



## Preparation and Properties of Luminomagnetic Nanoparticles with Magnetic Core and Terbium Complex Shell

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(Received: 23 December 2010;

Accepted: 27 June 2011)

AJC-10101

Novel luminomagnetic nanoparticles with magnetic core and terbium complex shell have been developed using a modified Stöber method combined with a layer-by-layer assembly process.  $\text{Fe}_3\text{O}_4$  nanoparticles as the magnetic core were firstly coated by a silica shell. Then, a kind of modified monomer (abbreviated as SA-Si) synthesized by grafting the coupling agent 3-isocyanatepropyltriethoxysilane (ICPTES) to salicylic acid (SA) was used as the ligand for coordination with  $\text{Tb}^{3+}$  ions. The ternary  $\text{Tb}^{3+}$  complex (denoted as SA-Si-Tb) served as the luminescent marker was covalently bonded to the silica surface. Subsequently, an outer shell of silica was introduced to allow for versatile surface functionalities. The architecture has been characterized by Fourier transform infrared spectra (FT-IR), transmission electron microscopy (TEM), vibration sample magnetometer (VSM) and photoluminescence (PL) spectra. The resultant luminomagnetic nanoparticles exhibited favourable superparamagnetic behaviour and photoluminescence properties, which had potential application in biolabelling, bioseparation, immunoassay and pathogenic diagnosis.

**Key Words:** Nanoparticles, Luminescence, Magnetic property, Terbium complex, Core-shell.

### INTRODUCTION

Multifunctional nanomaterials possessing mainly magnetism and fluorescence have recently become an attractive research field. Magnetic moieties allow manipulation of the particles by external magnetic fields and luminescent moieties provide a possibility to detect the presence and movements of the particles<sup>1</sup>.

Among all of magnetic particles, superparamagnetic nanoparticles (usually  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) have received much attention because they do not retain any magnetism after they are removed from the magnetic field. This unique feature has led to several successful applications, including contrast enhancement in magnetic resonance imaging<sup>2-4</sup>, site-specific drug delivery<sup>5</sup>, hyperthermia treatment for malignant cells<sup>6</sup>, magnetic separation of labelled cells and other biological entities<sup>7</sup>. The luminescent moieties mainly include various organic fluorescent molecules<sup>8,9</sup>, quantum dots (QDs)<sup>10,11</sup>. But the poor photostability of the fluorescent dyes and the potential toxicity of the quantum dots make them suffer from some limitations in biomedical applications<sup>12</sup>.

Lanthanide complexes are a class of useful luminophores because of their long lifetimes, sharp luminescence spectra and high colour purity, large Stokes' shift, avoiding the overlapping spectra currently observed with most organic fluore-

scent probes and the natural background fluorescence of biological materials<sup>13</sup>. These characteristics can provide very low detection limits and enhanced sensitivity in luminescence based detection schemes.

Lanthanide complexes with aromatic carboxylic acids are generally used as structural and functional probes in systems of biological system<sup>14,15</sup>. Salicylic acid has excellent coordination ability with rare earth ions and the luminescence of lanthanide ions by salicylic acid plays an important role in the analyses of trace salicylic acid and its derivatives in biological systems and in fluorimetric immunoassay<sup>16-18</sup>.

The combination of  $\text{Fe}_3\text{O}_4$  and lanthanide complexes with salicylic acid into a single micro- or nanocomposite system will allow the development of a novel multifunctional biomedical platform for multimodal imaging and simultaneous diagnosis.

In this work, we attempt to modify active hydroxyl groups of salicylic acid (SA) by ICPTES bearing tri-alkoxysilyl group as a functionalized organic ligand (SA-Si), then we designed a new multifunctional core-shell magnetic silica nanocomposites, with the  $\text{Fe}_3\text{O}_4$  core coated by a silica shell, to which luminescent complexes (SA-Si-Tb) were covalently attached and further encapsulated with an additional layer of silica shell core-shell.

## EXPERIMENTAL

$\text{Fe}_3\text{O}_4$  nanoparticles with the average size of 13 nm were synthesized according to the literature procedures<sup>19</sup>. Tetraethoxysilane (TEOS) was provided by Tianjin chemical reagent factory. Salicylic acid was provided by Shanghai chemical reagent factory. 3-Isocyanatepropyltriethoxysilane (ICPTES) was purchased from Aladdin.  $\text{TbCl}_3$  ethanol solution was obtained by a reaction of  $\text{Tb}_4\text{O}_7$  (99.999 %, Lianyungang Ligang Rare Earth Manufacturin Co., Ltd) and  $\text{HCl}$  (6.0 mol/L). Deionized water was used throughout the experiments. All other materials were of analytical grade and used without any further purification.

