Synthesis, and Characteristic Luminescence of Core-Shell SiO_2@Eu(MABA-Si)·(phen) Microspheres

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Abstract. Monodispersed SiO_2@Eu(MABA-Si)·(phen) core-shell microspheres were synthesized by silane coupling agent method. The core-shell microspheres was used the europium complex Eu(MABA-Si)·$(phen)_2$·$(ClO_4)_3$·$2H_2O$ as shell and SiO_2 as the inorganic core. The europium complex shell has grafted to silica surface through forming a Si-O-Si bond. The europium complex was synthesized by $HOOCC_6H_4N$- $(CONH(CH_2)_3Si(OCH_2CH_3)_3)_2$ (denoted as MABA-Si) and phen coordinated europium perchlorate. The europium complex has been characterized by element analysis, molar conductivity, ^{1}HNMR and IR. The TEM and SEM showed that the diameter of SiO_2 core was about 400 nm and the thickness of the europium complex shell was about 20 nm. Fluorescence spectra illustrated that the core-shell microspheres have stronger fluorescence intensity than the europium complex which was 1.87 times.

1 Introduction

Core-shell nanometer microspheres are a kind of nanomaterial with a core-shell structure that can be widely applied in making functional fluorescent materials, magnetic materials, electronics, medicine, and so on. By coating a layer of organic alkoxysilane complexes, the luminescence properties of core-shell materials can be changed *including* luminescence intensity, fluorescence quantum efficiency, stability and fluorescence lifetime [1-3].

Silica probably is the most popular inorganic material because of its good mono-disperse, flexibility of controlling the particle size, low cost, low toxicity, and more mechanical stability. Owing to the external hydrogen bonds of its surface, SiO_2 is easy to bond with different materials through chemical bonds or electrostatic interactions [4-6]. At present, silane coupling agent is used to prepare the coating structure nanomaterials that was generally described as $Y(CH_2)nSiX_3$. Y group is the organic functional group that can combine with the rare earth ions. X represents the hydroxyl groups which combined with

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Si-OH of the surface of SiO_2. As a result, RE^{3+} and SiO_2 can be incorporated through silane coupling agent which plays a role of the "molecular bridge".

In this article, we have controlled prepared ternary europium complex Eu(MABA-Si)·$(phen)_2$·$(ClO_4)_3$·$2H_2O$. The MABA-Si is a kind of silane coupling agent, which can be easily coordinated with Eu^{3+} ions through the carboxyl oxygen atoms of MABA-Si groups, and the second ligand phen also can be coordinated with Eu^{3+}. Furthermore, the monodispersed SiO_2@Eu(MABA-Si)·(phen) core-shell microspheres synthesized by the europium complex grafting to silica surface through forming a Si-O-Si bond. The luminescent properties of europium complex and core-shell microspheres SiO_2@Eu(MABA-Si)·(phen) was discussed in detail.

2 The experiment

2.1 Materials.

Eu_2O_3(99.99%), $HClO_4$(1 mol·L^{-1}), phen, m-aminobenzoic acid, TEOS, 3-(Triethoxysilyl)-propyl isocyanate (96%, TEPIC, Aldrich), All other reagents were analytically grade.

2.2 Physical measurements.

Elemental analysis was carried on PF-2400 Elemental Analyzer. Conductivity was measured by DDS-11D Conductivity Meter. The europium ion content was measured by EDTA titration, Xylenol-Orange as indicator. The IR was determined by Nicolet NEXUS-670 FT-IR spectrophotometer. The ^{1}HNMR spectra was determined in the DMSO-d_6 by Bruker AC-500 nuclear magnetic resonance spectrophotometer.The morphology of the products was observed by Scanning Electronic Microscope (Hitachi S-4800) and Transmission Electronic Microscope (FEI Tecnai F20). Fluorescence properties were determined via FLS980 (slit width: 1 nm). Fluorescent decay curves were recorded by FLS980 Combined Steady State and Lifetime Spectrometer.

2.3 Preparation of the europium ternary complex.

The ligand MABA-Si was synthesized according to the method of the literature [7]. 1 mmol MABA-Si and phen were added into 1 mmol $Eu(ClO_4)_3$·nH_2O, anhydrous ethanol solution drop by drop under the magnetic stirring. White precipitate was obtained by washing for several times with anhydrous ethanol and distilled water.

