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Luminescent properties of encapsulation of europium complex into meso-structured silica monoliths

Yu Chen [a], Qi Chen [a,b,*], Li Song [b], Hui-ping Li [b], Feng-zhen Hou [b]

[a] Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
[b] Department of Inorganic Materials, East China University of Science and Technology, Shanghai 200237, China

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A B S T R A C T

Meso-structured silica monoliths using PEG (PEG = polyethylene glycol) as a low-cost template and synthesized via sol–gel methods were used as host materials for incorporation of europium complexes Eu(BA)$_3$Phen (BA = benzoic acid and Phen = 1,10-phenanthroline). The meso-structured silica was silylated by 3-aminopropyltriethoxysilane (APTES) or 3-glycidoxypropyltrimethoxysilane (GPTMS) before wet impregnation. Samples were characterized by BET, diffuse reflectance (DR) spectroscopy, infrared spectroscopy and fluorescence measurements. The results showed that the emission quantum efficiency of GPTMS silylated meso-structured silica with larger pore size was up to 44.6%. Also, the lifetime measurement showed the complex encapsulated in this rigid matrix had longer lifetime than the pure complex in solid or liquid.

1. Introduction

Lanthanide ions are useful for their ability to exhibit characteristic emission wavelength, but their poor adsorption abilities in the UV region make the direct excitation process very difficult. To solve this problem, lanthanide ions are chelated with organic ligands, which have strong absorption bands in the UV region. The ion-centered luminescence originates from the intramolecular energy transfer through the excited state of the ligand to the emitting level of the lanthanide ions, which is known as the antenna effect [1]. The lanthanide complexes display a long emission life in the millisecond time scale and high-quantum yields at room temperature. However, owing to the poor thermal and photostability of lanthanide complexes, they are prevented from having more applications. Therefore, the complexes have to be incorporated into stable rigid matrices for practical use. Silica hosts with mesoporous structure such as MCM-41 [2], MCM-48 [3] and FDU-1 [4] have been used in encapsulation of lanthanide complexes. Whereas recent studies on mesoporous materials encapsulated with lanthanide complexes were mainly focused on luminescent powders or films using M41S as support materials. We developed meso-structured monoliths, using polyethylene glycol (PEG) as a low-cost template, as host materials for the incorporation of lanthanide complex Eu(BA)$_3$Phen [5]. In this paper, particularly, detailed information of the assemblies systems was studied by the investigation of luminescent properties of lanthanide complex Eu(BA)$_3$Phen encapsulated in silylated silica with mesoporous structure.

2. Experimental section

2.1. Synthesis of mesoporous monoliths and lanthanide complex

The mesoporous monoliths and the ternary lanthanide complex were prepared by the same method described in the previous work [5], except that the smaller pore size samples were obtained by heat treatment at 600 °C (873 K) with heating rate at 0.5 K(°C)/min. The silylation and encapsulation process were also carried in the same way shown in the Ref. [5], except that another silylation agent 3-glycidoxypropyltrimethoxysilane (GPTMS) was used in this work.

2.2. Characterization

Adsorption and desorption isotherms were measured with a Micromeritics surface area and porosimetry system analyzer (ASAP 2010N). Specific surface area was evaluated using the BET

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[*] Corresponding author at: Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China. Tel.: +86 21 6425 3466; fax: +86 21 6425 0882.
E-mail address: qichen@ecust.edu.cn (Q. Chen).

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method. Pore size distribution (PSD) was calculated in the way of BJH algorithm. Fluorescence measurements at room temperature were recorded by an Edinburgh Instrument (FLS920) spectrofluorimeter with a double grating monochromator, and a 450 W xenon lamp as excitation source. The CHN elemental analysis, carried on VarioEL β analyzer, determined the C%, H% and N% of the complex. Also, the amount of Eu^{3+} was performed by complex on metric titration with EDTA.

2.3. Naming of samples

In this paper, Sample **S3-0** and **S6-0** stand for silica under heat treatment at 623 and 873 K. **E-p** and **E-s** are Eu-complex powder and complex solvated in DMF (diluted by EtOH). Assembly samples **A3-1, A6-1, G3-1** and **G6-1** are 3-aminopropyltriethoxysilane (APTES)-silylated silica (heat treatment at 623 K), APTES-silylated silica (heat treatment at 873 K), GPTMS-silylated silica (heat treatment at 623 K) and GPTMS-silylated silica (heat treatment at 873 K), respectively. All these assembly samples were impregnated in 9×10^{-3} mol L^{-1} Eu-complex solution.

3. Results and discussion

3.1. Analysis of structure of europium complex and meso-structured silica

The elemental analysis data presented in Table 1 are in concordance with the formulas $Eu(BA)_3Phen$. Also, TG analysis shows the complex has no obvious weight loss in the range of 50–230 °C, which indicates no water molecule exists in the complex.

