Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Dual-mode color tuning based on upconversion core/triple-shell nanostructure

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Experimental section

Synthesis of $NaErF_4$ NCs. $Er(Ac)_3$ (0.8 mmol) and NaAc (0.8 mmol) ware added into a 50 mL three-necked bottle containing 8 mL OA. The mixture was heated at 155 ^oC for 30 min to remove water from the solution. Then 12 mL ODE was quickly added to the above solution and the resulted mixture was heated at 150 ^oC for another 30 min to form a clear solution, and then cooled down to room temperature. Afterwards, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 ^oC for 30 min. After the methanol was evaporated, the solution was further heated at 290 ^oC under N_2 for 120 min and then cooled down to room temperature. The products were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for three times, and finally re-dispersed in 4 mL cyclohexane. The preparation of $NaErF_4$: 2Eu and $NaErF_4$: 5Yb NCs are similar with that of $NaErF_4$ NCs except adding the corresponding precursors into the initial solution.

Synthesis of $NaErF_4$@$NaYF_4$ core-shell particles. $Y(Ac)_3$ (0.8 mmol) and NaAc (0.8 mmol) was added into a 50 mL three-necked bottle containing OA (8 mL). The mixture was heated at 150 ºC for 30 min to remove water from the solution. A solution of ODE (12 mL) was then quickly added and the resulted mixture was heated at 150 ^{o}C for another 30 min to form a clear solution, and then cooled down to 80 ^{o}C. Thereafter, the pre-prepared $NaErF_4$ core NCs in 4 mL cyclohexane was added to the above solution and kept at 110 ^{o}C for 40 min. After the removal of cyclohexane, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 ^{o}C for 30 min. After the methanol was evaporated, the solution was further heated at 290 ^{o}C under N_2 for 120 min, and finally cooled down to room temperature.

Synthesis of $NaErF_4$@$NaYF_4$@$NaYbF_4$:0.5Tm core-shell-shell particles. $Yb(Ac)_3$ (0.796 mmol), $Tm(Ac)_3$ (0.004 mmol) and NaAc (0.8 mmol) was added into a 50 mL three-necked bottle containing OA (8 mL). The mixture was heated at 150 ºC for 30 min to remove water from the solution. A solution of ODE (12 mL) was then quickly added and the resulted mixture was heated at 150 ^{o}C for another 30 min to form a clear solution, and then cooled down to 80 ^{o}C. Thereafter, the pre-prepared $NaErF_4$@$NaYF_4$ core-shell NCs in 4 mL cyclohexane was added to the above solution and kept at 110 °C for 40 min. After the removal of cyclohexane, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 °C for 30 min. After the methanol was evaporated, the solution was further heated at 290 °C under N_2 for 120 min, and finally cooled down to room temperature.

Synthesis of $NaErF_4$@$NaYF_4$@$NaYbF_4$:0.5Tm@$NaYF_4$ core-shell-shell particles. It is similar with that of $NaErF_4$@$NaYF_4$ NCs except replacing $NaErF_4$ core by $NaErF_4$@$NaYF_4$@$NaYbF_4$:0.5Tm core-shell-shell NCs.

Calculation of the UC luminescence life-time

The life-time of Er^{3+}/Tm^{3+} in Er@3S NCs can be fitted well by a bi-exponential function as

$$I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

Where I is the UC luminescence intensity, A_1 and A_2 are constants, and τ_1 and τ_2 are the corresponding decay times. The mean lifetimes are calculated by the following equation:

