



SYNTHESIS AND CHARACTERIZATION OF PURE and Zn DOPED CdSe NANOPARTICLES BY ULTRASONICATION TECHNIQUE

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Abstract: Synthesis of nanoparticles of cadmium selenide (CdSe) was carried out using sonochemical method with cadmium acetate and sodium selenite as precursors. Hydrazine hydrate and ammonia were used to control the size of the nanoparticles. The crystalline nature and particle size of the samples were characterized by powder X-Ray Diffraction analysis. The FTIR results show that the frequency of absorption at 890 cm^{-1} decreases as the concentration of dopant increases. The absorption exhibit blue-shift with decreasing nanoparticle size, which is attributed to quantum confinement effect. The refractive index and dielectric constant is dependent on absorbance. The extinction coefficient values increases with particle size.

I. Introduction

Among the various kinds of semiconductor nanoparticles, CdSe colloidal nanoparticles are most widely investigated as their emissions can be easily tuned to cover a broad spectrum (from red to blue) with decreasing nanoparticle size [1]. Semiconductor nanoparticles are well-known for their widespread fundamental research and industrial applications [2–4]. II–VI compound semiconductor nanocrystals have been paid great attention due to their unique optical properties that can be tuned not only by changing the particle size but also by changing the composition of the alloy. Cadmium Selenide (CdSe) is a solid, binary compound of cadmium and selenium. CdSe nanoparticles can be prepared by diverse methods such as co-precipitation, electrodeposition[5], pulsed sonoelectro chemical[6], solvothermal[7] and hot injection methods[8]. Among these, sonochemical is suitable, effective and low cost method for production of CdSe nanoparticles. CdSe nanocrystalline semiconductors have attracted immense interest over the past years because the various properties and applications in light-emitting diodes, lasers, holographic optical memories, photonic band-gap crystals, ultrafast photonic switches, and biomedical tags for fluoroimmuno assays, nanosensors and biological imaging [9,10]. In the present work, different concentrations of Zn are doped at the lattice of CdSe to understand the structural and optical properties of Zn doped CdSe nanocrystals. The Zn doped CdSe nanocrystals $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ (where $x = 5, 1, 0.2, 0.04$) were synthesized by sonochemical method and characterized by powder X-Ray Diffraction analysis, FTIR and UV visible spectroscopy.

II. Experimental Detail

A. Synthesis of Pure CdSe Nanoparticles:

For the sonochemical synthesis of pure cadmium selenide (CdSe) nanoparticles following steps were performed: First, took 2.36 g analytic reagent grade selenium powder, 9.48 g analytic grade sodium sulphite and dissolved them into 120 ml of water to get sodium selenosulphate. Stirred the solution for 8 hours, continuously and kept it overnight. Filtered the solution and after filtration clear solution was obtained. Took 25 ml of this stock sodium solution of selenosulphate for further precipitation reaction. Added 1 ml of hydrazine hydrate drop wise with continuous stirring into 25ml of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$) aqueous solution. Then a white turbid solution was obtained. Then added ammonia solution till the turbidity of the solution is removed. Added 1M NaOH solution to the above solution and adjusted the pH 11.6 with the help of pH meter. After setting the pH, the solution was placed in the ultrasonicate bath to achieve reaction solution temperature 70°C then switch off ultrasonicate and monitor the temperature till it reaches 60°C . Then added 25ml sodium selenosulphate as prepared in step above, then ultrasonicated the resulting solution for 3-4 hours until the red precipitates were observed. Take out the solution from ultrasonicate bath to cool down to room temperature and the resulting precipitate were filtered and dried it in oven and crush it [11].

B. Synthesis of Doped CdSe Nanoparticles:

For the synthesis of Zn doped cadmium selenide (CdSe) nanoparticles following experimental steps were

performed:

All the other synthesis steps were similar to the synthesis of pure (CdSe) nanoparticles, only difference involve in the addition to dopant precursors after step 5 of the above procedure.

