

Supporting information

Lanthanide doped upconverting colloidal CaF₂ nanoparticles prepared by a single-step hydrothermal method: toward efficient materials with near infrared-to-near infrared upconversion emission

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Experimental details

Synthesis

Ln³⁺/Yb³⁺ (Ln=Er, Ho or Tm) co-doped CaF₂ nanoparticles (Ca²⁺:Yb³⁺:Ln³⁺= 0.78 : 0.20 : 0.02 metal ratios) were prepared by hydrothermal synthesis. In a 50 ml Teflon vessel, stoichiometric quantities of CaCl₂·2H₂O (Baker, >99%), YbCl₃·6H₂O (Aldrich, 99.99%) and ErCl₃·6H₂O (Aldrich 99.9%), TmCl₃·6H₂O (Aldrich, 99.9%) or Ho(NO₃)₃·5H₂O (Aldrich, 99.9%) (total metal amount of 3.5·10⁻³ mol), were dissolved in 7 ml of deionized water. 20 ml of 0.47 M sodium oleate (cis, Sigma-Aldrich, purum) solution was added dropwise under vigorous stirring and after few minutes a milky suspension was formed. An aqueous solution of NH₄F (Baker, 99%) was added in the previous suspension, in order to have a small excess of fluoride ions with respect to the stoichiometric amounts ((Ca+Yb+Ln):F=1:2.5, Ln=Er, Ho or Tm). The obtained dispersion was put in a pressure digester (DAB-2, Berghof) and heat treated in an oven at 180°C for 8 h or 200°C for 4 h, under autogenous pressure. The autoclave was then cooled to room temperature and after centrifugation (at 7000 rpm for 20 m) the calcium fluoride nanoparticles are collected. After a proper washing with deionized water, absolute ethanol (Carlo Erba, purum) and acetone (Carlo

Erba, purum), the obtained oleate paste was dried at room temperature for 12 h. All the calcium fluoride nanoparticles can be easily dispersed in apolar solvents, such as chloroform or toluene (Carlo Erba, purum), with a typical concentration of 10 mg/mL. Lanthanide doped CaF_2 nanoparticles in water solution are also directly obtained in the supernatant liquid after the centrifugation procedure. The extraction of the CaF_2 nanoparticles dispersed in CHCl_3 was obtained by mixing a NPs colloidal dispersion in CHCl_3 (1 ml, 1%wt) and sodium oleate aqueous solution (1 ml, 0.23 M) under vigorous stirring and subsequent centrifugation in order to quickly separate the two phases.

X-Ray powder diffraction

X-ray-diffraction (XRD) data were taken with a Thermo ARL X'TRA powder diffractometer, operating in Bragg-Brentano geometry equipped with a Cu-anode X-ray source (K_α , $\lambda=1.5418 \text{ \AA}$) and using a Peltier Si(Li) cooled solid state detector. The spectra were collected with a scan rate of $0.0033^\circ/\text{s}$, with a measurement time of 9.0 s/step and 2θ range of 24° - 90° . The phase identification were performed with PDF-4+ 2008 database provided by the International Centre for Diffraction Data (ICDD). The instrumental X-ray peaks broadening was determined exploiting LaB_6 standard reference material (SRM 660a) provided by NIST, the cell parameters were precisely determined using α - SiO_2 as an internal standard. The samples were carefully homogenized in a mortar, suspended in a few drops of ethanol and deposited in a low-background sample stage. Before starting the X-ray diffraction pattern collection the ethanol was completely evaporated.

Mid infrared spectra

Room temperature infrared absorption spectra were measured in the mid infrared (MIR) region using a FTIR spectrometer (Nicolet, Magnet-IR 760) with a spectral resolution of 2 cm^{-1} . For the measurements, the powder samples were dispersed in KBr (3 wt%) and pressed to obtain a pellet.

Electron Microscopy setup

Transmission Electron Microscopy (TEM) and high resolution TEM (HRTEM) images were taken with a JEOL 3010 high resolution electron microscope (0.17 nm point-to-point), operating at 300 KV, equipped with a Gatan slow-scan CCD camera (model 794) and an Oxford Instrument EDS microanalysis detector (Model 6636). The powder was dispersed in a toluene solution and deposited on a holey carbon film.

