

Preparation, and Luminescence Properties of SiO₂@Sm(MABA-Si)phen Core-Shell Structure Nanometer Composite

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Abstract. A novel ternary samarium complex was prepared using HOOCC₆H₄N(CONH(CH₂)₃Si-(OCH₂CH₃)₃)₂ (MABA-Si) as first ligand, and phen as second ligand. The corresponding SiO₂@Sm(MABA-Si)phen core-shell structure nanometer composite was synthesized as well, and the silica spheres was the core, and the ternary samarium complex was the shell layer. The ternary samarium complex has been characterized by element analysis, molar conductivity and IR spectra. The results show that the chemical formula of the complex is Sm(MABA-Si)(phen)₂(ClO₄)₃·2H₂O. The fluorescent spectra illustrate that the luminescence properties of the samarium complex are superior. The core-shell structure of SiO₂@Sm(MABA-Si)phen nanometer composite is characterized by SEM, TEM and IR spectra. The SiO₂@Sm(MABA-Si)phen core-shell structure composites exhibit stronger emission intensity than the ternary samarium complex. The fluorescence lifetime of the complex and core-shell structure composite is measured as well.

1. Introduction

The core-shell nanometer composite is a novel orderly assembled structure material. It can be formed by chemical bonds or physical adsorption. Therefore, it is a higher level of nanometer composite structure material. The core-shell nanometer composite differs from the unary substance because of its unique property, and it was intensely studied in the past decades [1-2]. By coating with a layer of other material, the surface of nanometer particle can be changed. So the chemical and optical properties of nanometer particles can be greatly improved. Hence, the core-shell structure composite has the advantages that the unary material doesn't have.

Our work is to prepare the core-shell structure materials. SiO₂ Sphere is the core, and the rare earth organic complex is the shell, and they were connected together by silane coupling agent. By using silane coupling method, the core-shell materials were formed through chemical bond linkages which were formed between the SiO₂ core and outer material. In this way, the core-shell structure material was stable and the chemical bond was

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not easy to break, so the morphology of core-shell material was easy to control. In this kind of core-shell structure materials, rare earth organic complex was used as cladding layer, and the thickness was magnitude nanometer. So the dosage of rare earth organic complexes can be reduced. As a result, the cost of materials can be greatly decreased. At the same time, compared with the hybrid materials [3,6], rare earth organic complex can be fixed by SiO₂ core easily, and the luminous efficiency of core-shell structure materials can be improved greatly.

In this paper, a novel ternary samarium complex Sm(MABA-Si)phen₂(ClO₄)₃·2H₂O has been synthesized for the first time. The SiO₂@Sm(MABA-Si)phen core-shell structure nanometer composite has been prepared as well. The samarium ions and SiO₂ core were connected together through MABA-Si silane coupling agent. The SiO₂@Sm(MABA-Si)phen core-shell structure composite exhibited stronger emission intensity than the ternary samarium complex.

2. The experiment

2.1 Materials

All chemicals were analytical grade and were used as received without further purification. Sm₂O₃ (purity > 99.99 %) were all supplied by Beijing Chemical Reagent Company. The Sm(III) perchlorate was prepared from dissolving in 2 mol·L⁻¹ HClO₄, and then evaporated and dried in vacuum. phen, Tetraethoxysilane (TEOS, Aldrich), 3-(triethoxysilyl)-propyl isocyanate (96%, TEPIC, Aldrich).

2.2 Physical measurements

Elemental analysis was carried out on a HANAU analyzer. Conductivity measurement was made by using a 1×10⁻³mol/L solution in dimethylformamide on a DDS-11D conductivity meter. The dysprosium content of the complex was determined by EDTA titration using xylenol-orange as indicator. The infrared spectra was determined by the KBr pressed disc method on a Nicolet NEXUS-670 FT-IR spectrophotometer. The ¹HNMR spectra was determined in the DMSO-d₆ by Bruker AC-500 nuclear magnetic resonance spectrophotometer. Luminescence properties were determined on a FLS980 fluorescence photometer with the slit width of 1nm. Fluorescent decay curves were recorded by FLS980 Combined Steady State and Lifetime Spectrometer. The microstructure were recorded by scanning the electronic microscope (Hitachi S-4800), transmission electron microscope (FEI Tecnai F20)

2.3 Synthesis of the ternary samarium complex

The ligand MABA-Si was synthesized according to the method of the literature [7,8]. The product has been characterized by ¹HNMR spectra. ¹HNMR data: δ0.56ppm(4H), δ1.04-1.51ppm(18H), δ2.93ppm(4H), δ3.33-3.47ppm(12H), δ3.73ppm(4H), δ7.43-7.57ppm(2H) and δ12.4 ppm(1H). Yield: 40%. mp: 46~48°C.

