Supporting Information

A novel upconversion core-multishell nanoplatform for a highly efficient photoswitch

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Experimental

Materials

$ErCl_3·6H_2O$ (99.99%), $YCl_3·6H_2O$ (99.99%), $YbCl_3·6H_2O$ (99.99%), $TmCl_3·6H_2O$ (99.99%), oleic acid (OA, > 90%), 1-octadecene (ODE, > 90%), NaOH (> 97%), NH_4F (> 98%), methanol (≥ 99.9%), cyclohexane (> 99.5%), ethanol (≥ 99.7%) were purchased from Aladdin and used as received without further purification.

Synthesis of core nanoparticles

As for the synthesis of $NaErF_4$:0.5%Tm nanoparticles, 1 mmol of $RECl_3$ (RE = rare earth) containing 0.995 mmol of $ErCl_3$ (1 M, 0.995 mL) and 0.005 mmol of $TmCl_3$ (0.1 M, 0.05 mL) were added into a 100 ml three-necked flask containing 6 mL of OA and 15 mL of ODE. The mixture was stirred at 105 °C for 40 min to remove residual water, and then heated to 150 °C for another 40 min to form a transparent solution (RE-oleate precursors). After that, the solution was cooled down to 50 °C. Subsequently, 10 mL of methanol solution containing 2.5 mmol of NaOH (0.1 g) and 4 mmol of NH_4F (0.148 g) was added into the above solution and stirred for 30 min. Then the solution was heated to 75 °C and kept for half an hour to remove the methanol. Thereafter, the reaction mixture was raised to 300 °C for 1.5 h under argon atmosphere. After reaction, the resulting solution was cooled down to room temperature. The products were washed by ethanol several times, and purified by centrifugation at 10000 rpm for 10 min. Finally, the obtained nanoparticles were dispersed in 10 mL of cyclohexane. $NaErF_4$:*x*Tm nanoparticles (*x* = 0, 0.2%) and $NaYF_4$:*x*Yb, 0.2%Tm nanoparticles (*x* = 20, 50, 80, 99.8%) were prepared by a similar process as described above.

Synthesis of core-shell nanoparticles

As for the synthesis of $NaErF_4$:0.5%Tm@$NaYF_4$ nanoparticles, 0.25 mmol of YCl_3 (1 M, 0.25 mL) was added into a 100 ml three-necked flask containing 6 mL of OA and 15 mL of ODE. The mixture was stirred at 105 °C for 40 min to remove residual water, and then heated to 150 °C for another 40 min to form a transparent solution (Y-oleate precursors). After that, the solution was cooled down to 50 °C. Then 0.25 mmol of the as-prepared $NaErF_4$:0.5%Tm core nanoparticles in cyclohexane were added into the flask and the solution was stirred at 85 °C for 30 min to remove the cyclohexane. After that, the solution was cooled down to 50 °C. Subsequently, 10 mL of methanol solution containing 0.625 mmol of NaOH (0.025 g) and 1 mmol of NH_4F (0.037 g) was added into the above solution and stirred for 30 min. Then the solution was heated to 75 °C and kept for half an hour to remove the methanol. Thereafter, the reaction mixture was raised to 300 °C for 1.5 h under argon atmosphere. After reaction, the resulting solution was cooled down to room temperature. The products were washed by ethanol several times, and purified by centrifugation at 10000 rpm for 10 min. Finally, the obtained core-shell nanoparticles were dispersed in 2.5 mL of cyclohexane. $NaErF_4$:*x*Tm@$NaYF_4$ nanoparticles (*x* = 0, 0.2%) were prepared by a similar process as described above.