$$\tau = \frac{A_1 \cdot \tau_1 + A_2 \cdot \tau_2}{A_1 + A_2} \quad (2)$$

Figure S1-S13

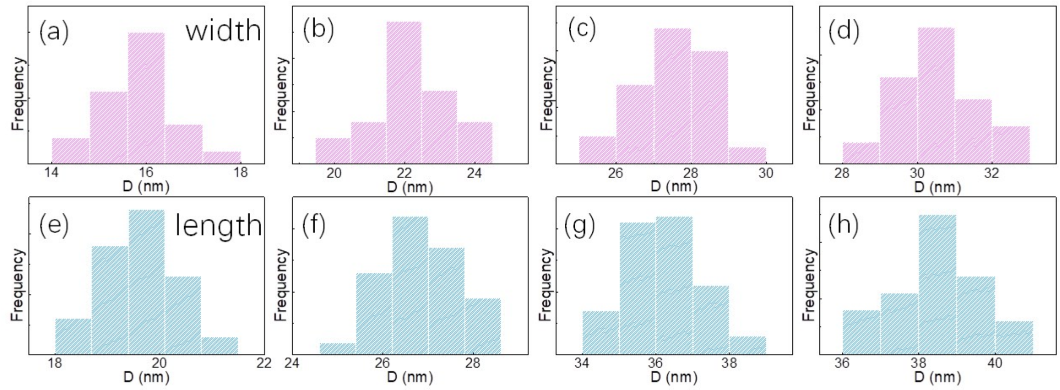

Figure S1 Size distributions of widths and lengths for the $NaErF_4$:2Eu core (a, e), $NaErF_4$:2Eu@$NaYF_4$ core-shell (b, f), $NaErF_4$:2Eu@$NaYF_4$@$NaYbF_4$:0.5Tm core-shell-shell (c, g) and ErEu@3S core-shell-shell-shell (d, h) NCs, respectively.

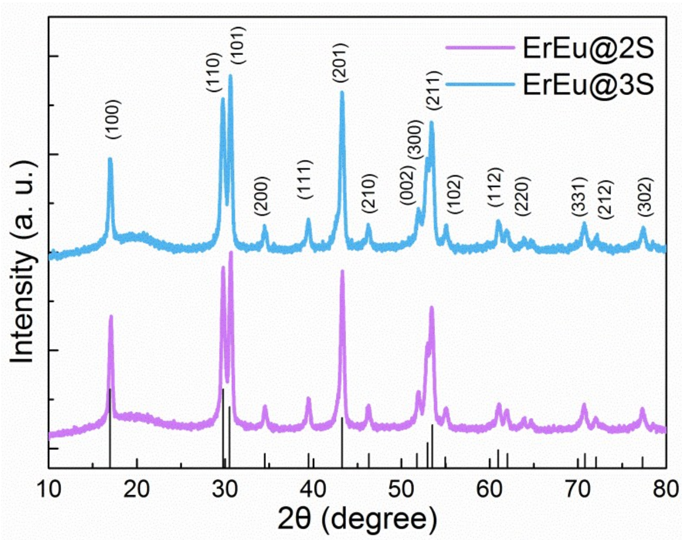

Figure S2 XRD patterns of $NaErF_4$:2Eu@$NaYF_4$@$NaYbF_4$:0.5Tm core-shell-shell (ErEu@2S) and ErEu@3S NCs, respectively.

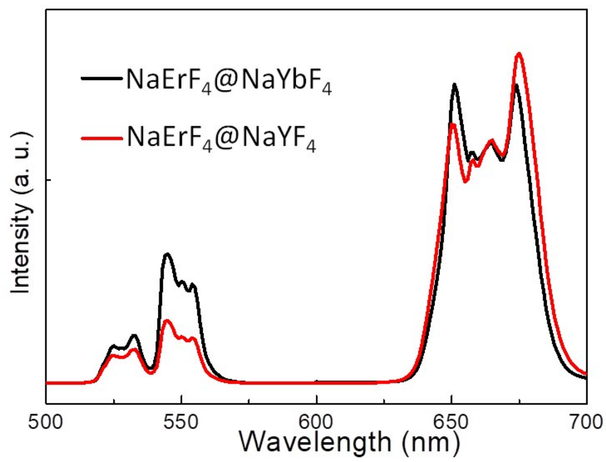

Figure S3 UC emission spectra of $NaErF_4$@$NaYbF_4$ and $NaErF_4$@$NaYF_4$ NCs under 980 nm laser excitation, which are normalized to 660 nm.

