CHAPTER 3

EFFECT OF ZnO AND SILICA CAPPING ON NASCENT ZnS NANOSTRUCTURES

3.1 INTRODUCTION

Nanoscaled semiconductor inorganic particles exhibit attractive photophysical properties (Lee et al. 2000; Parak et al. 2002; Han et al. 2001) owing to their size dependent behaviour and quantum confinement effects. Various core-shell nanocomposites were explored, among which the selection of inorganic materials for core-shell nanocomposites has been one of the most popular strategies to provide dense surface protection in one case and the combination of higher or lower bandgap materials in the other. For example, surface passivation of the nanocrystals by a thin semiconductor shell not only modify the absorption and emission wavelengths, but also increase the quantum yield up to 50-70%, e.g., CdSe/ZnS, CdSe/CdS and ZnSe/Zn core/shell structures (Xu et al. 2000; Peng et al. 1997). With higher band gap energy than that of the core, the ZnS shell didn’t absorb the emission from the core and helped to eliminate the broadband emission of the QDs. ZnO-coated ZnS nanoparticles were also prepared by some groups (Karar et al. 2004; Dinsmore et al. 2008) but their X ray diffraction (XRD) results indicated poor crystallinity. Daixun (2009) studied the influence of ZnO shell thickness on the luminescence properties of Mn-doped ZnS nanoparticles. As ZnS is a non-toxic material and ZnO has a very high binding energy as well as good chemical and thermal stability, so the core-shell combination of ZnS/ZnO seems to be very attractive. However, very less work has been reported so far in case of nanocomposites comprising of ZnS and ZnO as seen from the review of literature. In the present chapter, a simple method to prepare crystalline core/shell ZnS/ZnO nanocomposites is reported, with emphasis on the tunability in morphological and optical properties which can be brought by altering the concentration of ZnO for a fixed amount of nascent ZnS nanoparticles.

The nascent as well as core-shell nanostructures were prepared by chemical precipitation method starting with the synthesis of nascent ZnS nanoparticles. ZnO and Silica were used as capping agents with varying concentrations viz. 0.1, 0.3, 0.5 and 1.0% for ZnO and 0.25, 0.5, 0.75, 1.0% for silica (SiO₂). Figure 3.1 presents a schematic of the capping.
Subsequent sections present a detailed discussion on the synthesis and characterization of inorganically capped ZnS quantum dots.

### 3.2 ZnO CAPPED ZnS QUANTUM DOTS

#### 3.2.1 Chemicals Used

Table 3.1 gives a list of the chemicals used in the present investigation for the synthesis of core-shell ZnS quantum dots.

**Table 3.1. List of chemicals for synthesis of inorganically capped ZnS QDs**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc acetate dehydrate (99.5 %)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>Sodium Sulfide (99.1%)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>Zinc Nitrate (99 %)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>Sodium Hydroxide (99 %)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>De-ionized water</td>
<td>Nice</td>
</tr>
</tbody>
</table>

#### 3.2.2 Synthesis of Nascent ZnS Quantum Dots

The ZnS quantum dots were synthesized by chemical precipitation method. The synthesis reaction was carried out in the aqueous medium. Figure 3.2 gives a schematic for the synthesis of nascent ZnS quantum dots. Homogeneous solutions of 0.5 M zinc acetate (Zn(CH$_3$COO)$_2$.2H$_2$O) and 0.5 M sodium sulfide (Na$_2$S) were prepared by dissolving 5.49 gm of zinc acetate and 1.95 gm of sodium sulfide in 50 ml of water separately and stirring for 30 minutes. The 0.5 M sodium sulfide solution was gradually added to the 0.5 M solution of zinc acetate. Soon after the addition of sodium sulfide solution, precipitation phenomenon initiated and the concentration of precipitates increased with the successive addition of sodium sulfide solution. The stirring was allowed for 30 minutes at room temperature using a magnetic stirrer. Then the particles were centrifuged at 4000 rpm for 5 minutes. The precipitated particles were filtered using Whatman 40 filter paper. The particles were then washed several times using de-ionized water to remove the traces of adhered impurities. The washed particles (Nascent ZnS QDs) were then dried at 60°C for 24 hours in vacuum oven to obtain nascent ZnS QDs.
3.2.3 Synthesis of ZnO Capped ZnS Core-Shell Quantum Dots

