Fabrication of silica-coated magnetic nanoparticles with highly photoluminescent lanthanide probes†

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Bi-functional nanoparticles (NPs) that consist of silica-coated magnetic cores and luminescent lanthanide (Ln) ions anchored on the silica surface *via* organic linker molecules are reported. Compared to individual Ln ions, the hybrid NPs show a drastically enhanced photoluminescence due to the efficient ligand-to-metal energy transfer in the Ln-loaded NPs: the new bi-functional NPs could be used in a variety of biological applications involving magnetic separation and optical detection.

Nanometer scale composites having multifunctional properties, which construct materials possessing desirable properties in a single entity, are attracting tremendous interest largely due to their unique coupled behaviours. For instance, materials with both photo-luminescent and magnetic properties could be used in a wide range of applications in biological systems, since they can serve as luminescent markers as well as magnets controlled by an external field.[1] Several methods of preparing the bi-functional composites have been investigated. Wang *et al.* reported the synthesis of core/shell type nanocomposites that consist of superparamagnetic core Fe_3O_4 NPs and a layer of luminescent CdSe/ZnS quantum dots on their surface.[1a] Another novel method described by Gaponik *et al.* involves the simultaneous encapsulation of luminescent CdTe NPs and magnetic ferrite (Fe_3O_4) NPs in polymer microcapsules.[1b] In these methods, NPs based on cadmium chalcogenides were used as emitting sources, which exhibit brighter emission band whose position is tuned by the particle size and are more stable toward photo-oxidation and photo-bleaching compared to organic dyes. For biomedical applications, however, they have the drawback that cadmium is an extremely toxic metal even though cadmium NPs are encapsulated in shells such as silica and bio-compatible polymer.

This limitation has led to extensive efforts to develop non-toxic luminescent markers such as cadmium-free NPs and inorganic or organic dyes that can easily combine with magnetic NPs.[1d,1f,2] In this respect, Ln compounds have been considered as an alternative emitting material. The Ln complexes coordinated with proper ligands have shown strong and narrow emission bands in the UV, visible, and infrared regions through the energy transfer from the ligands to the Ln ions.[3] Unlike organic dyes that often exhibit a photo-bleaching effect or a quenched luminescence, moreover, they have better photo-stability and enhanced signal sensitivity. The photoactive Ln complexes have thus been exploited to detect and monitor signals in specific regions generated by various biological interactions.

In this article we report the fabrication of silica-coated magnetic ferrite NPs functionalized by luminescent Ln ions in which the Ln ions are attached to the silica surface through the 2,2′-bipyridine-4,4′-dicarboxylic acid (BDA) molecule. As schematically illustrated in Fig. 1, new magnetic NPs with built-in optical probes have been developed. An important finding is that the SiO_2@Fe_3O_4/BDA/Ln^{3+} hybrid NPs exhibit a significantly enhanced luminescence compared to the free Ln ions. Accordingly, the magnetic NPs with luminescent probes have potential applications in medical diagnostic such as magnetic resonance imaging for clinical diagnosis, DNA detection, magnetic drug delivery, and enzyme immobilization.[4]

The silica-coated ferrite NPs were used to fabricate the bi-functional materials with luminescent Ln ions, since they have better chemical stability and biocompatibility than the uncoated ferrite NPs. On the basis of their TEM images, the coated NPs have core/shell structure (SiO_2@Fe_3O_4) where each silica sphere appears to contain one ferrite NP. The average diameter of the coated NPs is about 150 ± 10 nm. X-ray powder diffraction revealed that the core Fe_3O_4 NPs adopt a typical cubic spinel structure.†

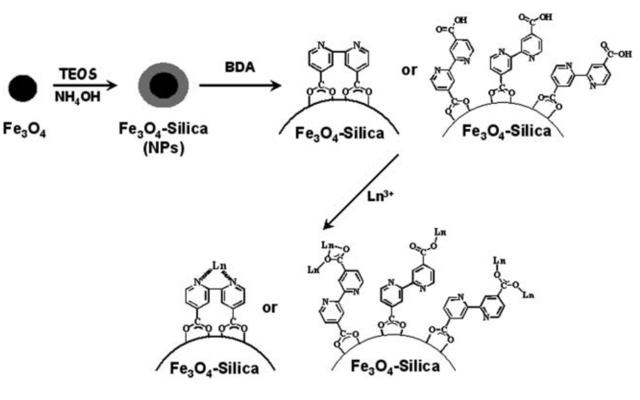

Fig. 1 Schematic drawings for the overall process to fabricate bi-functional NPs, SiO_2@Fe_3O_4/BDA/Ln^{3+}. Top right: Enlargement of a particle showing the two representative coordination modes of BDA. Bottom: Possible coordination modes of Ln ion on SiO_2@Fe_3O_4/BDA/Ln^{3+} showing the chemical structure.

