

Electronic Supplementary Information

Electrospinning Preparation and Upconversion Luminescence of Yttrium Fluoride Nanofibers

*Renyuan Yang, Weiye Song, Shusen Liu, Weiping Qin**

5 State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering,

Jilin University, Changchun 130012, P. R. China

E-mail: wpqin@jlu.edu.cn

1. Experimental Procedure

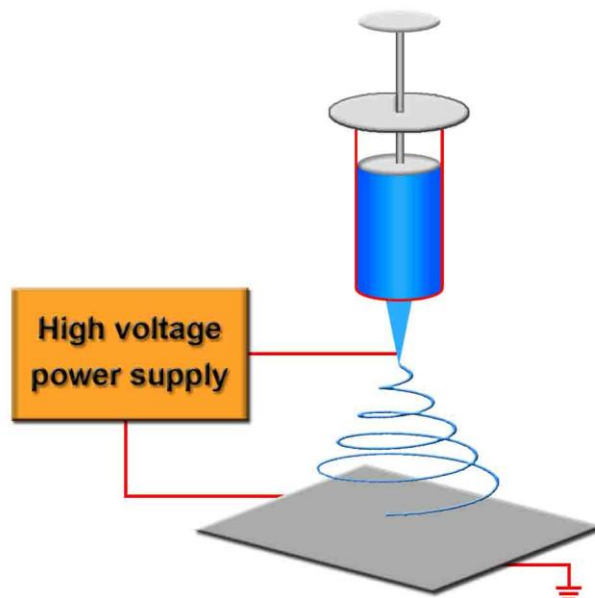


Fig. S1 Schematic illustration of electrospinning of PVP/RE(CF₃COO)₃ composite fibers.

5 Synthesis of PVP/RE(CF₃COO)₃ fibers (RE = Y, La, Nd, Gd, Tm and Yb):

All the chemicals were used as received without purification. REO₂ (purity ≥ 99.99%) were supplied by Shanghai Chemical Reagent Company. Trifluoroacetic acid, PVP ($M_w \approx 1\,300\,000$) and NH₄HF₂ were purchased from Aldrich Company.

Polymer solution was prepared by dissolving 0.4 g PVP in 8 mL of ethanol and stirred for 6 h. Water solution of RE(CF₃COO)₃ was prepared by mixing RE₂O₃ (1.0 mmol) in deionized water (0.5 mL) and trifluoroacetic acid (1.6 mL). The mixture was then put in water bath at 50 °C. After the mixture became clear, it was added into polymer solution. After magnetic stirring for 2 h, uniform precursor solution for electrospinning was obtained.

As shown in Fig. S1, the precursor solution was loaded into a 1 mL plastic syringe. The solution flow rate was about 0.2 mL/h during electrospinning. The operation voltage was switched to 15.0 kV.

The distance between the syringe tip and collector was 12 cm. The relative humidity was less than 30%. Non-woven mat consisted of composite fibers was obtained on grounded aluminum foil. It was preserved carefully in a desiccator free from humidity.

Calcination of REOF fibers and REF₃ fibers:

5 The as-fabricated mat was calcined at 300 °C for 24 h and then at 600 °C for 3 h in air so that PVP could be eliminated thoroughly. The temperature rose from room temperature and the rising rate was 5 °C/min. The calcinated sample cooled down to room temperature naturally. The as-calcinated fibers were loaded in a small crucible. A large crucible contained 5 g NH₄HF₂. The small crucible was put in the large one, making sure that REOF fibers did not directly contact with the NH₄HF₂. The large
10 crucible was sealed and heated in a furnace at 400 °C for 6 h. The temperature rose from room temperature, with a heating rate of 5 °C/min. After fluoridization reaction, REF₃ fibers were obtained. In order to prepare YF₃ fibers codoped with Yb³⁺ and Tm³⁺, stoichiometric amounts of Yb(CF₃COO)₃ and Tm(CF₃COO)₃ were mixed in the precursor solution for electrospinning. The preparation procedure of YF₃:Yb³⁺,Tm³⁺ fibers was same as that of YF₃ fibers.

