Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Protected excitation-energy reservoir for efficient upconversion luminescence

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Experimental Details

Reagents: YCl_3•$6H_2O$ (99.9%), $YbCl_3$•$6H_2O$ (99.9%), $ErCl_3$•$6H_2O$ (99.9%), $GdCl_3$•$6H_2O$ (99.9%), NaOH (98+%), NH_4F (98+%), 1-octadecene (90%), oleic acid (OA) (90 %), Rose bengal (Dye content 95 %), IGEPAL® CO-520 (average Mn 441), (3-aminopropyl) triethoxysilane (APTES) (99%), tetraethyl orthosilicate (TEOS) (98%), N-(3-Dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC) (98%), N-Hydroxysuccinimide (NHS) (98%) were purchased from Sigma-Aldrich and used as received without further purification.

Synthesis of $NaYF_4$:Yb,Er UCNPs**:** $NaYF_4$: 20%Yb, 2%Er nanoparticles were synthesized following a previously reported protocol with modifications[1]. YCl_3 (0.78 mmol), $YbCl_3$ (0.20 mmol) and ErCl3 (0.02 mmol) were mixed with 6 mL of oleic acid and 15 mL of 1-octadecene in a 100 mL flask. The solution was heated to 150 °C to form a homogenous solution and then cooled down to room temperature. A solution of 4 mmol NH_4F and 2.5 mmol NaOH in 10 mL of methanol was added to the flask and stirred for 30 min. Subsequently, the solution was heated to 100 °C to remove the methanol. After methanol was evaporated, the solution was heated to 300 °C and incubated at that temperature for 1 hour under an argon atmosphere and then cooled to room temperature. The UCNPs were precipitated with 10 mL of acetone, collected after centrifugation, then washed thrice with ethanol/water (1:1 v/v) and finally dispersed in cyclohexane for subsequent use.

Synthesis of $NaYF_4$:Yb@$NaYF_4$:Er core-shell UCNPs*:* $NaYF_4$:Yb@$NaYF_4$:Er core-shell UCNPs were synthesized through two-step synthesis, in which the $NaYF_4$:Yb core UCNPs were synthesized in the first step, followed by a growth of the $NaYF_4$:Er shell onto the as-prepared core UCNPs in the second step.

Typically, $NaYF_4$:20%Yb core UCNPs were synthesized following a previously reported protocol with modifications[1]. YCl_3 (0.80 mmol) and $YbCl_3$ (0.20 mmol) were mixed with 6 mL oleic acid and 15 mL 1-octadecene in a 100 mL flask. The solution was heated to 150 °C to form a homogenous solution and then cooled down to room temperature. A solution of 4 mmol NH_4F and 2.5 mmol NaOH in 10 mL of methanol was added to the flask and stirred for 30 min. Subsequently, the solution was heated to 100 °C to remove the methanol. After methanol was evaporated, the solution was heated to 300 °C and incubated at that temperature for 1 hour under an argon atmosphere and then cooled to room temperature. The UCNPs were precipitated with 20 mL of acetone, collected after centrifugation, then washed thrice with ethanol/water (1:1 v/v) and finally dispersed in cyclohexane for subsequent use.

The $NaYF_4$:Er shell was grown onto the as-prepared core UCNPs following a previously reported protocol with modifications[2]. In a typical synthesis of $NaYF_4$:20%Yb@$NaYF_4$:2%Er, 0.98 mmol YCl_3 and 0.02 mmol $ErCl_3$ were mixed with 6 mL oleic acid and 15 mL 1-octadecene in a 100 mL flask. The solution was heated to 150 °C to form a homogenous solution and then cooled down to room temperature. A suspension of the $NaYF_4$:20%Yb core nanocrystals dispersed in cyclohexane that obtained from the previous step was added to the flask. The solution was maintained at 110 °C to remove the cyclohexane solvent and then subsequently cooled down to room temperature. A solution of 4 mmol NH_4F and 2.5 mmol NaOH in 10 mL of methanol was added to the flask and stirred for 30 min. Subsequently, the solution was heated to 100 °C to remove the methanol. After methanol was evaporated, the solution was heated to 300 °C and incubated at that temperature for 1 hour under an argon atmosphere and then cooled to room temperature. The nanocrystals were precipitated with 10 mL of acetone, collected after centrifugation, then washed thrice with ethanol/water (1:1 v/v) and finally dispersed in cyclohexane for subsequent use.

