Synthesis and luminescence properties of hybrid organic–inorganic transparent titania thin film activated by *in-situ* formed lanthanide complexes

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Abstract

Stable transparent titania thin films were fabricated at room temperature by combining thenoyltrifluoroacetone (TTFA)-modified titanium precursors with amphiphilic triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO, P123) copolymers. The obtained transparent titania thin films were systematically investigated by IR spectroscopy, PL emission and excitation spectroscopy and transmission electron microscopy. IR spectroscopy indicates that TTFA coordinates the titanium center during the process of hydrolysis and condensation. Luminescence spectroscopy confirms the *in-situ* formation of lanthanide complexes in the transparent titania thin film. TEM image shows that the *in-situ* formed lanthanide complexes were homogeneously distributed throughout the whole thin film. The quantum yield and the number of water coordinated to lanthanide metal center have been theoretically determined based on the luminescence data.

1. Introduction

Luminescent lanthanide organic complexes are of both fundamental and technical interest due to their characteristic luminescence properties, e.g., extremely sharp emission bands, long lifetime, and potential high internal quantum efficiency. This has drawn much attention because of their versatile applications, such as planar waveguide amplifiers, plastic lasers, and light-emitting diodes [1]. For technological applications, these complexes have to be incorporated into a stable solid matrix [2–7]. Lanthanide complexes are generally incorporated into different substrates or matrixes, including sol–gel materials, supramolecules, and porous materials. An enhanced thermal stability, mechanical stability, and luminescent properties compared with the corresponding pure lantha-nide complexes have been observed in these systems. Among them, mesostructured materials fabricated from polymerizable silica species and organic structure-directing agents are much more attractive because they have led to a number of advanced optical applications thanks to the ability to integrate specific functional molecules into distinct regions of the mesostructures [5,6,8,9], for instance, when a laser dye is incorporated selectively into the organic domains of the mesostructure, silica-based hybrids perform a number of advanced optical applications, including optical switching and sensing, and low threshold wave-guide microlasing [8,9]. However, optical devices fabricated from silica have a limited refractive index ($n = 1.43$) and must be supported by ultralow refractive index materials when efficient waveguiding is important [9]. This obstacle could be overcome by using a higher refractive index inorganic component such as mesostrucutred titania, which has been demonstrated recently by the fabrication of dye-doped hybrid waveguides with trifluoroacetate

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(TFA)-modified titania frameworks [10–13]. The obtained transparent thin films have a high effective index of refraction ($n = 1.6$–1.7). The stability and optical quality of the hybrid thin film obtained by this new approach can be ascribed to the presence of chelating TFA ligands within the titania network suppressing continued condensation of titainia network [12,13]. Carboxylic acid and β-diketones are used to moderate the reactivity of titanium precursor, thus transparent titanium gel can be obtained [12–14]. Nevertheless, to the best of our knowledge, stable transparent titania thin films combined with the interesting luminescent properties of lanthanide compounds have not been reported yet due to the high activity of the titanium precursor.

Herein we report a controlled synthesis procedure for organic–inorganic transparent titaina thin film exhibiting sharp emission lines due to the *in-situ* formed highly luminescent 1,10-phenanthroline (phen) Eu^{3+} or Tb^{3+} complex by employing a TTFA stabilized titania precursor. The obtained organic–inorganic composites are composed of hydrophobic regions and the rigid inorganic framework due to the presence of Pluronic P123, enabling them act as ideal host materials for organic guest molecules because the hydrophobic regions are compatible with organic guest species and the rigid inorganic framework can protect the included molecules.

2. Experimental

2.1. Materials

Eu_2O_3, Tb_4O_7, $Ti(O^iPr)_4$, P123, TTFA, 1,10-phenanthroline purchased from Aldrich. They were used without further purification. $EuCl_3 \cdot 6H_2O$ and $TbCl_3 \cdot 7H_2O$ were obtained by dissolving Eu_2O_3, Tb_4O_7 in HCl.

2.2. Synthesis of hybrid organic–inorganic titania thin film

Appropriate amount of $EuCl_3 \cdot 6H_2O$ (or $TbCl_3 \cdot 7H_2O$) and 1,10-phenanthroline (molar ratio Eu^{3+}:phen of 1:3) were added to 15 mL of EtOH containing 1 g of P123. Separately, 5.5 mL of $Ti(O^iPr)_4$ was reacted under stirring with 4.13 g of TTFA and 0.7 mL of concentrated HCl. After 10 m, the two solutions were mixed together and further stirred for 15 min. The molar ratio of $Eu^{3+}(Tb^{3+})/$ $Ti(O^iPr)_4$ and that of phen/TTFA were kept as 1:186 and 3:186, respectively. Thin films were prepared by dip-coating onto glass sides at the rate of 10 cm min^{-1} and stored at 70% relative humidity for 24 h. The films were then removed from the humidity chamber and allowed to full dry. No heat treatment was necessary to stabilize the structure.