1 mmol MABA-Si and 2 mmol phen anhydrous ethanol was added into 1 mmol Sm(ClO₄)₃·nH₂O anhydrous ethanol solution drop by drop under the magnetic stirring for 2 h. A white precipitate was formed. The resulting white solid precipitates were filtered, washed several times with anhydrous alcohol. (yield>80%)

2.4 Synthesis of the core-shell structure nanometer composite SiO₂@Sm(MABA-Si)phen

2.4.1 Synthesis of SiO₂@MABA-Si

Firstly, mono-disperse SiO₂ were synthesized by the well-known Stöber[9] method. Then 0.1 g SiO₂ was dissolved in 20 mL mixture solution of anhydrous alcohol and distilled water under stirring at 12 hours. 0.2 g MABA-Si was dissolved in 15 ml anhydrous alcohol, adding drop-wise to the activated SiO₂ microspheres solution that mentioned above under stirring for 10 h. A white precipitate was centrifuged separation, and washed by distilled water and anhydrous ethanol several times, then dried at 40 °C.

2.4.2 Synthesis of core-shell structure nanometer SiO₂@Sm(MABA-Si)phen

SiO₂@MABA-Si was dispersed in 10 mL anhydrous ethanol. The molar ratio of Sm³⁺: MABA-Si: phen equals 1:1:2, the phen was dissolved in 5 ml anhydrous alcohol and was added into the SiO₂@MABA-Si anhydrous ethanol drop by drop, The appropriate amount samarium perchlorate was dissolved in 5 ml anhydrous ethanol and then added into the anhydrous ethanol solution of phen and SiO₂@MABA-Si drop by drop. The mixture was stirred 5 h, centrifuged separation. The product was washed by anhydrous ethanol several times and then dried. A white precipitate was obtained.

3 Results and discussions

3.1 The composition and Properties of the complex

The elemental analysis data of ternary samarium complex was shown as follows: C, 39.54; N, 6.33; H, 4.45 (Anal. Calcd: C, 40.33; N, 6.47; H, 4.63), and it was conformed to Sm(MABA-Si)(phen)₂(ClO₄)₃·2H₂O. The complex was white powder, and it was stable in atmospheric condition and soluble in DMF and DMSO. The result of molar conductivity value (149 S·cm²·mol⁻¹) of the complexes in DMF was formulated 1:2 electrolytes [10].

3.2 SEM and TEM

In our work, the core-shell structure composite was formed by hydrolysis between the ethoxy of MABA-Si and hydroxyl groups of the SiO₂ surface. Then the carboxyl oxygen atoms of MABA-Si groups and the double nitrogen of phen can be coordinated with Sm³⁺ ions. As a result, the SiO₂ cores and Sm ions were connected together through the "molecular bridge", the MABA-Si. The peripheral of SiO₂ cores was coated by Sm(MABA-Si)L complex successfully. The core-shell structure was observed by SEM, TEM and Infrared spectra.

SEM and TEM images of SiO₂ microspheres and core-shell structure composites were shown in the Fig 1,2. Fig.1. could be seen that the SiO₂ had the regular micro-structure, smooth surface and good dispersity. The average particle size of SiO₂ spherical was about 400nm. Core-shell structure nanometer SiO₂@Sm(MABA-Si)phen can be seen in Fig.2. Resulted from TEM photographs, the interface of the core-shell structure micro-spheres show that the surface is much rougher than the pure SiO₂ micro-spheres. The thickness of the gray shell layer of the composites was about 20 nm.

