting properties.⁵¹ Recently, much attention has been paid to the synthesis of binary⁵², ternary⁵³ and core-shell nanocrystals⁵⁴. Binary QDs of group II-VI has been proven to be potential candidates for solar cells, Light-emitting diodes (LED) and lasers but ternary semiconductor QDs have compositional dependent optoelectronic properties. Optoelectronic properties like fluorescence lifetime, fluorescence intensity, PL and PL QY can be tuned by varying the composition of Ternary QDs.⁵⁵ To govern the optoelectronic properties of QDs, the bandgap is the predominant factor. QDs with a binary composition having discrete band gaps which limits their applications whereas ternary QDs having continuously tunable bandgap energy⁵⁶. As the bandgap of ternary and quaternary QDs can be engineered by regulating their size, composition, and structures so their optical properties can be tuned which is not possible in binary QDs. This can be attained by alloying two or more semiconductors having different bandgap energies. It is observed that

the bandgap energy is increased when the concentration of semiconductor either chalcogenide component i.e., anion or metal component i.e., cation having broad bandgap is increased.⁵⁷

Moreover, in binary QDs heavy metals of group IV-VI, group III-V, and group II-VI are used which are highly toxic and cause a quenching effect i.e., fluorescence decreases by time or by other chemicals, therefore, they are not biocompatible. To overcome this difficulty ternary or quaternary alloyed semiconductors have been used. Nonetheless, ternary QDs gain so much attention, they are considered as potential substitutes for binary QDs and they have high PL, PL QYs with less toxic components. The commonly used nontoxic ternary QDs involve AgInS, CuInS and AgCuS.⁵⁸

1.10.1 ZnCdS quantum dots

1.10.1.1 Zinc

Among group II-VI group, Zn-based QDs are chemically most stable, cost-effective, eco-friendly and nontoxic elements but they may become toxic to humans when a high concentration of Zn is used. As, Zn is eco-friendly, so it is very useful for wastewater treatments, photocatalytic and biological applications. Moreover, Zn content in ZnCdS QDs decreases its size which results in a remarkable quantum confinement effect.

1.10.1.2 Cadmium

As cadmium is carcinogenic metal, indium metal is the secondary compound, but many researchers found that indium is 10 times more noxious than cadmium. Other secondary options do exist, but they don't have comparable efficiency and commercially not easily available, so cadmium is the primary choice. Cadmium-based QDs having high luminating properties among other group II members which include broad absorption peak, narrow emission peak, high photostability and bright photoluminescence which make them highly efficient in many applications as in photovoltaic devices, sensors, electroluminescence (EL), bio-imaging, etc.

1.10.1.3 Why ZnCdS combination?

ZnCdS QDs have earned so much attention in recent decades due to their tremendous advantages of the direct bandgap, high absorption coefficient in blue and UV region, size-tunable and compositional tunable bandgap. The novel properties and bandgap energy of alloyed ZnCdS lie between the bulk CdS (2.4 eV) and ZnS (3.7 eV). ZnCdS

alloyed QDs formation following the Hume-Rothery rule.⁵⁹ First, the difference between the size of a solute atom and parent metal should be small i.e., less than 15%, second, there should be a small electronegativity difference and the third crystalline structures of solute and solvent should be same to get complete solubility. Zn atoms containing 1.6 electronegativity and 142pm atomic radius whereas Cd atoms containing 1.7 electronegativity and 161pm atomic radius so they have small electronegative difference and small atomic size difference (12%)⁶⁰ additionally both ZnS and CdS binary QDs having same zinc blende cubic structure and their lattice constants are 5.406 and 5.835 Å So low lattice mismatch allow Zn to introduce into CdS lattice and form ZnCdS colloidal QDs, that is the practical way to manufacture blue emitter with higher bandgap emission efficiency. Ternary ZnCdS QDs are brilliant entrants as blue emitters. The solubility product of CdS and ZnS is 8.0×10^{-27} and 2.0×10^{-25} respectively so CdS growth rate is higher than ZnS. By changing Zn/Cd ratio in ZnCdS QDs, the absorption and emission spectra can be altered. Increase Zn contents will decrease the size of ZnCdS QDs which leads to a remarkable Quantum confinement effect.⁶¹ PL QYs, chemical and thermal stabilities of ZnCdS QDs are also compositional dependent.

1.10.1.4 Applications of ZnCdS quantum dots

ZnCdS QDs occupies an important position in the application of photoconductive devices, photocatalysis and heterojunction solar cells due to their broad bandgap.⁶² They are a substitute for CdS quantum dots in solar cells since they reduce the possibilities of absorption loss in solar cells. Based on the convenient eco-friendly process the optical properties of ternary ZnCdS fluorescent alloy QDs with adjustable composition are verified.⁶³ It is foreseeable that such alloyed fluorescent QDs provide multiple possibilities for bandgap tailoring and can be used in a variety of applications, such as biomarking and bioimaging in nanomedicine, or environmental use in water treatment as nano photocatalyst.⁶⁴

1.11 Capping agents

Surface defects in QDs act as temporary traps which alters the electron-hole recombination, this causes the blinking effect and quantum yield declines. So, passivation or capping off a surface is essential for the advancement of QDs that are photostable. The

key to other innovations in QDs is the latest development of QD surface chemistry by combining with suitable functional molecules.⁶⁵ By modifying the surface of quantum dots, more QDs are accessible to interact with target analytes.⁶⁶ Moreover, the surface modification of QDs avert them from agglomeration, also their stability and luminescent quantum yields magnified⁶⁷ for numerous applications. Primarily the applications of QDs may be limited if modification is done by highly noxious organic reagents. Appropriate surface modification is a key challenge to maintain QD colloid and photostability under intracellular or intercellular environments. Surface modification is commonly done by dumping either inorganic or organic coating over QDs. Two techniques are used for surface modification that is in situ and ex-situ. In situ technique, the surface modification is only performed during the synthesis of the nanoparticles whereas in an ex-situ technique the binding of capping agent to the surface occurs to the prefabricated QDs. The former technique is more efficient due to more grating density of capping agent on the nanoparticle surface.⁶⁸ When QDs surface is capped by chemical agents, they can amend the morphology, mechanical stability, toxicity, particle size optical properties and even photocatalytic activities.