Spectroscopy setup

Upconversion emissions were measured upon 980 nm using a diode laser as the excitation source (CNI Optoelectronics Tech). The emission signal was analysed by a half-meter monochromator (HR460, Jobin Yvon) equipped with a 1200 lines/mm grating and detected with a CCD detector (Spectrum One, Jobin Yvon). The spectral resolution of the emission spectra is 0.1 nm. The upconversion luminescence images were acquired with a Canon multiple CCD camera.

Zeta Potential measurements

Zeta potential data were measured using a Malvern Zetasizer Nano ZS90 operating with a He-Ne laser at 633 nm. Water dispersions with a 0.1 g/L concentration of lanthanide doped CaF_2 nanoparticles were used.

Table S1. Energies (in cm^{-1}) and assignment of the vibrational modes [S1, S2] for oleic acid, sodium oleate and capped CaF_2 nanoparticles (NPs).

oleic acid	sodium oleate	capped NPs	Assignment
1711	-	1716	C=O stretch
	1561	1561	antisym CO_2^- stretch
1465	1463	1466	CH ₂ scissoring and CH ₃ deformation
~1455		1458	
	1447	~1445	
1438			
	1425	~1420	
1413			sym CO_2^- stretch
-	1405	~1405	

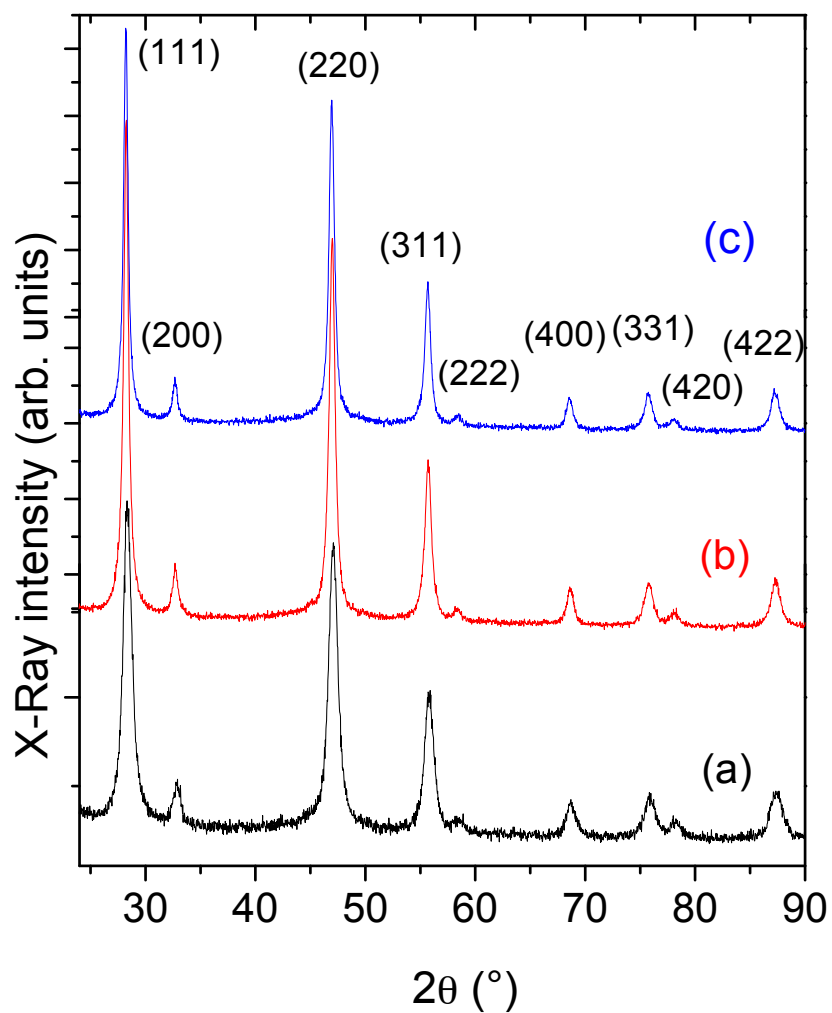


Figure S1. X-Ray powder diffraction patterns of (a) $\text{CaF}_2:\text{Yb}^{3+},\text{Tm}^{3+}$, (b) $\text{CaF}_2:\text{Yb}^{3+},\text{Er}^{3+}$, (c) $\text{CaF}_2:\text{Yb}^{3+},\text{Ho}^{3+}$ prepared after a heat treatment of 180 °C for 8 h.

