Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Highly intense upconversion luminescence in Yb/Er: $NaGdF_4@NaYF_4$ core-shell nanocrystals with complete shell enclosure on core

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Experimental section

Materials. All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout. $LnCl_3·6H_2O$ (Ln=Gd, Y, Yb, Er), NaOH, NH_4F, 1-octadecene (ODE), oleic acid (OA), cyclohexane and ethanol were all supplied by Sinopharm Chemical Reagent Company.

Synthesis of Yb/Er: $NaGdF_4$ NCs. $GdCl_3·6H_2O$ (0.8mmol×0.78), $YbCl_3·6H_2O$ (0.8mmol×0.2), $ErCl_3·6H_2O$ (0.8mmol×0.02) dissolved in 1 mL aqueous solution was added to a 100 mL flask containing 8 mL OA. The mixture was heated at 150ºC for 30 min to remove water from the solution. Then 12 mL ODE was quickly added to the flask and the resulted mixture was heated at 150 °C for another 30 min to form a clear solution, and then cooled down to room temperature. Afterwards, 10 mL methanol solution containing NH_4F (3 mmol) and NaOH (2 mmol) was added and the solution was stirred at 50 °C for 30 min. After the methanol was evaporated, the solution was heated at 80 °C for 5 min, and further heated at 280 °C under N_2 for 90 min and then cooled down to room temperature. The products were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for several times, and finally re-dispersed in 6 mL cyclohexane. The modification of the core size is achieved by controlling NH_4F content and reaction temperature/time.

Synthesis of Yb/Er: $NaGdF_4@NaYF_4$ core-shell NCs. 1 mL aqueous solution of $YCl_3·6H_2O$ (0.8 mmol) was added to a 100 mL flask containing OA (8 mL). The mixture was heated at 150 ºC for 30 min to remove water from the solution. A solution of ODE (12 mL) was then quickly added to the flask and the resulted mixture was heated at 150 °C for another 30 min to form a clear solution, and then cooled down to 80 °C. Thereafter, the pre-prepared core NCs in 6 mL cyclohexane was added to the above solution and kept at 110 °C for 30 min. After the removal of cyclohexane, 10 mL methanol solution containing NH_4F (3 mmol) and NaOH (2 mmol) was added and the solution was stirred at 50 °C for 30 min. After the methanol was evaporated, the solution was kept at 80 °C for 5 min, and further heated at 280 °C under N_2 for 180 min, and finally cooled down to room temperature. The products were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for several times, and finally re-dispersed in cyclohexane. The modification of the shell thickness is realized by introducing different contents of $YCl_3·6H_2O$ in the synthesis.

Characterizations. XRD analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu-K_a radiation (λ=0.154 nm). The size, shape and uniformity of the products were studied using a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive X-ray spectroscope (EDS). The high-angle annual dark-field scanning transmission electron microscopy (HAADF-STEM) observations were performed on an FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope operated at 200 kV. TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon coated copper grid. UC emission spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with an adjustable laser diode (976 nm) and a xenon lamp (450 W) as the excitation sources respectively. To enable comparison of the UC emission intensities among different samples, the emission spectra were measured with the same instrumental parameters (for example: same mass of samples, same excitation wavelength and power, same excitation and emission slits, and so on). All the measurements were carried out at room temperature.

