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ORIGINAL PAPER

Photoluminescence and Energy Transfer Study of Eu^{3+} Codoped with CdS Nanoparticles in Silica Glass

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Abstract The CdS nanoparticles along with Eu^{3+} ions were embedded in silica xerogel by sol gel technique. The samples were studied by TGA, DTA and fluorescence techniques. The result suggested that doping of CdS nanoparticles enhanced the luminescence properties of Eu^{3+} even in the gel stage itself and this avoids the need of heating gel at higher temperature. The effects of CdS nanoparticles on the Eu^{3+} luminescence were discussed.

Keywords Photoluminescence · Sol-gel technique · Nanoparticles · Energy transfer

Introduction

Luminescent properties of the rare-earth (RE) elements hosted in several matrices are widely used because of their technological application [1–4]. Sol-gel silica glasses are considered as very good materials for hosting rare-earth ions along with semiconductor nanoparticles. These glasses allow incorporation of CdS, ZnS, CdSe etc. at low temperature with predetermined concentration [5, 6]. A semiconductor nanoparticle in the glass matrix shows very attractive properties completely different from those of bulk materials. The application of semiconductor nanoparticles incorporated in the glass matrix has been studied for non-linear optical devices [7]. Lanthanide impurities in semiconductor quantum dots have been considered as promising candidate for building a new class of light emitting devices (LEDs). For examples, GaN quantum dots doped with Eu, Sm or Pr (red emission), Tm (blue emission) and Ho, Er, Tb (green) may have potential applications in full color displays [8]. It is expected that Eu^{3+} ions is incorporated in CdS nanoparticles because the ionic radius of the Cd ion (0.98 Å) is close to the Eu^{3+} ions (0.95 Å). It is reported that Eu ions appear to form a solid solution with the CdSe sample with random ion displacement of the cadmium cation site by the substitution guest Eu^{3+} ions[9]. Moreover, nanoparticles can transfer energy to another nanoparticle via electronic interactions (i.e. long range resonance transfer), which suggested that such process could be used to improve the luminescence properties. This mechanism of energy transfer is very similar to that observed for transfer of energy between ions in a host matrix or vice versa. Nanoparticles could behave like sensitizers (donor) in a host matrix and luminescence from activator ions in the host matrix could be increased by embedding nanoparticles into the host matrix [10]. Among rare earth ions, Eu^{3+} ion is the best candidate to be used as a probe to investigate the local structure around rare-earth ions as well as crystal field effect. Knowledge of local structure surrounding rare-earth ions in glass is important not only for interpreting their optical properties; it is also useful for designing laser glasses or phosphors [11, 12]. T. Hayakawa et al. [13, 14] have reported an increased in the emission intensities from Eu^{3+} doped SiO_2 gel, which has been immersed into CdS sol. They suggested the possibility of energy transfer from CdS nanoparticles to activator ions. They also show the increased in the photoluminescence (PL) intensities because of segregation of Eu^{3+} ions to the interface between the nanoparticles and the host matrix. Evidence for energy transfer, such as photoluminescence excitation (PLE) spectra was not reported. An active research has been focused on the optical properties of rare-earth doped semiconductor nanoparticles to find out the potential application in photonics. From the fundamental point of

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view, the physical understandings of the luminescent properties of RE ions in nanoparticles are very important with changes in size, crystal phase and dopant concentration. Particles in the nano size regime exhibit quantum confinement effect, the evidence of which is a blue shift in the optical spectrum [15]. The quantum confinement effect of semiconductor nanoparticles creates photo-generated carriers, which may have an interaction with f-electrons. That is an important factor for influencing the optical properties. Among the rare earth ions, terbium and europium ions have absorption and emission in the visible range and sharp green and red fluorescence can be used for display applications.

In this paper we report fluorescence enhancement and local field properties of different concentration of CdS nanoparticles on Eu^{3+} ions embedded in the silica xerogel.

