

In situ composition and photoluminescence of Tb, Eu centers / PMMA hybrid polymeric thick films

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The transparent hybrid thick films composed by terbium (or europium) coordination polymers and polymethyl methacrylate (PMMA) have been prepared through an in-situ composition technology. They show homogeneous interpenetrating polymeric network micromorphology because both of them possess similar polymeric microstructure. The luminescence properties and energy transfer for these polymeric composite films were studied by absorption spectra, fluorescent excitation and emission spectra. All the hybrid thick films with terbium and europium coordination polymers show characteristic emission of the lanthanide ions.

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1. Introduction

Luminescent rare earth organic complexes are of both fundamental and technical interest due to their characteristic luminescent properties, such as extremely sharp emission bands, long lifetime, and potential high internal quantum efficiency, which make them suitable candidates for applications as light emitting diode (LED), laser materials, optical signal amplification, and fluoroimmunoassay [1-5]. The luminescence of rare earth ions stems from the intra-4f transitions, which in principle are forbidden transitions, resulting in relatively low emission efficiency. An effective approach to increase the luminescent efficiency is to modify the complexes with different kinds of ligands that have broad and intense absorption bands so that the absorbed photon energy has a large chance to transfer to the higher energy levels of rare earth ions [6-8]. Several papers were published on the luminescence behavior of Eu^{3+} and Tb^{3+} complexes with β -diketones [9, 10], aromatic carboxylic acid [11, 12] and heterocyclic ligands [13, 14] in sol-gel derived host materials. Unfortunately, it is not easy to obtain transparent and uniform material and the inorganic matrix has some disadvantages such as poor mechanistic properties that restrict its practical application.

The growing importance of polymer films in integrated optic technology makes interesting to study the incorporation of rare-earth complexes in a polymer. Rare-earth complexes doped polymers are important because they possess the properties of the complexes while they can be processed from solution and are mechanically flexible. In recent years, rare earth ions-containing polymers have attracted much attention for their potential applications for fluorescence and laser systems, optical communication devices, such as polymer optical fiber amplifier and integrated waveguide [15, 16]. The main reason is that polymer-based rare earth luminescent materials can be processed easily, which is an advantage in the fabrication of optical components. In addition to that,

encapsulation of rare earth ions with organic ligands makes it possible to incorporate them into polymers hosts up to higher concentrations. The concentration quenching sets in at high concentrations [17]. Rare-earth ions transition that is most influenced by the environment is observed. The metastable-state lifetime should be maximized for efficient laser property [18]. As an optical polymer material, particular interest in PMMA arises from its low cost, simple synthesis, refractive index tailorability depending on molecular weight, best optical transparency and resistance to laser damage. These characteristics make it suitable as a host material for rare earth ions and organic dye doping.

In this paper, the hybrid thick films were prepared by two kinds of rare earth complexes: $[\text{Tb}(\text{2-OHnic})_3 \cdot 2\text{H}_2\text{O}]_n$ and $[\text{Eu}(\text{2-OHnic})_3 \cdot 2\text{H}_2\text{O}]_n$, which have chain-like polymeric structure. The PMMA were got by in situ polymerization method using the initiator action of BPO. The luminescence properties of these hybrid polymeric thick films were studied. SEM microscope indicates that the luminescent hybrid thick films show very homogenous and uniform structure.

2. Experiment

Methyl methacrylate (MMA) was previously treated using dilute sodium hydroxide solution in order to get rid of impurity which hinders the polymerization of monomers. The $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}$) and the 2-hydroxynicotinic acid (the molar ratio 3:1) were dissolved into ethanol solvent, then the pH value of the result solutions were adjusted to about 7, respectively. After stirred several minutes, 7.5 ml methyl methacrylate was added to mixtures. Then benzoyl peroxide (BPO) (about 0.005 g), used as the initiator and catalyst for polymerization, was added into the mixed solution. After heat treatment for several minutes, the mixture solution became viscous and then put along the microscopic glass

slides. The thick films were achieved after drying at 60 °C in the oven.

