

Electronic Supplementary Information

Monodisperse upconversion $\text{Er}^{3+}/\text{Yb}^{3+}$: MFCl (M=Ca, Sr, Ba) nanocrystals synthesized via a seed-based chlorination route

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Experimental details

Chemicals: All chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout. $\text{Sr}(\text{NO}_3)_2$, MCO_3 (M=Ca, Sr, Ba), $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Ln_2O_3 (Ln=Yb, Er), sodium oleate (NaOA), cyclohexane, ethanol, and HF (40 wt%) were all supplied by Sinopharm Chemical Reagent Company. Oleic acid (OA), trifluoroacetic acid (CF_3COOH , TFA), trichloroacetic acid (CCl_3COOH , TCA), tribromoacetic acid (CBr_3COOH , TBA) and 1-octadecene (ODE) were purchased from Aladdin Chemical Reagent Company.

Preparation of $\text{M}(\text{CF}_3\text{COO})_2$ and $\text{Ln}(\text{CF}_3\text{COO})_3$ precursors: The metal trifluoroacetates were prepared from the corresponding metal oxides and TFA followed by the literature method (Roberts, J. E. J. Am. Chem. Soc., 1961, 83, 1087). In a typical synthesis of $\text{M}(\text{CF}_3\text{COO})_2$, 4 mmol of MCO_3 were added into a solution containing 10 mL H_2O and 10 mL TFA with continuous stirring, which was kept refluxing so as to form an optically transparent solution. The resulting solution was dried in an oven at 80 °C for 24 h to obtain $\text{M}(\text{CF}_3\text{COO})_2$ powders. The same process is also used to prepare $\text{Ln}(\text{CF}_3\text{COO})_3$ powders.

Synthesis of MF_2 seed-nanocrystals by a thermolysis route: The synthesis was carried out using the standard oxygen-free procedure. A typical procedure was described as follows. A given amount of $\text{M}(\text{CF}_3\text{COO})_2$ (0.5 mmol) were added into the mixture solution of 10 mL OA and 10 mL ODE in a three-necked flask (100 mL) at room temperature. Then, the slurry was heated to 100 °C and kept for 30 minutes to remove water and oxygen with vigorous magnetic stirring under vacuum in a temperature-controlled electromantle and thus to form an optically transparent solution. The solution was then heated to 280~310 °C and kept for 1-6 hour under an inert N_2 atmosphere. On cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of ethanol into the reacted solution, followed by washing with ethanol and cyclohexane and drying in an oven at 80 °C for 24 h. The as-prepared dried nanocrystals can be easily dispersed in various nonpolar organic solvents such as cyclohexane. The $\text{Yb}^{3+}/\text{Er}^{3+}$: SrF_2 seed-nanocrystals were similarly synthesized by introducing the corresponding rare earth trifluoroacetates with designed concentrations to the reaction system.

Synthesis of MFCl nanocrystals by a MF₂-seed based chlorination route: Upon cooling to room temperature for the above-mentioned thermolysis solution, the mixture of 0.5 mmol trichloroacetic acid (TCA), 10 ml OA and 10 ml ODE was quickly added into the solution and then heated at 100 °C for 30 min to remove water and oxygen under vacuum. Subsequently, the chlorination reaction was carried out to fabricate MFCl nanocrystals when heating the solution at 120~280 °C for 30 min. After cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of ethanol into the reacted solution, followed by washing with ethanol and cyclohexane and drying in an oven at 80 °C for 24 h. The as-prepared dried nanocrystals can be easily redispersed in various nonpolar organic solvents such as cyclohexane. The Yb³⁺/Er³⁺: SrFCl nanocrystals were similarly synthesized by adopting Yb³⁺/Er³⁺: SrF₂ nanocrystals as seeds.

Synthesis of SrFCl nanocrystals by a direct co-thermolysis route: A given amount of Sr(CF₃COO)₂ (0.500, 0.250, or 0.125 mmol) and the same mole content of trichloroacetic acid were added into the mixture solution of 10 mL OA and 10 mL ODE in a three-necked flask (100 mL) at room temperature. Then, the slurry was heated at 100 °C for 30 minutes to remove water and oxygen with vigorous magnetic stirring under vacuum in a temperature-controlled electromantle and thus to form an optically transparent solution. The solution was then heated to 280 °C and kept for 30 min under an inert N₂ atmosphere. On cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of ethanol into the reacted solution, followed by washing with ethanol and cyclohexane and drying in an oven at 80 °C for 24 h.

Synthesis of Yb³⁺/Er³⁺: SrF₂ nanocrystals with the similar size and shape to those of Yb³⁺/Er³⁺: SrFCl ones by a solvothermal route: For a typical synthesis, an aqueous solution of Sr(NO₃)₂, Yb(NO₃)₃, Er(NO₃)₃ (total 0.5 mol/L) was mixed with ethanol (10 mL), oleic acid (10 mL) and NaOA (2.5 g) under thorough stirring. Then, 4mL HF (1.0 mol/L) solution was dropwise added to the mixture. After vigorous stirring at room temperature for about 30 min, the colloidal solution were transferred into a 40 mL Teflon-lined autoclave, sealed and heated at 180 °C for 84 h. The final products were collected by centrifugation, washed several times with ethanol/cyclohexane, and drying in an oven at 80 °C for 24 h. The as-prepared dried nanocrystals can be easily redispersed in various nonpolar organic solvents such as cyclohexane.

Synthesis of Yb³⁺/Er³⁺: α-NaYF₄ nanocrystals by a solvothermal route: For a typical synthesis, an aqueous solution of Y(NO₃)₃, Yb(NO₃)₃, and Er(NO₃)₃ (total 0.2 mol/L) was mixed with ethanol (5 mL), oleic acid (5 mL) and NaOH (0.3 g) under thorough stirring. Then, 1mL NH₄F (2.0 mol/L) solution was dropwise added to the mixture. After vigorous stirring at room temperature for about 30 min, the colloidal solution were transferred into a 20 mL Teflon-lined autoclave, sealed and heated at 160 °C for 12 h. The final products were collected, washed several times with ethanol/cyclohexane, and purified by centrifugation.