Figure S1-S4

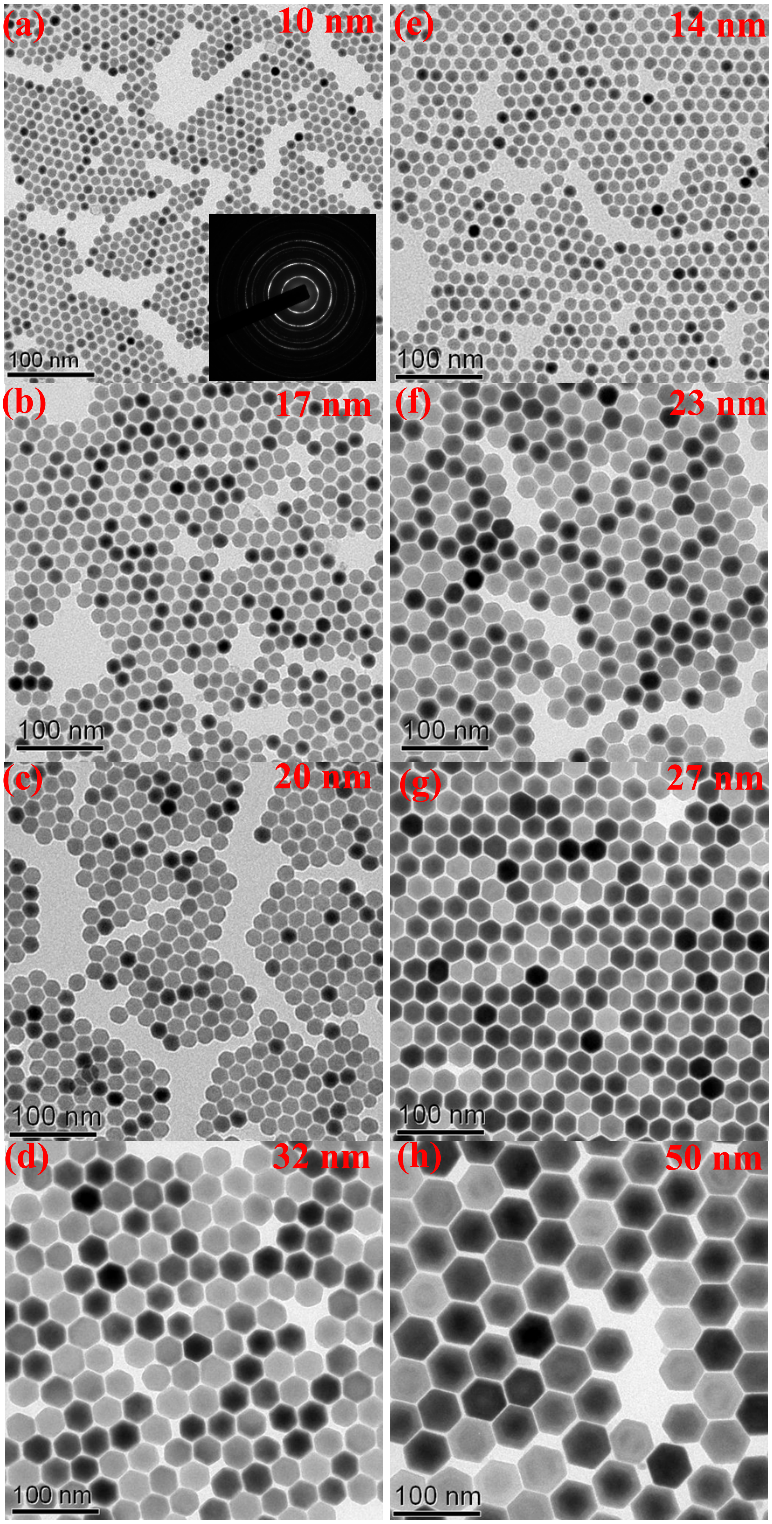

Fig. S1. TEM images of Yb/Er: $NaGdF_4$ core NCs (left: a-d) and the corresponding Yb/Er: $NaGdF_4$@$NaYF_4$ core-shell NCs (right: e-h); inset of (a) is the corresponding SAED pattern.

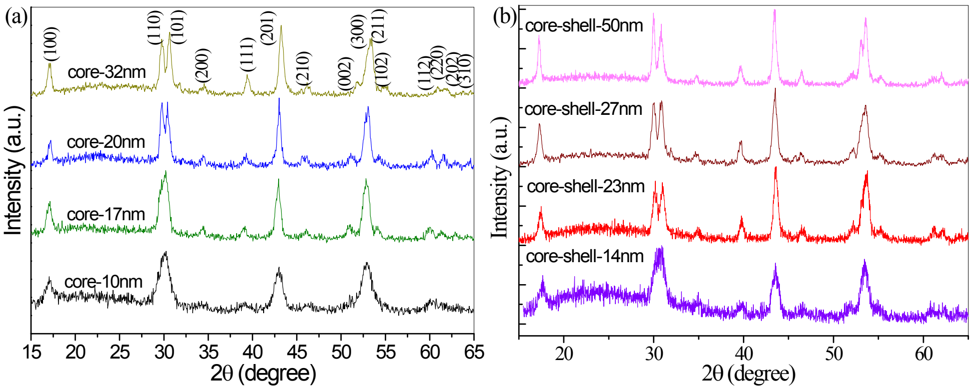

Fig. S2. XRD patterns of (a) Yb/Er: $NaGdF_4$ core and (b) Yb/Er: $NaGdF_4$@$NaYF_4$ core-shell NCs

