Supplementary Information

Engineering Homogeneous Doping in Single Nanoparticle to Enhance Upconversion Efficiency

Xiaomin Li, Rui Wang, Fan Zhang, Dongyuan Zhao**

Department of Chemistry and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, P.R. China;

*To whom correspondence should be addressed.

E-mail: zhang_fan@fudan.edu.cn; dyzhao@fudan.edu.cn

I. Supplementary Methods

Materials.

Gadolinium (III) chloride anhydrous ($GdCl_3$, 99.99 %), yttrium (III) chloride anhydrous (YCl_3, 99.9 %), ytterbium (III) chloride anhydrous ($YbCl_3$, 99.9 %), erbium (III) chloride anhydrous ($ErCl_3$, 99.9 %), thulium (III) chloride anhydrous ($TmCl_3$, 99.9 %), sodium trifluoroacetate (Na-TFA, 98 %), 1-octadecene (ODE, 90 %), oleic acid (OA, 90 %), polyvinylpyrrolidone (PVP 10000) (10000 g mol^{-1}) was purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 96 %), ammonium fluoride (NH_4F, 96 %) was obtained from Beijing Chemical Reagents Co. Ltd. All chemicals were used as received without any further purification.

Preparation of shell precursors.

Y-OA (0.10 M) host precursor: A mixture of YCl_3 (2.50 mmol), OA (10.0 mL), and ODE (15.0 mL) was loaded in a reaction container and heated at 140 °C under vacuum with magnetic stirring for 30 min to remove residual water and oxygen. Then, the colorless Y-OA precursor solution (0.10 M) was obtained.

Gd-OA(0.05 M), Yb-OA (0.05 M), Er-OA (0.05 M) and Tm-OA (0.05 M) precursor: The synthesis of Gd-OA, Yb-OA, Er-OA and Tm-OA precursors were carried out all the same as that of the Y-OA precursor except 1.25 mmol of $GdCl_3$, 1.25 mmol of $YbCl_3$, 1.25 mmol of $ErCl_3$, 1.25 mmol of $TmCl_3$ were used instead of 2.5 mmol of YCl_3, respectively. ***Na-TFA-OA precursor:*** A mixture of Na-TFA (4.00 mmol) and OA (10.0 mL) was loaded in a container at room temperature under vacuum with magnetic stirring to remove residual water and oxygen. Then the colorless Na-TFA-OA precursor solution (0.40 M) was obtained. For specific requirements, the Na-TFA-OA precursor could also be prepared with the concentration of 0.20 M.

Synthesis of $NaGdF_4$:Yb,Er heterogeneous doping core (HEC) nanoparticles.

The synthesis of the $NaGdF_4$:Yb,Er HEC nanoparticles with a size of ~ 10 nm in this work was similar to that reported previously by van Veggel et *al*.[1] In a typical procedure, $GdCl_3$ (0.75 mmol), $YbCl_3$ (0.23 mmol), $ErCl_3$ (0.02 mmol), oleic acid (OA, 4.0 mL) and 1-octadecene (ODE, 15.0 mL) were mixed together and heated to 140 °C under vacuum until a clear solution formed, after that, the solution was cooled down to room temperature. A solution of NaOH (2.5 mmol) and NH_4F (4.0 mmol) in methanol (10 mL) was added and the mixture was stirred for half an hour. The reaction mixture was then heated to 70 °C and maintained for half an hour to remove the methanol. Afterward, the solution was heated to 290 °C and maintained for 100 min under a gentle argon flow. Small amount of aliquots were taken at different time intervals by using glass syringe. The aliquots were centrifuged at high speed of 16500 rpm/min and washed twice with ethanol for further characterization. Subsequently, the solution was cooled down to room temperature and the nanoparticles were

centrifuged and washed twice with ethanol. The nanoparticles were finally dispersed in 10 mL of cyclohexane for further use.

Synthesis of $NaGdF_4$:Yb,Er homogeneous doping core (HOC) nanoparticles.