Characterizations: XRD analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using CuKα radiation (λ=0.154 nm). The size and shape of the samples were observed by a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive x-ray spectroscope (EDS). TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon-coated copper grid. Upconversion luminescence spectra were carried out upon 980 nm excitation with a pump power of ~200 mW (power density ~20 W/cm²), provided by a power-controllable 980 nm diode laser (DPL-II, Module-HTL98M10) with the maximum power output of 9 W. To enable comparison of the upconversion emission intensities among different samples, the emission spectra were measured

with the same instrumental parameters (for example: same excitation wavelength and power, same excitation and emission slits). Upconversion decay lifetimes were measured with a customized UV to mid-infrared steady-state and phosphorescence lifetime spectrometer (FSP920-C, Edinburgh) equipped with a digital oscilloscope (TDS3052B, Tektronix) and a tunable mid-band OPO pulse laser as excitation source (410-2400 nm, 10 Hz, pulse width ≤ 5 ns, Vibrant 355II, OPOTEK). All photoluminescence studies were carried out at room temperature.

Figure S1-S13

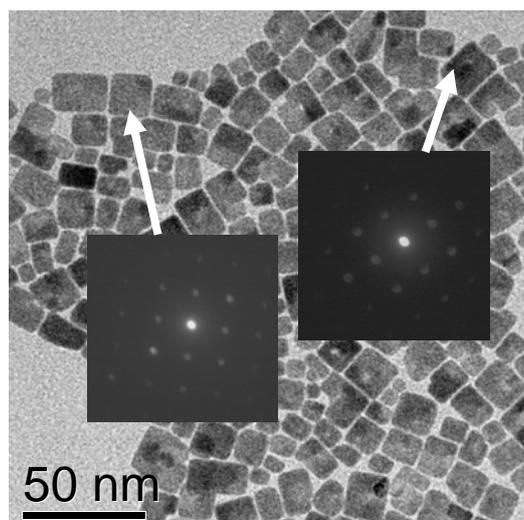


Figure S1. TEM micrograph of SrFCl NCs, insets shows NBED patterns of two different NCs

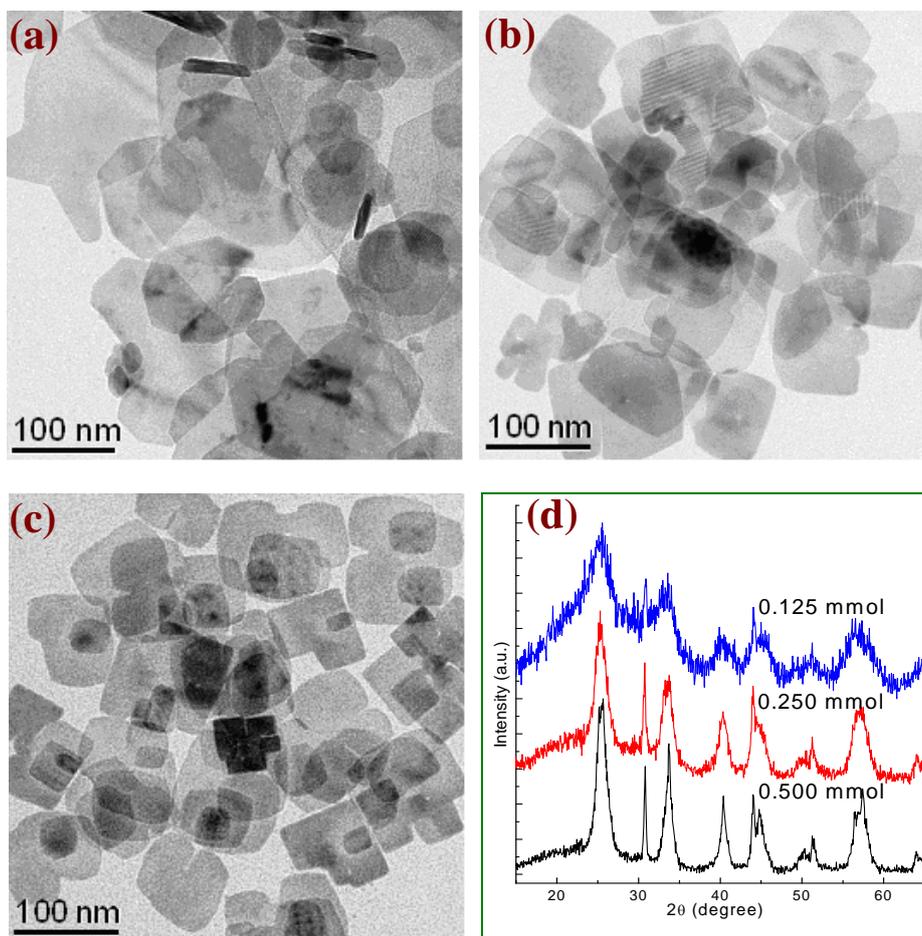


Figure S2. TEM micrographs of SrFCl NCs prepared by direct co-thermolysis of x mol% Sr(CF₃COO)₂ and x mol% TCA in OA and ODE solution: (a) x=0.500, (b) x=0.250, (c) x=0.125. (d) XRD patterns of the corresponding SrFCl samples.