Figure 3.3 presents a schematic for the synthesis of inorganically (ZnO) capped ZnS QDs. In this process, 0.2 g ZnS nanocrystals powder was put into 200 ml deionised water and ultrasonically dispersed for 1 hr. Then appropriate amount (10, 30, 40, 50, 100 ml) of 0.05 M Zn(NO$_3$)$_2$ aqueous solution was added into the ZnS suspension under vigorous stirring. Drops of 0.1 M NaOH aqueous solution were then gradually added to attain the pH value of 10, when ZnO precipitated to form ZnS/ZnO nanocomposite. The nucleation and growth of a separate ZnO particle were suppressed by the addition of very low concentration of NaOH in the ZnS suspension and centrifuged at 4000 rpm for 5 minutes. This process was then followed by filtering and washing with double distilled water. Subsequently, particles were vacuum dried at 60ºC. The size of ZnS/ZnO nanocomposite was controlled by varying the dosage of Zn(NO$_3$)$_2$. This synthesis route was followed to coat the ZnO on the surface of ZnS. The synthesized QDs were studied for morphological and optical properties through various characterization techniques (XRD, TEM, FTIR, UV-vis and PL).
Figure 3.1. Schematic for Capping agents and the capping concentrations for ZnS QDs
Figure 3.2. Schematic for synthesis of nascent ZnS QDs.
Ultrasonically dispersed for 1 hr

Magnetic stirring

Magnetic stirring

Magnetic stirring

Magnetic stirring

Magnetic stirring

Centrifugation

Filteration

Vacuum Oven drying at 60°C

Extraction of powder containing ZnO capped ZnS: Mn nanoparticles

0.2 gm ZnS QDs + 200 ml deionized water

10ml/30ml/50ml/100ml 0.05 M Zinc Nitrate

0.1 M sodium Hydoxide solution

Figure 3.3. Schematic for the synthesis of inorganically (ZnO) capped ZnS QDs.
3.3 CHARACTERIZATION OF ZnO CAPPED ZnS QUANTUM DOTS

The uncapped ZnS quantum dots and ZnO capped ZnS quantum dots in various capping concentrations (0.1, 0.3, 0.5 and 1.0%) were characterized by employing powder X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transformation infrared (FTIR) spectroscopy, UV-visible spectroscopy and energy resolved Photoluminescence spectroscopy.

3.3.1 X-Ray Diffraction

X-ray diffraction (XRD) patterns of synthesized ZnS/ZnO core shell nanoparticles were collected on Rigaku, model D–max IIIC diffractometer with Cu Kα radiation. Figure 3.4 shows the XRD pattern of Nascent ZnS QDS together with ZnO capped QDs. Pure zinc-blende crystal structure and three broad peaks corresponding to the (111), (220) and (311) planes were observed in the XRD pattern (Fig. 3.4a). It correspond those of the β-ZnS (cubic) reported in the JCPDS Powder Diffraction (File No.5-0566) at 2θ values of 29.0°, 48.1° and 56.4° respectively.

Some new diffraction peaks appeared at about 31.8°, 34.4°, 36.2°, 62.9°, 67.9°, and 69.0° (Figures 3.4 b–e). These peaks correspond to (100), (002), (101), (103), (112) and (201) diffraction peaks from the standard card (JCPDS No. 80-0074), respectively, indicating that the ZnO possess a wurtzite structure. It was also observed that with the increase in the amount of ZnO shell, the intensity of the diffraction peaks increases (Figures 3.4 b-e). Broadening of XRD peaks shows the formation of nanocrystals. Crystallite size of nanoparticles was calculated by Scherer’s equation as shown by equation 3.1:

\[ D = \frac{0.9\lambda}{\beta \cos\theta} \]  

