

## Electronic Supplementary Information

# Shape-Controlled Synthesis and Self-Assembly of Highly Uniform Upconverting Calcium Fluoride Nanocrystals

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## Experimental Section

**Materials.** All chemicals were used as obtained without further purification. Calcium carbonate ( $\text{CaCO}_3$ , 99.9%), lithium fluoride (LiF, 99.99%), erbium oxide (99.99%), thulium oxide (99.9%), ytterbium oxide (99.99%), oleic acid (OA, technical grade, 90%), and 1-octadecene (ODE, technical grade, 90%), were purchased from Sigma–Aldrich. Trifluoroacetic acid (99.5+%) was purchased from Alfa Aesar.

**Synthesis of  $\text{CaTFA}_2$  precursors.** Calcium trifluoroacetate ( $\text{CaTFA}_2$ ) precursors were synthesized by dissolving 10 g of  $\text{CaCO}_3$  in 100 mL of a trifluoroacetic acid/deionized water mixture (50/50 vol%) at room temperature. Evolution of  $\text{CO}_2$  gas was observed for a few seconds after adding  $\text{CaCO}_3$  in the TFA solution. The solution was stirred for additional two hours. The  $\text{CaTFA}_2$  precursors were collected by removing the solution *via* vacuum distillation.

**Synthesis of  $\text{LnTFA}_3$  precursors.** Lanthanide trifluoroacetate ( $\text{LnTFA}_3$ ) precursors were synthesized by dissolving 10 g of lanthanide oxide (eg.  $\text{Er}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{Tm}_2\text{O}_3$ ) in 100 mL of a trifluoroacetic acid/deionized water mixture (50/50 vol%) and stirred under refluxing until oxide precursors were completely dissolved. The  $\text{LnTFA}_3$  precursors were collected by vacuum distillation.

**Synthesis of  $\text{CaF}_2$  spherical NCs.**  $\text{CaTFA}_2$  (2 mmol), LiF (6 mmol), OA (30 mL), and ODE (30 mL) were added into a 125 mL three-neck flask and degassed at 125 °C for one hour. The mixture was then heated to 300–320 °C and kept at this temperature for 30 min. After cooling the reaction mixture to room temperature, the nanocrystals were precipitated by adding excess ethanol and collected by centrifugation at 4000 rpm for two minutes. The purification was performed twice by re-dispersing in hexane and precipitation with ethanol. After purification, hexane was added to the

precipitates to disperse the NCs in the solution. Residual LiF was removed by centrifugation at 3000 rpm for two minutes. The thermal decomposition of CaTFA<sub>2</sub>

**Synthesis of truncated CaF<sub>2</sub> octahedra.** LiF (6 mmol), OA (15 mL), and ODE (15 mL) were added into a 125 mL three-neck flask and degassed at 125 °C for one hour. CaTFA<sub>2</sub> (2 mmol), OA (15 mL), and ODE (15 mL) were added into the other 125 mL three-neck flask and degassed at 125 °C for one hour. The mixture containing LiF was then heated to 300–320 °C and then the solution of CaTFA<sub>2</sub> was slowly injected into the mixture of LiF and OA/ODE for 15 min. The reaction was kept for an additional 15 min. After cooling the reaction mixture to room temperature, the NCs were precipitated by adding excess ethanol and collected by centrifugation at 4000 rpm for two minutes. The purification was performed twice by re-dispersing in hexane and precipitation with ethanol. After purification, hexane was added to the precipitates to disperse the NCs in the solution. Residual LiF was removed by centrifugation at 3000 rpm for two minutes.

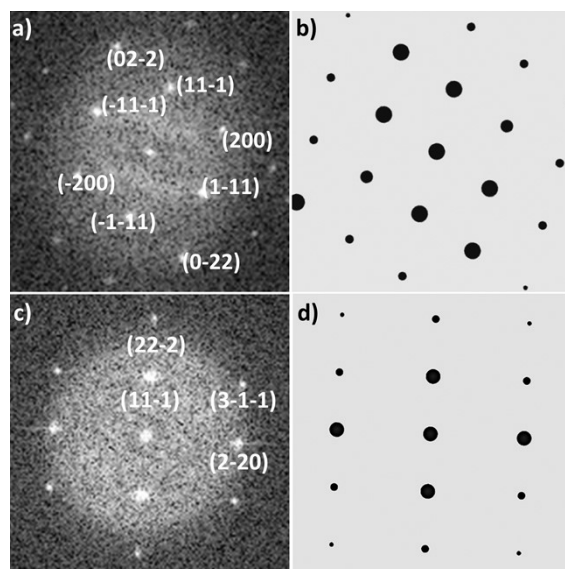
**Synthesis of CaF<sub>2</sub> NWs.** CaTFA<sub>2</sub> (2 mmol), OA (1 mL), and ODE (59 mL) were added into a 125 mL three-neck flask and degassed at 125 °C for one hour. The mixture was then heated to 280 °C and kept at this temperature for 30 min. The NWs were purified using the same procedure as for the spherical CaF<sub>2</sub> synthesis.