2.3. Characterization

IR spectra were recorded on a Nicolet impact F410 FTIR spectrometer from KBr pellets. Transmission elec-

tron microscopy image was recorded on a JEOL2010F (200 keV) microscope. Sample obtained by scratching the film from the substrate was suspended in methanol, followed by sonication for 5 min in an ultrasonic bath. Carbon-coated copper used as the sample holder. Photoluminescence emission spectra and decay curves were recorded on SPEX FluoroLog 3 spectrofluorometer with 450 W ozone-free Xe source.

3. Results and discussion

The obtained titania thin films are stable under ambient conditions for several months without heat treatment for stabilization via conventional inorganic-acid-based route. This can be ascribed to the chelating of TTFA to titanium alkoxide, which can prevent extended three-dimensional cross-linking of the molecular titania units and enable the room temperature formation of stable glassy composite. The reaction of TTFA with $Ti(O^iPr)_4$ can be confirmed by the FTIR spectra as shown in Fig. 1. Fig. 1 displays the FTIR spectra of TTFA (a) and the organic–inorganic hybrid thin film (b). Bands centered at 1663 and 1581 cm^{-1} in Fig. 1a can be ascribed to the stretch vibration of carbonyl group, which are replaced by bands at 1602 and 1541 cm^{-1} in Fig. 1b due to the chelating of TTFA to the titanium center in the final hybrid materials [15].

The microstructure of the hybrid titania thin film was investigated by transmission electron microscopy as shown in Fig. 2. From Fig. 2, we can observe the wormlike mesostructure. There is structural homogeneity in the obtained thin film. This means the *in-situ* formed lanthanide complexes are homogeneously distributed in the throughout the thin film.

Fig. 3 shows the excitation and emission spectra of the obtained hybrid organic–inorganic hybrid materials activated by the *in-situ* formed Eu^{3+}–phen complex. The emission spectrum was recorded at room temperature by
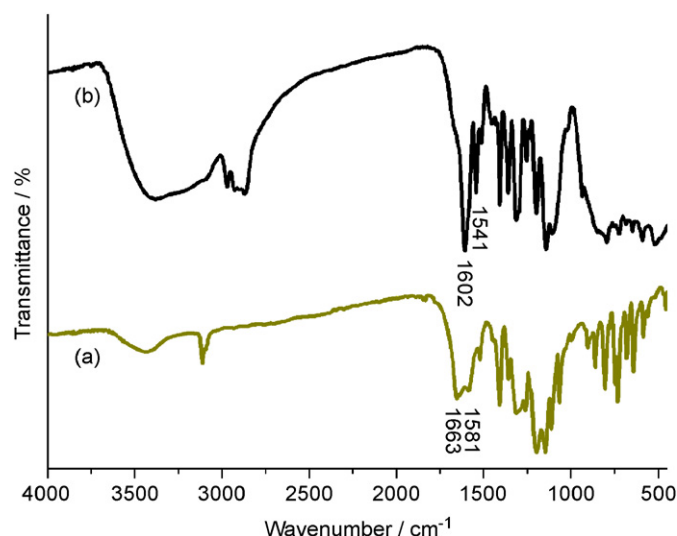

Fig. 1. FTIR spectra of TTFA (a) and the hybrid thin film (b).
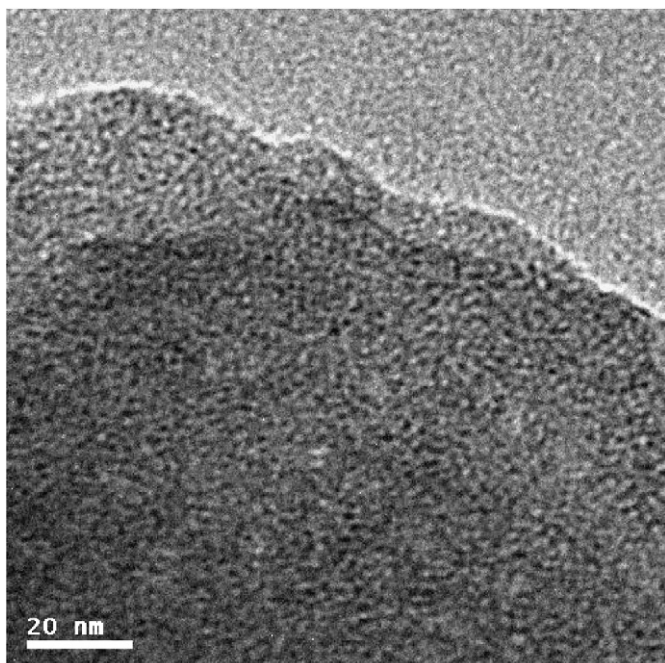
Fig. 2. Transmission electron micrographs of hybrid titania thin film activated with *in-situ* formed lanthanide complex.
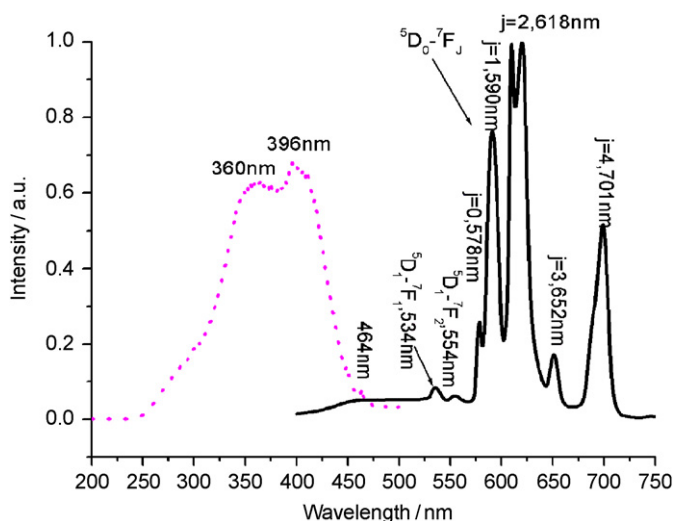

