

Preparation and spectroscopic study of water-soluble β -NaYF₄:Yb³⁺/Er³⁺@NaGdF₄ crystal particle and its application in bioimaging

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Materials

Dissolving Gd₂O₃ (99.99% Sigma-Aldrich) into Y(NO₃)₃ by nitric acid. We stirred the solution at 50°C for a few hours to evaporate overdosed nitric acid. Then it was dissolved with deionized water and filtered to get rare-earth nitrate solution. Er(NO₃)₃·5H₂O (99.9%), Yb(NO₃)₃·5H₂O (99.9%), and Y(NO₃)₃·6H₂O (99.8%) were bought from Sigma Aldrich. C₆H₅Na₃O₇·2H₂O (99.0%), NaNO₃ (99.0%) and NaF (98.0%) with analytical grade were purchased from Sino pharm Chemical Reagent Co., Ltd. (China). Dulbecco's Modified Eagle's Medium (DMEM), Fetal bovine serum (FBS) were purchased from Gibco.

Synthesis of β -NaYF₄:Yb³⁺/Er³⁺ particles

β -NaYF₄:Yb³⁺/Er³⁺ particle was prepared by hydrothermal method¹. Specifically, first, (1.26 g) trisodium citrate was added to the 32 ml deionized water, then 0.75 mL RE(NO₃)₃ (0.375 mmol; RE: 78 mol% Y³⁺, 20 mol% Yb³⁺ and 2 mol% Er³⁺) was added in turn. After stirring for 30 minutes, (3.21 g) NaNO₃ and (0.27 g) NaF were added into the solution. In order to make the predecessor mixed enough, the above solution was stirred for about half an hour or twenty minutes of ultrasound. Finally, the solution was added into 50 ml Teflon-lined autoclave at 180°C for 20 hours. Then obtained β -NaYF₄:Yb³⁺/Er³⁺ powder was centrifuged and washed several times with deionized water after natural cooling to room temperature. White powder was collected for at 50°C about 10 hours after drying in a vacuum drying box and was dispersed in deionized water for subsequent testing.

Synthesis of β -NaYF₄:Yb³⁺/Er³⁺@NaGdF₄ particles

The method for the synthesis of the core-shell structure was described as follows. First, weighing the above synthetic white powder sample about 23 mg was dispersed into 9 ml deionized water for stirring about 30 minutes, marked the solution of A. The method for synthesizing the core-shell structure was similar to that of the β -NaYF₄:Yb³⁺/Er³⁺ particle. (0.25 g) trisodium citrate was added into the solution A, and then 0.12 ml (0.50 M) Gd(NO₃)₃ was added into the mixture solution marked

B. After stirring about 30 minutes, (0.64 g) NaNO_3 and (0.05 g) NaF were added into the solution B. It was stirred to the color of the solution to be transparent for approximately 30 minutes. Finally, the final solution was added into 50 ml Teflon-lined autoclave at 180°C for 20 hours, then the synthesized $\beta\text{-NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@/\text{NaGdF}_4$ powder was centrifuged and washed several times with deionized water after natural cooling to room temperature. The thickness of the shell was controlled by adjusting the amount of precursor required for the NaGdF_4 shell. In the discussion of this work, we use $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@/\text{NaGdF}_4$ (0.20), (0.25), (0.33), (0.50) and (1.00) to indicate the molar amount of NaGdF_4 reaction precursor, which are 0.20, 0.25, 0.33, 0.50 and 1.00 times, respectively of the $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ particle.

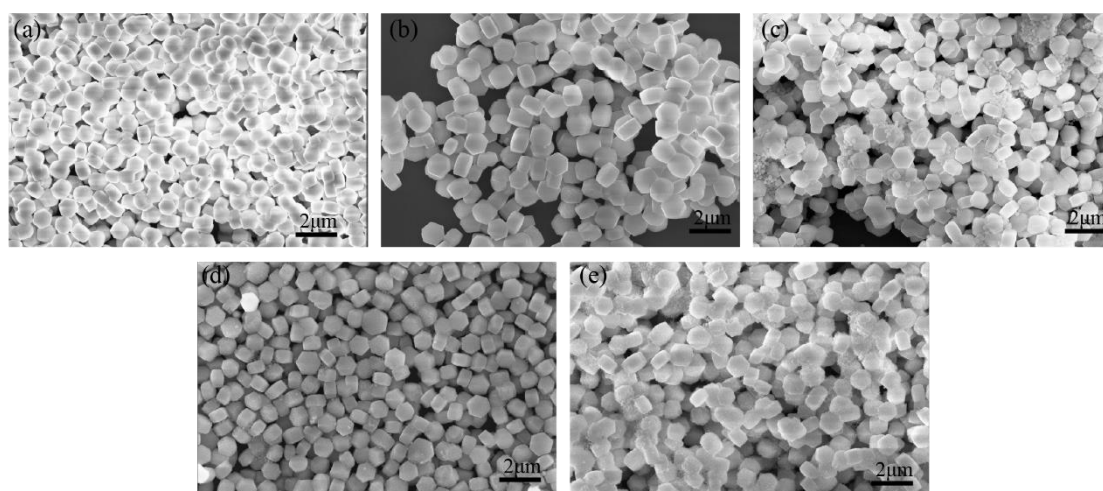


Fig.S1. The SEM images of the $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@/\text{NaGdF}_4$ particles prepared with hydrothermal method. (a) $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@/\text{NaGdF}_4$ (0.20); (b) NaGdF_4 (0.25); (c) NaGdF_4 (0.33); (d) NaGdF_4 (0.50); (e) NaGdF_4 (1.00).

