

SYNTHESIS AND STRUCTURAL PROPERTIES OF WURTZITE TYPE CdS NANOPARTICLES

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CdS semiconductor nanoparticles were synthesized by chemical precipitation method using cadmium chloride as cadmium source and sodium sulphide as sulphur source. Structural characterization of as synthesized semiconductor nanoparticles were performed by X-ray diffraction pattern (XRD) and Raman spectroscopy while optical characterization were done by Photoluminescence spectroscopy and UV-Visible absorption spectroscopy. XRD pattern showed the as synthesized CdS nanoparticles have wurtzite structure with 6-10 nm average crystallite size. Raman spectrum also confirmed the as synthesized sample was of CdS nanoparticles having first Longitudinal optical phonon (1LO) mode at 299 cm^{-1} and 2LO at 601 cm^{-1} . UV-Visible absorption spectrum showed the blue shift in absorption edge w.r.t. bulk CdS. Photoluminescence study was performed to investigate the several defects and vacancy levels in the synthesized CdS nanoparticles.

(Received May 13, 2009; accepted September 12, 2009)

Keywords: CdS, Wurtzite, Nanoparticle, Synthesis, XRD, UV-Vis, Semiconductor

1. Introduction

Nanoparticles have attracted great interest in recent years because of their unique chemical, physical, optical, electrical and transport properties which are different from those of either the bulk materials or single atoms[1,2]. Due to the vast surface area, all nanostructured materials possess a huge surface energy and thus, are thermodynamically unstable or metastable. One of the great challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the nanomaterials from growth in size driven by the reduction of overall surface energy. Due to high surface energy of the nanoparticles, they are extremely reactive and most systems without protection or passivation of their surfaces undergo aggregation[3]. Organic stabilizers are usually used to prevent nanoparticles from aggregation by capping their surfaces[4].

CdS is an II –VI semiconductor. Bulk CdS has hexagonal wurtzite -type structure [5], melting point $1600\text{ }^{\circ}\text{C}$ [6] and band gap $E_g=2.42\text{ eV}$ [7] at room temperature and pressure. As the semiconductor nanoparticles exhibit size dependent properties, the melting point of 2.5 nm CdS crystallites is as low as $\sim 400\text{ }^{\circ}\text{C}$ [6], the band gap of 0.7 nm CdS crystallites is 3.85 eV [8] and at very high pressure phase changes from hexagonal wurtzite type to rock salt cubic phase [9]. Since CdS has 2.42 eV (515 nm) band gap, so it is most promising candidate among II-VI compounds for detecting visible radiation. As CdS has wide band gap, it is used as window material for hetero junction solar cells to avoid the recombination of photogenerated carriers which improves the solar cells efficiency [10]. It has also application in light emitting diodes [11], photo detectors [12], Sensors [13], address decoders [14], and electrically driven lasers [15].

In this paper we report a simple chemical precipitation synthesis route at room temperature without using any capping agent. CdS nanoparticles were synthesized by several other methods given as controlled precipitation reaction method, rapid hot-injection based synthesis method, photochemical method and physical methods etc.

2. Experimental

All chemicals were of analytical grade and used as received without further purification. CdS nanoparticles were grown by the chemical precipitation method at room temperature. In synthesis procedure 100 ml aqueous solution of the reactants was prepared. 0.1 M CdCl₂ and 0.1 M Na₂S were used as the reactant materials. Freshly prepared aqueous solution of 0.1M Na₂S was mixed drop by drop in the 0.1 M CdCl₂ solution using vigorous stirring. 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 then washed several times with ethanol and centrifuged. The precipitate collected from centrifugation was dried at 50°C for few hours. This dried CdS powder was used to characterized XRD pattern, Raman spectroscopy and Photoluminescence spectra. While, for recording UV-Visible absorption spectrum, CdS powder was dispersed in DMSO and ultasonicated.