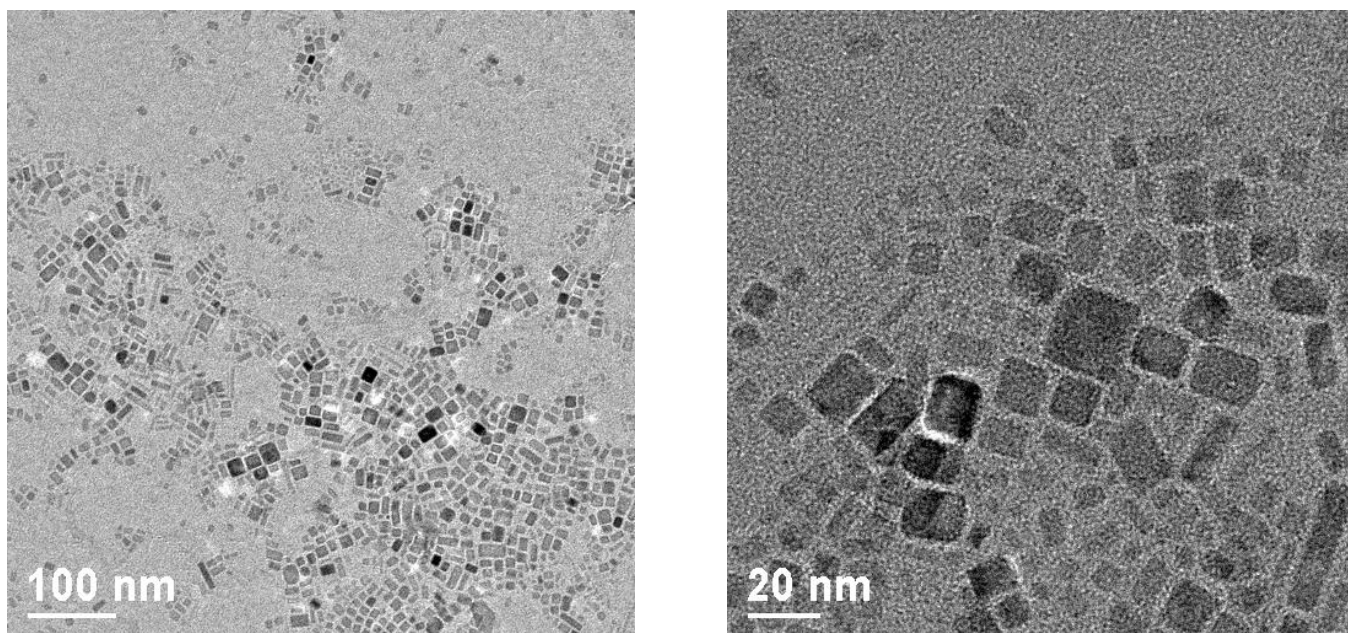


Figure S2. Representative TEM images for the oleate capped CaF₂ nanoparticles prepared after a heat treatment of 180 °C for 8 h.

