Supplementary information

Porous Upconversion Materials-Assisted Near Infrared Energy Harvesting by Chlorophylls

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Experimental procedures:

Synthesis

Synthesis of $NaYF_4$:Yb,Er particles

All chemicals were purchased from Sigma-Aldrich without further purification. Deionized water was used throughout. In a typical procedure, $Y(NO_3)_3$ (0.264 mmol), $Yb(NO_3)_3$ (0.03 mmol) and $Er(NO_3)_3$ (0.006 mmol) were dissolved in 5 mL of sodium dodecyl sulphate (0.15mmol) solution under vigorous stirring. Then 10mL of NaF solution (3.6 mmol) was dropped into the above solution. After stirring for 0.5 h, the mixed solution was transferred into a 20 mL autoclave and heated to 160 °C for 3 h and naturally cooled down to room temperature. White precipitates were collected from the solution after centrifugation then placed in distilled water (50 mL) and incubated for 24 h. The transparent supernatant was removed. Then the obtained precipitates were washed with ethanol and water for three times, respectively, and dried in a vacuum at 80 °C for 48 h.

Extraction of chlorophylls

In order to preserve the natural composition, chlorophylls were simply extracted from plants without further separation and purification. 100 g of spinach leaves was cut and ground, and then soaked in 50 ml of ethanol for an hour. The supernatant was centrifugated to obtain the stock chlorophylls solution. Two sample solutions (denoted as ×1/2 and ×1/5 chlorophylls) were prepared by diluting the stock solution 2 or 5 times.

Investigation of fluorescence resonance energy transfer from upconversion materials to chlorophylls

5 mg of $NaYF_4$:Yb,Er particles was added into 1 mL of ethanol, followed by the addition of different volume of original chlorophylls. Here 0, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900, 1000, 2000μL of chlorophylls was tried. And the corresponding upconversion fluorescence spectra were recorded. Then ×1/2 and ×1/5 chlorophylls was added into the $NaYF_4$:Yb,Er suspension, respectively. The other conditions were identical with the above experiments.

Control experiments: Pure ethanol was added into the $NaYF_4$:Yb,Er suspension, instead of chlorophylls. Here 0, 200, 400, 600, 800, 1000, 2000 μL of ethanol was tried.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with high-intensity Cu $K\alpha_1$ irradiation (λ=1.5406 Å). The general morphology of the products was characterized by a field-emission scanning electron microscope (FESEM, FEI, Quanta 400 FEG) equipped with an energy-dispersive spectroscopy (EDS) instrument. TEM images were taken on a Philips CM-120 electron microscopy instrument. HRTEM images were obtained by employing a Tecnai F20 microscope (FEI, 200 kV). Room temperature upconversion fluorescence spectra were recorded on a Acton SpectraPro-300i monochromator integrated with an Princton Instruments thermoelectrically cooled CCD (TE/CCD-1024-E/1), which was cooled to -50 °C. A commercial IR laser working at 976.5 nm wavelength with tunable power was used for excitation. UV-vis spectra were recorded on a Varian Cary 500 Scan UV-visible system. Room-temperature fluorescence spectra of the pure chlorophylls were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

