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In situ synthesis of monodisperse luminescent terbium complex-silica nanocomposites

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A facile strategy for the *in situ* synthesis of terbium complex-silica nanocomposites is described. The resultant spherical nanocomposites possess good monodispersity and exhibit luminescent properties of terbium complex.

Introduction

Recently, a variety of methods have been developed for the design of the lanthanide complexes with organic ligands due to their excellent luminescence characteristics from the electronic transitions between the 4f energy levels.[1–5] However, the poor thermal stability and the mechanical properties of lanthanide complexes limit to great degree their practical application as luminescent sources. To improve their disadvantages, lanthanide complexes are generally incorporated into different substrates or matrixes, including LB films,[6] sol–gel materials,[7–9] supramolecules,[10] and porous materials[11–14] *et al.* Studies indicated that the resulting materials often exhibited improved thermal stability, mechanical and emission properties compared to the pure lanthanide complexes. For example, Zambon *et al*[9] first prepared different organic complexes that are functionalized with alkoxysilyl groups, and then the as-obtained silylated monomers are submitted to complexation with rare-earth ions and are used as the siloxane network precursors. The resultant materials exhibit a series of improved properties. Moreover, effective strategies to design tailored materials are required to meet the ever-increasing technical demands placed on the materials synthesis and performance by many advanced technologies such as nanotechnology. Unfortunately, the fabrication of nanostructured material containing lanthanide complexes is often impeded by the difficulty in encapsulation of lanthanide complexes into suitable matrices while preserving the monodisperse nanostructure of the ultimate materials. Few papers,[14] to the best of our knowledge, have been published in this field.

In this paper, we report a facile strategy for *in situ* synthesis of monodisperse nanostructured material containing terbium complex. The proposed approach has two essential features: (1) *in situ* synthesis of a terbium complex on the surface of a silica nanosphere, and (2) good monodispersity of as-prepared nanocomposites with luminescent properties of terbium complex.

Experimental section

Materials

Tetraethylorthosilicate (TEOS), *p*-aminobenzoic acid, and isocyanatopropyltriethoxysilane were obtained from Aldrich. Terbium oxide (Tb_4O_7, 99.99%) was purchased from YueLong Chemical Plant (Shanghai, China). Dry tetrahydrofuran (THF), petroleum ether, absolute ethanol, NH_4OH, and HCl were purchased from Beijing Chemical Reagents Industry. All chemicals were used as supplied.

Preparation of TbCl$_3$ solution

$TbCl_3$ ethanol solutions were prepared as follows: The rare earth oxide (Tb_4O_7) was dissolved in concentrated HCl and the surplus HCl removed by evaporation. The residue was diluted with 95% ethanol.

Synthesis and characterization of PABI molecules

5 mmol of *p*-aminobenzoic acid was dissolved in 15 ml of dry tetrahydrofuran (THF). To this solution 7.5 mmol of isocyanatopropyltriethoxysilane (ICPTES) was then added. The resultant solution was refluxed for 8 h. White precipitate was observed when 50 ml of petroleum ether was added to the above solution. The precipitate was filtered off and washed with petroleum ether to remove excess ICPTES. Finally, the purified precipitate was dried on a vacuum line to get 1.8 g of PABI at a 95% yield.

The product was confirmed by ^1H NMR and MS as follows: ^1H NMR (DMSO, 400 MHz) δ/ppm 12.45 (1H, bs, COOH), 8.79 (1H, s, HN), 7.78 (2H, d, ArH, $J = 8.8$ Hz), 7.47 (2H, d, ArH, $J = 8.8$ Hz), 6.31 (1H, t, NH, $J = 5.6$ Hz), 3.75 (6H, q, OCH_2, $J = 6.8$ Hz), 3.07 (2H, q, NCH_2, $J = 6.4$ Hz), 1.48 (2H, quint, CH_2, $J = 8.0$ Hz), 1.15 (9H, t, CH_3(OEt), $J = 6.8$ Hz), 0.56 (2H, t, $SiCH_2$, $J = 6.8$ Hz). MS(ES) $m/z = 407.4$ (M + Na^+).

