

Supporting Information

Establishment of core-shell nanoparticles based on interfacial energy transfer for red emission and highly-sensitive temperature sensing

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I. Experimental section

1. Experimental

1.1 Materials: 1-Octadecene (ODE; 90%), oleic acid (OA; 90%), and $\text{Re}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ were purchased from Alfa Aesar. Ammonium fluoride (NH_4F), sodium hydroxide (NaOH), methanol, cyclo-hexane, and ethanol were purchased from Tianjinzhiyuan Chemical Reagent Co. All $\text{Re}(\text{CH}_3\text{COO})_3$ were dissolved in deionized water, NaOH and NH_4F were dissolved in methanol solution. All materials purchased were used directly without further purification.

1.2 Synthesis

Synthesis of the $\text{NaYF}_4:\text{Er}^{3+}, \text{Tm}^{3+}$ core nanoparticles: All UC nanoparticles were prepared by the co-precipitation method^[1]. Firstly, 12 mL OA and 28 mL ODE were added into a 100 mL-flask, and then mixed with aqueous solution (8 mL) containing 1.6 mmol $\text{Re}(\text{CH}_3\text{COO})_3$. The resulting mixture was heated to 150 °C for 30 min with constant stirring to obtain lanthanide-oleate complexes, and then cooled down to room temperature. Further, the methanol solution of 4 mL NaOH (4 mmol) and 16 mL NH_4F (6.4 mmol) were added into the lanthanide-oleate complexes and insulated at

50 °C for 40 min. Methanol and oxygen were removed by heating up to 100 °C in Argon (Ar) atmosphere. After that, the solution was quickly heated (in 15 min) to 300 °C and kept for 1.5 h. Then the core UC nanoparticles of $\text{NaYF}_4:\text{Er}^{3+},\text{Tm}^{3+}$ were obtained after cooling down to room temperature. The resulting nanoparticles were precipitated by addition of ethanol, collected by centrifugation at 9000 rpm for 5 min, and washed with ethanol for several times. The core UC nanoparticles were dissolved in 10 mL cyclohexane for further shell coating.

Synthesis of $\text{NaYF}_4:\text{Er}^{3+},\text{Tm}^{3+}@\text{NaYF}_4:\text{Yb}^{3+}$ core-active shell UC nanoparticles with different shell thickness: The core-active shell UC nanoparticles with different shell thickness precursor were prepared by adding $\text{Y}(\text{CH}_3\text{COO})_3\cdot 4\text{H}_2\text{O}$, and $\text{Yb}(\text{CH}_3\text{COO})_3\cdot 4\text{H}_2\text{O}$ (total 0.4 mmol) into a mixture of OA (3 mL) and ODE (7 mL), and then the mixed solution was heated to 150 °C for 45 min. After cooling down to room temperature, x mmol $\text{NaYF}_4:\text{Er}^{3+},\text{Tm}^{3+}$ core (x=0.4, 0.8, 1.6) along with methanol solution of 1 mL NaOH (1 M) and 4 mL NH_4F (0.4 M) were added into the solution. Subsequently, the solution was kept at 50 °C for 50 min. After evaporating methanol at 100 °C in Ar atmosphere, the mixture solution was quickly heated up to 300 °C (in 15 min) and kept for 1 h for the coating of inert shell. The resultant dual-layered core-shell UC nanoparticles were obtained by repeating the washing processes described in the core preparation.

Synthesis of $\text{NaYF}_4:\text{Er}^{3+},\text{Tm}^{3+}@\text{NaYF}_4$ core-inert shell UC nanoparticles with different shell thickness: The coating procedures of active shell were similar to that of inert shell. Here the $\text{Y}(\text{CH}_3\text{COO})_3\cdot 4\text{H}_2\text{O}$ were used as the precursor, and x mmol $\text{NaYF}_4:\text{Er}^{3+},\text{Tm}^{3+}$ core (x=0.4, 0.8, 1.6) nanoparticles were used as seeds for the growth of core-active shell UC nanoparticles.

1.3 Characterization

Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED) measurements were carried out by using a JEM-2100F transmission electron microscope. The UC luminescence spectra were measured by a Edinburgh FS5 fluorescence spectrometer equipped with a power-tunable 980 nm laser diode (LD) (maximum power: 2 W). The

photos of UC luminescence were obtained digitally by a Canon EOS 5D camera. Luminescence decay curves were measured by HJY TRIAX550 spectrometer equipped. Uv-vis reflective spectra were carried out by a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Temperature-dependent luminescence characteristics of the as-prepared sample were measured in the temperature range of 300-480 K by the self-manufactured temperature heating instrument (DMU-TC450).