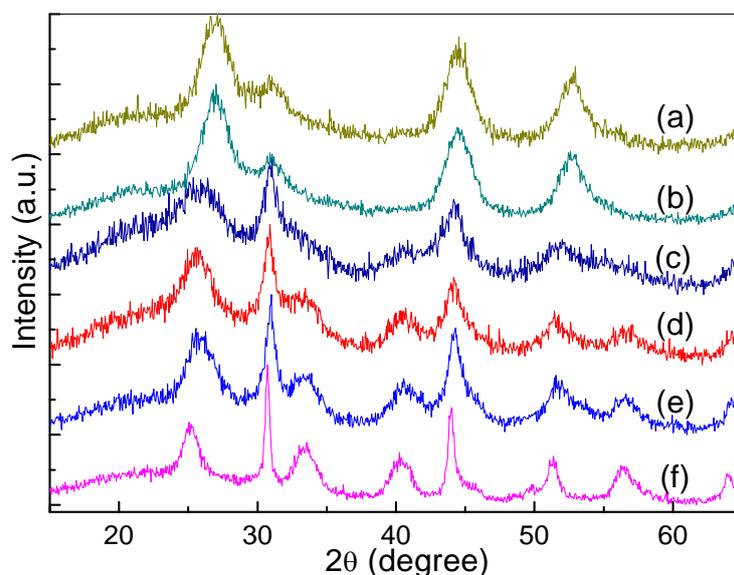


Figure S3. XRD patterns of the SrF₂ seed-based chlorination products obtained by heating at various temperatures: (a) un-treated, (b) 120 °C, (c) 160 °C, (d) 200 °C, (e) 240 °C, and (f) 280 °C.

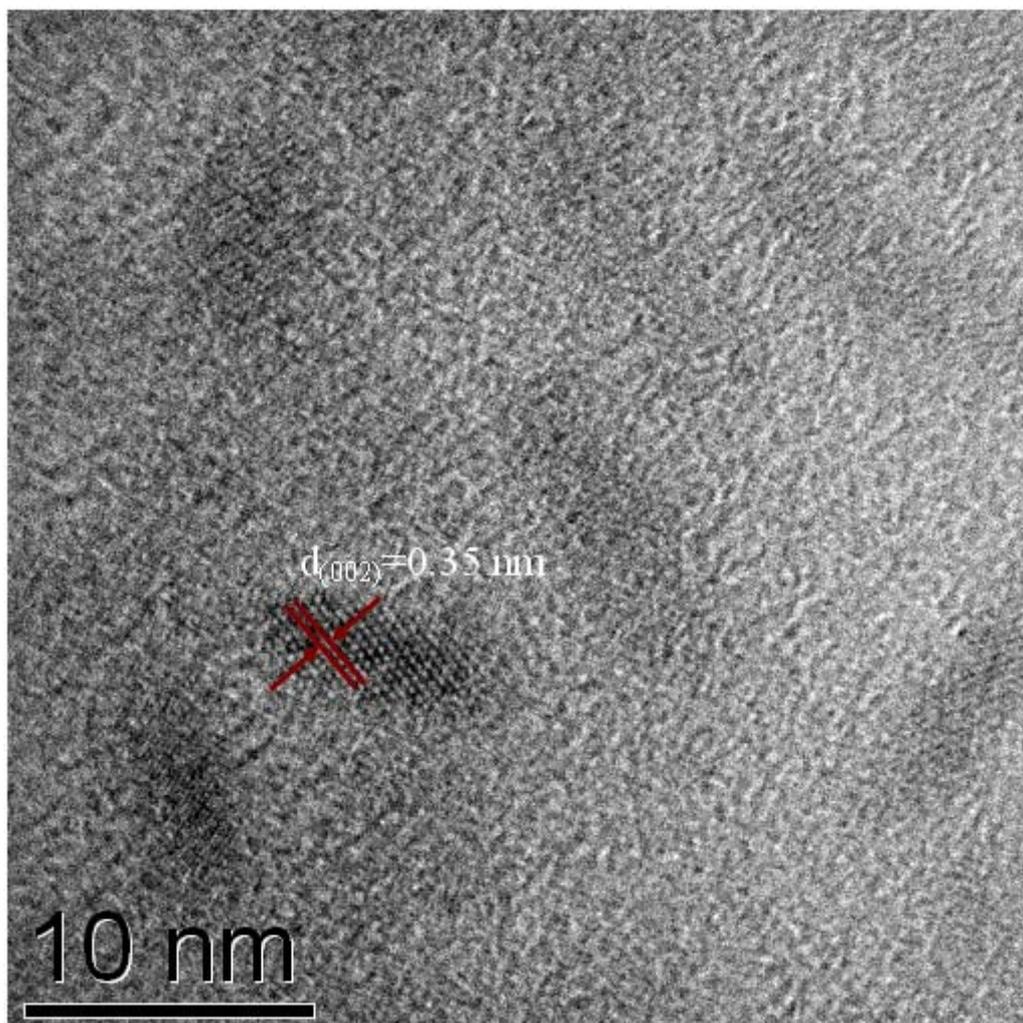


Figure S4. HRTEM image of the chlorination product obtained by heating at 160 °C, showing the co-existence of the SrFCl nanocrystals and the amorphous phase. The measured interplanar spacing of $\sim 0.35 \text{ nm}$, corresponding to the distance of (002) plane of tetragonal SrFCl, is also provided.

