

Preparation and characterization of CdS nano particles using chemical precipitation method for solar cell applications

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Cadmium sulfide (CdS) nanoparticles were prepared using cadmium sulphate and sodium sulphide as precursor by chemical precipitation method. The synthesized CdS material was annealed at 300, 400 and 500°C to study the effect of temperature on size and surface morphology. The prepared CdS was characterized using X-ray diffraction (XRD), Ultra-violet spectroscopy (UV-Vis), scanning electron microscopy (SEM) and photoluminescence (PL). The XRD pattern of CdS reveals the nano-sized hexagonal crystalline structure at 300°C. The hexagonal structure of the CdS was converted into cubic CdO and monoclinic CdSO₃ at 400 and 500°C by partial oxidation. The average crystallite size of the CdS, CdO and CdSO₃ obtained at 300, 400 and 500°C was 24, 26 and 31 nm, respectively. It shows the particle size of the materials was slightly increased at elevated temperature. The SEM analysis of CdS shows that the CdS particles are agglomerated particles at 300°C. It also reveals that the morphology of CdO and CdSO₃ at 400 and 500°C is changed into cluster structure. The UV-Vis absorption spectroscopy reveals that the optical absorption increased from 425 to 490 nm from 300 to 500°C. At the same time, the band gap energy of the CdS decreased from 2.91 to 2.53 eV. The average particle sizes of the different forms of CdS were 39, 47 and 49 nm at 300, 400 and 500°C, respectively. The present study reveals that the synthesized CdS could be used as a material for solar cell applications.

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1. Introduction

Cadmium sulfide an important II-VI compound semiconductor with a bandgap of ~2.4 eV at room temperature, has been considered as an excellent visible-light-responsive material for optoelectronic devices [1]. However CdS is unstable material and can easily change into other materials on heating in air. Nanostructure sulfides and selenides (E.g. CdSe, ZnSe, CdS and ZnS) have been extensively studied with a view to find the relationship between structure, size and optical properties [2].

CdS is one of the important materials for application in electro-optic devices such as laser materials, transducers, photoconducting cells, photosensors, optical wave-guides and non-linear integrated optical devices [3]. Nano particles have attracted significant interest due to their tunable electronic, optical and catalytic properties arising from the quantum confinement effect [4].

In 20th century, few reports have been available in the literature on cubic to hexagonal phase transformation in

CdS. CdS generally shows dimorphism of (i) zinc blende type (cubic form) and wurtzite type (hexagonal form) at relatively low temperatures, and (ii) only wurtzite type at relatively high temperatures. The complete transformation has been observed from cubic to hexagonal phase around 600°C [5].

There are various methods reported in the literature to fabricate nanoparticles by physical [6, 7], chemical methods [8] and ion implantation [9]. Recently, nano structured CdS with different size, shape and dimensionality has been fabricated and characterized by different groups [10].

CdS nanoparticles have been prepared by various cadmium source precursors such as cadmium nitrate, cadmium acetate, cadmium chloride, cadmium oleate and cadmium sulphate [11-13]. A number of sulfur sources for preparation of CdS nanoparticles have been reported. Sodium sulphide [14], hydrogen sulphide gas [15] and thiourea [16] are the most commonly used for solution-based preparation of nanosized CdS. Few researchers used

cadmium sulphate and sodium sulphide but the detailed study has not been reported [13,17].

2. Experimental

In the present study, Cadmium sulphate (CdSO_4) Sigma Aldrich, sodium sulphide ($\text{Na}_2\text{SxH}_2\text{O}$) Loba chemie, Mumbai and de-ionized water were used to prepare CdS nanoparticles without any further purification.

The structural properties of the CdS sample powders were determined by X-ray diffractometer (XRD, X'Pert Pro; PANalytical, Netherlands) using $\text{Cu K}\alpha$ as a radiation source ($\lambda=1.5406 \text{ \AA}$) which operated at 30 kV and 15 mA. The samples were scanned in the (2θ) range from 10 to 80° . The average crystallite sizes of all the samples were calculated from 2θ position of FWHM by Scherrer's formula. The surface morphology of CdS particles was inspected using a scanning electron microscope (SEM, JSM-6390LV; JEOL, Tokyo, Japan) with an accelerating voltage of 20 kV. X-ray fluorescence spectrometry (XRF, EDX-720, and Shimadzu, Japan) was used to identify the concentration of the elements presented in nano powder with way of qualitative and quantitative elemental analysis. The infrared (IR) absorption spectra of all samples were recorded at room temperature using the fourier transform infrared spectroscopy (FTIR; Spectrum 100; PerkinElmer, USA) in the wave number range from 4000 to 400 cm^{-1} . The study was carried out with KBr material and explored the present functional groups. UV spectrophotometer (JASCO, V-650 Japan) was investigated to analyze the optical properties in the wavelength range from 200-900 nm at room temperature.

