

Electronic Supplementary Information

A facile aqueous synthesis strategy for hexagonal phase NaGdF₄ nanorods

Rongyao Gao^{a, †}, Liyuan Sun^{a, †}, Luoyuan Li^b, Tingting Pan^a, Limin Fu^{a, *}, Xi-Cheng Ai^a, Jian-Ping Zhang^a

^a. *Department of Chemistry, Renmin University of China, Beijing 100872, China.*

^b. *School of Pharmaceutical Sciences, Tsinghua University, Beijing 100084, P. R. China.*

**To whom correspondence should be addressed*

E-mail: lmfu@ruc.edu.cn; Tel: +86 010 62516604

Experiment

1.1 Materials

Rare-earth oxides, Gd_2O_3 (99.99%), Lu_2O_3 (99.99%), Y_2O_3 (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%) and Tm_2O_3 (99.99%) were purchased from Foshan Lansu Chemical Industry Company. NH_4F (98%) and NaCl (98.5%) were purchased from J&K Chemical. β -cyclodextrin were purchased from Sinopharm Chemical Reagent Co., Ltd. Rare-earth chlorides (GdCl_3 , LuCl_3 , YCl_3 , YbCl_3 , ErCl_3 and TmCl_3) were prepared by the transformation of their respective rare-earth oxides (Gd_2O_3 , Lu_2O_3 , Y_2O_3 , Yb_2O_3 , Er_2O_3 and Tm_2O_3).

1.2 Characterization

The crystal phase of the nanomaterial was analyzed by Shimadzu XRD-7000 X-ray diffraction (XRD, Shimadzu Corporation, Japan). The radiation source was $\text{Cu K}\alpha$ line ($\lambda=0.154056$), the scanning speed was $2^\circ/\text{min}$, and the scanning range was $10^\circ\sim 70^\circ$. The reference data comes from the Joint Committee on Powder Diffraction Standards (JCPDS). The morphologies of the upconversion nanorods were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010) at an accelerating voltage of 5 kV and JEOL JEM-2010 transmission electron microscope (TEM) low to high resolution transmission electron microscope (HRTEM) at 200 kV. FT-IR spectra were obtained on a Bruker TENSOR 27 Fourier transform IR spectrometer (Karlsruhe, Germany). We disperse all the nanomaterials in ethanol for further spectral testing. The steady-state upconversion luminescence spectra were measured using a FLS980 fluorescence spectrometer (Edinburgh Instruments, UK). The excitation range was 500-700 nm. The excitation source was an external continuous 980 nm diode laser ((MDL-H-980-5W, Changchun New Industrial Optoelectronics). Technology Co., Ltd).

1.3 Synthesis

In this synthesis procedure, 18 mg β -cyclodextrin (β -CD) mixed with 1 mmol RECl_3 (0.78 mmol MCl_3 (M: Gd, Lu, Y), 0.2 mmol YbCl_3 and 0.02 mmol NCl_3 (N:Er,Tm)) and 2.5 mmol NaCl were dissolved in 30 mL deionized water under vigorous stirring.

Subsequently, 5 mL NH_4F aqueous solution (with 4 mmol NH_4F) was dropwise added into the mixed solution slowly and raised the temperature to $60\text{ }^\circ\text{C}$ for 40 min. When the colorless transparent mixed solution becomes milky white, the solution cooled down to the room temperature. The UCNPs was precipitated by centrifugation with ethanol for three times then dried in air at $60\text{ }^\circ\text{C}$ before further characterization.