Synthesis of core-shell-shell nanoparticles

As for the synthesis of $NaErF_4$:0.5%Tm@$NaYF_4$@$NaYbF_4$:0.2%Tm nanoparticles, 0.5 mmol of $RECl_3$ containing 0.499 mmol of $YbCl_3$ (1 M, 0.499 mL) and 0.001 mmol of $TmCl_3$ (0.1 M, 0.01 mL) were added into a 100 ml three-necked flask containing 6 mL of OA and 15 mL of ODE. The mixture was stirred at 105 °C for 40 min to remove residual water, and then heated to 150 °C for another 40 min to form a transparent solution (RE-oleate precursors). After that, the solution was cooled down to 50 °C. Then 0.25 mmol of the as-prepared $NaErF_4$:0.5%Tm@$NaYF_4$ core-shell nanoparticles in cyclohexane were added into the flask and the solution was stirred at 85 °C for 30 min to remove the cyclohexane. After that, the solution was cooled down to 50 °C. Subsequently, 10 mL of methanol solution containing 1.25 mmol of NaOH (0.05 g) and 2 mmol of NH_4F (0.074 g) was added into the above solution and stirred for 30 min. Then the solution was heated to 75 °C and kept for half an hour to remove the methanol. Thereafter, the reaction mixture was raised to 300 °C for 1.5 h under argon atmosphere. After reaction, the resulting solution was cooled down to room temperature. The products were washed by ethanol several times, and purified by centrifugation at 10000 rpm for 10 min. Finally, the obtained core-shell-shell nanoparticles were dispersed in 2.5 mL of cyclohexane.

Synthesis of core-shell-shell-shell nanoparticles

As for the synthesis of $NaErF_4$:0.5%Tm@$NaYF_4$@$NaYbF_4$:0.2%Tm@$NaYF_4$ nanoparticles, 0.25 mmol of YCl_3 (1 M, 0.25 mL) was added into a 100 ml three-necked flask containing 6 mL of OA and 15 mL of ODE. The mixture was stirred at 105 °C for 40 min to remove residual water, and then heated to 150 °C for another 40 min to form a transparent solution (Y-oleate precursors). After that, the solution was cooled down to 50 °C. Then 0.25 mmol of the as-prepared $NaErF_4$:0.5%Tm@$NaYF_4$@$NaYbF_4$:0.2%Tm core-shell-shell nanoparticles in cyclohexane were added into the flask and the solution was stirred at 85 °C for 30 min to remove the cyclohexane. After that, the solution was cooled down to 50 °C. Subsequently, 10 mL of methanol solution containing 0.625 mmol of NaOH (0.025 g) and 1 mmol of NH_4F (0.037 g) was added into the above solution and stirred for 30 min. Then the solution was heated to 75 °C and kept for half an hour to remove the methanol. Thereafter, the reaction mixture was raised to 300 °C for 1.5 h under argon atmosphere. After reaction, the resulting solution was cooled down to room temperature. The products were washed by ethanol several times, and purified by centrifugation at 10000 rpm for 10 min. Finally, the obtained core-shell-shell-shell nanoparticles were dispersed in 2.5 mL of cyclohexane.

Characterization

X-ray diffraction (XRD) characterization was performed by using the D-Max 2200VPC XRD from Rigaku Company with Cu-Kα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) and energy dispersive spectrum (EDS) were carried out by the JEM-2010HR TEM operated at 120 kV and 300 kV from JEOL equipped with energy dispersive X-ray spectrometer. UC emission spectra and lifetime measurement were obtained by an Edinburgh FLS980 equipped with fuorescence lifetime and 2 W 980/1532 nm diode lasers. The decay lifetime was calculated based on the function: $\tau = \int I(t)dt/I_P$, where $I(t)$ and I_P denote the emission intensity at time t and the maximum intensity, respectively.

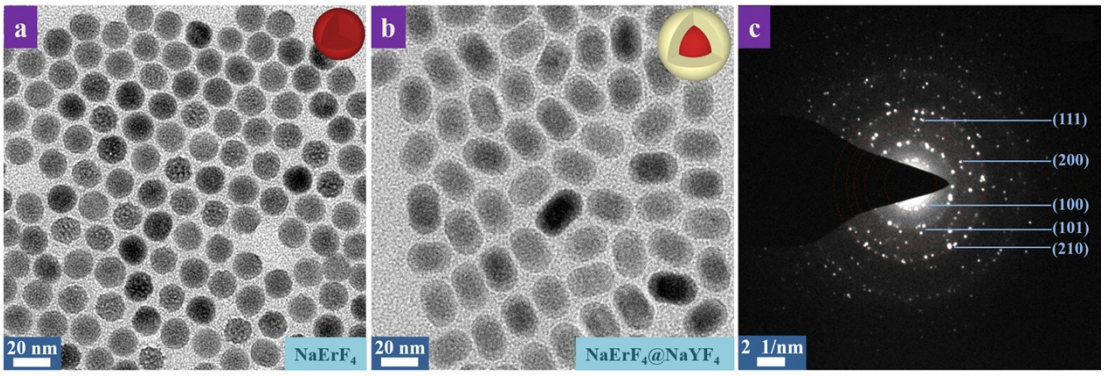

Fig. S1 TEM images (a,b) of $NaErF_4$ and $NaErF_4@NaYF_4$ nanoparticles, respectively. (c) is the corresponding selected-area electron diffraction (SAED) pattern of $NaErF_4@NaYF_4$ nanoparticles. As can be seen, the SAED pattern indicates the pure hexagonal structure of $NaErF_4@NaYF_4$ nanoparticles.

