Electronic Supplementary Information

Synthesis of colour tunable lanthanide ions doped $NaYF_4$ upconversion nanoparticles by controlling temperature

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Experimental section

Materials: Rare earth oxides Y_2O_3 (99.99%), Yb_2O_3 (99.99%), Er_2O_3(99.99%), Tm_2O_3 (99.99%), Ho_2O_3 (99.99%) were purchased from Sinopharm Chemicals Reagents Co., Ltd. (Shanghai, China). Na_2CO_3, oleic acid (OA), octadecylamine (OM), trifluoroacetic acid were purchased from Tianjing Kermel Chemical Reagents Development Center (Tianjing, China). The other chemicals were supplied by Shengyang Chemical Reagents Company and used directly without further purification.

Synthesis of lanthanide ions doped $NaYF_4$ UCNPs: Rare earth trifluoroacetates ($RE(CF_3COO)_3$) and sodium trifluoroacetate (CF_3COONa) were prepared by the literature method.[1] For a typical synthesis of $NaYF_4$:20%Yb,2%Er nanoparticles, a mixture of 0.01 mmol of Er_2O_3, 0.10 mmol of Yb_2O_3, 0.39 mmol of Y_2O_3, and 0.50 mmol of Na_2CO_3 was dissolved in 10 mL of 50% aqueous trifluoroacetic acid at 80 °C. The residual water and acid were slowly evaporated to dryness at 70 °C in a three-necked flask. Then, a mixture of OA (5.0 mmol) and OM (50.0 mmol) was added. The reaction solution was heated to 120 °C and maintained for 30 min under reduced pressure to remove residual water and oxygen during which time the flask was purged periodically with dry nitrogen. The resulting solution was heated to a given temperature and maintained for 1 h under a nitrogen atmosphere. After heating was stopped, the temperature was cooled and the $NaYF_4$:20%Yb,2%Er upconversion nanoparticles were isolated by addition of absolute ethanol and centrifugation. This procedure was repeated at least for two times.

Instrumentation: Upconversion fluorescence spectra were obtained on Hitachi F-4500 fluorescence spectrophotometer under the excitation of a 980 nm laser. Powder X-ray diffraction patterns were measured on a Rigaku D/MAX-2400 with Cu-Kα radiation. The scanning step size was 0.02º 2θ. TEM measurements were carried out on a Tecnai F20 S-TWIN microscope operated at 200 kV. IR spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrometer.

