SYNTHESIS AND CHARACTERIZATION OF UNCAPPED AND CAPPED ZINC SULFIDE (ZnS) QUANTUM DOTS

A PROJECT REPORT

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Submitted By

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CANDIDATE'S DECLARATION

I, SAGAR SINGH ADHIKARI, Roll No. 2K16/NST/07, hereby declare that the project Dissertation titled "**Synthesis and characterization of uncapped and capped zinc sulfide (ZnS) quantum dots"** which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in the partial fulfillment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associate ship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled "**Synthesis and characterization of uncapped and capped zinc sulfide (ZnS) quantum dots"** which is submitted by SAGAR SINGH ADHIKARI, 2K16/NST/07, Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the students under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any degree or diploma to this university or elsewhere.

Place: Delhi

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ABSTRACT

Zinc sulfide (ZnS) quantum dots have been synthesized via chemical route. The results of uncapped and poly-vinyl alcohol capped ZnS quantum dots (QDs) are compared. X-ray diffraction (XRD) shows synthesized ZnS QDs are in cubic phase (zinc blende). Effect of poly-vinyl alcohol concentration on synthesized ZnS QDs is significant. The crystalline size of uncapped and poly-vinyl alcohol capped ZnS QDs are 2.4 nm and 1.8 nm respectively. Photoluminescence spectrum of poly-vinyl alcohol capped ZnS QDs is blue shifted in comparison to uncapped QDs. The emission peaks are obtained at 433 nm and 425 nm for uncapped and poly-vinyl alcohol capped ZnS QDs respectively. Poly-vinyl alcohol has affected the particle growth because particle size changes with the concentration of poly-vinyl alcohol.

Keywords: ZnS, QDs, XRD, and poly-vinyl alcohol.

CONTENTS

List of Figures

CHAPTER 1

INTRODUCTION

1.1 Overview

Quantum dots are zero dimensional (0D) units. They are tiny semiconductor particles, whose diameter range is about 2- 10 nm (10~15 atoms long). Their properties are similar to an atom than bulk material hence; they are nick named artificial atoms. Mark Reed coined the term “quantum dot” in 1986 [1]. Alexey Ekimov in glass matrix and Louis Brus in colloidal solution first discovered them [2-4]. In recent years, quantum dots have attracted lot of attention due to its vast application in the field of optics, biomedical, chemical and quantum computing etc.

The electronic and optical properties of semiconductor material changes significantly when the size of material decreases due to increase in surface to volume ratio, lattice contraction, and quantum effect. Quantum confinement changes the electronic structure of nanoparticle when its size is equal to Bohr exciton radius of that material. When the particle size is less than the Bohr radius, the energy band gap is widened, leading to band shift in energy band and in emission spectrum. The recombination of an exciton at the surface plays significant role in modifying the optical properties of nanoparticle. As the size of material decreases, surface to volume ratio of that material increases and recombination of an exciton at surface is dominant [5]. These size dependents properties have many potential application solar cells, chemical and biological sensors, light emitting diodes etc. [6-8].

1.2 Quantum confinement

The movement of free carrier (electron or hole) in solid is restricted by bottom-up approach and top-down approach resulting in the formation of discreet energy levels and charge localization. Depending on the direction of confinement, possible nano-structures are quantum well, quantum wire and quantum dots.

(a) Quantum well (2D): In this, charge carriers movement is restricted in one direction but allowed to move in other two directions.

(b) Quantum wire (1D): In this, charge carriers movement is restricted in two directions but is free to move along third direction.

(c) Quantum dot (0D): In this configuration, charge carriers experiences strong quantum confinement along all direction. In quantum dot, all the dimensions are smaller or at least equal to Bohr exciton radius.

(d) Bulk material (3D): Here charge carriers do not experience quantum confinement in any direction.

The density of state (DOS) represents changes in electronic properties of low dimensional system. The Density of state is defined as the number of electrons (or holes) for unit volume per unit energy for a given energy level.

In bulk 3D system Density of state (g (E) dE) of volume $a^{3\ given}$ by:

$$g(E)dE = \frac{a^3}{2\Pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}\ dE \qquad (1.1)$$

For bulk system, DOS is directly proportional to square root of energy and the energy states are continuous.

For 2D systems (quantum well) DOS (g (E) dE) of area a^2 is given in equation (1.2). It exhibit staircase like character and DOS is independent of energy. The equal height of staircase corresponds to quantized electronic states.

$$g(E)dE = \frac{a^2 m}{\Pi\hbar^2}\ dE \qquad (1.2)$$

In 1D, (quantum wire) system confinement is in two directions and DOS is like array of spikes and inversely proportional to square root of energy.

$$g(E)dE = \frac{1}{\hbar\Pi}\left(\frac{m}{2E}\right)^{\frac{1}{2}} dE \qquad (1.3)$$

In (0D) quantum dot, electrons or holes are confined in all direction. In this case, DOS is given by Dirac function:

$$g(E)dE = 2\delta(E - E_C) \qquad (1.4)$$

DOS of 0D is dependent on energy and gives discreet energy level that is similar to characteristics individual atoms/molecules thus, also called artificial atoms. The enhanced energy band gap and discreet energy level of quantum dots make them useful in wide range of application. Fig 1.1 shows the schematic diagram of density of states of various confinement configurations and their energy response.

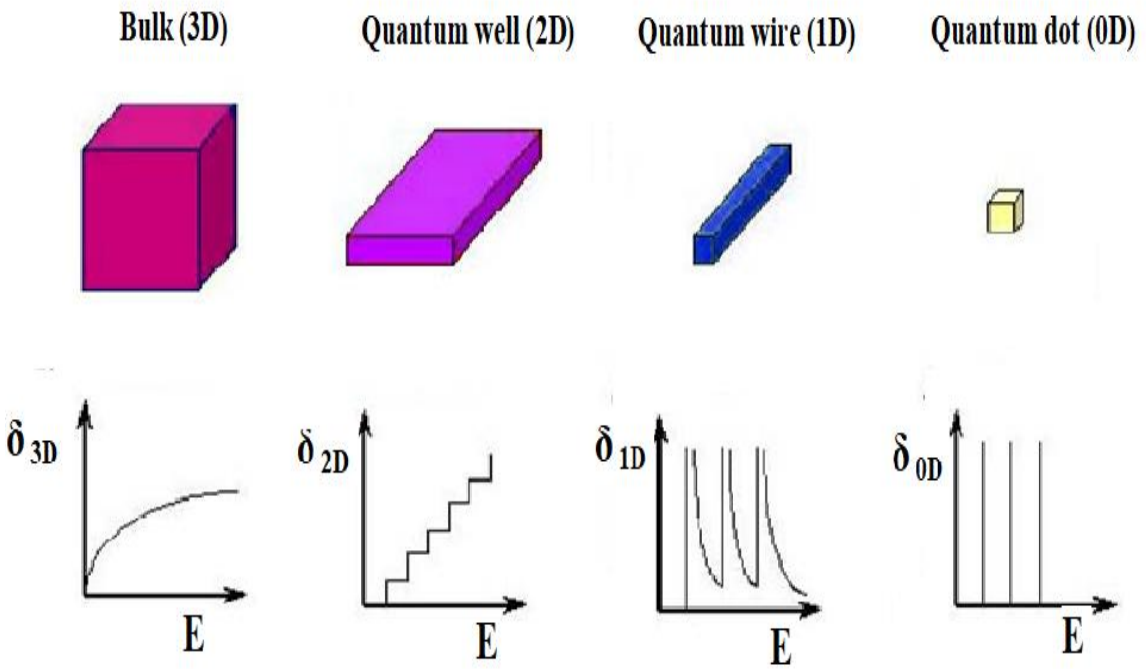

Fig.1.1 Density of states vs Energy response of different quantum states.

1.3 Bohr exciton radius

An exciton is a bound electron hole pair formed via columbic interaction [9]. When semiconductor material is excited by an external energy, it absorbs a photon; electrons in the valence band are excited and hopped into the conduction band of that material, leaving behind a positive charge (or hole). This hole is bound with electron via columbic interaction and bound electron hole pair is called an exciton. The probable distance between electron and hole is Bohr's radius of an exciton given by:

$$a_B = 4\Pi \frac{\varepsilon_\circ \varepsilon \hbar^2}{m_\circ e^2} \left\{\frac{1}{m_e^*} + \frac{1}{m_h^*}\right\} \quad (1.5)$$

where, m_e* and m_h* are effective mass of electron and effective mass of hole and ε dielectric constant of material. As it is evident from the above equation that Bohr radius is dependent on effective mass and dielectric constant of the material hence, it is different for different materials.

In the strong confinement region, radius of the material is less than or equal to the Bohr radius, the confinement energy is greater than columbic interaction potential. In this region, an electron and hole are viewed as an individual particle. In weak confinement region, however, an exciton expected as quasi particle moving around quantum dot with weak coulomb interaction.

1.4 Types of Quantum Dots

Based on their composition and structure quantum dot are classified into three categories as follows:

(a) Core-Type Quantum Dots

These types of quantum dots are single module consist of uniform composition of selenides, sulfides, or telluride's etc. of group II metals such as lead, zinc, and cadmium. Examples are ZnS, CdSe, PbS, etc. The photo-luminescence properties of this type of quantum are modified easily by varying its crystalline size.

(b) Core-Shell Type Quantum dots (CSQD)

In this type, quantum dot of one material are embedded into another with wider band gap to enhance the efficiency and luster of semiconductor nanocrystal.

These are further divided into three categories based on the arrangement of relative conduction band (CB) and valence band (VB) of core and shell.

In the Type I CSQD, core of the quantum dot has smaller band gap than shell. The CB and VB of the core lie within the band gap of shell that confines an electron and holes in the core. Examples are CdSe/CdS, CsSe/ZnS, and ZnO/MgO.

In the Reverse type, the core has wider band gap and the CB and VB of shell lie in the core. The emission wavelength changes by varying thickness of the shell. ZnSe/CdSe and MgO/ZnO are few examples of this type.

In the Type II configuration, CB and VB edges of the shell is either lower or higher than the core band edges. Examples are ZnTe/CdSe, CdTe/CdSe, and CdS/ZnSe.