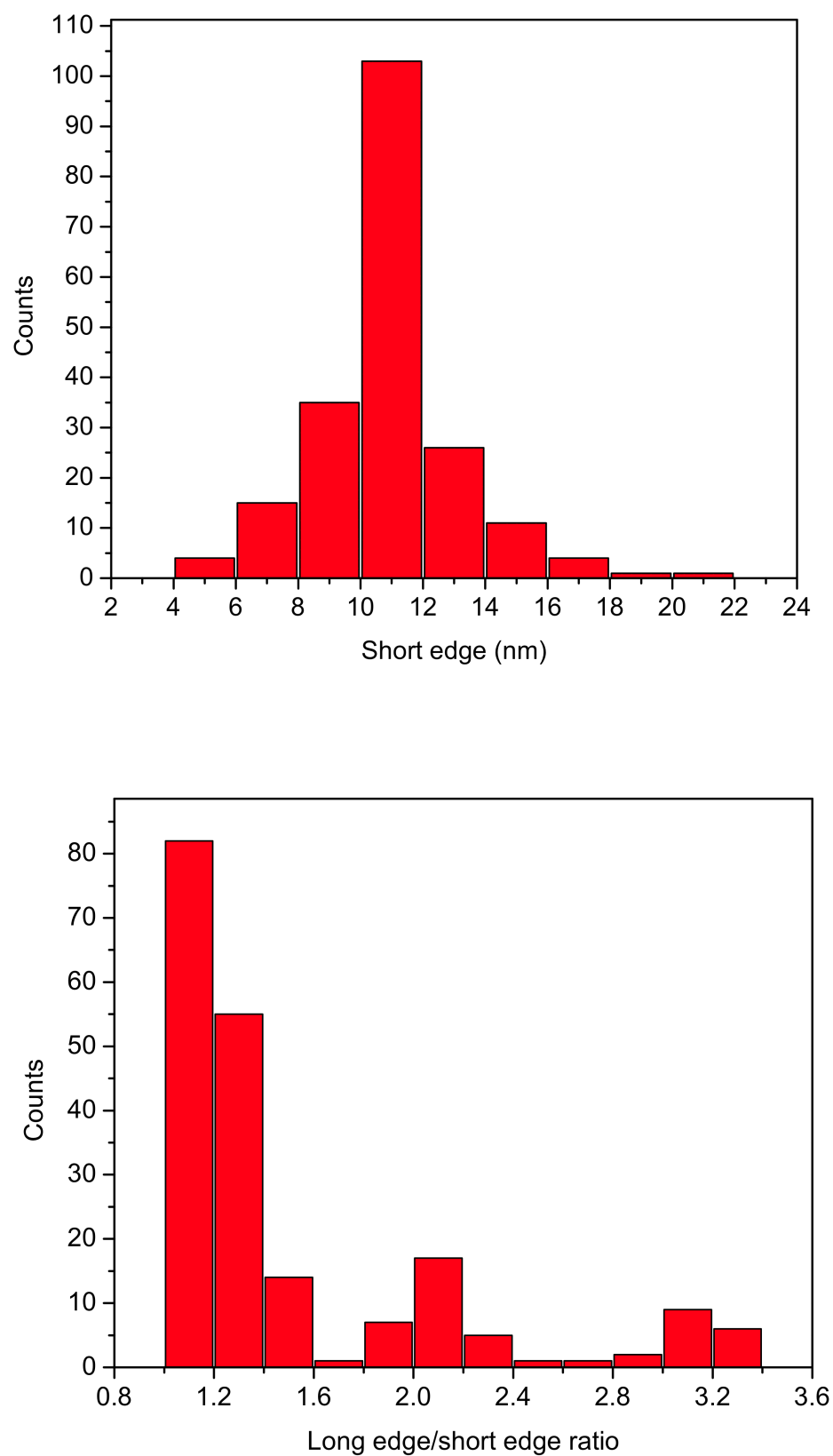


Figure S3. Size dispersion (upper figure) and aspect ratio (lower figure) for a representative sample of capped CaF_2 nanoparticles prepared after a heat treatment of 180 °C for 8 h.

