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Synthesis and structural and optical characterization of Mn^{2+} doped cadmium sulphide nanoparticles stabilized in DETA matrix

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ABSTRACT

Mn^{2+} doped cadmium sulphide nanoparticles were prepared with different pH values by chemical precipitation method, at room temperature. Diethylene triamine (DETA) was used as stabilizing agent to control the particle size and prevent agglomeration. The samples were characterized with X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM), energy dispersive X-ray analysis (EDAX), diffuse reflectance spectroscopy (DRS), Fourier transform infrared (FTIR) spectroscopy and photoluminescence (PL) studies. The average size of the Mn^{2+} doped cadmium sulphide nanoparticles, exhibits both cubic and hexagonal structure, calculated from Debye–Scherrer formula was of the order of 2–6 nm. The above value of the particle size was confirmed by using Williamson–Hall plot as well as Henglein's formula. X-ray peak broadening analysis was done using Williamson–Hall plot. The HRSEM images showed the formation of nanoclusters and EDAX spectra confirms the presence of cadmium, sulphide and manganese elements in the sample. The DRS UV–vis spectra of the samples show blue shift, revealing the strong quantum confinement effect of nanoparticles. The formation of DETA capped Mn^{2+} doped CdS nanoparticles were confirmed by FTIR analysis. The synthesized samples show photoluminescence emission, ranging from 400 to 600 nm, in the visible region of the electromagnetic spectrum.

1. Introduction

Recent investigations in nanotechnology implies that nanoscale inorganic semiconductor materials finds wide range of applications such as optoelectronics, telecommunications, sensors and photo catalytic activities, due to their novel size dependent characteristics [1–3]. Semiconductor nanocrystals, displaying interesting electronic and optical properties attributed to the quantum confinement effect and the large surface to volume ratio of atoms are both fundamental and technological interest. Cadmium sulphide (CdS), with a direct band gap of 2.43 eV at room temperature is an important semiconducting material, owing to its unique electronic, electrical, magnetic and optical properties [4,5]. In view of the tunable band gap, optimized structural characteristics, high adaptability, CdS nanoparticles with metal dopants at various concentration and size controlling surfactant can be explored for potential device applications in the frontier areas such as, bioimaging, sensors, solar cell fabrication and photocatalysis [6–10]. In the present era CdS nanocrystals have attracted considerable interest among the researchers because of its discrete energy levels, tunable band gap, size dependant optical properties and well developed synthetic protocols, good chemical stability and easy preparation techniques [11]. It is also observed that the evolution of CdS crystal structure from cubic to hexagonal under the synergistic effect of ultrasound with microwave irradiation is an effective tool to synthesize nanomaterials with enhanced properties [12]. CdS nanoparticles have been prepared and characterized by several methods and their important technological applications are explored [13–16]. Monte et al. [17] synthesized CdS nanoparticles embedded in polymeric microsphere templates and studied their optical properties. Nanosized CdS particles were also prepared by melting nucleation method within a hosting glass template [18]. In this paper, we report the synthesis of Mn^{2+} doped CdS nanoparticles at different pH values by chemical precipitation method using DETA, a non toxic, water soluble and inherently biodegradable matrix, as surfactant. The effect of DETA on the structural and optical properties of Mn^{2+} doped CdS nanoparticles have been discussed in detail.

2. Experimental details

2.1. Synthesis

High quality Mn^{2+} doped CdS nanoparticles, stabilized in DETA was prepared by chemical precipitation method at different pH values using cadmium chloride ($CdCl_2$), sodium sulphide (Na_2S) and manganese chloride ($MnCl_2$) as synthesizing materials. Double distilled water and diethylene triamine (DETA) were used as sol-

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vent and capping agent respectively. All the reaction procedure was performed at room temperature (32 °C) and standard pressure. Initially 100 mL solution of 0.07 mol/L $CdCl_2$ and 0.14 mol/L diethylene triamine were prepared separately using double distilled water and mixed throughly under vigorous stirring. In this mixture, 7% of $MnCl_2$ solution was added and the pH of the samples was adjusted to two by adding hydrochloric acid (0.07 mol/L) appropriately. Thereafter Na_2S (100 mL) solution was added drop by drop with constant magnetic stirring in the reaction process. As the reaction proceeded, the colour of the reaction changed from transparent to yellowish orange. The precipitate thus obtained as the final product of the reaction was recovered by centrifugation, washed several times with acetone to remove the impurities, un-reacted reactants and dried in air oven at 60 °C for 5 h. The sample synthesized at pH values 2, 4 and 6 were named as PH1, PH2 and PH3, respectively. In our study, the bare CdS nanoparticles are encapsulated within the template formed from DETA molecules and got stabilized in DETA matrix.

2.2. Characterization

The Mn^{2+} doped CdS nanoparticles stabilized in DETA matrix were characterized with structural and optical properties. The X-ray diffraction patterns for the samples were recorded using Schimadzu Labx XRD 6000 X-ray powder diffractomer with CuKα radiation with 2θ ranging from 10° to 90° at a scanning rate of 10° per minute. FEI quanta FEG 200 high resolution scanning electron microscope was used to study the surface morphology and compositional analysis of Mn^{2+} doped CdS samples stabilized in DETA matrix for all the three pH values. The optical properties of Mn^{2+} doped CdS samples were studied using a Varian CARRY 5E spectrophotometer. Fourier transform infrared (FT-IR) measurements were carried out using a FT-IR Perkin Elmer spectrometer by KBr pellet technique in the wave number range 400–4000 cm^{-1}. The photoluminescence spectra of the samples were recorded using a Perkin Elmer spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction studies