Preparation of Eu^{3+} Doped Sol-gel Silica Glass Containing CdS Nanoparticles

Silica gel containing 0.1 M of Eu^{3+} and varying concentration of CdS were prepared by sol-gel process with tetraethylorthosilicate (TEOS), as a precursor in the presence of methanol, water and nitric acid [16–18]. First, a desired amount of europium oxide was dissolved in methanol and water in presence of nitric acid. Then to this mixture TEOS was added and stirred for 30 min. Second, the methanol solution of cadmium nitrate and thiourea was added into the above mixture and stirred. Cadmium nitrate and thiourea were as cadmium and sulfur sources, respectively. After being stirred for 60 min, the mixture was poured into polyethylene container, seal tightly and gelatinized at room temperature. The xerogel obtained was aged for 24 days. Finally, the xerogel was annealed at 150 °C for 1 h. The color of the xerogel turned from white into yellow, which shows the presence of CdS in our sample.

The excitation and fluorescence spectra were measured using a FluoroMax-4P spectrofluorometer equipped with 100 W Xenon lamp source. All the spectra were measured at room temperature. The TGA and DTA were recorded using Perkin-Elmer, model: Pyris Diamond TG/DTA apparatus. The fresh samples in the cell were heated in air at 10 °C/min from 40 °C to 800 °C.

Result and Discussion

Absorption and Emission Spectra of CdS Alone Doped Sol-gel Silica Glass

The absorption and photoluminescence spectra of CdS alone-doped silica xerogel were already shown in our previous reports [16–18]. The absorption band at 424 nm is consistent with the formation of CdS nanoparticles [13]. It is well known that the diameter of the particles is related with the absorption edge. The blue shift of the band gap energy is described by effective mass approximation (EMA) [19, 20]. After excitation at 370 nm, we observed the emission peaks at 454 nm, markedly blue shifted relative to that of the bulk CdS (515 nm); the emission arising from the electron-hole recombination after relaxation (band edge emission). The particles size was calculated by using EMA model and found to be 2.9 nm.

Thermal Analysis of Eu^{3+} Doped with and Without CdS Nanoparticles in Sol-gel Silica Glass

Figure 1(a) and (b) shows the TGA and DTA diagram of Eu^{3+} co-doped with and without CdS nanoparticles in sol-gel silica glass. In Eu^{3+} doped sol-gel glass a strong endothermic peak is observed at 94.68 °C in the DTA thermogram indicating the loss of 14.46% of water as observed in TGA profile, followed by one exothermic peak at 223.06 °C, which is caused by the decomposition of ethoxy and butoxy groups remaining in the solid [21]. While in the DTA thermogram obtained for Eu^{3+}: CdS nanoparticles doped sol-gel glass the endothermic peak is observed at 95.44 °C due to elimination of 13.84% of water. The strong exothermic peaks is observed at 204.92 °C corresponds to 66.25% of weight loss, after which no any weight loss occur; as observed from its corresponding TGA profile. This may be the temperature at which CdS particles get crystallized.

PL Studies of Eu^{3+} Ions Doped with and Without CdS Nanoparticles in Sol-gel Silica Glass

Emission spectra of Eu^{3+} doped sol-gel silica glass with and without CdS nanoparticles under the irradiation of 399 nm excitation are shown in Fig. 2. The characteristic peaks from Eu^{3+} ions are observed with the dominated peaks at 616 nm being ≈20 times more intense for Eu^{3+} ions with CdS nanoparticles in compare to without CdS nanoparticles. The possible explanations is that CdS nanoparticles doped in the network of SiO_2-RE xerogel would increase the Si dangling and oxygen vacancy in the network of the silica xerogel. In this way, more electron or hole can be easily excited and radiant recombinations are increased. So the emission intensity of the doped sample markedly increased. Addition to this the band edge emission of CdS nanoparticles themselves should be one of the contributing factors. Similar results have been reported by G. Ehrhart et al. [22] on sol-gel derived ZrO_2 thin film. The peak at 464 nm is due to CdS nanoparticles and peak at 592, 616, 652 and 694 nm are due to Eu^{3+} ions. In order to

