

Supplementary information

Chemical stability of up-converting fluoride nanoparticles in aqueous suspensions

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Experimental description

2.1 Chemicals

All the reagents were used as received without any additional purification. NaCl (min. 99%), $\text{LnCl}_3 \cdot x(\text{nH}_2\text{O})$ ($\text{Ln} = \text{Y}$ (99.99%), Gd (99.9%), Yb (99.9%), Tm (99.9%), La (99.99%)), $\text{Ln}(\text{NO}_3)_3 \cdot x(\text{nH}_2\text{O})$ ($\text{Ln} = \text{Y}$ (99.9%), Gd (99.9%), Yb (99.9%), Tm (99.9%), La (99%)), NaF (99%), NH_4F (98%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), ethylene glycol (EG, 99%) and citric acid (CA, 99%) were all purchased from Alfa Aesar. Polyethylene imin (PEI, branched, $M_r \sim 2500$) was purchased from Aldrich. NaOH ($\geq 99\%$), NaBF_4 ($\geq 97\%$) and methanol were purchased from Merck. Ethanol ($\geq 99.9\%$), acetone (99.8%) and hexane ($> 95\%$) were purchased from CarloErba Reagents. HNO_3 , HCl and diethyl ether (DE) (99.5%) were purchased from Applichem. Deionized water was used in all the experiments. To ensure the proper stoichiometry of the products, the Ln^{3+} content in the reagents was determined using an optical emission spectrometer with inductively coupled plasma (ICP-OES, Agilent 720).

2.2 Synthesis of nanoparticles

The HT synthesis of the $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ (NaY-HT) NPs was carried out at 180 °C for 1 h as described previously.¹ In short, 2 mmol of Ln nitrates in a stoichiometric ratio were dissolved in 9 ml of water. This solution was admixed to 18 ml of aqueous solution of Na citrate (the molar ratio of citrate ion: $\text{Ln}^{3+} = 4:1$). The Na citrate was prepared by dissolving a stoichiometric ratio of NaOH and CA in water. After vigorous stirring for 30 min, 27 ml of aqueous solution containing 25 mmol of NaF was admixed into the above solution, transferred into a 70 ml-Teflon vessel in a stainless-steel autoclave, and heated with 3 °/min to 180 °C with a holding time of 1 h. As the autoclave was naturally cooled to room temperature, the precipitates were separated by a centrifugation at 5000 rpm for 5 min, washed with ethanol and deionized water, and then dried in air or they were suspended in water.

The ST synthesis of the $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ (NaY-ST) NPs was carried out in EG, similar to ref.² Some 0.45 g of PEI was dissolved in 27 ml of EG during the stirring at 40 °C. Some 3.6 mmol of

¹ C. Li, Z. Quan, J. Yang, P. Yang and J. Lin, *Inorg. Chem.*, 2007, **46**, 6329.

² F. Ventrone, R. Naccache, A. Zamarron, A. J. dela Fuente, F. Sanz-Rodriguez, L. M. Maestro, E. M. Rdoriguez, D.

NaCl, and 1.8 mmol of LnCl_3 in a stoichiometric ratio were added to the solution, which was kept at 40 °C for 1 h. Then, 7.2 mmol of NH_4F was admixed together with 17 ml of EG into the above solution and the mixture was stirred for another 30 min. The slurry was transferred into the autoclave, as above, and heated to 200 °C with a holding time of 24 h. The product was purified as above.