Synthesis of the 2.5 nm seed: The synthesis of the $NaGdF_4$:Yb,Er initial seeds with a size of ~ 2.5 nm was carried out similar as that of $NaGdF_4$:Yb,Er HEC nanoparticles. Typically, $GdCl_3$ (0.78 mmol), $YbCl_3$ (0.20 mmol), $ErCl_3$ (0.02 mmol), OA (4.0 mL) and ODE (15.0 mL) were mixed together and heated to 140 °C under vacuum until a clear solution formed, after that, the solution was cooled to room temperature. A solution of NaOH (2.5 mmol) and NH_4F (4.0 mmol) in methanol (10 mL) was added and the mixture was stirred for a few hours. The reaction mixture was then heated at 70 °C to remove the methanol. Afterward, the solution was heated to 270 °C and maintained for 10 min under a gentle argon flow. Finally, the 2.5-nm $NaGdF_4$:Yb,Er seed with a doping concentration of 22 % and 2.3 % for Yb^{3+} and Er^{3+} was obtained. Then the solution was cool down to room temperature and the nanoparticles were centrifuged and washed twice with ethanol. The nanoparticles were finally dispersed in 10 mL of cyclohexane for further use.

Synthesis of $NaGdF_4$:Yb,Er HOC nanoparticles (~ 10 nm): The Gd-Yb-Er-OA (0.05 M) shell precursor was firstly obtained from a mixture of Gd-OA (0.05 M), Yb-OA (0.05 M) and Er-OA (0.05 M) in a 78:20:2 ratio. Then, 2.5 mL of the purified 2.5-nm $NaGdF_4$:Yb,Er initial seed solution was mixed with 4.0 mL of OA and 6.0 mL of ODE. The flask was pumped at 70 °C for 30 min to remove cyclohexane and residual air. Subsequently, the system was switched to Ar flow and the reaction mixture was further heated to 280 °C at a rate of ~ 20 °C/min. Then Gd-Yb-Er-OA (0.05 M) and Na-TFA-OA (0.20 M) host shell

precursors were alternately introduced by dropwise addition at 280 °C and the time interval between each injection was 15 min. The amounts of the shell precursors for each addition were calculated and summarized in Table S1. Finally, the obtained $NaGdF_4$:Yb,Er homogeneously doping cores were centrifuged and washed as above and dispersed in cyclohexane.

Synthesis of $NaGdF_4$:Yb,Er/$NaYF_4$ HOC/shell (HOC/S) nanoparticles.

All of the purified $NaGdF_4$:Yb,Er HOC nanoparticle solutions were mixed with 4.0 mL of OA and 6.0 mL of ODE. The flask was pumped at 70 °C for 30 min to remove cyclohexane and residual air. Subsequently, the system was switched to Ar flow and the reaction mixture was further heated to 280 °C at a rate of ~ 20 °C/min. Then Y-OA (0.10 M, 1.0 mL) and Na-TFA-OA (0.40 M, 0.5 mL) host shell precursors were alternately introduced by dropwise addition at 280 °C and the time interval between each injection was 15 min. Finally, the obtained $NaGdF_4$:Yb,Er/$NaYF_4$ HOC/S nanoparticles were centrifuged, washed and dispersed in cyclohexane for further use.

Synthesis of $NaGdF_4$:Yb,Er/$NaYF_4$ HEC/shell (HEC/S) nanoparticles.

2.5 mL of the purified $NaGdF_4$:Yb,Er HEC nanoparticle solution was mixed with 4.0 mL of OA and 6.0 mL of ODE. The synthesis of $NaGdF_4$:Yb,Er/$NaYF_4$ HEC/S nanoparticles was carried out similar to that of $NaGdF_4$:Yb,Er/$NaYF_4$ HOC/S nanoparticles.

Characterization.

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field imaging in the scanning TEM (HAADF-STEM) observations were performed on JEM-2100F transmission electron

microscope with an accelerating voltage of 200 kV equipped with a post-column Gatan imaging filter (GIF-Tri-dium) and Tecnai G^2 20 transmission electron microscope. The doping concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an IRIS Advantage Duo ER/S (Thermo Fisher Scientific). X-ray diffraction (XRD) measurements were carried out at room temperature with a Bruker D8 diffractometer using Cu Kα radiation (wavelength = 1.5406 Å). The UC luminescence emission spectra were recorded on Hitachi Fluorescence Spectrometer F4500 instrument, but the excitation source using an external 980 nm semiconductor laser (Changchun New Industries Optoelectronics Tech. Co., Ltd.) with an optic fiber accessory, instead of the Xeon source in the spectrophotometer (Unless otherwise specified, all spectra were collected under identical experimental conditions). Single particle imaging was done using Olympus IX71 microscope equipped with the SP 2360 spectrometers and Pro EM CCD camera (Princeton Instruments Inc.). According to the literature reported previously, we can define that the luminescent spots are captured from single UCNP if most of the luminescent spots in a fixed area exhibit the similar intensities of UCL.[2] 980-nm CW laser was used as the excitation source, in combination with a short pass optical filter (750SP from Chroma Corp) (Figure S6). In vivo UC luminescence imaging was performed with a modified LB983 NightOWL II (Berthold Technologies GmbH & Co.KG, Germany) using an external 0 ~ 2 W adjustable 980 nm CW laser as the excited source.

