# Supporting Information

## Synthesis of Oil-dispersible Hexagonal-phase and Hexagonal-shaped $NaYF_4$:Yb,Er Nanoplates

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### 1, TEM and FE-SEM Studies on the $NaYF_4$:Yb,Er nanocrystals

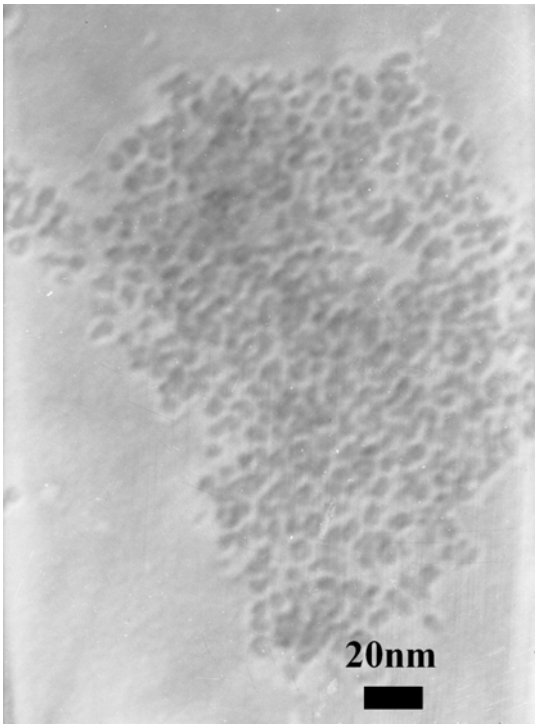



