

High luminescence quantum efficiency of green mesophase silicate thin film incorporated with rare earth complex

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ABSTRACT

Mesophase silica thin film doped with in-situ formed binary terbium (Tb) complex was synthesized through a simple one-step evaporation-induced self-assembly method. In this process, the precursors of rare earth complex and surfactant were added into hydrolyzed tetramethoxy-silane (TMOS) together and the inorganic/organic mesophase thin film was formed after spin coating. The mesophase structure was characterized as a 2D-hexagonal structure by X-ray diffraction (XRD) analysis. The excitation spectra ($\lambda_{em} = 544$ nm) and emission spectra ($\lambda_{ex} = 315$ nm) indicated that the binary complex, Tb(SA)₃, formed in-situ during the formation of the film. Under the UV excitation, the mesophase silica thin film showed bright and consistent green luminescence. The luminescence quantum efficiency of the hybrid thin film was confirmed to be 35.2%.

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1. Introduction

Luminescent thin films are receiving considerable attention for their potential applications in flat panel display and lighting system. These thin films should possess high luminescence quantum efficiency and could be fabricated easily. Recently, organic–inorganic mesophase thin films have attracted a great deal of attention due to their promising applications in chemical sensors, optical devices, and electronic devices [1–5]. In the field of optical applications, such thin films have been intensively studied because many different types of photo-active dopants can be incorporated into the mesoporous thin films [6–8]. The organic luminescent compounds, such as dyes and rare earth complexes, can be used as photo-active dopants [9–11]. The obtained organic–inorganic mesophase thin films have some advantages. It is known that the dyes and rare earth complexes possess high luminescence quantum efficiency when they are well dispersed without aggregation. Incorporating them into the mesopores of the mesophase thin films can efficiently avoid their aggregations and the inorganic framework can provide additional protection for them. Both the optical and chemical properties of the luminescent components are improved. In particular, these organic–inorganic mesophase thin films can be fabricated easily

using the sol-gel method which is a low-cost, low temperature processing route. It means the cost of the fabrication is low. Therefore, such kind of mesophase organic–inorganic hybrid thin films has gained considerable attention in the field of new luminescence materials.

Terbium (Tb) complexes exhibit extensive green luminescence due to the strong absorption of the ligands in the ultraviolet region and efficient energy transfer from the ligands to the central Tb ions. For technological applications, these complexes have to be incorporated into a stable solid matrix [11]. It had been reported that the 1,10-phenanthroline (phen) Tb complex was incorporated in mesostructured thin films and the luminescence efficiency was between 17 and 25% according to the Tb–phen complex concentrations ranging from 2 to 6 wt% [11]. However, for optical applications, the luminescence efficiency should be improved. In this paper, we explore another binary Tb complex as luminescence dopants to enhance the luminescence intensity and the quantum efficiency of the mesophase organic–inorganic hybrid thin film.

In our experiments, a transparent silica mesophase thin film doped with brightly green luminescent binary terbium complex was synthesized by an in-situ method [11]. In this process, the organic ligand salicylic acid, rare earth chloride and surfactant were added into hydrolyzed tetramethoxy-silane solution together. The surfactant is acted as structure-directing agent for the mesophase structure. The silica species are assembled outside the surfactant micelles to form the silica framework and the functional organic components are concurrently incorporated into the surfactant micellar interiors. All the components can be combined at the

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nanoscopic level in a single thin film. Here, the mesophase silicate thin film was chosen as framework because of its optical transparency in the visible region making green photoluminescence possible. Salicylic acid (SA) was used as organic ligand to form the binary Tb complex. During the synthesis of this mesophase thin film, the acid condition was necessary for the hydrolyzation of silica precursor. The organic ligand, SA, could efficiently complex with Tb^{3+} under acid condition. Therefore, the luminescence efficiency of the obtained mesophase organic-inorganic hybrid thin film is higher than that of similar hybrid thin film doped with Tb-phen complex.

