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Electronic Supplementary Information

Redispersible and water-soluble LaF_3:Ce,Tb nanocrystals *via* a microfluidic reactor with temperature steps

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Detail Experimental

Raw materials: $Ln(NO_3)_3{\cdot}6H_2O$ (Ln=La, Ce, Tb) (99.99%, Shanghai Yuelong New Materials Co., Ltd.), and NH_4F (96.0%, analytical reagent, A. R., Beijing Beihua Chemicals Co., Ltd.) were used as precursor materials without further purification. Diethylene glycol (DEG, 99%, Sinopharm Chemical Reagent Co., Ltd) was used as solvent after boiling at 105 °C for 1 h for purification and degasification. Rhodamin 6G (Sigma-Aldrich, Ltd.) was used as the standard reference in calculating the quantum yield of luminescent nanoparticles.

Synthesis of LaF₃: Ce, Tb nanoparticles. The molar ratio of La^{3+}: Ce^{3+}: Tb^{3+} is 40: 45: 15 in $Ln(NO_3)_3$ reagent. Stoichiometric amounts of $Ln(NO_3)_3{\cdot}6H_2O$ (Ln=La, Ce, Tb) were dissolved in DEG at 70 °C under stirring for an hour to form a clear solution with 0.01 M Ln^{3+}. The reagent 0.03 M NH_4F was obtained in the same way. Then two clear solutions were encased in two glass syringes separately and inject in a blender by syringe push pump. And then the mixture were injected in a microcapillary (300 μm diameter, made of Polytetrafluoroethylene (PTFE), without any further inner surface treatment) and heated to 180 °C in oil bath for a very short time (like 3 s). After that, the mixture in the microcapillary went to the other oil bath rapidly at 100 °C for a longer time (like 30 s). Finally a small bottle was used to collect the products. The residence time in microcapillary could be calculated by the driving-speed, the diameter and length of microcapillary. Three samples of LaF_3: Ce, Tb nanocrystals were collected from the different regions: i) outlet of microcapillaries in an oil bath at 180 °C for 3 s (sample 1); ii) collecting the colloid to a bottle from the outlet of microcapillaries in an oil bath at 180 °C for 3 s, and then placing the bottle in an oven at 100 °C for 30 min (sample 2); and iii) outlet of microcapillaries, which was initially in an oil bath at 180 °C for 3 s, and then in an oil bath at 100 °C for 30 s (sample 3).

The obtained suspension (about 10 ml) was diluted with 80 ml of acetone to precipitate the particles. The flocculent was centrifuged at a speed of 6000 rpm for 5 min to separate the particles from the suspension. To remove residual DEG and the unreacted raw reagents, the particles were dispersed in acetone and centrifuged for 2 more times. The final solid particles were redispersed and stored in about 10ml deionized water for characterizations.

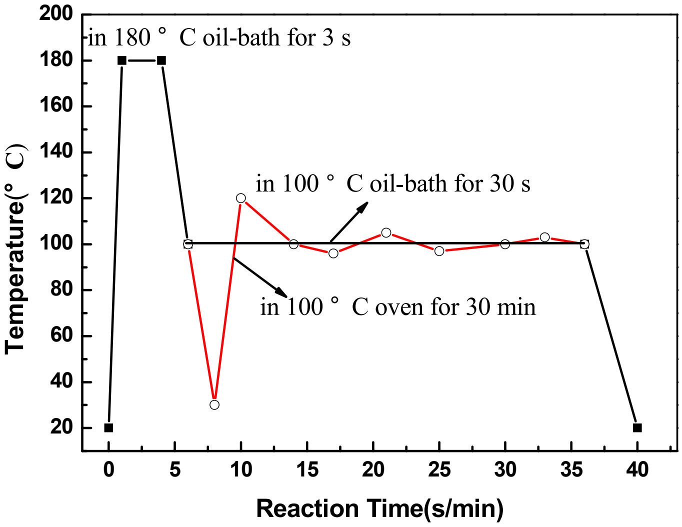

Fig. S1. Curves of steep reaction temperature steps in two temperature zone microfluidic systems and in oven for the synthesis of LaF_3: Ce, Tb nanoparticles.

The time needed from room temperature (like 20 °C) to the expected temperature (like 180 °C) in microcapillary is about 0.2 s, calculated from the heat-exchange formula:

$$\frac{\partial \mathrm{T}}{\partial t}=\kappa\frac{\partial T}{\partial^{2} x} \tag{1}$$

The rapid increase and decrease of reaction temperature in microcapillary realize the rapid temperature transformation for rapid thermal and mass transfer, towards separation of nucleation and growth stages.

Characterization. X-ray diffraction (XRD) was carried out on a Rigaku-Dmax 2550 PC (Japan) diffractometer with Cu Kα radiation (λ=0.15405 nm). Transmission electron microscope (TEM) images were obtained using a JEM-2100 F TEM (JEOL Tokyo Japan) operating at 200 kV. The UV-Vis absorption spectra were measured on a Lambda 35 (Perkin Elmer, America) spectrophotometer. The fluorescence spectra of excitation and emission were taken on an F-6600 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The FT-IR spectrum were measured on a NEXUS-670 (Nicolet, America) FTIR-Raman.

