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STRUCTURAL AND OPTICAL CHARACTERIZATION OF PVA CAPPED CADMIUM SULPHIDE NANOPARTICLES BY CHEMICAL COPRECIPITATION METHOD

L. SUJATA DEVI[a], K. NOMITA DEVI[b*], B. INDRAJIT SHARMA[a], H. NANDAKUMAR SARMA[c],
[a]*Department of Physics, Assam University, Silchar-788011, Assam, India*
[b]*Department of Physics, North Eastern Regional Institute of Science and Technology (NERIST), Nirjuli, Arunachal Pradesh-791109, India*
[c]*Department of Physics, Manipur University, Canchipur, Imphal-795003, India*

CdS nanoparticles have been synthesized by chemical co-precipitation method using PVA as a capping agent. Structural characterization of the as synthesized CdS nanoparticles were performed by X-ray diffraction (XRD) study which showed hexagonal structure with average crystallite size of 11 nm and lattice constants a=4.106 Å, c=6.637 Å. Optical characterization of nanocrystalline thin films prepared by Vacuum Evaporation Method from the synthesized powder were done by Photoluminescence spectroscopy and UV-Visible absorption spectroscopy. UV-Visible absorption spectrum showed blue shift in absorption edge with respect to bulk CdS. The photoluminescence spectrum of the CdS film exhibited green emission band with a maximum at 528 nm. Radius of the synthesized CdS nanoparticle has been evaluated from the absorption spectrum by using the effective mass approximation formula.

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Keywords: Chemical method, CdS nanoparticle, Vacuum evaporation, XRD, UV-VIS spectrum, Photoluminescence.

1. Introduction

The synthesis of nanoparticle of group II-VI semiconductors in powder form has been a rapid area of research due to their unique chemical, physical, optical, electrical and transport properties. Cadmium Sulphide (CdS) is one of the most studied materials among II-VI compounds due to its potential technological applications in field effect transistors, solar cells, photovoltaic light emitting diodes, photocatalysis, infrared photoconductor and biological sensors [1-7]. There are many reports about CdS nanoparticles obtained by different methods and from different precursors [8-13]. Sizes of the nanoparticles depend strongly upon their preparation condition and methods [14-16]. Polymer capped nanoparticles composite have been increasingly studied because of their enhanced optoelectronics and optical properties. Polymer is a good choice as stabilizer as they can interact with metal ion by complex or ion-pair formation and can be designed to certain physical properties of semiconductor nanoparticle.

In this paper, we report a simple chemical co-precipitation synthesis method using polyvinyl alcohol (PVA) as a capping agent. Different techniques of synthesis have been developed to obtain CdS naopaticles in the solid phase (17), precipitation in the liquid phase (18) and growth in nanosize micells (19). Although many methods for the synthesis of CdS nanocrystals have been developed, it is still a challenge to synthesize CdS nanocrystals in the quantum confinement range.

*Corresponding author: nomita_k@rediffmail.com

2. Experimental

CdS nanoparticles were grown by chemical co-precipitation method using PVA as a capping agent. All the chemicals reagents used were of analytical grade. The matrix solution were prepared by adding 0.1 M solution of cadmium sulphate ($CdSO_4$) to an aqueous solution (2%) of PVA with constant stirring at constant temperature 70^0C maintained for one and half hour until the solution became a transparent liquid which indicates the complete dissolution of $CdSO_4$. The pH of the solution was maintained at around 11 by slowly adding NH_4OH solution. Then an equimolar solution of thiourea (CH_4N_2S) was added to the matrix solution while stirring constantly at constant temperature until the solution turned into pale yellow and forms precipitates. The precipitates were filtered out separately and washed thoroughly with de-ionized water and dried at 60^oC. CdS nanocrystalline thin films of thickness ~1.2 μm were prepared by evaporating the synthesized powder onto glass substrates held at 200 ^{0}C from a molybdenum boat in a vacuum of about 10^{-5} torr using a vacuum coating system (Make: HINDHIVAC; MODEL:12A4DM). The glass substrates were cleaned with warm dilute chromic acid, detergent solution, distilled water and isopropyle alcohol in that order. The substrates were placed directly above the source at a distance of nearly 12 cm.

The structure and phase of the as synthesized sample were determined by X-ray diffraction using PAnalytical X-ray diffractometer using Cu-K_α (λ=1.54Å) radiation. Diffraction patterns have been recorded over the *2θ* range of 20^o to 70^o at the scan rate of 2^o/min. The optical absorbance spectra for CdS films are recorded using Perkin Elmer UV-VIS spectrophotometer (Model:Lamda 35) in the wavelength range 300 nm-900 nm. The measurements were done in the wavelength scanning mode at room temperature in the normal incidence and using uncoated glass slides as the reference. Photoluminescence spectra of the sample are recorded using Perkin Elmer LS 55 with an excitation light wavelength of 390 nm.