The particle size distribution was determined with a sub micrometer particle size analyzer (Nanophox, Sympatec, Germany) according to the dynamic light scattering technique. The particle size of all the samples were measured in the range of 1-100 nm at the scattering angle of 90° . Three dimensional photon cross-correlation techniques were used for the simultaneous measurement of particle size. The photoluminescence spectrum (Cary Eclipse WinFLR) was recorded in the wavelength range from 200 nm to 1200 nm.

CdS nanoparticles were prepared by chemical precipitation route with two precursor solutions. First solution was prepared with 0.1 M of cadmium sulphate (CdSO_4) dissolved directly in 25 ml of de-ionized water at room temperature and stirred for 10 min. Second solution with 0.1 M of sodium sulphide (Na_2S) was prepared with same process as mentioned above. The second solution was mixed drop by drop with first solution under stirring for 20 min. During this process, instantly yellow colour wet precipitation was obtained. It was dried in hot air oven at 80°C for 48 h. Finally yellow coloured CdS nano powders were obtained and the powder samples were annealed at three different temperatures of 300, 400 and 500°C for 1 h. The chemical reaction took place for preparation of cadmium sulfide nano particles was $\text{CdSO}_4 + \text{Na}_2\text{S} \rightarrow \text{CdS} + \text{Na}_2\text{SO}_4$.

3. Results and discussion

3.1. Structural properties

XRD measurements of CdS nanoparticles were taken by varying the annealing temperature from 300°C , 400°C and 500°C for 1h. Fig. 1 shows the observed XRD pattern at 300°C exhibit hexagonal structure of CdS nanoparticles (JCPDS: 41-1049), which is evidence from the observed three prominent peaks (100) (002) (101) matching with the lattice parameter $a = 4.140 \text{ \AA}$ and $c = 6.71 \text{ \AA}$. Furthermore, at higher annealing temperature 400°C and 500°C , CdS is observed with the partial oxidation of CdO and CdSO_3 [15, 16]. This structural transformation can be interpreted as a result of size- driven structural transformation by annealing process [17]. The traces of CdO (cubic structure) and CdSO_3 (monoclinic structure) are matched with the [JCPDS: 75-0592] and [JCPDS: 78-1473], respectively, results in structural transformation from CdS hexagonal structure. It is noted that the oxidation process takes place from $400^\circ\text{C} - 500^\circ\text{C}$ onwards. Further, it is found that when the annealing temperature increased, the crystallites size also increased [18]. The average crystallite sizes (D) were found to be within the range 24 to 31nm as shown Table 1 depends upon the above properties these nano sized particles are used in solar cell applications [19].

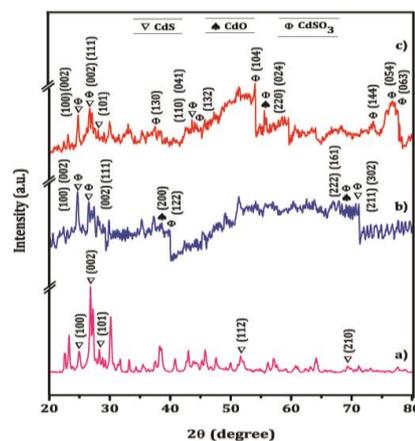


Fig.1. XRD pattern of CdS nanoparticles annealed at (a) 300°C (b) 400°C (c) 500°C

Table 1. The Values of annealed temperature, Crystallite size (nm), Wave length (nm), and Energy band gap (eV) of CdS nanocrystalline

S.No	Annealed temperature ($^\circ\text{C}/\text{h}$)	Crystallite size from XRD (nm)	Wave length (nm)	Energy Bandgap E_g (eV)
1.	300/1	24.81	425	2.91
2.	400/1	26.02	470	2.63
3.	500/1	31.15	490	2.53

X-ray fluorescence spectrometry (XRF) measurements which were made on the samples annealed

at three different temperatures of 300, 400 and 500°C are shown in Table 2. The analysis reveals that the precipitation route yielded confirms the presence of CdS

found to be around Cd (77%) and S (20%) after annealing temperature.

Table 2. XRF chemical analysis for CdS nanoparticle

300°C		400°C		500°C	
Elements	Weight %	Elements	Weight %	Elements	Weight %
Cd	77.802	Cd	78.414	Cd	77.376
S	20.315	S	20.456	S	20.354
K	1.832	K	1.012	K	1.791
Cu	0.051	Fe	0.068	P	0.435
		Cu	0.05	Cu	0.044
Total =100%					

3.2. Morphological properties

The SEM image of CdS particle is shown in the Fig. 2. It shows that clearly indicates the formation of clusters with compact crystalline nature. As annealing temperature increases the CdS particles are agglomerated and in turn form clusters. This morphological feature is due to the increase of grain size and it can be measured by surface morphology micrographs.