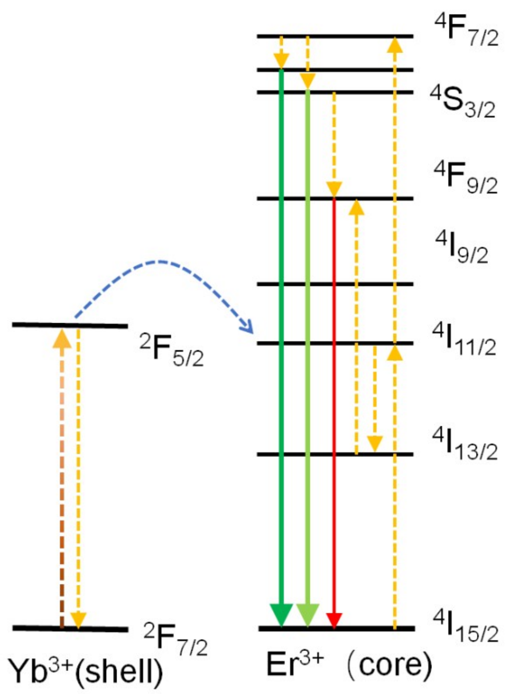

Figure S4 Proposed energy transfer mechanism in $NaErF_4$@$NaYbF_4$ NCs.

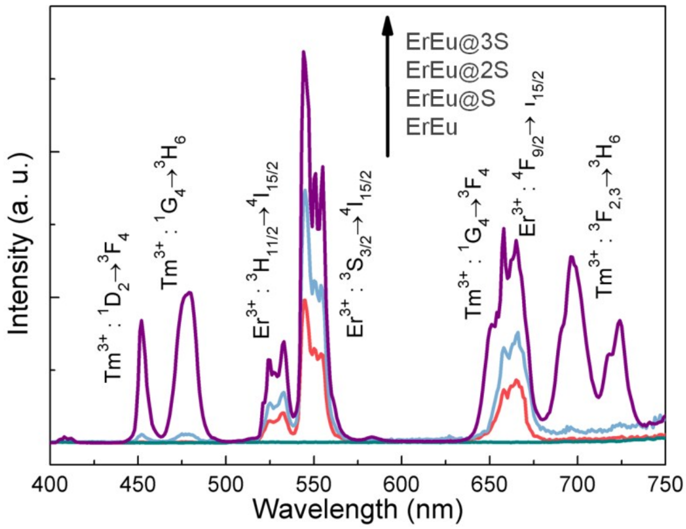

Figure S5 UC emission spectra of $NaErF_4$:2Eu core (ErEu), $NaErF_4$:2Eu@$NaYF_4$ core-shell (ErEu@S), $NaErF_4$:2Eu@$NaYF_4$@$NaYbF_4$:0.5Tm core-shell-shell (ErEu@2S) and $NaErF_4$:2Eu@$NaYF_4$@$NaYbF_4$:0.5Tm@$NaYF_4$ core-shell-shell-shell (ErEu@3S) NCs, respectively.

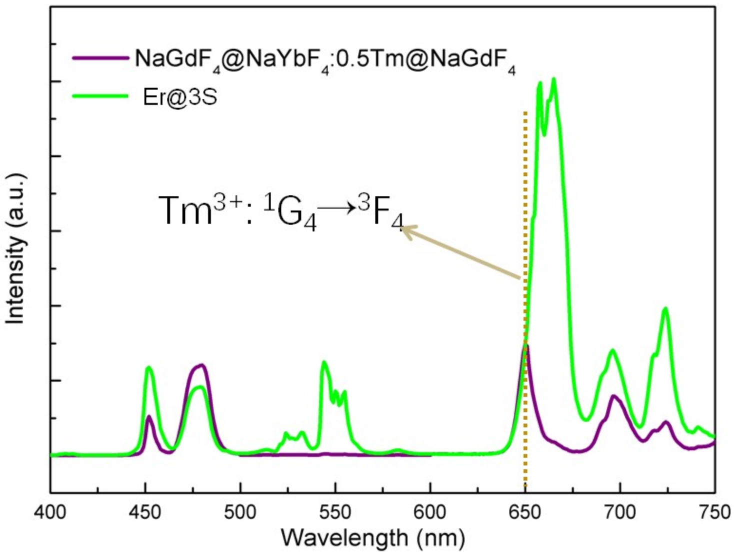

Figure S6 UC emission spectra of $NaGdF_4$@$NaYbF_4$:0.5Tm@$NaGdF_4$ and $NaErF_4$ @$NaYF_4$@$NaYbF_4$:0.5Tm@$NaYF_4$ (Er@3S) NCs, respectively.

