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Structural and optical properties of CdS nanorods and CdS/ZnS nanoslabs

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ABSTRACT

CdS nanorods having diameter, 22 nm, and CdS/ZnS nanoslabs, having thickness of ~85 nm, have been synthesized solvothermally at 160 °C, using ethylenediamine (En) as the solvent and the chelating ligand. In this two-step solvothermal process, CdS nanorods synthesized in the first step have been used as an ingredient for the second step, resulting in CdS/ZnS nanostructures with CdS nanorods embedded in ZnS nanoslabs. Both the samples have been compared structurally, morphologically and optically using, respectively, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–vis absorption studies and photoluminescence (PL) studies. CdS and CdS/ZnS nanostructures have hexagonal wurtzite phase of CdS and ZnS. Fourier transform infrared spectroscopy (FTIR) has been carried out to find the organic composition of the samples, especially to confirm the presence of En. Comparison between the PL spectra of the two samples has shown distinct peaks centered at 420 and 484 nm due to the presence of ZnS, in addition to the CdS related luminescence peaks centered at 530 and 544 nm.

1. Introduction

The properties of nanomaterials can be tailored by passivating or functionalizing their surface with organic or inorganic materials. Encapsulation of the core nanostructures with a shell of desired material leads to a new class of materials, known as core/shell nanostructures, having modified optical, conductive and catalytic properties [1]. Owing to a variety of applications of these core/shell nanocomposities as compared to their individual single-component nanostructures, like in solar photovoltaic devices, chemical/biological sensors, light-emitting diodes, and optical switches [2–7]; it has led to the fabrication and study of the metal and semiconductor-based core/shell nanostructures. Many efforts have been made in the recent years to synthesize and characterize the semiconductor-based core/shell nanostructures, like: CdSe/ZnS, CdSe/CdS, ZnO/ZnS, TiO_2/CdS, CdS/SiO_2, CdS/ZnS, CdS/ZnS/SiO_2, etc. [7–12], but most of them are focused on nanoparticles. However, there are some reports on CdS/ZnS based 1-D nanorods also [1,13]. CdS and ZnS are direct band gap II–VI chalcogenides having the band gap values of respectively, 2.42 and 3.67 eV. We have passivated CdS nanorods with a wider band gap material, ZnS, to increase the luminescence intensity.

In this paper, we demonstrate the successful fabrication of CdS/ZnS nanostructures, using the solvothermal technique in two steps (6 h each), with ethylenediamine (En) as the solvent. The structural and optical properties have been studied to compare the changes in the properties of the core and the core/shell nanostructures. Also, the morphology of the synthesized nanostructures and the FTIR spectra have been studied.

2. Experimental

The synthesis of CdS and CdS/ZnS nanostrustures [1,13] has been carried out in a closed cylindrical teflon-lined stainless steel chamber, using solvothermal technique. The schematic diagram of the chamber has been shown in Fig. 1. All of the chemical reagents used in this experiment were of analytical grade and used without any further purification. Desired molar ratio of cadmium acetate $[Cd(ac)_2 \cdot 2H_2O]$ and thiourea $[CSN_2H_4]$ was taken with 70 mL of ethylenediamine (En), which acted as the solvent, in the teflon chamber (capacity ~100 mL). The solution was stirred, at room temperature, for around 2 min, inside the teflon chamber. The chamber was sealed and placed in a preheated oven, at 160 °C, for 6 h [13], and then it was allowed to cool normally to room temperature. The yellow colored product, so obtained, was precipitated and washed several times, with double distilled water and ethanol. The paste, so obtained, was divided into two parts, out of which, one was dried and considered at the core part, whereas the other part was again added to the teflon chamber along with appropriate concentration of zinc acetate and 70 mL of En. The drying had been carried out in a vacuum oven at 70 °C for 24 h, followed by crushing the dried paste to obtain fine powder using a pestle–mortar. The sealed chamber was then placed in the preheated oven, at 160 °C, for 6 h, and then it was allowed to cool

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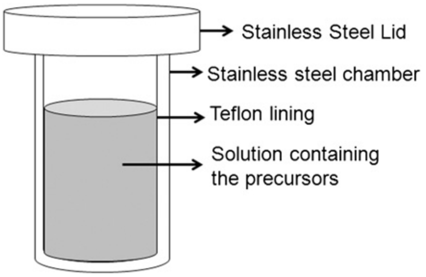

Fig. 1. Schematic diagram of the teflon-lined stainless steel chamber used for the solvothermal synthesis of the nanostructures.

normally to room temperature. The light yellow colored product so obtained was precipitated, washed and dried. The powders obtained in both the steps were used for further characterization.

3. Characterization

To check the crystalline quality of the deposits, the synthesized CdS and CdS/ZnS power was placed on the sample holder, without any further specimen preparation, and X-ray diffraction of the nanostructures has been carried out with the Panalytical's X'Perto Pro X-ray diffraction machine using copper characteristic wavelength, 1.5418 Å. The morphological studies of the nanostructures have been done through scanning electron microscopy (SEM; FEI Nova Nanolab), and transmission electron microscopy (TEM; Technai G220 S-Twin, FEI Netherlands; and Hitachi). The specimen preparation was done by placing the powered sample on the SEM stub and then coating it with a fine layer of gold–palladium alloy with a sputter. However, for TEM, a drop of finely dispersed particles in spectroscopic grade ethanol, was applied to carbon coated copper grid and then dried.

FTIR spectroscopy has been used to investigate the organic chemical components present on the surface of the synthesized samples. Powered samples have been used with FTIR Spectrum BX-II (Perkin Elmer) spectrometer, without any further specimen preparation.