15 2. Characterization

XRD of samples was performed by X-ray diffractometer (mode Rigaku RU-200b), using nickel-filtered Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The size and morphology of the fibers before and after calcination process were inspected using a Hitachi S-4800 field emission scanning electron micrograph (FE-SEM). JEOL-2000ex TEM was employed to record the TEM images and selected area electron
20 diffraction (SAED) images. Fourier transform infrared spectra (FTIR) of KBr powder-pressed pellets were recorded on a Fourier transform spectrometer (Perkin-Elmer, Spectrum 1). UC fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrophotometer with a 980 nm diode laser

acting as excitation source. The spectral resolution was 1.0 nm. The high voltage of photomultiplier tube was 400 V. All measurements were performed at room temperature.

3. XRD Pattern of $\text{YF}_3 \cdot 1.5\text{NH}_3$

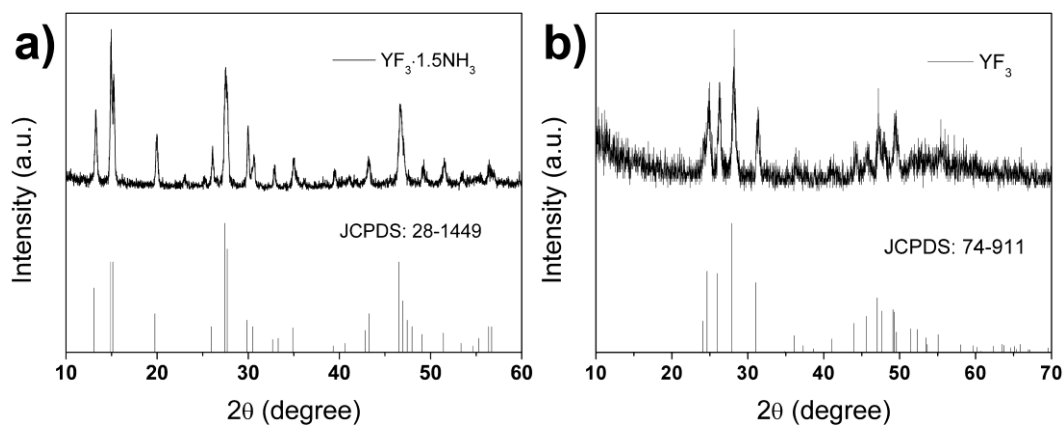


Fig. S2 (a) XRD pattern of $\text{YF}_3 \cdot 1.5\text{NH}_3$; (b) XRD pattern of YF_3 .

When YOF fibers were calcinated at 200 °C in NH_3 -HF atmosphere, the final product turned to be $\text{YF}_3 \cdot 1.5\text{NH}_3$. The corresponding XRD pattern is shown in Fig. S2a. In comparison, when the temperature in the fluorination process rose to 250 °C, YF_3 was formed. The corresponding XRD pattern is shown in Fig. S2b. Compared with the noise signal in the pattern, intensity of diffraction peaks are weak, indicating poor crystalline of YF_3 crystals.

4. FTIR Spectra of Fibers

FTIR spectra of fibers are shown in Fig. S3. Characteristic absorption peaks of PVP and $\text{RE}(\text{CF}_3\text{COO})_3$ can be detected. When the composite fibers were calcined at 500 °C, the weak peaks suggested that the organic ingredients were not eliminated completely. After the calcination at 600 °C, these peaks disappeared, indicating the removal of organic ingredients. The CO_2 contributed to the band at about 2360 cm^{-1} . The wide absorption bands at $\sim 500 \text{ cm}^{-1}$ were assigned to YOF and YF_3 .

