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Structural and optical studies of $Zn_{1-x}Cd_xS$ quantum dots synthesized by *in situ* technique in PVA matrix

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ABSTRACT

$Zn_{1-x}Cd_xS$ (x = 0.1, 0.2, 0.3, 0.4, 0.5 . . . 0.9) quantum dots were synthesized successfully using novel *in situ* technique in polyvinyl alcohol (PVA) matrix. The PVA acted as a capping agent as well as a reducing agent. The structural and optical properties of the samples were studied by X-ray diffraction (XRD), TEM analysis, UV–Visible absorption and photoluminescence spectroscopy (PL). X-ray diffraction patterns revealed cubic zinc blende phase of the samples with lattice parameter in the range 5.47–5.75 Å. Optical band gap values were calculated from the absorption spectra and observed a decreasing band gap with increasing Cd:Zn ratio. The Raman spectra were recorded using conventional Micro Raman technique. Photoluminescence spectra showed asymmetric broad emission with multiple maxima. The concentration dependent quenching of PL intensity with increasing Cd:Zn ratio was observed along with a red shift. The nonlinear optical (NLO) and limiting properties were studied using Z-scan technique.

1. Introduction

Synthesis and characterization of luminescent semiconducting nano-sized materials are an important and interesting research field in recent times due to their unique optical and electrical properties. Among the various semiconductor nano-sized materials, II–VI semiconductors have attracted proper attention because of their potential applications such as catalysts, electronic and optoelectronic nano devices mainly due to the shape and size controlling flexibility of their nanocrystals [1,2]. Capping of nanoparticles has been one of the most important methods to provide chemical passivation and also improve the surface state of the nanoparticles which in turn has significant influence on their optical and electronic properties [3]. Polymers carrying functional groups have been used as specific stabilizers and capping agents in the synthesis of semiconducting nanoparticles [4]. Previously different authors have reported studies on polymer capped semiconductor nanoparticles with improved properties [5–7]. Composition controlled structural, UV absorption and photoluminescence of nano sized ZnCdS in various geometrical shapes like nanoparticles, nanosheets and nanowires were synthesized by different synthesis methods [8–10]. Ni doped ZnCdS and Cu doped ZnCdS were synthesized by coprecipitation and microwave assisted methods [11–13].

In this paper we focused on the structural, optical absorption, photo luminescence, optical nonlinear and optical limiting properties of PVA capped $Zn_{1-x}Cd_xS$ nanoparticles synthesized by *in situ* technique. So far this kind of study is not reported to the best of our knowledge. One of the earliest and easiest method for nanoparticles synthesis is the *ex-situ* method [14,15], where the nanoparticles are first synthesized and then directly incorporated into the polymer matrix. Another important and general method is the *in situ* approach, where the nanoparticles are generated from the respective metal precursor within the polymer matrix [16–19] itself. In this work, we adopted the *in situ* technique for the synthesis of $Zn_{1-x}Cd_xS$ nanoparticles using polyvinyl alcohol (PVA) as the matrix by an ion exchange reaction. PVA is a good solute to multi phase systems, providing uniform and close gaps distributed in the form of arrays [20]. Nanoparticles may readily aggregate due to their large specific surface energy [21]. The characteristic structure of the polymer network can stabilize the nanoparticles and prevent them from aggregation by covering the large surface area of the nanoparticles. Hence the capped form of nanoparticles in polymer matrix is more stable and prone to external chemical influences than the uncapped nanocrystals or thin films. The crystalline

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structure and particle size of the samples were characterized using X-ray diffraction technique, the optical properties were analyzed using UV–Visible absorption spectroscopy and photoluminescence spectroscopy. Band gap of the synthesized quantum dots were calculated from the UV data [22] and the nonlinear optical properties were studied using the Z-scan technique.

2. Experimental

Materials used in the present synthesis were zinc acetate, cadmium acetate, sodium sulfide (Na_2S) as sulphur source, polyvinyl alcohol (PVA) as the capping and dispersing matrix. In a typical procedure, aqueous stock solutions of 1 M zinc acetate and 1 M cadmium acetate were mixed at various volume ratios of (9:1), (8:2), (7:3), (6:4) ... (1:9). The prepared precursor was mixed with 5 wt% solution of PVA in water under stirring rate of 300 rpm at 50 °C for 5 h. 10 ml of 1 M sodium sulfide solution was added drop by drop to the PVA metal complex till the color changes from white to yellow, depending on the Cd:Zn ratio and continued stirring for 5 h. The synthesized particles were collected by centrifugation at 10,000 rpm for 10 min. The collected particles were washed with deionized water and methanol to remove the last traces of adhered impurities and dried at 50 °C. Structural characterization of the samples were carried out by X-ray diffraction technique. X-ray data were collected for 2θ range from 5° to 70° using PAnalytical diffractometer with Cu Kα irradiation ($\lambda = 1.5406$ Å) UV–Visible absorption spectra were recorded in the wavelength range 200–800 nm using SHIMADZHU UV PC 2501 PC spectrophotometer. Photoluminescence spectra of the samples were collected at an excitation wavelength of 340 nm using florescence spectrophotometer (FLUROMAX-4). The Micro-Raman scattering were recorded using Labram HR-800 spectrometre equipped with excitation radiation at wavelength 514 nm from an argon ion laser at a spectral resolution of about 1 cm^{-1}. The nonlinear and optical limiting properties of the semiconducting nanoparticles were studied using Z-scan technique. Measurements of the parameters were carried out in a 5 ns pulse width laser in continuous wave (Nd-YAG) mode with $\lambda = 532$ nm. Nanoparticles were dispersed in 2-propanol and kept in a quartz cuvette of path length 1 mm in the translate stage and can move in the direction of propagation of transmitted laser beam [23]. The measurement of NLO properties were carried out with the transmission detector fully open, commonly known as open aperture Z-scan. This measurement technique allowed to measure nonlinear absorption coefficient (γ). The optical limiting properties of the $Zn_{1-x}Cd_xS$ nanoparticles in 2-propanol at different Cd concentrations were investigated with intensity – dependent transmittance measurements at 532 nm. The linear transmittances of all the solutions were adjusted to 57%. All the experiments were carried out at room temperature.

