CHAPTER – III

ORGANIC LIGANDS PASSIVATED ZnSe
NANOSTRUCTURES AND FUNCTIONAL PROPERTIES

3.1 INTRODUCTION

Semiconductor nanocrystals have size tunable optical properties that open up possibilities for revolutionary advances. The study of nanomaterials provides an opportunity to observe the evolution of material properties with crystal structure, size and shape. Altering the size of the particles changes the degree of confinement of electrons, which affects the electronic structure of the solid especially the band gap edges. As the dimensions of the particle become comparable or less than the Bohr radius of the exciton, its electronic properties changes significantly by quantum confinement effect, which can be observed as a blue shift in the band gap or exciton energy. The quantum confinement effect in bulk semiconductors and nanoparticles were explained based on the spatial electronic state concept. In small particles, as the size drops down from the micron to nanometre range, the optical properties change drastically [103 –105].
ZnSe is a direct band gap semiconductor with room temperature band gap energy and an emission at 2.7 eV, which suggests that ZnSe is applicable for photo electronic devices. ZnSe also has potential application in optically controlled switching due to its giant photo resistivity \([106 – 109]\). Therefore, it is of great interest as a model material in such forms as thin films, quantum wells and bulk crystals. Many methods have been used to synthesize ZnSe nanoparticles such as surfactant – assisted chemistry, sonochemical method, solvothermal route, wet chemical route, hydrothermal method, vapor phase synthesis, microwave assisted preparation \([110 – 115]\). However, solution methods have several draw backs such as agglomeration of particles due to Ostwald ripening growth and irregular shape formation.

In order to avoid the Ostwald ripening, agglomeration and to enhance the luminescence property, surface passivation technique is used. In general, the surface defects act as a non – radiative relaxation centers for electron hole recombination. During the growth of ZnSe nanostructures, the organic molecules passivate the surface defects of ZnSe nanostructures and thus results in the enhanced optical properties with suppressed defect level emissions.

In this present work, the organic ligands such as amines, thiols and polymer molecules were used as capping agents to synthesize the monodispersed ZnSe nanostructures. The role of these organic ligands in the formation of ZnSe nanostructures and its functional characteristics has been investigated.
3.2 Synthesis and characterization of edamine capped ZnSe nanowires

3.2.1 Structure

Figure. 3.1 Molecular Structure of Edamine

Edamine is an organic compound with the formula of $\text{C}_2\text{H}_4(\text{NH}_2)_2$. This is a colorless liquid with ammonia-like odor. It is a strongly basic amine. It is widely used building block in various chemical syntheses. Because of its bi-functional nature, having two amines, it readily forms heterocycles such as imidazolidines. Edamine is a well-known chelating ligand for coordination compounds. In the present work, edamine was used as a surface capping agent in the synthesis of ZnSe nanostructure.

3.2.2 Synthesis

All the reagents used were of analytical grade and used without further purification. All the reactions were carried out in pure de-ionized water. In a typical procedure, 0.2 M of zinc acetate and 0.1 M of sodium selenite were deliquesced in 20 ml of deionized water. 0.2 M of Edamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$) (EDA) was injected drop by drop into the above solution under continuous stirring and the reaction was allowed for 36 hours. The resultant product was finally dried at 110° C for 8 hours in hot air oven. The
synthesized product have been characterized by X-Ray diffraction (XRD), UV-Visible spectroscopy, Photoluminescence, Fourier Transform Infrared spectrometry, Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM).

### 3.2.3 Reaction Mechanism

Figure 3.2 represents the growth mechanism of Edamine capped ZnSe nanowires. During the reaction, Zn$^{2+}$ ions were released from Zinc acetate and Se$^{2-}$ ions were released by sodium selenite. Meanwhile, the addition of Edamine will facilitate the nucleation of Se$^{2-}$:Zn$^{2+}$:(NH$_2$)$_2$C$_7$H$_8$ without agglomeration due to the chemisorption of the lone pair electron present in the nitrogen atom of Edamine. After that, thermal treatment at 110°C leads to the formation of nanowires.

![Figure 3.2 Reaction mechanism of Edamine capped ZnSe nanowires](image)

### 3.2.4 Optical studies

The UV - Vis spectrum of EDA capped ZnSe is displayed in Figure 3.3(a). From the spectrum, it is observed that the onset of peak appears
at 372 nm whereas, the bulk ZnSe has an absorption onset at 467 nm. The shift towards shorter wavelength in absorption spectrum (blue shift) is due to the strong quantum confinement. Juan Yang et al., reported that the absorption peak of EDA capped ZnSe nanoplates is at 310 nm [116]. Yuan Tao Chen et al., reported that the EDA capped ZnSe flower like structures have the absorption peak is at 280 nm [117].

The PL spectrum is shown in Figure 3.3 (b) and it is observed from the spectrum that the near band edge emission peak is at 442 nm. The Se defects related emissions have not been observed in the mid visible region. Similar results have been observed by Ruitan lv et al., and it was reported that the PL emission peak was at 453 nm for the ZnSe nanorods [118] and Jin Du et al., reported that the PL emission peak was at 453 nm for ZnSe nanoflakes [119].

