

## Supporting Information

### Sensitizer-rich core-shell-shell upconversion nanoparticles for enhancing luminescence by spatial separation

Yujiao Zhang<sup>a</sup>, Pengli Wang<sup>b</sup>, Jiabin Li<sup>b</sup>, Jia Geng<sup>\*a</sup>, Cuisong Zhou<sup>\*b</sup>

<sup>a</sup>State Key Laboratory of Biotherapy, West China Hospital, Sichuan University, Chengdu 610041, P. R. China

\*Email: geng.jia@scu.edu.cn

<sup>b</sup>College of Chemistry, Sichuan University, Chengdu 610064, P. R. China

\*Email: zcs@scu.edu.cn

#### Experimental

##### Materials.

Yttrium oxide (Y<sub>2</sub>O<sub>3</sub>), ytterbium oxide (Yb<sub>2</sub>O<sub>3</sub>), erbium oxide (Er<sub>2</sub>O<sub>3</sub>), gadolinium oxide (Gd<sub>2</sub>O<sub>3</sub>), sodium oleate (NaC<sub>18</sub>H<sub>33</sub>O<sub>2</sub>) and sodium trifluoroacetate (NaCF<sub>3</sub>COO) were purchased from Shanghai Macklin's Biochemical Technology Co. Ltd. 90% 1-octadecene (ODE), 90% oleic acid (OA), and 70% oleylamine were purchased from Aladdin. Ammonium fluoride (NH<sub>4</sub>F), cyclohexane and acetone were purchased from Chengdu Kelong Chemical Co., Ltd. Ethanol was purchased from Chengdu Jinshan Co., Ltd. All chemicals are used directly without further purification.

LnCl<sub>3</sub> (Ln=Yb, Er, Y and Gd) and Ln (AC)<sub>3</sub> (Ln=Er, Y and Gd) were obtained by dissolving their corresponding metal oxides with hydrochloric acid or acetic acid and then evaporating the water completely.

##### Characterization.

Powder X-ray diffraction (XRD) data were obtained using a Shimadzu XRD-6100 diffractometer with Cu-Kα radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 30 mA. The

morphology and size of the as-prepared UCNPs were determined on JEOL 2100 Plus transmission electron microscopy (TEM). The up-conversion luminescence emission spectra were recorded on F-7000 fluorescence spectrophotometer, which attached to a 980 nm laser (MDL-XF-980-10W) purchasing from Changchun New Industry. Unless otherwise specified, the test conditions were as follows (concentration: 10 mg/mL; power: 50 mW; solvent: cyclohexane). The UC emission enhancement factor (EF) is defined as the ratio of the integrated intensity of the red/green UC emission under the different power excitation to the intensity under 50 mW. Fluorescence lifetime decay was taken on Fluorolog-3 steady-state transient near-infrared micro-fluorescence spectrometer under 980 nm irradiation. The ultraviolet–visible (UV–vis) absorption and Fourier infrared spectrum were obtained on a U-2900 ultraviolet–visible spectrophotometer and a Nicolet-6700 Fourier infrared spectrophotometer, respectively.

#### **Synthesis of NaYF<sub>4</sub>:x%Yb cores of CSS (x=20, 40, 60, 80, 100).**

A mixture of YbCl<sub>3</sub> (0.4/0.8/1.2/1.6/2 mmol), YCl<sub>3</sub>(1.6/1.2/0.8/0.4/0 mmol), OA (18.25 mL), and ODE (20 mL) was put in a 100 mL three necked flask. The flask was stirred under vacuum and heated to 110 °C for 1 h. 6.25 mmol of sodium oleate, 10.9 mmol of NH<sub>4</sub>F, 6.25 mL of oleyl amine and 8.75 mL of ODE were added after the flask cooled to 30 °C. The flask was placed in a vacuum again and stirred at room temperature for 30 min. Then, the flask was heated rapidly to 315 °C in a nitrogen atmosphere for 45 min. After rapid cooling, the reactant was transferred to five centrifuge tubes containing 200 mL mixture (ethanol and acetone, v:v=1:1) to be precipitated the nanoparticles and then centrifuged at 7500 rpm for 10 min. Subsequently, the white products were dispersed in 25 mL of cyclohexane and then centrifuged and washed with ethanol. Finally, the nanoparticles were dispersed in 50 mL of cyclohexane.