Synthesis of $NaYF_4$:Er@$NaYF_4$:Yb core-shell UCNPs: Synthesis of $NaYF_4$:Er core UCNPs and coating of $NaYF_4$:Yb onto the core UCNPs were similar to the synthesis above but the lanthanides chloride was changed accordingly.

Synthesis of $NaYF_4$:Yb@$NaYF_4$:Yb,Er core-shell UCNPs with enhanced doping concentration: Synthesis of $NaYF_4$:Yb@$NaYF_4$:Er core-shell UCNPs with enhanced doping concentration were similar to the synthesis above but the amount of lanthanides chloride was changed accordingly. In order to keep similar size of the $NaYF_4$:Yb core UCNPs doped with different concentrations of Yb^{3+}, certain amounts of Gd^{3+} were co-doped to tune and maintain the core particle size.

Nanoparticle concentration control: The same nanoparticle synthesis and post processing protocols were used throughout this study. These protocols were empirically very reliable, yielding very similar production rate of nanoparticles for all batches. The particle concentrations were accordingly controlled by considering the moles of ions added in the synthesis. Although there could be batch-to-batch variation in the synthesis, this approach for nanoparticle concentration comparison is widely accepted and adopted in the field of nanotechnology.

References

1. Li, Z.; Zhang, Y. *Nanotechnology* **2008**, 19, 345606.

2. Qian, H.-S.; Zhang, Y. *Langmuir* **2008**, 24, 12123-12125.

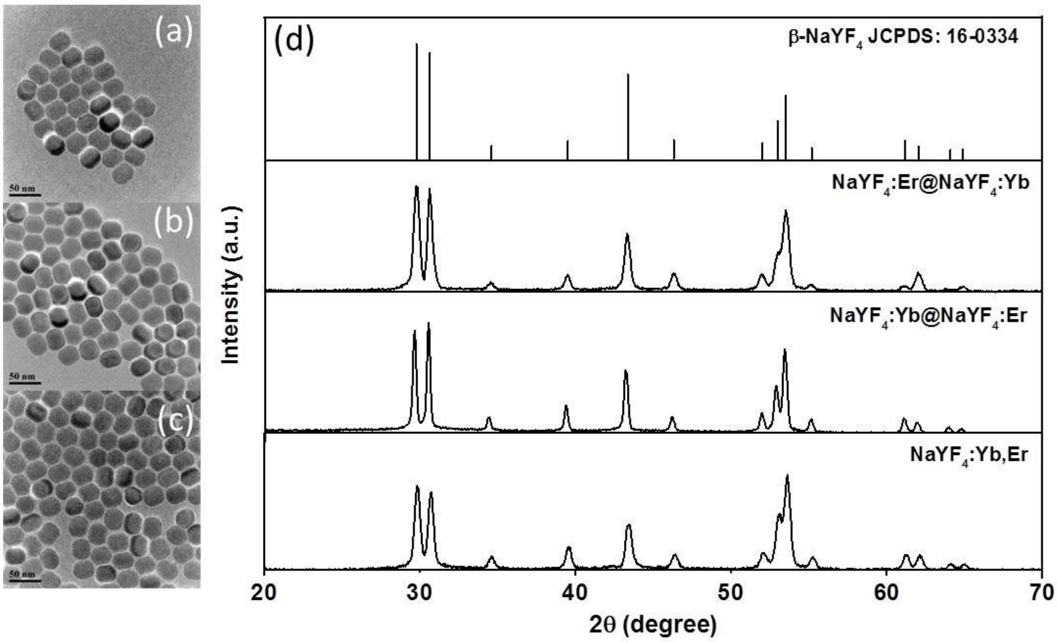


Figure S1. TEM images of (a) $NaYF_4$:2%Er@$NaYF_4$:20%Yb, (b) $NaYF_4$:20%Yb@$NaYF_4$:2%Er, and (c) $NaYF_4$:20%Yb,2%Er UCNPs. (d) XRD patterns of $NaYF_4$:2%Er@$NaYF_4$:20%Yb, $NaYF_4$:20%Yb@$NaYF_4$:2%Er, and $NaYF_4$:20%Yb,2%Er UCNPs. The diffraction pattern at the top shows the data from hexagonal $NaYF_4$ crystal (Joint Committee Powder Diffraction Standards #16-0334).

