Synthesis and Characterization of Europium Complex Nanowire

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A new compound of benzyl 2-{2-[ethyl(phenyl)amino]-2-oxoethoxy}-1,1-bis{2-[ethyl(phenyl)amino]-2-oxoethoxy-methyl}ethylcarbamate (L) was synthesized. The Eu(III) complex nanowires were fabricated by a template method and characterized by elemental analysis, IR spectrum and TEM. The longer luminescence lifetime was found for the Eu(III) complex nanowire in comparison with that of Eu(III) complex powder which is prepared by deposition reaction in solvent.

Organic and inorganic materials on the nanometer scale have many peculiar properties that can not be normally found in traditional materials.[1–3] These properties are currently under intense study for potential uses in rechargeable battery, condensers, restoring of data, biochemical analysis and a host of other applications.[4–8] Recently, attempts have been made to synthesis nanoscopic fibrils and tubules using template synthesis method to achieve this objective.[9,10] This method entails synthesis of the desired material within the pores of a nanoporous membrane, including polymers, metals, semiconductors, and carbon.[11–15] Because the membranes employed have linear, cylindrical pores of uniform diameters, monodispersed nanostructrues of the desired material can be obtained in each pore.

Luminescent lanthanide complex have many potential applications in supramolecular devices, fluorescent sensors, or luminescent probes[16,17] due to their intense emission peaks in the visible and near-infrared region under an UV excitation. Much effort has been devoted to the design of available ligands that can efficiently optimize the luminescent properties of lanthanide ions by facilitating the well-known light conversion process, i.e. ligand absorption, ligand-to-metal energy transfer, and metal emission.[16,18] Recently, there is a proliferation interesting in the study of the incorporation of lanthanide complexes in a polymer to create a suitable organic/inorganic cage capable of encapsulating the luminescent centers, protecting them from deleterious quenching processes.[19,20] But so far, no pure lanthanide complex nanomaterials have been prepared. It is our motivation to design a new growth process and to fabricate complex nanowires for lanthanide luminescent materials. In this work, we firstly synthesized nanowires of Eu(III) complex based on anodic aluminum oxide (AAO) template method and briefly discuss their better photoluminescence properties in comparison with Eu(III) complex powder.

All solvents prior to use were dried by conventional procedures. Europium picrate, 2-chloro-*N*-ethyl-*N*-phenylacetamide, benzyl 2-hydroxy-1,1-bis(hydroxymethyl)-ethylcarbamate[21,22] were prepared by the reported methods. Benzyl 2-{2-[ethyl(phenyl)amino]-2-oxoethoxy}-1,1-bis-{2-[ethyl(phenyl)amino]-2-oxoethoxymethyl}ethylcarbamate (L) was obtained by the modified literature method.[23] The complex powder was obtained directly by the reaction of L with $Eu(Pic)_3$ in absolute ethanol.

The dried AAO template was put into a dilute solution of L and dried in vacuum. Then the AAO template was immersed into a dilute ethanol solution of $Eu(Pic)_3$ for 2 h. After washed ultrasonically in ethanol and dried in vacuum, the resulted AAO template changed to yellow and emitted red fluorescent light under UV light radiation, indicating the deposition of Eu(III) complex within the pores of AAO membrane. The Eu(III) complex materials dispersed in the pores were liberated by dissolving the AAO membranes in 6 mol·L^{-1} NaOH and washed by pure water.

The C, H, N elemental analyses were performed using an Elementar Vario EL. The Eu(III) were determined by EDTA titration using Xylenol Orange as indicator. IR spectra were obtained by using a Nicolet AVATAR-360 fourier transform infrared (FTIR) spectrometer. The FTIR spectra showed only the absorption of the complex. TEM analysis was performed using a JEOL-2010 microscopy at 200 kV. The room temperature photoluminescence (PL) spectra were obtained by a Shimadzu RF-530/PC spectrofluorophotometer. The luminescence decay transients were recorded using a Nd:YAG laser at 77 K.

The analytical data listed in Table 1 reveals the composition of $[Eu(Pic)_3]_6L_5$ to both of the complexes. The almost equal values indicate that the different synthesis methods did not change the stoichiometry of the complex.

Table 1. Analytical data for the $[Eu(Pic)_3]_6L_5$ complexes (wt/%)

	C	H	N	Eu
Calculated values	43.84	3.31	11.90	10.47
Nanowire	44.38	3.77	11.86	11.35
Powder	44.41	3.26	12.02	10.32

Figure 1 shows the IR spectra of L, Eu(III) complex powder and nanowire. The spectrum of L shows bands at 1752, 1671 and 1126 cm^{-1} which may be assigned to $\nu_{C=O}$ (-OCO, -CH_2CO) and $\nu_{C–O–C}$, respectively. While in the complex nanowire, these bands (1733, 1617 and 1076 cm^{-1}) show shifts by ca. 19, 54 and 50 cm^{-1} towards lower wave numbers, indicating carbonyl and ether O atoms of L take part in the coordination to Eu(III). For the complex powder, the fact that these main bands can also be seen but with a little higher wave numbers than that of nanowire, proves that the carbonyl and ether O atoms are also the coordinated molecular but with a little different coordination situation.