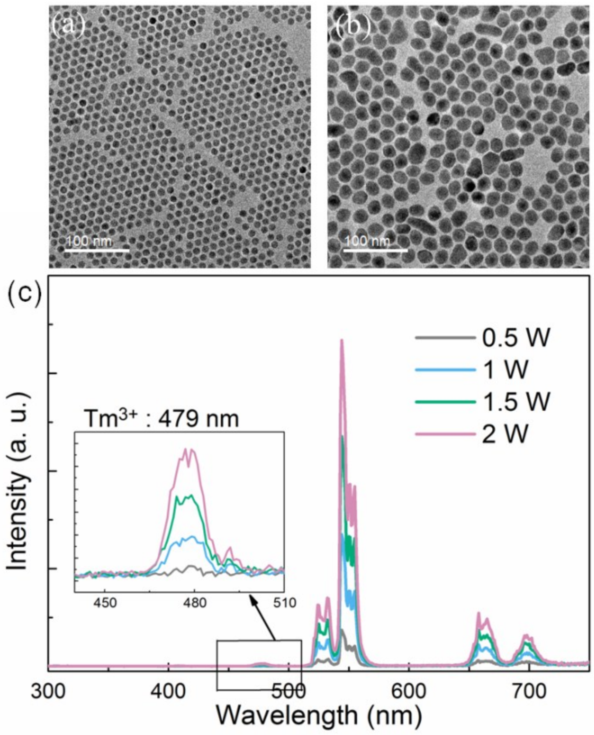

Figure S7 TEM images of $NaErF_4$: 2Eu (a) and $NaErF_4$: 2Eu @$NaYF_4$@$NaYbF_4$:0.5Tm@$NaYF_4$ (b) NCs. (c) UC emission spectra of $NaErF_4$: 2Eu @$NaYF_4$@$NaYbF_4$:0.5Tm@$NaYF_4$ NCs versus excitation power. Inserts of (c) is the enlarged spectra ranging from 440 to 510 nm.

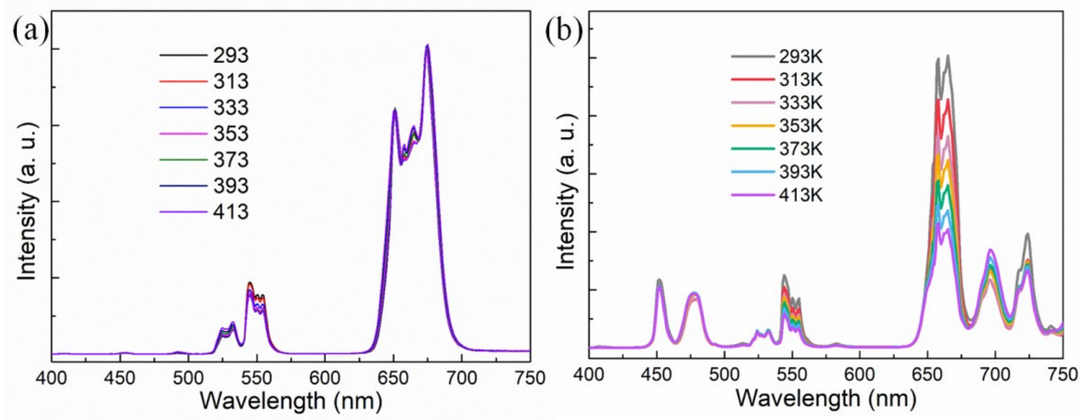

Figure S8 Temperature dependent UC emission spectra of $NaErF_4@NaYF_4$ (a) and $NaErF_4@NaYF_4@NaYbF_4$:0.5Tm@$NaYF_4$ NCs under 980 nm laser excitation.

