

Electronic Supplementary Information

Synthesis of Water-soluble β -NaYF₄ Nanocrystals in a Green Way

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Experimental details

Materials. All chemicals were of analytical grade and used as received without further purification. Deionized (DI) water was used throughout. Rare earth oxides were supplied by Guangdong Zhujiang Rare Earths Co., Ltd., China. Sodium fluoride, sodium oxalate, poly(acrylic acid) (PAA, $M_w \approx 1800$) were purchased from Guangzhou Chemical Reagent Factory, China.

Rare earth oxides were dissolved in diluted nitric acid under heating, the excess nitric acid was driven off by gentle heating the clear solution to dry, and DI water was added to prepare 0.5 mol L⁻¹ of Ln(NO₃)₃ stock solution.

Characterizations. The solid products were characterized using powder X-ray diffraction (Rigaku D/MAX 2200 VPC) at a scanning rate of 5°/min, with Cu K α radiation ($\lambda = 0.1541$ nm). The morphology of the as-prepared particles was observed using transmission electron microscopy (TEM) performed on a JEOL 2010 microscope operated at 120 kV. All samples were

first dispersed in ethanol and then collected using copper grids covered with carbon films for measurements. Photoluminescence spectra were measured on a Fluorolog-3 spectrofluorometer (Jobin Yvon Inc./Specx) equipped with a 450 W Xe lamp, double excitation monochromators and single emission monochromator. Up-conversion emission spectra were detected by the same instrument equipped with an external 980 nm diode laser and a R928P photomultiplier tube.

Synthesis of β -NaYF₄ at 55 °C. 0.5 ml of Ln(NO₃)₃ (0.25 mmol) and 27.5 ml of ethanol were mixed in a 50 ml of flask under vigorous stirring, then 0.268 g of sodium oxalate (2.0 mmol) was added. After stirring for 10 minutes, 0.084 g of NaF (2.0 mmol) and 2.0 ml of DI water was added. The mixture was maintained at 55 °C for 2 h with stirring. 10 ml of the mixture was taken for solvothermal reaction (if necessary). The remaining was collected by centrifuging, washed with DI water for three times, and dried under vacuum at room temperature.

For doped samples, corresponding Ln(NO₃)₃ was used instead of Y(NO₃)₃ in the feedstock.

Synthesis of water-soluble up-converting β -NaYF₄. 10 ml of the mixture for solvothermal reaction was transferred into an autoclave with 15 ml capacity of Teflon cup. The capped autoclave was put into an oven with 220 °C inside, and kept for 2 h. After the reaction, the precipitate in the bottom of the cup was collected and dispersed in water and centrifuged. The washing procedure was repeated for three times. One half of the product was dried under vacuum for powder XRD (Fig.S1d) and FT-IR characterization (Fig. S4a). The other part was dispersed in 10 ml of DI water containing 0.25 g of PAA for up-conversion luminescence detection (Fig.3c). After washing and centrifuging for 3 times, the vacuum-dried powder was used for FT-IR measurement again (Fig. S4b).

Preparing transparent thin film. A glass substrate (2.0×2.0 cm) was soaked in dilute NaOH solution for 10 minutes, rinsed with DI water, soaked in dilute HCl solution for 10 minutes and rinsed with DI water again, then ultrasonicated in ethanol for 10 minutes. The cleaned glass substrate was dipped into the mixture solution of PAA and the nanoparticles for 5 minutes, and pulled out slowly (about 2.0 cm/min.). The glass substrate was dried in an oven with 100 °C inside for 20 minutes. This dip-coating and drying procedure could be repeated several times to make a thicker film.

Figures

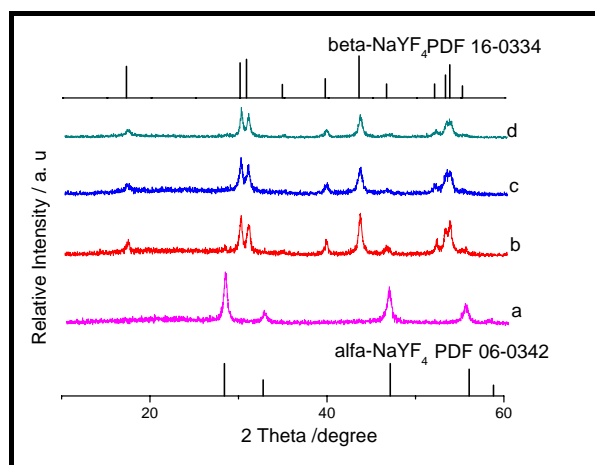


Fig. S1. Powder XRD patterns of samples doped with Eu^{3+} (5 mol %, a, b), and co-doped with Yb^{3+} (20 mol %) and Er^{3+} (2 mol %) (c, d). Solvent: 30 ml of DI water for sample a, 27.5 ml of ethanol and 2.5 ml of water for b and c; sample a, b, and c were prepared at 55 °C for 2 h; sample d was obtained from sample c after it was solvothermally treated at 220°C for 2 h.

