Green Route Synthesis of High Quality CdSe Quantum Dots

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Cadmium precursors with acetylacetonate, less toxic than Me_2Cd give one-step synthesis procedure for CdSe quantum dots (QDs). Powder Xray diffraction shows hexagonal structure of QDs. TEM and HRTEM images of QDs reveal that they are almost mono disperse and size is of the order of 5 nm. It is observed that the precursor and reaction time affect size. The size of QDs increases with reaction time. The temporal growth was monitored by UV–Vis spectroscopy (up to 20 min).

Keywords: Cadmium selenide, X-ray diffraction, Temporal growth.

1. INTRODUCTION

QDs (Quantum dots), also known as colloidal semiconductor nanocrytals, are generally composed of II-VI and III-V groups of table of elements. Their optical and electrical properties are strongly size dependent [1-4]. High quality semiconductor nanocrystals have many applications such as thin film light-emitting devices, non-linear optical devices, solar cells and life science [5-8]. On the other hand, most of chemical materials which used for their production are toxic, expensive, and even explosive. Cadmium selenide (CdSe) can have both of solid hexagonal or cubic crystal structures with dark red appearance. It is an n-type semiconductor material with a band gap of 1.74 eV at 300°K. The molecular weight of CdSe is 191.37g/mol where Cd is 58.74% and Se is 41.26% [5]. Bulk form of CdSe is not very interesting but CdSe nanoparticles are one of the most interesting semiconductors which many current researches have focused on their characteristics and applications. Researchers are concentrating on developing controlled synthesis of CdSe nanoparticles. It has useful properties for optoelectronic devices, laser diodes, nanosensing, biomedical imaging and high efficiency solar cells [5-7].

In this study, CdSe nanoparticles were prepared and the crystal structure, particles size distribution and optical properties of them were investigated. The optical properties of the CdSe nanoparticles were also assessed at different temperatures.

2. EXPERIMENTAL DETAILS

The reagent grade cadmium(II) acetate hydrate (99.99%), cadmium(II) acetylacetonate (99.99%), selenium (99.5%, 100 mesh), trioctylphosphine oxide (TOPO), trioctylphosphine (TOP), 1-octadecene (ODE), oleic acid (OA), octadecylamine (ODA)

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Anil Kumar Malik

were procured from Aldrich (USA) and used as received. All organic solvents (HPLC grade) were obtained from Merck (India). Other chemicals were procured locally.

The synthesis of CdSe QDs was conducted in a moisture and oxygen-free atmosphere. CdSe, QDs were synthesized using a one-step process involving reduction of cadmium(II) acetylacetonate or acetate. A 0.1 mmol of Se was dissolved in 1 mL of tri-noctylphosphine (TOP) and kept in a syringe as TOPSe. A 0.1 mmol of cadmium precursor (cadmium(II) acetylacetonate or acetate) and 0.4 mmol of oleic acid (OA) were added to 4 mL of 1-octadecene (ODE) and heated to 240 °C with continuous stirring under an N₂ atmosphere until a colorless solution was obtained. The temperature was lowered to room temperature and 1.5 g of octadecylamine (ODA) and 1.5 g of tri-noctylphosphine (TOPO) were added to the mixture, which was further heated to 300 °C under N_2 atmosphere with continuous stirring. After attaining a constant temperature, TOPSe solution was injected swiftly in the reaction mixture. The temperature fell down to 270 °C and the reaction mixture was allowed to reflux. Aliquots of the reaction mixture were withdrawn at various intervals. They were diluted with hexane and subjected to photoluminescence and UV absorption spectral studies to understand the formation and size of the QDs. The reaction mixture was cooled down and washed thrice with a 1:1 mixture of hexane and methanol, allowing separation of the QDs in hexane and the unreacted precursors. Finally, the QDs were precipitated by adding ethanol to the hexane layer, separated by centrifugation and redissolved in hexane.

3. PROPERTIES ASSESSMENT

UV-visible spectra (200-800) were recorded at room temperature with a Lambda Bio 20 (Perkin Elmer) UV-visible spectrophotometer. The photoluminescence (PL) spectra were taken on a Horiba Scientific, Fluoromax-4 spectrofluorometer fitted with a PMT emission detector with 5 nm excitation and emission slits. The excitation wavelength was kept at 400 nm for all of the measurements reported here. The same sample was used for absorption and photoluminescence measurements and the concentration was kept low so as to get an absorbance below 0.1. The scan range chosen for each sample was 200-800 nm using a 0.5 s integration time. The diluted solution was placed in a quartz fluorescence cell with 10 mm path length. The powder XRD measurements were made on a Bruker D8 advanced powder X-ray diffractometer with 20 range 10 to 70° with the step size of 0.05° and step time 1 s. A Cu radiation source was used along with a polycapillary lens and a Ni filter to provide the incident beam. The power settings on the X-ray generator were 45 kV and 40 mA. The samples of CdSe used for the powder XRD measurements were prepared by placing a colloidal solution of CdSe, QDs on a glass slide and the solvent was removed by drying in a vacuum oven at 30°C for several hours. TEM images were recorded on a Philips instrument model CM-12 operated at an accelerating voltage of 100 kV and high resolution TEM on an instrument model FEI Technai G220 with accelerating voltage of 200 kV. Samples were prepared on 200-mesh carbon coated Cu grids by dropping 10 L of solutions the QDs in hexane and allowing the solvent to evaporate.