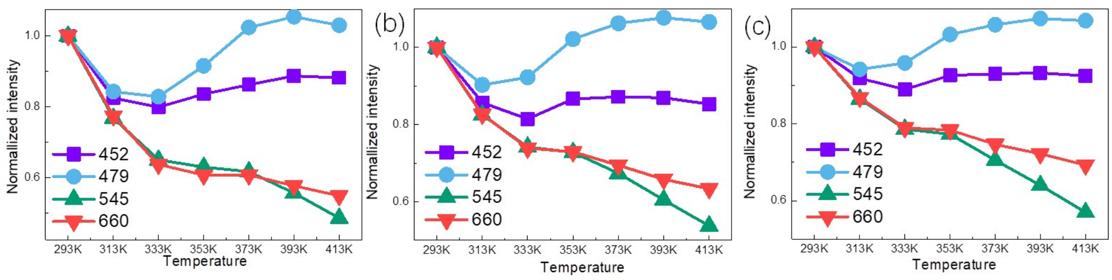

Figure S9 Temperature dependent UC emission intensity of different transitions in $NaErF_4@NaYF_4@NaYbF_4$:0.5Tm@$NaYF_4$ NCs under 980 nm laser excitation at 100 mW (a), 200 mW (b) and 400 mW (c).

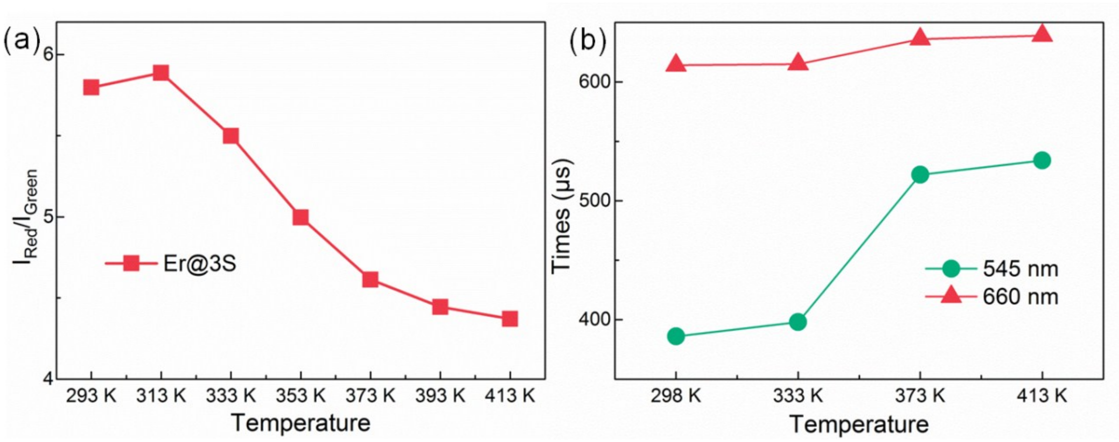

Figure S10 (a) UC emission intensity of red to green versus temperature. (b) life-time variation trends of green and red versus temperature.

