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Strong quantum confinement effect in nanocrystalline CdS

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Abstract CdS quantum dots have been prepared by chemical method. The X-ray diffraction results indicated the formation of CdS nanoparticles with hexagonal phase and grain size 2.5 nm. The HRTEM analysis reveals the formation of CdS quantum dots with an average grain size of ~2.5 nm. The X-ray photoelectron spectroscopy spectra exhibit the $3d_{5/2}$ and $3d_{3/2}$ peaks corresponding to cadmium and the $S2p_{3/2}$ peak corresponding to sulphur. Optical studies by UV–vis spectroscopy show a blue shifted absorption at 471 nm because of the quantum confined excitonic absorption. The photoluminescence spectra of CdS exhibited a broad green emission band centred at around 494 nm.

Introduction

Nanotechnology refers to the research and technology development at atomic, molecular and macromolecular scales, which leads to the controlled manipulation and study of structures and devices with length scales in the range from 1 to 100 nm. CdS is one of the most important II–VI semiconductor compound, possessing excellent optical properties. A tremendous amount of effort has been devoted to the synthesis and optical property study of CdS related nanoparticles and quantum dots [1]. In recent years, nanosize semiconductor crystallites also called quantum dots have received a lot of attention. CdS, in particular, has been extensively studied due to its potential applications in field effect transistor, light emitting diodes, photocatalysis and biological sensors [2–4]. The use of CdS quantum dots in biological applications has increased dramatically because of its unique spectral properties, which enable simultaneous multiplex labelling and detection [5, 6]. Most importantly, the spectral properties of these semiconductor nanocrystals can be controlled effectively by tuning the size, composition, surface properties and crystal structure of the nanocrystals [7]. Lee and Chang [8] have reported an efficient and non-corrosive polysulphide electrolyte for CdS quantum dot sensitized solar cell application. By using a photoelectrode of FTO/TiO_2/CdS, the efficiency of the CdS-sensitized solar cell obtained was 1.15% [8]. Chalcogenide semiconductors such as CdS are important materials for solar cell and optoelectronic applications [9]. Bulk CdS shows an absorption onset of 2.42 eV and absorbs in the visible region. Semiconductor nanoparticles are known to exhibit unique size dependent optical properties, which render them attractive from the viewpoint of integrated photonic devices. There is significant change in the properties when the dimensions of the nanocrystallites become comparable or less than the Bohr radius of the exciton wave function. In molecular terminology, this corresponds to the widening of the energy gap as size decreases. Because of the quantum confinement effect, semiconductor nanocrystals exhibit size dependent, molecular like discrete electronic and optical transitions. In CdS, such quantum size

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effect is observed for crystallite dimensions below 5 nm which is approximately the Bohr exciton diameter of CdS [10]. Nanocrystalline CdS has been prepared by different workers using various techniques such as pulsed laser deposition, chemical bath deposition, spray pyrolysis, successive ionic layer adsorption and reaction, screen printing and sol–gel spin coating method [11–16]. Chemical method is a simple and really inexpensive method. In this paper, we report about the structural and optical properties of the prepared CdS quantum dots.

Experimental

In the present study, CdS quantum dots have been synthesized through chemical precipitation technique. Aqueous solution of cadmium acetate ($(CH3COO)_2$ $Cd{\cdot}2H_2O$) was stirred for 1 h at room temperature. Aqueous solution of sodium sulfide (Na_2S) was added drop wise to cadmium acetate solution and was stirred for 2 h. A precipitate with yellowish orange colour was formed soon after the addition of the Na_2S. The nanoparticles were initially purified by precipitating the particles with excess double distilled water and the solution obtained was centrifuged at 2000 rpm for 5 min. CdS nanoparticles were obtained as precipitate after being dried at room temperature.

X-ray diffraction studies have been carried out using PANalytical X-ray diffractometer, high resolution transmission electron microscope (HRTEM) images of the prepared CdS have been recorded using a Philips TECNAI F20 microscope. The optical properties have been studied using the absorbance spectrum recorded by spectrophotometer (JASCO V-570) and the photoluminescence spectra have been recorded using the Cary Eclise WinFLR photoluminescence device.

Results and discussion

The properties of nanomaterials are related to the confinement of (quasi) particles (electrons, hole, excitons, phonons, etc.,) in volumes with radii less than 10 nm. To explain the possibility of these materials as potential candidates for different applications it is necessary to have an accurate knowledge of the mean particle size and the size distribution. The most reliable technique for the determination of particle size is high resolution transmission electron microscopy (HRTEM). The other commonly used technique is X-ray diffraction method, where Debye Scherre's equation is used for the determination of particle size. Figure 1 shows the X-ray diffraction pattern of the prepared CdS nanoparticles. The X-ray diffraction peaks are found to be very broad indicating very fine size of the grains. The X-ray diffraction pattern exhibits prominent broad peaks at 2θ values of 26.82°, 44.75° and 52.63° which could be indexed to the (002), (110) and (112) direction of the hexagonal phase. The lattice parameters were calculated from and are found to be $a = 6.63$ Å and $c = 4.05$ Å, which are in close agreement with JCPDS (01-0783) data. The average grain size of the sample is determined using full width at half-maximum (FWHM) of the most intense peak with of the help Scherre's equation [17].