1.11.1 Organically capped QDs

Mostly the development of monodispersed QDs is done by using an organic molecule that plays a role as a capping agent and adsorbs on the surface of QDs. Some of the advantages of organically capped semiconductor QDs involve the ability to bio-conjugate the QDS and colloidal suspension. Though, the choice of organic capping ligand is a crucial issue for surface modification. Mercaptans(-SH) or Phosphenes (tri-n-octyl phosphene oxide-TOPO) are mostly used. Capping a surface with organic ligands may cause steric hindrance due to due to large size and distorted size of ligand than surface sites.

1.11.1.1 Mercaptoacetic acid:

Mercaptoacetic acid (MAA) is a widely used organic ligand having the formula $\text{HSCH}_2\text{CO}_2\text{H}$ shown in Figure 1.7. MAA is also known as thioglycolic acid (TGA). It contains both carboxylic acid and mercapto (thiol) functional group. Due to the presence of a carboxylic functional group, MAA is considered a weak acid. MAA is highly reactive so it is unsuitable with bases, oxidizers, active metals i.e., Na, P, Ca, or Mg and with air. The extensive use of MAA as a capping agent is due to the following reasons.

- It is highly reactive.
- It is easily available and cost-effective.
- Due to its small size, it causes a low steric hindrance to the surface of QDs.



Fig 1.7. Formula of mercaptoacetic acid (MAA)

1.12 Aims and objectives

The aims and objectives of the work follows as

- To synthesize ZnCdS QDs
- To control the size of ZnCdS QDs by using different concentrations of capping ligand (MAA) and by fixing the ratio of other precursors
- To study the effect of capping ligand on UV-Vis absorption spectra
- To study the effect of changing the concentration of MAA on PL emission spectra and PL lifetime

Chapter 2
EXPERIMENTAL

2.1 Chemicals required for the experimental work

All the chemicals used for experimental work are given below in Table 2.1 along with their chemical names, molar masses, chemical formulas, percentage purities, and suppliers. These chemicals were of analytical grade with a high purity level, therefore, were used as received without any further purification.

Table.2. 1 List of the chemicals used in experimental work.

Sr. No	Compound	Chemical formula	Molar mass (g/mol)	Purity (%)	Suppliers
1	Zinc Sulphate	$ZnSO_4 \cdot 2H_2O$	287.60	≥ 98	Sigma-Aldrich
2	Cadmium chloride (hemi-pentahydrate)	$CdCl_2 \cdot 5H_2O$	228.34	≥ 99	Sigma-Aldrich
3	Mercaptoacetic acid (MAA)	$HSCH_2COOH$	92.12	≥ 98	Sigma-Aldrich
4	Sodium Sulphide (nonahydrate)	$Na_2S \cdot 9H_2O$	240.18	≥ 99.9	Sigma-Aldrich
6	Sodium hydroxide solution	NaOH	39.99	≥ 99	Sigma-Aldrich

2.2 Synthesis procedure

2.2.1 Synthesis of MAA capped ZnCdS QDs via colloidal method

ZnCdS QDs were synthesized by using the most accessible and inexpensive way as reported in the literature.⁶⁹ Colloidal method was used to synthesize ternary QDs. 0.1 M of $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$ (4mL) and 0.1 M $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (12mL) both prepared in deionized water was added in a three-necked round bottom flask. The mixture was stirred at 300 RPM with 80°C temperature under a nitrogen atmosphere. After homogenous mixing of both cationic precursors capping ligand MAA was added. This synthetic scheme was repeated five-time for ZnCdS-I, ZnCdS-II, ZnCdS-III, ZnCdS-IV and ZnCdS-V by changing the concentration of MAA 0.5 M, 1 M, 1.5 M, 2 M, 2.5 M respectively. The pH of the solution was maintained by adding NaOH solution dropwise till pH becomes 9-10. Under vigorous stirring, the anionic precursor $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added which is the source of sulphur. The whole reaction mixture was kept and monitored for 1h. The minimum amount of ethanol was added to the reaction mixture to remove organic impurities and to precipitate QDs. QDs were separated and centrifuged by using distilled water to remove other impurities. This procedure was repeated four times to remove excess salts. After washing, the QDs were dried in an oven at 75°C. Finally, the desired ZnCdS was obtained in the form of pale-yellow powder which was subjected to various characterization techniques.

2.2.2 Flow chart for the synthesis of maa capped ZnCdS QDs

The flow chart for the synthesis of ZnCdS using various concentration of MAA is given in Figure 2.1.

