Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Nd^{3+}-Sensitized Multicolor Upconversion Luminescence from A Sandwiched Core/Shell/Shell Nanostructure

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Materials. Ytterbium (III) oxide (Yb_2O_3, 99.9%), thulium (III) oxide (Tm_2O_3, 99.99%), erbium (III) oxide (Er_2O_3, 99.99%), neodymium (III) oxide (Nd_2O_3, 99.99%), calcium hydroxide ($Ca(OH)_2$,96.8%), sodium hydroxide (NaOH,98%), sodium trifluoroacetate (CF_3COONa, 98%), trifluoroacetic acid (CF_3COOH, 99%), oleic acid (90%, tech grade), oleylamine (70%, tech grade), octadecene (90%, tech grade) and TWEEN 20 were obtained from Sigma Aldrich Reagent Company. Hexane (ACS reagent grade, ≥98.5%) was purchased from Fisher Scientific. All chemicals were used as received.

Synthesis. The α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+}@CaF_2:30%Nd^{3+}@CaF_2:20%Yb^{3+},5%Er^{3+},1%Nd^{3+} sandwich-structured upconversion nanoparticles were synthesized using a three-step procedure adapted from a recent thermolysis approach[1]. The first step involves the preparation of core α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+} (cubic phase) nanoparticles. The steps 2 and 3 involve the coating of the CaF_2:30%Nd^{3+} interlayer onto the cubic core, and the CaF_2:20%Yb^{3+}, 5%Er^{3+},1%Nd^{3+} outmost layer onto the α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+}@CaF_2:30%Nd^{3+} core/shell nanoparticles through seed-mediated epitaxial growth processes, respectively.

Step 1. Synthesis of α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+} core: In a typical procedure, Yb_2O_3 (0.4925 mmol), Tm_2O_3 (0.0025 mmol) and Nd_2O_3 (0.005 mmol) were first mixed with 5 mL of deionized water and 5ml of 50% trifluoroacetic acid in a 100 mL three-necked flask, and refluxed at 95 °C until getting dissolved completely. Subsequently, the clear solution was evaporated to dryness under argon gas purge to yield 1.0 mmol $RE(CF_3COO)_3$ (RE=Yb+Tm+Nd) solid precursor. Then, sodium trifluoroacetate (2.0 mmol), oleic acid (8 mL, 90% tech grade), oleylamine (8 mL, 70% tech grade), and octadecene (12 mL, 90% tech grade) was added together into the three-neck bottle. After degassed at 120 °C for 30 min under argon gas protection, the resulting solution was heated to 300 °C at a rate of ~15 °C/min and kept at this temperature for 30 minutes before naturally cooling down to room temperature. Lastly, the resulting nanoparticles were collected by adding 10 mL ethanol into the solution and being centrifuged at 7500 rpm for 5 minutes. The collected precipitate was finally dispersed in 10 mL hexane for further uses.

Step 2. Synthesis of α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+}@CaF_2:30%Nd^{3+} core@shell nanoparticles: The $Ca(OH)_2$ (2 mmol) and Nd_2O_3 (0.6 mmol) was first dissolved in 50% concentrated trifluoroacetic acid at a temperature of 95°C in a three-neck flask, yielding a transparent solution. Following that, the solution was evaporated to dryness under argon gas to produce the $Ca(CF_3COO)_2$ and $Nd(CF_3COO)_3$ precursor. Subsequently, the α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+} core (0.5 mmol) in hexane, 7 mL oleic acid and 7 mL octadecene were all added into the flask. The mixture was then heated at 80 °C for 30 min to remove hexane, degassed at 120 °C for 30, and finally heated, at a rate of~15 °C/min, to 300 °C for 45 minutes. After naturally cooling down to room temperature, the solution was added with 10 mL ethanol, and centrifuged at 7500 rpm for 5 minutes. The precipitate was finally dispersed in 10 mL hexane for further uses.

Step3. Synthesis of α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+}@CaF_2:30%Nd^{3+}@CaF_2:20%Yb^{3+}, 5%Er^{3+}, 1%Nd^{3+} sandwich-structured core/shell/shell nanoparticles: The $Ca(CF_3COO)_2$, $Yb(CF_3COO)_3$, $Er(CF_3COO)_3$ and $Nd(CF_3COO)_3$ precursor was first prepared by mixing $Ca(OH)_2$ (2 mmol), Yb_2O_3, Er_2O_3 and Nd_2O_3 with 50% concentrated trifluoroacetic acid, refluxing at 95°C to yield a clear solution, and being evaporated to dryness under argon gas purge in a three-neck flask. Subsequently, the α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+}@CaF_2:30%Nd^{3+} core/shell (0.5 mmol) in hexane, 7 mL oleic acid and 7 mL octadecene were added into the flask. After that, the mixture was heated at 80 °C for 30 min to remove hexane, and then degassed at 120 °C for 30 min under argon gas protection. Lastly, the resulting solution were heated to 300 °C at a rate of ~15 °C/min and kept at this temperature for 45 minutes before naturally cooling down to room temperature. 10 mL ethanol was then added into the solution to precipitate the nanocrystals, followed by centrifugation at 7500 rpm for 5 minutes. The resulting precipitate was finally dispersed in 10 mL hexane for further uses.