2.4 The synthesis of core-shell SiO_2@Eu(MABA-Si)·(phen) microspheres.

SiO_2 was synthesized through the so-called Stöber [8] method. 0.2 g MABA-Si was added into 15 ml SiO_2 anhydrous ethanol solution under magnetic stirring for 12h. Then appropriate concentration of europium perchlorate and phen were added into above solution. The white precipitate core-shell microspheres SiO_2@Eu(MABA-Si)·(phen) were formed by washing for several times with anhydrous ethanol and distilled water.

3 Results and discussions

3.1 The composition of the europium complex.

The composition and structure of the europium complex have been identified by element analysis, molar conductivity, ^{1}HNMR and IR. The element analysis showed that Anal. Calcd for $C_{28}H_{49}N_3O_{10}Si_2$ (MABA-Si): C, 51.35%; H, 7.76%; N, 6.66%, found: C, 50.80 %; H, 7.82%; N, 6.55%. The results demonstrated that the experimental value was close to the theoretical value. The molar conductivity value was 167 $S{\cdot}cm^2{\cdot}mol^{-1}$, (DMF as solvent). The ^{1}HNMR (DMSO) spectra of europium complex's chemical shift appeared at δ0.56 ppm, δ1.04-1.51 ppm, δ2.93 ppm, δ3.33-3.47 ppm, δ3.73 ppm, δ7.43-7.57 ppm and δ12.4 ppm. It showed that MABA-Si synthesized successfully. Fig. 1 displayed the IR spectra of MABA-Si, phen and Eu(MABA-Si)·(phen)·$(ClO_4)_3{\cdot}2H_2O$. The peak located at 1700, 1417, and 1314 cm^{-1} were belonged to the $\nu_{C=O}$, ν_{C-OH} and δ_{O-H} of carbonyl, which prove the presence of MABA-Si. Compared with MABA-Si, the europium complex not only exhibit similar infrared absorption bands as MABA-Si but also the peak at 1527, 716 and 848 cm^{-1} range in phen with red shift, indicating that europium ion was bonded with MABA-Si and phen through the carbonyl group and double nitrogen atoms [9]. It was found that ClO_4^- absorption band around 1145, 1115, 1083, and 625 cm^{-1}, which were assigned C_{2v} symmetry of the perchlorate group [10]. The above analysis shows that the composition of the complex was Eu(MABA-Si)·$(phen)_2{\cdot}(ClO_4)_3{\cdot}2H_2O$.

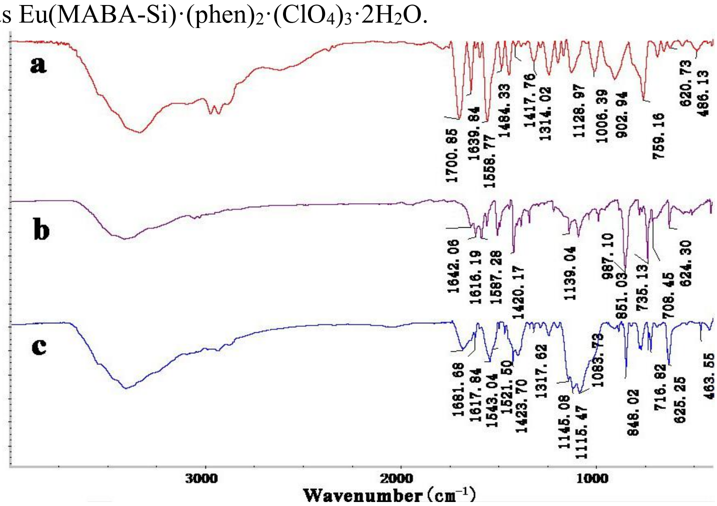

Fig. 1. IR Spectra of a. MABA-Si; b. phen; c. Eu(MABA-Si)·$(phen)_2{\cdot}(ClO_4)_3{\cdot}2H_2O$

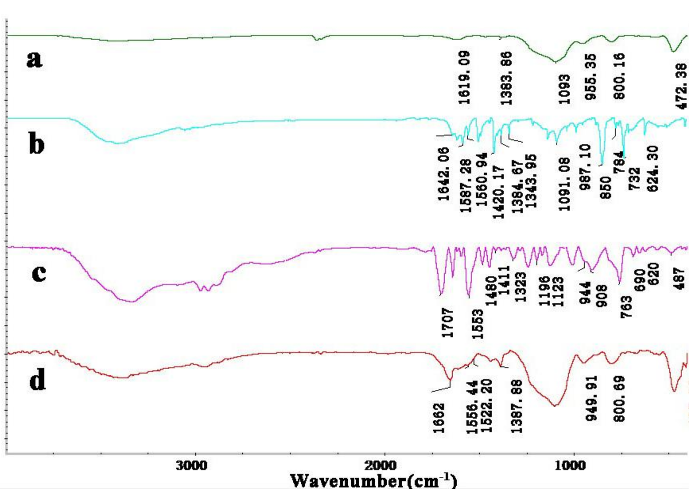

Fig. 2. IR Spectra of a.SiO_2; b. MABA-Si; c. phen; d. SiO_2@Eu(MABA-Si)·(phen)

