

Electronic Supplementary Information (ESI)

# Nonlinear Spectral and Lifetime Management in Upconversion Nanoparticles by Controlling Energy Distribution

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For a simplified two-step energy transfer upconversion emission process, as shown in **Fig. 3**, according to the proposed energy transfer process, the time-resolved rate equations of each energy states are derived as follows:

$$\frac{dN_0}{dt} = -W_0 N_b N_0 + R_2 N_2 + R_1 N_1 \quad (S1)$$

$$\frac{dN_1}{dt} = W_0 N_b N_0 - W_1 N_b N_1 - R_1 N_1 \quad (S2)$$

$$\frac{dN_2}{dt} = W_1 N_b N_1 - R_2 N_2 \quad (S3)$$

where  $N_b$  is the population density of excited state of sensitizer (normally  $\text{Yb}^{3+}$ ) at any given time;  $N_i$  ( $i = 1, 2$ ) represents the population density of emitter on level  $i$ ;  $R_1$  and  $R_2$  are the total emission rate constants of emitter ( $\text{X}^{3+}$ ) from state 1 and 2;  $W_0$  and  $W_1$  are the energy transfer rates from  $\text{Yb}^{3+}$  to  $\text{X}^{3+}$  in states 0 and 1. As the emission intensity remains unaltered at the steady state, we should obtain a constant emission density of each energy state at different time intervals as defined by

$$\frac{dN_0}{dt} = \frac{dN_1}{dt} = \frac{dN_2}{dt} = 0 \quad (S4)$$

Then, the population density of the upconversion emission state 2 in emitter is

$$N_2 = \frac{W_0 W_1 N_0 N_b^2}{W_1 R_2 N_b + R_1 R_2} \quad (S5)$$

which can be simplified as

$$N_2 = \frac{N_b^2}{A \cdot N_b + B} \quad (S6)$$

where  $A$ , and  $B$  are constants.  $A = W_1 R_2 / W_0 W_1 N_0$ ,  $B = R_1 R_2 / W_0 W_1 N_0$ . Under a low excitation power density,  $W_1 \ll R_1$ ,  $A \ll B$ ,

$$N_2 \propto N_b^2 \quad (S7)$$

Under a high excitation power density,  $R_1 \ll W_1$ ,  $B \ll A$ ,

$$N_2 \propto N_b \quad (S8)$$

Since

$$N_b = N - N_a \quad (S9)$$

Where  $N_a$  is the population density of ground state of  $\text{Yb}^{3+}$  ions, and  $N$  is the total density of  $\text{Yb}^{3+}$  ions which is a constant value. The time-resolved rate equations of each energy state of  $\text{Yb}^{3+}$  are derived as follows:

$$-\frac{dN_a}{dt} = \frac{dN_b}{dt} = \frac{\sigma P}{h\nu} N_a - (W_0 N_0 + W_1 N_1 + W_D N_D + R_b) N_b \quad (S10)$$

where  $\sigma$  is the absorption cross-section of  $\text{Yb}^{3+}$  ions and considered independent of the laser power;  $P$  is the excitation power density;  $h$  is Planck's constant;  $\nu$  is the frequency of the excitation light;  $R_b$  is the radiative decay rate of  $\text{Yb}^{3+}$  at its excited state;  $N_D$  represents the population density of added energy distributors; and  $W_D$  is the energy transfer rate from the sensitizer to the energy distributors. At steady state emission,

$$\frac{dN_a}{dt} = \frac{dN_b}{dt} = 0 \quad (\text{S11})$$

$$\frac{\sigma P}{h\nu} (N - N_b) - (W_0 N_0 + W_1 N_1 + W_D N_D + R_b) N_b = 0 \quad (\text{S12})$$

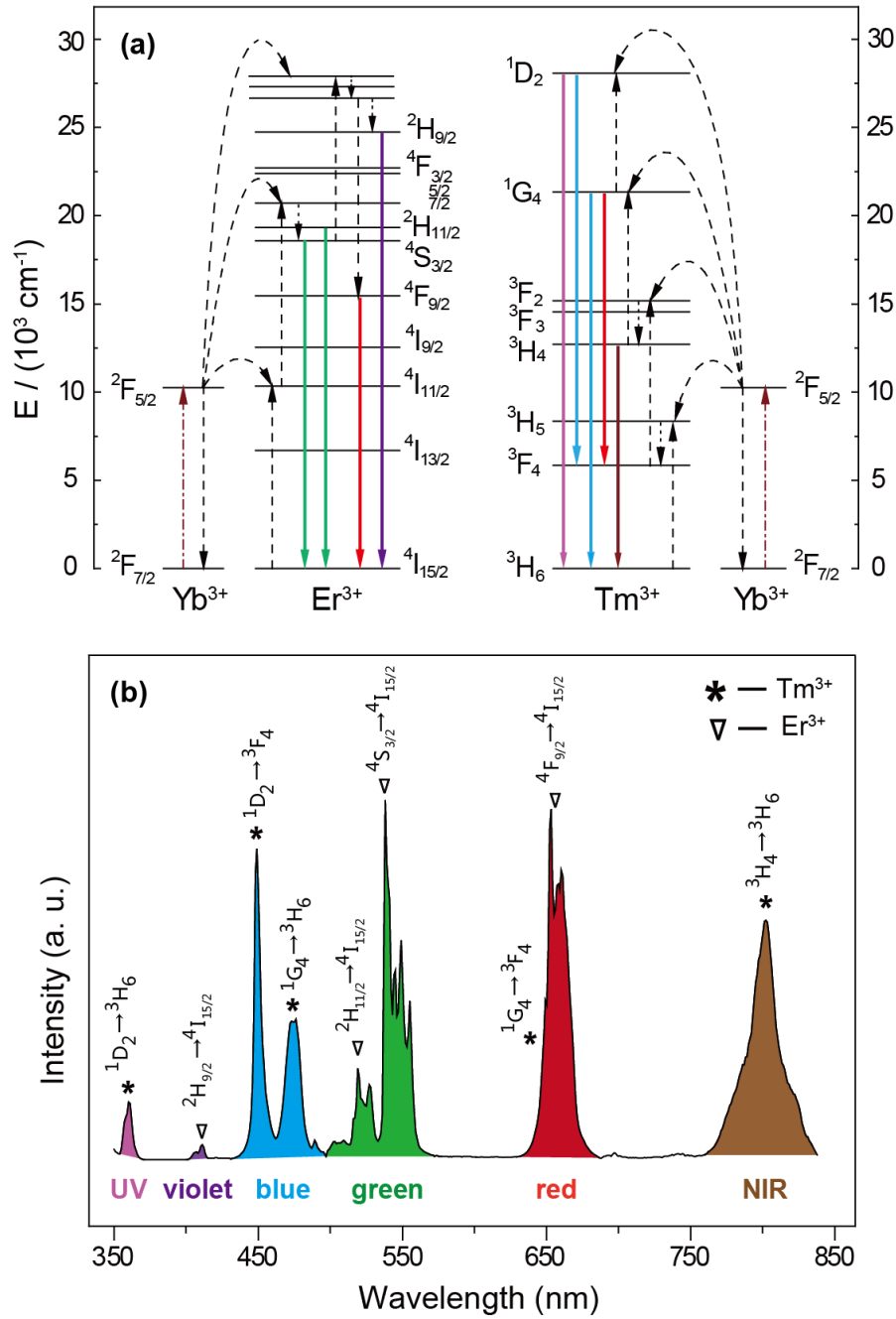
Thus, the relationship of  $N_b$  and  $P$  can be expressed as

$$N_b = \frac{\frac{\sigma N}{h\nu} \cdot P}{W_0 N_0 + W_1 N_1 + W_D N_D + R_b + \frac{\sigma}{h\nu} \cdot P} \quad (\text{S13})$$