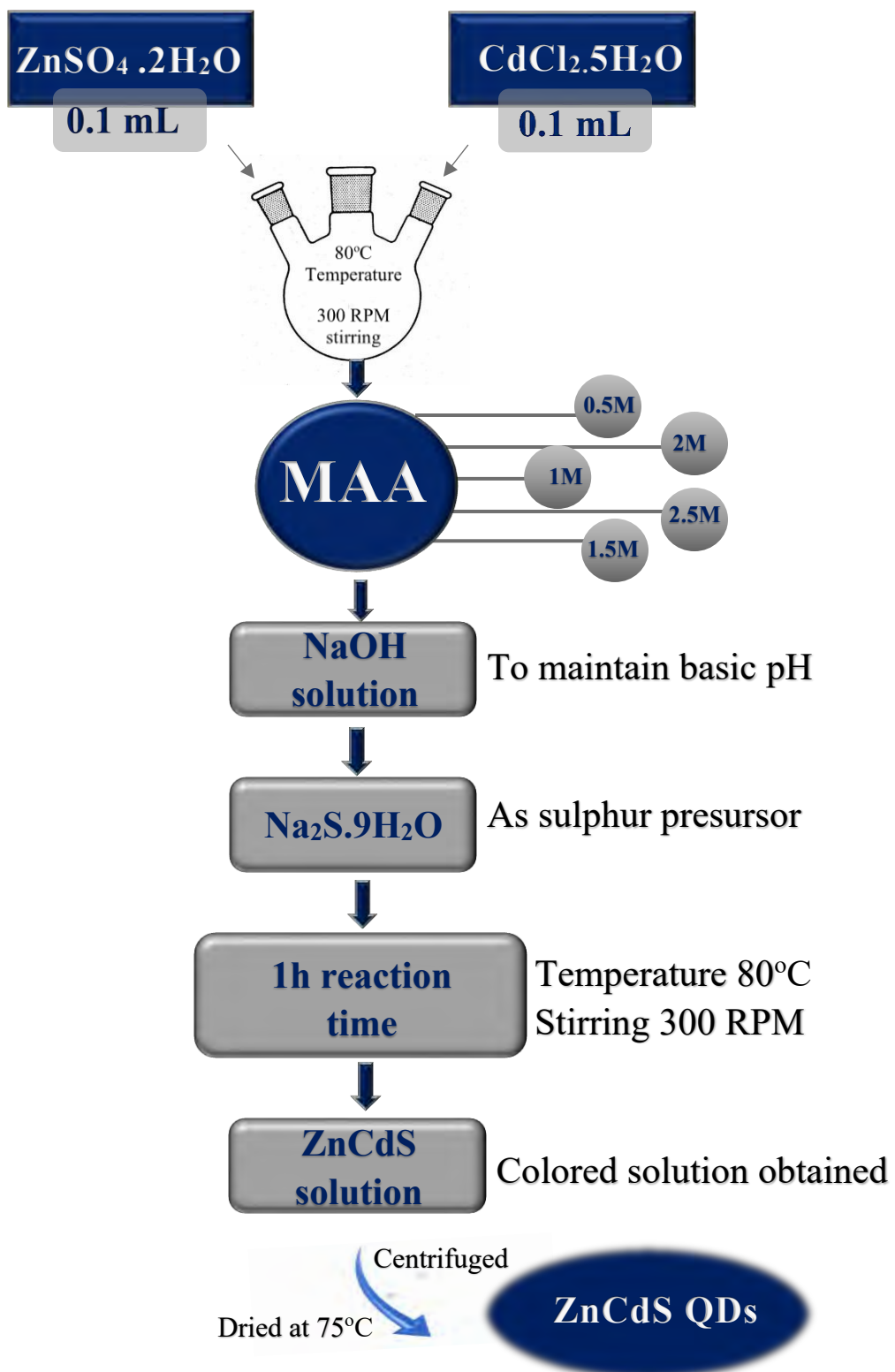


Fig.2.1. Flowchart for the preparation of ZnCdS QDs via colloidal method.

2.3 Characterization Techniques

After the synthesis of ZnCdS QDs, the characterization was carried out to study optical properties, band gaps energies, fluorescence lifetime, crystalline structure and particle size of QDs. The techniques used are listed below.

1. Fourier-transform infrared (FTIR) spectroscopy
2. X-ray diffraction (XRD) analysis
3. UV-visible spectroscopy
4. Steady-state photoluminescence (SSPL)
5. Time-resolved photoluminescence (TRPL)

2.3.1 Fourier-Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectroscopy analysis of ZnCdS QDs was performed in the region of 4000-500 cm^{-1} by using BRUKER TENSOR-II FT-IR spectrometer. The response of the sample was monitored against the reference beam and different signals at the detector were plotted as Infrared Spectrum. The FT-IR study was employed to investigate the chemical structure of as-synthesized nanocrystals and to identify the molecules that were used for capping, stabilization and reduction.

2.3.4 X-Ray Diffraction Analysis (XRD)

The crystal structure of CuCdS QDS was determined by using PANalytical X-ray diffractometer model 3040/60 X'Pert PRO of 45kV and 40mA source having $\text{CuK}\alpha$ ($\lambda=1.54\text{\AA}$) radiation over an angle range of 10 - 80°. The XRD analysis was carried out to determine crystal structure, calculation of crystallite size, d-spacing, and lattice parameters, and size confirmation of QDs. Every crystal has a different X-ray diffractogram that follows Bragg's law. By using Debye Scherrer's equation, the average crystallite size was calculated from XRD data.

2.3.1 UV-Visible Spectroscopy

The UV-VIS spectroscopy analysis of ZnCdS QDs was performed by using the instrument model UV-Vis 1601 Shimadzu spectrophotometer under the absorbance mode in the wavelength range of 200-800 nm. This instrument consists of a light source (UV lamp), dispersive element, sample holder and detector. To determine the stability and

formation of QDs, various absorption bands were observed in UV-Vis spectra. Bandgaps of ZnCdS QDs were calculated from the absorption spectra using Tauc method.

2.3.2 Steady-State and Time-Resolved Photoluminescence (PL) Spectroscopy

PL analyses were performed by using the instrument model Pico-Quant Fluo Time-300 steady-state and time-resolved, time-correlated single-photon counting (TCSPC) setup. The PL of the samples were collected at room temperature after exciting at 306 nm with a pulsed LED laser coupled to TCSPC setup. Both the PL spectra and PL decay kinetics of the synthesized ZnCdS QDs by altering the amount of MAA were studied

Chapter 3

RESULTS AND DISCUSSION

3.1 FTIR analysis of MAA capped ZnCdS QDs

By performing FTIR analysis, different functional groups are detected that are associated with a sample. All functional groups have characteristic fingerprint regions. Figure 3.1 shows the FTIR analysis of MAA capped ZnCdS QDs. A broad peak appears at 3190 cm^{-1} that corresponds to O-H stretching. The characteristic peaks for C-O and C=O stretching mode appeared at 1397 and 1648 cm^{-1} respectively. The peak of C-H bending vibrational mode appeared between 1100 - 1300 cm^{-1} . The stretching vibrational modes of ZnCdS QDs occurred at 555 cm^{-1} and 624 cm^{-1} which are per the recorded value for ternary composition i.e., in the range between 530 - 670 cm^{-1} .⁶⁰ Different functional groups that are present in MAA along with their modes of vibrations and peak positions are listed in Table 3.1. No characteristic peak was observed between 2550 - 2620 cm^{-1} for S-H stretching mode that indicates the strong interaction between S-H with the surface of ZnCdS QDs. Hence, it can be inferred that ZnCdS QDs were successfully capped by MAA.