**Preparation of luminomagnetic nanoparticles:** The synthetic procedure for functionalized luminomagnetic nanoparticles is shown in Fig. 1. SA-Si was prepared using the method already described<sup>20</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 10.38 (1H, s), 7.93 (1H, d), 7.53 (1H, t), 7.02 (1H, d), 6.94 (1H, t), 4.00 (6H, m), 3.26 (2H, m), 1.70 (2H, m), 1.25 (9H, t), 0.88 (2H, t).  $\text{Fe}_3\text{O}_4$  nanoparticles (0.1 g) were dispersed in a mixture of ethanol (40 mL) and water (8 mL), followed by  $\text{NH}_3\cdot\text{H}_2\text{O}$  (1 mL, 28 %) and TEOS (0.5 mL) under mechanical stirring and the reaction was continued for 4 h at room temperature. The  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  nanoparticles were obtained by magnetic separation and washed with water and ethanol, separately, for 4 times. A solution of SA-Si (10 mg) dissolved in DMF (10 mL) was added to the ethanol-dispersed silica-coated  $\text{Fe}_3\text{O}_4$  nanoparticles (100 mL) with stirring and the mixture was heated to reflux overnight. After the reaction, the SA-Si modified  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  nanoparticles were obtained and redispersed in ethanol (100 mL). Then, an excess solution of  $\text{TbCl}_3$  was added to the above solution and allowed to react at 80 °C for 6 h. The resultant  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{SA-Si-Tb}$  nanoparticles were washed with ethanol three times. An ethanolic solution (30 mL) of TEOS (0.2 mL) was added to a mixture of  $\text{NH}_3\cdot\text{H}_2\text{O}$  (0.5 mL),  $\text{H}_2\text{O}$  (10 mL) and the previously obtained  $\text{Tb}^{3+}$  complex-modified magnetic nanoparticles in ethanol (10 mL) with stirring. The hydrolysis and condensation of TEOS onto the surface of the nanoparticles were completed at room temperature within 4 h. The luminomagnetic nanoparticles were collected and washed with ethanol three times.

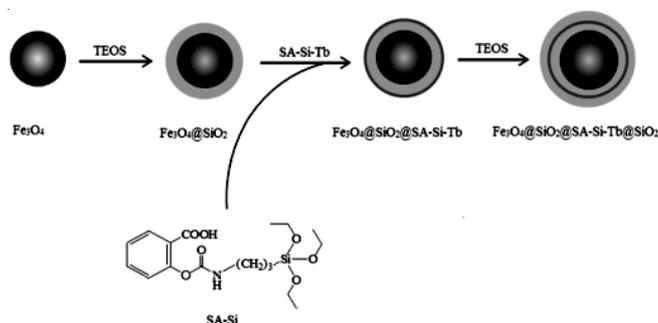


Fig. 1. Schematic illustration of preparation the luminomagnetic nanoparticles

**Detection method:** The morphologies and sizes of the as-prepared samples were observed under a transmission electron microscope (Hitachi H-600). Magnetic properties were

investigated using a vibrating sample magnetometer (VSM-5 Model manufactured by Toei Kogyo Co., Ltd.). Photoluminescence (PL) spectra were measured at room temperature by a RF-5301 (Shimadzu, Japan) spectrofluorimeter equipped with a xenon lamp as the excitation light source at room temperature.

## RESULTS AND DISCUSSION

Successful covalent linking of SA-Si on the surface of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  could be proven by infrared experiments. The corresponding FT-IR spectra are presented in Fig. 1. The peaks at 1731 and 1285  $\text{cm}^{-1}$  could be assigned to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$  of the  $-\text{COOH}$  in SA-Si, respectively and the occurrence of the grafting reaction was supported by the band located at 1631  $\text{cm}^{-1}$ , which originated from the absorption of amide groups ( $-\text{CONH}-$ ) (Fig. 2a). The presence of the bending vibration ( $\delta_{\text{NH}}$ , 1566  $\text{cm}^{-1}$ ) is another evidence for the formation of amide groups. In addition, the peaks located at 2927 and 2865  $\text{cm}^{-1}$  are due to the vibrations of methylene ( $-\text{CH}_2-$ ) in the 3-isocyanatepropyltriethoxysilane (ICPTES), proving that ICPTES has been successfully grafted on to salicylic acid. The presence of iron oxide could be identified by the absorption peak at 568  $\text{cm}^{-1}$ , which was stemming from the stretching vibration of the Fe-O functional group. The bands at 1097 and 467  $\text{cm}^{-1}$  correspond to Si-O-Si and Si-O-Fe stretching vibrations of the silica shell (Fig. 2b). In the FT-IR spectrum of the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{SA-Si-Tb}$  nanoparticles (Fig. 2c), the two new bands appear at 1562 and 1403  $\text{cm}^{-1}$  are attributed to  $\nu_{\text{as}}(-\text{COO}-)$  and  $\nu_{\text{s}}(-\text{COO}-)$  correspondingly, which suggests the coordination of the carboxylic group to  $\text{Tb}^{3+}$  with the oxygen atoms.