**Figure S1.** TEM image of α-$NaYF_4$:Yb,Er nanoparticles obtained at 210°C

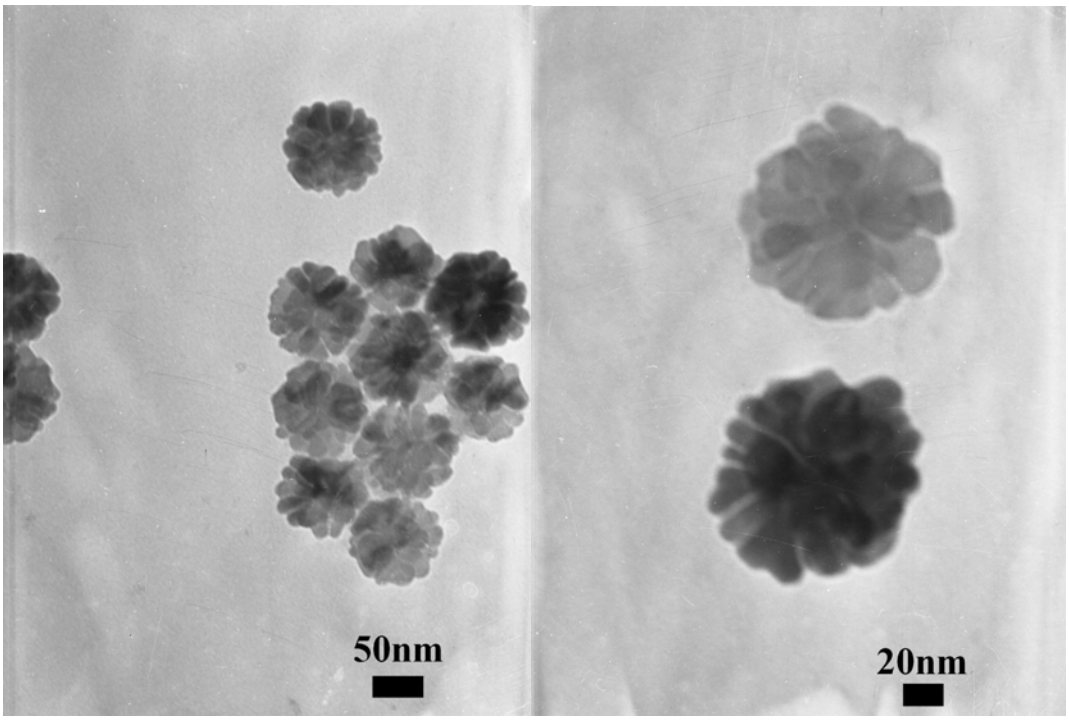



**Figure S2.** TEM images of $NaYF_4$:Yb,Er nanocrystals obtained at 230°C

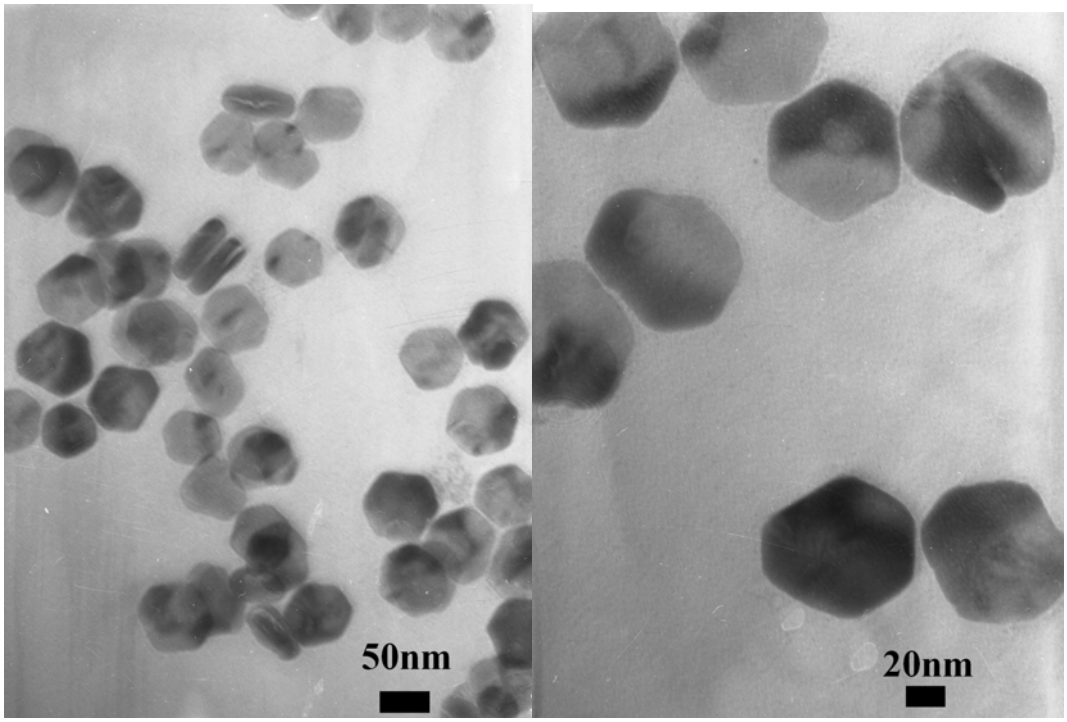
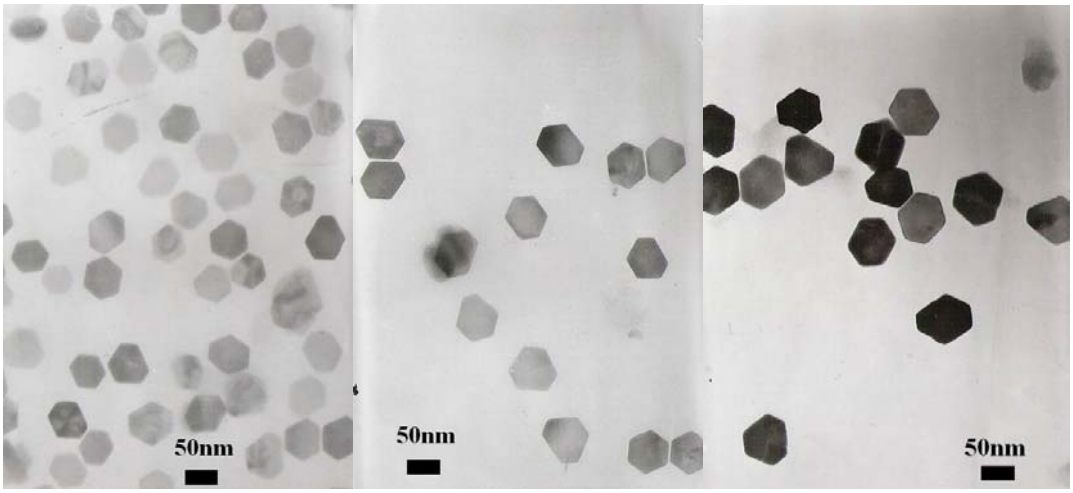