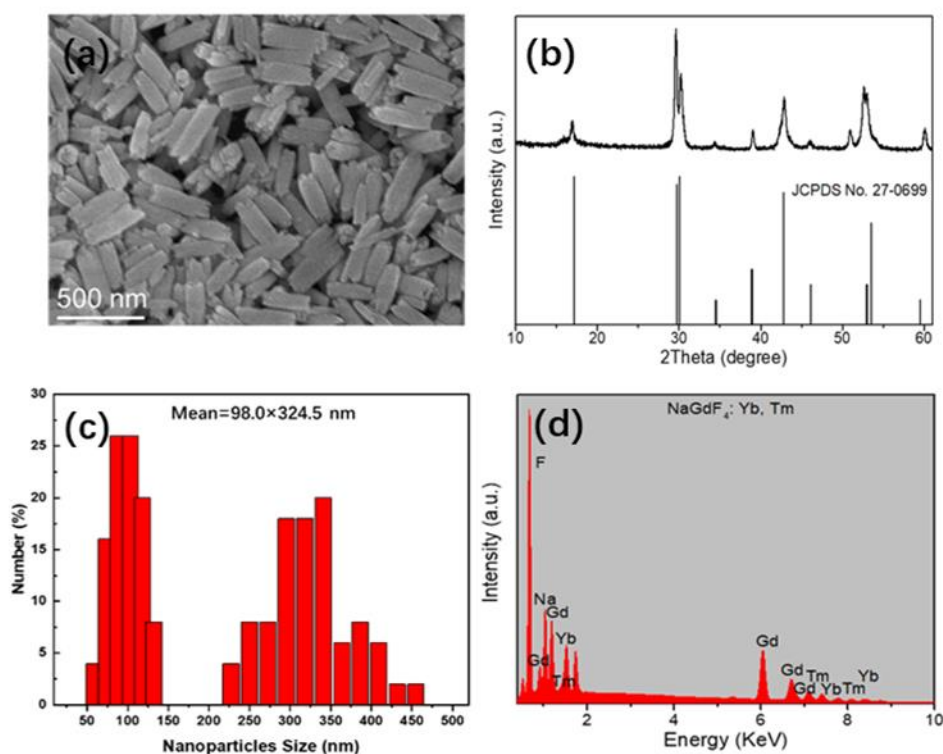


Fig. S1 (a) SEM image. of the $\beta\text{-NaGdF}_4\text{: Yb}^{3+}/\text{Tm}^{3+}$ nanorods. (b) XRD pattern of the $\beta\text{-NaGdF}_4\text{: Yb}^{3+}/\text{Tm}^{3+}$ nanorods (JCPDS card No.27-0699). (c) Size distribution histograms of $\beta\text{-NaGdF}_4\text{: Yb}^{3+}/\text{Tm}^{3+}$ nanorods. (d) Energy-dispersive X-ray spectroscopy (EDS) of $\beta\text{-NaGdF}_4\text{: Yb}^{3+}/\text{Tm}^{3+}$ nanorods.

Nearly rodlike shape of the prepared $\beta\text{-NaGdF}_4\text{: Yb/Tm}$ nanoparticles was shown in Fig. S1 (a). The size distribution histograms of the UCNPs was shown in Fig. S1 (c), the average diameter of the nanorods was 98.0×324.5 nm. As shown in Fig. S1 (b), the XRD pattern of the UCNPs was well confirm to the standard hexagonal phase card (JCPDS No. 27-0699), which indicated that the acquired UCNPs was pure hexagonal. The compositions of $\beta\text{-NaGdF}_4\text{: Yb}^{3+}/\text{Tm}^{3+}$ nanorods were confirmed by EDS spectroscopy (Fig. S1 (d)), and the presence of the elements Yb and Tm in the NaGdF_4

matrix directly prove the successful doping of the dopants.