![Figure 3.3](image)
3.2.5 Structural analysis

Figure 3.4 shows the X-ray diffraction (XRD) pattern of EDA capped ZnSe nanowires. The position of the diffraction peaks were indexed to wurtzite crystal phase of ZnSe. The positions of two theta were in good agreement with the standard JCPDS card no: 89-2940. The sharp peaks indicate that the product is crystalline in nature [120].

![XRD pattern of EDA capped ZnSe nanowires.](image)

3.2.6 Morphological studies

The FESEM and TEM images of EDA capped ZnSe nanowires are shown in Figures 3.5(a),( b) and 3.5 (c), (d) respectively. From the FESEM images, it is clearly seen the formation of one dimensional ZnSe nanowires. All the nanowires have monodispersed shape and thickness. The length of the
nanowires is in the range of few micrometres. In order to elucidate the length, high magnification TEM images were taken. From the TEM images, it is found that the ZnSe nanowires have an average diameter of 200 nm.

Figure 3.5 (a,b) FESEM and (c,d) TEM images of Edamine capped ZnSe nanowires
3.2.7 Functional properties

The FTIR spectrum of EDA capped ZnSe nanowires is shown in Figure. 3.6(a). It illustrates the vibration bands related to EDA (C$_2$H$_8$N$_2$). The sharp band observed at 1119 cm$^{-1}$ is due to C-N vibrations of edamine. The peak identified at 2925 cm$^{-1}$ is attributed to C-H stretching vibrations. N-H stretching of edamine vibration appears at 3393 cm$^{-1}$ [121]. This corroborated that the presence of edamine molecules and is adequately incorporated on the surface of the ZnSe nanowires. The chemical compositions are confirmed with the EDAX measurement and is shown in Figure.3.6 (b) [122]. No other peaks due to impurities are observed here.

![Figure 3.6(a) FTIR and (b) EDAX of Edamine capped ZnSe nanowires](image-url)
3.3 Synthesis and characterization of N-Methylaniline passivated ZnSe nanorods.

3.3.1 Structure

![Molecular Structure of N-Methylaniline](image)

Figure 3.7 Molecular Structure of N-Methylaniline

The structure of N - Methylaniline (NMA) is shown in Figure.3.7. It is a secondary amine in aniline class, is used as a latent and coupling solvent. N-Methylaniline molecules contains a lone pair of electrons in the nitrogen atoms. And these will facilitate the coordination bond formation with the metal ions.

3.3.2 Synthesis

Analytically pure zinc acetate and sodium selenite were procured and were used as such. Zinc acetate and sodium selenite were used as precursors. In a typical synthesis, 0.2 M of zinc acetate and 0.2 M of sodium selenite were dissolved in 50 ml of de-ionized water under vigorous stirring at 50 °C to which 0.1 M of N – Methylaniline (NMA) was added drop by drop. This process was continued for 8 h. After a yellowish precipitate was obtained, it was collected and washed with absolute ethanol for several times. Finally, the product was dried in hot air oven for 6 h at 170 °C. The synthesized product was characterized by XRD, UV - Vis, PL, FTIR, TEM and SEM.
3.3.3 Optical studies

Figure 3.8  (a) UV – Visible absorption and photoluminescence spectra and (b) band gap plot of NMA capped ZnSe nanorods.
Figure 3.8 (a) shows the UV–Visible absorption and PL spectra of NMA capped ZnSe nanorods. It is found that the absorption edge start at 350 nm. It exhibits blue shift when compared to that of bulk ZnSe. The PL emission peaks appeared at 322 nm, 335 nm, 349 nm and 399 nm. The first three strong emission bands are attributed to the band emission and the weak emission band at 399 nm is caused by the Se defects [123].

The optical band gap is obtained by plotting \((a\nu)^2\) and \(h\nu\) as shown in Figure 3.8 (b). It gives the band gap as 3.5eV. It is larger than that of ZnSe bulk crystal (2.7 eV). This shift of absorption edges towards shorter wavelength is due to the quantum confinement of ZnSe nanoparticles.

3.3.4 Structural analysis

![XRD of NMA capped ZnSe nanorods.](image)

Figure 3.9. XRD of NMA capped ZnSe nanorods.
The crystallinity and crystal phase of the ZnSe were studied by XRD patterns. Figure 3.9 shows a typical XRD pattern for the NMA capped ZnSe nanorods. All the diffraction peaks are indexed to cubic structure with the lattice constant $a = b = c = 5.633 \text{ Å}$ which is in good agreement with the reported data (JCPDS card no: 70-0777). No significant broadening is observed in the peaks.

3.3.5 Morphological studies

![FESEM and TEM images of NMA capped ZnSe nanorods.](image)

**Figure 3.10** (a) FESEM and (b, c, d) TEM images of NMA capped ZnSe nanorods.
FESEM image of NMA capped ZnSe nanorods is shown in the Figure. 3.10 (a). This image clearly shows that the nanorods are randomly oriented and the diameter of the nanorods is in the range of 100 to 200 nm and the lengths up to several micrometres.

The detailed morphologies of the NMA capped ZnSe nanorods are investigated using TEM and are presented in Figure.3.10 (b), (c) and (d). Figure. 3.10 (b) represents the image of the individual rod, which clearly indicates there is a break in the structure (marked region). This trend is attributed due to the oriented attachment of the nanoparticles moving randomly during the thermal treatment. Greater fraction of each nanoparticle merges with its immediate neighbors to form the nanorods. Figure. 3.10 (c) and (d) depicts the magnified images of the encapsulated ZnSe nanorods. The TEM results are in good agreement with the FESEM results.

