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Improved Photobleaching for (1,10-phenanthroline)tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato]europium(III) Particle Embedded in Sol-Gel Derived Glass Film

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In this research, we investigated improved photobleaching characteristics of (1,10-phenanthroline)tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato]europium(III) by forming nano-particles embedded into a sol-gel derived silica glass film by a conventional sol-gel process. The relative photoluminescence intensities after the UV irradiation for 90 min were 88, 76, and 67% for nano-particles in the sol-gel derived glass film, powders in the sol-gel derived glass film, and raw powders, respectively. This result indicates that the phtobleaching of this Eu-complex can improved by forming nano-partcile structures by a reprecipitation method and embedding in the sol-gel derived silica glass.

Keywords $Eu(TTA)_3phen$; reprecipitation method; sol-gel derived silica glass film

Introduction

Eu-complexes have number of useful spectroscopic characteristics such as near ultraviolet (UV) excitation, sharp photoluminescence (PL) peak at a red wavelength region, high PL quantum yield, and superior long term stability compared to other organic molecule. Therefore, Eu-complexes have been expected for several applications, such as fluorescent biological image sensors [1], organic light-emitting diodes [2], wavelength conversion films for silicon photovoltaic cells [3], optical fiber lasers [4], and white light-emitting diodes [5].

One of the most serious problem is photobleaching in the presence of ultraviolet (UV) light irradiation. This is because that the bond strength between the Eu^{3+} ion and the organic ligand is lower than those of conventional inorganic materials. Therefore, the chemical structure of the Eu-complex easily changes under UV-irradiation, resulting in a decrease in the PL intensity [6].

Recently, several researchers have demonstrated that highly stable Eu-complexes can be realized by encapsulating into sol-gel derived inorganic materials, which prevent the

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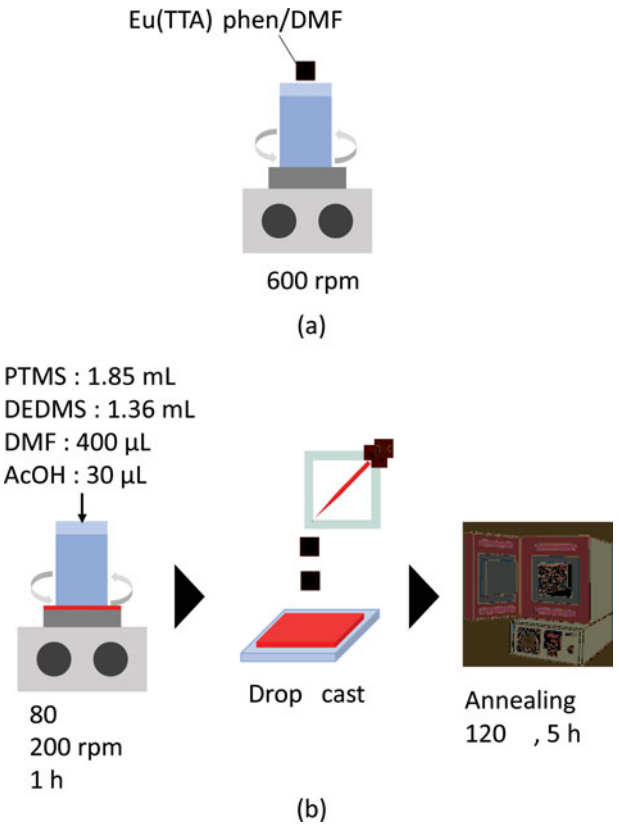

Figure 1. Fabrication of process of (a) $Eu(TTA)_3phen$ colloidal aqueous solution and (b) sol-gel derived silica glass film containing the $Eu(TTA)_3phen$ nanoparticles.

chemical structure change of Eu-complex [7–12]. As a result, the photobleaching can be prevented against the UV light irradiation. In addition, another approach for improving photobleaching of Eu-complex is a formation of nanoparticles by the reprecipitation method. In previous papers, photobleaching of Eu-complex were successfully improved by embedding into sol-gel derived networks and polymers [13, 14]. However, further improved stability should be realized for practical applications.

In this paper, we investigated the long term stability of (1,10-phenanthroline)tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato]europium(III) ($Eu(TTA)_3phen$) nano-particles by embedding into the sol-gel derived glass film. Especially, the long term stability was estimated as the PL intensity change while irradiating with UV light.