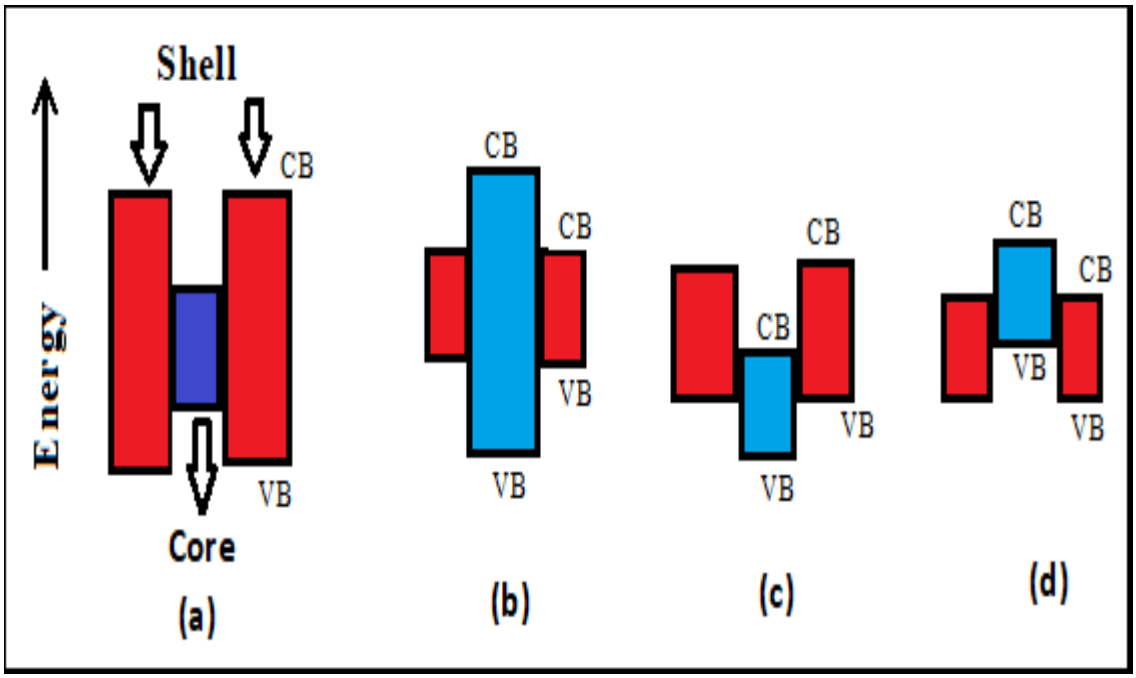

Fig.1.2: Types of Core-Shell Quantum dots: (a) Type I; (b) Reverse Type; (c, d) Type II .The upper edge and lower edge are the conduction band and valence band edge of core (blue) and shell (red).

(c) Alloyed Quantum dots

The optical and electrical properties tuned by varying the crystalline size but the problem arises with the size restriction. Multicomponent QDs can tune the electrical and optical properties without altering crystalline size. Alloyed QDs changes the properties by simply varying the composition of the constituents in the dot and internal structure.

Alloyed QDs formed by alloying two semiconductor materials of different band gap. They have properties that are different from their parent semiconductor and bulk material. Apart from quantum confinement, these types of dots have added composition- tunable properties.

1.5 Material selection

Metal chalcogenides of group II-VI elements were chosen for this study. These group elements in nano-crystalline form have unique non-linear optical properties, enhanced luminescent properties and other important chemical properties. Their properties dependent on size and varies significantly with the effect of quantum confinement.

Zinc sulfide compound selected for this project because of its various unique characteristics. Zinc sulfide has a wide band gap of about 3.68 eV (bulk) that is fitting for optoelectronics devices such as photovoltaic cells, light-emitting diodes (LED). It has high refractive index (2.35) and high transmission in visible range that made it suitable for reflectors and dielectric filter [10-11]. Zinc sulfide has a 40 meV exciton binding energy and high thermal stability.

1.6 Selection of synthesis process

There are various numbers of techniques to synthesize different types of nano-material. Various synthesis processes shown in fig. 1.3. They are classified into physical, chemical, biological and hybrid techniques. Synthesis techniques plays vital role in determining shape, size, chemical, optical and electronic properties of synthesize nanoparticles.

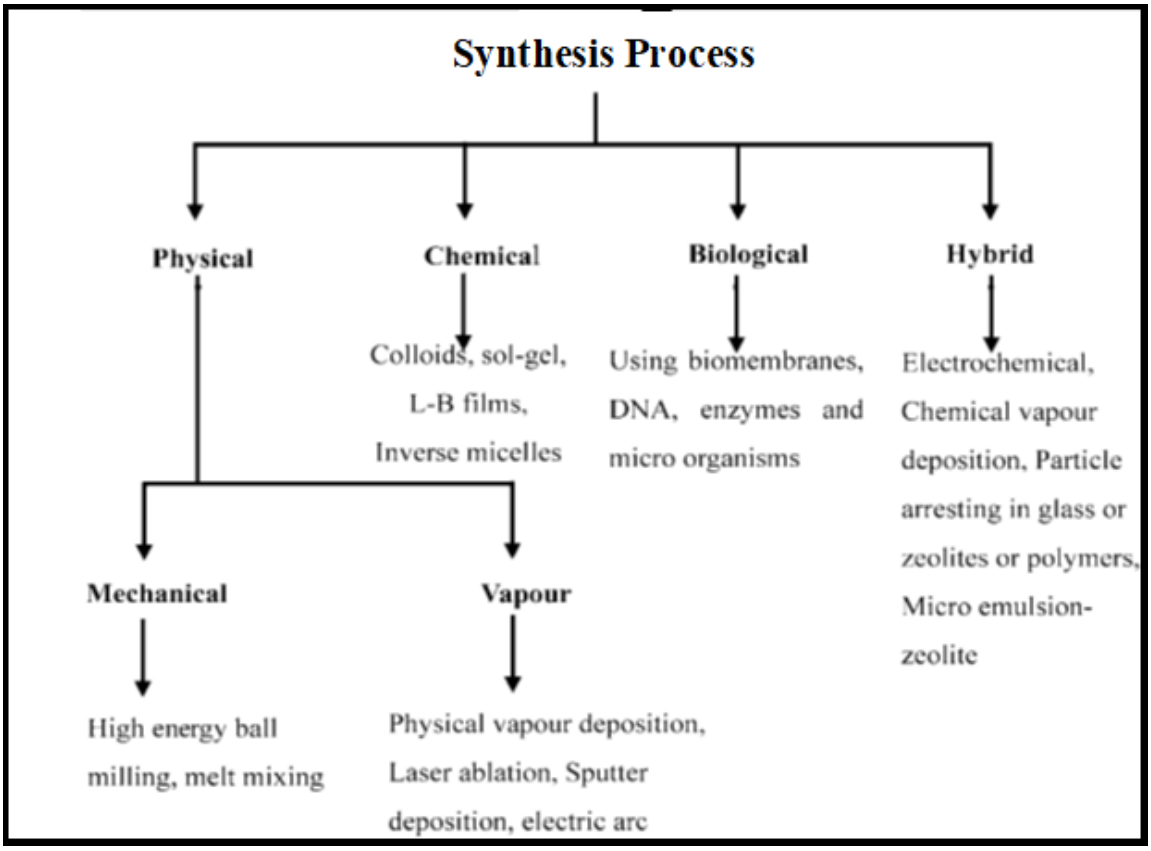

Fig.1.3: Various synthesis processes of nanomaterials.

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In this project, chemical process preferred for the synthesis of zinc sulfide nanoparticles because of its simplicity, requirement of an inexpensive and simple instruments, shorter synthesis time, low deposition temperature, possibility of surface passivation, and possibility of capping synthesized nanoparticles as per desired stoichiometric proportion. In addition, it is much easier to control the size and morphology of the particle by chemical route. The shape and size of nanoparticles tailored by changing the concentration of reactants, pH of the solution, temperature of the reaction, capping agent concentration and stirring rate.

1.7. Applications

Quantum dot small sizes and composition make them highly valuable entity in the field of optics. Their tunable size and energy band gap make them emit light of different wavelength and varying intensity. Larger quantum dot emit red color light at larger wavelength and blue color light emitted by smaller quantum dot.

In biological field, quantum dots have been able to replace organic dye due to its high brightness and stability. Their brightness is approximately 20 times more than traditional dye. Quantum dot can emit entire spectrum, and have minute degradation over time thus superior to organic dyes in biomedical applications. They are used in cellular imaging, drug delivery, tumor targeting.

In photovoltaic devices, due to wide band gap and high extinction coefficient of quantum dots they are used in light harvesting devices such as different types of solar cells to increase their efficiency and cost. Quantum dot ability to tune an entire spectrum makes them useful in liquid crystal display (LCD). In conventional LCD fluorescent lamp are color filtered to yield different color light that is power-consuming technology.

CHAPTER 2

LITERATURE REVIEW

Synthesis overview

Kirpal et al. [12] synthesized Zn: Mn^{+2} using co-precipitation method. The crystalline size reported from XRD studies was around 2-4 nm that is smaller than size estimated by TEM images. Photoluminescence spectrum varies with the concentration of Mn^{+2} and gives orange color emission. UV-Absorption studies shows blue shift in comparison to bulk counterpart.

Kanemeto et al. [13] discussed the photo-catalytic properties of ZnS nanocrystals and studied the effect of defects on the luminescence features of quantum dots. Photoluminescence spectroscopy gives emission peak at 325 nm (3.82 eV). The emission peak was due to promotion of trapped electron to valence band. It was reported that capping agent are important for the removal of ZnS dangling orbitals. The red shift observed in photoluminescence because of unsaturated sp^3 hybridized sulfur atom on the surface.

Manzoor et al. [14] reported pyridine capped and polyvinyl pyrrolidone (PVP) capped ZnS nanoparticle by wet chemical methods. The Photoluminescence studies revealed that the emission from pyridine capped ZnS nano-crystal is due to energy released through band-to-band excitation. The energy bands of PVP in the excitation spectrum confirm the transfer of energy from the absorbed PVP molecules to dopant sites in ZnS nanoparticles.

Nazerdeylami et al. [15] reported PVP capped ZnS: Mn^{+2} nanoparticles in aqueous solution by chemical route. Average crystalline size reported from XRD studies is approximately 2nm and structure of ZnS is cubic. The absorption edge observed at 292 nm and band gap of particle remain unaffected from the concentration of Mn^{+2}. The emission peak observed at 592 nm in PL spectrum has orange-red color and its intensity increase with the increase in concentration of Mn^{+2}.

