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Convenient preparation and photoluminescence properties of polymer microspheres based on europium complex

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Abstract The preparation and properties of luminescent polystyrene (PS) composite microspheres with rare earth (RE) organic complexes Eu(DBM)$_3$(Phen) (DBM = dibenzoylmethanate, Phen = 1,10-phenanthroline) entrapped in the microspheres are presented. The luminescent composite microspheres are readily obtained by the soaking pre-existing particles method. The morphologies of resulting composite microspheres are characterized by field emission scanning electron microscope. The photoluminescence properties of the composite microspheres are also investigated. The results show that the existence of the rigid PS matrix can improve the photostability of the RE complex under UV irradiation and elongate the fluorescence lifetime of the RE complex. The improvement of the properties, the convenient preparing method, and brilliant red emission make the composite microspheres promising candidates for *in cellulo* applications.

Introduction

Luminescent rare earth (RE) organic complexes have gained increasing attention in fundamental studies and technological applications because of their unique optical properties, such as extremely sharp emission bands, long lifetime, and potential high internal quantum efficiency. Their excellent photoluminescence properties endow them with considerable applications in tracking assays [1–3] or responsive probes [4–7]. Recently, lanthanide complexes have been reported that are taken up by live cells and can be observed by fluorescence-based microscopy techniques [8–12]. However, pure RE complexes usually do not have good thermal stability and high mechanical strength, which strongly restricts them to promising extensive photophysical applications. To overcome these shortcomings, different methods to introduce RE complexes into organic, inorganic, or organic/inorganic hybrid matrixes [13–17] have been developed. An interesting result is that the RE complexes incorporated in the polymer matrixes show improved photoluminescence properties and thermal stability [18–24]. Moreover, recent progresses in nanoscience and nanotechnology provide a panel of synthetic methods that allows one to control both the size and the functionalization of nanoparticles, thus permitting their linkage to target molecules and bioconjugation. Of the many different polymers, polystyrene (PS) which is rigid, transparent, and easy to process (shrinkage is low) can provide a rigid environment to protect the pure complexes. In this case, it is necessary to prepare PS particles based on europium complex which may be good candidates for *in cellulo* applications.

To date, several different synthesis and fabrication methods have been developed to incorporate fluorescent dyes into polymer particles, such as copolymerization with reactive fluorophores [25, 26], entrapment of classical dyes introduced in the monomer before polymerization [27–30], or by soaking pre-existing particles [31–34]. Among these methods, the later method is a simple, versatile, and effective technique to incorporate water-insoluble dyes within the core of hydrophobic particles in an aqueous environment. The dye-load can be easily controlled by the soaking conditions, so that particles containing tunable numbers of dye-per-particle are accessible from one set of particles.

In this article, luminescent composite microspheres of Eu(DBM)$_3$(Phen)/PS (DBM = dibenzoylmethanate, Phen = 1,10-phenanthroline) were prepared by the soaking

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pre-existing particles method. The fluorescence properties of the composite microspheres were studied in comparison with that of the pure europium complex in detail. The presence of the polymer matrixes can improve the stability of the RE complex under UV irradiation and elongate the fluorescence lifetime of the RE complex.

Experimental procedure

Materials

2,2-Azobis(isobutyronitrile) (AIBN), styrene, and acrylic acid were purchased from Tianjin chemical reagents Corp. (China). Poly(vinylpyrrolidone) (PVP, Mw = 1,300,000), dibenzoylmethanate (DBM), and 1,10-phenanthroline (Phen) were purchased from Aldrich. Styrene was washed with 1 M NaOH and deionized water to remove inhibitor, purified through vacuum distillation, and stored at −20 °C before use. Acrylic acid was added to anhydrous $MgSO_4$ to remove residual water, purified through vacuum distillation, and stored at −20 °C before use. The water used in our study was deionized. In all the experiments, the chemicals were analytical grade and used without any further purification.

Synthesis of europium organic complexes

Europium chloride ($EuCl_3$) was prepared by dissolving Eu_2O_3 in concentrated hydrochloric acid (HCl). $Eu(DBM)_3$(Phen) was synthesized and characterized according to the method described in Ref. [35].