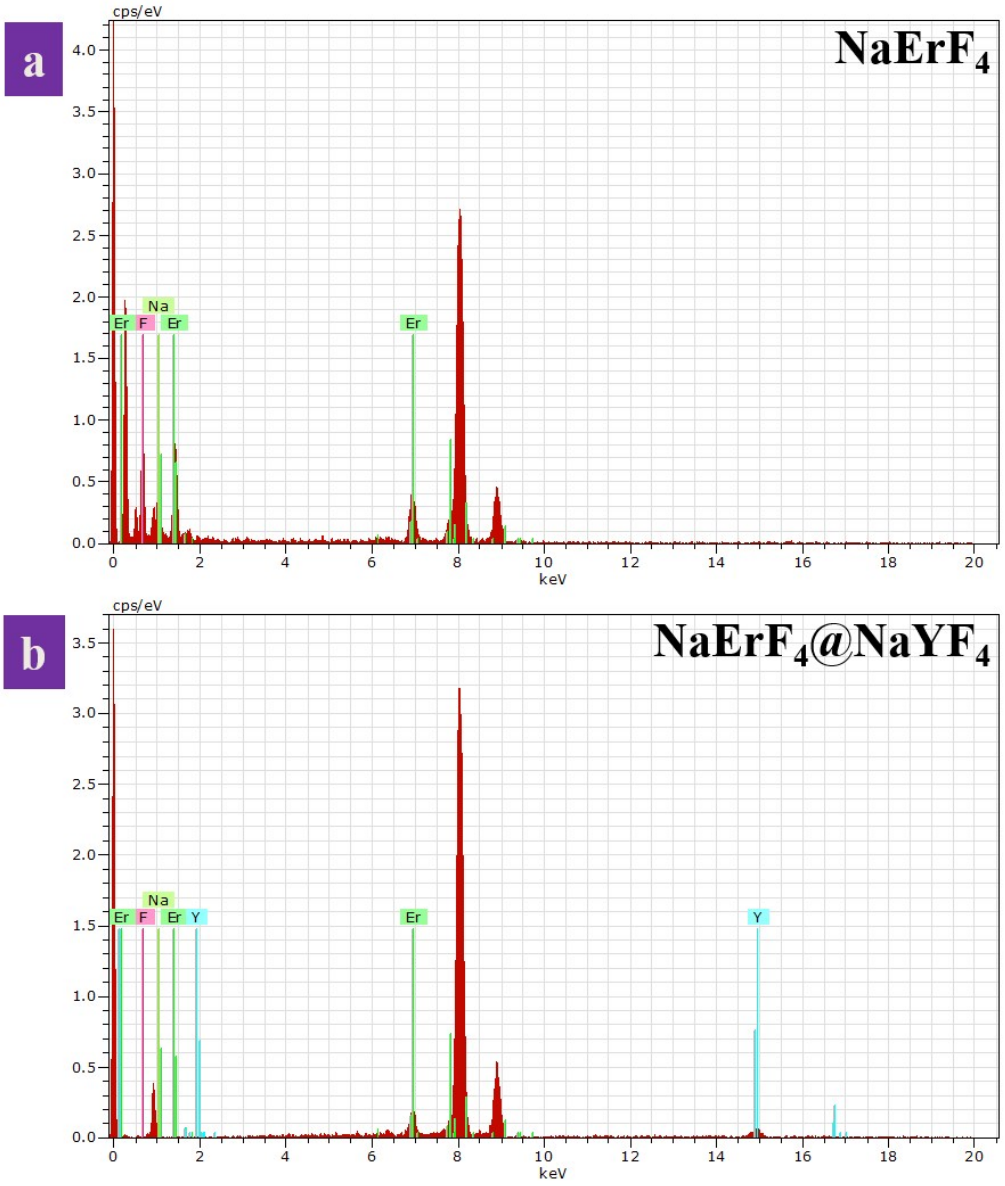

Fig. S2 EDS (a,b) of $NaErF_4$ and $NaErF_4$@$NaYF_4$ nanoparticles, respectively. As can be seen, the Na, F, Er elements and Na, F, Er, Y elements are clearly present in $NaErF_4$ and $NaErF_4$@$NaYF_4$ nanoparticles, respectively.

