

Luminescence of doped CdS nanocrystals: effect of doping and capping agent

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Cu and Fe doped cadmium sulfide nanoparticles were prepared with a wet chemical synthesis by mixing the reactants in double distilled water solvent. Thioglycerol (TG) was employed as the capping agent and also the reaction catalyst. The estimated particle size of prepared samples was found in the range 3–4 nm. Properties of particles were investigated using photoluminescence spectroscopy (PL) and X-ray diffraction analysis (XRD). XRD pattern of samples reveals a hexagonal crystal structure at room temperature. We have studied effect of doping and TG concentration on the luminescence of doped CdS nanocrystals. There is a noticeable increase of the PL intensity when TG concentration increased. The PL spectra include two bands, due to emission of traps and surface state.

Keywords: nanoparticles, doping, luminescence, crystal structure, capping agent.

1. Introduction

CdS, an II–VI semiconductor with a direct band gap of 2.42 eV at room temperature, is a very good luminescence material and an attractive material for a green light emitting diode [1] used as photoconducting, photovoltaic or optoelectronic materials. CdS powder is used in the production of light sources emitting in the green region, in the technology of solar cells and photocells [2]. Also it is used in devices such as laser screen materials, projection color TVs, nuclear radiation detectors [3–5]. Due to the quantum confinement effect, the band gap of nanomaterials can be tuned by changing the particle size that leads to tunable band edge light emission and hence exhibits novel optical properties [6–8]. Much research has been done on doped nanocrystals such as ZnS:Mn and CdS:Mn to improve emission activity [9–13]. PL emission covering the whole visible region from Mn²⁺ doped CdS nanoparticles was reported previously [14–21]. Keeping in mind the above discussion, an effort has

been made to study the optical response of doped CdS nanoparticles. The doping of Fe impurity in semiconductor nanocrystals is intense activity at this time due to their electrical and magneto-optical effects. The synthesis of doped CdS remains a topic of interest for researchers, from physical and technological points of view.

In this research, we reported an efficient method for preparation of Cu and Fe doped CdS nanoparticles with controllable and narrow size distribution, which involves the use of TG as stabilizer. Also, we investigated crystal structure and the influence of copper and iron doping concentration and the effect of capping agent concentration on the luminescence behaviors of samples.

2. Experiment

2.1. Chemicals

All the chemicals used in synthesis were of analytical grade and used without further purification. Cadmium chloride (Anhydrous, Merck), copper chloride – $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and sodium sulfide – $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ (Merck), thioglycerol (Fluka).

2.2. Synthesis

Experiments were carried out in a dry nitrogen atmosphere, 50 ml of CuCl_2 was added into 50 ml of aqueous solution of CdCl_2 , under stirring. Thioglycerol (TG) was added dropwise into the mixture and aqueous solution as a surfactant in order to prevent agglomeration of nanoparticles in the solution. Then 50 ml of Na_2S solution was injected drop by drop into the above solution under stirring. Final mixture was stirred for 60 minute. The samples were then separated from solution by centrifugation (3500 rpm for 10 minutes) and washed with acetone to get rid of unreacted solvent. For drying, the particles are kept in a Petri dish for about 12 hours and then ultrasonically agitated for breaking the agglomerated particles. (Cu, Fe) doped CdS nanoparticles were prepared in different concentrations of TG, CdCl_2 and $(\text{Cu, Fe})\text{Cl}_2$.

2.3. Characterization

X-ray diffraction (XRD) measurements were performed on a Philips PW 1840 diffractometer with $\text{Cu-K}\alpha$ radiation (40 kV, 40 mA), scan rate $0.02 \text{ } 2\theta/\text{s}$, the range of 2θ being $20\text{--}70 \text{ deg}$. XRD patterns were recorded using an automatic divergence slit system. Absorption spectra were measured using a Scan Cary 100 UV/vis spectrometer. The photoluminescence (PL) measurement was carried out at room temperature using Shimadzu RF-5000.

3. Results and discussion

3.1. Structural characterization

The structures of the doped CdS nanoparticles with different doping concentration of Cu^{2+} and Fe^{2+} ions have been studied at room temperature using X-ray diffractometer.

