

## Synthesis, Structural and Optical Investigation of CdSe semiconductor Quantum Dots

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### ABSTRACT

In this paper, we present a simple synthetic route for the development of high quality CdSe quantum dots TGA capped in aqueous solutions. CdSe semiconducting Quantum dots were prepared by a chemical method at room temperature. The crystal structure, morphology, spectral and compositional properties were analyzed from powder X-ray Diffraction, High resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV-Vis absorbance and Photoluminescence (PL), Fourier transform infrared (FTIR) and Fourier transform RAMAN (FT-RAMAN) techniques. The XRD results depicted the formation of CdSe quantum dots with the average crystallite size of 3 nm and 4 nm, which is in accordance with observations from HRTEM and TEM micrographs predict an average particle diameter of the QDs range between 2-3 nm. The UV-Vis absorbance peaks indicate the broad absorption behavior of the synthesized CdSe quantum dots. The calculated band gap energy was 2.55 eV and further it is found the particle size estimated from the maximum excitonic peaks for CdSe 2.7 nm. The photoluminescence studies evidenced that the luminesce property of quantum dots can be varied by systematically tuning precursor concentrations. The PL emission spectrum depicts the strong excitation peaks for the synthesized CdSe QDs with peaks centered at 603 nm. The capping of TGA was confirmed from FTIR and FT-RAMAN studies. From the FTIR spectra it is observed that, for the synthesized CdSe QDs almost all the peaks are common with slightly shifting behavior towards larger and shorter wave numbers. FT-Raman analysis was performed to study the sample qualities such as microcrystallinity, homogeneity and surface conditions for the as synthesized CdSe quantum dot. The resulting colloids are very stable, and no precipitate is observed over a period of 6 months.

**Keywords:** CdSe quantum dots, XRD, photoluminescence, TEM, SEM, FT-IR, FT-Raman.

### 1. Introduction:

Nanostructured materials have attracted a great transaction of attention in the last few years for their unique characteristics that cannot be obtained from conventional



macroscopic materials. Owing to the quantum size effects and surface effects, nanoparticles can display novel optical, electronic, magnetic, chemical and structural properties that might find many important technological applications. In the past decade, colloidal II-VI semiconductor nanocrystals, often referred to as quantum dots or QDs, have attracted scientists' intensive attention in the preparation methods, fundamental studies, because of their size-dependent (and thus tunable) photo- and electro-luminescence properties and promising applications in optoelectronics and biomedical applications [1]. QDs, whose size falls in the range of 1~10 nm, have been made to be the ideal fluorescent labels for the wavelength-luminance multichannel transmission system, because of their unique optical properties. The recognition of strongly size and shape dependent physical/chemical properties of nanostructure materials has stimulated efforts towards the fabrication of nanocrystals in a systematic and controlled way [2]. Chemically synthesized nanostructures and their assembly are of fundamental importance due to their unique dimension dependent properties and their potential applications as building blocks in nanoelectronics, nano-optonics, nanosensors & actuators, and in biology [3-4]. Recently much interest has been aroused in the preparation and assembly of semiconductor QDs due to their narrow and intensive emission spectra, continuous absorption band, high chemical and photo bleaching stability, processability and surface functionality. There is a wide range of very efficient light emitting QDs, which can be synthesized both in organic or as aqueous solutions [5-6].

## **2. Experimental Details**

### **2.1. Sample preparation:**

All the chemicals used in the present work were of analytical grade, and the reactions were carried out under open-air conditions using triply distilled water. Selenium (99.99%), cadmium chloride ( $\text{CdCl}_2$ ) powder (99.9%), thioglycolic acid (TGA) (98% pure) were obtained from Sigma-Aldrich and hydrazine hydrate ( $\text{N}_2\text{H}_4\text{H}_2\text{O}$ ) (99%) and acetone (AR) were obtained from Sd-Fine Chemicals, India.

0.1M of highly pure  $\text{CdCl}_2$  powder and 0.2 M of thioglycolic acid (TGA) are added in 250 ml of deionised water and stirred for 10-15 minutes which resulted into a white buffer solution. 0.05M of pure elemental Selenium (99.9%) is added with 0.05 M of Hydrazine hydrate. This dark brown solution is added to the white buffer solution drop by drop at room temperature. Initially the colour of the solution was light orange and after 1-2 hours the solution turns out to yellow colour.