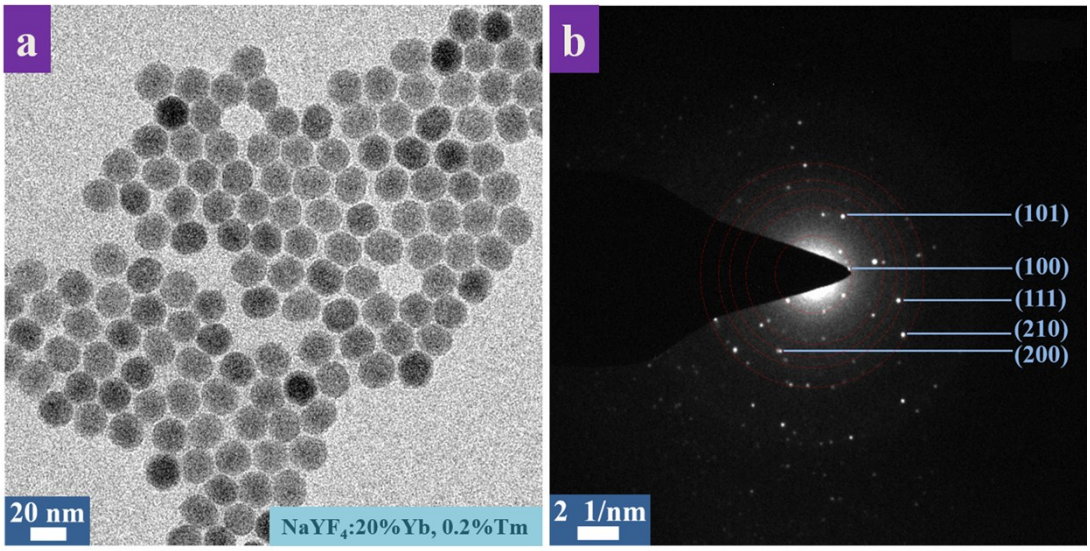

Fig. S3 TEM image and the corresponding SAED pattern of $NaYF_4$:20%Yb, 0.2%Tm nanoparticles. As can be seen, the SAED pattern indicates the pure hexagonal structure of $NaYF_4$:20%Yb, 0.2%Tm nanoparticles.