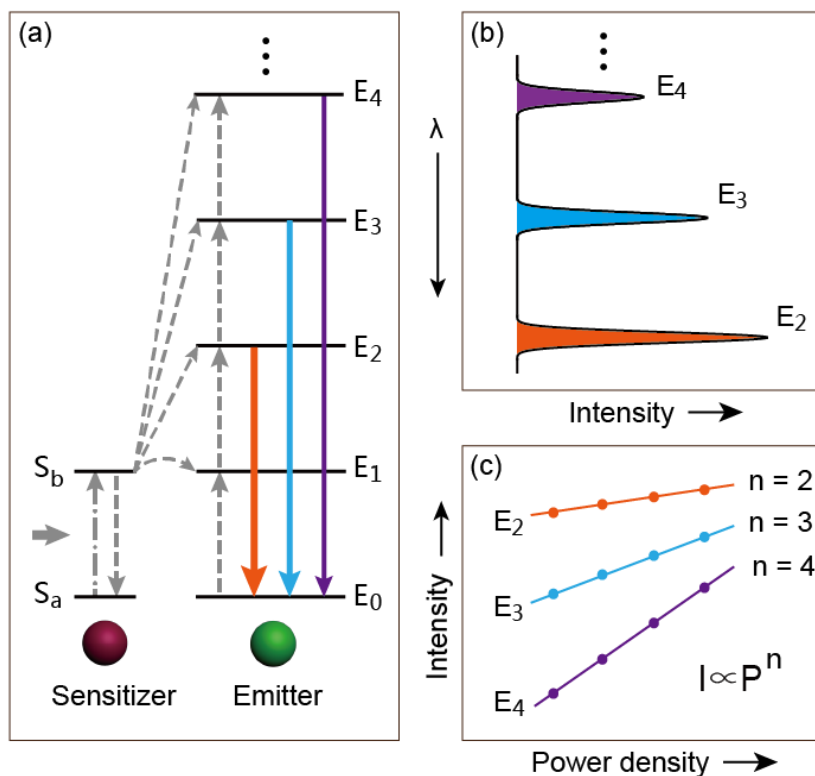
which can be further simplified as

$$N_b = \frac{P}{C + D \cdot P} \quad (\text{S14})$$

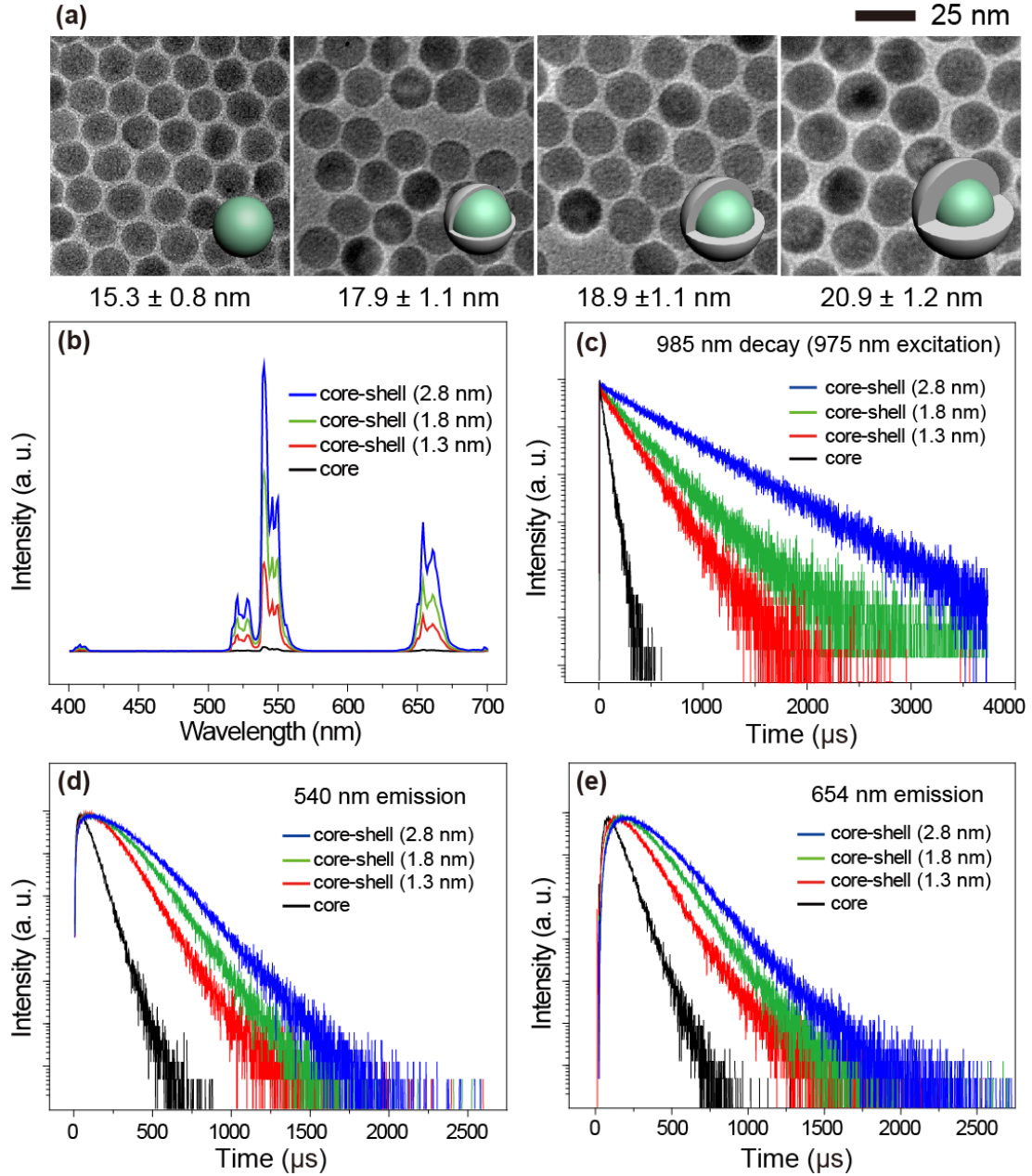
where  $C$  and  $D$  are constants.  $C = (W_0 N_0 + W_1 N_1 + W_D N_D + R_b) h\nu / \sigma N$ ,  $D = 1/N$ .