Pandey et al. [16] synthesized histidine capped manganese doped ZnS nanoparticles via co-precipitation method. The homogeneous solution of zinc and manganese salts were mixed to obtained precipitate. XRD gives crystalline size of order 5 nm. PL results reported emission peak at 590 nm.

Thottoli [17] discusses the wet chemical method for the synthesis of ZnS nanoparticles in cubic and hexagonal structure. ZnS nanaocrystal of about 1.54 nm that is smaller than Bhor's exciton radius have been obtained using poly-vinyl alcohol as a capping agent. ZnS nanoparticles of hexagonal structure were prepared at low temperature by simultaneously using specific concentration of trisodium citrate and poly-vinyl alcohol with the precursors.

Toprak et al. [18] reported new method for synthesis of ZnS QDs. The chemical reaction was carried out between zinc ions and freshly prepared sulfur ions in ethanol. Zinc chloride and elemental sulfur were used precursors and hydrazine hydrate as a reducing agent. The absorption shows absorption peak at 253 nm corresponding to 4.9 eV band gap. Photoluminescence emissions were observed at 314 nm and 439 nm.

Vacassy et al. [19] synthesized ZnS nanoparticles in powder for via co-precipitation method from the homogeneous solution of zinc compound and S^{2-} formed by decomposition of thioacetamide. It was observed that nucleation enhanced by acetic acid but particle growth restricted due to formation of complex zinc cations that decreases the concentration of free cations in the solution.

Ghosh et al. [20] reported PVP encapsulated ZnS nanoparticles using zinc acetate and thiourea as precursors and PVP as capping agent. The crystalline size observed was 2-3 nm that is less than the size of uncapped ZnS nanoparticles. Quantum confinement confirmed by the blue shift in absorption edge in comparison to bulk ZnS.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF UNCAPPED ZINC SULFIDE (ZnS) QUANTUM DOTS

3.1 Synthesis of uncapped ZnS QDs.

0.1 M solution of zinc acetate dehydrate (Zn $(CH_3COO)_2.H_2O$) and 0.1 M sodium sulfide (Na_2S) were prepared separately by mixing 1.097 gm. of zinc acetate dehydrate with 50 ml distilled water and 0.39 gm. of sodium sulfide with 50 ml of distilled water at room temperature and under continuous magnetic stirring. Then prepared 0.1 M sodium sulfide solution added drop wise into 0.1 M zinc acetate solution that results in growth of white precipitate. The pH value of the mixture was maintained at 6.5. As white precipitate phenomena occurred, stirring continued for further 30 minutes to allow the thorough mixing of sodium sulfide solution in zinc acetate solution. After mixing precipitate was allowed to settle down for 20 minutes and then centrifuged at 10000 rpm for 10 minutes. After the completion of centrifugation process, precipitate particles filtered and washed 3-4 times in distilled water to remove any impurities present in the particles. The particles dried in oven at 75°C for 4 hours to obtain an uncapped zinc sulfide (ZnS) quantum dot (QDs).

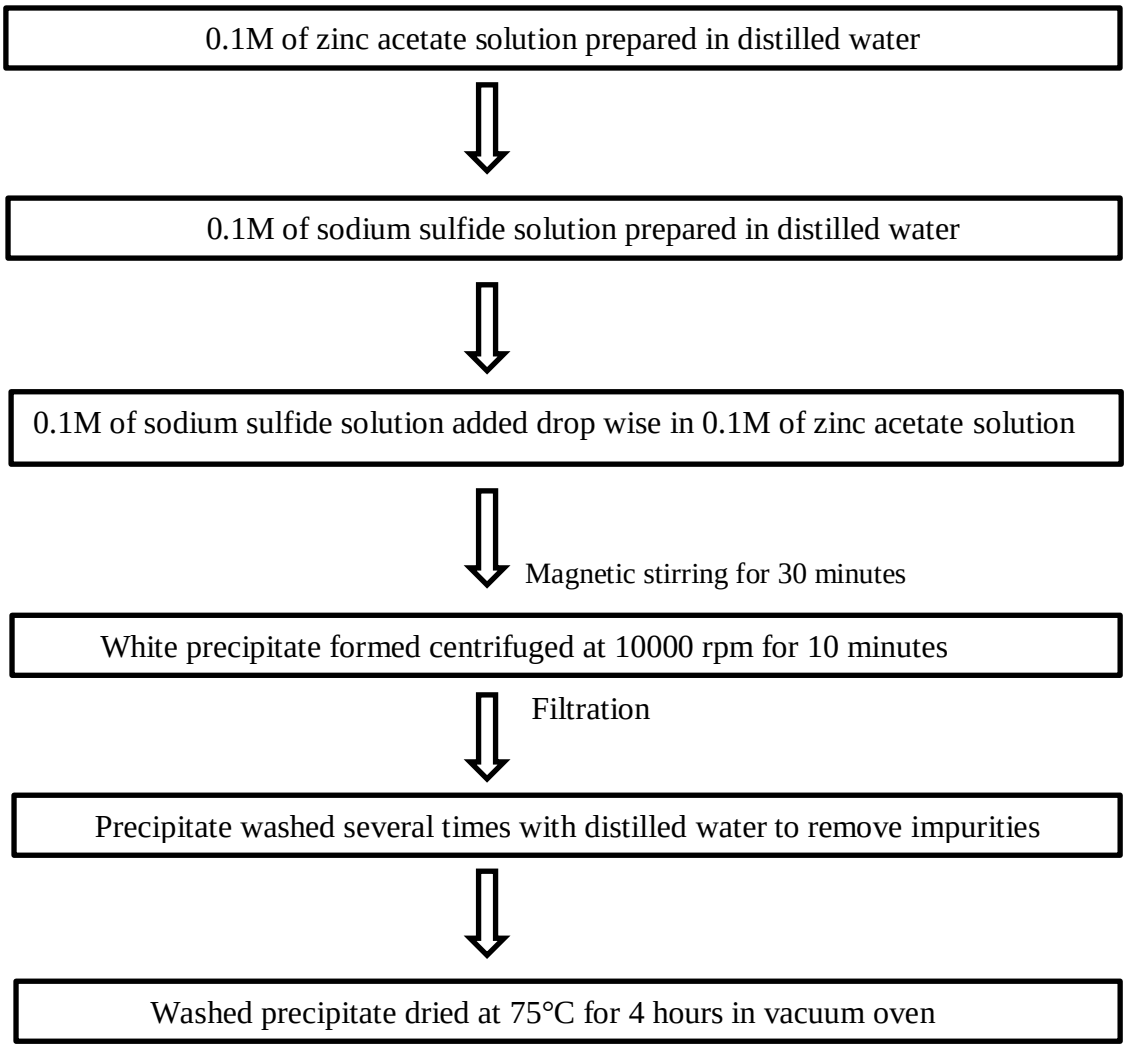

Fig 3.1: Flow chart of synthesis of uncapped zinc-sulfide quantum dots.

3.2 Characterization of uncapped ZnS QDs.

The characterization of the sample is broadly divided into two categories one is structural characterization, which includes XRD and SEM analysis and the other one is optical characterization in which absorption and photoluminescence (PL) of uncapped ZnS QDs is done. The prepared uncapped ZnS QDs were characterized by X-ray diffractometer, absorption by Perkin Elmer Lambda 750 spectrophotometer UK, scanning electron microscopy (SEM) (CARL ZESIS EVO 50) and PL analysis from Fluorolog-3 spectroflurometer (Horba Jobin Yyon, UK).

3.2.1 X-ray diffraction analysis

In X-ray diffraction analysis of prepared nascent zinc sulfide quantum dot three broad crystalline Bragg peaks were obtained at 28.79°, 47.9° and 57.24°. These peaks corresponds to (111), (220) and (311) planes respectively which were matched with zinc blend (cubic phase) reported in ASTM data. The peak at lower Bragg angle considered for calculation of crystal size because of high intensity and was broader than the peaks at higher Bragg angle. The broadening of peaks in XRD attributes to formation of nanoparticle. XRD pattern of synthesized uncapped ZnS QDs shown in fig.3.2

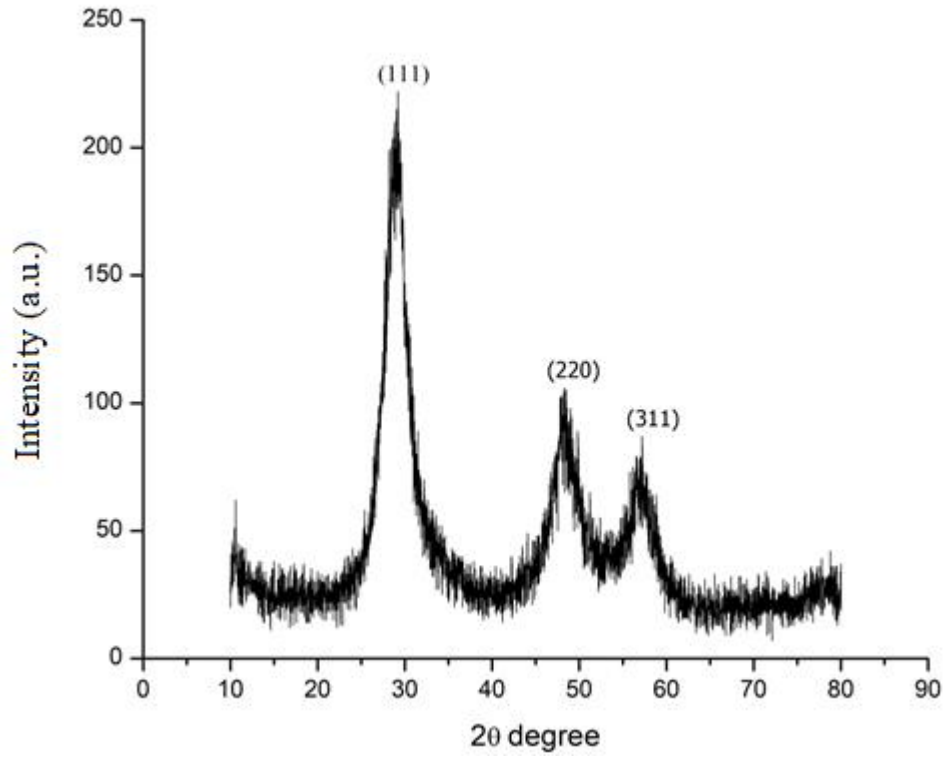

Fig. 3.2: XRD pattern of uncapped ZnS QDs.