TWEEN modification of sandwich-strucured UCNPs. In a typical process, 100 μL of TWEEN 20 was added into a 20 mL flask containing 5 ml of sandwich-structured UCNPs (2mg/ml) hexane solution, and the solution was ultrasonicated for 10 min at room temperature. Then, 10 mL of deionized water were poured in the flask and the dispersion was kept in a 80 °C water bath for 3 h. During this period, the hexane was evaporated and these UCNPs were gradually transferred into the water. The TWEEN coated UCNPs were obtained by centrifugation at 13000 rpm for 20 minutes.

Characterization. The powder X-Ray diffraction (XRD) pattern was carried out on a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Kα source (λ=0.154056 nm). The 2θ angle of the XRD spectra was recorded at a scanning rate of 5°/min. The size and morphology of colloidal α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+} core, α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+}@CaF_2:30%Nd^{3+}core/shell, and α-$NaYbF_4$:0.5%Tm^{3+},1%Nd^{3+} @CaF_2:30%Nd^{3+}@CaF_2:20%Yb^{3+},5%Er^{3+},1%Nd^{3+} sandwich-structured core/shell/shell nanoparticles were characterized by transmission electron microscope (TEM, Tecnai G2 Spirit Twin 12) operating at 200 kV. The data of the size distributions was obtained through evaluation of ~200 nanocrystals in the TEM image. Upconversion luminescence (UCL) spectra were recorded using a calibrated Fluorolog-3.11 Jobin Yvon spectrofluorometer. The UCL signal of the sample in the cuvette was collected at 90° relative to the excitation light. Laser excitation of both 800 and 980 nm was provided by a Ti: Sapphire laser (Chameleon from Coherent). Photographic UCL images of colloidal nanocrystals were taken by a digital camera (Canon Power Shot SX100 IS) without adding any filter.

Supporting Figures

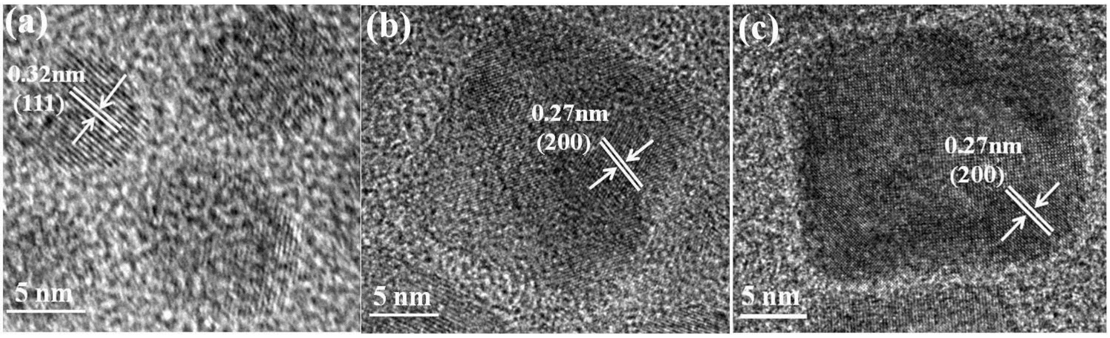


Figure S1. HRTEM images of the (a) $NaYbF_4$:Nd,Tm core, (b) $NaYbF_4$:Nd,Tm@CaF_2:Nd core/shell NPs, and (c) $NaYbF_4$:Nd,Tm@CaF_2:Nd@CaF_2:Nd,Yb,Er sandwich-structured core/shell/shell NPs.