**Figure S3.** TEM images of β-$NaYF_4$:Yb,Er nanoplates obtained at 260°C




A B C

**Figure S4.** TEM images of β-$NaYF_4$:Yb,Er nanoplates obtained at 260ºC after different reaction time: 2h (A); 4h (B); 6h (C) .

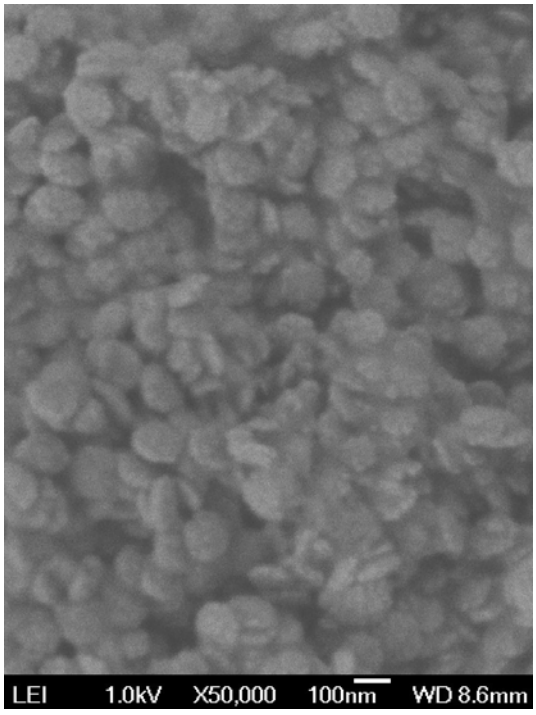



**Figure S5.** FE-SEM image of $NaYF_4$:Yb,Er nanocrystals obtained at 230°C

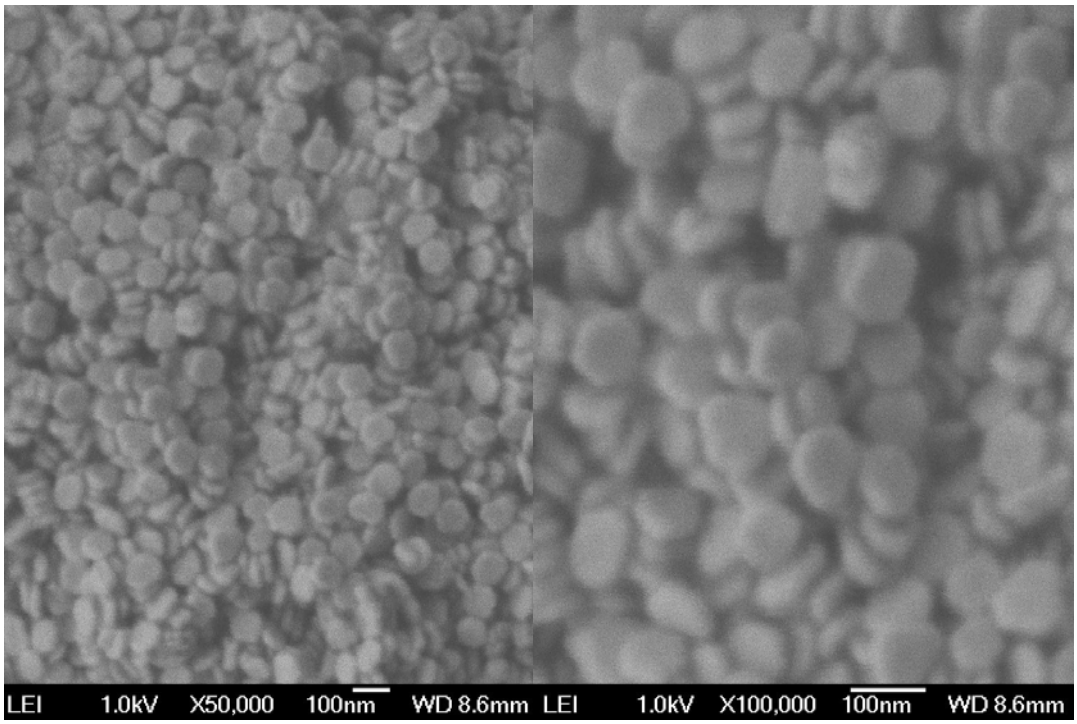