Measurement of upconversion absolute quantum yield.

According to the method reported by van Veggel et al.,[3] fluorescence spectroscopy (Edinburgh LFS920) was modified by using Ocean Optics UV-VIS-NIR CCD (QE65000) as a detector for collecting the 980 nm light and the UC emissions. An integrating sphere was also used to measure the efficiency data. The response of the detection systems in photon flux

was determined using a calibrated VIS-NIR lamp (Ocean Optics LS-1-CAL). The quantum yield of UC emission of the nanoparticles was calculated with the following equation.

$$QY = \frac{\text{Photons emitted}}{\text{Photons absobed}} = \frac{E_{sample}}{A_{blank} - A_{sample}}$$

Where QY is the quantum yield, E_{sample} is the photons emitted per unit time of the sample in the UC emission range, A_{blank} and A_{sample} are the photons emitted per unit time by the excitation light in the absence and presence of the UCNPs samples, respectively.

Animal experiments and *in-vivo* imaging.

Male Kunming mice (weighing 30 ~ 40 g) were purchased from Shanghai SLAC Laboratory Animal Co., Ltd. (Shanghai, China). All animal experimental procedures were in agreement with institutional animal use and care regulations. *In-vivo* UC luminescence imaging was performed with a modified LB983 NightOWL II (Berthold Technologies GmbH & Co.KG, Germany) using an external 0 ~ 2 W adjustable 980 nm CW laser as the excitation source. After the mice were anesthetized (with 100 μL of 10 % chloral hydrate), the water-soluble UCNPs aqueous solution (100 μL, 1 mg/mL) in 0.9 % NaCl saline solution was subcutaneously injected. Then the optical whole body images of mice were recorded on the modified LB983 NightOWL II instrument.

Calculate the amount of shell precursor for the growth of each monolayer.

The spherical concentric shell model (CSM) was employed to calculate the amount of shell precursor necessary for the growth of each monolayer (ML).[4, 5] This model has been used extensively for the hexagonal CdS and ZnS shell deposition during the quantum dots

core/shell nanocrystal synthesis process.[1] Because of the highly symmetric structure of the CdS, the ML was inferred to a thickness equal to half the c-lattice parameter. Although the $NaGdF_4$ shell adopted here has also hexagonal structure ($P6_3/m$, a = 6.02 Å, c = 3.60 Å), the cation sites are of three types. A onefold site occupied by RE^{3+}, another site occupied randomly by $1/2Na^+$ and $1/2RE^{3+}$, and a twofold site occupied randomly by Na^+ and vacancies.[5, 6] Therefore, referral to a $NaGdF_4$, the ML could be taken to mean a thickness equal to the c-lattice parameter of the bulk material, 0.36 nm in the case of the hexagonal NaGdF4. The required Gd-OA precursor amount for every layer of one particle can be calculated by the following equations:

$$m_{layer(n)} = m_{particle(n)} - m_{particle(n-1)} = \rho(V_{particle(n)} - V_{particle(n-1)}) = \rho\frac{4}{3}\pi(r_{particle(n)} - r_{particle(n-1)}) \quad (1)$$

Density of the $NaGdF_4$ materials (ρ) is calculated as follows:

$$\rho = \frac{m}{V} = \frac{M}{(N_A * c * \frac{\sqrt{3}}{2}a^2)/N'} \quad (2)$$

Here M represents relative molecular mass of the material of $NaGdF_4$, N' means the number of $NaGdF_4$ units that one crystal cell contains and according to crystal structure of the hexagonal $NaGdF_4$, N' = 1.5. So, for $NaGdF_4$, the cell parameter is a = 6.02 Å, c = 3.60 Å, molecular weight (M) = 256.3, and ρ = 5.65 g/cm^3. For $NaYF_4$, cell parameter is a = 5.96 Å, c = 3.53 Å, molecular weight M = 187.9, and ρ = 4.31 g/cm^3.