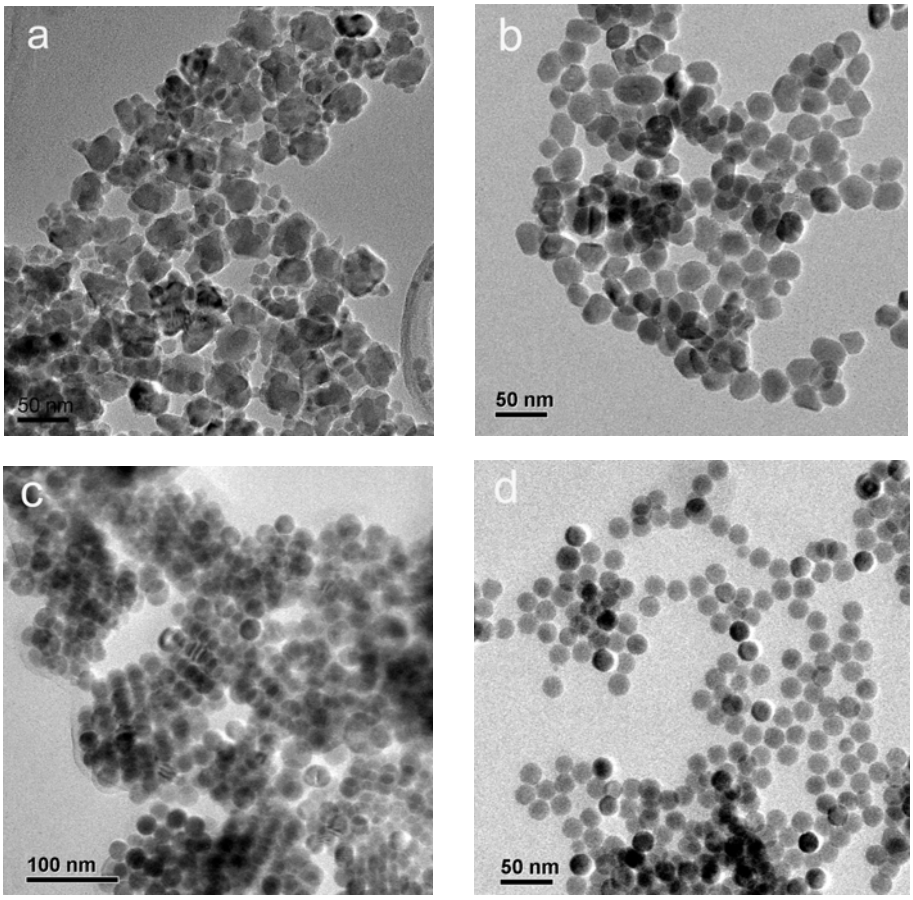

Fig. S1 TEM images of $NaYF_4$:20%Yb,2%Er UCNPs prepared at 260 °C (a), 280 °C (b), 300 °C (c), 320 °C (d) (*t*= 1h, OA/OM=5/50).

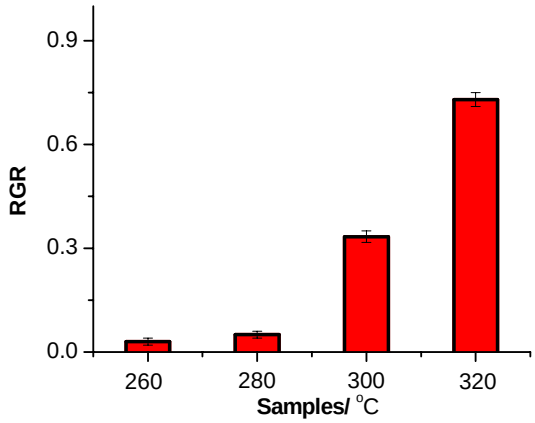

Fig. S2 The intensity ratio of green to red emissions of $NaYF_4$:20%Yb,2%Er UCNPs prepared at different temperature.

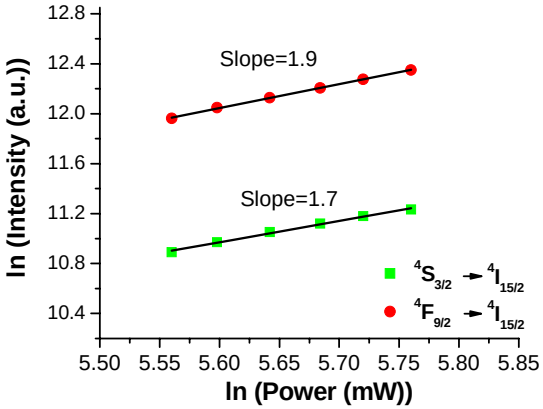

Fig. S3 Power dependence of the green and red upconversion intensity of $NaYF_4$:20%Yb,2%Er nanoparticles prepared at 300 °C.

According to recent report[2], the characteristic Er^{3+} emission at ~410 nm ($^2H_{9/2} \rightarrow {}^4I_{15/2}$) is a three-photon process.

It is known that the upconversion intensity (I) depends on the excitation power (P) according to the power law $I = A\ P^n$, (A is constant) where the number of pumping photons (n) required to excite ions from the ground state to the emitting state can be determined from the slope of the photoluminescence intensity versus the laser excitation power in a log-log plot.

