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Ultraviolet-visible and photoluminescence spectroscopy of newly synthesized CdSe nanostructures

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Abstract – Cadmium selenide (CdSe) nanorods were synthesized using isopropyl amine as both solvent and template. The length of the as prepared CdSe nanorods were varying from 200 to 300 nm and its breadth were varying from 40 to 80 nm, which were calculated from field emission scanning electron micrograph. From x-ray diffraction pattern we observed well crystalline CdSe nanostructures which were prepared using isopropyl amine. We have found that the band gap energy of the CdSe nanorods is changing from 2.0 to 3.0 eV depending on its geometrical configuration. The high band gap energy of these products is consistent with the length and breadth of the CdSe nanorods. Due to its high band gap energy these CdSe products can be used in photovoltaic devices like solar cells.

Index terms – Luminescence, Nanostructures, Sol-gel chemistry, X-ray diffraction.

I. INTRODUCTION

During the past decade, one-dimensional (1-D) and quasi 1-D semi conducting nanostructures were matter of great attention due to their unique chemical and physical properties [1-2]. CdSe was belonging to II-VI semiconductor group having a direct band gap of 1.24 eV at room temperature, and widely used in photovoltaic devices, electroluminescence, and catalysts [3-5]. Besides these CdSe has wide potential applications in solar cells, biological labelling, and so on [6-7]. Till date various synthetic methods have been reported such as chemical vapour deposition (CVD), solvothermal and hydrothermal method to produce II-VI group semiconductor nanocrystals with different structures and morphologies [8-14]. Synthesis of 1-D ME (M=Zn, Cd; E=S, Se) nanocrystals using ethylenediamine as both solvent and template has been reported [15].

To the best of our knowledge preparation of CdSe nanorods using isopropyl amine as both solvent and template is not reported. In this study, we prepared CdSe nanorods using isopropyl amine as both solvent and template and the size of the nanorods can easily be changed by simply changing the reactants' composition at low temperature.

II. EXPERIMENTAL SECTION

All the reactants were of analytical grade and were used without further purification. In a typical procedure to synthesize CdSe nanorods, 3.00gm of Cd(NO₃).4H₂O was put into a glass beaker filled with 60 ml of isopropyl amine (IPA). The mixture was stirred for 10 minutes at room temperature forming a whitish solution and then 0.56 gm of selenium (Se) powder was added. The final mixture was stirred for 5 minutes. 5ml of N₂H₄.H₂O was added to the previous mixture and then the new mixture was stirred for 30 minutes at room temperature. The colour of the solution was deep yellow. Then the solution was put into a Teflon lined stainless steel autoclave. The autoclave was maintained on average at 170^oC for 2 hours and on average at 124^oC for 5 hours 45 minutes, and then it was allowed to cool naturally approaching to room temperature. The resulted very dark brown precipitate was filtered, subsequently washed with double distilled water and absolute ethanol. The products were dried in air at 65^oC for 3 hours to obtain a type of CdSe nanostructures (CdSe1). For obtaining nanostructures with different dimension, we repeated the previous experiment with different molar ratios at different temperatures. For obtaining the new CdSe nanorods (CdSe2), we used 3 gm of Cd(NO₃).4H₂O, 0.22 gm selenium powder, 5 ml of hydrazine hydrate and 55 ml of isopropyl amine and the mixture was kept in a Teflon lined stainless steel autoclave at the temperature of 126^oC for 12 hours. Similarly for obtaining the next CdSe nanorods (CdSe3), we used 2 gm of Cd(NO₃).4H₂O, 0.067 gm selenium powder, 5 ml of hydrazine hydrate and 40 ml of isopropyl amine and the mixture was kept in a Teflon lined stainless steel autoclave at the temperature of 126^oC for 12 hours.



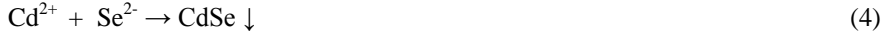
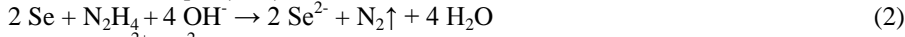
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With the increase of Se the percentage of zinc blende CdSe nanorods are increased compared to the wurtzite nanorods. Reactant's composition plays the key role in controlling the morphology and the structure of the CdSe nanocrystals. In this present work the reactions can be formulated as follows:



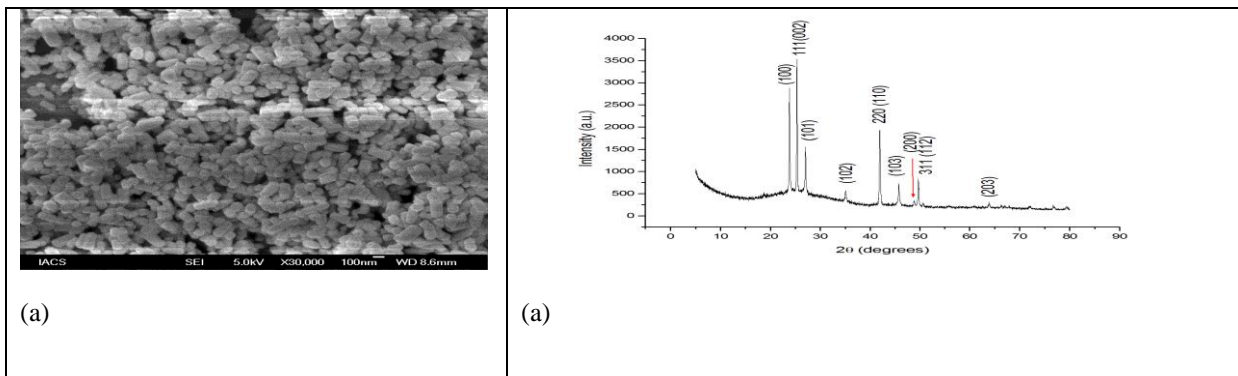
The concentration of Se^{2-} ions is the decisive factor leading to different products. When Se^{2-} ions are excessive in the system, the electrostatic interaction between Se^{2-} and Cd^{2+} is very much stronger than that of IPA and Cd^{2+} .

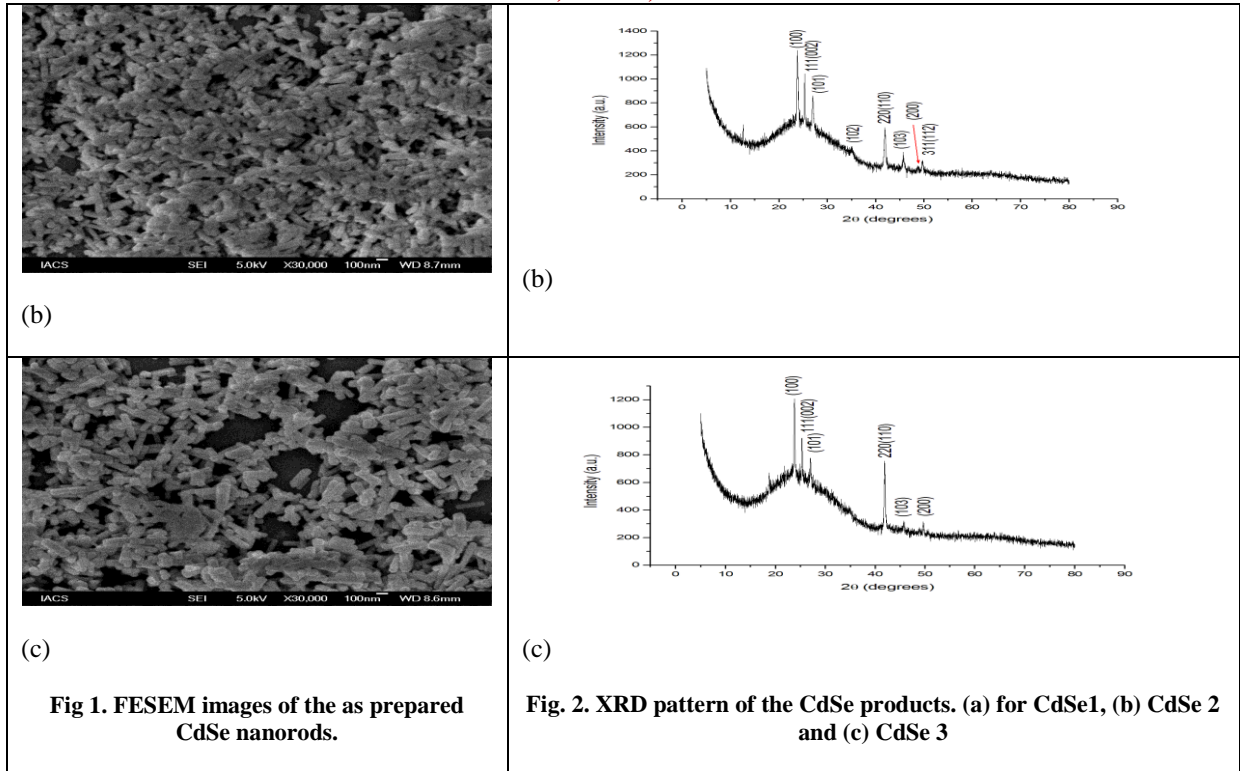
Crystalline structure of the obtained products were characterised by X-ray diffraction studies (XRD) using a diffractometer (Bruker D8 Advance) with Cu $K\alpha$ line ($\lambda=1.5418 \text{ \AA}$), IACS, Jadavpur, Kolkata. The morphology of these products was obtained by field emission scanning electron microscopy (FE-SEM). The FE-SEM photos were taken with a JSM-6700F, JEOL, Japan at 5.0 kV, IACS, Jadavpur, Kolkata. The SEM measurements were done on the glass substrate coated with requisite samples using a programmable Spin Coater, Apex Instruments Co. with model No. SCU-2008 C. UV-vis spectrophotometer (Model: TCC-240A, UV-2401 PC, Shimadzu, Japan) was used to record the electronic absorption spectra of the obtained products at room temperature. Photoluminescence spectra were recorded on a LS55, Fluorescence spectrometer, PerkinElmer using excitation source of the 400 nm line of a He-Cd laser.