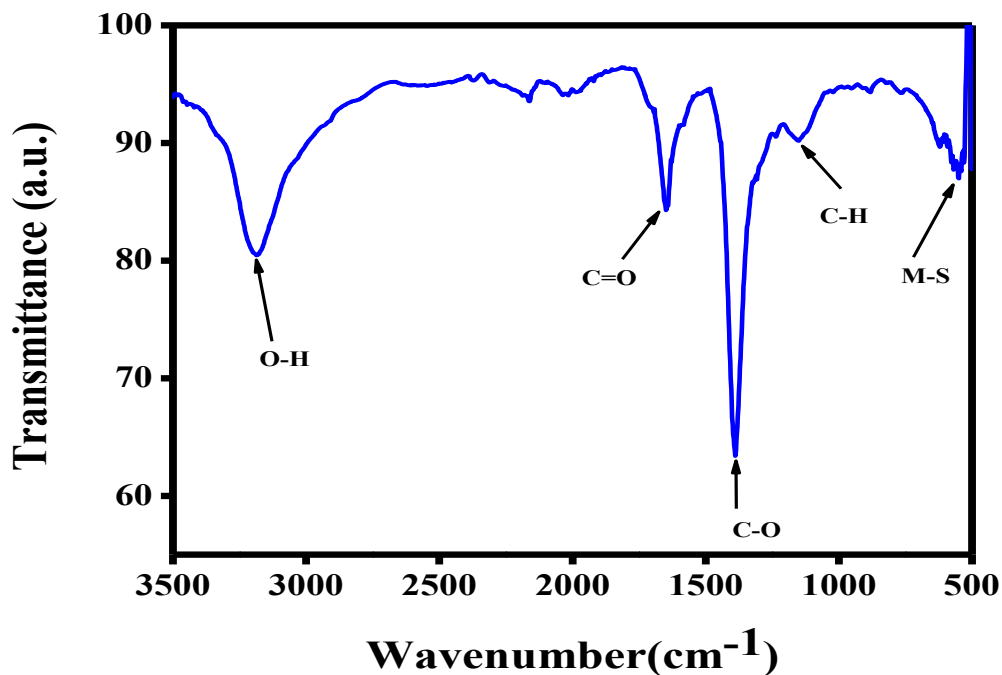


Fig.3.1 FTIR spectrum of ZnCdS QDs capped with MAA.

Table.3. 1 Different functional groups of MAA capped ZnCdS QDs in FTIR spectrum.

Sr. No	Bond	Wavenumber (cm⁻¹)	Mode of vibrations
1.	O-H	3381	stretching
2.	C=O	1648	stretching
3.	C-O	1397	stretching
4.	C-H	1150	bending
5.	M-S	530-670	stretching

3.2 XRD analysis of ZnCdS QDs capped with MAA

The powder XRD technique is used to determine the crystallinity of the material. It is also used to calculate the phase purity and crystallite size of a material. Here, the XRD technique was used to get the crystallite size, as well as the structure of ZnCdS QDs, capped with MAA. The XRD pattern has been displayed in Figure 3.2. The crystal nature are in close agreement with standard reference card confirming the cubic structure of MAA capped ZnCdS QDs. With different concentration of MAA from 0.5M to 2M there observed a slight variation in intensity and peak broadening. The bpeak broadening is clear evidence of formation of ultra-small sized QDS from 1.90nm to 1.65nm.

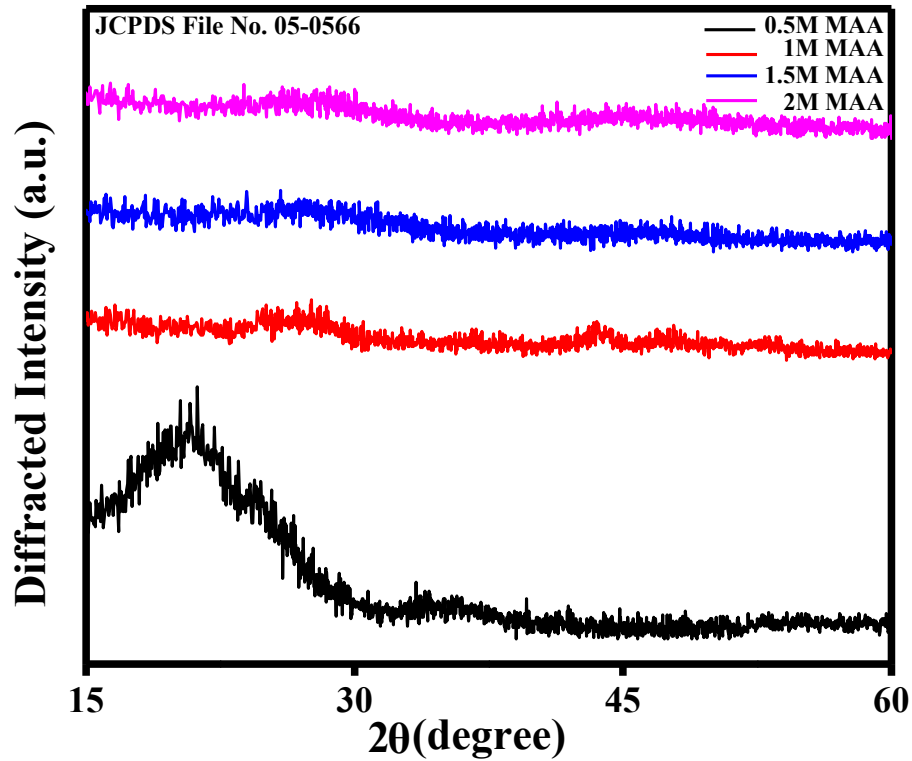


Fig.3.2 XRD pattern of MAA capped ZnCdS QDs.