3.3.6 Functional properties

![FTIR Spectrum of NMA capped ZnSe nanorods](image)

Figure 3.11 FTIR Spectrum of NMA capped ZnSe nanorods.
The presence of NMA in the synthesized ZnSe nanorods was examined by FTIR spectrum. KBr pellet technique was employed. The spectrum was recorded in the range of 4000–400 cm\(^{-1}\). Figure 3.11 shows the FTIR spectrum of NMA capped ZnSe nanorods. FTIR spectrum consists of various organic vibrations related to NMA. Further, it is to be noted that the absorption peaks at 1666 cm\(^{-1}\), 3355 cm\(^{-1}\) and 1046 cm\(^{-1}\) are due to C–H stretching, N–H stretching and C–N stretching respectively. This is due to the formation of coordinate bond between the nitrogen atom of NMA and Zn\(^{2+}\) ions [124].

3.4 Synthesis and characterization of Hexamethylenetetramine capped ZnSe nanorods.

3.4.1 Structure

Hexamethylenetetramine is a heterocyclic organic compound with the formula \((\text{CH}_2)_6\text{N}_4\). It has lone pair electrons in the four nitrogen atoms. Moreover, the longer chain length of this molecule will alter the chemical kinetics of the nucleation in solution. This white crystalline compound is highly soluble in water and polar organic solvents.

![Figure 3.12 Molecular Structure of Hexamethylenetetramine](image-url)
3.4.2 Synthesis

All the chemical reagents used for the synthesis were of analytical grade and used without further purification. In a typical synthesis, 0.2 M of zinc acetate and 0.2 M of sodium selenite were dissolved in 50 ml of de-ionized water under vigorous stirring at 50 °C to which 0.1 M of Hexamethylenetetramine (HMTA) was added drop by drop. This process was continued for 8 h. The final product was collected and washed with absolute ethanol for several times. Finally, the product was dried in hot air oven for 6 h at 170 °C. XRD, UV - Vis, PL, FTIR, TEM and SEM studies were carried out for the synthesized product.

3.4.3 Optical studies

The UV absorption spectrum of HMTA capped ZnSe dispersions in ethanol is shown in Figure. 3.13 (a). The absorption onset is observed at 377 nm and it is shifted towards shorter wavelength when compared to that of bulk counterparts (460 nm). The band gap plot of HMTA capped ZnSe nanorods is displayed in Figure 3.13 (b) and the band gap value is found to be 3.05 eV. The shift in band gap towards higher energy can be due to the quantum confinement effect. K.Vijaianand et al., [125] have synthesized the HMTA capped Zinc Sulphide (ZnS) nanoparticles and investigated the thermal stability and the optical properties. They have reported from the UV absorption studies that the HMTA capped ZnS nanoparticles exhibit strong quantum confinement. This was due to significant increase in the optical energy band gap when compared with that of the bulk ZnS. The observed results are in consonance with the results obtained.
Figure 3.13  (a) UV – Visible absorption spectrum and (b) band gap plot of HMTA capped ZnSe.

The PL spectrum of the HMTA capped ZnSe is shown in Figure 3.14. The PL measurement exhibits a strong green emission in addition to the band edge emission. The excitation wavelength of the sample is at 350 nm. The emissions are observed at 408 nm and 600 nm.
The emission at 408 nm is attributed to band edge emission. It is also noted that there is a broad emission in the region of 500 – 700 nm with peak at 600 nm. Generally, the emission peaks appearing at higher wavelength are mostly assigned to recombination of electron from the zinc interstitial defect centers with the photo generated hole at valence band. Hence, the emission peak detected at 600 nm is therefore assigned to the transition between zinc interstitial defect centers and selenium interstitial, a shallow acceptor above the valence band of ZnSe [126].

3.4.4 Structural properties

XRD pattern of HMTA capped ZnSe nanorods is shown in Figure 3.15. The appearance of the diffraction peaks corresponding to (1 1 1), (2 2 0) and (3 1 1) planes indicate the cubic structure of ZnSe nanorods. All the diffraction peaks can be assigned to face centered cubic with lattice constants \((a = b = c = 5.670 \text{ Å})\) which are in good agreement with the JCPDS card no: 88-2345.
3.4.5 Morphological studies

Figure 3.16. shows typical TEM images of HMTA capped ZnSe nanocrystals of rod like structure. The long nanorods with lengths up to several micrometre are observed. The diameter is of about 100 nm. Yu C. Chang et al., have synthesized Zinc oxide (ZnO) nanorods by an aqueous chemical method. Zinc nitrate hexahydrate and HMTA was used as source materials. They have reported that the size of the particles can be effectively controlled with an appropriate mixture of zinc nitrate and HMTA [127].

Kelvin M. Mc et al., have prepared ZnO nanowires and determined that the HMTA absorbs on the ZnO surfaces and acted as a capping agent that facilitates anisotropic growth of ZnO nanowires. By using ATR – FTIR spectroscopy studies, they have concluded that nanowires growth does not involve absorption of HMTA, instead, the role of HMTA in ZnO nanowires is
to keep the crystallization of ZnO under thermodynamic control by the slow release of OH ions [128].

