



Effect of annealing and dopants on the physical properties of CdS nanoparticles

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ABSTRACT

For the synthesis of cadmium sulfide (CdS) nanoparticles, microwave assisted solvothermal method with ethylene glycol as the solvent was used in this work. The cadmium acetate and thioacetamide were used as the cadmium source and sulphide source. Semiconductor nano particles doped with transition metal ions have attracted wide attention due to their excellent luminescent properties. The nano-structured materials of CdS prepared with different annealing periods were characterized by XRD method. The size of the crystallites were determined by XRD method to be 10 nm depending on the amount of the molar ratio of the reactants. The effect of different annealing temperature, concentration of dopants and ionic radii of dopants are also studied.

Key words: Nanoparticles; semiconductor; microwave-assisted method; ethylene glycol; XRD; annealing; doping

INTRODUCTION

Cadmium sulfide (CdS) is an important II–VI group semiconductor with many excellent physical and chemical properties, which has numerous applications in the field of photochemical catalysis, gas sensor, detectors for laser and infrared, solar cells, nonlinear optical materials, luminescence devices, optoelectronic devices, environmental sensors, biological sensors and so on [1-14]. There are various methods developed for the fabrication of nanoparticles [15-19]. Recently, the solvothermal process as a powerful method for the synthesis of materials has attracted tremendous attentions [20, 21]. Comparing with the synthesis route based on colloid chemistry, solvothermal method takes the advantage of obtaining pure and clean nanoparticles in high degree of crystallinity. Efforts have been devoted to the preparation of high quality CdS nanoparticles and the investigation of optical properties [22]. The possibility of tuning the properties of particles by controlling their sizes and shapes can be carried out by the preparation of nanoparticles by solvothermal method. Many papers have been reported by the synthesis of chalcogenides with solvothermal method [23-33]. In this paper, We choose thioacetamide as the sulphide source and it is much easier for thioacetamide to release sulphide ions. A microwave oven has been used for heating the solution containing the reactants and the effects of annealing and dopants on the physical properties of CdS nanoparticles have been analyzed.

EXPERIMENTAL SECTION

In this study, thioacetamide and cadmium acetate were added in the ratio 1:1 molar ratio and were mixed with 30 ml of ethylene glycol and stirred well at room temperature to get a clear transparent solution. The solution was subjected to microwave irradiation of 800 W for 20 minutes. The orange coloured CdS nanocrystallites were separated out from the productive mixtures and washed with de-ionized water for four times and then with alcohol twice.

The sample was finally annealed at about 200 °C for 12 minutes, 20 minutes and 120 minutes to get phase-pure nanoparticles of CdS samples and the samples be called as sample 1, sample 2 and sample B respectively for various annealing times.

In the same way, the as CdS nanoparticles were annealed for different temperatures such as 100 °C for 120 minutes, 200 °C for 120 minutes and 300 °C for 120 minutes and these samples be termed as sample A, sample B and sample C respectively.

In order to synthesize CdS:Cu²⁺ nanoparticles, 1 mol%, 2 mol% and 3 mol% of copper acetate were added to the solutions of thioacetamide and cadmium acetate and these samples were annealed at about 100 °C for 2 hours. Let the copper doped CdS samples be called as sample C1, sample C2 and sample C3.

To understand the effect of ionic radii of Zn²⁺, Mn²⁺, and Cu²⁺ on the CdS nanoparticles, different dopants were added to the host CdS and the samples be called as sample A3, sample B3 and sample C3 for zinc doped, manganese doped and copper doped CdS nanoparticles.

The as-prepared undoped CdS and doped CdS nanoparticles obtained by solvo-thermal route in the present work were characterized by powder X-Ray diffraction technique. The structure and phase purity of the powders were examined by powder X-ray diffraction (XRD) technique using an X-ray diffractometer (Model Bruker AXS D-8) with Nickel filtered Cu-K_α radiation (Cu K_α: λ = 1.5406 Å) with 2θ ranging from 10° to 80° at the speed of 2° min⁻¹.