**Figure S6.** FE-SEM images of β-$NaYF_4$:Yb,Er nanoplates obtained at 260°C

## 2, Structural characterization of β-$NaYF_4$:Yb,Er nanoplates

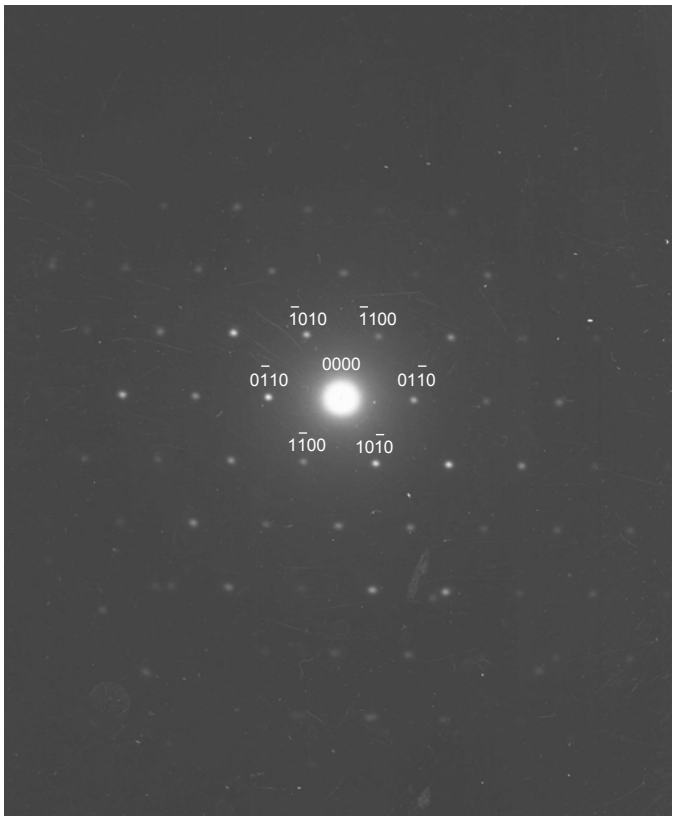



**Figure S7.** SAED patterns of β-$NaYF_4$:Yb,Er nanoplates obtained at 260°C

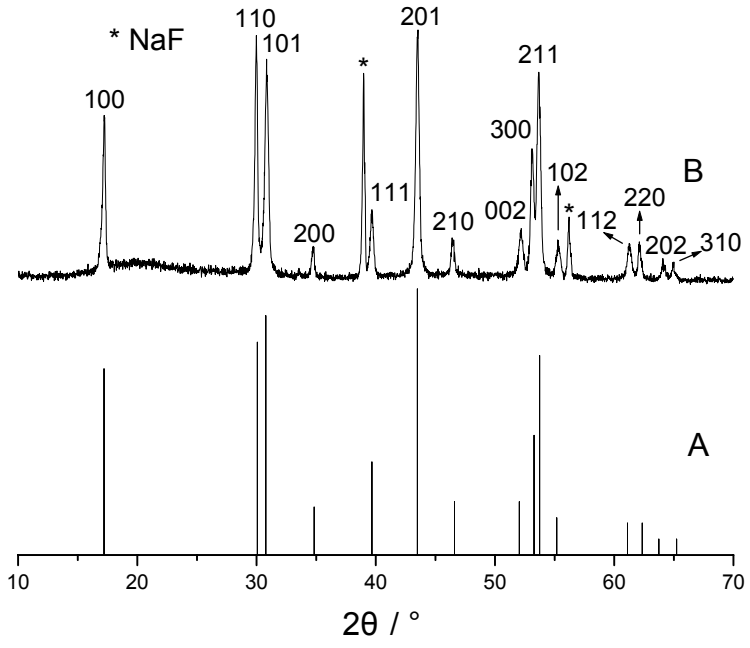



**Figure S8.** Calculated line pattern (A) and experimental powder XRD data for the β-$NaYF_4$:Yb,Er nanoplates obtained at 260ºC after 2h reaction (B)

