

## Electronic supplementary information

### A longwave optical pH sensor based on red upconversion luminescence of NaGdF<sub>4</sub> nanotubes

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#### Experimental sections

##### 1. Materials synthesis

All the chemicals were of analytical grade and used as received without further purification. The rare earth (RE) nitrate aqueous solution was obtained by dissolving RE nitrate in deionized water. The Gd(OH)<sub>3</sub> nanotubes were prepared according the reference.

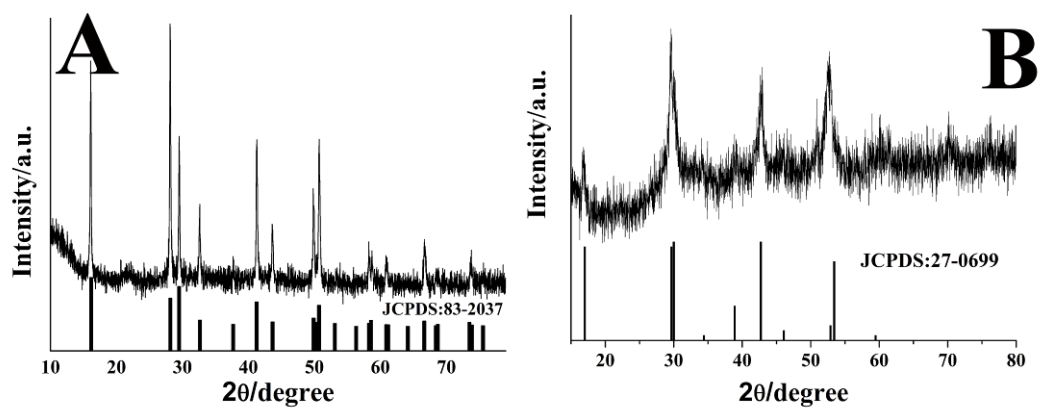
In a typical procedure, 1 mL NH<sub>3</sub>·H<sub>2</sub>O (14 M) was added in the 10 mL aqueous solution containing 0.1 mmol Gd(NO<sub>3</sub>)<sub>3</sub> under vigorous stirring. Then the system was additional agitated by vigorous magnetic stirring for 10 min. The resultant solution was transferred to a 20 mL autoclave and maintained at 160 °C for 2 h. Finally, the autoclave was cooled to room temperature naturally. The precipitates were separated by centrifugation, followed by washing with deionized water for several times. The obtained Gd(OH)<sub>3</sub> nanotubes was dried at 80 °C in air for about 12 h.

After 0.15 g Gd(OH)<sub>3</sub> nanotubes dispersed in 8 mL water by ultrasonic, 0.1 g NaF and 3 mL HF(0.1 M) were added in the aqueous solution by vigorous stirring. After vigorous magnetic stirring for 10 min, the system was transferred into a 15 mL autoclave and maintained at 120 °C for 4 h. The autoclave was cooled to room temperature naturally. And the precipitates were separated by centrifugation, followed by washing with deionized water for several times. The obtained NaGdF<sub>4</sub> nanotubes was dried at 80 °C for about 12 h and calcined at 400 °C for 4 h in air. The Ln<sup>3+</sup>-doped NaGdF<sub>4</sub> nanotubes were prepared by the same procedure, except for adding corresponding relevant Ln<sup>3+</sup> (Ln<sup>3+</sup> = Yb<sup>3+</sup> and Er<sup>3+</sup>) into the solution of Gd(NO<sub>3</sub>)<sub>3</sub> at the initial stage.

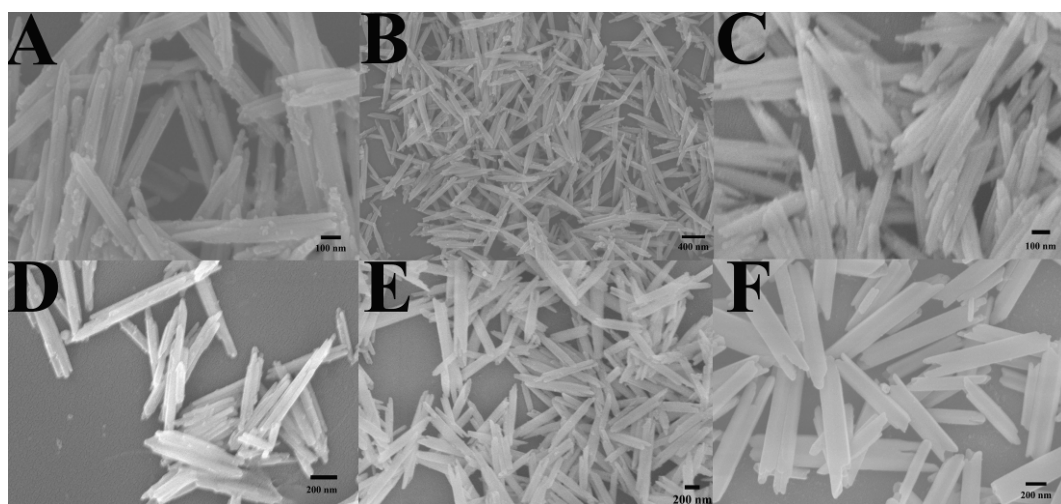
The pH measurement was carried out by the following procedure. The NaGdF<sub>4</sub> nanotubes were dispersed in water to get a 10 mg/mL aqueous solution. And the BTB was dissolved in ethanol to get a 0.04 % (weight) solution. The buffer solution from 3-8 was obtained by use citric acid and disodium hydrogen phosphate system. 20 μL BTB solution and 200 μL NaGdF<sub>4</sub> nanotubes solution were added into 3 mL buffer solution and dispersed by ultrasonic. Then the system was transferred to a quartz cuvette to finish the absorption and UC PL spectra test.