The TD synthesis of the $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ (NaY-TD) NPs was based on ref.³ A total of 12 ml of OA and 30 mL of ODE were added to 2 mmol of stoichiometric amounts of Ln chlorides in a 100 ml flask. The solution was heated to 156 °C for 30 min and then cooled to room temperature. A solution of NH_4F (8 mmol) and NaOH (5 mmol) in 10 ml of methanol was added to the above and stirred at 50 °C for 30 min. After the evaporation of methanol, the solution was heated to 300 °C in an Ar atmosphere for 1.5 h and then cooled to room temperature. The Ln-NPs were precipitated with acetone, collected after centrifugation (at 5000 rpm for 5 min), washed with ethanol to remove the OA, and with deionized water to remove the NaCl. Finally, they were re-dispersed in hexane. Oleate-capped NaY-TD NPs in hexane were transferred into water through a modified ligand-free protocol.⁴ The dried Ln-NPs were immersed in water (10 ml) and the pH value was decreased to 2–4 using 0.1-M HCl. The mixture was sonicated in an ultrasound bath for about 4 h, while maintaining the pH value of 2–4 by adding 0.1-M HCl every 30 min. The carboxylate groups of the oleate ligand were gradually protonated to yield OA. After completion of this process, the aqueous solution was mixed with DE to remove the OA by extraction. The procedure was repeated several times until the solution became transparent. The ligand-free Ln-NPs in water were recovered by centrifugation at 5000 rpm for 5 min after precipitation with acetone. The product was again immersed in acetone, centrifuged at 5000 rpm for 5 min and finally dispersed in water.

The HT synthesis of binary fluoride Ln-NPs, $\text{LaF}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ (La-HT) and $\text{GdF}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ (Gd-HT) was carried out in a similar way as the NaY-HT, from Ln nitrates and at 180 °C for 6 h. However, in this case NaBF_4 was used instead of NaF.⁵ In short, 5 ml of stoichiometric amounts of Ln nitrates (total of 1 mmol) were added to 10 ml of aqueous solution of Na citrate (2 mmol), prepared as described above. After stirring, 15 ml of aqueous solution of NaBF_4 (25 mmol) was introduced into the nitrate solution. The pH of the mixture was adjusted to pH ~ 1 with HNO_3 (c = 1 M). After agitation for 15 minutes the mixture was transferred into an autoclave (as above) and the subsequent procedure was similar to that described above.

The ST synthesis of the $\text{LaF}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ (La-ST) and $\text{GdF}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ (Gd-ST) was carried out in EG at 180 °C for 6 h using a slightly modified procedure from ref.⁶ The NaBF_4 (8 mmol) was dissolved in 20 mL of EG, and afterwards a solution of 2 mmol of Ln chlorides in a

Jaque, J. G. Sole and J. A. Capobianco, *ACS Nano*, 2010, **4**, 3254.

³ H. S. Qian and Y. Zhang, *Langmuir*, 2008, **24**, 12123.

⁴ N. Bogdan, F. Vetrone, G. A. Ozin, and J. A. Capobianco, *Nano Lett.*, 2011, **11**, 835.

⁵ C. X. Li, J. Yang, P. P. Yang, H. Z. Lian and J. Lin, *Chem. Mater.*, 2008, **20**, 4317.

⁶ X. Qu, K. Y. Yang, J. W. Chung, B. K. Moon, B. C. Choi, J. H. Jeong and K. H. Kim, *J. Solid State Chem.*, 2011, **184**, 246.

stoichiometric ratio in 20 ml of EG was added under vigorous stirring. The ST synthesis and purification of the product were carried out in a similar way as the HT syntheses above.

2.3 Characterization of nanoparticles and suspensions

The crystal structure of the synthesized Ln-NPs was verified by X-ray diffraction (XRD) with an X-ray diffractometer (Philips X'Pert PRO MPD Diffractometer, PANalytical with $\text{CuK}\alpha$ radiation, $\lambda_{\text{CuK}\alpha 1}=1.5406 \text{ \AA}$). The morphology of the Ln-NPs was inspected with a transmission electron microscope (TEM, Jeol 2100). The TEM samples were prepared by dropping a diluted dispersion of Ln-NPs onto a copper grid. The equivalent diameters of the Ln-NPs were determined from their surfaces using Gatan Digital Micrograph Software. A minimum of 150 Ln-NPs per sample was counted for the statistics. An energy-dispersive X-ray spectroscopy (EDXS) and selected-area electron diffraction (SAED) were also performed during the TEM analyses.

