Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Unravelling Phase and Morphology Evolution of $NaYbF_4$ Upconversion Nanoparticles via Modulating Reaction Parameters

Xuechun Pan, Jilou Ren, Jianfeng Zeng, Mingyue Liu, Zhenlan Fang, Qiang Ju*

Preparation of $Lu(CF_3COO)_3$ precursors

$Lu(CF_3COO)_3$ precursors were prepared using the following procedure. Firstly, 2 mmol corresponding rare earth oxides were dissolved in 20 mL trifluoroacetic acid solution of 50% (v/v) under heating at 90 °C in a three-neck flask, yielding a transparent solution. Subsequently, the solution was evaporated to dryness under nitrogen protection. Finally, white powder was collected for further uses.

Preparation of Lu-OA precursors

The Lu-OA precursors were prepared using the following procedure. Typically, 4 mmol $Lu(CF_3COO)_3$ was added into a 100 mL 3-neck flask containing 4 mL oleic acid (OA), 1 mL oleylamine (OM) and 6 mL 1-octadecene (ODE). Then, the mixture solution was heated to 120 °C and maintained at this temperature for 45 min under nitrogen protection, yielding a clean and slightly yellow solution. After naturally cooling down to room temperature, the viscous precursor liquid was stored in a glass vial for further uses.

Preparation of Na-OA shell precursors

4 mmol CF_3COONa was added into a 20 mL glass vial containing 4.5 mL OA and 4.5 mL ODE. The mixture was ultrasounded until a complete dissolution of the solid CF_3COONa, yielding a clear solution. Then, the vial was stored at room temperature for further uses.

Synthesis of the cubic-phase $NaYbF_4$: 2 mol% Er@$NaLuF_4$ UCNPs

The cubic $NaYbF_4$: 2 mol% Er@$NaLuF_4$ UCNPs were prepared following a literature hot-injection method (*J.Am.Chem.Soc.* 2020, **142**, 2023−2030) with adaptations. Typically, 1.0 mL (0.2 mmol) cyclohexane dispersed cubic-phase $NaYbF_4$: 2 mol% Er UCNPs as core was first mixed with 6 mL OA and 15 mL ODE in a 3-neck flask (250 mL), the mixture was heated to 120 ℃ for 30 min, and then to 300 ℃ at a rate of 30 ℃/min under nitrogen protection. Subsequently, an aliquot of energy migration shell precursors (0.5 mL) that contains 0.1 mmol Lu-OA and 0.1 mmol Na-OA was consecutively injected into the solution per an interval of 10 min. After completion of shell growth, the reaction was allowed to cool down to room temperature by removing the heating mantle. The resultant cubic-phase $NaYbF_4$: 2 mol% Er@$NaLuF_4$ were dispersed in 1.0 mL cyclohexane for further uses.

Synthesis of silica-coated UCNPs loading with MB (UCNPs@SiO_2−MB)

UCNPs@SiO_2−MB was synthesized according to the literature method (*Biomaterials* 2012, **33**, 1079−1089) with a modified reverse microemulsion method. Igepal CO-520 (1 mL) was mixed with cyclohexane (19 mL) and stirred for 1 h at room temperature. Then $NaYbF_4$: 2 mol% Er@$NaLuF_4$ (0.2 mmol@2 mmol, 19.0 nm) UCNPs in cyclohexane (0.05 mmol) were added into the flask, and the mixture was stirred for 3 h. Then MB aqueous solution (200 μL) was added and stirred for 1 h. After that, 150 μL of $NH_3 \cdot H_2O$ was added dropwise to the mixture and stirred for 2 h. Subsequently, the system was sealed and stirred for 24 h at room temperature after slowly adding 200 μL of TEOS. The products were precipitated with methanol and washed with ethanol for several times.

Determination of the absolute UCQYs

The measurement was conducted according to previous protocols (*Nat Commun*., 2018, **9**, 3462). The absolute upconversion quantum yields were measured on a customized absolute upconversion quantum yields measurement system combined with a fiber optic spectrometer (QE65pro, Ocean Optics), a standard barium sulfate coated integrating sphere (150 mm in diameter, Edinburgh), a 980 nm CW diode laser (MDL-III-980-2W, Changchun New Industries Optoelectronics Tech Co., Ltd.) as the excitation source, and a neutral density filter to attenuate the excitation light. Pure cyclohexane solution for reference were mounted in the integrating sphere. The UCQYs were then calculated by:

$$QY = \frac{N^e}{N^a} = \frac{L^s}{E^R - E^s}$$

where N^e and N^a are the photons emitted and absorbed, respectively; L^S is the emission intensity, E^R and E^S are the intensities of the excitation light in the presence of the reference and the samples, respectively.

Table S1. The obtained $NaYbF_4$ nanoparticles under different reaction parameters.