The mean crystalline size calculated by using Scherrer formula (Scherrer 1918):

$$D = \frac{k\lambda}{B\ Cos\theta} \qquad (3.1)$$

Where, D is the mean size of crystal, ƛ is the wavelength of X-ray wavelength (Kα(Cu) = 0.154056 nm), B is the full width at half maxima (FWHM) of diffraction peak, θ is the Bragg diffraction angle and K is shape factor with value close to unity. Typical value of k is 0.94 and it is dimensionless. In the above equation, FWHM of peak at lowest Bragg

angle is 3.67°. The mean size of crystal is 2.4 nm, and thus confirmed the formation of nascent quantum dots.

3.2.2 Absorption spectroscopy

The absorption spectrum of an uncapped ZnS QDs is shown in fig.3.3. For absorption measurement small amount of prepared precipitate dispersed in 10 ml of dimethyl sulfide (DMS) and the mixture was sonicated for five minutes, and after that sonicated mixture used for optical characterization. The peak observed at 319 nm is blue shifted in comparison to bulk ZnS. This shows decrease in particle size and quantum confinement effect.

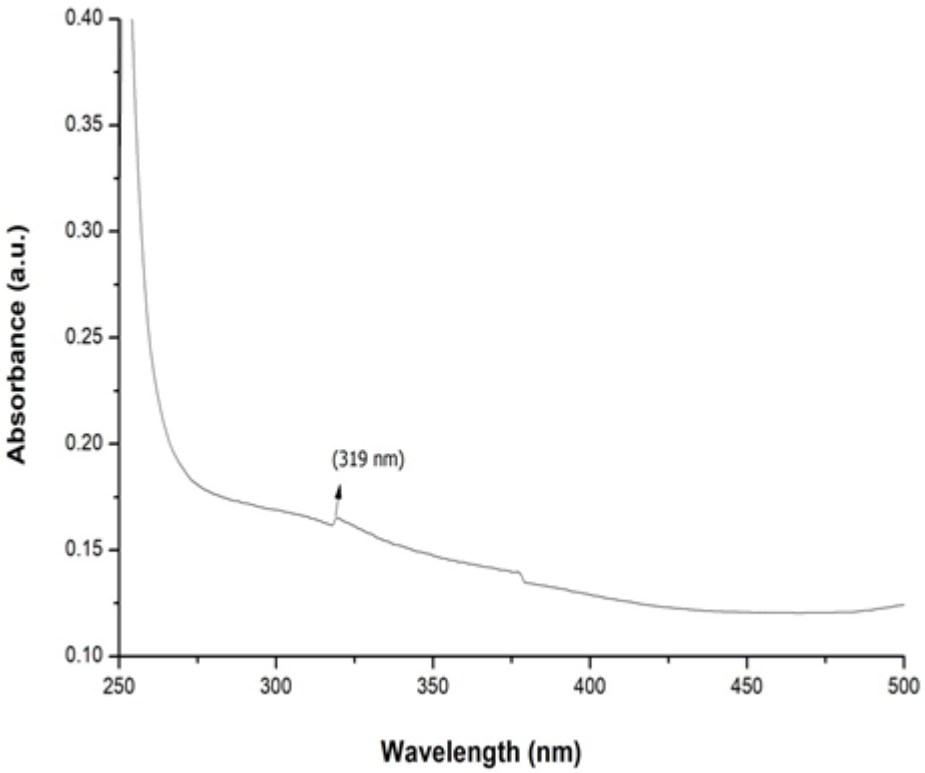

Fig. 3.3: Absorption spectrum of uncapped ZnS QDs. The absorption peak obtained at 319 nm.

The Tauc relation used for obtaining optical band gap of sample and this optical band gap is further used in Brus equation to determine particle size. Tauc relation for obtaining the optical band gap of nascent ZnS QDs is given in equation (3.2).

$$(ahv)^n = A(hv - E\mathrm{g}) \qquad (3.2)$$

Where, hv is the photon energy, E_g is optical band gap of ZnS QDs, A is constant and the value of n is 2 for direct band gap materials.

To get the optical band gap of the uncapped ZnS QDs, the graph shown in fig. 3.4 is extrapolated towards abscissa and the intercept point gives us the value of optical band gap of the material. From tauc relation optical band gap of the sample comes out to be 3.9 eV, which shows that due to decrease in particle size the absorption edge shift towards higher energy.

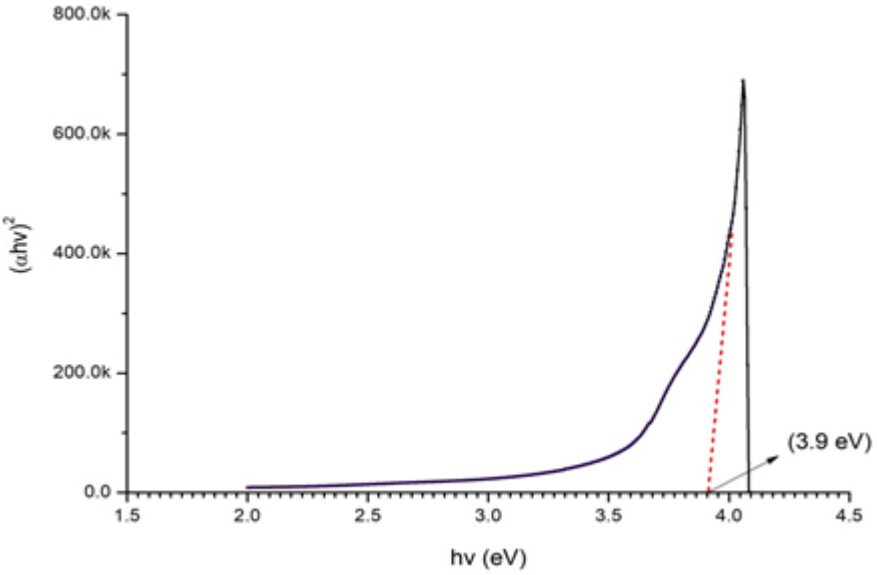

Fig. 3.4: Tauc plot of prepared uncapped ZnS QDs. Optical band gap (E_G) is 3.9 eV.

3.2.3 Particle size calculation

The average particle size of synthesized quantum dot can be determined from effective mass approximation method also known as Bruss equation. The exciton peak position at 319nm obtained in UV-absorption of the sample shown in fig 3.3 used in equation (3.3)

$$E = \frac{hc}{\lambda} \cong \frac{1240}{\lambda}\ ev \qquad (3.3)$$

Where, E is the energy band gap of nanoparticle in electron-volt (eV), λ is wavelength at which peak is observed, h is planck constant ($6.63 * 10^{-34}$ J-s), and c is the speed of light ($3 * 10^{8}$ m/s). The value of energy band gap of synthesized uncapped ZnS QDs is approximately 3.9 eV.

The effective mass approximation equation is:

$$E = E_G + \frac{h}{8r^2}\left[\frac{1}{m*_e} + \frac{1}{m*_h}\right] - \frac{1.8e^2}{4\Pi\varepsilon\varepsilon_\circ r} \quad (3.4)$$

Where, E is the energy band gap of nanoparticle in electron-volt (eV), ƛ is wavelength at which peak is observed, h is planck constant ($6.63 * 10^{-34}$ J-s), and c is the speed of light ($3 * 10^8$ m/s), r is the radius of synthesized nanoparticle, m^*_e and m^*_h are the effective mass of electron (ZnS m^*_e= 0.25 m_e) and hole (ZnS m^*_h=0.60 m_h).

According to equation (3.4), the average particle size calculated is 3.94 nm, which is greater than the mean size 2.4 nm calculated from Scherrer formula. This discrepancy in results is may be due to the presence of interband transition, which affects the absorption of nanoparticles. The band gap calculated at crystalline size 2.4 nm by using Bruss relation is 4.27 eV. Hence, Bruss relation may be quantitatively incorrect or gives approximation results for nanoparticles.

3.2.4 Photoluminescence of uncapped ZnS QDs.

Photoluminescence is a phenomenon in which particle emits a light of particular wavelength when it absorbs a photon. For PL measurement same process is followed which is discussed in (section 3.2.2). PL spectrum of ZnS QDs is shown in fig.3.5 in which emission peak observed at 433 nm is blue shifted from bulk ZnS (440nm). PL spectrum was smoothened and non-linearly curve flitted according to Gaussian function by using ORIGIN8.

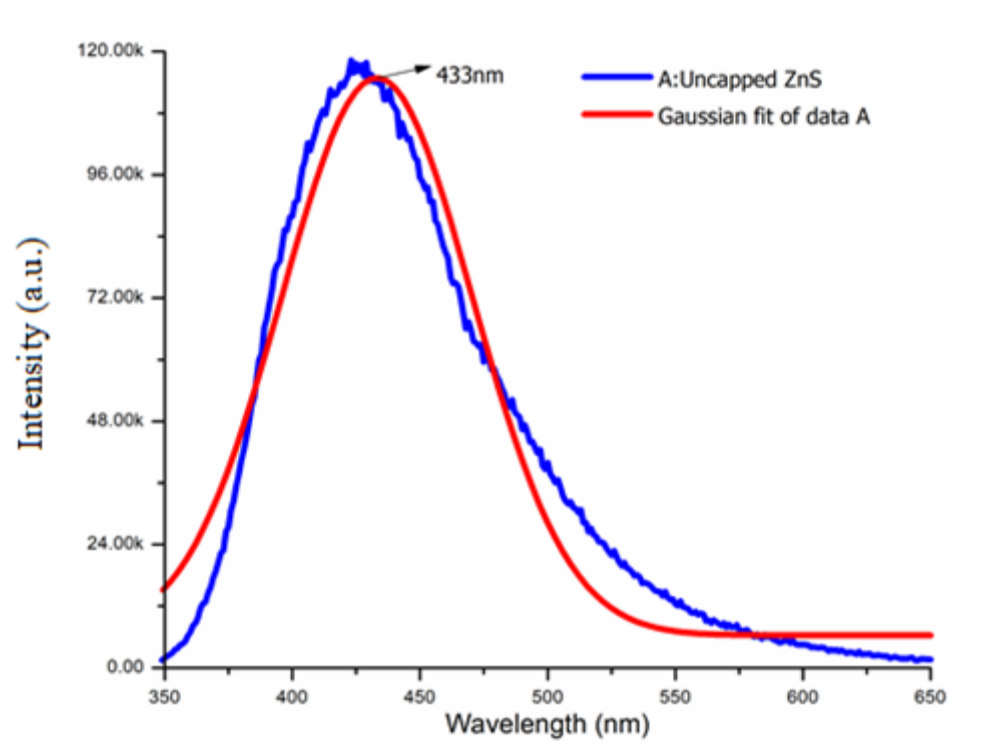

Fig. 3.5: PL spectrum of uncapped ZnS QDs. The emission peak at 433 nm was excited at 330 nm.

CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF CAPPED ZINC SULFIDE (ZnS) QUANTUM DOTS

4.1 Synthesis of PVA capped ZnS QDs.

0.5M of zinc acetate dihydrate ($Zn(CH_3COO)_2.H_2O$) and sodium sulfide (Na_2S) homogeneous solution were prepared separately by mixing 3.407 gm. zinc acetate in 50 ml of distilled water and 1.95 gm. of sodium sulfide in 50 ml of distilled water under continuous magnetic stirring for 30 minutes. A solution of poly- vinyl alcohol (PVA) with different concentration of PVA was prepared by mixing PVA in distilled water at 80°C for 1 hour. Two different concentration of PVA prepared were 0.04gm/ml and 0.004gm/ml. PVA polymer is soluble in water at high temperature and used as capping and reducing agent in nanoparticle synthesis. After PVA solution was prepared, 0.5M of zinc acetate solution slowly added in it and stirring continued for 30 minutes. The pH value of the mixture was maintained at 8.5. After 30 minutes, solution of sodium sulfide was added drop wise in the mixture of PVA and zinc acetate solution under continuous stirring, addition of sodium sulfide solution in mixture results in formation of white precipitate. After stirring prepared precipitate centrifuged at 10000rpm for 10 minutes and washed several times with ethanol to remove impurity present in precipitate. The washed precipitate dried in vacuum oven at 75°C for 4 hours to remove moisture and to get the capped zinc sulfide nanoparticles.

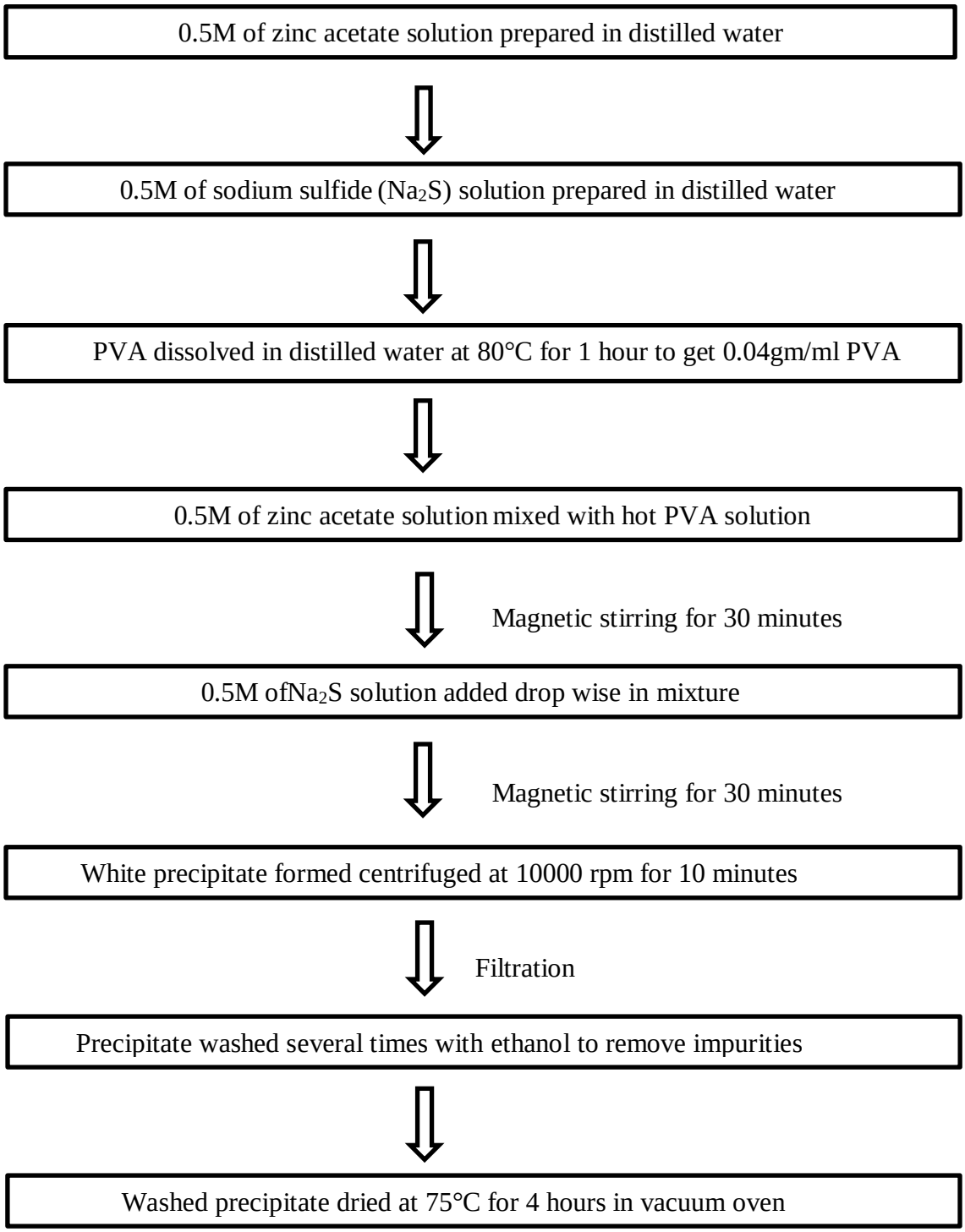

Fig 4.1: Flow chart of synthesis of PVA capped ZnS quantum dots.

4.2 Characterization of PVA capped ZnS QDs.

The results of PVA capped ZnS QDs are compared with uncapped ZnS QDs. The effects of PVA on structural properties, optical properties and particle size of synthesize QDs were analyzed.

4.2.1 X-ray diffraction analysis

The X-ray diffraction analysis of sample PVA-1 in which concentration of PVA is 0.04gm/ml gives us three broad Bragg peak at 28.91°, 48.65° and 57.67°. The plane links to above-mentioned peaks are (111), (220), and (311). These planes are similar to planes calculated in uncapped ZnS quantum dot, which shows that neither new phase is formed and nor crystalline structure changes due to addition of poly-vinyl alcohol. X-ray diffraction of sample PVA-1 shown in fig. 4.2.

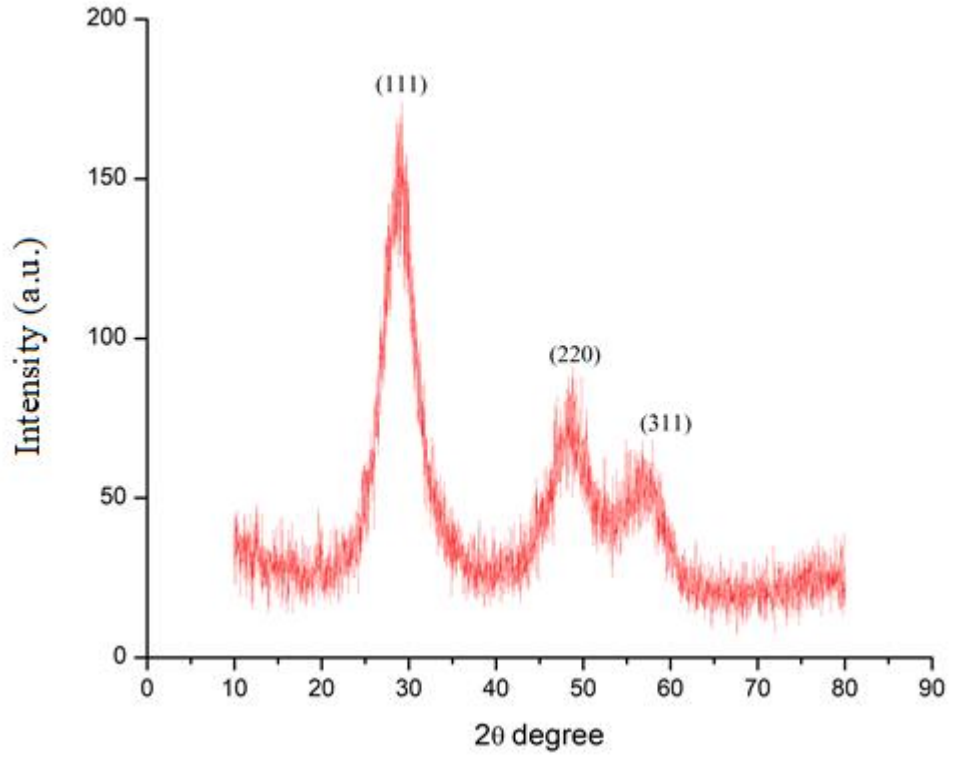

Fig. 4.2: XRD pattern of sample PVA-1 (0.04 gm/ml PVA capped ZnS QDs).

At peak, 28.91° full width at half maxima is 4.91° that is used in Scherrer formula equation (3.1) to get mean particle size of nanoparticle. The mean particle size of sample PVA-1 is 1.8 nm, which is less than the particle size of uncapped ZnS quantum dot (2.4 nm) and less than the Bohr exciton radius of ZnS. Since particle size is less than Bohr radius thus, quantum dot formation confirmed.

XRD of sample PVA-2 in which PVA concentration of 0.004gm/ml gives Bragg peak at 28.82°, 48.42°, and 57.42° corresponding to same plane as in sample PVA-1. The full width at half maxima of peak 28.82° is 4.11°. The mean particle size of PVA-2 sample is 2.2 nm, which is smaller than uncapped zinc sulfide nanoparticle but slightly bigger than sample PVA-1, which states the fact that with the increase in concentration of capping agent particle size decreases. XRD of sample PVA-2 is shown in fig. 4.3.