Figure 3.16. TEM images of HMTA capped ZnSe nanorods.

Xin Ping Li et al., synthesized CdS hollow nanospheres by hydrothermal method. The Polyvinylpyrrolidone (PVP) and HMTA were used as capping agents. They have investigated the effects of HMTA by varying the concentrations whereas the concentration of PVP was fixed [129]. Chens et al., have reported that HMTA was used to prepare 3D CdS nanocrystals with flower like structure [130]. They have proposed that HMTA could selectively absorb on certain faces of CdS seeds. From these phenomena, one can conclude that HMTA could form complex compounds with bivalent ions. The lone pair involved nitrogen atoms of HMTA molecules can selectively bind or be absorbed on certain faces of ZnSe to influence the growth of these faces and aggregation of small nanoparticles.
3.4.6 Functional group analysis

FTIR spectrum of hexamethylenetetramine capped ZnSe nanowires is shown in Figure 3.17. Various vibrations of organic functional groups have been identified from the FTIR spectrum. The peak observed at 2929 cm\(^{-1}\) due to the C-H stretching of HMTA. Peaks at 1500 cm\(^{-1}\), 1392 cm\(^{-1}\) and 1053 cm\(^{-1}\) are attributed to C-H bending vibrations. These absorption peaks indicate that the synthesized ZnSe nanorods are successfully capped by HMTA molecules [131].

Figure 3.17. FTIR spectrum of HMTA capped ZnSe nanorods
3.5 Synthesis and characterization of Octylamine passivated ZnSe nanospheres

3.5.1 Structure

Octylamine is a mono-alkylamine that is used as building block in various end molecules. This material is chemically stable under normal and anticipated storage and handling conditions.

![Molecular Structure of Octylamine](image)

Figure 3.18. Molecular Structure of Octylamine

3.5.2 Synthesis

The typical synthesis procedure is as follows: zinc acetate and sodium selenite (analytical grade) without further purification were used as precursors. Initially, 0.2 M of zinc acetate and 0.2 M of sodium selenite were dissolved in 50 ml of de-ionized water under vigorous stirring at 50°C. 0.1 M of octylamine was added drop wise to the above mixture. This mixture was allowed to continuous stirring for 8 hours. The collected precipitates were washed with water and ethanol for several times. Finally the product was dried in hot air oven for 6 h at 180°C. The synthesized products have been characterized by XRD, UV - Vis, PL, FTIR, TEM, and SEM.
3.5.3 Optical studies

Figure 3.19 (a) UV – Visible absorption spectrum and (b) the band gap plot of Octylamine capped ZnSe nanospheres.
The UV-Vis absorption spectrum of octylamine capped ZnSe nanospheres is shown in Figure 3.19 (a). From the spectrum, it is observed that there is an absorption peak at 422 nm. The plot $hv$ versus $(ahv)^2$ is presented in Figure 3.19 (b). The optical band gap of the synthesized nanoparticles is obtained by extrapolating the straight line region and is found to be 2.83 eV. It suggests that the energy band gap shifted towards blue region, which is due to the confinement effect.

![Photoluminescence spectrum of octylamine capped ZnSe nanospheres.](image)

The room temperature photoluminescence of octylamine capped ZnSe nanospheres is presented in Figure 3.20. Two emission bands are observed from the spectrum. The band centered at 420 nm could be attributed to the transition between the band edges and the band centered at 575 nm.
could be attributed to the selenium vacancies related emission. R. Comparelli et al., have prepared oleic acid capped quantum dots by thermal decomposition in the non coordinating solvent. They have investigated the optical properties, capping exchange procedures using alkyamines. Enhancement of band edge emission was observed in CdS nanocrystals using octylamine as a capping ligand [132]. Gomez et al., have demonstrated that by using single quantum dot experiments, the blinking statistics could be modified by adding octylamine, which passivate unsaturated dangling bonds at the surface of the CdSe quantum dots [133].

3.5.4 Structural studies

The X-ray diffraction pattern of the Octylamine capped ZnSe nanospheres is demonstrated in the Figure. 3.21. All the diffraction peaks (1 1 1), (2 2 0) and (3 1 1) can be indexed to the ZnSe cubic crystalline structure. The diffraction pattern is well matched to JCPDS data (card no - 88-2345)

![Figure 3.21. XRD of octylamine capped ZnSe nanospheres.](image)
3.5.5 Morphological studies

![TEM images of Octylamine capped ZnSe nanospheres.](image)

Figure 3.22. TEM images of Octylamine capped ZnSe nanospheres.

Characteristic TEM images for illustrative octylamine capped ZnSe nanospheres are shown in the Figure. 3.22. These images reveal the formation nanospheres with narrow distribution. From the TEM images, the average diameter was found to be 50nm. The diameters of the individual particles were obtained by averaging the dimensions along the longest axis of the particulate and an axis perpendicular to it. The spherical morphology of octylamine capped ZnSe nanostructures indicates that the octylamine molecules were successfully passivated the ZnSe in all spatial directions during the growth.

3.5.6 Functional group analysis

FTIR spectrum of octylamine capped ZnSe nanospheres is shown in Figure.3.23. The broad peak at 3420 cm\(^{-1}\) is corresponds to N-H vibration of octylamine.
Figure 3.23. FTIR spectrum of Octylamine capped ZnSe nanospheres.