#### **Synthesis of NaYF<sub>4</sub>:x%Yb,20%Gd,2%Er core UCNPs for CS (x=5, 10, 20, 40, 78).**

YCl<sub>3</sub> (1.46/1.36/1.16/0.76/0mmol), ErCl<sub>3</sub> (0.04 mmol), YbCl<sub>3</sub> (0.1/0.2/0.4/0.8/1.56 mmol), GdCl<sub>3</sub> (0.4 mmol),16.25 mL of OA, and 20 mL of ODE were put into a

50 mL flask. The mixture was vigorously stirred under vacuum and then slowly heated to 110 °C for 1 h. The flask was then cooled to 30 °C and then 6.25 mmol (5 mmol) of sodium oleate, 10 mmol (8 mmol) of  $\text{NH}_4\text{F}$ , 6.25 mL (5 mL) of oleyl amine and 8.75 mL (7 mL) of ODE were added. Vacuum was pulled again for 30 min, then the flask was cycled with nitrogen gas three times prior to heating rapidly to 315 °C for 45 min and then the flask was quickly cooled to 75 °C. The specific washing process is consistent with the  $\text{NaYbF}_4$  core in CSS structure.

### **Synthesis of $\text{NaYF}_4$ :20%Yb,20%Gd,2%Er, $\text{NaYF}_4$ :20%Yb,20%Gd and $\text{NaYF}_4$ :2%Er,20%Gd Cores.**

Synthesis of the three core UCNPs was similar to the above procedures, but the lanthanide chloride was changed accordingly. 0.0928 mmol of  $\text{YCl}_3$ , 0.0032 mmol of  $\text{ErCl}_3$ , 0.032 mmol of  $\text{YbCl}_3$  and 0.032 mmol of  $\text{GdCl}_3$  were used for  $\text{NaYF}_4$ :20%Yb core. 0.032 mmol of  $\text{YbCl}_3$ , 0.032 mmol of  $\text{GdCl}_3$  and 0.096 mmol of  $\text{YCl}_3$  were used for  $\text{NaYF}_4$ :20%Yb,2%Er,20%Gd. And 0.032 mmol of  $\text{GdCl}_3$ , 0.0032 mmol of  $\text{ErCl}_3$  and 0.1248 mmol of  $\text{YCl}_3$  were used for  $\text{NaYF}_4$ :2%Er,20%Gd core.

### **Preparation of Shell Precursors.**

0.1 mol/L OA-Ln: 2.5 mmol of acetic acid Ln (Ln= Y, Er, Yb, Gd), 10 mL of OA, and 15 mL of ODE were added to a 50 mL three necked flask. The flask was stirred vigorously under vacuum and slowly heated to 110 °C for 15 min and then the temperature was fixed at 160 °C until dissolved.

0.4 mol/L Na-TFA-OA: 45 mL of OA and 18 mmol of sodium trifluoroacetate were added to a 100 mL flask. The solution was vigorously stirred under vacuum at room temperature until dissolved.