General procedure for terbium complex-silica nanocomposites

Scheme 1 presents an overview of our approach. Monodisperse silica nanospheres with a diameter of 84 nm were synthesized using the previously reported method.[15] An excess solution of PABI molecules (~ 300 μL, 1.6 mmol) was added to a 100 ml of solution of silica nanospheres while vigorously stirring and allowed to react for 2 h at room temperature (step 1). After stirring ceased, the PABI–modified silica nanospheres were
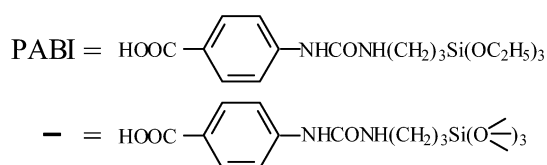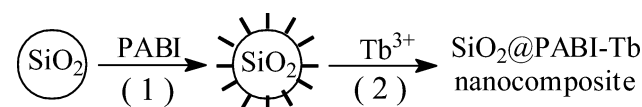
Scheme 1 Procedure for the synthesis of SiO_2@PABI-Tb nanocomposites.

observed to precipitate to the bottom. Removing excess PABI molecules *via* centrifuging and washing with water, the purified PABI-modified silica nanospheres were redispersed in water (100 mL). Then, an excess solution of $TbCl_3$ (10 mM in ethanol) was added to the above solution with vigorously stirring and allowed to react for 6h at room temperature (step 2). The resultant SiO_2@PABI-Tb nanocomposites were purified by further centrifuging and redispersing in water.

UV–vis spectra

The purified SiO_2@PABI-Tb nanocomposites were redispersed in water (100 mL). A 2 mL of above solution was added to quartz cell for UV–vis measurement. In comparison, same molecular amount of purified SiO_2@PABI were also redispersed in 100 mL water. Similarly, 2 mL of SiO_2@PABI solution was added to other quartz cell for UV–vis measurement.

Characterization

^{1}H NMR spectra were recorded on a Bruker AC400 spectrometer. FT–IR spectra were measured on a Perkin-Elmer model 580B infrared spectrophotometer. TEM measurement was carried out on a JEOL 2000-FX transmission electron microscopy. The UV–vis absorption spectra were taken with aTU-1901 spectrophotometer. The fluorescence excitation and emission spectra were recorded on a SPEX Fluorolog-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetime measurements were performed on a SPEX 1934D phosphorimeter using a 7 W pulsed xenon lamp as the excitation source.

Results and discussion

Fig. 1(a) and (b) shows the IR spectra of PABI molecules and SiO_2@PABI-Tb nanocomposites, respectively. The bands corresponding to the $\nu_{C=O}$ and ν_{C-O} for the –COOH of PABI are situated at 1689 cm$^-$ and 1292 cm$^-$, respectively. However, the two bands in the SiO_2@PABI-Tb nanocomposites disappear and two new bands are observed at 1418 cm$^-$ and 1548 cm$^-$. It is known that carboxylic acid salts have a characteristic band in the 1610–1550 cm$^-$ region due to the asymmetric stretching vibration of CO^{2-}. The symmetric stretching vibration of this group gives rise to a band in the range 1420–1335 cm$^-$. Therefore, the appearance of the band at 1418 cm$^-$ corresponding to the $\nu_{s(-COO^-)}$ and the band at 1548 cm$^-$ corresponds to the $\nu_{as(-COO^-)}$ in the SiO_2@PABI-Tb nanocomposites evidences the synthesis of SiO_2@PABI-Tb nanocomposites.

Fig. 2(a) and (b) shows representative TEM images of SiO_2 nanoparticles and SiO_2@PABI-Tb nanocomposites, respectively. As observed from Fig. 2, SiO_2 nanoparticles are
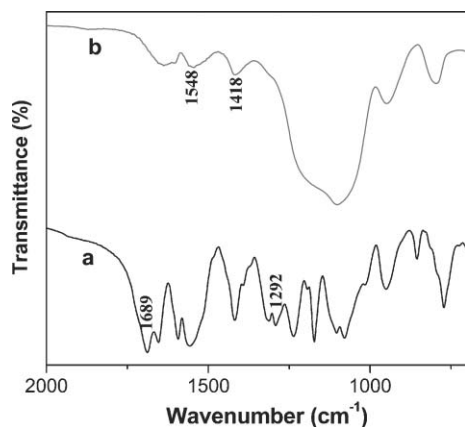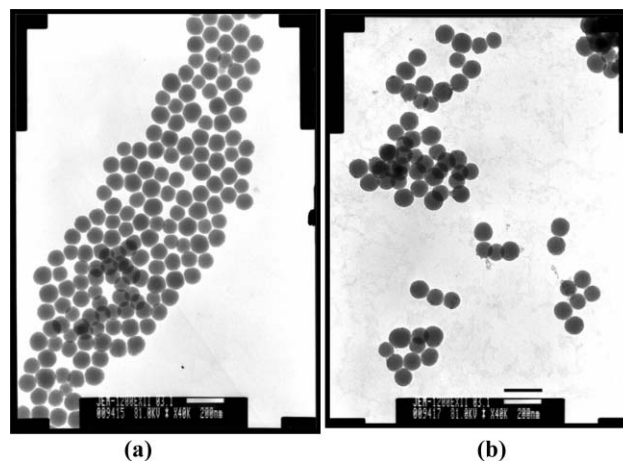

