

Optical characterization of Fe³⁺ doped CdS nanoparticles synthesized by wet-chemical route

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Abstract

Fe³⁺ doped CdS nanoparticles using Mercaptoethanol as a capping agent were prepared by colloidal wet-chemical method. UV-VIS spectra show that Fe-doping can effectively tune energy band structure, i.e. a large blue shift (~ 30 nm) with increasing Fe concentration. PL measurement of doped CdS nanoparticles shows an additional emission band at ~ 532 nm, which can be due to radiative transition of dopant level to ground state. X-ray diffraction patterns studies revealed cubic crystal phase. TEM micrographs show a spherical shape and nearly well distribution with an average particle size of ~ 4 nm.

Key Words: Nanoparticles, Photoluminescence, II-VI semiconductor

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1. Introduction

In recent years, semiconductor nanoparticles have drawn much research attention due to their unique optical properties originating from size quantization effect [1]. Cadmium sulphide (CdS), a compound of direct band gap (~ 2.4 eV) semiconductor, is a suitable material for optoelectronic applications [2, 3] and biological labels [4, 5]. Currently, modification of CdS properties by impurity/dopant incorporation has become a hot topic. Doping with proper metal elements via introducing acceptor or donor level in host nanocrystals is an effective approach to tune materials properties [6]. Up to now, various capping agents such as polyethylene glycol (PEG), thioglycerol (TG), etc., have been used to synthesize nanomaterials. In this study Fe doped CdS nanoparticles using Mercaptoethanol as a capping agent were prepared by colloidal wet-chemical method, and characterized by XRD, TEM, UV-VIS and PL spectroscopy. The effect of dopant content on the optical and structural properties is discussed.

2. Experimental

2.1. Synthesis

All the chemicals were purchased from commercial sources (analytical grade) and used without further purification. De-ionized water was used as a solvent in all the experiments. Typical ME-capped CdS nanoparticles were synthesized by the procedure reported in our previous work [7–9] as follows: 0.148 g of CdCl₂ and 0.008 g FeCl₃ were dissolved in 50 ml of de-ionized water under stirring in a three-necked round bottom flask. To prevent of particle agglomeration, ME aqueous solution (0.01 M) was slowly added into above suspension. Finally, aqueous solution of Na₂S (0.01 M) was dissolved in 50 ml of DDW, and then added dropwise (12 drop/min) to the former solution. Under an Argon flow, the resulting solution was stirred for 30 min. At the end of reaction, the precipitate was centrifuged (3000 rpm), washed several times with de-ionized water, and then dried in a laboratory oven at 20 °C.

2.2. Characterization

X-ray patterns of the powders were recorded using a Bruker D8-ADVANCE diffractometer (Cu K_α radiation: $\lambda = 1.5418 \text{ \AA}$). Particle size, shape and distribution of doped NPs were characterized using a transmission electron microscope (Jeol 1200 EX II, operating TEM). Samples for TEM were prepared by dropping diluted colloids on carbon coated TEM grids followed by controlled drying. UV-VIS absorption spectra were taken on a Perkin-Elmer Lambda 2 spectro-meter. To record the optical absorption spectra, 1mg of prepared samples were dispersed in 10 ml of de-ionized water and sonicated for 25 min. Then the diluted colloidal solution of nanoparticles was placed in quartz cells (1 cm path length). PL measurements were recorded using Perkin-Elmer LS-55 spectrophotometer with Xe lamp as excitation source at room temperature ($\sim 25 \text{ }^\circ\text{C}$).

3. Result and discussion

3.1. Optical study

UV-VIS absorption spectra of doped samples, along with the undoped sample, are shown in Figure 1. Broad and less symmetric absorption peak of undoped is observed at about 449 nm, that is effectively blue shifted compared to the bulk band gap wavelength at 515 nm. Blue shifting absorption peak is attributed to the quantum size effect [11], whereas the broadening and asymmetry are due to the wide size distribution of synthesized particles. Different size of particles give number of excitonic peaks that appear at different energies and overlapping of these peaks produces a broadening in absorption spectra [12]. It is clearly shown in Figure 1, the absorption edges reveals a large shifting with Fe-doping ($\sim 30 \text{ nm}$), which the possible reason for this result may be come due to ionic radii (R_i) of cadmium and dopant. Using the well-known Brus equation [13] the particles size was estimated to be around $2 \pm 0.5 \text{ nm}$. Figure 2 shows the variation of band gap energy and particles size versus Fe concentration.

