

# Fluorescence Enhancement in $\text{Tb}^{3+}/\text{CdS}$ Nanoparticles Doped Silica Xerogels

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**Abstract** Cadmium sulfide semiconductor nanoparticles along with terbium ions were incorporated in silica xerogels through sol–gel route. The optical absorption and emission spectra confirmed the formation of CdS nanoparticles along with terbium ions in the silica gel. The optical bandgap and size of the CdS nanoparticle were calculated from the absorption spectrum. The TEM measurement was also used to evaluate the average size of the CdS nanoparticles. The fluorescence spectra reveal that the intensity of characteristic emission of terbium ions increases considerably in the presence of CdS nanoparticles even in the gel stage itself and this avoids the need of heating gels at high temperatures. The branching ratios were calculated from the emission spectra using the standard procedure.

**Keywords** Sol–gel · Nanoparticles · Rareearths · Fluorescence enhancement

## Introduction

Semiconductor nanoparticles have attracted much attention due to their novel properties and varieties of promising potentials in extensive applications [1–3]. Semiconductor nanoparticles with sizes of a few nanometers in a glass matrix show very attractive properties completely different from those of bulk materials. The application of semiconductor nanocrystals incorporated in glass matrices has been studied for nonlinear optical devices and phosphors [4].

Among II–VI semiconductors, CdS nanoparticles have been widely studied because of their many applications in optoelectronics.

Among the different techniques used to prepare the semiconductor nanocrystals, sol–gel method has certain attractive features and the protection offered by the sol–gel environment can prevent crystal growth and aggregation [5]. Silica gels and glasses doped with rare earth ions are of technological interest for a variety of applications in solid-state lasers, fiber optics and wave-guide devices. Studies have revealed that rare-earth doped luminescent II–VI materials are promising candidates for applications in color thin film electroluminescent devices [6–8]. Further rare earth ions/semiconductors doped gels and glasses have attracted much attention in respect of luminescence properties, high quantum efficiencies and energy transfer processes [9]. The optical properties play a crucial role in such applications and fluorescence can particularly serve as the basis for spectroscopic applications [10]. Recently, a lot of work has been done on the preparation and fluorescence properties of  $\text{Eu}^{3+}/\text{CdS}$  in sol–gel derived silica matrices [11, 12]. There have been reports on the influence of CdS nanoparticles on the enhancement of fluorescence from  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  doped zirconia sol–gel films [13].

Among the rare earth ions, terbium ions have absorption and emission in the visible range and its sharp green fluorescence can be used for display applications. Here we report the fluorescence enhancement of terbium ions in the presence of CdS nanoparticles embedded in the silica xerogel. The enhanced fluorescence observed even in the gel stage avoids the need of heating gels at high temperatures. The fluorescence enhancement and the estimated branching ratio suggest a potential laser transition for  $\text{Tb}^{3+}$  ions at 542 nm in the investigated samples.

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## Experimental

Silica gels containing 3 wt.% of  $Tb^{3+}$  and varying concentrations of CdS were prepared by sol–gel process [14] with tetraethyl orthosilicate (TEOS), as precursor in the presence of ethanol and water. The dopants were added in the form of cadmium acetate, thiourea and terbium nitrate. Cadmium acetate and thiourea were used as cadmium and sulfur sources respectively. Measured volume of 1M  $HNO_3$  was added as catalyst. The mixture (sol) is poured into polypropylene containers, which is sealed and kept to form stiff gel for one month. The following codoped samples were prepared.

Sample A (CdS 1 wt.% Tb 3 wt.%)

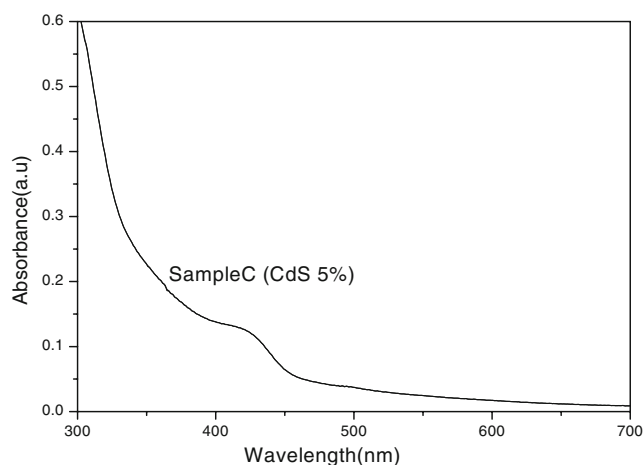
Sample B (CdS 3 wt.% Tb 3 wt.%)