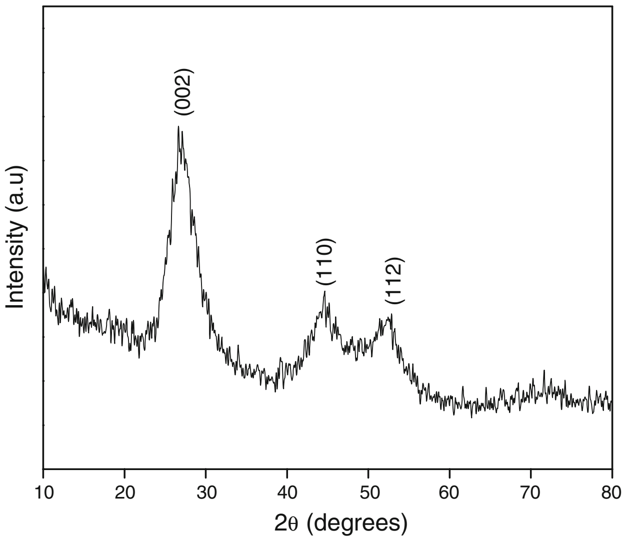

Fig. 1 X-ray diffraction pattern of CdS quantum dots

$$D = k\lambda/\beta\cos\theta$$

where, D is the grain size, k is a constant taken to be 0.94, λ is the wavelength of the X-ray radiation, β is the FWHM and θ is the angle of diffraction. The grain size is found to be 2.5 nm.

Figure 2a shows the HRTEM image of prepared CdS quantum dots. The HRTEM image gives a grain size of ~2.5 nm and this is in agreement with X-ray diffraction result. Figure 2b is the HRTEM image which shows the interplanar lattice spacing of the planes and it is found to be 3.33 Å corresponding to (002) plane of hexagonal CdS.

Figure 3a, b shows the X-ray photoelectron spectroscopy(XPS) spectra of nanocrystalline CdS. In XPS spectra, each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by photon energy and the respective binding energies. The presence of peaks at particular energy indicates the presence of a specific element in the sample under study. In the XPS spectra of CdS shown in Fig. 3a, b, the $3d_{5/2}$ and $3d_{3/2}$ peaks corresponding to cadmium and $S2p_{3/2}$ peak corresponding to sulphur are present confirming the formation of CdS. The peaks of $3d_{5/2}$ and $3d_{3/2}$ are observed at 405.6 and 412.2 eV, respectively. The cadmium $3d$ spectrum exhibits a doublet feature due to spin

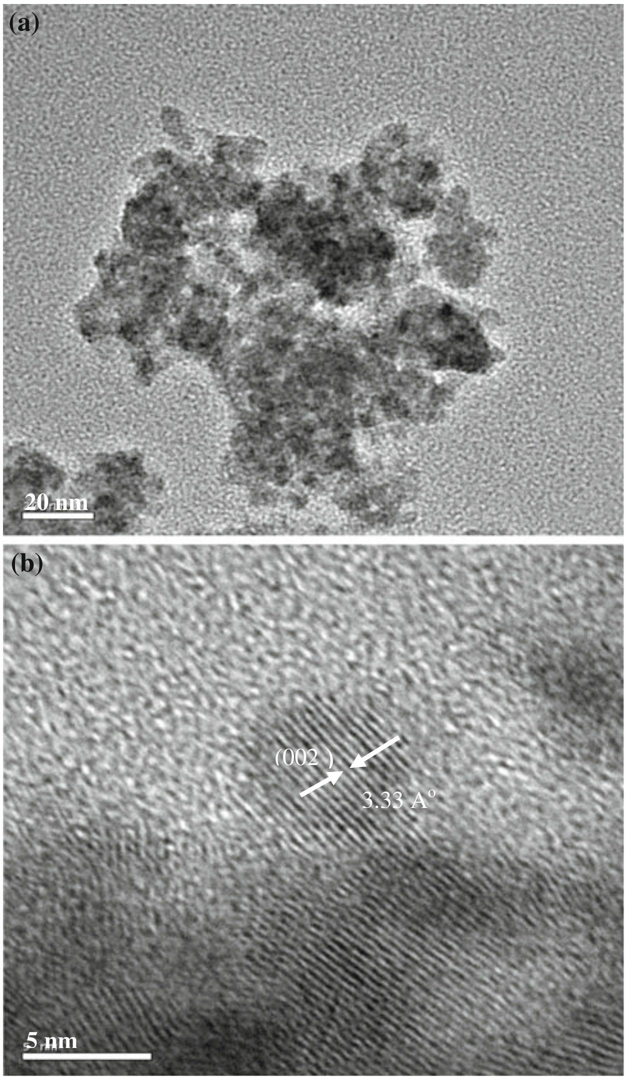

Fig. 2 HRTEM image of CdS quantum dots **a** agglomeration of CdS, **b** lattice fringes of CdS

