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STRUCTURAL AND OPTICAL ANALYSIS OF CdS NANOCRYSTALS PREPARED BY LOW TEMPERATURE THERMOLYSIS

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CdS nanoparticles were synthesized via low temperature thermolysis method using cadmium chloride and thiourea as cadmium and sulphur sources respectively. XRD analysis of nanocrystals prepared with three different synthesis times showed the crystalline nature, structure as well as particle size of the prepared CdS particles. From the peaks position of XRD spectra, the dependence of phase of CdS nanoparticles with the synthesis time has also been found. The absorption spectra enabled to visualize the blue shift in absorption onset. The bandgap of the prepared nanoparticles are found to be in the range 3.6-3.86eV. SEM, TEM and SAED images of CdS nanoparticles showed their morphology, particle size and crystallinity respectively. From the structural and SEM analysis it has been confirmed that phase change can be achieved by annealing the samples.

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1. Introduction

In the present study CdS nanocrystals have been synthesized based on low-temperature thermolysis of single-source organometallic precursor in noncordinating solvent ethanol. This technique has the ability to achieve high temperature stable phase at very low temperature. It provides not only an economically viable route for applications but also opens a new avenue to study structural kinetics and chemistry of semiconductor nanocrystals [1]. In the present study CdS nanocrystals have been synthesized based on low-temperature thermolysis of one single-source organometallic precursor in noncordinating solvent ethanol. The organometallic precursor was prepared by using cadmium chloride, thiourea and sodium hydroxide in ethanol solution. Another advantage of this method are that protective inert gas or vacuum is not needed. Moreover no toxic material is used, and is easy to reproduce. It is mainly focused on the dependence of parameters such as synthesis time and temperature on the effect of size of nanoparticles and also on their structural, optical and morphological behavior.

2. Experimental

Using ethanol as solvent, solution A was prepared by dissolving 36mg of cadmium chloride ($CdCl_2$) and 12mg of thiourea($(NH_2)_2CS$) in to 30ml of ethanol in a flask under magnetic stirring at 60^0 C. Solution B was prepared by dissolving 10mg of sodium hydroxide (NaOH) in 10ml ethanol. Solution B was rapidly injected in to solution A. The mixed solution was held at 60^o C under magnetic stirring. Following rapid injection, a white precursor was obtained. The reaction system gradually becomes transparent and the color changes slowly to yellow. The nanoparticles are then separated by centrifugation and washed with acetone to get

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rid of unreacted solvent. All chemicals used are of analytical grade and the whole experiment was conducted in air atmosphere.

3. Reaction mechanism

This method makes use of cadmium chloride and thiourea as cadmium and sulphur sources. The synthesis mechanism can be described as Cd^{2+} cations reacting with s^{2-} anions released from decomposition of thiourea in solution. The reaction solution was made alkaline by the addition of NaOH. The white precursor formed immediately after the injection of NaOH solution is an organometallic precursor which could not formed if the NaOH solution was first added to the solution of $CdCl_2$ before adding$(NH_2)_2CS$. CdS nanocrystals cannot be formed without adding NaOH or other latescent reagents. The possible composition of the organometallic precursor is $[Cd(OH)_2]SC(NH_2)_2]_{ads}^{2+}$. The metastable complex decomposes and CdS is formed according to the equation

$$[Cd(OH)_2]SC(NH_2)_2]_{ads}^{2+} \rightarrow CdS + CN_2H_2 + 2H_2O \qquad (1)$$

It is observed that as soon as CdS is formed the colour of the precursor changes from off white to pale yellow and then to dark yellow.

In this study nanocrystals are prepared by changing the volume of the reactants and also the time of reaction /synthesis time (Ts). The volumes of reactants are optimized first and then Ts is varied as 2, 5 and 10hrs respectively for 3 samples which are named as D2, D5 and D10 respectively. The nanocrystals prepared were then analyzed to monitor the growth and phase transitions.

4. Results and discussion

4.1 Structural analysis

In the present study the structural characterization of CdS nanocrystals has been carried out using Shimadzu (Lab X-6000) x-ray diffractometer using Cu kα(λ = 1.5406 Å) line in 2θ range from 20 – 80^0. The x-ray powder diffraction pattern of CdS nanocrystals prepared for three different times is shown in Fig. 1.

