Supporting Information

A Core-Multiple Shell Nanostructure Enabling Concurrent

Upconversion and Quantum Cutting for Photon Management

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1. Synthetic Procedures for Each Type of Nanoparticles

Synthesis of NaYF4:2%Tb³⁺,x%Yb³⁺ (x=0, 20, 40, 60 and 80)

In a typical procedure, totally 0.02 mmol TbCl₃•6H₂O, x mmol YbCl₃•6H₂O and 0.98x mmol YCl₃•6H₂O (x=0, 0.2, 0.4, 0.6 and 0.8) were added into a 100 ml flask containing 3, 3, 7, 11, 15 ml oleic acid corresponding to x=0, 0.2, 0.4, 0.6 and 0.8 respectively and 15 ml octadecene. The mixture was heated to 160 °C at a rate of 12 °C/min, kept this temperature for 60 min under a gentle argon gas purge, and then cooled down to room temperature. Subsequently, a solution of 4 mmol NH₄F and 2.5 mmol NaOH in 10 ml methanol was added and stirred for 30 min. The reaction mixture was then heated at 100 °C for 30 min to remove the methanol, followed by heating up to 300 °C at a rate of 12 °C/min and keeping at 300 °C for 60 min before cooling down. A syringe needle was used to let the argon gas out during the synthesis. The mixture was cooled to room temperature naturally and precipitated by excess ethanol and collected by centrifugation at 18144 rcf for 7 minutes. The precipitate was washed with ethanol several times, and the nanocrystals were dispersed in hexane.

Synthesis of NaYF4:10%Er³⁺

In a typical procedure, totally 0.1 mmol $ErCl_3 \cdot 6H_2O$ and 0.9 mmol $YCl_3 \cdot 6H_2O$ were added into a 100 ml flask containing 7 ml oleic acid and 15 ml octadecene. The mixture was heated to 160 °C at a rate of 12 °C/min, kept this temperature for 60 min under a gentle argon gas purge, and then cooled down to room temperature. Subsequently, a solution of 4 mmol NH₄F and 2.5 mmol NaOH in 10 ml methanol was added and stirred for 30 min. The reaction mixture was then heated at 100 °C for 30 min to remove the methanol, followed by heating up to 300 °C at a rate of 12 °C/min and keeping at 300 °C for 60 min before cooling down. A syringe needle was used to let the argon gas out during the synthesis. The mixture was cooled to room temperature naturally and precipitated by excess ethanol and collected by centrifugation at 18144 rcf for 7 minutes. The precipitate was washed with ethanol several times, and the nanocrystals were dispersed in hexane.

Synthesis of NaYF4:10%Er³⁺@NaLuF4 with different thickness of NaLuF4

The NaYF₄:10%Er³⁺@NaLuF₄ core-shell nanoparticles are synthesized by thermal decomposition method. 0.25, 0.5, 0.75 and 1 mmol of Lu₂O₃ respectively was dissolved in 50% trifluoroacetic acid at 95 °C in a three neck flask. Then, the solutions were evaporated to dryness under an argon gas purge. Next, 10 mL of oleic acid, 10 mL of 1-octadecene, 1, 2, 3 and 4 mmol sodium trifluoroacetate respectively and 1 mmol NaYF₄:10%Er³⁺ core were added into the flask. The resulting solution was then heated at 120 °C with magnetic stirring for 45 min to remove water and oxygen under a gentle argon gas purge. The brown solution was then heated to 320 °C at a rate of about 12 °C/min under argon gas protection and kept at this temperature under vigorous stirring for 45 min. A syringe needle was used to let the argon gas out during the synthesis. The mixture was cooled to room temperature naturally and precipitated by excess ethanol and collected by centrifugation at 18144 rcf for 7 minutes. The

precipitate was washed with ethanol several times, and the nanocrystals were dispersed in hexane.

Synthesis of NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺

The synthesis procedure of NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺ core-shell nanoparticles are like the one for preparation of NaYF4:10%Er³⁺@NaYF4. The only difference is using 0.39 mmol of Y₂O₃, 0.1 mmol of Yb₂O₃ and 0.01 mmol of Tb₂(CO₃)₃•H₂O to form the precursor, and 2 mmol sodium trifluoroacetate adding into 1 mmol NaYF4:10%Er³⁺@NaLuF4 core-shell nanoparticles.