	NH_4F (mmol)	NaOH (mmol)	Heating rate (°C/min)	Tempe rature (°C)	Reaction time (min)	Crystalline phase	Diameter (nm)
1	2.4					α	8.2±0.5
2	2.6					α&β	7.8±0.5 198.5±1.8
3	2.8					α&β	5.7±0.4 89.2 ± 1.5
4	3.0					α&β	5.2±0.6 82.7±1.3
5	3.2	2.0	20	310	40	β	39.2±1.1
6	3.6					α&β	/
7	4.0					α&β	/
8	4.4					α&β	/
9	4.8					β	/
10	5.6					β	/
11	6.4					β	/
12		0.8				α	9.2±0.6
13		1.2				α&β	/
14	4.0	2.0	20	310	40	α&β	12.5±1.1 48.5±1.3
15		3.0				α&β	/
16		4.0				β	81.4±1.6
17		6.0				β	/
18	3.12	2.0	8.5	290	90	β	118.0±1.8
19			18.6			α&β	11.4±0.8

							106.2±1.4
20			27.3			α&β	/
21			45.5			α	6.6±0.5
22	3.2	2.0	45.0	230	40	α	/
23				270		α	10.5±0.7
24				290		α	/
25				300		α&β	/
26				310		α&β	13.1±1.1 34.0±1.5
27				320		β	/
28				330		β	53.5±1.8
29	2.4	2.0	25.0	330	10	α	4.2±0.4
30					15	α&β	/
31					20	α&β	/
32					25	α&β	5.0±0.5 119.0±1.4
33					30	β	139.5±1.7

	Intensity*	**UCQY**	**Lifetime (655 nm, ms)**
β-$NaYF_4$: 2 mol% Er, 18 mol% Yb (20.5 nm)	100.0	0.069%	0.22
α-$NaYbF_4$: 2 mol% Er (8.2 nm)	0.7	\	0.07
α-$NaYbF_4$: 2 mol% Er@$NaLuF_4$ (19.0 nm)	108.1	0.071%	1.30
α-$NaYbF_4$: 2 mol% Er@$NaLuF_4$ (27.8 nm)	210.6	0.095%	1.93
β-$NaYbF_4$: 2 mol% Er (39. 2nm)	12.9	\	0.30

Table S2. The upconversion performance of obtained UCNPs

* The upconversion intensity of hexagonal-phase $NaYF_4$: 2 mol% Er, 18 mol% UCNPs was set to 100, and the intensities of other UCNPs were calculated based on $NaYF_4$: 2 mol% Er, 18 mol% UCNPs.

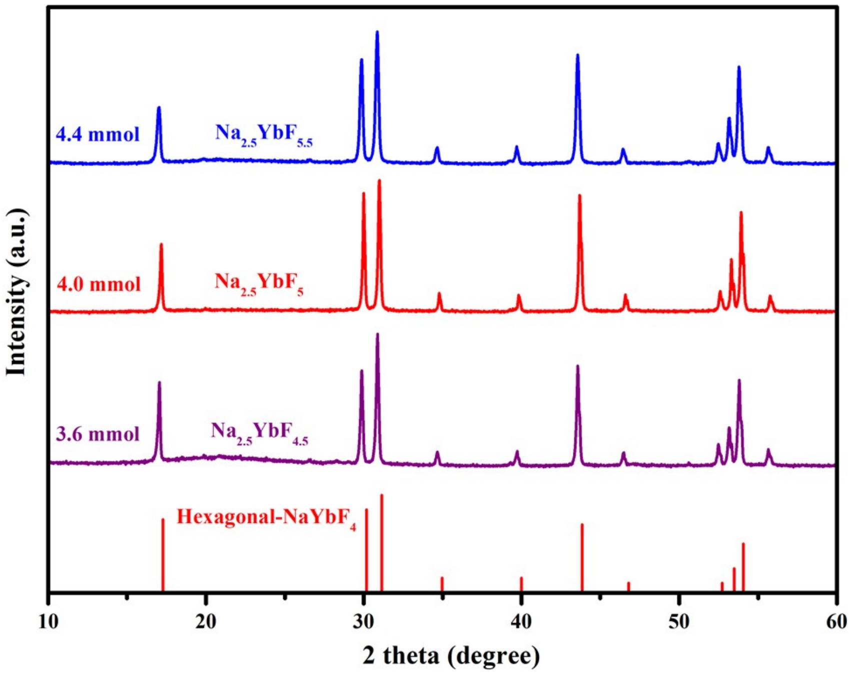

Figure S1. XRD patterns of $Na_{2.5}YbF_{4.5-5.5}$ nanoparticles obtained at varied amounts of NH_4F (3.6-4.4 mmol, which can also be symbolized as $NaYbF_{4.5-5.5}$). The amount of NaOH, heating rate, reaction temperature, and reaction time were set to 2.0 mmol, 20 °C/min, 310 °C, and 90 min, respectively. The corresponding line patterns are literature references for hexagonal-phase $NaYbF_4$ (JCPDS standard card no. 27−1427).

