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Synthesis and optical characterization of monodispersed Mn^{2+} doped CdS nanoparticles

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ABSTRACT

Monodispersed Mn^{2+} doped CdS nanoparticles with average size as small as 1.8 nm have been synthesized through chemical method. The nanostructures of the prepared nanoparticles have been confirmed through X-ray diffraction (XRD), ultraviolet-visible (UV-vis) absorption and transmission electron microscope (TEM) measurements. The photoluminescence emission covering 450–650 nm of the visible region is observed under ultraviolet light excitation, from Mn^{2+} doped CdS nanoparticles dispersed in dimethyl sulfoxide (DMSO).

1. Introduction

Recently, transition metal ion-doped II–VI semiconductor nanoparticles have attracted much attention because such doping can modify and improve the optical properties of II–VI semiconductor nanoparticles by a large amount [1–20]. Extensive research work have been undertaken [10–14] on the doped nanocrystalline semiconductors like ZnS : Mn or CdS : Mn, etc., to improve their emission activity. Photoluminescence (PL) emission covering the whole visible region from Mn^{2+} doped CdS nanoparticles were reported previously [15–18]. Nag et al. [15] recently reported visible light emission from Mn^{2+} doped CdS nanoparticles prepared through chemical method. They [15] used 1-thioglycerol as capping agent and the reaction mixture was heated at high temperature in the 45–130 °C temperature range and after 12 h of stirring of the mixture they obtained CdS : Mn nanoparticles of average diameter of 1.8 nm.

In this work it is reported that it is possible to prepare monodispersed Mn^{2+} doped (0.19%) CdS nanoparticles (CdS : Mn) with average size of nanoparticles as small as 1.8 nm through chemical method capped with polyvinyl pyrolidone (PVP) in only 5 h stirring of the reaction mixture maintained at 55 °C temperature. The nanostructures of the prepared CdS : Mn nanoparticles are confirmed from X-ray diffraction (XRD) peak broadening and transmission electron microscope (TEM) measurements. The optical absorption properties of the prepared nanoparticles are also measured and the absorption edge was found to be blue shifted from their corresponding bulk values due to the quantum confinement effect. The prepared Mn^{2+} doped CdS (i.e., CdS : Mn) nanoparticles show photoluminescence emission covering almost the whole visible range of 450–650 nm wavelength of the electromagnetic spectrum, under 290 nm ultraviolet excitation.

2. Experimental details

To synthesize CdS nanoparticle the chemicals used were $Cd(CH_3COO)_2{\cdot}2H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$, polyvinylpyrolidone (PVP), and Na_2S. All the chemicals were used as received (Merck & SD fine chemicals) without further purification. $(4-y)$ mmol of $Cd(CH_3COO)_2{\cdot}2H_2O$ was taken into 20 ml DMSO and $y = 0.12$ mmol of $Mn(CH_3COO)_2{\cdot}4H_2O$ was taken into 20 ml of DMSO; 0.1 gm PVP dissolved in 20 ml DMSO was added to this solution. The reaction mixture was kept at a temperature of 55 °C in a beaker of 40 ml capacity under continuous stirring. Na_2S was added drop-wise for 5 minutes. Two samples S1 and S2 of Mn^{2+} doped CdS (CdS : Mn) nanoparticles were collected after 3 h and 5 h stirring, respectively. The nonsolvent acetone was added in excess to reaction mixture to precipitate out nanoparticles. The solution was centrifuged and washed with methanol to get rid of any Mn^{2+} and other unreacted ions remaining outside the clusters.

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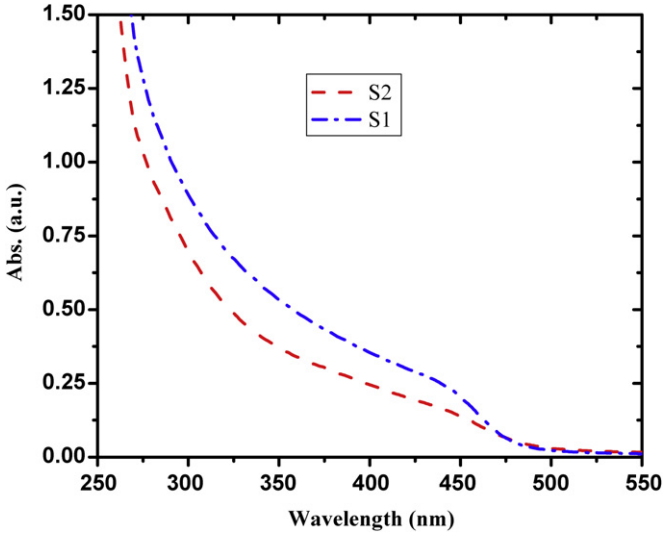
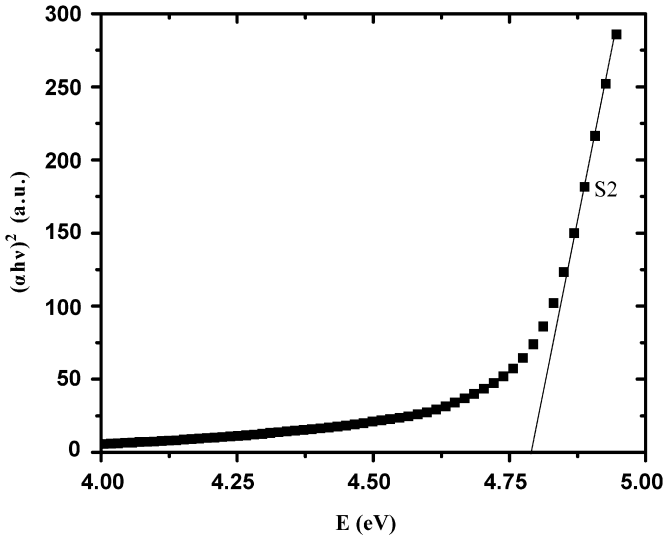


(a)



(b)

Fig. 1. (a) UV-vis absorption characteristics of the prepared CdS nanoparticles dispersed in DMSO. S1 and S2 are obtained after 3 and 5 h stirring, respectively. (b) Variation of $(\alpha h\nu)^2$ versus $E(=h\nu)$ is shown for the calculation of the direct bandgap of the prepared CdS : Mn nanoparticles. By extrapolating the straight portion of the graph to E axis gives the value of bandgap = 4.79 eV for S2 sample.