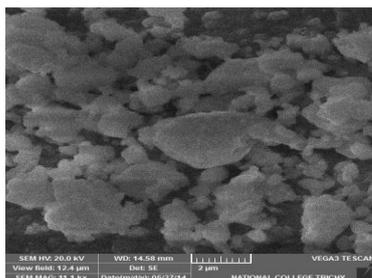
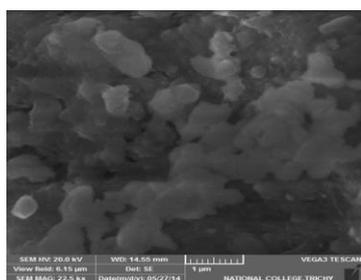
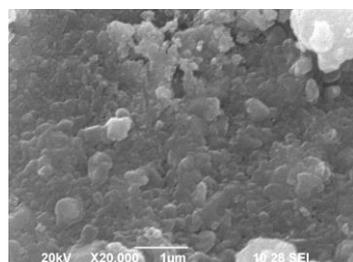


Fig. 2. SEM image for annealed CdS nanocrystalline (a) 300°C (b) 400°C (c) 500°C

3.3. FTIR analysis

Fig. 3 shows the FTIR spectra of CdS nanoparticles. A medium absorption peak at 3504.05 cm^{-1} was assigned to O-H stretching vibration of water molecules, due to presence of moisture in the sample [12]. CdS nanoparticles shows that on stretching bands, asymmetric and symmetric around 2923.92 cm^{-1} gets associated with C-H stretching [5, 20]. The observed weak peak 1333.59 and 1623.66 cm^{-1} , are possibly due to stretching vibrations of sulphate group [5] and also traces absorption at 984.96 and 1101.17 cm^{-1} were assigned to SO_4^{4-} [20]. In addition, IR characteristic revealed a strong absorption band at 613.46 cm^{-1} was assigned to stretching vibration of Cd-S [5]. Hence, the existences of absorption spectra identify the presence of CdS along with reduced impurities.

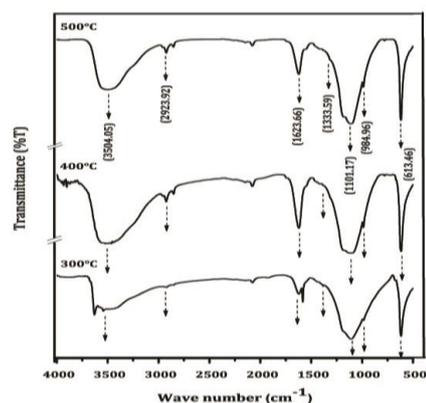


Fig. 3. FTIR spectra of CdS powder

3.4. UV-Vis analysis

The optical absorption of CdS nanoparticles was recorded by UV-Vis absorption spectroscopy. Optical measurement constitutes the most important means of shaping the band structures of semiconductors. CdS nano powders prepared at different annealing temperatures is

shown in Fig. 4. Optical absorption spectra of CdS nanoparticle exhibits an absorption peak at 425, 470 and 490 nm respectively for 300, 400 and 500°C. The bulk CdS material exhibits an absorption peak at around 515nm. Optical band gap is calculated from the absorption coefficient signifies the blue shift in direct band gap from 2.91 to 2.53 eV respectively (Table 1). The change in band gap with the different temperature is attributed to quantum confinement effects [18, 21, 22].

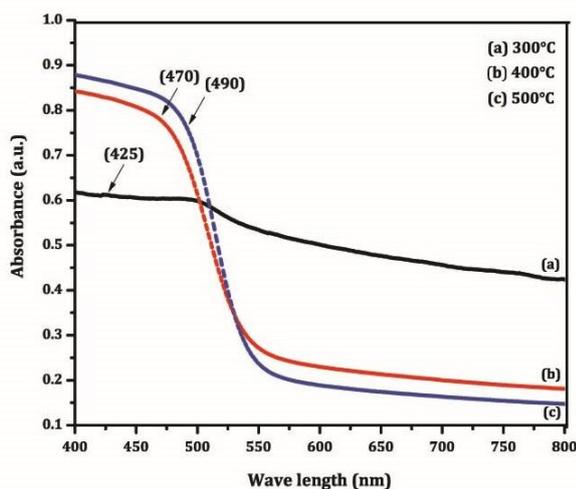


Fig. 4. Optical absorption spectra of CdS annealed at 300°C, 400°C and 500°C

3.5. Particle size analysis

The particle size distribution of CdS nanoparticles after annealing in different temperature are shown in Fig. 5. The average particles size distribution of CdS nanoparticles is 39, 47 and 49 nm respectively at 300, 400 and 500°C. It is found that particle size increases with increase in the annealing temperature. This is mainly due to crystalline size growth during the annealing temperature, which is more evident in observed XRD pattern (Fig. 1).

