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SYNTHESIS, STRUCTURAL AND OPTICAL CHARACTERIZATION OF CdS NANOPARTICLES

D. K. DWIVEDI*, DAYASHANKAR[a], MAHESHWAR DUBEY[a]
Department of Physics, M.M.M.Engineering College, Gorakhpur – 273010 (India)
[a]Department of Physics, University of Lucknow – 226007 (India)

CdS nanoparticles have been synthesized by chemical synthesis method using ethylenediamine as a capping agent. The nanoparticles were characterized using techniques such as X-ray powder diffraction (XRD), transmission electron microscope (TEM) and UV-Vis absorption spectroscopy. The grown sample is ultrasonicated in ethylenediamine. The dispersed sample is characterized using electron diffraction technique. The optical absorption of the CdS nanoparticles is studied in the range of 200-800 nm. Raman spectroscopy showed that the product were hexagonal wurtzite CdS with the 1st and 2nd harmonic modes at 300.1 and 601.34 cm^{-1} respectively. The optical properties of CdS nano particle were investigated by the UV-Vis-NIR absorption spectroscopy. The band gap of CdS nano particles has been determined.

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1. Introduction

In recent years, the synthesis of chalcogenides has attracted significant interest and still is the subject of intense investigation owing to their important non-linear properties, luminescent properties, quantum size effects and other important physical and chemical properties [1-6]. Among these materials, CdS is the most interesting owing to its high photosensitivity and attractive application in photo conducting cells, in particular in the observation of the dependence of these properties on size. The study of optical constants of CdS nano particles is interesting in view of the importance of this material as a "model" photoconductor. Moreover, the study of optical constants in the sub band gap region is often of interest for using this material in solar cells and in other optoelectronic device designs. Consequently, much effort has been expended in the synthesis of these small quantum size particles. CdS particles were successfully synthesized in a variety of media, such as non-aqueous solvents [4,7,8], reversed micelles [9,10], vesicles [11], zeolites [12,13] and other methods [2,14]. 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. The precipitation of Cd^{2+} with S^{2-} is faster than their homogeneous mixing, the in homogeneity at early stages results in a broadening size distribution. 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 [15], but most of these are toxic, readily hydrolyzed and oxidized and hence difficult to handle. So finding a simple synthesis method is a topic of semiconductor CdS materials. Cadmium sulphide is an important semiconductor and has many optoelectronic applications including solar cells, photodiodes, light emitting diodes, nonlinear optics and heterogeneous photocatalyis. In the present work we have synthesized CdS nanoparticles of size

*Corresponding author: dwivedidkphys@rediffmail.com

~2.6 nm by chemical precipitation technique. The particles are characterized using XRD, UV-Vis absorption spectroscopy, TEM and Raman spectroscopy.

2. Experimental

Nanoparticles of CdS are synthesized in aqueous medium through chemical precipitation technique starting from analar grade cadmium salt and sodium sulfide, and using ethylinedieamine as capping agent. The nanaoparticles are separated from the reaction medium by centrifugation, washed and dried at 80^0 C. The structure and phase of the sample are determined by X-ray diffraction using Bruker X-ray difractometer and using CuK_α radiation. UV-visible spectrum of the nanoparticels dispersed in alcohol is recorded using Varian Cary Model 5000 spectrophotometer in the wavelength range 200-800 nm. The Raman spectroscopy of the CdS nano particle was performed using a Horiba Jobin Yvon laser Spectrometer 64000 and Olympus Inverted Microscope with Ar-ion laser at room temperature.

3. Results and discussion

3.1 Structural properties

Fig. 1 shows the X-ray diffraction pattern of the CdS nanoparticle. The XRD peaks are found to be very broad indicating very fine size of the grains of the sample.

