Chapter-V

ENHANCEMENT IN OPTICAL PROPERTIES OF Ce$^{3+}$-DOPED ZnS NANOCRYSTALS BY POLYMER EDTA

5.1 Introduction

In this chapter, synthesis of optimum concentration of Ce$^{3+}$ doped ZnS nanocrystals by simple chemical precipitation method using ethylenediaminetetraacetic acid (EDTA) as the capping agent has been explained. The effect of EDTA capping in the preparation of nanostructures has been studied by many researcher (Muhammad, et al., 2000; Dong En Zhang, et al., 2006; Saifullah, et al., 2009; Bo Liu, et al., 2010; Oihana Barrutia, et al., 2010; Hongxing Dong, et al., 2010; Shulan Zhao, et al., 2011; Hejuan Song, et al., 2013). The possible capping mechanisms of EDTA are briefly explained.

5.2 Results and discussion

5.2.1 X-ray diffraction (XRD)

The XRD patterns of uncapped and various concentrations of EDTA capped ZnS: Ce$^{3+}$ nanocrystals are shown in Fig. 5.1. All samples exhibit a predominantly zinc blende crystal structure with planes in the (111), (220) and (311) directions. No diffraction peaks from other crystalline forms were detected, which indicates a high purity and well crystallinity of the synthesized products. However, on capping the broadening of peaks in the diffraction patterns is noted. The broadening can be indexed from micro straining of the nanocrystal structure, which arises from dislocation and twinning. From the X-ray diffraction peak
widths, the diameter of the nanocrystals was estimated through Scherrer formula. The estimated particle sizes are 22, 12, 7.27, 15.12 and 2.88 nm for uncapped and nanocrystals capped with 1.25, 2.5, 3.75 and 5% of EDTA respectively. When compared with uncapped particles, all the capped particles show reduced size as result of capping.

The mechanism behind the formation of size reduced particles is explained as follows. After introducing polymer into the reaction mixture, Zn$^{2+}$ ions form a complex with EDTA, this results in particle capping upon nucleation. Upon titration of thiourea into preformed Zn-EDTA complex, a competition for the metal between the sulfide and EDTA is introduced with the reaction further proceeding, formation of EDTA capped ZnS progresses by displacement of EDTA with S$^2$ at the Zn–EDTA complex. By using appropriate amounts of EDTA and thiourea, the conditions described here allow efficient incorporation of the sulfide into Zn–EDTA complex to form nanocrystals. During the process, the introduction of EDTA not only stabilized the small particles and inhibited their agglomeration but rendered the ZnS nanocrystals hydrophilic surface due to the existence of –COOH group in EDTA molecules which absorbed in the particle surface.

The nanoparticle formation takes place due to agglomeration of the primary particles, which in this case is the single ZnS unit. Agglomeration number specifies the number of primary particles or molecules contained in a single nanoparticle of a given size. The calculated agglomeration numbers for various concentrations of EDTA are given in (Table 5.1). From the table, the lowest value of agglomeration number is predicted for the 5% of EDTA addition confirming its optimum capping level.
Fig. 5.1: XRD patterns of uncapped and different concentrations of EDTA capped ZnS: Ce$^{3+}$ nanoparticles.
Table: 5.1

The calculated agglomeration number for various concentrations of EDTA

<table>
<thead>
<tr>
<th>Polymer concentrations in volume percentage</th>
<th>Nanoparticle Radius (r)</th>
<th>Agglomeration number (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>6</td>
<td>22,852</td>
</tr>
<tr>
<td>2.50</td>
<td>3.63</td>
<td>5060</td>
</tr>
<tr>
<td>3.75</td>
<td>7.56</td>
<td>45714</td>
</tr>
<tr>
<td>5</td>
<td>1.44</td>
<td>316</td>
</tr>
</tbody>
</table>

5.2.2 UV-Vis absorption spectra

UV-Visible absorption analysis is an eminent technique for the study of semiconductor nanoparticles in the nanoscale. The absorption spectrum may provide sufficient information regarding the size of the particles. The UV-Vis absorption spectra of present study samples are shown in Fig.5.2. The absorption peaks were observed around 298, 295, 293, 297, and 290 nm corresponding to uncapped and EDTA capped at 1.25, 2.5, 3.75 and 5% respectively. When compared with uncapped particles all the absorption peaks of capped particles exhibit appreciable blue shift as a result of quantum confinement effect.

