Journal of Zhejiang University SCIENCE
ISSN 1009-3095
http://www.zju.edu.cn/jzus
E-mail: jzus@zju.edu.cn

***Science Letters:***

# In-situ synthesis and luminescence properties of titanium oxide gels containing 1,10-phenanthroline europium(III) complex*

XIE Fei (谢 飞)[1], YANG Hui (杨 辉)[†1], XU Cun-jin (徐存进)[2], ZHANG Xi-he (张细和)[1]

([1]*Institute of Inorganic Nonmetal Materials, School of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China*)

([2]*Department of Chemistry, Hangzhou Teachers College, Hangzhou 310012, China*)

[†]E-mail: yanghui@zju.edu.cn

Received Jan. 23, 2005; revision accepted Apr. 8, 2005

**Abstract:** It is difficult to directly dope europium complexes in gel because the excessive water or high acidic condition may lead to their decomposition. We prepared a novel homogeneous $TiO_2$ gel containing Eu-phen complexes by using an in-situ synthesis method. The formation of Eu-phen complexes in sol-gel derived $TiO_2$ was confirmed by luminescence excitation spectra. The effects of temperature and aging time on in-situ synthesis are discussed. The luminescence spectra of gel containing europium complexes were also compared with the pure Eu-phen complexes.

**Key words:** In-situ synthesis, Europium complex, Titanium dioxide gel, Luminescence
**doi:**10.1631/jzus.2005.A0619 **Document code:** A **CLC number:** O614. 33

## INTRODUCTION

Europium(III) ion is a lanthanide ion with excellent luminescent properties and wide applications in luminescence materials due to the good monochromaticity and high quantum yields the ion's red light emits at 615 nm (Calefi *et al.*, 1999; Reisfeld, 2004). But the absorption coefficients of Eu(III) ion are very small, limiting its actual applications. In order to overcome these shortcomings, Eu(III) ions are usually chelated with ligands having broad intense absorption bands such as those of carboxylic acid derivatives, heterocyclic and $\beta$-diketone compounds. When Eu(III) complexes are irradiated by UV light, the organic ligands are first excited by light absorption, followed by energy transfer from the ligands to the excited levels of Eu(III), resulting in enhanced lanthanide fluorescence.

As well known, Eu(III) complexes normally are difficult to incorporate into a suitable host material as their structure can easily be destroyed during production and processing. While, sol-gel technique is a very common and efficient method to create functional transparency solid bulk-glass or thin film, whose relatively gentle synthetic conditions make it possible to form homogeneous composite gel by adding some guest materials, such as organic dyes or inorganic materials. But many rare earth complexes exhibit low solubility in sol-gel precursor solutions, even precipitate from the precursor solutions, so sometimes these complexes cannot be directly added into sol-gel solutions (Reisfeld *et al.*, 2000).

Qian *et al*.(1997) successfully doped Eu(III) complex in silica gel using an in-situ method. Zhang *et al*.(1999) reported synthesis of europium complexes in silica matrix by using a two-step sol-gel process. However, until now, there are few reports on doping Eu(III) complexes in titanium dioxide by sol-gel method. In this work, we used an in-situ synthesis method to prepare a homogeneous titanium dioxide gel containing Eu-phen complex. The lumi-

*Project (No. 2004C210023) supported by Science Planning Project of Zhejiang Province, China

nescence properties of the resulting homogeneous gel were studied in detail by changing temperature and aging time during the in-situ synthesis procedures.

## MATERIAL AND METHODS

### Chemicals

Titanium tetrabutoxide, absolute ethanol, 1,10-phenanthroline (phen) were obtained from Zhejiang University. Europium chloride was prepared by dissolving $Eu_2O_3$ in excessive 6 mol/L HCl, then hydrated europium chloride was obtained by evaporating away excess HCl from the solution.

### Sample preparation

The doped titanium gels were prepared by the acidic ($HNO_3$) hydrolysis of titanium tetrabutoxide in ethanol solution (Wang *et al.*, 2003). First, phen was dissolved in absolute ethanol under stirring. After several minutes, titanium tetrabutoxide and a certain amount of ethanol solution of europium chloride (molar ratio Ti:Eu=50:1) were added to the above mixture. Then $HNO_3$ aqueous solution (pH=2) was added to promote the hydrolysis and condensation reaction of titanium tetrabutoxide. The molar ratio of titanium tetrabutoxide:ethanol:$H_2O$ was 1:33:3. The mixture was stirred at room temperature for several hours to ensure homogeneous mixing and complete hydrolysis.