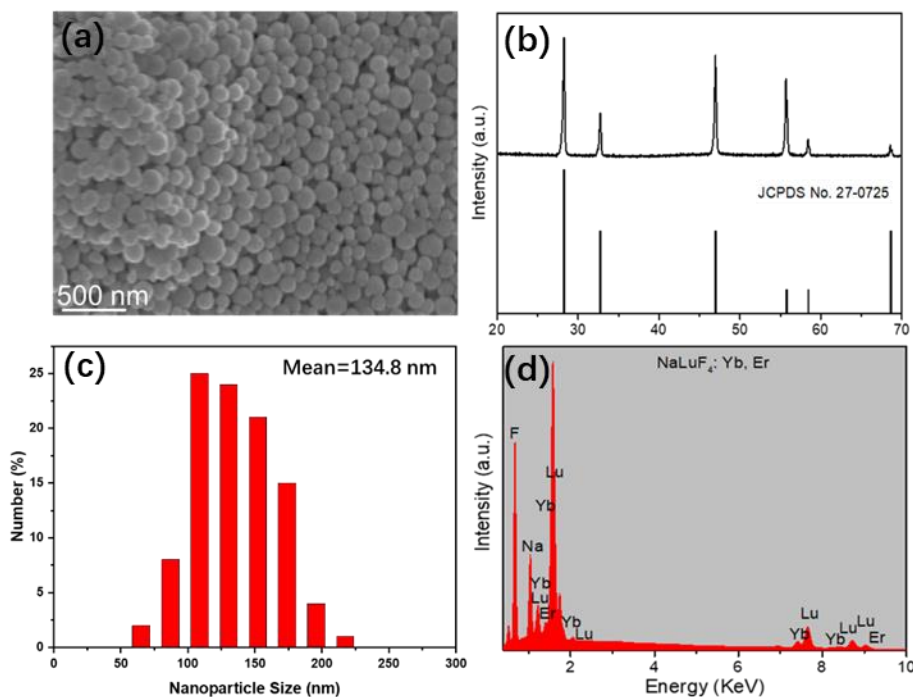


Fig. S2 (a) SEM image of the α -NaLuF₄: Yb³⁺/Er³⁺ nanoparticles. (b) XRD pattern of the α -NaLuF₄: Yb³⁺/Er³⁺ nanoparticles (JCPDS card No.27-0725). (c) Size distribution histograms of α -NaLuF₄: Yb³⁺/Er³⁺ nanoparticles. (d) Energy-dispersive X-ray spectroscopy (EDS) of α -NaLuF₄:Yb³⁺/Er³⁺ nanoparticles.

As shown in Fig. S2(a), the spherical morphology and size of α -NaLuF₄: Yb³⁺/Er³⁺ nanoparticles were characterized by scanning electron microscopy (SEM). The size of nanoparticles was 134.8 nm from Fig. S2 (c). The XRD pattern of the UCNP was well indexed to the standard cubic phase card (JCPDS No. 27-0725), which indicated that the acquired UCNP was pure cubic phase that shown in Fig. S2 (b). Energy-dispersive X-ray spectroscopy (EDS) observed in Fig. S2 (d) confirmed the presence of the elements Na, F, Lu, Yb, and Er of the NaLuF₄: Yb/Er nanoparticle, demonstrating the successful doping of the dopants.