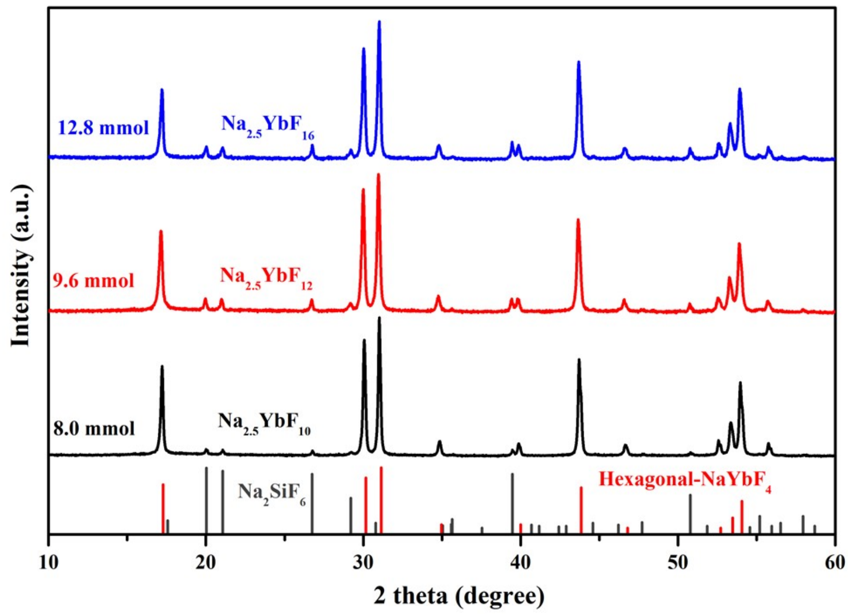

Figure S2. XRD patterns of $NaYbF_4$ nanoparticles obtained at varied amounts of NH_4F (8.0-12.8 mmol, which can also be symbolized as $NaYbF_{10-16}$). The amount of NaOH, heating rate, reaction temperature, and reaction time were set to 2.0 mmol, 20 °C/min, 310 °C, and 40 min, respectively. The corresponding line patterns are literature references for hexagonal-phase $NaYbF_4$ (JCPDS standard card no. 27−1427) and Na_2SiF_6 (JCPDS standard card no. 33-1280), respectively.

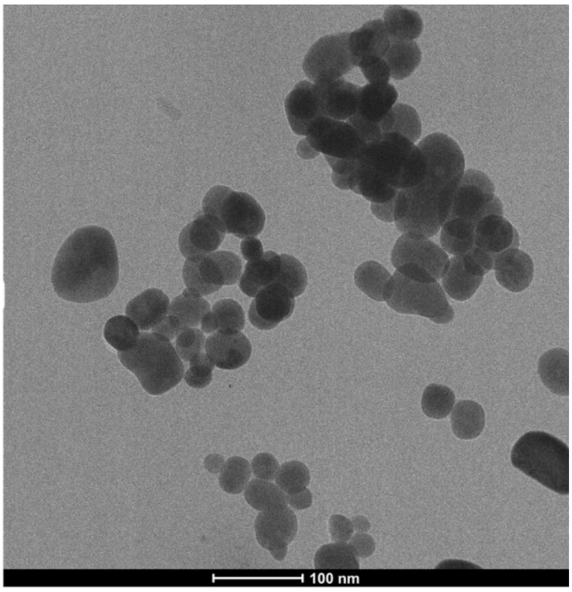

Figure S3. TEM image of $NaYbF_4$ nanoparticles synthesized with 6.4 mmol NH_4F ($Na_{2.5}YbF_8$). The amount of NaOH, heating rate, reaction temperature, and reaction time were set to 2.0 mmol, 20 °C/min, 310 °C, and 40 min, respectively.