Synthesis of NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺@NaYF4

The synthesis procedure of NaYF4:10%Er³⁺@NaYF4@NaYF4:10%Ho³⁺@NaYF4 core-shell nanoparticles are like NaYF4:10%Er³⁺@NaYF4. The only difference is using 0.5 mmol of Y_2O_3 to form the precursor, and 2 mmol sodium trifluoroacetate adding into 1mmol NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺ core-shell nanoparticles.

Control of the shell thickness

An spherical concentric shell model was employed to calculate the relationship between the shell precursor dosage and the thickness of shell layers. The required amount of precursor to produce a desired thickness can be calculated by the following equations: $m_{layer(n)} = m_{particle(n)} - m_{particle(n-1)} = \rho(V_{particle(n)} - V_{paricle(n-1)})$

$$= \frac{4}{3}\pi\rho N \times 10^{-21} \times [r_{particle(n)}^3 - r_{particle(n-1)}^3]$$
(S1)

Here $m_{layer(n)}$ represents the mass of the layers, N represents the number of core, $m_{particle(n)}$, $V_{particle(n)}$, and $r_{particle(n)}$ represents the mass, volume and radius of the number n layer, respectively. The $r_{particle(n-1)}$ is the radius of the core/multishell nanoparticles with (n-1) shell layers.

Density of NaYF₄ core and NaLuF₄ shell materials (ρ), particle number of one molar(N) are calculated as follows:

$$\rho = \frac{m}{v} = \frac{M \times n}{c \times \frac{\sqrt{3}}{2}a^2} = \frac{M \times N'}{N_A \times c \times \frac{\sqrt{3}}{2}a^2}$$
(S2)

Here M represents relatice molecular mass of the materials. N' means the number of the NaLuF₄ and NaYF₄ units that one crystal cell contains, according previous report, N' = 1.5.

For NaYF₄, cell parameter is a= 5.96 Å, c= 3.53 Å, molecular weight (M)= 187.9, and $\rho = 4.31$ g/cm³. For NaLuF₄, cell parameter is a= 5.90 Å, c= 3.45 Å, molecular weight (M)= 273.9, and $\rho = 6.56$ g/cm³



Here, $r_0 = 11$ nm; M, ρ represent molecular weight and density of NaYF₄ or NaLuF₄.

According to equations (S1), (S2) and (S3), the mass of the n shell layer, $m_{layer(n)}$ can be calculated as follows:

 $m_{layer(n)} = 0.206 \times (r_{particle(n)}^3 - r_{particle(n-1)}^3)$

Equation (S4) was utilized to calculate the predicted radius of the resulting core-shell naonparticles with NaLuF₄ shell layers with the employed precursor dosages. The predicted radius versus the measured radius of these core/multishell nanoparticles are listed in Table S1, displaying a good agreement.

Table S1. The measured radius vs predicted radius of $NaYF_4:10\% Er^{3+}@NaLuF_4$ nanoparticles with different dosage of $NaLuF_4$ layer.

Dosage of NaLuF ₄ Layer	Measured Radius r _m	Predicted Radius r _p (nm)
0	11	11
0.5	12.5	12.59
1	14	13.86
1.5	15	14.93
2	16	15.86

2. Supporting Figures



Figure S1. PL excitation spectra of Tb³⁺ emission at 532 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ and Yb³⁺ emission at 980 nm (${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$) in NaYF₄:2%Tb³⁺, 20%Yb³⁺ nanoparticles.



Figure S2. Decays of PL emission at (a) 542 nm from the ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ transiton of Tb³⁺ ions (excited at 355 nm) and (b) 1000 nm from the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transiton of Yb³⁺ ions (excited at 980 nm) in nanoparticles of NaYF₄:2%Tb³⁺,x%Yb³⁺ (x=0, 20, 40, 60 and 80%).

In Figure S2 a, the decays of PL peaked at 542 nm from the Tb^{3+} ions are shown for nanoparticles with different concentrations of Yb^{3+} , further illustrating ET between Tb^{3+} and Yb^{3+} . The PL of single dopant, Yb^{3+} -free NaYF₄:2%Tb³⁺ nanoparticles exhibits a nearly single exponential decay with a decay time of 4.89 ms. With introduction of Yb^{3+} and increase in its doping concentration, the PL decay time decreases in sequence and eventually reaches 2.03 ms for the NaYF₄:2%Tb³⁺, 80%Yb³⁺ nanoparticles. The dramatical reduction of PL decay time with an increase of Yb³⁺ concentration can evidently be explained by the enhanced energy transfer (ET) from Tb³⁺ to Yb³⁺ ions (the quantum cuttting process), which is supposed to enhance the NIR PL from Yb³⁺ when excited at 488 nm or 355 nm. On the other hand, we measured the decay curves for PL from Yb³⁺ (${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition) at ~1000 nm under excitation at 980 nm (Figure S2 b). It is found that the lifetime for PL of Yb³⁺ decreased with an increase of Yb³⁺ ions, indicating the occurence of the concentration quenching effect. The competion between the high Yb³⁺-enhanced quantum cutting process and the high Yb³⁺-induced concentration quenching effect, results in an observation of the strongest NIR PL for Yb³⁺ concentration of 20% (Figure 3). The decay results for VIS PL of Tb³⁺ at 542 nm (excited at 355 nm) and the NIR PL of Yb³⁺ at 1000 nm (excited at 980 nm) are compiled in Table S2.