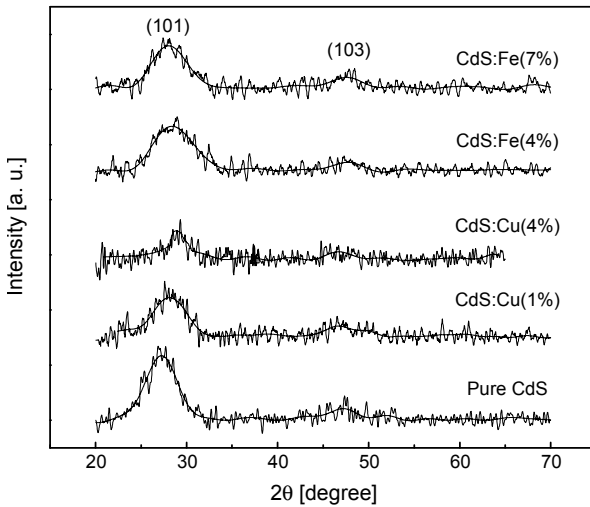


Fig. 1. X-ray diffraction patterns of the doped CdS nanoparticles. The samples have hexagonal phase. ($[TG] = 0.09 \text{ M}$).

The XRD pattern of doped CdS nanoparticles is shown in Fig. 1. The two diffraction peaks in the pattern correspond to crystal planes (101) and (103). This reveals that the prepared nanoparticles exhibit a hexagonal crystal structure. Due to the size effect, the XRD peaks tend to broaden and their widths become larger as the particles become smaller. As no extra peak was observed in the XRD pattern, clearly this indicated the phase purity and absence of impurity phases. The average crystallite size can be calculated from the full width at half maximum (FWHM) of the diffraction peaks using the Debye–Scherer formula [18]:

$$R = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

Here, R is the mean grain size, λ is the X-ray wavelength, β is the full width of half maximum (FWHM) intensity of diffraction line and θ is the diffraction angle. The grain size of the samples was calculated from Eq. (1) using (101) reflection in the XRD pattern. The values of particle size for different doping concentrations are listed in Tab. 1, from which it is clear that the particle size decreases with the increase of Cu and Fe doping concentration.

Also, for particle size investigation, we consider the absorption spectra of samples. As shown in Fig. 2, the excitonic peak shifted to smaller wavelength due to size quantum effects, which means that the band gap (or first excitonic transition energy)

T a b l e 1. Particle size variation with doping concentration from XRD analysis.

	Pure CdS	Cu (1%)	Cu (4%)	Fe (4%)	Fe (7%)
Grain size [nm]	4.22	3.85	4.07	3.71	3.54

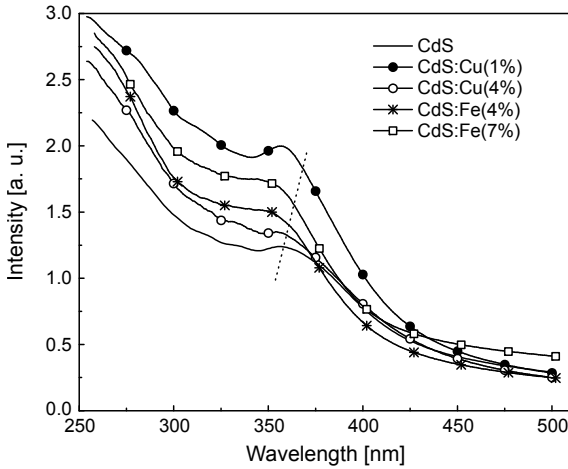


Fig. 2. Absorption spectra of undoped and doped CdS nanoparticles at various doping concentrations.

Table 2. The estimated particle size at different doping concentrations from absorption spectra.

	Pure CdS	Cu (1%)	Cu (4%)	Fe (4%)	Fe (7%)
Optical size [nm]	4.06	3.69	3.88	3.43	3.31

increased and therefore the size of the nanoparticle is reduced. The size variation of (Cu, Fe) doped CdS nanoparticles can be attributed to surface modification of CdS nanoparticles with (Cu^{2+} , Fe^{2+}) and it has also been suggested that Cd^{2+} ion is replaced by Cu^{2+} and Fe^{2+} ion in the CdS lattice. The optical size of nanoparticles can be determined using Brus equation [19]. The optical size of pure and doped CdS nanoparticles is given in Tab. 2. It can be noted that the particle size estimated from UV–vis absorption analysis is in the same size regime as obtained from the X-ray line width measurements described above (Table 1).