Sample C (CdS 5 wt.% Tb 3 wt.%)

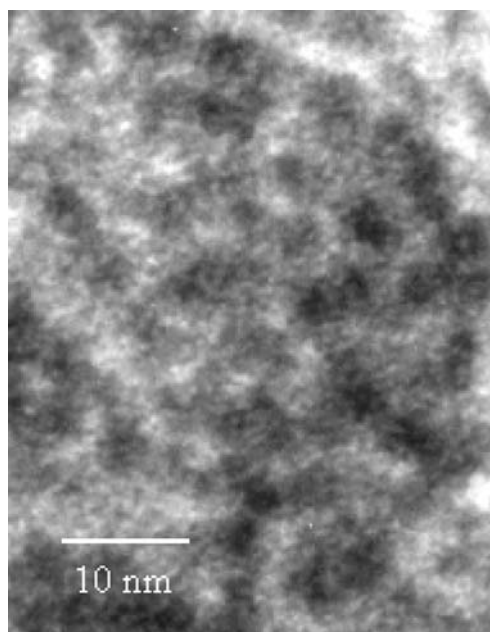
Sample D (CdS 7 wt.% Tb 3 wt.%)

As references for optical measurements, 3 wt.%  $Tb^{3+}$  (sample E) and 5 wt.% CdS (sample F) were also prepared following the same procedure. Finally the samples were annealed at 60°C for 2 days. The colour of the samples C, D and F turned into yellow showing the presence of CdS whereas samples A and B remain colourless indicating the poor formation of CdS as these concentrations are not sufficient for the formation of CdS nanoparticles at this temperature. The colouration of the samples depends on the concentration of the semiconductor and annealing temperature.

The excitation and emission spectra were taken using spectrophotofluorimeter (Shimadzu-RFPC 5301) and the absorption with U-V visible spectrophotometer (Shimadzu-UVPC 2401). The particle size was measured with Tecnai F30 S-Twin transmission electron microscope (TEM) at 300 kV. All the measurements were done at room temperature.



**Fig. 1** Absorption spectrum of CdS alone doped sample recorded at room temperature



**Fig. 2** TEM micrograph of CdS embedded xerogel

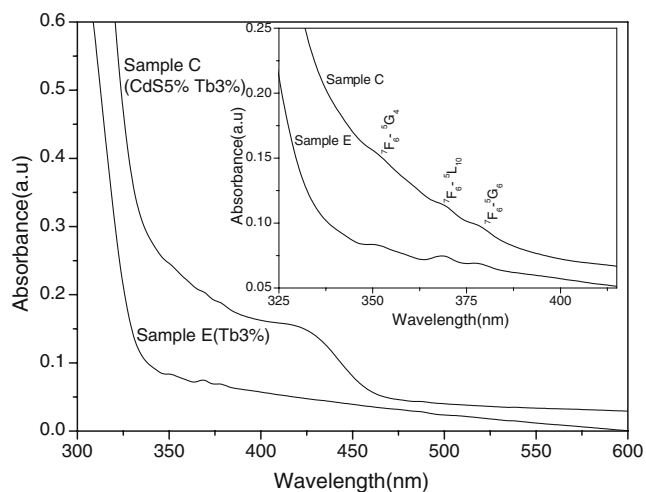
## Results & discussion

The absorption spectra corresponding to CdS alone doped silica xerogel is shown in Fig. 1. The absorption band at 425 nm is consistent with the formation of CdS nanoparticles [15]. The blueshift of the absorption edge can be explained by the effective mass approximation model, developed by Brus [16] and Kayanuma [17]. In the strong exciton confinement regime of nanoparticles (particle radius  $<a_b^*$ ), the energy  $E(R)$  for the lowest 1S excited state as a function of cluster radius ( $R$ ) given by

$$E(R) = E_g + \frac{\pi e a_b^*}{8\epsilon R^2} - \frac{1.786e^2}{4\pi\epsilon R} + 2.48E_R$$

where  $a_b^*$ , Bohr radius of the exciton (for CdS 2.8 nm),  $\epsilon$  is the dielectric constant of the nanocrystallite (for CdS, 8.36) and  $E_R$  is the bulk exciton Rydberg energy (for CdS 0.029 eV). The first term is the band gap energy for bulk material and it is 2.42 eV for CdS. The second term is the quantum confinement localization for the electrons and holes, which leads to the blueshift. The third term is the Coulomb term leading to red shift, while the fourth term gives the spatial correlation energy, which is small and of minor importance. For our CdS alone doped silica xerogel, the lowest energy of 1S transition was observed at  $\sim 2.92$  eV (425 nm), which showed the presence of CdS nanoparticles [18]. The particle size was determined to be 4.8 nm using Brus formula, by considering this to be in the strong confinement region.