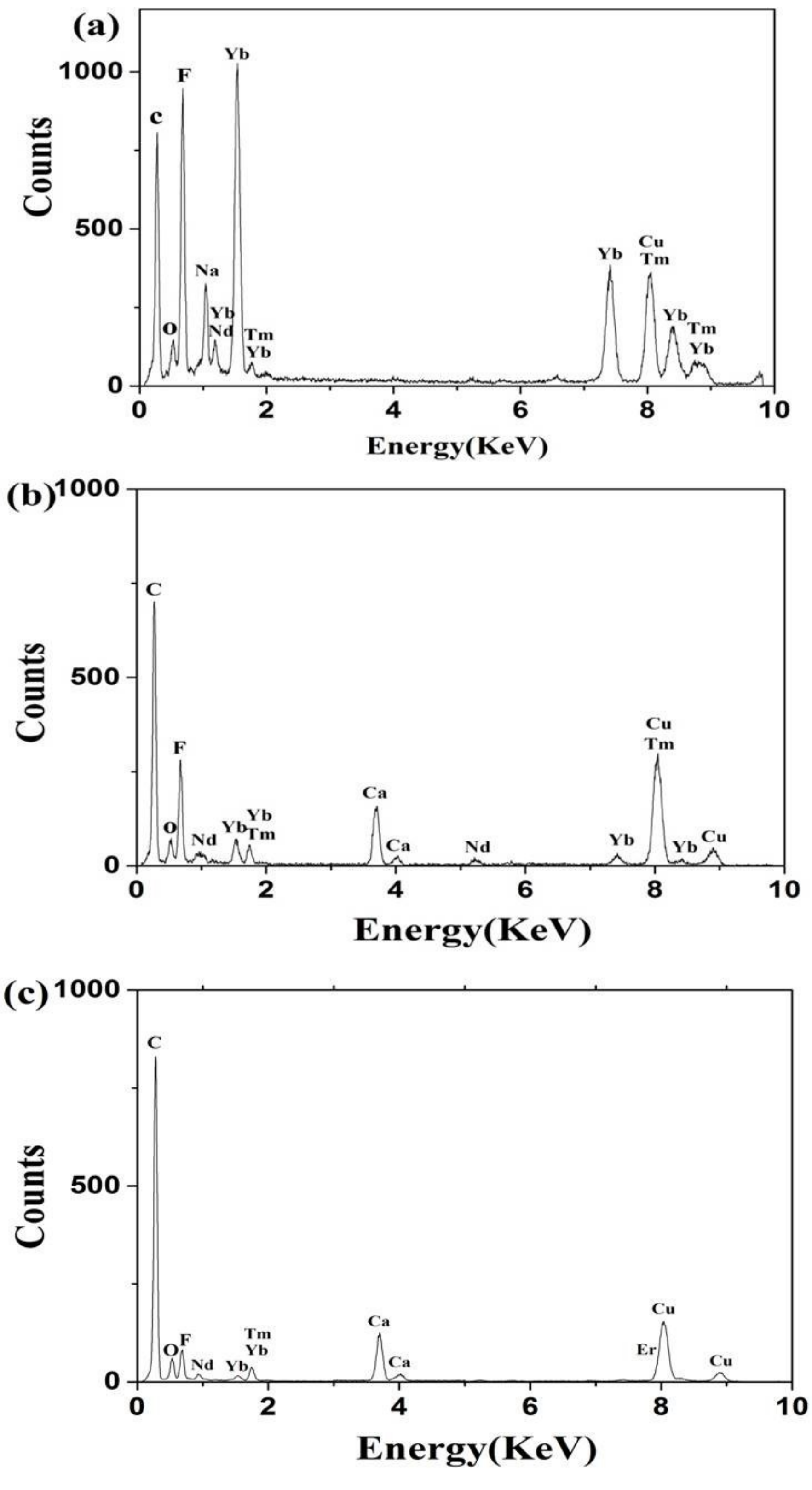


Figure S2 Energy-dispersive X-ray spectra (EDX) of the (a) NaYbF$_4$:Nd,Tm core, (b) NaYbF$_4$:Nd,Tm@CaF$_2$:Nd core/shell, and (c) NaYbF$_4$:Nd,Tm@CaF$_2$:Nd@CaF$_2$:Nd,Yb,Er sandwich-structured core/shell/shell NPs.

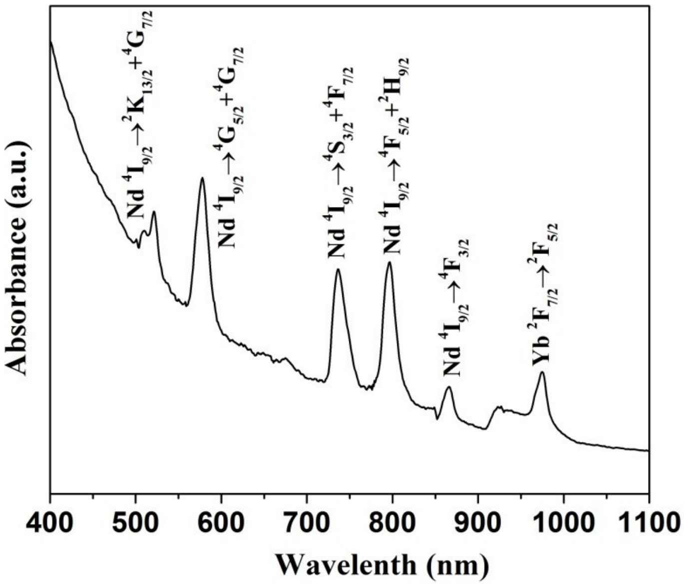


Figure S3. The absorption spectrum of the sandwich-structured $NaYbF_4$: 0.5%Tm, 1%Nd@CaF_2:30%Nd@ CaF_2:20%Yb,2%Er,1%Nd core/shell/shell UCNPs. A strong absorption peak at 800 nm was observed, corresponding to the ground state absorption of the $^4I_{9/2}\rightarrow{}^4F_{5/2}/{}^2H_{9/2}$ transition of Nd^{3+} ions.

