



Synthesis, Structural and Optical Characterization of Zinc Doped Cadmium Sulphide Nanoparticles

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Nanocrystals of undoped and zinc doped cadmium sulphide ($\text{Cd}_{1-x}\text{Zn}_x\text{S}$, where $x = 0.00$ to 0.10) were synthesized by chemical precipitation method. Structural characterization of as synthesized semiconductor nanoparticles was performed by X-ray diffraction pattern while optical characterization were done by UV-Visible absorption spectroscopy. XRD pattern showed that the synthesized Zn doped CdS nanoparticles have wurtzite hexagonal structure with 3-39 nm average crystallite size. Optical absorption measurements indicated red shift in the absorption band edge upon Zn doping. Direct allowed band gap of undoped and Zn-doped CdS nanoparticles measured by UV-Visible spectrophotometer were 2.4 to 2.2 eV at 500 °C.

Key Words: CdS, Nanoparticles, X-ray diffraction, Absorption spectroscopy, Chemical precipitation.

INTRODUCTION

Nanoparticles have attracted great interest in recent years because of their unique size dependent chemical, physical, optical and transport properties, which are different from those of either the bulk materials or single atoms^{1,2}. Due to the large surface area, all nanostructure materials possess a high surface energy and are extremely reactive without protection of their surfaces and undergo aggregation³. Organic stabilizers are used to prevent nanoparticles from aggregation by capping their surfaces⁴. Bulk CdS has hexagonal wurtzite type structure⁵, melting point 1600 °C⁶ and band gap $E_g = 2.42$ eV⁷ at room temperature and pressure, so it is most promising candidate among II-VI compounds for detecting visible radiation. It is used as window material for heterojunction solar cells to avoid the recombination of photo generated carriers which improves the solar cell efficiency because of its wide band gap and stability⁸. It has also application in light emitting diodes⁹, photo detectors¹⁰, sensors¹¹ and electrically driven lasers¹².

Cadmium sulphide particles were successfully synthesized in a variety of media, such as non-aqueous solvents¹³⁻¹⁵, reversed micelles^{16,17}, vesicles¹⁸, zeolites^{19,20} and other methods²¹. However some of the above methods use Cd^{2+} ions and H_2S , which are in separate phase and mixed unevenly, the formation and the aggregation of CdS particles are uneven. CdS nano particles can also be obtained using Cd^{2+} ion with Na_2S . In addition, deoxygenation and fresh Na_2S aqueous stock solution are

necessary in these methods to avoid the formation of colloidal sulfur and other species because of the instability of Na_2S . Organometallic precursors can be used to provide another synthetic route to CdS ²², but most of these are toxic, readily hydrolyzed and oxidized and hence difficult to handle.

In the present work Zn doped CdS nanoparticles were synthesized by chemical precipitation method using a polyethylene glycol as a capping agent and discussed the structural and optical properties of the prepared nanoparticles.

EXPERIMENTAL

For the preparation of undoped and Zn-doped CdS nanoparticles, the materials used were cadmium sulphate [$\text{M} = 769.52$, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$], zinc sulphate [$\text{M} = 288$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$], sodium sulphide [$\text{M} = 78$, Na_2S] and polyethylene glycol [$\text{M} = 6000$, $\text{OH}(\text{OCH}_2\text{CH}_2)_n\text{H}$; PEG]. All chemicals used were AR grade from Sigma Aldrich and used without further purification.

Synthesis: Zinc doped cadmium sulphide ($\text{Cd}_{1-x}\text{Zn}_x\text{S}$, where $x = 0.00$ to 0.10) were synthesized by chemical precipitation method. 0.1 M cadmium sulphate, 0.1 M zinc sulphate and 0.1 M sodium sulphide were used as reactant materials. Freshly prepared 50 mL of aqueous solution of 0.1 M sodium sulphide was mixed drop by drop in 50 mL of 0.1 M solution of cadmium sulphate and 50 mL of 0.1 M solution of zinc sulphate using vigorous stirring and then added 0.5 g of

polyethylene glycol as a capping agent. As the reaction was started; the reaction system gradually changed from transparent to light yellow and after completion of reaction this turn to dark yellow. The precipitate was separated from the reaction mixture, washed several times with distilled water. The wet precipitate was dried and thoroughly ground and then calcined at 100, 500 and 700 °C in muffle furnace.