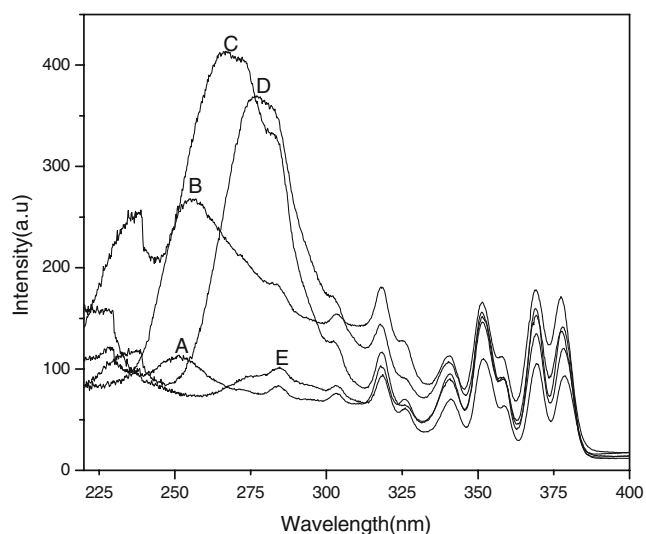
Figure 2 shows the TEM micrograph of CdS alone doped silica xerogel. The irregularly shaped dark particles in the



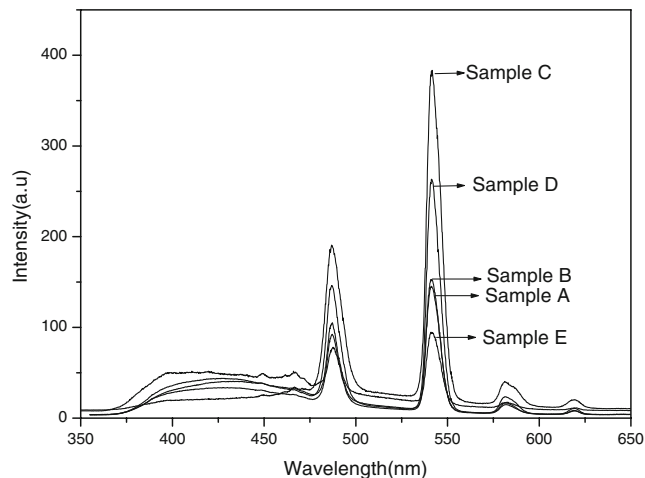
**Fig. 3** Absorption spectra of samples C and E recorded at room temperature. *Inset* shows the prominent transition levels of terbium ions

micrograph are CdS nanoparticles. The CdS nanoparticles are embedded in irregular, porous silica xerogel network. The calculated average size is found to be 4.2 nm, which is in agreement with the estimation by optical analysis.

Figure 3 shows the absorption spectra of Tb and CdS/Tb (sample C as a representative one) doped gel. The absorption bands of Tb<sup>3+</sup> ions corresponding to the forbidden 4f–4f transitions are usually weak in sol–gel silica matrices. In our samples, the prominent levels of terbium ions observed are assigned to the appropriate electronic transitions as <sup>7</sup>F<sub>6</sub>→<sup>5</sup>G<sub>4</sub> (352 nm), <sup>7</sup>F<sub>6</sub>→<sup>5</sup>L<sub>10</sub> (368 nm), <sup>7</sup>F<sub>6</sub>→<sup>5</sup>G<sub>6</sub> (378 nm). The absorption spectrum of sample C confirms the formation of CdS nanoparticles along with terbium ions in the matrix.



**Fig. 4** Excitation spectra of samples recorded at room temperature ( $\lambda_{em}=542nm$ )



**Fig. 5** Fluorescence spectra of samples recorded at room temperature at an excitation wavelength of their 4f<sup>8</sup>→4f<sup>7</sup>5d transitions