Synthesis of polymer microspheres

The monodisperse PS microspheres were subjected to dispersion polymerization method in ethanol medium with PVP as stabilizer and AIBN as initiator. 90 mL ethanol solution with 0.4 g of PVP was first poured into the flask. After the temperature was increased to 70 °C under nitrogen atmosphere, 5 mL of styrene and 0.1 mL of acrylic acid containing 0.06 g of AIBN were charged. The polymerization reaction was kept 24 h at 70 °C under nitrogen atmosphere. After cooling to room temperature, the resulting precipitates were washed repetitively with deionized water and absolute ethanol, and then dried at 40 °C under vacuum.

Synthesis of luminescent composite microspheres

Appropriate volumes of $Eu(DBM)_3(Phen)/CH_2Cl_2$ solution (0.01 g/mL) was added to the aqueous PS microspheres suspensions (10 mL). The sample tube was then uncapped, and the solution was stirred in the dark at room temperature for 24 h to allow the diffusion of the dye within the polymer matrix and the progressive evaporation of dichloromethane. The dispersion of microspheres remained stable during loading. After exhaustive evaporation of the solution, the stained microspheres were repeatedly centrifuged and washed by alcohol for three times to remove the residual fluorescent dyes.

Characterization

Field emission scanning electron microscope (FESEM, XL30, FEI) was applied to observe the morphologies of PS microspheres. The fluorescence excitation and emission spectra were obtained with a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. In the measurements of fluorescence dynamics, 355-nm light from the Nd^{3+}:YAG (yttrium aluminum garnet) laser combined with a third-harmonic generator was used as the pump. An oscilloscope was used to record the decay dynamics.

Results and discussion

The RE organic complexes used in this study were synthesized according to a general method [35]. Then, the RE-capped luminescent composite microspheres were prepared in two steps. First, the PS microspheres were obtained by dispersion polymerization of styrene in the presence PVP as stabilizer and AIBN as initiator in ethanol medium. Herein, the addition of acrylic acid avoided the conglutination of the PS microspheres. Furthermore, the size of polymer particles can be controlled by varying the feed ratio of styrene and acrylic acid, the initiator concentration, etc. Figure 1a and b shows FESEM images of PS microspheres. As shown in Fig. 1a and b, PS microspheres have uniform diameter and regular morphology. In a second step, the soaking pre-existing particles method was utilized to form highly bright fluorescent beads. Fluorescent PS microspheres are readily obtained by swelling the polymer particles with dichloromethane solutions of europium organic complexes. Dichloromethane swells the polymer particles and, thereby, allows the diffusion of the hydrophobic dye within the shrinked particles after evaporation of the solvent [33]. Note that the extent of swelling depends strongly on the amount of dichloromethane solution. Figure 2 shows FESEM images of luminescent composite microspheres. When adding into 0.6 mL of dichloromethane solution, the obvious conglutination of the PS microspheres appears (Fig. 2a). With the decrease of dichloromethane solution, the conglutination is rarely obtained (Fig. 2b). When adding into 0.3 mL of

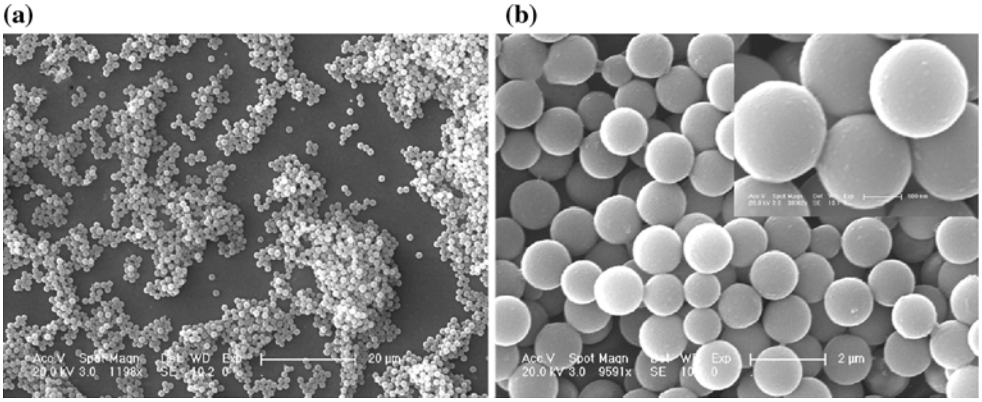

Fig. 1 **a** and **b** low and high magnification FESEM images of PS microspheres

