

## Supporting Information

### **Green Synthesis of Upconversion Nanocrystals by Adjusting Local Precursor Supersaturation in an Aqueous Condition**

## Experimental Section

**Synthesis of UCNs using sodium acrylate or sodium octanoate as stabilizer.** In a typical synthesis, 0.60 g of sodium acrylate (or 1.06 g of sodium octanoate) and 14 mL of deionized water were mixed with stirring at room temperature to get a pellucid solution. Then, an amount of 4 ml of aqueous solution containing 0.2 g of  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.1 g of  $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 7.2 mg of  $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was added to the prepared pellucid solution, which was stirred intensively for 5 min. After then, 2 mL of freshly prepared  $\text{NH}_4\text{F}$  solution (0.05 g/mL) was added to the above reaction mixture to form an emulsion. After stirring for 10 min at room temperature, the mixture was transferred into a 40 mL autoclave, sealed and heated respectively at 120 °C, 150 °C, 170 °C and 200 °C for 8 h. After the reaction was finished, the system was then allowed to cool to room temperature. After centrifugation at 10000 rpm, the powder products were collected. And then the powders were purified with deionized water several times to remove sodium acrylate and other remnants.

**Synthesis of  $\alpha$ -UCNs using sodium oleate as stabilizer.** In a typical synthesis, 1.6 g of sodium oleate, 4 ml of ethanol and 10 mL of deionized water were mixed with stirring at room temperature to get a pellucid solution. Then, an amount of 4 ml of aqueous solution containing 0.2 g of  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.1 g of  $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 7.2 mg of  $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was added to the prepared pellucid solution, which was stirred intensively for 5 min. After then, 2 mL of freshly prepared  $\text{NH}_4\text{F}$  solution (0.05 g/mL) was added to the above reaction mixture to form an emulsion. After stirring for 10 min at room temperature, the mixture was transferred into a 40 mL autoclave, sealed and heated respectively at 120 °C, 150 °C and 170 °C for 8 h. After the reaction was finished, the system was then allowed to cool to room temperature. Toluene or chloroform was used to extract the prepared UCNs in the vessel. The samples were deposited by adding ethanol to the sample-containing cyclohexane or chloroform solution, and the solution was centrifuged to get the powder samples. And then the powders were purified with ethanol several times to remove sodium oleate and other remnants.

**Synthesis of  $\beta$ -UCNs using sodium oleate as stabilizer.** In a typical synthesis, 1.6 g of sodium oleate, 4 ml of ethanol and 10 mL of deionized water were mixed with stirring at room temperature to get a pellucid solution. Then, an amount of 4 ml of aqueous solution containing 0.05 g of  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.025 g of  $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 1.8 mg of  $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was added to the prepared pellucid solution, which was stirred intensively for 5 min. After then, 4 mL of freshly prepared  $\text{NH}_4\text{F}$  solution (0.05 g/mL) was added to the above reaction mixture to form an emulsion. After stirring for 10 min at room temperature, the mixture was transferred into a 40 mL autoclave, sealed and heated respectively at 150 °C, 170 °C for 8 h. After the reaction was finished, the system was then allowed to cool to room temperature. Toluene or chloroform was used to extract the prepared UCNs in the vessel. The samples were deposited by adding ethanol to the sample-containing cyclohexane or chloroform solution, and the solution was centrifuged to get the powder samples. And then the powders were purified with ethanol several times to remove sodium oleate and other remnants.