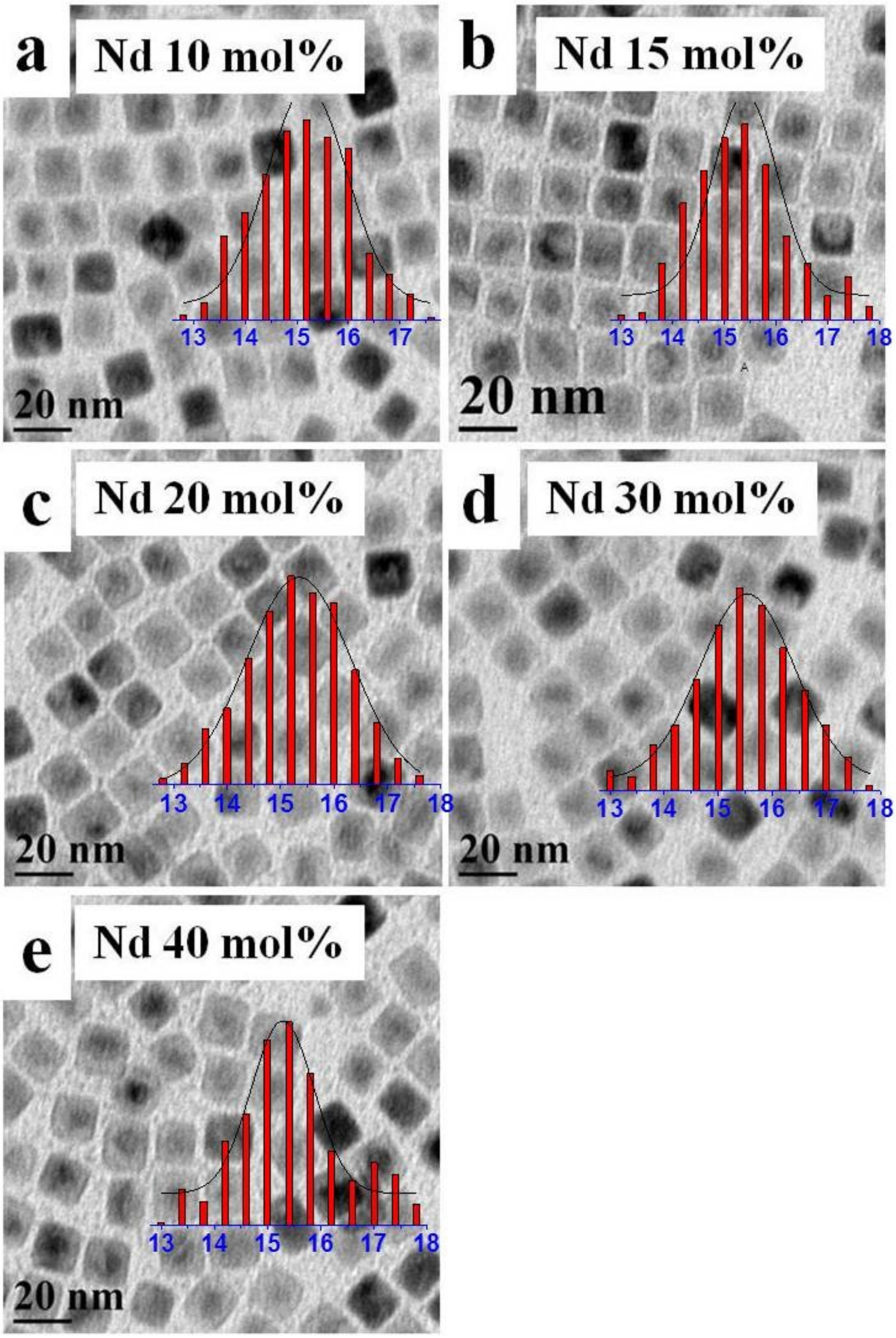


Figure S4. TEM images of $NaYbF_4$:0.5%Tm,1%Nd@CaF_2:Nd core/shell UCNPs with Nd^{3+} concentration of (a) 10%, (b) 15%, (c) 20%, (d) 30% and (e) 40% in the CaF_2 shell, respectively. From these images, one can see that the as-prepared core/shell UCNPs all have uniform cubic shape with an average side length of ~ 15.2 nm.