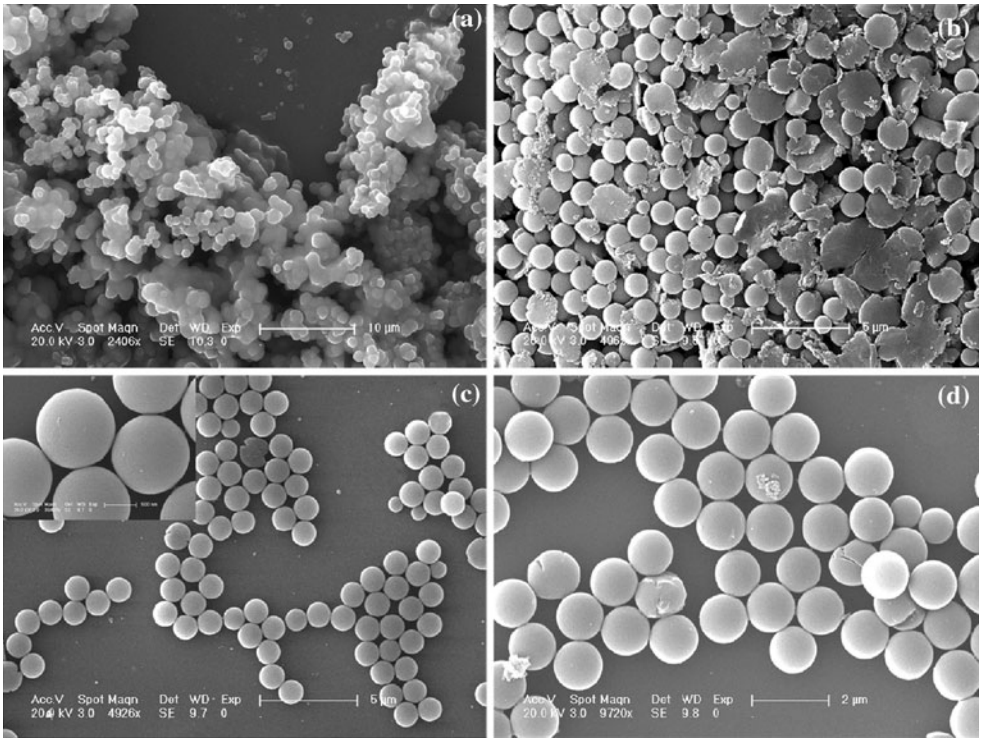

Fig. 2 FESEM images of luminescent composite microspheres swelled by different volumes of dichloromethane solution (**a** 0.60 mL, **b** 0.45 mL, **c** 0.30 mL, and **d** magnified FESEM image of 0.3 mL)

dichloromethane solution, the resulting microspheres show more uniform diameter and regular morphology; therefore, 0.3 mL of dichloromethane solution is chosen as an optimum experimental condition.

The fluorescent properties of the Eu(DBM)$_3$(Phen)/PS composite microspheres were investigated and compared with that of the pure Eu(DBM)$_3$(Phen) complex. Figure 3 depicts the excitation and emission spectra of these samples. In all the excitation spectra, broad bands that appeared in the range of 250–500 nm are assigned to the π–π* transitions of conjugated double bonds in the aromatic β-diketonate dibenzoylmethane (DBM) ligands [36]. However, the differences in the surrounding also lead to differences in the fluorescent properties. First, in the pure europium complex, two bands are identified, peaking at 314 and 411 nm, respectively. In comparison to the pure complex, for the Eu(DBM)$_3$(Phen)/PS composite microspheres, the excitation bands blue shift and split obviously into two components, with peaks at around 281 and 381 nm, respectively. This phenomenon can be ascribed that due to the existence of the surrounding PS media in the composite microspheres, the site symmetry of the Eu^{3+} ion is distorted and decreased [37]. Second, in the pure complexes the $^7F_0$–$^5D_2$ excitation line appears, while in the composites the line disappears,