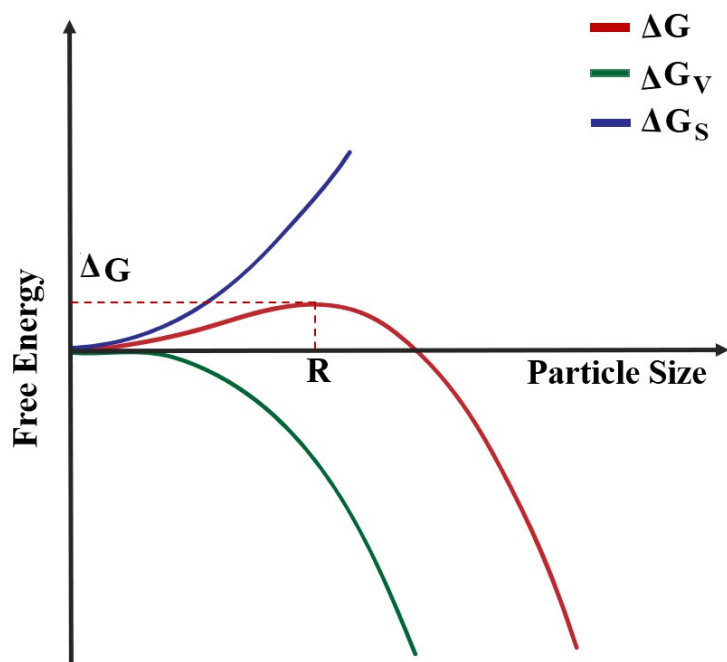
**Carbonyl groups functionalization of the prepared UCNs.** Firstly, a certain amount of UCNs with original alkyl ligands were dispersed in 0.1 M hydrochloric acid solution by ultrasonication with 40-60 °C for 1-2 h to remove the oleate ligands. After the reaction, the UCNs were collected via centrifugation at 14000 rpm for 30 min, washed twice with deionized water, and re-dispersed in 1 mL of deionized water. A certain amount of new ligands such as poly (acrylic acid) (average molecular weight = 1500~10000) was first dissolved in 9 mL of deionized water by adjusting the pH to 8 using a NaOH solution (0.1 M in deionized water) under vigorous stirring at room temperature. Thereafter, 0.5 mL of the above ligand-free UCNs was added drop by drop, followed by stirring for another 2 h. The water dispersion was then added to 8 mL of diethylene glycol, and the mixture was stirred at 105 °C for 1 h to remove water. Finally, the diethylene glycol dispersion was transferred to a 20 mL Teflon-lined autoclave and incubated at 160 °C for 2 h. The obtained UCNs were collected via centrifugation at 14000 rpm for 30 min, washed several times with ethanol and deionized water, redispersed in 10 mL of deionized water, and stored in a fridge at 4 °C.

**Characterization.** The powder X-ray diffraction (XRD) patterns were recorded by a Bruker D2-Phaser XRD using Cu K $\alpha$  radiation ( $\lambda=0.15418$  nm). The size and morphology of the prepared UCNs were determined by a JEOL JEM-1200EX transmission electron microscope (TEM) at 100 kV, and a JEOL JEM 3010 TEM high-resolution transmission electron microscope (HRTEM) at 200 kV. Samples were prepared by placing a drop of a dilute chloroform dispersion of UCNs onto carbon-coated copper grids with excess solvent evaporated. Dynamic light scattering (DLS) were measured on a Nano ZS ZEN3600 particle sizer (Malvern Instruments). Measurement of upconversion luminescence was carried out in a quartz cuvette, which was inserted into an integrating sphere in the Horiba Fluoromax-4 (Horiba Jobin-Yvon spectrofluorometer).

