Chapter 5

Synthesis and Characterization of Luminescent Cadmium Selenide Quantum Dots

5.1. Introduction

Colloidal semiconductor nanocrystals or quantum dots (QDs) have been an attractive class of nanometer sized building blocks due to their prodigious size-dependent optoelectronic properties and flexible processibility [1-4]. As a result, these materials find potential applications in large number of areas such as solar light harvesting [5], light emitting diodes [6], low cost thin film transistors [7], photocatalysis [8], bio-imaging [9], bio-sensing [10] and chemo-sensing [11] etc. The high density of surface charge traps, either due to intrinsic surface states or the functionality of capping molecules, can be utilized for the specific charge and energy transfer processes to design a new and unexplored kind of sensors/electronic devices [12]. Further, for fluorescence-tagging applications, QDs are advantageous over organic fluorophores due to their sharp and intense absorption associated with narrow and symmetric emission [13].

Among various semiconductor QDs, cadmium chalcogenides (II-VI compounds: CdX (X= S, Se, Te)) are more attractive materials since their emission spectra covers most of the visible region due to quantum confinement effect [14]. Different strategies for the synthesis of these nanomaterials have been developed, so that their composition, size, shape, and surface properties can be systematically controlled with an exceptionally high degree [15]. Each one of these techniques has its own advantages and disadvantages; an interesting and exhaustive recent review
covers various aspects of colloidal synthesis of various QDs [16]. The aqueous approach is an advantageous alternative to the traditionally used organic (organometallic) phase; it is mainly due to the simplicity, less toxicity, easy up-scalable for large quantity synthesis and easy functionalization with vast number of molecules, the last aspect yields more biocompatible materials. The main disadvantage of this route is the mild synthetic conditions, particularly the temperature, leading in poor crystallinity and size distribution [17]. Recently Subila et al. have nicely demonstrated the influence of crystallinity on fluorescent properties of CdSe QDs [18]. Nevertheless, with time the aqueous synthesis of nanomaterials has been gaining momentum, still many improvements are awaited.

Selenium oxide (SeO₂), which is easily water solvable, can be thought of as an alternative source of selenium (Se) ions in the synthesis of CdSe QDs. Further, it is low cost and less toxic as compared to other compounds of Se [19]. However, there are limited efforts to utilize this precursor by both aqueous and non-aqueous routes [20, 21]. Recently Wang et al. reported the CdSe QDs synthesis using SeO₂ as Se source and thioglycolic acid (TGA) as capping molecule in an aqueous medium. But the fluorescence quantum yield of their nanoparticles is low that is 4.1 % [22]. For last couple of years we have been working on the synthesis of CdSe QDs, we reported a good quality CdSe using hydrazine hydrate-Se as air stable complex [23]. It is our continued effort to replace the use of hazardous hydrazine hydrate by simple precursor. Herein, we report the synthesis of stable CdSe colloids of different size associated with tunable emission using a simple and water soluble Se precursor that yields good luminescent CdSe QDs.

**5.2. Preparation of CdSe Quantum Dots**

Cadmium chloride monohydrate (CdCl₂·H₂O), selenium dioxide (SeO₂), ammonia
(24%), Rhodamine B (with PL QY of 89 % in ethanol) was obtained from sd-Fine chemicals, India. 3-mercaptopropionic acid (3-MPA) was obtained from Sigma-Aldrich. All the chemicals were of analytic grade and were used without further purification. Double distilled water was used to prepare and process the nanoparticles.

