Synthesis and Characterization of [Eu(DBM)₃phen]Cl₃@SiO₂–NH₂ Composite Nanoparticles

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Fluorescent rare earth complex Eu(DBM)₃(phen)Cl₃@SiO₂–NH₂ nanoparticles were synthesized by combination of solvent precipitation method and Stöber method. The morphologies, structure, surface and optical properties of the samples were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and fluorescence spectrophotometer (FS). The observation from FE-SEM images indicate that the obtained samples are spherical and uniform nanoparticles with a tunable average sizes from 140 nm to 300 nm. TEM results verify a core–shell structure of the nanoparticles. The FTIR spectrum confirms the characteristic vibration absorption peaks of the complex [Eu(DBM)₃(phen)]Cl₃@SiO₂–NH₂. TGA result indicates that the complex is stable below 200 °C. The photoluminescence analysis shows that the complex has Eu³⁺ characteristic red luminescence and broader excitation peak from 200 nm to 450 nm that can meet the demands of fluorescent confocal imaging. The amino groups are directly introduced to the [Eu(DBM)₃(phen)]Cl₃@SiO₂–NH₂ nanoparticles surface by using APS (3-aminopropyl triethoxysilane). This makes the surface modification and bioconjugation of the nanoparticles easier. The nano-sized spheres could be provided a basis for further expansion of its application in biomedical imaging, biological detection and fluorescent nanoprobes.

Keywords: Rare Earth, Eu, Fluorescent Nanoparticle, Solvent Precipitation, Photoluminescence.

1. INTRODUCTION

In recent years, fluorescent nanoparticle as potential optical and fluorescent materials have attracted considerable interest due to their high photostability, good luminescence efficiency, and fluorescent nanoprobe property.¹⁻³ Recently, fluorescent rare earth complex nanoparticles have especially gained attention in biomedical field such as luminescent probes, fluorescent confocal imaging and time-resolved fluorescence imaging because of their photophysical properties such as the chemical stability, high color purity and long-lived fluorescence.⁴⁻⁶ However, the rare earth complexes have several drawbacks (e.g., the poor hydrophilicity, low thermal- and photo-stability and poor biocompatible) which limited their applications in biomedical research. Inorganic material silica (SiO₂) is relatively inert, hydrophilic, optically transparent, and biocompatible. Combination of the rare earth organic complex and inorganic material has attracted intense attention due to their potential applications in simultaneous biolabeling, fluorescent probe, and fluorescence imaging. Yuan’s group⁷⁻⁹ has reported several types of fluorescent lanthanide complex-doped silica nanoparticles which can be used for biolabeling and time-resolved fluorescence biosays. Zhao et al.¹⁰ synthesized a set of rare earth complex-doped silica hybrid nanospheres which exhibit intense narrow emission band and can be used as luminescent and optical material in EL and PL fields. After the introduction of silica shell, water-solubility, chemical stability, biocompatibility and surface functionality of the rare earth nano-sized complex obtain striking improvement. The silica coating, on one hand, can provide an effective barrier to prevent fluorophores from quenching by solvent molecule (e.g., water). On the other hand, the silica surface can be
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Easily functionalized by various fluorescent and biological species through chemical bonding. Incorporation of the rare earth fluorescent complex into the silica shell should be a good choice for biomedical applications.

In this work, we successfully synthesized the Eu(DBM)3(phen)Cl3@SiO2–NH2 composite nanoparticles with a well-defined core–shell structure by using combination of solvent precipitation method and Stöber method. The morphologies, structure, surface properties, thermal stability and optical properties of the samples were characterized by FE-SEM, TEM, FTIR, TGA-DSC and FS.