The phases of the sample can be identified and the maxima can be assigned by comparing the XRD spectra to ASTM data. The prominent peaks of the spectra confirm that the synthesized particles have crystalline structure. The estimated d' spacing of (hkl) planes are given in Table 1.

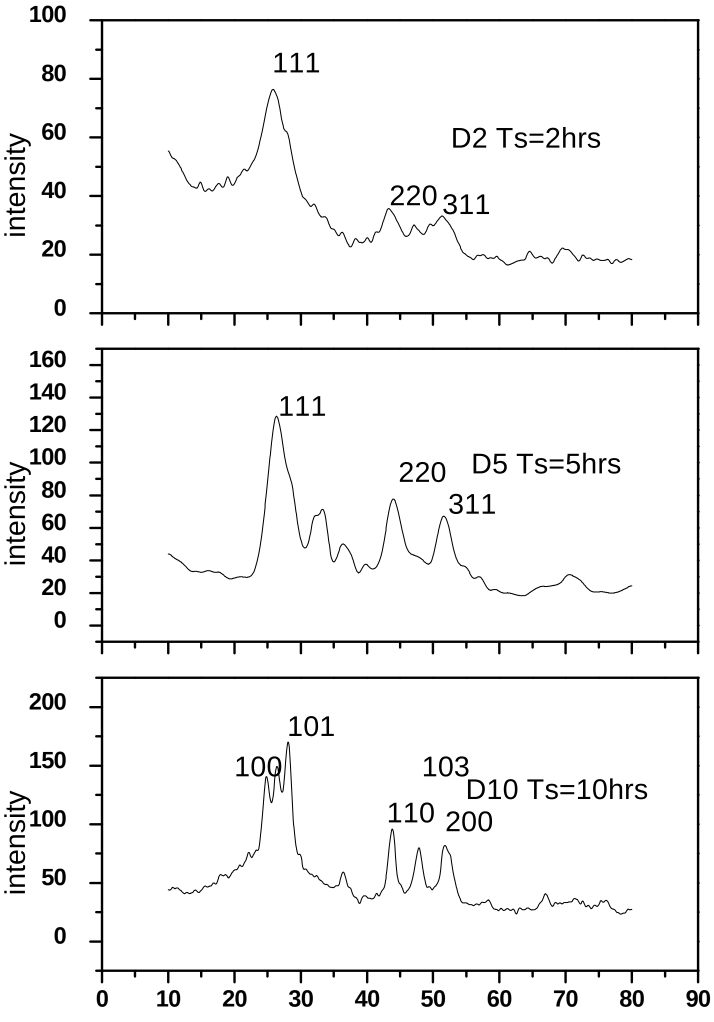


Fig. 1 XRD profiles of CdS nanocrystals.

size were estimated and presented in Table 1. It has been observed that there are typical peaks belonging to CdS particles and the peak broadening suggested the formation of nanocrystals of size about 4nm. The observed peaks show that the nanocrystals formed show a change in phase from cubical to hexagonal as reaction time increases [1]. The average crystal size has been estimated using Scherrer formula [2] and is presented in Table 1.

Lattice constants of the samples are evaluated using equations (2) and (3) and are tabulated in Table 2. It is seen that the lattice constants of the sample D10 coincide with that of hexagonal structure and lattice constants of samples D2 and D5 coincides with that of cubic structure. As reaction time increases a gradual increase in particle size is observed and when the synthesis time is 10 hours hexagonal phase (Wurzite) is seen which is the structure of bulk CdS.

From (hkl) planes the lattice constants for hexagonal structure can be evaluated using the relation

