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Laser selective spectroscopy of europium complex embedded in colloidal silica spheres

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Abstract

Monodisperse colloidal silica spheres embedded with Eu(DBM)$_3$phen complex were synthesized by a modified Stöber method. The europium complex dispersed in the hybrid spheres display the characteristic luminescence of the Eu^{3+} ions. Low-temperature laser selective spectroscopy and decay dynamics were performed to study the luminescence properties of the pure europium complex and the hybrid spheres. Our results indicate that the method of incorporating the Eu complex into the SiO$_2$ spheres may have a great potential to reduce the contribution of non-radiative processes and optimize the luminescence quantum yield of lanthanide complexes.

1. Introduction

Silica-coated colloidal particles have stimulated great research interest due to their tunable optical [1–3], electric [4,5], magnetic [6,7], and catalytic properties [8]. These excellent functions make the colloids widely used in many fields such as biology [9,10], photonic crystal [11–13], and material science [14]. The silica colloids can be easily processed as monodisperse spheres with smooth surfaces, thus can form regular three-dimensional (3D) photonic crystals via self-assembly [15]. Photonic crystals with a complete or almost complete band gap have the ability to manipulate both the propagation and the spontaneous emission of photons in new and exciting ways. Such an effect can be studied by placing luminescent probes inside the crystal [16]. Commonly, laser dyes can be chemically incorporated into the SiO$_2$ particles during synthesis for this purpose [17,18]. 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 [19]. 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 addition, RE ions do not exhibit photo bleaching commonly observed for laser dyes. Thus, RE-doped colloids appear to be ideal probes in photonic crystals.

So far, two methods have been used to incorporate RE ions as luminescent probes in colloids, i.e. ion implantation [20] and wet-chemical processing [19]. The ion implantation can be used to put the RE ions at well-defined depth in monodisperse spherical particles, while it is difficult to gain large amount of optical particles. The acid-catalyzed wet-chemical reaction can introduce the RE ions into the SiO$_2$ spheres, but results in large size polydispersity. Although the base-catalyzed reaction (Stöber method) can be well controlled to yield the spherical SiO$_2$ particles with low size polydispersity [21], it fails to incorporate RE ions directly under base condition because the RE ion immediately forms an insoluble RE hydroxide. Dood et al. [19] has exploited the acid-based wet chemical synthesis route using a seeded growth process to obtain monodisperse RE ions doped silica colloids with large quantities. However, the RE

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ions inside the silica network are exposed to the strong vibrations of Si–O bonds, which increase the non-radiative transition probability and quench the luminescence, resulting in a relatively low luminescence efficiency. RE complex with π-conjugated ligands such as β-diketonnato is a kind of material with excellent luminescence properties. The RE ions surrounded by the ligands are excited via intramolecular energy transfer from the triplet excited states of the ligands, which leads to a high inner quantum efficiency [22]. In this Letter, the europium complex as a luminescent probe was introduced into the monodisperse colloidal silica spheres by a modified Stöber method. In the hybrid spheres, the Eu complex molecules or clusters are scattered in the silica host and still remain their original molecular conformations as in the pure Eu complex. Low-temperature laser selective spectroscopy was performed to study the luminescence properties for both the Eu complex and the hybrid sphere.

2. Experimental

The monodisperse colloidal SiO_2 spheres embedded with RE complex were formed by two steps process using the base-catalyzed wet-chemical synthesis. First, the Eu tris(dibenzoylmethanato)phenanthroline [Eu(DBM)$_3$phen] complex was prepared as follows. Three mol of the negative charged dibenzoyl methane (Aldrich) unit and 1 mol of $EuCl_3$ ethanol solution are used to form 1 mol of the hexacoordinated neutral complex. One additional mol of 1,10-phenanthroline is used to get the stable and water free octacoordinated form. The precipitate was obtained under weak basic condition, washed with absolute ethanol thoroughly. Second, the silica colloid is formed by the Stöber method [21], i.e., base-catalyzed hydrolysis and polycondensation of tetraethoxysilane (TEOS). The purified complex was dissolved into acetone (Aldrich). After complete dissolving, the mixture was poured into ethanol bath containing $NH_3 \cdot H_2O$ (Aldrich, 28% NH_3) and distilled water under well stirring for an additional hour. A stable sol formed. Then a tetraethoxysilane (Aldrich) solution was added drop wise to the stable sol under continuous stirring for an hour. The samples were rinsed thoroughly with ethanol and dried in air. The white particles were acquired. A set of spherical particles with different diameters can be obtained through the well-controlled concentrations of the reagents.