The X-ray diffraction patterns of samples PH1, PH2 and PH3 are shown in Fig. 1a–c, respectively. The XRD patterns of Mn^{2+} doped CdS samples synthesized at pH values 2 and 4 are in good agreement with the reported value of the cubic phase of standard CdS (JCPDS 80-0019). The three main peaks at 26°, 43° and 51°, respectively were also assigned to the cubic phase of (1 1 1), (2 2 0), (3 1 1) CdS crystal planes [19]. However, the XRD pattern of Mn^{2+} doped CdS nanoparticles synthesized at pH value 6 is agreed with the hexagonal phase of standard CdS (JCPDS 80-0006) having peaks at 27°and 47°. The lattice parameters and cell volumes of Mn^{2+} doped CdS nanoparticles at pH values 2, 4, 6 have been compared with the standard CdS value and presented in Table 1. The 2θ values of the corresponding hkl planes for the Mn^{2+} doped CdS nanoparticles at pH values 2, 4, 6 compared with the standard CdS are presented in Table 2.

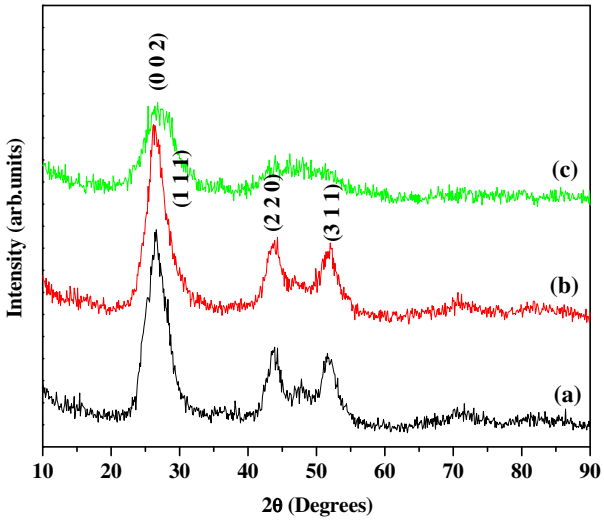

Fig. 1. X ray diffraction patterns of Mn^{2+} doped CdS nanoparticles: (a) pH1, (b) pH2 and (c) pH3.

The three major peaks of Mn^{2+} doped CdS nanoparticles at different pH values are varies slightly from that of the standard CdS which confirms the isomorphic substitution of Cd^{2+} ions by Mn^{2+} ions. Also the modification of cell parameter and cell volume of Mn^{2+} doped CdS nanoparticles confirms the replacement of Cd^{2+} ions by Mn^{2+} ions in the lattice of CdS.

The full width at half maximum (FWHM) can be expressed as a linear sum of FWHM of size, FWHM of strain and FWHM of instrument [20].

$$\beta_{tot} = \beta_{size} + \beta_{strain} + \beta_{instrumental} \quad (1)$$

Here the instrumental broadening β_{hkl} was corrected corresponding to each diffraction peak and fitted with a Lorentzian profile.

The broadening of diffraction peaks provides information about the crystalline size, as the width of the diffraction peaks increases, the particle size decreases. The presence of broad diffraction peaks in Mn^{2+} doped CdS samples confirms the size of the particles. From the XRD results, the crystallite size was estimated using Debye–Scherer formula as

$$D = K\lambda/\beta\cos\theta \quad (2)$$

where λ is wavelength of copper Kα line (1.5406 Å), Θ is the angle between the incident beam and the reflection lattice planes, β is full width at half maximum of the peak and D is average particle size (nm).

The average grain size of all the samples estimated by using Eq. (1) is in the order of 2–6 nm. It is observed from the X-ray analysis that the crystal structure of CdS nanoparticles is not affected by changing the pH from 2 to 4. However, for the samples prepared at pH value 6, a change of crystal structure from cubic to hexagonal has been observed. It is important note that similar phase transition from cubic to hexagonal was already observed in CdS and reported by Udaya et al. [21]

Generally, local distortion of the lattice generates strain in the lattice and its contribution to peak broadening is known as strain broadening. By considering uniform strain in all crystallographic directions and the isotropic nature of the crystal, the strain broadening can be written as,

$$\varepsilon = \beta_{hkl}/4\tan\theta \quad (3)$$

Substituting the values for β_{size} and β_{strain} in Eq. (1) we obtain,

$$\beta_{hkl} = K\lambda/D\cos\theta + 4\varepsilon\tan\theta$$

By rearranging the above equation the relation is,

$$\beta_{hkl}\cos\theta = K\lambda/D + 4\varepsilon\sin\theta \quad (4)$$

where the microstrain parameter is $\varepsilon = \Delta D_{hkl}/D_{hkl}$.

A graph is drawn between $4\sin\theta$ and $\beta_{hkl}\cos\theta$, for the as-prepared CdS nanoparticles. From the linear fit to the data plot, the particle size and strain were calculated. It is found that the particle size calculated from the Scherrer's equation (2–6 nm) closely agreed with that of the particle size estimated from the W–H plot (2 nm). The microstrain evaluated from the graph shown in Fig. 2, corresponding to the sample PH3 is found to be −0.0204. The negative slope of Williamson–Hall plot indicates the occurrence of compressive strain on the particles for the sample prepared at pH value 6.

3.2. Morphological studies

The HRSEM images of Mn^{2+} doped CdS samples prepared at pH values 2, 4 and 6 are shown in Fig. 3a–c and the respective EDAX