Effect of pH on the Optical Properties of Doped CdS (Cu, Fe) Nanoparticles Incorporated in TG as the Capping Agent

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Cu and Fe doped cadmium sulfide nanoparticles with controllable and relatively narrow size distribution were prepared using a facile and efficient wet chemical route by mixing the reactants in water solvent. It was found that the mixture pH plays an active role in the growth procedure of nanoparticles. Diverse physical properties of the prepared nanoparticles were investigated using UV-vis absorption, photoluminescence spectroscopy, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy. The average particle size of samples was estimated to be about 5 nm by using transmission electron microscopy measurement. The pH optimization study implies that pH $\approx$ 7 would yield an enhancement in photoluminescence intensity. There are two bands in photoluminescence spectra which related to deep and shallow traps.

1. Introduction

Nanoscale materials have stimulated great interest owing to their importance in basic scientific researches and potential technological applications [1]. During the past decade, the preparation and characterization of chemically deposited CdS thin films have been widely studied due to their potential applications [2] but there are limited investigations of physical properties. The study of CdS nanostructures has attracted many research groups because of their excellent optical and electronic properties. Due to the unique size-dependence of the optical, magnetic, electronic and electrochemical properties [4–6], these materials have a wide range of applications such as efficient phosphors, superior biological labels [7], solar cells, laser sources [8], UV-NIR sensors and tunnel diodes [9].

Semiconductor nanophosphors, especially sulfides, doped with transition metal ions and rare earth ions, have been studied extensively because of their excellent luminescence properties [10]. Recently, the researchers are highly interested in investigating of the properties doped CdS nanoparticles [11–15].

Pure and doped CdS nanocrystals and thin layers are often used as photoconducting, photovoltaic or optoelectronic materials. CdS powder is used in the production of light sources emitting in the green region, solar cells and photocells [16]. Different synthesis methods have been reported for CdS nanoparticles, but chemical methods are probably the most extensively explored approach for the synthesis of doped CdS nanoparticles. Doping with transition metal ions such as Mn, Cu, Co etc. opens up

possibilities of forming a new class of materials and new properties of the materials are expected.

In the case of chemical synthesis, there are many factors (concentration solvent, temperature, reaction rate, solution pH, etc.); those can affect physical and optical properties (energy gap, crystal structure, luminescence, etc.) of nanoparticles. In our previous work, we investigated the effect of Cu doping [17] and also capping agent [18] on the optical and structural properties of CdS nanocrystals.

This paper reports some interesting results obtained by presenting an efficient and facile method for preparation of Cu and Fe doped CdS nanoparticles with a controllable and narrow size distribution, which involves the use of thioglycerol (TG) as the stabilizer. Gao et al. [19] observed that reactions in presence of thiols (mercaptans), which contain SH group attached to carbon atom, leads to surface modification of the nanoparticles and reduction of the nonradiative local surface traps which, in turn, gives rise an enhancement of the quantum yield of the excitonic transitions. Thioglycerol is one of such thiols and has been found to act as capping agent [20]. We also investigated the effect of pH on the luminescence features of CdS:Cu and CdS:Fe nanoparticles.

2. Experimental details

2.1. Materials

Cadmium chloride (anhydrous, Merck), copper (ferrous) chloride dihydrate, sodium sulfide×H_2O and mercaptopropionic (MPA, Merck), thioglycerol (TG, Fluka) were used as the feedstock to prepare CdS (Cu, Fe) nanopowders.

2.2. Procedure method

Cu and Fe doped cadmium sulfide nanoparticles in different Cu/Cd and Fe/Cd molar ratios were prepared as follows: in a dry nitrogen ambient, 50 ml of $CuCl_2$

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($FeCl_2$) (5×10^{-4} M) was added to 50 ml of aqueous $CdCl_2$ (5×10^{-2} M) solution under stirring. Afterward, 50 ml of TG (9×10^{-2} M) was poured dropwise into the mixture. Subsequently, 50 ml of Na_2S solution (5×10^{-2} M) was injected dropwise into the above solution under stirring. Eventually, the final mixture was stirred for 1 h at room temperature. The doped CdS nanoparticles were then separated by centrifugation (3500 rpm for 10 min) and washed with acetone to get rid of unreacted solvent and other impurities perfectly. For drying, the particles were kept in a Petri dish for about 12 h. To adjust the pH, NaOH/acetic acid was added before injecting $CuCl_2$/$FeCl_2$. To ensure the reproducibility of the procedure presented in this paper, it was repeated and it was observed that the results are reproducible.