## 3, Procedure for remove the residual NaF from products

After reaction was completed, the reaction mixture solution was washed three times with deionized water in a separatory funnel to remove the residual NaF. The reaction mixture solution was also mixed with a mixture solvent composed of 50 mL ethanol, 60 mL distilled water and 100 mL hexane. The resulting solution was added into a 500-mL round-bottomed flask with a reflux condenser, and then heated to 60°C and kept at that temperature for half an hour under vigorous stirring. However, these two methods were not effective enough to remove all the residual NaF.

After drying the nanocrystals under vacuum, about 0.2g dried powdered products were dispersed in 100 mL hexane under ultrasonication, then the nonpolar solution was mixed with 50 mL ethanol and 60 mL distilled water. The resulting solution was

added into a 500-mL round-bottomed flask with a reflux condenser, and then heated to 60°C and kept at that temperature for half an hour under vigorous stirring. Then the mixture was put into a separatory funnel, the upper nonpolar layer was separated and washed again in the same way. The nanocrystals were separated by centrifugation. As shown in Figure S9, NaF could be removed completely from the products.

In solution, the binding strength of oleic acid to the nanocrystals and NaF was strong, thus it was not easy to remove the hydrophobic NaF from the products. However, in the dry powder form, the binding strength of oleic acid to the nanocrystals and NaF became weak, after dispersing the dried powdered products in nonpolar solvent, the more hydrophilic NaF could be removes by the polar solvent.

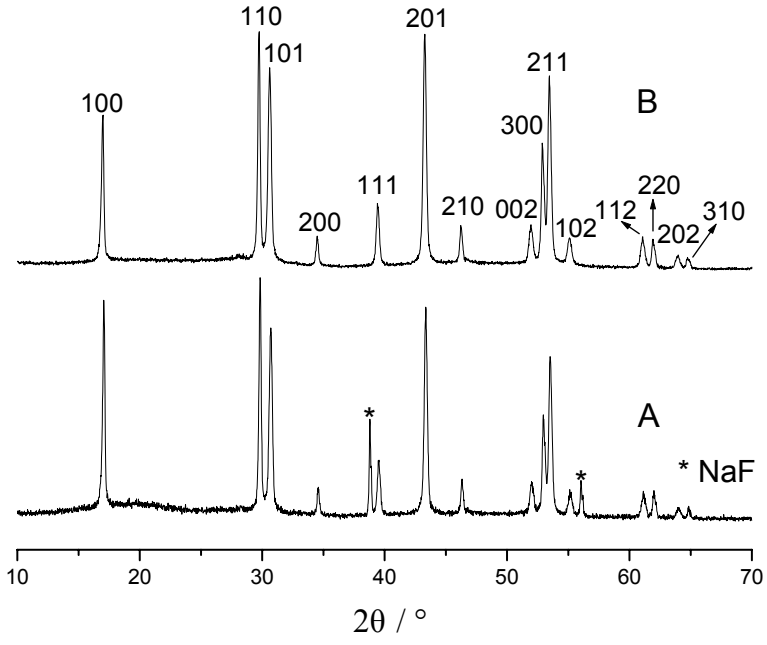



**Figure S9.** Powder XRD data for the β-$NaYF_4$:Yb,Er nanoplates before (A) and after (B) remove residual NaF completely

## 4, Glycerol-mediated preparation of α-$NaYF_4$:Yb, Er nanoparticles

**Materials.** Sodium fluoride (NaF) and glycerol were obtained from Beijing Chemical Corporation (Beijing, China). Yttrium oxide ($Y_2O_3$, 99.99%), ytterbium oxide ($Yb_2O_3$, 99.99%) and erbium oxide ($Er_2O_3$, 99.99%) were obtained from Grirem Advanced Materials Co., Ltd. (Beijing, China), and were of SpecPure grade. Rare earth chlorides ($RECl_3 \cdot 6H_2O$ with RE = Y, Yb, Er) were prepared by dissolving the corresponding rare earth oxides in hydrochloric acid at elevated temperature then evaporating the solvent at vacuum.