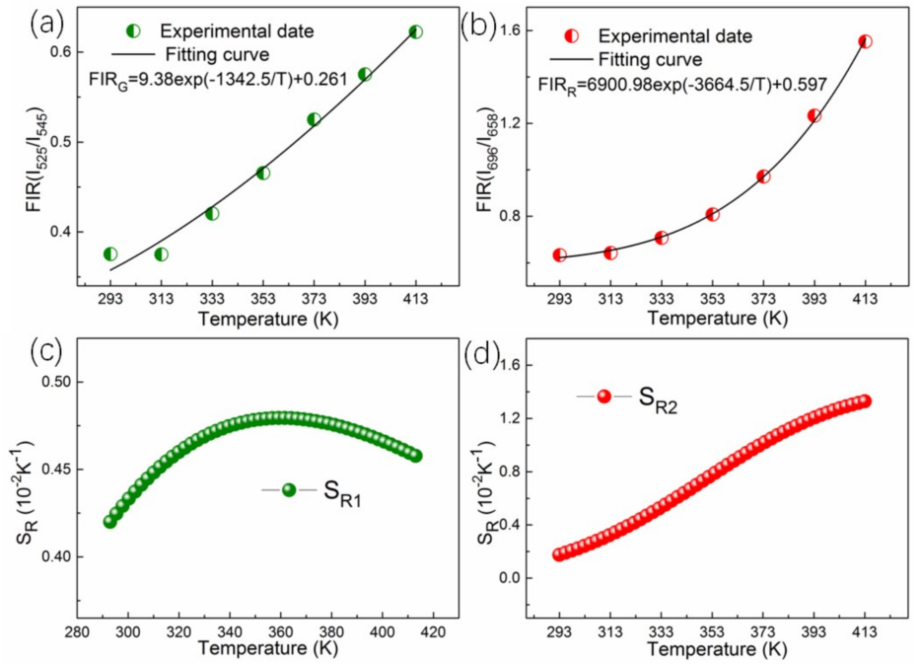

Figure S11 Dependence of FIR values on temperature in ErEu@3S NCs: (a) I_{525}/I_{545} and (b) I_{696}/I_{658}. The fitting curves are also provided. (c) and (d) are the dependence of relative sensitivities on absolute temperature corresponding to (a) and (b), respectively.

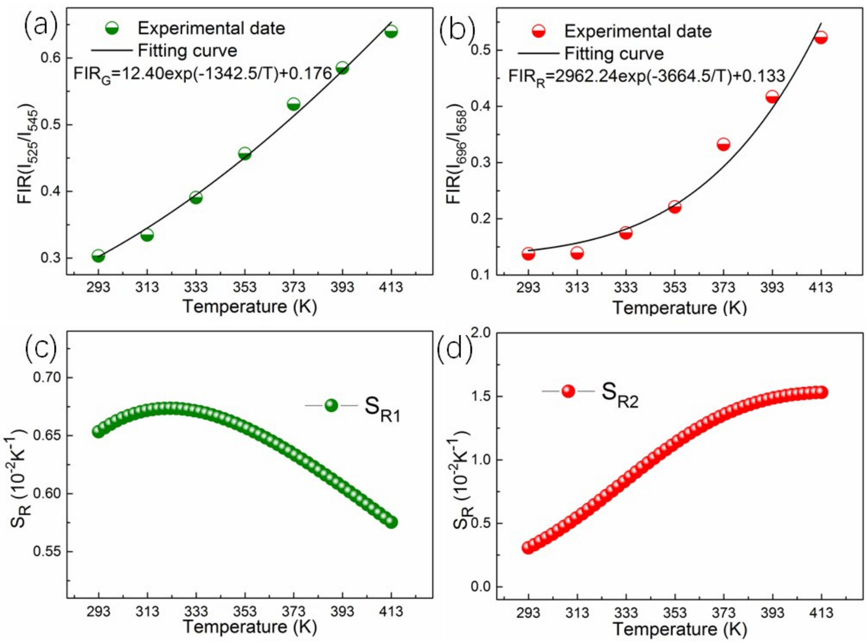

Figure S12 Dependence of FIR values on temperature in ErYb@3S NCs: (a) I_{525}/I_{545} and (b) I_{696}/I_{658}. The fitting curves are also provided. (c) and (d) are the dependence of relative sensitivities on absolute temperature corresponding to (a) and (b), respectively.

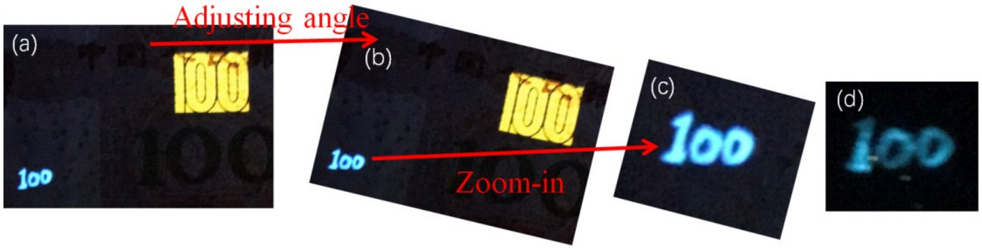

Figure S13 (a) Pattern of Figure 7d in the main-text. (b) angle-tuned of (a). (c) Zoom-in of the number “100” in (b). (d) Pattern of Figure 7e in the main-text.