This quantum confinement can be used as a measure of particles size and size distribution (Zhu, et al., 2006; Sarhaddi, et al., 2010). According to the formula $E_g = \frac{hc}{\lambda}$ eV, the calculated band gap values are 4.19, 4.22, 4.16, and 4.27 eV for 1.25, 2.5, 3.75 and 5% of capped particles respectively. For uncapped
particles the value is 4.15 eV. From this result, it is realised that the size of the particles might have controlled by surfactant addition.

![Graph showing UV-Vis absorption spectra of uncapped and different concentrations of EDTA capped ZnS: Ce$^{3+}$.

5.2.3 Photoluminescence (PL)

Fig. 5.2 shows the PL spectra of uncapped and capped nanocrystals. All the spectra exhibit mainly two emission peaks one at UV and other at visible ranges. These two emission bands are caused by Ce$^{3+}$ ions. The valid transition processes are shown in Fig. 3.3 (b and c), ZnS nanocrystals absorbed energy from the excitation source and transferred it nonradiatively to
luminescent centres (Ce\(^{3+}\) ions). Now the single electron in the 4f orbital of Ce\(^{3+}\) gets transferred to 5d level. The 5d excited configuration is split by the crystal field into two components (\(^2\text{D}_{5/2}\) and \(^2\text{D}_{3/2}\)), and 4f ground state configuration yields two components (\(^2\text{F}_{7/2}\) and \(^2\text{F}_{5/2}\)) due to spin orbital coupling. The Ce\(^{3+}\) emission originates from the lowest crystal field component of the 5d configuration to the two levels of the ground state giving rise to two emission peaks one at UV region and the other at visible region, by the 5d→4f transitions of Ce\(^{3+}\) ions. When compared with uncapped sample, all the concentrations of EDTA encapsulated samples (except 1.25%) show a red shift for both UV and visible bands, indicating quantum size effect (Table.5.2).

Fig.5.3a: PL emission spectra of uncapped and different concentrations of EDTA capped ZnS: Ce\(^{3+}\).
Fig. 5.3b: The intensity ratio of UV emission to visible emission calculated from PL spectra as a function of EDTA concentration. 0 volume percentage indicates without EDTA.

Fig. 5.3b shows the intensity ratio of UV emission to visible emission of the nanoparticles as a function of EDTA concentration from 0 to 5%. The PL intensity ratio initially decreases and then slightly increases, reaching its higher value at 5% concentration of EDTA. The obtained value is more than two fold the value for uncapped ZnS: Ce$^{3+}$. The PL intensity ratio is on evidence to evaluate the crystals quality. If higher is the crystal quality, greater should be the PL intensity ratio.
Table: 5.2

The PL transition behaviour of uncapped and EDTA capped ZnS: Ce$^{3+}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Emission due to Ce$^{3+}$ transition</th>
<th>Calculated size from Scherrer formula(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2D_{(5d_0)}$$\rightarrow$$^4F_{5/2}$</td>
<td>$2D_{(5d_0)}$$\rightarrow$$^4F_{7/2}$</td>
</tr>
<tr>
<td>ZnS: Ce$^{3+}$(1.5g)</td>
<td>353</td>
<td>602</td>
</tr>
<tr>
<td>EDTA (1.25%) capped Zn: Ce$^{3+}$</td>
<td>351</td>
<td>597</td>
</tr>
<tr>
<td>EDTA (2.5%) capped Zn: Ce$^{3+}$</td>
<td>356</td>
<td>607</td>
</tr>
<tr>
<td>EDTA (3.75%) capped Zn: Ce$^{3+}$</td>
<td>356</td>
<td>592</td>
</tr>
<tr>
<td>EDTA (5%) capped Zn: Ce$^{3+}$</td>
<td>358</td>
<td>606</td>
</tr>
</tbody>
</table>

5.2.4 Functional group analysis

FT-IR spectra of uncapped and EDTA capped nanocrystals are shown in Figure 5.4. A broad intense absorption centred in the range of 3350–3410 cm$^{-1}$ corresponding to –OH vibration, because all FTIR spectra were recorded by mixing samples with KBr, there may be some adsorbed water vapour, as KBr is hygroscopic. The peak positioned at 2365 cm$^{-1}$ is due to microstructures formation of the sample. The peak at 1578 cm$^{-1}$ is due to N-H bending, and the absorption at 1409 cm$^{-1}$ can be ascribed to CH$_2$ bending of C=O. A sharp absorption at 1111 cm$^{-1}$ indicates the presence of C-O stretching of carboxylic acid.
Fig. 5.4: FT-IR spectra of uncapped and different concentrations of EDTA capped ZnS: Ce$^{3+}$.