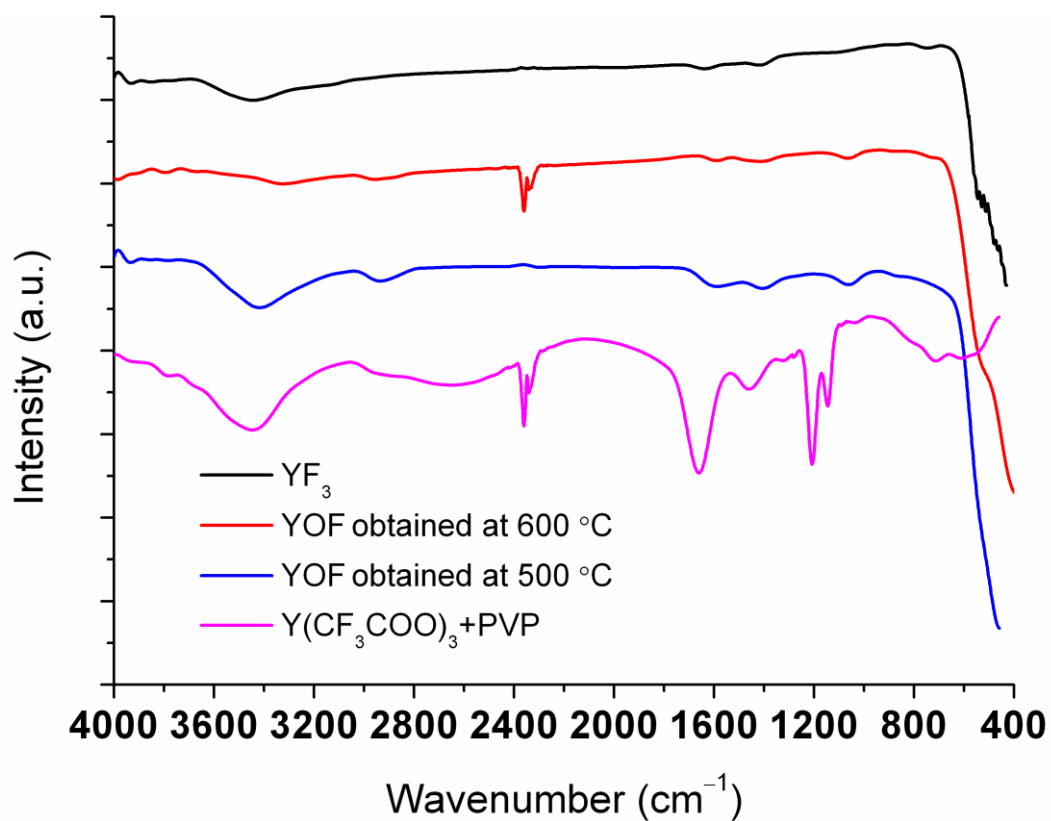


Fig. S3 FTIR spectra of fibers.