### **Synthesis of Core-shell-shell or Core-shell UCNPs by Using the Successive Layer-by-Layer (SLBL) Method**

Stock  $\text{NaYbF}_4$  core nanoparticles (2.7 mL), OA (4 mL) and ODE (6 mL) were added into a 50 mL flask and stirred violently under vacuum and was heated to 70 °C for 30 min. Nitrogen gas was introduced all the time and the mixture was heated at 300 °C for 5 min, before the injection table below was followed (Table S1). Each cycle included injections of Ln oleate solution with a waiting time of 15 minutes and

sodium trifluoroacetate solution. The first four cycles were carried out to fabricate the middle shell, and the last 4, 6, 8 or 10 cycles were to fabricate the inert shell. In each cycle of middle shells, the proportion of Er, Y and Gd was x%, (80-x) % and 20%, respectively. In each cycle of inert shells, the proportion of Y and Gd was 80% and 20%, respectively. After being held at 300 °C for 30 min, the flask was rapidly cooled to 75 °C and centrifuged at 7500 rpm for 10 min after adding a 30 mL mixture (ethanol and acetone, v:v=1:1). The nanoparticles were dissolved in 5 mL cyclohexane, added with 35 mL of ethanol and centrifuged at 7500 rpm for 10 min. Finally, the nanoparticles were dissolved in cyclohexane (5 mL).

Table S1: Shell precursor injections

Cycle number	1	2	3	4	5	6	7	8	9	10
Ln-OA (mL)	0.28	0.36	0.44	0.52	0.62	0.72	0.83	0.95	1.07	1.19
Na-TFA-OA (mL)	0.14	0.18	0.22	0.26	0.31	0.36	0.42	0.48	0.54	0.60

### Fabrication of the UCL membrane

Ligand exchange: In detail, 5 mL of CSS UCNPs dispersed in cyclohexane was added to 5 mL of DMF. Afterward, 0.05 mmol NOBF<sub>4</sub> solids were added and stirred for 60 min. Then the mixed solution was transferred to a centrifuge tube and centrifuged at 12000 rpm for 20 min, the product was redispersed in DMF (5 mL).

Approximately 0.4 g of PS powder (Mw=350 000) was dissolved into 2 ml of the above CSS/DMF solution. This composite solution was then transferred to a plastic syringe for electrospinning. The applied negative voltage was fixed at 10 kV and the collection distance was closed at 15 cm. The temperature and humidity were 27 °C and 30%, respectively.

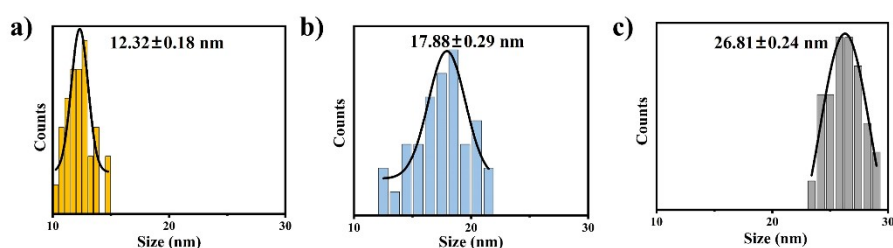


Figure S1. Size distribution of the core (a), the core-shell (b), and the final CSS UCNPs (c).

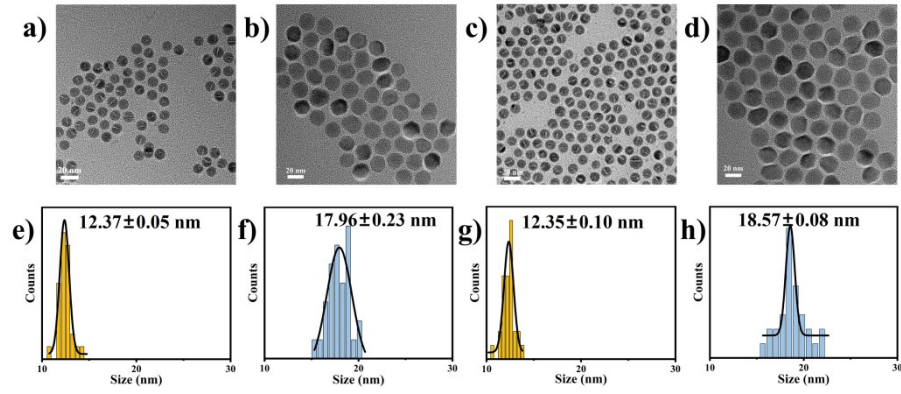


Figure S2. TEM images and size distribution diagrams of the core (a, e) and the core-shell (b, f) of Yb@Er@Y, and the core (c, g) and the core-shell of Er@Yb@Y (d, h).