Fig. 2 TEM images of (a) SiO_2 nanospheres and (b) SiO_2@PABI-Tb nanocomposites. The scale bar is 200 nm

uniformly spherical in morphology and approach monodispersity. The average particle size is determined to be 84 nm by counting 250 particles from the enlarged TEM image. After addition of PABI molecules to the solution of silica nanospheres, these PABI molecules bond to the surface of the silica nanospheres and extend their –COOH groups outward. In this case, the self-assembly of PABI molecules on the silica nanospheres will yield the PABI monolayer of approimately 70% coverage that is evaluated from the experimental data. When a solution of Tb^{3+} is mixed with SiO_2@PABI, Tb^{3+} ions can react with SiO_2@PABI *via* –COOH groups. It is evident that the modification of silica nanosphere with PABI molecules and the reaction between SiO_2@PABI and Tb^{3+} have little effect on the morphology of silica nanospheres except that the size of SiO_2@PABI-Tb nanocomposites become a little larger as determined by TEM images. These resultant monodisperse SiO_2@PABI-Tb nanocomposites with good monodispersity represent attractive building blocks from which to create ordered and complex luminescent materials.

UV–vis spectra of SiO_2@PABI and SiO_2@PABI-Tb nanocomposites are shown in Fig. 3(a) and (b), respectively. As seen from Fig. 3, a strong absorption is observed at $\lambda = 270$ nm for the spectrum of SiO_2@PABI. A red shift (from 270 nm in Fig. 3(a) to 278 nm in Fig. 3(b)) is seen upon addition of excess Tb^{3+} ions to SiO_2@PABI, further indicating the formation of SiO_2@PABI-Tb nanocomposites.

The excitation spectrum of SiO_2@PABI-Tb nanocomposites by monitoring the Tb^{3+} emission at 544 nm is indicated (Fig. 4b) together with UV–vis spectrum of SiO_2@PABI (Fig. 4a). A maximum peak appears at 306 nm in Fig. 4b, which is the characteristic absorption of lanthanide complex
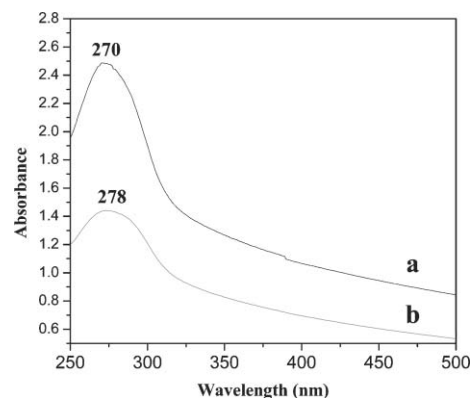

Fig. 1 IR spectra of (a) PABI and (b) SiO_2@PABI-Tb nanocomposites

Fig. 3 UV–vis spectra of (a) SiO_2@PABI and (b) SiO_2@PABI-Tb nanocomposites.