$$1/d^2=4/3\{(h^2+hk+h^2)/a^2\} + (l/c^2) \qquad (2)$$

For cubic structure the lattice constant can be evaluated using the formula

$$a = d^*(h^2+k^2+l^2)^{½} \tag{3}$$

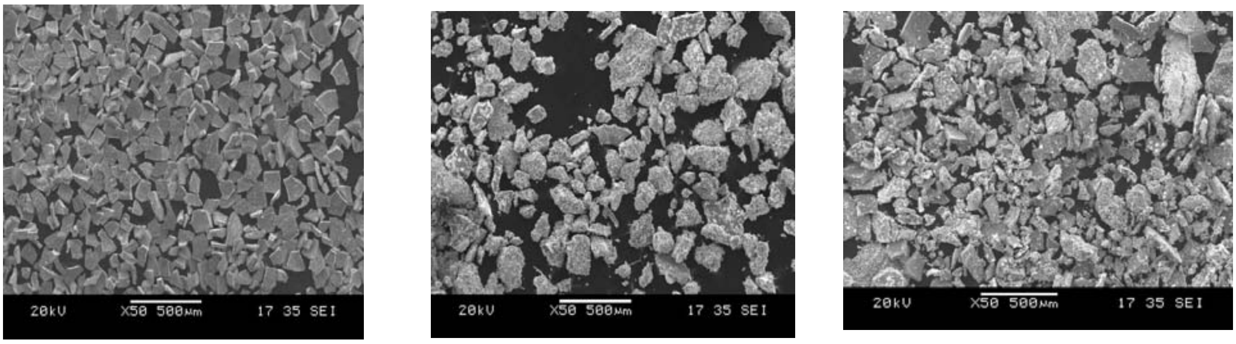
Samples D5 and D2 contain peaks around 26°, 43° and 52° (2θ) corresponding to reflections from (111), (220) and (311) planes of β-CdS (the cubic phase of CdS) having zinc blende structure. In sample D10, there are 3 diffraction peaks located at 24.8°, 28.15° and 47.5° (2θ) which correspond to (100), (101) and (103) reflections of the hexagonal phase of CdS [2]. In sample D10 were the nanocrystal diameter is the largest, there is a combination of hexagonal phase and the cubic phase. The presence of the hexagonal phase is identified without ambiguity from the (103) reflection observed in the sample, which is characteristic of hexagonal CdS [3]. In bulk CdS crystals the diffracted intensity in all directions other than those satisfying the Bragg condition will be zero due to destructive interference. However, for crystals of finite size, this destructive interference will not be complete, leading to a finite width of the diffraction peaks. It is interesting to note that irrespective of the structure, the particle size increases with synthesis time
In order to further elucidate the size, shape and crystal structure of the clusters, SEM analysis was carried out using JEOL-Japan-JSM 6360. Fig.2 shows SEM images prepared at 60 °C for 2, 5 and 10 hrs respectively. From Fig.2, it is clear that the particles show crystalline nature and the reaction time affects the morphology of nanocrystals [1, 3].

Table. 1 XRD data of CdS nanocrystals.

Sample	Angle(2θ) (degrees)		d(Å)	(hkl)	Particle size (nm)
	ASTM	Observed			
D10 (Ts =10hrs)	24.828 26.449 28.216 36.648 43.735 47.885 52.072 66.867	24.85 26.45 28.15 36.40 43.80 47.50 51.65 66.95	3.579 3.366 3.166 2.465 2.064 1.912 1.768 1.396	100 002 H/111(C) 101 102 110 H/220(C) **103** 220H/311(C) 203	7.52
D5 (Ts =5hrs)	26.514 43.983 52.094	26.35 44.00 51.65	3.378 2.056 1.768	111 220 311	6.02
D2 (Ts =2hrs)	26.514 43.983 52.094	26.41 43.85 51.65	3.371 2.062 1.758	111 220 311	4.12

Table. 2 Structure and lattice constants of CdS nanocrystals

Sample	Structure	Lattice constants			
		a		c	
		observed	ASTM	observed	ASTM
D10 (Ts = 10hrs)	Hexagonal	4.129	4.136	6.788	6.713
D5(Ts = 5hrs)	Cubic	5.813	5.818	-	-
D2 (Ts = 2hrs)	Cubic	5.830	5.818	-	-



D2 **D5** **D10**

Fig. 2 SEM images of CdS nanocrystals

B Optical analysis

Absorbance can be calculated using Beer-Lambert law. The Beer-Lambert law is the linear relationship between absorbance and concentration of an absorbing species. The Beer-Lambert law states the absorbance is proportional to the transmitted intensity i.e.

$$A= - \log_{10} (I/I_0) \tag{4}$$

where A is the measured absorbance and I_0 is the maximum intensity of the incident light and I is the transmitted intensity. The ratio I/I_0 is called the transmittance and is usually expressed as (%T). The absorbance A is based on the transmittance T, i.e.

$$A= -\log (\%T) \tag{5}$$

Size of the particle can be calculated using Brus equation [4]:

$$E_{np}=E_g+ \left(\left(h^2/8r^2\right)*[(1/m_e^*)+(1/m_n^*)] \right) -(1.8e^2/4\Pi\varepsilon\, \varepsilon_0\, r) \tag{6}$$

E_{np} is calculated from the excitation absorption peak of the nanoparticles in Joules, E_g is the bulk semiconductor band gap in joules, r is the radius of nanoparticles in meters, m_e^* is the effective mass of electron, m_e is the mass of an electron in kg, m_h^* is the effective mass of the hole, m_h is the mass of a hole in kg, e is the charge of an electron, ε is the dielectric constant of the material and ε_0 is the vacuum permittivity constant in $C^2N^{-1}m^{-2}$.

