Electronic Supplementary Information

Ultra-broadband near-infrared excitable upconversion core/shell nanocrystals

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Experimental details

Chemicals: All chemicals were used as received without further purification. Deionized water was used throughout. $GdCl_3 \cdot 6H_2O$ (99.99%), $ErCl_3 \cdot 6H_2O$ (99.99%), $HoCl_3 \cdot 6H_2O$ (99.99%), NaOH (98%), NH_4F (98%), $NH_3 \cdot H_2O$ (25%),1-octadecene (ODE, 90%), oleic acid (OA, 90%), tetraethylorthosilicate (TEOS) and CO-520 were purchased from Aladdin Chemical Reagent Company.

Synthesis of Er^{3+}: $NaGdF_4$ NCs: In a typical synthesizing procedure, 2 mL aqueous solution of $GdCl_3$ and $ErCl_3$ (total 1 mmol) was added to a 100 mL flask containing 8 mL OA. The mixture was heated at 150 °C for 60 min to remove the water from the solution, then 12 mL ODE was quickly added to the flask and the resulting solution was heated at 150℃ for another 60 min before cooling to 60℃. Subsequently, a methanol solution (10 mL) containing NaOH (2 mmol) and NH_4F (3 mmol) and the solution was stirred for 120 min. After the methanol was evaporated, the solution was heated to 280 °C for 90 min under an inert N_2 atmosphere. On cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of ethanol into the reacted solution, followed by washing with ethanol and cyclohexane and drying in an oven at 80 °C. The as-prepared dried nanocrystals can be easily dispersed in various nonpolar organic solvents such as cyclohexane.

Synthesis of Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$ NCs: The Ho^{3+}: $NaGdF_4$ shell precursor was first prepared by mixing an 2 mL aqueous solution of $GdCl_3$ and $HoCl_3$ (total 1 mmol) with 8 mL OA in a 100 mL flask and subsequently heating at 150 °C for 60 min to remove the water. Then 12 mL ODE was quickly added to the flask and the resulting solution was heated at 150 °C for another 60 min before cooling to 60 °C. Er^{3+}: $NaGdF_4$ core NCs in cyclohexane (8 mL) were added along with a methanol solution (10 mL) of NaOH (2 mmol) and NH_4F (3 mmol) and the solution was stirred for 120 min. After the cyclohexane and methanol were evaporated, the solution was heated to 280 °C for 90 min under an inert N_2 atmosphere. On cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of ethanol into the reacted solution, followed by washing with ethanol and cyclohexane and drying in an oven at 80 °C. The as-prepared dried nanocrystals can be easily dispersed in various nonpolar organic solvents such as cyclohexane.

Synthesis of Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$@$NaGdF_4$ NCs: The $NaGdF_4$ shell precursor was first prepared by mixing an 2 mL aqueous solution of $GdCl_3$ (1 mmol) with 8 mL OA in a 100 mL flask and subsequently heating at 150℃ for 60 min to remove the water. Then 12 mL ODE was quickly added to the flask and the resulting solution was heated at 150 °C for another 60 min before cooling to 60 °C. Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$ core/shell NCs in cyclohexane (8 mL) were added along with a methanol solution (10 mL) of NaOH (2 mmol) and NH_4F (3 mmol) and the solution was stirred for 120 min. After the cyclohexane and methanol were evaporated, the solution was heated to 280 °C for 90 min under an inert N_2 atmosphere. On cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of ethanol into the reacted solution, followed by washing with ethanol and cyclohexane and drying in an oven at 80 °C. The as-prepared dried nanocrystals can be easily dispersed in various nonpolar organic solvents such as cyclohexane.

Synthesis of SiO_2 coating Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$ NCs: The coating of silica on the surface of core/shell NCs was performed by mixing the synthesized Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$ NCs (13 mg) dispersed in 4 mL cyclohexane with 350 uL of CO-520 and 3 mL of cyclohexane. After 30 min stirring, $NH_3 \cdot H_2O$ (200 uL) was added to the above solution and stirred until the mixture become transparent. Subsequently, TEOS (40 uL) was added and stirred for 12 h. The silica-coated core/shell NCs were separated by adding acetone, and then washed with ethanol/water for several times.

Characterizations: XRD analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu*K*α radiation (λ=0.154 nm). The size and shape of the samples were observed by a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive x-ray spectroscope (EDS). TEM specimens were prepared by directly drying a drop of a dilute cyclohexane or water dispersion solution of the products on the surface of a carbon-coated copper grid. UC emission, excitation spectra and UC decay curves were measured with a customized UV to mid-infrared steady-state and phosphorescence lifetime spectrometer (FSP920-C, Edinburgh) equipped with a digital oscilloscope (TDS3052B, Tektronix) and a tunable mid-band OPO pulse laser as excitation source (410-2400 nm, 10 Hz, pulse width≤5 ns, Vibrant 355II, OPOTEK). All photoluminescence studies were carried out at room temperature. To enable comparison of the UC emission intensity, the same amount of NCs were dispersed in cyclohexane solution, and the emission spectra were measured with the same instrumental parameters.

Figure S1-S5

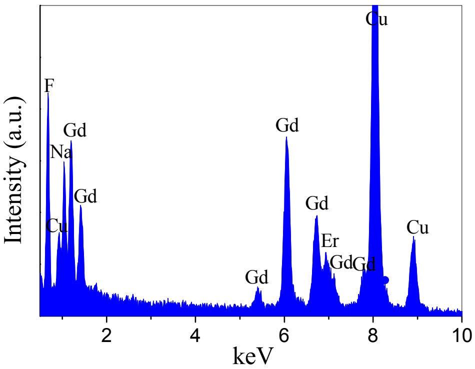

Fig. S1 EDS spectrum taken from Er^{3+}: $NaGdF_4$ NCs, showing the existence of Na, Gd, F and Er elements (Cu signals come from the copper grid).