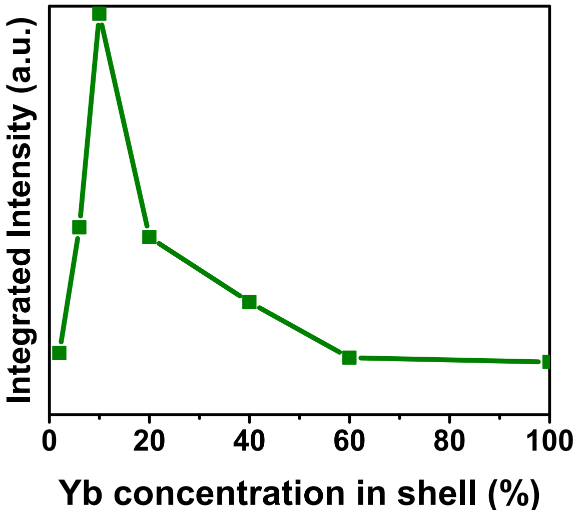


Figure S2. The dependence of the green emission intensity at 543 nm on the concentration of Yb^{3+} ions confined in the shell for Er@Yb UCNPs.

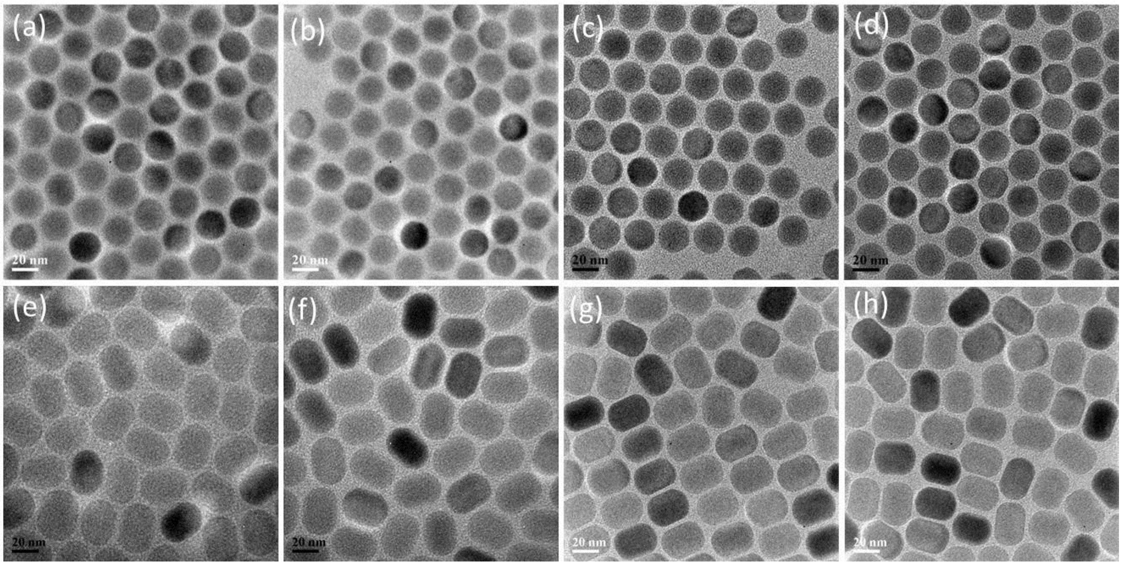


Figure S3. TEM images of (a) NaY(Gd)F_4:20%Yb, (b) NaY(Gd)F_4:30%Yb, (c) NaY(Gd)F_4:50%Yb, (d) NaY(Gd)F_4:70%Yb, (e) NaY(Gd)F_4:20%Yb@NaYF_4:2%Er, (f) NaY(Gd)F_4:30%Yb@NaYF_4:2%Er, (g) NaY(Gd)F_4:50%Yb@NaYF_4:2%Er, and (h) NaY(Gd)F_4:70%Yb@NaYF_4:2%Er upconversion nanoparticles.