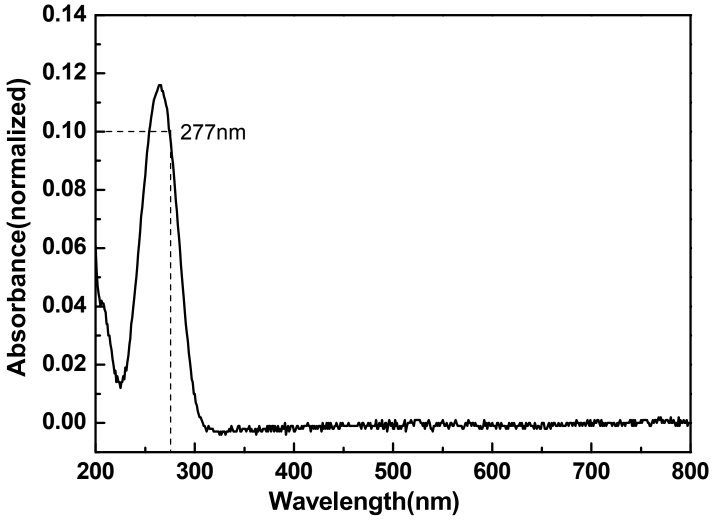

Fig. S2 UV-Vis absorption spectrum (with the absorbency of 0.1 at 277 nm) of LaF_3: Ce, Tb nanoparticles (sample 3) redispersed in deionized water solution.

The spectra of each sample were obtained from the colloidal (water) solutions of LaF_3: Ce, Tb nanoparticles with the absorbency of 0.1 at 277 nm. The spectrum shows there's almost no absorption in 320−800nm, which suggests the solution is transparent in visible light.

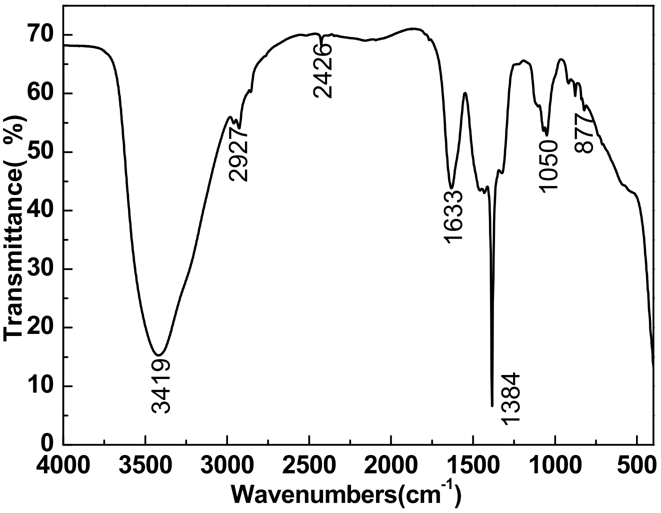

Fig. S3. FT-IR spectrum of the LaF_3: Ce, Tb nanoparticles (sample 3).

The absorption bands at around 3419 cm^{-1} and 1633 cm^{-1} are attributed to O−H stretching and bending vibrations respectively. The absorption band around 2927 cm^{-1} and 1384 cm^{-1} are attributed to C−H group. Other absorptions due to groups brought by DEG. The strongest absorption bands render the nanocrystals water solubility.

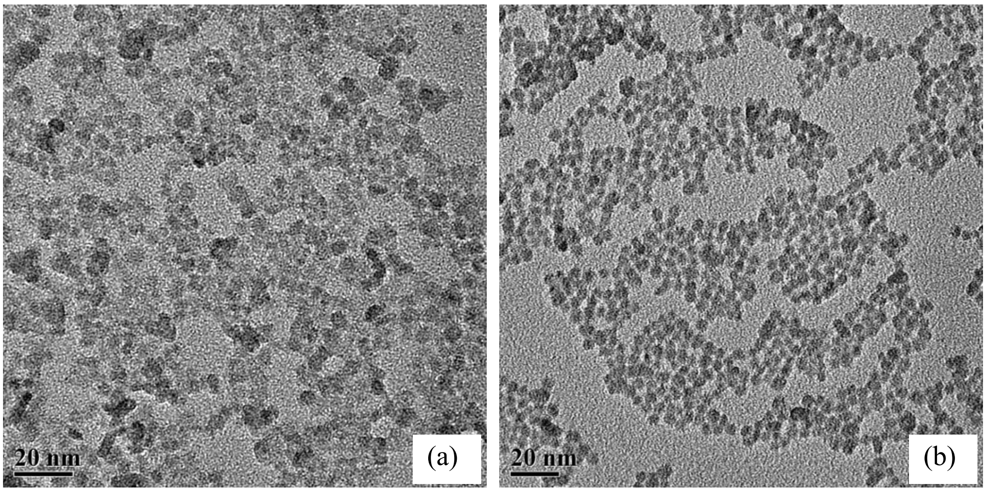

Fig. S4. TEM images of LaF_3:Ce, Tb nanoparticles of sample 2 (a) and sample 3 (b).

The particle size of sample 2 is obviously larger than that of sample 3, and the dispersibility and size distribution are also worse than those of sample 3. We believe that the fluctuant temperature in oven resulted in the Ostwald Ripening of sample 2.

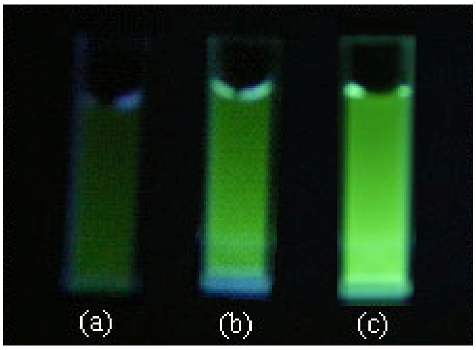

Figure. S5. Chromophotographs (under irradiation of a 254 nm UV lamp) of dispersion of LaF_3: Ce, Tb nanoparticles in de-ionized water solution of sample 1 (a), sample 2 (b) and sample 3 (c).