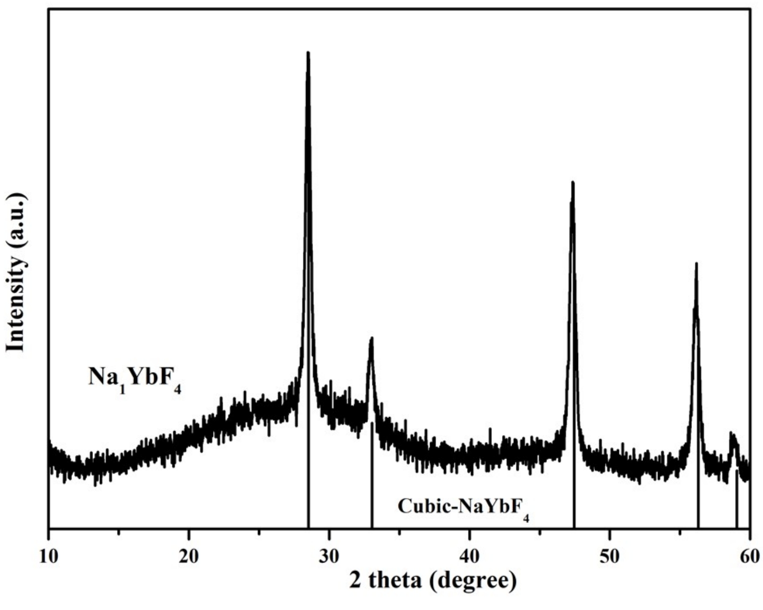

Figure S4. XRD patterns of $NaYbF_4$ nanoparticles. The amount of NH_4F, amount of NaOH, heating rate, reaction temperature, and reaction time were set to 3.2 mmol, 0.8 mmol, 20 °C/min, 310 °C, and 40 min, respectively. The corresponding line pattern is cubic-phase $NaYbF_4$ (JCPDS standard card no. 77−2043).

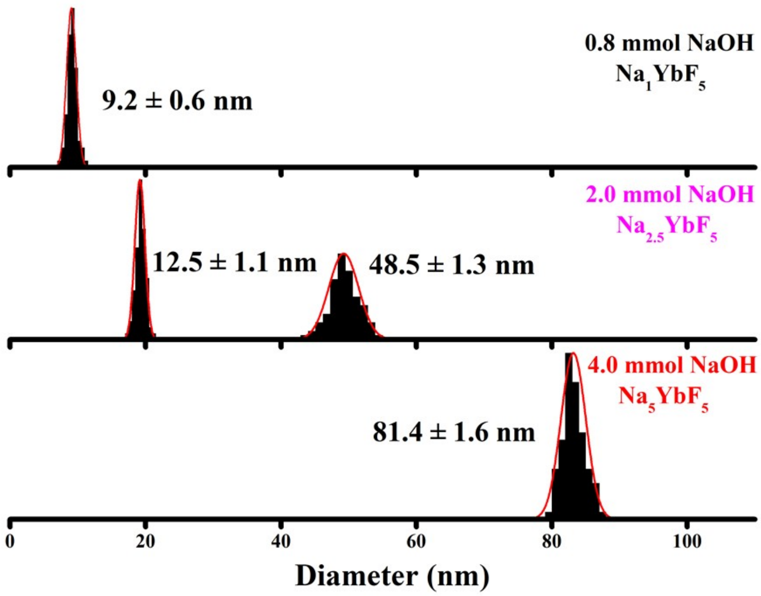

Figure S5. Corresponding size distributions of $NaYbF_4$ nanoparticles obtained at varied amounts of NaOH. The amount of NH_4F, heating rate, reaction temperature, and reaction time were set to 4.0 mmol, 20 °C/min, 310 °C, and 40 min, respectively.

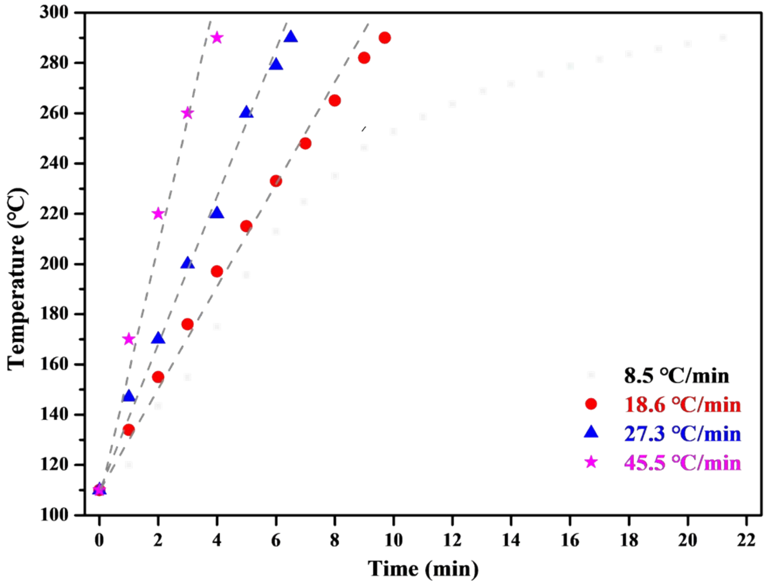

Figure S6. The temperature varying with the time under different heating rate.