Ultraviolet absorption spectra were measured with Agilent 8453 spectrophotometer. The fluorescence (excitation and emission) spectra were determined with Perkin– Elmer LS-55 spectrophotometer with excitation slit width = 10 nm, emission slit width = 5 nm respectively. The micrographs recorded with scanning electronic microscope (SEM, Philips XL-30).

3. Results and discussion

The two kinds of hybrid thick films were synthesized by the same method and the properties were studied in detail. Fig. 1 shows the ultraviolet absorption spectra of the hybrid thick film composed with the two lanthanide ions coordination polymers. They all exhibit two absorption bands at the range of 250 – 350 nm with the maximum absorption peak of 260 and 325 nm, which corresponds to the characteristic absorption of pyridine cycle's $\pi \rightarrow \pi^*$ transition. This indicates that the nicotinic acid derivative is still the energy absorption donor for the luminescence of rare earth ion in the hybrid thick films.

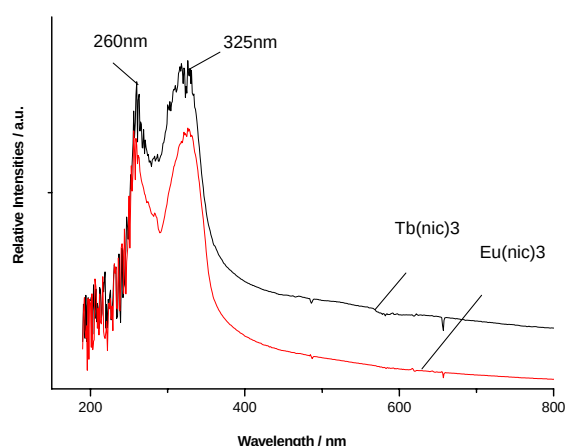


Fig. 1. Ultraviolet absorption spectra of terbium and europium centered polymeric hybrids thick film.

Fig. 2 exhibits the excitation spectra of the terbium coordination polymer which has two broad peaks from 250 to 370 nm in every spectrum. In the low concentration (0.015 mmol / 7.5 ml) the peak around 300 nm is obviously sharper and stronger than the peak around 350 nm, but in the high concentration the figure of two broad peaks is similar except intensity of the excitation peak around 330 nm appreciably high. We found that for the concentration up to 0.025 mmol / 7.5 ml the excitation peak is the greatest one not only in intensity but also in extension, then decrease with increasing the quantum energy of terbium complex. The excitation peak of europium coordination polymer has the similar feature i.e. has two broad peaks in long wavelength ultraviolet region (Fig. 3). However, comparing to the terbium coordination polymer, the extension of excitation is only from 290 nm to 340 nm and the intensity of the later peak is obviously weaker than

that of the former. The intensity for different doping concentrations do not show significant difference. According to the energy match principle and intramolecular energy transfer mechanism, 2-hydroxynicotinic acids absorb the energy in ultraviolet region and then transfer the energy to the resonant emissive level of lanthanides ions with intramolecular energy transfer process. Both energy transfer rate constants depend on the energy differences between the triplet level of the ligands and the resonant emission energy of Ln^{3+} . From the spectra we can deduce that in the PMMA environment the degree of energy matching between the terbium ion and 2-hydroxynicotinic acids is much better than that between the europium ion and the 2-hydroxynicotinic acids.

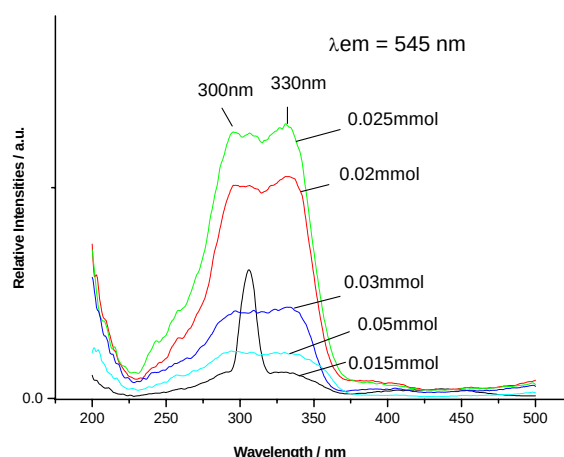


Fig. 2. Excitation spectra of terbium centered polymeric hybrids thick film.