The absorption peak at 2900 cm\(^{-1}\) is corresponded to stretching vibrations of C-H bonds and the peak at 1627 cm\(^{-1}\) is assigned to the bending vibrations of N-H bonds [134]. The above functional group vibrations indicate that the ZnSe nanospheres were capped by octylamine molecule.

3.6 Synthesis and characterization of Tripropylamine capped ZnSe spherical nanoparticles.

3.6.1 Structure

Tripropylamine is a colorless liquid the relative density of 0.754. Boiling point of 156.5°C, with ethanol and ether phase immiscibility slightly soluble in water.
Tripropylamine is a tertiary amine which belongs to the class of trialkylamines. The main application of tripropylamine is the production of quaternary ammonium cations, which are used as phase transfer catalyst. Smaller volumes are used as proton scavenger or as molecular template in the production of micro porous inorganic catalysts.

### 3.6.2 Synthesis

In the typical preparation, zinc acetate and sodium selenite were used as precursors. 0.2 M of zinc acetate and 0.2 M of sodium selenite were dissolved in 50 ml of de-ionized water under vigorous stirring at 50 °C to which 0.1 M of Tripropylamine (TPA) was added drop by drop. This process was continued for 8 h. After a white precipitate was obtained, it was collected and washed with absolute ethanol for several times. Finally the product was dried in hot air oven for 6 h at 180 °C. XRD, UV - Vis, PL, FTIR, TEM and SEM studies were carried out for the synthesized product.
3.6.3 Optical Properties

Figure 3.25 (a) UV – Visible absorption spectrum and (b) the band gap plot of TPA capped ZnSe nanoparticles.
Figure 3.26 Photoluminescence spectrum of TPA capped ZnSe nanoparticles.

The UV absorption spectrum of TPA capped ZnSe is shown in the Figure 3.25 (a). Generally, the wavelength of the maximum exciton absorption ($\lambda_{\text{max}}$) decreases as the particle size decreases due to the quantum confinement of the photo generated electron – hole carriers. It is noticed that TPA capped ZnSe nanoparticles exhibit a blue shift in the absorption onset. The absorption onset of TPA capped ZnSe nanoparticles is observed at 365 nm. The blue shift in the absorption spectrum is mainly attributed to the confinement of charge carriers in the nanoparticles. The band gap is calculated by extrapolating the straight line portion of plot shown in Figure 3.25 (b). Zero absorption coefficient value gives the direct band gap $E_g$ of the synthesized products. Thus, the band gap energy is found to be 3.46 eV. The emission spectrum of the sample was recorded upon excitation at 325 nm.
The two emission peaks centered at 383 nm and 440 nm of the as synthesized TPA capped ZnSe is shown in the Figure. 3.26. This is attributed to the band edge emission [135, 136].

3.6.4 Structural studies

![XRD of TPA capped ZnSe](image)

Figure 3.27. XRD of TPA capped ZnSe

Figure 3.27 shows X-ray diffraction pattern of the TPA capped ZnSe spherical particles. The observed diffraction peaks match the standard peaks at (1 1 1), (2 2 0) and (3 1 1) planes of cubic ZnSe. No other peaks related to any impurity phases are observed in XRD graph. The XRD pattern is well matched to joint committee powder diffraction data (card no: 80 - 0021). The similar structure was observed by the reported literature [137].
3.6.5 **Morphological studies**

TEM and HRTEM images of TPA capped ZnSe nanoparticles are shown in Figure 3.28. The TEM images clearly depict the formation of spherical particles with monodispersity in size and morphology. The average size of the particles is found to be 5 nm. The HRTEM image shows the crystalline fringes which indicate the well crystalline nature of TPA capped ZnSe nanoparticles.

![TEM and HRTEM images of TPA capped ZnSe nanoparticles](image)

*Figure 3.28 TEM and HRTEM images of TPA capped ZnSe nanoparticles*

3.6.6 **Functional group analysis**

FTIR spectrum of TPA capped ZnSe nanoparticles is shown in Figure 3.29. The presence of tripropylamine in ZnSe nanoparticles have been confirmed from the vibration peaks from 3500 cm\(^{-1}\) to 1000 cm\(^{-1}\). Vibrational peaks at 3348 cm\(^{-1}\) and 1655 cm\(^{-1}\) are due to N-H stretching of tripropylamine. The peaks at 1446 cm\(^{-1}\) and 1105 cm\(^{-1}\) are due to C-H bending of TPA. From
the FTIR spectrum, it is apparently evident that the tripropylamine was capped with ZnSe nanoparticles.

![FTIR spectrum](image)

**Figure 3.29.** FTIR spectrum of TPA capped ZnSe nanoparticles

### 3.7 Synthesis of Triethylamine passivated zinc selenide bean like nanostructures

#### 3.7.1 Structure

Triethylamine is a chemical compound with the molecular formula of N(CH₂CH₃)₃. The molecular structure of Triethylamine is shown in Figure 3.30.
Triethylamine is a tertiary amine; it is a clear, colorless liquid with ammonia like odor. It is commonly encountered in organic synthesis as a base. The lone pair of electrons of the nitrogen atom makes this compound an efficient stabilizing agent.