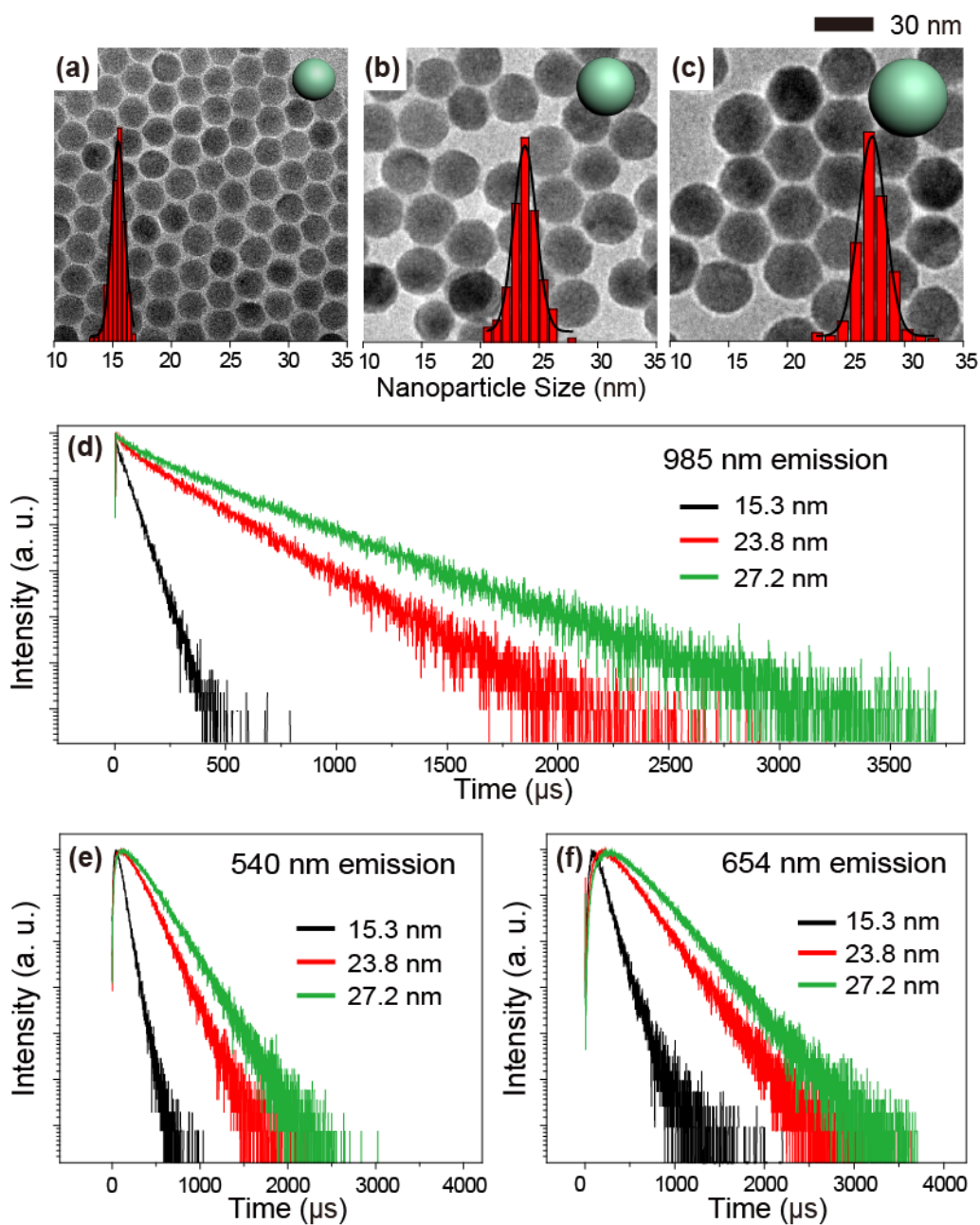
**Figure S1.** (a) Proposed steady-state upconversion mechanism in the Yb<sup>3+</sup>-Er<sup>3+</sup> and Yb<sup>3+</sup>-Tm<sup>3+</sup> codoped systems. (b) Typical upconversion emission spectrum, in the range of UV to NIR region, of Yb<sup>3+</sup>-Er<sup>3+</sup>-Tm<sup>3+</sup> triply-doped NaYF<sub>4</sub> nanoparticles upon 975 nm excitation. Emission peaks marked with stars and triangles are attributed to Tm<sup>3+</sup> and Er<sup>3+</sup> ion, respectively.



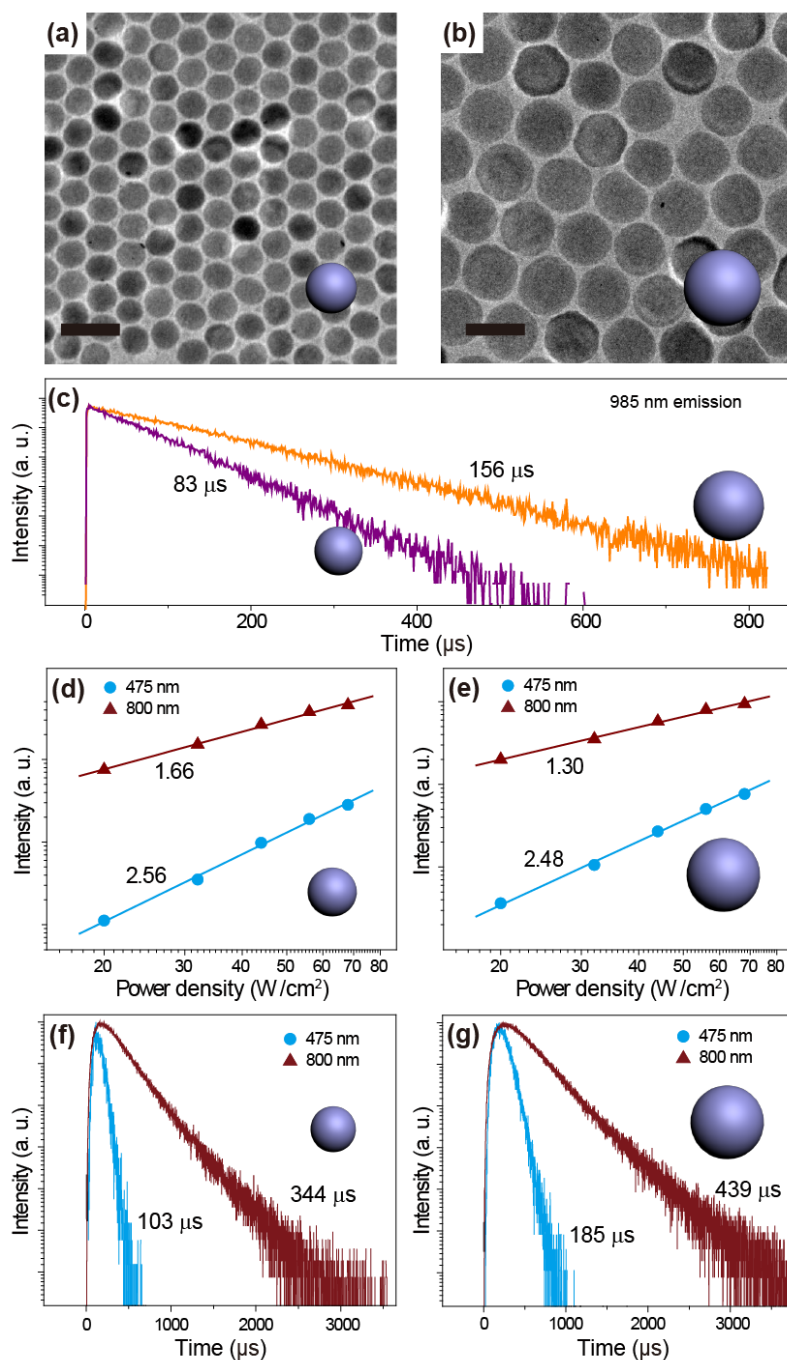
**Figure S2.** (a) Simplified energy transfer upconversion processes involving sensitizer and emitter ions. The dashed-dotted, dashed and full arrows represent photon excitation, energy transfer, and emission processes, respectively. (b) Schematic of corresponding emission spectrum of the system shown in a. (c) Proposed emission intensity profiles from different excited states of the emitter vs pump power density.



**Figure S3.** (a) TEM images of NaYF<sub>4</sub>:Yb/Er(20/2%) core nanoparticles with different NaYF<sub>4</sub> shell thickness. Scale bars are 25 nm. (b) Corresponding upconversion emission spectra of the samples under 975 nm irradiation with a power density of 50 W/cm<sup>2</sup>. (c) Decay curves of 985 nm emission (<sup>2</sup>F<sub>5/2</sub>→<sup>2</sup>F<sub>7/2</sub> transition of Yb<sup>3+</sup>) from the four samples. (d-e) Decay curves of 540 nm (<sup>4</sup>S<sub>3/2</sub>→<sup>4</sup>I<sub>15/2</sub> transition of Er<sup>3+</sup>) and 654 nm (<sup>4</sup>F<sub>9/2</sub>→<sup>4</sup>I<sub>15/2</sub> transition of Er<sup>3+</sup>) emissions of the four samples.