RESULTS AND DISCUSSION

3.1 Powder XRD of pure CdS nanoparticles

The powder XRD result for CdS nanoparticle is shown in the figure 1. It contains cubic phase with a little hexagonal phase of CdS. Cubic CdS phase was most often found in synthesized colloidal CdS particles, but the macroscale phase of CdS is normally with the hexagonal structure [34]. In solvothermal synthesis, the hexagonal phase is more common [35-37]. The coexistence of cubic and hexagonal phases has also been reported [35]. We also obtain cubic phase as well as hexagonal phase in the present system.

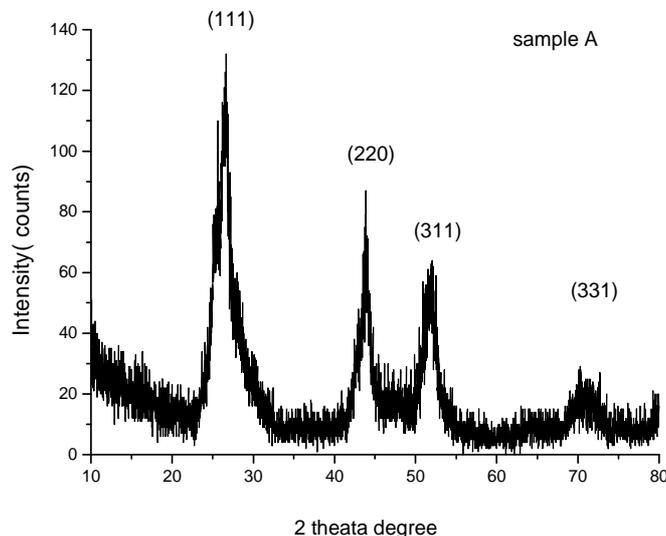


Figure 1: XRD pattern for pure CdS nanoparticles

The XRD pattern consists that there are three distinct peaks at three different angles. From the XRD pattern, it observed that the synthesized sample belongs to pure CdS phase. The XRD peaks are broadened and this is due to the nanocrystalline nature of particles. The nanocrystals have lesser lattice planes compared to bulk, which contributes to the broadening of the peaks in the diffraction pattern. This broadening of the peak could also arise due to the micro-straining of the crystal structure arising from defects like dislocation and twinning etc. These defects are believed to be associated with the chemically synthesized nanocrystals as they grow spontaneously during chemical reaction [38,39]. Broad and diffused pattern of XRD lines are indicative of the small size of the CdS nanoparticles and the 'hkl' values are compared with the standard JCPDS file (10-454) [40]. The XRD pattern exhibits prominent, broad peaks at 2θ values of 26.60, 44.30 and 52.03 which could be indexed to scattering from (1 1 1), (2 2 0) and (3 1 1) and planes respectively of cubic CdS [41-48]. It is evident from the table 1 that the data

obtained in this work are well matched with the standard values. The lattice parameter values were calculated using XRDA software and the values are found to be $a = b = c = 5.4500 \text{ \AA}$.

Table 1: Comparison between experimental and standard XRD data for pure CdS sample

Standard JCPDS			Experimental values		
(hkl)	d-spacing	2θ (degrees)	(hkl)	d-spacing	2θ (degrees)
(111)	3.16	28.218	(111)	3.34	26.66
(220)	1.93	47.046	(220)	2.06	43.78
(311)	1.64	56.029	(311)	1.75	51.95

The grain size of nanocrystalline CdS was calculated from the Scherrer's equation [49-52]. The Scherrer's formula is given by:

$$D = 0.9\lambda/\beta\cos\theta$$

Where D is the crystallite size in nm, λ is the wavelength of the X-rays (1.5406 Å), β is the full width at half maximum and θ is the diffraction peak angle. The average particle size of the sample is obtained to be 16.65 nm.