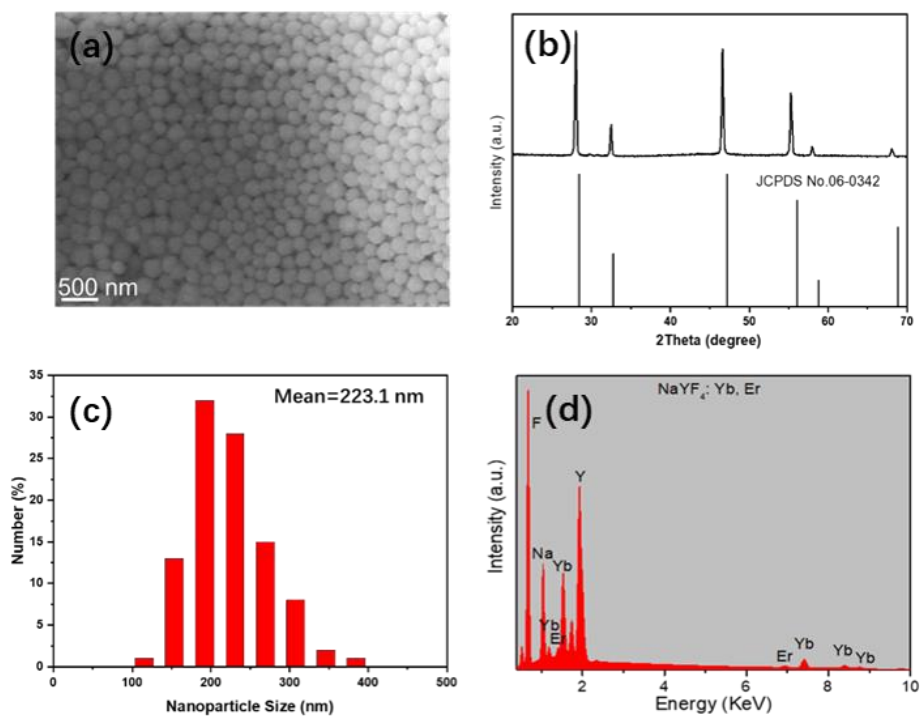


Fig. S3 (a) SEM image of the α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles. (b) XRD pattern of the α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles (JCPDS card No.06-0342). (c) Size distribution histograms of α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles. (d) Energy-dispersive X-ray spectroscopy (EDS) of α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles.

The SEM image (Fig. S3 (a)) shows that the morphology of α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles was nearly spherical. The average size of UCNPs was 223.1 nm according to the size distribution histograms (Fig. S3 (c)). As shown in Fig. S3 (b), the XRD pattern of the UCNPs were in good agreement with the standard cubic phase card (JCPDS No. 06-0342). The compositions of α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles were confirmed by EDS spectroscopy (Fig. S3 (d)), and the presence of the elements Yb and Er in the NaYF₄ matrix directly prove the successful doping of the dopants.

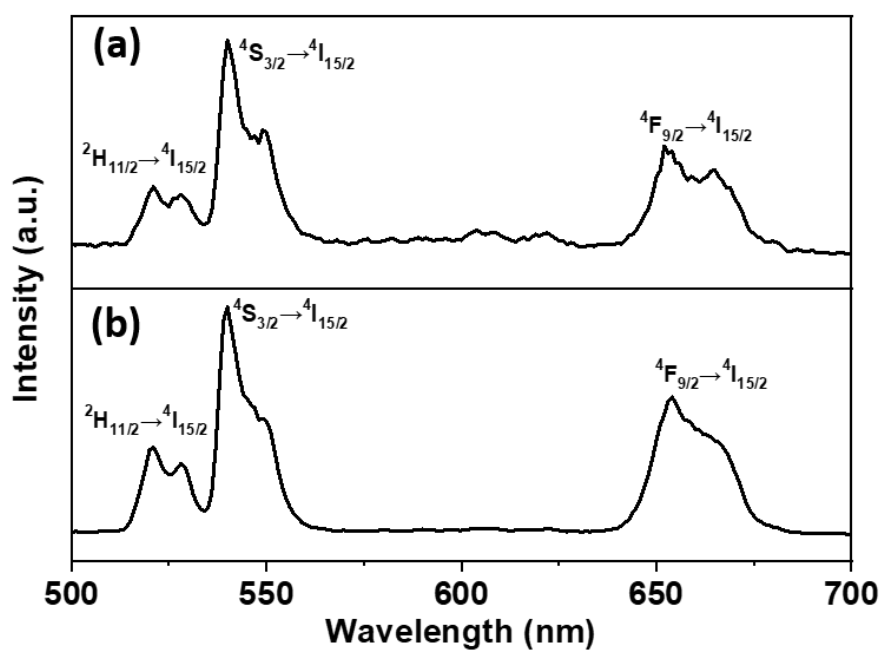


Fig. S4 Upconversion luminescence spectra of (a) α -NaLuF₄: Yb³⁺/Er³⁺ nanoparticles and (b) α -NaYF₄: Yb³⁺/Er³⁺ nanoparticles under 980 nm laser excitation.