where D is the crystallite size (Å), \( \lambda \) (Å) =1.54 be the wavelength of Cu Kα radiation and \( \beta \) corrected half width of the diffraction peak. The primary crystallite size of nascent ZnS was around 1.8 nm; however, it tends to increase with core-shell combination. For (111) peak of ZnS phase, the average crystallite size for all the samples were estimated from the half width of diffraction peaks (Table 3.2). For (101) peak of ZnO phase, grain size was found to be 17.97 nm, 27.42 nm, 18.43 nm and 15.05 nm corresponding to 0.1, 0.3, 0.5 and 1.0% concentration of ZnO respectively as shown in Table 3.3.
Figure 3.4. X-Ray Diffraction spectra for (a) pure ZnS and (b-e) ZnS/ZnO core-shell nanoparticles
### Table 3.2. Crystallite size of uncapped ZnS and ZnS/ZnO capped quantum dots

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm) from (111) peak of ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncapped and Undoped ZnS</td>
<td>1.80</td>
</tr>
<tr>
<td>0.1% ZnO capped ZnS</td>
<td>1.80</td>
</tr>
<tr>
<td>0.3% ZnO capped ZnS</td>
<td>1.80</td>
</tr>
<tr>
<td>0.5% ZnO capped ZnS</td>
<td>4.92</td>
</tr>
<tr>
<td>1.0% ZnO capped ZnS</td>
<td>4.71</td>
</tr>
</tbody>
</table>

### Table 3.3. Crystallite size from (101) peak of ZnS/ZnO capped quantum dots

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm) from (101) peak of ZnO phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% ZnO capped ZnS</td>
<td>17.97</td>
</tr>
<tr>
<td>0.3% ZnO capped ZnS</td>
<td>27.42</td>
</tr>
<tr>
<td>0.5% ZnO capped ZnS</td>
<td>18.43</td>
</tr>
<tr>
<td>1.0% ZnO capped ZnS</td>
<td>15.05</td>
</tr>
</tbody>
</table>

### 3.3.2 Transmission Electron Microscopy

TEM studies were carried out using a Transmission Electron Microscope, Hitachi (H-7500) 120 kV, having a resolution of 0.36 nm (point to point) with 40-120 kV operating voltage and magnification capacity of 6 lakh times in high resolution mode. Figures 3.5 show the TEM of ZnS nanoparticles with and without ZnO. TEM studies confirm the formation of nascent as well as ZnS/ZnO nanocomposites. TEM micrograph reveals that uncapped ZnS nanoparticles are agglomerated (Figure 3.5a); the phenomenon is attributed to high surface to volume ratio. On the other hand, ZnO capped ZnS nanoparticles are monodispersed in nature. Hence, presence of ZnO capping on ZnS nanoparticles can prevent their agglomeration. The size of nascent ZnS nanoparticles was observed to be 4-5 nm. With increase in ZnO concentration, particle size increases from 3-200 nm, until it shows pure wurtzite structure (Figures 3.5 b-d).
Figure 3.5. Transmission electron micrographs showing formation of (a) pure ZnS, (b) 0.1\% ZnO, (c) 0.3\% ZnO and (d) 1.0\% ZnO.
3.3.3 Fourier Transforms Infra-Red (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded in range of 4000–400 cm\(^{-1}\) with Perkin Spectrum RXI (40). Figures 3.6 show FTIR spectra of ZnS nanoparticles with and without ZnO. Remadevi et al (2007) reported that the existence of bands around 3000-3600 cm\(^{-1}\) in ZnS QDs were due to the hydrogen stretching frequency (OH stretching). However, the bands around 900-1500 cm\(^{-1}\) were due to the oxygen stretching.