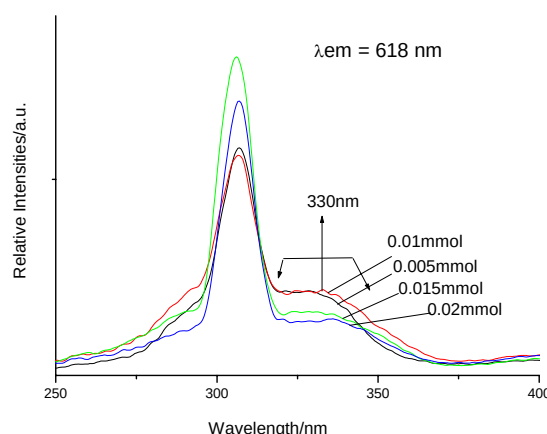


Fig. 3. Excitation spectra of europium centered polymeric hybrids thick film.

Figs. 4 and 5 show different doping concentration emission spectra of hybrid polymeric thick films composed by $[\text{Tb}(\text{2-OHnic})_3(\text{H}_2\text{O})_2]_n$, $[\text{Eu}(\text{2-OHnic})_3(\text{H}_2\text{O})_2]_n$ and MMA respectively. Fig. 3 exhibits clearly that

concentration quenching of activator appears at high concentration of $[\text{Tb}(\text{2-OHnic})_3 \cdot (\text{H}_2\text{O})_2]_n$ when the thick films are excited under the excitation wavelength of 330 nm. Similar to bulk materials the intensity shows a maximum at a doping level of about 0.025 mmol/7.5 ml and decreases at higher terbium concentrations by metal ions aggregation. This partial quenching of the luminescence at high terbium concentration is a typical property of lanthanide-doped systems due to mutual Tb^{3+} - Tb^{3+} interaction. The characteristic emission can be seen obviously at 489 and 546 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_J$, $J = 6, 5$), originating from low energy transfer of Tb^{3+} . Besides, we can also observe the weak emission (586, 620 nm) corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 4, 3$) transition of Tb^{3+} from its high excited state of $^5\text{D}_4$ level. Upon UV excitation, we also obtain the emission spectra of $[\text{Eu}(\text{2-OHnic})_3 \cdot (\text{H}_2\text{O})_2]_n/\text{PMMA}$ (Fig. 5). From the spectra, we also get the concentration quenching when the doping amount is up to 0.01 mmol / 7.5 ml due to the mutual Eu^{3+} - Eu^{3+} interaction. As for the Eu^{3+} , the characteristic emission can be observed ($^5\text{D}_0 \rightarrow ^7\text{F}_J$) ($J = 1, 2$). This emission line originates from low energy transfer of Eu^{3+} . The dominated red peak is located at about 613 nm, which comes from the hypersensitive transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ with $J = 2$. As well known, in the bulk material the emission of the Eu^{3+} comprises the weak emission (536.5, 556.5 nm) corresponding to the $^5\text{D}_1 \rightarrow ^7\text{F}_J$ ($J = 1, 2$) transition of Eu^{3+} from its high excited state of 5D_1 level excepting the characteristic emission ($5\text{D}_0 \rightarrow ^7\text{F}_J$) ($J=1,2$). However, it is difficult to exhibit these emissions in europium complex. In the emission spectra of two lanthanide ion all exhibit the concentration quenching phenomena, so it can be estimated that there are not chemical bond between terbium complex and the PMMA, but occurs only physical dispersion.

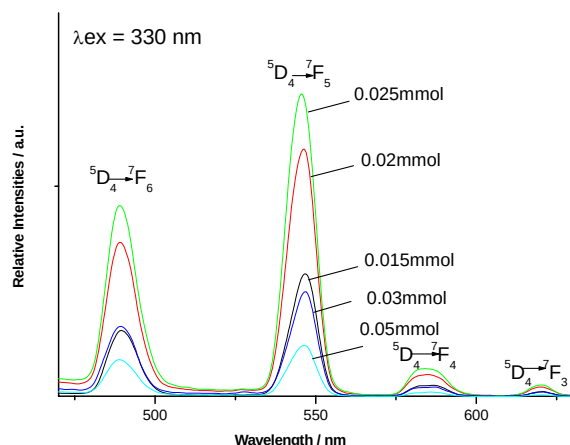


Fig. 4. Emission spectrum of terbium centered polymeric hybrids thick film.