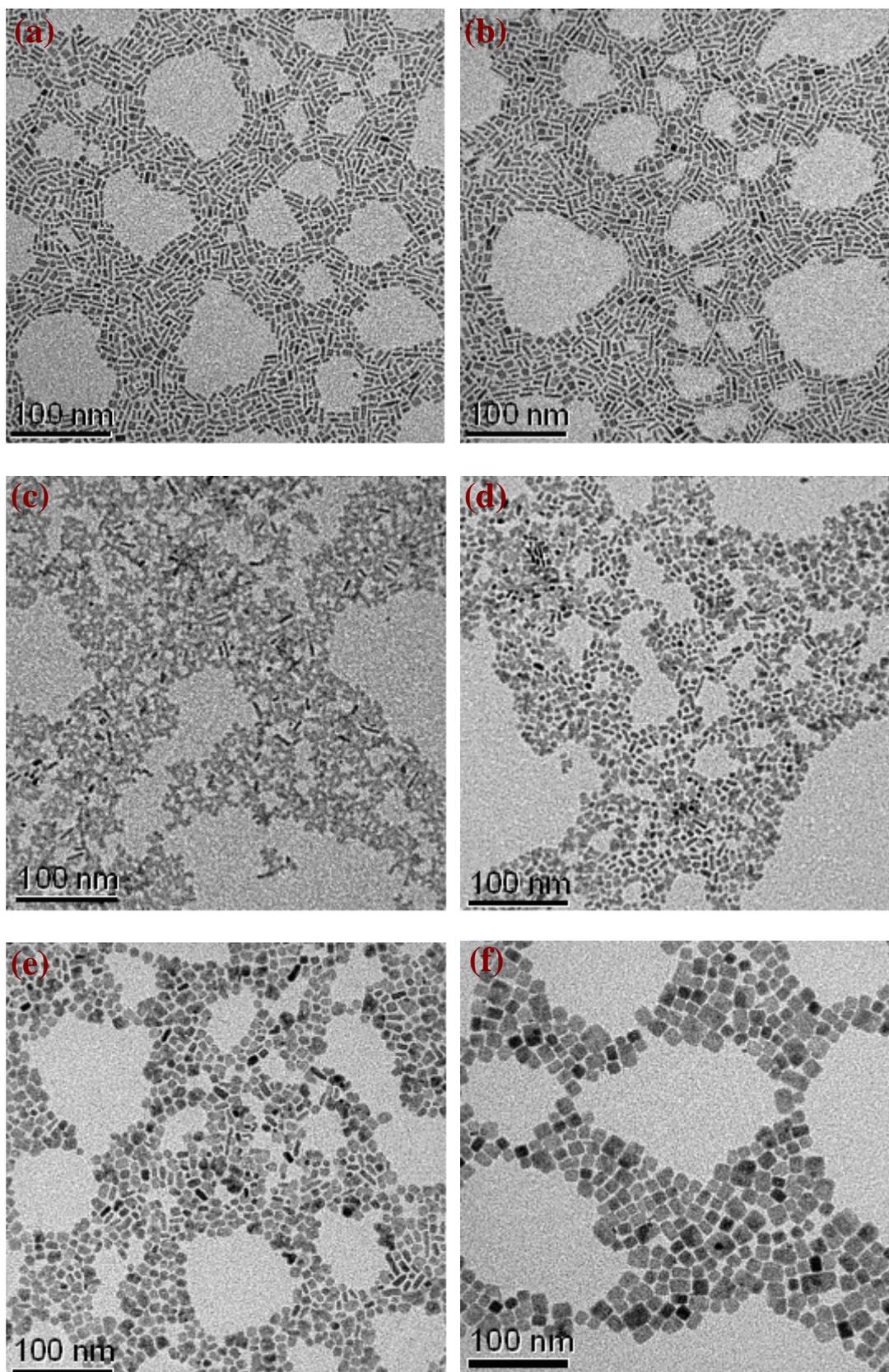


Figure S5. TEM micrographs of SrF₂ nanorod-based chlorination products obtained by heating at various temperatures: (a) un-treated, (b) 120 °C, (c) 160 °C, (d) 200 °C, (e) 240 °C and (f) 280 °C.