III. RESULTS AND DISCUSSION

A. Morphology

We obtained FESEM micrograph with the variation of concentration of Se powder and duration as shown in fig. 1. Fig. 1(a) represents the SEM micrograph of CdSe nanorods (CdSe1) prepared from 0.56 gm Se powder with 60 ml IPA which indicates the dimension of nanorods are 80 nm in breadth and 200-300 nm in length. Fig. 1(b) represents the SEM micrograph of CdSe nanorods (CdSe2) prepared from 0.22 gm Se powder with 55 ml IPA which indicates the dimension of nanorods are 50 nm in breadth and 200-300 nm in length. Fig. 1(c) represents the SEM micrograph of CdSe nanorods (CdSe3) prepared from 0.067 gm Se powder with 40 ml IPA which indicates the dimension of nanorods are 40 nm in breadth and 200-300 nm in length. From all FESEM micrographs we observe that the shape of the nanorods is straight.





The length of the nanorods is about 250 nm on average and ranging from 200 to 300 nm. The breadth of the nanorods is about 60 nm on average and ranging from 40 to 80 nm.

The XRD patterns of the three precipitates of the CdSe nanorods are shown in fig. 2 (a-c). The XRD patterns of CdSe nanorods clearly show the characteristic zinc blende planes of (111), (220) and (311) located at 25.38, 42.06 and 49.76°, respectively, in the 2θ range of 0° – 80° as similar to earlier reported results [16]. It is interesting that the XRD patterns also show the wurtzite plane of the as prepared CdSe nanorods. The wurtzite planes (in parentheses) are (100), (002), (101), (102), (110), (103), (200), (112) and (203) located at 23.82, 25.38, 27.08, 35.02, 42.06, 45.74, 48.87, 49.76 and 63.88°, respectively, in the 2θ range from 0 – 80° [16].

In addition, the intense and sharp diffraction peaks appear at (100), 111 (002), (101) etc. planes depicted in fig. 2(a – c). This suggests that the obtained products are well crystallized. By using the XRD analysis, the d-spacing of the CdSe nanorods have been calculated for both wurtzite and zinc blende structures and compared with the standard JCPDS data (Table 1). The calculated zinc blende lattice parameter is 6.089 Å which is in good consistent with the value in JCPDS (19-191, a=6.077 Å) [JCPDS (8-459) for wurtzite structure and JCPDS (19-191) for zinc blende structure]. The Debye-Scherrer Equation connected with particle size is given below [17]:

$$d = 0.9 \lambda / \beta \cos \theta \quad (5)$$

Where d is the breadth of the nanorods, λ is the wavelength of the CuKα radiation (λ=1.5418 Å), β is full width half maxima (FWHM) of the XRD peaks, θ is the angle at which the corresponding peaks occur. By using Debye- Scherrer equation we calculated the average breadth of the nanorods. The obtained values of breadths of the as prepared CdSe nanorods are 41.39 nm for CdSe1, 27.19 nm for CdSe2 and 35.68 nm for CdSe3.