XRD patterns of the as synthesized sample was recorded on a Rigaku X-ray diffractometer using rotating anode with Cu-K_α line ($\lambda = 1.54 \text{ \AA}$) operating at 18 kV. The 2θ scanning range was from 15° to 55°. Raman spectra were recorded on RENISHAW inVia Raman spectrometer (RM 2000) integrated with a lica microscope. UV-Vis absorption spectra were recorded on Lambda 35 Perkin Elmer spectrophotometer in the range 250 to 600 nm. All the spectra were recorded by 514 nm Ar ion laser at room temperature. LS 55 Perkin elmer spectrophotometer was used for recording of photoluminescence of CdS nanoparticles samples with 400 nm and 430 nm excitation wavelength.

3. Results and discussion

Raman is a nondestructive technique for structural study of the material. It is an inelastic process in which incoming photons exchange energy with the crystal vibrational mode. Fig (1) showed the Raman spectra of bulk CdS and CdS nanoparticles. One can clearly see two characteristics bulk CdS longitudinal optical (LO) phonons peaks at about 297.5 cm⁻¹ and 599 cm⁻¹ corresponding to the 1LO and 2LO [16]. While, CdS nanoparticles have 1LO peak at 299 cm⁻¹ and 2LO peak at 601 cm⁻¹. Fig (2) clearly showed the shift in 1LO peak position of CdS nanoparticles towards lower wavelength side. Spanier et al [17] reported that phonon confinement, strain, defects and broadening associated with the size distribution are mainly factors which affect the Raman spectra. Due to phonon confinement and strain effect (fig not shown here) we observed the shift in 1LO and 2LO peak position of CdS nanoparticles w.r.t. bulk CdS.

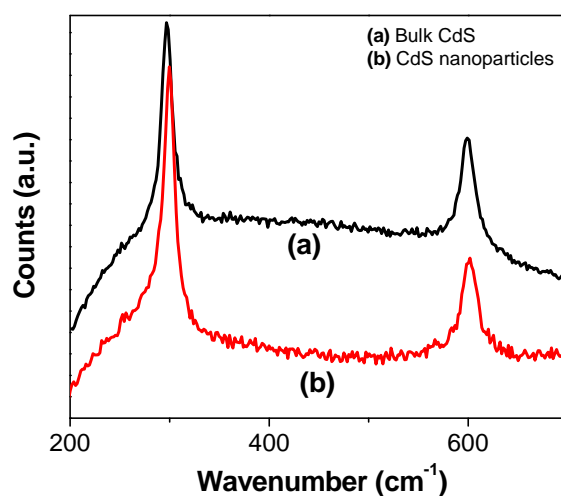


Fig 1. Raman spectra of (a) Bulk CdS (b) synthesized CdS nanoparticles in the range 200 to 700 cm⁻¹.

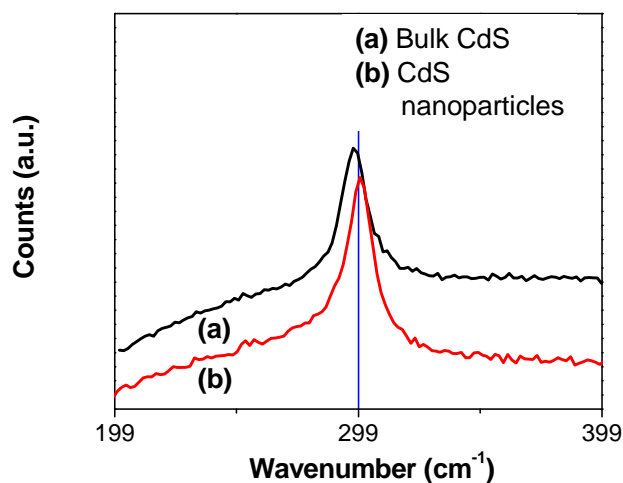


Fig 2. Raman spectra of (a) Bulk CdS (b) synthesized CdS nanoparticles in the range 199 to 399 cm^{-1} . This figure clearly showed the shift in 1LO peak position of as synthesized nanoparticles w.r.t. bulk CdS sample.

Using conventional Raman equipment we could observed only the optical phonons not acoustic phonons. As the crystal lattice has infinite periodicity which gives the $\Delta q = 0$ selection rule, where q stands for momentum[18]. However, if the periodicity of the crystal is interrupted, as in the case of Nanocrystalline materials, this rule is relaxed. The phonon uncertainty goes roughly as $\Delta q = 1/d$, where d is the grain size or nanoparticle diameter.