Particle number of one molar (N) the $NaGdF_4$ (N) is calculated as follows:

$$N = \frac{V_{per\ molar}}{V_{per\ particle}} = \frac{\frac{M_0}{\rho_0}}{\frac{4}{3}\pi r_0^3} \quad (3)$$

Here, we supposed that the reactants were complete reacted after the reaction prolong 100 min (the synthesis of the HEC). So, in the above equation, r_0 = 5 nm. Because the particle number is constant during the particle growth from smaller to bigger, so the particle number of the obtained initial seed, which was used for the synthesis of HOC, is nearly the same as N. According to equation (1), (2), (3), the calculations of the doses of the precursors for the HOC growth with different ML are shown in Table S1.

II. Supplementary Tables

Table S1. Calculation of the doses of the precursors for the HOC growth with different ML, and statistics average diameter and predict diameter of the obtained HOC UCNPs with different ML growth.

Monolayers	Precursors (mL)		Average Measured Diameter (nm)	Predicted Diameter (nm)
	Re-OA (0.05 M)	Na-TFA-OA (2 M)		
0	-	-	2.50	-
1	0.1	0.05	3.32	3.22
2	0.15	0.075	3.89	3.94
3	0.21	0.105	4.55	4.66
4	0.3	0.15	5.41	5.38
5	0.38	0.19	6.22	6.1
6	0.48	0.24	6.91	6.82
7	0.6	0.3	7.58	7.54
8	0.72	0.36	8.42	8.26
9	0.85	0.425	9.11	8.98
10	1	0.5	9.89	9.7
11	1.2	0.6	10.53	10.42

III. Supplementary Figures

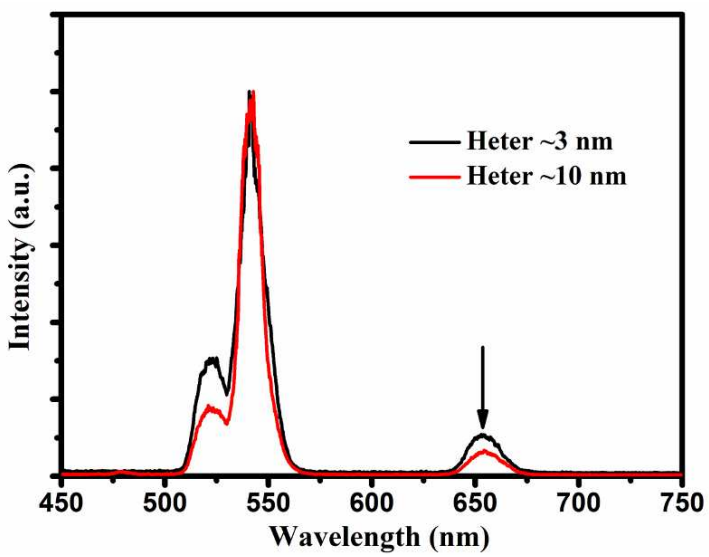

Figure S1. UC emission spectra of the HEC nanoparticles during the spontaneous growth with different crystal sizes under 980 nm excitation.

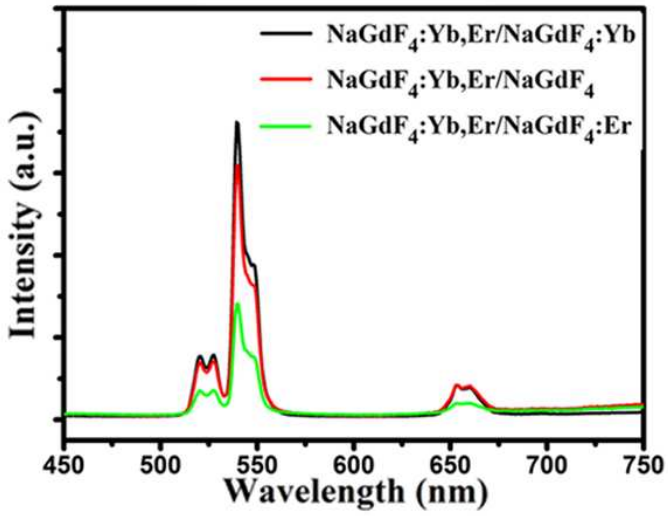

Figure S2. UC emission spectra of the $NaGdF_4$:Yb,Er/$NaGdF_4$, $NaGdF_4$:Yb,Er/$NaGdF_4$:Er, and $NaGdF_4$:Yb,Er/$NaGdF_4$:Yb under 980 nm excitation obtained at identical experimental conditions.