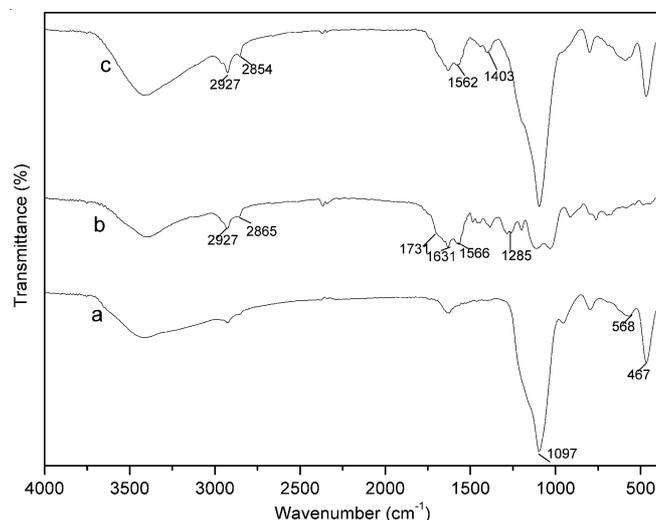


Fig. 2. IR spectra of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  nanoparticles (a) SA-Si-Tb (b) and  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{SA-Si-Tb}@ \text{SiO}_2$  nanoparticles (c)

The morphology of the luminomagnetic nanoparticles were investigated by TEM. From Fig. 3a one can see that  $\text{Fe}_3\text{O}_4$  nanoparticles are spherical in shape and the average effective diameter is about 13 nm. As shown in Fig. 3b, the luminomagnetic nanoparticles have a mean particle size of 70 nm and a regular spherical shape is present in most of the samples. It is obviously that the diameter of the bifunctional nanoparticles is larger than the bare  $\text{Fe}_3\text{O}_4$ , which can be attributed to the wrapped silica layers and terbium complex.

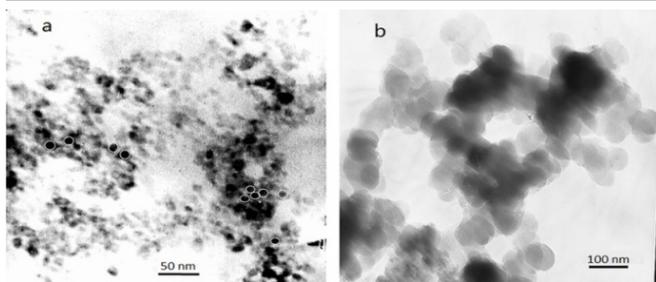


Fig. 3. TEM images of the  $\text{Fe}_3\text{O}_4$  nanoparticles (a) and the luminomagnetic nanoparticles (b)

The magnetic hysteresis loops of  $\text{Fe}_3\text{O}_4$  (a)  $\text{Fe}_3\text{O}_4@SiO_2$  (b) and  $\text{Fe}_3\text{O}_4@SiO_2@SA-Si-Tb@SiO_2$  (c) are shown in Fig. 4. All samples exhibit negligible coercivity and remanence, which demonstrates that the superparamagnetic properties of the nanoparticles are retained. Their saturation magnetization ( $M_s$ ) was 78.47, 30.18 and 5.12 emu/g, respectively. The lower saturation magnetization of these functional nanoparticles could be attributed to the presence of the middle and outermost silica shells.

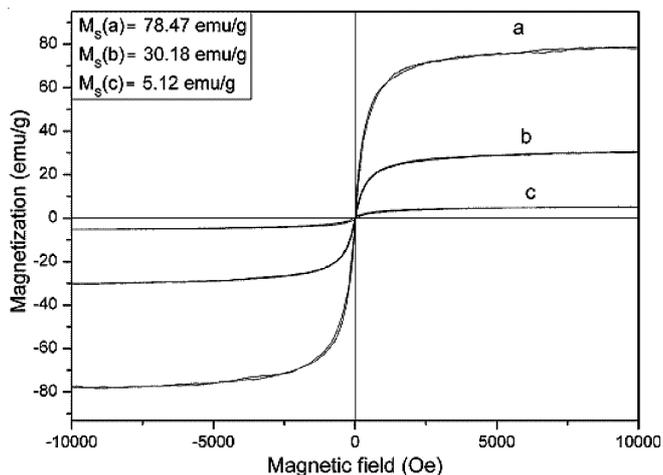


Fig. 4. Measured magnetic hysteresis loops of  $\text{Fe}_3\text{O}_4$  (a)  $\text{Fe}_3\text{O}_4@SiO_2$  (b) and  $\text{Fe}_3\text{O}_4@SiO_2@SA-Si-Tb@SiO_2$  (c)