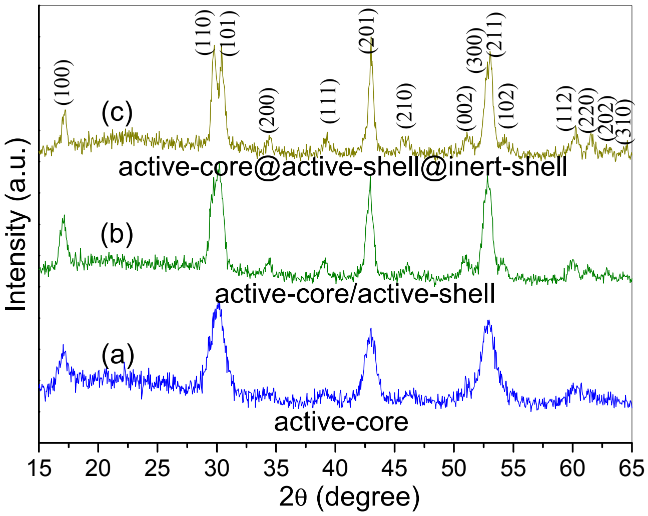

Fig. S2 XRD patterns of (a) Er^{3+}: $NaGdF_4$, (b) Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$, and (c) Er^{3+}: $NaGdF_4$@Ho^{3+}: $NaGdF_4$@$NaGdF_4$ core/shell NCs, showing that all peaks can be well indexed in accordance with hexagonal $NaGdF_4$ phase (JCPDS 27-0699).

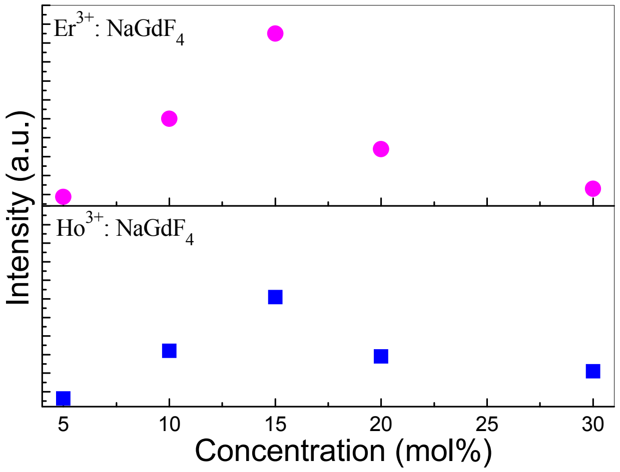

Fig. S3 Dependence of UC emission intensity of Er^{3+}: $NaGdF_4$ or Ho^{3+}: $NaGdF_4$ NCs on Er^{3+} or Ho^{3+} concentration.

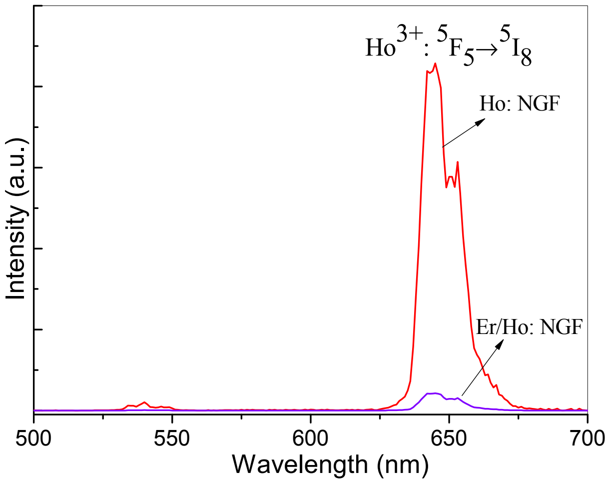

Fig. S4 UC emission spectra of Ho^{3+}: $NaGdF_4$ and Er^{3+}/Ho^{3+}: $NaGdF_4$ NCs under 1160 nm excitation.

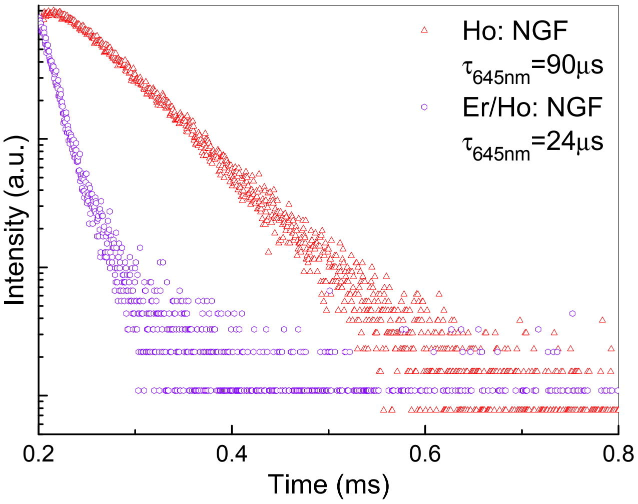

Fig. S5 UC decay curves of Ho^{3+}: $^5F_5$ excited state in Ho^{3+}: $NaGdF_4$ and Er^{3+}/Ho^{3+}: $NaGdF_4$ NCs, under 1160 nm excitation.