3. Results and discussions

3.1 XRD studies

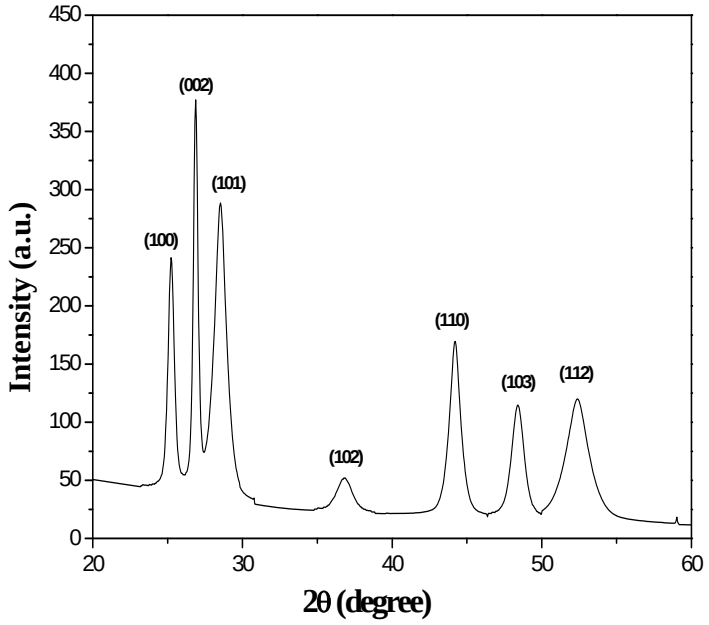

Fig. 1: XRD spectrum of as synthesized CdS nanopowder

Fig.1 shows the X-ray diffraction pattern of the as synthesized CdS powder. The XRD pattern indicates the synthesized CdS powder having a hexagonal phase due to the presence of (100), (002), (101) reflection planes in the angular region between 20° and 30°. The presence of (102), (110), (103), (112) also supports the existence of hexagonal phase. In fig 1 all diffraction peaks can be indexed as the hexagonal CdS with lattice constants a= 4.106 Å, c=6.637 Å which is very consistent with the values in the standard card (JCPDS 80-006). From the full width at half maximum (FWHM) of the most intense peak, the particle size has been calculated by using Scherrer formula [20].

$$D = \frac{K\lambda}{\beta_{1/2}\cos\theta} \quad (1)$$

where K is a constant taken to be 0.94, λ the wavelength of X-ray used, $\beta_{1/2}$ is the FWHM in radians of the XRD peak and θ is the angle of diffraction. The evaluated crystallite size is found to be 11 nm.

3.2 Absorption Studies

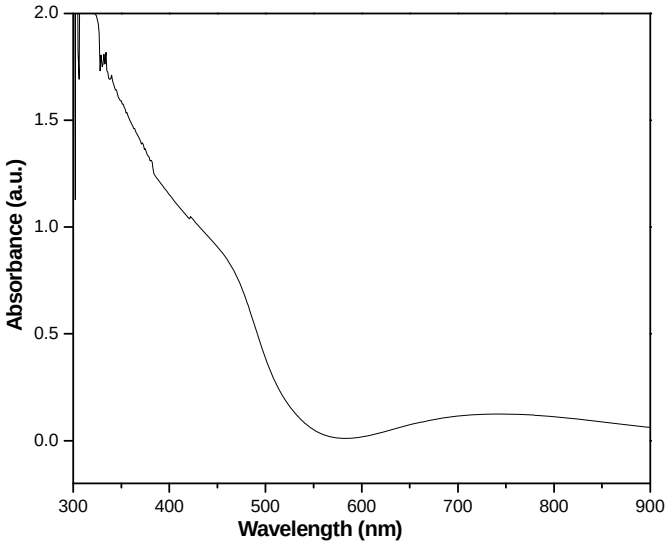

Fig. 2. Absorption spectrum of CdS nanoparticles

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The spectrum which is obtained by absorption of electromagnetic radiation is called absorption spectra. Fig 2 shows the room temperature optical absorption spectrum of CdS film and as can be seen from the spectrum the optical absorption excitonic peak is shifted to the lower wavelength side relative to that of bulk CdS (~530 nm) crystals. This result is in agreement with the value of the reported literatures. [21, 22]. The energy band gap of the material is calculated using the Tauc relation [23]

$$(\alpha h\nu)^{1/n} = A(h\nu - Eg) \quad (2)$$

where A is a constant and Eg is the band gap of the materials and exponent n depends on the type of transition. For direct allowed transition n=1/2, indirect allowed transition n=2, direct forbidden transition n=3/2 and forbidden indirect transition n=3. To determine the possible transitions $(\alpha h\nu)^2$ vs $h\nu$ is plotted and shown in Fig. 3. The value of α is obtained from the relation

$$\alpha = 2.3026(A/t) \quad (3)$$

where A is the absorption and t is the thickness of the sample. The extrapolation of straight line to $(\alpha h\nu)^2=0$ gives the value of the energy band gap of the prepared materials. The direct band gap value of the sample is found to be 2.54 eV and this value is shifted about 0.12 eV compared with the bulk value (2.42eV) and this could be a consequence of quantum-size effect in the sample.