**Figure 3.6.** FTIR spectra of (a) pure ZnS, (b-e) ZnS/ZnO core shell nanoparticles of different capping concentration.
and bending frequency. The additional weak bands and shoulders at 2921, 2847, 2353, 1634 and 1409 cm\(^{-1}\) may be attributed to the microstructural changes. Bands around 1200 and 1100 cm\(^{-1}\) were due to the characteristic frequency of inorganic ions. The peak at 612 cm\(^{-1}\) was assigned to the ZnS band (i.e., corresponding to sulphides). According to the standard values in case of ZnO (Viswanatha et al 2012) the band located near 600 cm\(^{-1}\) can be attributed to the Zn-O stretching mode. The bands at 3200 to 3600 cm\(^{-1}\) corresponds to the stretching vibration of \(-\text{OH}\) bond and at around 1680 cm\(^{-1}\) at wavelength just half of 3200 to 3600 cm\(^{-1}\) has been assigned to the first overtone of fundamental stretching mode of \(-\text{OH}\). These stretching vibrations correspond to the water molecule bound on the surface. FTIR spectra in the present studies are in accordance with the standard values given in the literature both for nascent ZnS as well for ZnS/ZnO nanocomposite. However, the small changes can be attributed to the formation of nano phase. It was also observed that in case of ZnS/ZnO nanocomposite formation, the FTIR peak intensity varies appreciably with the slight modification in wave number.

### 3.3.4 UV-visible Absorption Spectroscopy

Figure 3.7 shows the absorption spectra of pure ZnS nanoparticles together with ZnS/ZnO core-shell QDs. The absorption edges were observed at 274 for pure ZnS QDs and 273, 274.5, 288 and 289 nm corresponding to 0.1%, 0.3%, 0.5%, and 1.0% ZnO concentrations respectively. In 0.5% and 1.0% two major peaks of ZnO were also observed at absorption edge of 384 and 398 nm. For obtaining the absorption characteristic, at first the transmittance (T) at different wavelengths were measured using different values of absorbance and then absorption coefficient (\(\alpha\)) at the corresponding wavelengths were calculated using the Beer-Lambert’s relation as shown in equation 3.2,

\[
\alpha = (1/d) \ln (1/T)
\]  

(3.2)

where \(d\) is the path length (1cm). The relation between the incident photon energy (\(h\nu\)) and the absorption coefficients (\(\alpha\)) is given by the following relation,

\[(\alpha h\nu)^{1/m} = c (h\nu - E_g)\]

where, \(c\) is a constant, \(E_g\) the band gap of the material and the values of exponent \(m\) depends on the type of the transition. For direct and allowed transition \(m = 1/2\), for
indirect transition \( m = 2 \), and for direct forbidden \( m = 3/2 \) (Themlin et al 1990). The optical band gaps were determined from the first peak of every curve in Figure 3.7 by plotting a graph between \((\alpha h\nu)^2\) and \(h\nu\). The bandgap values were found to be 3.925eV for nascent ZnS, and 3.93eV, 4.0eV, 3.98eV and 4.12eV respectively, corresponding to 0.1%, 0.3%, 0.5% and 1.0% ZnO in ZnS/ZnO nanocomposite as shown in Figure 3.8. From the UV-visible analysis of all samples, it was observed that in case of 1.0% ZnO, maximum bandgap of 4.12eV is observed, which exhibits better confinement effect compared to other samples, while quantum confinement effect is almost observed in all the samples in comparison to the bulk ZnS which has a band gap of 3.68 eV. Rough bandgap of ZnO calculated from the second UV-visible peak for 0.5% and 1.0% ZnO was found to be 3.22 eV and 3.11 eV respectively, which indicates the tendency for the bulk formation of ZnO after a certain concentration.

**Figure 3.7.** UV-Visible absorption spectra of ZnS nanoparticles with and without ZnO.
Figure 3.8. Plot of $h\nu$ vs $(\alpha h\nu)^2$ for (a) Pure ZnS and (b-e) ZnS/ ZnO core shell nanoparticles of different capping concentration
3.3.4.1 Particle size

Particle size was calculated by Brus equation (3.3). A computer code, for Brus equation was used for the calculation of particle size of ZnS. For these findings, nano-particle band gap \((E_{np})\) as calculated from the \((ahv)^2\) versus \(hv\) graph was used.