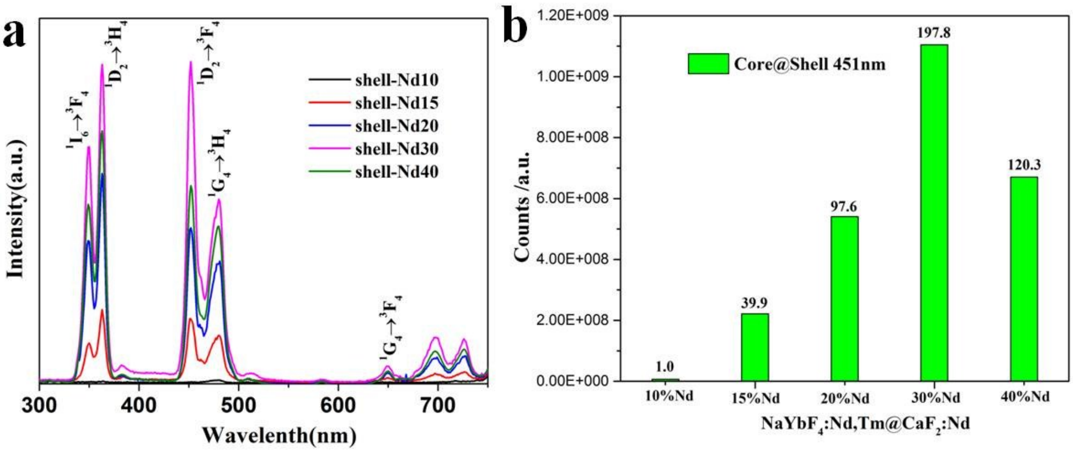
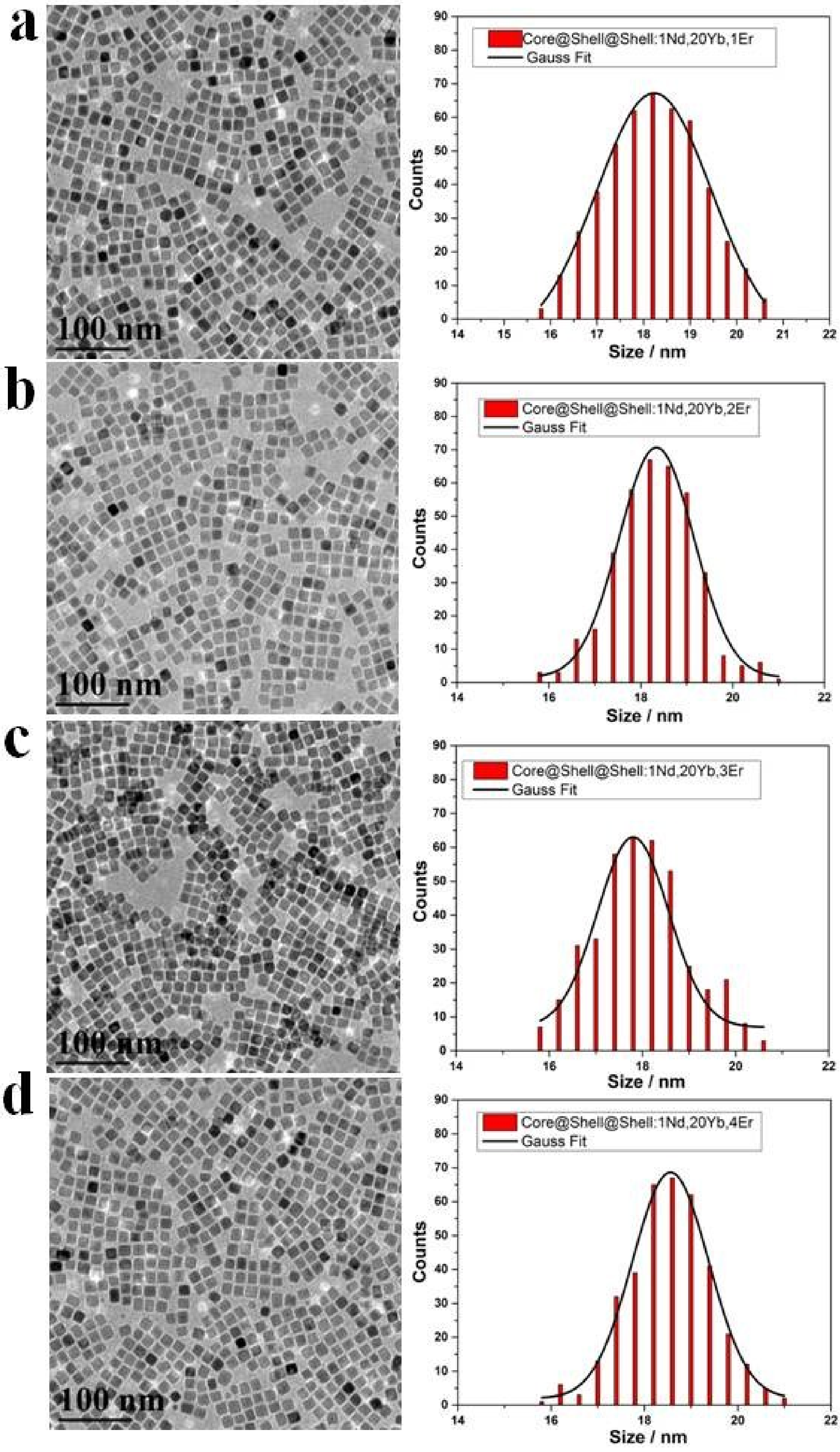


Figure S5. (a) The UCL spectra from $NaYbF_4$:0.5%Tm,1%Nd@CaF_2:Nd x% core/shell/shell UCNPs (x=10, 15, 20, 30, and 40). (b) The UCL peak intensity at 451 of the $^1D_2 \rightarrow ^3F_4$ of Tm from $NaYbF_4$:0.5%Tm,1%Nd@CaF_2:Nd x% UCNPs (x=10, 15, 20, 30, and 40). Excitation at 800 nm of 6.0 W/cm^2. The optimized Nd content was determined to be 30%, achieving 197.8-fold enhancement when compared with the sample doped with 10% Nd^{3+} in shell.