5. SEM Images and XRD Patterns of REOF and REF_3

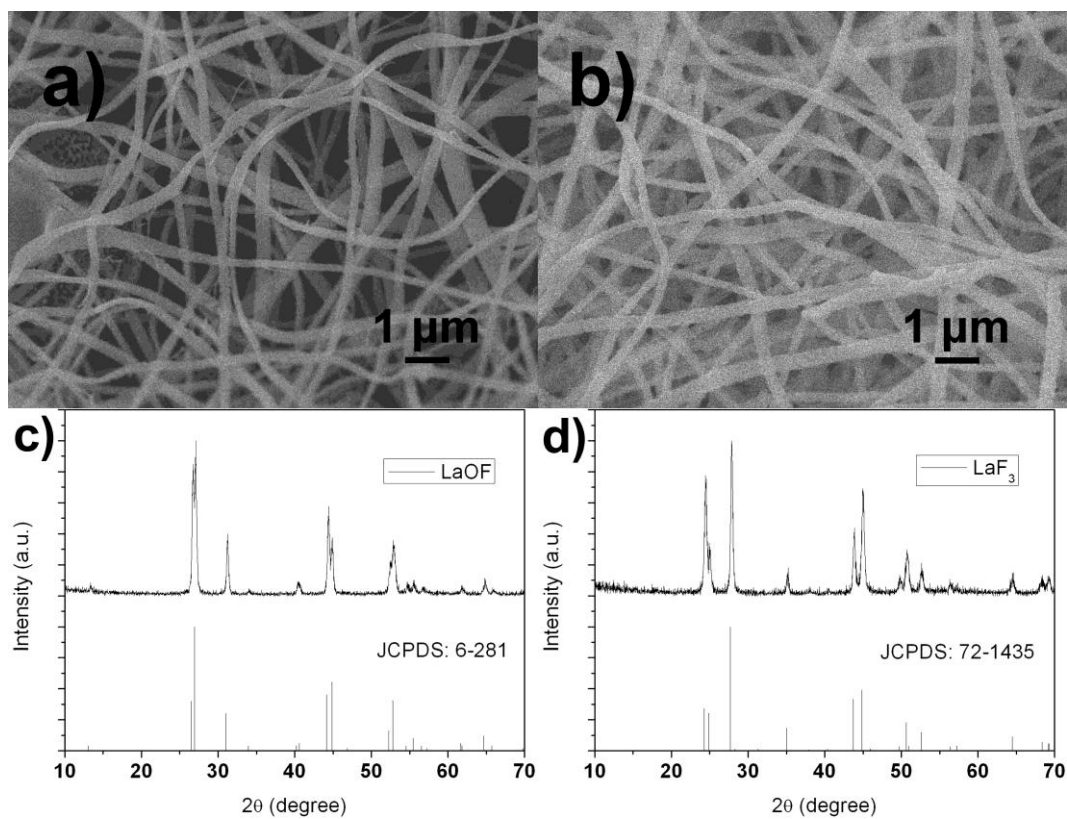


Fig. S4 (a, b) SEM image of LaOF and LaF₃ fibers, respectively. (c, d) XRD patterns of LaOF and LaF₃ fibers, respectively.

