

THE EFFECT OF CAPPING AGENTS, EDTA AND EG ON THE STRUCTURE AND MORPHOLOGY OF CdS NANOPARTICLES

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In this work we report the effect of capping agents, ethylenediaminetetraacetic acid (EDTA) and ethylene glycol (EG) on the structure, morphology and characteristic properties of CdS nanoparticles. The samples were prepared by co-precipitation method at 90 °C using Cadmium acetate and thioacetamide as source materials. Characterization of as prepared samples was carried out using X-ray diffraction (XRD) patterns which revealed formation of well crystallized hexagonal and cubic structures for CdS@EDTA (Cd-1) and CdS@ EG (Cd-2) nanoparticles respectively. The average nanocrystalline sizes calculated using Scherrer formula indicated 7.6 nm and 8.5 nm for Cd-1 and Cd-2 respectively. Band gaps calculation of the prepared samples, using absorbance onset at about 309.2 and 463 nm confirming a blue shift for both the cases showed an increase of band gaps from 2.55 eV to 3.45 eV due to the change of surfactants, EG by EDTA. The morphological study of the prepared CdS nanoparticles by SEM revealed well distributed CdS spherical nanostructure for both the cases with a smaller grain size for EDTA-capped CdS nanoparticles. This observation was in conformity with the results of decreased crystallite sizes for Cd-1 obtained by using Scherrer formula.

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Keywords: CdS nanoparticles, capping agents, Energy band gaps, Hexagonal and cubic semiconductors, Ethylenediaminetetraacetic acid, Ethylene glycol

1. Introduction

Preparation of II-VI semiconductor nanoparticles are very interested because of their applications in optoelectronics and photonics purposes. It was found that, the physical and chemical properties of these nanomaterials are size and shape dependent and we have examined in this work. In fact, the size and shape dependence can be related to the change of surface to volume ratio with size (1) and quantum confinement effect (2). Quantum confinement can modifies the density of states (DOS) near the band – edges [1, 2] and leads therefore to a blue shift of band - gap energy, when the particle size falls below a particular size depending on the semiconductor species [3-6]. CdS is a good and most popular example for group II–VI semiconductor [7] with a direct bandgap energy of 2.42 eV [7- 9] at room temperature, and it shows great potential for uses in photochemical catalysis, solar cells, nonlinear optical materials, bioimaging and various luminescence devices [10-17]. Extensive research has focused on the synthesis of various CdS nanostructures. However, to get well defined and optimized properties, it is necessary for synthesizing particles to narrow size distribution [18-21]. In recent papers many suitable capping agents, such as saccharides, (glucose, lactose, chitosan, starch and...) [22-27], thiols [28, 29] or polymers have been used to obtain CdS (QDs) [30-33]. In this work, we report preparation of CdS nanoparticles at 90 °C by co-precipitation method using two different capping agent, ethylene glycol (EG) and ethylenediaminetetraacetic acid (EDTA). Characterization of the CdS nanoparticles obtained was carried out by XRD, SEM and UV–vis spectra.

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2. Experimental

2.1 Materials

All the chemicals were of analytical grade and used without any further purification. Cadmium acetate as a source of cadmium ions, sodium thiosulfate, EDTA and EG used as capping agents were supplied by Merck.

2.2. Characterization

The crystal structure of the samples were examined using X-ray diffraction technique (X'per PRO (PANalytical)) with a graphite monochromator, Cu K α radiation ($k\alpha = 1.5418 \text{ \AA}$) in 2θ ranging between 10° and 80° at room temperature while the tube voltage and electric current were held at 40 kV and 20 mA. Field Emission Scanning Electron Microscopic images and Energy Dispersive X-ray analysis (FESEM-EDAX) were obtained using Hitachi F4160, Oxford. A NICOLET 5700 Instrument was used to record FT-IR spectra and a Varian Cary 100 Spectrophotometer in the range of 200-800 nm was used to record UV-Vis absorption spectra.