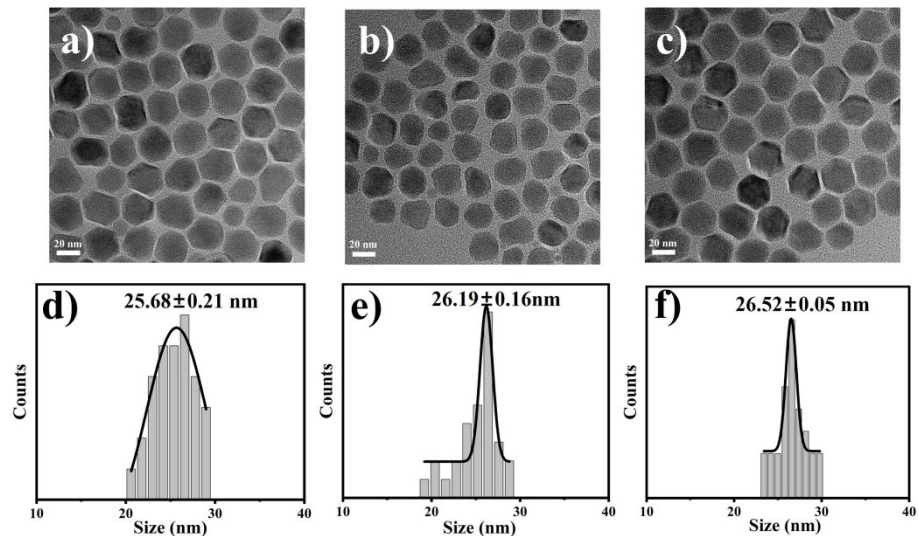


Figure S3. TEM images and size distribution diagrams of Yb@Er@Y (a, d), Yb,Er@Y (b, e) and Er@Yb@Y (c, f).

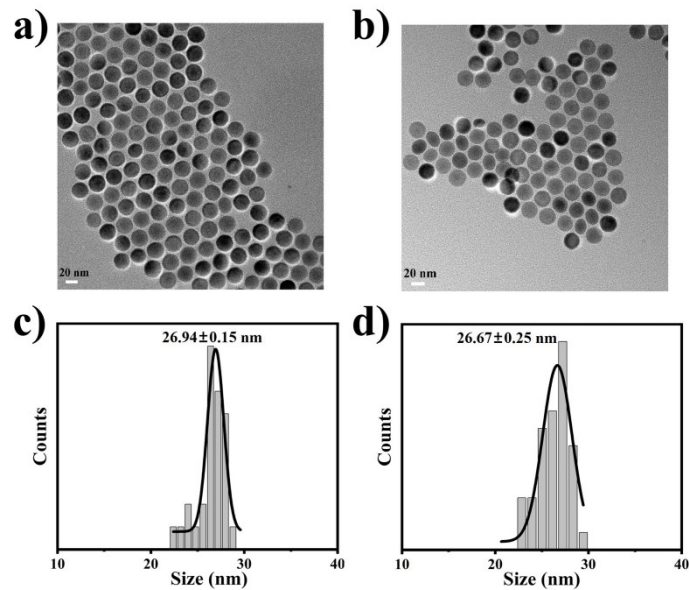


Figure S4. TEM images and size distribution diagrams of  $\text{NaYF}_4:20\%\text{Yb}@$   
 $\text{NaYF}_4:2\%\text{Er},20\%\text{Gd}@$  $\text{NaYF}_4:20\%\text{Gd}$  (a, c) and of  $\text{NaYF}_4:60\%\text{Yb}@$  $\text{NaYF}_4:2\%\text{Er},$   
 $20\%\text{Gd}@$  $\text{NaYF}_4:20\%\text{Gd}$  (b, d).