**Synthetic procedure.** 0.3g NaF and 40 mL glycerol was filled in a 250 mL round-bottomed flask with a reflux condenser. The mixture was heated to 260ºC under vigorous stirring. 1.35 mmol rare earth chlorides (Y: Yb: Er = 0.80: 0.17: 0.03) were dissolved in 50 mL glycerol under ultrasonication, then the rare earth chlorides solution was added into the NaF solution. The reaction mixture was stirred for 6 hours at 260ºC. Solid material was collected by centrifugation and washed by water and ethanol for several times.

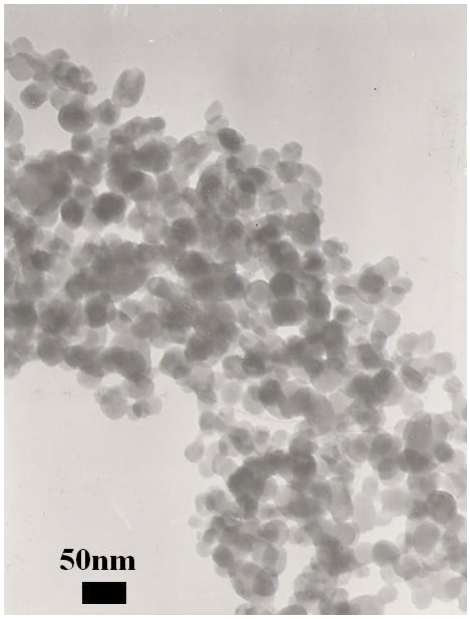



**Figure S10.** TEM image of α-$NaYF_4$:Yb,Er nanoparticles obtained after 6h glycerol-mediated reaction at 260ºC.

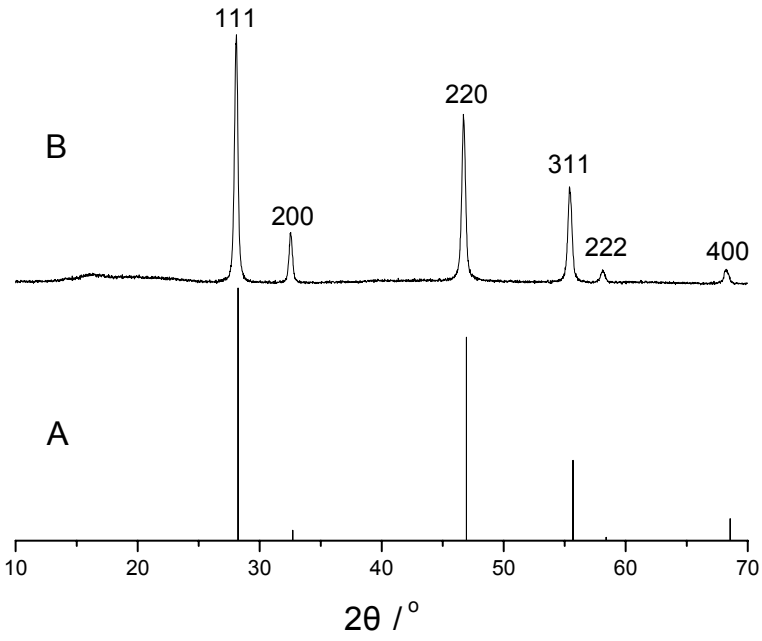



**Figure S11.** Calculated line pattern (A) and experimental powder XRD data for the α-$NaYF_4$:Yb,Er nanoparticles obtained after 6h glycerol-mediated reaction at 260ºC (B)

## 5, Mechanisms for upconversion fluorescence of β-$NaYF_4$:Yb,Er nanoplates

Room temperature upconversion fluorescence spectra of β-$NaYF_4$:Yb,Er nanoplates obtained at 260ºC in the wavelength region of 400-700 nm using different laser power for excitation are shown in Figure S12. There are three major bands in the curves, centered at 522, 542, and 654nm, respectively.