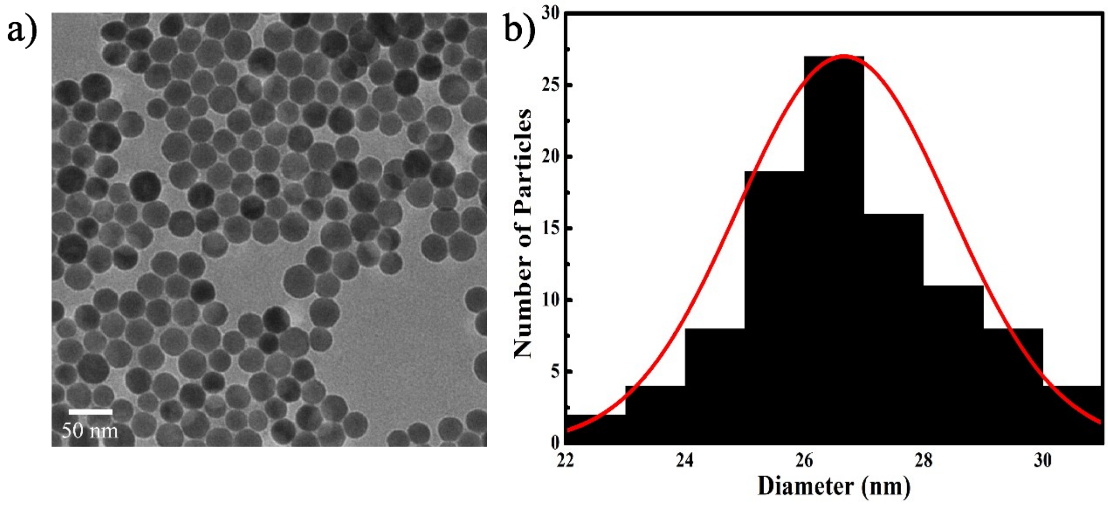

Figure S7. a) TEM image and b) corresponding size distribution of hexagonal-phase $NaYbF_4$ nanoparticles. The amount of NH_4F, amount of NaOH, heating rate, reaction temperature, and reaction time were set to 3.2 mmol, 2.0 mmol, 45 °C/min, 320 °C, and 20 min, respectively. The average size is calculated to be 26.2 nm.

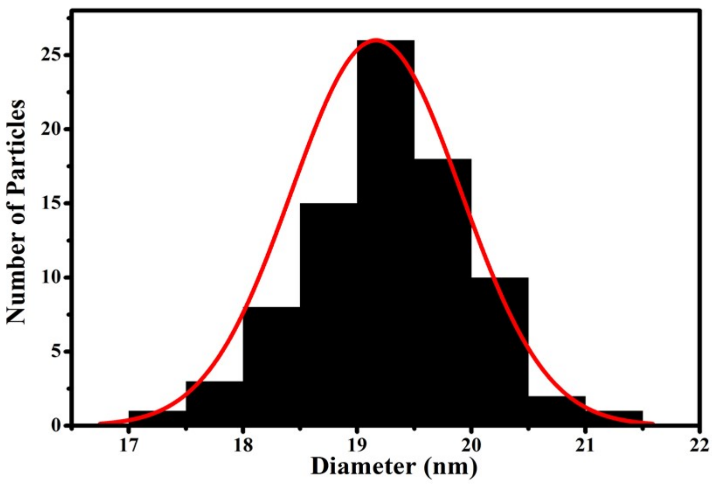

Figure S8. Corresponding size distribution of cubic-phase $NaYbF_4$: 2 mol% Er@$NaLuF_4$ (0.2 mmol@2 mmol) UCNPs. The average size is calculated to be 19.0 nm.

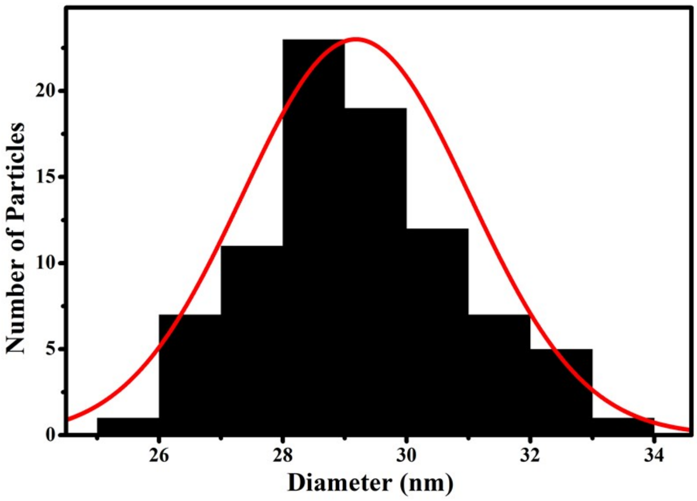

Figure S9. Corresponding size distribution of cubic-phase $NaYbF_4$: 2 mol% Er@$NaLuF_4$ (0.2 mmol@4 mmol) UCNPs. The average size is calculated to be 27.8 nm.

