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Modified spontaneous emission of europium complex nanoclusters embedded in colloidal silica spheres

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Abstract

Europium complex nanoclusters were encapsulated inside silica colloidal spheres by a wet-chemical method. The hybrid spheres were characterized to possess a core-shell structure by transmission electron microscopy. The spheres present strong characteristic emissions of Eu^{3+} ions, and the fluorescence decay time decreases when the spheres are dispersed in two dielectric polymers. Temperature-dependent decay dynamics indicates that europium complex in sphere-polymer systems display higher spontaneous emission rate compared with free hybrid spheres in air. Our results are suggestive for optimizing the luminescence quantum yield of lanthanide complexes, and also provide a promising probe to investigate modified spontaneous emission in photonic crystals.

1. Introduction

Spontaneous emission can be interpreted as a consequence of interaction between an atomic dipole and the electromagnetic vacuum field. It is therefore not a property of the atom only, but also depends on the local optical surrounding. Previous experiments, examining a fluorescent layer very close to a flat mirror, have demonstrated that the fluorescence decay time could be modified because the vacuum fluctuations were altered by the reflections from boundaries [1]. Such modifications were subsequently observed for Rydberg atoms [2,3], for atoms placed in microcavities [4], in thin films [5,6], close to dielectric interfaces [7], and inside dielectric nanospheres [8]. Particularly, with the introduction of the concept of photonic crystal [9,10], there has been a growing interest in the use of photonic band-gap material to modify the rate of spontaneous emission. In crystals with a full band-gap, spontaneous emission at frequencies inside the band-gap will be fully inhibited because the optical mode does not exist. Such a radical effect is still waiting to be experimentally demonstrated [11,12].

Monodisperse silica colloids with smooth surfaces have great potential as building blocks for creation of three-dimensional (3D) photonic crystal, which have the ability to manipulate both the propagation and the spontaneous emission of photons in new and exciting ways. Such effects can be studied by placing luminescent probes inside the crystal [12,13]. Generally, laser dyes can be chemically incorporated into the SiO_2 particles during synthesis for this purpose [14,15]. However, to study the effect of the photonic crystal on spontaneous emission or to probe the local optical density of states, dyes are impractical since their emission spectrum is often broader than the photonic feature under study [16]. In contrast, rare earth (RE) ions display narrow-line intra-4f transitions and the mean energy of which is almost independent of the local environment. In

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addition, most of the RE ions do not exhibit photo bleaching commonly observed for laser dyes. Thus, RE-doped silica colloids appear to be ideal probes in photonic crystals.

In our earlier Letter [17], europium complex as a luminescent probe was introduced into monodisperse colloidal silica spheres by a modified Stöber method. Low-temperature laser selective spectroscopy and decay dynamics were performed to study the luminescence properties of the pure europium complex and the hybrid spheres. In this Letter, we have demonstrated that the spontaneous emission of the europium complex embedded in the silica colloids could be modified by dispersing the hybrid spheres in different dielectric polymers. Temperature-dependent decay dynamics was studied on the sphere-polymer systems, which clarifies that the europium complex in such systems displayed higher spontaneous emission rate compared with free hybrid spheres in air. Our results are suggestive for optimizing the luminescence quantum yield of lanthanide complexes, and also provide a promising probe to study photonic crystal effect.

2. Experimental

The monodisperse colloidal SiO_2 spheres embedded with europium complex were formed by two-step process using the base-catalyzed wet-chemical synthesis, which has been described in detail elsewhere [17]. Briefly, the Eu tris(dibenzoylmethanato)phenanthroline [$Eu(DBM)_3phen$] complex was prepared under weak basic condition, and then washed with absolute ethanol thoroughly. The purified complex was dissolved into acetone (Aldrich). After complete dissolving, the solution was poured into ethanol bath containing $NH_3 \cdot H_2O$ (Aldrich, 28% NH_3) and distilled water under well stirring till a stable sol formed. Then a tetraethoxysilane (Aldrich) solution was added drop wise to the sol dispersion under continuous stirring for an hour. The samples were rinsed thoroughly with ethanol and dried in air. The hybrid spheres were dispersed in two dielectric polymers, polymethyl methacrylate (PMMA) and polystyrene (PS), which have the refractive indices of 1.45 and 1.59, respectively.