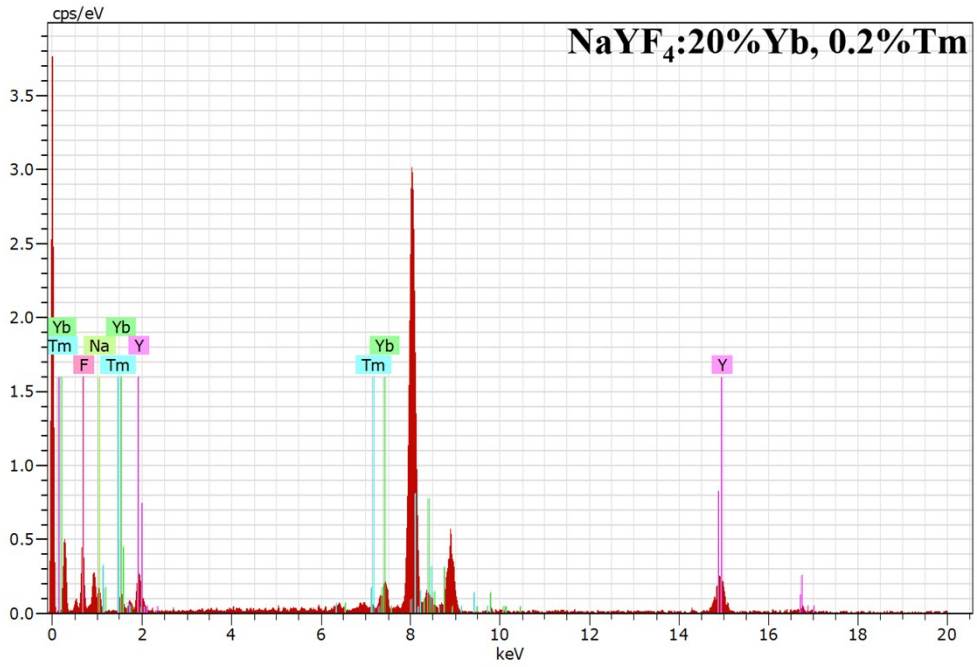

Fig. S4 EDS of $NaYF_4$:20%Yb, 0.2%Tm nanoparticles. As can be seen, the Na, F, Yb, Tm, Y elements are clearly present.

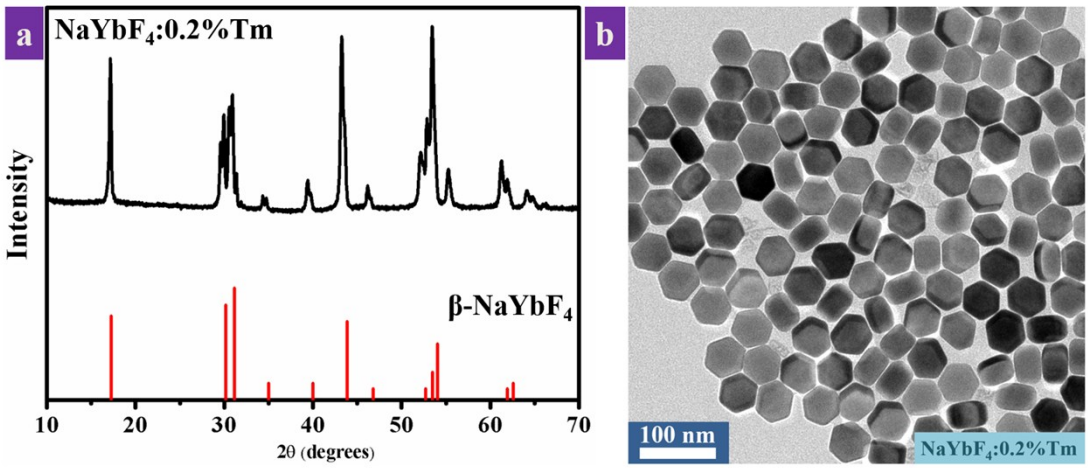

Fig. S5 XRD pattern (a) and TEM image (b) of $NaYbF_4$:0.2%Tm nanoparticles. The vertical red lines in (a) are the standard profiles of hexagonal $NaYbF_4$.