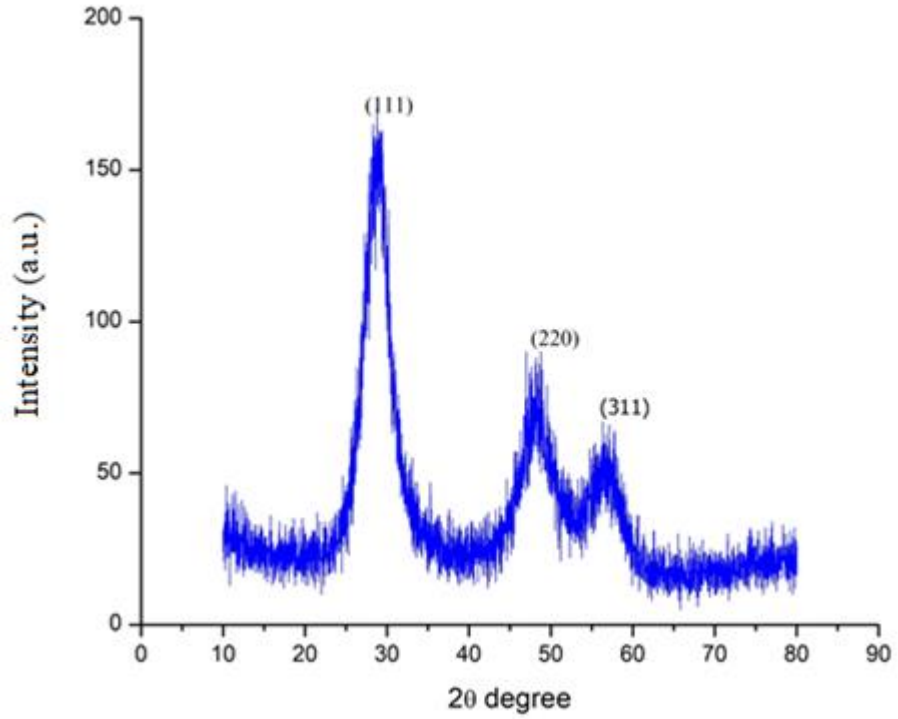

Fig. 4.3: XRD pattern of sample PVA-2 (0.004 gm/ml PVA capped ZnS QDs).

Comparison of XRD pattern of uncapped and poly-vinyl alcohol capped ZnS QDs is shown in fig. 4.4, which clearly shows that the addition of polyvinyl alcohol hinders the growth of ZnS and reduction in agglomeration of synthesized particles. The broadening of XRD peaks in PVA capped ZnS QDs confirms the reduction in particle size.

Table 4.1: Comparison of crystalline size of uncapped and PVA capped ZnS QDs.

Sample	PVA density (gm/ml)	Crystalline size (nm)
Uncapped ZnS	0	2.4
PVA-1	0.04	1.8
PVA-2	0.004	2.2

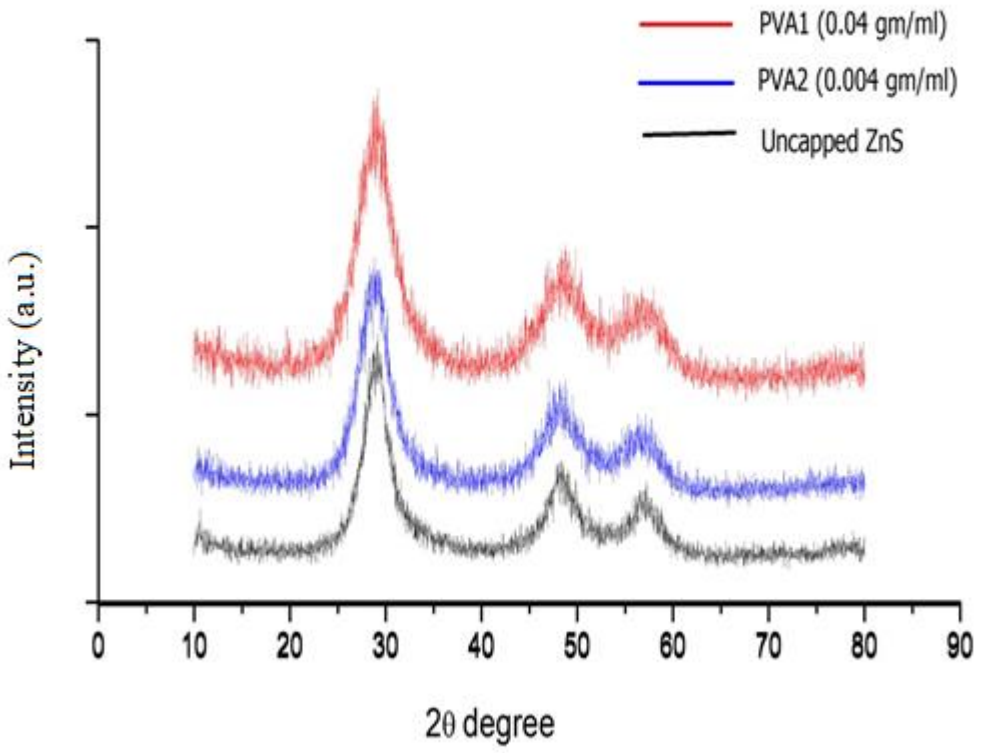

Fig. 4.4: XRD comparison of uncapped and PVA capped ZnS QDs.

4.2.2 Absorption spectroscopy

The energy band gap is fundamental property of semiconductor material and with the decrease in particle size the energy band gap of material increases, thus allowing more absorption of UV rays. The energy band gap of bulk ZnS is 3.68 eV that should increase as the quantum confinement effect occur. Absorption spectrum of sample PVA-1 shown

in fig. 4.5 in which absorption peak observed at 312 nm. The optical band gap of PVA-1 sample is 4.75 eV obtained from tauc plot (discussed in section 4.2.5).

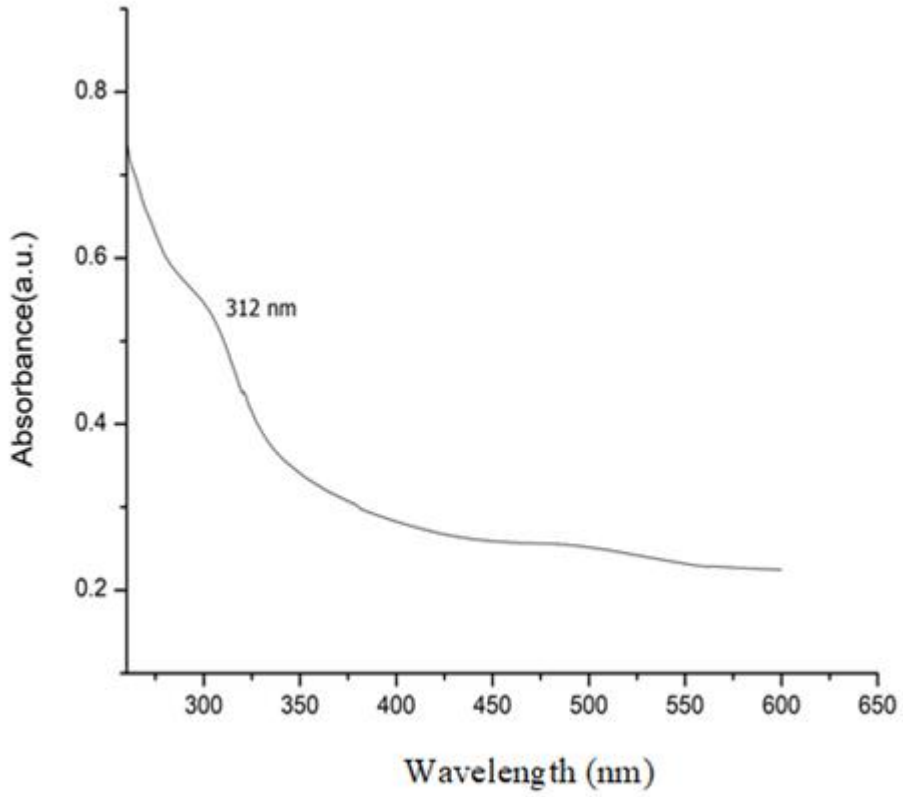

Fig. 4.5: Absorption spectrum of sample PVA-1 (0.04 gm/ml PVA capped ZnS QDs).

The approximated optical band gap of sample PVA2 (0.004gm/ml PVA capped ZnS) is 4.38 eV, calculated by substituting the value of its crystalline size i.e. 2.21 nm in Bruss equation (discussed in chapter 3 equation 3.4).

4.2.3 Photoluminescence of PVA capped ZnS QDs

Photoluminescence spectroscopy is a study that confirms the quantum confinement effect in the particle. The blue light emitted at shorter wavelength, which means particle size is less than Bohr exciton radius and strong quantum confinement in the particle. The emission of red light attribute to larger particle size as they emit at larger wavelength and shows weak quantum confinement. For PL measurement same process is followed which is discussed in (section 3.2.2). PL spectrum of sample PVA-1 (PVA capped ZnS) in fig. 4.6 gives low intensity emission peak at 425 nm. The peak obtained in PL spectrum is

blue shifted when matched with uncapped ZnS QDs thus confirming the quantum confinement phenomena in the particle.

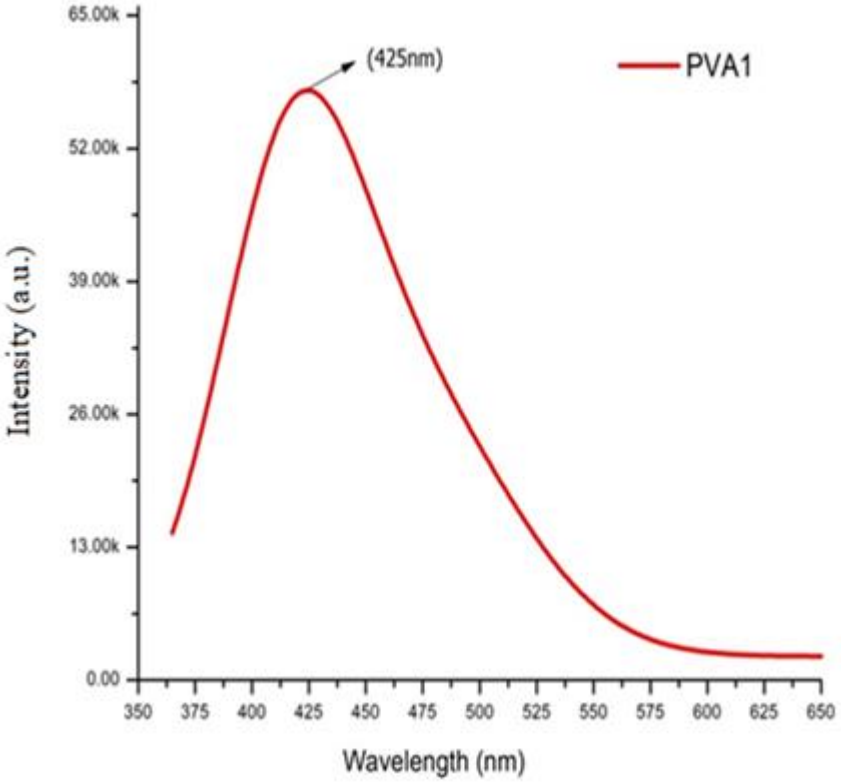

Fig. 4.6: PL spectrum of sample PVA-1 (0.04 gm/ml PVA capped ZnS QDs). The emission peak observed at 425 nm was excited at 350 nm.