3.2 IR spectra analysis of core-shell microspheres

Fig. 2 displays the IR spectra of SiO_2, MABA-Si, phen, and SiO_2@Eu(MABA-Si)·(phen). The absorption band Si-O-Si was appeared at 1096 and 800 cm^{-1}(Fig. 2a and 2d), which confirmed that the europium complex shell has grafted to silica surface through forming a Si-O-Si bond. In Fig. 2b, 2c and 2d, it was similar to above complex that the stretching frequency red shifted to 1656, 1619, 1553 cm^{-1} (MABA-Si) and 1568 cm^{-1} (phen). Compared with 1700, 1639 and 1558 cm^{-1} (MABA-Si) and 1587 cm^{-1} (phen). The above information indicated that europium ion coordinated with through C=O oxygen atom of MABA-Si and double nitrogen of phen.

3.3 The SEM and TEM analysis of core-shell microspheres.

The morphology was revealed by SEM and TEM images (Fig. 3a and 3b). The d3iameter of SiO_2 core was about 400 nm. The TEM images of the core-shell SiO_2@Eu(MABA-Si)·(phen) microspheres were presented in Fig. 3c and 3d, the thickness of coating layer was about 20 nm. The core-shell microspheres showed rougher surface than pure SiO_2 particles. In addition, characteristic peaks of europium was found in the EDX spectrum of core-shell microspheres, which confirmed that Eu(MABA-Si)·(phen) exist in the cladding layer of core-shell microspheres (Fig. 4).

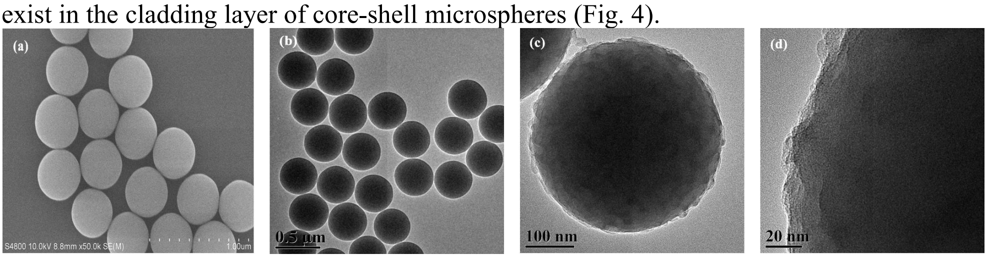

Fig. 3. a, the SEM of SiO_2; b, TEM of SiO_2; c and d, SiO_2@Eu(MABA-Si)·(phen)

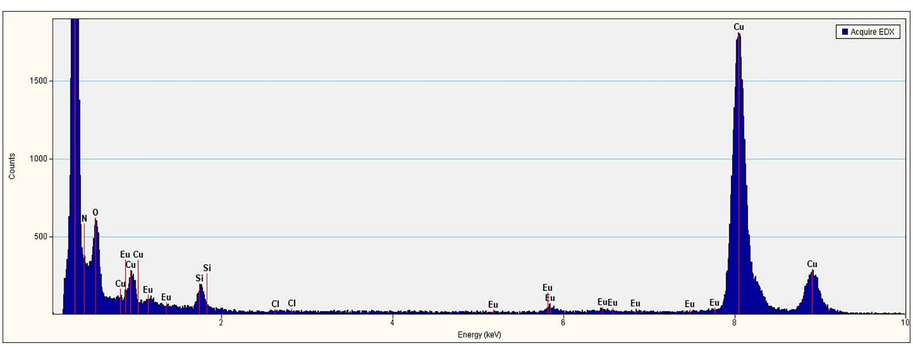

Fig. 4. EDX spectrum of core-shell microsphere

3.4 Luminescent properties.

The emission spectra of the europium complex (Fig. 6b) and core-shell microsopheres SiO_2@Eu(MABA-Si)·(phen) (Fig. 6a) were recorded under excitation wavelength at λex=272 nm that exhibited the characteristic transitions $^5D_0 \rightarrow {}^7F_J$ (J=0-4) of Eu^{3+}, and the peaks are appeared at 579, 593, 612, 652 and 699 nm respectively. The strongest emission peak appears at 612 nm, which was assigned to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. The emission intensity of the core-shell microspheres (36282456 a.u.) stronger than the europium complex (19425658 a.u). The fluorescent lifetime value of the europium complex and core-shell microspheres (Fig. 5a) were calculated by the double exponential mode. The core-shell microspheres lifetime was 1009.67 μs which langer than 389.55 μs of the europium complex (Fig. 5b).