The general morphology of the hybrid spheres was characterized by a scanning electron microscope (SEM, KYKY 1000B), and the detailed structure analysis was carried out by a transmission electron microscope (TEM, JEOL 2010). The specimens for SEM observations were supported by copper substrate, and those for TEM investigations were placed on holey copper grid with carbon film. The room-temperature emission spectra were measured under a 355-nm excitation from the third harmonic generation of a Nd:YAG pulsed laser. Fluorescence signals were dispersed through a Spex 1403 double-grating monochrometer, detected by a photomultiplier tube, averaged with a boxcar integrator and processed by a computer. For temperature-dependent fluorescence dynamics, the samples were mounted in the helium exchange gas chamber of a closed cycle refrigeration system, where the temperature varied from 10 to 300 K. The decay curves were recorded by a Tektronix TDS 3052 digital oscilloscope.

3. Results and discussions

3.1. Morphology and structure of the hybrid spheres

The morphology and structure of the silica colloids embedded with Eu complex were characterized by SEM and TEM observations. Fig. 1a shows a typical SEM image of the as-synthesized colloids. The sample possesses a spherical morphology and appears to be relatively uniform, with an average diameter of ~300 nm. The size polydispersity is estimated to be 3% by analyzing 100 particles. The samples for SEM observations were prepared by placing small drops of the colloids dispersion on copper substrate. After the samples were dried at room temperature, the monodisperse spherical colloids have a tendency to organize themselves into a close-packed structure, as indicated in the SEM image. It suggests that the hybrid spheres can be used as building blocks to fabricate photonic crystals under well-controlled conditions. TEM measurements provide further insight into the structure of the hybrid spheres. As shown in Fig. 1b, all the spheres were well dispersed and have smooth surfaces. From a magnified image in Fig. 1c, the diffraction contrast can be clearly identified between the central part and the outer layer of an individual sphere. The central part consists of many light spots that may originate from the europium complex nanoclusters while the outer shell was mainly composed of silica. Thus, the hybrid spheres possess a core-shell structure where the Eu complex nanoclusters inside the spheres are isolated from the outside environment by the silica shell.

3.2. Fluorescence properties of the hybrid spheres dispersed in dielectric polymers

Europium complex was chosen as fluorescent probe for several reasons. In the complex system, lanthanide ion is chelated with ligands which have intense broad absorption bands. There is an efficient intermolecular energy transfer from the excited state of the ligands to the emitting levels of the Eu^{3+} ion, which overcomes the very small absorption coefficient of the lanthanide ion [18]. Fig. 2 shows the energy transfer and the emission mechanism for the $Eu(DBM)_3phen$ complex. Furthermore, in the hybrid spheres the Eu^{3+} ion can be