Experimental Method

Figure 1(a) shows a fabrication process of $Eu(TTA)_3phen$ colloidal aqueous solution. At first, $Eu(TTA)_3phen$ powder was dissolved in *N,N*-dimethylformamide (DMF) at concentrations ranged from 1 to 3 mg/mL. Then, the resulting solution (400 μL) was injected

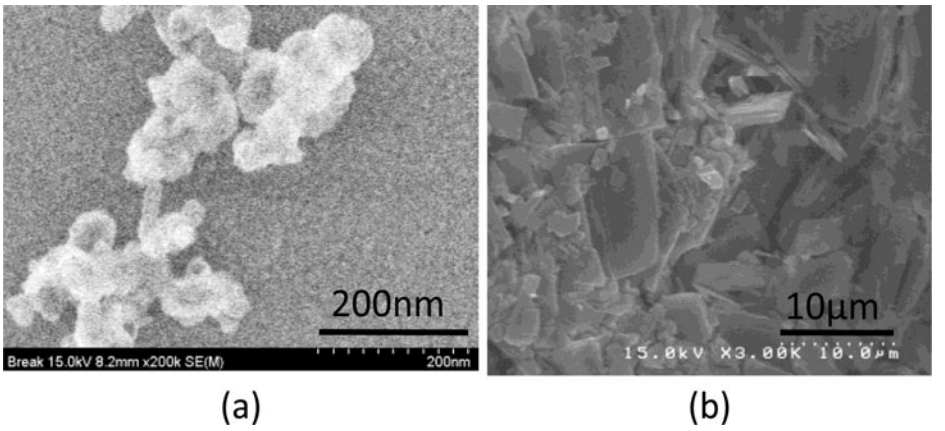

Figure 2. SEM images of $Eu(TTA)_3phen$ (a) nanoparticles and powders.

slowly into a pure water (2.69 mL) while stirring at 600 rpm. As a result, $Eu(TTA)_3phen$ colloidal aqueous solution was obtained.

Figure 1(b) shows a fabrication process of sol-gel derided glass film containing $Eu(TTA)_3phen$ colloid. At first, the colloidal $Eu(TTA)_3phen$ solution was added into 1.85 mL of phenyltrimethoxysilane (PTMS), 1.36 mL of diethyldimethoxysilane (DEDMS), 400 μL of DMF, and 30 μL of acetic acid (AcOH). Then, the resulting solution was stirred at 200 rpm, 80°C, for 1 h. The previous research indicates that this condition is suitable for fabricating the transparent silica glass thin film containing the Eu-complex [15].

The PL and PL excitation (PLE) spectra were measured using the spectrofluorometer (FluoroMax3, Horiba Jovin Yvon). The excitation wavelength for PL spectrum measurement was 340 nm, and the monitor wavelength of PLE spectrum was 612 nm, corresponding to the transition between $^5D_0$ and $^7F_2$ [16, 17]. The PL decay curve was also measured using the spectrofluorometer (FluoroMax3, Horiba Jovin Yvon), and excitation and monitored wavelengths were 340 and 612 nm, respectively. The particle shape was measured using the scanning electron microscopy (SEM).

Results and Discussion

Figures 2(a) and 2(b) show SEM images of $Eu(TTA)_3phen$ (a) nanoparticles and (b) powders, respectively. The $Eu(TTA)_3phen$ powder showed a size of several μm with a rectangular shape. However, a round shape was observed after the reprecipitation method as shown in Fig. 2(a). The diameters of $Eu(TTA)_3phen$ nanoparticles were about 100 nm, which are small enough for the wavelength conversion film of the photovoltaic cells. Because the optical transmittance will be negligible due to the little effect of Layleigh scattering against the visible light.