## 2.2. Characterization:

The structural properties of the synthesized samples were studied using powder X-ray diffraction on a Rich Seifer with monochromatic nickel filtered Cu K $\alpha$  radiation ( $\lambda = 1.5461$  Å) in the  $2\theta$  range of  $10^\circ$  to  $80^\circ$ . The size and shape of the synthesized nanocrystals were estimated using the JEOL JEM 2100. High Resolution Transmission Electron Microscopy (HR-TEM) with an accelerating voltage of 200 kV coupled with EDS. Scanning electron microscopy (SEM) was applied to investigate the size and morphology, which was carried out under JEM-3010 with an operating voltage 200 kV. Transition electron microscopy (TEM) was obtained using a JEOL JEM-2100 instrument with accelerating voltage of 200 kV.

UV-Vis spectroscopy analysis was carried out to study the optical properties using Analytica spectrophotometer in the wavelength range of 200 nm to 800 nm. The photoluminescence spectra of the samples were recorded with a Jobin Yvon Fluorolog-3-11 spectrofluorimeter with Xenon lamp 450W as source at room temperature using 400 nm as the excitation wavelength. The FTIR spectra of the samples were obtained by the conventional KBr pellet technique, in a Perkin Elmer spectrometer operating in the range of 4000 to 400  $\text{cm}^{-1}$ . The FT-RAMAN spectra of the samples were obtained by using Bruker's FT-Raman Spectrometer 2010.

## 3. Results and Discussion

### 3.1. Structural analysis:

X-ray powder patterns were recorded in the powder of nanoparticles, and the pattern is shown in Figure 1. The peaks of CdSe have been obtained due to diffraction corresponding to (1 1 1), (2 2 0), (3 1 1) reflections, which is in a very good agreement with cubic CdSe structure. The information on the particle size ( $A$ ) of CdSe Qd's has been obtained from the following Scherrer relations,

$$A = 0.94 \lambda / \beta \cos\theta$$

The peak broadening indicated the fine nanocrystalline nature and the reduced size for the synthesized samples.

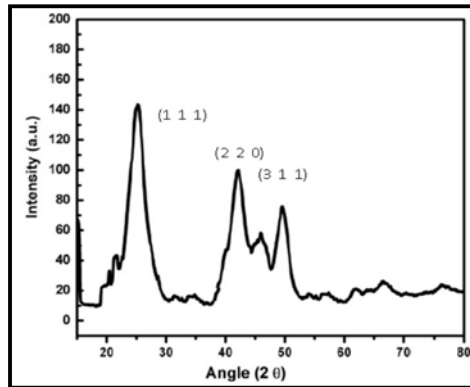


Figure 1. X-ray powder patterns of TGA capped CdSe nanoparticles.

**3.2 Spectroscopic Analysis:** In order to study the optical properties of the as-synthesized CdSe QDs UV-Vis absorption and photoluminescence studies were carried out and shown in Figure 2. The absorption spectra consisted of an absorption shoulder at 482 nm. The particle size estimated from the maximum excitonic peaks for CdSe, 2.7 nm.

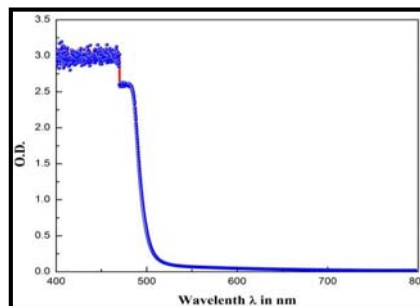


Figure 2. UV-VIS spectrum of TGA capped CdSe QD.

The Tauc Plot of TGA capped CdSe QDs is shown in Figure 3. The standard band gap value for CdSe bulk semiconductor is 2.6 eV. Further, the room temperature photoluminescence spectra of CdSe QDs capped with TGA is recorded using 450 nm excitation wavelength for the sample with the help of a computer controlled rationing luminescence spectrometer and given in Figure 4. The PL emission spectrum depicts the strong excitation peaks for the synthesized CdSe QDs with peaks centered at 603nm.