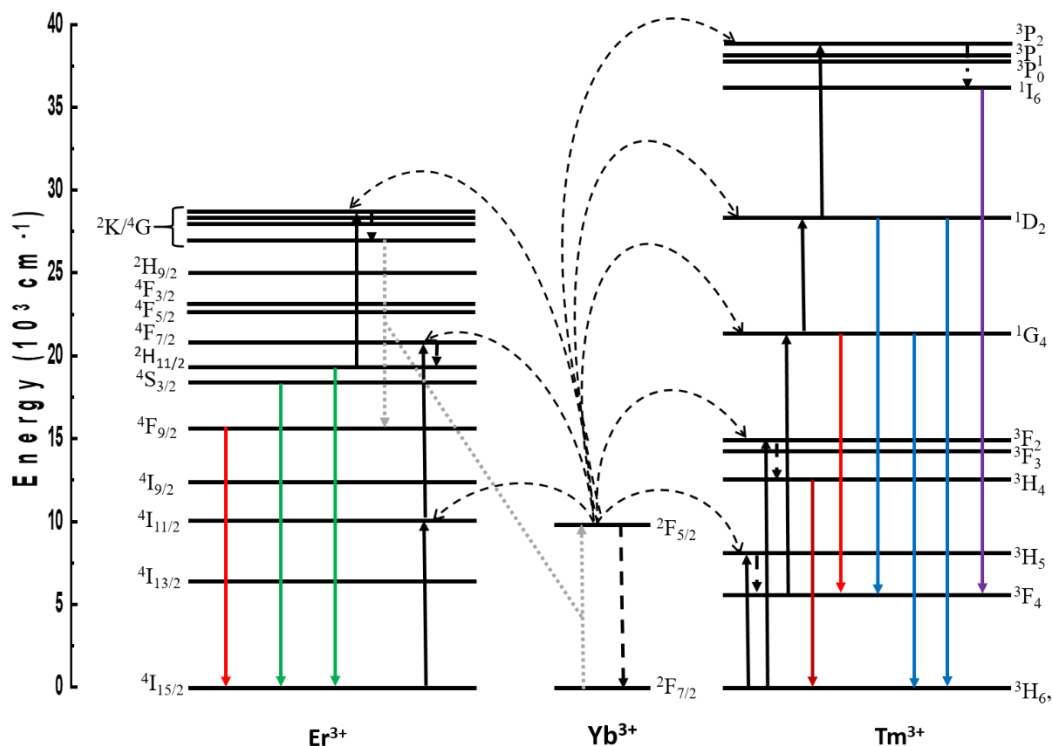


Fig. S5 Energy level diagram and possible transitions of Yb^{3+} , Er^{3+} and Tm^{3+} ions.¹⁻⁵

The role of the NH_4F is to provide F^- ions for NaREF_4 nanoparticles, other soluble fluorides can replace the NH_4F . For example, we use NaF instead of NH_4F for NaGdF_4 nanocrystals by this facile method. XRD and steady-state luminescence spectra were performed to characterize the crystal-phase and the upconversion property of the prepared nanoparticles. The XRD pattern (Figure S6) of the sample was well indexed to the standard hexagonal phase card (JCPDS No. 27-0699), which indicated that the acquired NaGdF_4 : Yb/Er nanocrystals was pure hexagonal phase. The steady-state luminescence spectra (Figure S7) show the typical emissions centered at 521 nm, 540 nm and 654 nm of Er^{3+} ions originated from the transitions of $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$, respectively. Therefore, we can use other soluble fluorides for NaLnF_4 nanoparticles by our synthesis method.

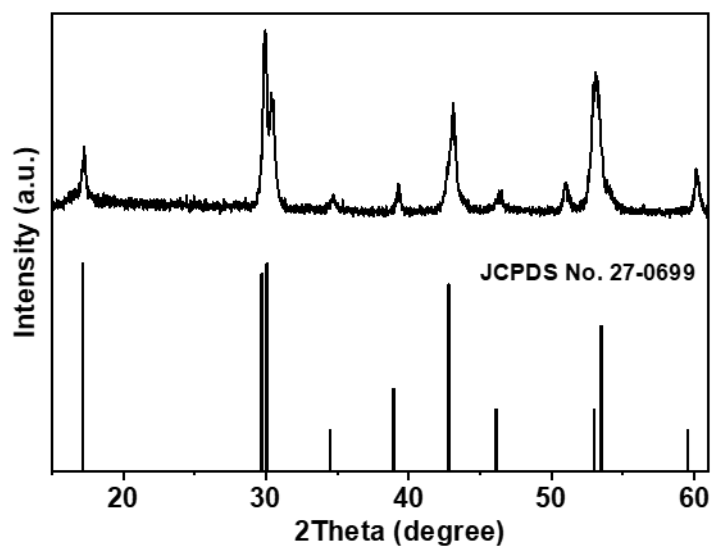


Figure S6. XRD pattern of the β -NaGdF₄: Yb³⁺/Er³⁺ nanocrystals that obtained by using NaF instead of NH₄F in our synthetic method (JCPDS card No.27-0699).

