

ON THE EFFECT OF COMPLEXING AGENTS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CdS NANOCRYSTALS

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In the present work a simple chemical method is followed to grow CdS nanocrystals at room temperature. In order to study the effect of using complexing agents we grow three CdS nanocrystals, two of them with complexing agents and the third without complexing agents. The synthesized nanocrystals were characterized using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and UV-visible spectrophotometry. The yield, elemental analysis, lattice parameters, crystallite sizes, microstrains and the band gap energy of the three CdS nanocrystals were evaluated. Best results were obtained for CdS nanocrystals which was grown without using complexing agents.

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1. Introduction

Nanoparticles of II-VI group semiconductor materials have been investigated by material scientists due to their excellent optical, structural, electrical, magnetic, dielectric, piezoelectric and optoelectronics properties, which are absent in bulk materials since nanoparticles have a wide number of surface atoms than that of bulk [1-4]. Among II-VI compounds, CdS with a direct band gap, $E_g = 2.40$ eV, is an important semiconductor with non-linear optical properties has potential applications such as solar battery, photoelectrocatalysis, Biological sensors and photodiodes [5-9].

Many synthetic methods have been employed to prepare CdS nanoparticles including solidstate reaction, sol-gel process and microwave heating [10-16]. Moreover, reports on the effect of complexing agents on preparation of CdS nanocrystals and their structural and optical properties are nil.

This paper deals with fabrication of CdS nanocrystals by simple chemical reaction method. In this work we aimed to study the effect of complexing agents on preparing CdS nanocrystals, and comparative evaluation of their structural and optical properties.

2. Experimental

2.1 Preparation of CdS nanocrystals

The used initial elements for the synthesis of CdS nanocrystals are high pure chemicals. In this work we used simple chemical reaction method for preparing CdS nanocrystals under three different cases, two with complexing agent and the third without using complexing agent as follow:

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Synthesis of CdS (1):

CdS (1) was prepared according to R. Eiiilarassi [17] method as follows:

$\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.025 mole, 7.7 gm) and thiourea (0.025 mole, 1.9 gm) were dissolved in 100 ml 0.05 M NaOH solution. The reaction mixture was kept under constant magnetic stirring and 50 ml 0.1 M of ammonium hydroxide NH_4OH was added to the stirred solution. A white precipitate was formed in the beginning, which gradually became transparent and the color changed from white to yellow after 15 min., and then the reaction mixture was further stirred for one hour. The yellow precipitate formed of CdS was filtered off, washed with water and dried at 100 °C .

Synthesis of CdS (2):

50 ml of aqueous solution of $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.025 mole, 7.7 gm) and 50 ml of aqueous solution of thiourea (0.025 mole, 1.9 gm) were added to 100 ml 0.05 M NaOH solution. The reaction mixture was kept under constant magnetic stirring and then 50 ml aqueous solution of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) (0.025 mole, 1.72 gm) was added to the stirred solution. A white precipitate was formed in the beginning, which changed to yellow precipitate after 1 hour. The reaction mixture was further stirred for additional one hour. The yellow precipitate formed of CdS was filtered off, washed with water and dried at 100 °C .

Synthesis of CdS (3):

50 ml of aqueous solution of $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.025 mole, 7.7 gm) and 50 ml of aqueous solution of thiourea (0.025 mole, 1.9 gm) were added to 100 ml 0.05 M NaOH solution. The reaction mixture was kept under constant magnetic stirring. A white precipitate was formed in the beginning, which gradually changed to yellow precipitate after 10 min., and then the reaction mixture was further stirred for one hour. The precipitate was then filtered off, washed with water and dried at 100 °C.

2.2 Characterizations

The grown CdS nanocrystals were analyzed by energy dispersive x-ray analysis, X-ray diffractograms and transmission electron microscopy.

The X-ray diffractograms were measured stepwise with angle/second value of 0.02° at ambient temperature with a model D 5000 Siemens diffractometer (Germany). High resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL JEM 2100 microscope (Japan). The chemical composition of the samples was determined using an energy dispersive x-ray analysis (EDX) spectrometer (Elemental Analyzer EDXRF, JSX3222, JEOL, Japan) attached to the scanning electron microscope. The UV–VIS absorption spectra were measured on a UV–Visible spectrometer.