Characterization: X-ray diffraction (XRD) patterns were recorded on a Rigaku mini desktop diffractometer using graphite filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 40 KV and 100 mA with a scanning rate of 3° per min (from $2\theta = 20^\circ$ to 80°).

Optical absorption spectra were recorded on a Shimadzu double beam double monochromator spectrophotometer (UV-2550), equipped with an integrated sphere assembly ISR-240A in the range of 190 to 900 nm.

RESULTS AND DISCUSSION

X-ray diffraction studies: Fig. 1(a-c) show the XRD patterns of undoped and zinc doped cadmium sulphide ($\text{Cd}_{1-x}\text{Zn}_x\text{S}$, where $x = 0.00, 0.03, 0.05$ and 0.10) powder samples at 100, 500 and 700 °C temperatures indicating that all the samples were composed of hexagonal phase. The XRD pattern of annealed samples at 100, 500 and 700 °C exhibit peaks at (2θ) values of $26.70^\circ, 28.3^\circ, 43.90^\circ, 52.1^\circ$ and 72.8° , which could be indexed to scattering from (002), (101), (110), (112) and (114) crystal planes. The measured d-spacing 3.34, 3.14, 2.06, 1.75 and 1.29 Å correspond to the reflection from (002), (101), (110), (112) and (114) crystal planes of the wurtzite hexagonal structure. Besides these additional peaks at 500 and 700 °C are also observed at angles (2θ) of $24.9, 36.8, 48.1, 51.1, 53.1, 54.9, 58.6, 67.1, 69.6, 71.2, 75.9$ correspond to the reflection from (100), (102), (103), (200), (201), (004), (202), (203), ((210), (211), (212) planes. All these peaks correspond to hexagonal cadmium sulphide structure. The measured d-spacing 3.56, 2.43, 2.06, 1.78, 1.72, 1.67, 1.57, 1.39, 1.34, 1.32, 1.25 Å correspond to the reflection from (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (203), ((210), (211), (212) crystal planes of the wurtzite structure. All the diffraction peaks agreed with the reported JCPDS card no. 80-0006. X-ray diffraction data reveals that the diffraction peak of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ at (100) plane shifts to larger angle and lattice constant decreases with increasing zinc concentration, which is due to the replacement of Cd ions with ionic radii 0.96 Å with smaller ionic radii Zn ions of 0.60 Å in the host lattice. No additional peaks correspond to the secondary phases of zinc sulphide were obtained for $x = 0.00$ to 0.10 at all temperatures calcined in the present work, which indicates that the wurtzite structure is not disturbed by the Zn addition.

A definite line broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer range. It was clearly observed from the XRD patterns that with the increased in temperature of calcination upto 700 °C, the diffraction peaks become sharper and stronger; which suggest that the crystal quality of the nanoparticles are improved and the particles sizes are increased. The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherrer formula:

$$D_{\text{hkl}} = 0.9\lambda / (\beta_{\text{hkl}}\cos\theta)$$

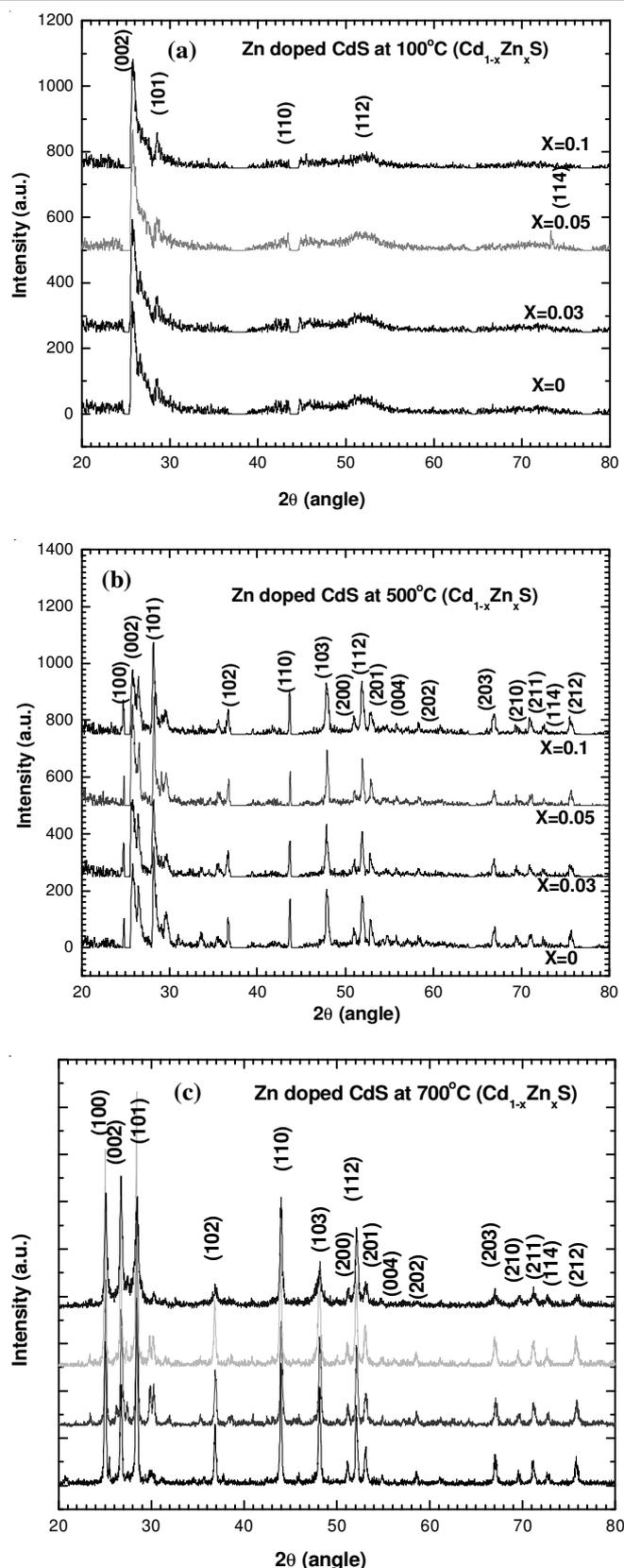


Fig. 1. XRD patterns of undoped and 3, 5 and 10 % Zn-doped CdS nanoparticles calcined at (a) 100, (b) 500 and (c) 700 °C with PEG

where, D is the average crystalline diameter, λ is the wavelength in Å, β is the line width at half-maximum and θ is the Bragg angle. We used the most intense peak (100) in the XRD patterns to calculate the average crystalline size. The calculated

values of particles size are presented in Table-1 for undoped and Zn doped CdS (3-10 %) at 100, 500 and 700 °C. It can be seen that the average size of nanoparticles increases as the heating temperature is increased and decreases as the doping percentage of zinc is increased. This is due to the change of growth rate between the different crystallographic planes. The particles sizes are in the range of 3 to 39 nm at 100, 500 and 700 °C corresponding to the $Cd_{1-x}Zn_xS$ ($x = 0.0$ to 0.1) nanoparticles respectively.

Percentage of doping of Zn (%)	Average size of particles for sample annealed at temperature 100 °C (nm)	Average size of particles for sample annealed at temperature 500 °C (nm)	Average size of particles for sample annealed at temperature 700 °C (nm)
0	3	7	32
3	9	9	36
5	9	11	39
10	8	6	28

Optical studies: The optical absorption spectra of undoped and zinc-doped cadmium sulphide ($Cd_{1-x}Zn_xS$ where, $x = 0.00, 0.03, 0.05, 0.10$) samples by a UV-VIS spectrophotometer in the range of 200 to 800 nm are presented in figure 2 at 500 °C. It can be seen from Fig. 2 that the intensive absorptions are present in the ultraviolet-visible range of about 250 - 515 nm. The absorption edge shifted towards the longer wavelength side in Zn-doped CdS nanoparticles.