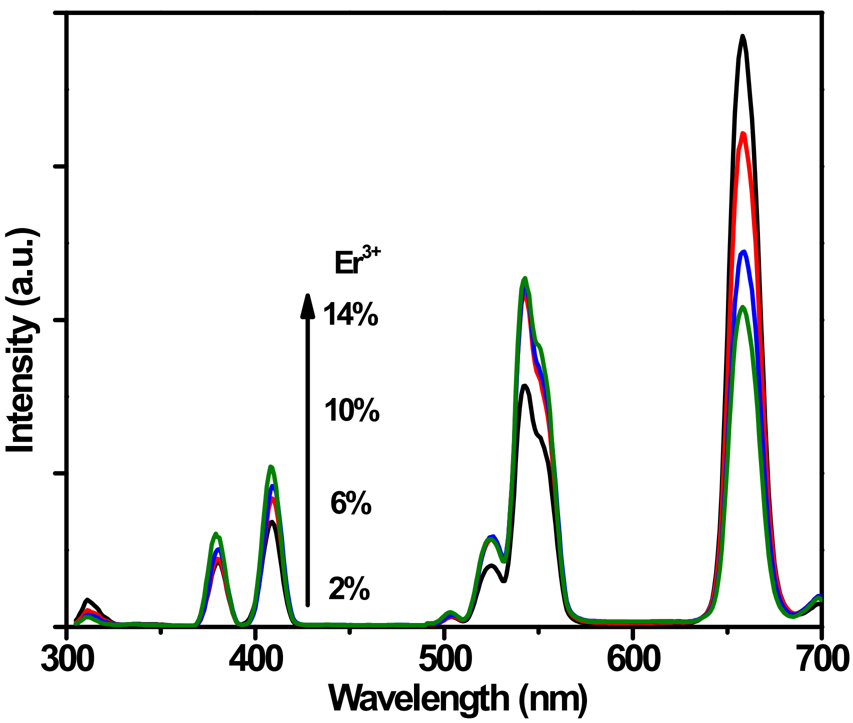


Figure S4. Photoluminescence spectra of Yb@Er UCNPs with different Er^{3+} concentration in the shell (Yb^{3+} 70% in the core).

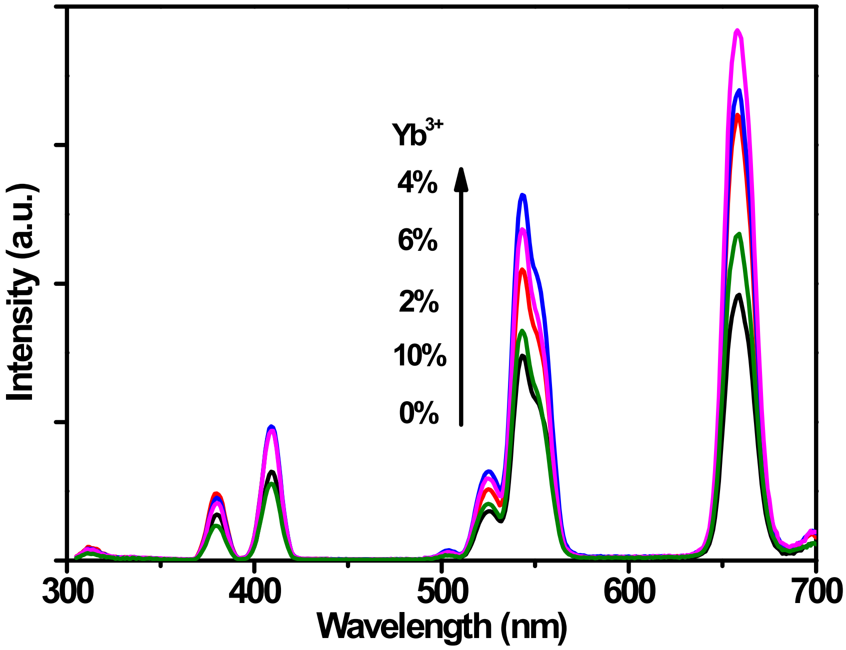


Figure S5. Photoluminescence spectra of Yb@(Yb)Er UCNPs with different bridging Yb^{3+} concentration in the shell (Yb^{3+} 70% in the core, and Er^{3+} 6% in the shell).