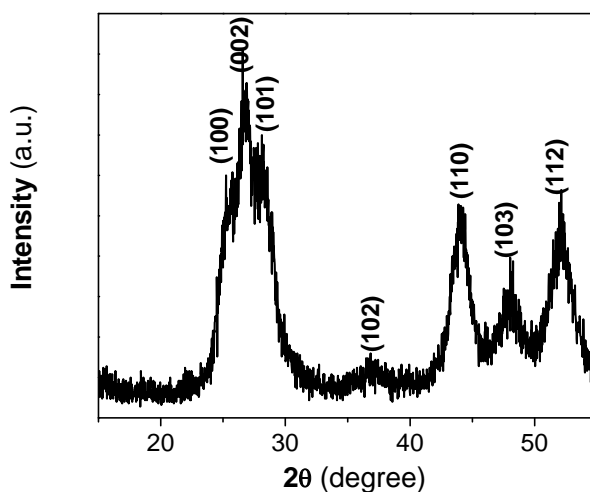


Fig 3. XRD spectrum as synthesized wurtzite type CdS nanoparticles.

XRD pattern provided information about crystalline phase of the nanoparticles as well as the crystallite size. Fig (3) shows the X-ray diffraction pattern of the as synthesized CdS nanoparticles. The XRD pattern indicate the synthesized CdS nanoparticles have a hexagonal phase due to presence of (100), (002) and (101) reflection planes in the angular region between 20° and 30° . The presence of (102), (110), (103) and (112) also supports the existence of hexagonal phase [19]. Crystallite size were calculated from using Scherrer's formula [19, 20]

$$D = 0.91 \lambda / \beta \cos\theta \quad (1)$$

Where D is the crystallite size, λ is the wavelength of the $\text{CuK}\alpha$ line (1.54 \AA), θ is the angle between the incident beam and the reflection lattice planes and β is the full width at half maxima (FWHM) of the diffraction peak in radian. The average crystallite size was found 6-10 nm. The lattice constant was calculated by using formula $1/d^2 = 4/3(h^2 + hk + k^2)/a^2 + (l/c)^2$ [20]. The lattice constant $a = 0.41 \text{ nm}$ and $c = 0.68 \text{ nm}$ calculated from XRD data which also support the results earlier reported by Ayyub et al [8].

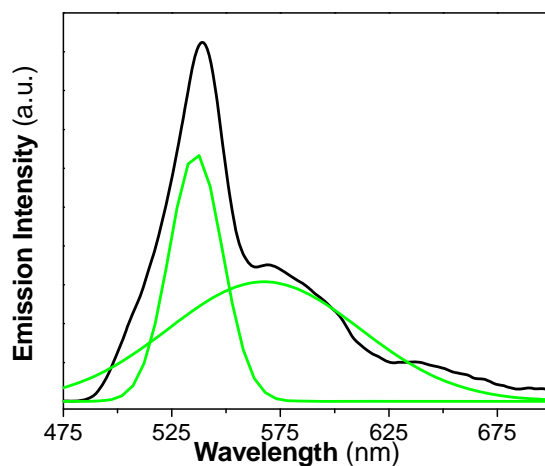


Fig 4. Photoluminescence spectrum of as synthesized CdS nanoparticles at 400 nm excitation wavelength.

The photoluminescence emission spectra of the synthesized CdS nanoparticles were shown in fig (4) at excitation wavelength 400 nm and fig (5) at excitation wavelength 430 nm. Fig (4) exhibits two broad bands centered at 536 nm and 567 nm while fig (5) shows bands centered at 525 nm and 576 nm. The bands corresponding to 536 nm and 525 nm provide Green emission while bands at 567 nm and 576 nm give Yellow emission. In fig [4] we also observed a small band at 639 nm corresponding to Red emission. The Green emission band was associated with the emission due to electronic transition from the conduction band to an acceptor level due to interstitial sulfur (I_S) [21]. The Yellow emission was attributed to recombination via surface localized states [22], a transition from interstitial cadmium (I_{Cd}) to valence band [23]. Red emission was observed due to the presence of sulphur vacancies [24].

