Electronic Supplementary Material (ESI) for Dalton Transactions

Separation and Phase Conversion Investigation of Yb^{3+}/Er^{3+} Codoped $NaYF_4$ Nanoparticles

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Experimental

Experimental details

Materials: All the chemicals were A. R. grade, bought from Beijing Chemical Reagent Co., Inc., and used as received without further purification.

1. Synthesis of $NaYF_4$:Yb/Er

In the typical synthesis, 1.2 g NaOH was dissolved in 5 mL deionized water, mixd with 7 mL ethanol and 20 ml oleic acid, To the mixture added 1 mL 0.5 mol/L $RE(NO)_3$ (RE= Y, Yb, Er, volume ratio: 78:20:2) and 3ml 1mol/L NaF under stirring. The solution was then transferred into a Teflon-lined autoclave (40 mL) and heated to 200 °C and aged at that temperature for 20 h. The finally products were collected by centrifugation, washed with ethanol and cyclohexane twice, and finally re-dispersed in cyclohexane for separation.

2. Separation of NaYF4 :Yb/Er

(1) Density gradient preparation

All separation experiments were performed using a Beckman Optima L8-80M ultracentrifuge. Typically a five-layer step gradient was made using 30%, 40%, 50%, 60%, and 70% concentrations (by volume) of solutions of CCl_4 in cyclohexane. For instance, a volume ratio of CCl_4:cyclohexane = 7:3 was used to make the 70% solution. A step gradient was created directly in Beckman centrifuge tubes (polyallomer) by adding layers to the tube with decreasing density (i.e., lower CCl_4 concentration).

To make a (30% + 40% + 50% + 60% + 70%) gradient, 2 mL of 70% solutions of CCl_4 in cyclohexane was first added to the centrifuge tube, then 2 mL 60% solutions of CCl_4 in cyclohexane was slowly layered above the 70% layer. The subsequent layers were made following the same procedure and resulted in a density gradient along the centrifuge tube.

(2) Separation of $NaYF_4$: Yb/Er

0.4 mL of $NaYF_4$: Yb^{3+}/Er^{3+} colloid solution was added on top of the five-layer step gradient, and centrifuged at 10,000 rpm for 10 minutes (a photograph of the ultracentrifuge tube after separation is shown in Fig. 1A). The gradient medium containing separated nanocrystal was manually sampled in fractions of 400 μL for characterization.

3. Characterization of nanocrystals

Transmission electron microscopy (TEM): A transmission electron microscope (Hitachi H-800, operated at 200 kV) was used to evaluate nanorod size and shape. Fractions obtained by gradient separation were directly dried on carbon film supported on copper grids. X-ray diffraction (XRD): XRD patterns of samples were recorded on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (40 kV, 30 mA, λ = 1.5418 Å). The optical properties of the NPs were characterized using a Hitachi F-4600 fluorescence spectrophotometer operated at room temperature with a 980 nm diode laser with a fiber optic accessory (Beijing Hi-Tech Optoelectronic Co.).