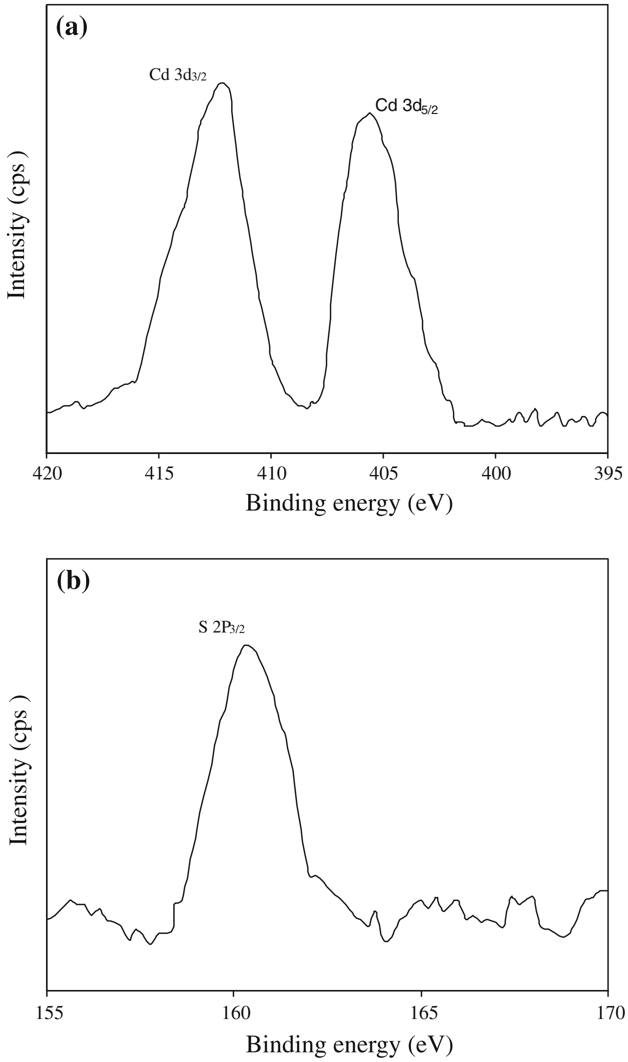

Fig. 3 XPS spectra of CdS. **a** $3d_{5/2}$ and $3d_{3/2}$ peaks of Cd. **b** $S2p_{3/2}$ peak of S

orbit splitting resulting into $3d_{5/2}$ and $3d_{3/2}$ peaks with spin orbit separation of 6.6 eV. The $S2p_{3/2}$ peak corresponding to sulphur is observed at 160.4 eV.

Optical properties which are directly related to the size of nanoparticles can be studied using the absorption spectra of CdS. The absorption spectra of CdS is shown in Fig. 4. The absorption onset wavelength is 471 nm, which is blue shifted compared to the absorption onset (515 nm) of bulk CdS. This blue shift is because of the quantum confinement effect [18]. When semiconductor absorbs enough light to excite charge carriers from ground state, the electron is allowed to move somewhat freely through the crystal or material. However, as the electron moves from the parent unit cell, a positive charge is left behind. The positive charge is called a hole and can move throughout the nanoparticle just like an electron. Due to attractions of positive and negative ions, the electrons and holes appear to move with an effective mass and not with the true mass. The mean size of the grains was calculated for the sample using Henglein's empirical formula [19], which relates the size of particle and optical absorption onset. Radius, R_{CdS}, of the CdS nanocrystals is given by

$$2R_{\mathrm{cds}}(\mathrm{nm}) = \frac{0.1}{(0.1338 - 0.0002345\,\lambda_{\mathrm{e}})}$$

where λ_{e} is the wavelength of absorption onset. The particle size has been calculated and is 2.1 nm. It is particularly interesting to see what happens when the size of the nanoparticle becomes smaller than or comparable to the radius of the orbit of the electron–hole pair. There are two situations, called the weak confinement and the strong confinement regime. In the weak regime, the particle radius is larger than the radius of the electron–hole pair, but the range of motion of the exciton is limited, which causes a