After being kept in static condition for one day at room temperature, the precursor solution converted into transparent wet gel. The wet gel was further aged for one day, then oven dried at different temperature, and stored in a desiccator for further measurements.

Meanwhile, in order to compare above gel containing Eu-complexes, another solid gel only doped with europium was prepared by a similar procedure. The pure solid europium complex with phen was prepared the method reported by Yang *et al.*(1998).

### Analytical methods

The luminescence excitation and emission spectra were measured at room temperature on a Hitachi 850 Spectrofluorometer with a xenon lamp as the excitation source. The bands pass for the excitation and emission monochromators were set at 2.5 nm.

## RESULTS AND DISCUSSION

### In situ synthesis of Eu(III) complex with 1,10-Phenanthroline

Fig.1 shows that the excitation spectrum (Curve 2 in Fig.1a) of the gel aged at 10 °C for one month is similar to that of the $TiO_2$ gel doped with pure $EuCl_3$ (Curve 1 in Fig.1a), both with several sharp bands appearing between 320 and 450 nm with a maximum peak at 396 nm, which is ascribed to the $^5L_6$ level of $Eu^{3+}$, indicating the absence of europium complexes in the $TiO_2$ gel aged at 10 °C. However, when the gels were further aged at 20 °C for half a month, a broad band appeared between 218 and 400 nm in the excitation spectrum (Curve 3 in Fig.1a) in addition to the original sharp band at 396 nm, implying that higher ageing temperature resulted in the formation of the Eu(III) complexes composition. The peak at 396 nm is due to the unreacted europium chloride. We suppose the mechanism is as follows: as the titanium dioxide gel is codoped with europium and phen, the phen molecules are isolated and may tend to adsorb

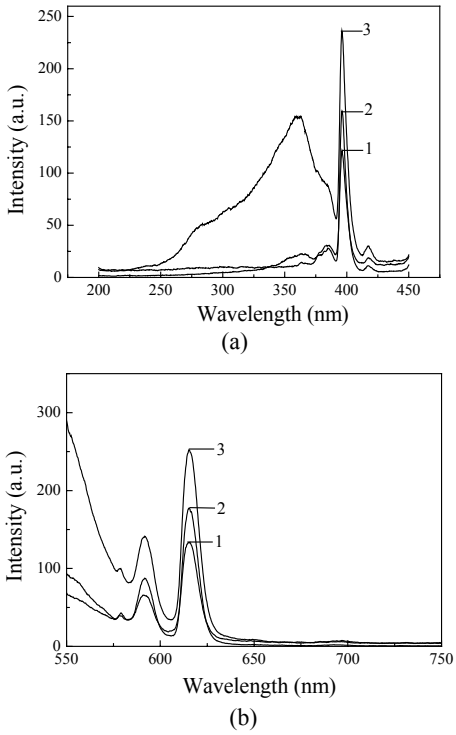


**Fig.1 Luminescence spectra of the excitation (a) and emission (b) of titania gel codoped with (1) europium, (2) europium and phen kept at 10 °C for one month, and (3) europium and phen kept at 20 °C for half a month**

on the pore wall of the titanium oxide network, thus resulting in producing more reacting sites in the gel structure. At lower temperature, the phen molecules are somewhat not very active in colliding with Eu(III) ions; while at higher temperature, phen molecules should have more energy to collide with Eu(III) ions, thus Eu(III)-phen complexes were formed in the Ti-O network. Thus showing the ageing temperature plays an important role in forming the Eu-phen complexes in the $TiO_2$ gel.

Moreover, the emission spectra of the above samples (Fig.1b) are consistently similar to their excitation spectra. With increasing ageing temperature, the intensities of the spectrum were enhanced due to the formation of Eu-phen complexes at higher temperature. The several bands between 580 nm and 700 nm are due to the $^5D_0 \rightarrow {}^7F_J$ ($J$=1,2,3 and 4) of $Eu^{3+}$. It is clearly seen that the order of the luminescence intensity is Curve 3>Curve 2>Curve 1.