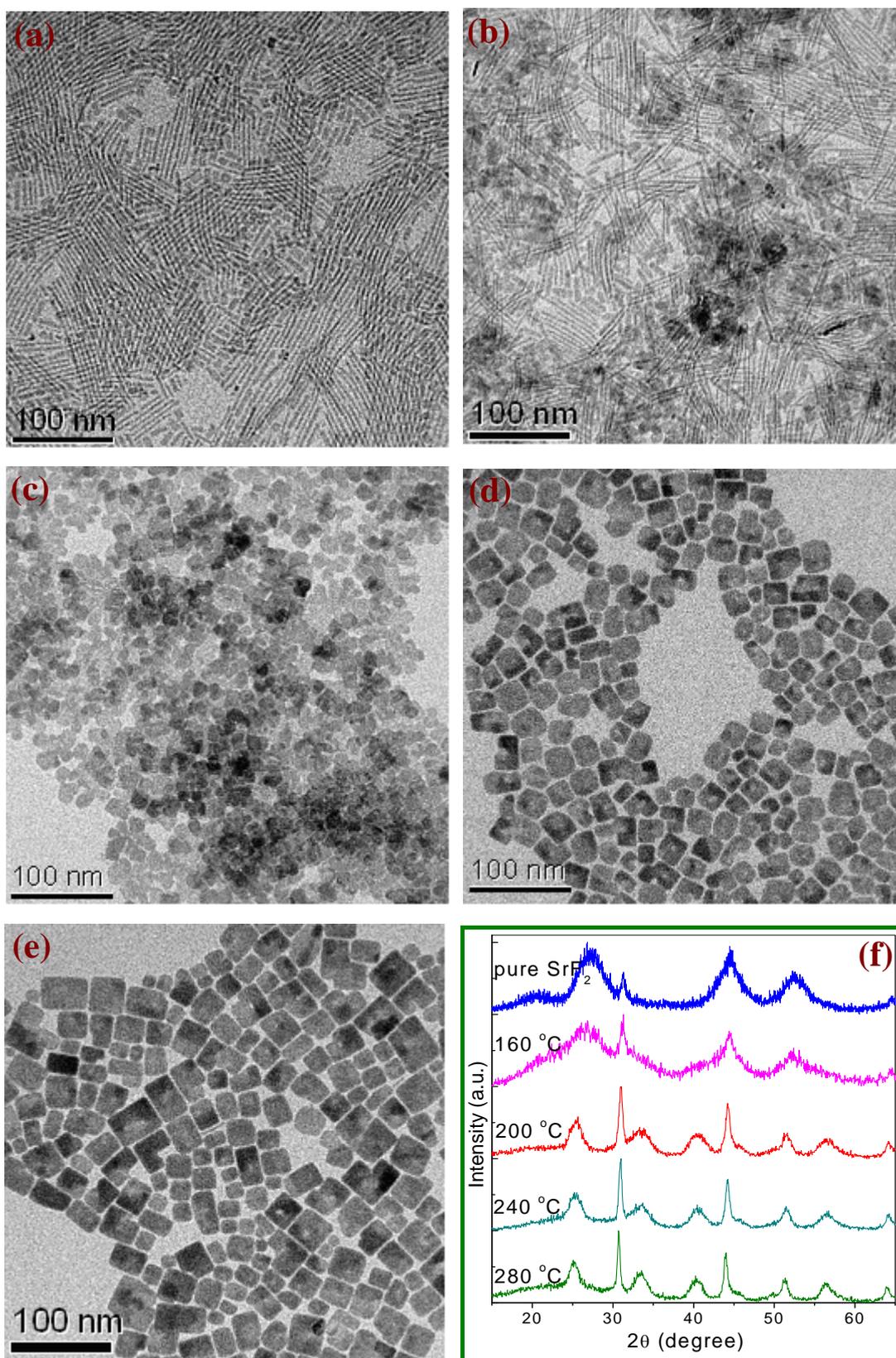


Figure S6. (a)-(e) TEM micrographs of SrF₂ nanowire-based chlorination products obtained by heating at various temperatures: (a) un-treated, (b) 160 °C, (c) 200 °C, (d) 240 °C and (e) 280 °C. (f) XRD patterns of the corresponding samples. Noticeably, the chlorination reaction is not complete at 160 °C, i.e., Only part of SrF₂ nanowires are chlorinated into SrFCl ones at this temperature.

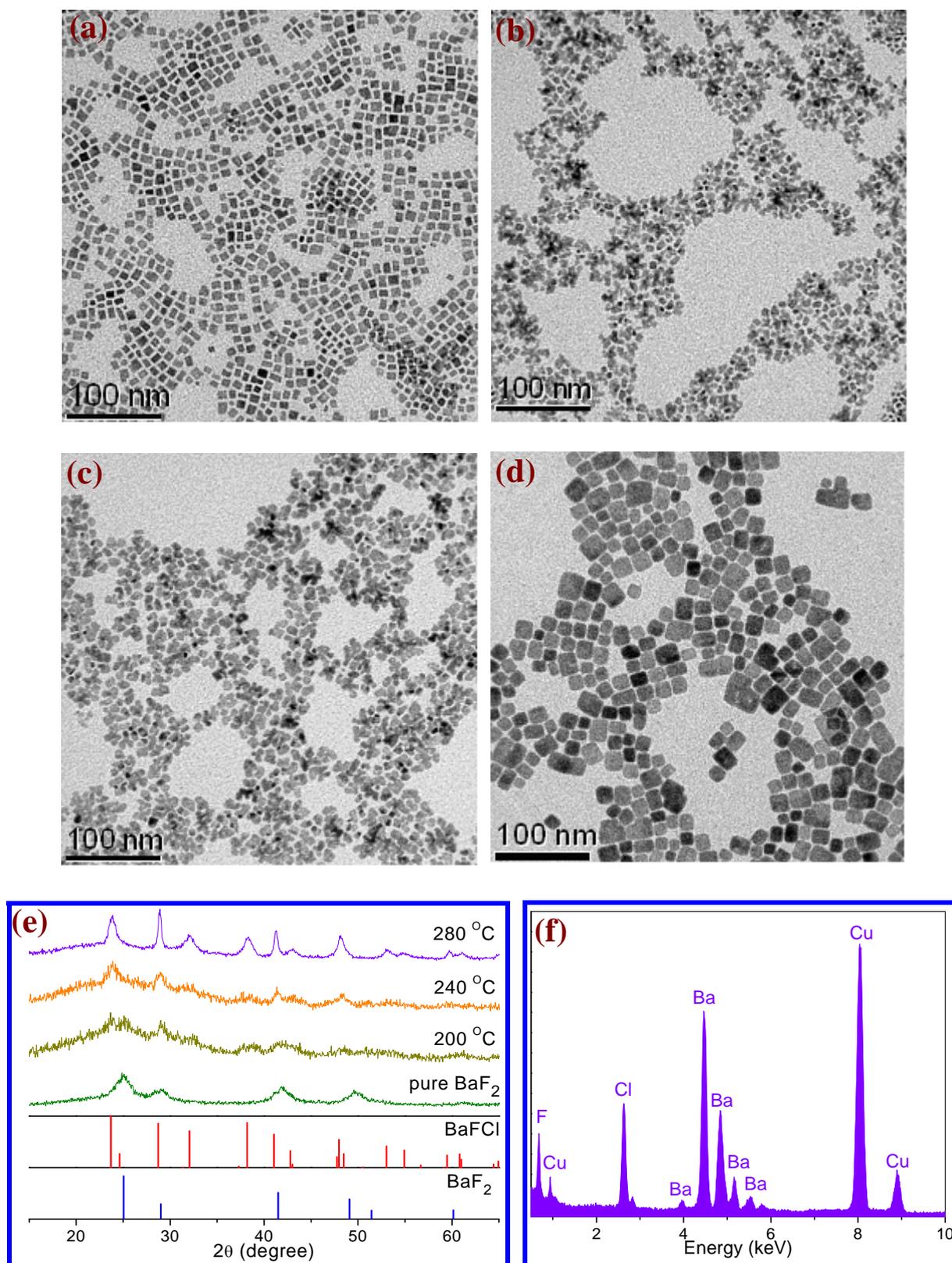


Figure S7. (a)-(d) TEM micrographs of BaF₂ nanocube-based chlorination products obtained by heating at various temperatures: (a) un-treated, (b) 200 °C, (c) 240 °C and (d) 280 °C. (e) XRD patterns of the corresponding samples; the standard cubic BaF₂ crystal data (JCPDS 88-2466) and the standard tetragonal BaFCl crystal data (JCPDS 84-0631) are also provided. (f) EDS spectrum

taken from sample (d), showing the existence of Ba, F, and Cl signals (Cu signals come from the copper grid).