3. Results and discussion

3.1. UV–Vis spectroscopic analysis

The UV–Visible absorption spectra of synthesised $Zn_{1-x}Cd_xS$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5 \ldots 0.9$) quantum dots are shown in Fig. 1. The spectra of $Zn_{1-x}Cd_xS$ exhibit steep absorption edge and is successively shifted from 470 nm to 520 nm when Cd:Zn ratio increases. The steep absorption edge indicates visible light absorption due to band gap transition rather than impurity level transition [11].The absorption edges of the spectra are related to the Zn and Cd concentrations, it is shifted towards the higher wavelength side on increasing the Cd:Zn ratio from 10% to 90%. Similar type of edge shifting was observed by varying the elemental composition of the semiconducting nanoparticles [12]. The shift in

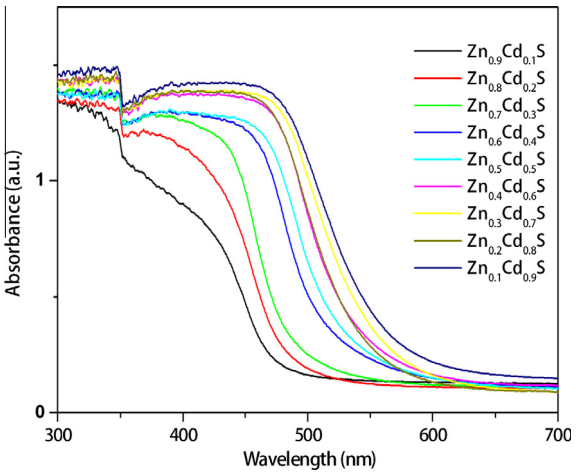

Fig. 1. UV–Visible absorption spectra of $Zn_{1-x}Cd_xS$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5 \ldots 0.9$) quantum dots.

absorption edge of the quantum dots at different Cd:Zn ratios reflect the variation in the band gap energy. Band gap of the synthesized samples are estimated from the absorption spectrum, which corresponds to the energy difference between the top of the valance band and the bottom of the conduction band. The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$), can be written as [24]

$$\alpha h\nu = K(h\nu - Eg)^n \quad (1)$$

where K is a constant, Eg is the band gap of the material and the integer "n" depends on the type of transition. For direct band gap material $n = ½$, for indirect band gap material $n = 2$ and for direct forbidden band gap material $n = 3/2$. The value of the optical band gap is obtained by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. $h\nu$ plot to $\alpha h\nu = 0$ [25] as shown in Fig. 2. The band gap value of the synthesized $Zn_{1-x}Cd_xS$ quantum dots varied from 2.25 eV to 2.7 eV related to Cd:Zn ratio, and is well matched with the reported values of $Zn_{0.4}Cd_{0.6}S$ nanoparticles [10]. $Zn_{0.1}Cd_{0.9}S$ and CdS nanoparticles of similar size showed almost same band gap values while a large difference in band gap is observed for $Zn_{0.9}Cd_{0.1}S$ and pure ZnS nanocrystals of same size. Fig. 3 shows the plot of band gap vs. percentage of Cd for the synthesized

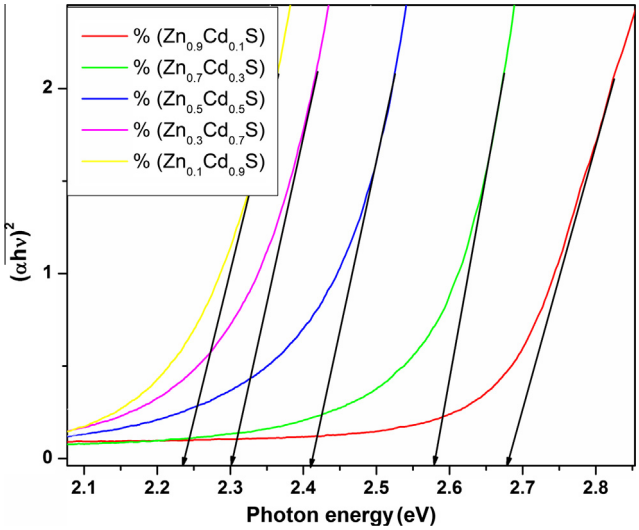

Fig. 2. Band gap of the $Zn_{1-x}Cd_xS$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9$) quantum dots.