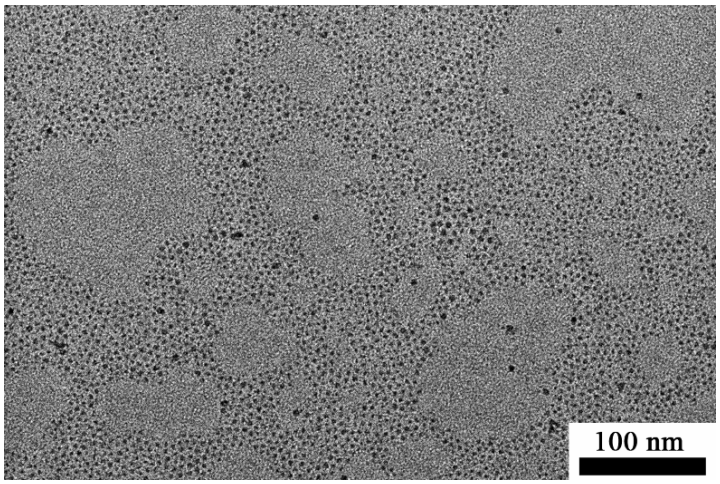

Figure S3. The TEM image of the initial seeds (~ 2.5 nm) used in the synthesis of HOC nanoparticles.

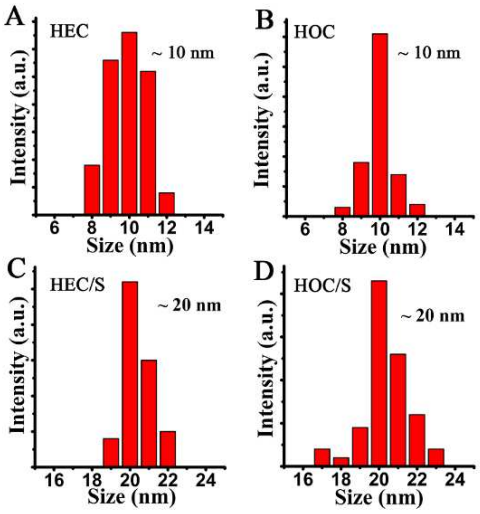

Figure S4. Histograms of the particle sizes of HEC, HOC, HEC/S, HOC/S UCNPs, which were measured by TEM images shown in Figure 4.

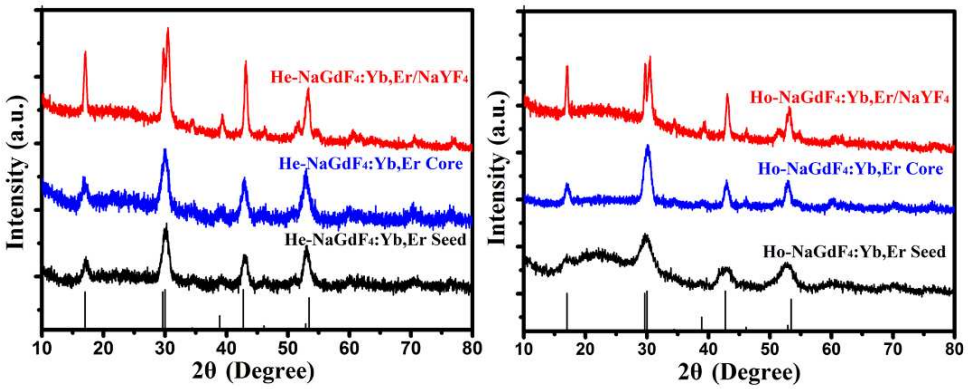

Figure S5. XRD patterns of hexagonal HEC, HOC, HEC/S, HOC/S, and the initial seed.

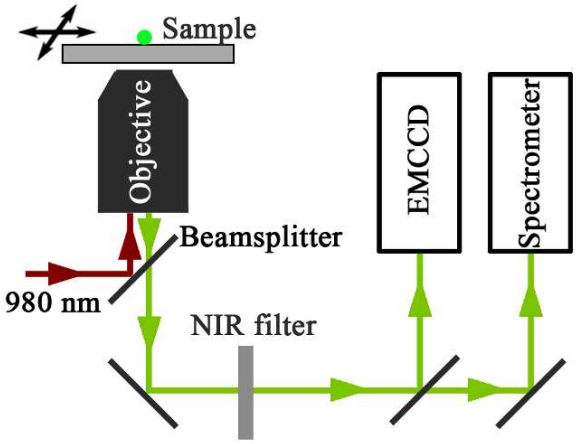

Figure S6. Scheme setup to get the single particle imaging and local spectral analysis of the nanoparticle.