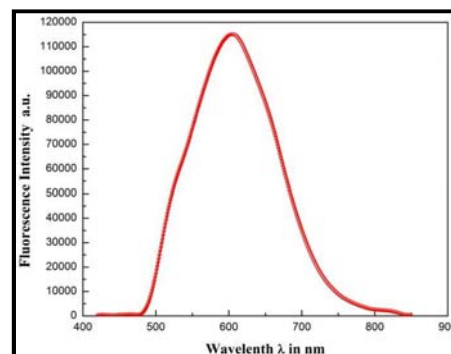
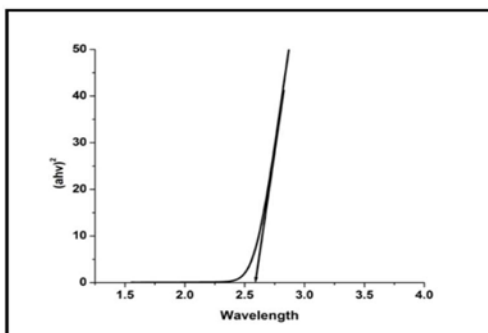


Figure 3. Tauc Plot of TGA capped CdSe QDs      Figure 4. PL spectra of TGA capped CdSe QDs

The surface morphology and the particle size of the synthesized CdSe QDs were analyzed from HRTEM studies. The Figure 5 is a typical HRTEM of this sample. The clear display of lattice fringes in the micrographs reveals the good crystalline nature of the samples. The QDs were found to be well dispersed, spherical and monodisperse without any agglomeration. The average particle diameter of the QDs is found in the range between 2-3 nm. The sizes and shapes of the CdSe quantum dots were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are given in Fig.6 (a) and Fig. 6(b). The SEM image demonstrated that the QDs were spherical morphology. To further elucidate the particle size of QDs, TEM study was performed to record the TEM images of samples. The particle sizes were found in the range of 2-4 nm, spherical in shape and are polycrystalline in nature.

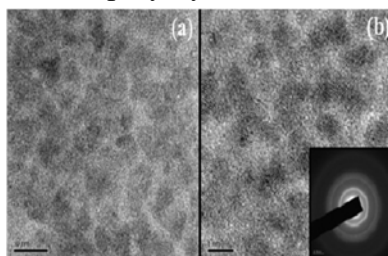


Figure 5. HRTEM pictures of TGA capped CdSe nanoparticles.

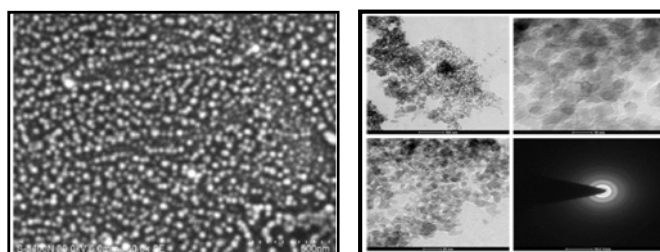


Figure 6. (a) SEM and (b) TEM pictures of TGA capped CdSe QD

In order to determine the chemical composition and to confirm the capping of TGA in the synthesized CdSe QDs the FTIR analysis was performed. Infrared spectroscopy furnished information about the bond that originated between the surface ligand and the CdSe surface. For illustration, Figure 7 contains the infrared spectra of the pure TGA, ligand and of the CdSe QDs stabilized with this ligand. Additionally, the Figure 8 presents the assignment of the main FT-IR band and provides a scheme that represents how the surface ligand binds to the CdSe QDs.