a
100 nm
Core@Shell@Shell:1Nd,20Yb,1Er
Gauss Fit
Counts
Size / nm
0
10
20
30
40
50
60
70
80
90
14
15
16
17
18
19
20
21
22
b
100 nm
Core@Shell@Shell:1Nd,20Yb,2Er
Gauss Fit
Counts
Size / nm
0
10
20
30
40
50
60
70
80
90
14
16
18
20
22
c
100 nm
Core@Shell@Shell:1Nd,20Yb,3Er
Gauss Fit
Counts
Size / nm
0
10
20
30
40
50
60
70
80
90
14
16
18
20
22
d
100 nm
Core@Shell@Shell:1Nd,20Yb,4Er
Gauss Fit
Counts
Size / nm
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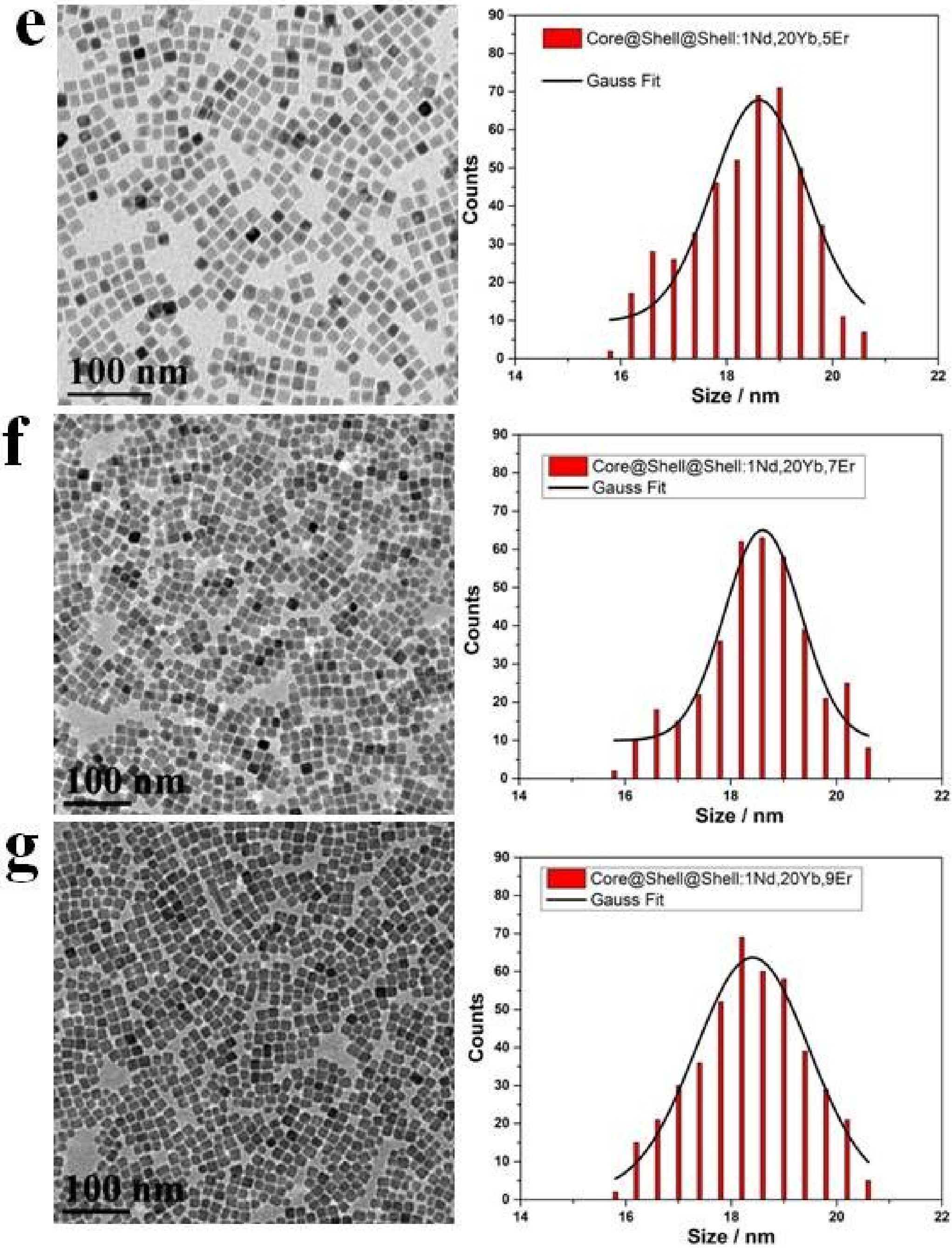

Figure S6. TEM images and size distributions of $NaYbF_4$:0.5Tm,1Nd@CaF_2:30Nd @CaF_2:1Nd,20Yb,Er sandwich-structured core/shell/shell UCNPs. The Er^{3+} doping level in the outmost layer was (a) 1%, (b) 2%, (c) 3%, (d) 4%, (e) 5%, (f) 7 %, and (g) 9%, respectively. It can be seen that all the obtained sandwich-structured UCNPs have a uniform cubic shape with an average side length of ~ 18.4 nm.