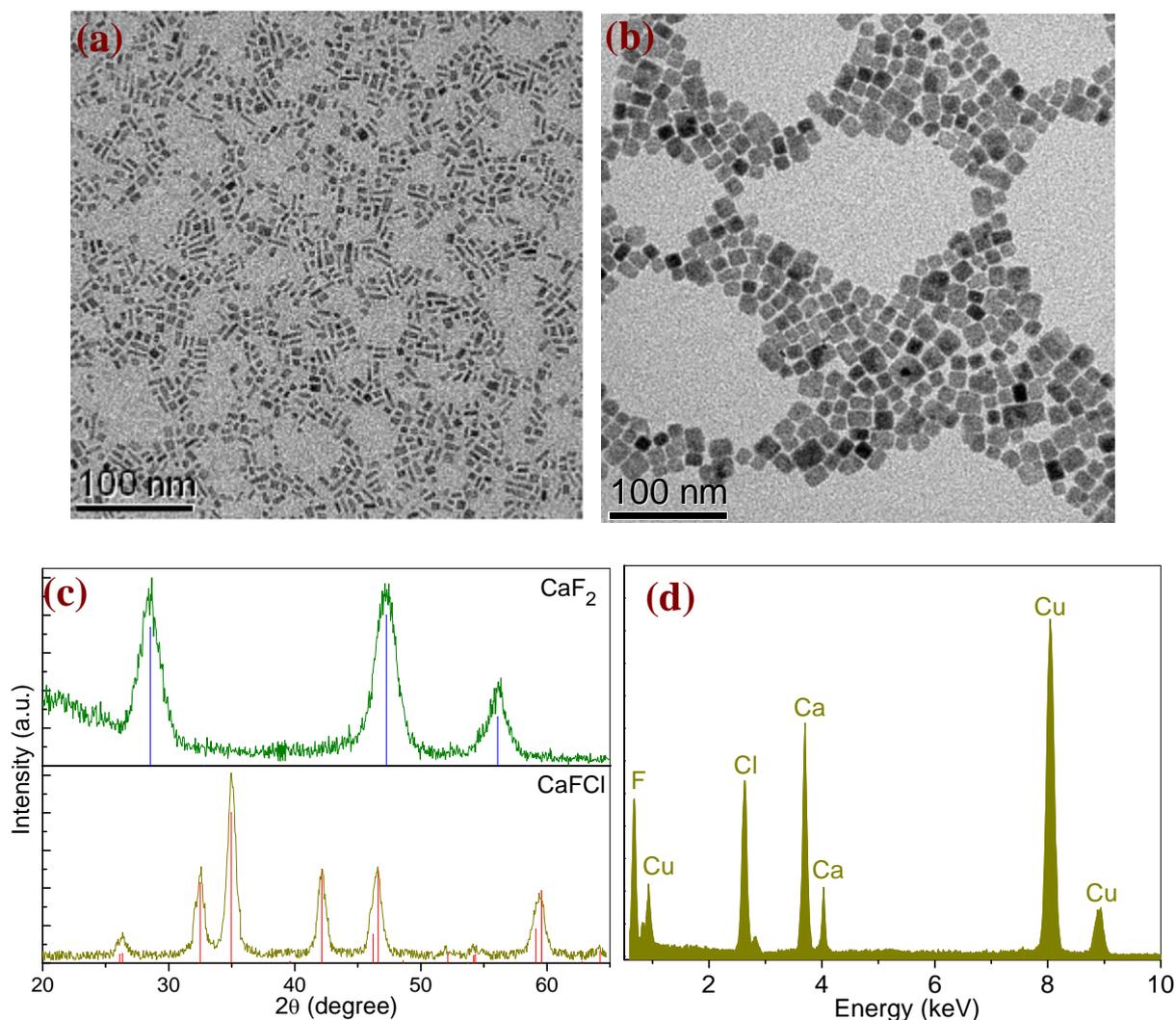


Figure S8. TEM micrographs of (a) CaF₂ precursor NCs, and (b) chlorination product CaFCl NCs. (c) XRD patterns of the corresponding samples; the standard cubic CaF₂ crystal data (JCPDS 35-0816) and the standard tetragonal CaFCl crystal data (JCPDS 70-0483) are also provided. (e) EDS spectrum taken from CaFCl NCs, showing the existence of Ca, F, and Cl signals (Cu signals come from the copper grid).

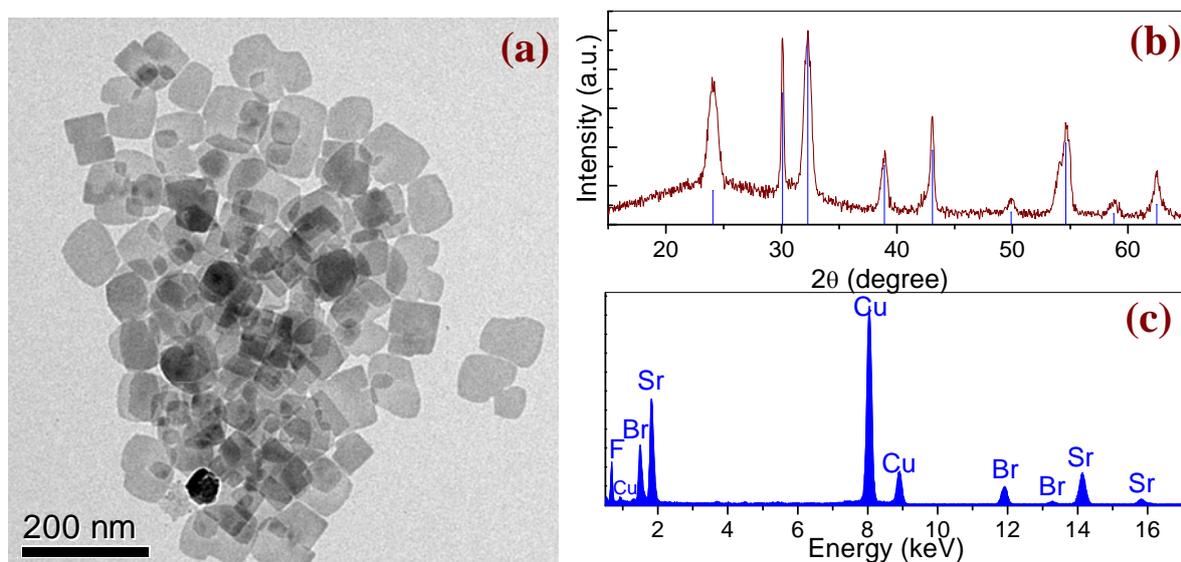


Figure S9. (a) TEM micrograph of SrF₂ seed-based bromination product SrFBr NCs. (b) XRD pattern of SrFBr NCs; the standard tetragonal SrFBr crystal data (JCPDS 76-1287) are also provided. (c) EDS spectrum taken from SrFBr NCs, showing the existence of Sr, F, and Br signals (Cu signals come from the copper grid).