2.3. Synthesis of CdS@EDTA nanoparticles (CdS-1)

In a typical synthesis process, 2 mmole cadmium acetate ($\text{Cd}(\text{CH}_3\text{Coo})_2 \cdot 2\text{H}_2\text{O}$) was dissolved in 30 mL deionized water to get Cd^{2+} solution and was added 0.87gr of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) (4 mmole) stirring at room temperature. The mixture obtained was called solution A. Now 0.057 mol/L of EDTA was added into the solution A under magnetically stirring at room temperature for 30min. The reacting system was further stirred at 90°C for 5 h. The precipitate was finally washed several times with ethanol and acetone and dried at 70°C for 4 h.

2.4. Synthesis CdS@ EG nanollparticles (CdS-2)

To a solution of 2 mmole of cadmium acetate dissolved in 30 mL EG and 2ml deionized water to get Cd^{2+} solution (solution A), a solution of 4mmole sodium thiosulfate dissolved in 30 ml EG (solution B) was added dropwise under vigorously stirring for 30min. The reacting system was further stirred at 90°C for 5 h. The precipitate was washed several times with ethanol and acetone and dried at 70°C for 4 h [34].

3. Results and discussion

3.1 UV-Visible study

Fig. 1 shows the UV-visible absorption spectra of CdS-1 in comparison with CdS-2 measured at the room temperature in the range of 200-700 nm. This figure shows that the absorbance onsets appeared at 309.2 and 463 nm for CdS- 1 and CdS-2 are significantly blue-shifted from the value for the bulk CdS which is at about 515 nm (2.4 eV) and is due to the quantum confinement of the particles [35-36].

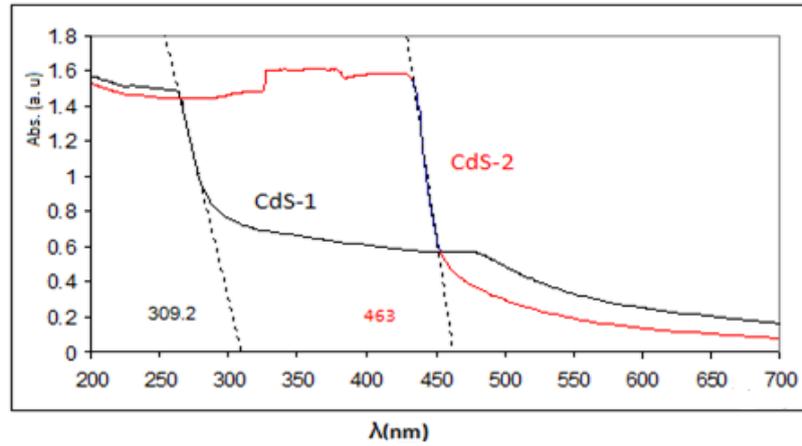


Fig 1. Absorption spectra of CdS-1 and CdS-2 nanoparticles

The absorption edge corresponding to the electron excitation from valance band to conduction band can be used to determine the nature and value of the optical band gap of the prepared CdS nanoparticles. To obtaining these absorption characteristics we have calculated, at first the transmittance (T) measured at different wavelengths (λ) and then absorption coefficients (α) at the corresponding wavelengths λ are calculated using the Beer-Lambert' s relation (Eq. (1)).

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (1)$$

Where d is the path length. The relation between the incident photon energy ($h\nu$) and the absorption coefficients (α) is given by the following relation:

$$(\alpha h\nu)^{1/m} = c(h\nu - E_g) \quad (2)$$

Where c is a constant and E_g is the band gap of the material and the exponent m depends on the type of the transition. For direct and allowed transition $m=1/2$, indirect transition $m=2$, and for direct forbidden $m=3/2$. For calculating the direct band gap value, we plotted the value of $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 2. By extrapolating the straight portion of the graph on $h\nu$ (eV) axis at $\alpha=0$, the optical band gaps were calculated and the results obtained are given in Table 1. The increase observed in the band gap energies as compared with bulk value of CdS (2.42eV) is due to quantum confinement effect created by used surfactants [37-40].