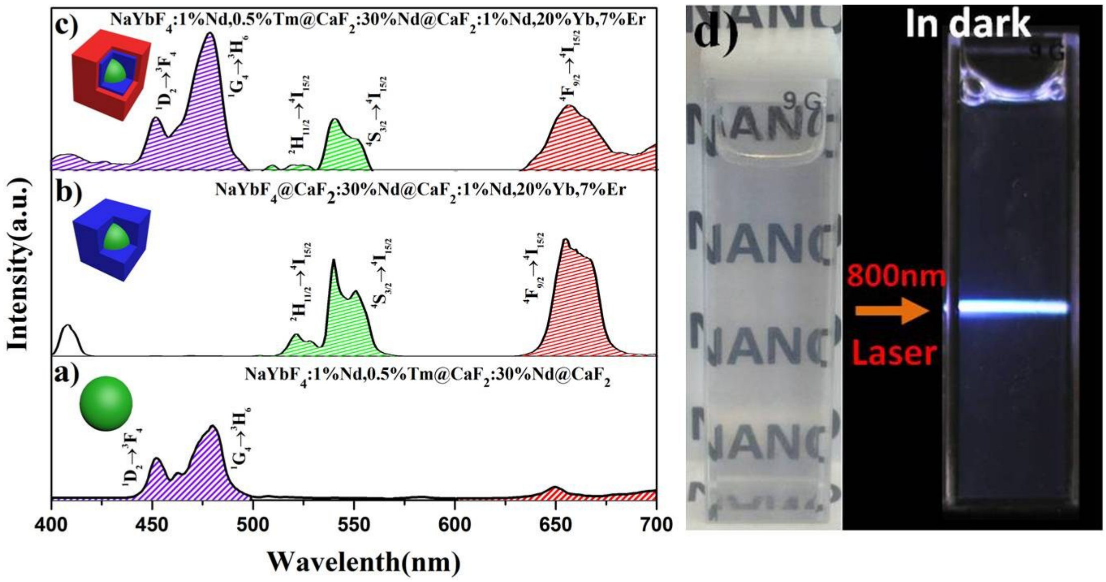

Figure S7. UCL spectra of a) $NaYbF_4$:1%Nd,0.5%Tm@CaF_2:30%Nd@CaF_2, b) $NaYbF_4$ @CaF_2:30%Nd@CaF_2:1%Nd,20%Yb,7%Er, and c) $NaYbF_4$:1%Nd,0.5%Tm@CaF_2:30%Nd CaF_2:1%Nd,20%Yb,7%Er UCNPs (hexane dispersion). (d) Photographic (left) and UCL (right) images of $NaYbF_4$:1%Nd,0.5%Tm@CaF_2:30%Nd@CaF_2:1%Nd,20%Yb,7%Er nanoparticles (hexane dispersion). Excitation at 800 nm of 6.0 W/cm^2. As one can see in (d), bright white UCL was obtained from the sandwiched core/shell/shell $NaYbF_4$:1%Nd,0.5%Tm@CaF_2:30%Nd CaF_2:1%Nd,20%Yb,7%Er UCNPs. This white UCL is produced through mixing blue UCL at 451 and 476 nm from Yb/Tm ion pair in the core, as well as the green at 540 nm and the red at 660 nm from the Yb/Er pair in the outmost shell layer (see Figure S5 a-c).