2.3. Characterization

UV-vis absorption spectra were measured using a Scan Cary 100 UV/Vis spectrometer. The photoluminescence (PL) measurements were carried out at room temperature using a Shimadzu RF-5000 spectrometer. Transmission electron microscopy (TEM) images were taken using a Philips CM10 system. Scanning electron microscopy (SEM) image was obtained using a S360 Cambridge SEM. Quantitative analyses were obtained by an energy dispersive X-ray analysis (LEO, 1430VP) with accelerating voltage 17 kV.

3. Results and discussion

In Fig. 1, the absorption spectra of CdS:Cu (1%) nanoparticles with different pH are shown. (1%) indicates the molar ratio of Cu to Cd. The pH is determined using Microbench TI 2100. No precipitate was observed in pH = 9.65 while the low amount of precipitate was obtained in pH = 8.45 that caused the emergence of $Cd(OH)_2$ and $Cu(OH)_2$ instead of CdS which decreased the precipitate rate. In the meantime, for pH less than 7.5 high precipitate occurred. As shown in Fig. 1, a more monodispersed particle size distribution was obtained with pH varying in the range 4.54 to 7.45. The sample of pH = 4.54 shows the best narrowing size distribution.
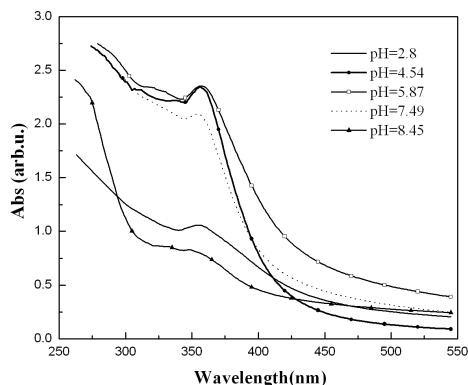

Fig. 1. Absorption spectra of CdS:Cu(1%) prepared at different pH values (2.8–8.45).
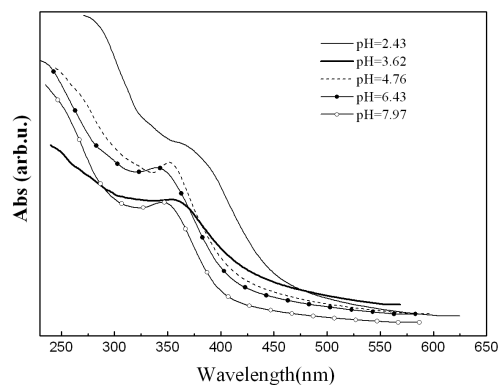

Fig. 2. Absorption spectra of CdS:Fe(1%) prepared at different pH values (2.43–7.97).

Also Fig. 2 shows the absorption spectra of CdS:Fe(1%) at various pH values (2.43–7.97). As shown in Fig. 2, a striking and sharp excitonic peak is obtained at pH = 4.76. Figures 1 and 2 indicate clearly that at the pH value between 4 and 5, there are monodispersed and narrowing size distributions.

Using the above mentioned absorption data the band gap energy E_g can be estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ according to the well-known Tauc formula. Besides, applying Brus equation for quantum confinement effect within nanoparticles would give the particle size [17]. The variation of band gap value and size of Cu and Fe doped CDs nanoparticles versus pH values is shown in Fig. 3. As shown, in acidic media the particle size increases when the pH value decreases. This may be due to increasing concentration of H^+ with the decrease of pH. That is why; H^+ ions can reduce the effect of capping agent and therefore increase the particle size. On the other hand, in an alkaline medium, the particle size increases as the pH value increases. As mentioned before, there is a high possibility to produce a $Cd(OH)_2$ and $Cu(OH)_2$ (or $Fe(OH)_2$) in the alkaline medium. This makes the system more complicated so that doped CdS and those hydroxides coexist and the different growth probabilities broaden the size distribution and eventually would increase the particle size.

Figure 4 shows SEM images of the CdS:Cu(1%) (pH = 4.54) and CdS:Fe(1%) (pH = 4.76) samples. From the SEM images, the shape of the nanoparticles is quasi-spherical but the actual size of the nanoparticles cannot be distinguished from the SEM image merely, because SEM shows the topographical image. The inset of Fig. 4a illustrates the energy dispersive X-ray spectroscopy (EDX) of CdS:Cu sample that shows copper to be in a stoichiometric atomic ratio. Also, the inset of Fig. 4b depicts the EDX spectrum of CdS:Fe. As it can be seen from the spectra, the peaks correspond to Cd, S and Cu/Fe are strikingly obvious in the figure as it was expected.