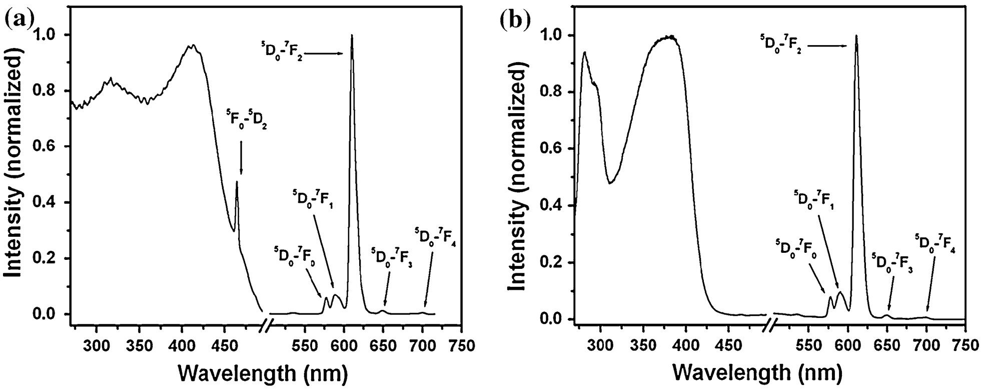

Fig. 3 Excitation spectra (λem = 610 nm) and emission spectra (λex = 365 nm) for the $^5D_0 \rightarrow {}^7F_J$ transitions of Eu^{3+} in pure Eu(DBM)$_3$(Phen) (**a**) and Eu(DBM)$_3$(Phen)/PS composite microspheres swelled by 0.3 mL of dichloromethane solution (**b**)

which suggests that in the composites the f–f inner-shell transitions are quenched through the non-radiative energy transfer from the higher excited states to some uncertain defect levels, substituting for the non-radiative relaxation to $^5D_0$ [21, 22].

In all the emission spectra, characteristic emission peaks of the europium ion are observed and which are assigned to the transitions $^5D_0 \rightarrow {}^7F_0$ (578 nm), $^5D_0 \rightarrow {}^7F_1$ (590 nm), $^5D_0 \rightarrow {}^7F_2$ (610 nm), $^5D_0 \rightarrow {}^7F_3$ (650 nm), and $^5D_0 \rightarrow {}^7F_4$ (700 nm) with the $^5D_0 \rightarrow {}^7F_2$ transition at 610 nm being the dominant emission peak. The five expected peaks for the $^5D_0 \rightarrow {}^7F_{0\text{–}4}$ transitions are all well resolved, and the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is very intense, pointing to a highly polarized chemical environment around the Eu^{3+} ion that is responsible for the brilliant red emission of these samples. And the $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic-dipolar transition and is insensitive to the local structure environment. Thus, the intensity (the integration of the luminescent band) ratio of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition can be used as a reference to compare different chemical environments of europium complex, that is, it can be used as an indicator of Eu^{3+} site symmetry [38]. The ratios in the pure complex and composite microspheres are determined to be 13.78 and 10.39, respectively. It is obvious that the intensity ratio of $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition in the composites decreases a little over the pure complex. The results suggest that incorporating Eu(DBM)$_3$(Phen) into PS decreases the symmetry of the coordination environment for Eu^{3+} ions.

The instability of RE complexes under UV irradiation is one of the problems for their practical application. To compare the photoluminescence stability of the Eu(DBM)$_3$(Phen)/PS composite microspheres and corresponding pure complexes (in the solid state), ultraviolet light irradiation-induced spectral changes were investigated, and the dependence of emission intensity on irradiation time at room temperature was given in Fig. 4. The monitored emission wavelength is 610 nm ($^5D_0 \rightarrow {}^7F_2$) for Eu^{3+}-centered luminescence (λex = 365 nm). As shown in Fig. 4, the emission intensity of $^5D_0 \rightarrow {}^7F_2$ in the pure complex decreases remarkably with the increasing exposure time, whereas in complex microspheres the fluorescence intensity is weakened with a slower rate of decline than for pure complexes. Thus, incorporating europium complexes into PS polymer matrixes could improve the photoluminescence stability under UV irradiation. This result has also been observed by the previous literatures [20–24] and can be interpreted as that the PS can provide a relatively rigid environment for the complexes to reduce the energy consumption on vibration of ligands and intermolecular collision of the complexes. Thus, the rigid PS can protect the complexes from decomposing under UV irradiation.