The TEM images of Eu(III) complex nanowires and powder are shown in Figure 2. The TEM image of nanowires exhibits the presence of uniform complex nanowires with diameter and length of ca. 10 nm and 260 nm, respectively. Some nanowires grow together with each other due to physical adsorption on the surface

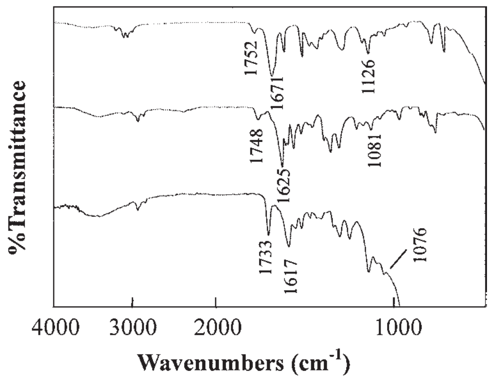

Figure 1. IR spectra of L (above), Eu(III) complex powder (middle), and nanowire (below).

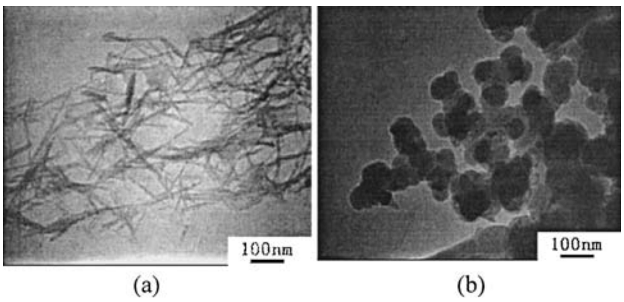

Figure 2. TEM images of (a) Eu(III) complex nanowires and (b) Eu(III)complex powder.

of the wires. From the TEM image of complex powder, only several particles can be seen, which connected to each other, the others are badly aggregated to form a big mass with a coarse surface. The sizes of particles are much different to each other.

Both of the Eu(III) complexes show a high luminescence peak at about 617 nm when excited with 396 nm radiation, which can be attributed to the $^5D_0 \rightarrow {}^7F_2$ transition. The fluorescence decay curves were obtained of the $^5D_0$ level, from which resulted in the lifetimes of 0.35 and 0.43 ms for the complex powder and nanowires respectively. The longer lifetime of the nanowires may be due to the better surface structure and higher surface-to-volume ratio than complex powder.

In summary, Eu(III) complex nanowires fabricated by our group is a new type of one-dimensional nanomaterial, which exhibits a better microstructure and a longer luminescent lifetime in comparison with the corresponding complex powder. It is also reasonable to speculate that there must have many other unique properties and applications to investigate further. Work along these lines should be in progress.

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References

1 A. P. Alivisatos, *Science*, **271**, 933 (1996).
2 A. J. Nojik, F. Williams, M. T. Menadovic, T. Rajh, and O. E. Micic, *J. Phys. Chem.*, **89**, 397 (1985).
3 A. Henglein, *Chem. Rev.*, **89**, 1861 (1989).
4 J. Heinze, *Synth. Met.*, **41–43**, 2805 (1991).
5 F. H. Winslow, W. O. Baker, and W. A. Yager, *J. Am. Chem. Soc.*, **77**, 4751 (1955).
6 A. Mohammadi, M. A. Hasan, B. Liedberg, L. Hungstom, and W. R. Salaneck, *Synth. Met.*, **14**, 19 (1986).
7 S. Kuwabata, S. Ito, and H. Yoneyama, *J. Electro. Chem. Soc. Electrochem. Sci. Technol.*, **135**, 1691 (1988).
8 S. Naitoh, K. Sanui, and N. Ogata, *J. Chem. Soc., Chem. Commun.*, **1986**, 1349.
9 G. H. Pontifex, P. Zhang, and Z. Wang, *J. Phys. Chem.*, **95**, 9989 (1991).
10 C. K. Preston and M. Moskovits, *J. Phys. Chem.*, **97**, 8495 (1993).
11 R. P. Burford and T. Tongtam, *J. Mater. Sci.*, **26**, 3264 (1991).
12 C. A. Foss, G. L. Hornyak, J. A. Stockert, and C. R. Martin, *Adv. Mater.*, **5**, 135 (1993).
13 C. B. Gorman, H. A. Biebuyck, and G. M. Whitesides, *Chem. Mater.*, **7**, 526 (1995).
14 B. B. Lakshmi, C. J. Patrissi, and C. R. Martin, *Chem. Mater.*, **9**, 2544 (1997).
15 T. Kyotani, B. K. Pradhan, and A. Tomita, *Bull. Chem. Soc. Jpn.*, **72**, 1957 (1999).
16 N. Sabbatini, M. Guardigli, and J.-M. Lehn, *Coord. Chem. Rev.*, **123**, 201 (1993).
17 P. Guerriero, S. Tamburini, and P. A. Vigato, *Coord. Chem. Rev.*, **139**, 17 (1995).
18 V. Alexander, *Chem. Rev.*, **95**, 273 (1995).
19 V. Z. Bermudez, R. A. Ferreira, and L. D. Carlos, *J. Phys. Chem. B*, **105**, 3378 (2001).
20 Q. Li, T. Li, and J. Wu, *J. Phys. Chem. B*, **105**, 12293 (2001).
21 A. J. Speziale and P. C. Hamm, *J. Am. Chem. Soc.*, **78**, 2556 (1956).
22 P. Köberle, A. Laschewsky, and D. Boogaard, *Polymer*, **33**, 4029 (1992).
23 S. Huang, Y. J. Yan, and B. Z. Tian, *Hecheng Huaxue*, **2**, 230 (1994).