For any unsaturated upconversion mechanism, the output intensity $I_{out}$ is proportional to some power $n$ of the excitation intensity $I_{exc}$, i.e., $I_{out} \propto (I_{exc})^n$, where $n$ is the number of IR photons absorbed per upconversion photon emitted. The exponent $n$ could be determined from the slope of the linear regression in a double logarithmic plot of the emitting intensity versus the excitation laser power. The values of $n$ for above emissions are obtained from Figure S13: 1.9 for 522nm, 1.8 for 542nm, and 1.7 for 654nm, respectively.

Under the 980nm excitation, $Yb^{3+}$ could be exited from ground state $^2F_{7/2}$ to excited state $^2F_{5/2}$. When the excited $Yb^{3+}$ return to the ground state, the energy released from above process could be transferred to $Er^{3+}$ nonradiatively to excite it up to corresponding excited level. As illustrated in Figure S14, the emission bands at 522, 542, and 654nm could be assigned to $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$, and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions of $Er^{3+}$ ion respectively. There exists only one possible pumping route for the green emissions. However, for red emission at 654nm, there exist two possible excitation routes to populate $Er^{3+}$ on corresponding exited state $^4F_{9/2}$. It is difficult to determine the relative probabilities of these two competitive mechanisms, different pumping routes were reported as the main excitation route in the literature.[S1-S3] In the

actual upconversion process, these two competitive mechanisms may contribute to the upconversion emissions together. From the energy level diagram, it is obvious that two 980nm photons are required to excite the $Er^{3+}$ to corresponding excited levels to produce the 522, 542, and 654nm upconversion fluorescence, respectively. This mechanism is in good agreement with the slopes of 1.9 for 522nm, 1.8 for 542nm, and 1.7 for 654nm, which are derived from the experimental data in the double logarithmic plots.

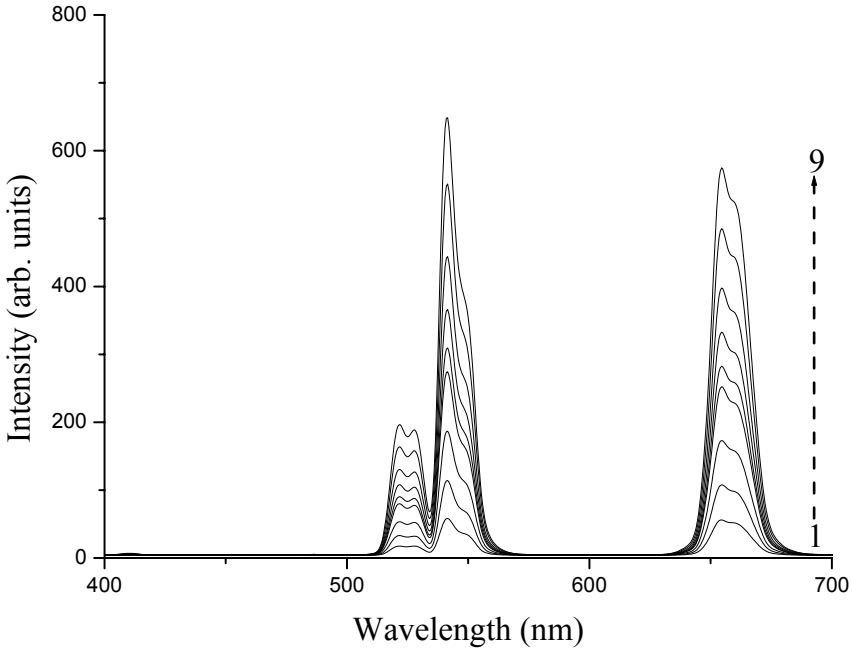



**Figure S12.** Upconversion emission spectrum of β-$NaYF_4$:Yb,Er nanoplates obtained at 260ºC using different laser power for excitation (the laser power varies from 81mW to 307mW, the emission slit is 5nm)