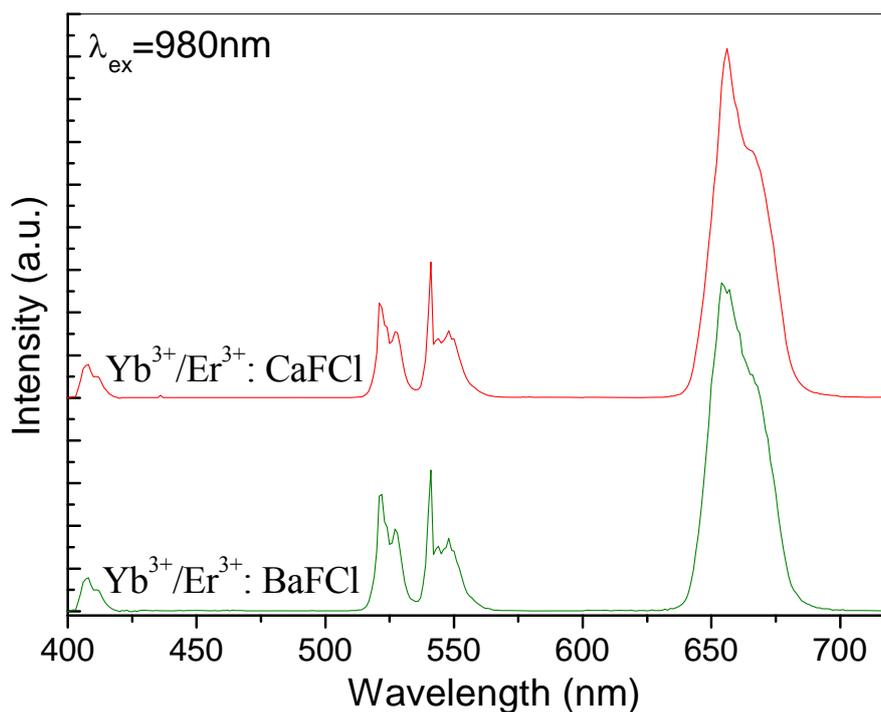


Figure S10. UC emission spectra of Yb³⁺/Er³⁺ (20/2 mol%) co-doped CaFCl and BaFCl NCs

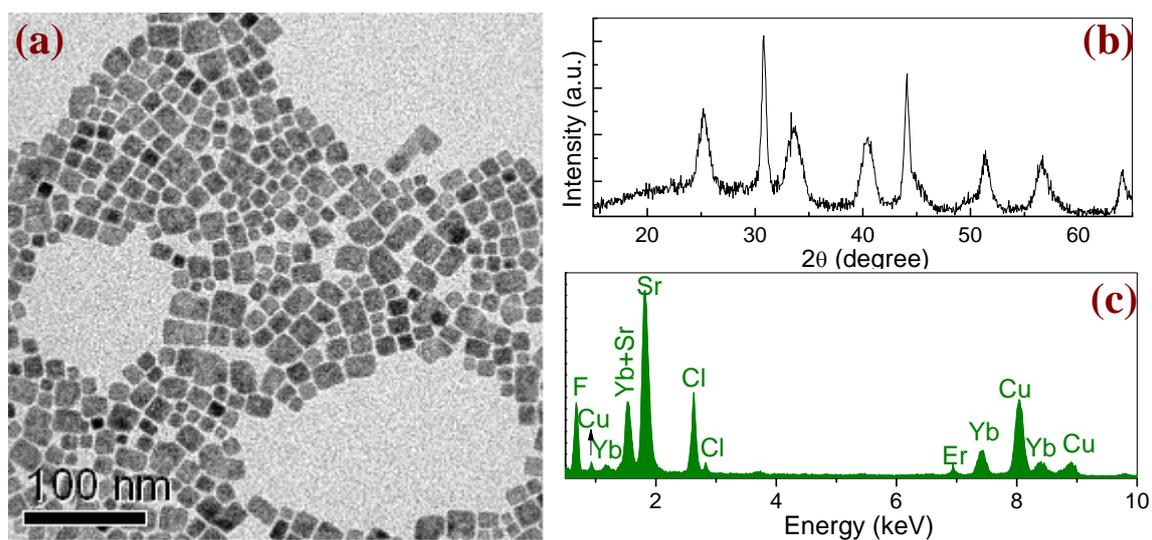


Figure S11. (a) TEM micrograph, (b) XRD pattern, and (c) EDS spectrum of $\text{Yb}^{3+}/\text{Er}^{3+}:\text{SrFCl}$ nanocubes. EDS spectrum evidences the existence of Sr, F, Cl, Yb and Er signals (Cu signals come from the copper grid).