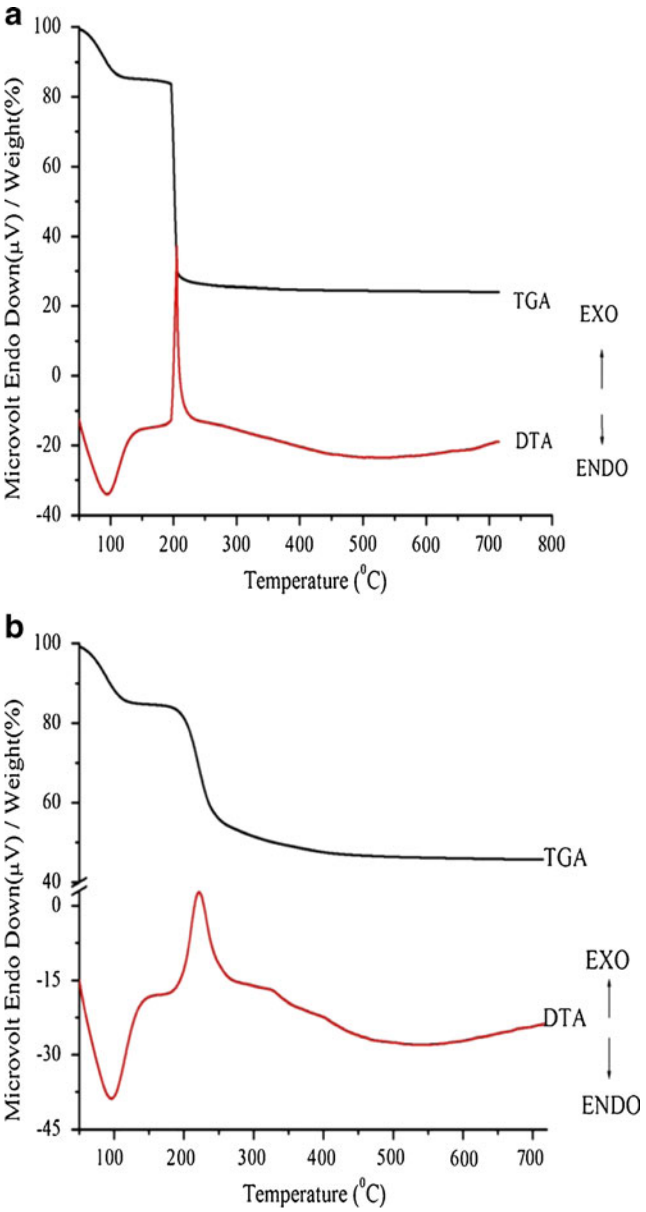

Fig. 1 **a** Thermogram of Eu^{3+}: CdS nanoparticles doped sol-gel silica glass. **b** Thermogram of Eu^{3+} alone doped sol-gel silica glass

clarify whether the emission at 464 nm is from Eu^{2+} or CdS, we oxidized the sample by heating it in air at 150 °C. Since Eu^{2+} is not stable in an oxidizing atmosphere, it can be oxidized to Eu^{3+} easily via Eu^{2+}→Eu^{3+} + e. The electron may be trapped at the surface states or defect of the CdS particles. The PLE spectra for the 616 nm peak are shown in Fig. 3. The excitation spectra exhibit the band associated with Eu^{3+} 4f-4f transition at 362 ($^7F_1$→$^5D_4$), 380 ($^7F_0$→$^5G_3$), 394 ($^7F_0$→$^5L_6$), 414 ($^7F_0$→$^5D_3$), 465 ($^7F_0$→$^5D_2$), 520 ($^7F_0$→$^5D_1$) and 534 nm ($^7F_1$→$^5D_1$). Thus when CdS is not crystallized, even if CdS aggregate are present, the excitation feature are characteristic of Eu^{3+} ions. The energy transfer (ET) from CdS nanoparticles to Eu^{3+} can be explained by the