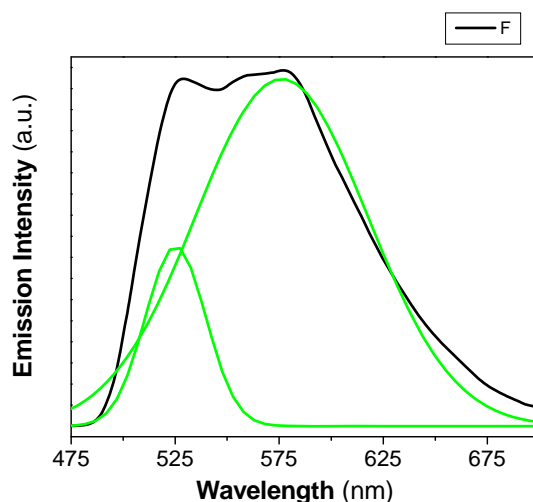


Fig 5. Photoluminescence spectrum of as synthesized CdS nanoparticles at 430 nm excitation wavelength.

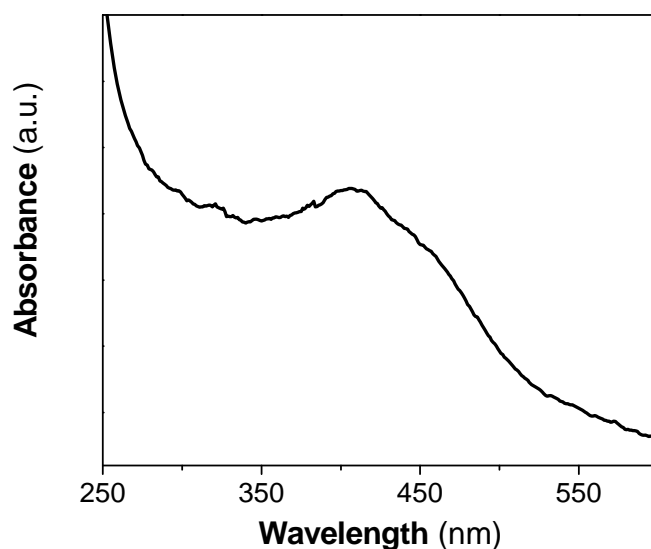


Fig 6. UV-Visible absorption spectrum of as synthesized CdS nanoparticles.

The spectrum which is obtained by absorption of electromagnetic radiations is called absorption spectra. Fig (6) shows the room temperature UV-Vis absorption spectrum of the CdS nanoparticles. The absorption edge was found at 515 nm (2.42 eV) in bulk CdS while in as prepared sample the absorption peak position was at lower wavelength which indicates the blue shift in absorption edge. Brus had derived Effective mass approximation formula [EMA][25] to explain the blue shift. The Effective mass approximation formula is given as

$$E_g^{\text{eff}} = E_g + \hbar^2 \pi^2 / 2\mu R^2 - 1.8 e^2 / 4\pi\epsilon \epsilon_0 R \quad (2)$$

Where $[1/\mu = 1/m_e^* + 1/m_h^*]$, m_e^* is the effective mass of electron ($0.19 m_e$), m_h^* is the effective mass of hole ($0.8 m_e$), R is the the radius of the particle, ϵ is the dielectric constant (5.7) and ϵ_0 is the permittivity of free space. The second term in the equation is the quantum confinement for electrons and holes which lead to the blue shift [26] while third term is the coulomb energy term [27].

4. Conclusions

A chemical precipitation method has been successfully developed to synthesize CdS nanoparticles without using any capping agent at room temperature. X-ray diffraction patterns revealed that the synthesized CdS nanoparticles have hexagonal structure. The peak position of first order Raman line in bulk CdS at 297.5 cm^{-1} is shifted towards higher energies as the particle size gets smaller. UV-Visible absorption spectrum shows the blue shift in absorption edge. Photoluminescence spectrum revealed the presence of I_S , I_{Cd} and V_S corresponding to the green, yellow and red emission.

Acknowledgement

Authors wish to acknowledge Dr A C Pandey, Nanophospher Application Center, University of Allahabad for providing all the characterization facility. We are also thankful to Prof Ram Gopal, Department of Physics, University of Allahabad, for providing UV-Visible facility

and another facility available with him.. One of the author Vineet Singh would like to acknowledge CSIR, India for providing Junior Research Fellowship.

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