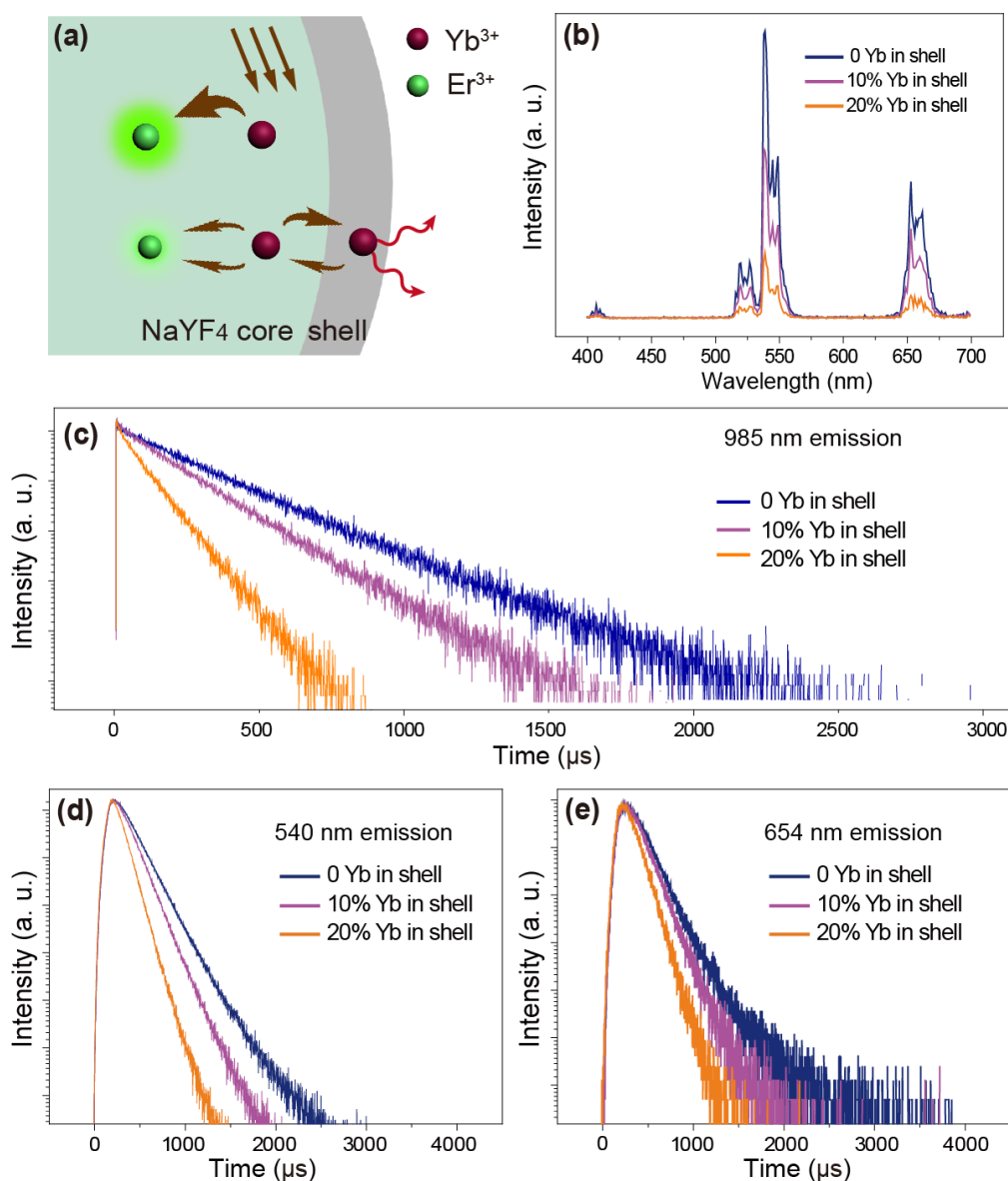


**Figure S4.** (a-c) TEM images and size distribution diagrams of NaYF<sub>4</sub>:Yb/Er(20/2%) UCNPs with average diameters of  $15.3 \pm 1.1$  nm,  $23.8 \pm 2.1$  nm and  $27.2 \pm 2.0$  nm, respectively. Scale bars are 30 nm. (d-f) Decay curves of 985 nm, 540 nm and 654 nm emissions of the three UCNPs samples.

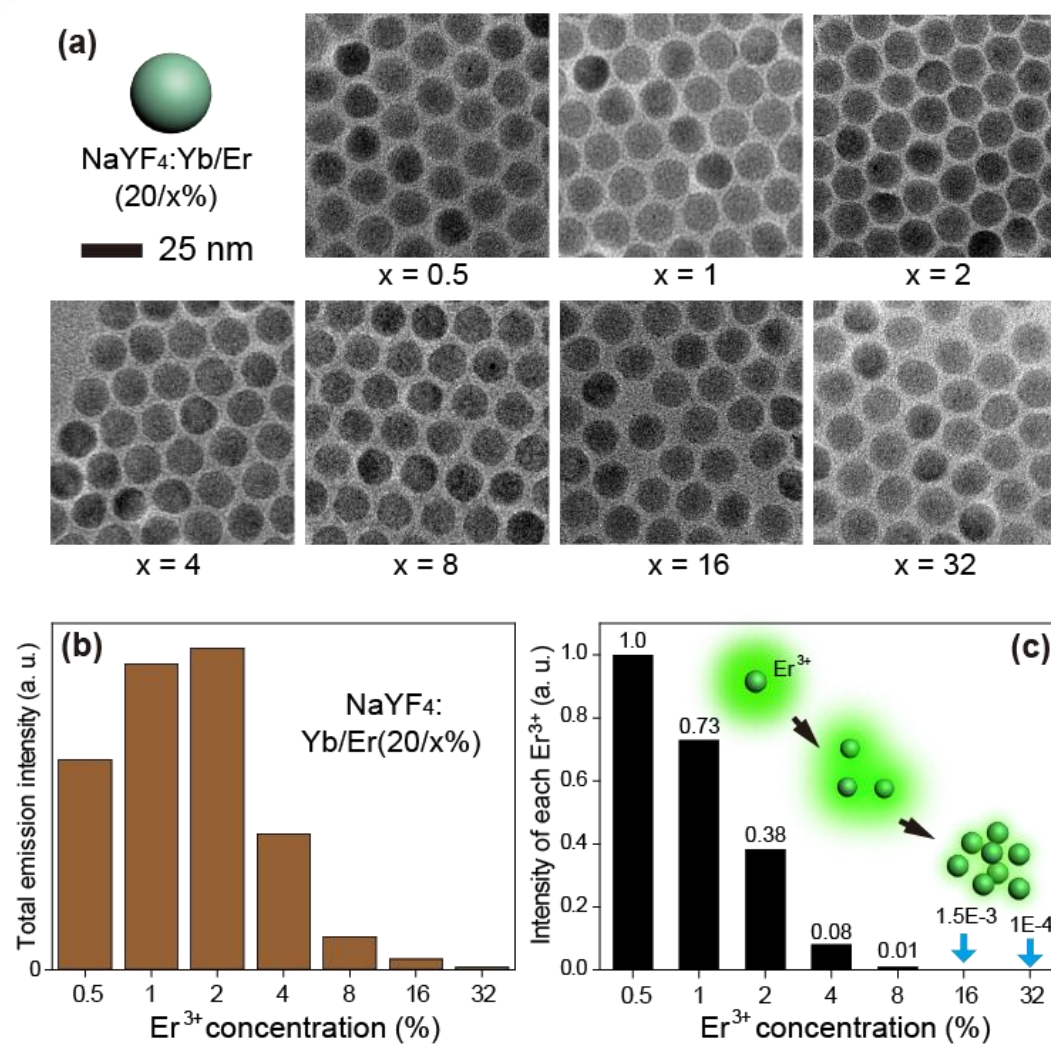


**Figure S5.** (a-b) TEM images (scale bar: 50 nm) of NaYF<sub>4</sub>:Yb/Tm(50/0.5%) UCNPs with average diameters of 23 nm and 46 nm. (c-d) Power-dependent luminescence intensities of 23 nm and 46 nm NaYF<sub>4</sub>:Yb/Tm(50/0.5%) nanoparticles, respectively. (e-f) Decay curves of 475 nm and 800 nm emissions of the two samples, respectively. Emissions at 475 nm and 800 nm are attributed to the  $^1G_4 \rightarrow ^3H_6$  and  $^3H_4 \rightarrow ^3H_6$  transitions of Tm<sup>3+</sup>.

