

Supporting Information

Employing Shell to Eliminate Concentration Quenching in Photonic Upconversion Nanostructure

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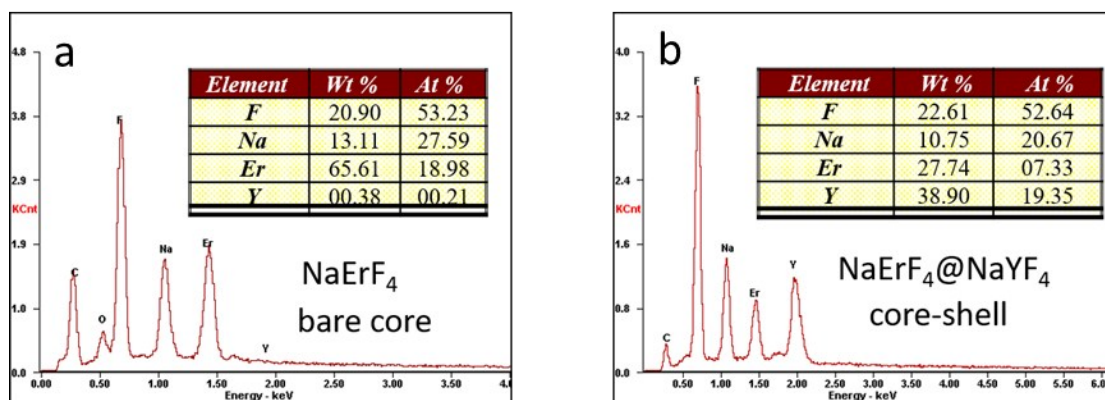


Figure S1. The element analysis results of (a) NaErF₄ bare core and (b) NaErF₄@NaYF₄ core-shell nanoparticle.

As shown in the Figure S1, in the NaErF₄ bare core, the atom ratio of Er:Y is over 90:1, while in the NaErF₄@NaYF₄ core-shell nanoparticle, the atom ratio of Er:Y is 0.38:1. These results well according with the calculation results relies on the uniformed core (20 nm) size and shell thickness (5 nm).

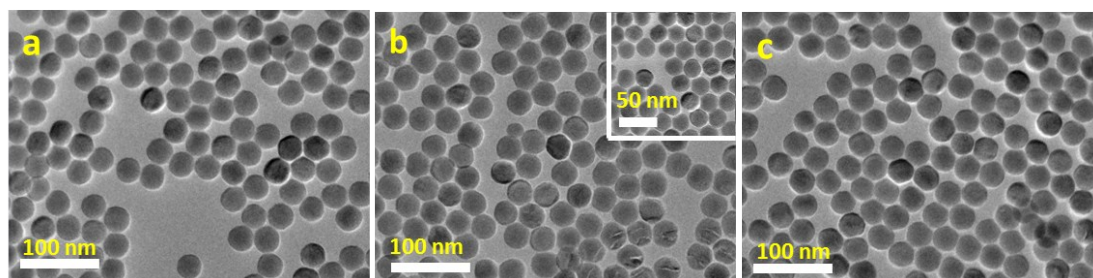


Figure S2. The TEM images of contrast samples (a) NaYF₄: 20% Yb, 2% Er@NaYF₄ nanoparticles. (b) NaYF₄: 20% Yb, 2% Er@NaYF₄: 20% Yb (2.5 nm) @NaYF₄: 10% Nd (2.5 nm) nanoparticles, inset: the TEM image of intermediate product NaYF₄: 20% Yb, 2% Er@NaYF₄: 20% Yb nanoparticle. (c) NaYF₄: 20% Er@NaYF₄ nanoparticles. All the samples are in the same size with 20 nm core and 5 nm shell.