The Brus equation is given by:

\[
E_{np} = E_g + \frac{\hbar^2}{8r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r}
\]

(3.3)

where, \(E_{np}\) is nanoparticle band gap

- \(E_g = 3.68\) eV, is band gap of bulk ZnS
- \(r\) is the radius of the nanoparticle, in meters
- \(m_e^*\) is the effective mass of the electron, \(m_e\) is the mass of an electron
  - For ZnS, \(m_e^* = 0.25m_e\)
- \(m_h^*\) is the effective mass of the electron, \(m_h\) is the mass of a hole
  - For ZnS, \(m_h^* = 0.60m_e\)
- \(e\) is the charge on the electron
- \(\varepsilon\) is the dielectric constant of material and for ZnS, \(\varepsilon = 8.3\)
- \(\varepsilon_0 =\) vacuum permittivity constant

Using Brus equation, the average particle size of ZnS comes out to be 2.36 nm for nascent and 2.34 nm, 2.12 nm, 2.18 nm and 1.86 nm, corresponding to 0.1\%, 0.3 \%, 0.5\% and 1.0\% ZnO respectively in core shell nanocomposites. As the bohr exciton radius for ZnS is 5 nm, the average particle size of less than 5 nm confirms the quantum confinement effects of ZnS even in ZnS/ZnO nanocomposites.

3.3.5 Photoluminescence

Figure 3.9 shows the emission spectra of ZnS and ZnS/ZnO core shell nanoparticles. The emission spectra were recorded at a fixed excitation wavelength of 300 nm. Pure ZnS shows its characteristic defect related emission at around 415 nm (Sharma et al 2010). With increase in ZnO concentration in ZnS/ZnO core-shell nanocomposites, the luminescence shifted to around 400 nm and may be attributed to near band edge emission,
which originates due to the combination of free excitons through an exciton–exciton collision process. Other emission peaks around 450, 475, 480, 490, and 560 nm were also observed. It has been reported that the zinc interstitials, zinc vacancies, and oxygen vacancies were responsible for the visible emissions in ZnO (Mishra et al 2010; Peng et al 2006; Vanheusden et al 1996; Pal and Santiago 2005; Nyffenegger et al 1998). Zinc interstitials were responsible for the emission around 450 nm, while the emission at 480 nm and 490 nm may be originated from the transition due to the oxygen antisite vacancy defects (Kundu et al 2011; Schroer et al 1993; Kale et al 2007; Bhatti et al 2013). The green emission at around 560 nm can be originated from the transition by the defect level of surface or the oxygen vacancy centers. However, the major emission wavelength peak of core-shell ZnS/ZnO nanocomposites was observed to be tunable towards blue region with the increase in ZnO concentration.

Figure 3.9. Emission spectra of ZnS and ZnS/ZnO core shell nanostructures.
3.4 SILICA CAPPED ZnS QUANTUM DOTS

Zinc Sulphide (ZnS) / silica core-shell nanostructures were studied to exploit the effect of silica concentration on the ZnS nanoparticles. The core-shell nanostructures were prepared by chemical precipitation method starting with the synthesis of ZnS nanoparticles. The changes in the morphological and optical properties of core-shell nanoparticles with varying the concentration of silica in a core-shell combination were investigated. Before coating the fluorescent quantum dots with any capping agent, it is very important to optimize the quantum dots without any dopant. Therefore, the aqueous synthesis of uncapped ZnS, silica capped ZnS QDs for different capping concentrations (0.25%, 0.5%, 0.75% and 1.0%) have been discussed. These core-shell ZnS/silica nano-composites may be very suitable material for specific kind of tunable optoelectronic devices and biological applications.

For biological applications, the fluorescent intensity per quantum dot is an important factor. Various methods have been proposed to enhance the intensity of the photoluminescence. The single-crystalline nature of the ZnS core ensures high-quality semiconductor material characteristics, while the amorphous silica shell should help to prevent mechanical or radiation damage and suppress chemical reactivity, which often leads to oxidation and contamination in bare ZnS nanomaterials. For biorelated applications, the low toxicity of both ZnS and silica is highly desirable. In fact, some researchers have observed that amorphous SiO\textsubscript{2} exhibits low toxicity even in systems that do not respond well to its crystalline form. This section reports the enhancement effects of SiO\textsubscript{2} nanoparticles on pure ZnS. Generally, silica shell is chemically inert and optically transparent, so it is a feasible and effective way to avoid uncontrollable surface effects, thus improving the reliability and long-term stability of the devices. Therefore, the ZnS nanoparticles passivated by SiO\textsubscript{2} shell, would exhibit good photostability and high luminescent efficiency. A simple method to prepare core/shell ZnS/silica nanostructures is reported, with the emphasis on the tunability in morphological and optical properties which can be brought by altering the concentration of silica (0.25%, 0.5%, 0.75% and 1.0%) for a fixed amount of nanoparticles. The subsequent sections elaborate the synthesis and characterization of inorganically capped ZnS quantum dots.
3.4.1 Chemicals Used