3. Results and discussion**3.1 Effect of complexing agents on the elemental analysis of CdS nanoparticles**

Nanocrystalline cadmium sulfide particles were prepared at room temperature starting from cadmium nitrate and thiourea in aqueous alkaline medium in the presence of different complexing agents such as ammonium hydroxide, hydroxylamine hydrochloride or without complexing agents. From Table 1 we can find that the complexing agents affected the yield amount and the elemental analysis of the obtained compound. As we see when we didn't use complexing agents we get the best yield and elemental analysis near the calculated one for CdS.

Table 1 Effect of complexing agents on the elemental analysis of the obtained CdS nanocrystals

Sample	Complexing agent	Yield	Elemental analysis		Calculated elemental analysis for CdS
			Cd	S	
CdS (1)	NH ₄ OH	3.11 gm (86%)	78.65%	21.35%	Cd = 77.78% S = 22.22%
CdS (2)	NH ₂ OH.HCl	1.5 gm (41%)	78.11%	21.89%	
CdS (3)	Without	3.35 gm (93%)	77.07%	22.93%	

3.2 Effect of complexing agents on the crystalline property of CdS nanoparticles

HRTEM was employed to obtain direct information about the size of the produced CdS nanoparticles. Figure 1 presents a typical HRTEM image of CdS (1) sample as a representative sample. It shows that practically monodisperse particles with an average size about 4 nm were loosely distributed on the grid. The fact that no large dense flocs were observed in the HRTEM image already indicates that the prepared CdS nanoparticles were well-dispersed in the solution.

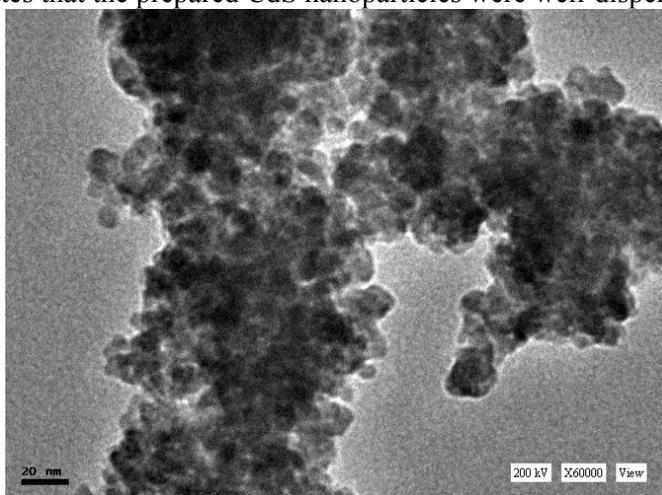


Fig. 1. The HRTEM image of CdS (1) nanocrystals

Figure 2 depicts the X-ray diffractograms for the prepared CdS nanocrystals. The spectra confirm the crystalline nature of the prepared crystals. XRD measurements showed agreement with Cross-Ref PDF No. 89-0440.

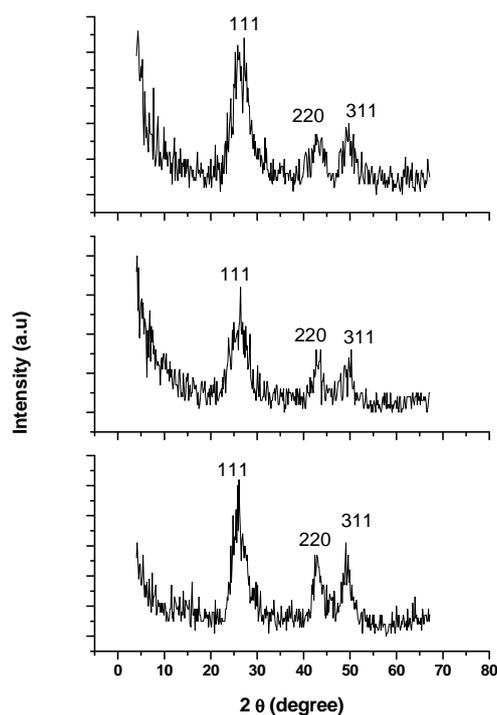


Fig.2. X ray powder diffraction pattern of CdS (1), CdS (2) and CdS (3) samples

Using known equations [18, 19] we can obtain the most accurate lattice parameter for the grown CdS nanocrystals. Figure 3 shows the relation between the lattice parameters a for the three samples vs. angular function $F(\theta)$. From this figure, the lattice parameters for the obtained crystals are $a = 5.89$, 5.93 and 5.85 \AA for CdS (1), CdS (2) and CdS (3) respectively, where the lattice parameters for the standard CdS is 5.83 \AA , [20]. These results verify the identity between the grown crystals and the standard one, also CdS (3) sample is the most closely to the standard CdS. We suggest that this is due to the correspondence between Cd and S ratio in sample CdS (3) and the standard one.