Low-cost, greener and water soluble reagents have been used for the synthesis of CdSe QDs. A typical synthetic procedure of CdSe QDs is briefly described below. Firstly, 200 mM CdCl$_2$.H$_2$O is dissolved in distilled water to which 250 mM 3-MPA is added. The solution is not completely clear and hence ammonia is added drop by drop till a clear solution was obtained. In a separate flask, 50 mM SeO$_2$ is dissolved in water, it is readily soluble in water. This mixture is slowly added to the above solution. The pH value of the reaction mixture plays a very important role in the aqueous synthesis of semiconductor quantum dots, ensuring their stability and providing control to their growth. The optimum pH value for the QD synthesis depends strongly on the nature of the stabilizer [24]. In the present synthesis protocol, the initial pH of cadmium precursor solution after the addition 3-mercaptopropionic acid was ~ 4.5. The pH of the solution was adjusted to 11 by dropwise addition of ammonia to get a clear solution. In the absence of ammonia and keeping the other synthetic parameters fixed, a relatively fast and uncontrolled growth of QDs was observed. Similarly, in case of selenium dioxide (SeO$_2$), for the formation of selenium ions the presence of ammonia is a crucial parameter. The precursors are converted to CdSe QDs by refluxing the reaction mixture close to 100 °C under open air conditions with condenser attached. Samples S1, S2 and S3 were prepared by choosing the volume ratio of Cd/Se as 1:1, 1:1 and 1:2 respectively. Temperatures for all the samples were maintained at 100 °C and the solutions were refluxed for different time to obtain different sizes of CdSe QDs. Initially the solution is clear, just after 15 min
of heating the sample turns light turbid. For S1, the sample is heated for ~30 min till it turns white in color; for S2 the same solution is heated for one hour till it turns yellow in color and for S3 the solution is heated for one and half hours till it turns orange in color. Later, all the colloids are allowed to cool under open conditions. Reactions were also carried out for a longer duration that gives red color precipitate that appears to be more close to the bulk. It is observed that the last sample is very weak fluorescent and hence it is not taken for further studies. The precipitates of S1, S2 and S3 were then vigorously stirred under room temperature before filtering, rinsed with distilled water and finally centrifuged and dried. The samples viewed in ambient light vary from white to orange in color.

5.3. Results and Discussion

5.3.1. Air Stable Selenium Precursor for Aqueous Synthesis

In the present report, SeO$_2$ has been used to generate aqueous source of selenium ions. It has a very good solubility in water (39.5 g /100 ml of water at 25°C) and gives a colorless, transparent selenious acid solution. Mixing of this solution with cationic solution of cadmium in water did not yield any precipitate of CdSe nanoparticles even after prolong heating at the boiling point of water. This indicates that Se is not in anionic form and hence there is no formation of CdSe. It is observed that the addition of 3-MPA to SeO$_2$ give s a white precipitate with time that slowly turns into reddish color precipitate. In order to get a clear solution of anionic source of Se, the starting solution of 50 mM SeO$_2$ was added with a drop of ammonia that gives a clear solution and finally, 250 mM 3-MPA is added, within 15 seconds it turns to yellow color and finally it becomes red. These solutions are shown in figure 5.1. (inset). It shows that addition of 3-MPA to aqueous solution of SeO$_2$ under the presence of little ammonia generates Se ions that is suitable for the development of aqueous synthesis of CdSe.
The optical absorption of this solution (reddish color) and the solution of SeO$_2$ prior to addition of 3-mercaptopropionic acid added results in selenium colloid (red color).

Figure 5.1: UV-Vis absorption spectra of (a) 50 mM SeO$_2$ dissolved in water (clear solution) in presence of 20 µl ammonia. (b) 50 mM SeO$_2$ dissolved in water in presence of 20 µl ammonia and 250 mM 3-mercaptopropionic acid added results in selenium colloid (red color).

nanoparticles. It is expected that it is the formation of Se colloid and hence this was subjected to further studies. The optical absorption of this solution (reddish color) and the solution of SeO$_2$ prior to addition of 3-MPA are shown in figure 5.1. The Se
The colloid shows absorption edge at 630 nm and the unreduced at 250 nm. The absorption edge at 630 nm is nothing but band gap absorption of Se nanoparticles [25]. An inset in figure 5.1 shows the room light photograph of these solutions. Further to confirm that it is Se, the collected precipitate was used for energy dispersive analysis of X-ray (EDAX) analysis and its morphology was done by SEM. The elemental analysis by EDAX clearly confirms that it is selenium (spectrum is not shown). The SEM picture is shown in figure 5.2, it is interesting to note that the precipitated powder gives sponge like structure having well connected tubular, the tube diameters are not uniform and the average bottle-neck diameter is in the range 200 to 250 nm.