The chemicals used in the present investigation for the synthesis of core-shell ZnS quantum dots are listed in Table 3.4.

**Table 3.4.** List of chemicals for synthesis of silica capped ZnS QDs

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc acetate dehydrate (99.5 %)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>Sodium Sulfide (99.1%)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>Tetra ethyl orthosilicate (TEOS) (99 %)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>Ammonia water (99 %)</td>
<td>Loba chemicals</td>
</tr>
<tr>
<td>De-ionized water</td>
<td>Nice</td>
</tr>
</tbody>
</table>

3.4.2 Synthesis of Silica Capped ZnS Quantum Dots

Synthesized QDs were studied for morphological and optical properties through various characterization techniques. For synthesis of silica capped ZnS 0.8 gm ZnS nanoparticles taken into a reaction flask with 0.5 ml of ammonia water and 5 ml of distilled water. Another flask was taken containing 0.25 ml of TEOS and 20 ml ethanol. Solution of first flask was mixed into second flask. After stirring for one hour, TEOS treated ZnS nanoparticles were obtained through filtering and drying process at 90\(^0\) in a vacuum oven. Different samples of ZnS/SiO\(_2\) were prepared by changing the concentration of TEOS (0.25%, 0.50%, 0.75% and 1.00%). The size of ZnS/SiO\(_2\) nanocomposite was controlled by varying the dosage of TEOS. Figure 3.10 presents a schematic for the synthesis of silica capped ZnS QDs.
Figure 3.10. Schematic for synthesis of inorganically silica capped ZnS QDs
3.5 CHARACTERIZATION OF SILICA CAPPED ZnS QUANTUM DOTS

The uncapped ZnS quantum dots and silica capped ZnS quantum dots (in various capping concentrations) were characterized by employing powder X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transformation infrared (FTIR) spectroscopy, UV-visible spectroscopy and energy resolved Photoluminescence spectroscopy.

3.5.1 X-Ray Diffraction

Bulk ZnS, exhibits two basic structures: the cubic zinc-blende structure and the hexagonal wurtzite structure. The most stable form of ZnS is the cubic structure and in the bulk it transforms to wurtzite structure at 1020 °C. The X-ray diffractograms of nascent and silica capped (0.25%, 0.50%, 0.75% and 1.00%) ZnS quantum dots are shown in Figure 3.11.

All the samples revealed pure zinc blende crystal structure and three broad peaks corresponding to the (111), (220) and (311) planes at 2θ values 28.95°, 48.34° and 56.95° respectively. It may be noted that the three peaks observed in the XRD pattern corresponds to those of the β-ZnS (cubic) reported in the JCPDS Powder Diffraction (File No: 5-0566). Broadening of XRD peaks represents the formation of nanocrystals of ZnS. These nanocrystals have lesser lattice planes compared to the bulk, which contributes to broadening of the peaks in the diffraction pattern. Broad diffraction peaks are attributed to small particle size effects (Qadri et al 1999). They are matched with a cubic (zinc blende) phase. From the XRD results, it is also observed that the intensity of the diffraction peaks slightly increases with the increase in the amount of SiO₂ concentration (Figure 3.11); but the shape and location of peaks did not change with the input amount of silica which signifies that neither any new phase was formed nor the crystalline structure changed with the addition of silica. Crystallite size of nanoparticles was calculated by Scherer’s formula (equation 3.1). The average crystallite size of all the samples was estimated from the half width of diffraction peaks (Table 3.5). It can be concluded that the crystallite size of synthesized silica capped ZnS QDs for various concentrations of silica are approximately 2 nm and silica capping on ZnS nanoparticles.
Figure 3.11. X-ray diffraction spectra of pure ZnS (inset), (a-d) ZnS/SiO$_2$ of different capping concentration core shell nanoparticles.
changes the crystallite size as seen with the broadening of XRD peaks. These results indicate that growth of ZnS was inhibited by silica capping.