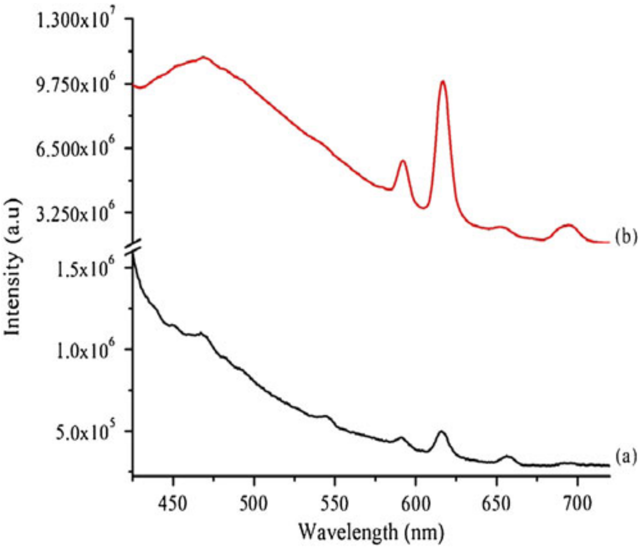

Fig. 2 Emission spectra of Eu^{3+} doped sol-gel silica glass (**a**) without (**b**) with CdS nanoparticles

spectral overlap [23]. The emission spectrum of CdS is a broad band ranging from 350 to 550 nm, which overlap with most of the excitation lines of Eu^{3+}. As a result, the emission energy of CdS can be absorbed by the Eu^{3+} ions, via their f-f transitions and ET from CdS to Eu^{3+} takes place. However after thermal-induced CdS crystallization all the excitation bands lying in the absorption range of CdS nanoparticles disappear; shows only a broad excitation band with maximum at 535 nm and a small peak at 394 nm, presumably from residual direct Eu^{3+} excitation at the most intense f-f transition. The disappearance of excitation bands from multiplets in resonance with the CdS absorption

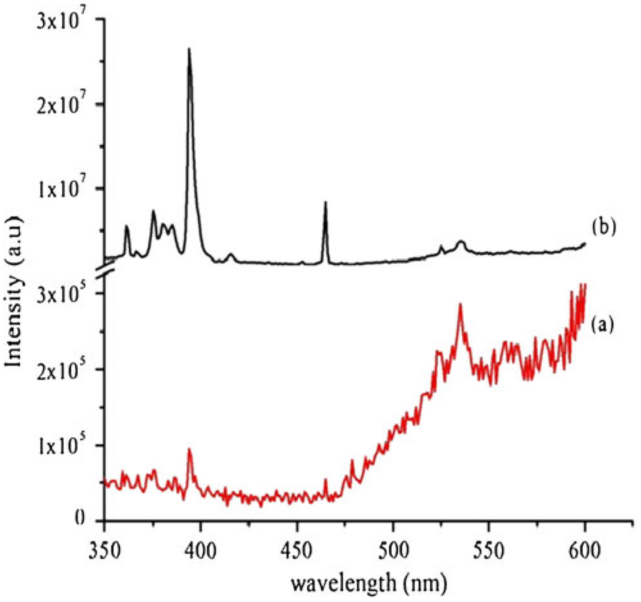

Fig. 3 Excitation spectra of Eu^{3+}:CdS doped sol-gel silica glass, (**a**) annealed at 300 °C, (**b**) without annealed

