Optical Properties Of ZnS And CdS Quantum Dots

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Abstract: In this study we adopt convenient chemical route for the synthesis of ZnS and CdS quantum dots of two different size distributions. They have been characterized by UV/Vis absorption spectroscopy and transmission electron microscopy. Fluorescence spectroscopy is performed to investigate their optical emission with size-variation. By UV/Vis spectroscopy, a blue-shift is revealed and the band gap is calculated in each case.

Key words: ***ZnS,CdS,Quantum Dots, Blue Shifts, Photoluminescence.***

1. Introduction

Semiconductor physics has been advanced significantly in the field of research and industry in the past few decades due to its numerous practical applications. There is immense interest in developing those materials, which maintain their required properties under extreme environmental conditions. One of the most important fields of current interest in material science is the fundamental aspects and applications of semiconductor Quantum dots. Many studies in this area focus on the development of new techniques to synthesize high-quality quantum dots with high-luminescence quantum yield and to measure their photo physical properties in organic and aqueous media (Y Chen and Z Rosenzweig et al., 2002). The properties exhibited by the semiconductor QDs can be utilized in manufacturing electronic devices such as light emitting devices (LEDs), photovoltaics (PVs), electronic switches etc. with more efficiency and compatibility and with faster response speed (Yu *et al.*, 2003, Kim *et al.*, 2009, Mohonta *et al*., 2006).
In the present investigation, we focus on the synthesis, characterization and fluorescence study of ZnS and CdS QDs (Rita John, S Sasi Florence,2010,Wenzhong Wang, Igor Germanenko *et al* 2002) of different size distributions. The samples are examined by UV/Vis absorption spectroscopy (UV/Vis analysis)) to ensure nanocrystal formation and by transmission electron microscopy (TEM analysis) to explore their size and morphology. Fluorescence spectroscopy (FL analysis) reveals the energy state in ZnS and CdS QDs that causes luminescence. Since ZnS and CdS QDs show size-dependent electrical and optical properties we prepare QDs of two different size-distributions.

2. Experimental

The synthesis of ZnS and CdS nanoparticles was carried out by aqueous chemical method using zinc chloride and sodium sulfide (Rita John, S Sasi Florence, 2010), cadmium chloride and sodium sulfide (T. Tsuzuki, P.G. McCormick 1997) as source materials respectively. All the chemicals required for the synthesis are purchased from Merck and fisher scientific and are used without further purification. The chemicals required are Zinc Chloride, Cadmium chloride and Sodium sulfide. All steps of the synthesis were performed at low temperature and ambient conditions.
2.1 Synthesis of ZnS Quantum dots: As a first step we take 6 grams of polyvinyl Alcohol (PVA) and are dissolved into 100 ml double distilled water (T. Tsuzuki, P.G. McCormick 1997,Daniele Gerion,Fabien Pinaud *et al* 2001). These mixture is then taken in three necked flask fitted with thermometer pocket and N2 inlet. The solution is then stirred in a magnetic stirrer at a stirring rate of 200 rpm at a constant temperature of 75^0C for 2.5 hours. Thus a water solution of PVA has been prepared.

In the similar way $Zncl_2$ solution is made by dissolving 3 grams of $Zncl_2$ in 50 ml double distilled water. The solutions are degassed by boiling N_2 for 3 hours .Now PVA solution and $Zncl_2$ solution have been mixed and few drops of HNO_3 is added to the mixture followed by moderate stirring while aqueous solution of Na_2S is put into it slowly by means of a dropper unless the whole solution appears completely milky. This solution is kept in dark chamber at room temperature for 14 hours for its stabilization followed by its casting over glass substrate and drying it in oven at 50^0 C.This casted film contains ZnS (1) quantum dots embedded in PVA matrix. Similarly ZnS (2) quantum dots prepared by dissolving 2 grams $Zncl_2$ in 50 ml double distilled water.

2.2 Synthesis of CdS Quantum dots:

To prepare CdS quantum dot take 6 grams of polyvinyl Alcohol (PVA) and are dissolved into 100 ml double distilled water. These mixture is then taken in three necked flask fitted with thermometer pocket and N2 inlet. The solution is then stirred in a magnetic stirrer at a stirring rate of 200 rpm at a constant temperature of 75^0C for 2.5 hours. The solution is stirred until get a transparent solution PVA. Thus a water solution of PVA has been prepared.