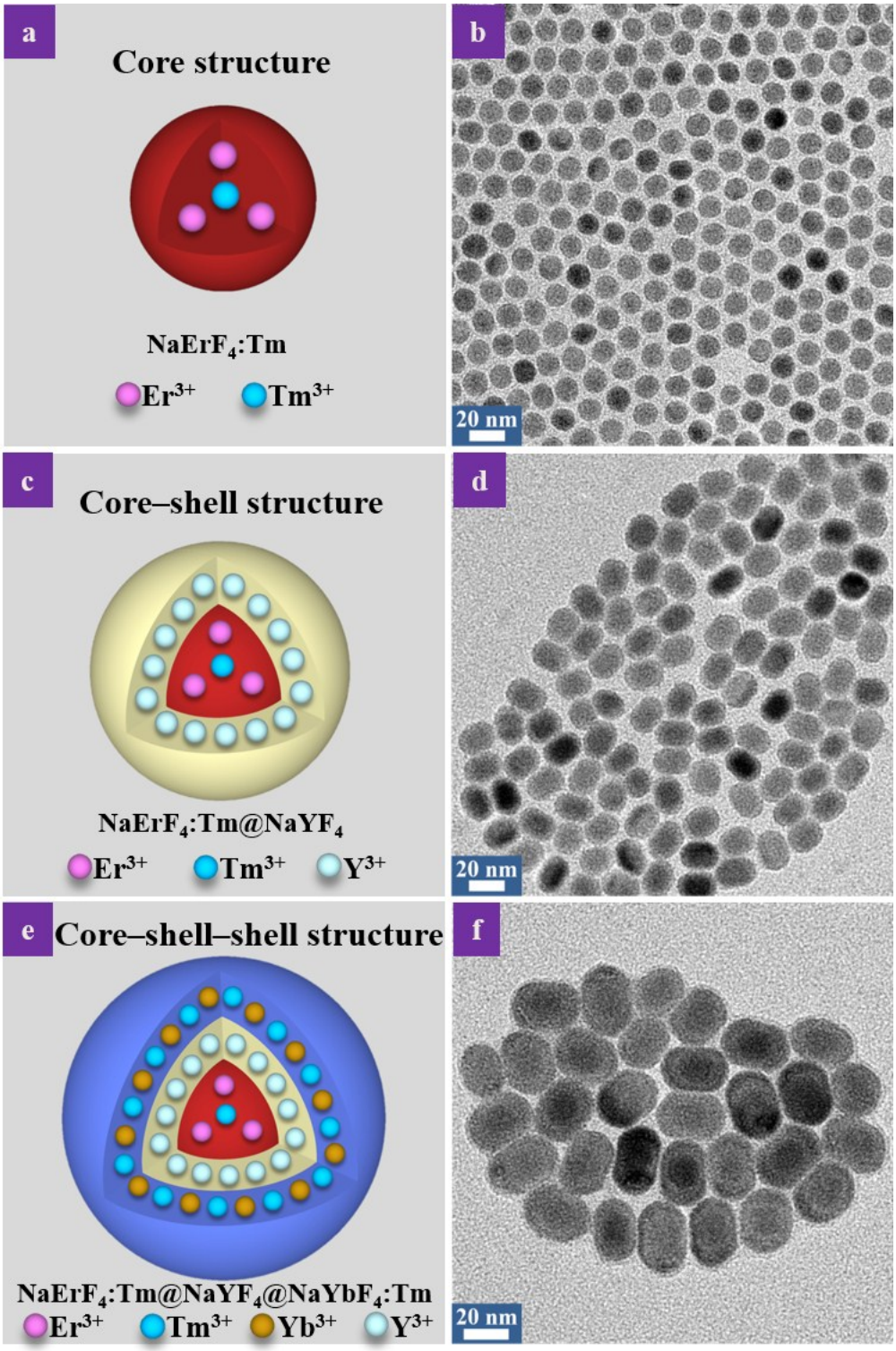

Fig. S6 Schematic models (a,c,e) and the corresponding TEM images (b,d,f) of $NaErF_4$:0.5%Tm (core), $NaErF_4$:0.5%Tm@$NaYF_4$ (core-shell) and $NaErF_4$:0.5%Tm@$NaYF_4$@$NaYbF_4$:0.2%Tm (core-shell-shell) nanoparticles.

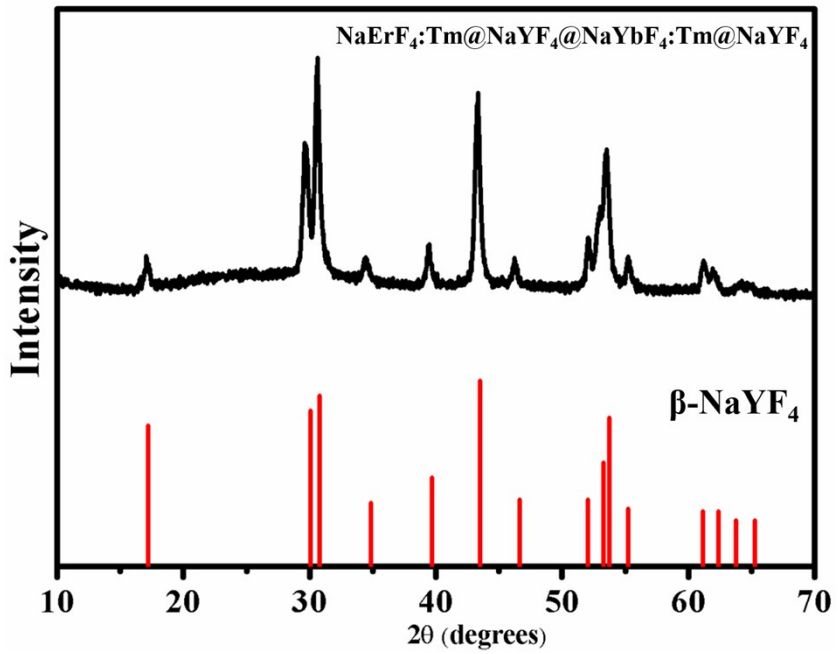

Fig. S7 XRD pattern of $NaErF_4$:0.5%Tm@$NaYF_4$@$NaYbF_4$:0.2%Tm@$NaYF_4$ nanoparticles. The vertical red lines are the standard profiles of hexagonal $NaYF_4$.