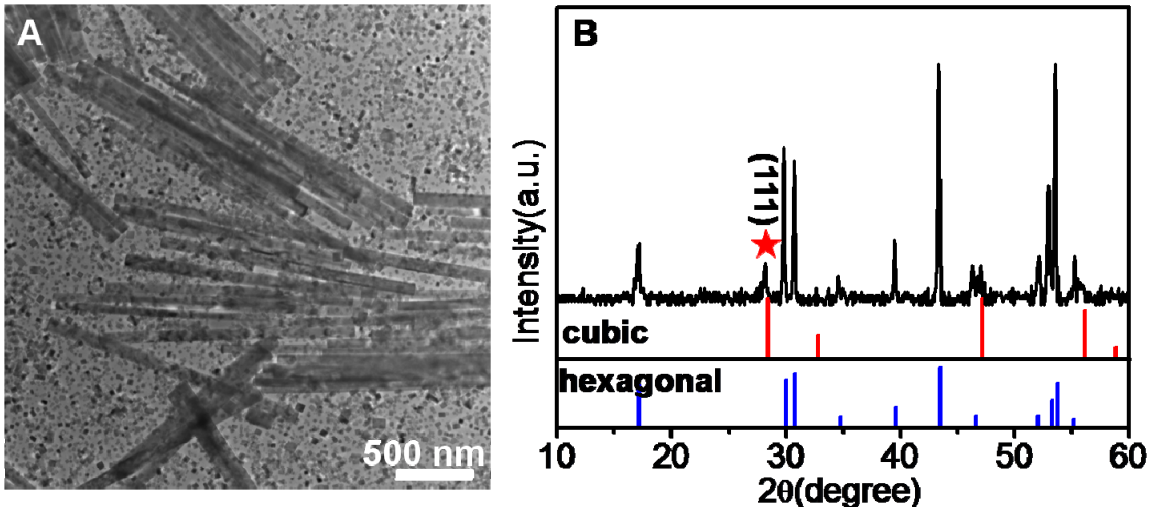

Fig. S1 (A) TEM image of $NaYF_4:Yb^{3+}/Er^{3+}$; (B) XRD patterns of prepared $NaYF_4:Yb^{3+}/Er^{3+}$ and standard dates for cubic and hexagonal of $NaYF_4:Yb^{3+}/Er^{3+}$.

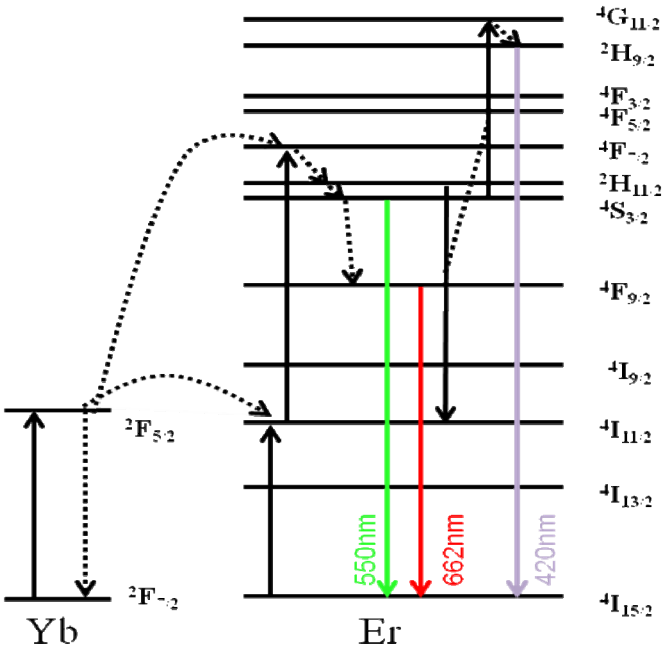

Fig. S2 Energy-level diagram of $NaYF_4:Yb^{3+}/Er^{3+}$ and UC process under 980 nm excitation

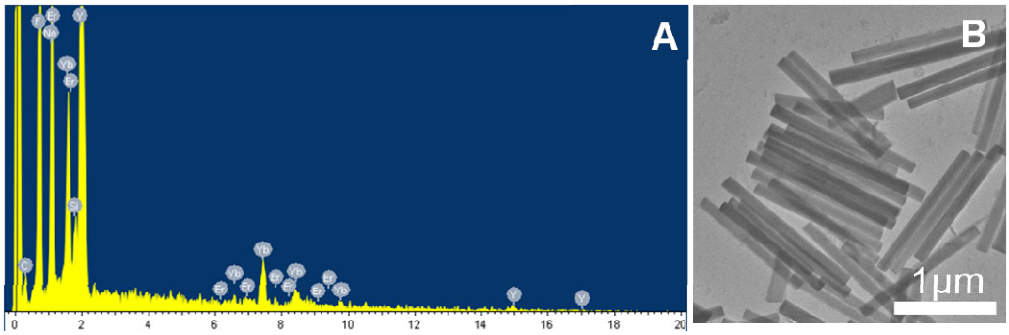

Fig. S3 Energy dispersive spectrum (A) and TEM images (B) of $NaYF_4$:Yb^{3+}/Er^{3+} after 7 days .