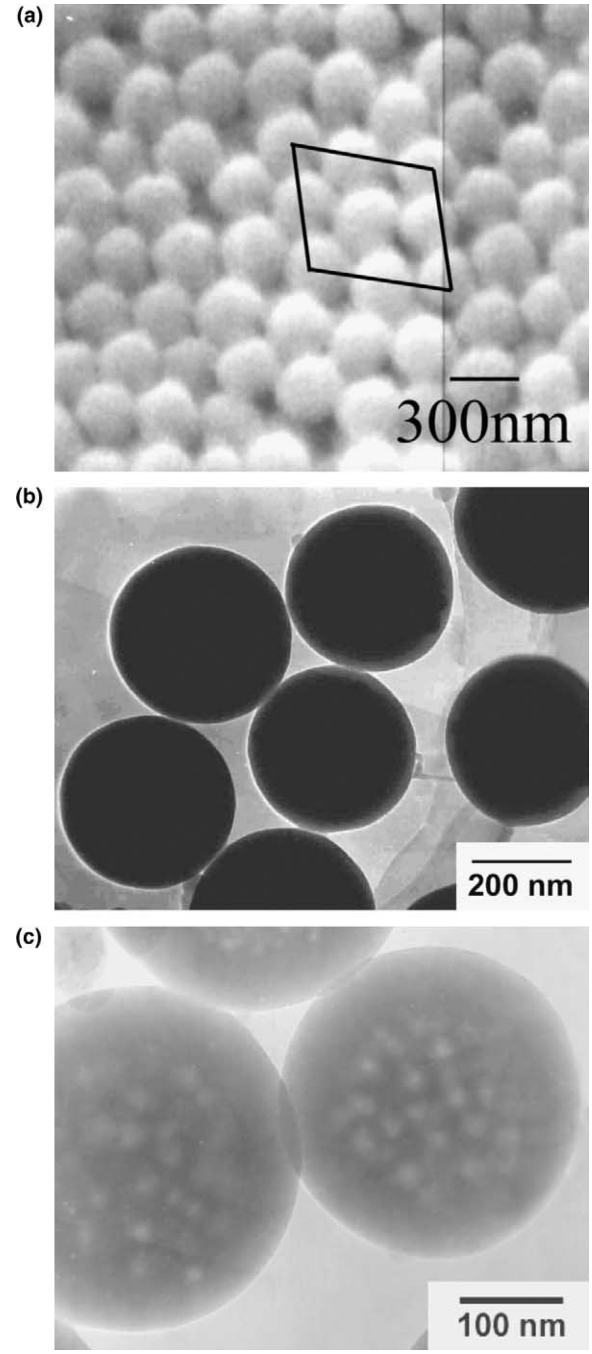

Fig. 1. (a) SEM image of Eu(DBM)$_3$ phen/silica hybrid spheres (b)TEM image of hybrid spheres (c) magnified TEM image of an individual hybrid sphere with core-shell structure.

largely isolated from the strong vibrations of the silica network by placing it in organic ligand cages, thus restricting the influence of the host to its luminescence properties. Under the 355-nm excitation of third harmonic of Nd:YAG pulsed laser, the hybrid spheres present a strong characteristic emission of Eu^{3+} ions, as shown in Fig. 3. The luminescence of the hybrid spheres is dominated by the forced electric dipole transitions

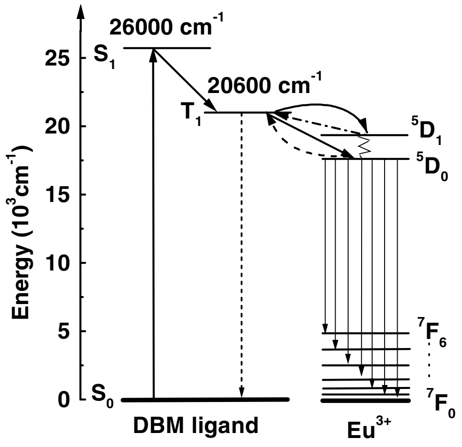

Fig. 2. Energy transfer and emission mechanisms for the Eu(DBM)$_3$phen complex.

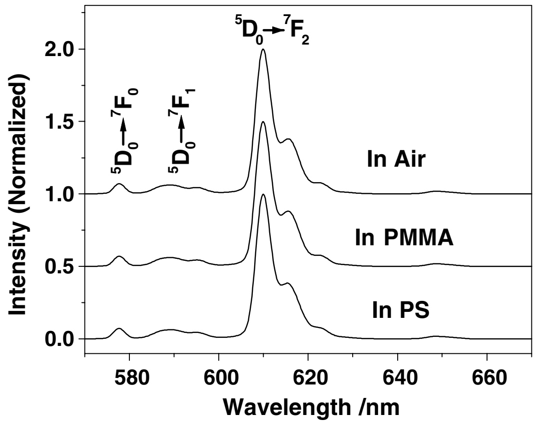

Fig. 3. Emission spectra of the hybrid spheres dispersed in air, PMMA and PS.

($^5D_0 \rightarrow {}^7F_2$), which is highly sensitive to the environment around the Eu^{3+} ion. The features of this transition and its intensity can be altered due to variations in the ligand field and site symmetry occupied by the Eu^{3+} ion. As can be seen from Fig. 3, there is no observable change for the emission spectra, when the hybrid spheres were dispersed in two different dielectric polymers, PMMA and PS. In these cases, the dielectric environment outside the hybrid spheres cannot affect the local structures around the Eu^{3+} ions because the Eu complex nanoclusters locate inside the silica spheres, and the silica shells protect the emitters far from the outside surroundings. However, the fluorescence decay times for three systems were quite different. In following discussions, we will focus on this and demonstrate that the difference in lifetime derives from the change of the spontaneous emission rate.

Fig. 4 shows the luminescence decay traces of the three systems by monitoring the peak emission at 611 nm. All the decay curves can be well fitted with a second order exponential decay function. Two components

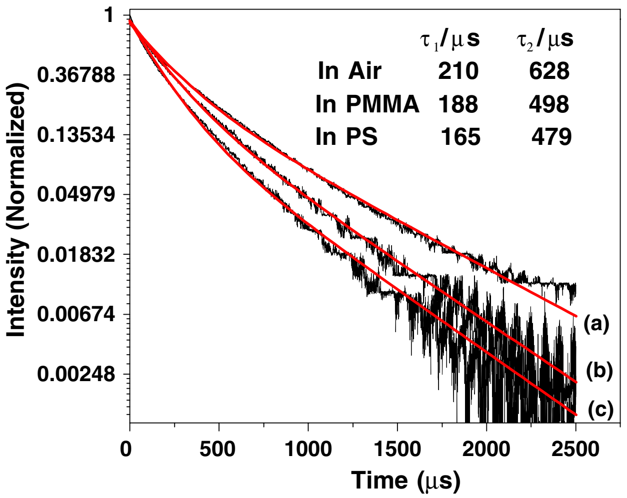

Fig. 4. Luminescence decay curves for the hybrid spheres dispersed in air (a), PMMA (b) and PS (c).