## **2. Characterization**

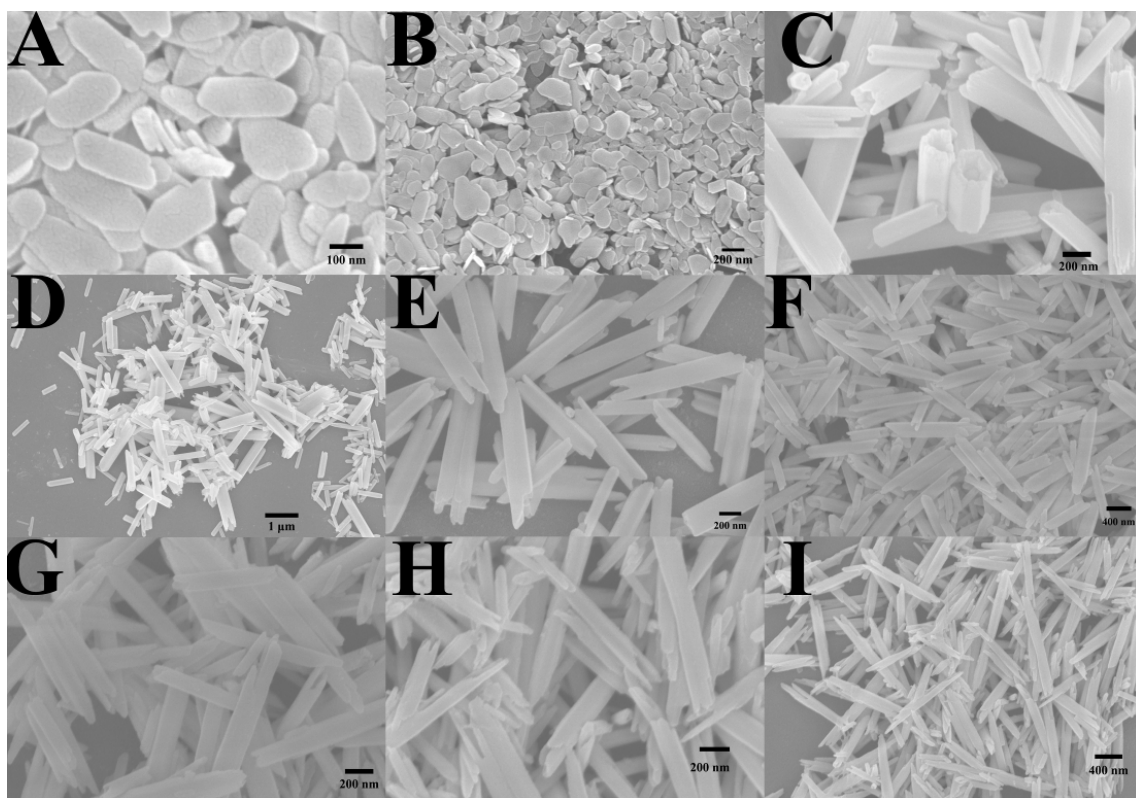
The crystalline and phase purity of the products were examined by powder XRD. Measurements were performed on a Rigaku X-ray diffractometer with Cu Ka radiation with an accelerating voltage and applied current of 40 kV and 40 mA, respectively. The size, general morphology and structure of the as-synthesized samples were characterized using field-emission scanning electron microscopy (SEM) (Hitachi S4800) at an accelerating voltage of 10 kV and Hitachi 8100 transmission electron microscope (TEM) at an operation voltage of 200 kV. The UC spectra were obtained by using a 980 nm laser diode. The emission attributed to the transitions between 350 and 800 nm was dispersed by a triple grating monochromator (Spectra Pro-2758, Acton Research Corporation, USA) equipped with a Photomultiplier (Hamamatsu R928). The absorption spectra were obtained by using UV-3600 (SHIMADZU) from 300 nm to 700 nm.