The colloidal spheres were characterized by using a JEOL-2010 transmission electron microscope (TEM). Infrared absorption spectra in KBr suspensions were registered by a Bio-Rad Fourier transform infrared (FTIR) spectrometer, in the range of 4000–400 cm^{-1}. Room-temperature emission spectra and luminescence decay were measured under the excitation of a third harmonic (355 nm) of a Nd:YAG pulsed laser. Laser selective spectroscopy was perform at 77 K by mounted the sample in the liquid nitrogen. A Rodamine 6G dye laser pumped by a second harmonic (532 nm) of a Nd:YAG pulsed laser was used as the excitation source. Photoluminescence signals were dispersed with a Spex 1403 double-grating monochromator, detected by a photomultiplier, averaged with a boxcar integrator and processed by a computer.

3. Results and discussions

The TEM images of the Eu(DBM)$_3$phen/SiO_2 colloidal spheres are shown in Fig. 1. As can be seen in Fig. 1a, the sample displays a spherical morphology with a uniform diameter of 300 nm. Each hybrid sphere possesses a smooth surface. The size polydispersity was estimated to be 3% by analyzing 50 particles. Fig. 1b presents a magnified image of an individual sphere. Although it looks like a core-shell structure, we believe that inside the sphere the Eu(DBM)$_3$phen complex is interconnected with the SiO_2 host and there is no obvious interface. The diffraction contrast can be identified between the central part and the outer layer. The central part consists of many light spots which may originate from some big europium complex clusters, while the outer shell was mainly composed of silica. The hybrid spheres were synthesized by the modified Stöber method, while the Eu complex can form optically active

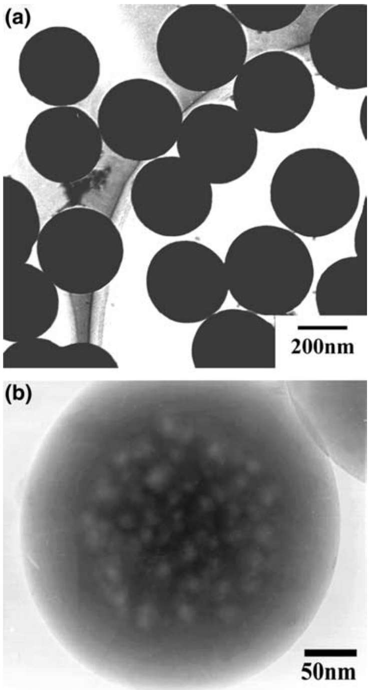

Fig. 1. (a) TEM image of the hybrid spheres. (b) Magnified TEM image of an individual sphere.

clusters under the base condition. In our experiments, the diameter of the spheres could be tuned from 30 to 300 nm through the well-controlled concentrations of the reagents. It should be noted that the introduction of rare earth complex do not change the spherical morphology and the smooth surfaces, although the sphere size deviates a little from the original data described in [21]. In the following discussions, we focus our attention on the luminescence and laser spectroscopy of the 300 nm hybrid spheres.