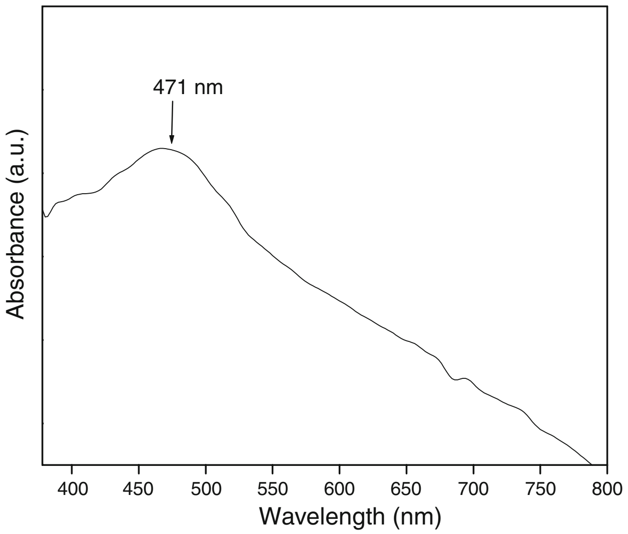

Fig. 4 Optical absorption spectra of the prepared CdS quantum dots

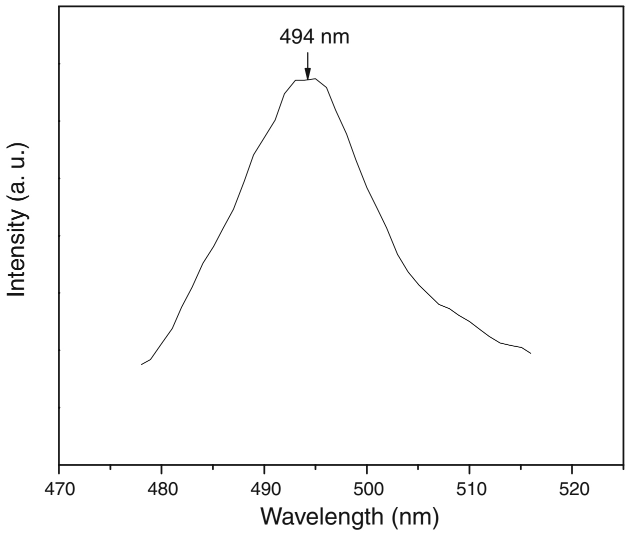

Fig. 5 Photoluminescence spectra of CdS quantum dots

blue shift of the absorption spectrum. When the radius of the particle is smaller than the orbital radius of the electron–hole pair, the motion of electron and hole become independent and the exciton does not exist. The hole and the electron have their own set of energy levels. Here also there is a blue shift [20]. As the particle size obtained from X-diffraction, HRTEM and optical absorption studies is smaller than the Bohr radius of 3 nm for CdS, the strong confinement effect can be assumed to be present in the CdS quantum dots.

Photoluminescence behaviour of semiconductor nanoparticles could give information on the energies and dynamics of photogenerated charge carriers as well as on the nature of the emitting states. Emissions from semiconducting nanoparticles originate from electrons in the conduction band, excitonic states and trap states [21–24]. It is well known that emission is very sensitive to the nature of the surface of nanoparticles and this is due to the presence of gap surface states arising from surface non-radiative recombination and they enhance luminescence efficiency. Broad low energy PL spectrum is usually attributed to trap state emission arising from surface defect sites [25]. In CdS, defects consist of cadmium vacancies, sulphur vacancies, interstitial sulphur and cadmium atoms adsorbed on the surface [26]. Sharp emission band at the absorption onset is due to the radiative recombination of free charge carriers or excitonic fluorescence, whilst broad PL peak is attributed to the recombination of charge carriers in deep traps of surface localized states [27, 28]. In this study, the PL spectra of CdS were recorded at room temperature with excitation wavelength of 320 nm. PL spectra are observed to be broad and emission occurred at a lower energy value than that corresponding to the excitonic emission band. This could be attributed to the recombination of the charge carrier trapped in the surface states [29]. The PL emission spectra of CdS shown in Fig. 5 are found to exhibit an emission peak centred around 494 nm. The emission band present at 494 nm is known as green emission band of CdS. According to Peng and co-workers [30], CdS nanoparticles with PL peaks at 509, 535, 569 and 585 nm correspond to particle size of 1.6, 2.2, 3.1 and 3.4 nm, respectively. Therefore, the PL peak at 494 nm observed in the present study can be said to correspond to a particle size of ∼2 nm again supporting the results obtained from structural and optical studies.

Conclusion

CdS quantum dots have been prepared by a simple chemical method. The prepared CdS quantum dots have been characterized using X-ray diffraction method, high resolution transmission electron microscopy UV–vis and photoluminescence spectra. The results indicated that the prepared CdS have a particle size of ∼2.5 nm which is smaller than the Bohr radius. This reveals that strong quantum confinement effect is present in the prepared CdS nanoparticles.

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