II Supplementary Figures

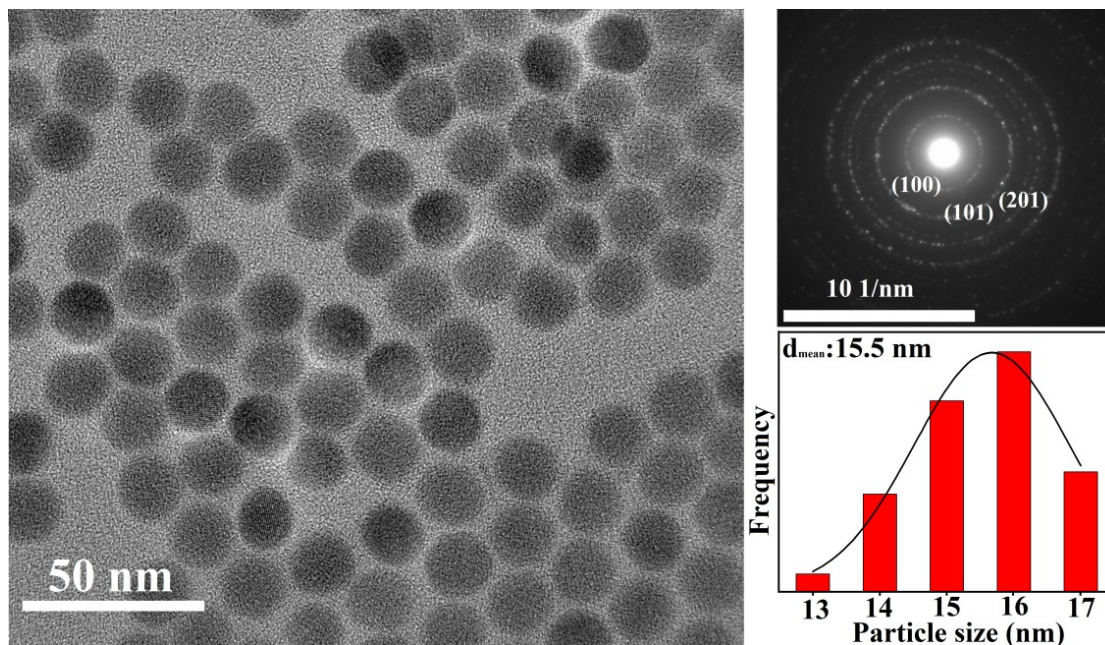


Figure S1 TEM image, corresponding particle-size histogram of $\text{NaYF}_4:\text{Er}^{3+}, \text{Tm}^{3+}$ core UCNs, and electron diffraction of as-prepared UCNs indicates the $\beta\text{-NaYF}_4$ crystals.

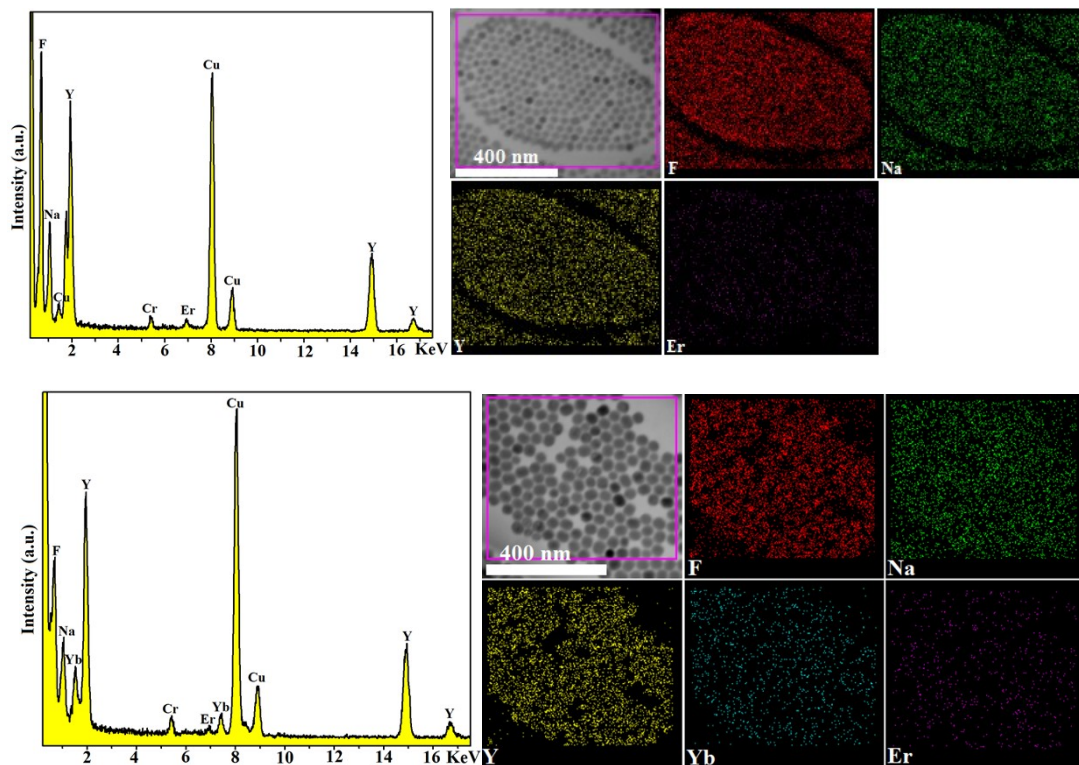


Figure S2 EDX analysis and STEM images of $\text{NaYF}_4:\text{Er}^{3+}, \text{Tm}^{3+}@ \text{NaYF}_4$ and $\text{NaYF}_4:\text{Er}^{3+}, \text{Tm}^{3+}@ \text{NaYF}_4:\text{Yb}^{3+}$ UCNs. The corresponding element distribution maps of F, Na, Y, Er and Yb of the core-inert shell (up) and core-active shell (below) UCNs.