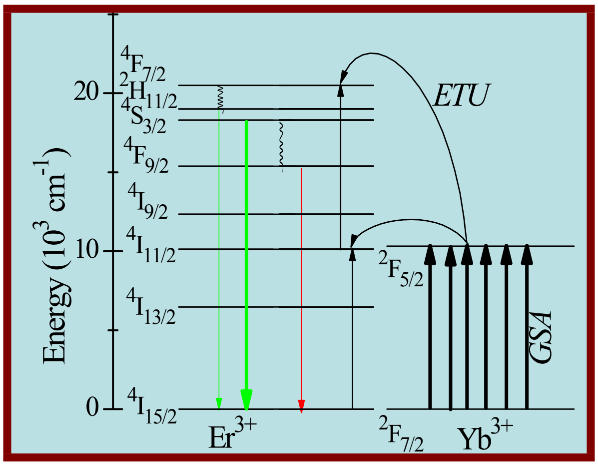

Fig. S3. Energy level diagrams of Er^{3+} and Yb^{3+} ions, showing possible energy transfer mechanisms for red and green UC emissions of Er^{3+} activators in the hosts; GSA and ETU represent ground state absorption and energy transfer upconversion, respectively.

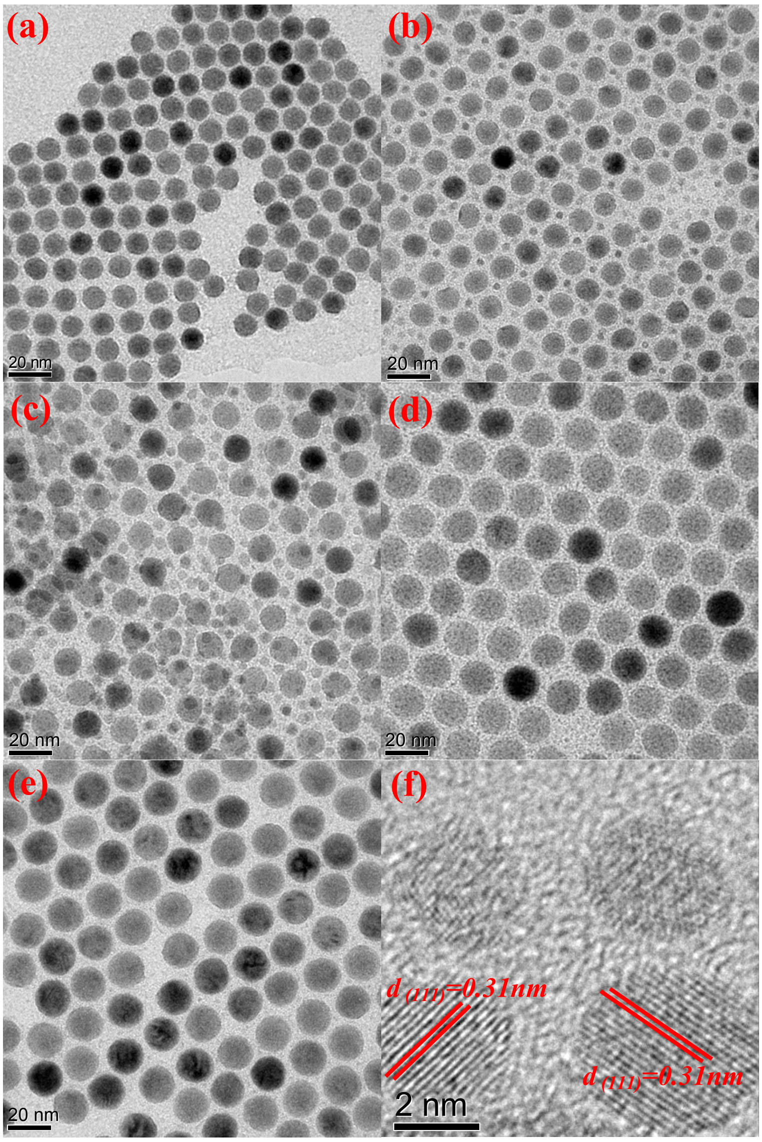

Fig. S4. TEM images of (a) Yb/Er: NaGdF$_4$ core NCs, and (b-e) Yb/Er: NaGdF$_4$@NaYF$_4$ CS NCs reacted for different durations (1 min, 30 min, 60 min and 90 min) at 280 ^{o}C; (f) HRTEM micrograph of cubic NaYF$_4$ NCs formed during the reaction.