

Rare-earth doped hexagonal NaYbF₄ nanoprobcs with size-controlled and NIR-II emission for multifunctional application

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Supporting information

Materials: $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{TmCl}_3 \cdot x\text{H}_2\text{O}$ (99.99%), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (99%), Oleic acid (OA, 90%), 1-Octadecene (ODE, 90%), NaOH (96%), NH_4F (98%), Y_2O_3 (98%), trifluoroacetic acid (TFA, AR), distearoyl phosphatidylethanolamine-polyethylene glycol (DSPE-mPEG₂₀₀₀, 95%), ethanol absolute (99.7%), cyclohexane (AR). All raw materials are utilized without further treatment.

Synthesis of NaYbF_4 :2% Tm^{3+} , 30% Gd^{3+} , 2% Ce^{3+} Nanoparticles: 0.66 mmol $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 0.02 mmol TmCl_3 , 0.3 mmol $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, 0.02 mmol $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, 6 ml OA and 15 ml ODE were mixed together in a 250 ml round reaction flask with branch pipe, vacuumized under stirring in a high temperature rotor, heated to 150 °C for 30. A syringe was used to rapidly add 10 ml of methanol solution dissolved with NaOH (2.5 mmol) and NH_4F (4 mmol). Then vacuum and heat to 120 °C for 15 min. Then, it was heated to 290 °C for 2 h under nitrogen protection. Naturally cooled to room temperature, 20 ml ethanol was added to precipitate nanocrystals, and the products were washed with cyclohexane for many times. Then the obtained NaYbF_4 : Tm^{3+} , Gd^{3+} , Ce^{3+} core nanocrystals were dispersed in 10 ml cyclohexane as a stock solution.

Synthesis of NaYbF_4 :2% Tm^{3+} , 30% Gd^{3+} , 2% Ce^{3+} @ NaYF_4 nanoparticles: First, 0.5 mmol Y_2O_3 was added to a 50ml flask, and then 5 ml deionized water and 5 ml trifluoroacetic acid (TFA) were added. The solution was heated at 90 °C to be transparent, and then the solvent was evaporated at this temperature to obtain a shell precursor of calcium trifluoroacetate ((CF_3COO)Y). After (CF_3COO)Y powder was

obtained, 10 mL OA, 10 mL ODE and the prepared β -NaYbF₄:Tm³⁺, Gd³⁺, Ce³⁺ (0.5 mmol) cyclohexane solution were added. Then vacuum degassing at 120 °C to remove water, oxygen and cyclohexane. Subsequently, the solution was heated to 300 °C at a rate of 15 K·min⁻¹ under nitrogen protection. After maintaining at 300 °C for 1 hour, the reaction was stopped and cooled to room temperature. Wash with ethanol twice, cyclohexane twice, dispersed in 10 ml cyclohexane for later use.

Synthesis of NaYbF₄:2% Tm³⁺, 30% Gd³⁺, 2% Ce³⁺@NaYF₄@PEG nanoparticles : In a typical process, the core-shell nanoparticles dissolved in 5ml chloroform (concentration of 1 mg/ml), add 20 mg distearoyl phosphatidylethanolamine-polyethylene glycol (DSPE-mPEG₂₀₀₀) mixed in a flask vigorously stirred 20 min after the evaporation of chloroform, in order to ensure that chloroform evaporated dry use 50 °C rotary evaporation. The resulting film was hydrated with 5 mL deionized water, then centrifuged and washed several times and dispersed in PBS for later use.