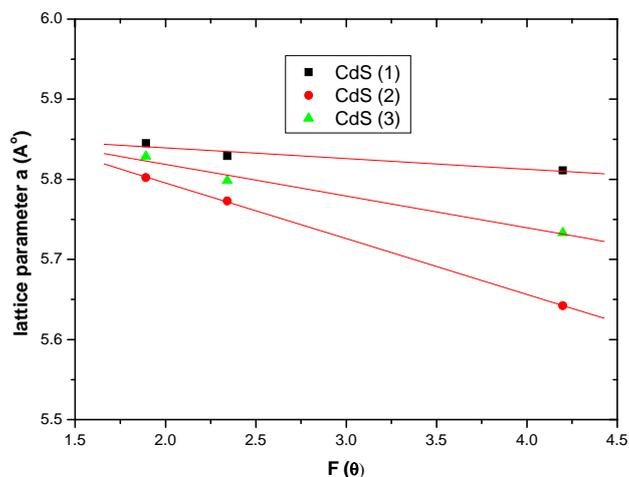


Fig. 3. The relation between the lattice parameters and $F(\theta)$ of CdS (1), CdS (2) and CdS (3) samples

To estimate the particle size using X-ray powder diffraction measurements, the Scherrer equation is the most used method [21]. The particle size (D) can be calculated using the Scherrer equation [22]:

$$D = k\lambda / \beta \cos \theta$$

where k is the shape coefficient for the reciprocal lattice point and shape coefficient for crystal in the direct space [23], λ is the wavelength of the incident radiation, β is the full-width at half-maximum (FWHM) of the peak and θ is the Bragg angle.

The Scherrer equation gives us a rough estimate of particle size. Despite the well-known accuracy of this method, it neglects the importance of the microstrain, ϵ , and its effects in the powder diffraction pattern [24].

A simple method to separate the contributions of particle size and microstrain to the line broadening in the XRPD patterns is the Williamson–Hall (WH) plotting [25]. This analysis supposes that particle size (D) and microstrain (ϵ) contribute to the line broadening with Lorentzian profiles described by:

$$\beta = \beta_D + \beta_\epsilon$$

where β is considered as the sum of the peak width due to the microstrain and due to particle size. WH plotting assumes that those contributions to the peak width are convoluted in the Full Width at Half Maximum (FWHM) of the diffraction peak. The WH equation can be written as [25]:

$$\frac{\beta}{\lambda} \cos \theta = \frac{k}{D} + \frac{4\epsilon}{\lambda} \sin \theta$$

Figure 4 shows the WH plotting for our three samples. This WH plotting method proved that average particle size $D=3.7$, 5.4 and 3.2 nm and microstrain is about 0.0028, 0.0015 and 0.0075 for CdS (1), CdS (2) and CdS (3) respectively. The positive signal of the microstrain indicates a lattice expansion; this result is in a good agreement with the results obtained from Fig. 3. These results suggest that the obtained CdS nanocrystals are homogenous in size and microstrain.

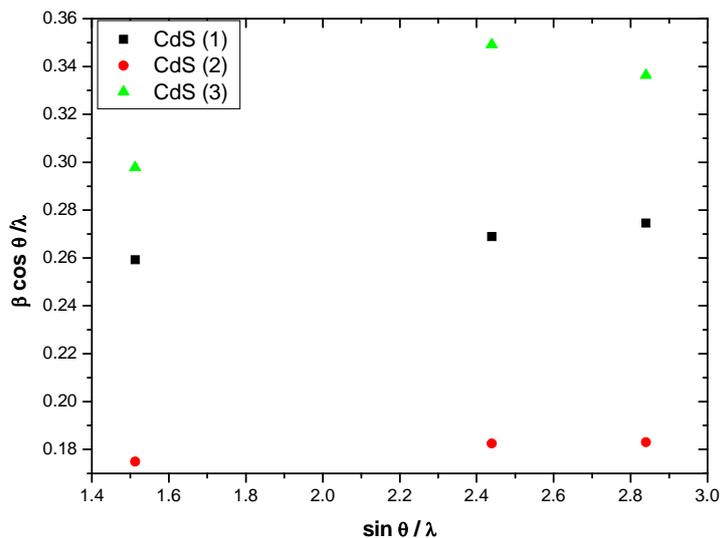


Fig. 4. Williamson – Hall plotting of CdS (1), CdS (2) and CdS (3) samples

As can be seen in Table 2 the average particle size obtained from the Scherrer equation is 3.5, 5.2 and 2.9 nm while the average particle size calculated using the WH plotting is 3.7, 5.4 and 3.2 nm for CdS (1), CdS (2) and CdS (3) respectively, the obtained results for our grown nanocrystals are better than the published data [17]. Nanoparticle size estimated from Scherrer

equation is quite different from that obtained by WH plotting. This difference can be explained: the microstrain can induce a greater broadening in the diffraction peak while in the Scherrer equation, the full width of the diffraction peak is considered in the calculation. The WH procedure presents a correction for this problem.