could be attributed to an ET from Eu^{3+} ions to CdS nanoparticles [24]. In europium, the $^5D_0 \rightarrow {}^7F_1$ (592 nm) transition mainly a magnetic-dipole transition while $^5D_0 \rightarrow {}^7F_2$ (616 nm) is a hypersensitive forced electric dipole transition being allowed only at low symmetries with no inversion center. Thus the intensity ratio I ($^5D_0 \rightarrow {}^7F_2$)/I($^5D_0 \rightarrow {}^7F_1$) serves as an effective spectroscopic probe of the site symmetry in which europium is situated, i.e., the higher the ratio, the lower the site symmetry. From Fig. 2 it is clear implying that Eu^{3+} ions in silica xerogel prepared by sol gel process were situated at low symmetry sites for CdS doped sample. It is well known that the f–f transitions arise from forced electric dipole which are parity forbidden and become partially allowed when the ion is situated at a low symmetry site. Such situation allows intermixing of the f-states with higher electronic configuration [25] and as a result the optical transition probability increases, i.e. the radiative emission rate increases. This reason will explain the changes in the luminescence intensity with increasing the concentration of dopant. These results reveal that site symmetry of ions depends on the concentration of dopant ions and it plays an important role on the photoluminescence properties.

Effect of CdS Concentrations and Annealing Temperature on the Luminescent Enhancement

From Fig. 4, it is clearly observed that the emission intensity of Eu^{3+} doped sol-gel silica glass varied with varying the CdS concentration. Increasing the CdS concentration up to 0.2 M, increased the fluorescence intensity while increasing the concentration further there was decreased in the intensity. In particular, in the network modifier case CdS nanoparticles concentration lower than 0.3 M, the CdS nanoparticles contribute to disrupting the silica structure and produce non-bridging CdS-O groups; which can coordinate with europium ions as a result reduces Eu-Eu interaction and increases emission intensity. Moreover, there is possibility of ET from the CdS nanoparticles to the Eu^{3+} ions, owing to the electron or hole trapped surface levels. The photogenerated electron is first trapped in the surface level of CdS particles and they interact with the Eu^{3+} ions located close to the surface CdS. Secondly, the electron in the surface trapped recombines with a valence band free hole and the energy is non-radiatively transferred to the Eu^{3+} ions. Additionally, the band edge emission of CdS nanoparticles themselves could be one of the contributing factors.

To further clarify the role of CdS nanoparticles in the emission of the rare-earth ions, the emission spectra of the samples were measured under excitation of 350 nm, no characteristics emission of $^5D_0 \rightarrow {}^7F_j$ (j=0–4) observed from Eu^{3+}:CdS doped silica glass. It is interesting to note that characteristics emission of Eu^{3+} ions appear for Eu/CdS co-doped silica glass at 399 nm excitations. This indicates that there exist effective ET between CdS nanoparticles and Eu^{3+} ions. Generally defect states play an important role in ET between RE ions and semiconductors nanoparticles. The ET in this system involves relaxation to defect states of CdS nanoparticles before the energy transfer to the Eu^{3+} ions, as shown in Fig. 5. The

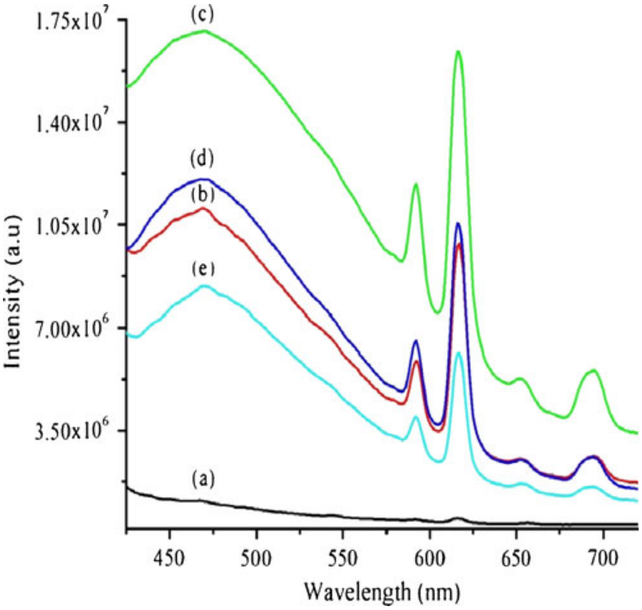

Fig. 4 Emission spectra of Eu^{3+} doped sol-gel silica glass with (**a**) 0.0 M CdS, (**b**) 0.1 M CdS, (**c**) 0.2 CdS, (**d**) 0.3 M CdS and (**e**) 0.4 M CdS