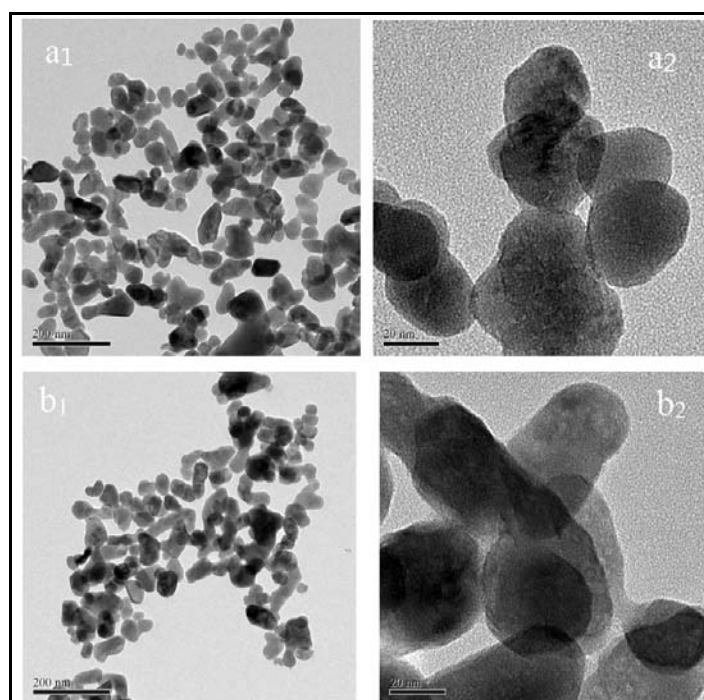


Fig. S2. TEM images of $\beta\text{-NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ nanocrystals corresponding to samples in Fig. S1c and S1d before (a) and after (b) solvothermal treatment.

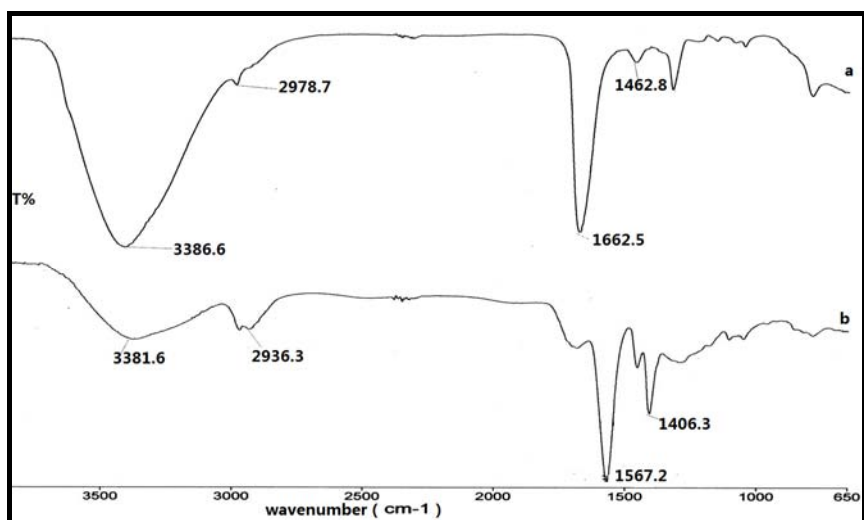


Fig. S3. FT-IR spectra of samples before (a) and after (b) PAA treatment.

The absorption bands around 3386 cm⁻¹ and 1662 cm⁻¹ in Fig S4a can be assigned to the stretching and deformation vibrations of OH groups. The peaks at 2978 cm⁻¹ can be assigned to the asymmetric and symmetric stretching vibration modes of CH₂ groups, respectively, suggesting the presence of ethanol at the surface of the nanoparticles. The peaks from -COOH (1567 and 1406cm⁻¹) in Fig S4b indicate that the surface of the NPs was capped by PAA.