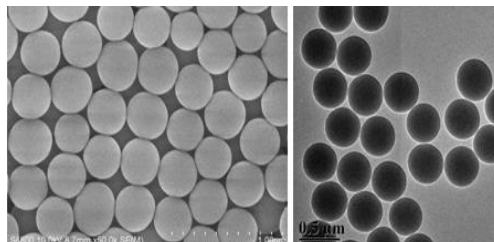


Fig. 1. The SEM (L) and TEM(R) photographs of 400nm SiO₂

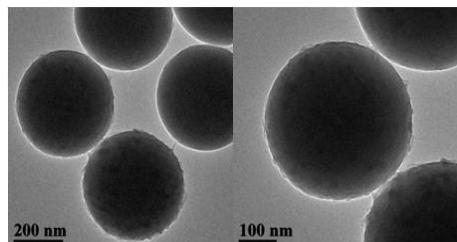


Fig. 2. The TEM photographs of core-shell structures SiO₂@Sm(MABA-Si)phen

3.3 Infrared spectra

Based on Fig.3a-c, For MABA-Si, the $\nu_{C=O(COOH)}$, $\nu_{C-OH(COOH)}$ and $\delta_{O-H(COOH)}$ appeared at 1700 cm⁻¹, 1447 cm⁻¹, and 1316 cm⁻¹. After coordinating with Sm³⁺, they shifted to lower wave number which appeared at 1682 cm⁻¹, 1398 cm⁻¹, 1242 cm⁻¹. The results showed that rare earth samarium ion bonded with MABA-Si through the COOH group [11,13]. For phen, $\nu_{C=N}$ shifted to 1521 cm⁻¹, and the δ_{C-H} shifted to 716 cm⁻¹ and 848 cm⁻¹ respectively, comparing with pure phen (the $\nu_{C=N}$ appeared at 1587 cm⁻¹, and δ_{C-H} appeared at 735 cm⁻¹ and 851 cm⁻¹ respectively). The results showed that rare earth samarium ion bonded with phen through the double nitrogen atoms. In the samarium complex, there were four perchlorate group absorptions at 1142 cm⁻¹, 1115 cm⁻¹, 1079 cm⁻¹, and 625 cm⁻¹. Combined the molar conductivity, one perchlorate group bonded with the Sm(III) ion by the oxygen atoms, and the coordination was bidentate. The IR spectrum of SiO₂ cores, MABA-Si, phen, SiO₂@Sm(MABA-Si)phen can be seen in Fig.4a-d. In the IR spectrum of MABA-Si and the core-shell structure nanometer composite, the $\nu_{C=O(COOH)}$ appeared at 1700 cm⁻¹, 1656 cm⁻¹, respectively. The ν_{CONH} of MABA-Si appeared at 1639cm⁻¹ and 1558 cm⁻¹ respectively. However in the core-shell composite, the ν_{CONH} group shifted to lower wave number which appeared at 1619 cm⁻¹ and 1556 cm⁻¹ respectively. Similarly, the $\nu_{C=N}$ of phen group and the core-shell composite appeared at 1587 cm⁻¹, 1522 cm⁻¹. These results suggested that the Sm-MABASi-phen complexes were formed in the shell layer of core-shell composites.

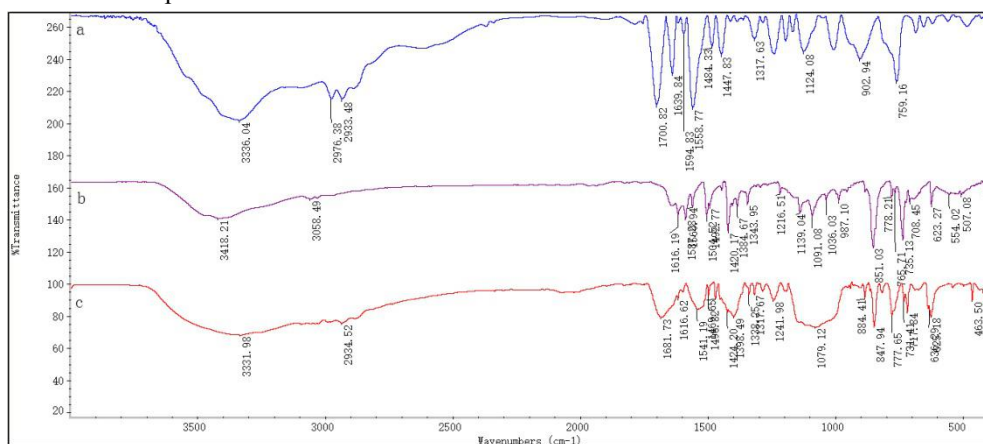


Fig. 3. The IR Spectra of (a). MABA-Si ; (b). phen; (c). Sm(MABA-Si)(phen)₂(ClO₄)₃·2H₂O