3.2. Photoluminescence (PL) properties

Photoluminescence is a process in which an electron, excited by monochromatic photon beam of certain energy undergoes radiative recombination either at valence band (band edge emission) or at traps-surface states within the band gap. Figure 3 presents the room temperature PL spectra of CdS and doped CdS nanoparticles with different Cu^{2+} and Fe^{2+} doping concentration in the energy range of 2.2–2.5 eV. The excitation energy is 3.45 eV. The PL intensity of CdS nanoparticles decreases on adding Cu^{2+} . Also, the PL intensity of Cu^{2+} samples decreases as the Cu^{2+} -doped ratio is increased. The PL spectra consist of two broad bands (*A* and *B*) which can be attributed to deep and shallow traps, respectively. The transition due to the deep traps (peak *A*) should not change their energy with decreasing or increasing nanoparticle

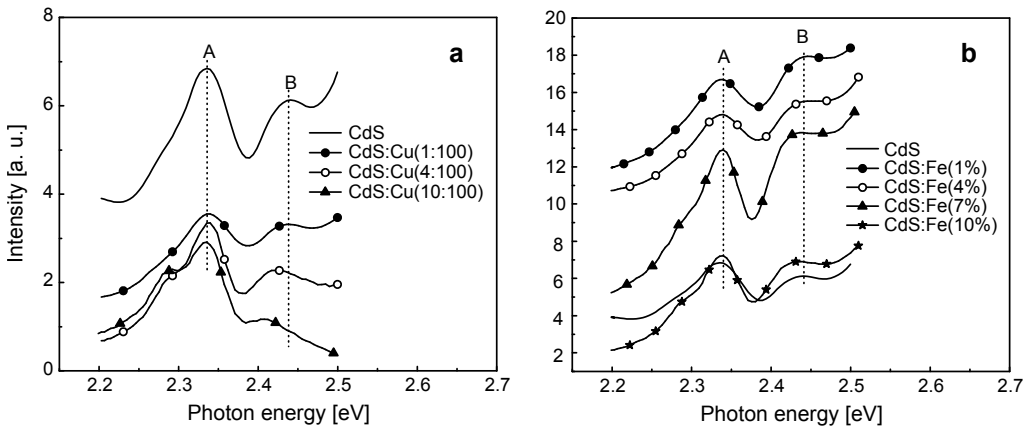


Fig. 3. PL spectra of pure CdS and doped CdS nanoparticles ($[TG] = 0.09$ M) at different ratio of doping: Cu^{2+} doped samples (a); Fe^{2+} doped samples (b). The excitation energy is 3.45 eV.

size because the shift of deep traps is negligible. But transition due to the shallow traps (peak B) moves along with the intrinsic band as the nanoparticle size decreases [22]. Hence, the luminescence bands can be identified with transitions involving donors, acceptors and surface states. The luminescence mechanism of the CdS nanoparticles doped with Cu^{2+} can be described as follows: when CdS nanoparticles absorb photons, the electrons are excited from the valence band to the conduction band and are trapped by defects. The recombination of the defects and excitation states induced by Cu^{2+} modified surface trap states which enhances and shifts and broadens the luminescence band [23]. The transition mechanism for copper doped ZnS has been thoroughly discussed by PEKA and SCHULZ [24]. They explained that the green copper luminescence is due to a transition from the conduction band of ZnS to the t_2 level of excited $\text{Cu}^{2+}(d^9)$ in the ZnS band gap. Also, this model can be used for Cu^{2+} doped CdS nanoparticles. As shown in PL spectra of Fe^{2+} doped CdS nanoparticles (Fig. 3b), the PL intensity enhanced with increasing Fe^{2+} concentration. When Fe^{2+} doped CdS nanoparticles are irradiated, more electron-hole pairs are created. Due to the fact that the electron-hole pairs recombine immediately and emit more photons, the fluorescence intensity is increased. When the luminescence centers of Fe^{2+} ions are formed, the luminescence center may trap electron and holes; and therefore the fluorescence efficiency is increased.