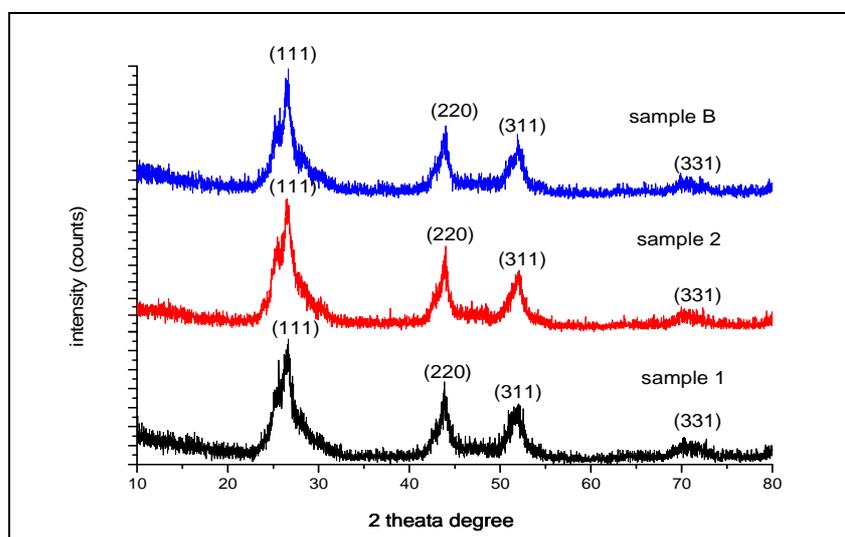


Figure 2: The XRD patterns of pure CdS prepared at different annealing times

Table 2: The size of the pure CdS nanoparticles prepared at different annealing times

Name of the sample	Temperature	Annealing time (min)	Peak height (counts)	Angle (2-Theta) (111),(220),(311)	Particle size (nm)
Sample 1	200 °C	12	121.32	26.53,43.83, 51.83	14.06
Sample 2	200 °C	20	328.47	26.57,43.90,51.98	18.33
Sample B	200 °C	120	403.74	26.66,43.94,52.02	21.05

3.2 Effect of annealing on particle size

In this study sample 1 is annealed at 200°C for 12 minutes, sample 2 is annealed at 200 °C for 20 minutes and sample B is annealed at 200°C for 120 minutes and the XRD patterns of the samples are presented in the figure 2. The XRD pattern reveals that there are three distinct peaks at three different angles. From the XRD pattern, it is observed that the synthesized sample belongs to pure CdS phase. In all the XRD patterns, the three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes, respectively. It exhibits that all three samples of CdS nanoparticles are in cubic as well as hexagonal phase. The XRD patterns of samples annealed at different times for the temperatures of 200 °C shows that with increasing the annealing time, the conversion of amorphous to crystalline phase started. It seems that the effect of temperature on crystal phase formation is more predominant than annealing time. It contains cubic phase with a little hexagonal phase of CdS. Cubic CdS phase was most often found in synthesized colloidal CdS particles, but the macroscale phase of CdS is normally with the hexagonal structure. As the annealing time increases, the diffraction peaks become sharper and narrower, and the intensity increases which indicates that the intensification in crystallinity [53]. Moreover, it is found that annealing time does not show any change in the particle size of the nano particle. The results are given shown in Table 2. The angle 2-

theta of (111) peak is shifting from 26.53 to 26.66, the peak (220) is shifting from 43.83 to 43.94 and the peak (311) is shifting from 51.83 to 52.02. The grain size of the nanocrystalline samples of CdS is also calculated from the Scherrer's equation.

3.3 Effect of annealing temperature on particle size

In this study sample A is annealed at 100 °C for 120 minutes, sample B is annealed at 200 °C for 120 minutes and sample C is also annealed at 300 °C for 120 minutes and the XRD patterns of the samples are shown in the figure 3. In all the XRD patterns, the three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes respectively. From table 3, it is found that the peak width increases with the decrease of annealing temperature, which is an indication of particle size decreases with the decrease of annealing temperature. Also peaks seem to be slightly shifted towards 26.68 which imply that the particle becomes more crystallized as the annealing temperature increases. The particle size is found to increase with increase in annealing temperature. In heating process when the particles are formed, they collide and either coalesce with one another to form a larger particle or coagulate [54]. The process which occurs depends upon the temperature and available energy, that's why particle size increases with increasing temperature. The grain size of the nanocrystalline samples of CdS is also calculated from the Scherrer's equation. A slight variation in 2θ value is also shown when the annealing temperature increases from 100 °C to 120 °C. The results were shown in Table 3. The 2-theta of (111) peak is shifting from 26.40 to 26.68, the peak (220) is shifting from 43.73 to 43.94 and the peak (311) is shifting from 51.90 to 52.95. This shifting occurs for the variation of annealing temperature from 100 °C to 120 °C. and it is clear that the annealing process can increase the size of the grains.