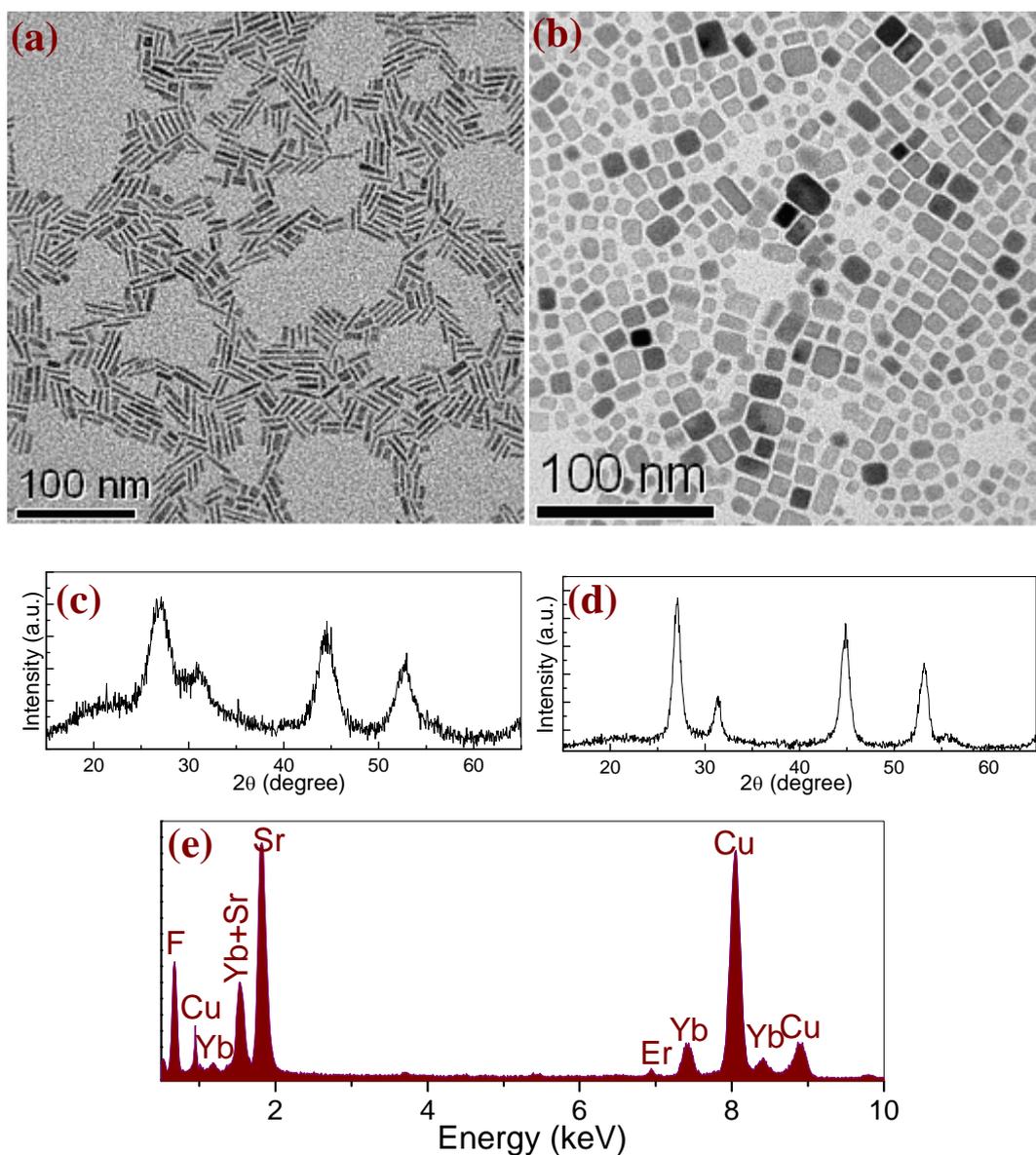


Figure S12. TEM micrographs of (a) $\text{Yb}^{3+}/\text{Er}^{3+}$: SrF_2 seed nanorods, and (b) $\text{Yb}^{3+}/\text{Er}^{3+}$: SrF_2 nanocubes with the same size to that of $\text{Yb}^{3+}/\text{Er}^{3+}$: SrFCl nanocubes. (c)-(d) XRD patterns of these two SrF_2 samples; (e) EDS spectrum taken from sample (b), showing the existence of Sr, F, Yb and Er signals (Cu signals come from the copper grid).

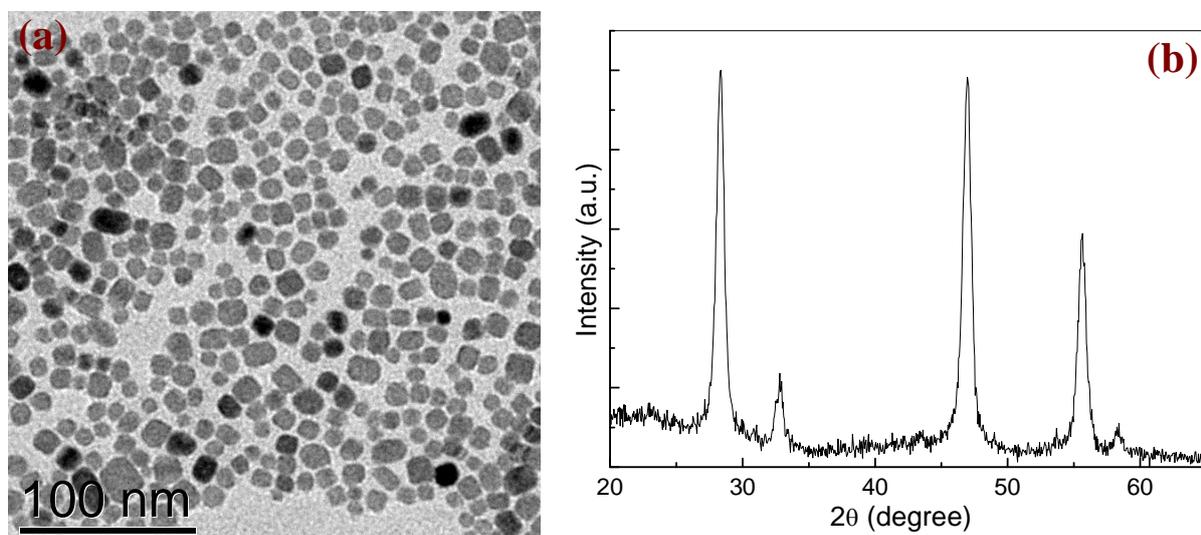


Figure S13. (a) TEM micrograph and (b) XRD pattern of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\alpha\text{-NaYF}_4$ NCs