2. Experimental details

2.1. Synthesis process

The mesophase organic-inorganic hybrid thin film was prepared using a one-step synthesis method at room temperature. For the synthesis procedure, tetramethylorthosilicate (TMOS, Shanghai Jingchun Chemical Company, 98%) was hydrolyzed in distilled water at room temperature. The hydrochloric acid (HCl, Shanghai Jingchun Chemical Company, 37%) was employed as catalyst in the hydrolysis reaction. Pluronic P123 (Aldrich, $M_{AW} = 5750$) was dissolved in methanol (CH_3OH , Shenyang Chemical Company, 99.8%) to form a template solution. Terbium(III) chloride was from terbium oxide (Tb_4O_7 , Shanghai Yuelong Rare Earth Company, 99.99%). TbCl_3 and salicylic acid (SA, Shenyang Chemical Company, 99%) were dissolved in methanol to form the complex solution. After the hydrolyzation of TMOS, the template solution was added while stirring the solution. The complex solution was then added into the mixture. The final mole ratio of the various components before spin-coating was $2\text{TbCl}_3 : 6\text{SA} : 100\text{TMOS} : 845\text{H}_2\text{O} : 0.9\text{HCl} : 1.05\text{P123} : 2469\text{MeOH}$. The transparent solution was stirred for 15 min and filtered through a $0.45 \mu\text{m}$ -sized Teflon filter to remove impurities and gas bubbles. The solution was then deposited onto p-type Si(100) wafer by spin coating at 4000 rpm for 40 s to form the mesophase thin film. To measure the luminescence quantum yield of this sample, the as-deposited thin film was also spin-coated on transparent quartz substrate. The as-deposited thin film was heated at 550°C in air to obtain the calcined sample.

2.2. Characterization

The thickness of the hybrid thin film was obtained from the image which was obtained using a Philips XL 30 scanning electron microscope (SEM). The mesophase structure of the organic-inorganic hybrid thin film was investigated by X-ray diffraction (XRD) measurements with $\text{CuK}\alpha$ radiation ($\lambda = 0.15417 \text{ nm}$) with a 0.01° step width and 1 s step time on a Rigaku D/MAX-RC diffractometer (40 kV, 80 mA). Transmission electron microscope (TEM) image of the calcined film was recorded using a JEOL JEM-2000EX electron microscope operating at 200 kV. The photographs of the photoluminescence from the mesophase thin films were taken by a commercial camera using a Hg/Xe lamp (Oriel 82511, with a power density of 70 mW cm^{-2} with a spectral range of around 220–260 nm) as the excitation source at room temperature. Room-temperature emission spectra and luminescence decay were measured using a HeCd laser (325 nm laser) as an excitation source. The luminescence decay traces were obtained with a digitizing oscilloscope. The excitation and emission spectra were measured at room temperature with a Hitachi F-4500 fluorescence spectrometer.

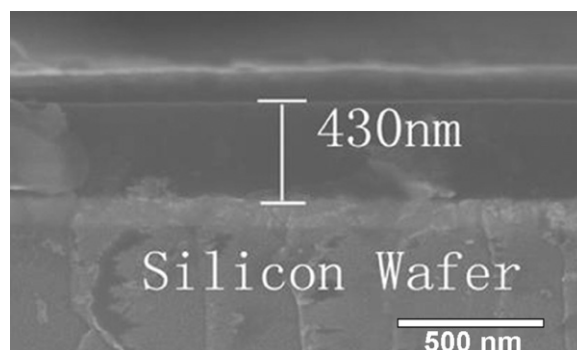


Fig. 1. SEM image of a cross-section of the as-deposited thin film.

3. Results and discussion

3.1. Structure of mesophase hybrid thin film

In our experiments, surfactant Pluronic P123 triblock copolymer (P123) was acted as a template. In the synthesis process, the hydrophobic moieties of the P123 enhanced the solubility of organic ligands and separated the in-situ Tb complex molecules in hydrophobic regions uniformly. After spin coating, the luminescence dopants were incorporated into the hydrophobic core of the template and a continuous homogenous 2D-hexagonal silica skeleton was formed with direction of the template. The scanning electron microscopy image of a cross-section of the mesophase thin film shows that the film is dense and continuous on silicon wafer (Fig. 1). The thickness is about 430 nm. The mesophase structure of the as-synthesized sample was confirmed by XRD pattern (Fig. 2). The XRD pattern of the thin film shows two peaks, at $2\theta = 0.88^\circ$ and 1.68° , which indicate (1 0 0) and (2 0 0) reflections of a general 2D-hexagonal structure, respectively [12]. The unit cell parameter (a_0) including the internal pore diameter and silica wall thickness can be calculated using this formula: $a_0 = 2d(100)/3^{1/2}$, where d spacing is from $d(100) = \lambda/2 \sin \theta$ [12]. The calculated unit cell parameter is obtained as 11.3 nm. The mesostructure of the hybrid thin film is distinguished between 2D-hexagonal and lamellar by calcining the sample at 550°C to get rid of the organic component. The XRD pattern of the calcined thin film shows that the two peaks still remain. It suggests that the calcined thin film has a similar structure to the as-synthesized one and the oriented hexagonal meso-structure does not collapse after calcinations. Therefore the as-deposited