Table 2: Effect of complexing agents on structural parameters and energy gap.

Sample	Crystallographic directions	Scherrer equation	WH plotting		Lattice parameter	Energy gap
	{hkl}	D (nm)	D (nm)	ϵ	a (Å)	Eg (eV)
CdS (1)	{111}	3.62	3.7	0.0028	5.89	4.6
	{220}	3.49				
	{311}	3.42				
CdS (2)	{111}	5.37	5.4	0.0015	5.93	4.3
	{220}	5.15				
	{311}	5.13				
CdS (3)	{111}	3.41	3.2	0.0075	5.85	4.75
	{220}	3.17				
	{311}	2.19				

3.3 Effect of complexing agents on the optical properties of CdS nanoparticles

UV–Visible absorption spectra for CdS nanocrystals prepared from different complexing agents are shown in Fig. 5. Comparing the absorption edge of bulk CdS with that of CdS (1), CdS (2) and CdS (3) samples, it is seen that a blue shift in the onset of absorption is observed in these samples. This phenomenon of blue shift of absorption edge has been ascribed to a decrease in particle size. This results in a shift in the absorption edge to a lower wavelength region. The absorption edge of samples CdS (1), CdS (2) and CdS (3) is about 300, 340 and 280 nm. Compared with the absorption edge of bulk materials (515 nm), the amount of blue shift is 215, 175 and 235 nm respectively. The main reasons for the blue shift are the quantum dimensional effect of the nanoparticles, which will induce the wider band gap and the blue shift of absorption band due to the decrease of particle size, and the surface effect of the nanoparticles, because the large surface force will cause crystal lattice aberration and a small crystal constant. At the same time, the short band length will induce the increase of the bond intrinsic oscillation frequency of nanoparticles, leading the blue shift of the absorption band. Therefore, the nanoparticle size is smaller, and the blue shift is more obvious [26].

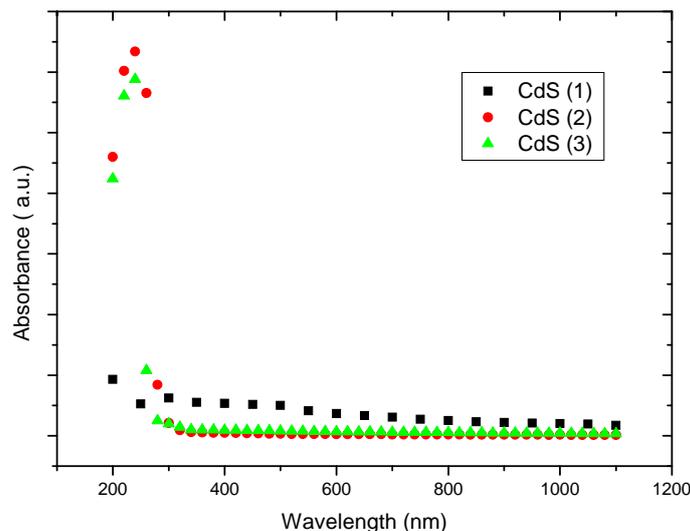


Fig. 5. UV-Visible absorbance spectra of CdS (1), CdS (2) and CdS (3) samples

From the onset of the adsorption edge, the band gap of the CdS particles was calculated using the method of Tandon and Gupta [27]. In Table 2, the band gap is found to increase in the order CdS (3) > CdS (1) > CdS (2). It is well known that in case of semiconductors the band gap between the valence and conduction band increases as the size of the particle decreases in the nanosize range [28]. The obtained values for energy gap are in a good agreement with published data [29].

4. Conclusion

Without using complexing agents CdS nanocrystals were obtained with properties better than the other two samples which were grown with complexing agents. On the other hand CdS nanocrystals which were prepared using NH_4OH as complexing agents have properties better than those prepared using $\text{NH}_2\text{OH.HCl}$.

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