Then, we calculated the number of pumping photons (n). The experimental data for 550- and 670-nm emission bands of $NaYF_4$:20%Yb,2%Er have been fitted with a straight line with a slope of ~ 2, which confirms the two-photon absorption process. Therefore, it is rational that no emission of 410 nm was showed, because two photons were involved in present report.

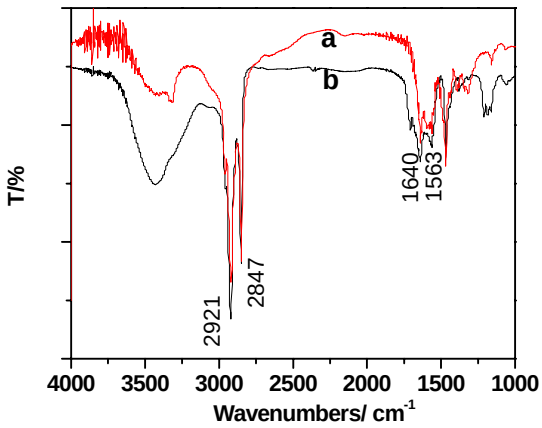

Fig. S4 IR spectra of $NaYF_4$:20%Yb,2%Er UCNPs prepared in OM (a) and OA/OM (b, 5/50).

The IR spectrum shows the bonding of the ligand molecules on the surface of nanoparticles. They play an important role for the preparation of monodisperse particles. The peaks at 2847 and 2921 cm^{-1} are due to the symmetric and asymmetric $\upsilon(CH_2)$ stretching modes. The spectrum shows a broad peak at 3350 cm^{-1}, which originates either from the υ(N-H) stretching of the NH_2 group of octadecylamine or the υ(O-H) stretching mode of water, whereas the peak at 1563 cm^{-1} arises from the υ(N–H) scissoring mode and indicates that the N-H bonds are intact and that octadecylamine binds to the nanoparticles surface. The absorption band at 1640 cm^{-1} became

stronger, which ascribed to the coordinated carbonyl groups.[2,3]

Effect of the composition of reaction solution: In the present synthesis, the composition of reaction solution plays an important role in the manipulation of multicolour emissions of $NaYF_4$:20%Yb,2%Er UCNPs by controlling temperature. When octadecylamine (OM) was used only, the obtained $NaYF_4$:20%Yb,2%Er UCNPs showed green emissions even reacted at 260°C. However, the obtained $NaYF_4$:20%Yb,2%Er UCNPs at different temperature were all in nearly red emissions when the molar ratio of oleic acid (OA) to octadecylamine (OM) was 25/30. Although it is rational that the crystallinity of $NaYF_4$:20%Yb,2%Er UCNPs increased gradually with the rise of temperature, the color output almost did not vary.