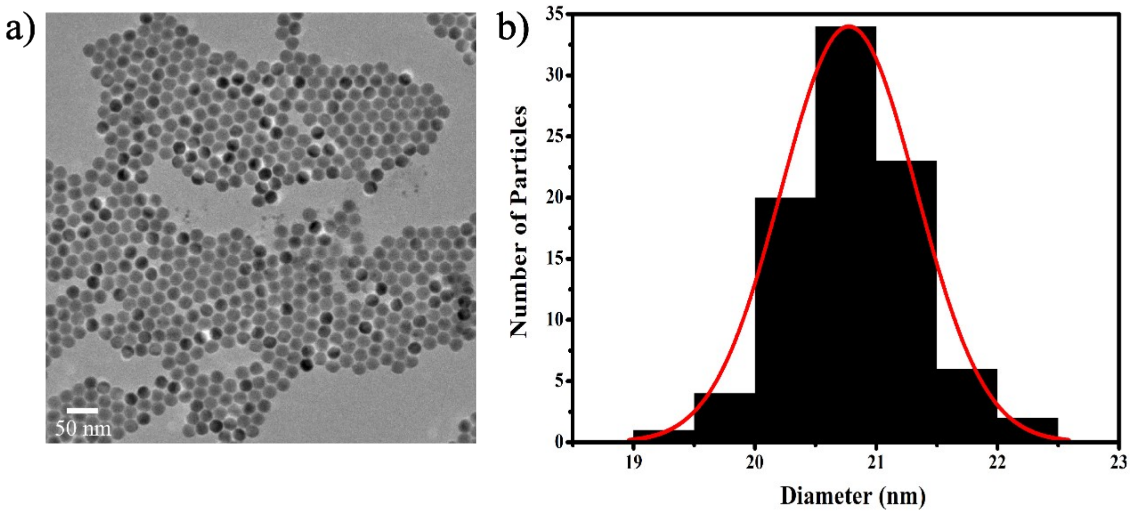

Figure S10. a) TEM image and b) corresponding size distribution of hexagonal-phase $NaYF_4$: 18 mol% Yb, 2 mol% Er UCNPs. The average size is calculated to be 20.5 nm.

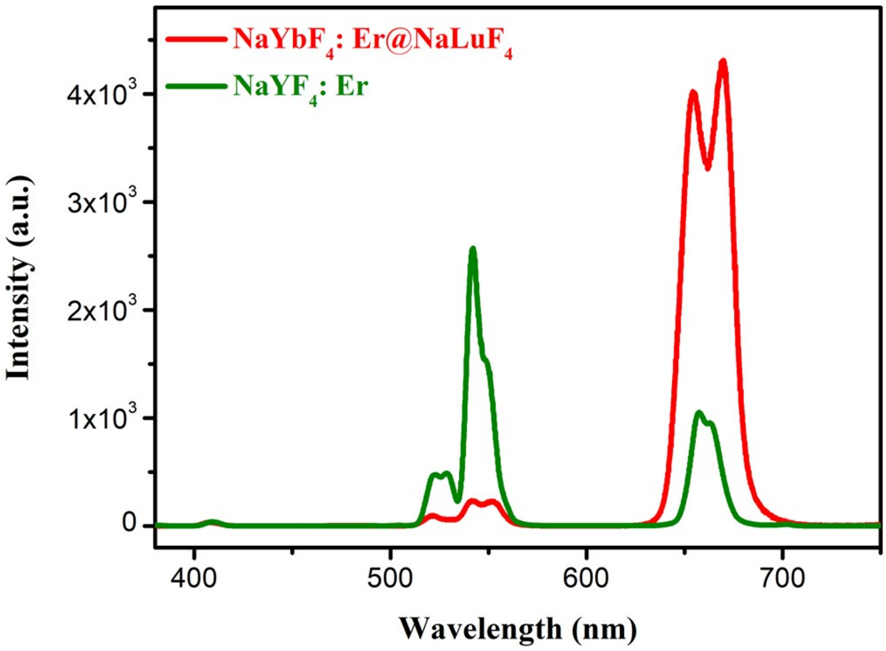

Figure S11. Upconversion spectra of cubic-phase $NaYbF_4$: Er@$NaLuF_4$ core-shell UCNPs (0.2 mmol @2.0 mmol) (red line) and hexagonal-phase $NaYF_4$: Yb, Er UCNPs (green line) after removing surface-capping OA.