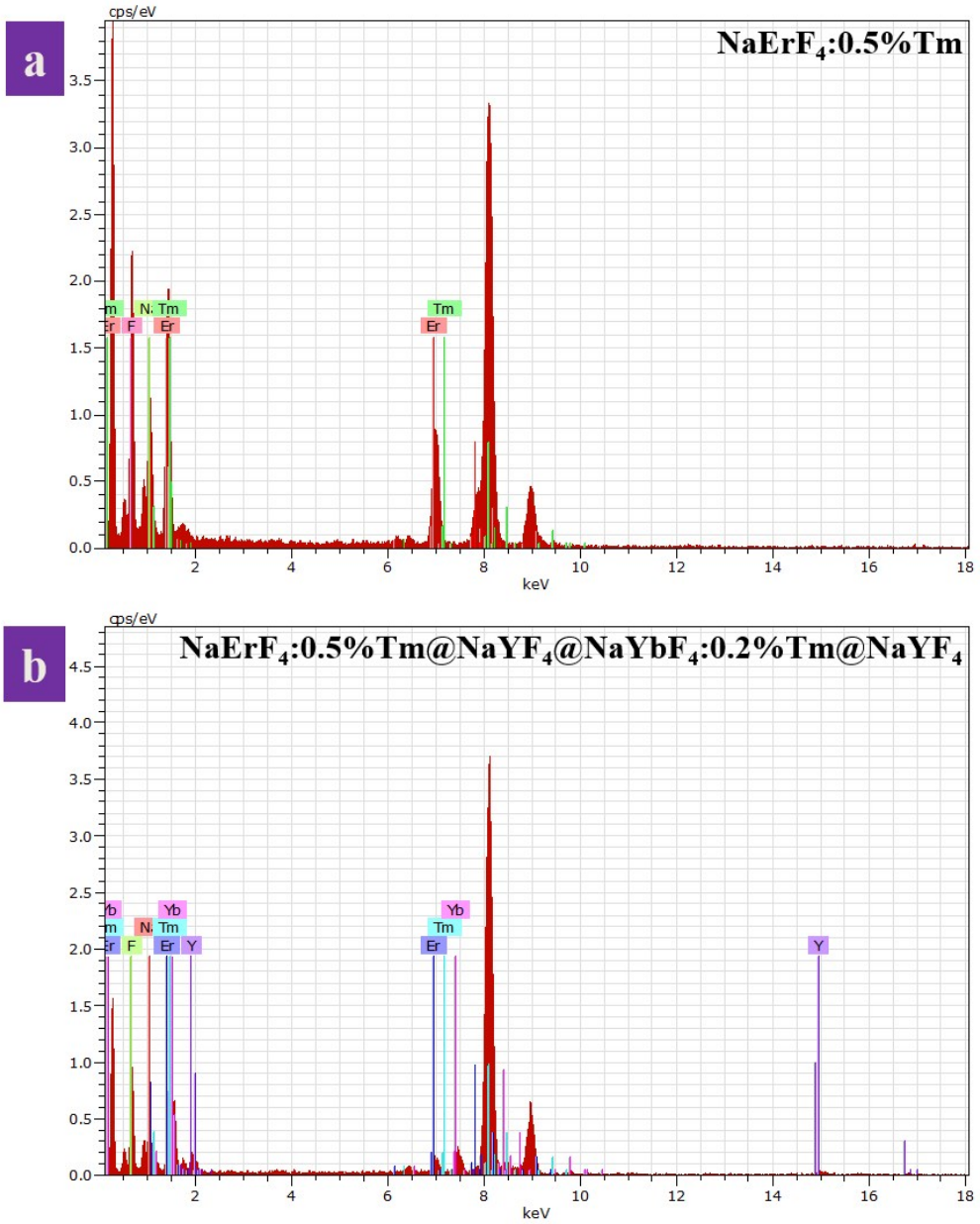

Fig. S8 EDS (a,b) of $NaErF_4$:0.5%Tm and $NaErF_4$:0.5%Tm@$NaYF_4$@$NaYbF_4$:0.2%Tm@$NaYF_4$ nanoparticles, respectively. As can be seen, the Na, F, Er, Tm elements and Na, F, Er, Tm, Yb, Y elements are clearly present in $NaErF_4$:0.5%Tm and $NaErF_4$:0.5%Tm@$NaYF_4$@ $NaYbF_4$:0.2%Tm@$NaYF_4$ nanoparticles, respectively.

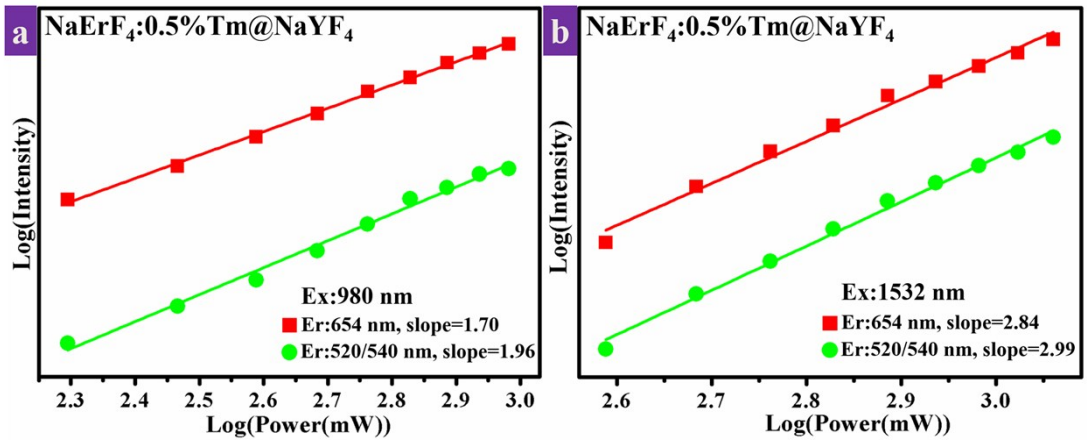