Table 3.5. Crystallite size of uncapped and silica capped ZnS QDs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm) from (111) peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncapped and Undoped ZnS</td>
<td>1.80</td>
</tr>
<tr>
<td>0.25% silica capped ZnS</td>
<td>2.34</td>
</tr>
<tr>
<td>0.50% silica capped ZnS</td>
<td>2.22</td>
</tr>
<tr>
<td>0.75% silica capped ZnS</td>
<td>2.21</td>
</tr>
<tr>
<td>0.1% silica capped ZnS</td>
<td>2.20</td>
</tr>
</tbody>
</table>

3.5.2 Transmission Electron Microscopy

The specimen preparation has been done by finely dispersing the nanoparticles in spectroscopic grade ethanol and then putting a drop of the dispersed solution on the carbon coated copper grid. Figure 3.12 shows TEM image of uncapped and silica capped ZnS nanoparticles. TEM micrographs revealed the agglomeration of pure ZnS nanoparticles; this effect is attributed to the high surface to volume ratio. On the other hand, silica capped ZnS nanoparticles are monodispersed in nature. Hence, presence of silica capping on ZnS nanoparticles can prevent their agglomeration. The diameters of most of the particles lie in the range of 2 to 4 nm, which is in accordance with those obtained through XRD. It was also observed that the particle size increases to 5-8 nm with increasing concentration of SiO₂.
Figure 3.12. Transmission electron micrographs showing formation of (a) uncapped ZnS (b) 0.50% silica capped ZnS and (c) 1.0% capped ZnS QDs
3.5.3 Fourier Transforms Infra-Red (FTIR) Spectroscopy

A small amount of quantum dots were mixed with KBr and then pressed into a disc for FTIR analysis in order to investigate the surface properties of synthesized core-shell QDs. Figure 3.13 shows the FTIR spectra of uncapped ZnS, silica capped (0.25%, 0.50%, 0.75% and 1.00%) ZnS quantum dots. Different features were observed in the wave number range of 500 - 4000 cm\(^{-1}\). Wang et al (2010) reported that the existence of bands around 3000 – 3600 cm\(^{-1}\) for ZnS, is due to the hydrogen stretching frequency (OH stretching). The broad absorption peaks around 3200 cm\(^{-1}\) and 2550 cm\(^{-1}\) were attributed to O-H stretching and peaks around 2900 cm\(^{-1}\) were due to C-H (acetate) stretching. The absorption peaks in the range of 2300 - 2400 cm\(^{-1}\) were attributed to the existence of CO\(_2\) molecule in air. Bands around 900-1500 cm\(^{-1}\) were due to the oxygen stretching and bending frequency. Two principal absorption peaks were observed between 1650 and 1400 cm\(^{-1}\) corresponding to the asymmetric and symmetric stretching of the carboxyl group (C=O). The deformation bands of C=O can also be observed around 1019 cm\(^{-1}\) (Alaria et al 2005). However, bands around 1200 and 1100 cm\(^{-1}\) were attributed to the characteristic frequency of inorganic ions. The peak 486 cm\(^{-1}\) was assigned to the metal – oxygen bonds while the peak at 617 cm\(^{-1}\) originate from ZnS bond, possibly due to Zn-S stretching (Staurt 2004). Viswanatha et al (2012) reported that the band near 600 cm\(^{-1}\) can be attributed to the Zn-O stretching mode. The broad absorption peak in the range of 3000 -3600 cm\(^{-1}\) corresponding to OH group indicates the existence of water absorbed in the surface of nanocrystals.