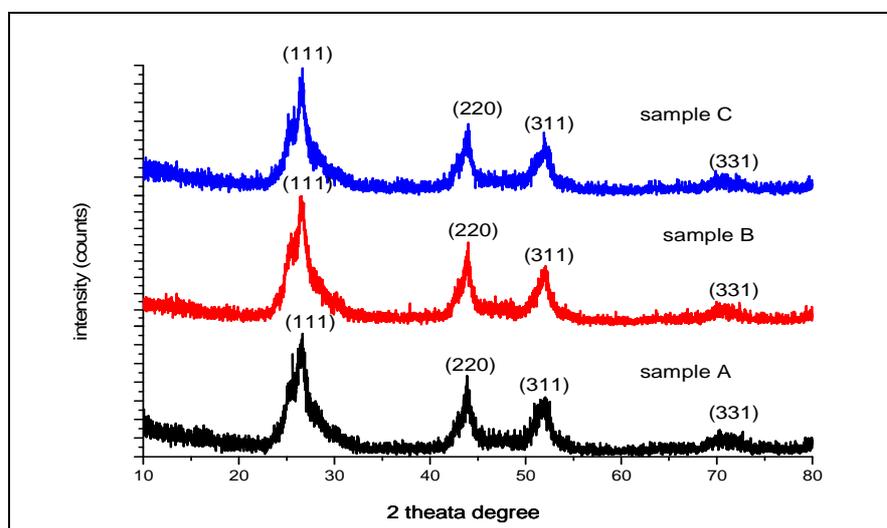


Figure 3: The XRD patterns of pure CdS due to the effect of annealing temperature

Table 3: The size of the pure CdS nano particles due to annealing temperature

Name of the sample	Temperature (°C)	Annealing time (min)	Peak height (counts)	Max. Peak (2 theta) (111), (220), (311)	FWHM	Particle size (nm)
Sample A	100 °C	120	370.67	26.40,43.73,51.90	0.2676	16.65
Sample B	200 °C	120	403.74	26.66,43.78,51.93	0.4684	21.05
Sample C	300 °C	120	410.24	26.68,43.94,51.95	0.4587	23.36

3.4 Powder XRD studies of doped CdS nanoparticles

Figure 4 shows the XRD patterns stack view of CdS doped with Cu^{2+} ions. The effect of doping concentration of Cu^{2+} is studied for 1 mol%, 2 mol% and 3 mol% respectively. In all the XRD patterns, the three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes, respectively. It is clearly seen that all the XRD patterns correspond to cubic as well as hexagonal structure of CdS. It shows that with increase the doping concentration of Cu^{2+} ion, however, the intensity of the diffraction peaks decrease and full width at half maximum (FWHM) is gradually increased and similar findings are made in the work of L.S Ravangave [55]. The increase of doping concentration results the decrease of crystallinity and increase of disorder effect which resulted in the broadening and decrease of intensity of the XRD peaks. It is clearly seen that all the XRD patterns correspond to cubic structure of CdS. It is observed that there are no peaks for the doped metal, sulfides or any binary cadmium metal phase in any of the XRD patterns of doped CdS samples. With the increment of doping percentage, the peak positions shifts slightly to lower angles, which indicates the slight increment of lattice parameters and the data are given in table 4. This is

presumably results from the substitution of metal ions with a large ionic radius. Moreover here it is observed that there was one extra peak (331) in the pure CdS sample.

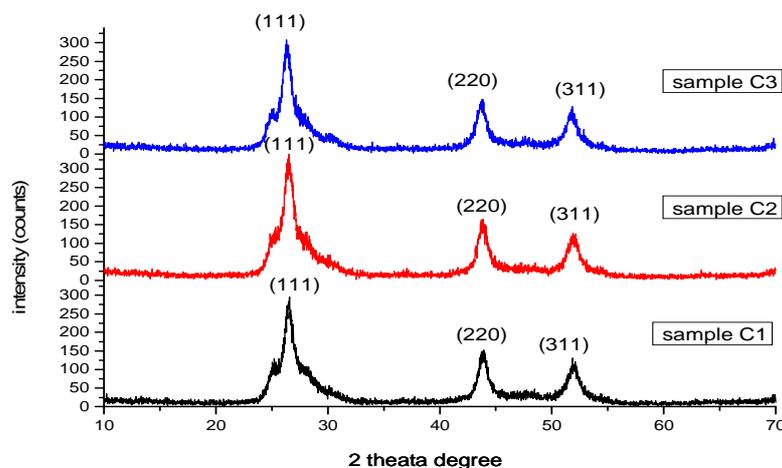


Figure 4: The XRD patterns of copper doped CdS nanoparticles

Table 4: Maximum 2θ values, FWHM and particle size for pure and copper doped CdS samples

