Supporting Information

Constructing Small Core-Multishell Nanostructure for Ho-

Based Red Upconversion Emission

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Experimental

Materials.

HoCl₃·6H₂O (99.99%), TbCl₃·6H₂O (99.99%), YCl₃·6H₂O (99.99%), GdCl₃·6H₂O (99.99%), YbCl₃·6H₂O (99.99%), TmCl₃·6H₂O (99.99%), NaOH (> 97%), NH₄F (> 98%), oleic acid (OA, > 90%), 1-octadecene (ODE, > 90%), cyclohexane (> 99.5%), methanol (\geq 99.9%) and ethanol (\geq 99.7%) were purchased from Aladdin. All chemicals were used as received without further purification.

Preparation of shell precursors.

Tb-OA (0.04 M) precursor: 2 mmol of TbCl_3 (1 M, 2 mL), 20 mL of OA and 30 mL of ODE were added into a 100 ml three-necked flask. The mixture was stirred at 105 °C for 1.5 h to remove residual water, and then heated to 150 °C for another 1.5 h. After that, the Tb-OA precursor solution (0.04 M) was obtained. Y-OA (0.04 M) precursor, Gd-OA (0.04 M) precursor, Yb-OA (0.04 M) precursor and Tm-OA (0.004 M) precursor were prepared by a similar process as described above.

Preparation of core nanoparticles.

As for the synthesis of NaHoF₄ nanoparticles, 1 mmol of HoCl₃ (1 M, 1 mL), 15 mL of OA and 20 mL of ODE were added into a 100 ml three-necked flask and stirred at 105 °C for 40 min to remove residual water. After that, the mixture was heated to 150 °C for 40 min to form the Ho-OA precursor solution, and then cooled down to 50 °C. Subsequently, a methanol solution (10 mL) containing NaOH (2.5 mmol) and NH₄F (4 mmol) was added and stirred at 90 °C for 1 h to remove the methanol. Then the mixture was heated to 280 °C for 1 h under a gentle argon flow. After cooled down to room temperature, the resulting nanoparticles were centrifuged and washed with ethanol several times. Finally, the nanoparticles were dispersed in cyclohexane. NaYF₄ nanoparticles were prepared by a similar process as described above.

Preparation of core/multi-shell nanoparticles.

As for the synthesis of NaHoF4@NaYF4:75%Tb@NaGdF4:49%Yb,1%Tm@NaYF4 nanoparticles, 0.025 mmol of Y-OA (0.04 M, 0.625 mL), 0.075 mmol of Tb-OA (0.04 M, 1.875 mL), 10 mL of OA and 15 mL of ODE were added into a 100 ml three-necked flask and stirred for 10 min. Then 0.1 mmol NaHoF4 core nanoparticles were added and stirred at 90 °C for 45 min to remove the cyclohexane. After the mixture was cooled down to 50 °C, a methanol solution (6 mL) containing NaOH (0.25 mmol) and NH4F (0.4 mmol) was added and stirred at 90 °C for 40 min to remove the methanol. Then the mixture was heated to 280 °C for 1 h under a gentle argon flow. After reaction, NaHoF4@NaYF4:75%Tb core/shell nanoparticles were prepared, and the mixture was cooled down to 50 °C. Subsequently, 0.05 mmol of Gd-OA (0.04 M, 1.25 mL) were added and stirred at 90 °C for 40 min to remove the for 20 min. After that, a methanol solution (6 mL) containing NaOH (0.25 mmol) was added and stirred at 90 °C for 40 min to remove the mixture was heated to 280 °C for 1 h under a gentle argon flow. After reaction, NaHoF4@NaYF4:75%Tb core/shell nanoparticles were prepared, and the mixture was cooled down to 50 °C. Subsequently, 0.05 mmol of Gd-OA (0.04 M, 1.25 mL) were added and stirred for 20 min. After that, a methanol solution (6 mL) containing NaOH (0.25 mmol) and NH4F (0.4 mmol) was added and stirred at 90 °C for 40 min to remove the methanol. Then the mixture was heated to 280 °C for 1 h under a gentle argon flow. After reaction, NaHoF4@NaYF4:75%Tb@NaGdF4:49%Yb,1%Tm core/shell/shell nanoparticles were prepared, and the mixture was heated to 280 °C for 1 h under a gentle argon flow. After reaction, NaHoF4@NaYF4:75%Tb@NaGdF4:49%Yb,1%Tm core/shell/shell nanoparticles were prepared, and the mixture was cooled down to 50 °C. Subsequently, 0.1 mmol of Y-OA (0.04 M, 2.5 mL)

were added and stirred for 20 min. After that, a methanol solution (6 mL) containing NaOH (0.25 mmol) and NH₄F (0.4 mmol) was added and stirred at 90 °C for 40 min to remove the methanol. Then the mixture was heated to 280 °C for 1 h under a gentle argon flow. After reaction, NaHoF₄@NaYF₄:75%Tb@NaGdF₄:49%Yb,1%Tm@NaYF₄ core/shell/shell nanoparticles were prepared, and the mixture was cooled down to room temperature. Then the resulting nanoparticles were centrifuged and washed with ethanol several times. Finally, the nanoparticles were dispersed in cyclohexane. NaHoF₄@NaYF₄:xTb@NaGdF₄:49%Yb,1%Tm@NaYF₄ (x = 0, 10, 25, 50, 100%), NaYF₄@NaYF₄:xTb@NaGdF₄:49%Yb,1%Tm@NaYF₄ (x = 25, 75%), NaHoF₄@NaGdF₄:75%Tb@NaGdF₄:49%Yb,1%Tm@NaYF₄, NaHoF₄@NaYF₄:75%Tb@ NaYF₄:30%Tb@NaYF₄ and NaHoF₄@NaYF₄@NaYF₄ nanoparticles were prepared by a similar process as described above.