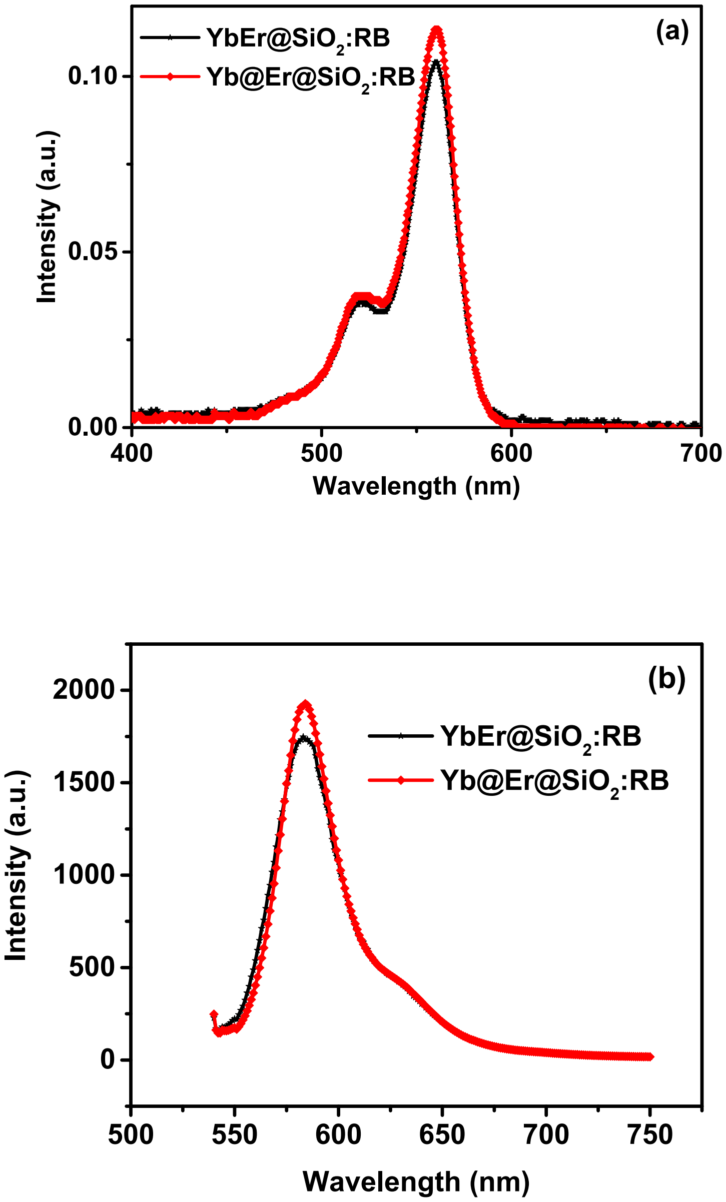


Figure S6. (a) UV-visible absorption spectra of RB-doped UCNP@SiO_2 nanospheres. (b) Photoluminescence spectra of RB-doped UCNP@SiO_2 nanospheres excited by a 532 nm continuous-wave laser.

