Characterization of chemically synthesized CdS nanoparticles

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Abstract. II–VI semiconductor nanoparticles are presently of great interest for their practical applications such as zero-dimensional quantum confined materials and for their applications in optoelectronics and photonics. The optical properties get modified dramatically due to the confinement of charge carriers within the nanoparticles. Similar to the effects of charge carriers on optical properties, confinement of optical and acoustic phonons leads to interesting changes in the phonon spectra. In the present work, we have synthesized nanoparticles of CdS using chemical precipitation technique. The crystal structure and grain size of the particles are studied using XRD. The UV–visible absorption, photoluminescence and Raman spectra of the sample are recorded and discussed briefly.

Keywords. Nanoparticles; optical properties; cadmium sulfide.

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1. Introduction

Nanometer-sized semiconductor particles belong to a state of matter in the transition region between molecules and solids. During the past two decades, research on quantum size semiconductor particles has increased enormously due to their exciting novel properties [1–4]. The colour tunability of semiconductor nanoparticles as a function of size is one of their most attractive characteristics. The control and improvement of the luminescence properties of quantum dots have been a major goal in synthetic procedures of nanoparticles. II–VI semiconductor nanoparticles are currently of great interest for their practical applications such as zero-dimensional quantum confined materials, and in optoelectronics and photonics. Numerous reports are available in the literature on synthetic techniques as well as potential applications of nano-sized semiconductor particles [5–9]. Colloidal methods provide effective routes to preparing semiconductor nanocrystals that are soluble in organic solvents and which have a narrow size distribution. Surface chemistry is an efficient tool not only to organize and immobilize the nanocrystals, but also to effectively modify the emission properties. It is also possible to manipulate the synthesized nanocrystals by proper modification of the surface using capping agents thereby rendering them compatible in almost any chemical environment and soluble

in organic solvents. Large-scale synthesis of semiconductor nanoparticles such as solid powder is critically important not only for the study of their physical properties but also for industrial applications in the areas of catalysis, photocatalysis and microelectronics. Recent progress in the chemical synthesis of monodispersed II–VI semiconductor nanoparticles on a gram scale has proved the efficiency of this method [10,11].

Cadmium sulphide is an important semiconductor and has many optoelectronic applications including solar cells, photodiodes, light emitting diodes, nonlinear optics and hetergeneous photocatalysis. In the present study we have synthesized CdS nanoparticles of size $\sim$2.6 nm through chemical precipitation technique. The particles are characterized using XRD, UV–visible, photoluminescence 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 triethanolamine as capping agent. The nanoparticles are separated from the reaction medium by centrifugation, washed and dried at 80°C. The structure and phase of the sample are determined by X-ray diffraction using Bruker X-ray diffractometer and using CuK_α radiation. UV–visible spectrum of the nanoparticles dispersed in alcohol is recorded using Varian Cary Model 5000 spectrophotometer in the wavelength range 190–900 nm. Also, photoluminescence of the sample is recorded using Shimadzu RF-5301 spectrofluorometer for different excitation wavelengths. Finally, Raman spectrum of the sample is recorded using SPEX-RAMALOG spectrometer employing the 514.5 nm line from Ar$^+$ ion laser at a laser power of $\sim$50 mW.

3. Results and discussions

Figure 1 shows the X-ray diffraction pattern of the nanoparticle sample of CdS. The XRD peaks are found to be very broad indicating very fine size of the grains of the sample. The XRD pattern exhibits prominent, broad peaks at 2θ values of 26.60, 44.30 and 52.03° and a shoulder at $\sim$31.5° which could be indexed to scattering from 1 1 1, 2 2 0, 3 1 1 and 2 0 0 planes respectively of cubic CdS [11,12]. The absence of peaks at 28.4 and 53° which are associated only with hexagonal phase eliminates the possibility of incorporation of hexagonal phase of CdS in the sample [11]. The average grain size of the sample is determined to be $\sim$2.6 nm from the full width at half maximum of the most intense peak making use of the Scherrer's equation, $D = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray radiation, β is the FWHM in radians of the XRD peak and θ is the angle of diffraction.