Fig 4.7 shows comparison between PL spectrum of uncapped ZnS and PVA capped ZnS QDs. It is clearly visible from the figure that emission peak of PVA capped ZnS sample shifted towards the lower wavelength i.e. blue shifted in comparison to uncapped ZnS QDs.

The decrease in intensity is clearly visible in PL spectrum of sample PVA-1 when matched with uncapped ZnS QDs. This shows that PL intensity is dependent on pH value of the solution. The pH of PVA-1 sample is 8.5 and that of uncapped zinc sulfide is 6.4, which indicates that high pH value of the solution quenched the PL intensity of synthesized nanoparticles. This fall in PL intensity is may be due to amalgamation of cations in solution. Thus, sodium Na ions can be responsible for quenching PL intensity.

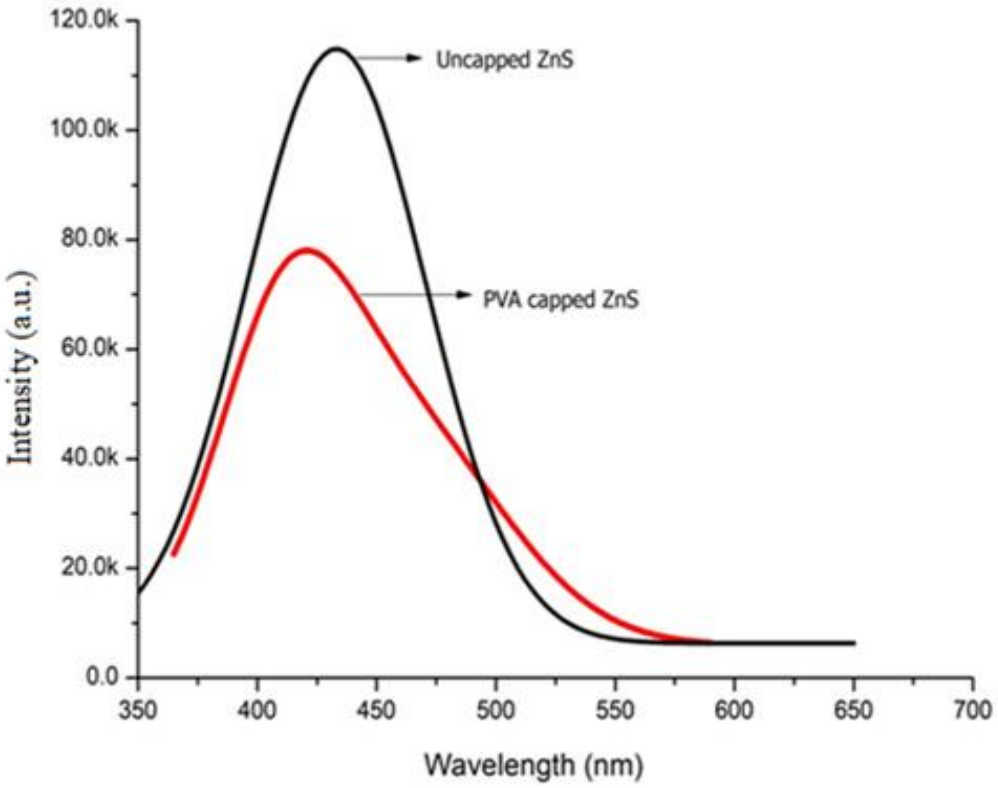

Fig. 4.7: PL spectrum comparison of uncapped and PVA capped ZnS QDs.

4.2.4 Particle size calculation

The average particle size of synthesized quantum dot can be determined from effective mass approximation method also known as Bruss equation.

The effective mass approximation formula as discussed in chapter 3:

$$E = E_G + \frac{h}{8r^2}\left[\frac{1}{m*_e} + \frac{1}{m*_h}\right] - \frac{1.8e^2}{4\Pi\varepsilon\varepsilon_\circ r} \qquad (4.2)$$

The optical band gap of sample PVA1 is 4.75 e V calculated from tauc plot shown in fig. 4.8. By substituting this value in Bruss relation the average particle size calculated is 1.78 nm.

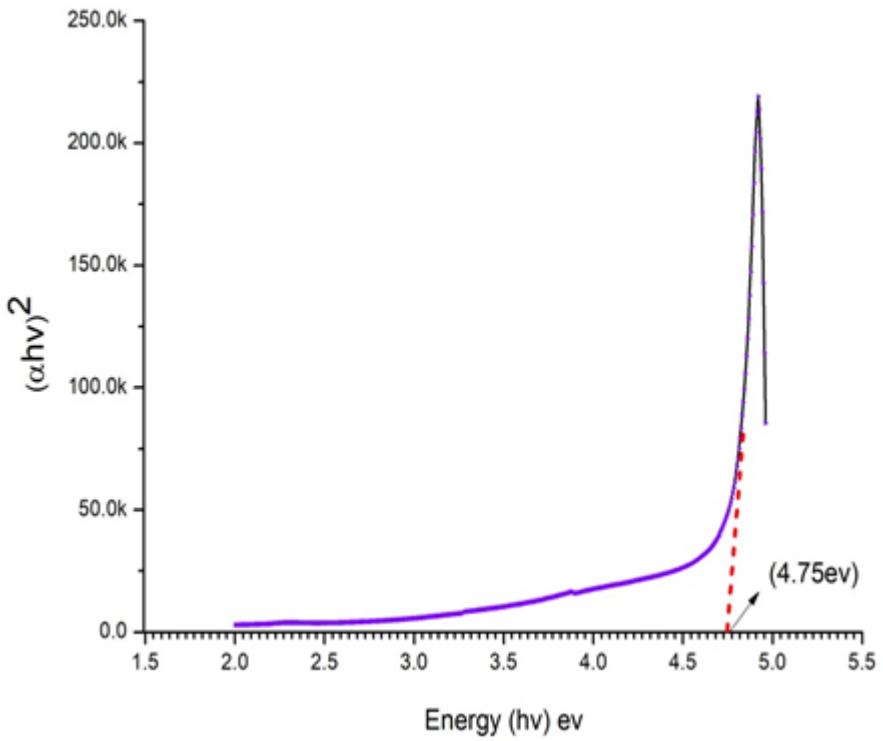

Fig. 4.8: Tauc plot of sample PVA-1 (0.04 gm/ml PVA capped ZnS QDs). Optical band gap (E_G) of sample PVA-1 is 4.75 eV.

The optical band gap of the material is dependent on the particle size. As the particle size decreases the energy band gap is widened. The variation in the optical band gap as the crystalline size changes is shown in fig.4.9. In this, the graph has been plotted between band gap (E_G) and crystalline size that clearly shows as the size of the particle decreases the band gap of the material increases.

Table 4.2: Comparison between optical band gap and crystalline size of synthesized samples.

Sample	Crystalline size (nm)	Optical band gap E_G (eV)
Uncapped ZnS	2.4	3.9
PVA1	1.8	4.75
PVA2	2.2	4.38

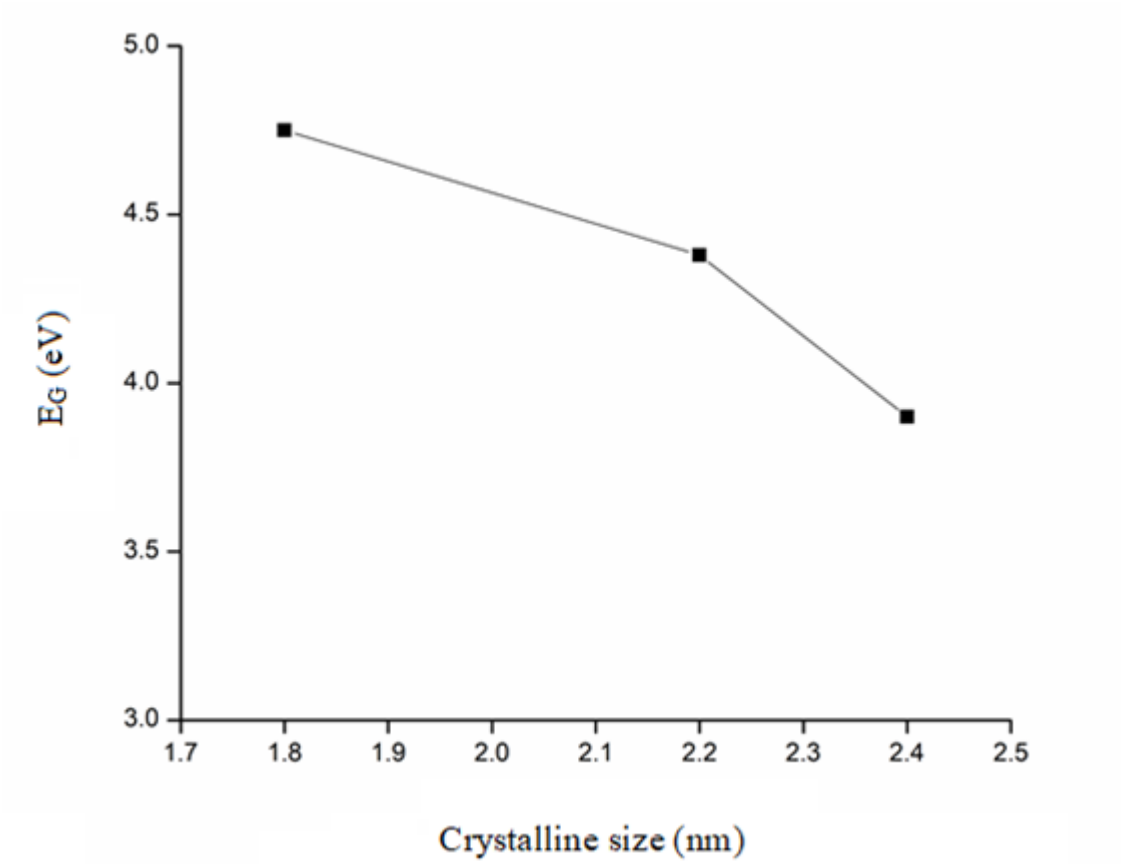

Fig. 4.9: Plot between E_g (eV) and crystalline size (nm).