**Effects of temperature and ageing time on the fluorescence properties**

Fig.2 shows the excitation and emission spectra of titanium dioxide gel containing Eu-phen complexes heated at the temperature of 60 °C, 80 °C, 100 °C and 120 °C, respectively. Obviously, there is a broad band at 365 nm together with a sharp peak at 396 nm for all samples, meaning all samples contain europium complexes. The peak at 396 nm represents unreacted $Eu^{3+}$. However, as the heating temperature increased, the intensities of the excitation and emission spectra both decrease gradually, and the intensities of the excitation and emission maximize at 60 °C (Curve 2 in Figs.2a and 2b); moreover, we found the intensities in the excitation (Fig.2a) and emission (Fig.2b) spectra both significantly increased with the extension of ageing time at 80 °C from one to two days (Curve 1 in Figs.2a and 2b). We will discuss this phenomenon elsewhere in detail.

**Comparison of fluorescence spectra in titanium dioxide gel codoped with Eu(III) and phen, and pure Eu(III) complex with phen**

Fig.3 shows the fluorescence spectra of pure sample of Eu(III)-phen complexes and titanium dioxide gel codoped with Eu(III)-phen complexes respectively. Compared to the pure Eu(III)-phen complex, the maximum excitation wavelengths of the gel

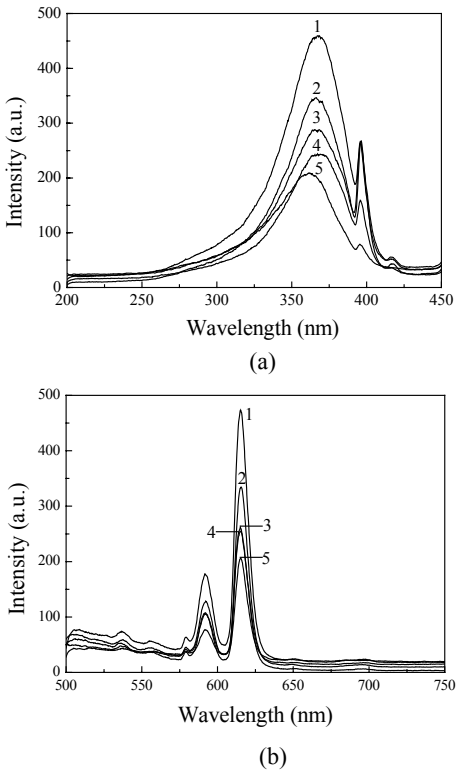


**Fig.2 Luminescence spectra of excitation (a) and emission (b) of the $TiO_2$ gel codoped with europium(III) and phen heated at different temperature: (1) 80 °C for 48 h, from (2) to (5) corresponding to 60 °C, 80 °C, 100 °C, and 120 °C for 24 h, respectively**

codoped with europium-phen complexes have almost no change, implying that Eu(III)-phen complexes in the $TiO_2$ gel have the same composition as the pure Eu-phen complexes. Both of their emission spectra present characteristic transitions of $Eu^{3+}$ with $^5D_0 \rightarrow {}^7F_2$ as the dominant group. While, we can see that the emission intensity of the pure Eu(III)-phen complexes powder is more than one hundred times stronger than that of the gel doped with europium and phen. Here, we should say that the total content of Eu-phen complexes in the gel composite is much lower than that of pure Eu-phen complexes. Thus, adequate luminescent effect can be observed even in the presence of small amount of Eu(III)-phen complexes in the $TiO_2$ gel. This is very important in practical applications. On the other hand, compared to the gel codoped with Eu-phen complexes, the emission spectra of the pure Eu-phen complexes show two sharp bands due to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition of electron (Yang *et al.*, 1998), this result is similar to that for the silica gel

codoped with terbium complexes described by Zhang *et al*.(1999). While the $TiO_2$ gel composite only shows one peak because the Eu-complexes were trapped in the micropores of the non-crystalline titanium dioxide matrix. Thus, complex molecular fixed in the pores are highly dispersed, so fewer lines are observed.