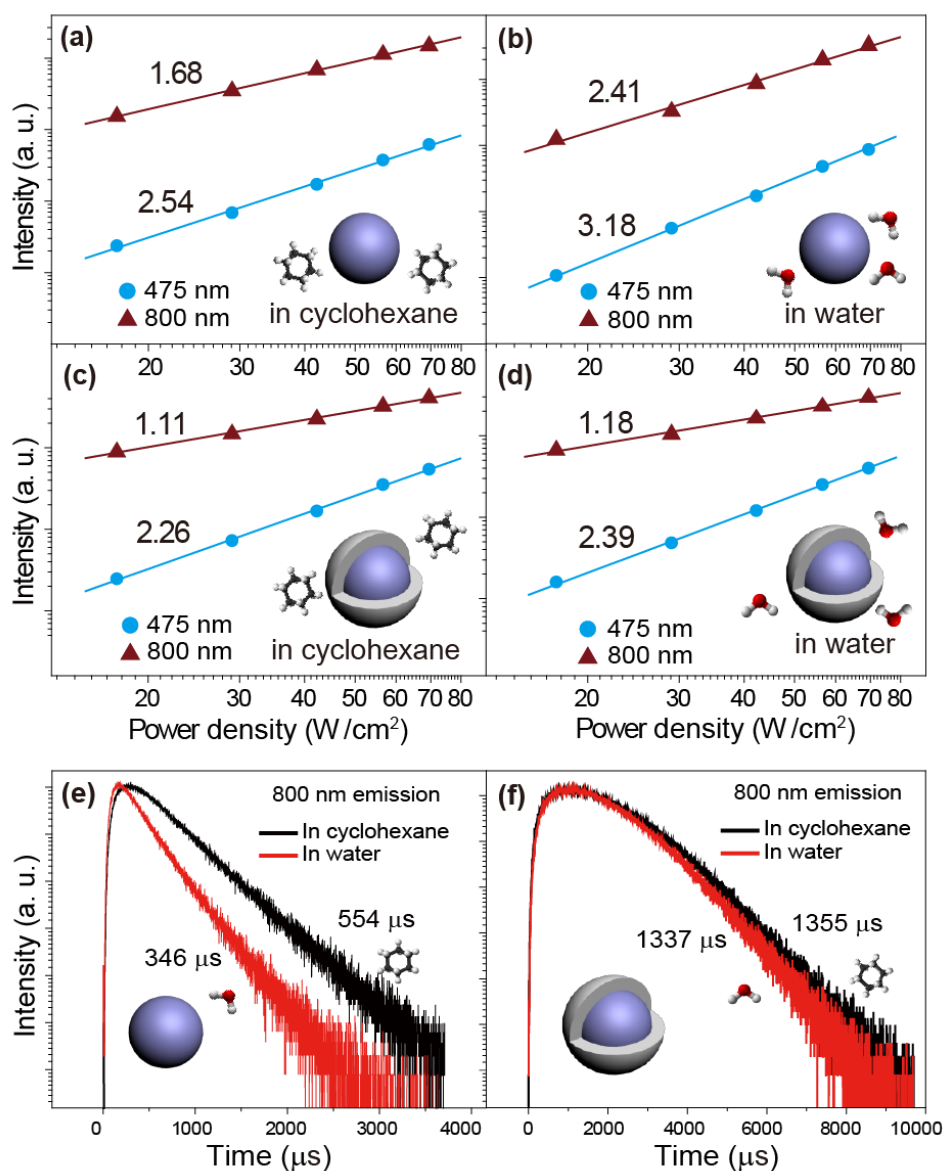




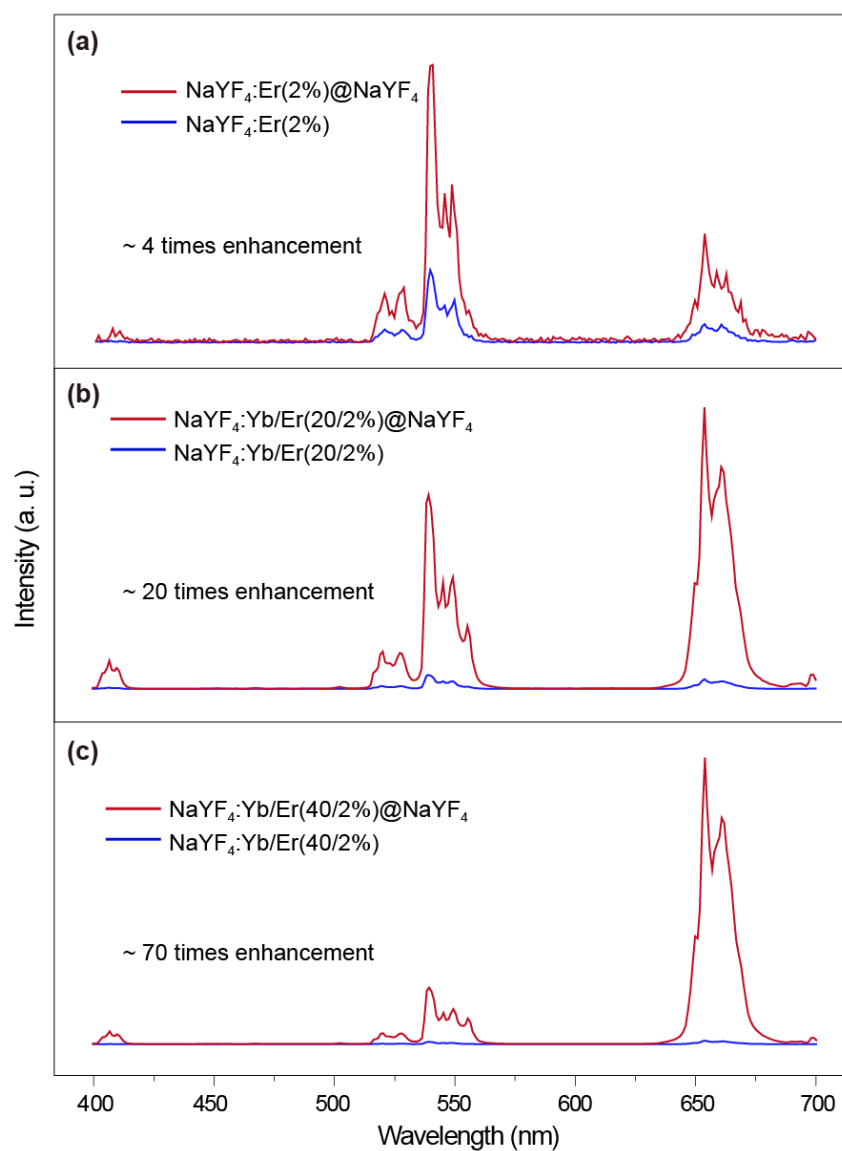
**Figure S6.** (a) Schematic of energy transfer pathways in active-shell-coated NaYF<sub>4</sub>:Yb/Er nanoparticles. (b) Upconversion luminescence spectra of NaYF<sub>4</sub>:Yb/Er(20/2%)@NaYF<sub>4</sub>:Yb(x%) (x = 0, 10, and 20) nanoparticles excited by a 975-nm diode laser (power density: ~ 50 W/cm<sup>2</sup>). (c-e) Decay curves of 985 nm, 540 nm and 654 nm emissions from NaYF<sub>4</sub>:Yb/Er(20/2%)@NaYF<sub>4</sub>:Yb(x%) (x = 0, 10, and 20) nanoparticles.