Sample	Maximum Peak Value of 2θ (degrees)	FWHM	Particle size (nm)
Pure CdS	26.40	0.2676	16.65
Sample C1	26.38	0.5353	15.83
Sample C2	26.22	0.5353	13.31
Sample C3	26.15	0.6691	12.78

3.5 Effect of ionic radii of dopant

Figure 5 shows the XRD pattern stack view of CdS doped with Zn^{2+} , Mn^{2+} and Cu^{2+} ions. The sample A3 is doped with 3 mol% of Zn, sample B3 is doped with 3 mol% of Mn and sample C3 is doped with 3 mol% of Cu. In all the XRD patterns, the three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes, respectively.

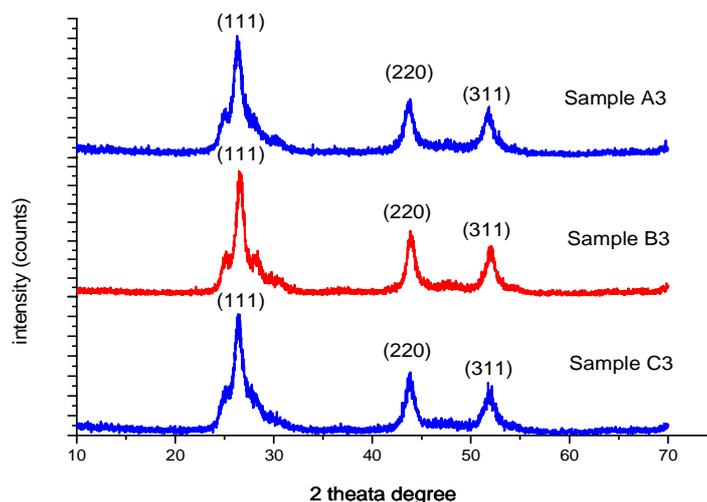


Figure 5: The XRD patterns of 3 mole % of dopants in CdS nanoparticles

The effect of ionic radii of 3% doped Zn^{2+} , Mn^{2+} , and Cu^{2+} CdS nano particles were studied. The d -spacings for (111) peak in the XRD patterns of the Mn^{2+} , Cu^{2+} , and Zn^{2+} doped CdS nanoparticles are in the range of 334-338 pm, this indicates the expansion after doping for (111) peak. In contrast, a shrinkage was occurred for other peaks also. The different changes in the microstructure infer that two kinds of species might exist in the doped CdS nanoparticles [56]. The crystallite sizes in the CdS nanoparticles also increased or decreased depending on the nature of the dopants. The crystallite size of the pure CdS nano particles was calculated to be 16.65 nm and incorporation of Mn^{2+} , Cu^{2+} , and Zn^{2+} dopants reduced the crystalline sizes to 10.28 from 12.78 nm. All the results are given in the table 5.

Table 5: Effect of ionic radii on pure and doped samples

Dopants	Ionic radii (pm)	d-spacing (Å)	Particle size (nm)
Pure CdS	109	3.343	16.65
Zn ²⁺	88	3.389	10.28
Cu ²⁺	87	3.378	12.12
Mn ²⁺	72	3.346	12.78

CONCLUSION

From the above results we can conclude that the cubic as well as hexagonal phase of CdS nanoparticles can be fabricated through the microwave assisted solvothermal process. In the above process ethylene glycol was used the solvent and thioacetamide was used the sulphide source. The particles are in high degree of crystallization. The XRD results reveal that the annealing effect had increased the crystalline size of the CdS nanoparticles. Moreover, the particle size of the metal ion doped nanoparticles decreases with the concentration. The studies have revealed that the CdS nanoparticles doped with various concentrations of copper decreases the crystallinity and also we found that the ionic radii determine the particle size of the doped CdS nanoparticles.

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