Fig. 3. Excitation (dotted line) and emission (solid line) spectra of the hybrid thin film.

direct excitation of the ligand at 360 nm. Only sharp emission peaks arise from transitions between $^5D_0-^7F_J$ crystal field components ($J = 0$, 1, 2, 3, 4), no broad emission band resulting from free phen molecules in the blue region can be observed. This is in striking difference from systems where only inorganic SiO_2 or TiO_2 matrices without the P123 surfactant where both broad blue band and sharp lines from Eu^{3+} are observable [5,16]. The great difference means that the presence of P123 surfactant is helpful for the *in-situ* formation of lanthanide complexes due to the good solubility of phen in the more hydrophobic environment provided by P123 surfactant, which is in good

agreement with the published result [5]. However, the interaction between the ethylene oxy groups from P123 europium ions could not be avoided. The typical red color of europium emission is mostly attributed to the strongest transition ($^5D_0-^7F_2$) centered at 614 nm. The fine splitting of the $^5D_0-^7F_2$ peak into distinct crystal field component, rather than an amorphous one, indicating in fact $Eu^{3+}-$ phen complex is formed *in-situ* during synthesis of the hybrid organic–inorganic hybrid thin film. On the contrast, the luminescence emission of titania without P123 reported in Ref. [16] display strong inhomogeneous broadening and unresolved emissions. This great difference could be could be ascribed to the presence of P123 surfactant and the mesostructure in our systems. In addition, another two sharp peaks centered at 534 and 554 nm arising from transitions $^5D_1-^7F_1$ and $^5D_1-^7F_2$ were also observed from the emission spectrum, which were rarely observed in other sol–gel-derived systems [2–7]. The excitation spectrum was recorded by monitoring the emission of Eu^{3+} ions at 618 nm. A broad band ranging from 250 to 500 nm superimposed by narrow f–f transition lines of Eu^{3+} ions (394 and 465 nm) is observed, the broad band can be assigned to absorption of the phen and indicates the red emission arise from non-radiative energy transfer of the triplet state of the phen ligand to the central Eu^{3+} ions. The decay curve of the Eu^{3+} ions in the hybrid organic–inorganic thin film is singly exponential, confirming that all Eu^{3+} ions lie in the same average environment, from which the luminescence lifetime was determined as 0.43 ms.

On the basis of the luminescence data discussed above, we can estimate the $^5D_0$ radiative (k_r), non-radiative (k_{nr}) transition probabilities, the $^5D_0$ quantum efficiency (q) and the number of the water molecules, n_w, coordinated to the Eu^{3+} ion [17]. Assuming that only non-radiative and radiative processes are involved in the depopulation of the $^5D_0$ state, q may be defined as

$$q = \frac{k_r}{k_r + k_{nr}}, \tag{1}$$

where k_r and k_{nr} are the radiative and non-radiative probabilities, respectively. The radiative contribution maybe calculated from the relative intensities of the $^5D_0-^7F_J$ ($J = 0$–4) transitions and can be expressed as

$$k_r = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^{4} \frac{S_{0-J}}{E_{0-J}}, \tag{2}$$

where A_{0-1} is Einstein's coefficient of spontaneous emission between the $^5D_0$ and $^7F_1$ level, usually considered to be equal to $50\,s^{-1}$, and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $^5D_0-^7F_J$ transitions, respectively [18].