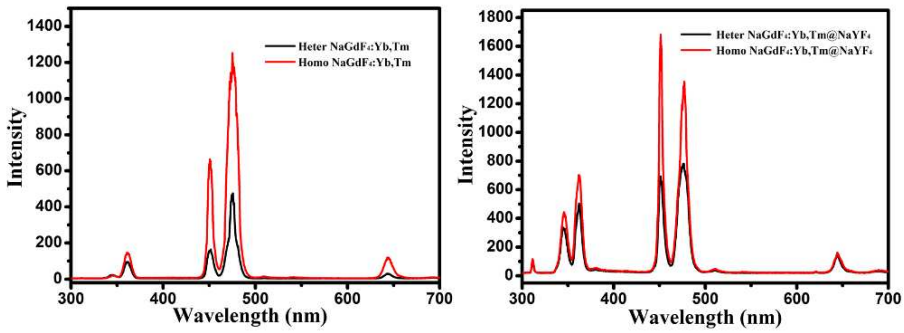

Figure S7. UC emission spectra of the $NaGdF_4$:Yb,Tm HEC, HOC and $NaGdF_4$:Yb,Tm/$NaYF_4$ HEC/S, HOC/S nanoparticles under identical experimental conditions.

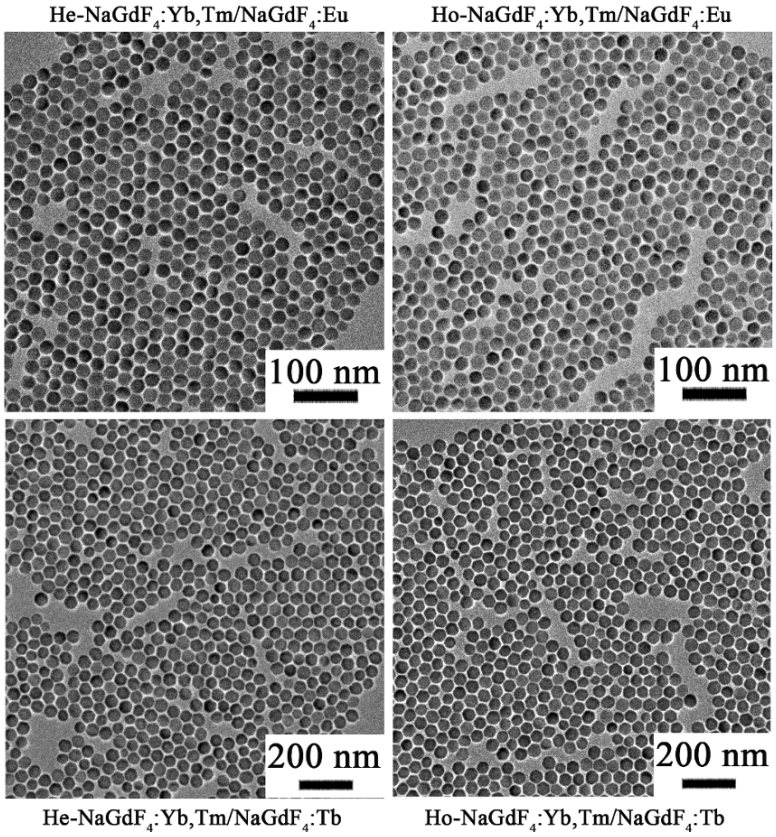

Figure S8. TEM images of the $NaGdF_4$:Yb,Tm/$NaGdF_4$:Tb and $NaGdF_4$:Yb,Tm/$NaGdF_4$:Eu UCNPs with the heterogeneously and homogeneously doping core.