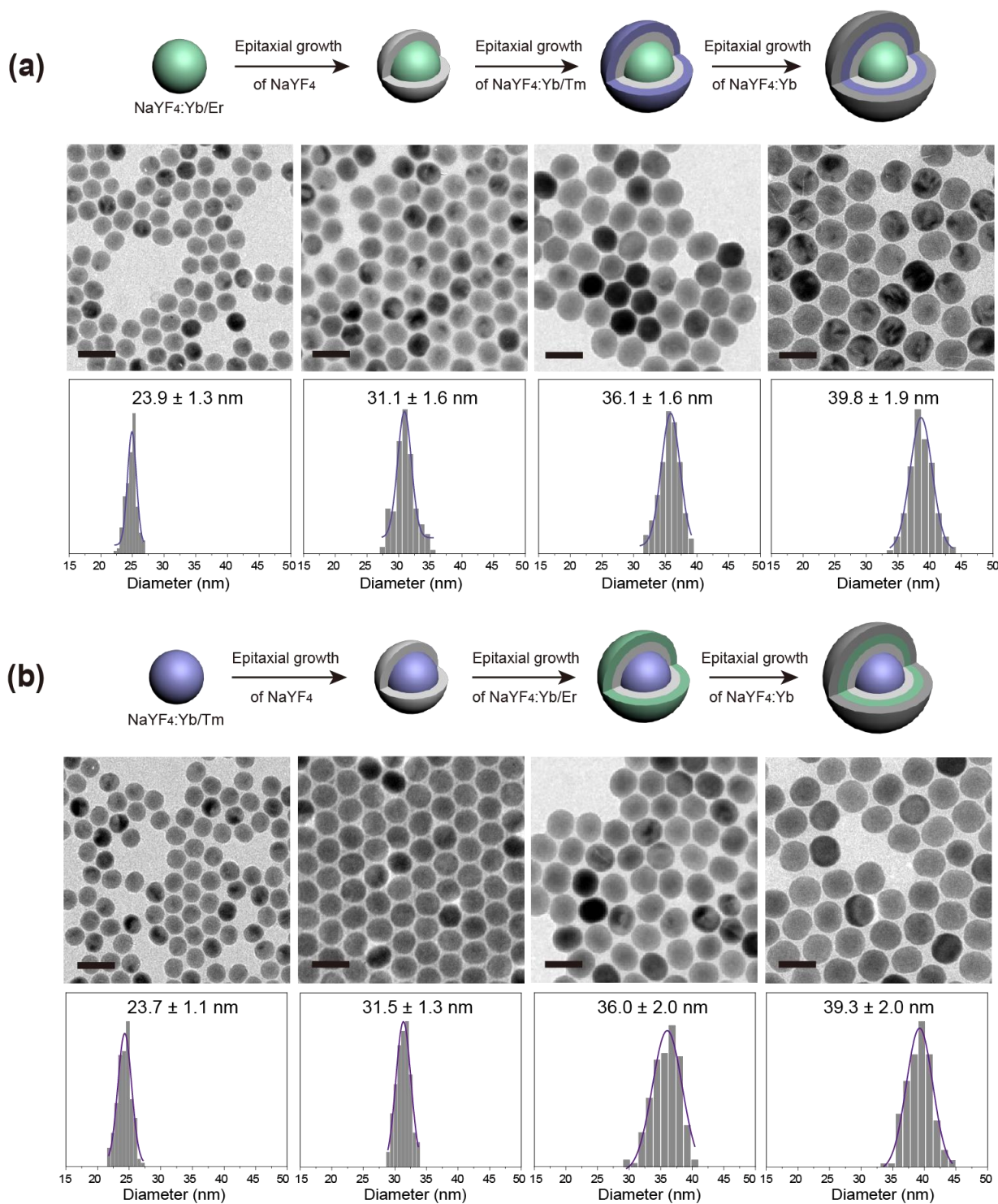
**Figure S7.** (a) TEM images of NaYF<sub>4</sub>:Yb/Er(20/x%) (x = 0.5, 1, 2, 4, 8, 16 and 32) nanoparticles. Scale bars are 25 nm. (b) Integrated total upconversion emission intensities of NaYF<sub>4</sub>:Yb/Er(20/x%) nanoparticles under 975 nm laser irradiation (power density: ~50 W/cm<sup>2</sup>). (c) Relative emission intensities of each Er<sup>3+</sup> ion (total emission intensity/the number of Er<sup>3+</sup> dopants), obtained from NaYF<sub>4</sub>:Yb/Er(20/x%) nanoparticles with different Er<sup>3+</sup> concentrations.



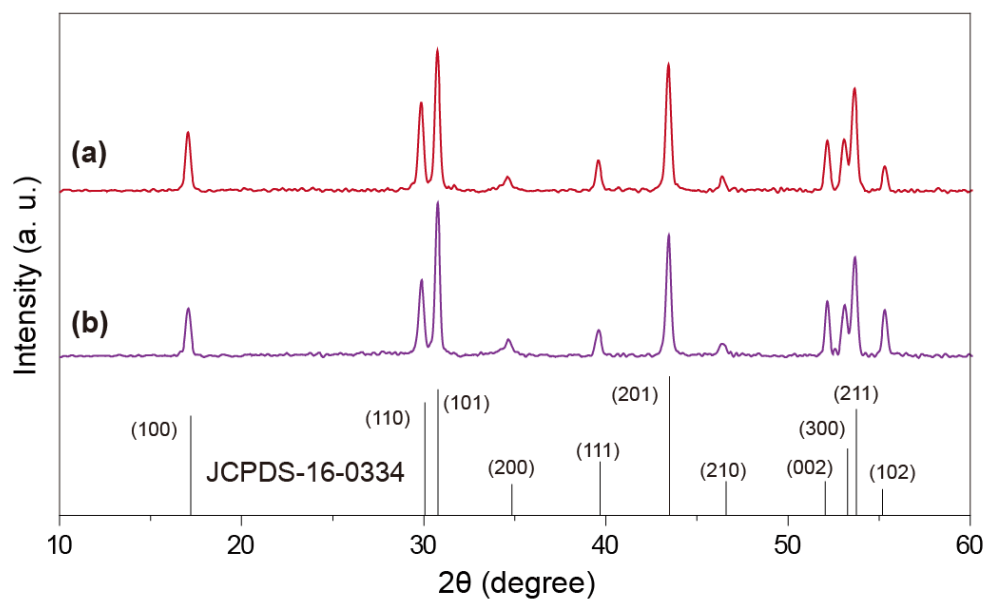
**Figure S8** (a and b) Pump-power-dependent luminescence intensities of NaYF<sub>4</sub>:Yb/Tm(50/0.5%) nanoparticles dispersed in cyclohexane and water, respectively. (c and d) Pump-power-dependent luminescence intensities of NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub> nanoparticles dispersed in cyclohexane and water, respectively. (e and f) Decay curves of 800 nm emission of NaYF<sub>4</sub>:Yb/Tm(50/0.5%) and NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub> nanoparticles, respectively, dispersed in cyclohexane and water.