The number of water molecules (n_w) coordinated to the metal ions in the hybrid thin film can be estimated by modified Horrock's equation, which can be written as

$$n_w = 1.11 \times [k_{exp} - k_r - 0.31], \tag{3}$$

Table 1
$^5D_0$ lifetime (τ), radiative (k_r) and non-radiative (k_{nr}) transition probabilities, quantum efficiency (q), and the number of water molecules coordinated to Eu^{3+} in the hybrid thin film

Sample	τ (ms)	k_r (m s^{-1})	k_{nr} (m s^{-1})	q (%)	n_w
Hybrid thin film	0.46	0.229	2.101	9.8	1.9
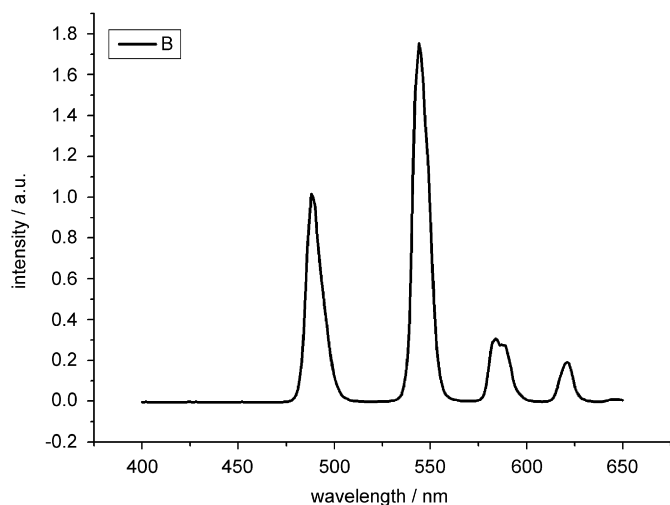
Fig. 4. Emission spectrum of titania thin film activated by *in-situ* formed Tb–phen complex.

Fig. 5. Structural modal of the hybrid titania thin film.

where k_{exp} is the reciprocal value of the $^5D_0$ lifetime. The data obtained using Eqs. (1)–(3) are summarized in Table 1. From these results, it is reasonable to assume that the number of water molecules coordinated to the Eu^{3+} in the hybrid thin film is about 2.

Very similar results were obtained when the Eu^{3+} was replaced by Tb^{3+} in the titania thin film. The Tb^{3+}–phen emission spectrum (Fig. 4) displays four main transitions between the Russell–Saunder multiplets $^5D_0$–^7F_J ($J = 6, 5, 4, 3$). The most intense peak centered at 544 nm is assigned to the $^5D_4$–$^7F_5$ transition and is responsible for the pure green emission color. The decay curve of titania thin film activated by *in-situ* formed Tb^{3+}–phen complex is singly exponential, from which the luminescence lifetime was determined to be 900 μm.

4. Conclusions

Concluding, novel stable luminescent organic–inorganic hybrid titania thin film with high transparency activated by *in-situ* formed lanthanide complexes have been obtained at room temperature via a simple one-pot synthesis approach by using TTFA-modified titanium precursor with amphiphilic triblock copolymer P123. The obtained hybrid thin film displays bright red (or green), near-monochromatic luminescence due to the *in-situ* formed lanthanide complex. We can ascribe our result to the presence of chelating TTFA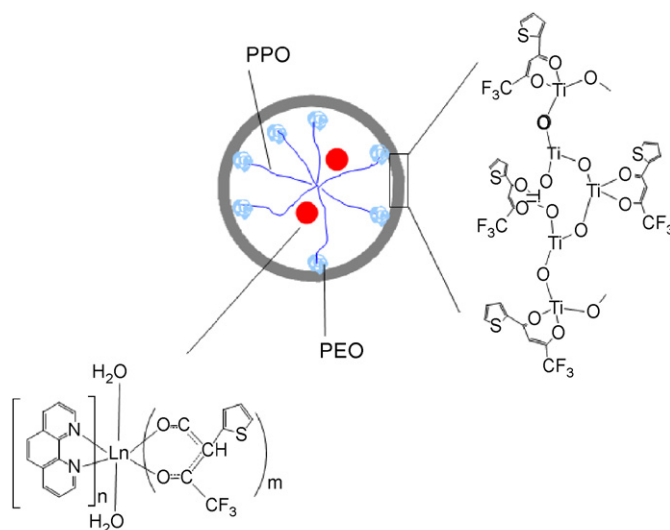 ligands within the titania network suppressing continued condensation of titania network and the addition of the copolymer P123 which can facilitate the *in-situ* formation of lanthanide complexes and the homogenous distribution of them within the thin film (Fig. 5). Furthermore, synthesis conditions are now being optimized to get ordered mesostrucutred thin film, and the work on the extension of photoluminescence to Nir region is also undertaken.

Acknowledgment

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