### 3.7.2 Synthesis

All the reagents were of analytical grade and used without further purification. Synthesis was carried out by a wet chemical process using zinc acetate and sodium selenite as source materials. In a typical preparation, solution of 0.2 M zinc acetate was prepared in 50 ml of deionized water and then the solution of 0.2 M sodium selenite was added to the solution which was kept on stirring using a magnetic stirrer at 50 °C. In order to provide stability and size control of the particles, 0.1 M of Triethylamine (TEA) as a capping agent was added drop wise to the solution and stirred vigorously for 36 hours. The resultant product was finally dried at 120 °C for 10 hours. The structure of the dried TEA capped ZnSe nanoparticles were characterized by XRD, UV, PL, AFM, and FTIR.
3.7.3 Optical studies

Figure 3.31 UV–visible absorption, photoluminescence spectrum (inset: plot of $E_g$ Vs $(a h\gamma)^2$) of TEA capped ZnSe nanostructures

Figure 3.31 shows the UV–visible absorption and photoluminescence spectrum of TEA capped ZnSe nanostructures. It exhibits the absorption edge of ZnSe nanostructures at 350 nm, which is blue shifted from that of bulk ZnSe (460 nm) [138, 139]. The band gap of ZnSe nanostructures was calculated as 3.5 eV, from the plot between the $h\nu$ Vs $(a h\nu)^2$ and it is depicted in the inset of Figure. 3.31. The broadened peak that occurs at 255 nm is due to the size distribution and differences in morphologies of the nanostructures. The two emission peaks observed at 401 nm and 424 nm when excited at 350 nm are attributed to the band edge.
emission of ZnSe [140]. These two strong emission bands are blue shifted due to the quantum size effect of ZnSe nanostructures.

3.7.4 Structural studies

Figure 3.32. XRD pattern of TEA capped ZnSe nanostructures

The crystal structure and phase purity of the product are characterized by XRD. Figure 3.32 shows the XRD pattern for TEA capped ZnSe nanoparticles. All the reflection peaks can be indexed to hexagonal with the lattice constant of \(a=3.974 \text{ Å}, c=6.506 \text{ Å}\), which is in good agreement with the reported data (JCPDS card no: 80-0008). No other peak related to impurities was detected within the detection limit of XRD. These results suggest that the growth of ZnSe is good.
3.7.5 Morphological studies

Figure 3.33 AFM images of (a,b) bean-like morphology, (c) roughness analysis (d), (e) 3D view and (f) profile of size measurement TEA capped ZnSe nanostructures.
AFM images of TEA capped ZnSe nanostructures are shown in 3.32 (a) and (b). The morphology of the ZnSe resembles the bean-like nanostructure. This image indicates that there exist two different crystalline domains in the asgrown nanostructure. It is due to mechanical breakdown occurring at the dislocations where the two domains meet. Thermal heating may cause this mechanical breakdown [141] and also the self-aggregation of the particles lead to the formation of such structures. All the particles were easily distinguishable. Figure.3.33 (c) shows the roughness analysis of the TEA capped ZnSe. It is observed that the height of the particle from the substrate is uniform and clearly seen that roughness of the bean-like ZnSe nanostructures were in monodispersity. This is consistent with the UV result. Figure.3.33 (d) shows the three dimensional view of the ZnSe nanostructures. It shows the unidirectional growth of the particles with unique size distribution. Figure.3.33 (e and f) shows the three dimensional view and size measurement profile of an individual ZnSe nanostructure. Size of the structure is found to be 205 nm with monodistribution

3.7.6 Functional group analysis

The FTIR spectrum for TEA capped ZnSe nanostructure is presented in Figure. 3.34 and it indicates the presence of TEA in ZnSe nanostructures. The C–N stretching and C–H bonding vibrations usually appear in the range 1000–1180 cm\(^{-1}\) and 1400–1300 cm\(^{-1}\) respectively [142]. In this spectrum, the two peaks observed correspond to C–N stretching (1020 cm\(^{-1}\)) and C–H bonding (1331 cm\(^{-1}\)) of TEA. This shows that the TEA molecules were effectively bound with the vacant shell of the Zn\(^{2+}\) in ZnSe nanostructures.
3.8 Synthesis and Characterization of 3–Mercapto–1,2–propanediol capped ZnSe and 3–Mercapto–1,2–propanediol capped ZnSe in Polyvinylpyrrolidone

3.8.1 Structure

3–Mercapto–1,2–propanediol is clear to yellowish viscous solution and it is stable under normal conditions. The only existing three-carbon sugar alcohol (triitol) is glycerol. Polyvinylpyrrolidone is a long chain polymer molecule with various chain lengths and it is widely used in chemical reactions.
3.8.2 Synthesis