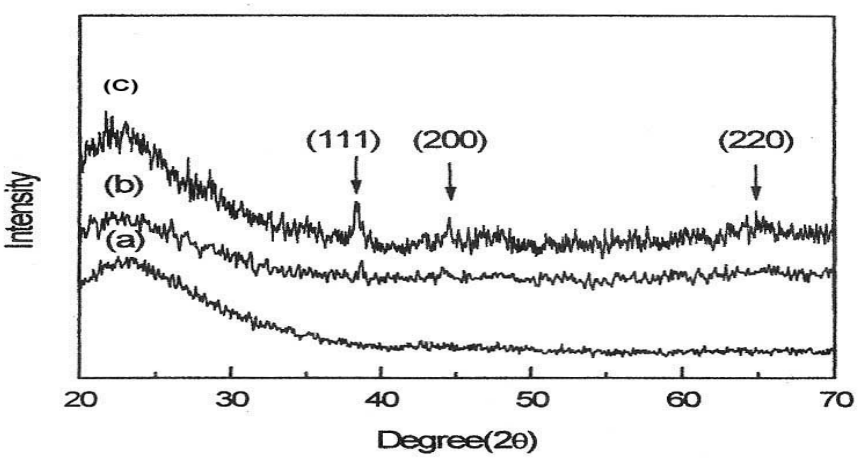

Fig. 1. X-ray diffraction pattern of CdS nanoparticles prepared at (a) 500^0C (b) 600^0C (c) 700 ^{o}C

The XRD pattern exhibits prominent, broad peaks at 2θ values of 27.50^0, 43.50^0 and 50.01^0 and the shoulder at ~30.5^0 which could be indexed to scattering from 111, 200, and 220 planes respectively of cubic CdS [12, 13]. The absence of peaks at 28.4^0 and 53^0 which are associated only with hexagonal phase eliminates the possibility of incorporation of hexagonal phase of CdS in the sample [12]. The average grain size of the sample is determined to be ~2.3 nm from the full width at half maximum of the most intense peak making use of the Scherrer's equation.

$$D=0.9\lambda/\beta \cos\theta \quad (1)$$

where λ is the wavelength of the X-ray radiation, β is the FWHM in radians of the XRD peak and θ is the angle of diffraction. TEM image of the CdS (Fig. 2(a)) reveals that small particles aggregate into secondary particles because of their extremely small dimensions and high surface

energy. Therefore the diameter and the size distribution of the nanoparticels are difficult to determine precisely by simply viewing the TEM image. Figure 2(b) indicates that the nanoparticles synthesized have good crystalline nature and in the cubic form. The diffraction rings in selected area electron diffraction (SAED) patterns (Fig. 2(c)) also indicate that the powder is cubic CdS phase. The average particle size obtained using the diffraction pattern is found to be 2.6 nm.

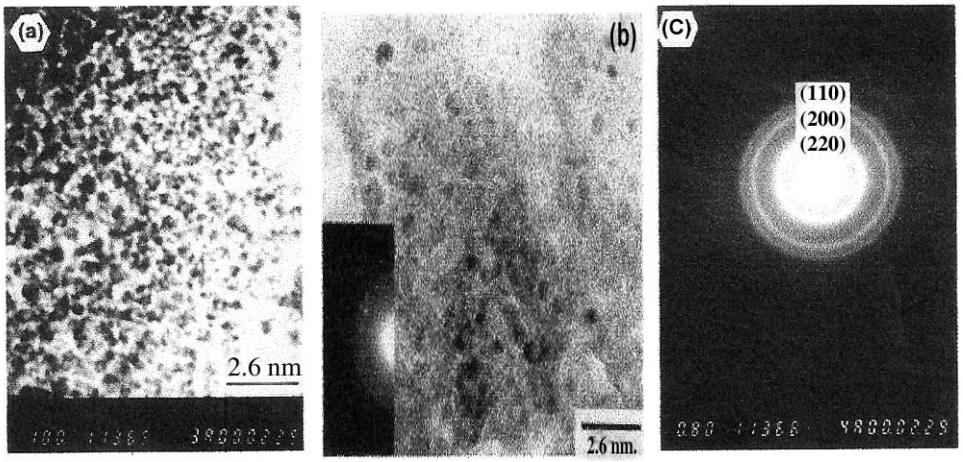

Fig. 2. Transmission electron microscope and electron diffraction pattern of CdS nanoparticles prepared at (a) 500^{0}C (b) 600^{0}C (c) 700^{0}C