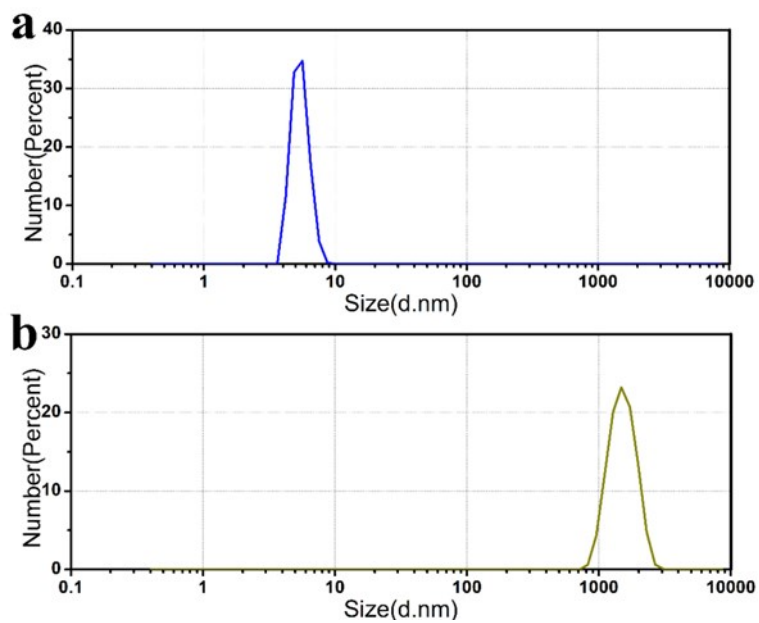
**S1 Mechanism of the crystallization approach.** As shown in Figure S1, a plot for Gibbs free energy change ( $\nabla G$ ) versus nano-particle size change in solution is used to explain for the energy barrier of the nucleation. From the energy equation,  $\nabla G = \nabla G_S + \nabla G_V$ , where  $\nabla G_S$  is the surface free energy change, which is positive and proportional to the surface area of particle (in general, which is proportional to  $R^2$  for 3-dimensional particle,  $R$  = radius of particle), and  $\nabla G_V$  is the volume free energy change which is negative and proportional to the volume of particle (in general,  $\nabla G_V = - (RT/V_m) \ln S$ , where  $S$  is the supersaturation,  $V_m$  is the molar volume of nanocrystal). The surface-to-volume ration will be very high due to the very small-sized nucleus, and  $\nabla G$  is positive when the size of particle is small enough. A maximum Gibbs free energy ( $\nabla G^*$ ) will be existed when the critical condition  $d(\nabla G)/dr = 0$ . Therefore, the formation of nano-particle in solution must breakthrough the free energy barrier ( $\nabla G^*$ ) to form small nucleus that can further grow into larger particle ( $R > R^*$ ).

According to the classical nucleation theory, production of nanocrystal in a solution must first overcome the energy barrier ( $\Delta G$ ) to form stable nano-nucli which can further grow into larger particles (Fig. S1 in Supporting Information (SI)).  $\Delta G = \Delta G_s + \Delta G_v$  is determined by the surface free energy change ( $\Delta G_s$ ) and the volume free

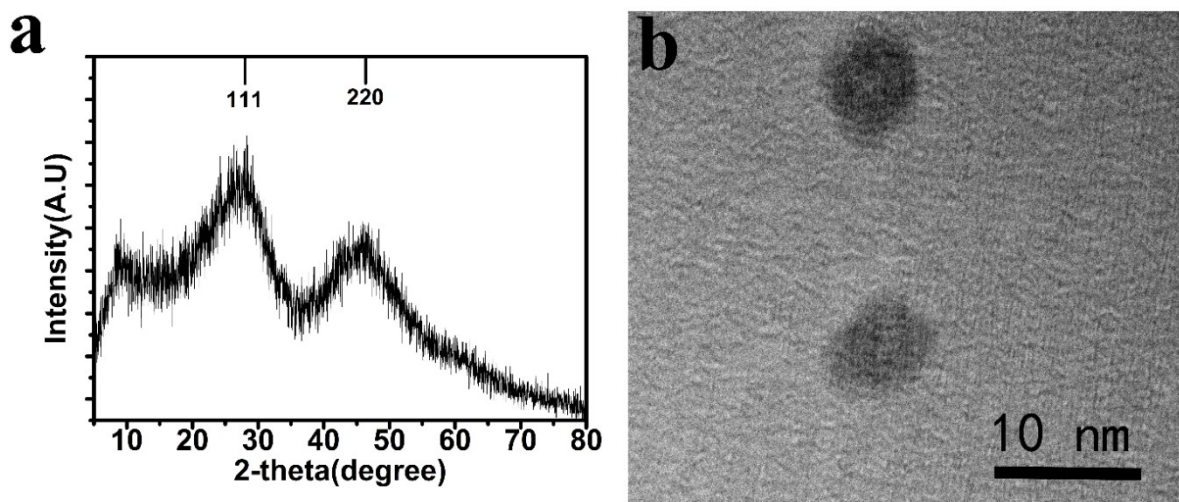
energy change and  $\Delta G_v = -\left(\frac{RT}{V_m}\right) \ln S_n$ , where  $S_n$  is the supersaturation of the precursor,  $V_m$  is the molar volume of nanocrystal. Therefore,  $S_n$  needs to be high to lower  $\Delta G$  for nucleation to occur, which should be much higher than the concentration needed to sustain the nucleus growth ( $S_g$ ).