The peaks centred at ~475 and 625 cm$^{-1}$ are assigned to the Zn-S stretching vibrations. The obtained results are well matched with the reported results (Vijayalakshmi, et al., 2011). However, on increasing the level of capping, the functional groups of capping agent embedded with the sample are started to
diminish and completely removed on 5% of capping. This shows that 5% of capping is optimum for the harvest of small sized well dispersed nanoparticles.

5.2.5 Field Emission Scanning Electron Microscopy (FESEM)

Fig. 5.5a shows the FESEM image of 1.5g of cerium doped ZnS nanorods. The FESEM image reveals the aggregate of nanorods and the aggregate is actually flower-shape structured with multiple petals. All the petals are joined together through their bases in such a way that the flower exhibits a spherical shape. Each petal of this flower shaped structure is about 24 - 26 nm in diameter and about 120-130 nm in length.

The change in morphology of the cerium doped ZnS as a function of EDTA capping is evidenced by the FESEM image presented in Fig.5.5b. On 5% of EDTA capping, variation from rod to spherical morphology is observed. The possible mechanism behind the change in morphology is explained as follows. When polymer is added to the reaction mixture, they simply attach to the surface of growing particles by either steric or electrostatics repulsion and prevents the further growth of the particles. Here EDTA plays an important role in preventing the flocculation of particles, controlling the particle size and its morphology (Ajji, 2007; Wang, et al., 2005).
Fig. 5.5: FESEM images of (a) uncapped ZnS: Ce$^{3+}$ and (b) EDTA Capped ZnS: Ce$^{3+}$ (c) EDS spectrum of EDTA capped ZnS: Ce$^{3+}$ nanocrystals.

The nitrogen and oxygen atoms of EDTA can easily attach to the surface of ZnS and may slow down the growth speed of the crystal facets by reducing the surface free energy. As a kinetic controller, EDTA adsorbed on specific crystalline surfaces could significantly decrease their growth rate and lead to nanosized particles.
The EDS analysis was carried out on the capped ZnS: Ce$^{3+}$ and the results are shown in Fig.5.5 (c). In EDS spectrum, numerous well defined peaks were predicted to Zn, S and Ce which clearly indicate that the synthesized particles are incorporated with cerium.

5.2.6 High Resolution Transmission Electron Microscopy (HRTEM)

The morphology and particle sizes of the uncapped and EDTA capped cerium doped nanoparticles are further confirmed from the HRTEM studies, as shown in Fig. 5.6. The Fig. 5.6 (a) shows the HRTEM image of uncapped ZnS doped with 1.5g of Ce$^{3+}$.

Fig. 5.6 (b, c and d) shows the HRTEM image and SAED pattern of capped ZnS: Ce$^{3+}$. As shown in the figures, particles are highly mono dispersed and show perfect spherical morphology. From the HRTEM image the estimated particle size is about 4 nm and is consistent with the XRD result.

The SAED pattern consists of broad diffuse rings due to the smaller size (Fig.5.6c). The diffraction rings are indexed to (111), (220) and (311) planes, which confirm the presence of cubic phase.
Fig. 5.6: HRTEM images of (a) uncapped ZnS: Ce$^{3+}$, (b, c) EDTA capped ZnS: Ce$^{3+}$ and (d) SAED pattern of EDTA capped ZnS: Ce$^{3+}$. 
5.3 Conclusions

We have presented the synthesis of different sized cerium doped ZnS nanocrystals by simple chemical precipitation method using different volume percentages of capping agent. The results of XRD and HRTEM reveal that 5% of EDTA addition yields small sized particles and the mean crystallite size range was between 3 and 4 nm. Among the different capping concentrations, PL intensity ratio exhibits best result for 5% of capping. The change in morphology from nanorods of flower like structure to spherical particles as a result of capping was confirmed by FESEM. Considering the above results, 5% of EDTA addition as capping agent is very efficient for the preparation of cerium doped ZnS nanoparticles in order to control the particle size and also for modern optoelectronic applications.