Fig. 2a presents the low-temperature (77 K) emission spectra under the 355 nm excitation which corresponds to the absorption of the β-diketonnato ligands. The hybrid spheres present the characteristic emissions of Eu^{3+} ions. The peak at 611 nm is due to the forced electric dipole transition ($^5D_0 \rightarrow {}^7F_2$), which is allowed on condition that the europium ion occupies a site without inverse center. Its intensity is hypersensitive to crystal environments. The peak around 580 nm corresponds to the $^5D_0 \rightarrow {}^7F_0$ transition, and those near 590 nm derive from the allowed magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$). In the emission spectrum of the hybrid spheres, the emission peak near 618 nm corresponding to one of the Stark splittings of $^5D_0 \rightarrow {}^7F_2$ transition becomes relatively weak, compared with that of the pure Eu(DBM)$_3$phen complex. The luminescence decay curves at the liquid nitrogen temperature were shown in Fig. 2b. The decay dynamics of the hybrid spheres was very different from that of the Eu(DBM)$_3$phen complex. The decay curve for the pure Eu(DBM)$_3$phen complex can be well fitted with a single exponential function and the lifetime of 473 ± 1.9 μs was obtained. But for the hybrid spheres, the decay curve cannot be fitted with single exponential function, as denoted by the dashed line, while a biexponential function may reproduce the decay data well and lead to two lifetimes of 224 ± 7.6 and 626 ± 7.1 μs. The relative contribution of the exponentials to the decay of the hybrid spheres is about 0.45:0.56. Energy transfer process between different Eu^{3+} ions can be neglected in Eu(DBM)$_3$phen/SiO$_2$ system. Therefore, the decay process indicates that at least two types of emission centers are contained in the hybrid spheres. In order to confirm the proposition, laser selective spectroscopy was performed to distinguish the emission centers in the hybrid spheres.

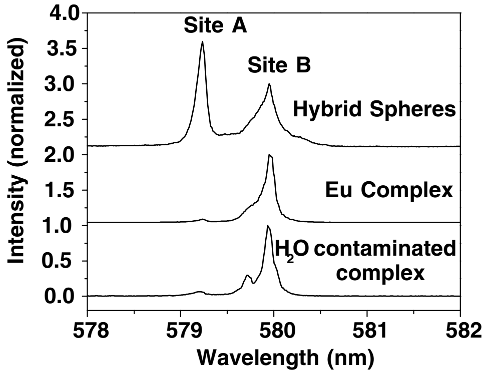

Fig. 3. Low-temperature (77 K) excitation spectra for the hybrid spheres, the pure Eu(DBM)$_3$phen complex and the H_2O contaminated complex by monitoring the emission wavelength of 611 nm.

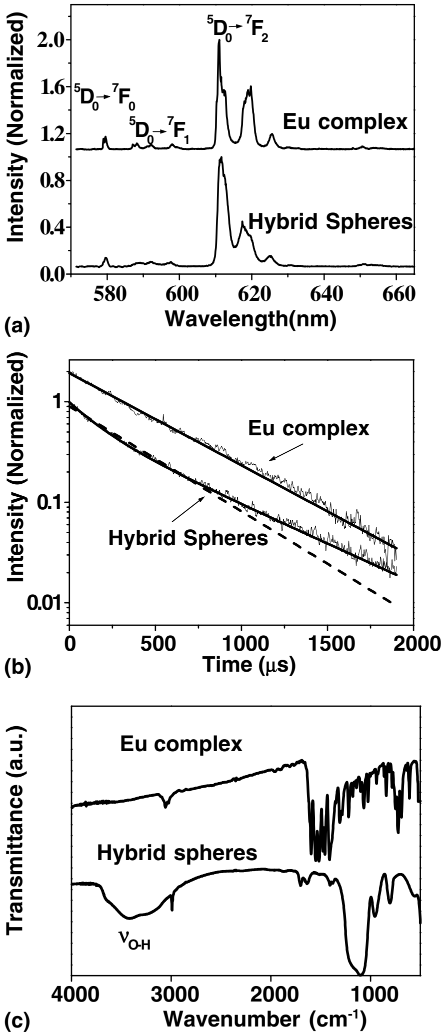

Fig. 2. (a) Emission spectra and (b) luminescence decay curves for the pure Eu complex and the hybrid spheres under the 355 nm excitation at 77K. (c) Infrared absorption spectra of the pure Eu(DBM)$_3$phen complex and the hybrid spheres.