Optical absorption spectra have been recorded with UV–vis absorption spectrophotometer, Specord 205, Analytik Jena, using spectroscopic grade ethanol as the reference media, and the room temperature photoluminescence studies were carried out by Fluorescence spectrophotometer (Carry Varian) employing excitation wavelength of 400 nm. The nanostructures have been dispersed finely in the spectroscopic grade ethanol using an ultrasonicator.

4. Results and discussion

Fig. 2 shows the XRD pattern of CdS and CdS/ZnS nanostructures synthesized using the solvothermal technique, using ethylenediamine (En) as the solvent and the chelating ligand. Fig. 2(a) shows the XRD pattern of the CdS core, synthesized in the first step of the solvothermal process. The diffraction peaks positioned at 2θ values of 25.1°, 26.8°, 28.5°, 36.9°, 44.0°, 48.2° and 52.1° match well with the respective, (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) crystal planes of the hexagonal wurtzite phase of CdS, according to the standard JCPDS data card no. 41-1049. XRD pattern of the CdS/ZnS nanostructures, synthesized in the second step of the solvothermal process, shows the diffraction peaks due to the hexagonal wurtzite crystalline phases of both CdS and ZnS. In case of the CdS/ZnS nanostructures, the diffraction peaks due to the presence of CdS are in coherence with that of the CdS core, as shown in Fig. 2(a) and (b). Whereas, the peaks positioned at 2θ values of 27.8°, 29.3°, 31.5°, 41.7°, 47.6° and 49.0°, match well with the respective, (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) crystal planes of hexagonal wurtzite-2H phase of ZnS, according to the JCPDS data card no. 36-1450. On comparing the CdS diffraction peaks in Fig. 2(a) and (b), it is found that the preferential orientation of the CdS nanorods is along the (0 0 2) plane, as its intensity is highest, however, in the case of CdS/ZnS nanostructures, the intensity of the peak corresponding to (1 0 0) has become comparable to that of (0 0 2), showing the change in the preferred crystallographic orientation. Apart from this, there are some diffraction peaks at 2θ values of 10.2°, 17.2°, 20.6°, 22.4°, 33.1°, 34.2°, 53.1° and 53.5°, which are due to the presence of CdS/ZnS–En complexes [14,15]. In the reaction mechanism, En ($H_2NCH{=}CHNH_2$) has two NH_2 groups to chelate, with the Cd^{2+} and Zn^{2+} ions. Moreover, En is known to have a relatively weak intermolecular coordination interaction, which allows it to act as a molecular template for the growth of the CdS, ZnS and CdS/ZnS nanostructures, offering a less rigid confinement for the crystal growth [16]. Therefore, the preferred growth direction of the crystal can change easily.

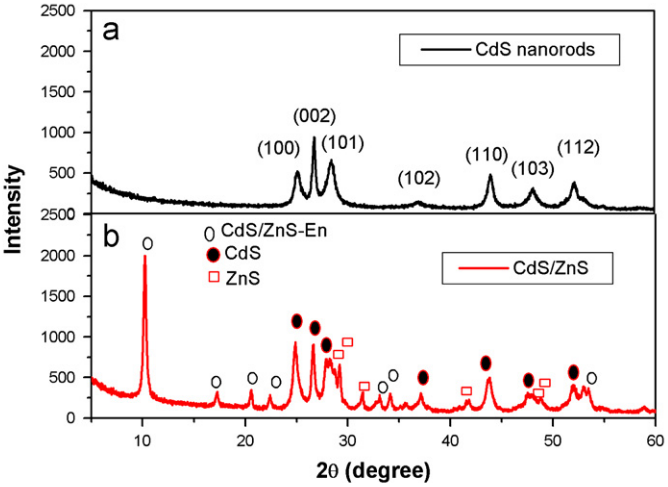

Fig. 2. XRD pattern of (a) CdS nanorods and (b) CdS/ZnS core/shell nanostructures.

The reactions following the CdS and CdS/ZnS nanostructures using the solvothermal technique in two steps, with En as the solvent can be formulated as follows:

Step I

$$Cd^{2+}+2(En)\rightarrow[Cd(En)_2]^{2+} \quad (1)$$

$$[Cd(En)_2]^{2+}+S^{2-}\rightarrow CdS\cdot 0.5\,(En)\rightarrow CdS+En \quad (2)$$

These reactions have been supported by many researchers of Refs. [14,17]. However, as seen from the FTIR spectra, Fig. 6 (discussed ahead), there is a presence of En in the product, showing incomplete transfer of $CdS\cdot 0.5\,(En)$ molecules to CdS and En.

Step II

$$Zn^{2+}+2(En)\rightarrow[Zn(En)_2]^{2+} \quad (3)$$

$$[Zn(En)_2]^{2+}+S^{2-}\rightarrow ZnS\cdot 0.5\,(En)\rightarrow ZnS+En \quad (4)$$

$$CdS+En+ZnS\rightarrow[CdS\text{–}En\text{–}ZnS] \quad (5)$$

En molecules interact with Cd and Zn ions to form Cd–En and Zn–En complexes, which react with S ions to give CdS–En and ZnS–En complexes. Due to high temperature and pressure, these complexes break up into the CdS or ZnS crystal structures along with En molecules, according to Eqs. (2) and (4). However, there is a possibility of the formation of CdS–En–ZnS complexes, in the second step of the solvothermal technique, used to synthesize CdS/ZnS nanostructures. This can be justified from the XRD pattern as shown in Fig. 2(b), as there are CdS/ZnS–En related diffraction