RSC Advances Supporting Information

Monodisperse bifunctional Fe_3O_4@$NaGdF_4$:Yb/Er@$NaGdF_4$:Yb/Er core-shell Nanoparticles

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Experimental section

Reagents and materials. Ammonium fluoride (NH_4F), sodium hydroxide, methanol and HCl were obtained from Yili Chemical Corporation (Beijing, China). Rare earth oxides (Gd_2O_3, Yb_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, 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. $LnCl_3$ 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. Fe_3O_4 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 Fe_3O_4@$NaGdF_4$:Yb/Er NPs, $GdCl_3$ (0.80 mmol), $YbCl_3$ (0.17 mmol), $ErCl_3$ (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 Fe_3O_4 was then added the solution. After the cyclohexane was removed, a solution of 4 mmol of NH_4F (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_3O_4@$NaGdF_4$:Yb/Er@$NaGdF_4$:Yb/Er NCs were prepared using Fe_3O_4@$NaGdF_4$:Yb/Er as seeds through the above process. Fe_3O_4@$NaGdF_4$:Yb/Tm@$NaGdF_4$:Yb/Tm and Fe_3O_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

1. J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang and T. Hyeon, *Nat. Mater.* 2004, **3**, 891–895.

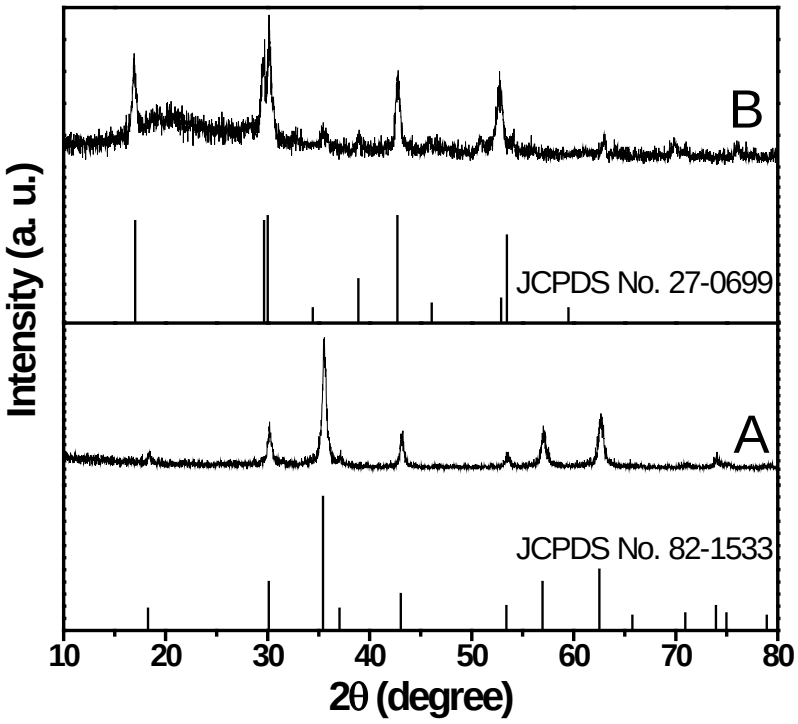

Fig. S1 XRD patterns of the as-prepared Fe_3O_4 core NCs (A) and core-shell Fe_3O_4@$NaGdF_4$:Yb/Er@$NaGdF_4$:Yb/Er NCs (B). The standard data for cubic Fe_3O_4 phase (JCPDS no. 82–1533) and hexagonal $NaGdF_4$ phase (JCPDS no. 27–0699) are shown as references.

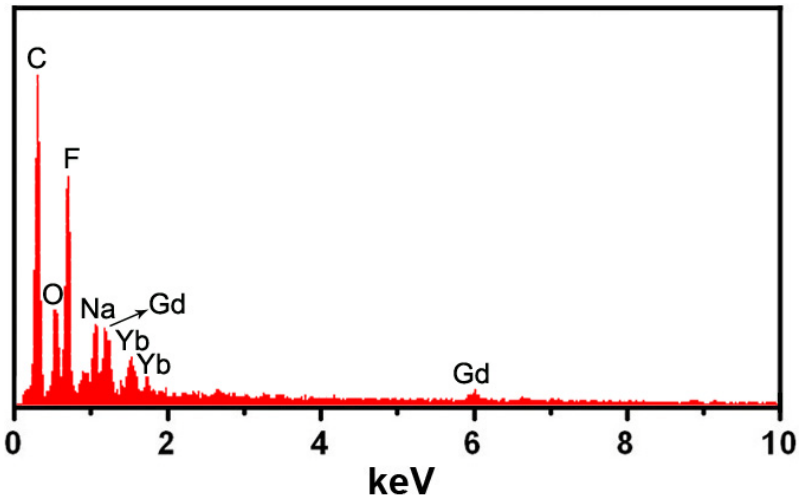

Fig. S2 EDS spectrum of core-shell Fe_3O_4@$NaGdF_4$:Yb/Er@$NaGdF_4$:Yb/Er NCs.

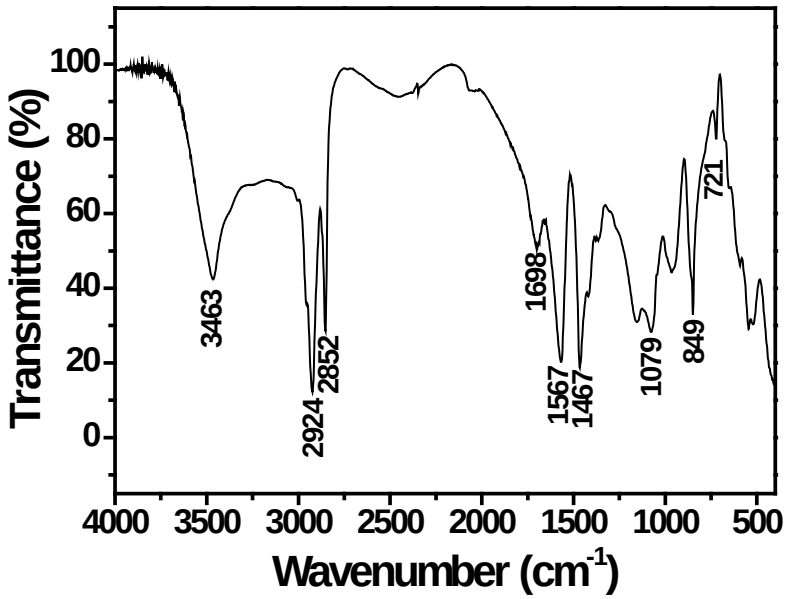

Fig. S3 FT-IR spectrum of core-shell Fe_3O_4@$NaGdF_4$:Yb/Er@$NaGdF_4$:Yb/Er NCs.