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Synthesis and study of optical and thermal properties of Mn doped CdS nanoparticles using polyvinylpyrrolidone

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ABSTRACT

High quality and monodispersed CdS:Mn (1–5%) nanoparticles were synthesized by chemical precipitation method using PVP as surfactant. The structure and morphology of the CdS:Mn were investigated by means of XRD, FT-IR, TEM, UV–visible, PL, EPR and TG-DTA. XRD study was confirmed the formation cubic structured CdS:Mn nanoparticles. The optical absorption of Mn doped CdS nanoparticles was found to be 420–432 nm, which is significantly decreased from the bulk CdS material. Photoluminescence spectroscopy of the CdS:Mn nanocrystals showed a strong emission peak at 535 nm near the band edge along with a week green emission around 575 nm. The PL property of annealed (255 °C–850 °C) samples was also investigated under different excitations. The presence of PVP on the CdS:Mn surface and incorporated the Mn ion into CdS lattice were identified by FT-IR and EPR spectroscopy, respectively. TEM result showed spherical with monodispersed particles with typical size of 3.8–4.3 nm, which is a favorable characteristic for many applications. The major weight loss and gain were found in the thermogravimetric analysis (TGA) which corresponds to the decomposition and oxidation of the samples.

1. Introduction

Semiconductor nanoparticles have unique chemical and physical properties, which are different from bulk materials [1]. Their high specific surface area results in high chemical reactivity. The decrease of their size also leads to an increase in the band-gap energy which is known as a quantum size effect [2]. This effect can be simply observed by a blue-shift of the luminescent [3] and absorption [4–6] spectra of nano-sized semiconductors. Cadmium Sulfide (CdS) is an important II–VI group semiconductor material that has attracted much interest owing to its unique electronic and optical properties and their potential applications in solar energy conversion, photoconducting cells, non-linear optics, heterogeneous photocatalysis and electroluminescence devices [7–9]. Freshly prepared nanoparticles tend to agglomerate; therefore, the particles were stabilized using various polymers and surfactants or inorganic layer. The surface passivation is provided through saturation of the dangling bonds on the nanoparticles surface.

We have prepared undoped, Mn doped CdS nanoparticles in the solution at room temperature controlling the size of the aggregates through the use of a surface-capping agent, polyvinylpyrrolidone (PVP) which at the same time provides surface functionality. The influence of surface passivation on particles size control has been investigated by many researchers using PVP [10–12]. PVP, a water-soluble polymer, was used as capping polymer molecules to stabilize the nanoparticles. It was found that PVP adsorbed on the surface of the nanoparticles by interaction of the C–N and C=O with the nanoparticle's surface, thereby affording protection from agglomeration by steric hindrance [10]. Through the surface passivation by PVP, monodisperse CdS:Mn nanoparticles were prepared, which exhibited enhanced luminescence and chemical stability, as the introduction of PVP can greatly improve the efficiency and reproducibility of the composite nanoparticles.

2. Experimental methods

2.1. Materials

To synthesize undoped CdS and CdS:Mn^{2+}, the following materials were used. The chemical reagents used were analytical reagent grade without further purification. Cadmium Acetate ($Cd(CH_3COO)_2 \cdot 2H_2O$), Manganese Chloride ($MnCl_2 \cdot 4H_2O$), Sodium Sulfide ($Na_2S \cdot xH_2O$) obtained from Nice Chemical company, Kochi, India were used as precursors. Polyvinylpyrrolidone (PVP-40,000) was obtained from Aldrich. All the glasswares used in this experimental work were acid washed. Ultrapure water was used for dilution and sample preparation.

2.2. Synthesis of undoped and Mn^{2+} doped CdS nanoparticles

The CdS nanoparticles and doped with Mn^{2+} (1–5%) were synthesized in deionized water in air atmosphere. In a typical experiment, 2.66 g (0.1 M) of $Cd(CH_3COO)_2 \cdot 2H_2O$ in 100 ml aqueous

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and different concentrations (1–5%) of $MnCl_2 \cdot 4H_2O$ in 25 ml aqueous were mixed. The mixture was stirred magnetically at 80 °C until a homogeneous solution was obtained. Then, 1.1 g (0.1 M) of 100 ml Na_2S was added drop by drop to the above mixture. After the Na_2S injection, a yellow voluminous precipitate appeared. It slowly dissolved under formation of CdS:Mn^{2+} nanoparticles with stirring for 30 min at 120 °C. The yellow color colloidal solution was purified by dialysis against de-ionized water acetone and ethanol, several times to remove impurities. The products were dried in hot air oven at 80 °C for 2 h. In addition, for synthesis of surfactant (PVP) capped particles different amounts (0.5–2.5 g) of PVP were added in Cadmium acetate solution before the addition of Manganese chloride. The undoped CdS nanoparticles were also synthesized following the same procedure without Manganese chloride solution.

2.3. Characterization

Crystal structure and size of the products were determined by X-ray diffraction (XRD) pattern using an X'pert PRO diffractometer with Cu K_α radiation ($\lambda = 1.54060$ Å) at room temperature. The optical transmission/absorption spectra of the particles in de-ionized water were recorded using a UV-1650PC SHIMADZU Spectrophotometer. The size and morphology of the nanoparticles were obtained using TEM (Technai 20G2, FEI). Particle size was measured using a Nanotrac (FLEX 10.5.2) particle size analyzer. Fluorescence measurements were performed on a RF-5301PC Spectrophotometer. Electron Spin Resonance (EPR) spectra of the CdS:Mn^{2+} powders were measured on an EPR spectrometer (Bruker EMX Plus) at room temperature. The thermal analysis of the CdS:Mn was carried out using a SDT Q600 20 thermometer.