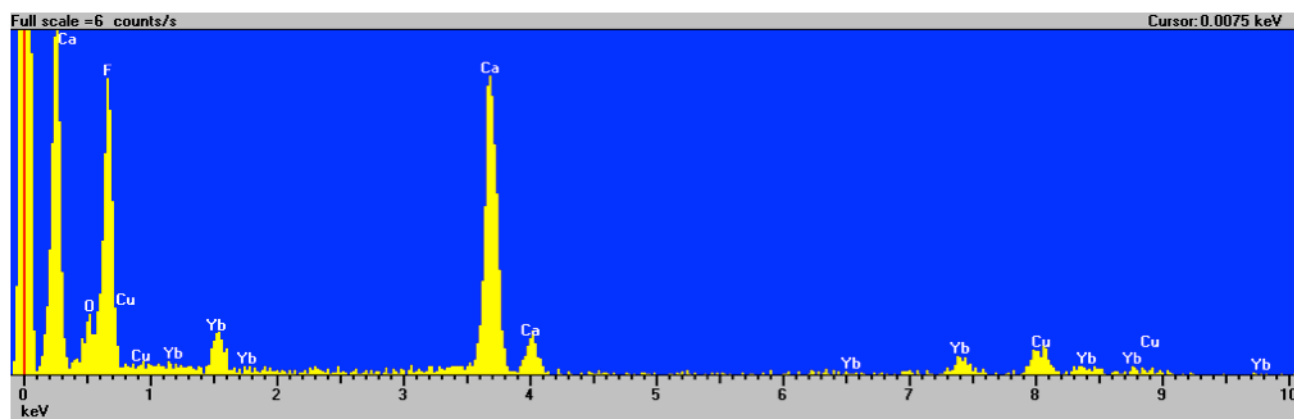
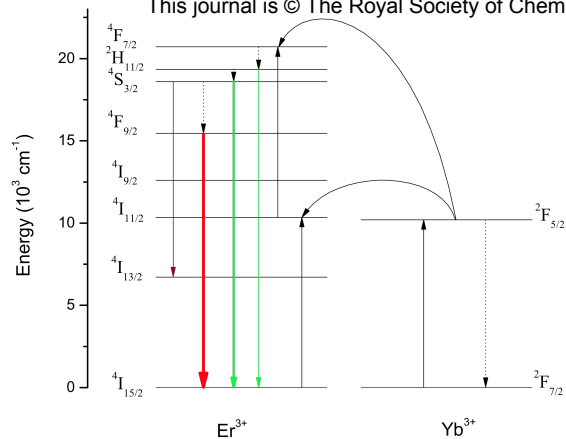
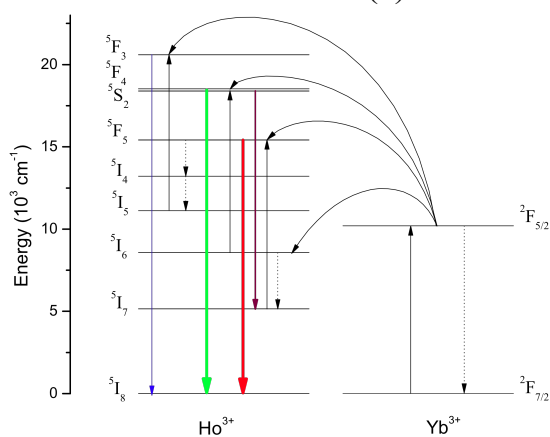


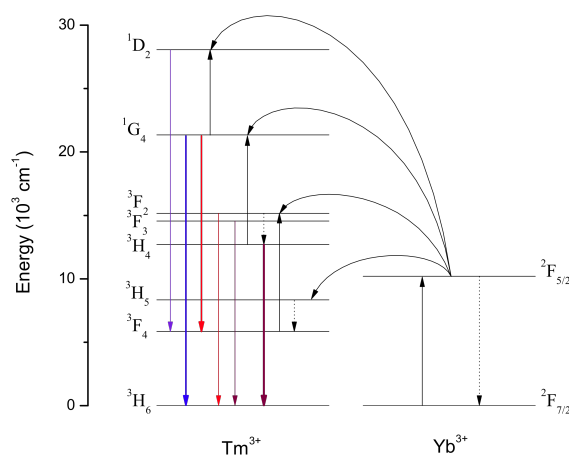
Figure S4. EDS pattern for $\text{CaF}_2:\text{Tm}^{3+}, \text{Yb}^{3+}$ nanoparticles prepared after a heat treatment of 180 °C for 8 h.



(a)



(b)



(c)

Figure S5. Schematic representation of energy transfer UC processes for $\text{Er}^{3+}/\text{Yb}^{3+}$ (a), $\text{Ho}^{3+}/\text{Yb}^{3+}$ (b) and $\text{Tm}^{3+}/\text{Yb}^{3+}$ (c) systems upon excitation at 980 nm.



Figure S6. Extraction of the CaF_2 nanoparticles from a CHCl_3 dispersion (lower layer) to a sodium oleate aqueous solution (upper layer). The aqueous solution is perfectly transparent (left image) and the UC emission is very bright upon laser excitation at 980 nm (right image). The lower layer is milky due to a partial transfer of the oleate molecule into the CHCl_3 dispersion.

References

- [S1] N. Wu, L. Fu, M. Su, M. Aslam, K. C. Wong and V. P. Dravid, *Nano Lett.* **2004**, *4*, 383-386.
- [S2] D. G. Cameron, J. Umemura, P. T. T. Wong and H. H. Mantsch, *Colloids Surfaces* **1982**, *4*, 131-145.