As the Cu^{2+} and Fe^{2+} doped CdS nanocrystals are prepared from a chemical route, it is expected to have a size distribution which in turn results in a tailing in optical absorption spectra and influences the luminescence properties [22]. In preparation of semiconductor nanocrystals the choice of the capping molecules is critical. The bonding between the capping molecules and the precursors needs to be neither too weak nor too strong. If the bonding between capping molecule and

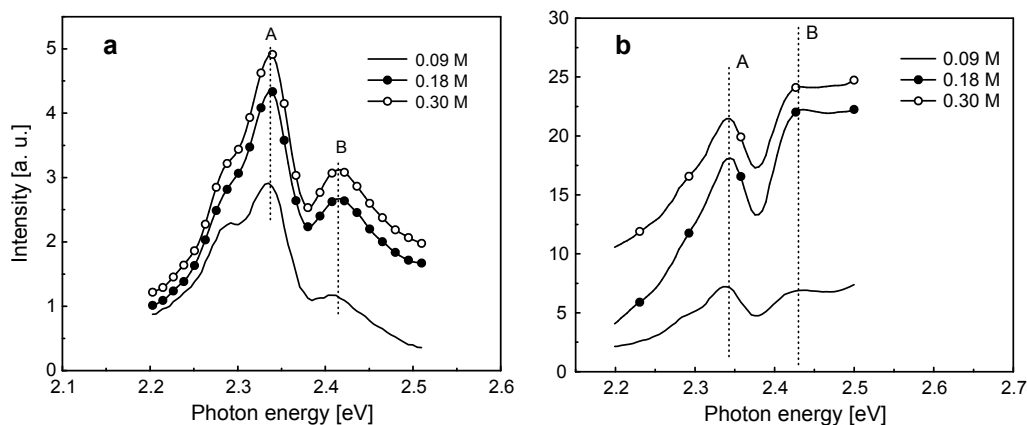


Fig. 4. PL spectra of the samples for different TG concentration: Cu^{2+} doped samples (10%) (a), Fe^{2+} doped samples (10%) (b). The excitation energy is 3.45 eV.

nanocrystal precursor is too weak, particle growth is fast and bigger crystallites are formed. If the binding is too strong, the nanocrystals will not be formed. The rate at which the capping molecules attach and de-attach the surface, influences the growth rate and thus the final size of the particles. By the choice of the type and concentration of capping molecules and the temperature, the dynamics of attaching and de-attaching can be influenced and the particle size can be tuned. At lower capping molecule concentrations, the concentration of the cation capping molecule complex is lower resulting in a faster particle growth. At higher capping molecule concentrations, the reaction is slower yielding well passivated and more monodisperse particles. The emission spectra of the (Cu, Fe) doped CdS nanoparticles prepared with various TG concentration are shown in Fig. 4. It can be noted that the highest intensity is related to the highest capping molecule concentrations. The excitation energy is 3.45 eV. As shown, the PL intensity increases as the concentration of TG is increased due to masking of (Cu, Fe) by TG [25]. We observe that the shift of the band B is negligible and there is no shift in the position of the band A. This behavior is understandable because the radiative defects exist in the cores of CdS nanocrystals. The surface modification will not change the energy levels of the defects.

4. Conclusions

Cu^{2+} and Fe^{2+} doped CdS nanoparticles were synthesized using wet chemical technique in doubled distilled water solution. We used thioglycerol (TG) as capping agent. The formations of the nanoparticles were confirmed by the broadening of XRD peaks and result shows that the samples have hexagonal phase. The effect of doping and TG concentration on luminescence of samples has been studied. Photoluminescence (PL) emission covering the energy range of 2.2–2.5 eV energy of the electromagnetic spectrum, originates from the recombination of surface states. Two bands have been

shown at PL spectra related to shallow and deep traps. The PL spectra show that emission intensity decreases on increasing the Cu^{2+} concentrations and is enhanced as the Fe^{2+} dopant concentration increases. The doping is found to be an important parameter to induce or quench luminescence centers in nanocrystals. Also, the PL intensity increases as the concentration of TG is increased due to the masking of (Cu, Fe) by TG.

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