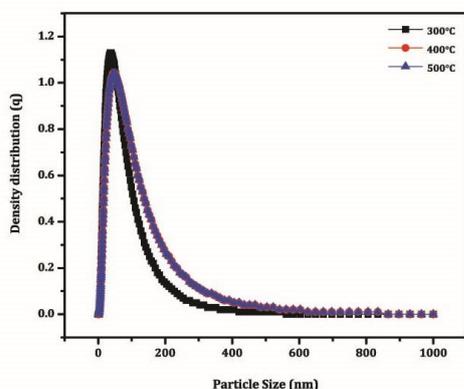


Fig. 5. Particles size distribution of CdS nanoparticles

3.6. Photoluminescence analysis

Photoluminescence (PL) spectra of CdS nanoparticles annealing in different temperature are shown in Fig. 6. Emission bands, such as 391 nm, 425 nm, 456 nm, 484 nm, 530 nm, 541 nm, 573 nm, 605 nm, 700 nm and 826 nm, reveal the green emission bands in CdS nanoparticles. Photoluminescence analysis in 400-650 nm emission wavelengths shows the 'well known' green emission band in CdS nanoparticle [12]. The green emission peaks around the bulk band-gap energy and is therefore assigned as the recombination of free electrons and holes [23]. In addition, the emission peak at 530 nm (2.34 eV), which was assigned to the surface trap induced fluorescence. This concerned the recombination of electrons trapped within a sulfur vacancy with a hole in the valence band of the CdS nanoparticles.

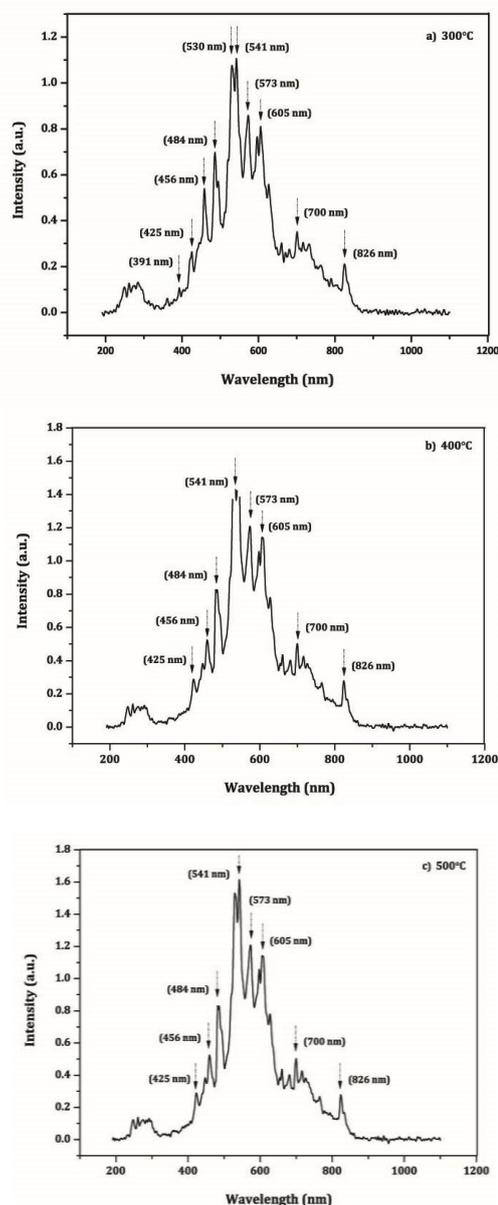


Fig. 6. Photoluminescence spectra of CdS nanoparticles

In general, at least two factors can increase the possibility of the hole-electron recombinations. First, as the size of these traps approaches that of the nanoparticle, the possibility of electron-hole recombination can become the predominant event. Secondly, surface protection has the effect of minimizing surface defects and may enhance the possibility of electron-hole recombination [24].

4. Conclusions

The cadmium sulfide nanocrystalline samples were prepared through precipitation from cadmium sulphate and sodium sulphide at room temperature. XRD pattern shows the synthesized CdS nanostructure has hexagonal structure and their evaluated crystallite size increase from 24 to 31 nm and the bandgap decreases from 2.91 to 2.53 eV with the increase of annealing temperature from 300°C to 500°C. The observed XRD pattern results reveal that, at higher annealing temperature 400°C and 500°C, CdS was observed with the partial oxidation of CdO and CdSO₃. The morphology of these particles was studied using SEM. The presence of CdS nanoparticles was also identified in the strong absorption bands at 613.46 cm⁻¹. UV-Vis absorption spectroscopy shows a blue shift from 425 to 490 nm. Among this nano sized result which in turn may be considered for the solar cell applications.

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