Next, we discuss the formation of Se precursor by the present route. Selenious acid or selenite (SeO$_3^{2-}$) has long been known to react with thiols to form relatively unstable derivatives [26]. Painter et.al in 1941 proposed the reaction between the thiols and SeO$_2$ in aqueous medium and it is as follows:

$$\text{SeO}_2 (s) + \text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{SeO}_3 (aq)$$  \hspace{1cm} (1)

It is expected that thiols react with selenious acid (H$_2$SeO$_3$) according to the reaction,

$$\text{H}_2\text{SeO}_3 + 4\text{RSH} \rightarrow \text{RSSeSR} + \text{RSSR} + 3\text{H}_2\text{O}$$  \hspace{1cm} (2)

The derivatives RSSeSR referred as selenotrisulphides are important intermediate in the selenite metabolic pathway in cellular systems [26], but are relatively unstable and decomposes to disulphide and elemental selenium as shown below,

$$\text{RSSeSR} \rightarrow \text{RSSR} + \text{Se}$$  \hspace{1cm} (3)

Thus, the reaction (3) produces Se due to the reduction of selenious acid by thiols. Presently, this new precursor of Se ions has been successfully implemented to develop a new aqueous method for synthesis of CdSe nanoparticles.
5.3.2. X-Ray Diffraction and Surface Morphological Study

The powder X-ray diffraction patterns of the CdSe QDs of three different sizes are shown in figure 5.3. The pronounced peaks of (111), (220) and (311) at 2θ = 26.7, 43 and 50° respectively are seen, which are the reflection characteristic of zinc-blende phase of CdSe nanocrystallites. Sample S1 shows only one broad peak belonging to (111) reflection, the other peaks belonging to (220) and (311) start appearing for S2 and these peaks are more pronounce in case of sample S3. These results clearly indicate that CdSe has purely cubic zinc blende structure (JCPDS file.19-0191) and the particle size increases from S1 to S3. The cubic zinc blende phase structure has been found to be the most preferred phase for thiol stabilized cadmium chalcogenides.

Figure 5.2: Scanning electron micrograph (SEM) of Se nanoparticles extracted from red color solution of figure 1 (b) results in selenium colloid (red color).
QDs prepared via aqueous route in the low temperature regime (100 -240 °C) rather than the hexagonal wurtzite phase that usually forms at elevated temperature (above 300 °C) using TOP/TOPO capping molecules in organic phase synthesis [27]. The

**Figure 5.3:** X-ray diffraction pattern of CdSe quantum dots of three different sizes capped with 3-mercaptopropionic acid.
particle diameter $D$ is estimated by FWHM of the (111) peak by using Scherrer formula, $D = \frac{0.9 \lambda}{\beta \cos \theta}$ where $\lambda$ is X-ray wavelength (1.5406 Å), $\beta$ is FWHM and $\theta$ is the Bragg’s diffraction angle. The estimated particle size of the samples S1, S2 and S3 are 1.67, 2.7 and 2.9 nm, respectively. Nanocrystals synthesized by the aqueous approach do not possess a good degree of crystallinity as compared to organic phase synthesis due to a high bath temperature in the latter case [17].

TEM measurements are done on these samples to estimate the size and shape of nanoparticles. Figure 5.4 shows TEM image for sample S2 along with the high resolution image of single CdSe QD and selected area electron diffraction pattern (SAED) pattern are shown as an inset. It can be observed that the particles are spherical in shape. The images clearly show that the particles are agglomerated which is common for many aqueous solutions of thiol capped nanocrystals [28]. The presence of lattice planes in the high resolution image confirms that the nanocrystals have better crystallinity which is further supported by the SAED pattern. The estimated average particle size in this case is 3.1 nm. Similarly, the estimated average particle size for S1 and S3 are 1.8 and 3.3 nm, respectively. In all the cases, the particles in TEM analysis appeared to be spherical in shape. The particle size estimated from the TEM is slightly higher than those estimated from the X-ray powder diffraction due to the fact that the Scherrer formula estimates the size of single-crystalline domain but not the actual particle size [27]. The extra layer on each particle could be a disordered material. Further, to analyze the composition of these quantum dots the energy dispersive analysis of X-ray (EDAX) spectra were recorded. In addition to cadmium and selenium, the presence of sulphur suggests that capping molecules effectively bind with these nanocrystals and remain intact even after the solution processing.
5.3.3. FTIR Analysis

FTIR spectra of the three samples are shown in figure 5.5. The preparation of CdSe QDs capped with various thiols is facilitated by the binding affinity between the S-H end group of molecules and CdSe surface atoms. All the spectra given in figure 5 are of similar kind except the intensity of peaks and hence we consider S1 spectra to
assign the absorption bands. A broad absorption peak at around 3440 cm$^{-1}$ is assigned to the O-H vibration and the bands at 2923 and 2855 cm$^{-1}$ are due to the stretching vibrations of the alkyl chains of 3-MPA molecules. The absence of S-H stretching band around 2557 cm$^{-1}$ clearly indicates that thiolates are connected to the Cd$^{2+}$ sites.