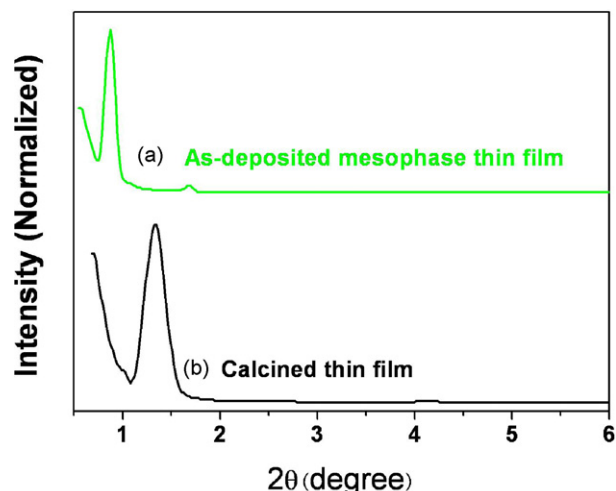


Fig. 2. XRD pattern of (a) the as-deposited and (b) the calcined thin film.

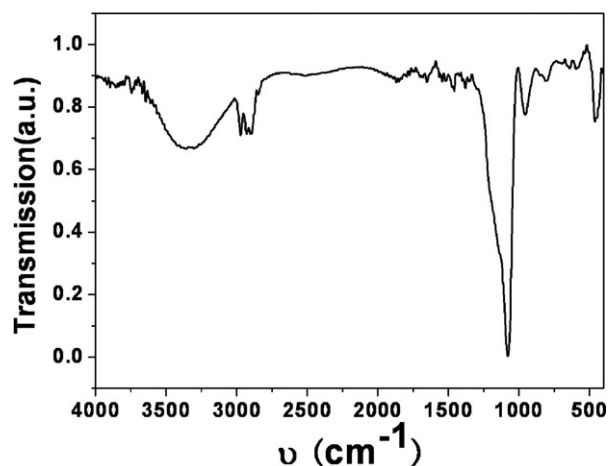


Fig. 3. FTIR spectrum of the as-deposited mesophase thin film.

thin film is proved possessing 2D-hexagonal mesostructure. The SEM image and XRD patterns confirmed that even the RE ions and organic ligand was added, the as-deposited mesophase thin film with a 2D-hexagonal structured silicate framework were formed successfully using the P123 block copolymer as template.

To confirm the organic components were incorporated in the as-deposited silica thin film, the FTIR spectrum was carried out. In the FTIR spectrum (Fig. 3), we can observe the bands at 1082, 807 and 461 cm^{-1} which are associated with the Si–O asymmetric stretching, Si–O symmetric stretching and Si–O–Si bending vibrations, respectively. Beside these bands of silica framework, the bands in the range of 2480–3008 cm^{-1} which are associated with C–H asymmetric stretching and symmetric stretching are also observed. The appearance of the vibration of organic components indicates that the as-deposited sample is organic-inorganic hybrid thin film. In addition, the broad band at 3450 cm^{-1} are attributed to the vibration of O–H groups [13]. According to the synthesis process of the thin film, the in-situ formed luminescence complexes should be combined at the nanoscopic scale and imbedded into the hydrophobic core of the template.

3.2. Luminescence properties of the as-deposited mesophase thin film

Fig. 4 shows the excitation (left) and emission (right) spectra obtained from the as-deposited mesophase thin film at room temperature. The color photo (Fig. 5) was taken under Hg/Xe lamp irradiation. From the photo, we can see that the as-deposited hybrid

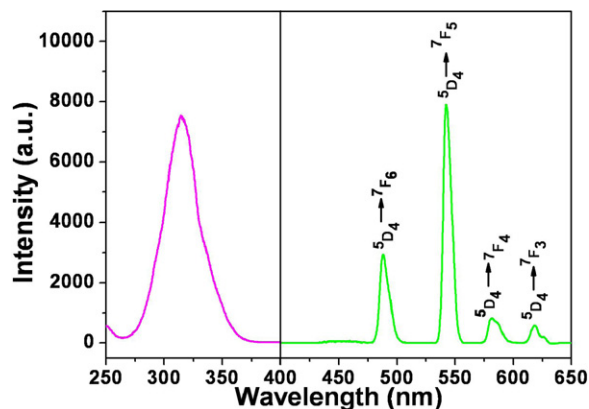


Fig. 4. Excitation (left) and emission (right) spectra of the as-deposited mesophase thin film.