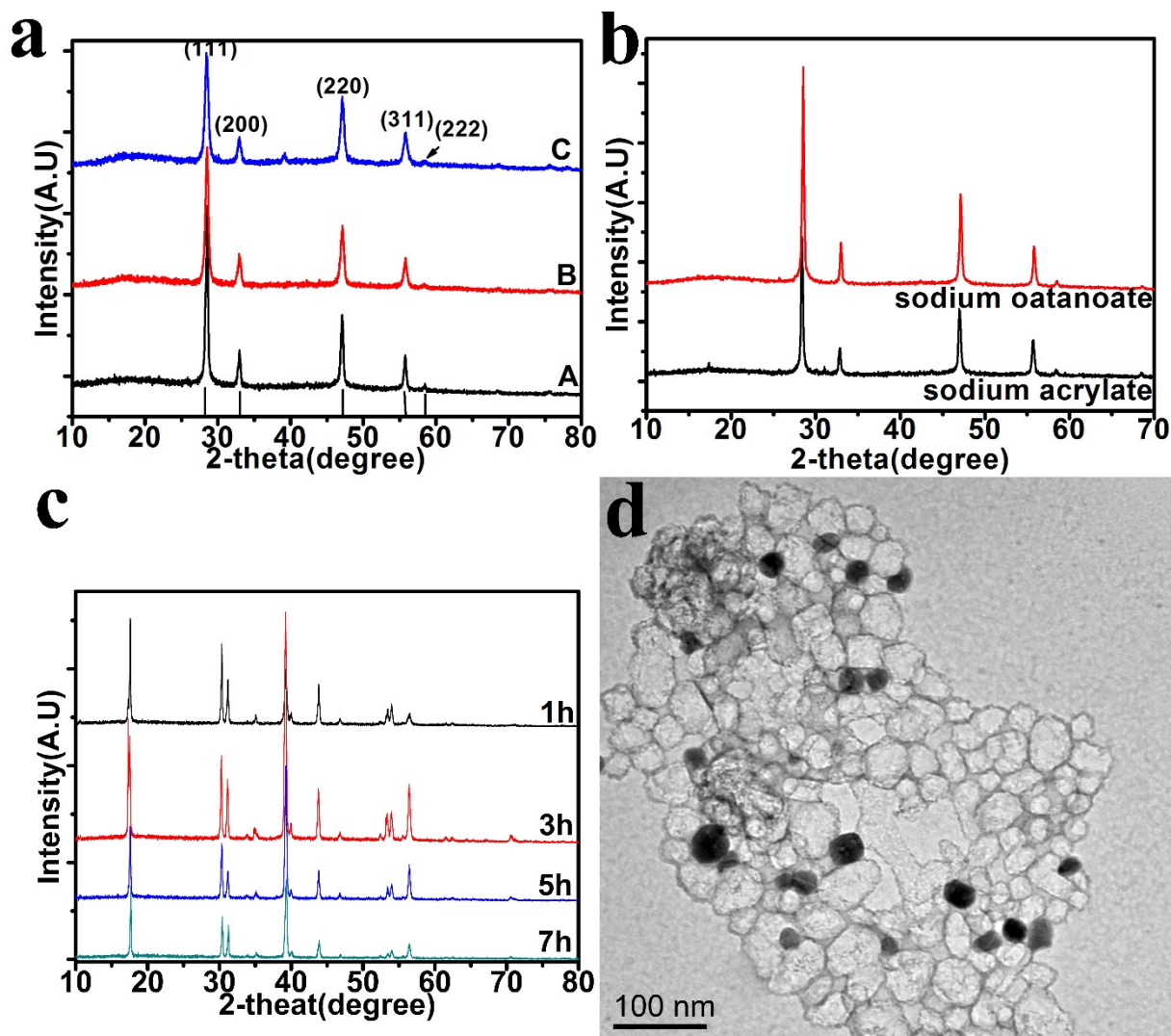
**Figure S1.** Energy plot for homogeneous nucleation in solution.