Fig. 3 gives the low-temperature excitation spectra for both the pure Eu(DBM)$_3$phen complex and the hybrid spheres, where the excitation peaks correspond to the transition $^7F_0 \rightarrow {}^5D_0$. The excitation spectra were taken by monitoring the emission wavelength of 611 nm, corresponding to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. An intense peak (579.94 nm, marked B) with a relatively weak peak (579.22 nm, marked A) at the high-energy side was observed in the spectrum of the Eu complex. The two peaks may denote two species (labeled as SA and SB, respectively) of the Eu complex. For the pure Eu complex, the luminescence of SA can be neglected due to its so less contribution to the 611 nm emission, which illustrates that the luminescence decay follows a single exponential process. However, in the case of the hybrid spheres, two intense peaks were clearly observed at the same positions. The luminescence of SA was enhanced greatly compared with the europium complex, thus both SA and SB make equivalent contributions to the 611 nm emission. Accordingly, the corresponding decay process follows multi-exponential functions.

It is well known that once the ligands (including H_2O molecules) coordinate with the Eu^{3+} ions, they may play important roles in the luminescence properties of europium complex [23–26]. The Eu(DBM)$_3$phen complex used to fabricate the hybrid spheres is a kind of non-hydrated complex, it can be proved by the absence of O–H stretching mode in the IR absorption spectrum for the pure Eu(DBM)$_3$phen complex in Fig. 2c. In fact, the hybrid spheres contain trace water due to the fabrication method (hydrolysis of tetraethoxysilane). The peak related to the H_2O vibrational mode appears at ~3400 cm^{-1} in the IR absorption spectrum of the hybrid spheres. However, the water molecules in the hybrid spheres do not modify the relative luminescence of SA and SB species, which can be confirmed by the following experiments. According to the synthesis process of the hybrid spheres, another sample, H_2O contaminated Eu(DBM)$_3$phen, was prepared to eliminate the influence of water. The sample was obtained by dissolving the pure Eu(DBM)$_3$phen into acetone, then pouring the solution into ethanol bath containing distilled water to get the precipitate. The excitation spectrum performed for the H_2O contaminated complex is shown in Fig. 3b, which is similar to that of the pure complex. The peak at 579.22 nm is rather weak and the luminescence of SA makes less contribution to the 611 nm emission in the H_2O contaminated complex. The comparison of the excitation spectra confirms that the water molecules in the hybrid spheres have nothing to do with the relative luminescence change of SA and SB species in the hybrid spheres. The luminescence enhancement of SA relative to SB does occur in the hybrid spheres, the reason for which is still pending.

Regardless of the intensity change, laser selective spectroscopy confirms that both SA and SB in hybrid spheres remain the same molecular conformations to those in the pure Eu complex. Fig. 4 presents the low-temperature (77 K) emission spectra of the Eu complex and the hybrid spheres by exciting the peak positions of SA (579.22 nm) and SB (579.94 nm). For both SA and SB, the emission intensities, the line-shapes, the numbers and peak positions of the Stark splittings in the Eu complex are perfectly identical with those in the hybrid spheres. In view of the high sensitivity of Eu^{3+} ion as a luminescent probe to its local structure [27], the compatibility in spectral properties indicates that SA and SB in the hybrid spheres still remain their original molecular conformations as in the pure Eu complex.

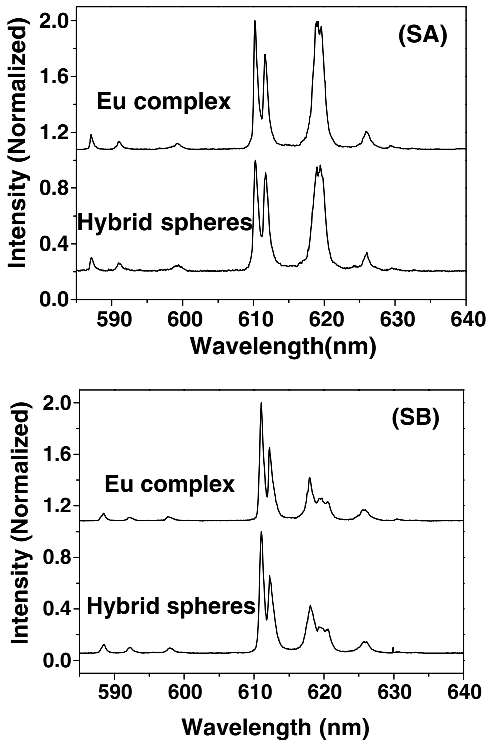

Fig. 4. Low-temperature (77 K) emission spectra of the Eu(DBM)$_3$phen complex and the hybrid spheres by exciting the peak positions of SA (579.22 nm) and SB (579.94 nm).