3.2 Optical properties

The UV-visible absorption spectroscopy has been used to monitor the optical properties of quantum-sized particles. The absorption spectrum of the nanoparticles of CdS is shown in Fig. 3. The spectrum exhibits a well-defined absorption feature (peak) at ~522 nm, which is considerably blue-shifted relative to the peak absorption of bulk CdS indicating quantum size effect [12,16]. The well-defined maximum at ~522 nm is assigned to the optical transition of the first excitonic state. Generally, this wavelength of the maximum exciton absorption decreases as the particle size decreases as a result of quantum confinement of the photo generated electron-hole pairs. The grain size of CdS nanoparticles can be determined using Brus equation [1].

$$E = E_g + h^2/8R^2[1/m_e^* + 1/m_h^*] - 1.8e^2/4\pi\varepsilon_0\varepsilon_\alpha R - 0.124e^4/\hbar(4\pi\varepsilon_0\varepsilon_\alpha)^2[1/m_e^* + 1/m_h^*]^{-1} \qquad (2)$$

where E is the onset of absorption of the sample. Eg is the bulk band gap, R is the radius of the particle, m_e^* and m_h^* are the reduced masses of the conduction band electron and valence band hole in units of the electron mass, ε_0 is the vacuum permittivity and ε_α is the high-frequency dielectric constant. The grain size of CdS nanoparticles using equation 2 is found to be 2.9 nm. Estimation of particle size of the present CdS nanoparticle using a value of 2.4 eV for Eg, gives a value of 5.4 nm.

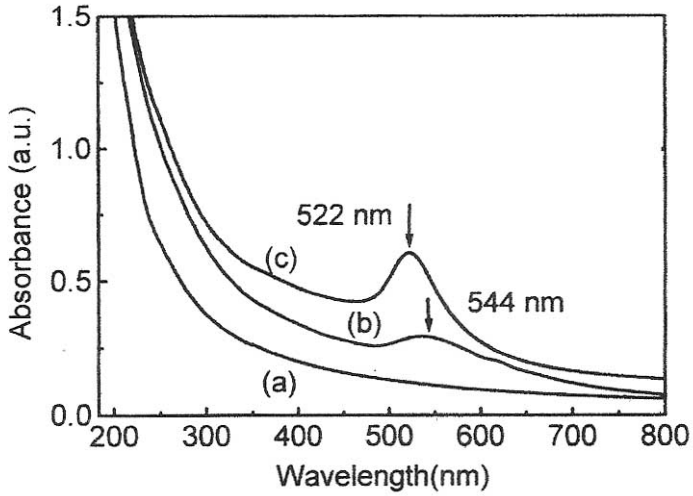

Fig. 3. UV-Vis Spectroscopy of CdS nanoparticles prepared at (a) 500^{0}C (b) 600^{0}C (c) 700 ^{o}C.

Optical transmission spectrum of CdS nanoparticles are shown in Fig. 4. All CdS particles show good transmission for wave length larger than 500 nm which is one of the prerequisites for optoelectronic devices, especially for solar cell window layers [17]. Transmittance of CdS nano particle increases with wavelength, while rise and fall in the transmittance is observed for a longer wavelength. These type of variations are recognized to be due to the interference of light transmitted through the CdS nanoparticles. Similar behaviors in the transmission spectrum of the CdS nanoparticles prepared by other techniques have been reported earlier [18-20]. In semiconductors, the relation connecting the absorption coefficient α, the incident photon energy $h\nu$ and optical band gap Eg takes the form

$$\alpha h\nu = A(h\nu - E_g)p \tag{3}$$

where k is constant related to the effective masses associated with the bands and p=1/2 for a direct band gap material, 2 for an indirect band gap material and 3/2 for a forbidden –direct energy gap. Since better linearity was obtained in the $(\alpha h\nu)^2$ vs $h\nu$ plot, which is shown in Fig. 5, the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis. The estimated E_g values are in the range 2.40-2.42eV.