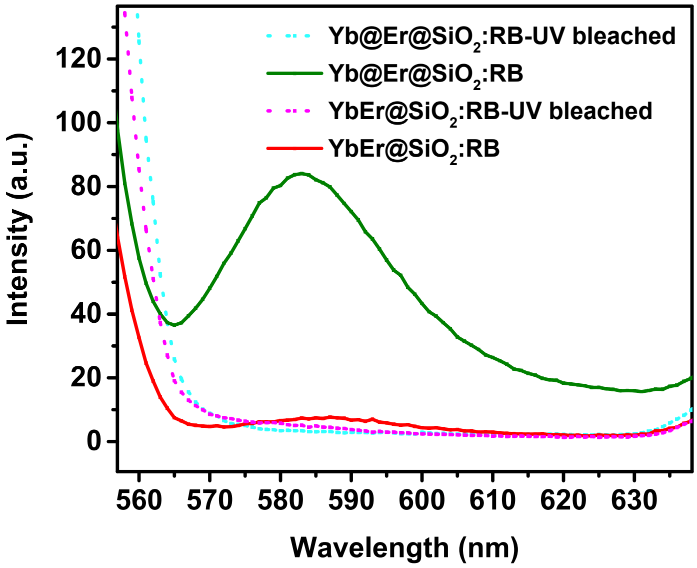
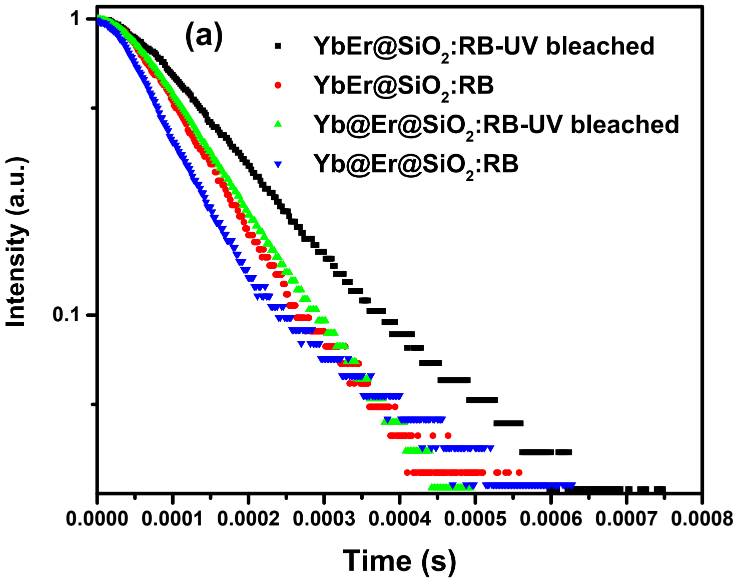


Figure S7. Photoluminescence spectra of RB-active and RB-UV-bleached UCNP@SiO2 nanospheres under excitation of 980 nm.



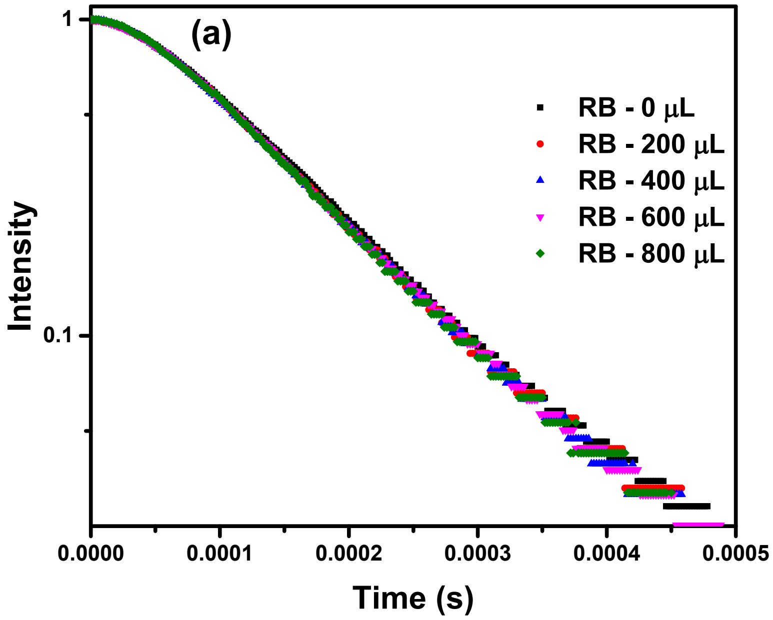


Figure S8. (a) Temporal behaviours of the 543 nm upconversion luminescence of RB-doped UCNP@SiO_2 nanospheres ($\lambda_{exc} = 980\ nm$). (b) Temporal behaviours of the 543 nm upconversion luminescence of Yb@Er@SiO_2 nanospheres when mixing with different volume of RB solutions (4 μg/mL). $\lambda_{exc} = 980\ nm$. The total amount of RB in the simple mixing cases was comparable with the case of RB-doped sample.