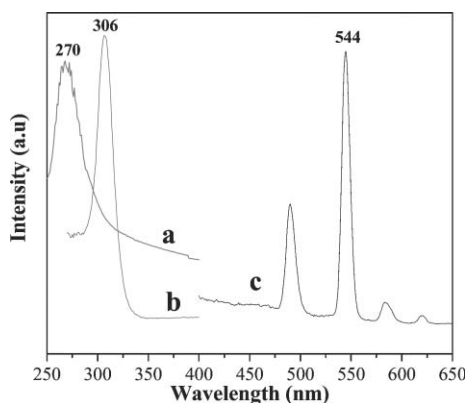**Fig. 4** (a) UV–vis absorption spectrum of SiO$_2$@PABI, and (b) excitation (λ_{em} = 544 nm) and (c) emission spectra (λ_{ex} = 306 nm) of SiO$_2$@PABI-Tb nanocomposites.

arising from the efficient transition based on the conjugated double bonds of the aromatic ligand. The observed overlap between the above two spectra show clearly that the typical sensitization of the Tb^{3+} by the heterocycle ligand, an antenna effect which is defined as a light conversion process *via* an absorption–energy transfer–emission sequence involving distinct absorption by a ligand and emission by a metal ion,[16–18] and thus confirms that Tb^{3+} are surrounded by ligands. Excitation into the ligand at 306 nm reults in a bright green emission (Fig. 4c). The line emissions of SiO$_2$@PABI-Tb nanocomposites are assigned to the transitions from the $^5D_4$ level to the ^7F_j (j = 6, 5, 4, 3) levels at 490, 544, 584, 620 nm, respectively, the $^5D_4 \rightarrow {}^7F_5$ emission being the most prominent one. No emission from the ligand is observed, which indicates that surrounding aromatic ligands absorb energy and transfer energy efficiently to the chelated terbium ions. Also, the half-widths of the strongest bands are less than 15 nm, indicating that the resultant SiO$_2$@PABI-Tb nanocomposites exhibit high fluorescence intensity and color purity.

We compare the luminescent property of SiO$_2$@PABI-Tb (Fig. 4c) and PABI-Tb (Fig. 5b). There is no obvious shift in wavelength of the luminescent emission peaks. However, the maximum excitation peak position depends on the coordinative environment, as shown in Fig. 4b and Fig. 5a. The maximum excitation wavelength of the PABI-Tb (316 nm) obviously shifts compared with that of SiO$_2$@PABI-Tb (306 nm). Moreover, the decay curves of PABI-Tb and SiO$_2$@PABI-Tb nanocomposites are measured. According to the decay curve, the luminescence lifetimes of PABI-Tb and SiO$_2$@PABI-Tb nanocomposites are determined to be 1.3 and 2.2 ms, respectively. It is evident that compared with PABI-Tb, the introduction of silica nanospheres to PABI-Tb obviously
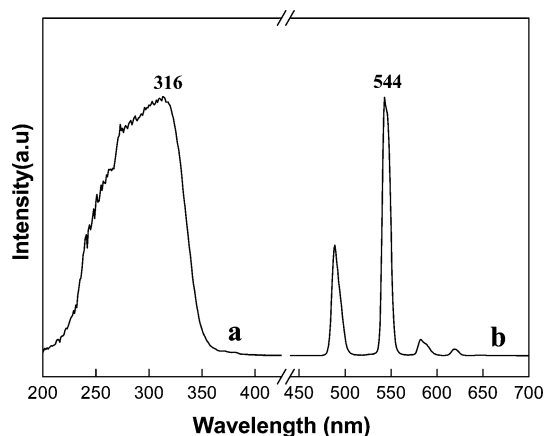
leads to a longer lifetime. The difference on the luminescence lifetime between PABI-Tb and SiO$_2$@PABI-Tb nanocomposites can be explained as follows: The relatively rigid structure of silica nanospheres restricts the vibrations of the ligands of Tb^{3+} and thus results in a decrease in non-radiative transition.[18] Similar results were also found in other lanthanide complexes incorporated into the silica matrix.[19–20] Also, the decay curve of SiO$_2$@PABI-Tb nanocomposites is double exponential, indicating that there are two different surroundings of the terbium ions.[18] Elemental analysis shows that there are some water molecules coordinate to the terbium ion in the SiO$_2$@PABI-Tb nanocomposites.

Conclusion

The proposed approach gives a new avenue for preparing SiO$_2$@ lanthanide complex nanocomposites. Through the judicious combination of organic ligands and lanthanide ions, the nanocomposite with different luminescent properties can be produced. Importantly, since the resultant nanocomposites possess monodispersity of silica nanosphere with the luminescent properties of lanthanide complexes, they can be used as biological probes, and building blocks from which to fabricate novel luminescent materials.

Acknowledgements

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Fig. 5 (a) Excitation (λ_{em} = 544 nm) and (b) emission spectra (λ_{ex} = 316 nm) of PABI-Tb.