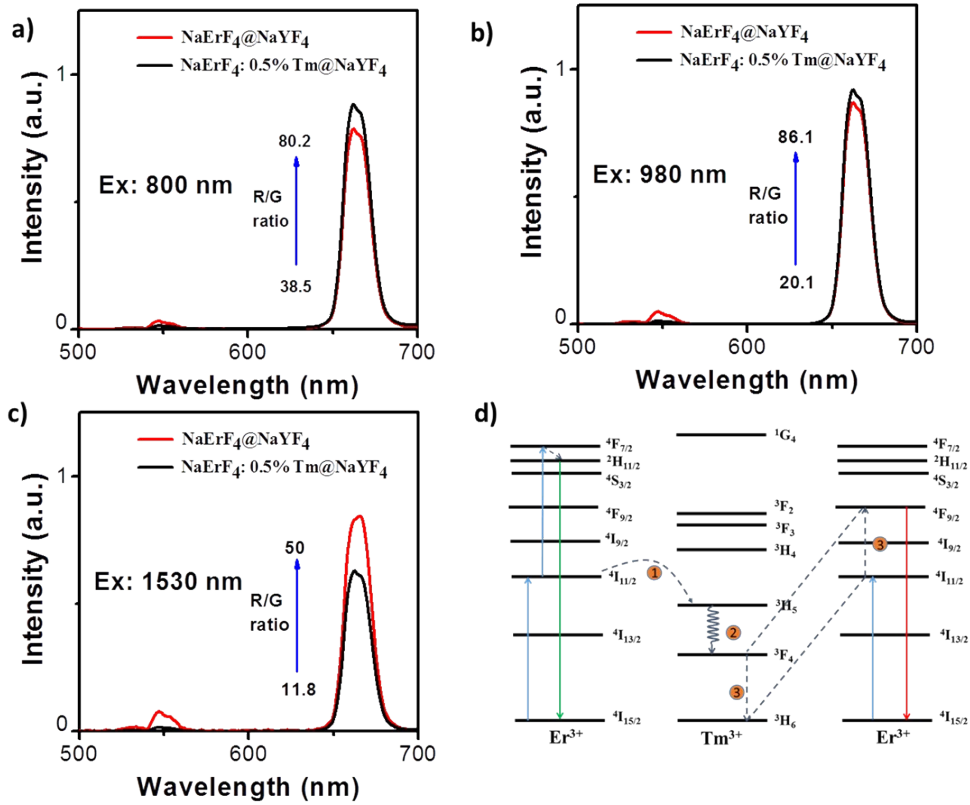


Figure S3. The UC emission spectra of NaErF₄@NaYF₄ and NaErF₄: 0.5% Tm@NaYF₄ nanoparticles under the excitation of (a) 800 nm (10 W/cm²), (b) 980 nm (10 W/cm²) and (c) 1530 nm (1 W/cm²), respectively. (d) The schematic of the energy transfer process between Er³⁺ and Tm³⁺.

As shown in the Figure S3, doping 0.5% Tm into the core area, all the R/G (red/green) ratios are significantly enhanced, from 38.5 to 80.2 (800 nm excitation), from 20.1 to 86.1 (980 nm excitation) and from 11.8 to 50 (1530 nm excitation), respectively. While the overall UC emission intensity is not changed obviously. The reason can be attributed to the energy transfer between Er³⁺ and Tm³⁺ (referred to Figure S3d), which will decrease the green emission of Er³⁺ efficiently, as described in previous report.^[1]

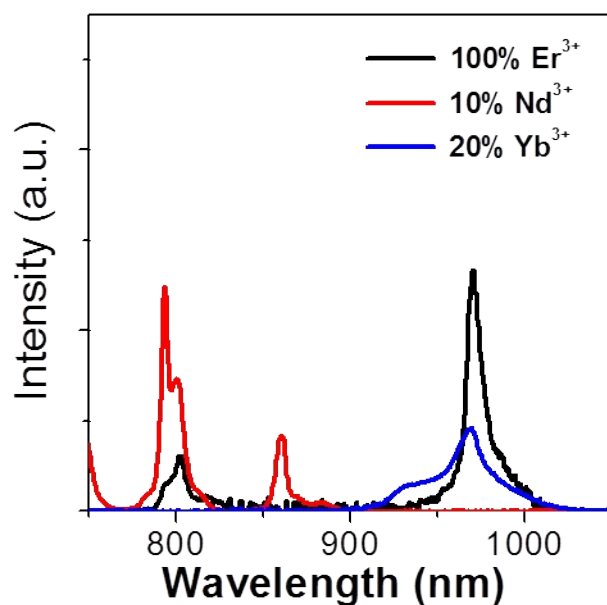


Figure S4. The absorption spectra of NaErF₄@NaYF₄ core-shell nanoparticles, NaYF₄: 10% Nd bare core and NaYF₄: 20% Yb bare core nanoparticles (normalized by the concentration of nanoparticle in cyclohexane).

As shown in the Figure S4, by raising the Er³⁺ doping concentration up to 100%, the absorption ability of NaErF₄@NaYF₄ nanoparticle becomes comparable with co-doping systems. More specifically, it reaches up to 33% of the NaYF₄: 10% Nd nanoparticle (integration from 770 nm to 830 nm) and 120% of the NaYF₄: 20% Yb nanoparticle (integration from 920 nm to 1040 nm).