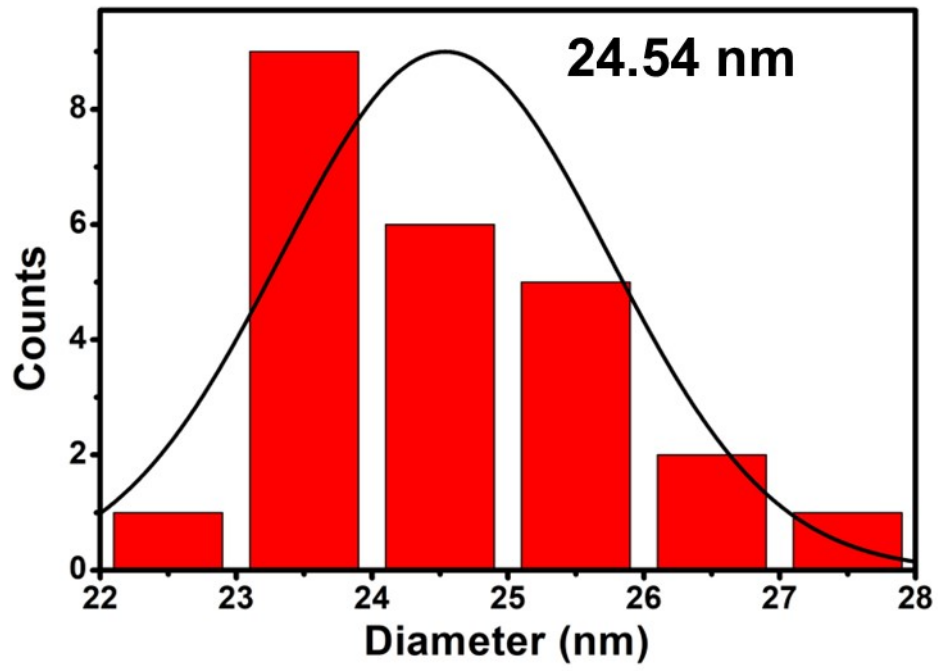


Figure S1. The corresponding particle size distribution of NaYbF₄: 5% Tm³⁺, 30% Gd³⁺, 2% Ce³⁺.