The three distinct peaks appear in XRD pattern that is indexed with a standard reference card of ZnS QDs that confirms the cubic structure of ZnCdS QDs capped with MAA. Moreover, using Debye Scherrer's equation.

$$D=0.9\lambda/\beta \cos \theta \quad (3.1)$$

Where,

D = Average crystallite size

K = dimensionless shape factor

β = Full width at half maxima (FWHM) in radians

λ = wavelength of X-ray source

θ = Bragg's diffraction angle

The measured average crystallite sizes by using this formula is given in the Table 3.2. MAA capped ZnCdS QDs using concentration from 0.5M to 2M have slight variation with in the range 1.90nm to 1.65nm that confirms the quantum confinement effect.

Table 3.2 Crystallite sizes of MAA capped ZnCdS QDs calculated via XRD pattern

Sr No.	Sample ID	Concentration of MAA (M)	Crystallite size (nm)
1.	ZnCdS-I	0.5	1.901
2.	ZnCdS-II	1	1.79
3.	ZnCdS-III	1.5	1.71
4.	ZnCdS-IV	2	1.65

3.3 UV-Vis absorption spectra of MAA capped ZnCdS QDs

UV-Visible absorption spectra of ZnCdS QDs synthesized via the colloidal method by varying the concentration of capping agent were measured using UV-VIS spectrometer. From UV-Vis absorption spectra optical properties, especially band gap as well as absorption edges of QDs having different sizes were estimated. The UV-Vis absorption spectra for capped ZnCdS QDs with different concentrations of capping ligand MAA are shown in Figure 3.3.

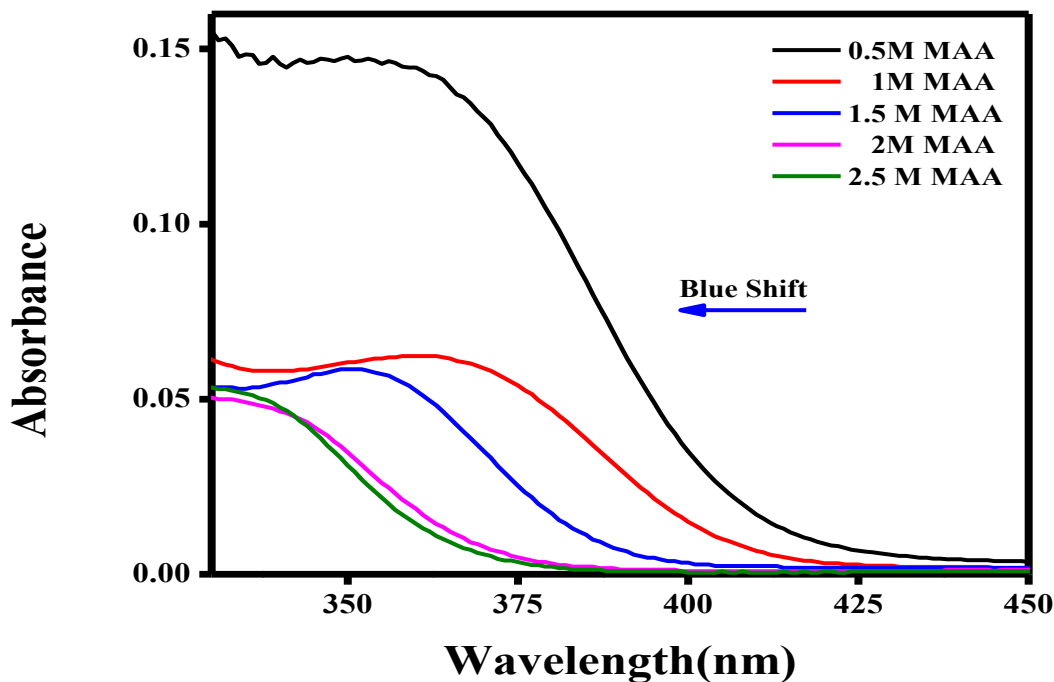


Fig.3.3 UV-Visible absorption spectra of ZnCdS QDS by capping with different concentrations of MAA.

ZnCdS QDs having a wide range of absorption edge lies in between bulk ZnS and CdS. The first sharp absorption peak is observed at 365nm with a 0.5 M concentration of MAA. By increasing the concentration of MAA, the blue shift is observed which is an indication of the quantum confinement effect. Due to the quantum confinement effect, the binding energy, as well as the coulombic interaction between the capping ligand and the surface of QDs increases. Moreover, when the concentration of the capping agent increases, more sites of QDs are capped that decrease the nucleation and the size decreases. A blue shift is observed in absorption spectra that corresponds to increase in band gap energy that is estimated from Tauc method.

3.2.1 Tauc plot of MAA capped ZnCdS QDs

By using Tauc equation 3.2, the optical band gap of ZnCdS QDs using different concentration of MAA were estimated. Tauc equation follow as;

$$(\alpha h\nu) = A(h\nu - E_g)^{\frac{1}{n}} \quad (3.2)$$

α is the absorption coefficient

A is an effective mass coefficient

E_g is the bandgap energy

n equals 2 for direct bandgap.