are determined from the fitting and the corresponding values for each curve are listed in Fig. 4. In previous Letter [17], we have identified two emission species in the hybrid spheres by low-temperature laser selective spectroscopy, which are responsible for the two components in fluorescence decay times. As can be seen in Fig. 4, there is an obvious decrease in fluorescence lifetime after the hybrid spheres were dispersed in polymers, compared with those in air. It is well known that the lifetime τ is determined by the radiative transition rate, W_{rad}, and the nonradiative transition rate, W_{nr}, which can be written as

$$\tau = \frac{1}{W_{\mathrm{rad}} + W_{\mathrm{nr}}(T)}. \tag{1}$$

The nonradiative relaxations in the rare earth complexes are governed by the energy difference between the emitting level and the next lower level, separated by the number of phonons of the host [19]. As for the hybrid spheres, W_{nr} depends on the local structures of the Eu^{3+} ions, having nothing to do with the surrounding polymers, because the europium complex nanoclusters are dispersed inside the central part and the silica shells isolate the emitters from outside surroundings. Therefore, the decrease in fluorescence lifetime reveals an increase of spontaneous emission rate (W_{rad}) in the sphere-polymer systems.

3.3. Modified spontaneous emission characterized by temperature-dependent decay dynamics

The dependence of the fluorescence lifetime on temperature was presented to quantify the contributions of the nonradiative relaxation and radiative transition rates. In the Eu complex system, the cross relaxations among Eu^{3+} ions and the concentration quenching can be neglected, for the reason that each Eu^{3+} ion is shielded in organic ligand cages [19,20]. Thus, the nonradiative relaxation is mainly a multiphonon process. In our experiments, for a given sample, the shorter component of lifetime varied little with increasing temperature, as shown in Fig. 5a. Fig. 5b shows the longer component of the lifetime as a function of the temperature for the three samples. Generally, W_{nr} increased remarkably with elevated temperature, while W_{rad} has little change. According to the theory of multi-phonon relaxation, W_{nr} can be given as [19,21,22],

$$W_{\mathrm{nr}}(T) = W_{\mathrm{nr}}(0)(1 + \langle n \rangle)^{\Delta E/\hbar\omega}, \tag{2}$$

where $W_{\mathrm{nr}}(0)$ is nonradiative transition rate at 0 K, ΔE is the average energy difference of the two states between which the multiphonon relaxation occurs, $\hbar\omega$ is the phonon energy, $\langle n \rangle = 1/(e^{\hbar\omega/kT} - 1)$ is the Bose–Einstein average occupation number of the phonon and k is Boltzmann's constant. According to Eqs. (1) and (2), the lifetime of $^5\mathrm{D}_0$ can be written as [21,22]

$$\tau = \frac{1}{\mathrm{W}_{\mathrm{rad}} + \mathrm{W}_{\mathrm{nr}}(0)[1 - \exp(-\hbar\omega/kT)]^{-\Delta E/\varpi}}. \tag{3}$$

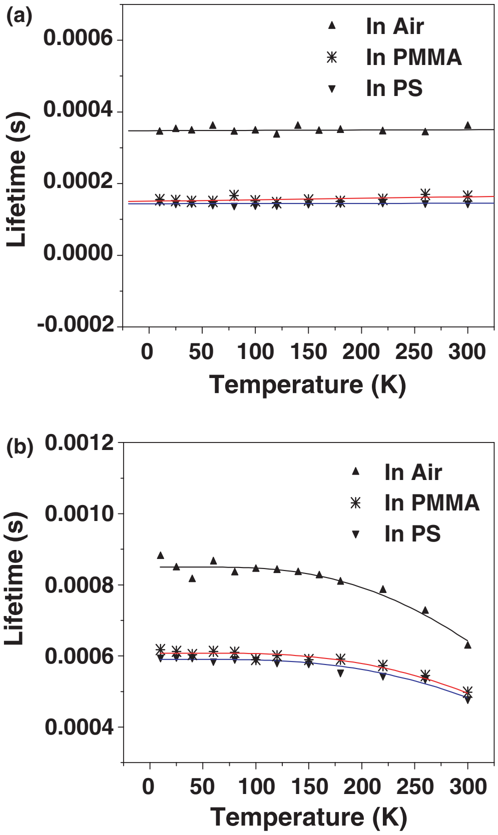

Fig. 5. Dependence of luminescence lifetimes for $^5\mathrm{D}_0$ lever on temperature for the hybrid spheres dispersed in air ($n = 1$), PMMA ($n = 1.49$) and PS ($n = 1.59$). (a) Temperature dependence of shorter component of lifetimes. (b) Temperature dependence of longer component of lifetimes. The solid lines are the fitting results.