Figure 3 shows PL and PLE spectra of $Eu(TTA)_3phen$ nano particle embedded in the sol-gel derived silica glass film (sample A), $Eu(TTA)_3phen$ powder embedded in the sol-gel derived silica glass film (sample B), and $Eu(TTA)_3phen$ powder (sample C). Rising wavelength of PLE spectra shifter toward shorter wavelength region for samples A and B compared to that of sample C, and this is a common effect of Eu-complex dissolved in the sol-gel derived silica glass networks [15]. Because the absorption spectrum of the

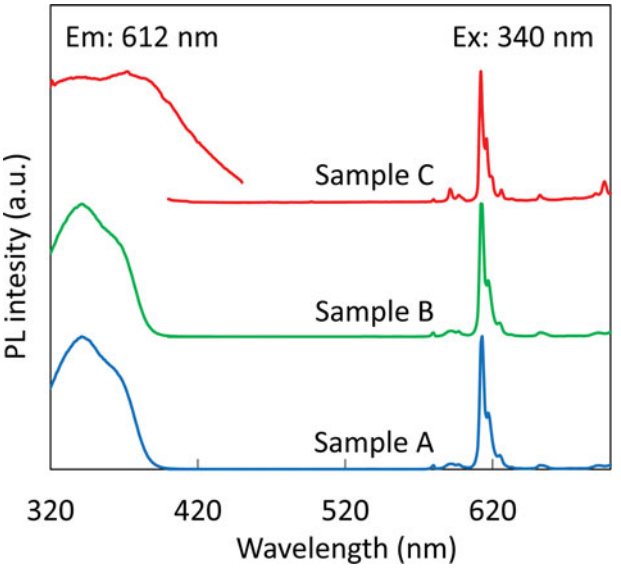

Figure 3. PL and PLE spectra of samples A, B, and C.

Eu-complex changes by the stacking condition. The PL quantum yields of samples A, B, and C were 73, 72, and 78%, respectively. This results indicate that all the samples showed the high PL quantum yield.

Figure 4 shows PL decay curves of samples A, B, and C. An optical intensity of excited light was 5 mW/cm^2. The relative PL intensities after UV irradiation for 90 min were 92, 59, and 67% for samples A, B, and C, respectively. By comparing samples A and B, the decreased PL intensity was suppressed by forming nanoparticle structures in the sol-gel derived silica glass film. This is because that the photobleaching is occurred by oxidizing

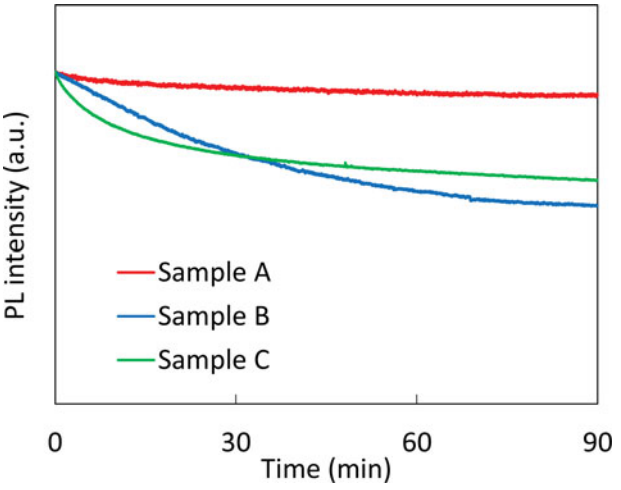

Figure 4. PL decay curve of sample A, B, and C while irradiating the UV light (340 nm and 5 mW/cm^2).

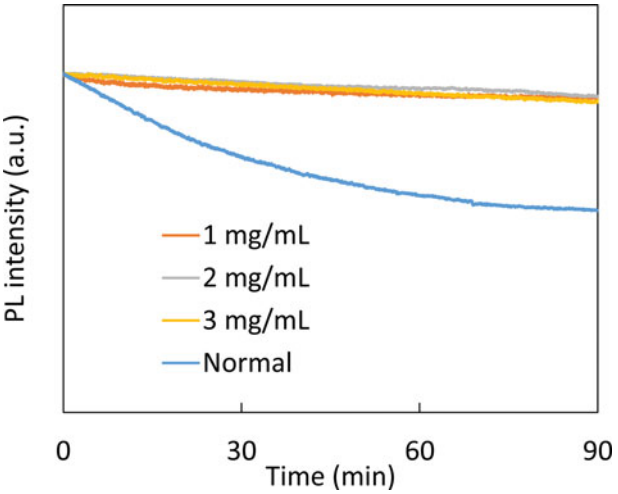

Figure 5. PL decay curve of $Eu(TTA)_3phen$ nanoparticles in sol-gel derived silica glass film with different concentrations.