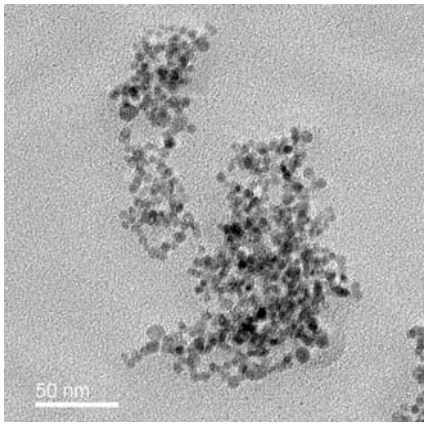

Fig. S5 TEM image (a) of $NaYF_4$:20%Yb,2%Er UCNPs prepared in OM at 260 °C

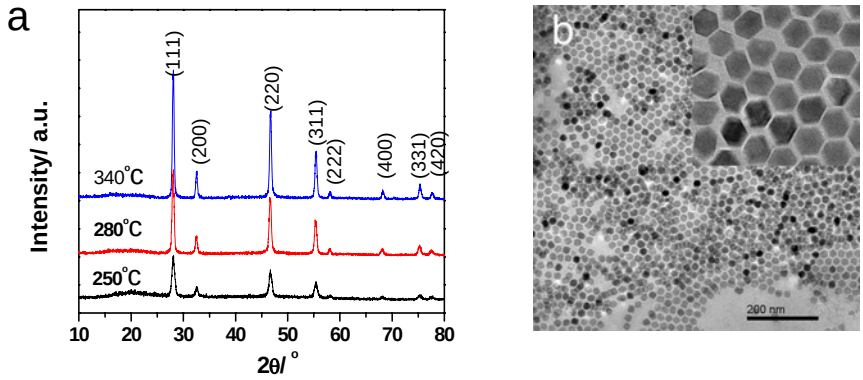

Fig. S6 XRD patterns (a) of $NaYF_4$:20%Yb,2%Er UCNPs prepared at different temperature (OA/OM=20/35, *t* =1h). And TEM image (b) of $NaYF_4$:20%Yb,2%Er UCNPs prepared at 280 °C (OA/OM=20/35, *t* =1h).

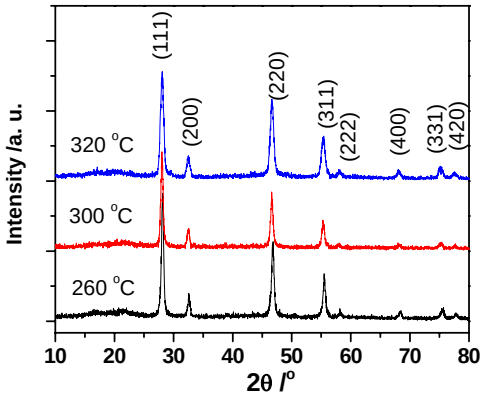

Fig. S7 XRD patterns of $NaYF_4$:20%Yb,2%Ho UCNPs prepared at different temperature (*t*= 1h, OA/OM=5/50).

For comparison, we had characterized the $NaYF_4$:20%Yb,2%Er UCNPs prepared at 260°C after annealing at 320°C. We could observe that they were still irregular in shape. Some of nanoparticles seemed aggregated and the size increased slightly to~33 nm.

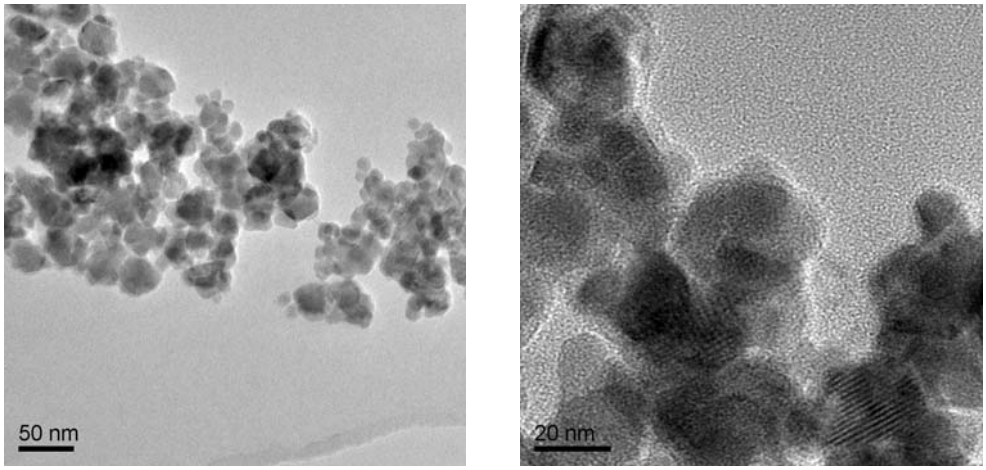

Fig. S8 TEM images of $NaYF_4$:20%Yb,2%Er UCNPs prepared at 260°C were annealed at 320°C.

References:

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