All the chemicals used for the synthesis were analytical grade and were used without further purification. Synthesis of 3–Mercapto–1,2–propanediol capped ZnSe and 3–Mercapto–1,2–propanediol capped ZnSe in Polyvinylpyrrolidone are as follows: 0.2 M of zinc acetate and 0.2 M of sodium selenite were dissolved in 50 ml of de-ionized water at 40 °C under vigorous stirring followed by addition of 0.5 ml of 3–Mercapto–1,2–propanediol. This reaction have been continued for 5 hours and then centrifuged in ethanol to remove the unreactant residues in the product. The collected colloids were dried at 110 °C for 6 hours. The obtained powder is denoted as 3–Mercapto–1,2–propanediol capped ZnSe quantum dots. For the preparation of 3–Mercapto–1,2–propanediol capped ZnSe in polyvinylpyrrolidone, the same procedure was followed up to the addition of 3–Mercapto–1,2–propanediol and then 0.002 M of polyvinylpyrrolidone
(molecular weigh 40,000) was added to the solution under stirring. The resultant product was centrifuged in ethanol and dried at 110 °C for 6 hours. The obtained product is denoted as 3–Mercapto–1,2–propanediol capped ZnSe in polyvinylpyrrolidone. The synthesized products have been characterized by XRD, UV-Vis, PL, FTIR and TEM.

### 3.8.3 Optical studies

![Absorption Spectrum](image)

**Figure 3.36** UV visible absorption spectra of (a) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots (b) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in Polyvinylpyrrolidone.

UV–visible absorption spectrum of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots is shown in Figure. 3.36 (a). It exhibited the ultraviolet absorption between 260 and 310 nm. Two excitonic absorption peaks
were observed at 264 and 301 nm as shown in the inset of Figure 3.36 (a). The excitonic absorption features of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots signified the shift in the optical transition towards higher energy range compared to that of bulk ZnSe absorption (460 nm). The possible reason for the above transition is that the existence of the different size of particles in the 3–Mercapto–1,2–propanediol capped ZnSe as shown in TEM and HRTEM images. In principle, the optical absorption spectrum is a collection of cumulative transitions over a wide range of spectral responses. In addition to that the histogram of the particle size distribution, from TEM and HRTEM images of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots distinctly strengthen the existence of two different sizes (3 – 5 nm).

On the other hand, the two or multi exciton generation extensively investigated in lead and cadmium chalcogenides quantum dots over the near infrared to visible region. Very recently, L.J. Zhang et al., [143] observed the multi exciton generation in ZnSe quantum dots in the deep UV region and the optical transitions were at 269 nm and 307 nm. The emission spectrum for 3–Mercapto–1,2–propanediol capped ZnSe consists of multiple emission peaks in the near band edge region as shown in Figure 3.36(c). Broad emission peak was centered at 378 nm with two satellite emission peaks of less intensity. Existence of multiple emission peaks within the bandgap of 0.3 eV confirmed the quantum size effect of the two different sizes of quantum dots. Difference in the absorption edge and luminescence peak center (i.e. stokes shift) of the 3–Mercapto–1,2–propanediol capped ZnSe
quantum dots was 0.49 eV. The deep level emission of 503 nm may be related to the defects or non-bonded dangling bonds on surface of the quantum dots.

Optical absorbance spectrum of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in polyvinylpyrrolidone is shown in Figure 3.36(b). Excitonic absorption peak is observed at 288 nm and no other optical transitions or excitonic peaks are observed, unlike 3–Mercapto–1,2–propanediol capped ZnSe. It indicated the presence of highly monodispersed quantum dots in confined energy level.

Figure 3.36 Photoluminescence spectra of (c) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots
Photoluminescence spectrum of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in polyvinylpyrrolidone is shown in Figure. 3.36 (d). The single emission peak is observed at 326 nm. This emission peak is near band edge luminescence in the deep ultra violet region. Photoluminescence intensity of the 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in polyvinylpyrrolidone was twofold increased to that of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots. This evidenced the stabilization of polymer ligands and passivation of dangling bonds on the surface of the quantum dots. Stokes shift of the optical transition is about 0.03 eV. It is almost the band edge luminescence behavior of ZnSe quantum dots. No other deep level emission has been observed.

Figure 3.36 Photoluminescence spectra of (d) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in polyvinylpyrrolidone.
3.8.4 Structural studies

Figure 3.37 XRD patterns of (a) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots, (b) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in Polyvinylpyrrolidone.

The XRD patterns for (a) 3–Mercapto–1,2–propanediol capped ZnSe and (b) 3–Mercapto–1,2–propanediol capped ZnSe in the polyvinylpyrrolidone are shown in Figure. 3.37. The comparative studies are done to monitor the effects of 3–Mercapto–1,2–propanediol and polyvinylpyrrolidone on ZnSe nanoparticles. All the peaks in the diffraction pattern are indexed to cubic structure of ZnSe where the lattice parameter \(a = 5.67 \text{ Å}\) is in good agreement with the standard JCPDS card no: 80-0021. The full width half maxima (FWHM) of the diffraction peaks of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in polyvinylpyrrolidone are broadened as compared to that of
3–Mercapto–1,2–propanediol capped ZnSe quantum dots. It suggested that the size of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots is smaller than that of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots. Further XRD analysis revealed no additional products in the samples.