4.2.5 SEM and EDX analysis

In this section, SEM micrograph of uncapped and poly-vinyl alcohol capped zinc sulfide quantum dots are studied. The SEM micrograph of uncapped sample in fig 4.10 (a) clearly shows the agglomeration of the particles in comparison to capped ZnS QDs shown in fig. 4.10 (b). The SEM images of synthesized samples also give the indication of homogeneous nature of nanoparticles.

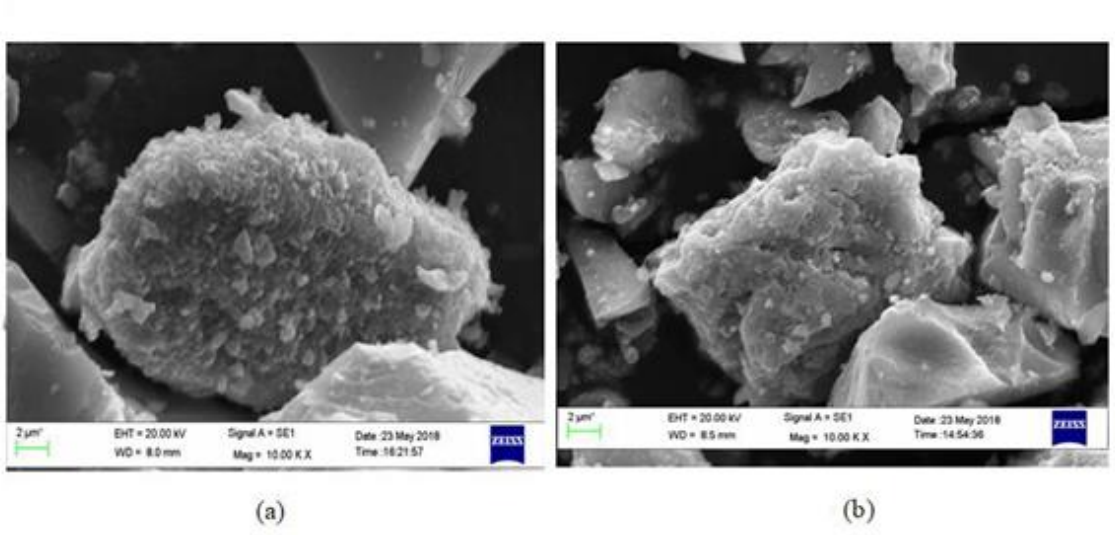

Fig. 4.10: SEM image of (a) uncapped ZnS QDs and (b) PVA capped ZnS QDs.

Energy dispersive X-ray analysis is used for elemental analysis or for determining chemical composition of the sample. Fig. 4.11 shows EDX analysis of uncapped zinc sulfide QDs. EDX analysis of synthesized uncapped ZnS QDs revealed the presence of zinc, sulfur, carbon, and oxygen with their weight percentage of 66.45 %, 23.28 %, 5.14 %, and 5.13 % respectively. The presence of oxygen in the synthesized sample is may be due to use of ethanol during washing of particle.

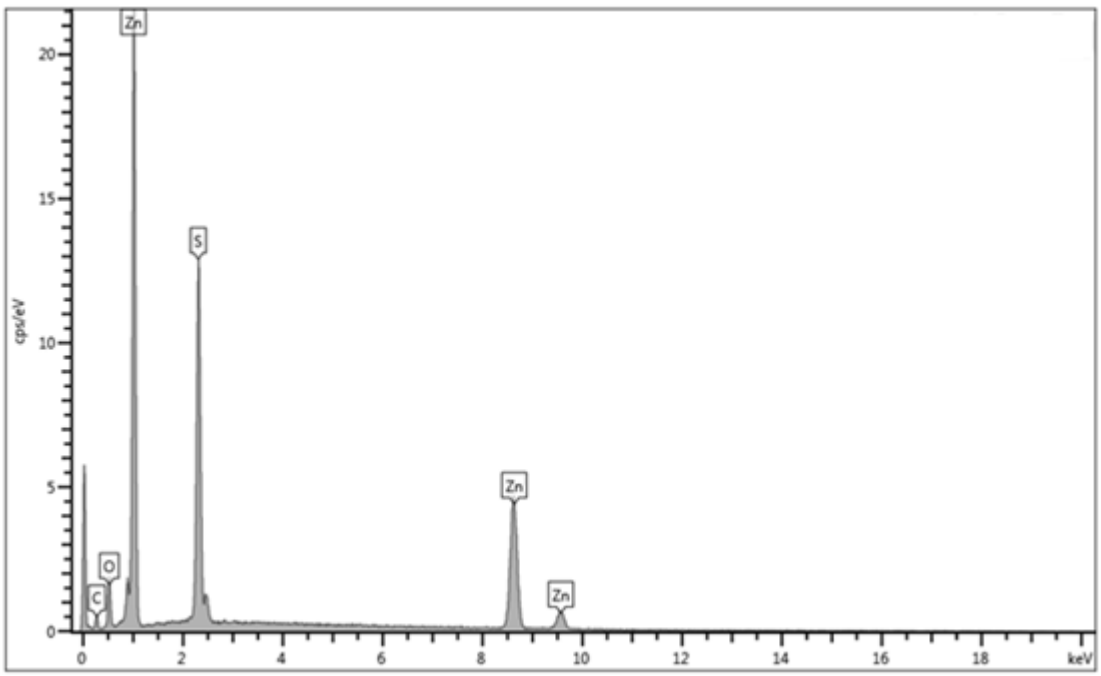

Fig. 4.11: EDX analysis of uncapped ZnS QDs.

In EDX analysis of PVA capped ZnS QDs shown in fig. 4.12 zinc, sulfur, carbon, sodium and oxygen elements were present with their weight percentage equal to 65.33 %, 22.64 %, 3.53%, 4.38 %, and 4.12 % respectively.

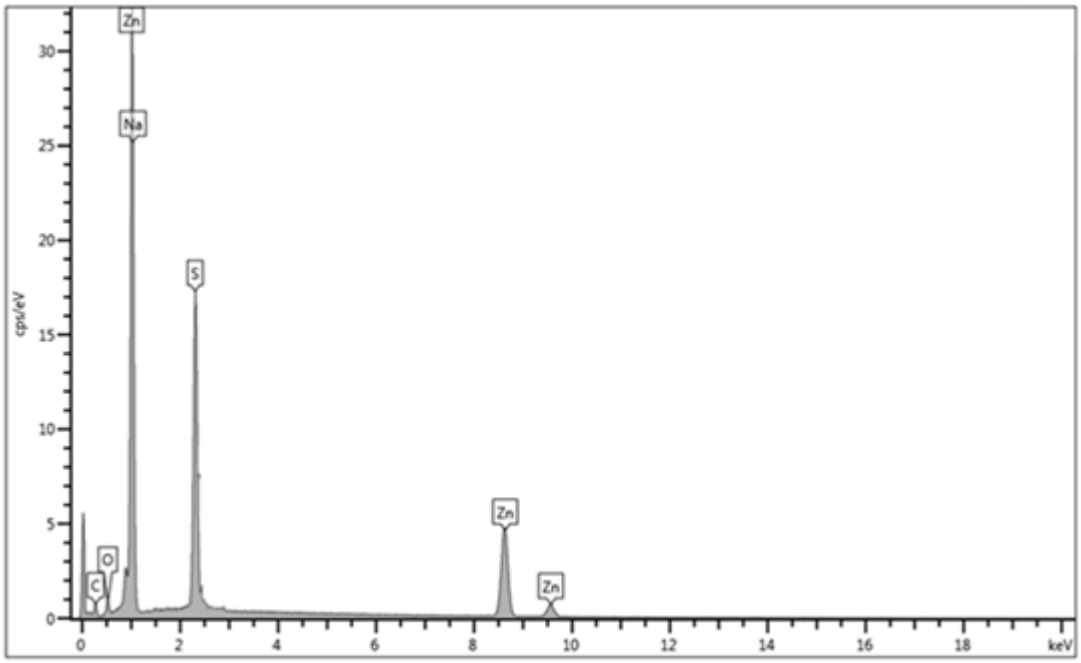

Fig. 4.12 : EDX analysis of PVA capped ZnS QDs.

Chapter 5

CONCLUSIONS

In this study, uncapped zinc sulfide and poly-vinyl alcohol capped quantum dots were synthesized by chemical co-precipitation method at room temperature. The particle size has been controlled by varying the pH value, concentration of PVA, stirring rate and molarity of the solution.

The characterization results of the synthesized samples were compared. The XRD analysis of the samples revealed that there was no new introduction of phase in ZnS by the addition of PVA but the crystalline size reduces. The cubic phase for PVA capped ZnS quantum dots was confirmed.

The UV-visible absorption spectrum shows the absorption peak of the sample PVA-1 (312 nm) was blue shifted in comparison to absorption peak of uncapped ZnS QDs (319 nm). The particle size calculated from Bruss relation is expected to be quantitatively incorrect due to quantum confinement effect in nanoparticle.

The photoluminescence spectra of prepared samples were recorded by Fluorolog-3 spectroflurometer (Habra Join Yon). The emission peak of PVA-1 obtained at 425 nm was blue shifted in comparison to uncapped ZnS QDs (emission peak at 433nm). The PL emission intensity was dependent on the pH value of the solution. PL emission intensity quenched as the solution became more alkaline.

5.1 Future scope

- In this study, zinc sulfide characterized by XRD, SEM, UV-absorption, and PL spectroscopy. In addition to this, characterization by Raman spectroscopy and X-ray photoelectron spectroscopy may provide additional information about growth and chemical composition.

- In future reaction should be carried out in ambient environment like in the presence of nitrogen or inert gasses to avoid contamination of the synthesized particles.

- Future work includes the synthesis of ZnS quantum dot at high temperature (>1000°C) and analyzes the changes in its properties. It has been reported that at high temperature wurtzite structure of ZnS is obtained.

- To study the effect of aging on PL intensity, UV absorption and particle size of the sample, synthesized quantum dot left in the solution and characterization recorded over a period.

- Due to ZnS wide band gap it can be used in photovoltaic, LED and in sensors.

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