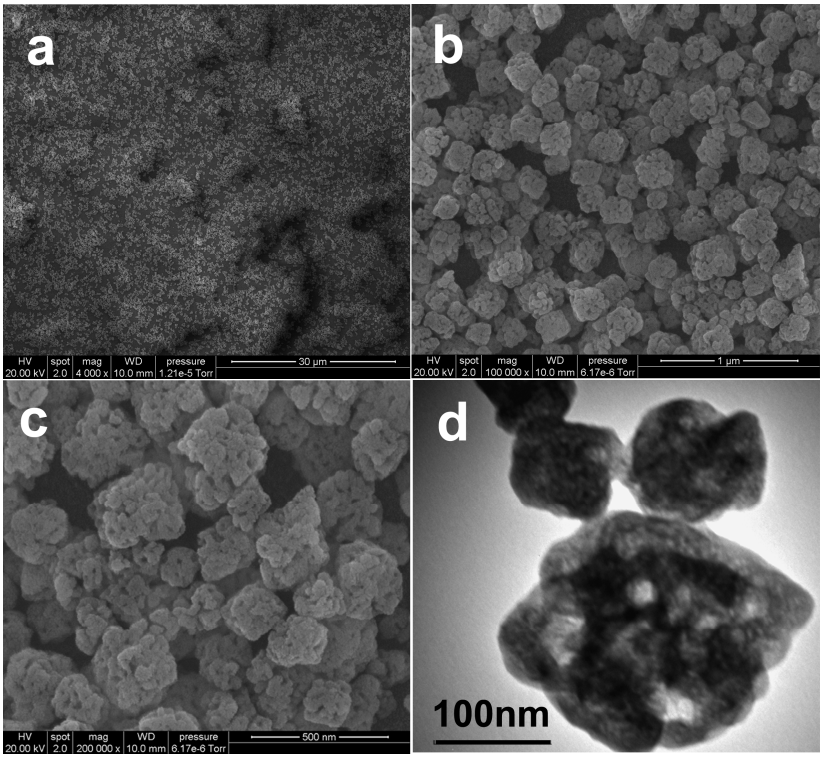

Figure S1. SEM and TEM images of the product obtained at 160°C for 3h with SDS concentration of 10mM

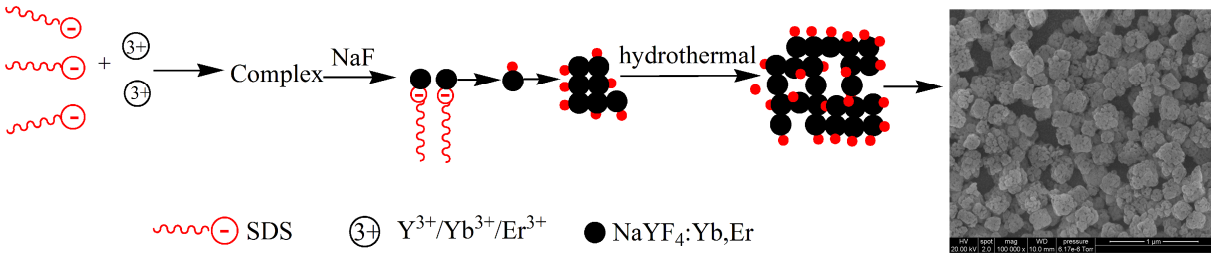

Figure S2. Schematic illustration for porous upconversion crystal growth in the presence of SDS

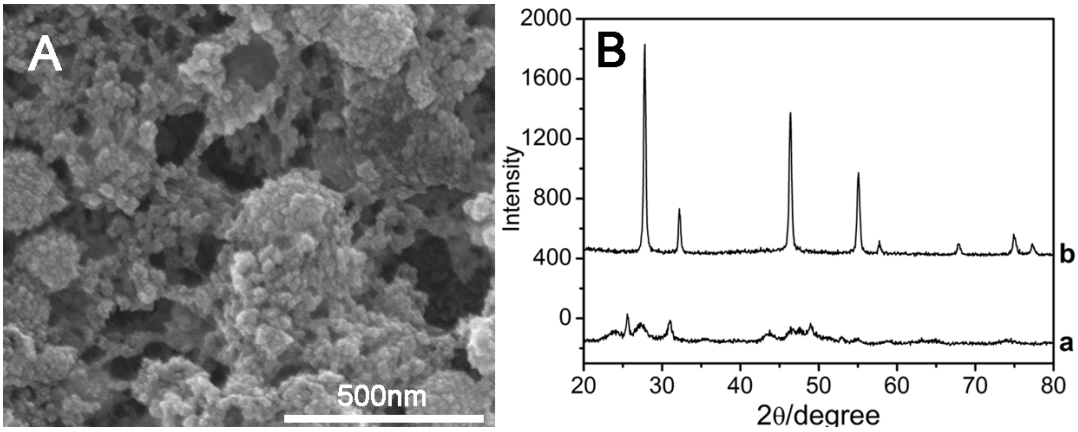

Figure S3. SEM image and XRD patterns of the products obtained at different reaction times (160 °C SDS=10 mM) (A, B-a) 0 h (B-b) 3 h