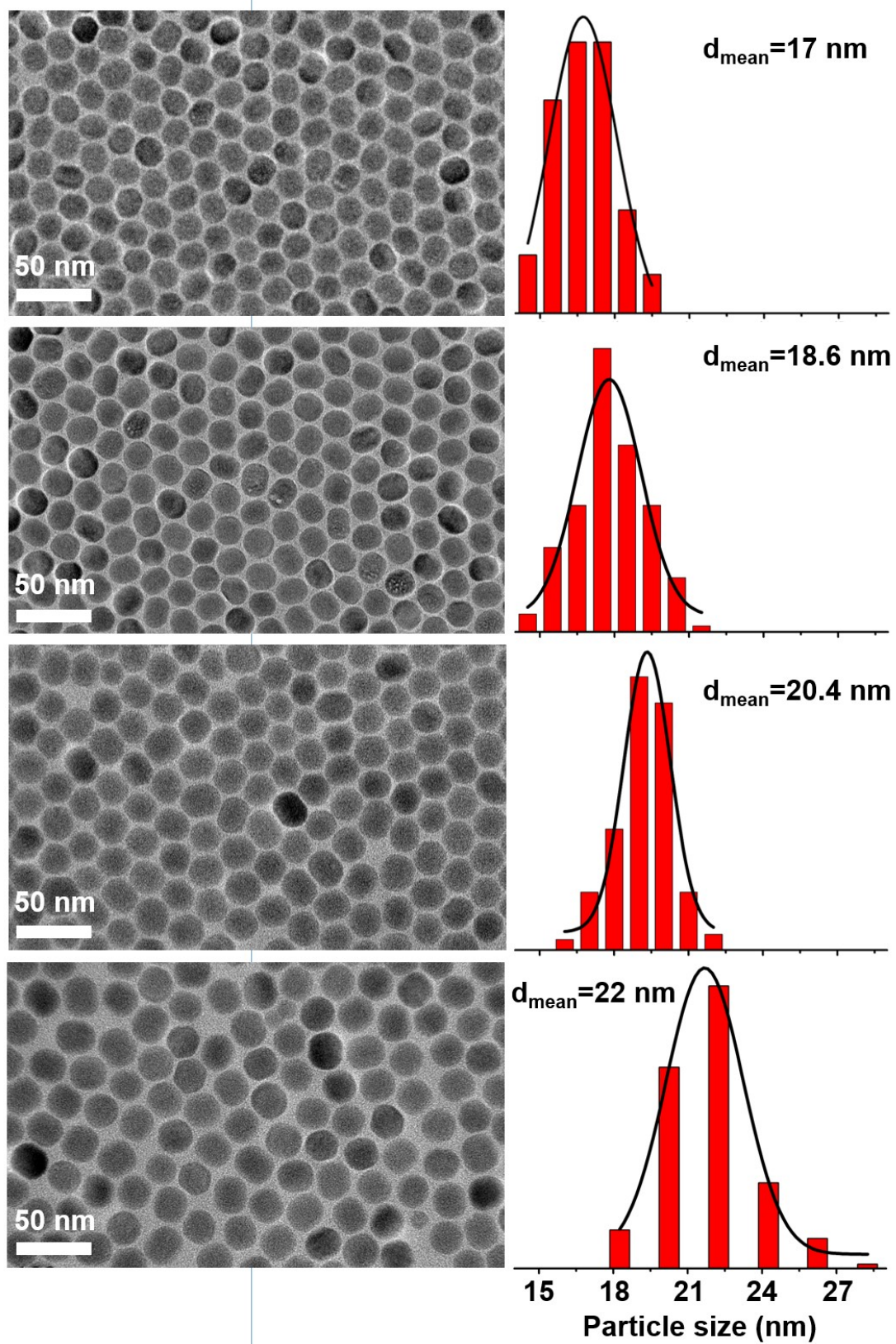


Figure S3 TEM imagers and corresponding size distributions of $\text{NaYF}_4:\text{Er}^{3+},\text{Tm}^{3+}@\text{NaYF}_4:\text{Yb}^{3+}$ with variable shell thickness.

References

- [S1] F. Wang, R. R. Deng, X. G. Liu. Preparation of core-shell NaGdF₄ nanoparticles doped with luminescent lanthanide ions to be used as upconversion-based probes. *Nat. Protoc.*, 2014, 9, 1634–1644.