The time-resolved intensity–decay curves of the composite microspheres and corresponding pure complexes (in the solid state) monitored at the $^5D_0 \rightarrow {}^7F_2$ transition (610 nm) of Eu^{3+} ion at room temperature were studied at room temperature. The fluorescence decay curves of composite microspheres and corresponding pure complexes are shown in Fig. 5. And the fitting parameters of these decay curves are summarized in Table 1. The fluorescence decay curve in pure complexes and composite microspheres could be fitted to a single- and bi-exponential decay curve,

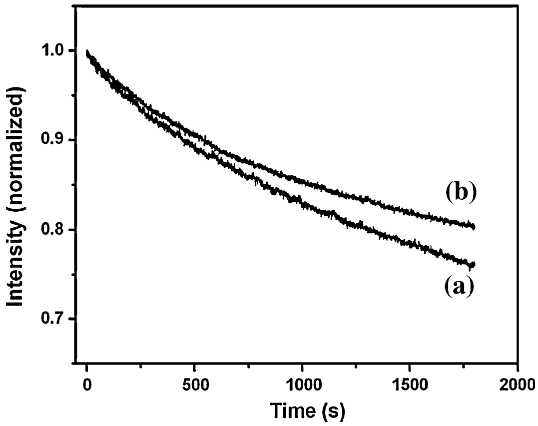

Fig. 4 Dependence of normalized intensity at 610 nm on irradiation time in pure Eu(DBM)$_3$(Phen) (*a*), Eu(DBM)$_3$(Phen)/PS composite microspheres swelled by 0.3 mL of dichloromethane solution (*b*). The samples were irradiated with 365 nm light

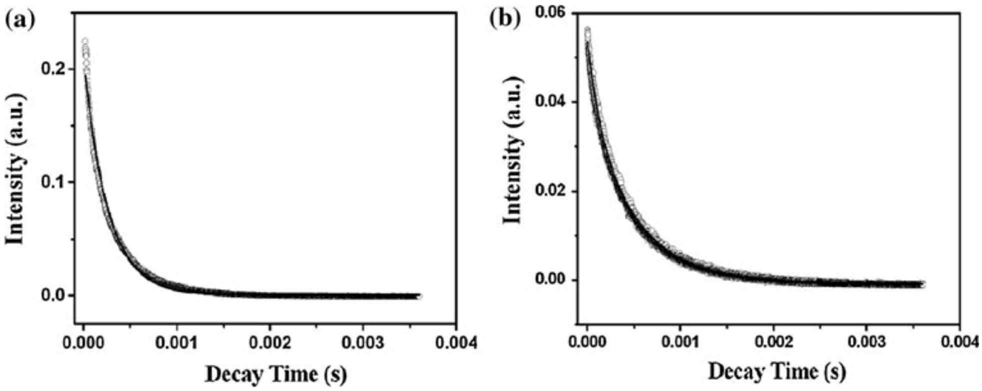

Fig. 5 Fluorescence decay curves of the $^5D_0 \rightarrow {}^7F_2$ transitions (λem = 610 nm) in pure Eu(DBM)$_3$(Phen) (**a**) and Eu(DBM)$_3$(Phen)/PS composite microspheres swelled by 0.3 mL of dichloromethane solution (**b**)

respectively [24, 39]. As seen from Table 1, we can find that the fluorescent lifetime of composite microspheres is longer than that of the corresponding pure complexes. This observation is in agreement with study carried out on RE complex/polymer system, which have also been shown to exhibit long fluorescent lifetime as compared with pure complexes [14, 20–24]. When the RE complex is swelled into the PS matrixes, the existence of the rigid PS matrix may bestow a certain degree of restriction on the rotation and vibration of RE complex molecules, thus reducing the non-radiation deactivation process of the electronic excitation state and elongating the fluorescence lifetime of composite microspheres.

Conclusion

Rare earth organic complex-doped fluorescent composite microspheres with brilliant red emission were prepared by the method of soaking pre-existing particles. The results show that it is a convenient and efficient approach for the preparation of fluorescent composite polymer microspheres. This study of the properties of composite microspheres also shows that PS polymer is valuable matrixes for improving the photostability of the RE complex under UV irradiation and elongating the fluorescence lifetime of the RE complex. Thus, we believe that the versatile method and the resulting composite microspheres might have potential biological applications.

Table 1 Time-resolved intensity decay constants for pure Eu(DBM)$_3$(Phen) and Eu(DBM)$_3$(Phen)/PS composite microspheres swelled by 0.3 mL of dichloromethane solution

Samples	α_1	τ_1 (ms)	α_2	τ_2 (ms)	τ (ms)	R^2
Eu(DBM)$_3$(Phen)	0.207	0.26	0.040	0.52	0.26	0.9928
Eu(DBM)$_3$(Phen)/ PS	0.015	0.14			0.33	0.9986

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