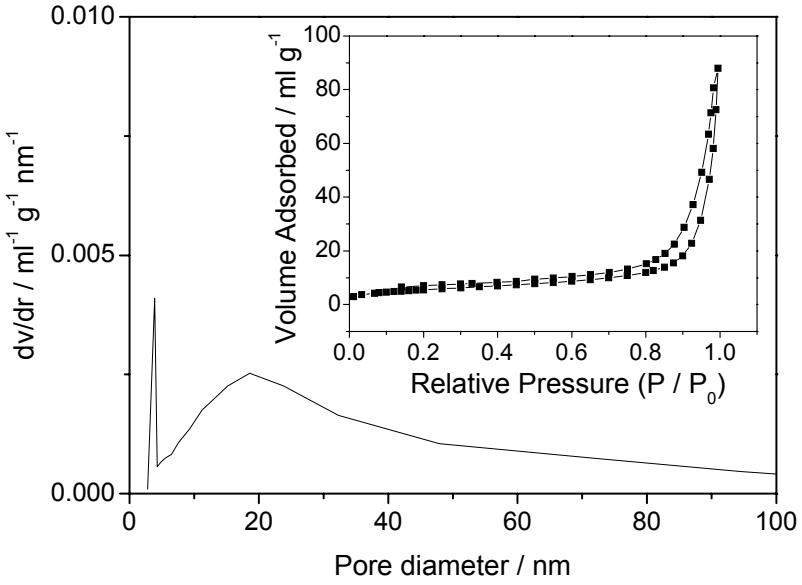

Figure S4. N_2 adsorption-desorption isotherm and the corresponding pore size distribution of the prepared porous upconversion materials

Figure S4 shows the nitrogen adsorption-desorption isotherms (inset) and pore size distribution plot for the porous upconversion materials. The specific surface area of the sample is $35 m^2 g^{-1}$ using the Brunauer-Emmett-Teller (BET) method. The average pore diameter is 24.9 nm (estimated using the desorption branch of the isotherm).

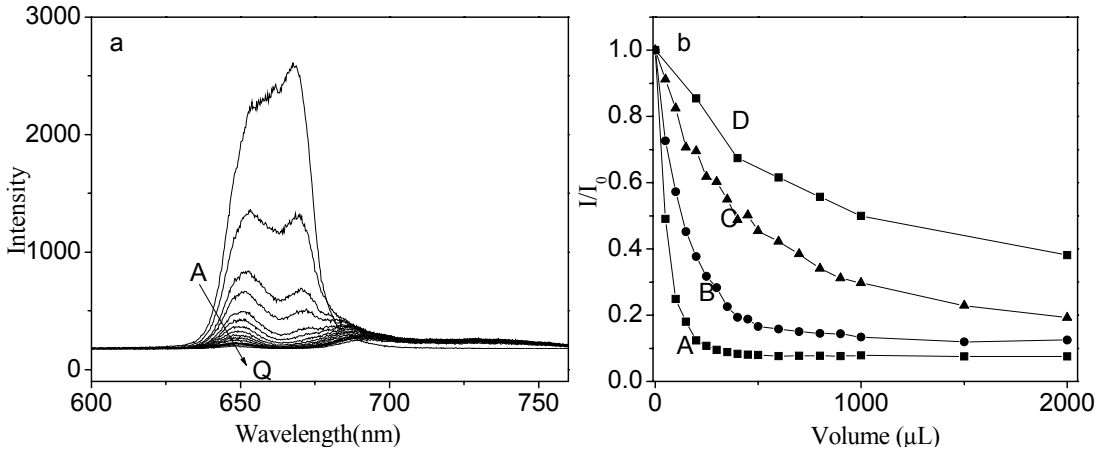

Figure S5. (a) Room temperature upconversion fluorescence spectra of the $NaYF_4$:Yb,Er ethanol suspension (1mL, 5mg/mL) with the addition of different volume of original chlorophylls. A-Q: 0, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900, 1000, 2000 μL, respectively. (b) The first-order plots for the upconversion emission intensity located at 660 nm and the volume of substance added. A-D: original, ×1/2, ×1/5 chlorophylls and pure ethanol, respectively. I_0 is the intensity at 660nm of the original upconversion suspension. I is the intensity after adding corresponding substance.