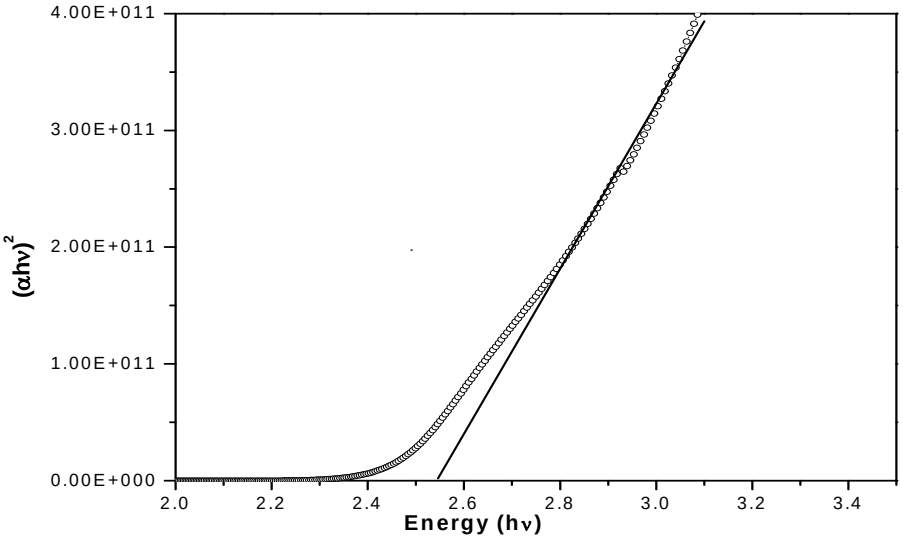

Fig 3. The band gap determination of as prepared CdS thin film

Particle size size can be calculated by the effective mass model that relates the change in band-gap energy to the radius of the particle [24]

$$Eg^{nano} = Eg^{bulk} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 r} \quad (4)$$

where Eg^{nano} is the band-gap energy of the nanoparticle as determined from the UV-Vis absorbance spectrum; Eg^{bulk} is the band gap of the bulk CdS at room temperature; r is the radius of the nanoparticles, m_e^* (0.19 m_e) and m_h^* (0.8 m_e) are the effective masses of the conduction band electron and valence band hole in CdS in units of electron mass; e is the electronic charge; h is the Planck's constant, ε_0 is the vacuum permitivity and ϵ is the high frequency dielectric constant of CdS (5.7). The average nanoparticle diameter calculated from the absorption spectra by using the effective mass model is 4.26 nm for the prepared CdS nanoparticles.

3.3 Photoluminescence Studies

Photoluminescence is a process in which an electron, excited by monochromatic photon beam of certain energy undergoes radiative recombination either at valence band or at surface states within the forbidden gap. The photoluminescence originates from the recombination of surface states [25]. Fig. 5 shows the photoluminescence emission spectra of CdS nanoparticles thin film at excitation wavelength 390 nm. The figure shows a high intense peak centered at 528 nm. The peak corresponding to 528 nm provide green emission band. The green emission band was associated with the emission due to electronic transition form the conduction band to an acceptor level due to interstial sulphur (I_s) site [26].

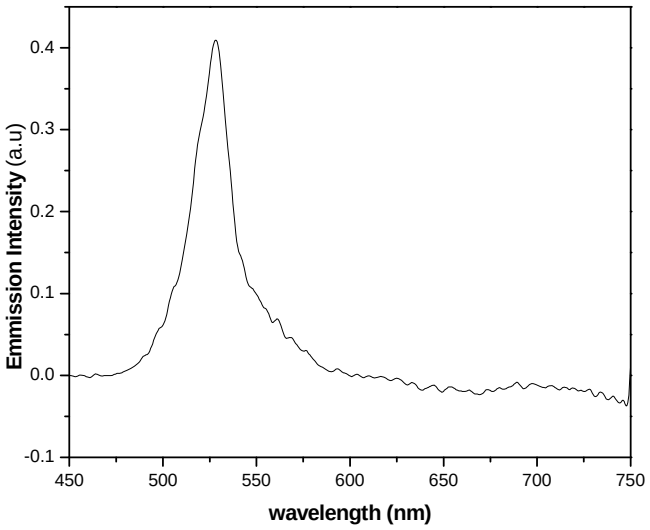

Fig. 4 Photoluminescence emission spectra of as prepared CdS nanoparticle thin film

4. Conclusion

CdS nanoparticles have been synthesized in the PVA matrix through chemical co-precipitation method. X-ray diffraction confirms the hexagonal structure and the particle size are 11 nm. UV-visible absorption showed a blue shift indicating quantum confinement of the particle. PL spectrum exhibits peaks centered at 528 nm because of interstial sulphur sites.

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