2. EXPERIMENTAL DETAILS

2.1. Materials

All chemicals were analytic reagent and used directly without further purification. Deionized water was used throughout. Eu2O3 (99.99%) were purchased from Shanghai Yuelong Chemical Factory. 1,10-phenanthroline (phen) was purchased from Beijing Yili Chemical Reagent. Dibenzoylmethide (DBM), tetraethyl orthosilicate (TEOS) and 3-Aminopropyltriethoxysilane (APS) were supplied by the Shanghai Jingchun Chemical Reagent. Absolute ethanol, concentrated ammonium hydroxide (NH3·H2O 25–28%) and concentrated hydrochloric acid (HCl) were supplied by the Beijing Chemical Factory.

2.2. Synthesis

0.20 mol/L europium chloride solution of pH 4–6 were prepared by dissolving Eu2O3 (0.10 mol) with 1:1 (v/v) HCl and removing residual HCl via evaporation under heating, and then fixed volume in a volumetric flask (500 mL) with deionized water at room temperature. [Eu(DBM)3phen]Cl3 was synthesized by adding solid DBM (3 mmol) and phen (1 mmol) into a solution of EuCl3 (1 mmol) in 20 mL of absolute ethanol, followed by the addition of concentrated NH3·H2O under magnetically stirring until pH∼7.11. [Eu(DBM)3phen]Cl3@SiO2–NH2 nanoparticles were synthesized by a solvent precipitation method and Stöber method. The synthetic procedure for functionalized luminescent nanoparticles and the chemical structure of the europium (III) complex are depicted in Scheme 1. In a typical synthesis, 100 mL deionized water was added into 50 mL of [Eu(DBM)3phen]Cl3 (0.18 mmol/L) ethanol solution in 250 mL of a beaker at room temperature under magnetically stirring. After 20 min, 20 µL of APS was injected into the above solution and then applied ultrasonication for 20 min. Next, 0.2 mL of the concentrated NH3·H2O was added into the above solution and kept stirring for 20 min. Then 0.2 mL of TEOS was injected into the above solution and the solution was stirred for 24 h at the room temperature. After the reaction completed, the resulting product was separated by centrifugation, washed with deionized water to remove any remaining ions from the final product, and dried at 80 °C in an air oven.

2.3. Characterization

Field emission scanning electron microscopy (FE-SEM) images were obtained by a HITACHI S4800 scanning electron microscope. The complex morphologies were observed using a FEI TECHAI G2 20 transmission electron microscope (TEM). The composition of the sample was detected by a BIO-RAD FTS135 Fourier-transform infrared (FTIR) spectrometer using the KBr pellet technique with a wave number from 4000 to 400 cm⁻¹. The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out by using a NETZSCH STA 449 F3 differential thermal analyzer at a rate of 10.0 °C/min in the range of 25–800 °C in air. The excitation and emission spectra were recorded on a HITACHI F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. Morphology of the Samples

Figure 1 shows FE-SEM images of the [Eu(DBM)3phen]Cl3@SiO2–NH2 nanoparticles. It can be seen that the particles are spherical and in a size of 140 to 300 nm. The sizes of the particles gradually increase by increasing the amount of APS.

Scheme 1. Synthetic scheme of the synthesis of functionalized [Eu(DBM)3phen]Cl3@SiO2–NH2 fluorescent nanoparticle.
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Fig. 1. SEM images of the Eu(DBM)₃(phen)Cl₃@SiO₂–NH₂ nanoparticles synthesized with different amount of APS: (a) 20 µL, (b) 30 µL, (c) 40 µL, and (d) 50 µL.

3.2. Structure

To investigate the core–shell structure, the TEM image of the typical [Eu(DBM)₃phen]Cl₃@SiO₂–NH₂ nanoparticle sample is exhibited in Figure 2. It can be clearly observed that the particles are composed of the gray [Eu(DBM)₃phen]Cl₃ cores of about 110 nm and dark silica shell with an average thickness of about 17 nm. The rare earth nanosized complex with protection of the SiO₂–NH₂ shell have improved their water solubility, chemical stability, and surface functionality and are in favor of in biomedical applications such as fluorescence labeling, bio-imaging, and biological fluorescent detection.