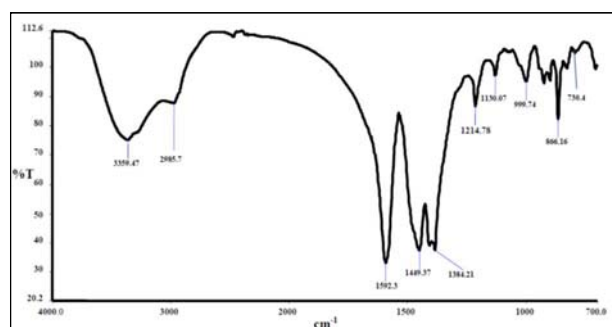


Figure 7. FTIR Spectra of TGA and TGA capped CdSe QD

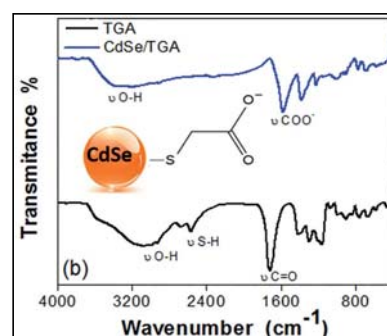


Figure 8. FTIR Spectra of TGA capped CdSe QD

From the FTIR spectra it is observed that, for the synthesized CdSe QDs almost all the peaks are common with slightly shifting behavior towards larger and shorter wave numbers. The peaks at  $1380\text{ cm}^{-1}$  are due to shifting of asymmetrical vibration of carboxylic group of in TGA. The peak at  $1672\text{ cm}^{-1}$  corresponds to the co stretching of carboxylic group. The peaks around  $2969$  and  $3225\text{ cm}^{-1}$  are due to  $\text{sp}^3$  stretching of C-H and due to vibration of O-H group present in TGA. The FT-IR assignments agreed with data recorded for similar systems such as water-soluble CdTe, which means that CdSe and CdTe QDs interact with thiol surface ligands in aqueous medium in much the same way. The Figure 9 depicts that, chemical reaction for the representation of TGA capped.

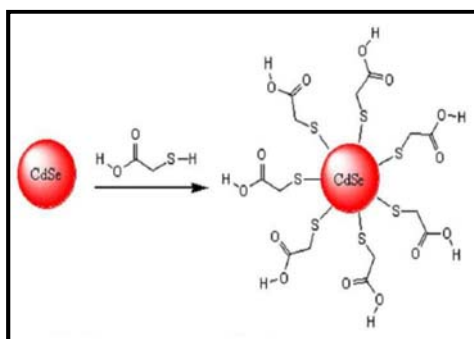


Figure 9. Pictorial representation of chemical reaction for the representation of TGA capped CdSe QD

The Figure 10 depicts FT-Raman analysis was also performed to study the sample qualities such as microcrystallinity, homogeneity and surface conditions for the as-synthesized CdSe quantum dot. The characteristic Raman peaks for CdSe-TGA QDs are observed at  $203\text{ cm}^{-1}$  and  $279\text{ cm}^{-1}$ . The peaks can be identified as transverse optical (TO) and longitudinal optical (LO) phonon mode, which are blue shifted from the corresponding phonon modes of bulk CdSe ( $\text{TO}=170\text{ cm}^{-1}$ ,  $\text{LO}=210\text{ cm}^{-1}$ ) system.

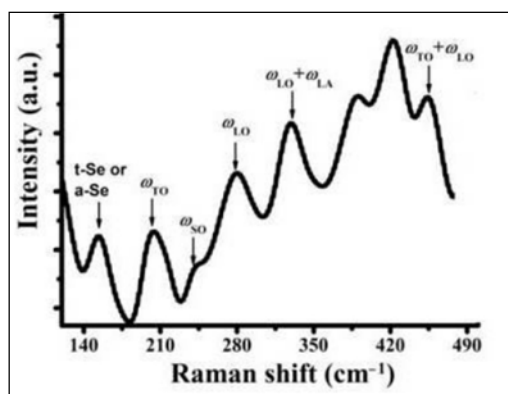


Figure 10. FT Raman spectra of TGA capped CdSe



For nanocrystallites, the confinement effect induces a broadening and downward shift of the Raman peaks. The Raman shifting due to the phonon confinement effect can be described by the confinement model. When the particle size decreases in the nanometer scale, a volume contraction occurs within the nanoparticle due to the size-induced radial pressure and this might lead to a substantial increment in the force constant value which in turn decreases interatomic distances. In vibrational transitions, the wave numbers vary approximately in proportion to  $k^{1/2}$ , where  $k$  is the force constant. Consequently, an enhanced magnitude of the force constant would be characterized by a shifting of the Raman band towards a higher wave number side. The respective LO and TO modes satisfy the well known Lydan-Sachs-Teller (LST) expression given by

$$\epsilon_{\infty} / \epsilon_d = \omega_{TO}^2 / \omega_{LO}^2$$

#### 4. Conclusions

In summary, stable, fluorescent colloids of CdSe QDs capped with TGA are prepared by simple chemical route under ambient conditions. A new precursor of selenium ions, that is, a hydrazine hydrate-Se complex, is proposed. The method is simple and the most viable solution route to prepare CdSe quantum dots. The size of nanoparticles is conveniently tuned by controlling the concentration of ions, volume of solutions and time of reaction. Colloids of different size are characterized by various experimental techniques such as X-ray powder diffraction, HRTEM, SEM and TEM optical absorption, photoluminescence, FTIR and FT-Raman measurements. It is found that these QDs are homogeneous, spherical, and small. Thus, the present synthesis is a simple and cost-effective in the preparation of high-quality CdSe nanoparticles.

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