The UC fluorescence of the Ln-NPs was characterized for irradiation with a continuously emitting 978-nm diode laser (MDL-III by CNI, Changchun, China). Focusing of the laser beam with an average power of 2 W produced an irradiant power density of $\sim 160 \text{ J/cm}^2$. The resulting UC fluorescence was collected with an integrating sphere (ISP-REF, Ocean Optics, Dunedin, FL) at an $\sim 90^\circ$ angle with respect to the beam axis and analysed using a compact diffraction spectrometer (USB4000, Ocean Optics, Dunedin, FL) in the 400–900 nm spectral range.

The concentration of Ln-NPs in suspension was determined thermogravimetrically. Water was evaporated at $70 \text{ }^\circ\text{C}$ during the night and the organic species (citrate, PEI, EG) were decomposed during the heating ($3 \text{ }^\circ\text{C/min}$) to $500 \text{ }^\circ\text{C}$ with a holding time of 1 h.

The dissolution analyses were performed from three-days-old aqueous suspensions. The solutions for the analyses were prepared by centrifugation of the suspensions at 5000 rpm for 5 min to remove the majority of the Ln-NPs, followed by an ultrafiltration (using a MW 30kDa filter) to eliminate any remaining Ln-NPs from the solution. An Orion 960 Autochemistry System with a temperature sensor and a combined fluoride ion selective electrode (Thermo, Orion model 96-09) was used for a potentiometric determination of the F^- using the multiple known addition method with a blank subtraction.⁷ The concentration of dissolved cations (Ln^{3+} , Y^{3+} and Na^+) was determined with ICP-OES.

⁷ M. Ponikvar, V. Stibilj, and B. Žemva, *Food Chem.*, 2007, **103**, 369.

XRD analysis

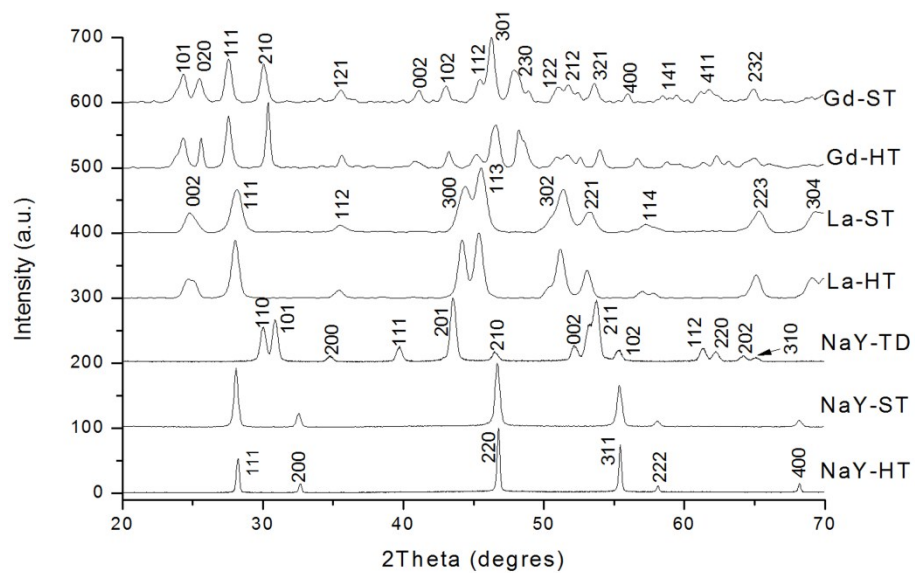


Fig. S1 XRD patterns of the as-synthesized Ln-NPs. The indices correspond, from bottom to top, to the α -NaYF₄ (JCPDS 77-2042), β -NaYF₄ (JCPDS 16-0334), hexagonal LaF₃ (JCPDS 32-0483), and orthorhombic GdF₃ (JCPDS 49-1804).