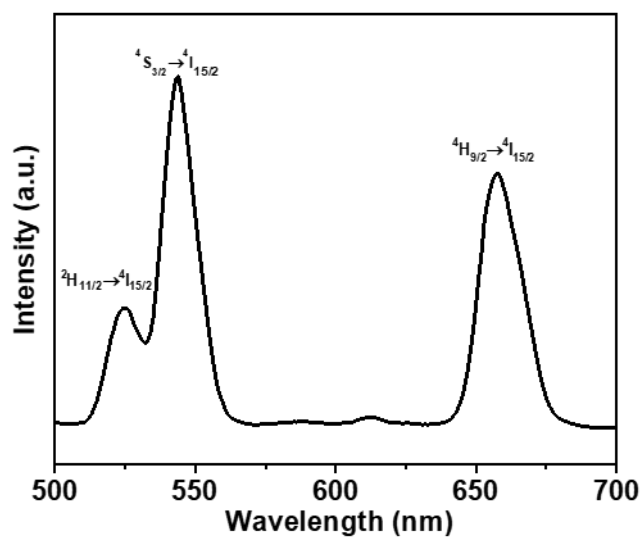


Figure S7. Upconversion luminescence spectra of the β -NaGdF₄: Yb³⁺/Er³⁺ nanocrystals that obtained by using NaF instead of NH₄F in our synthetic method.

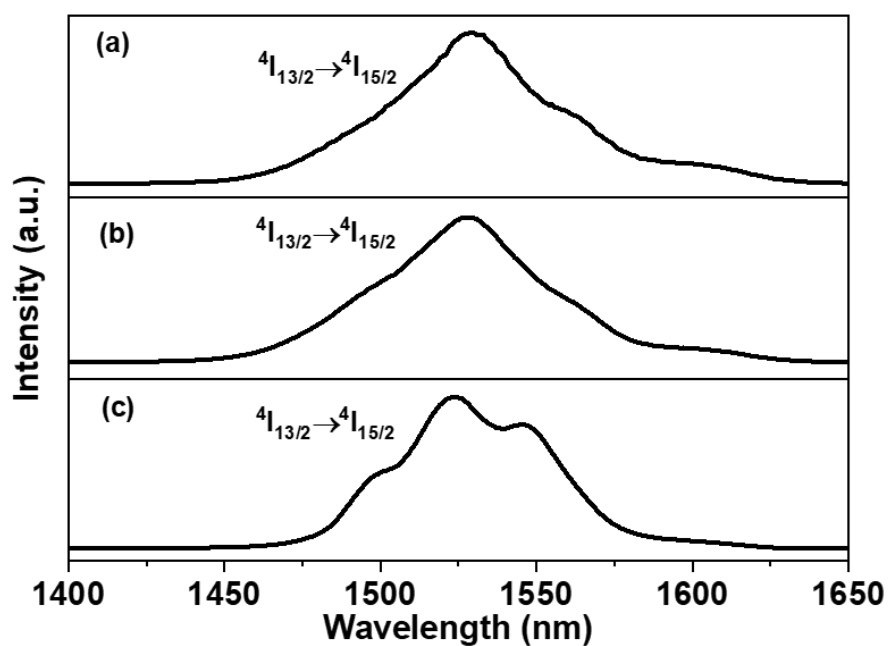


Fig. S8 The SWIR luminescence spectra of (a) NaLuF₄: Yb/Er, (b) NaYF₄: Yb/Er and (c) NaGdF₄: Yb/Er nanocrystals.

Reference

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