

## **Ionothermal Synthesis of Hexagonal-phase NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup>/Tm<sup>3+</sup> Upconversion Nanophosphors**

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### **SUPPORTING INFORMATION**

#### **Synthetic Procedures:**

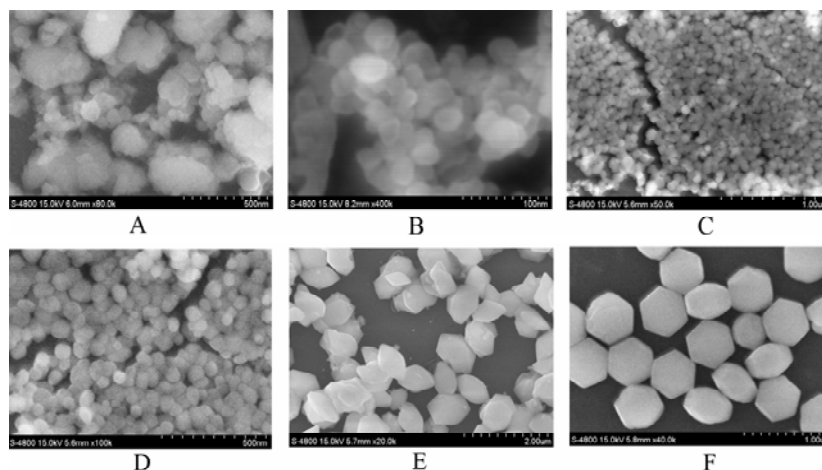
All reagents were analytical grade. Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Ln =Y, Yb, Er and Tm) salt was purchased from Beijing Chemical Plant (Beijing, China). [Bmim][BF<sub>4</sub>] was purchased from Shanghai Chengjie Chemical Co., Ltd., China (97%). These chemicals were used without further purification.

In a typical synthetic route, 0.056g NaCl, 0.2985g Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 0.093g Yb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 0.0093g Er(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O or 0.0093g Tm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added into a beaker containing 10 mL of BmimBF<sub>4</sub> and stirred for 30 min at 80 °C, the above mixed solution was then transferred into a 23 mL Teflon-lined autoclave and kept at 160 °C for 18 h, before being cooled to room temperature and diluted with the appropriate absolute ethanol or acetone. Finally, the precipitates were collected through centrifugation at a speed of 6000 rpm, washed by absolute ethanol, and dried in vacuum at 50 °C

#### **Characterization:**

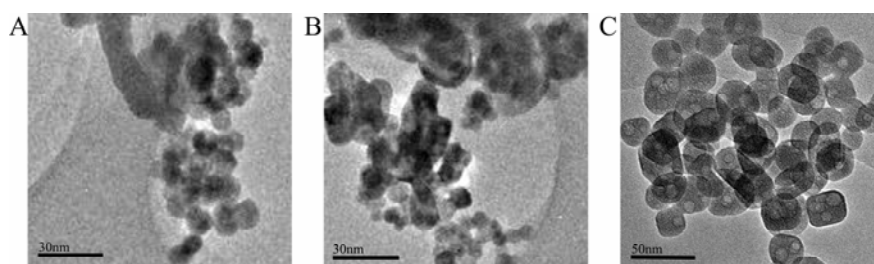
The structure and morphology of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup>/Tm<sup>3+</sup> NCs were characterized by X-ray powder diffractometer (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectra, and transmission electron microscopy (TEM). The obtained samples were characterized by XRD using a Bruker D8-advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The size and morphology of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup>/Tm<sup>3+</sup> NCs were characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-4800). FT-IR spectra were recorded at a Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. In making the KBr pellets, 1 mg of sample was diluted with approximately 100 mg of KBr power. The low- and high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-3010 electron microscope operated at 300 kV. The upconversion emission spectra of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup>/Tm<sup>3+</sup> NCs were acquired using a Jobin-Yvon LabRam Raman spectrometer system equipped respectively with 1800 and 600 grooves/mm holographic

gratings, respectively, and a Peltier air-cooled CCD detector. The samples were excited by a CW semiconductor diode laser at 980 nm.



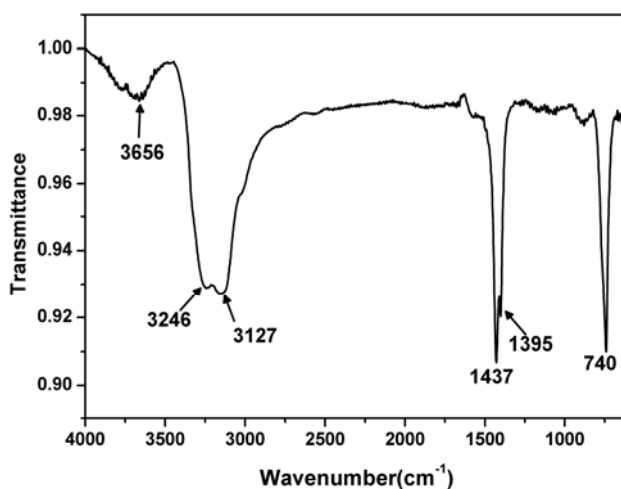
**Fig. S1** SEM images of the products obtained at 120 °C (A: amorphism); 140 °C (B: aggregate sphere with bad crystallization); 160 °C (C: 30-50 nm particle); 180 °C (D: 60-80 nm particle); 220 °C (E: spindle) and 240 °C (F: hexagonal flake).

Effect of the hydrothermal temperature on the size and morphology of the final products was examined. Varying the hydrothermal temperature between 120 °C and 240 °C resulted in completely different morphology and size of the product. Low hydrothermal temperature favors the formation of smaller hexagonal nanoparticles (C, D), whereas high hydrothermal temperature benefits the formation of submicrocrystals (E, F).



**Fig. S2** TEM images of particles with different hydrothermal time (A) 160 °C for 1h; (B) 160 °C for 3h; (C) 160 °C for 18h.

From the TEM images shown in Fig. S2, it is clear that the sample with hydrothermal time for 1h is aggregates of many primary particles with a coarse surface (A). When the hydrothermal time extends to 3 h, besides the aggregates, there exist some bigger particles of relatively smooth surface (B). The hydrothermal time extends for at least 18h, the particles with regular morphology and smooth surface can be obtained (C).



**Fig. S3** IR spectrum of hexagonal NaYF<sub>4</sub>: 2% Er<sup>3+</sup>, 20% Yb<sup>3+</sup> nanocrystals.

The broad band at 3656 cm<sup>-1</sup> corresponds to the O-H stretching vibration. The 3246 and 3127 cm<sup>-1</sup> transmission bands are related respectively with the stretching vibration of C-H in the ring and alkyl chain. The bands at 1437 and 1395 cm<sup>-1</sup> are ascribed to the C-C and C-N stretching vibration of the ring, respectively. The peak at 740 cm<sup>-1</sup> is attributed to the breathing vibration of the imidazole ring.