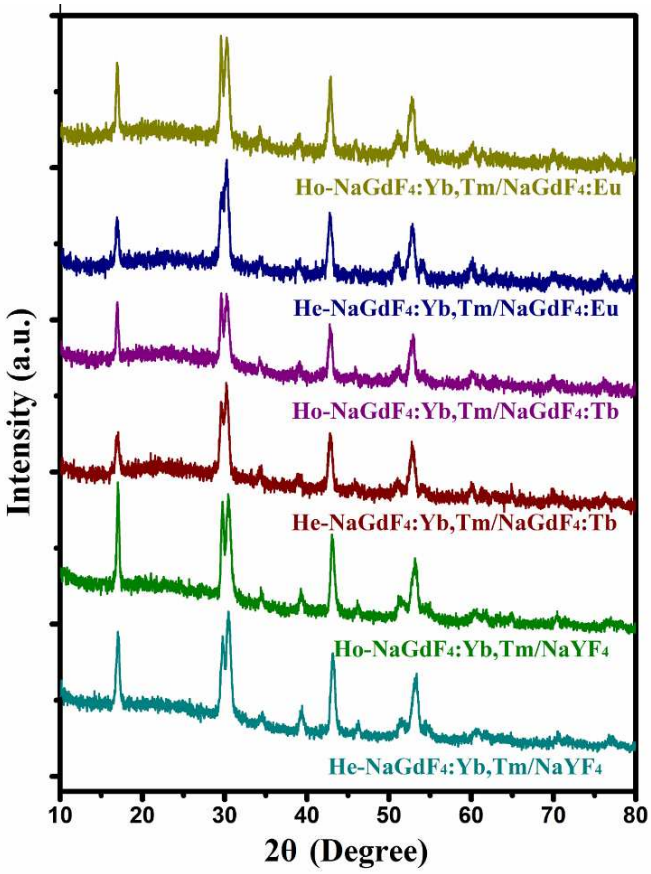

Figure S9. XRD patterns of HEC/S and HOC/S $NaGdF_4$:Yb,Tm/$NaYF_4$, $NaGdF_4$:Yb,Tm/$NaGdF_4$:Tb, $NaGdF_4$:Yb,Tm/$NaGdF_4$:Eu UCNPs with heterogeneous and homogeneous doping core, respectively.

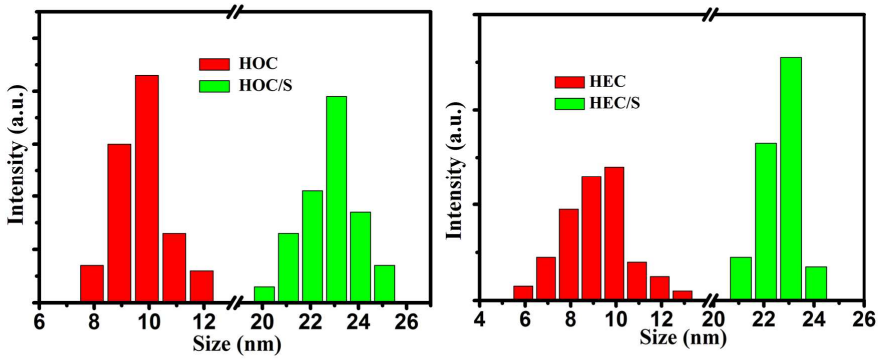

Figure S10. The size distributions of the HOC, HOC/S, HEC, HEC/S obtained from Figure 3E and I.