Tauc plot for ZnCdS QDs for different MAA concentrations is shown in Figure 3.4

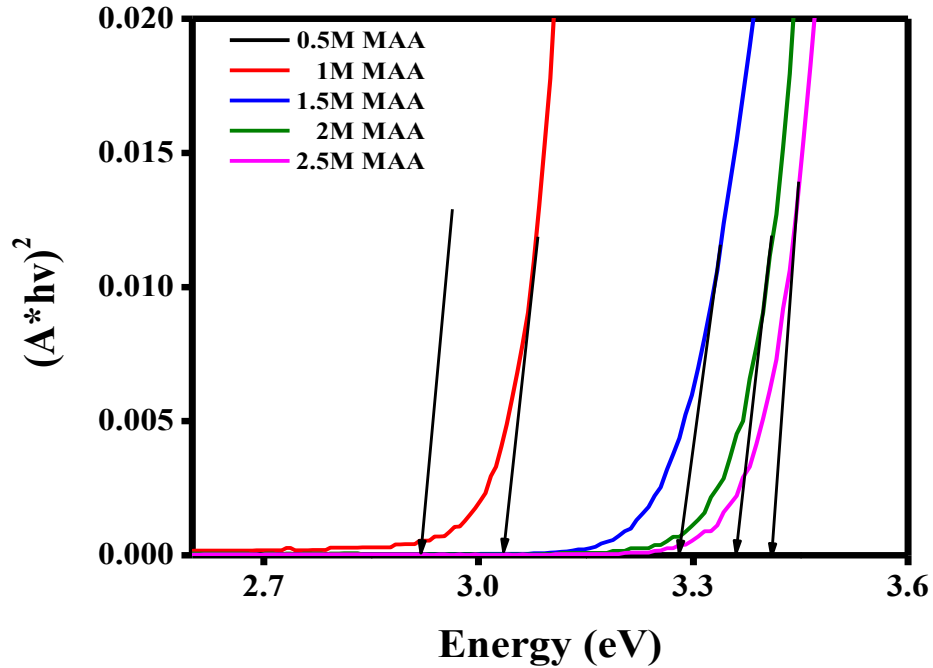


Fig. 3.4. Tauc plot for estimation of energy band gap of ZnCdS QDs capped with different concentrations of MAA.

As observed from the graph the value of band gap for ZnCdS QDs containing different concentrations of MAA is varied from 2.91 eV to 3.41 eV. The values of energy bandgap estimated with five different concentrations of MAA are listed in Table 3.3. A continuously high energy bandgap (blue shift in wavelength) is observed. The direct relation between the concentration of MAA with band gap is shown in Figure 3.5.

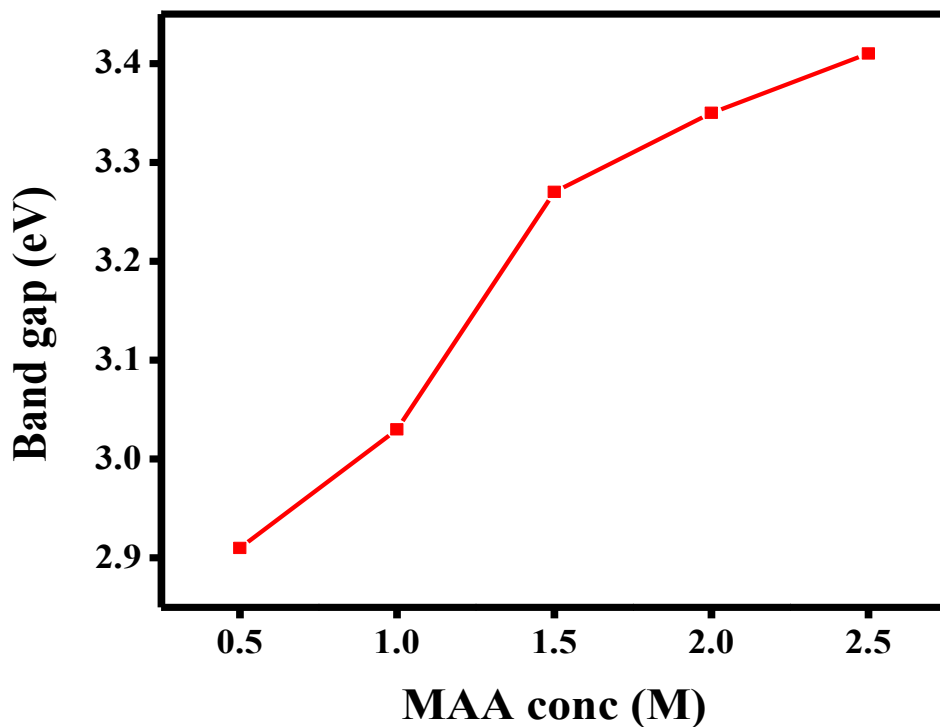


Fig.3.5. Relation between bandgap of ZnCdS QDs with the concentration of MAA.

From Figure 3.5 two important results can be concluded. First, a direct relationship between the concentration of MAA and bandgap. And second, a tunable bandgap for ZnCdS QDs from 2.91 to 3.41 by varying the concentration of MAA from 0.5 to 2.5 M is obtained. A wide range in tunability of bandgap is observed for ternary ZnCdS QDs in contrast to binary ZnS and CdS which gives direct bandgap energy. Hence, the tunable bandgap effect is confirmed in the case of ternary ZnCdS QDs.

Table.3. 3 Relation between the concentration of capping agent with bandgap and absorption wavelength of ZnCdS QDs.

Sample ID	Concentration of MAA (M)	Wavelength, λ (nm)	Bandgap (eV)
ZnCdS-I	0.5	365	2. 91
ZnCdS-II	1	361	3.03
ZnCdS-III	1.5	350	3.27
ZnCdS-IV	2	340	3.35
ZnCdS-V	2.5	335	3.41

3.3 Steady-state photoluminescence (SSPL)

The PL spectroscopy mechanism can briefly be explained as the photons having energy equal to or higher than the bandgap excite electrons from valance band or Zn^{+2} or Cd^{+2} levels to conduction band. The excited electron may decay back in two ways; radiatively and non-radiatively. First, the excited electron de-excite to surface states (non-radiatively) and then de-excite to valance band (radiatively) and emit photons having low energy. The valance band edge shifts downwards in energy as the particle size decreases, as a result emitted photon having high energy giving a blue shift in PL peak i.e., the PL occurs towards a shorter wavelength.