Interestingly, upon UV light irradiation, well dispersed aqueous luminomagnetic nanoparticles emit bright-green light originating from the characteristic emission of  $\text{Tb}^{3+}$  as shown in the digital photographs of Fig. 5a. When a handheld magnet was placed close to the glass vial, the nanoparticles were attracted to the magnet quickly and accumulated near it within several minutes, leaving the bulk solution clear and transparent. These aggregations emit green light accordingly (Fig. 5b). The fact is the direct evidence that SA-Si-Tb has been connected to  $\text{Fe}_3\text{O}_4@SiO_2$  nanoparticles.

The excitation and emission spectra of  $\text{Fe}_3\text{O}_4@SiO_2@Si-SA-Tb@SiO_2$  nanoparticles are shown in Fig. 6. The excitation spectrum was monitored at 545 nm with a broad band centered at 310 nm without absorption from terbium ions, which was due to light absorption by the ligand SA-Si-Tb. Upon excitation at 310 nm, four emission lines of the nanoparticles could be detected in the visible spectrum, corresponding to the transitions from the  $^5D_4 \rightarrow ^7F_J$  ( $J = 6, 5, 4, 3$ ) at around 489, 545, 584 and 619 nm of terbium ions. Among these emission peaks, the

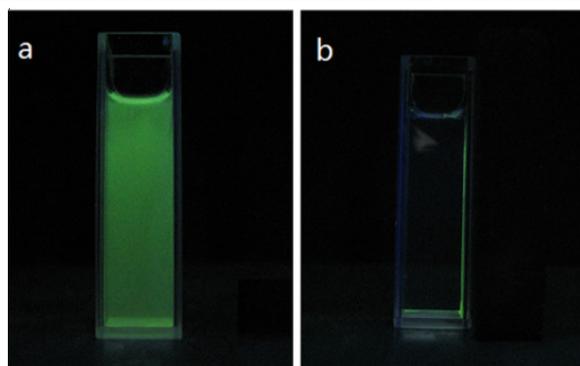


Fig. 5. Photographic images of the luminomagnetic nanoparticles under UV irradiation without (a) and with (b) an external magnetic field

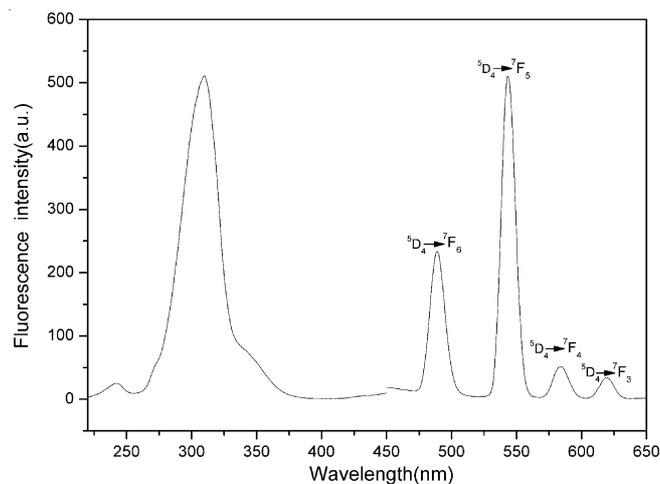


Fig. 6. Excitation ( $\lambda_{em} = 545$  nm) (a) and emission spectra ( $\lambda_{ex} = 310$  nm) (b) of luminomagnetic nanoparticles

green luminescence ( $^5D_4 \rightarrow ^7F_5$ ) was the most striking, which indicated that the effective energy transfer took place between the modified ligand SA-Si and  $\text{Tb}^{3+}$  ions. Both strong emission intensity and narrow emission half width (below 15 nm) are observed, showing the luminomagnetic nanoparticles high fluorescence intensity and colour purity. The spectrum testing results further confirm that the terbium complexes have been successfully grafted onto the silica coated magnetic nanoparticles.

## Conclusion

In summary, a novel luminomagnetic nanomaterial with magnetic core and terbium complex shell has been successfully synthesized combined with a layer-by-layer assembly process and it possesses both favourable superparamagnetic and unique lanthanide fluorescent properties. By reason of covalent coupling lanthanide complexes to the silica shell, higher chemical stability and photostability may be expected. This type of composite nanoparticles can be potentially used in biolabeling, imaging and cell separation.

## ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (No. J0730425) and the Main Nature Science Foundation of Gansu Province in China (No. 3ZS041-A25-009).

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