Table S2. The decay results for VIS PL of Tb^{3+} at 542 nm (excited at 355 nm) and the NIR PL of Yb^{3+} at 1000 nm (excited at 980 nm) from NaYF₄ nanoparticles doped with 2% Tb^{3+} and various concentrations of Yb^{3+} .

Yb concentration (%)	τvis (ms)	τnir (ms)
0	4.89	
20	4.28	0.471
40	3.56	0.348
60	2.54	0.257
80	2.03	0.133

Furthermore, the efficiency of ET from Tb^{3+} to Yb^{3+} can be determined using the decays for VIS PL shown in Figure S2a. The ET efficiency is defined as the ratio

between the number of Tb³⁺ ions, transfering their energy to Yb³⁺ ions, and the total number of the excited Tb³⁺ ions. It can also be expressed as $\eta_{x\%Yb} = 1 - \int I_{x\%Yb} dt / \int I_{0\%Yb} dt$ where *I* denotes intensity, x%Yb stands for the Yb³⁺ concentration^{S7}. The PL quantum efficiency QE could be defined as the ratio of the number of photons emitted to the number of photons absorbed, which is defined as $\eta =$ $\eta_{Tb}(1 - \eta_{x\%Yb}) + 2\eta_{x\%Yb}$, where QE for the Tb³⁺ ions η_{Tb} is set to 1^{S7}. No nonradiative losses are assumed to occur, in particular, the concentration effect of Yb³⁺ ions. The result is shown in table S3. For NaYF₄:2%Tb³⁺,80%Yb³⁺ nanoparticles the QE is determined to be around 173%, this means that for 73 out of 100 times a depopulation of the ⁵D₄ level of Tb³⁺ in occurs through excitation of two Yb³⁺ ions to the ²F_{5/2} level.

Table S3. Lifetime of Tb^{3+} ions and the theoretical QE of samples with different Yb^{3+} concentration.

Yb ³⁺ concentration	Lifetime of Tb ³⁺ (ms)	Theoretical QE
0	4.89	0
20	4.18	144.83%
40	3.46	159.27%
60	2.78	166.09%
80	2.03	172.38%



Figure S3. A comparsion of UC PL spectra from colloidal NaYF4:10%Er³⁺@NaYF4 and from NaYF4:10%Er³⁺@NaLuF4 nanoparticles dispsersed in hexane (1 wt%). Excited at ~ 1523 nm, 18 W/cm².



Figure S4. QC PL spectra of NaYF4:10% Er^{3+} @NaLuF4@NaYF4:20%Yb³⁺,2%Tb³⁺ with and without the outermost NaYF4 layer.



Figure S5. a) TEM imaging and b) size distribution of NaYF₄:10%Er³⁺ core.



Figure S6. Size distribution of $NaYF_4:10\% Er^{3+}@NaLuF_4$ with $NaLuF_4$ radius thickness of a) 1.5 nm, b) 3 nm, c) 4 nm and d) 5 nm.



Figure S7. NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺ with a NaLuF4

layer thickness of a) 0 nm, b) 1.5 nm, c) 3 nm d) 4 nm and e) 5 nm.



Figure S8. Size distribution of NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺

@NaYF4 with NaLuF4 layer thickness of a) 1.5 nm, b) 3 nm, c) 4 nm and d) 5 nm.