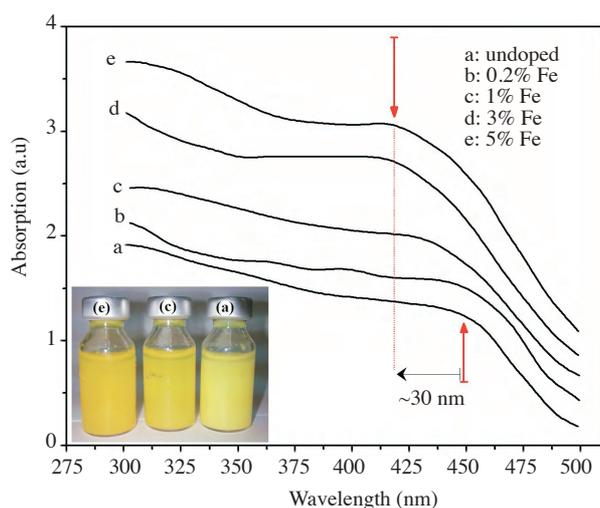


Figure 1. UV-VIS spectra of undoped and doped CdS nanoparticles. Inset shows the visual observation of as-prepared nanoparticles.

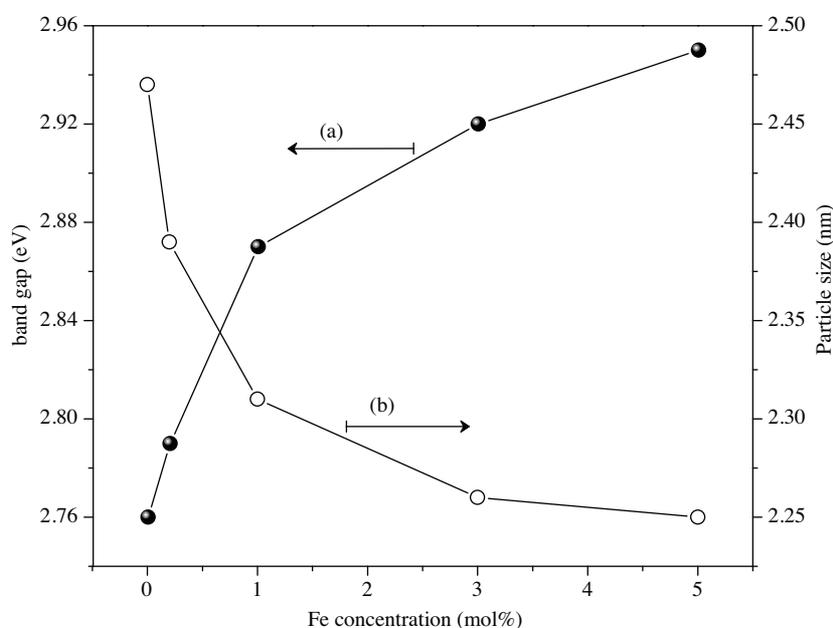


Figure 2. Plot of band gap and particles size of CdS nanoparticles as a function of dopant concentration, evaluated from UV-VIS spectra.

Figure 3 shows the room temperature PL spectra of Fe-doped CdS nanoparticles via different dopant content. A strong blue emission band located at ~ 492 nm and weaker green emission band at ~ 532 nm were observed. The blue emission band is attributed to radiative transition of defect states such as sulfur vacancies (i.e. V_s to Ground state). Moreover, green emission band can be related to impurity ions (i.e. Fe-dopant). Fe dopant occupies the Cd lattice site and behaves as a trap site for charge carriers.

Of Fe ions, previous works show that inclusion of Fe ions in a typical II-VI semiconductor such as ZnS, ZnSe, CdTe and CdS, due to crystal field effect leads to new energy states (i.e. 3T_1 , 5T_2 and 5E states) in

the band gap of these materials [14, 15]. Therefore, we interpret the emission band observed at ~ 532 nm may be attributed to the 3T_1 to Ground state radiative transition of Fe^{3+} dopant. Schematic diagram present in inset Figure 3 indicates the different transitions which are responsible for above mentioned emissions peaks.