The prepared nanoparticles were characterized for their optical and nanostructural properties. The optical transmission/absorption spectra of CdS : Mn nanocrystallites dispersed in DMSO were recorded using a UV-vis spectrophotometer (Hitachi U-3010). The formation of CdS : Mn nanocrystallites were confirmed by TEM (JEOL 2000 FX 11) micrograph. X-ray diffraction pattern was recorded with an X-ray diffractometer (PANLYTICAL) using CuK_α radiation of wavelength $\lambda = 0.15406$ nm in the scan range $2\theta = 20$–$90°$. Scanning electron microscope (FESEM with EDXA, Sirion) has been used for compositional analysis of the prepared CdS : Mn nanocrystallites. The photoluminescence (PL) spectrum of the CdS : Mn nanoparticles dispersed in DMSO has been measured using a spectrofluorimeter (F-2500 FL Spectrophotometer, Hitachi).

3. Results and discussion

Fig. 1(a) shows the ultraviolet-visible (UV-vis) absorption characteristics for S1 and S2 samples of the as-prepared CdS : Mn nanoparticles.

For measuring the absorption characteristics, the nanopowder was first dispersed in DMSO and taken in a quartz cuvette. For obtaining the absorption characteristics of the samples, at first the transmittance (T) at different wavelengths (λ) was measured and then absorption coefficient (α) at the corresponding wavelengths λ were calculated using the Beer–Lambert's relation (Eq. (1)).

$$\alpha = \frac{1}{l}\ln\left(\frac{1}{T}\right), \tag{1}$$

where l is the path length. From Fig. 1 it is clear that the absorption edge for S2 sample has been blue shifted more in comparison to that of S1, i.e., particle size for S2 sample is smaller than that of S1.

The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the value of the optical bandgap of the prepared CdS : Mn nanoparticles. The relation between the incident photon energy ($h\nu$) and the absorption coefficients (α) is given by the following relation.

$$(\alpha h\nu)^{1/m} = c(h\nu - E_g), \tag{2}$$

where c is a constant and E_g is the bandgap of the material and the exponent m depends on the type of the transition. For direct and allowed transition $m = 1/2$, indirect transition, $m = 2$, and for direct forbidden, $m = 3/2$. For calculating the direct bandgap value for S2 sample, for example, $(\alpha h\nu)^2$ versus $E(=h\nu)$ is plotted and it is shown in Fig. 1(b). By extrapolating the straight portion of the graph on E axis at $\alpha = 0$, the optical bandgap is calculated and it is 4.79 eV. The obtained value of the bandgap is higher than that of bulk value of CdS (2.43 eV). This blue shift of the bandgap takes place because of the quantum confinement effect [15–19]. The absorption edge for a suspension of nanoparticles is much broader and is determined by the distribution of particle size [16]. At the absorption edge, only the larger particles contribute to the absorbance. In the smaller wavelength range particles with smaller sizes contribute more and at the region of absorbance maximum, all particles contribute to the absorbance [16]. Following the Brus model [19], the relation between the bandgap shift (ΔE_g) and the nanoparticles radius (r) can be derived as,

$$\Delta E_g = \frac{2.43125}{r^2} - \frac{0.4684375}{r}. \tag{3}$$

Here, ΔE_g and r are in eV and nm units, respectively. For deriving Eq. (3), we have used $m^*_{e\mathrm{CdS}} = 0.19m_0$, $m^*_{h\mathrm{CdS}} = 0.80m_0$, $m_0 = 9.1 \times 10^{-31}$ kg, and the dielectric constant $\varepsilon_{\mathrm{CdS}} = 4\pi\varepsilon_r\varepsilon_0$ with $\varepsilon_r = 5.5$ and $\varepsilon_0 = 8.85 \times 10^{-12}$ Farad/m [15–19]. From the value of bandgap shift and using Eq. (3) the calculated value of the average size (diameter) of the CdS : Mn (S2 sample) nanoparticles is 1.8 nm. The particle size and its distribution have also been calculated from XRD peak broadening data and TEM measurements, respectively, which are presented below.

X-ray diffraction pattern of the prepared CdS : Mn samples were obtained and those are shown in Fig. 2. Three broad peaks at $2\theta = 27°$, $44°$, and $52.6°$ correspond to (111), (220), and (311) planes of cubic phase of CdS (JCPDS File No. 10-454). For S2 sample the peaks are much broader than those of S1, which indicates that the particle size for S2 sample is smaller than that of S1 sample. The appearance of diffraction peaks demonstrates that particles are not amorphous. The positions of diffraction peaks correspond to those of the cubic phase of cadmium sulfide. The average crystallite size is calculated, for example for S2 sample, from the full width at half maximum (FWHM) of the diffraction peaks using the Debye–Scherrer formula [21].

$$R = \frac{0.89\lambda}{\beta\cos\theta}. \tag{2}$$