Table 1
Radiative transition rate (W_{rad}) and nonradiative transition rate at 0 K ($W_{nr}(0)$) of the $^5D_0$ state of Eu^{3+} ions in hybrid spheres surrounded by dielectric materials with different refractive indices (n)

$Eu(DBM)_3phen/SiO_2$ spheres in	Air $n = 1$	PMMA $n = 1.49$	PS $n = 1.59$
W_{rad} (s^{-1})	1042.7 ± 17.0	1513 ± 15.6	1560.7 ± 16.6
$W_{nr}(0)$ (s^{-1})	134.1 ± 11.9	131.6 ± 10.9	133.6 ± 10.9

The radiative transition rate values are parameters obtained from the decay curves fitted by the Eq. (3).

The experimental data of the three samples can be well fitted by the Eq. (3), when the phonon energy was chosen as $\hbar\omega = 398\ cm^{-1}$, which was determined by micro-Raman scattering spectra of the three samples. In these Raman spectra, the $398\ cm^{-1}$ vibration mode is dominant in the region of 300–3000 cm^{-1}. In the fit, we had chosen $\Delta E = 3330\ cm^{-1}$, because the ΔE was taken as a variable parameter and all the energies of the three samples obtained were about $3330\ cm^{-1}$. The fitting lines go well with the data dots, which are shown as solid lines in Fig. 5b. The parameters W_{rad} and $W_{nr}(0)$ obtained by fitting are listed in Table 1.

It is well known that the presence of water or solvent molecules in the coordination cage of RE ion is often responsible for quenching of the luminescence via multiphonon relaxation. In the hybrid spheres, the overall RE complex molecules were incorporated into the silica matrix and there exists water molecules. However, in the metal complex system, the macrocyclic ligands cage shield the RE ions from the solvent quenching [20,23,24]. We also fitted the experimental data by taking $\hbar\omega = 3420$ and $\hbar\omega = 1100\ cm^{-1}$, which correspond to the energies of v(O–H) and v(Si–O) vibrations, respectively. The experimental data cannot be reasonably fitted. This fact can be interpreted as the less contribution of water and silica matrix to the multiphonon relaxation process in the hybrid spheres.

As the experimental results shown above, at the same temperatures, the luminescence lifetimes of the $^5D_0$ emitting level of Eu^{3+} ions are decreased with the increase of refractive indices of the surrounding dielectric polymers. As can be seen in Table 1, with the increase of refractive index, a clear increase of the radiative transition rate of Eu^{3+} ion is observed, while the nonradiative transition rate has little change. The modification of the spontaneous emission rate can be explained by the presence of dielectric boundaries, which modifies the local electric field fluctuations and changes the local optical density of states at the position of the Eu^{3+} ions in the hybrid spheres. According to Fermi's Golden Rule, the radiative decay rate can be written in terms of a local density of states ρ as [6,7,25]

$$W_{rad}(r) = \frac{\pi\omega}{\hbar\varepsilon(r)}|D|^2\rho(\omega, r), \tag{4}$$

where $\varepsilon(\mathbf{r})$ is the position-dependent dielectric constant, ω is the transition frequency, $|D|^2$ is the atomic dipole matrix element of the transition involved, and $\rho(\omega,r)$ describes the local optical density of states. The matrix element $|D|^2$ depends on the local environment of the emitting Eu ions and is not influenced by the optical properties of the interface or the presence of the polymers outside the silica shell. Therefore, the modification of the radiative decay rate is determined by the variation of the local optical density of states $\rho(\omega, r)$, which are influenced by the optical surroundings. When the hybrid spheres are dispersed in different polymers, the presence of the dielectric boundaries changes the local electric field fluctuations, resulting in the modification in the spontaneous emission rate.

4. Conclusions

Europium complex nanoclusters were encapsulated inside silica colloidal spheres by a wet-chemical method. The spheres present strong characteristic emissions of Eu^{3+} ions, and the fluorescence decay time decreases when the spheres are dispersed in two dielectric polymers. Temperature-dependent decay processes were investigated, which reveals that the spontaneous emission rate of the Eu ions in the sphere-polymer systems is enhanced compared to that of free spheres in air. This modification is due to the presence of dielectric boundaries that changes the local electric field fluctuations.

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