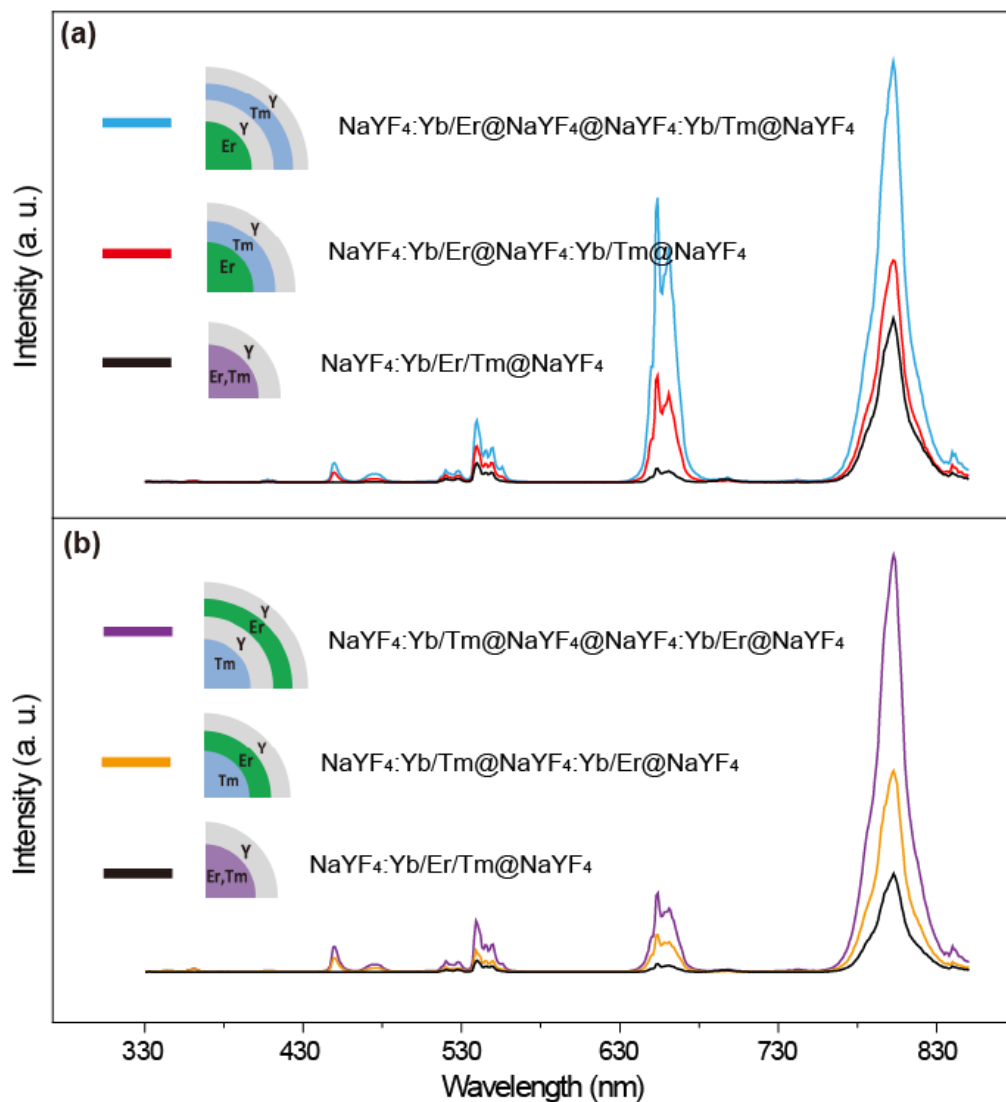
**Figure S9.** Comparison of upconversion luminescence spectra of NaYF<sub>4</sub>:Yb/Er core and NaYF<sub>4</sub>:Yb/Er@NaYF<sub>4</sub> core-shell UCNPs with a fixed Er<sup>3+</sup> doping concentration of 2% and a varied Yb<sup>3+</sup> concentration. (a-c) Yb<sup>3+</sup> concentration: 0, 20, 40%, respectively.




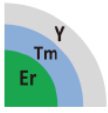
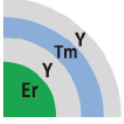
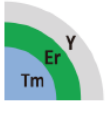

**Figure S10.** Schematic presentation showing the synthetic process, TEM images and size distribution histograms of multilayered core-shell nanoparticles: (a)  $\text{NaYF}_4:\text{Yb/Er}(50/2\%)@\text{NaYF}_4@\text{NaYF}_4:\text{Yb/Tm}(50/0.5\%)@\text{NaYF}_4:\text{Yb}(20\%)$  and (b)  $\text{NaYF}_4:\text{Yb/Tm}(50/0.5\%)@\text{NaYF}_4@\text{NaYF}_4:\text{Yb/Er}(50/2\%)@\text{NaYF}_4:\text{Yb}(20\%)$ . Scale bars are 50 nm.



**Figure S11.** (a-b) XRD patterns of  $\text{NaYF}_4\text{:Yb/Er@NaYF}_4\text{@NaYF}_4\text{:Yb/Tm@NaYF}_4\text{:Yb}$  and  $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4\text{@NaYF}_4\text{:Yb/Er@NaYF}_4\text{:Yb}$  nanoparticles, respectively. The diffraction pattern at the bottom is the literature reference for hexagonal-phased  $\text{NaYF}_4$  crystal (Joint Committee on Powder Diffraction Standards file number 16-0334).

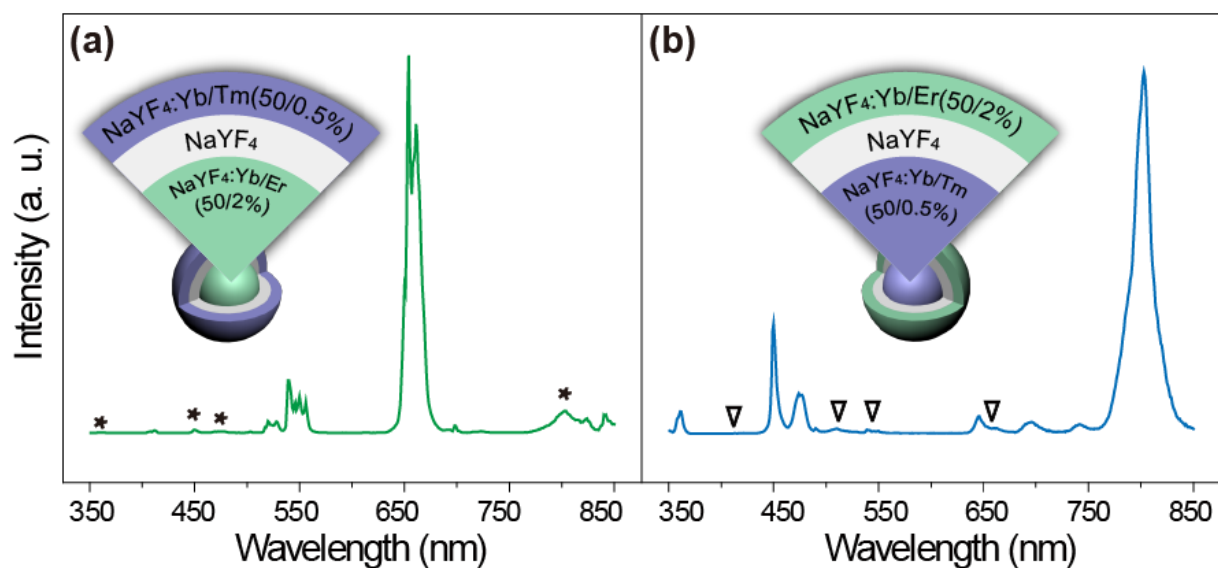


**Figure S12.** (a) Comparison of upconversion emission spectra of NaYF<sub>4</sub>:Yb/Er/Tm(50/2/0.5%)@NaYF<sub>4</sub>, NaYF<sub>4</sub>:Yb/Er(50/2%)@NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub>, and NaYF<sub>4</sub>:Yb/Er(50/2%)@NaYF<sub>4</sub>@NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub> nanoparticles. (b) Comparison of upconversion emission spectra of NaYF<sub>4</sub>:Yb/Er/Tm(50/2/0.5%)@NaYF<sub>4</sub>, NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub>:Yb/Er(50/2%)@NaYF<sub>4</sub>, and NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub>@NaYF<sub>4</sub>:Yb/Er(50/2%)@NaYF<sub>4</sub> nanoparticles. All spectra were taken under 975 nm irradiation with a power density of ~ 50 W/cm<sup>2</sup>.