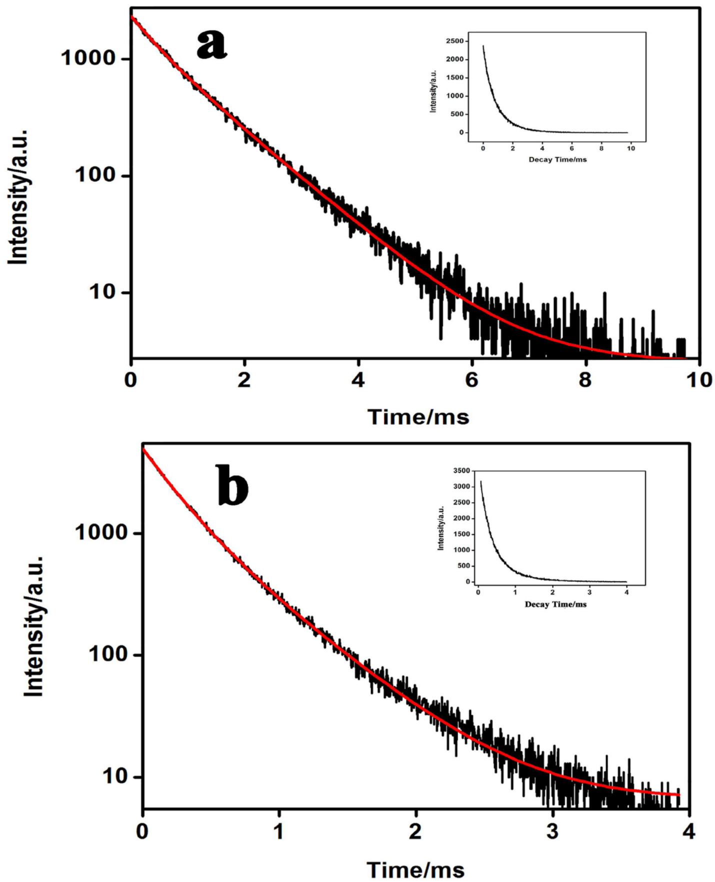

Fig. 5. Decay Curve and Fit Curve of core-shell microsphere (a) and europium complex (b)

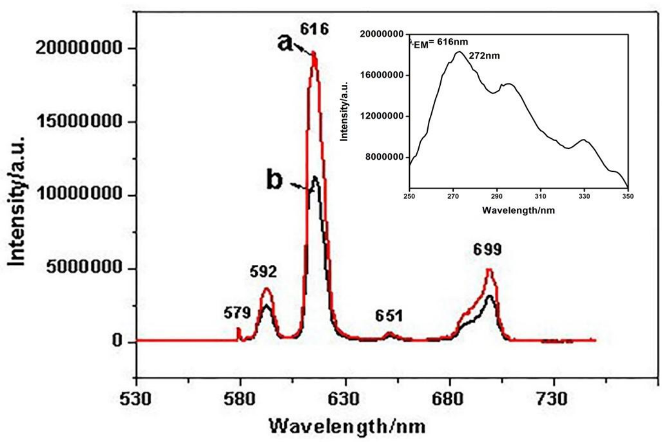

Fig. 6. excitation, emission spectrum of core-shell microspheres (a) and europium complex (b)

4 Conclusions

The novel europium complex of Eu(MABA-Si)$(phen)_2 \cdot (ClO_4)_3 \cdot 2H_2O$ and core-shell SiO_2@Eu(MABA-Si)(phen) microspheres were prepared. The core-shell microspheres was used the europium complex as shell and SiO_2 as the inorganic core. The europium complex shell has grafted to silica surface through forming a Si-O-Si bond. The emission intensity of core-shell microspheres was enhanced 1.87 times as great as the europium complex. And the core-shell microspheres have longer lifetime. The core-shell microspheres have a potential application as red luminescence nanomaterials, which will expand their applications in optical or electronic field.

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