FTIR spectra in the present investigations are in accordance with the standard values given in the literature both for nascent ZnS as well for ZnS/ nanocomposites. However, the small changes can be attributed to the formation of nanophase. A small absorption band due to Si–O–Si vibrations (Peng et al 1997; Swann and Patwardhan 2011 ) appearing at 1105 cm\(^{-1}\) (Figure 3.13d), at 814 cm\(^{-1}\)and 588 cm\(^{-1}\) (Figure 3.13c) was observed for silica-coated ZnS, which revealed that a Si–O–Si network formed as a component of the SiO\(_2\) shell structure. It was also observed that in case of ZnS/SiO\(_2\) nanocomposite formation, the FTIR peak intensity varies appreciably with the slight modification in wave number.
Figure 3.13. FTIR spectra of (a) uncapped ZnS, (b-e) silica capped ZnS QDs
3.5.4 UV-Visible Absorption Spectroscopy

The variations of optical absorbance as a function of wavelength for ZnS and silica capped ZnS quantum dots are shown in Figure 3.14. The absorption peaks were observed at 322 nm for pure ZnS, whereas at 323, 324, 320 and 324 nm wavelength corresponding to 0.25%, 0.5%, 0.75% and for 1.0% concentration of silica in capped ZnS quantum dots respectively. For calculating the direct bandgap value, a graph of \((ahv)^2\) versus \(hv\) was plotted (Figure 3.15). By extrapolating the straight portion of the graph on \(hv\) axis at \(\alpha = 0\), the optical band gaps were calculated and found to be 3.8 eV for pure, and 3.78, 3.775, 3.824 and 3.73 eV, corresponding to capping concentrations of 0.25%, 0.5%, 0.75% and 1.0% with silica respectively. A maximum band gap of 3.824 eV was observed corresponding to the capping concentration of 0.75% with silica, which represents better confinement effect. Moreover, the strong quantum confinement effects are manifested by the increased band gap in all the samples as compared to a band gap of 3.68 eV for bulk ZnS.

![Figure 3.14. UV-Visible Absorption spectra of uncapped ZnS and silica capped ZnS QDs](image-url)
Figure 3.15: Graph between $h\nu$ vs $(\alpha h\nu)^2$ for (a) pure ZnS and (b-f) for different ZnS:Mn/SiO$_2$ ratios.
3.5.5 Photoluminescence

In order to examine the tenability in the emission wavelength or emission intensity, energy resolved photoluminescence studies were conducted. The emission spectra were recorded at fixed excitation wavelength (300 nm). The recorded PL spectra have been smoothened using the Gaussian function of Nonlinear Curve Fit tool in the OriginPro 8®. Figure 3.16 shows the emission spectra of ZnS/SiO₂ core shell nanoparticles for different concentrations (0.25%, 0.50%, 0.75% and 1.00%) of SiO₂. Maximum PL was observed in 0.25% doped ZnS/SiO₂. Characteristic defect related emission for pure ZnS was observed at 415 nm (Mu et al 2005). The luminescence is blue shifted with increasing concentration of SiO₂ in ZnS/SiO₂ core-shell nanocomposites. The effect may be attributed to near band edge emission, which originates due to the combination of free excitons through an exciton–exciton collision process.

Figure 3.16. Emission spectra of uncapped ZnS and silica capped ZnS QDs.
In general, defect related emission is suppressed by the capping with silica (Figure 3.16). Existence of other emission peaks around 360, 450 and 575 nm was also observed. Existence of silica green band at 360 nm is attributed to the presence of Si-H species at the silica surface. It has been observed by many researchers that the zinc interstitials, zinc vacancies, and oxygen vacancies are responsible for the visible emissions in ZnS/SiO$_2$ (Karar et al 2004; Jiang et al 2009; Ashkarran 2014; Sen et al 2014; Warad et al 2005). Zinc interstitials are primarily responsible for the emission around 450 nm, (Ahemen et al 2013; Alaria et al 2005). The green emission around 575 nm can be originated from the transition by the defect level of surface or the oxygen vacancy centers. However, the major emission wavelength peak of core-shell ZnS/SiO$_2$ nanocomposites appears to be tunable towards the blue region with the increase in SiO$_2$ concentration.
REFERENCES