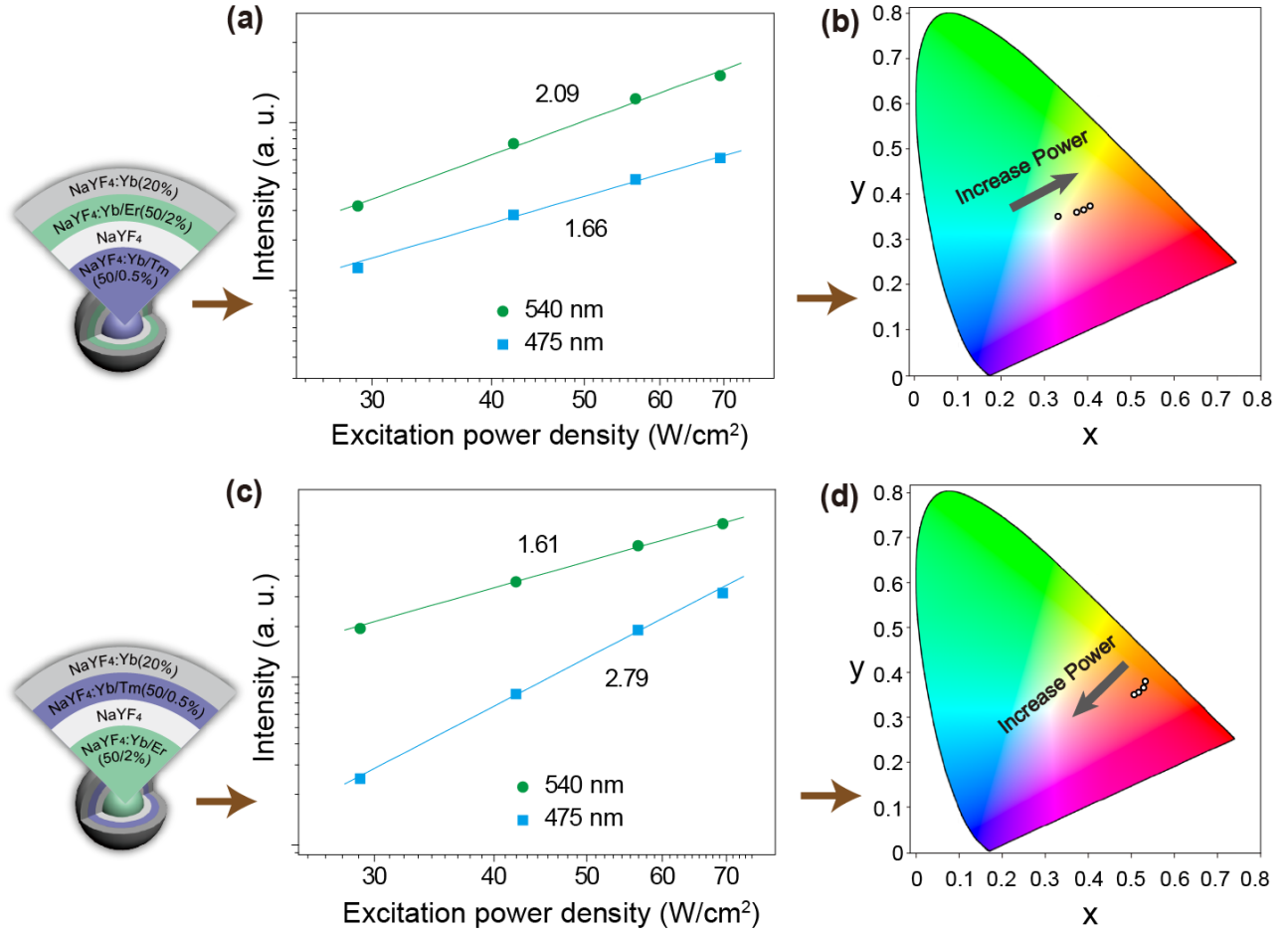
Sample	Structure	475 nm decay lifetime ( $^1G_4 \rightarrow ^3H_6$ in $Tm^{3+}$ )	540 nm decay lifetime ( $^4S_{3/2} \rightarrow ^4I_{15/2}$ in $Er^{3+}$ )
	NaYF <sub>4</sub> :Yb/Er/Tm(50/2/0.5%) @NaYF <sub>4</sub>	133 $\mu$ s	183 $\mu$ s
	NaYF <sub>4</sub> :Yb/Er(50/2%) @NaYF <sub>4</sub> :Yb/Tm(50/0.5%) @NaYF <sub>4</sub>	328 $\mu$ s	268 $\mu$ s
	NaYF <sub>4</sub> :Yb/Er(50/2%) @NaYF <sub>4</sub> @NaYF <sub>4</sub> :Yb/Tm(50/0.5%) @NaYF <sub>4</sub>	576 $\mu$ s	501 $\mu$ s
	NaYF <sub>4</sub> :Yb/Tm(50/0.5%) @NaYF <sub>4</sub> :Yb/Er(50/2%) @NaYF <sub>4</sub>	450 $\mu$ s	243 $\mu$ s
	NaYF <sub>4</sub> :Yb/Tm(50/0.5%) @NaYF <sub>4</sub> @NaYF <sub>4</sub> :Yb/Er(50/2%) @NaYF <sub>4</sub>	609 $\mu$ s	399 $\mu$ s

**Figure S13.** Decay lifetimes of 475 nm and 540 nm emissions of different structured UCNPs.





**Figure S14.** (a and b) Upconversion emission spectra of NaYF<sub>4</sub>:Yb/Er@NaYF<sub>4</sub>@NaYF<sub>4</sub>:Yb/Tm and NaYF<sub>4</sub>:Yb/Tm@NaYF<sub>4</sub>@NaYF<sub>4</sub>:Yb/Er nanoparticles, respectively. The peaks, marked with stars in a and with triangles in b, are attributed to the respective emission of Tm<sup>3+</sup> and Er<sup>3+</sup> doped at the surface layer. The power density of 975 nm laser excitation is ~ 50 W/cm<sup>2</sup>.



**Figure S15.** (a and c) Excitation-power-dependent upconversion emission intensities of NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub>@NaYF<sub>4</sub>:Yb/Er(50/2%)@NaYF<sub>4</sub>:Yb(20%) and NaYF<sub>4</sub>:Yb/Er(50/2%)@NaYF<sub>4</sub>@NaYF<sub>4</sub>:Yb/Tm(50/0.5%)@NaYF<sub>4</sub>:Yb(20%) nanoparticles, respectively, measured at both 540 nm and 475 nm. The 975 nm laser power densities under investigation are 29.0, 42.2, 56.6 and 69.4 W/cm<sup>2</sup>. (b and d) Corresponding Commission Internationale de l'Eclairage (CIE) chromaticity of coordinates recorded for the two samples under 975 nm excitation.