**Synthesis of lanthanide-doped CaF<sub>2</sub> NCs and NWs.** Lanthanide-doped CaF<sub>2</sub> NCs and NWs were synthesized using the same experimental conditions as those used for undoped samples except for the use of a mixture of CaTFA<sub>2</sub> and LnTFA<sub>3</sub> precursors.

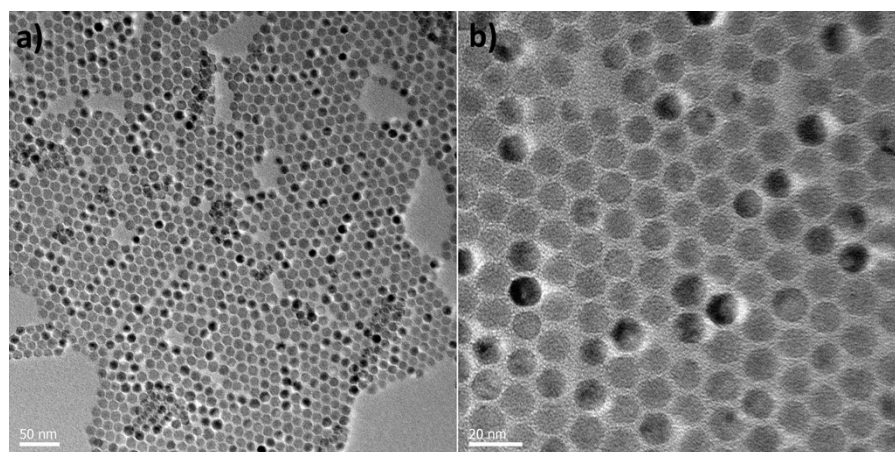
**Self-assembly of CaF<sub>2</sub> NCs and NWs.** Self-assembly of CaF<sub>2</sub> NCs and NWs was performed *via* liquid interfacial assembly procedure previously reported. Briefly, a Teflon well was filled with diethylene glycol subphase, and then 30 μL of NC dispersed in hexane solution was dropped on

top of subphase. A Teflon well was covered with a glass slide to induce slow evaporation of hexane. After self-assembled superlattices were formed, the films were transferred onto carbon-coated TEM grids for microscopic analysis.

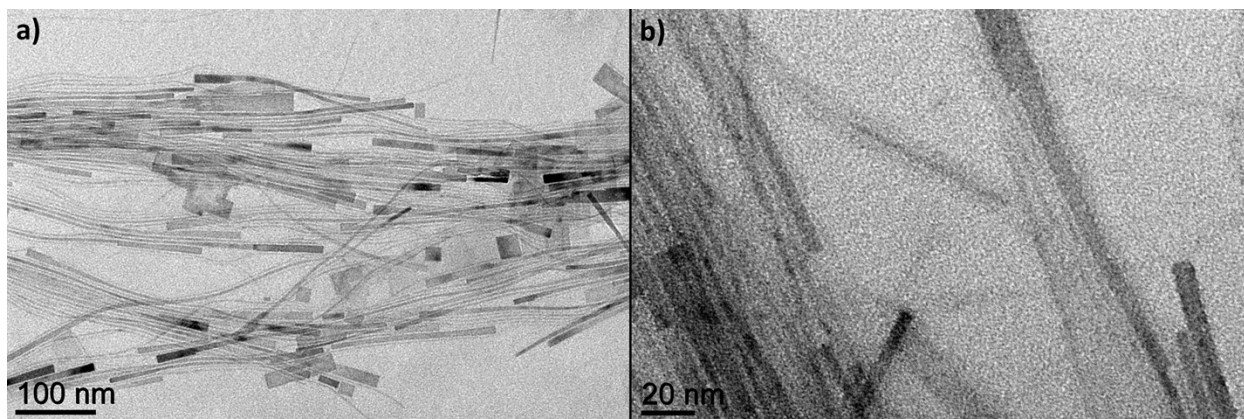
**Characterization.** The TEM images and SAED data were collected using a JEM-2100 microscope (JEOL, Ltd.) operating at 200 kV. The elemental compositions of Er<sup>3+</sup>, Yb<sup>3+</sup> doped CaF<sub>2</sub> NCs were collected via energy dispersive X-ray spectroscopy in scanning TEM (STEM-EDX) using a JEOL JEM-F200 system operated at 200 kV. Simulated electron diffraction patterns of CaF<sub>2</sub> NCs were obtained using the CrystalMaker software (Oxfordshire, UK). The atomic coordinates and sizes of the CaF<sub>2</sub> NCs were constructed from the cubic CaF<sub>2</sub> unit cell (JCPDS no. 87-0971). Powder X-ray diffraction measurements were performed using a Rigaku Smartlab high-resolution diffractometer (Rigaku Corporation). SAXS measurements were performed at the Multi-Angle X-ray Scattering Facility at the University of Pennsylvania. Information regarding the size and shape was extracted by the X-ray simulation of the SAXS results using Datasqueeze software. Photoluminescence spectra were collected using the Edinburgh FS5 spectrofluorometer (Edinburgh Instruments Ltd.). Upconversion luminescence was measured with excitation at 980 nm using a diode laser. The absorption spectra were collected using the JASCO-770 spectrophotometer (JASCO, Inc.).