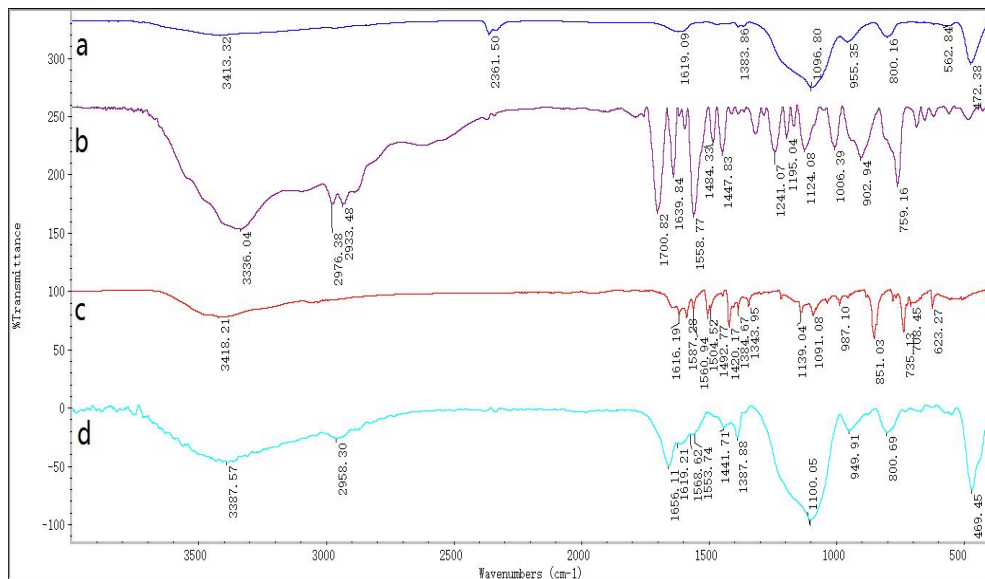


Fig. 4. The IR Spectra of (a). SiO₂ ; (b). MABA-Si; (c).phen; (d).SiO₂@Sm(MABA-Si)phen

3.4 Fluorescence spectra

The fluorescence excitation and emission spectrum of core shell structure composites and ternary samarium complex were measured in solid state at room temperature. The results were shown in Fig 5a,b There were three emission peaks, which were attributed to the characteristic transitions of Sm(III). The three peaks correspond to ⁴G_{5/2}-⁶H_{5/2}, ⁶H_{7/2}, ⁶H_{9/2} and the peaks were appeared at 561 nm, 596 nm, and 643 nm respectively. The strongest fluorescence emission intensity of core-shell structure composites and ternary samarium complex were 860847a.u. and 295259a.u. The fluorescence emission intensity of core-shell structure composites and ternary samarium complex was 2.92 times as great as the ternary complex system.

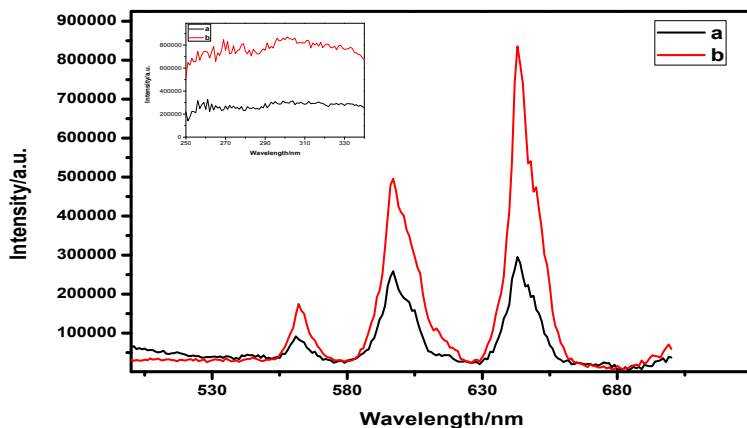


Fig. 5. Fluorescence excitation spectrum (inset) and emission spectrum of (a) Sm(MABA-Si)(phen)₂(ClO₄)₃·2H₂O,(b) SiO₂@Sm(MABA-Si)phen