For Zn doping, 4.4 ml of zinc acetate were added to the 22.5 ml of cadmium acetate solution in the stoichiometric proportion. For Zn doping, 22.5 ml of cadmium acetate and 5.0 ml of Zinc acetate were added. Four samples of each dopant with variable concentration (5%, 1%, 0.2%, 0.04% atomic weight percentage) have been synthesized. Added NaOH solution in the above solution and adjust the pH with the help of pH meter in the basic media (11.6). After setting the pH, the solution was placed in the ultrasonicate bath to achieve reaction solution temperature 70°C then switch off the ultrasonicate and monitor the temperature till it reaches 60°C. Then added 25 ml sodium selenosulphate as prepared in step 3, then ultrasonicated the resulting solution for 3-4 hours until the red precipitates were observed. Take out the solution from ultrasonicate bath to cool down to room temperature then the resulting precipitate were filtered and dried it in oven and crush it.

C. Characterization:

The materials phases analysis were obtained by using X-Ray Diffraction (XRD) using Cu K α radiation with $\lambda = 1.5418\text{\AA}$. The optical properties were conducted using UV Visible spectroscopy. FTIR was carried out using KBr Pallets.

III. Result and Discussion

A. Phase Characterization:

Figure 1(a), 1(b) shows the XRD patterns of Pure and Zn doped CdSe samples respectively. The hexagonal spinel structure of CdSe is confirmed by the diffraction pattern shown in figure 1(a). Crystallite size D was calculated using the Debye–Scherer equation [12]:

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

where λ is the wavelength of used radiation, β is the full width half maximum (FWHM) of diffraction peak, and θ is the Bragg angle.

The X-Ray Diffraction (XRD) measurements were carried out using Cu K α 1 radiation ($\lambda = 1.5418\text{\AA}$), average crystallite size D is 65 nm. However, all the peaks match with the crystalline phase of hexagonal spinel structure of CdSe (JCPD Card No. 77-2307)[13]. The diffraction peak shifts towards the lower angle a little with increase in Zn substitution. From the XRD pattern, it is clear from the broadening of diffraction peaks of that the particles crystallize at nanoscale regime. The intensity of the peaks indicates that the CdSe nanoparticles are crystalline and there is no trace of cubic phase. The peaks (100), (002), (101), and (103) are corresponding to the hexagonal phase. Usually, the (101) diffraction peak in hexagonal CdSe is strong and narrow, which may be attributed to the preferential growth along (101) plane of CdSe crystallites.

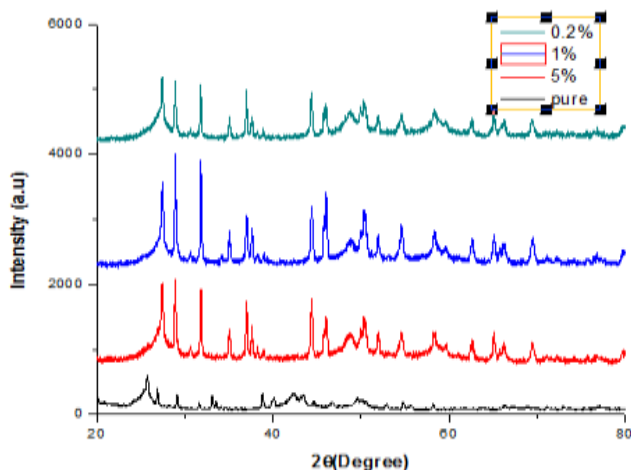


Fig. 1(a) XRD pattern of Pure CdSe, 5% Zn doped CdSe, 1% Zn doped CdSe, 0.2% Zn doped CdSe nanoparticles