3.3. FTIR

Figure 3 gives FT-IR spectra of the [Eu(DBM)₃phen]Cl₃@SiO₂–NH₂ nanoparticles. The peaks near 3339 cm⁻¹ and 2927 cm⁻¹ belong to the νN–H and νC–H stretching vibration respectively. The stronger peak at 462 and 565 cm⁻¹ can be assigned the Eu–O and Eu–N stretching vibration. The strongest peak at 1072 cm⁻¹ belongs to Si–O–Si stretching vibration. The peaks at 1654, 1603 and 1552 cm⁻¹ belong to the νC=O, νC=C

Fig. 2. TEM image of the Eu(DBM)₃(phen)Cl₃@SiO₂–NH₂ nanoparticles.

Fig. 3. FTIR of the Eu(DBM)₃(phen)Cl₃@SiO₂–NH₂ nanoparticles.
and $\nu_C=\text{N}$ stretching vibration originating from ligands of the DBM and the 1,10-phen, respectively. The peak at 794 cm$^{-1}$ can be assigned to C–Si stretching vibration. These characteristic peaks can further confirm formation of the [Eu(DBM)$_3$phen]Cl$_3$@SiO$_2$–NH$_2$ nanoparticles. Moreover, this indicates that APS has grafted to the particle surface. The amino groups from APS made the surface modification and bioconjugation easier.

### 3.4. TGA-DSC

Figure 4 shows the TG-DSC curves of the representative [Eu(DBM)$_3$phen]Cl$_3$@SiO$_2$–NH$_2$ nanoparticles. There are two major weight losses in the range of 60–126 and 200–700 °C, respectively. The first one is due to the removal of adsorptive water molecule, which is 1.6% of the total weight. The second one is due to the decomposition of the framework of the complex, which is 15.7% of the total weight. There is a strong exothermic peak near 457 °C in the corresponding DSC, where the ligands decomposed apparently. The decomposition and oxidation of the complex finished when the temperature was over 700 °C and finally formed a mixture containing oxides Eu$_2$O$_3$ and SiO$_2$.

### 3.5. Photoluminescence

Figure 5 gives the excitation and emission spectra of the [Eu(DBM)$_3$phen]Cl$_3$@SiO$_2$–NH$_2$ nanoparticle samples. The excitation spectra were measured by monitoring emission at 614 nm. There are two strong and broad excitation peaks at 285 nm (Eu–O charge shift transition) and 369 nm. The two shoulder peaks at 337 and 405 nm are due to light absorption by the diketonate ligands. To meet the demand of 405 nm excitation wavelength for a common fluorescent confocal imaging, the emission spectrum was examined under the 405 nm UV-light, as shown in Figure 5(b). The narrow emission peaks at 581, 593 and 614 nm originate from transition of the $^5D_0$ excited state level to the $^7F_J$ ($J = 0–6$) ground state levels. The strongest emission peak at 614 nm is due to the hypersensitive electric dipole transition of $^5D_0–^7F_2$. The photoluminescence analysis results indicate that the [Eu(DBM)$_3$phen]Cl$_3$@SiO$_2$–NH$_2$ nanoparticles have potential applications as luminescent nanoprobes for biological research and labeling agents for the fluorescent confocal imaging and time-resolved fluoroimmunoassay (TR-FIA).

### 4. CONCLUSIONS

In summary, we successfully synthesized Eu(DBM)$_3$(phen)Cl$_3$@SiO$_2$–NH$_2$ core–shell nanoparticles by combination of solvent precipitation method and Stöber method. The obtained nanoparticles are spherical and have a tunable average size range from 140 nm to 300 nm. They are stable under 200 °C in air and emit Eu$^{3+}$ characteristic red luminescence under excitation with 405 nm UV-light. These fluorescent nanoparticles can be used for a common fluorescent confocal imaging, time-resolved fluoroimmunoassay and luminescent nanoprobe for biological detection as they have excellent...
stability, water solubility, broad excitation band and narrow fluorescent emission.

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References and Notes

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