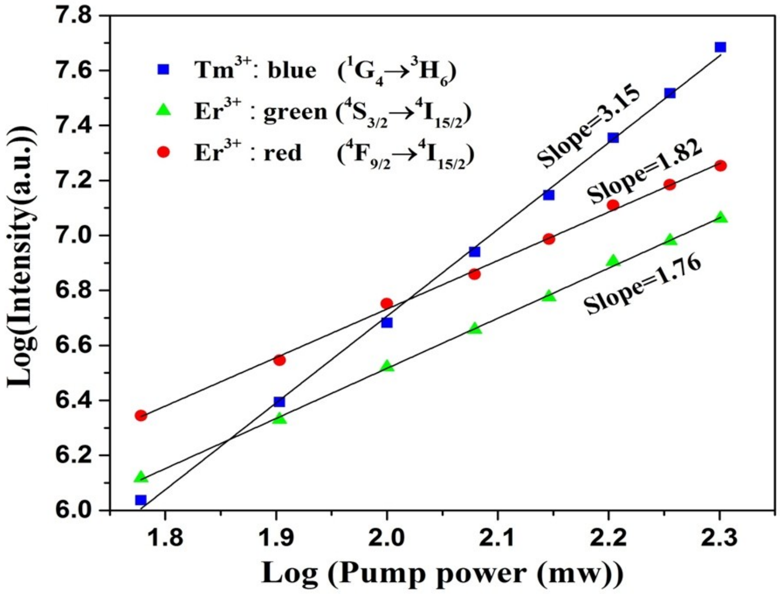

Figure S8. The dependence of the intensities of UCL at 480 nm (Tm), 540 nm (Er) and 660 nm (Er) on the excitation power in colloidal $NaYbF_4$:0.5Tm,1Nd@CaF_2:30Nd@CaF_2: 1Nd,20Yb,7Er UCNPs. The number of photon process can be derived from the relation, $I_f \propto P^n$, where I_f is the fluorescent intensity, P is the pump laser power and n is the number of the laser photons required to populate the upper emitting state under unsaturated condition. The value of n can be obtained from the slope of the fitting line in the plot of log I_f versus log p. A slope value of 3.15, 1.82, and 1.76 are observed for the blue emisson (Tm), green emission (Er) , and red emission (Er), illustrating an involvement of three-, two- and two-photon process in the generation of UCL at 480 nm, 540 nm and 660 nm, respectively.

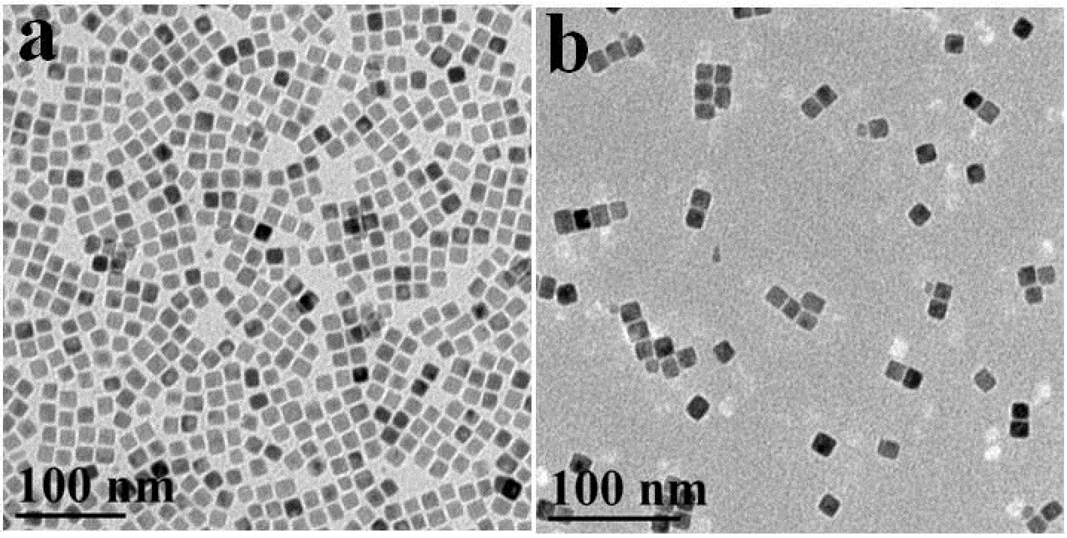

Figure S9. TEM images of NaYbF$_4$:0.5Tm,1Nd@CaF$_2$:30Nd@CaF$_2$:1Nd,20Yb,7Er UCNPs (a) before and (b) after TWEEN 20 modification. The result shows that surface modification does not affect their size and shape.

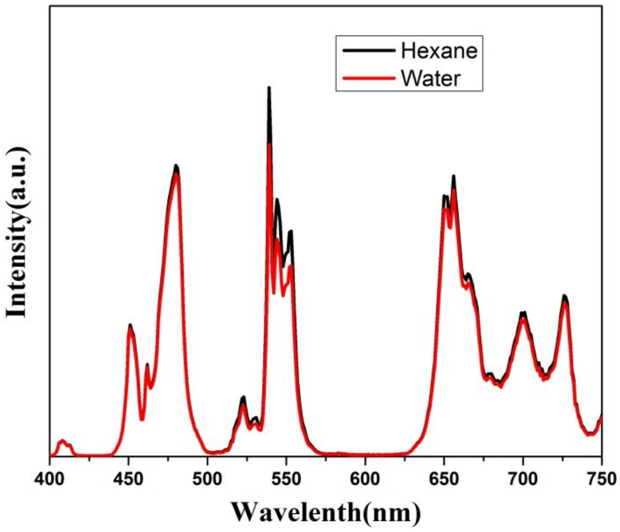

Figure S10. UCL spectra of NaYbF$_4$:0.5Tm,1Nd@CaF$_2$:30Nd@CaF$_2$:1Nd,20Yb,7Er sandwich-structured UCNPs dispersed in both hexane (black, before phase transfer) and water (red, after phase transfer). Excited at 800 nm of 6 W/cm^2. The phase transfer process of UCNPs from hexane to aqueous environment was implemented through surface modification with TWEEN 20 using the protocol described earlier. As one can see, the UCL intensity remains almost unchanged after the phase transfer process.