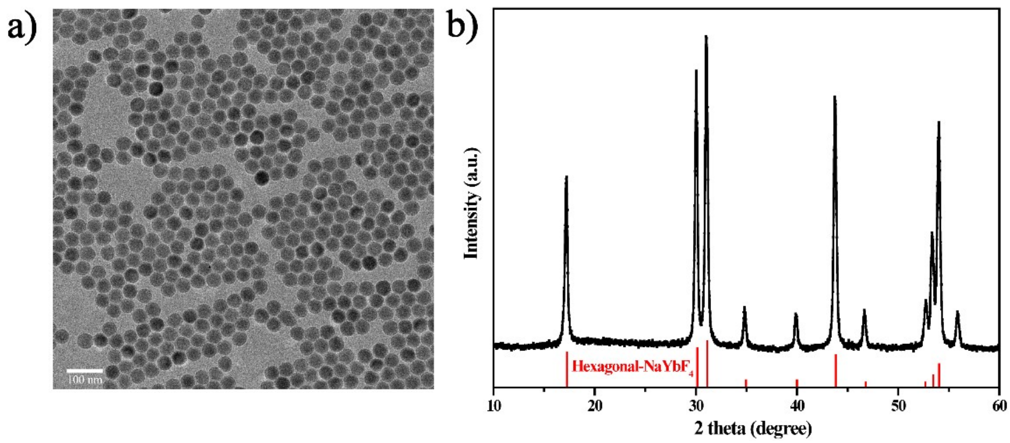

Figure S12. a) TEM image and b) XRD patterns of $NaYbF_4$: 2 mol% Er@$NaLuF_4$ UCNPs. The size for $NaYbF_4$: 2 mol% Er core and $NaYbF_4$: 2 mol% Er@$NaLuF_4$ core-shell nanoparticles were 39.2 nm and 42.4 nm, respectively. XRD pattern confirms the obtained $NaYbF_4$, Er@$NaLuF_4$ UCNPs are pure hexagonal-phase.

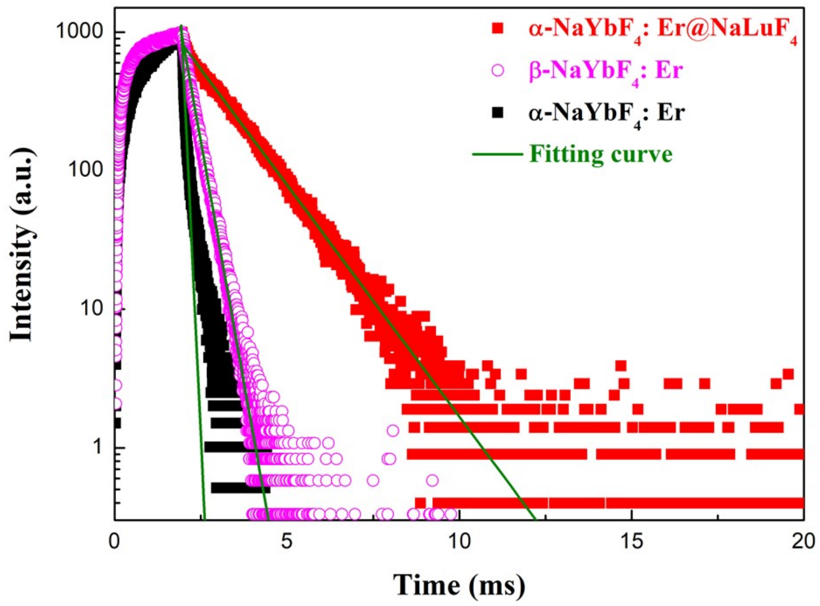

Figure S13. Upconversion luminescence decays of $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} in cubic-phase and hexagonal-phase $NaYbF_4$: 2 mol% Er UCNPs, cubic-phase $NaYbF_4$: 2 mol% Er@$NaLuF_4$ core-shell UCNPs. The corresponding lifetimes are calculated to be 0.07, 0.30, and 1.30 ms, respectively.

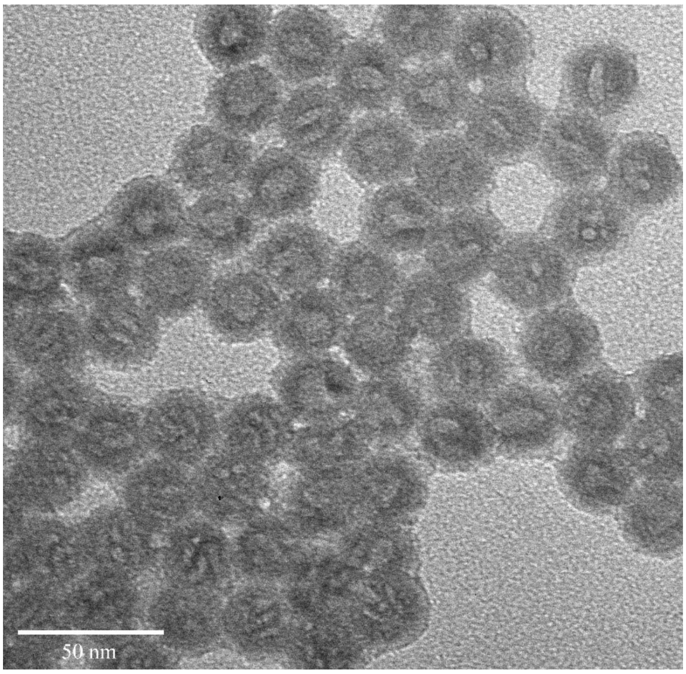

Figure S14. TEM image of $NaYbF_4$:2 mol%Er@$NaLuF_4$@SiO_2 nanoparticles. The SiO_2 shell is measured to be 2.5~3.5 nm.