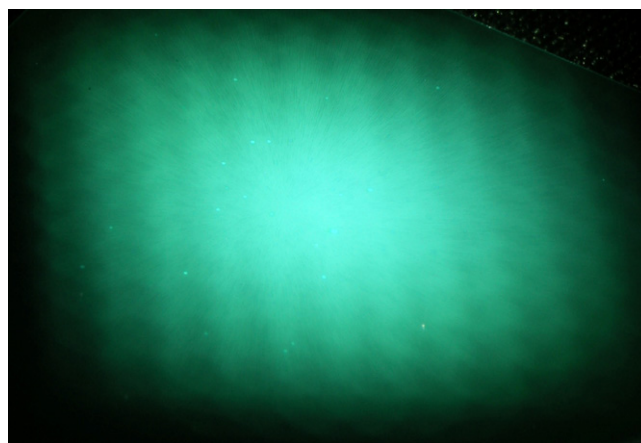


Fig. 5. Color photo of the as-deposited mesophase thin film under a Hg/Xe lamp irradiation. (For interpretation of the reference to color in the text for Fig. 5, the reader is referred to the web version of the article.)

thin film shows bright green luminescence. The emission spectrum of this hybrid thin film exhibits four characteristic emission peaks at 488, 544, 584, and 622 nm, which are attributed to the f–f transitions of the Tb^{3+} ion ($^5\text{D}_4 \rightarrow ^7\text{F}_{J=3-6}$) [13]. The peak at 544 nm is dominant, therefore the luminescence of the thin film is shown green in color. We also detected the excitation spectrum of the sample in a range of 250–400 nm by monitoring the 544 nm emission. The broad band in the range of 275–350 nm is attributed to absorption of the organic ligand (SA), which can be assigned to the $\pi-\pi^*$ electron transition. By monitoring the characteristic emissions of the Tb^{3+} ion, the presence of the typical absorption band of the SA ligand in the excitation spectrum indicates that the Tb^{3+} ion is coordinated to this organic ligand and the electrons of Tb^{3+} can be pumped efficiently via intramolecular energy transfer from the triplet excited state of the SA ligand. It also proves the in-situ formation of the $\text{Tb}(\text{SA})_3$ complex.

The luminescence lifetime is an important parameter in the photophysical description of luminescence dopant. The luminescence decay curve of the as-deposited mesophase thin film was shown in Fig. 6. It can be well fitted with a single exponential function (red line), and lifetime of $920 \pm 2.2 \mu\text{s}$ was obtained. The mono exponential decay process of the hybrid mesophase thin film is indicative of a single average site distribution for Tb^{3+} ions in the sample. It indicates that there exists only one emission center in the mesophase thin film and the in-situ formed Tb complex is well dispersed in the silica network.

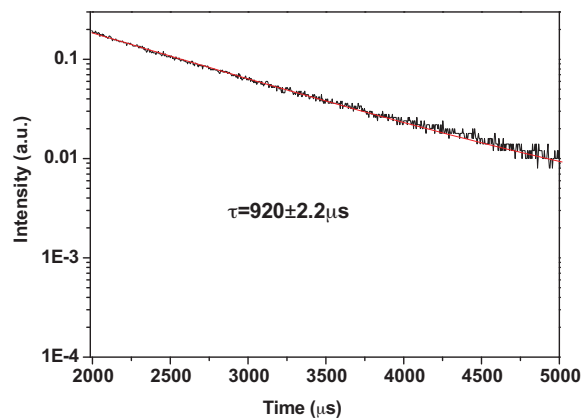


Fig. 6. Luminescence decay curve of the as-deposited mesophase thin film. (For interpretation of the reference to color in the text for Fig. 6, the reader is referred to the web version of the article.)

In our experiments, the luminescence quantum efficiency of the as-deposited mesophase thin film was measured to quantify the efficiency of the energy transfer. The method is an integrating-sphere technique similar to that described elsewhere [14–17]. Under the UV excitation (325 nm HeCd laser), the luminescence quantum efficiency of the as-deposited mesophase thin film reaches 35.2%. The value is higher than that of the similar thin film doped with other Tb complex reported in the reference (the quantum efficiency for the thin films doped with terbium–phen complex are between 17 and 25% according to the Tb complex concentrations ranging from 2 to 6 wt%) [11]. This result shows that using SA as the ligand can improve the luminescence quantum efficiency of such inorganic/organic mesophase thin film doped with binary Tb complex. It meets the requirements of high luminescence quantum efficiency for display and lighting applications.

4. Conclusions

Luminescent mesophase silica thin film doped with in-situ formed Tb(SA)₃ complex was prepared by a one-step synthesis method. XRD and SEM analyses confirm that the homogenous thin film has a typical 2D-hexagonal mesostructure. Under UV excitation, the mesophase thin film exhibits the strong characteristic emissions of Tb³⁺ ions. The emission and excitation spectra for the mesophase thin film suggest that the Tb(SA)₃ complex is in-situ formed during the synthesis of the composite films. The decay process indicates that only one luminescence center is contained in the mesophase thin film, and that the mesophase silica thin film is homogeneous. The luminescence quantum efficiency of the as-deposited mesophase thin film can reach 35.2% and it indicates that the green-color mesophase silica thin film phosphors

incorporated with in-situ formed Tb complex have promising applications in display field.

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