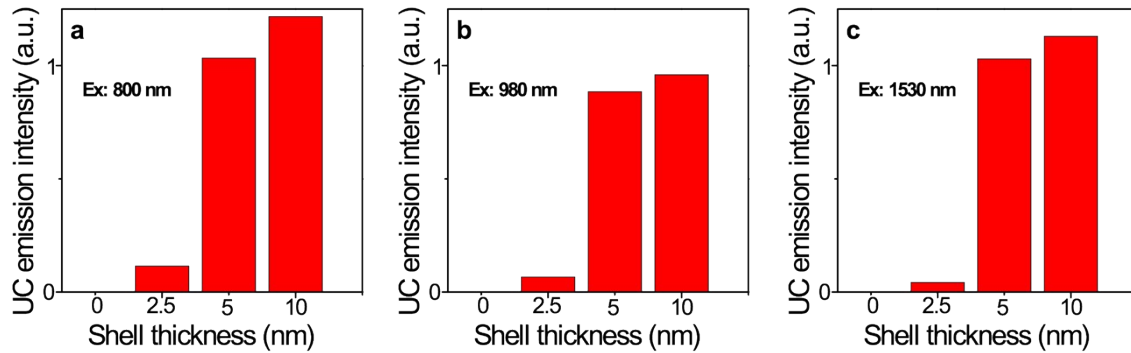


Figure S5. The shell thickness dependent UC emission intensity (integration from 500 nm to 700 nm) of NaErF₄@NaYF₄ nanostructure (0 nm shell corresponding to the NaErF₄ bare core), the excitation wavelength is (a) 800 nm (10 W/cm²), (b) 980 nm (10 W/cm²) and (c) 1530 nm (1 W/cm²), respectively.

It should be noticed that almost no UC emission could be observed for the NaErF₄ bare core structure (Fig. S5 a-c), due to the numerous defects located on the surface of nanoparticle. But after the NaYF₄ shell coating strategy to passivate the surface defects, the NaErF₄@NaYF₄ nanostructure generates a much more efficient UC emission. This protective effect nearly achieves saturation beyond 5 nm shell thickness in cyclohexane solution.

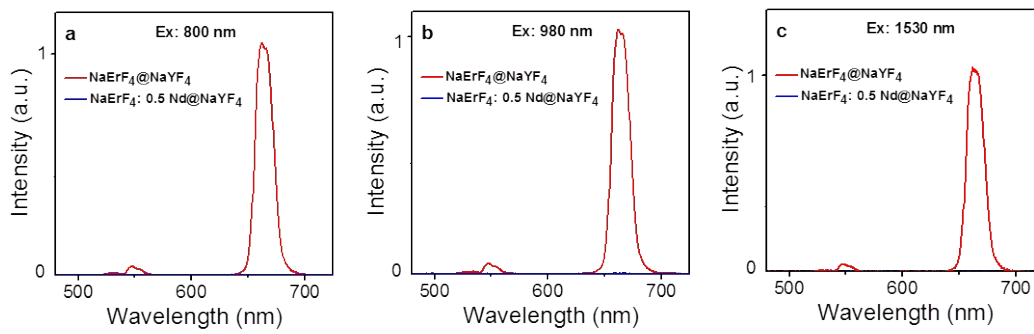


Figure S6. The UC emission spectra of the NaErF₄@NaYF₄ (20 nm core and 5 nm shell) and NaErF₄: 0.5 mol% Nd@NaYF₄ (20 nm core and 5 nm shell) nanoparticle under the (a) 800 nm, (b) 980 nm and (c) 1530 nm excitation, respectively.

As shown in the Figure S6, by introducing 0.5 mol% Nd³⁺ into the core area as energy trappers,^[2] which plays the role of bulk quenching sites, the UC emission will be almost completely quenched.