The infrared spectrum [5] of obtained meso-structured silica shows the absorption bands in the 1030–1250 cm^{-1} range which belong to asymmetric Si–O stretching vibration modes, whereas bands at 796 cm^{-1} are attributed to the symmetric Si–O stretching vibration. All these bands indicate the formation of silica network. In the infrared spectra of silylated samples, absence of absorption bands at about 953 cm^{-1} (surface –OH groups of mesoporous silica) and presence of absorption band (the stretching vibration of $–CH_2–$ of silylation agents) at about 2900 cm^{-1} indicates that surface –OH groups were consumed by silylation process.

Nitrogen adsorption and desorption isotherms, pore size distribution and BET surface area of samples **S3-0** and **S6-0** are shown in Figs. 1 and 2 and Table 2. In this work, it is found that **S6-0** has lower S_{BET} and total pore volume (V) than **S3-0**. However, the nitrogen adsorption and desorption isotherms shows the similar Type IV isotherms with Type H3 loops [6], which indicates the structure of mesopores has not been changed after heat treatment at different temperatures.

3.2. Diffuse reflectance (DR) spectra

The DR spectra of Eu-complex powder (**E-p**), APTES-silylated assembly (**A3-1**) and GPTMS-silylated assembly (**G3-1**) are shown in Fig. 3. There are two strong absorption bands of **E-p** peaking at around 258 and 295 nm, which are attributed to electronic transitions from the S_0 ground state level to the S_1 excited level of two ligands benzoic acid and 1,10-phenanthroline, respectively. The hypsochromic phenomena of $S_0 \rightarrow S_1$ absorption can be observed for the two impregnated samples with different silylation agents. The reasonable explanation for the blue-shift effect is that the polarity of the surrounding chemical environment of the Eu^{3+} has been changed when the complex is dispersed in the channels of mesopores. To better analyze the effect, the blue shift is visualized by plotting first derivative of the absorption curves. The position of the $S_0 \rightarrow S_1$ absorption onset value is defined as the same way described in the Ref. [3]. Table 3 shows onset values and blue shifts of all the samples. The results indicate that there are strong interactions between the mesopores of the silica and two ligands. The interactions cause the similar blue shifts effect on both two ligands.

Table 1
Elemental analysis of the europium complex.

	%C	%H	%N	$\%Eu^{3+}$
Calc.	56.98	3.29	4.01	21.86
Exp.	55.84	3.08	3.82	22.07

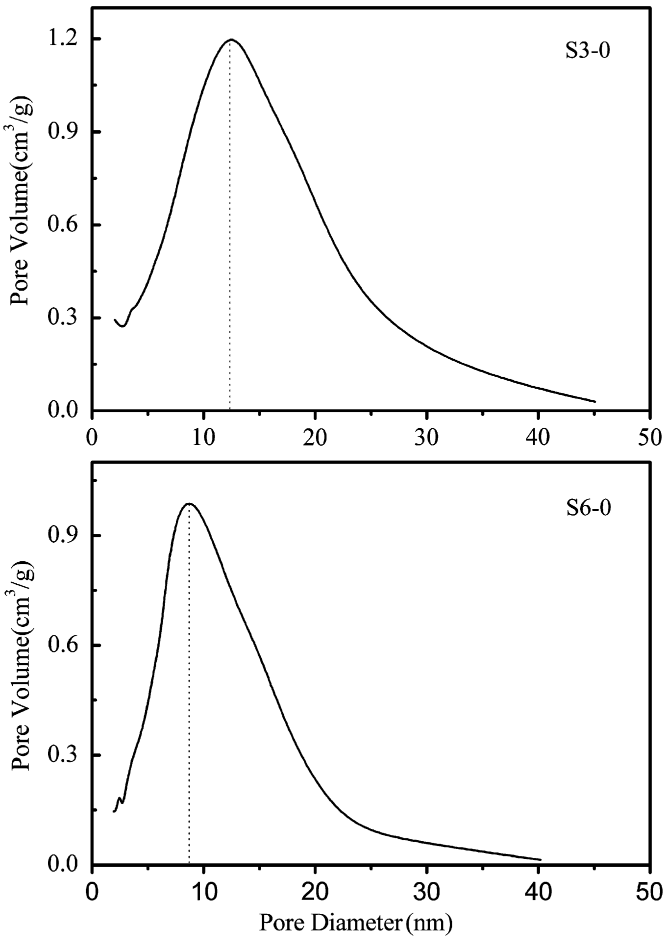

Fig. 1. Nitrogen adsorption and desorption isotherms of sample **S3-0** and **S6-0**.

3.3. Luminescence properties

3.3.1. Excitation spectra

The excitation spectra of the Eu-complex (**E-p**), APTES-silylated assembly (**A3-1**) and GPTMS-silylated assembly (**G3-1**) are shown in Fig. 4. All the excitation spectra were recorded at room temperature by monitoring at 615 nm. The neat complex exhibited broad bands of effective excitation wavelength ranging from 250 to 370 nm. The dominating band at about 350 nm can be ascribed to electric transition of 1,10-phenanthroline ligands as research work showed its absorption in the similar range [7]. The other relatively weaker band appearing at the high-energy side of excitation spectrum (about 290 nm) is assigned to benzoic acid ligands, since the absorption band of aromatic carboxylic groups appear in the