CdS is a typical direct band gap semiconductor. When the size of CdS nanocrystals becomes smaller than the exciton radius [1], a remarkable quantum size effect leads to a size dependent increase of the band gap and a blue shift in the absorption onset. Fig.3 shows the room temperature UV-VIS absorption spectrum for the CdS nanocrystals. Brus equation was used to calculate the particle size from the absorption peak. The value of electron effective mass (m_e^*) is $0.21m_e$ and the value of the effective mass of hole m_h^* is $0.80m_e$ for CdS where m_e is the mass of electron. The value of dielectric constant is 5.6 and E_g, the band gap energy of bulk CdS is taken as 2.42ev. From the characteristic absorption spectra, the size of CdS nanoparticles is estimated to be about 2.5nm in diameter.

Table. 3 Optical parameters of CdS nanocrystals.

Sample	Eg (nanoparticle) (eV)	Eg (bulk) (eV)	Particle radius(nm)
D10 (Ts=10hrs)	3.60	2.4	1.34
D5 (Ts=5hrs)	3.81	2.4	1.26
D2 (Ts=2hrs)	3.86	2.4	1.24

Fig 4 shows the variation of absorbance with energy. From graph the band gap of particle is determined by extrapolating the absorption onset edge to x axis [4]. Particle radius obtained for three different samples were presented in table 3 and the reduction in particle size gives a shift in the optical band gap. The absorption onset is about 330 nm corresponding to a band gap of 3.8eV which is higher than the band gap of bulk CdS (2.42eV). Moreover, the increment in band gap is