In the similar way $CdCl_2$ solution is made by dissolving 3 grams of in 50 ml double distilled water. The solutions are degassed by boiling N_2 for 3 hours .Now PVA solution and $CdCl_2$ solution have been mixed and few drops of HNO_3 is added to the mixture followed by moderate stirring while aqueous solution of Na_2S is put into it slowly by means of a dropper unless the whole solution appears completely yellow. This solution is kept in dark chamber at room temperature for 14 hours for its stabilization and finally CdS(1) quantum dots embedded in PVA matrix. Similarly CdS (2) quantum dots prepared by dissolving 1.5 grams $Cdcl_2$ in 50 ml double distilled water.

2.3 Characterization: All the samples are characterized by UV/Vis absorption spectroscopy and transmission electron microscopy (TEM). UV/Vis absorption spectra are recorded by UV/Vis Spectrophotometer,Perkin Elmer Lambda 35. For UV/Vis analysis, the specimens are dispersed in methanol and then exposed to ultra-violet and visible region of the electromagnetic spectrum, taking methanol as reference. TEM images are obtained with a JEOL, 100CXII, 100 KV system. The samples for TEM analysis are prepared by placing a drop of the ZnS and CdS QDs colloid on carbon-coated copper grid. The films on the grid are allowed to dry for a few hours after removing extra solution using blotting paper. Fluorescence spectroscopy is done by Perkins Elmer S2500, PL Spectro-photometer to investigate the internal energy state of the specimen which gives rise to luminescence.

3. Results and discussion

3.1. UV-Vis Absorption Analysis:

UV-Vis Absorption spectra are taken 4 minutes after the preparation of each sample (B. O. Dabbousi,J. Rodriguez-Viejo 1997) and are shown in Fig. (**1**) and (2). The first excitonic peaks of the samples ZnS(1)and ZnS(2) are found to be at 205nm and 208 nm respectively and that of CdS(1) and CdS(2) are found to be at 260nm and 274 nm respectively.. All the excitonic peaks infer that the absorption edge of ZnS and CdS quantum dots is strongly blue shifted with respect to the bulk specimen. By using hyperbolic band model the average size of ZnS(1), ZnS(2), CdS(1) and CdS(2) are respectively 7.40 nm, 7.42 nm, 1334 nm and 14.16 nm .

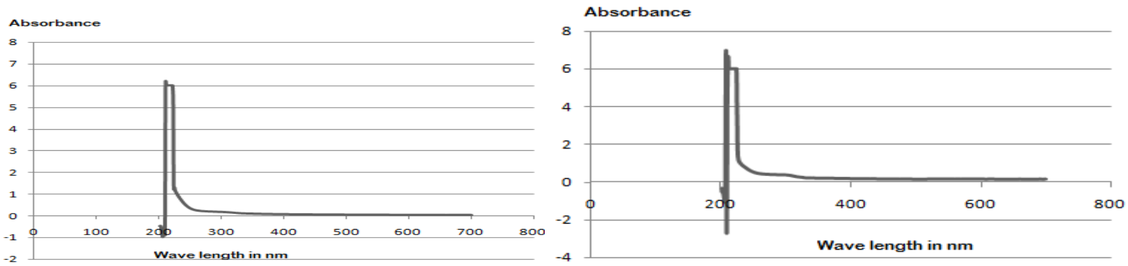

Figure 1: UV-VIS absorption spectra of ZnS(1) and ZnS(2) respectively.

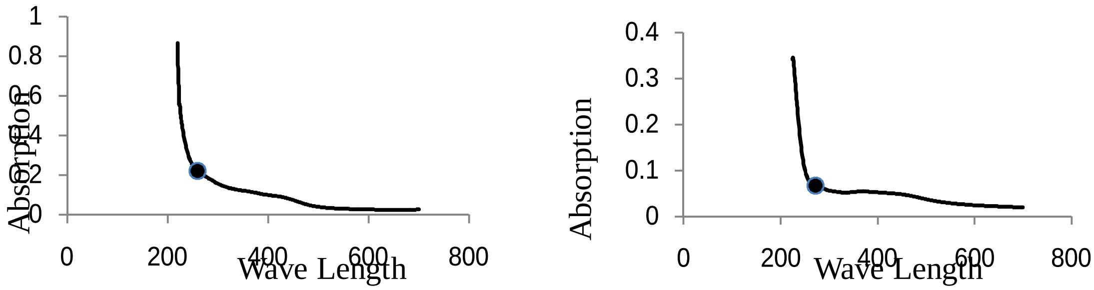

Figure 2: UV-VIS absorption spectra of CdS(1) and CdS(2) respectively.