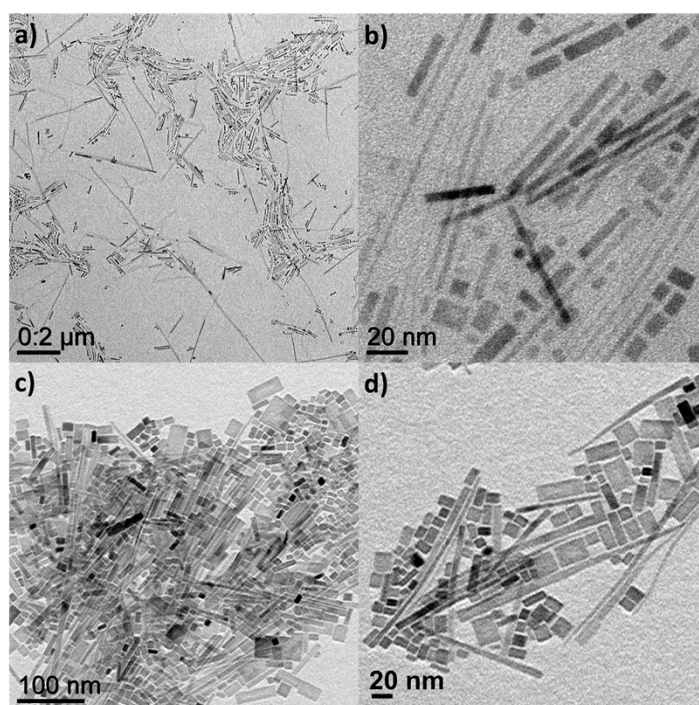
**Fig. S1** Fast Fourier transform of high-resolution transmission electron microscopy (TEM) images along the (a) [110] projection and (c) [112] projection and (b) and (d) the simulated electron diffraction patterns from the [110], and [112] zones, respectively.



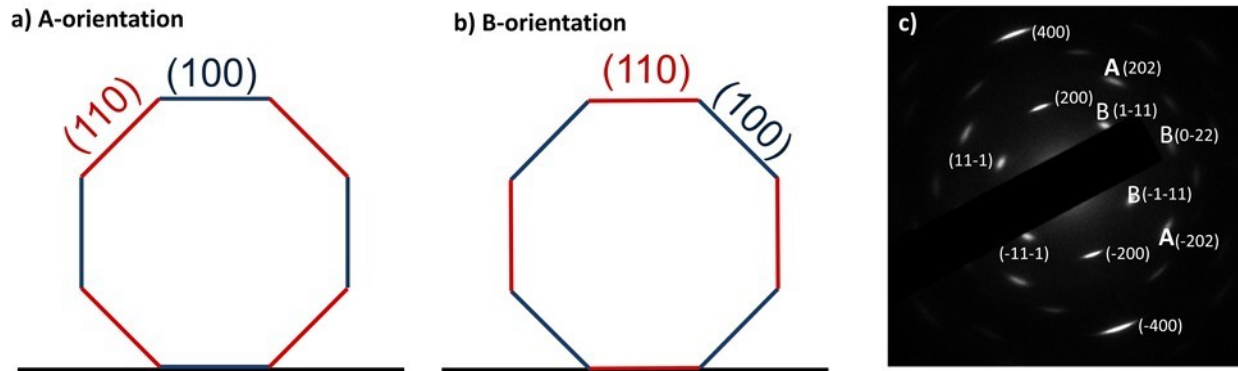
**Fig. S2** (a) Low-magnification and (b) high-magnification TEM images of  $\text{CaF}_2$  nanocrystals synthesized at 320 °C for one hour.