In SSPL spectroscopy, the increase in density of defect states was studied. Trap states are accountable to cause defects such as dangling bonds and vacancies on the surface of the QDs. As particle size is reduced the roughness on the surface decrease, which will change the densities of surface defects because of which PL peak shifted. The PL emission occur at longer wavelength compared to excitation wavelength i.e., 306 nm (Stokes Shift). This predicts the presence of surface states or impurities, as displayed by Figure 3.6. It shows the SSPL spectra with Stoke shifted PL appear at 587 nm, 572 nm, 539 nm, 508 nm, and 478 nm for five different concentrations of MAA 0.5 M, 1 M, 1.5 M, 2 M and 2.5 M respectively. As the concentration of MAA increases, a blue shift is observed which agrees with UV-Vis absorption spectra of ZnCdS QDs.

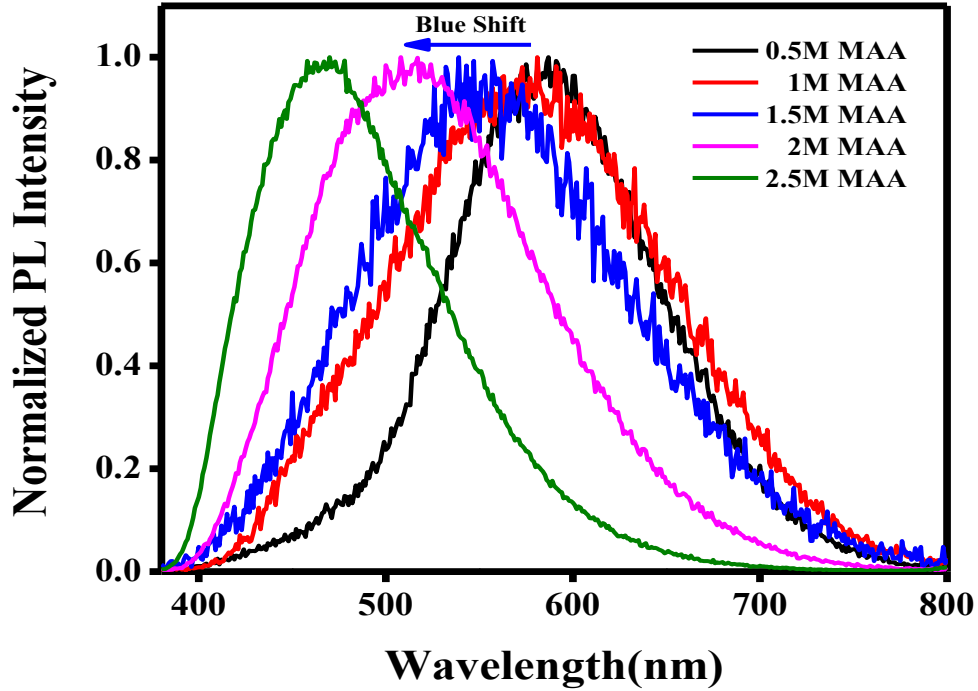


Fig.3.6. Normalized SSPL spectra of ZnCdS QDs capped with different concentrations of capping agent MAA.

3.4 Time-resolved photoluminescence (TRPL)

For each fluorescent QD, fluorescence decay time plays a major role. The TRPL measurement of excited state was performed to get the information about the PL lifetime of QDs. The PL is said to be fluorescence if singlet to singlet de-excitation occurs and PL lifetime will be shorter whereas triplet to singlet de-excitation occurs then lifetime will be longer and this is known as phosphorescence. PL kinetics measured after excitation at 306 nm. The lifetime for ZnCdS QDs is estimated by fitting the experimental PL kinetic data by bi-exponential decay model and τ_{average} is calculated by equation 3.3.

$$\tau_{\text{(average)}} = \frac{\sum_{i=1}^n A_i \tau_i}{\sum A_i} \quad (3.3)$$

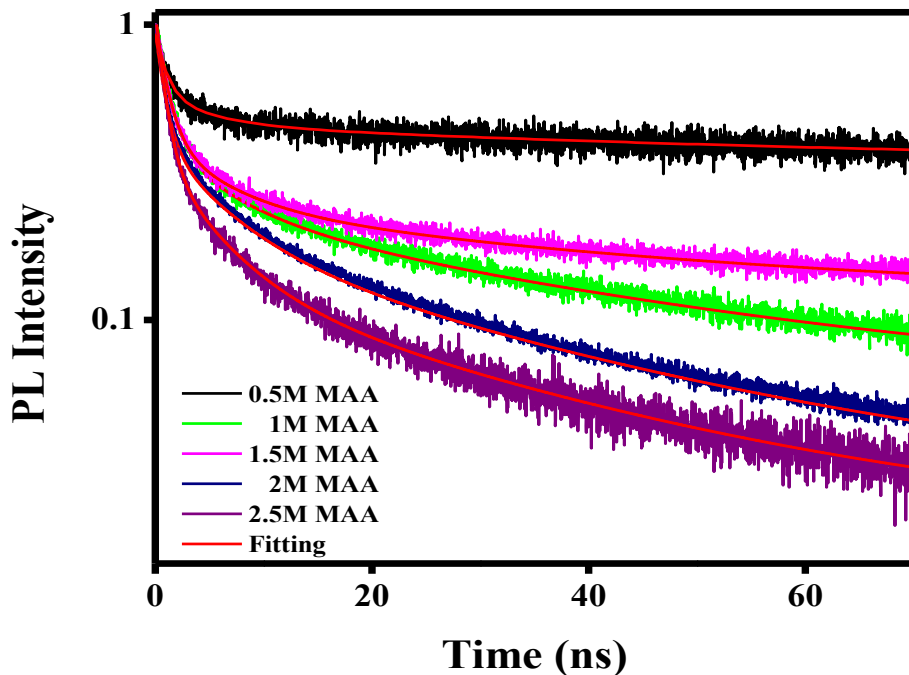


Fig.3.7. PL decay kinetics of ZnCdS QDs capped with different concentrations of capping agent MAA fitted with bi-exponential decay model (red traces).