To get straight information about the particles size and the pertinent distribution, it seems necessary to validate them by a direct measurement, such as TEM, which can
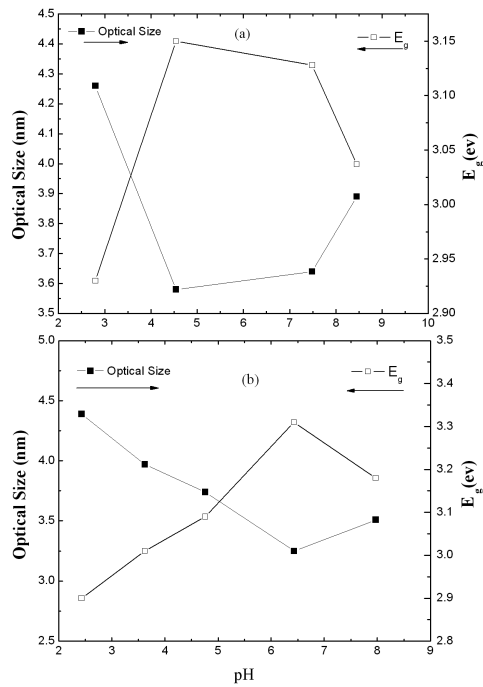
Fig. 3. Variation of band gap and optical size versus pH values for (a) CdS:Cu(1%) and (b) CdS:Fe(1%) nanoparticles.
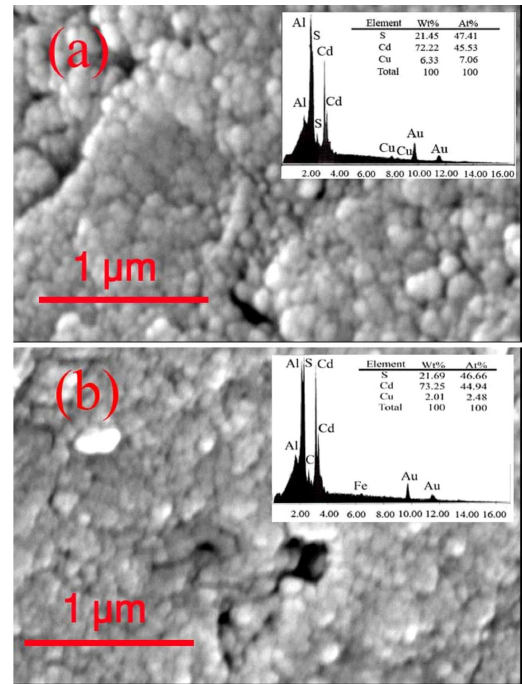

Fig. 4. Scanning electron micrograph images of (a) CdS:Cu (pH = 4.54) and (b) CdS:Fe (pH = 4.76) samples. Insets show the corresponding EDX spectrum.
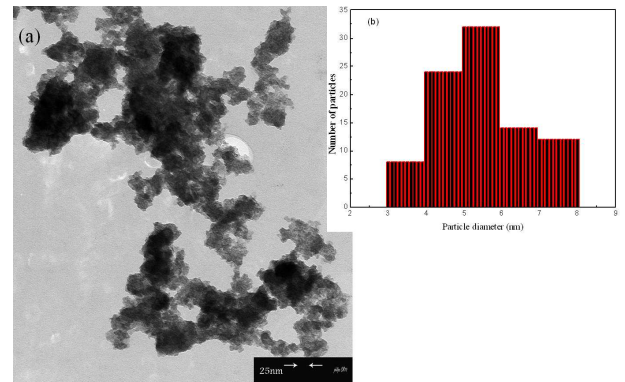

Fig. 5. (a) TEM image and (b) the particle size distribution of CdS:Fe(1%) nanoparticles.

reveal the size and morphology of particles. Figure 5a shows the TEM image of CdS:Fe(1%) nanoparticles that a nearly quasi-spherical particles aggregation can be seen. The particle size distribution histogram is demonstrated in Fig. 5b. 100 numbers of particles have been taken for calculating the particle size distribution. As can be seen, the diameter of the major number of particles lies in region of 5–6 nm and the average size of the particles is about 5.6 nm as obtained from the log-normal fitting of the particle size distribution.

In Fig. 6, the dependence of the emission spectrum on the pH is shown for CdS:Cu(1%) and CdS:Fe(1%) nanoparticles. The excitation energy is 3.45 eV and the measurement was carried out at room temperature. As shown, the highest intensity is related to pH = 7.49 for CdS:Cu and pH = 6.43 for CdS:Fe. Lower PL intensities were observed for other pH values. It seems that at about pH $\approx$ 7 yields an enhancement in PL intensity for both samples. The reduction of the PL intensity of samples under acidic condition may be attributed to increase in surface defect and trap states because of presence of H^+ which decreases the effect of capping agent. In Fig. 6b, the PL intensity decreases at pH = 7.97 that may be linked to the pH dependence of Na^+ incorporated in the CdS matrix that can help to induce the required density of impurity states in the energy gap of CdS [21]. In both figures, two bands (A and B) are clearly observed in the range of 2.2–2.5 eV. These bands are related to deep and shallow traps, respectively [17].