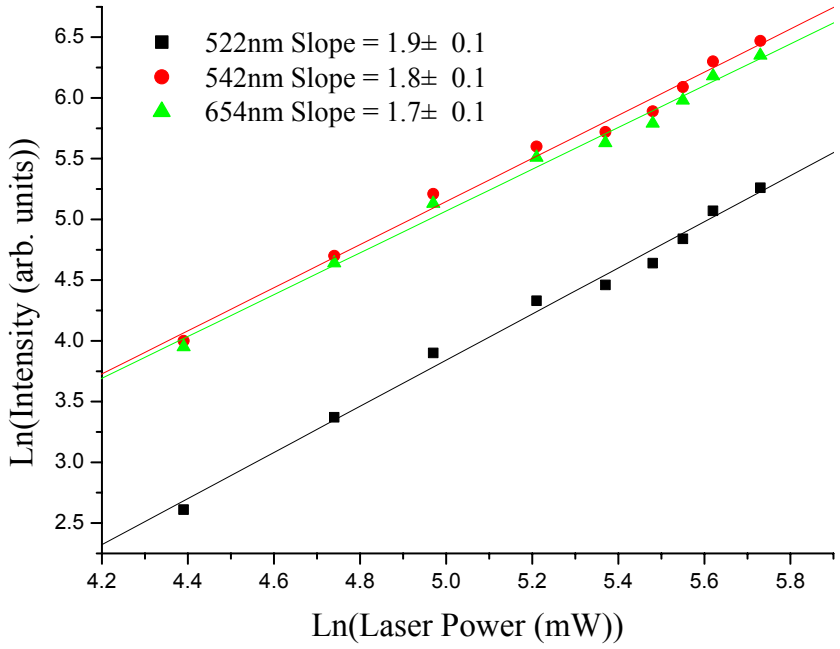



**Figure S13.** Power dependence of the upconversion fluorescence of β-$NaYF_4$:Yb,Er nanoplates obtained at 260ºC.

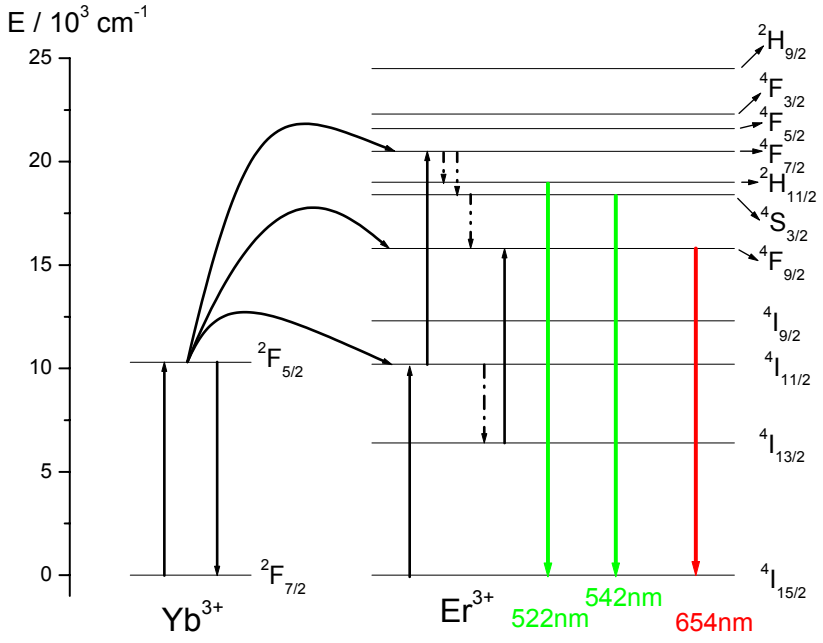



**Figure S14.** The energy level diagrams of the $Yb^{3+}$ and $Er^{3+}$ dopant ions and upconversion mechanisms of the β-$NaYF_4$:Yb,Er nanoplates under 980nm laser excitation

# References

(S1) Xu, S. Q.; Yang, Z. M.; Zhang, J. J.; Wang, G. N.; Dai, S. X.; Hu, L. L.; Jiang, Z. H. *Chem. Phys. Lett.* **2004**, 385, 263

(S2) Heer, S.; Kompe, K.; Gudel, H. U.; Haase, M. *Adv. Mater.* **2004**, 16, 2102

(S3) Yan, R.X.; Li, Y.D. *Adv. Funct. Mater.* **2005**, 15, 763