The low-temperature (77 K) decay curves of optically active Eu^{3+} ions embedded in the hybrid spheres and in the complex are measured by exciting the peak positions of SA and SB, as shown in Fig. 5. Each decay curve can be well approximated by a single exponential function. The luminescence lifetimes (τ_{obs}) obtained were listed in Table 1. As can be seen, the lifetimes of SA and SB in the hybrid spheres are longer than those in the pure Eu complex. Meanwhile, the two lifetimes for the hybrid spheres under the excitation of the $^7F_0 \rightarrow {}^5D_0$ absorption peaks deviated from those when exciting the absorption of ligands (355 nm). It is well known that the $^5D_0 \rightarrow {}^7F_0$ transition appears only when europium ions occupy at certain symmetry sites. Thus, the excitation peaks in Fig. 3 may not exhibit all the emission species contained in the hybrid spheres, while the luminescence with the excitation at 355 nm originate from all the emission species in the samples. This also means that the decay components of the hybrid spheres in Fig. 2 may include species which cannot be well observed in the excitation spectra. The total luminescence decay rate can be written as

$$W = W_r + W_{nr}, \tag{1}$$

where W_r and W_{nr} denote the radiative and nonradiative transition rates, respectively. On one hand, it is well

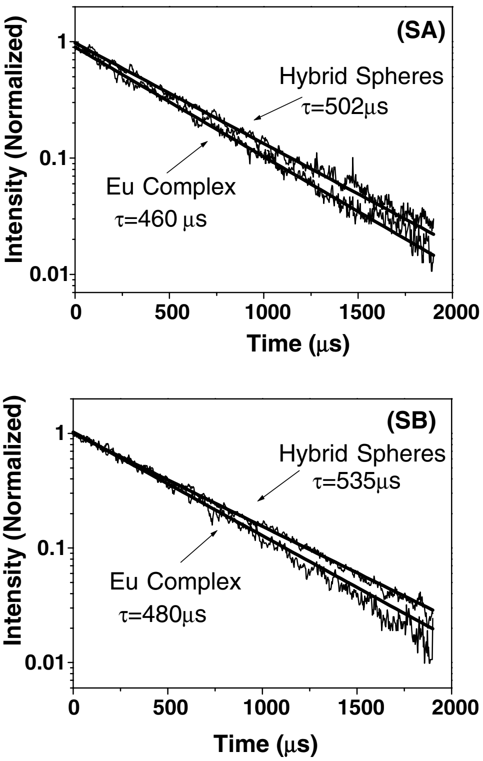

Fig. 5. Low-temperature (77 K) luminescence decay curves of SA and SB in the Eu complex and the hybrid spheres.

known that the decay times of the Eu^{3+} ion is highly dependent on its local structure such as the site symmetry and the nearest ligands. Laser selective spectroscopy have confirmed that the local structures around the Eu^{3+} ions remain unchanged. However, as described by Li et al. [28] in a similar material system, the relatively rigid structure of the silica sphere may limit the vibrations of the ligands, which leads to a decrease of the non-radiative transition rate (W_{nr}) caused by ligand vibrations. On the other hand, the spontaneous emission rate of an electric dipole located at an arbitrary location in a sphere of a given diameter has been calculated analytically by Chew [29]. According to Chew's calculations, the radiative decay rate W_r inside an infinitesimally small sphere is then expressed as