**Figure 5.5:** FTIR spectra of 3-mercaptopropionic acid capped CdSe quantum dots S1, S2 and S3.
on the CdSe nanocrystallite surface via sulphur atom of organic molecule. The sharp peak at 1540 cm\(^{-1}\) can be assigned to the vibration of the carboxylate anion of MPA molecules. The band at 1420 cm\(^{-1}\) is due to the symmetric stretching vibration C-O. It is interesting to note all the samples show a sharp, prominent peak due to carboxylate ions and this result in a net negative charge on the outer surface of the nanoparticles thus preventing the nanoparticles from coagulation that leads to stable colloids of these nanoparticles. In fact our colloids are quite stable over a long period of time (more than couple of months). Thus the organic capping of CdSe QDs by 3-mercaptopropionic acid is confirmed by FTIR spectroscopy. The presence of the carboxylate anion peak in CdSe capped with thioalkyl acids has been clearly observed by other groups also [29].

### 5.3.4. Optical Properties

Figure 5.6 shows the photographs of isolated CdSe nanoparticles of different sizes redispersed in ethanol viewed under normal light and under UV light (368 nm of 9 W power). Samples which are white, yellow and orange in color under normal light emit fluorescent green, bright yellow and orange respectively under UV excitation, which clearly indicates the size tunability of these nanoparticles. The absorption spectra of 3-mercaptopropionic acid stabilized CdSe nanoparticles of three different sizes are shown in figure 5.7. With increase in heating time of reaction, the absorption edge shifts towards red, thus indicating the enhancement in CdSe nanoparticle size. The absorption onset for the three samples appeared at 425 nm, 461 nm and 541 nm, respectively, which is obviously blue shifted compared with bulk CdSe absorption at 716 nm. The particle size is estimated using a simple model based on the geometry of the semiconductor as a sphere via eqn. \( \Delta E_g = \frac{\hbar^2}{8a^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \) where \( \Delta E_g = (E_{g}^{n} - E_{g}^{b}) \) is the difference between the band gaps of nanoparticle \( (E_{g}^{n}) \) and that of bulk.
(\(E_g^b\) (CdSe \(E_g^b = 1.74\) eV) [30]. The particle size obtained for S1, S2, S3 are 1.7, 2.85 and 3.0 nm respectively. These values are quite close to that are estimated by XRD and TEM measurements.

The normalized photoluminescence (PL) spectra of CdSe QDs redispersed in ethanol are shown in figure 5.8. These QDs have strong luminescent emission intensity under excitation of ultraviolet light. The emission maxima of the QDs can be tuned in a wider range from 510 to 650 nm by changing synthetic conditions. These quantum dots exhibit broad photoluminescence bands which may be attributed to defect related emission. The reason for the generation of defect-related emission is due to the fact that extremely small diameter has a very high surface-to-volume ratio and hence a high-density of dangling bonds or traps, who’s complete passivation is rather incomplete due to hindrance created by the size of capping molecules [31]. The peak positions of PL spectra of samples S1, S2 and S3 are at 505, 549 and 647 nm, respectively. These emissions are well below their respective critical band gap absorption edge, in each case it is almost by 100 nm, this clearly indicates that defect

**Figure 5.6:** Photographs of CdSe colloids under normal light and under ultra-violet light illumination.
Figure 5.7: UV-Vis absorption spectra of CdSe quantum dots redispersed in ethanol.

Figure 5.8: Photoluminescence spectra of CdSe quantum dots redispersed in ethanol for three different samples.
levels are predominantly involved in the light emission process due to photoexcited carriers. Further, the PL spectrum of sample 2 was recorded for the crude and the isolated particles redispersed in ethanol. The isolated particles exhibit high PL intensity (four times) as compared to the crude solution, indicating that the surrounding liquid medium significantly affects the emission properties of these nanoparticles. Defect related or deep trap emission is quite common in small (< 3 nm) nanocrystals usually referred as ultra-small nanocrystals. Recently Coughlin et al. reported the synthesis of cysteinate capped CdSe QDs via aqueous route for quantum dot solar cell applications. The PL FWHM is ~ 250 nm. These ultra-small nanocrystals exhibit broadband emission covering the whole visible spectrum (420-710 nm) while not suffering from coagulation [31-33].