XRD pattern of pure and doped CdS nanoparticles is shown in Fig. 7. As shown, the peaks are appearing due to reflections from (101) and (103) planes of the hexagonal phase of CdS. It indicates the phase purity and absence of impurity phases. Broadening of the XRD peaks indicates formation of curds nanocrystals. Lattice parameters a and c were calculated by the relations [22]:

$$d_{hkl} = \frac{2\pi}{|\boldsymbol{G}_{hkl}|}, \tag{1}$$

$$\boldsymbol{G}_{hkl} = h\boldsymbol{A} + l\boldsymbol{B} + k\boldsymbol{C}. \tag{2}$$

Here, $\boldsymbol{G}$ is reciprocal lattice vector. The value of a and c were obtained 2.073 and 3.871 Å, respectively, which yields $c/a = 1.867$ near to $c/a = 1.633$ reported for hexagonal structure.
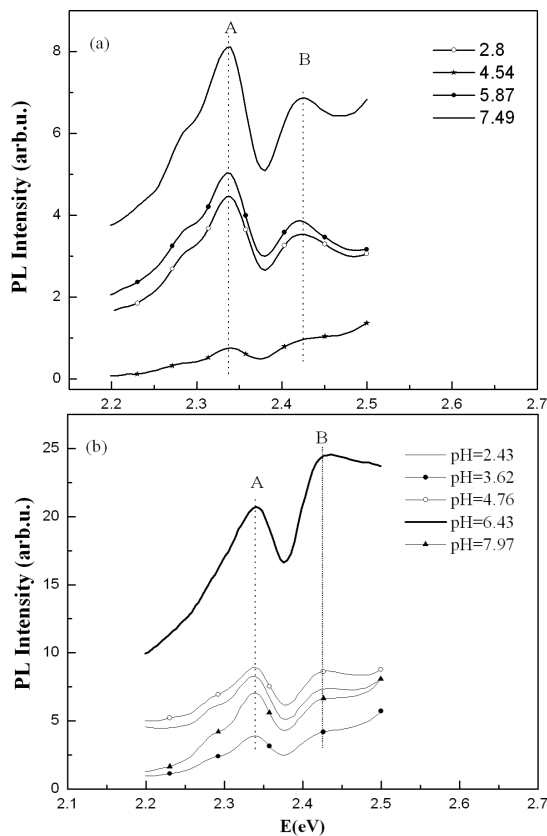
Fig. 6. Emission spectra for (a) CdS:Cu, (b) CdS:Fe prepared at different pH values. The excitation energy is 3.45 eV.
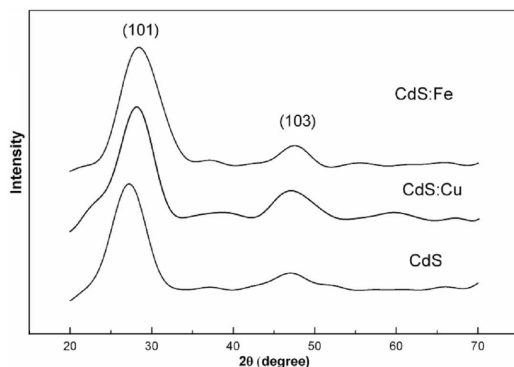

Fig. 7. X-ray diffraction patterns of the CdS, CdS:Cu (1%) (pH = 4.64) and CdS:Fe (1%) (pH = 4.76) nanocrystals. The samples have hexagonal crystal structure.

4. Conclusion

Well dispersed Cu and Fe doped CdS nanoparticles were prepared using a wet chemical technique in doubled distilled water solution and using TG as the capping agent. We investigated the effect of pH on the optical properties of doped CdS nanoparticles. Totally, the optical band gap increased with pH value while the determined optical size from the quantum confinement measurement decreased. To study the morphology and

having a direct measure on the particle size the TEM analysis was done and discussed in detail. The PL spectra show that the highest intensity is related to pH ≈ 7. Two bands related to deep and shallow traps are clearly observed in PL spectra. TEM image shows most of the particles are round in shape and the average size of the particles is 5.6 nm. The formations of the nanoparticles were confirmed by the broadening of XRD peaks and result shows that the samples have hexagonal phase.

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