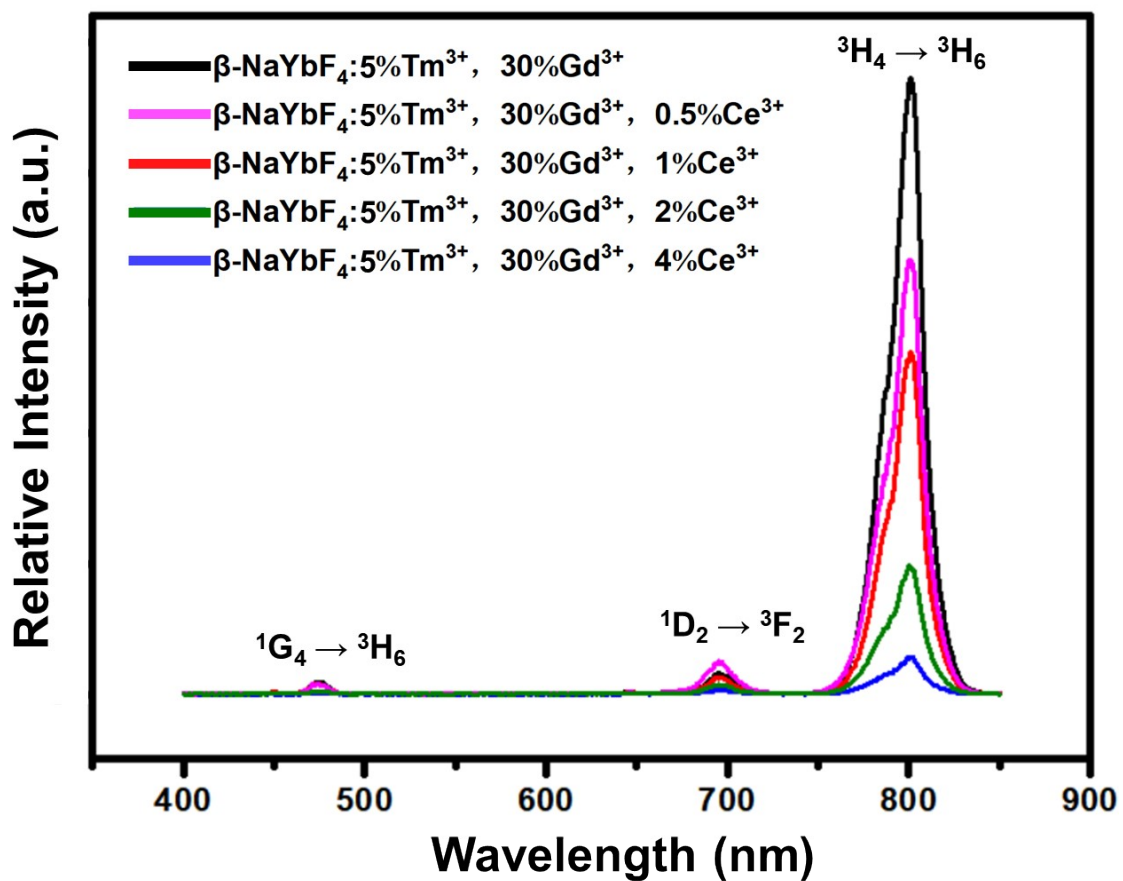


Figure S2. PL intensity of the product at 801 nm of β -NaYbF₄: 5% Tm³⁺, 30% Gd³⁺, X% Ce³⁺ (X = 0, 0.5, 1, 2, 4) ($\lambda_{ex} = 980$ nm).

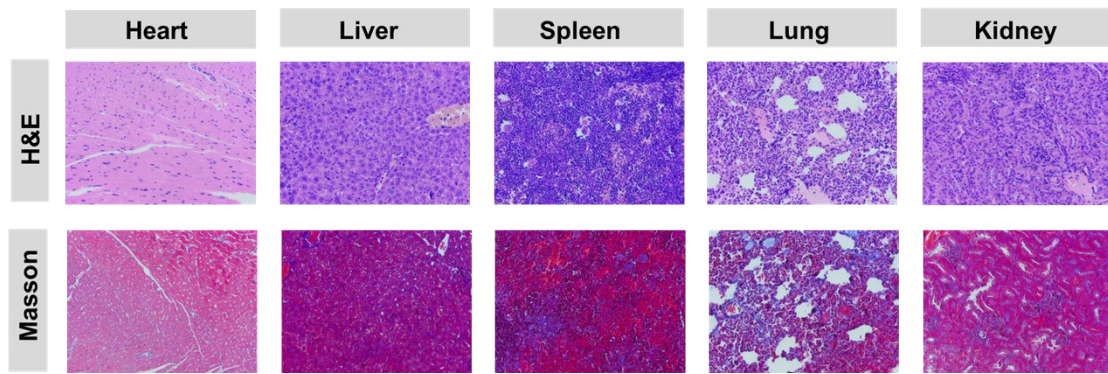


Figure S3. H&E staining and Masson staining images of organ sections of nude mice in control group after 14 days (tail vein injection of PBS).

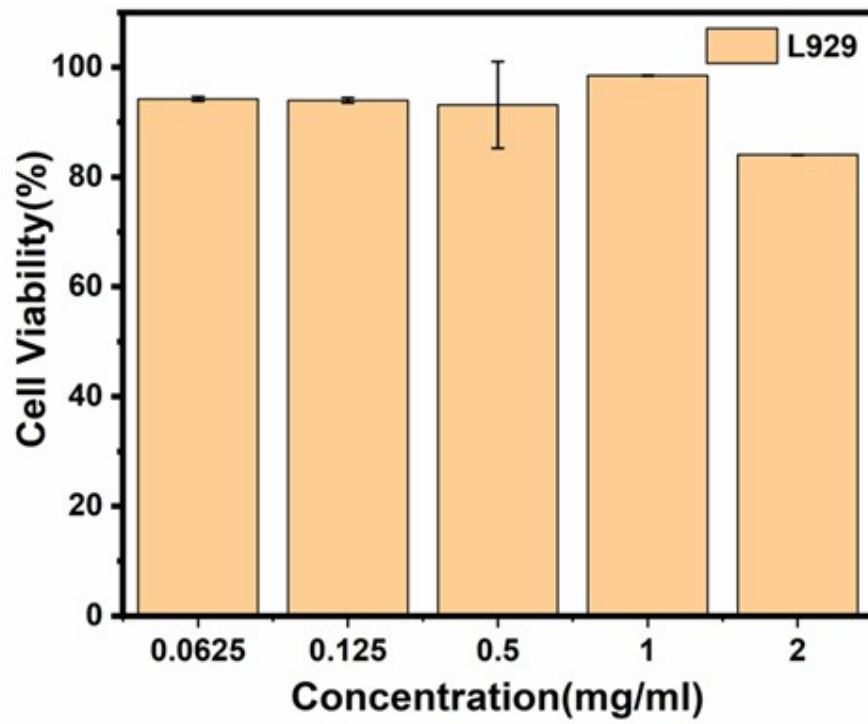


Figure S4. The toxicity test of NTC-PEG on L929 cells.