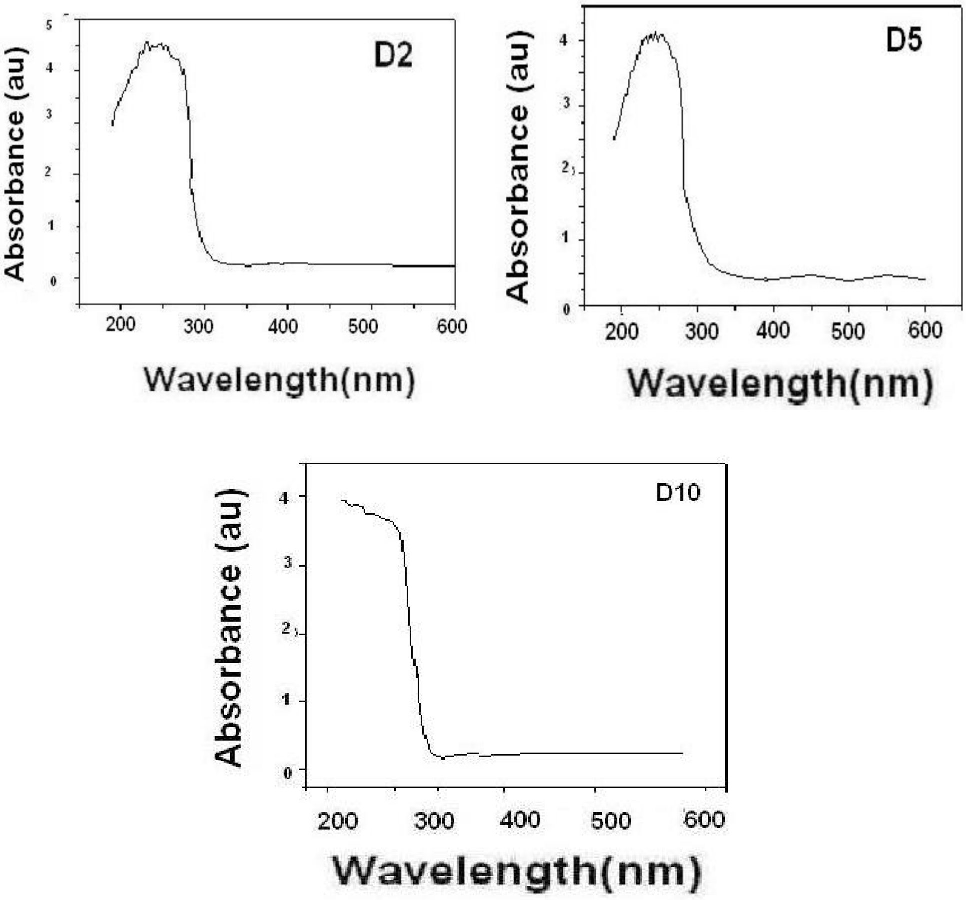


Fig 3 Absorbance spectra of CdS nanocrystals.

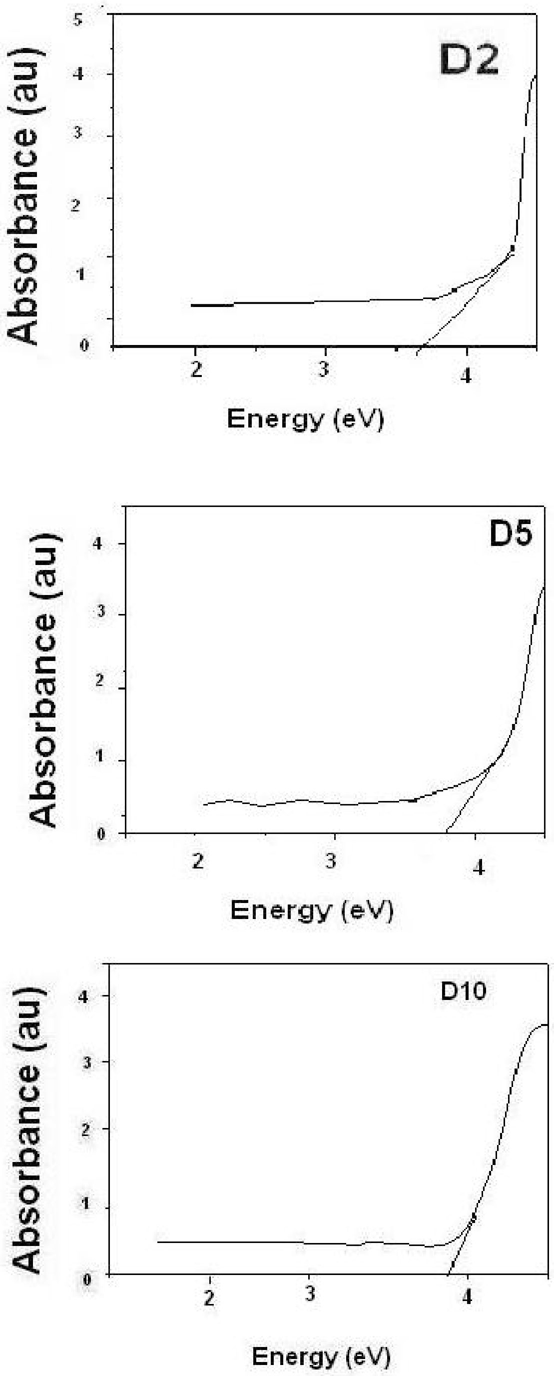


Fig 4 Estimation of Eg of CdS nanocrystals.

approximately inversely proportional to the square of the crystal size based on the effective mass approximation. The absorption edge is shifted to higher energy as the particle size decreases. The intensity of the absorption is also high because of the reduced particle size. Even though the same sample have been used for the structural and optical analysis it has been found that the particle size estimated from the optical absorbance analysis are much smaller from those of XRD analysis. This may be due to the way of using the sample for optical study. The sample has been placed as layers between the two glass plates and therefore the analysis of the absorbance of CdS may be due to 2 or more layers of CdS and not a single CdS nanocrystal. This may be the reason for decrease in particle size and in turn increase in bandgap.

5. Conclusions

XRD profiles of nanocrystals synthesised for 3 different times (2, 5 and 10 hours) show sharp peaks which indicates the crystalline nature of particles. Broadening of peaks is due to the reduced size of particles and also from the position of peaks it is seen that the particle shows a change in phase as synthesis time increases. Surface morphological studies have been carried out using SEM and it shows that the particles are of uniform shape and size and the surface morphology varies with reaction time. Absorbance spectra show a blue shift in absorption onset compared to bulk which is due to the reduced particle size.

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