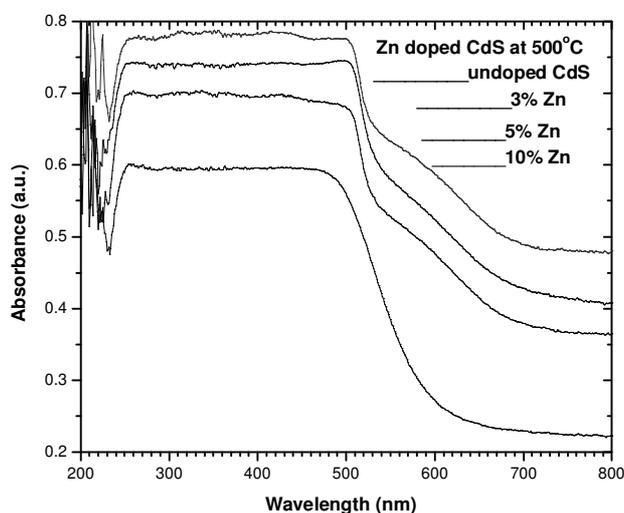


Fig. 2. Optical absorption spectra of undoped and 3, 5 and 10 % Zn-doped CdS nanoparticles calcined at 500 °C

A small red shift indicated the decrease of band gap energies for Zn doped CdS powders. Manificier model is used to determine the absorption coefficient from the absorbance data²³. Fundamental absorption corresponds to the transmission from valance band to conduction band is employed to determine the band gap of the material. The direct band gap energy can be estimated from a plot of $(\alpha hv)^2$ versus photon energy (hv). The energy gap was determined by using the relationship:

$$\alpha hv = A (hv - E_g)^n$$

where hv = photon energy, α = absorption coefficient ($\alpha = 4\pi k/\lambda$; k is the absorption index or absorbance, λ is the wavelength in nm), E_g = energy band gap, A = constant, $n = 1/2$ for the allowed direct band gap. The exponent n depends on the type of transition and it may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively²⁴. The value of band gap was determined by extrapolating the straight line portion of $(\alpha hv)^2 = 0$ axis; as shown in Fig. 3 at a temperature of 500 °C. The plots of $(\alpha hv)^2$ versus hv are presented in Fig. 3. The intercept of the tangent to the plot will give a good approximation of the direct band gap energies of the samples. The band gap energies of undoped and Zn-doped CdS powders calcined at 500 °C are depicted in Table-2. The band gap decreases from 2.4 eV to 2.2 eV with zinc (3, 5, 10 %) doping at temperature 500 °C.

Percentage of doping of Zn (%)	Band gap for sample annealed at temperature 500 °C (eV)
0	2.4
3	2.2
5	2.1
10	2.2

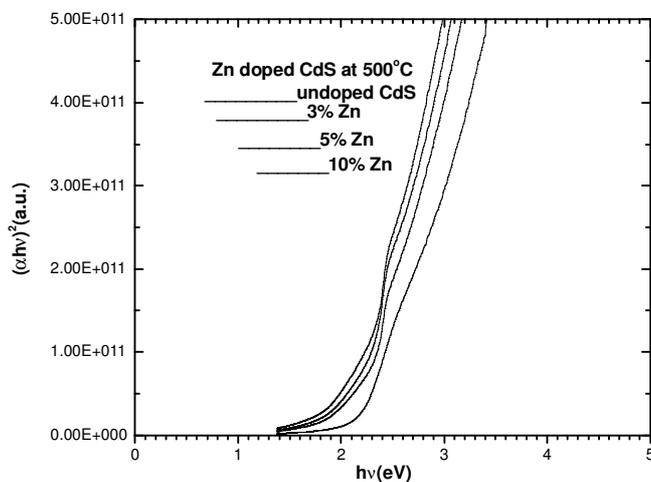


Fig. 3. $(\alpha hv)^2$ vs. photon energy (hv) for undoped and 3, 5 and 10 % Zn-doped CdS nanoparticles calcined at 500 °C

Conclusion

Chemical precipitation method was used successfully for preparation of Zn doped CdS nanoparticles. The XRD pattern of Zn doped CdS nanoparticles showed that the materials are in the nanometric size regime with a hexagonal phase. The sizes of nanoparticles are in range of 3-39 nm. The Zn doped CdS nanoparticles showed red shift in their UV-VIS absorption band edge. The band gap value of as prepared Zn-doped CdS samples were found to decrease as compared to undoped cadmium sulphide.

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