4. RESULTS AND DISCUSSION

4.1. Optical Properties

The quality of CdSe, QDs synthesized by present procedure in a non-coordinating solvent octadecene, was found good with nearly monodisperse size and shape. The temporal study was undertaken to investigate the crystal growth of CdSe, QDs. For these studies (i) the ratio of cadmium precursor cadmium(II) acetylacetonate to selenium, (ii) the moles of (TOPO) and ODA and (iii) the temperature of the reaction mixture over a 20 minutes time period were kept constant. From reaction mixture aliquots were taken and quenched in hexane at time intervals of 1, 3, 5, 10, 15, and 20 minutes from the start.

The progress of CdSe crystal growth in each aliguot was monitored by taking their UV-Visble and photoluminescence spectra. The results are shown in Figures 1 The changes observed in QDs were insignificant when reaction time was greater than 20 min. The sizes were calculated from UV-visible spectra [8] and were found in the range 4.32 with cadmium(II) acetylacetonate. It is worth noticing that the QDs obtained from two precursors under identical reaction conditions differ only marginally in size. The photoluminescence spectra reveal that the value of full width at half maximum (FWHM) of the photoluminescence peaks of QDs obtained after 20 min from cadmium(II) acetylacetonate is 23±2 nm. Our values are lower than those, reported [9] earlier (~30 nm) for CdSe, QDs obtained from cadmium(II) acetylacetonate precursor. The photoluminescence properties of QDs prepared by present procedure are superior to those reported earlier [9]. A red shift (color changed from green to wine red) in photoluminescence peaks of QDs with increasing reaction time of their synthesis, was observed for both the cadmium precursors indicating the dependence of their size on reaction time. In Figures 1 and 2, photoluminescence spectra recorded for varying reaction time are exhibited. A systematic increase in peak wavelength from 579 to 601 nm in case of cadmium(II) acetylacetonate precursor was observed. The red shifts were also observed in case of absorption spectra with increase in reaction time. The band gaps of CdSe, QDs obtained after 20 min reaction time using cadmium(II) acetylacetonate is 2.08. Figures 1 and 2 also show that wavelength of maximum absorption in UV-Vis spectra of QDs increases with reaction time.





Fig. 1: UV-VIS and photoluminescence spectra of CdSe, QDs synthesized from cadmium acetylacetonate.

4.2. XRD Analysis

The powder-XRD patterns obtained for QDs prepared from cadmium(II) acetylacetonate is shown in Figure 2. This suggest that CdSe, QDs have wurtzite structure. The wurtzite structure is commonly formed in high temperature ($\geq 270^{\circ}$ C) synthesis [10] of CdSe, QDs carried in TOPO (containing amine). This is consistent with our results. The low or room temperature synthesis results in zinc blende structure which sometimes also has faults

Anil Kumar Malik

[11]. Peng *et al.* [12] synthesized wurtzite structure (hexagonal) of CdSe in TOPO at 300°C. However in some other solvents different results have been reported. Sasamoto *et al.* [14] reported that CdSe synthesized at 60°C gave cubic particles and hexagonal at 80°C when sodium sulphite was used as a stabilizing agent and sodium dicarboxylate as a complexing agent. Palchik *et al.* [10] observed formation of cubic CdSe at 287°C when the solvent used was triethylene glycol and formation of hexagonal CdSe at 196°C in ethylene glycol. The small size of presently prepared CdSe, QDs is indicated by broad nature of X-ray diffraction peaks as shown in Figure 2. The average diameter of these QDs by Scherrer's formula [11] has been found to be 4.02 when particles were obtained from cadmium(II) acetylacetonate.





The TEM and HRTEM images of the QDs are given in Figure 3. The average diameter of QDs from TEM has also been found to be 4.12 nm for cadmium(II) acetylacetonate. This result about size are consistent with those obtained from powder XRD and absorption spectra. The TEM images suggest that QDs are nearly spherical and mono-disperse. The HRTEM images also reveal the high crystallinity of the QDs and their size of the order ≤ 4 nm.



Fig. 3: TEM (100 nm scale) and HRTEM (at corner, 5 nm scale) images of CdSe nanoparticles synthesized from cadmium acetylacetonate.

5. CONCLUSION

The similar hexagonal CdSe, QDs of good dispersity and small size of the order ≤ 4 nm have been prepared from cadmium(II) acetylacetonate. Their photoluminescence properties are better than those of earlier reports [8,12,13] in terms of narrow wavelength range as revealed by FWHM values (23±2 and 14±2 nm). The other advantages of the present route are: (i) the precursors, cadmium(II) acetylacetonate are less toxic, more stable and crystalline and (ii) solvents used are not expensive.

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