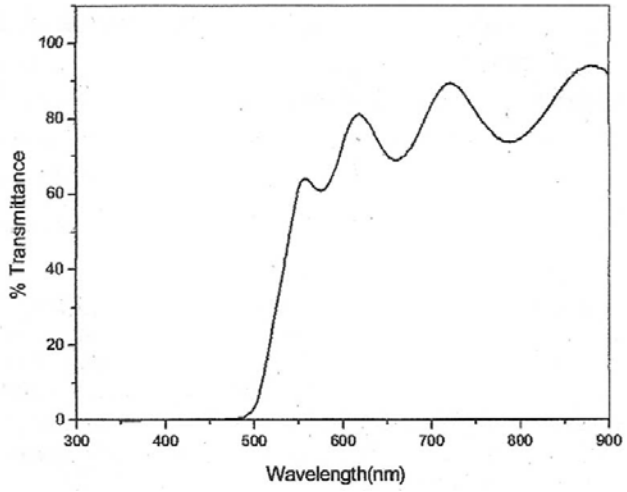

Fig. 4.Optical transmission spectrum of CdS nanoparticles.

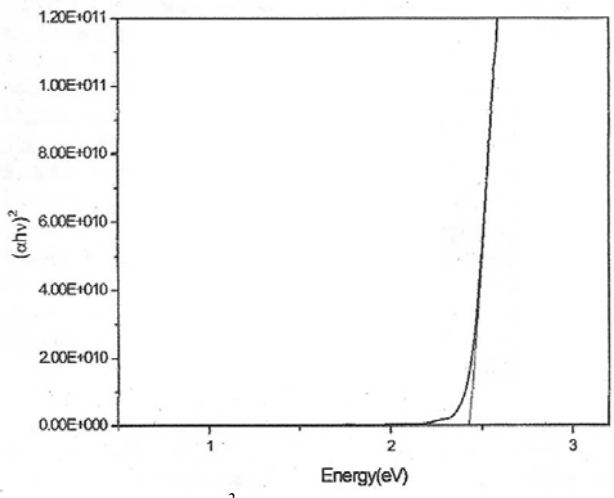

Fig. 5. $(\alpha h\nu)^2$ vs hν of CdS nanoparticles.

Raman spectrum of CdS nano particle is shown in Fig.6. Strong fundamental and weak overtone modes are detected at 300.1 and 601.34cm^{-1} respectively. The fundamental and overtone modes correspond to the 1LO (longitudinal optical) and 2LO Peaks, and are the result of phonon vibration [21-23]. These vibrations match well with vibrations of hexagonal wurtzite structure of CdS thin films reported at 297.0 cm^{-1} and 597.1 cm^{-1} by Thongtem et. al [24-25].

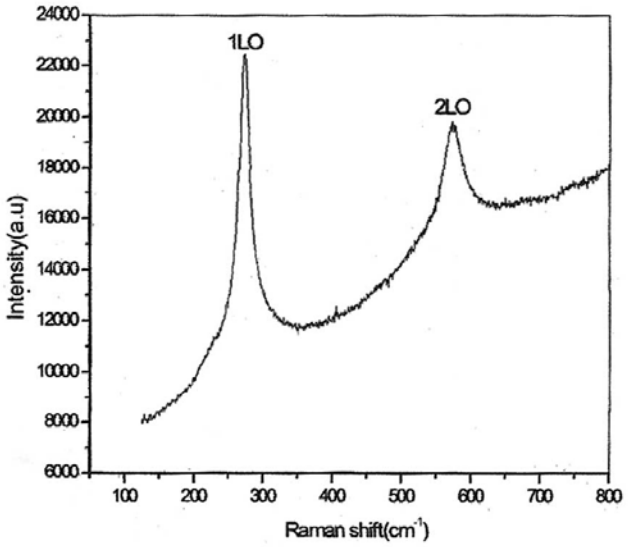

Fig. 6 Raman spectrum of CdS nanoparticles.

4. Conclusions

Nanoparticles of CdS are synthesized through chemical synthesis method. The crystal structure and grain size of the particles are determined using XRD and TEM. UV-Vis absorption spectrum showed a blue-shift indicating quantum confinement of charged particles. The grain size determined using the band gap of the nanostructured CdS sample employing the Brus equation is compared with that obtained making use of Scherrer's formula and it is found that the two values do not agree closely. The particle size of CdS nanoparticle is found to be 2.6 nm. The particle size changes with energy band gap because increasing energy band gap results into transformation of phase of CdS nanoparticle from hexagonal to cubic. The CdS nanoparticles have high

transmittance of about 70 and 85% in the UV-Vis-NIR regions; hence they could be used as thermal control window coatings for cold weather and antireflection coatings. The particles have a direct band gap of 2.42 eV.

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