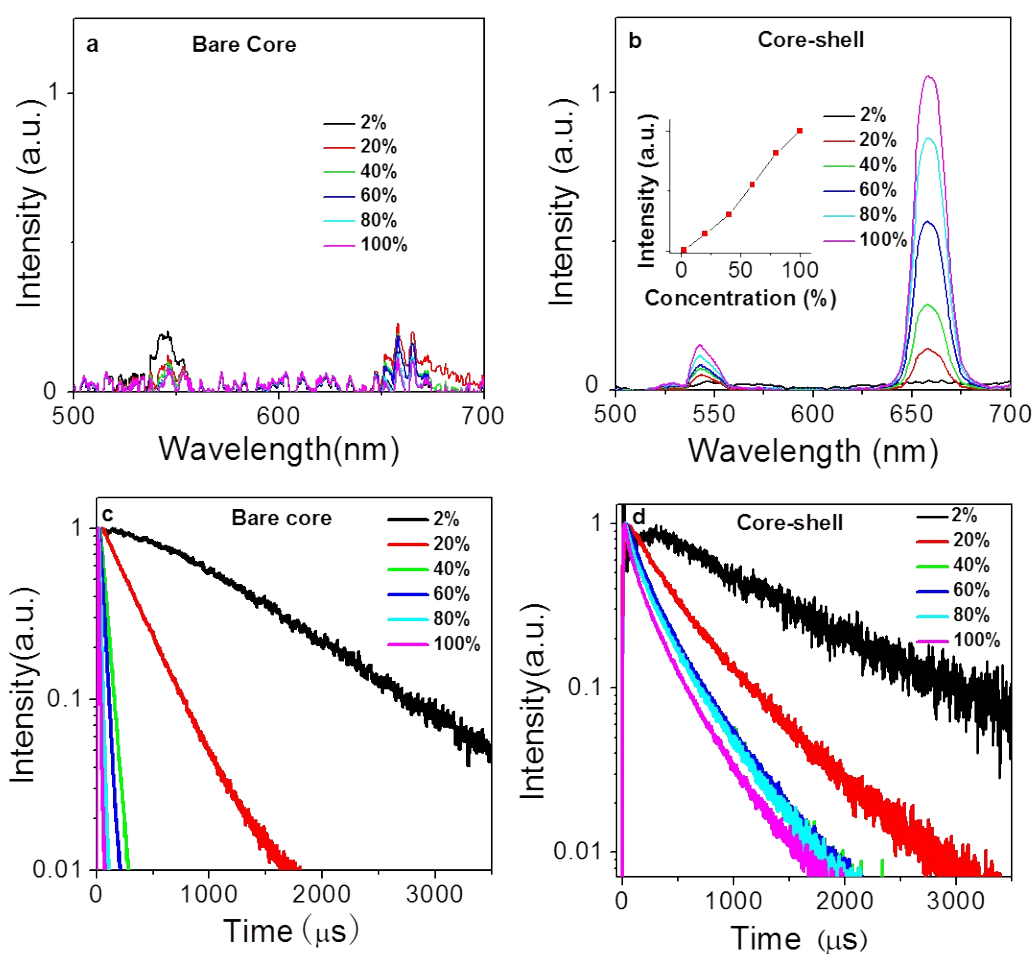


Figure S7. The UC emission spectra of solutions containing: a) NaYF₄: x% Er (x: 2-100) bare core, b) NaYF₄: x% Er (x: 2-100)@NaYF₄ core-shell nanoparticles in cyclohexane (~1 wt%, excited by 800 nm, 10 W/cm²). Insert in Fig S7b: the concentration dependent UC emission intensity (integration from 500 nm to 700 nm) in core-shell structure. And the corresponding decay curves of Er³⁺: ⁴F_{9/2} → ⁴I_{15/2} transition, *i.e.* ~ 650 nm, in c) NaYF₄: x% Er bare core and d) NaYF₄: x% Er @NaYF₄ core-shell nanoparticles. It should be noticed that the 800 nm excited bare core UC emission is too weak to be analyzed well.