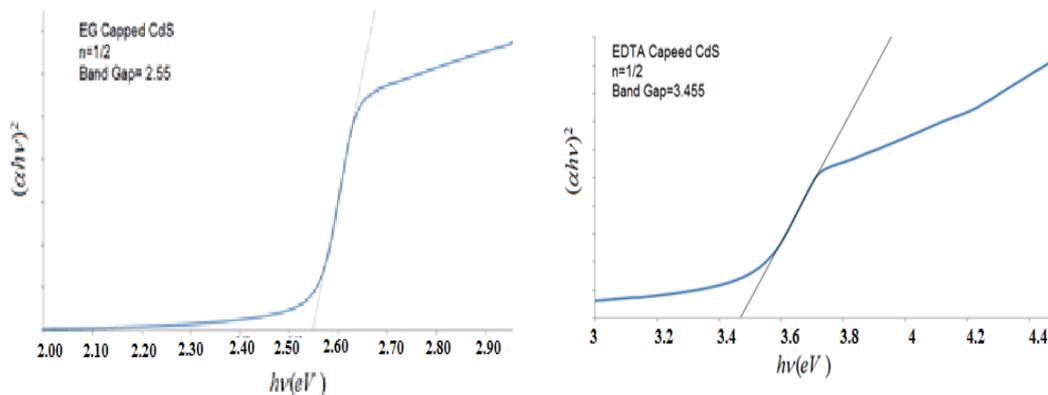


Fig 2. Evaluated direct band gap energy using UV-vis absorption spectra for CdS-1 and CdS-2 nanoparticles

Table 1. Calculated band gap for CdS-1 and CdS-2

samples	Band gap (ev) (Bulk)	Band gap (ev) (nano)	Blue shift of optical band gap (ev)
CdS-1	2.42	3.45	1.03
CdS-2	2.42	2.55	0.13

Brus et al., based on quantum mechanics for calculation of the size of nanoparticle, proposed an equation to describe the emission energy of quantum dot of semiconductor nanocrystals. This expression gives a [41] relationship between the E_g energy and the particle radius (r) as described by the following equation (Equation 3):

$$E_{(QD)} = E_{g(Bulk)} + \frac{\hbar^2 \pi^2}{2\mu R^2} - 1.786 \frac{e^2}{\epsilon R} - 0.248 E_{RY}^* \quad (3)$$

With:

$$\mu = \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]$$

Where $E_{(QD)}$ nano and $E_{(bulk)}$ are the band gap values of the nanoparticles and the bulk material, μ is the reduced mass of m_e^* and m_h^* or effective masses of electron ($0.21 m_0$ for CdS) in conduction band and holes ($0.80 m_0$ for CdS) in valance band respectively where, m_0 is the mass of electron, e is the electron charge and ϵ is the relative permittivity of the semiconductor, R is the radius of the particles and E_{RY}^* is the effective Rydberg energy. The second term of the equation 3 represents additional energy due to quantum confinement having a $1/R^2$ dependence on band gap energy and R (sphere radius) is associated to particle size. The third subtractive term stands for the columbic interaction energy of exciton in $1/R$ dependence, is often neglected due to high dielectric constant of the material [42-48]. Using our calculated bond gap energy in Brus equation, the particle size of CdS-1 and CdS-2 was found to be 7.8 nm and 8.7 nm respectively.

3.2 XRD study

Fig. 3a,b shows the powder XRD pattern of the synthesized CdS-1nanoparticle in comparison with the CdS pattern reported by [49]. In Fig.3a the six prominent peaks values observed at 24.4° , 26.7° , 28.4° , 44° , 47.8° and 51.9° 2θ angles can be readily be indexed to the reflections of (100), (002), (101), (220), (103) and (112) planes corresponding to the hexagonal CdS Wurtzite structure (space group: P63mc) with the lattice constant $a=4.0726 \text{ \AA}$ and $c=6.6895 \text{ \AA}$ (JCPDS Card No. 10-0454). This result was very close to that of those reported for hexagonal CdS values [49], noting that the higher intensities of (002) plane compared with other planes in the pattern suggests that the prepared sample have a preferential growth along the [002] direction [50-51].