Characterization.

The crystal structure was characterized by using the D-Max 2200VPC X-ray diffraction (XRD) from Rigaku Company with Cu-K α radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM), high-resolution TEM, selected-area electron diffraction (SAED) pattern, high-angle annular dark field scanning TEM (HAADF-STEM), elemental mapping and energy dispersive spectrum (EDS) were performed on TEM operated at 120 kV (FEI Tecnai G2 Spirit), 200 kV (JEM-2010HR) and 300 kV (FEI Tecnai G2 F30). UC emission spectra and decay curves were measured by Edinburgh Instruments FLS980 fluorescence spectrometer equipped with 980 nm diode laser.



Fig. S1 Schematic model (a) of core/shell structure and TEM images (b-d) of NaHoF₄@NaYF₄:xTb (x = 0, 25, 50%) core/shell nanoparticles.



Fig. S2 Schematic model (a) of core/shell/shell structure and TEM images (b-d) of NaHoF₄@NaYF₄:xTb@NaGdF₄:49%Yb,1%Tm (x = 0, 25, 50%) core/shell/shell nanoparticles.



Fig. S3 Schematic model (a) of core/shell/shell structure, TEM images (b-f) and the corresponding SAED patterns (g-k) of NaHoF₄@NaYF₄:xTb@NaGdF₄:49%Yb,1%Tm@NaYF₄ (x = 0, 10, 25, 50, 100%) core/shell/shell nanoparticles.



Fig. S4 XRD pattern of NaHoF₄@NaYF₄:75%Tb@NaGdF₄:49%Yb,1%Tm@NaYF₄ nanoparticles. The vertical red lines are the standard profiles of hexagonal NaHoF₄ (JCPDS 49-1896).



Fig. S5 EDS (a-e) of NaHoF₄, NaHoF₄@NaYF₄:75%Tb, NaHoF₄@NaYF₄:75%Tb@NaGdF₄:49%Yb,1%Tm, NaHoF₄@NaYF₄:75%Tb@NaGdF₄:49%Yb,1%Tm@NaYF₄ and NaHoF₄@NaYF₄:10%Tb@NaGdF₄:49%Yb,1%Tm@NaYF₄ nanoparticles, respectively. HAADF-STEM (f) of NaHoF₄@NaYF₄:75%Tb@NaGdF₄:49%Yb,1%Tm@ NaYF₄ nanoparticles.



Fig. S6 TEM image (a) and the corresponding SAED pattern (b) of $NaYF_4@NaYF_4:75\%Tb@NaGdF_4:49\%Yb,1\%Tm@NaYF_4$ nanoparticles. The upper right of (a) is the schematic model of core/shell/shell structure.



 $\label{eq:Fig. S7} {\it Fig. S7 Proposed UC mechanisms for NaYF_4@NaYF_4:Tb@NaGdF_4:Yb,Tm@NaYF_4 core/shell/shell nanoparticles under 980 nm excitation.}$



Fig. S8 Decay curves of Ho³⁺ 541 nm emission (${}^{5}F_{4} \rightarrow {}^{5}I_{8}$) in NaHoF₄@NaYF₄:*x*Tb@ NaGdF₄:49%Yb,1%Tm@NaYF₄ (*x* = 25, 50, 75%) nanoparticles under 980 nm excitation.



Fig. S9 Power density dependence of blue (Tm^{3+}), green (Ho^{3+}) and red (Ho^{3+}) UC emissions from NaHoF₄@NaYF₄@NaGdF₄:49%Yb,1%Tm@NaYF₄ nanoparticles under 980 nm excitation.



Fig. S10 Power density dependence of green (Ho^{3+}) and red (Ho^{3+}) UC emissions from NaHoF₄@NaYF₄:75%Tb@NaGdF₄:49%Yb,1%Tm@NaYF₄ nanoparticles under 980 nm excitation.



 $\label{eq:Fig.S11} Fig. \ S11 \ EDS \ of \ NaHoF_4 @ NaYF_4: 75\% Tb @ NaYbF_4: 30\% Tb @ NaYF_4 \ nanoparticles.$



Fig. S12 TEM images (a,b) of NaHoF₄@NaYbF₄ and NaHoF₄@NaYbF₄@NaYF₄ nanoparticles, and the corresponding SAED pattern (c) of NaHoF₄@NaYbF₄@NaYF₄ nanoparticles. The upper right of (a,b) are the schematic models of core/shell and core/shell/shell structures, respectively.



Fig. S13 UC emission spectra of NaHoF₄@NaYbF₄@NaYF₄ and NaHoF₄@NaYF₄:75%Tb@ NaGdF₄:49%Yb,1%Tm@NaYF₄ nanoparticles under 980 nm excitation. Note that the emission spectra are normalized to Ho³⁺ 541 nm emission.



Fig. S14 Power density dependence of red (Ho³⁺) and green (Ho³⁺) UC emissions from NaHoF₄@NaYbF₄@NaYF₄ nanoparticles under 980 nm excitation.