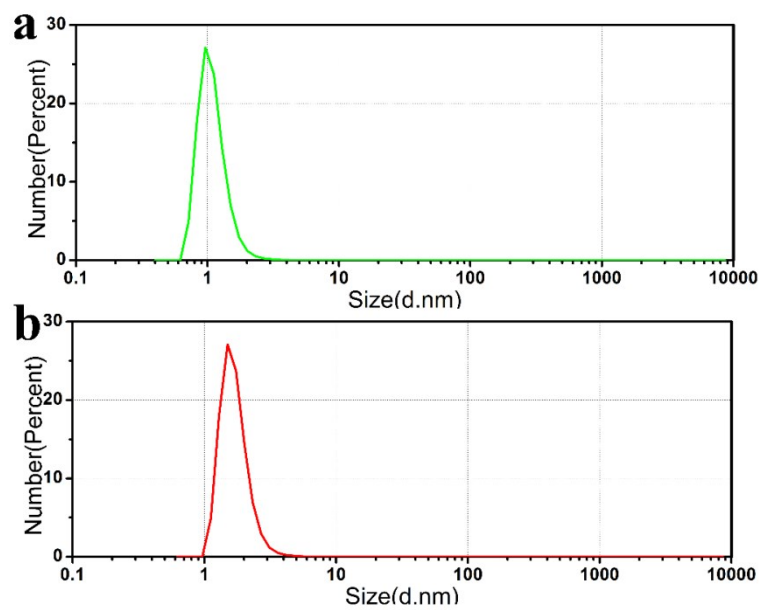
**Figure S2.** Dynamic light scattering (DLS) spectra of 0.44 M sodium oleate solution before (a) and after (b) the addition of rare earth metal ions.