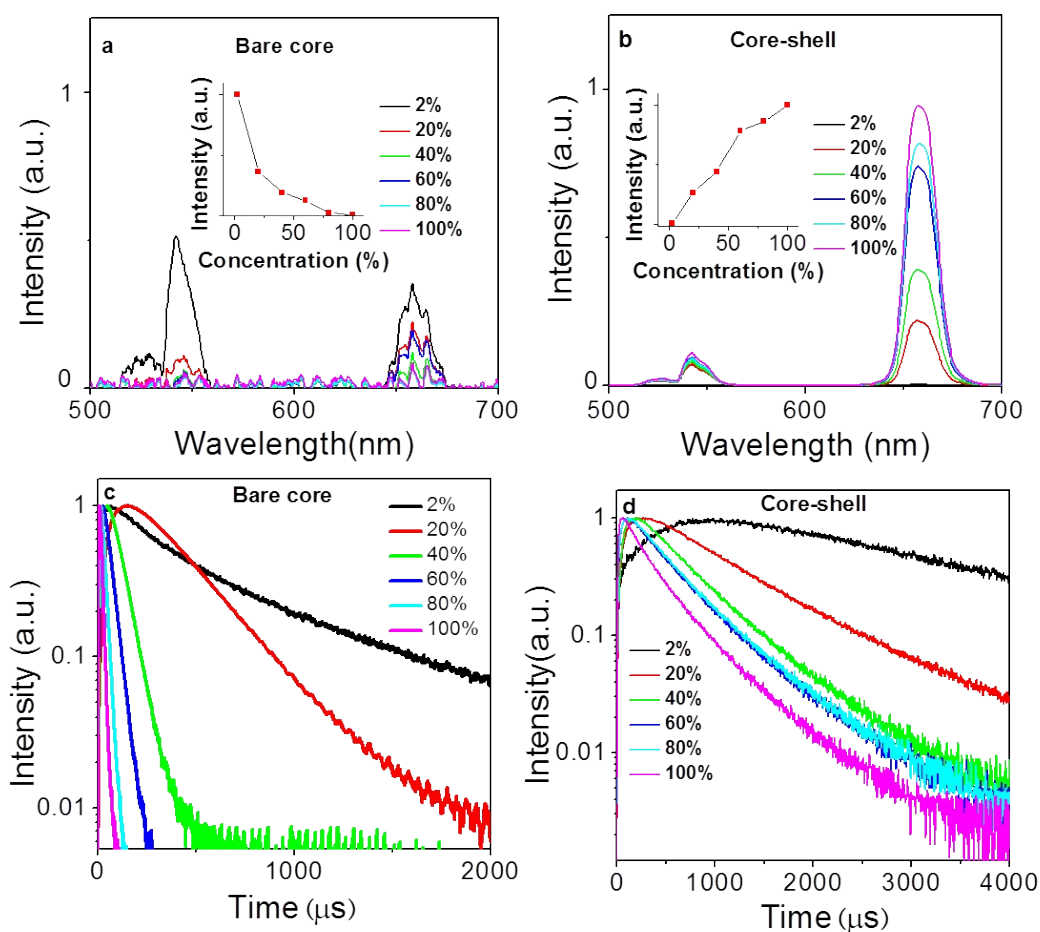


Figure S8. The UC emission spectra of solutions containing: a) NaYF₄: x% Er (x: 2-100) bare core, b) NaYF₄: x% Er (x: 2-100)@NaYF₄ core-shell nanoparticles in cyclohexane (~1 wt%, excited by 1530 nm, 1 W/cm²). Inserts in Fig S8a,b: the concentration dependent UC emission intensity (integration from 500 nm to 700 nm) in bare core and core-shell structures. And the corresponding decay curves of Er³⁺: ⁴F_{9/2} → ⁴I_{15/2} transition, *i.e.* ~ 650 nm, in c) NaYF₄: x% Er bare core and d) NaYF₄: x% Er@NaYF₄ core-shell nanoparticles.

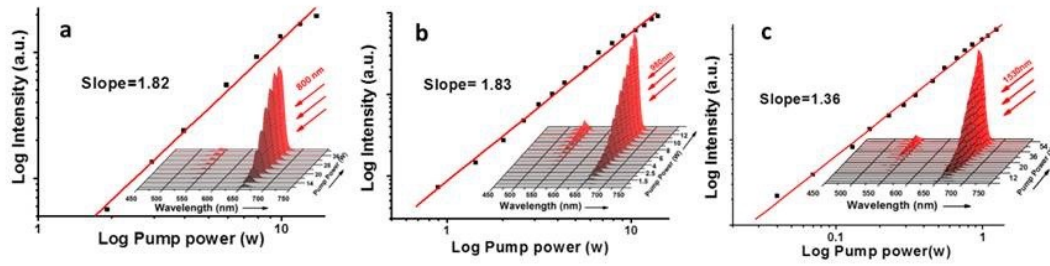


Figure S9. Log-log plots of the ~ 650 nm UC emission intensity of $\text{NaErF}_4@ \text{NaYF}_4$ nanoparticles as a function of pump power at (a) 800nm, (b) 980nm and (c) 1530 nm, respectively. The output slopes are measured as 1.82, 1.83 and 1.36, respectively, exhibiting the non-linear relationship between UC emission intensity and excitation power.

References

- [1] E. M. Chan, G. Han, J. D. Goldberg, D. J. Gargas, A. D. Ostrowski, P. J. Schuck, B. E. Cohen, D. J. Milliron, *Nano Lett.* **2012**, *12*, 3839-3845.
- [2] Y. T. Zhong, G. Tian, Z. J. Gu, Y. J. Yang, L. Gu, Y. L. Zhao, Y. Ma, J. N. Yao, *Adv. Mater.* **2014**, *26*, 2831-2837.