3.2. TEM Analysis

The TEM images of all the four samples are shown in Fig. (**3**) and (4). The QDs are nearly uniform and nearly equi-spaced (Yang Li, Eric Chun Yeung *et al* 2004). The average sizes of the QDs in samples ZnS(1), ZnS(2), CdS(1) and CdS(2) are respectively 7 nm, 7.4 nm 13 nm and 13.8 nm .

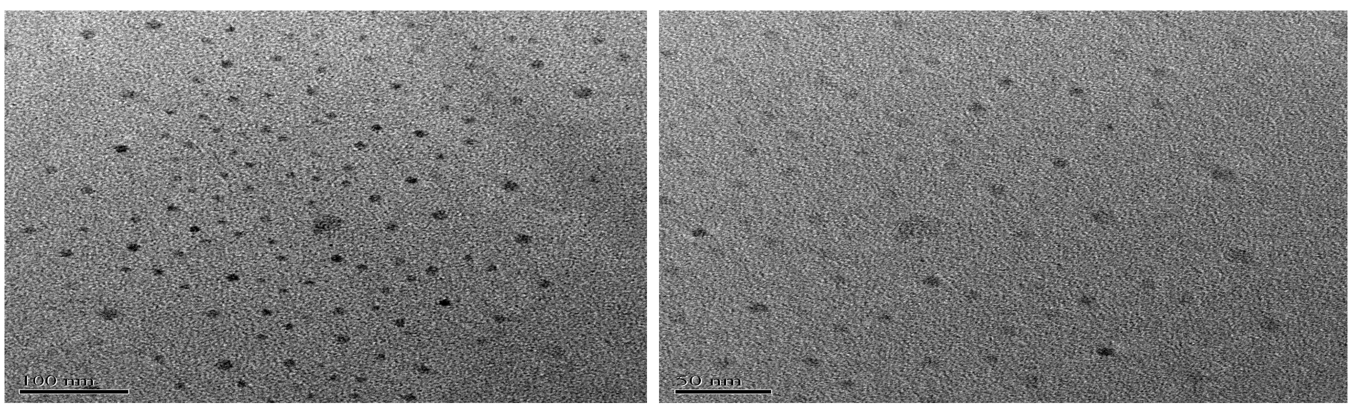

Figure.3 TEM images of *prepared ZnS (1) and ZnS(2) sample*

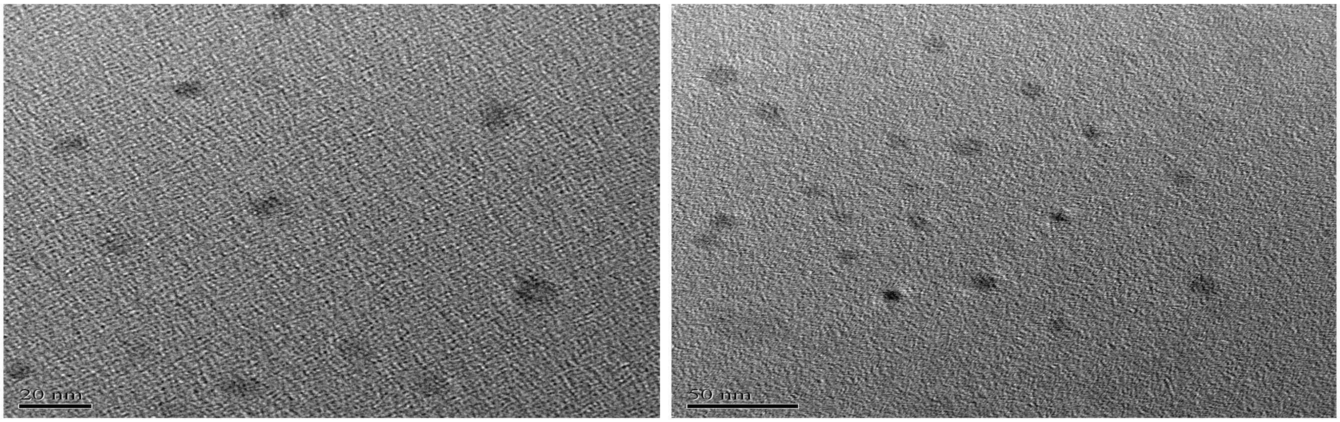

Figure 4.TEM images of *prepared CdS (1) and CdS(2) sample*

3.3. PL Spectra Analysis

Luminescence study is complementary to the UV-Vis absorption analysis (Yongfen Chen and Zeev Rosenzweig,2002). The FL spectra of the samples ZnS (1), ZnS(2) CdS (1) and CdS(2) are shown in the Fig. (**5**) and (6). Peaks are at 490nm, 495 nm,494 and 492 nm respectively.