TRPL gives an understanding of crystal defects including surface trap states i.e., shallow traps and deep traps. Compared with deep trap, surface trap offers local sites for recombination of excited electrons which results in a shortening of PL lifetime i.e., faster PL decay. Surface trap states are usually high in energy and considered as shallow traps. With shallow traps, the decay rate is faster whereas deep traps play a major role in slower PL decay rate.

The average PL lifetime for 0.5 M MAA is 12.24 ns and as the concentration of MAA increases, PL lifetime decreases accordingly as shown in Figure 3.7. The longer PL lifetime is observed at 0.5 M concentration of MAA this is because for large size QDs, energy levels are more closely spaced in which electron and hole can easily be trapped. Therefore, exciton (bound electron-hole) in large size QDs lived longer than small QDs. So, an increase in the concentration of MAA results in a decrease in particle size due to which PL lifetime decreases which is due to shallow traps. The relation between the concentration of capping agent and average PL lifetime is shown in Figure 3.8.

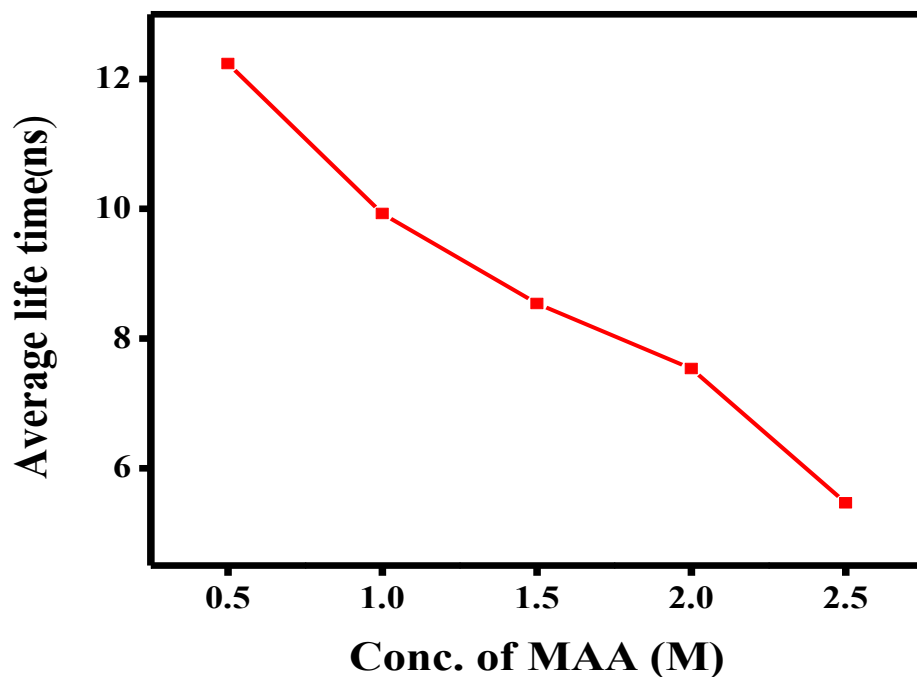


Fig.3.8 Relation between average PL lifetime with concentration of capping ligand MAA.

Table.3. 4 PL decay lifetime of ZnCdS QDS capped with different concentration of MAA.

Sample ID	[MAA] (M)	A ₁	τ_1 (ns)	A ₂	τ_2 (ns)	A ₃	τ_2 (ns)	τ_{average} (ns)
ZnCdS-I	0.5	84.35	41.99	237.6	1.68	---	---	12.24
ZnCdS-II	1	657.38	42.19	637.6	6.16	2152	1.18	9.93
ZnCdS-III	1.5	420.09	44.92	570.9	5.73	1839	1.09	8.54
ZnCdS-IV	2	1718.90	33.10	2328.3	5.94	6057	0.89	7.53
ZnCdS-V	2.5	273.64	30.22	502.2	5.11	1430.1	0.85	5.47

Conclusions

ZnCdS QDs of different sizes were synthesized via the most accessible and inexpensive way i.e., colloidal synthesis using five different concentrations of MAA. In FTIR analysis the absence of characteristic S-H peak from 2250- 2600 cm^{-1} confirmed the successful capping of QD surface with MAA. Three distinct peaks that appeared in the XRD pattern confirmed that ZnCdS QDs have been synthesized in the cubic phase.

Tuning of photophysical properties of ZnCdS QDs were performed by varying the concentration of MAA and was confirmed with the help of UV-VIS and SSPL spectroscopy. On increasing the concentration of MAA from 0.5 to 2.5 M, a blue shift in the wavelength range from 356-335 nm was observed in UV-VIS spectra. Moreover, this blue shift in wavelength was associated with an increase in bandgap energy from 2.91-3.41 eV that was estimated by Tauc method, which confirmed the quantum confinement effect in MAA capped ZnCdS QDs. A wide range of bandgap tunability was observed for ternary ZnCdS QDs in contrast to ZnS and CdS which gives direct bandgap energy. Stoke shifted PL was observed from 587-478 nm with changing concentration of MAA from 0.5 to 2.5 M which agreed with UV-VIS spectroscopy. Average PL lifetime decreased from 12.24-5.47 ns as the concentration of MAA increased from 0.5 to 2.5 M. This trend showed that in large-sized QDs, the electron-hole pair lived longer as compared to small-sized QDs.

The small-sized ZnCdS QDs find many applications in the optoelectronic field i.e., ZnCdS QDs are widely used in heterojunction solar cells, LEDs and photoconductive devices because of their wide bandgap energy i.e., from 2.91-3.42 eV.

Future prospects

- As the surface of ZnCdS QDs was successfully engineered by functionalizing with MAA, further attachment with many organic molecules is possible to enhance its properties and applications.
- To synthesize Cd-free QDs by replacing Cd with non-toxic metal.
- To synthesize ZnCdS QDs by changing the composition of Zn or Cd contents.
- To develop strategies for improving stability and for higher radiative lifetimes of ZnCdS QDs.
- To fabricate solar cells by using MAA capped ZnCdS QDs.

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