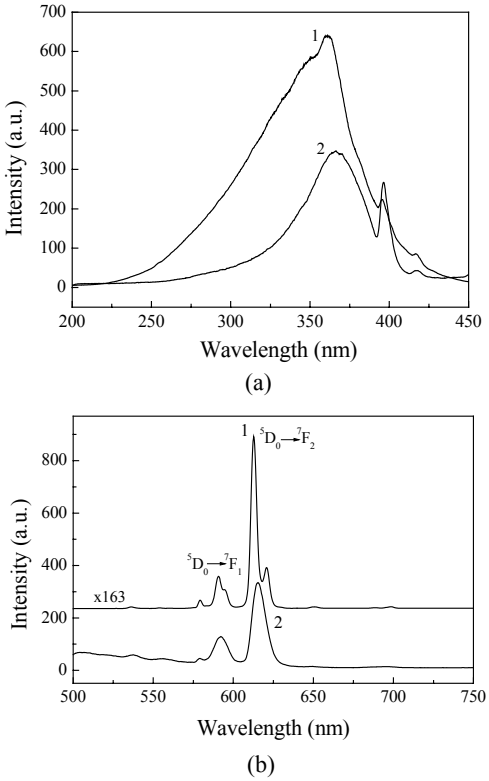


**Fig.3 Excitation spectra (a) and emission spectra (b) of the pure complex powder (1) and titanium dioxide gel codoped with europium and 1,10-phenanthroline heated at 60 °C for 24 h (2)**

The third difference is that the fluorescence intensity ratio of the $^5D_0 \rightarrow ^7F_2$ transition to the $^5D_0 \rightarrow ^7F_1$ transition in the pure complex is higher than that in the gel. This ratio is assumed to be an indication of the degree of asymmetry in the surroundings of $Eu^{3+}$ (Elhouichet *et al.*, 2003), and can also be ascribed to the relatively homogeneous distribution of the complex in gel.

## CONCLUSION

Eu(III)-phen complexes can be doped in $TiO_2$ gel matrix to form homogeneous composite gel by in-situ method. The formation of Eu-phen complexes in sol-gel derived $TiO_2$ gel was confirmed by luminescence excitation spectra. The composite gel exhibits the characteristic emissions of $Eu^{3+}$. Higher room temperature favors the formation of the complex, while when the gels are heated at 60 °C, 80 °C, 100 °C, 120 °C, the emission intensity falls gradually with the increase of the temperature. Longer ageing time also helps to improve the emission intensity. The emission spectra of the gels show fewer emission lines than the pure complexes, and the fluorescence intensity ratio of the $^5D_0 \rightarrow ^7F_2$ transition to the $^5D_0 \rightarrow ^7F_1$ transition is lower than that of the latter. That is all due to the highly ordered porous structure. The spectra of luminescence excitation and emission of gel containing europium complexes being similar to that of pure Eu-phen complexes, further confirms that the existing Eu-complex molecules in the gels are the same as those of the pure Eu-complexes.

## References

Calefi, P.S., Nassar, E.J., Neri, C.R., Serra, O.A., 1999. Synthesis and some properties of hybrid gels of titanium oxide containing europium(III). *Journal of Non-Crystalline Solids*, **247**:120-123.

Elhouichet, H., Othman, L., Moadhen, A., Oueslati, M., Roger, J.A., 2003. Enhanced photoluminescence of $Tb^{3+}$ and $Eu^{3+}$ induced by energy transfer from $SnO_2$ and Si nanocrystallites. *Materials Science and Engineering B*, **105**:8-11.

Qian, G.D., Wang, M.Q., Wang, M., 1997. In situ synthesis and fluorescence characterization of 2, 2'-dipyridyl-Eu(III) complex in silica xerogel prepared by the sol-gel process. *Journal of Photochemistry and Photobiology A-Chemistry*, **107**:121-124.

Reisfeld, R., 2004. Rare earth ions: their spectroscopy of cryptates and related complexes in glasses. *Structure and Bonding*, **106**:209-235.

Reisfeld, R., Zelner, M., Patra, A., 2000. Fluorescence study of zirconia films doped by $Eu^{3+}$, $Tb^{3+}$ and $Sm^{3+}$ and their comparison with silica films. *Journal of Alloys and Compounds*, **300-301**:147-151.

Wang, F.Q., Wang, L.P., Liu, L.J., Yang, X.H., 2003. Preparation of nanosized $TiO_2$ powders by Sol-Gel method. *Ningxia Engineering Technology (Ning Xia Gong Cheng Ji Shu)*, **2**(3):248-250 (in Chinese).

Yang, C.M., Wang, S.F., Fang, Z., 1998. A study on IR and fluorescence spectra of solid binary complex compounds of phen-Eu(III) codoped with $Y^{3+}$ and $Gd^{3+}$. *Chinese J. of Spectroscopy Laboratory*, **15**(2):10-13 (in Chinese).

Zhang, H.J., Fu, L.S., Wang, S.B., Meng, Q.G, Yang, K.Y., Ni, J.Z., 1999. Luminescence characteristics of europium and terbium complexes with 1,10-phenanthroline in-situ synthesized in a silica matrix by a two-step sol-gel process. *Materials Letters*, **38**:260-264.