B. Optical Properties

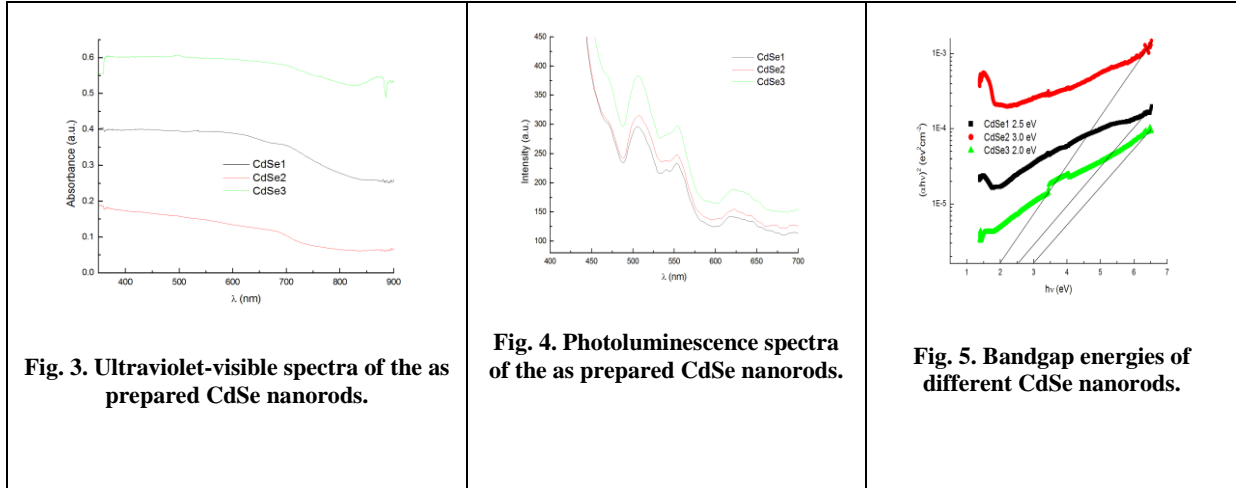


Fig. 3. Ultraviolet-visible spectra of the as prepared CdSe nanorods.

Fig. 4. Photoluminescence spectra of the as prepared CdSe nanorods.

Fig. 5. Bandgap energies of different CdSe nanorods.

The optical properties of semiconductor nanomaterials depend on the size and shape of the particles. The UV-Vis spectra recorded at room temperature of the as prepared CdSe are shown in fig. 3. The absorption edge of CdSe nanorods is about 700 nm and energy is approximately 2.5 eV. The excitonic absorption features are not very sharp.

Fig. 4 shows the photoluminescence spectra of the as prepared CdSe nanorods at room temperature. The influence of the width of the CdSe nanorods/nanosaws on the shifting behaviour in the PL spectrum has been reported by many researchers [18-19]. In the present work the emission property of the as prepared CdSe nanorods was studied from photoluminescence spectrum in the spectral region from 400 to 750 nm. Two sharp peaks are observed at 507 and 553 nm. Also there is a weak peak observed at 622 nm. Their corresponding energies are 2.45, 2.24 and 1.99 eV, respectively. The excitation was given at 400 nm and we got the first peak at 507 nm, and two consecutive peaks were observed at 553 nm and 622 nm. Therefore the energy loss for the first peak is 0.65 eV, for the second peak is 0.86 eV and for the third peak is 1.105 eV.

The optical band gap (E_g) for semiconductors can be evaluated with the following relation as given below [20-21]:

$$\alpha h\nu = A (h\nu - E_g)^n / h\nu \tag{6}$$

Where, A is a constant related to the effective masses associated with the bands and n is a constant and $n = 1/2$ for a direct band gap material, 2 for an indirect band gap material and 3/2 for a forbidden- direct energy gap, the estimated E_g values are in the range 1.70 – 2.30 eV as reported earlier [20]. α is calculated with the following relation as given below [21]:

$$\alpha = 1/t \ln(1/(1-A)) \tag{7}$$

We obtain the band gap of all CdSe nanorod products by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $(h\nu)$ as shown in fig. 5. Band gap is changing from 2.0 to 3.0 eV depending on different geometric configurations of CdSe nanorods. So we can tune band gap energies of such CdSe nanorods obtained by using the concentration of isopropyl amine.

IV. CONCLUSION

Precisely, the structure of the CdSe nanorods are changed by simply changing the reactant’s composition at low temperature. The particle size and morphology was verified by powder XRD and FESEM. Use of isopropyl amine as both solvent and template is new in this work. The optical properties are changed with the change of the dimension of the CdSe nanorods. This work provides a new way to synthesize CdSe nanostructure and other II-VI semiconductor using different solvent.

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