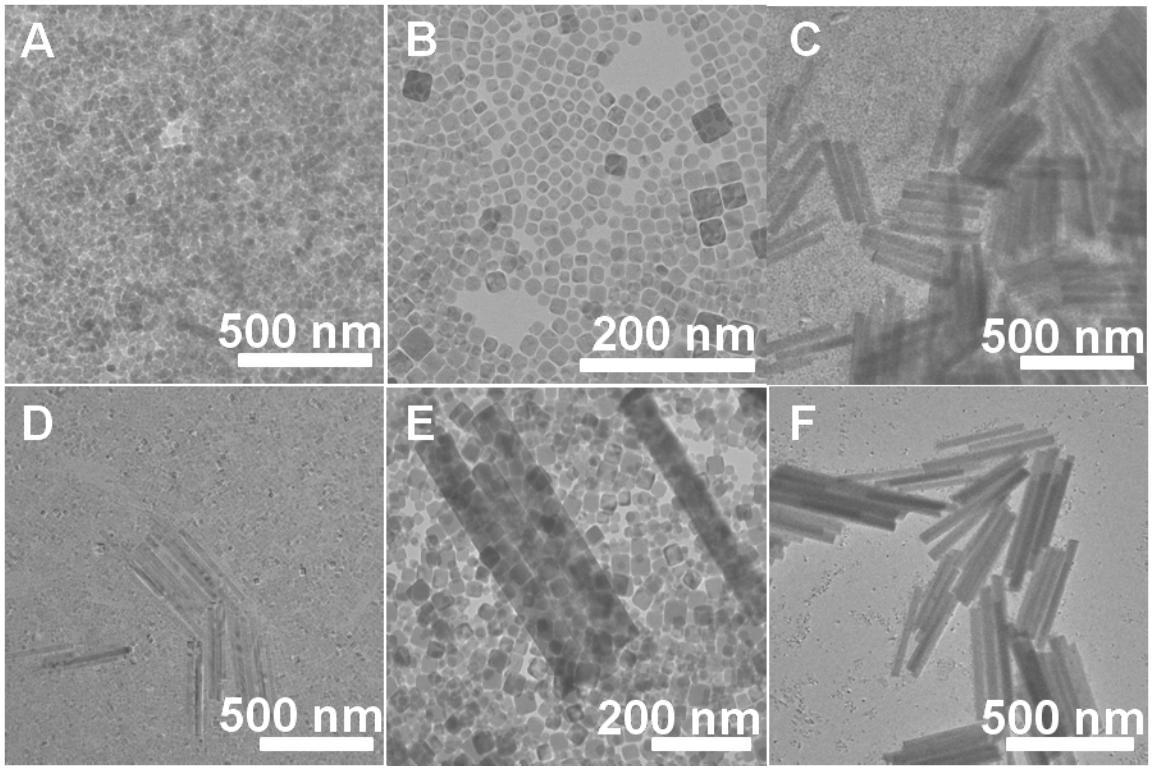

Fig. S4 TEM images of the samples heated with 1.5 h: (A) $NaYF_4$, (B) $NaYbF_4$, (C) $NaErF_4$; 2h: (D) $NaYF_4$, (E) $NaYbF_4$, (F) $NaErF_4$.

fraction	Y:Yb:Er	Average
f1	84:15:1	83:15:2
	83:15:2	
	83:14:3	
f14	84:14:2	82:16:2
	81:17:2	
	81:18:1	
f18	74:22:4	74:22:4
	75:22:3	
	72:24:4	

Figure S5. Energy dispersive spectra of typical fractions: f1, f14 and f18.