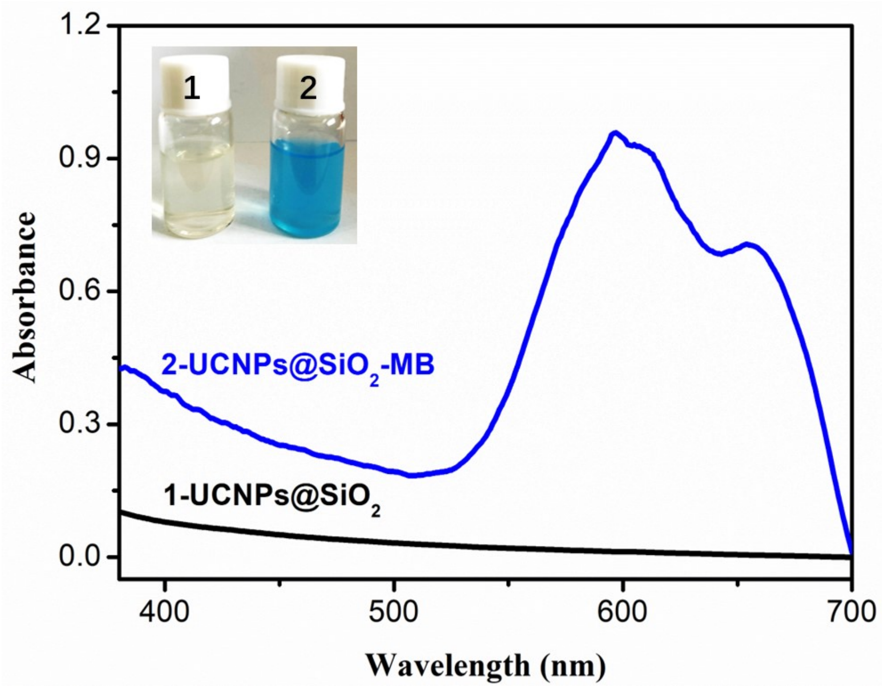

Figure S15. UV-vis absorbance spectra of UCNPs@SiO_2 and UCNPs@SiO_2-MB nanoparticles. Inset is the images of UCNPs@SiO_2 (1) and UCNPs@SiO_2-MB (2) solutions, indicating the presence of MB in UCNPs@SiO_2. The absorption band peaked at 590 nm can be attributed to the aborption of MB, confirming the successfully loading of MB in UCNPs@SiO_2 nanoparticles.

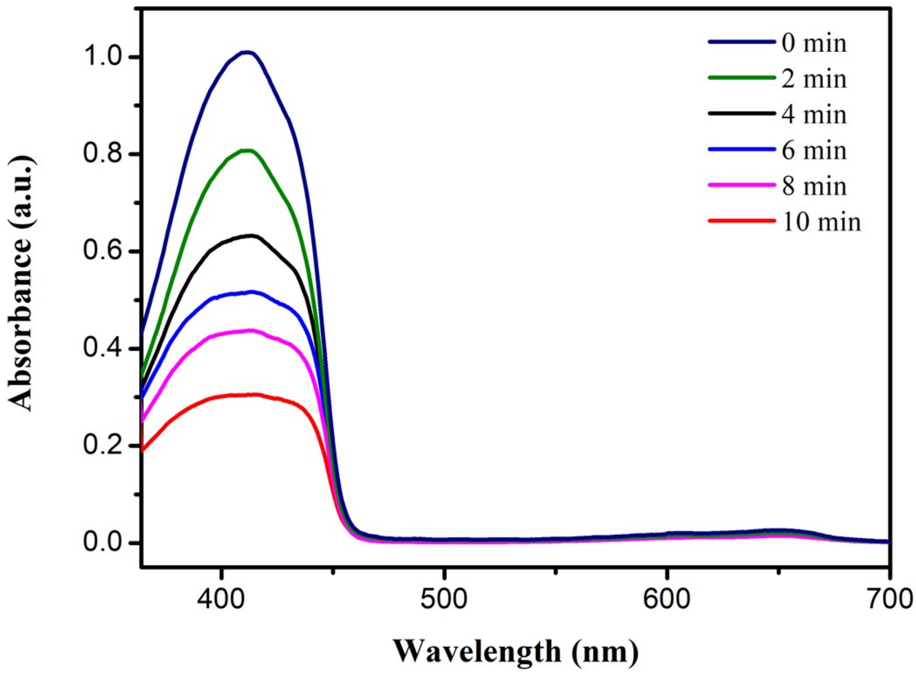

Figure S16. UV-vis absorbance spectra of UCNPs@SiO_2-MB with DPBF under 980 nm irradiation for different time**.**