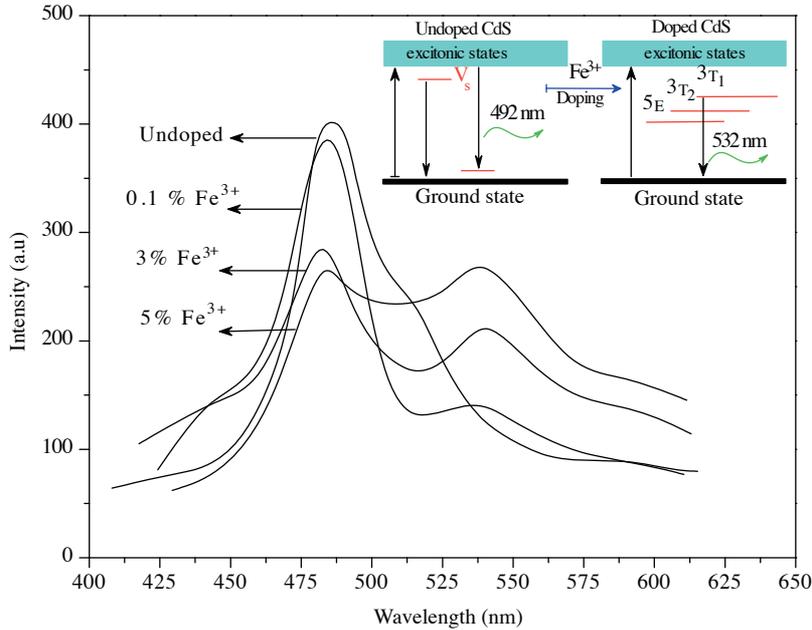


Figure 3. PL spectra of undoped and Fe-doped CdS nanoparticles. Schematic diagram of energy levels shows probable electronic transitions of doped CdS nanoparticles.

On the other hand, the first peak descends by increasing dopant content (i.e. Fe concentration), which may be due to increasing of transition probability from impurity level to ground state (i.e. more and more electron-holes due to effect of the luminescent centers are excited and radiative recombination). This leads to radiative recombination enhancement in 532 nm wavelength. Therefore fluorescence efficiency of the second peak increases. Therefore, Figure 4 (a) shows the value of I_{fp}/I_{sp} (intensity of first peak/ intensity of second peak) versus dopant content.

3.2. Structural study

The X-ray diffraction patterns of undoped and Fe-doped CdS nanoparticles are shown in Figure 5. The diffraction peaks are significantly broadened due to very small size of the nanoparticles. Figure 5 indicates three diffraction peaks at 2θ values; 26.54° , 42.95° and 50.6° corresponding to reflections from (111), (220) and (311) crystal planes of the cubic zinc blend phase and are well matched with the standard cubic CdS (JCPDS card No. 10-454). No characteristics peaks corresponding to impurity phases were detected. Using the Debye-Scherrer formula [16], average particle size of nanoparticles was calculated to be about 3 ± 0.5 nm. The substitution of the Fe ions ($r_{Fe^{3+}} = 0.72 \text{ \AA}$) with the different radius Cd ions ($r_{Cd^{2+}} = 0.97 \text{ \AA}$) results a small change in full width at half maximum (FWHM) of XRD, as shown in Figure 4(b). By increasing of Fe content in crystal structure, FWHM of patterns increases. This change FWHM gives the strong evidence for the incorporation of dopant ions into the host lattice which is also confirm by PL spectra.

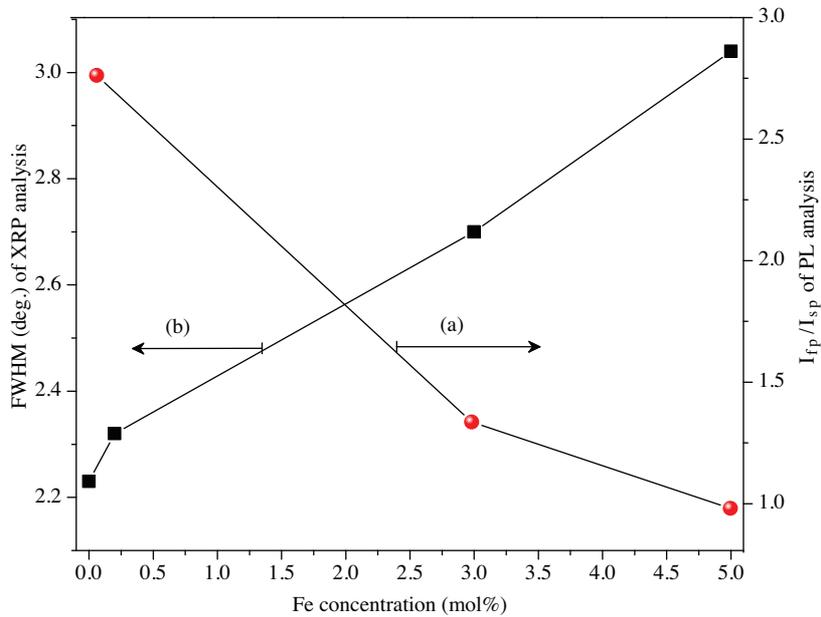


Figure 4. Plot of (a) I_{fp}/I_{sp} of PL and (b) FWHM of XRD versus dopant content.