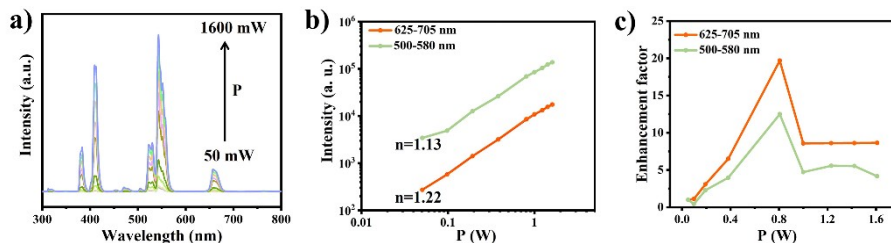


Figure S5. Up-conversion emission spectra of CSS UCNPs after irradiation with a 980 nm laser at different powers (concentration: 0.1 mg/mL) (a); Power-dependent red and green UC emission integrated intensity under 980 nm excitation (b); UC emission enhancement factor (EF) of CSS UCNPs measured at different power excitation (c).

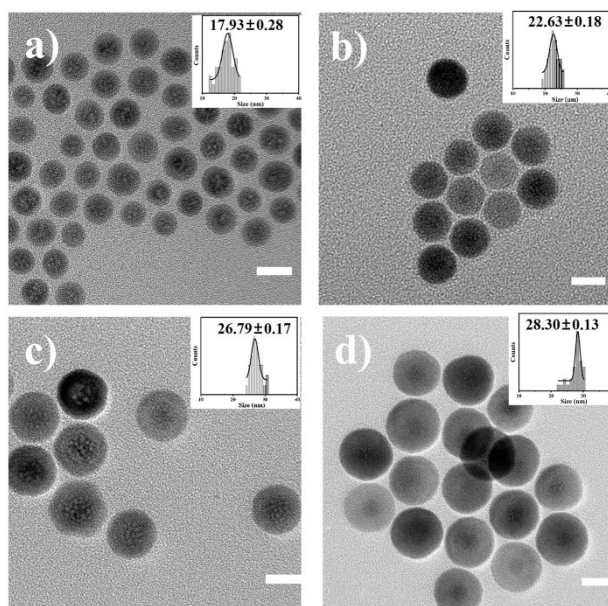


Figure S6 TEM and size distribution of CSS structure with different thicknesses of inert shells (a-d). All scale bars are 20 nm.

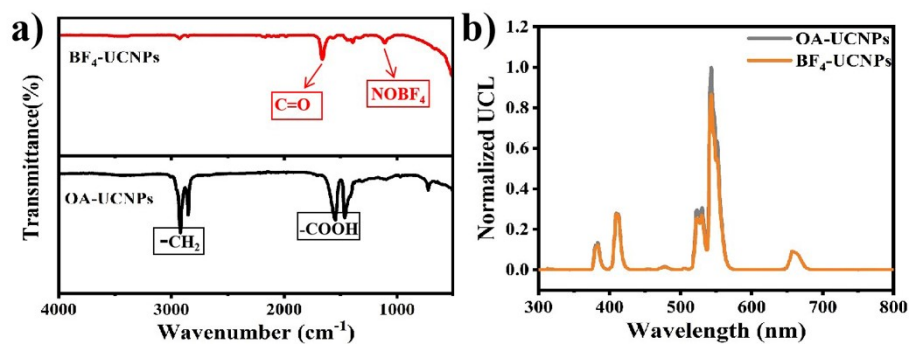


Figure S7. (a) FT-IR spectra of OA-UCNPs and  $\text{BF}_4\text{-UCNPs}$ . (b) Upconversion emission spectra of CSS UCNPs before and after the  $\text{NOBF}_4$  treatment (980 nm, 50 mW).