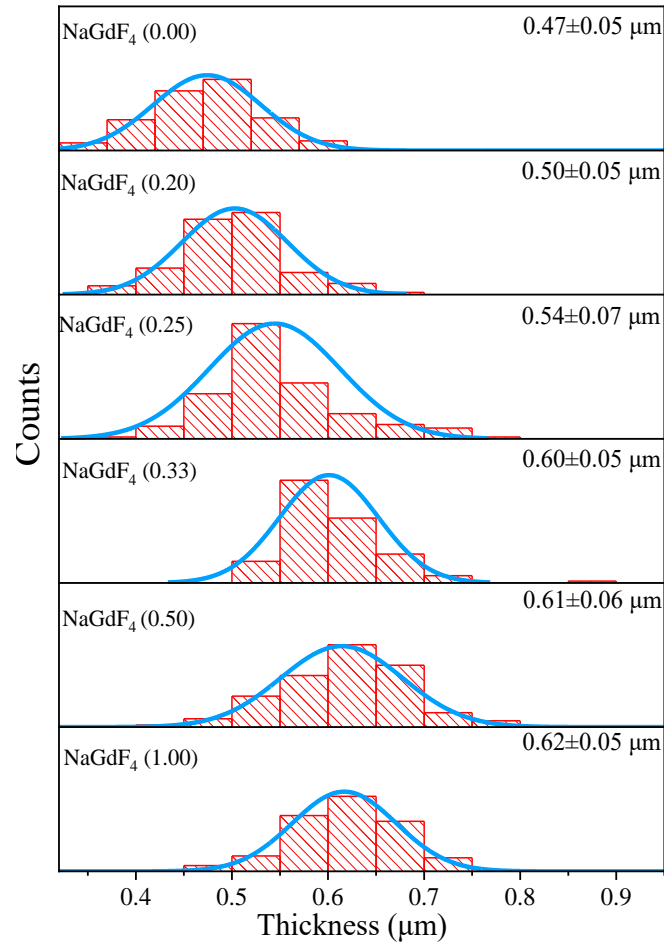


Fig.S2. Thickness distribution of NaYF₄:Yb³⁺/Er³⁺@NaGdF₄ particles as the molar amount of NaGdF₄ shell precursor change.

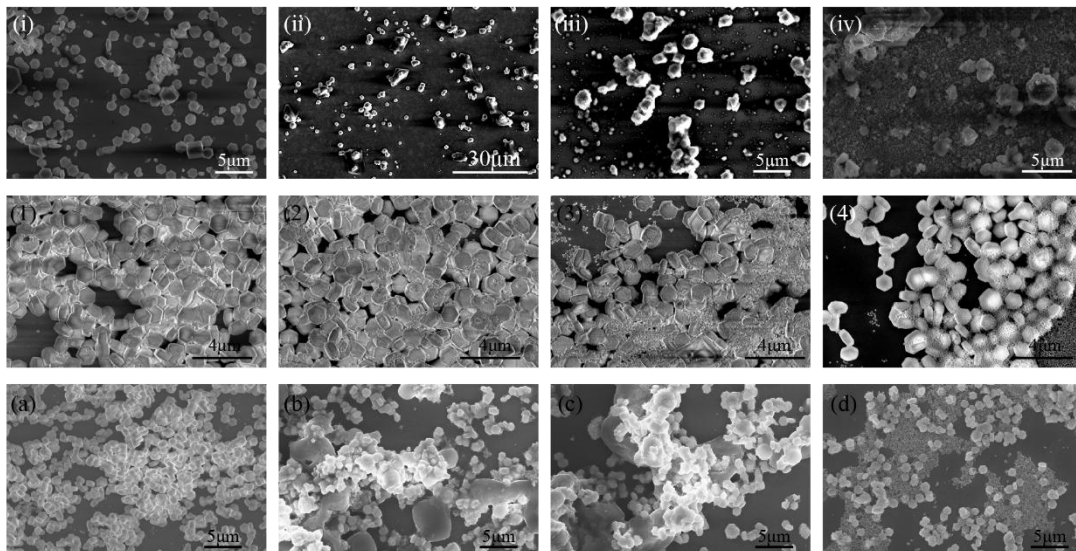


Fig.S3. Synthesis and SEM of NaYF₄:Yb³⁺/Er³⁺@NaGdF₄ under different reaction conditions (NaYF₄:Yb³⁺/Er³⁺@NaGdF₄ (0.20); (0.25); (0.33); (0.50)). (i)~(iv) Reducing the molar amount of NaYF₄:Yb³⁺/Er³⁺ crystal particles to 0.67 times the original, other reaction conditions remain unchanged; (1)~(4) Prolonging the reaction time of the core-shell crystal particles up to 36 h,

keeping other conditions unchanged; (a)~(d) Increasing the synthesis temperature to 200°C and the time to 24 h, maintaining other reaction conditions the same. No matter reducing the amount of nuclear precursor or prolonging the reaction time, raising the reaction temperature, the small particles β -NaGdF₄ produced during the formation of the core-shell structure could not be reduced, and it is even not easy to form a hexagonal disk with uniform morphology. Therefore, it is only under certain conditions that the samples can be synthesized and crystallized.