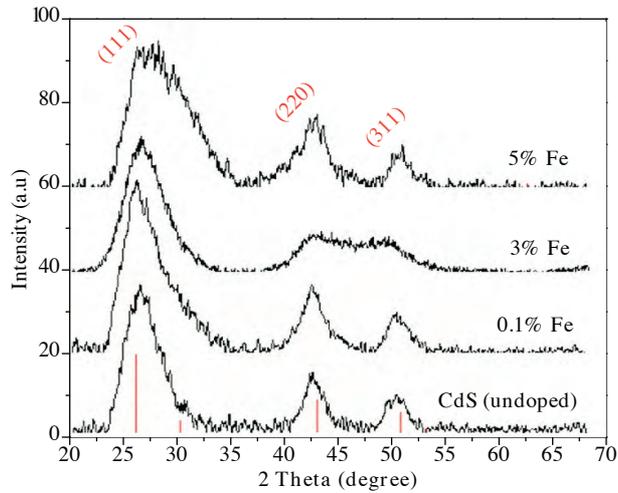


Figure 5. X-ray diffraction patterns of Fe-doped CdS nanoparticles.

It is necessary to obtain the particle size by direct measurement, which can reveal the size and morphology of the particles. Figure 6 shows a typical TEM micrograph of the Fe-doped CdS nanoparticle. Initially the particles shape is look like a spherical shape and an approximately well distribution with the average diameter of about 4 nm.

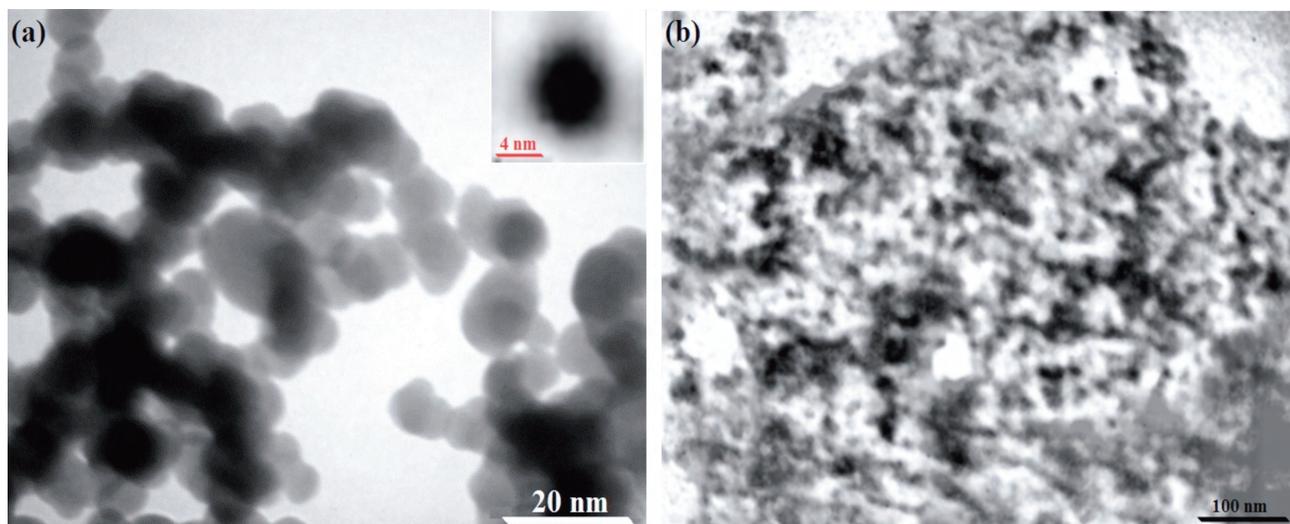


Figure 6. TEM micrograph of Fe-doped CdS nanoparticles.

4. Conclusion

In brief, Fe³⁺ doped CdS nanoparticles were synthesized through colloidal wet-chemical route. The UV-VIS spectra show a large blue shift (~ 30 nm) of the absorption band edge with increasing Fe doping. PL spectra show a strong blue emission band at ~ 492 nm, while Fe-doped CdS nanoparticles revealed an additional emission peak at ~ 532 nm, which may be due to radiative transition of dopant level to ground state. Moreover, by increase Fe content, fluorescence efficiency at second peak increased due to transitions enhancement from impurity levels to the ground state. Structural results demonstrate cubic phase, spherical shape and nearly well distribution with size of about ~ 4 nm.

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