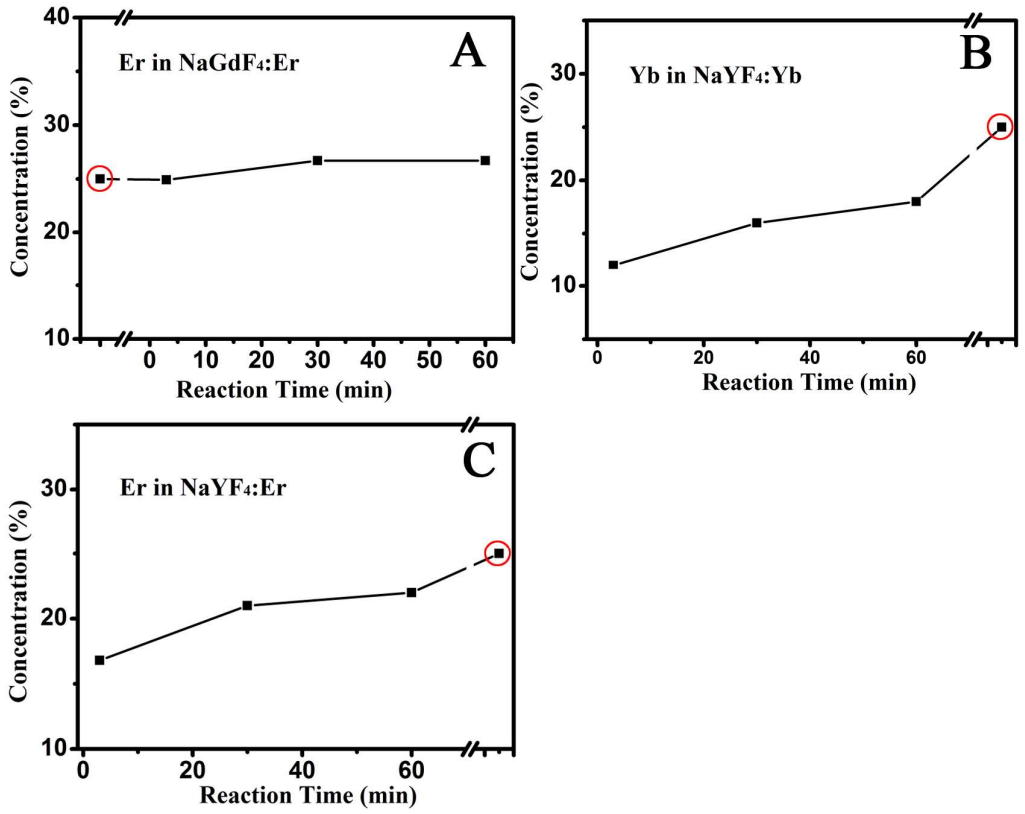

Figure S11. (A) The evolution of Er^{3+} doping concentration during the spontaneous growth process of $NaGdF_4$:25% Er^{3+} nanoparticles. (B) The evolution of Yb^{3+} doping concentration during the spontaneous growth process of $NaYF_4$:25 % Yb^{3+} nanoparticles. (C) The evolution of Er^{3+} doping concentration during the spontaneous growth process of $NaYF_4$:25 % Er^{3+} nanoparticles. The points marked with red circle show the initial macroscopic reactant feed ratio in the experiment.

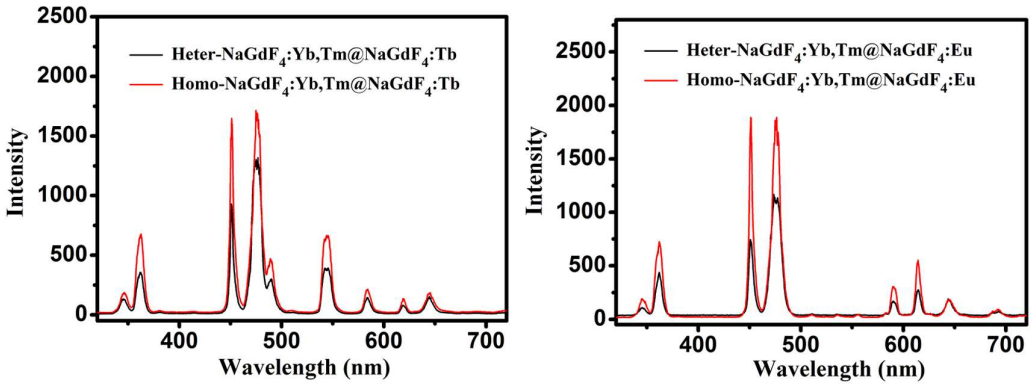

Figure S12. UC emission spectra of $NaGdF_4$:Yb,Tm/$NaGdF_4$:Tb and $NaGdF_4$:Yb, Tm/$NaGdF_4$:Eu nanoparticles based on HEC and HOC under identical experimental conditions.

IV. Supplementary References

1. N. J. J. Johnson, W. Oakden, G. J. Stanisz, R. Scott Prosser, F. C. J. M. van Veggel, *Chem. Mater.* **2011**, *23*, 3714.
2. S. Wu, G. Han, D. J. Milliron, S. Aloni, V. Altoe, D. V. Talapin, B. E. Cohen, P. J. Schuck, *Proc. Natl. Acad. Sci.* **2009**, *106*, 10917.
3. J.-C. Boyer, F. C. J. M. van Veggel, *Nanoscale* **2010**, *2*, 1417.
4. J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson, X. Peng, *J. Am. Chem. Soc.* **2003**, *125*, 12567.
5. F. Zhang, R. Che, X. Li, C. Yao, J. Yang, D. Shen, P. Hu, W. Li, D. Y. Zhao, *Nano Lett.* **2012**, *12*, 2852.
6. F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, X. Liu, *Nature* **2010**, *463*, 1061.