3.5 The fluorescence decay curve

The fluorescence decay curve of the ternary samarium complex and the core-shell structure composites was also measured. Fig.6-7 showed the fluorescence decay and double exponential fit curve of the $\text{Sm}(\text{MABA-Si})(\text{phen})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $\text{SiO}_2@\text{Sm}(\text{MABA-Si})\text{phen}$ respectively. The lifetime of the Sm(III) ion could be obtained from the Eq.

$$I(t) = I_0 + A_1 \exp\left(-\frac{t_1}{\tau_1}\right) + A_2 \exp\left(-\frac{t_2}{\tau_2}\right) \quad (1)$$

$$\langle \tau \rangle = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \quad (2)$$

Where I_0 was the fluorescence intensity varying with time t , and τ_1 and τ_2 were lifetime. The corresponding data were calculated. As the result, the lifetime of the ternary samarium complex was $31.27\mu\text{s}$. Moreover, the lifetime of the core-shell composites was $39.58\mu\text{s}$.

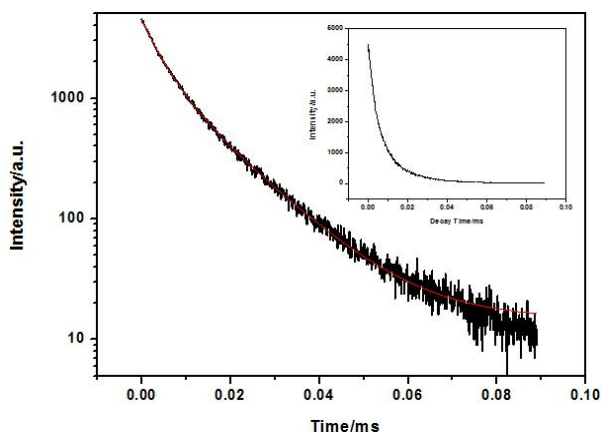


Fig. 6. Decay Curve (R) and Fit Curve (L) of $\text{Sm}(\text{MABA-Si})(\text{phen})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$

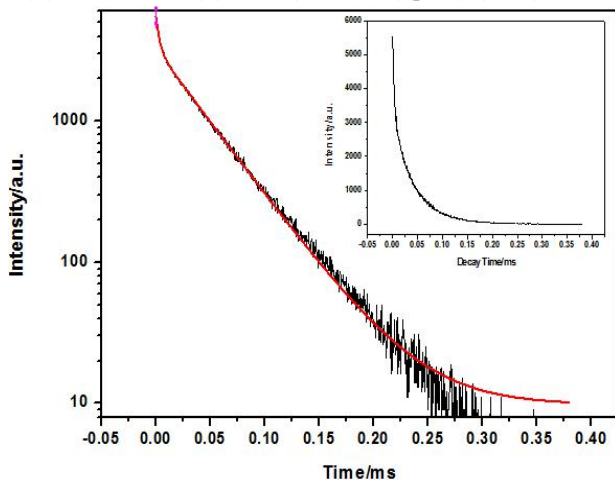


Fig. 7. Decay Curve (R) and Fit Curve (L) of $\text{SiO}_2@\text{Sm}(\text{MABA-Si})\text{phen}$

4 Conclusions

A novel ternary samarium complex $\text{Sm}(\text{MABA-Si})(\text{phen})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ and the corresponding core-shell structure composites $\text{SiO}_2@\text{Sm}(\text{MABA-Si})\text{phen}$ were prepared and characterized. Luminescence property was studied by the fluorescence spectrum. The results showed that they had excellent luminescent property. The fluorescence emission intensity of the core-shell structure composites system was 2.92 times as great as the corresponding ternary complex system. The result above showed that SiO_2 core and ligands played a mutually synergistic effect in the energy transfer process from the ligands to $\text{Sm}(\text{III})$ ion. The evidence illustrated that the fluorescence emission intensity of material can be greatly enhanced by the formation of core-shell structure. The $\text{SiO}_2@\text{Sm}(\text{MABA-Si})\text{phen}$ core-shell structure nanometer composites can be applied in luminescent materials. So this approach gave an applicable new choice for future study of novel luminescent materials. These studies can help us find more about samarium luminescent materials, as well as develop the application of rare earth elements samarium.

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