Figure S9. Absorption spectrum of

 $NaYF_4:10\% Er^{3+} @NaLuF_4 @NaYF_4:2\% Tb^{3+}, 20\% Yb^{3+} @NaYF_4 \\$



Figure S10. a) A comparision of QC PL spectra of colloidal NaYF₄:10%Er³⁺@NaLuF₄ @NaYF₄:2%Tb³⁺,20%Yb³⁺@NaYF₄ core/multishell nanoparticles and collidal NaYF₄:2%Tb³⁺, 20%Yb³⁺ @NaYF₄ core/shell nanoparticles under light excitation at 355 nm; a) A comparision of QC PL spectra of colloidal NaYF₄:10%Er³⁺@NaLuF₄ @NaYF₄:2%Tb³⁺,20%Yb³⁺@NaYF₄ core/multishell nanoparticles and collidal NaYF₄:10%Er³⁺@NaLuF₄ core/shell nanoparticles under light excitation at 488 nm.



Figure S11. A comparison of the UC spectra from the NaYF₄:10%Er³⁺@NaLuF₄@ NaYF₄:2%Tb³⁺,20%Yb³⁺ @NaYF₄ core-multishell nanoparticles and the reference

NaYF₄:10%Er³⁺@NaYF₄ core/shell nanoparticles dispersed in hexane. (Excited at ~ 1523 nm, 18 W/cm²). These two type of nanoparticles were of the identical concentration and measured using an exactly identical geometry in the same setup. The reference NaYF₄:10%Er³⁺@NaYF₄ core/shell nanoparticles have prepared following exactly the same procedure in our previously reported work.^{S1} The intensity of the NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺ @NaYF₄ core-multishell nanoparticles is about 0.93 times than that of the reference NaYF4:10%Er³⁺@NaYF4 Since the upconversion efficiency of the reference core-shell nanoparticles nanoparticles has been determined to be ~ 3.9% (corresponding upconversion quantum yield of ~ 1.7%) using an integrating sphere method, S1 this intensity difference indicates an upconversion efficiency of 3.6% (upconversion quantum yield of 1.6%) for the NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺ @NaYF₄ core-multishell nanoparticles. It should be noted that the upconversion efficiency (UCE) refers to an energy conversion efficiency, which is defined by the ratio between the emitted luminescence power and the absorbed excitation power. It relates to the upconversion quantum yield (UCQY) through the following equation (here the excitation wavelength is a constant, the UCQY is the spectral one),

$$UCE = \int UCQY(\lambda_{Emission}) (\frac{\lambda_{Exciation}}{\lambda_{Emission}}) d\lambda_{Emission}$$
(S5)

The luminescence quantum yield refers to the ratio between the number of emitted luminescence photons and the number of the absorbed excitation photons, which is an important parameter for the characterization of a luminescent process.^{S2-S6} The luminescence quantum yield for the quantum cutting process in our core-multishell colloidal nanoparticles samples was measured by an relative method, referencing to a standard with a known luminescence quantum yield (QY). Here, the Rhodamine 6G in ethanol with a known QY_R of 95% was utilized as the reference standard.^{S2} We utilized

the following equation to caculated the luminescence QY_S of our core-multishell colloidal nanoparticles:^{S3}

$$QY_S = QY_R \left(\frac{E_S}{E_R}\right) \left(\frac{A_R}{A_S}\right) \left(\frac{I_R}{I_S}\right) \left(\frac{n_S}{n_R}\right)^2$$
(S6)

Where E_S and E_R are the numbers of the emitted photons for the referenced standard sample and the measured sample, respectively; A_R and A_S are the numbers of the photons absorbed by the referenced standard sample and measured sample, respectively; I_R and I_S indicate the relative intensity of the exciting light for the referenced standard sample and measured sample, respectively; n_S and n_R are the refractive index of the solvent used for dissolving the referenced standard sample and the measured sample, respectively.



Figure S12. Determination of the luminescence quantum yield for a set of dye solutions with known quantum yields (Rhodamine 123 in ethanol, Rhodamine B in ethanol, and Fluorescein in 0. 1 0.1 M NaOH aq), using Rhodamine 6G as a standard reference. (a) The absorptions of Rhodamine 123, Rhodamine B, Fluorescein, and the standard reference Rhodamine 6G have been matched at ~ 488 nm. (b) The measured

photoluminescence spectra of Rhodamine 123, Rhodamine B, and Fluorescein versus the one of the standard reference Rhodamine 6G.

 Table S4. The measured luminescence quantum yields of a set of dye solutions in this

 work versus the well-established and reported values in literature.