Fig. 4a,b represents the powder XRD patterns of the CdS nanoparticles synthesized by using EG in comparison with the results reported by Nayereh soltani et al. [52]. In this figure the peaks observed at 2θ values of 26.66 , 43.40 and 52.01 are well matched with the (111), (220) and (311) crystallite planes corresponded to the face centered cubic structure of CdS (ICDD PDF 89-0440) with a crystal lattice parameter of 5.8 \AA and the cell volume of 198.2 \AA^3 . All the structural parameters shown in Table 2 were calculated using interplanar spacing values of d corresponding to the lattice plane h, k, l by Debye-scherrer formula:

$$d = \lambda / 2 \sin \theta \quad (4)$$

Table 2 shows also the average crystallite size of the samples calculated using Scherrer formula [53,54]:

$$D = k\lambda / \beta \cos\theta \quad (5)$$

Where, D is the mean crystalline size, K is a dimensionless shape factor, with a value close to unity which varies from 0.89 for spherical to 0.94 for cubic particles (usually, is taken 0.9 for particles in unknown size [54, 55]), λ is the X-ray wavelength, β is the full-width at half-maximum of the diffraction peaks (FWHM) and θ is the diffraction angle. Table 3, shows the average nanocrystallite sizes calculated for CdS-1 and CdS-2 respectively to be 7.8 nm and 8.5 nm. These values were obtained using the first intense peaks of (100) and (111) at 2θ value 24.4° and 26.66° for CdS-1 and CdS-2. Since, the peak broadening at lower angle is more meaningful for the calculation of particle size. The particle size obtained 7.8 nm and 8.5 nm were in good agreement with the crystallite size calculated from Brus model.

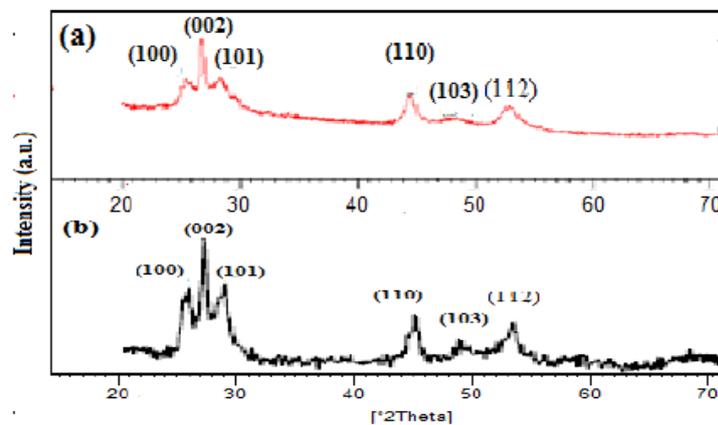


Fig 3. XRD pattern of: a) CdS-1 b) CdS nanoparticles as reported by [49].

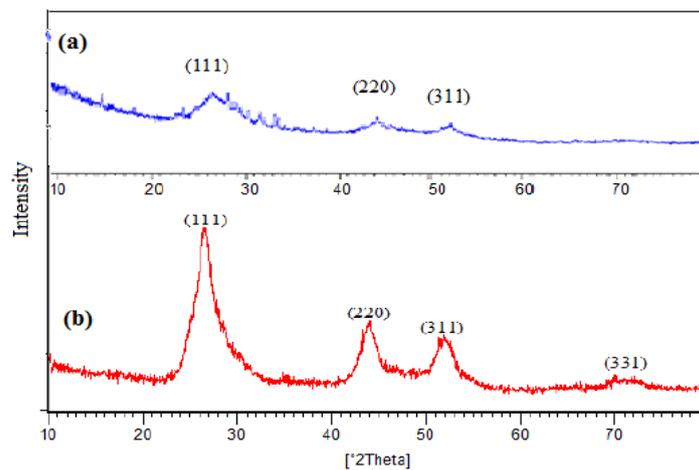


Fig 4. XRD pattern of: a) CdS-1 b) CdS nanoparticles as reported by [52]

Table2. Structural parameters of CdS nanoparticles calculated from the XRD patterns.