The most dramatic property of semiconductor nanoparticles is the size evolution of the optical absorption spectra. Hence UV–visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. The absorption spectrum of the nanoparticles of CdS is shown in figure 2. The spectrum exhibits a well-defined absorption feature (peak) at $\sim$480 nm which is considerably blue-shifted relative to the peak absorption of bulk CdS indicating
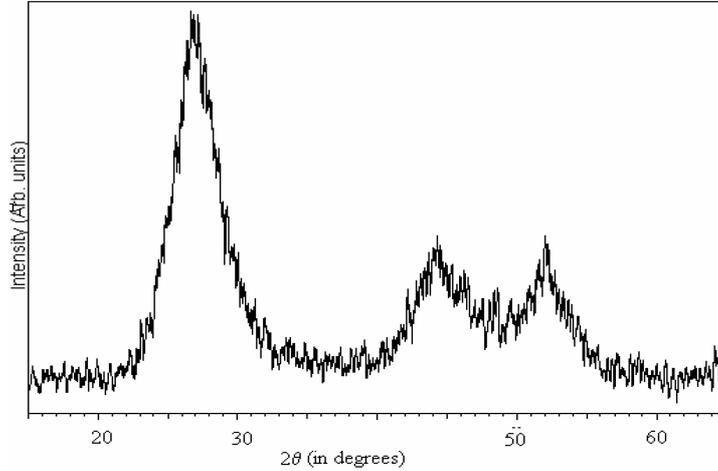
Figure 1. XRD pattern of nanoparticles of CdS.

quantum size effect [10,11]. The well-defined maximum at $\sim$480 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 photogenerated electron–hole pairs. The grain size of semiconductor particles can be determined using Brus equation [1]

$$E = E_\mathrm{g} + h^2/8R^2[1/m_\mathrm{e}^* + 1/m_\mathrm{h}^*]$$
$$-1.8e^2/4\pi\varepsilon_0\varepsilon_\alpha R - 0.124e^4/\hbar^2(4\pi\varepsilon_0\varepsilon_\alpha)^2[1/m_\mathrm{e}^* + 1/m_\mathrm{h}^*]^{-1},$$

where E is the onset of absorption of the sample, E_g 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. Estimation of particle size of the present CdS sample, using a value of 2.4 eV for E_g gave a value of 5.4 nm. This is more than twice the value of the grain size obtained by XRD technique. It has been shown by a number of experimental studies that the equation for E cannot be expected to be quantitatively correct for very small particles. This is due to the fact that for small particles the eigenvalues of the lowest excited states are located in a region of the energy band that is no longer parabolic. The particle-size dependence estimated from the above equation was shown to clearly overestimate the exciton energy and hence fail to account for the experimental size determined from XRD line width using Scherrer's equation. Also, how possible agglomeration of the nanoparticles of CdS might have effected the UV–visible absorption spectrum and thereby the value of particle size may also be a point to be investigated.

Figure 3 shows the photoluminescence (PL) spectra of nanoparticles of CdS for different excitation wavelengths of 300, 240 and 230 nm (energies 4.1, 5.1 and 5.4 eV). It is seen that there is a pronounced change in the intensity of the spectra with change in the excitation energy, while the general features of the spectra remain unaltered. The spectra generated by the higher excitation energies
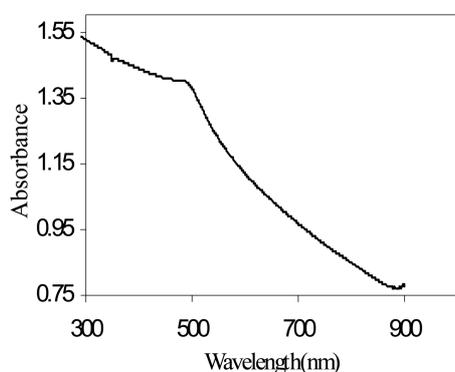
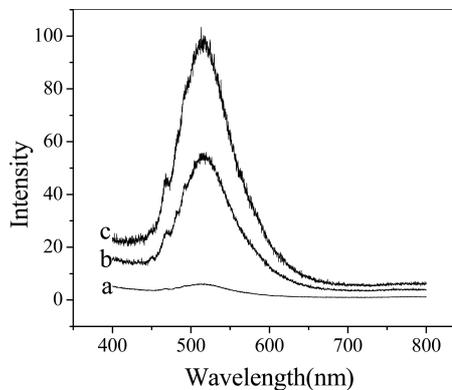**Figure 2.** UV–visible spectrum of nanoparticles of CdS.

Figure 3. Photoluminescence spectra of nanoparticles of CdS for different excitation wavelengths: (**a**) 300 nm, (**b**) 240 nm, and (**c**) 230 nm.