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As a linker molecule, BDA was chosen because it has bi-functional groups. The carboxylate groups in the BDA molecules readily bind to the silica surface and the bi-pyridinyl groups can be covalently bonded to the Ln ions. The BDA molecule was first anchored on the silica-coated ferrite NPs. From the absorption and emission spectra of BDA attached on the surface of $SiO_2@Fe_3O_4$, we found that BDA is covalently linked to the silica surface.† The BDA-attached NPs were then used as seeds. By adding the aqueous solution of the corresponding $LnCl_3$ to the NPs, the Ln-loaded magnetic NPs were fabricated. Hereafter, we denote the resulting bi-functional NPs as $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ (Ln = Eu, Tb).

The coordination modes of the BDA molecule anchored on the $SiO_2@Fe_3O_4$ surface were investigated by examining the Raman spectrum of the $SiO_2@Fe_3O_4/BDA$ complex (Fig. 2). A prominent feature in the spectrum is a strong peak at 1306 cm^{-1} due to the stretching mode of carboxylate groups in BDA, $\nu_s(CO_2^-)$, implying that the BDA molecules are coordinated to the silica surface as the carboxylate (CO_2^-) form. On the basis of the Raman data alone, however, it is hard to discern whether both carboxylate groups of BDA bind to the oxide surface or only one carboxylate group links to the surface. Earlier reports on the BDA linkage with the oxide surface suggested that the carboxylate groups are likely to be coordinated *via* a bridging or bi-dentate coordination to the corresponding metal ions rather than a uni-dentate one.[5] It is thus conceivable that in most BDA molecules both carboxylate groups are coordinated to the silica surface and for a few BDA molecules only one carboxylate group is participated in the bonding with the oxide surface, which are schematically illustrated in Fig. 1.

Emission spectra of the Ln-loaded magnetic NPs excited at 300 nm in aqueous solution at room temperature are presented in Fig. 3. For comparison, emission spectra of $LnCl_3$ and $SiO_2@Fe_3O_4/BDA$ NPs obtained at the same conditions were included. Free Eu^{3+} and Tb^{3+} ions show their characteristic luminescence although their intensities are very weak. The peaks at 578.5, 591.5, 617, 650, and 697.5 nm are the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, and 4) emission bands for Eu^{3+} ion and those at 489, 543.5, 584.5, and 620 nm correspond to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, and 3) lines of Tb^{3+} ion. As can be clearly seen in Fig. 3, $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ NPs show drastically enhanced luminescence peaks although their shapes and positions are not virtually changed. The intensities of luminescence observed from $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ NPs are much higher than those from free Ln^{3+} ions, which is attributed to the efficient ligand-to-metal energy transfer occurred in the Ln-loaded NPs. Namely, the Ln ion bonded to the $SiO_2@Fe_3O_4/BDA$ surface has a more efficient sensitization of its photoluminescence through the BDA ligand.

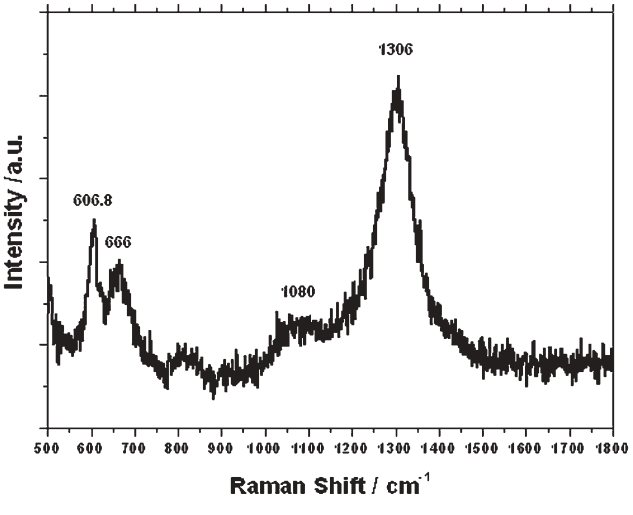

Fig. 2 Raman spectrum of $SiO_2@Fe_3O_4/BDA$ measured using the 633 nm line of a He-Ne laser.