Prepared nanoparticles	Crystallite Plane (hkl)	Standard Jcpds d values (Å)	Calculated d values (Å)	2 θ value		Crystallite size (nm)
				JCPDS	Expt.	
CdS-1	(100)	3.586	3.533	24.808	25.190	8.7
	(002)	3.360	3.357	26.507	26.531	21.3
	(101)	3.164	3.180	28.183	28.04	5.4
	(110)	2.070	2.063	43.682	43.854	9.4
	(103)	1.900	1.917	47.840	47.380	3.8
	(112)	1.763	1.759	51.825	51.953	6.8
CdS-2	(111)	3.341	3.333	26.660	26.720	8.5
	(220)	2.060	2.071	43.905	43.680	17.9
	(311)	1.754	1.753	52.108	52.141	23.1

Table3- Calculated Particles size using Brus and Sherrer formula

sample	UV-Vis Spectra λ (nm)	Calculated Particles size)	
		Using Brus's formula (nm)	Using Scherrer formula (nm)
CdS-1	309.2	7.8	7.6
CdS-2	463.0	8.7	8.5

3.3 Morphological study

Fig. 5 shows morphological image of the samples using SEM. This image demonstrates clearly the formation of spherical CdS nanoparticles for both the cases which are the same. From this figure, it also can be seen that, EDTA-capped CdS nanoparticles, in the form of nanoclusters had a smaller grain size than that of EG-capped CdS.

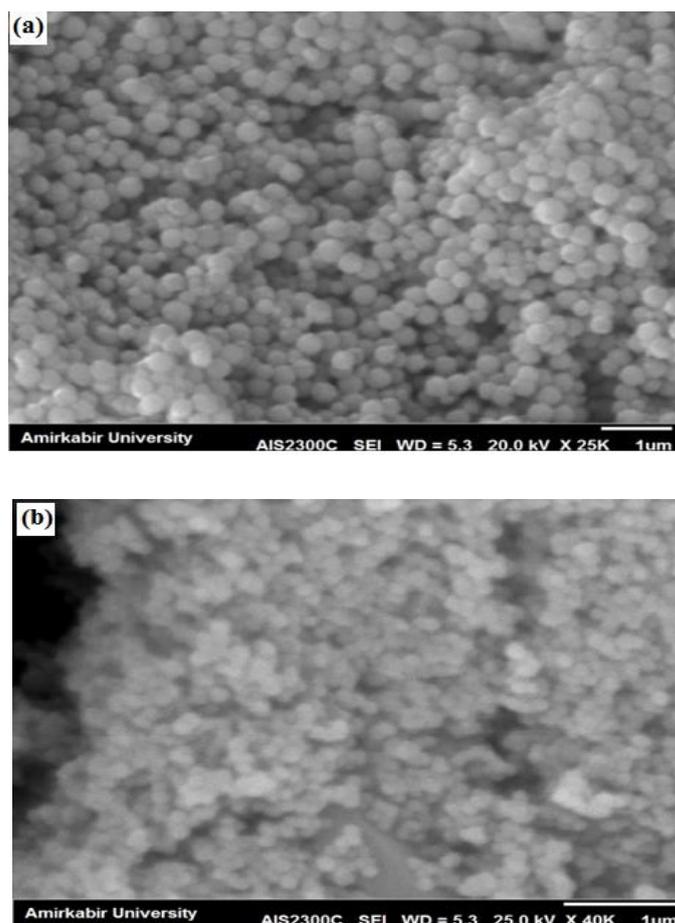


Fig 5. SEM images of CdS samples: a) CdS-1; b) CdS-2

4. Conclusions

We have successfully synthesized EDTA-capped and EG-capped CdS nanoparticles separately. The XRD analysis revealed formation of hexagonal form when we used EDTA as a surfactant agent. Whereas, a face centered cubic structure was obtained by using EG as surfactant agent. The absorbance onsets values appeared at 309.2 and 463 nm respectively for both the cases were significantly blue-shifted from the onset value of the bulk CdS due to the quantum confinement properties.

The broad peak nature of the XRD pattern confirms nanocrystallinity behavior of the samples with an average crystalline size of 7.6 and 8.5 nm for CdS-1 and CdS-2 respectively. These values were approximately in good accordance with the values calculated by Brus formula. The morphology of the samples studied by SEM images was in conformity with the results of decreased crystallite sizes for the samples calculated by using Scherrer formula.

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