3.8.5 Morphological studies

Figure 3.38 (a) TEM image, (b, c) HRTEM images and (d) SAED pattern of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots (inset of c is histogram of particle size distribution.)
In order to obtain the conclusive evidence of the size, shape and the structure of the nano particle, TEM measurement was carried out. Figure 3.38 (a) shows the TEM image of 3–Mercapto–1,2–propanediol capped ZnSe and it revealed the formation of spherical particles without conglomeration over the area of 200 nm × 200 nm on a small area of the carbon coated copper grid. Quantum dots with the size of about 3 – 5 nm can be clearly seen from high resolution TEM (HRTEM) images shown in Figure 3.38 (b, c). The crystal size calculated for the 3–Mercapto–1,2–propanediol capped ZnSe by XRD is nearly in good agreement with the particles size measured by TEM images. The columns of the atoms were periodically arranged. The formation of lattice fringes displayed the characteristic cubic pattern of <1 1 1> projection of zinc blende crystal structure and most of the quantum dots exhibited no defects such as stacking faults or coalescence. Lattice constant of 3–Mercapto –1,2–propanediol capped ZnSe quantum dots was measured to be 0.33 nm and it was well matched with calculated lattice constant value from X- ray diffraction pattern (JCPDS no: 80-0021) [137].

Selected Area Electron Diffraction Pattern (SAED) of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots is shown in Figure 3.38 (d). Ring patterns of the SAED are well apparent to the formation of the cubic phase of ZnSe. The ring patterns was indexed to (1 1 1), (2 2 0) and (3 1 1) planes and no more patterns for defect or other lattices are observed. Histogram of particles size distribution is presented in the inset of Figure 3.38 (c). From the histogram, it is evident to note that the sizes of the quantum dots are dispersed from 3.6 to 6.0 nm. However most of the quantum
dots are formed in the size of 5 nm. This variation of the quantum dots size distribution greatly influenced the optical transition as shown in the optical properties.

Figure 3.39 (a) TEM image, (b, c) HRTEM images and (d) SAED pattern of 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in Polyvinylpyrrolidone (inset of c is histogram of particle size distribution.

Figure 3.39 (a) and (b, c) shows TEM and HRTEM images for 3–Mercapto–1,2–propanediol capped ZnSe in polyvinylpyrrolidone, respectively. These images clearly depicted the formation of merely
monodispersed ZnSe quantum dots. The size of the quantum dots are in the range of 3.5 to 4 nm which is less than that of bulk excitonic Bohr radius of ZnSe (8.6 nm). Moreover, the HRTEM images affirmed the crystalline nature of quantum dots which could be evidenced by the array of lattice fringes. It can be seen that the 3–Mercapto–1,2–propanediol capped ZnSe nanocrystals are homogenously distributed on the chains of a polymer network which is formed by the chemical reaction of polyvinylpyrrolidone. These particles are uniform and no aggregation is observed when polyvinylpyrrolidone was used to stabilize ZnSe nanocrystals. Since the long chain molecules are coated on the surface of the nanocrystals, the dispersive force among the polarized molecules stabilized the nanocrystals in the colloid solution. This kind of polymer network is extended into the whole dispersion thus the ZnSe nanocrystals exhibited excellent stability.

Figure 3.39 (d) shows the SAED pattern of the 3–Mercapto–1,2–propanediol in polyvinylpyrrolidone and it clearly depicted the signature of zinc blende with (1 1 1), (2 2 0), (3 1 1) three planes and no more rings are observed. This indicates that the polymer ligands played the role in size confinement without the change in crystalline phase. The particle size distribution is presented in the histogram as shown in the inset of Figure. 3.39 (c). 3–Mercapto–1,2–propanediol capped ZnSe quantum dots distributed around the size of 4 nm.
3.8.6 Functional group analysis

![FTIR spectra](image)

**Figure 3.40** FTIR spectra of (a) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots and (b) 3–Mercapto–1,2–propanediol capped ZnSe quantum dots in Polyvinylpyrrolidone.

Functional groups in the ZnSe quantum dots have been confirmed by FTIR spectra--and are displayed in Fig.3.39 (a) and (b). Characteristic vibrations of 3–Mercapto–1,2–propanediol and PVP are observed in the spectra. Vibration peak at 886 cm\(^{-1}\) and 2600 cm\(^{-1}\) corresponds to S-H bond of thiol molecule. Peak at 2886 cm\(^{-1}\) and 3354 cm\(^{-1}\) corresponds to CH\(_2\)-S and O-H of thiol, respectively. These vibrations confirm the surface passivation of 3–Mercapto–1,2–propanediol on ZnSe nanoparticles. Whereas, spectrum of thiol capped ZnSe in PVP displays the weakened vibrations regions of 2300 cm\(^{-1}\) to 1600 cm\(^{-1}\) as shown in the inset. It indicates the presence of PVP in the quantum dots. PVP characteristic bonds such as C=O and C-N are observed at 1656 cm\(^{-1}\) and 1333 cm\(^{-1}\), respectively. Both thiol and PVP molecules effectively passivates the surface of ZnSe quantum dots.
3.9 Conclusion

In summary, ZnSe nanostructures have been prepared by simple wet chemical method with Edamine, N-Methylaniline, Hexamethylenetetramine, Octylamine, Tripropylamine, Triethylamine and as the organic ligands. The optical properties were investigated using absorption and photoluminescence techniques. The size confinement effects have been evident from the UV – visible absorption spectra, which showed blue shifts in the Excitonic absorption as compared to the bulk ZnSe. The structural properties were studied using X-ray diffractometry. The morphology of the nanostructures has been observed by SEM, TEM and AFM analysis. The presences of the organic ligands were confirmed by FTIR analysis.