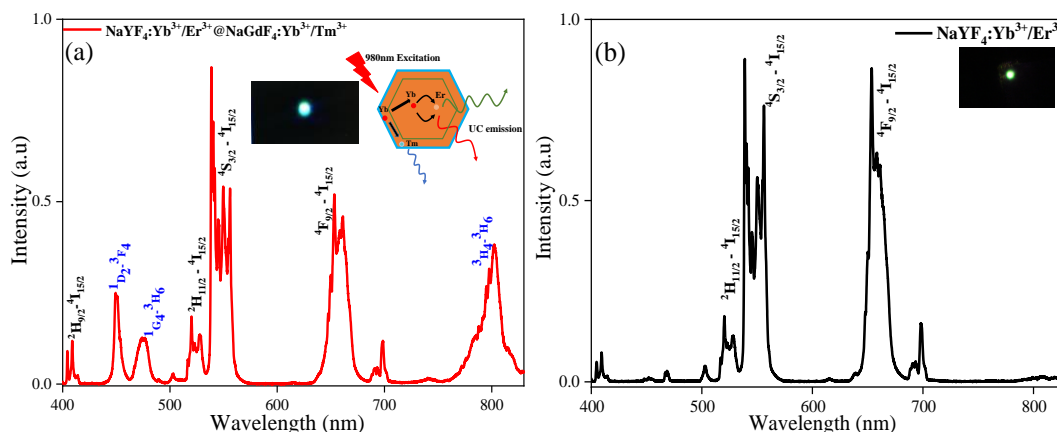


Fig.S4. (a) Fluorescence emission spectrum of the single NaYF₄:Yb³⁺/Er³⁺@NaGdF₄:Yb³⁺/Tm³⁺ core-shell particle at 980 nm excitation, the inset of the image is the fluorescence emission from a single NaYF₄:Yb³⁺/Er³⁺@NaGdF₄:Yb³⁺/Tm³⁺ (1.00) particle in microscopic dark field. (b) The fluorescence emission spectrum of single NaYF₄:Yb³⁺/Er³⁺ particle at 980 nm excitation. The illustration at upper right corner is the fluorescence emission of single NaYF₄:Yb³⁺/Er³⁺ particle in a microscopic dark field.

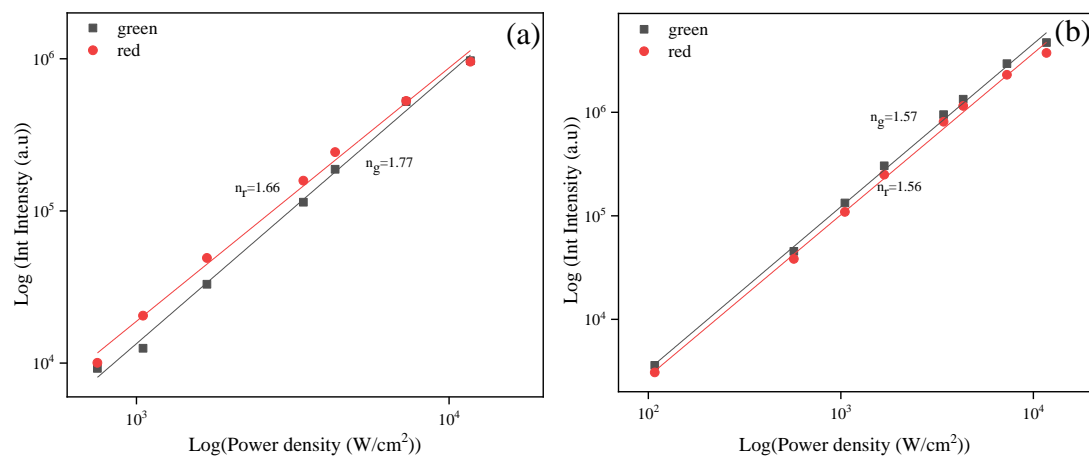


Fig.S5. (a) Log-log plot of the upconversion emission peak intensity for single NaYF₄:Yb³⁺/Er³⁺ particle as a function of power density. (b) Log-log plot of the upconversion emission peak intensity for single NaYF₄:Yb³⁺/Er³⁺@NaGdF₄ (0.50) particle as a function of power density. (black square: green emission at 535 nm, red circle: red emission at 655 nm).

Reference

1. C. Li, J. Yang, Z. Quan, P. Yang, D. Kong and J. Lin, *Chem Mater*, 2007, **19**, 4933-4942.