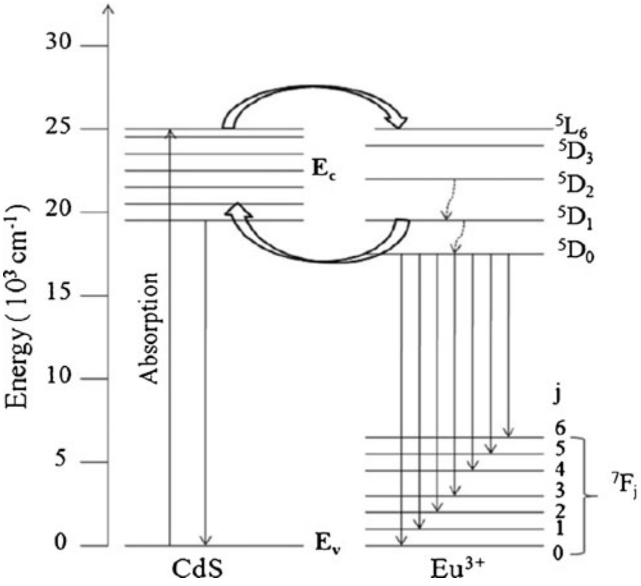

Fig. 5 Schematic diagram energy transfer process between Eu^{3+} ions and CdS nanoparticles

UV light energy is observed by CdS nanoparticles subsequently relax to the surface state. Then the surface state transfer the energy to the $^5D_0$ level of Eu^{3+} and emission can be observed after the relaxation between surface state and Eu^{3+} ions. We also observed that with increasing the annealing temperature up to 150 °C, the emission band intensity increased considerably, while the sample heated above 300 °C, the emission intensity were decreased. The possible mechanism i.e. defect mechanism has been proposed to explain the emission phenomena in sol gel derived silica gels. In the process of heat treatment, various defect centers were formed by the hydrolysis and condensation of hydroxysilane precursor. One hand, a strong electron phonon coupling caused the emission. On the other hand, the influence of high-energy vibration of the hydroxyl groups on the emission of Eu^{3+} was decreased, and the releasing energy from electrons and holes produced by the defect recombining was transferred to Eu^{3+} ions that were embedded in the network of silica xerogel, which enhanced the emission intensity of Eu^{3+} ions. Moreover, heat treatment leads to an increase in the in homogeneities of the local environment, owing to the cross-linking between silica chains and consequent shrinkage. Due to change in the geometry of silica, upon annealing at higher temperature producing an increased in the concentration of both Eu and CdS, which could results in the aggregation of Eu-Eu [26]. As the densification continues, clustering of Eu^{3+} induces strong ET even at lower concentrations and there is also the probability of back ET from Eu^{3+} to CdS nanoparticles, which is confirmed from the observed PLE spectra. The low fluorescent intensity of the gels was due to electron–phonon coupling with C-H and O-H groups.

Conclusions

Silica glass codoped with Eu^{3+} ions and CdS nanoparticles were prepared by sol gel technique. The enhancement of fluorescence intensity of Eu^{3+} ions in amorphous silica matrix in presence of CdS nanoparticles is due to the lower site symmetry of europium ions in silica glass and energy transfer between Eu^{3+} and CdS nanoparticles. A possible explanation refers to the effect of CdS nanoparticles on silica glass as glass modifier. In amorphous silica matrix, the energy transfer can be achieved between CdS and Eu^{3+} ions. The defects on the surface of CdS nanoparticles as surface transition state play an important role in the energy transfer.

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