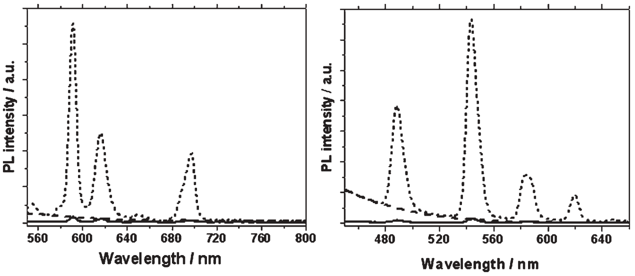

Fig. 3 Emission spectra of $LnCl_3$ (straight line), $SiO_2@Fe_3O_4/BDA$ NPs (dash line), and $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ (short dash line): (a) and (b) correspond to Eu- and Tb-coordinated materials, respectively. (The concentration of Ln^{3+} in all sample solutions was adjusted to be 1×10^{-5} M).

Now we turn to discuss how the Ln ions are bonded to the BDA molecule. It has been known that Ln ion has high coordination number and is well coordinated to the oxygen or nitrogen atoms of various ligands.[3b–c,6] In case both carboxylate groups of BDA are covalently bonded to the silica surface at the initial stage as previously explained, Ln ions bind solely to the bi-pyridinyl group. On the other hand, several coordination modes from carboxylate and bi-pyridyl groups illustrated in Fig. 1 are available if only one carboxylate group is coordinated to the oxide surface and the other group remains intact. Although we cannot precisely determine the coordination modes of Ln ion at this stage, our emission data support the latter scenario. A couple of groups reported that a $^5D_0 \rightarrow {}^7F_0$ transition with a narrow band width ($\sim$2 cm^{-1}) reflects the presence of single chemical environment for the Eu^{3+} ion while a broad $^5D_0 \rightarrow {}^7F_0$ band indicates polymorphic nature of the Ln coordination.[3c,7] Within this regard, the broad band width ($\sim$34 cm^{-1}) of a $^5D_0 \rightarrow {}^7F_0$ transition in our $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ system suggests that the Ln ions are coordinated to both carboxylate and bi-pyridyl groups in BDA.

We have measured the field-dependent magnetization of $SiO_2@Fe_3O_4$ and $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ NPs using a SQUID magnetometer. The M(H) data given in Fig. 4 suggest that the characteristic superparamagnetic features are observed at 10 and 300 K, which are typical of magnetic NPs. As anticipated, the $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ NPs show slightly reduced magnetization compared to the $SiO_2@Fe_3O_4$ NPs, which is due to the presence of BDA and Ln ion in the former. One thing to be mentioned is that no virtual magnetic change due to paramagnetic Ln ion was found. Although the europium content (5.9 weight%) determined by the EDS measurement is larger than the iron content (0.5 weight%) in the $SiO_2@Fe_3O_4/BDA/Eu^{3+}$ sample, the para-magnetic signal from the europium ion is apparently smeared out by strong magnetization induced by the ferrite core.

In conclusion, we have fabricated bi-functional $SiO_2@Fe_3O_4/BDA/Ln^{3+}$ NPs that consist of silica-coated magnetic cores and

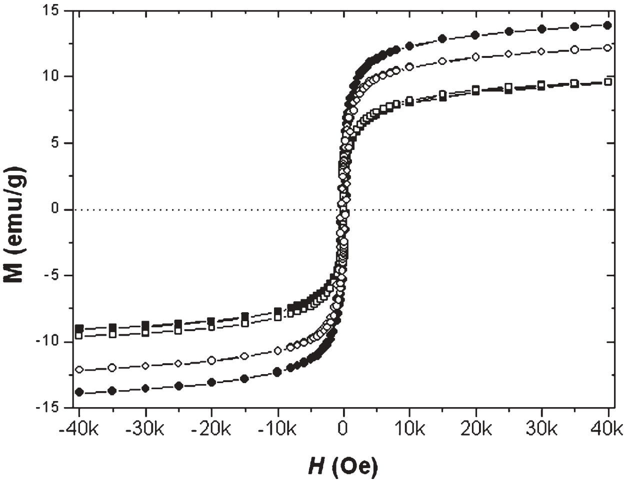

Fig. 4 Field-dependent magnetization curves measured at 10 K (circle) and 300 K (square) by a SQUID magnetometer. Closed and open symbols are magnetization data for $SiO_2@Fe_3O_4$ and $SiO_2@Fe_3O_4/BDA/Ln^{3+}$, respectively.

luminescent Ln ions for the first time. The biocompatible luminescent/magnetic NPs, in which Ln ions act as luminescent markers and silica-coated magnetic NPs serve as cores, show a significantly enhanced luminescence due to the ligand-to-metal energy transfer. Advantages of the bi-functional NPs are two-fold: one is the simple detection of the NPs by conventional optical means and the other is the easy manipulation by an external magnetic field. This simple method can extend to the fabrication of different types of bi-functional composites that can be used a variety of bio-analytical assays.

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