Most of the applications of semiconductor QDs demand a high fluorescence yield or simply quantum yield (PL QY). As mentioned above, PL QY of semiconductor QDs synthesized by aqueous route is quite poor as compared to organic phase synthesis. It is important to estimate this parameter of QDs, here we measured QY of CdSe nanoparticles using Rhodamine-B as a standard and ethanol as a solvent for dispersing both nanoparticles and dye molecules using the procedure given in Ref [34, 35] (QY of the dye is taken to be 89%). The formula used for quantum yield (QY) calculation is 

\[ Y = \text{QY}_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n^2_R} \]

Here R refers to Rhodamine B dye of known quantum yield (i.e. 89 %) and \( n \) refers to the indices of refraction of the respective solutions. ‘I’ is the fluorescence peak intensity. Since the sample and the Rhodamine dye were dispersed in the same solvent the ratio of refractive indices is equal to one. OD\(_R\) and OD are the optical densities of the reference dye and the sample in the solution respectively. At the excitation wavelength of respective samples the optical density (absorption intensity) of the
sample and the reference solutions are made equal by changing the concentration of dye [33]. The excitation wavelength of sample S1, S2 and S3 are 385, 395 and 475 nm respectively, these are chosen by measuring their absorption curves. The QY estimated is an average of three independent measurements for each sample. 

**Figure 5.9:** (a) Photographs of dry powders of CdSe of four different sizes. (b) One batch material synthesis of sample S2 filled in eppendorfs.
estimated QY for S1, S2 and S3 are 5, 24 and 2.6 % respectively. The aqueous synthesis was successfully carried out by us yielding up to 3 g of CdSe nanoparticles per synthesis and further scaling up is possible with good reproducibility. Figure 5.9 (a) photographs of dry powders of CdSe of four different sizes. The last sample is very weak fluorescent and hence is not taken into consideration. The sample S2 synthesized in a batch of 200 ml total solution yielded the final dried powder equal to 3 g. A photograph of this one batch material filled in eppendorfs along with scale is shown in figure 5.9 (b). The CdSe nanoparticles were thoroughly washed and kept in dry state under ambient conditions and they remained stable for more than a year and are readily redispersible in ethanol and aqueous solutions.

The highest QY reported by Wang et al. using SeO\textsubscript{2} as Se source is 4.1% and these particles have a broad PL emission (150 nm) [22]. Unfortunately, CdSe QDs synthesized with TGA in aqueous solution generally have broad PL emission, although, CdTe synthesized with 3-MPA or TGA as capping agent by aqueous route have a narrow PL band (30 nm) [36]. In the present work the FWHM of the PL bands of CdSe QDs is around 100 nm. The role of capping molecules and aqueous synthetic conditions (including temperature, molarity, pH etc) are needed to be studied in detail to improve the quality of these nanoparticles. Thus the present synthetic approach can be generalized for the formation of high-quality metal-selenide and metal-telluride nanocrystals using SeO\textsubscript{2} as Se source and Tellurium dioxide as tellurium source respectively.

5.4. Conclusions

An alternative approach for the synthesis of CdSe QDs using SeO\textsubscript{2} as selenium source in aqueous solution has been reported. In the present work, worth mentioning is the simplicity in synthesis (low cost and less hazardous precursors), scalability, good
reproducibility and stability (powders in dried form kept under ambient conditions remain stable for more than a year) of CdSe QDs. This results show a high photostability of as prepared QDs. These QDs display significant blue shift in optical absorption edge as compared to their bulk absorption edge (716 nm), indicating a strong quantum confinement effect due to particle size. These nanoparticles are good fluorescent and for one of QDs the fluorescent quantum yield is close to 24 %, which is reasonably superior in case of aqueous synthesis. Extending exploration of this synthesis protocol to synthesis CdSe QDs and other metal selenide nanocrystals using different thiols as effective size-regulating agents with its extensive structural and optical characterization has been an open issue for further investigation.
References