	Solvent	Measured quantum	Reported quantum	
		yield (Ψ_{exp})	yield (Ψ_{rep})	
Rhodamine 6G	Ethanol	0.95 ± 0.02 (this work)	0.95 ± 0.005 (ref.	
			S2)	
Rhodamine 123	Ethanol	0.87 ± 0.03 (this work)	0.90 (ref. S4)	
Rhodamine B	Ethanol	0.54 ± 0.03 (this work)	0.50 (ref. S5)	
Fluorescein	0.1 M NaOH	0.90 ± 0.02 (this work)	0.91 ± 0.02 (ref. S2)	

To test whether our calibrated system is able to measure luminesce quantum yield accurately, we used our calibrated spectroscopic system firstly to quantify a set of dye solutions that have widely investigated and accepted as reference standard alternatives (Figure S 11). Using the relative method and our calibrated setup, we determine the luminescence quantum yields for Rhodamine 123 in ethanol, Rhodamine B in ethanol, and Fluorescein in 0.1 M NaOH aq to be 0.87, 0.54, and 0.90, all in good agreement with well-established and reported values in literature (Table S3). Aftering vlidating our relative method, we proceed to quantify the luminescence quantum yield of NaYF4:10%Er³⁺@NaLuF4@ NaYF4:2%Tb³⁺, 20%Yb³⁺ @NaYF4 core-multishell nanoparticles.

The absorption of Tb^{3+} (~ 480 nm) in the NaYF4:10%Er³⁺@NaLuF4@ NaYF4:2%Tb³⁺, 20%Yb³⁺@NaYF4 core-multishell nanoparticles is hard to detect due to its low absorption cross section and low concentration inside the nanoparticle. We obtained the absorbption of Tb^{3+} in our core-multishell nanoparticles by scaling down from that of colloidal NaYF₄:20%Tb³⁺, 20%Yb³⁺ nanoparticles with high Tb³⁺ concentration but identical Yb³⁺ concentration. The scaling down factor was precisely determined through the compasion result of inductively coupled plasma optical emission spectrometry (ICP-OES) of two samples (see Table S4). Prior to the ICP-OES test, both samples have been matched at the absorption peak of Yb³⁺ ions to ensure that both testing solutions contains identical concentrations of Yb³⁺ ions, as confirmed in ICP-OES result in Table S5. The stoichiometric chemical nature of these nanoparticles, revealed in Table S5, ensure the scaling dwown factor to be a constant value of 10.

Table S5. The ICP-OES result of the Tb³⁺ and Yb³⁺ concentration (ppm), and thecalculatedconcentrationratioofTb/Ybforthecore-multishellNaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺, 20%Yb³⁺@NaYF4 nanoparticle and theNaYF4:20%Tb³⁺, 20%Yb³⁺ nanoparticle.

Measureme	Core-multishell		NaYF	4:20% Tb ³⁺	$,20\% Yb^{3+}$	
nt Times	Tb(ppm	Yb(ppm	Tb/Yb(Rati	Tb(ppm	Yb(ppm	Tb/Yb(Rati
1	0.0567	0.5574	2:20	0.547	0.5486	20:20

2	0.1058	1.101	2:20	1.063	1.1918	20:20
3	0.2257	2.187	2:20	2.113	2.095	20:20



Figure S13. The determination of the luminescence quantum yield for the quantum cutting process in the NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺@NaYF4 core-multishell nanoparticles. The absorptions a) of NaYF₄:10%Er³⁺@NaLuF₄@NaYF₄:2%Tb³⁺,20%Yb³⁺ @NaYF₄ and the referenced standard of Rhodamine 6G were matched at ~ 488 nm. The absorption of the coremultishell nanoparticles was obtained by scaling down from the absorption of NaYF₄: 20% Tb³⁺, 20% Yb³⁺ nanoparticles, taking into account of the ICP-OES-determined difference factor of the Tb³⁺concentration. b) The emission of the core-multishell $NaYF_4:10\% Er^{3+}@NaLuF_4@NaYF_4:2\% Tb^{3+},20\% Yb^{3+} @NaYF_4 nanoparticles in$ reference to that of the Rhodamine 6G standard with a quantum yield of ~ 95%. The integrated emission intensity (500-1100 of nm) the NaYF4:10%Er³⁺@NaLuF4@NaYF4:2%Tb³⁺,20%Yb³⁺ @NaYF₄ core-multishell nanoparticles is about 1.37 times stronger than that of the Rhodamine 6G standard,

indicating a luminescence QY of ~ 130% (\pm 3%). This experimental value is close to the theoretical quantum efficiency of ~ 144.83% in Table S3 for NaYF₄:2%Tb³⁺,20%Yb³⁺ nanoparticles with the minimized concentration quenching effect for the NIR PL of Yb³⁺ ions.



Figure S14. PL spectrum under different power densities at a) 1523 nm and b) 488 nm.

Supporting References:

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