(figures 3b, c) display a strong, broad green peak centered at 519 nm plus emissions which appear as fine structures on the higher energy side of the broad green emission. These emissions appear at wavelengths 493, 482, 470 and 450 nm for excitation wavelengths of 230 and 240 nm, both of which are much shorter than the onset of absorption of ∼515 nm for bulk CdS. The UV–visible spectrum given in figure 2 shows that the onset of absorption for the sample is ∼480 nm. Realising that our CdS nanoparticles sample may not be strictly monodispersed, the fine structure on the higher energy side of the broad green emission may be assigned as band-edge emissions from particles of different sizes. The green emission peaks around the bulk band-gap energy and is therefore assigned as the recombination of free electrons and holes. It is found that the green emission peak does not shift appreciably on changing the excitation wavelength, as expected. The low intensity of the spectrum for 300 nm excitation indicates that the CdS nanoparticles are not efficiently excited at this excitation energy. A few reports [13] on the effect of change in the excitation wavelength on the PL spectra of CdS and CdSe nanoparticles are available in the literature. Rodrigues *et al* [14] have studied the size selective photoluminescence of CdSe nanocrystals. They found the band-edge emission to be strongly dependent on the excitation photon energy ($h\nu_L$) where $h\nu_L$ is much higher than the fundamental absorption peak and this has been explained in terms of selectively excited photoluminescence. This idea was first proposed by Tews *et al* [15] to explain the dependence of donor–acceptor pair spectra on excitation photon energy. The observation of these selectively excited photoluminescence spectra depends very much on the size distribution of nanocrystals. If the distribution is very broad, a large number of particles of different sizes will always be excited. Hence, a broad PL spectrum with no distinct features will be observed independent of $h\nu_L$. But, if the distribution is extremely narrow, the emission peak will always occur at the same energy determined by the unique crystallite size. In the intermediate case of distribution which is not too broad nor too narrow, an appropriate excitation energy can excite several nanocrystals simultaneously producing a
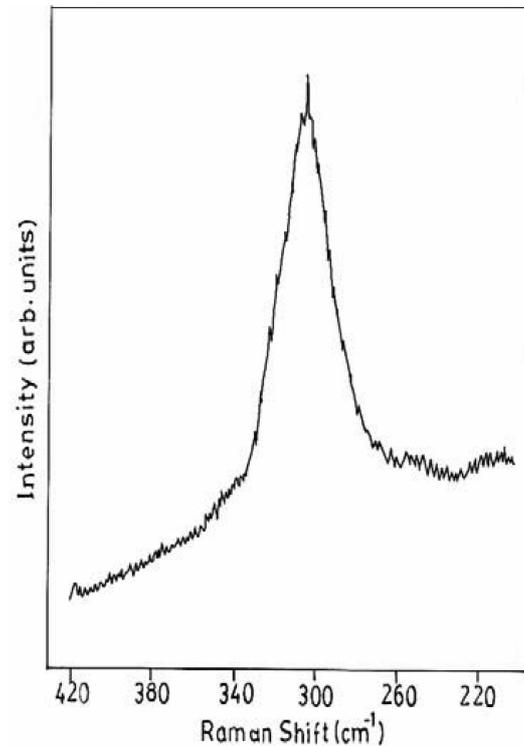
Figure 4. Raman spectrum of nanoparticles of CdS.

PL spectrum which contains more than one peak. The present sample may not be strictly monodispersed and the fine structure on the high energy side of the green emission may be attributed to selectively excited photoluminescence.

Similar to the effects of charge confinement on the optical spectra, confinement of optical and acoustic phonons leads to interesting changes in the phonon spectra. Confinement of the acoustic phonons may lead to the appearance of new modes in the low-frequency Raman spectra, whereas optical phonon line shapes develop marked asymmetry [16,17]. The Raman spectrum of nanoparticles of CdS in the range 180–400 cm^{-1} is shown in figure 4. The spectrum exhibits a strong but broad peak at $\sim$302 cm^{-1} corresponding to the LO phonon mode. There is noticeable asymmetry in the line shape indicating the effect of phonon confinement. This peak has also slightly shifted to lower frequency compared to the LO mode of bulk CdS (305 cm^{-1}).

Analysis of asymmetric broadening of first-order Raman peak within the framework of three-dimensional phonon confinement has been reported in the case of nanoparticles of different materials including Si, BN [18,19], CdS [17] and CdS$_x$Se$_{1-x}$ [20]. In bulk crystals, the phonon eigenstate is a plane wave and the wave vector selection rule for first-order Raman scattering requires $q \approx 0$. However, the confinement of the phonon to the volume of the nanocrystal results in the relaxation of the conservation of crystal momentum in the process of creation and decay

of phonons. This relaxation of the $q \approx 0$ selection rule results in the additional contribution of the phonon with $q \neq 0$ which causes the asymmetric broadening and low frequency shift of first-order LO-Raman peak.

4. Conclusion

Nanoparticles of CdS are synthesized through chemical precipitation technique. The crystal structure and grain size of the particles are determined using XRD. UV–visible 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 photoluminescence spectra recorded for different excitation light energies show a fine structure on the higher energy side of the spectrum which has been explained as due to selectively excited photoluminescence. The Raman spectrum of the sample showed the LO phonon mode with asymmetric broadening which is attributed to the effect of phonon confinement.

Acknowledgements

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