B. FTIR measurements:

Initially, the sample was washed with absolute ethanol and hot distilled water several times and then dried in an oven. Run IR spectrophotometer to determine the IR absorption of the prepared CdSe powder using KBr pallets. It is observed that the broad peak at 3221 cm^{-1} could be assigned to –OH stretching (hydrogen bonded) due to the small quantity of H_2O in the sample. N-H stretching vibration peak is also observed at 3100 cm^{-1} due to the presence of hydrazine hydrate in our sample as residue. The peak observed at 1578 cm^{-1} is assigned to OH of water absorbed from the molecular precursors. C-N stretching vibration peak is positioned at 1236 cm^{-1} is due to the interaction of ethylene glycol with the hydrazine hydrate and regular periodic structure of molecular precursors[14]. The FTIR results show that the frequency of absorption at about 890 cm^{-1} decreases as the concentration of dopant increases. The exact mechanism for the formation of CdSe nanoparticles is still unclear,

but it is reasonably concluded that the appropriate ratio of solvents volume may play the significant role for the formation of CdSe NPs. In the present work, Se source can be easily converted into Se^{2-} by N_2H_4 , which results in a high monomer concentration. In the initial step, hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) complexes with Cd^{2+} and forms the transparent soluble complexes solution, which effectively decreases the concentration of Cd^{2+} and avoids the precipitation of CdSeO_3 , and thus provides a more homogeneous solution for the reaction.

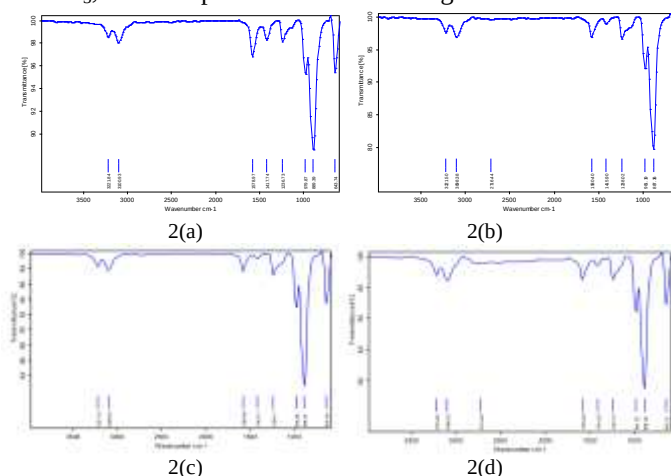


Fig. 2(a) FTIR spectrum of pure CdSe, 2(b) 5% Zn doped CdSe 2(c) 0.2% Zn doped CdSe 2(d) 0.04% Zn doped CdSe

C. Optical Characterization:

UV-visible absorption has been one of the most important measurements to investigate the optical properties of CdSe nanoparticles. UV-visible spectroscopy is a measurement of the wavelength and intensity of absorption of near-ultraviolet and visible light by a sample. It measures the intensity of emergent light through a sample (I) and compares it to intensity of incident light on the sample (I_0). The ratio of I and I_0 is called the transmittance, the relation between absorbance A and T is given by:

$$A = -\log T = -\log (I / I_0) \quad (2)$$

Optical characterization of synthesized nanoparticles has been done by UV-visible absorption spectroscopy. Band-gap, photo-catalytic activity, concentration of absorbing species solution can be calculated with the help of UV-visible absorption spectroscopy.

C.1 Absorption

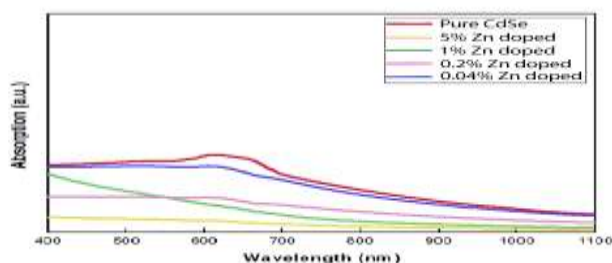


Fig. 3(a) Absorption spectra of synthesized pure and Zn doped CdSe nanoparticles.

Figure 3(a) shows the optical absorption spectra for pure, Zn doped CdSe nanoparticles. The absorption spectra demonstrate that high absorption occur at a wavelength of 604, 605 and 614 nm for pure, 0.04% Zn and 0.2% Zn doped CdSe nanoparticles respectively.