$Eu(TTA)_3phen$ molecules, and the smaller surface area of the nanoparticle structure prevent the oxidization. In addition, by comparing samples A (nanoparticle in silica glass) and C (powder), the improved long-term stability was occurred by embedding into the sol-gel derived silica glass, which protects oxygen and water transmittances. As a result, the highly long-term stability was successfully achieved for the sample A.

Figure 5 shows the PL decay curve of the sol-gel derived silica glass film containing $Eu(TTA)_3phen$ nanoparticles with different of concentrations. The relative PL intensities after UV irradiation for 90 min were 91, 93, and 92% for concentrations of 1, 2, and 3 mg/mL of $Eu(TTA)_3phen$ nanoparticles in the aqueous solution, respectively. These samples showed improved photostabilities than the sample B ($Eu(TTA)_3phen$ powder in the sol-gel derived silica glass film). This indicates that large particle size of $Eu(TTA)_3phen$ is an important role for improving photostability for all the concentrations by the reprecipitation method.

Conclusion

We demonstrated the improved long-term stability of $Eu(TTA)_3phen$ particle by encapsulating the sol-gel derived glass film. In addition, the highly long-term stability was achieved for all the concentrations of $Eu(TTA)_3phen$ nanoparticles in the sol-gel derived silica glass. A most likely cause of this result is that the degradation from the air was prevented due to the small surface area.

References

[1] Rai, P.; Mallidi, S.; Zheng, X.; Rahmanzadeh, R.; Mir, Y.; Elrington, S.; Khurshid, A.; & Hasan, T. (2010). *Adv. Drug Deliv. Rev*. *62*, 1094.
[2] Kido, J.; Nagai, K.; Okamoto Y.; & Skotheim, T. (1991). *Chem. Lett.*, *20*, 1267.
[3] Fukuda, T.; Kato, S.; Kin, E.; Okaniwa, K.; Morikawa, H.; Honda, Z.; & Kamata, N. (2009). *Opt. Mater.*, *32*, 22.
[4] Kuriki, K.; & Koike, Y. (2002). *Chem. Rev.*, *102*, 2347.

[5] Yan, V.; Wang, H.; He, P.; Shi, J.; & Gong, M. (2011). *Inorg. Chem. Commun.*, *14*, 1065.
[6] Lima, P. P.; Sá Ferreira, R. A.; Freire, R. O.; Paz, F. A. A.; Fu, L.; Alves Jr., S.; Carlos, L. D.; & Malta, O. L. (2006). *Chem. Phys. Chem.*, *7*, 735.
[7] Binnemans, K. (2009). *Chem. Rev.*, *109*, 4283.
[8] Li, H., Inoue, S., Machida, K., & Adachi, G. (1999). *Chem. Mater.*, *11*, 3171.
[9] Carlos, L. D.; Ferreira, R. A. S.; Bemudez, V. de Z.; Ribeiro, S. J. L. (2009). *Adv. Mater.*, *21*, 509.
[10] Lechevallier, S.; Jorge, J.; Silveira, R. M.; Ratel-Ramond, N; Neumeyer, D.; Menu, M. J.; Gressier, M.; Marçal, A. L.; Rocha, A. L.; Martines, M. A. U.; Magdeleine, E.; Dexpert-Ghys, J.; Verelst, M. (2013). *J. Nanomater.*, 918369.
[11] Cides da Silva. L. C.; Marins. T. S.; Filho. M. S.; Teotonio, E. E. S.; Isolani, P. C.; Brito, H. F.; Tabacniks, M. H.; Fantini, M. C. A.; Matos, J. R. (2006). *Micropor. Mesopor. Mater.*, *92*, 94.
[12] Fukuda, T.; Kato, S.; Akiyama, S.; Honda, Z.; & Kamata, N. (2012). *Opt. Mater.*, *35*, 5.
[13] Peng, H.; Wu, C.; Jiang, Y.; Huang, S.; & McNeill, J. (2007). *Langmuir*, *23*, 1591.
[14] Oh, M.; & Mirkinm C. A. (2005). *Nature*, *438*, 651.
[15] Fukuda, T.; Yamauchi, S.; Honda, Z.; Kijima, N.; & Kamata, N. (2009). *Opt. Mater*, *32*, 207.
[16] Fang, J.; & Ma, D. (2003). *Appl. Phys. Lett.*, *83*, 4041.
[17] Eilers, H.; & Tissue, B. M. (1996). *Chem. Phys. Lett.*, *251*, 74.