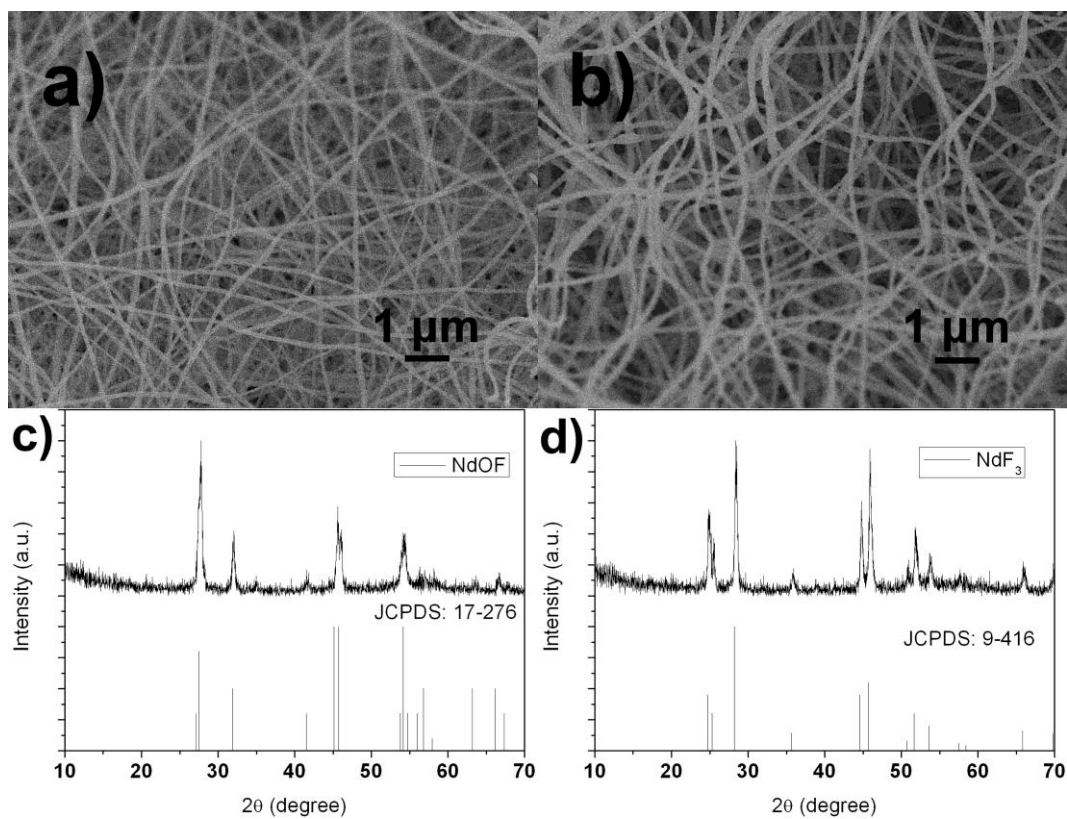


Fig. S5 (a, b) SEM image of NdOF and NdF₃ fibers, respectively. (c, d) XRD patterns of NdOF and NdF₃ fibers, respectively.

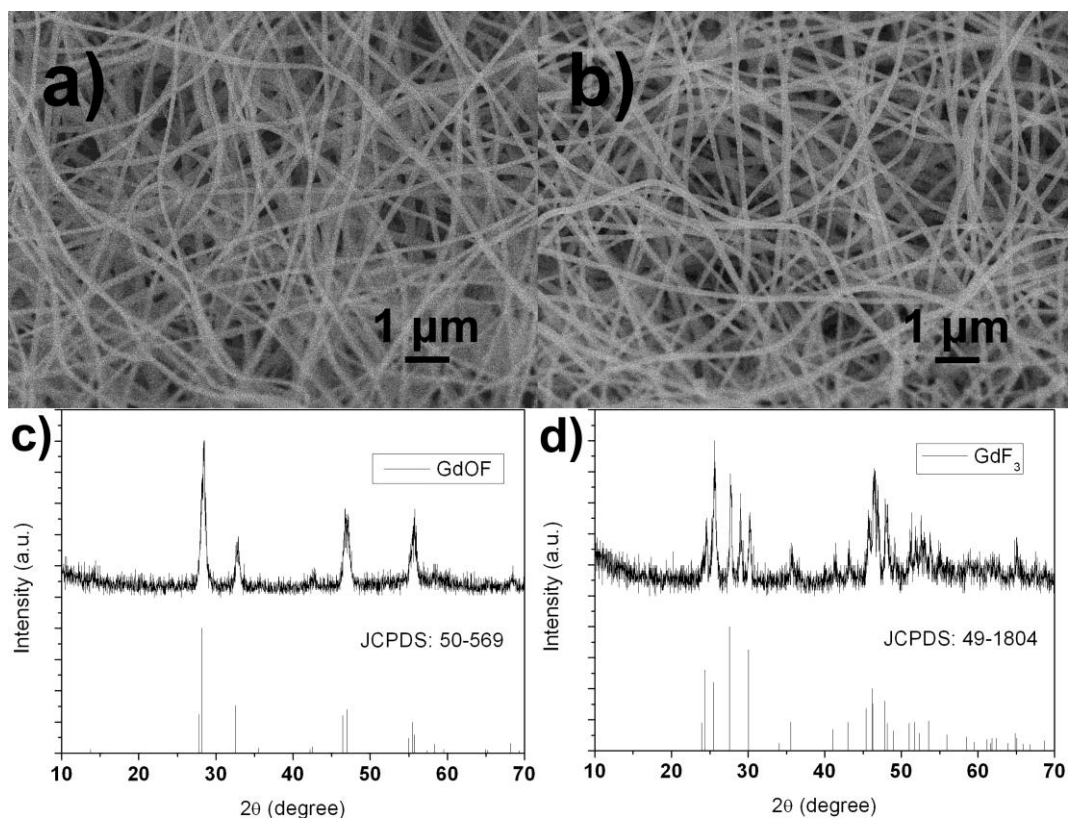


Fig. S6 (a, b) SEM image of GdOF and GdF₃ fibers, respectively. (c, d) XRD patterns of GdOF and GdF₃ fibers, respectively.