Supplementary information

Controlled synthesis of $NaYF_4$: Yb, Er nanocrystals with upconversion fluorescence via a facile hydrothermal procedure in aqueous solution

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Experimental details on the synthesis

All reagents were purchased from Shanghai Chemical Reagent Company and used without further purification. The aqueous solutions were prepared using ultrapure water (Mill-Q, Millipore, 18.2 MΩ resistivity). In a typical synthesis procedure, lanthanide oxides Y_2O_3 (0.195 mmol), Yb_2O_3 (0.05 mmmol) and Er_2O_3 (0.005 mmol) were dissolved in hot nitric acid (65℃) to acquire $Ln(NO_3)_3$. Solvent was evaporated after 6 h reaction. The as-obtained nitrate salts were added to 1.5 mmol trisodium citrate aqueous solution to form Ln-citrate chelates. Subsequently, a certain volume of ethanol was added into the above Ln-citrate solution (according to the volume ratio of ethanol to water, marked as Solution A, final volume 24 ml). Under vigorous stirring, another aqueous solution containing stoichiometric amount of NaF and certain volume of ethanol (according to F^-/Ln^{3+} molar ratio and volume ratio of ethanol to water, marked as Solution B, final volume 12 ml) was added dropwise to solution A. Note that the composition of solvents of solution A and B were the same with a

certain ethanol-to-water volume ratio. The pH of the mixture was adjusted to designed value with nitric acid and sodium hydroxide. Then the mixture (with a total volume 36 ml) was transferred into a 50 ml Teflon autoclave and heated to 240 ℃. After 2h hydrothermal treatment, the autoclave was cooled down to room temperature in air. A precipitate was obtained after evaporating the solvent. The precipitate was washed with water and absolute ethanol three times and finally dried under vacuum.

Characterization of the products

The crystal phase of the products were identified by a Brucker D8 Discover X-Ray Diffractometer (XRD) with 2θ range from 10° to 70° at a scanning rate of 4° per minute, with Cu Ka irradiation (k=1.5406 Å). The size and morphology of the samples were characterized by a JEM-2010 transmission electron microscope (TEM) operated at 200kV. A 980 nm CW laser (Beijing Hi-Tech Optoelectronic Co., Ltd.) was used as the excitation source with the power being set at 20 $W.cm^{-2}$. The upconverting fluorescence spectra were recorded on DCS200PC Photon Counting (Beijing Zolix Instruments Co., Ltd) with single-photon sensitivity through an Omni-λ500 monochromator (Beijing Zolix Instruments Co., Ltd).