C.2 Refractive Index

The refractive index has been determined from the reflectance data by using equation [15].

$$n = (1 + \sqrt{R}) / (1 - \sqrt{R}) \quad (3)$$

Where n is the refractive index and R is the reflectance.

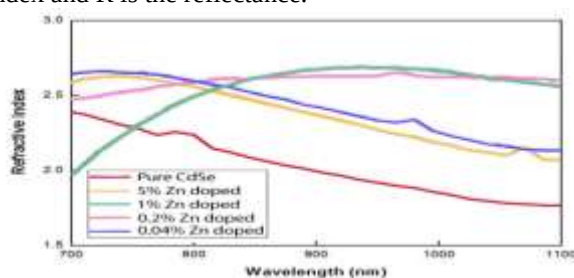


Fig. 4(a) Refractive index for pure and Zn doped CdSe nanoparticles.

The refractive index spectra demonstrate that high refractive index occur at 2.064, 2.0378 and 2.451 for 5% Zn, 1% Zn, 0.2% Zn doped CdSe nanoparticles respectively.

C.3 Extinction Coefficient

Extinction coefficient of CdSe nanoparticles determined using [15]

$$k = \alpha \lambda / 4\pi \quad (4)$$

Where $\alpha = 2.303(A/d)$, k is the extinction coefficient, α is the absorption coefficient, λ is the incident photon wavelength, A is the absorbance and d is the crystallite size of CdSe nanoparticles. The extinction coefficient values show a similar trend as the absorption spectra.

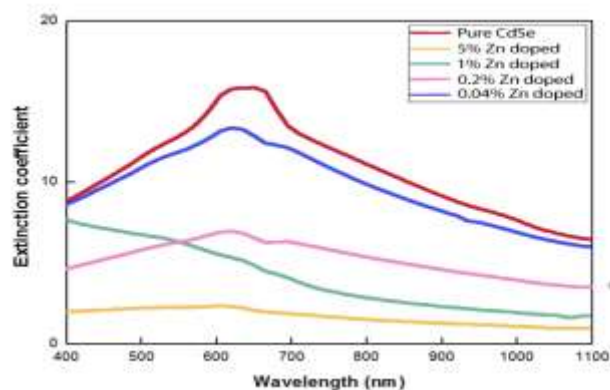


Fig. 5(a) Extinction coefficient for pure and Zn doped CdSe nanoparticles.

C.4 Dielectric Constant

Dielectric constant has been determined using equation [15].

$$\epsilon_r = n^2 - k^2 \quad (5)$$

Where n is refractive index and k is extinction coefficient. Theoretically, the real part of the dielectric constant is directly proportional to the refractive index.

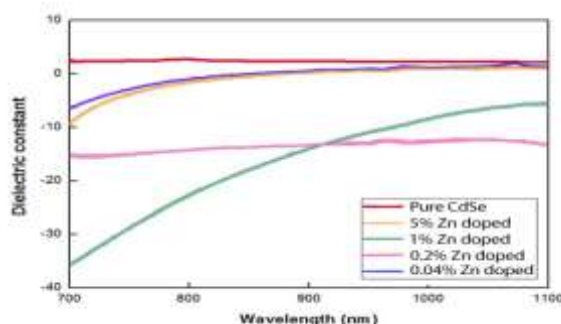


Fig. 6(a) Dielectric constant for pure and Zn doped CdSe nanoparticles

IV. Conclusions

Sonochemical method is a facile eco-friendly synthesis route for the preparation of intrinsic and extrinsic CdSe nanostructures. From the recorded XRD pattern average crystalline size of pure CdSe nanoparticles found to be 65 nm. Effect of change of dopant concentration is confirmed by Fourier Transform infra-red (FTIR) spectroscopy. The refractive index calculated is based on the reflectance. The extinction coefficient shows a similar behaviour as the absorption spectra. The calculated real dielectric constants are observed to be directly proportional to the refractive index and the calculated imaginary dielectric constants are directly proportional to the absorbance.

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