RSC Advances Supporting Information

Monodisperse bifunctional

$\text{Fe}_3\text{O}_4@\text{NaGdF}_4:\text{Yb/Er}@\text{NaGdF}_4:\text{Yb/Er}$ core-shell Nanoparticles

Chongna Zhong, a Piaping Yang,* a Xingbo Li, a Chunxia Li, b Dong Wang, a Shili Gai, a and Jun Lin*b

a Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, China.
b State Key laboratory of Rare Earth Resource utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

yangpiaoping@hrbeu.edu.cn; jlin@ciac.jl.cn
Experimental section

Reagents and materials. Ammonium fluoride (NH₄F), sodium hydroxide, methanol and HCl were obtained from Yili Chemical Corporation (Beijing, China). Rare earth oxides (Gd₂O₃, Yb₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, 99.99%), and oleic acid were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 1-Octadecene was purchased from Acros Organics. All the chemical reagents were used as received without further purification. LnCl₃ were prepared by dissolving the corresponding rare earth oxides in hydrochloric acid at elevated temperature followed by evaporating the solvent under vacuum.

Synthesis of core-shell structured NPs. Fe₃O₄ NPs seeds with a uniform diameter of 9 nm were obtained by high-temperature thermolysis using iron-oleate complexes in a solution of oleic acid surfactant and 1-octadecene solvent.¹ In a typical procedure for the synthesis of Fe₃O₄@NaGdF₄:Yb/Er NPs, GdCl₃ (0.80 mmol), YbCl₃ (0.17 mmol), ErCl₃ (0.03 mmol), oleic acid (6 mL) and 1-octadecene (15 mL) were added to a 100 mL flask. The solution was heated to 140 °C for 30 min to form a clear yellow solution and then cooled to 80 °C, the as-prepared Fe₃O₄ was then added the solution. After the cyclohexane was removed, a solution of 4 mmol of NH₄F (0.1482 g) and 2.5 mmol of NaOH (0.1 g) in 10 mL of methanol was added, and then the solution was kept at 50 °C for 30 min under vigorous stirring. After the methanol was evaporated, the solution was heated rapidly to 300 °C and kept at this temperature for 1 h under vigorous magnetic stirring in the presence of nitrogen. Subsequently, the mixture was allowed to cool to room temperature, and the core-shell structured NPs
were precipitated by the addition of ethanol and isolated by centrifugation. The final products were dispersed in non-polar cyclohexane solvent to form colloidal solution.

Fe$_3$O$_4$@NaGdF$_4$:Yb/Er@NaGdF$_4$:Yb/Er NCs were prepared using Fe$_3$O$_4$@NaGdF$_4$:Yb/Er as seeds through the above process. Fe$_3$O$_4$@NaGdF$_4$:Yb/Tm@NaGdF$_4$:Yb/Tm and Fe$_3$O$_4$@NaGdF$_4$:Yb/Ho@NaGdF$_4$:Yb/Ho core-shell structured NPs were synthesized by the similar procedure.

**Characterization.** X-ray diffraction (XRD) was examined on a Rigaku-Dmax 2500 diffractometer using Cu Kα radiation (λ = 0.15405 nm). The morphologies and composition of the as-prepared samples were characterized by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM), performed on a FEI Tecnai G$^2$ S-Twin transmission electron microscope with a field emission gun operating at 200 kV. Samples for TEM measurements were prepared by evaporating a drop of the colloid onto a carbon-coated copper grid. The energy spectra were obtained by energy-dispersive X-ray spectrum (EDS, JEOL JXA-840) equipped with scanning electron microscope (FESEM, S4800, Hitachi). Fourier-transform infrared (FT-IR) spectra were measured on a Perkin-Elmer 580B IR spectrophotometer using KBr pellet technique. The up-conversion emission spectra were obtained using a 980 nm laser from an OPO (optical parametric oscillator, Continuum Surelite, USA) as the excitation source and detected by a photomultiplier tube (HAHAMATSU R955) from 400 to 900 nm. All the measurements were performed at room temperature.
References

**Fig. S1** XRD patterns of the as-prepared Fe$_3$O$_4$ core NCs (A) and core-shell Fe$_3$O$_4$@NaGdF$_4$:Yb/Er@NaGdF$_4$:Yb/Er NCs (B). The standard data for cubic Fe$_3$O$_4$ phase (JCPDS no. 82–1533) and hexagonal NaGdF$_4$ phase (JCPDS no. 27–0699) are shown as references.
Fig. S2 EDS spectrum of core-shell Fe$_3$O$_4$@NaGdF$_4$:Yb/Er@NaGdF$_4$:Yb/Er NCs.
Fig. S3 FT-IR spectrum of core-shell Fe$_3$O$_4$@NaGdF$_4$;Yb/Er@NaGdF$_4$;Yb/Er NCs.