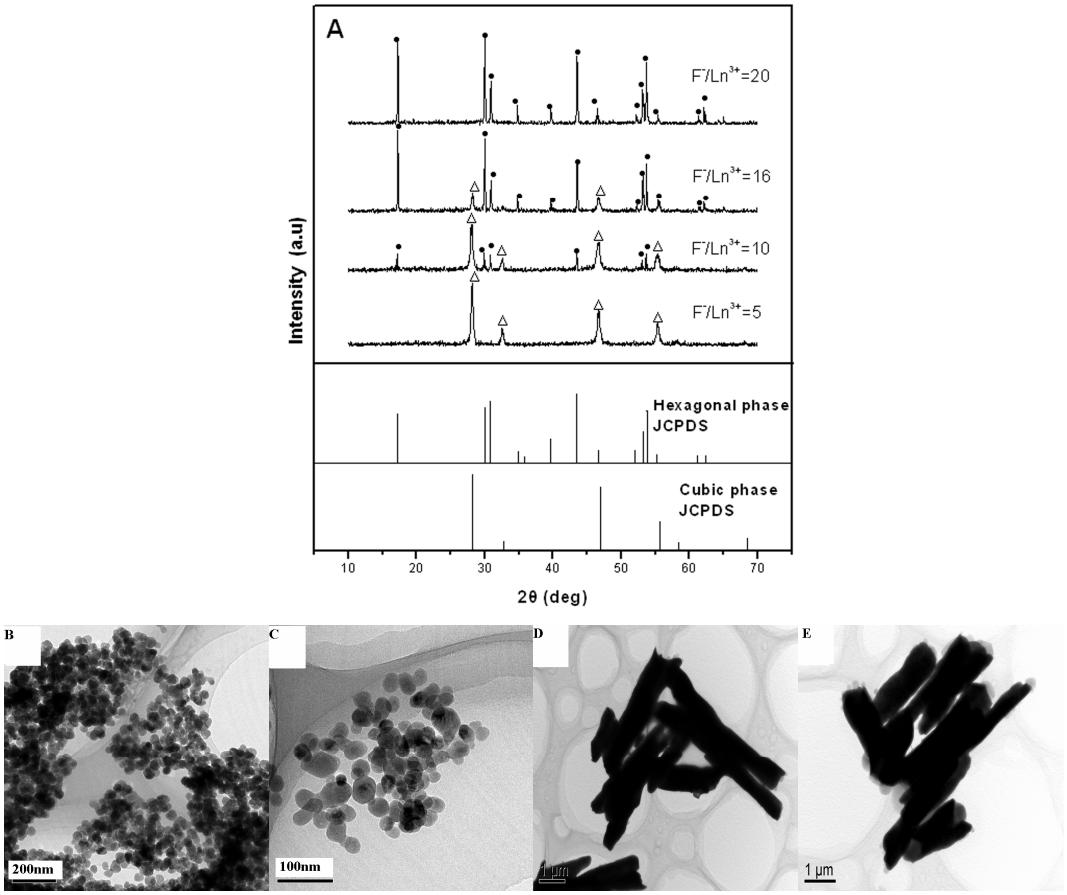

Fig. S1 XRD patterns of $NaYF_4$: Yb, Er nanocrystals synthesized in water with different F^-/Ln^{3+} ratio (A), and TEM images of the samples, in which F^-/Ln^{3+}=5 (B), 10 (C), 16 (D) and 20 (E), respectively. pH=3.0, hydrothermal time, 2h. Δ cubic phase $NaYF_4$: Yb, Er (JCPDS file no. 77-2042); ● hexagonal phase $NaYF_4$: Yb, Er (JCPDS file no. 28-1192).

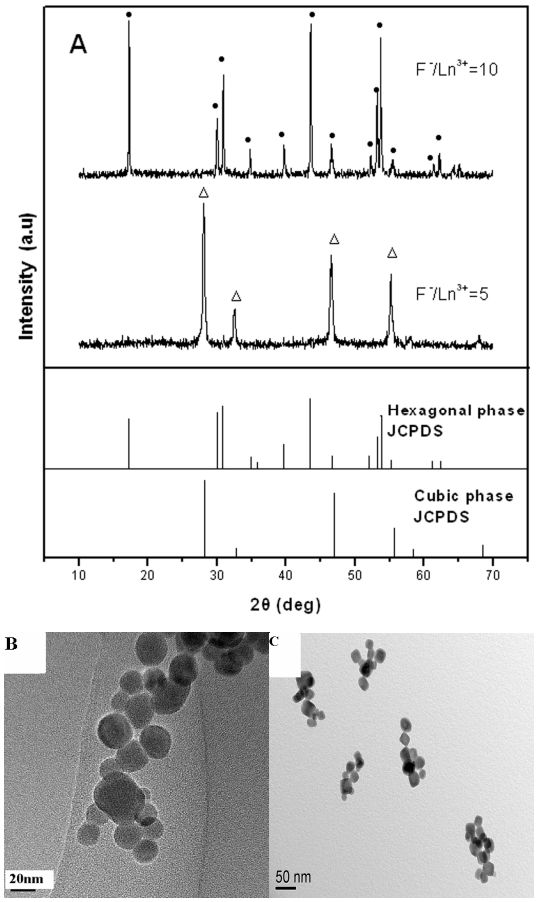

Fig. S2 XRD patterns of $NaYF_4$: Yb, Er nanocrystals with ethanol/water (1:1) as solvent (A), and TEM images of the samples, in which F^-/Ln^{3+}=5 (B) and 10 (C), respectively. pH=3.0, hydrothermal time, 2 h. Δ cubic phase $NaYF_4$: Yb, Er (JCPDS file no. 77-2042); ● hexagonal phase $NaYF_4$: Yb, Er (JCPDS file no. 28-1192).

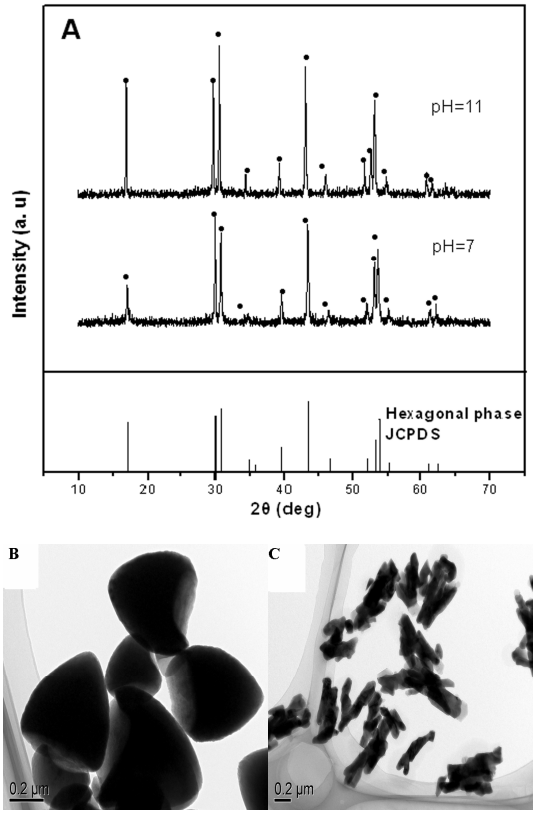

Fig. S3 XRD patterns of $NaYF_4$: Yb, Er nanocrystals with ethanol/water (1:1) as solvent (A), and TEM images of the samples where pH=7 (B), pH=11 (C), respectively. F^-/Ln^{3+}=10, hydrothermal time, 2 h. ● hexagonal phase $NaYF_4$: Yb, Er (JCPDS file no. 28-1192).