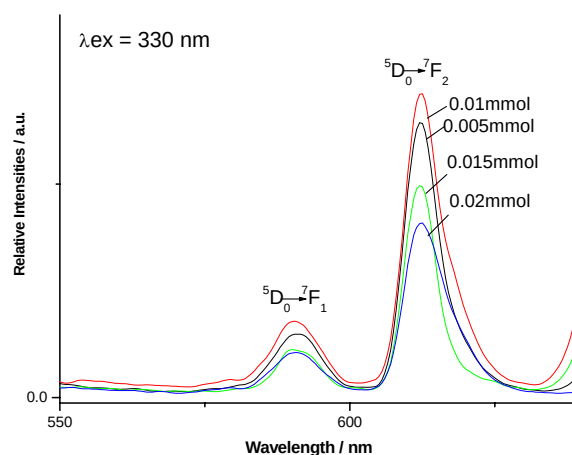
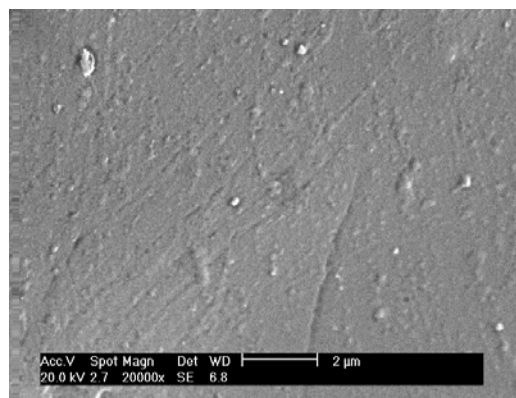
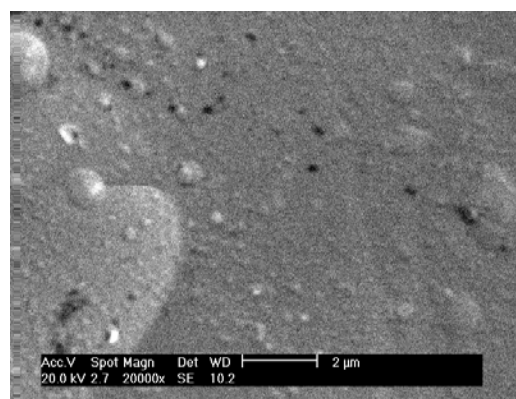


Fig. 5. Emission spectrum of europium centered polymeric hybrids thick film.

Finally we detected the SEM images of these hybrid polymeric thick films (shown in Figs. 6). It was observed that the two coordination polymers can be dispersed in the PMMA homogeneously and they mix very uniformly to interpenetrate together because both of them have similar polymeric structures: phase separation phenomenon, occurs.



(a)



(b)

Fig. 6. SEM of terbium centered (A) and europium centered (B) polymeric hybrids thick film.

4. Conclusions

By controlling the formation of terbium and europium coordination polymers accompanied by the polymerization of methyl methacrylate, two coordination polymers of $[\text{Tb}(\text{2-OHnic})_3 \cdot (\text{H}_2\text{O})_2]_n$ and $[\text{Eu}(\text{2-OHnic})_3 \cdot (\text{H}_2\text{O})_2]_n$, with infinite chain polymeric structures, were *in situ* composed with poly methyl methacrylate (PMMA). Thus, transparent hybrid polymeric thick films were obtained. The emission spectra indicate that all the hybrid thick films composed with terbium and europium coordination polymers show the corresponding characteristic emission of lanthanide ions. By comparing two kind of coordination polymers, we found that the hybrid composite polymeric film is a suitable substrate for the luminescence of two lanthanide complexes of 2-hydroxynicotinic acids.

Acknowledgements

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