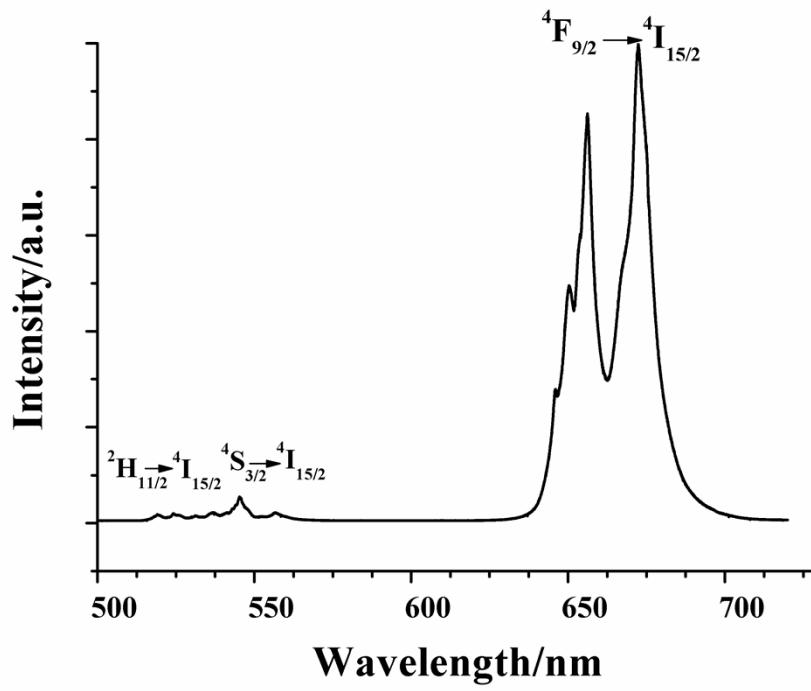
**Fig.S1** XRD patterns of (A) Gd(OH)<sub>3</sub> nanotube, and (B) NaGdF<sub>4</sub> nanotubes.



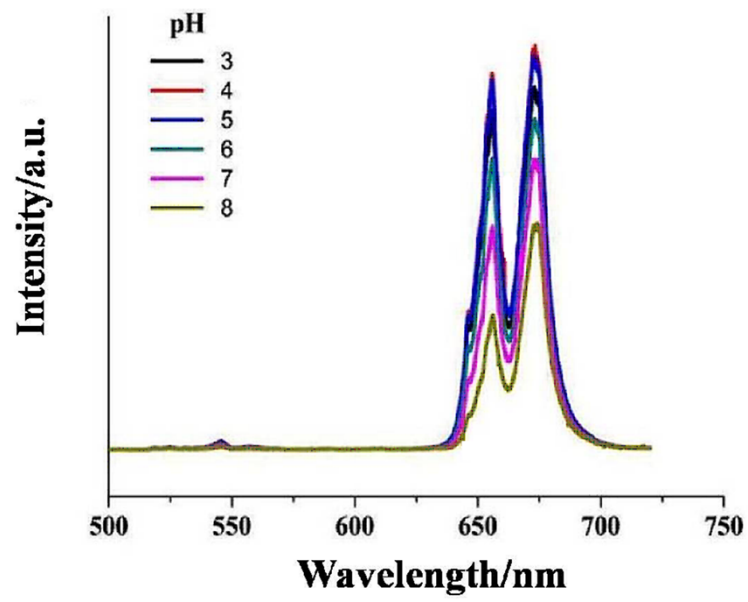
**Fig. S2** SEM images of Gd(OH)<sub>3</sub> nanotubes with different Gd<sup>3+</sup> concentration, (A, B) 1 mmol, (C, D) 2 mmol (E) 5 mmol, (F) 10 mmol.



**Fig. S3** SEM images of Gd(OH)<sub>3</sub> nanotubes with different amount of NH<sub>3</sub>·H<sub>2</sub>O: (A, B) 0.3 mL, (C, D) 0.6 mL, (E, F) 1 mL, (G) 2 mL, (H, I) 4 mL.



**Fig. S4** UC PL spectra of NaGdF<sub>4</sub>:20%Yb<sup>3+</sup>/2%Er<sup>3+</sup> nanotubes excited by 980 nm laser.



**Fig.S5** UC PL spectra of NaGdF<sub>4</sub>:20%Yb<sup>3+</sup>/2%Er<sup>3+</sup> nanotubes in buffer solutions at pH value from 3-8.