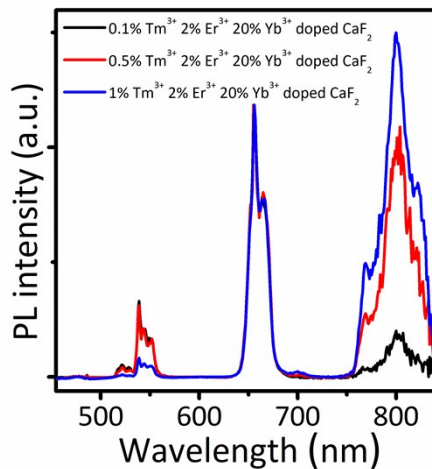
**Fig. S3** (a) Low-magnification and (b) high-magnification TEM images of  $\text{CaF}_2$  nanowires.



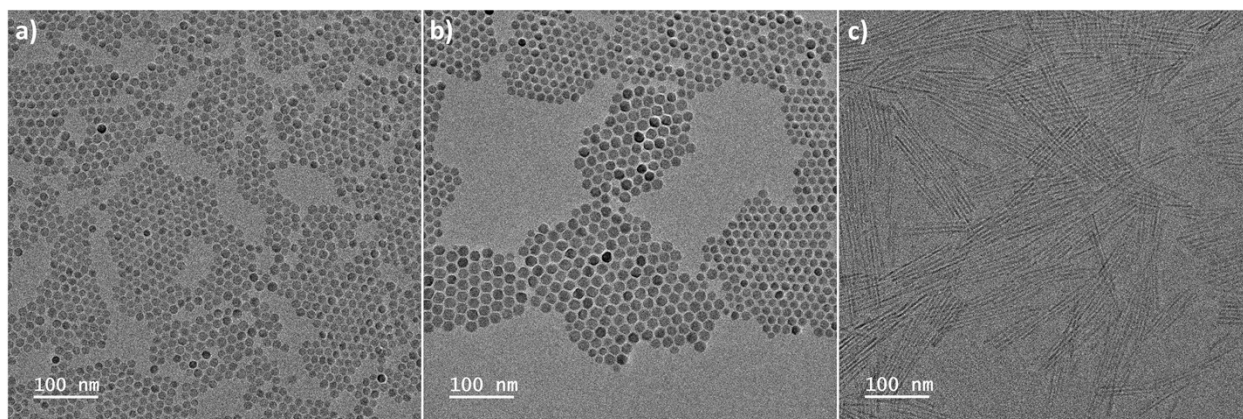
**Fig. S4** (a) TEM images of  $\text{CaF}_2$  nanowires synthesized at a, (b) 280 °C for one hour and (c, d) 290 °C for 30 min.



**Fig. S5** Schematics of the cross-sections of  $\text{CaF}_2$  nanowires placed along the (a) (100) and (b) (110) planes parallel to the substrate. (c) Electron diffraction pattern of self-assembled  $\text{CaF}_2$  nanowires. Mark “A” corresponds to the diffraction from the A-orientation of  $\text{CaF}_2$  and mark “B” is attributed to the electron diffraction of the B-orientation.



**Fig. S6** Upconversion luminescence spectra of  $\text{Tm}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+}$  triply doped  $\text{CaF}_2$  nanocrystals. The atomic concentrations of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  are 2% and 20%, respectively, and the concentration of  $\text{Tm}^{3+}$  is varied as 0.1%, 0.5%, and 1%. The emission spectra are normalized to the green emission peaks at 540 nm.



**Fig. S7** TEM images of (a)  $\text{CaF}_2$  nanospheres, (b)  $\text{CaF}_2$  nano-octahedra, and (c)  $\text{CaF}_2$  nanowires used for UC measurements.

**Table S1** Elemental composition of the  $\text{CaF}_2$  NCs.

	nanospheres	nano-octahedra	nanowires
Ca (at.%)	78.31	78.21	78.72
Er (at.%)	1.97	1.92	1.98
Yb (at.%)	19.72	19.87	19.30
Total (at.%)	100	100	100