The excitation spectra for the 542 nm emission of the terbium alone and codoped samples are shown in Fig. 4. In addition to the f–f transitions a broad band due to 4f<sup>8</sup>→4f<sup>7</sup>5d transition is observed for the CdS/Tb doped sample. We can observe the 4f<sup>8</sup>→4f<sup>7</sup>5d transition for terbium ions, which corresponds to the peaks or shoulders between 225 and 300 nm [19]. Normally this band will broaden only after heating the gels above 400°C [20]. These are related to the environment of Tb<sup>3+</sup> ions. Since the outer shell electrons screen the electrons of 4f shells, the presence of the surrounding lattice has little effect on the 4f–4f absorptions. In addition, the parity selection rule forbids these transitions. The 4f<sup>8</sup>→4f<sup>7</sup>5d transition is much affected by the surroundings of Tb<sup>3+</sup> ions. Here, the dominant peak for the codoped samples appear due to the transition of Tb<sup>3+</sup> affected by the surroundings of Tb<sup>3+</sup> ions in CdS/Tb doped silica xerogel. CdS nanoparticles are embedded in the network of the silica xerogel in sol–gel processing. So the nanoparticles can lead to form more Si dangling bonds and oxygen vacancies in the network of the silica xerogel [21, 22]. Because of the additional interaction induced by the influence of the ligand field, the 4f<sup>8</sup>→4f<sup>7</sup>5d transition probability of Tb<sup>3+</sup> ions increases and this transition band broadens.

**Table 1** The fluorescence branching ratio obtained for the sample C (CdS 5 wt.%Tb<sup>3+</sup> 3 wt.%) from the emission spectrum

Transition	Wavelength (nm)	Area (au)	Branching ratio (%)
<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>6</sub>	487	1,710	32
<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>5</sub>	542	3,311	62
<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>4</sub>	582	270	5
<sup>5</sup> D <sub>4</sub> → <sup>7</sup> F <sub>3</sub>	620	72	1

The excitation spectra are found to red shift with concentration of CdS implying the growth of CdS nanoparticles and the  $4f^8 \rightarrow 4f^7 5d$  transition band broadens to a maximum for sample C (CdS 5 wt.% Tb<sup>3+</sup> wt.%) compared to other samples. A 5 wt.% and above concentration of CdS is favoured for the formation of CdS nanoparticles when the samples are annealed at 60°C for 48 hours because the formation of CdS nanoparticle in sol–gel glasses depends on concentration, annealing temperature and heat treatment time. The CdS nanoparticle acts as network modifiers at small concentrations and this increases the presence of nonbridging oxygens and dangling bonds [23] and as a result the  $4f^8 \rightarrow 4f^7 5d$  transition band of sample C broadens to a maximum compared to sample D.

Figure 5 shows the relationship between emission intensity of SiO<sub>2</sub>-Tb<sup>3+</sup> xerogel and concentration of CdS nanoparticles doped in the silica xerogel. The Tb<sup>3+</sup> doped xerogel shows four fluorescence bands belonging to the  $^5D_4 \rightarrow ^7F_J$  ( $J=3, 4, 5, 6$ ) transitions. Here we observe that the fluorescence intensity of Tb<sup>3+</sup> is significantly dependent on the amount of CdS nanoparticles. The possible explanation is that CdS nanoparticles doped into the network of SiO<sub>2</sub>-Tb<sup>3+</sup> xerogel would produce nonbridging oxygen, which paved the way for the broadening of  $4f^8 \rightarrow 4f^7 5d$  transition band for the codoped sample. By exciting at this wavelength, the fluorescence intensity of the codoped sample is markedly increased compared to the Tb alone doped sample. The fluorescence intensity is found to be greater for sample C (Tb 3 wt.% CdS 5 wt %) and it is 4.3 times higher than that of Tb alone doped sample. The branching ratios were calculated for all the transitions using the standard procedure [24] and are summarized in Table 1 and the branching ratio with a value greater than 50% becomes a potential laser emission [25]. The highest branching ratio corresponds to the  $^5D_4 \rightarrow ^7F_5$  transition (542 nm) and this transition may therefore be considered to be a possible laser transition.

## Conclusion

Silica xerogels codoped with terbium ions and CdS nanoparticles were prepared through sol–gel route. The absorption spectrum confirms the formation of CdS nanoparticles along with terbium ions in the silica xerogel. The average size of the nanoparticle estimated from the optical analysis agreed well with that obtained from the TEM micrograph. The excitation spectrum shows strong  $4f^8 \rightarrow 4f^7 5d$  transition band of terbium ions in the presence of CdS nanoparticles. The fluorescence intensities of the terbium ions are found to be greatly enhanced by codoping with nanoparticles of CdS

even in the gel stage itself avoiding the need of heating gels at high temperatures. The fluorescence intensity of CdS/Tb doped sample is 4.3 times higher than that of Tb alone doped sample. This might be of interest for potential applications such as phosphor material for light-emitting devices.

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