Fig. S9 Power density dependence (a,b) of Er^{3+} emissions at 654, 520/540 nm in $NaErF_4$:0.5%Tm@$NaYF_4$ nanoparticles under 980 and 1532 nm excitations, respectively.

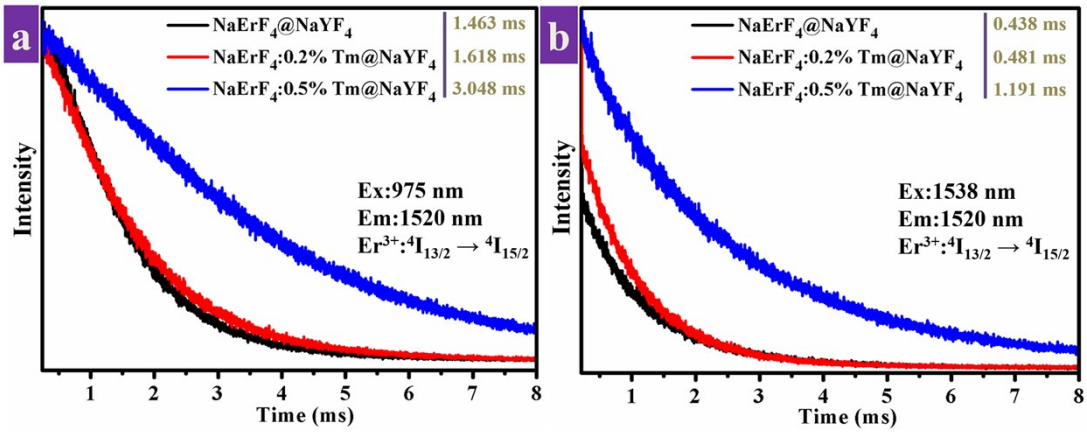

Fig. S10 Decay curves (a,b) of Er^{3+} measured at 1520 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) for $NaErF_4$:*x*Tm@$NaYF_4$ (*x* = 0, 0.2, 0.5%) nanoparticles under 975 and 1538 nm excitations, respectively.