$$\lim_{R\to 0} W_r = [9/(n^2+2)^2](W_r^{\text{bulk}}/n), \tag{2}$$

where W_r^{bulk} represents the radiative decay rate of the emitter inside a bulk dielectric and n is the refractive index of the dielectric. Schniepp and Sandoghdar [30] have explained this result by considering Fermi's golden rule and demonstrated experimentally that the spontaneous emission rate of ions placed in dielectric spheres is substantially reduced as one crosses the border from the superwavelength regime of Mie to the nanoscopic realm of Rayleigh scattering. In our experiments, the pure Eu complex forms molecular crystal with the crystallite size in the order of micrometers or larger. It can be regarded as a bulk dielectric ($n \approx 1.6$). Thus, the Eu complex embedded in the 300 nm SiO_2 spheres ($n \approx 1.5$) may possess a reduced radiative decay rate regardless of the small discrepancy in refractive index between the pure Eu complex and the hybrid spheres. The decreases in the radiative and nonradiative decay rates mentioned above both make contribution to the longer lifetime in the hybrid spheres. However, the possibility of additional effects cannot be completely eliminated. For example, the presence of dielectric boundaries changes the local electric field fluctuations and modifies the spontaneous emission rate [31]. In such a case, the long fluorescence lifetime can be partly attributed to the fact that the Eu complex embedded SiO_2 spheres are surrounded by air, causing the local optical density of states in the hybrid spheres to be lower than that of the bulk Eu complex [32,33].

From the corrected emission spectra at 77 K, the radiative lifetime (τ_R) and the quantum yield (Φ_{Ln}) of the two species in both the Eu complex and the hybrid spheres are calculated. The method used is described in details in [34] by Werts et al. The calculated results were all listed in Table 1. The quantum yield expresses how well the radiative processes compete with non-radiative processes

$$\Phi_{LN} = \frac{\tau_{obs}}{\tau_R}. \tag{3}$$

In our experiments, the quantum yields of SA and SB in the hybrid spheres are higher than those in the pure Eu complex. The higher quantum yields indicate that the luminescence pathway for Eu^{3+} in the hybrid spheres is more competitive with the channels of non-radiative depopulation of the excited state. The method of incorporating the Eu complex into the SiO_2 spheres may have a great potential to reduce the contribution of non-radiative processes and optimize the luminescence quantum yield of lanthanide complexes.

Table 1
Low-temperature luminescence lifetimes (τ_{obs}) of SA and SB in the hybrid spheres and the Eu complex excited at 579.22 and 579.94 nm, respectively

	SA			SB		
	τ_{obs} (μs)	τ_R (μs)	Φ_{Ln}	τ_{obs} (μs)	τ_R (μs)	Φ_{Ln}
Eu complex	460 ± 2.6	932	0.493	480 ± 2.6	1000	0.48
Hybrid spheres	502 ± 2.4	996	0.504	535 ± 1.9	1039	0.515

Radiative lifetimes (τ_R) calculated on basis of the low-temperature emission spectra, and the luminescence quantum yield (Φ_{Ln}) is found using Eq. (3).

4. Conclusions

By a modified Stöber method, the Eu(DBM)$_3$phen complex was introduced into the monodisperse silica colloids, forming the optically active hybrid spheres. TEM measurements confirm that each sphere possesses a spherical morphology and a smooth surface. Under the 355 nm excitation, the hybrid spheres present strong characteristic emissions of Eu^{3+} ions. Low-temperature luminescence decay curves indicate that the hybrid spheres follow a decay process different from that of the pure Eu(DBM)$_3$phen complex. Low-temperature laser spectroscopy was performed to distinguish the emission centers in the hybrid spheres. For each of the two species, SA and SB, the spectral properties in the Eu(DBM)$_3$phen complex are perfectly identical with those in the hybrid spheres, which means that SA and SB in the hybrid spheres still remain their original molecular conformations as in the pure Eu(DBM)$_3$phen complex. Several effects may result in the reduction of both radiative and nonradiative decay rates in the hybrid spheres. Accordingly, the lifetimes of the two species in the hybrid sphere are longer than those in the Eu(DBM)$_3$phen complex. The quantum yields of the Eu(DBM)$_3$phen complex and the hybrid spheres were calculated and the results show that the hybrid spheres possess higher quantum yields.

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