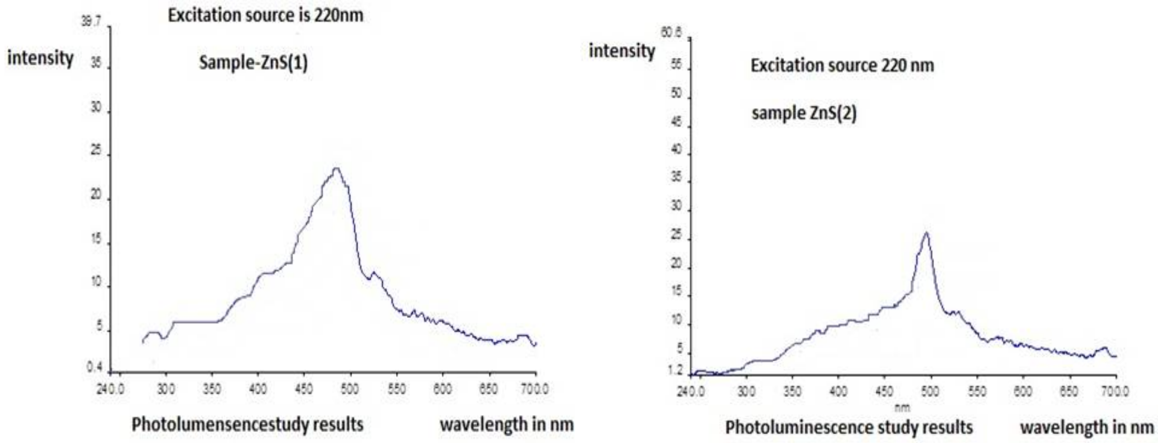

Figure 5: PL spectra of ZnSS(1) and ZnSS(2) with excitation sources at 220 nm.

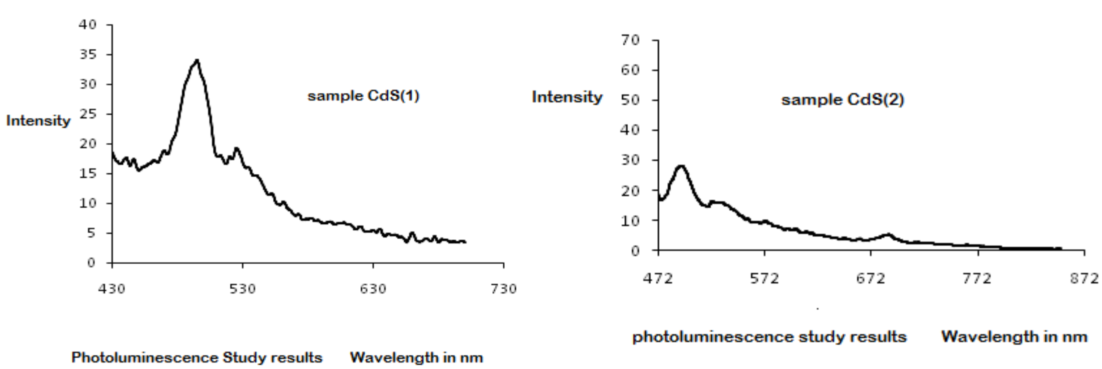

Figure 6: PL spectra of CdS(1) and CdS(2) with excitation sources at 215 nm at 220 nm respectively.

4. **Conclusions**

A good quality narrow size ranged ZnS and CdS QDs can be prepared through a chemical route by using are Zinc Chloride, Cadmium chloride, Sodium sulfide, PVA and de-ionised water. The prepared QDs are of narrow and non uniform size which promises a high quantum yield. The absorption and emission of the prepared sample reveal expected nonlinear phenomenon and blue shift with respect to bulk. There is a small difference between wavelengths corresponding to absorption edge and PL peak which is called 'Stokes Shift'.

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