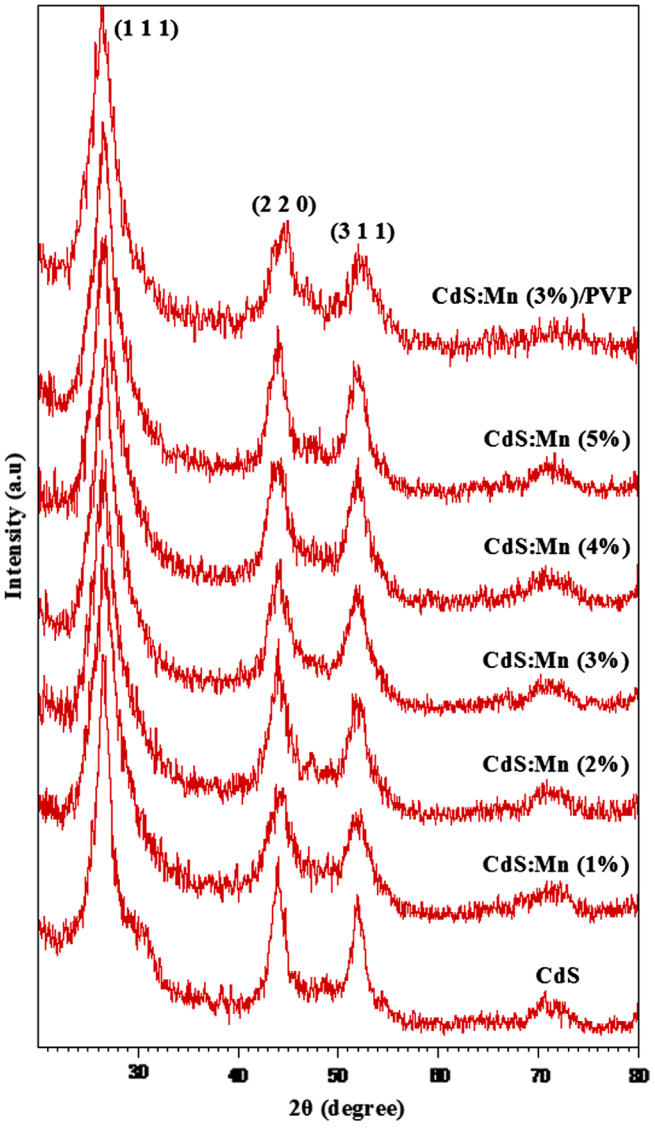

Fig. 1. X-ray diffraction patterns of CdS, CdS:Mn (1–5%) and CdS:Mn/PVP nanoparticles.

3. Results and discussion

3.1. Structure and morphology

Typical X-ray diffraction (XRD) patterns for the undoped CdS and doped CdS:Mn (1–5%) nanoparticles shown in Fig. 1. All the

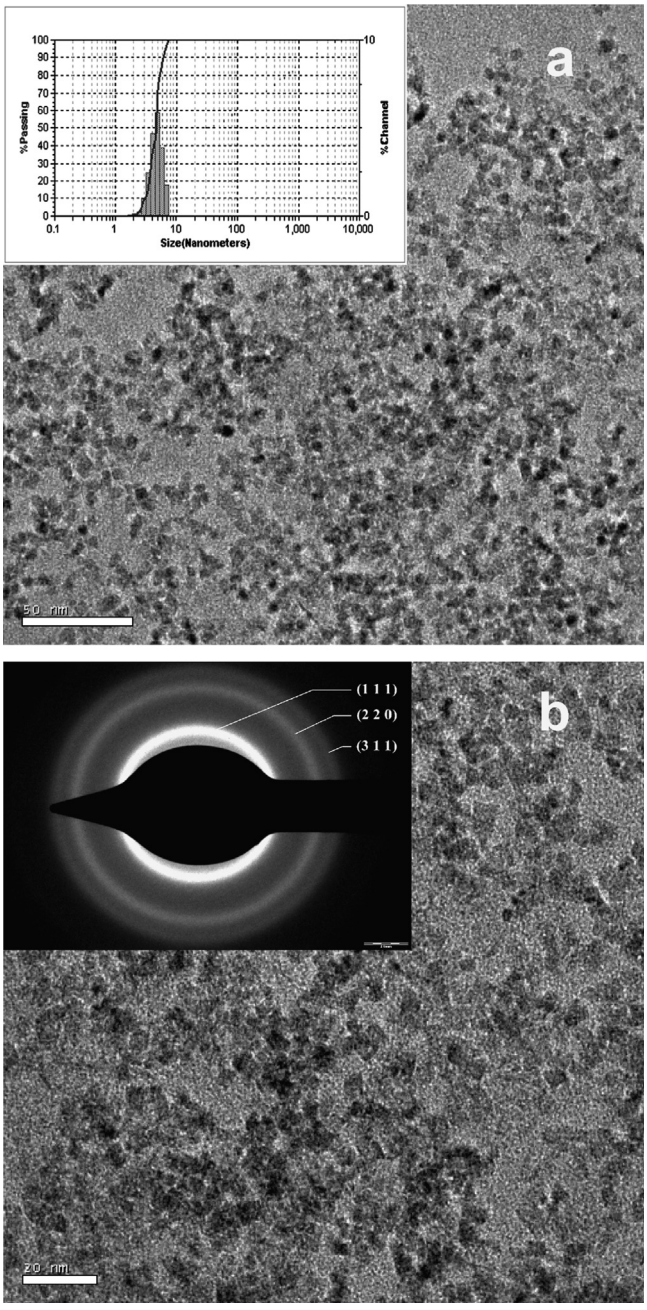

Fig. 2. TEM micrographs of CdS:Mn/PVP nanoparticles and corresponding particle size analyzer curve (inset) and SAED pattern (inset).