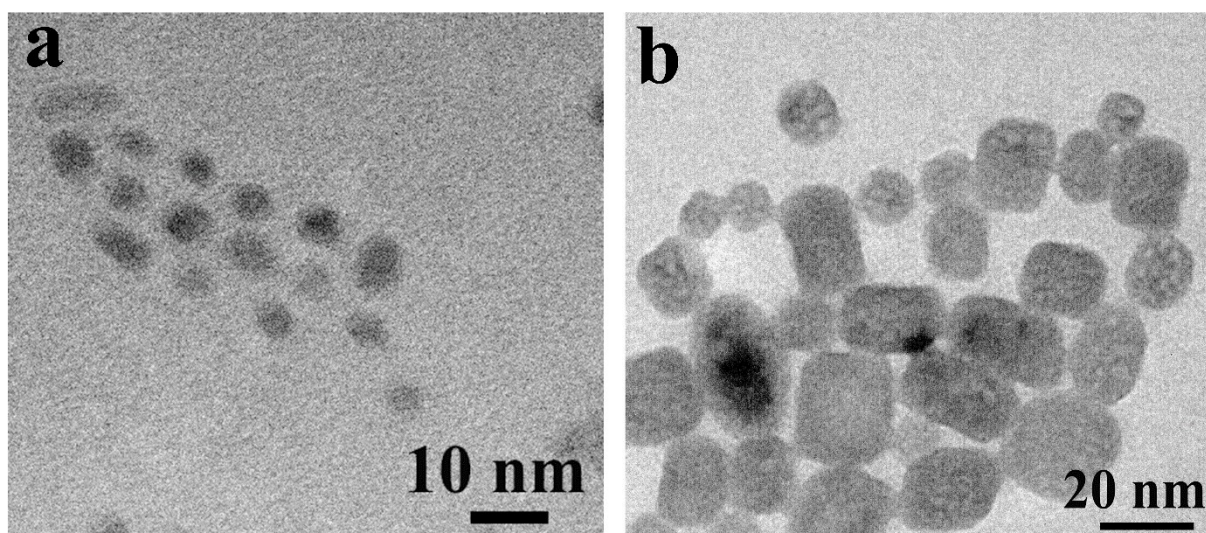
**Figure S3.** (a) XRD spectrum of UCN nucleations right after the supply of  $F^-$  ions at the ambient temperature. (b) TEM image of the finally obtained UCNs (120 °C hydrothermal reaction for 3h, in presence of sodium oleate).



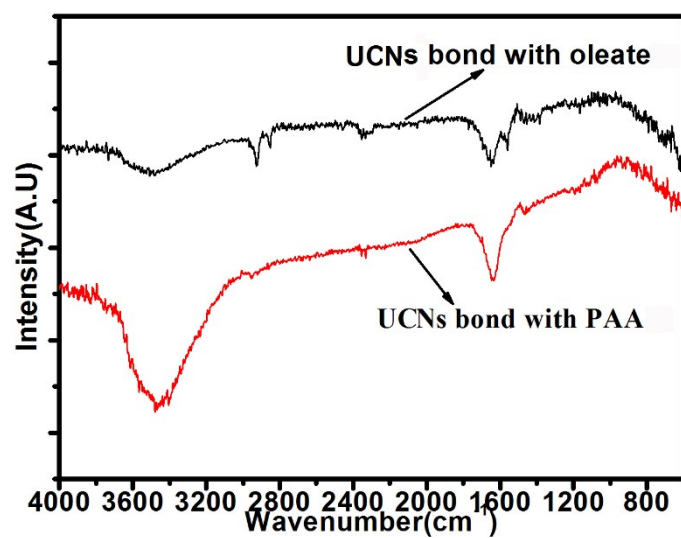
**Figure S4.** (a) XRD patterns of the prepared UCNs using different fatty acids including (A) sodium acrylate, (B) sodium oatanoate and (C) sodium oleate with  $F^-$  to  $Y^{3+}$  (4:1) in 120 °C hydrothermal reaction. PDF (no. 01-077-2042) of  $\alpha$ -phase UCN is indicated on the axis. (b) XRD spectra of the UCNs prepared at 200 °C using sodium acrylate or sodium oatanoate as the stabilizer with  $F^-$  to  $Y^{3+}$  ratio of 4:1. (c) XRD spectra of the UCNs prepared at 200 °C with  $F^-$  to  $Y^{3+}$  ratio of 32:1. (d) TEM image shows that  $\beta$ -UCNs are grown at the micelle interfaces.



**Figure S5.** DLS spectra of 0.44 M sodium acrylate solution (a) and sodium octanoate solution (b) within in rare earth metal ions.



**Figure S6** (a) TEM image of the prepared  $\alpha$ -phase  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals. (b) TEM image of the prepared  $\beta$ -phase  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals.



**Figure S7.** Fourier-transform infrared spectroscopy (FTIR) spectra of the UCNs capped with PAA.