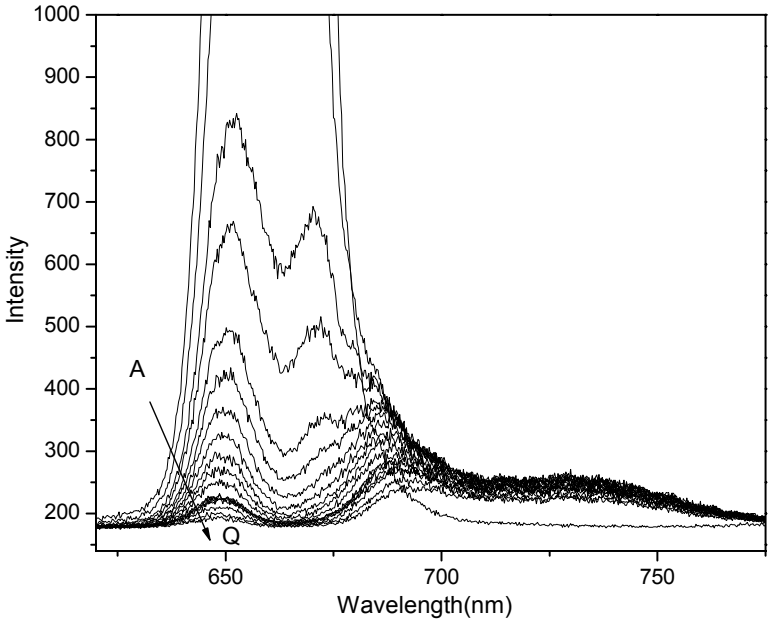

Figure S6. Magnified spectra of Figure S5a

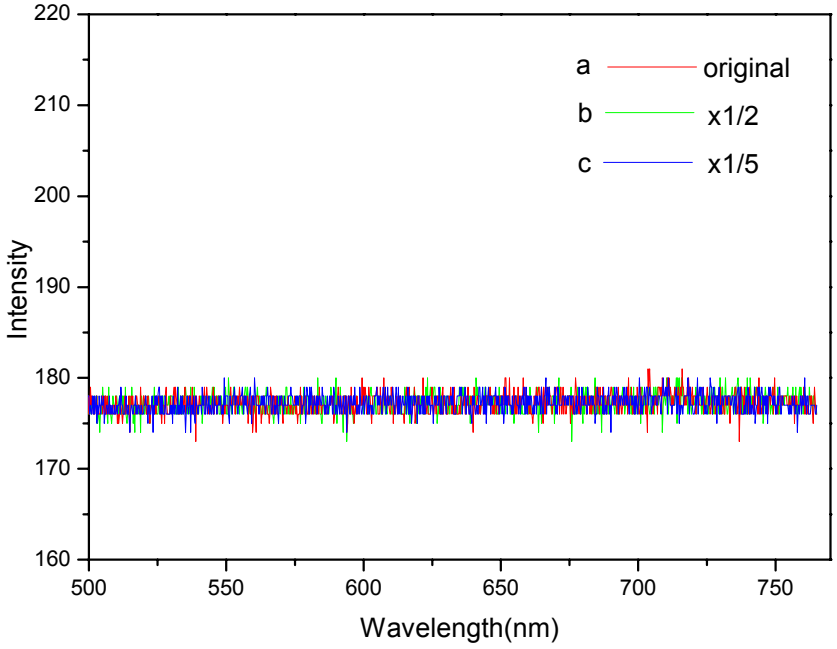

Figure S7. Room temperature upconversion fluorescent spectra of a) the original chlorophylls solution, b) two-times dilution, c) five-times dilution.

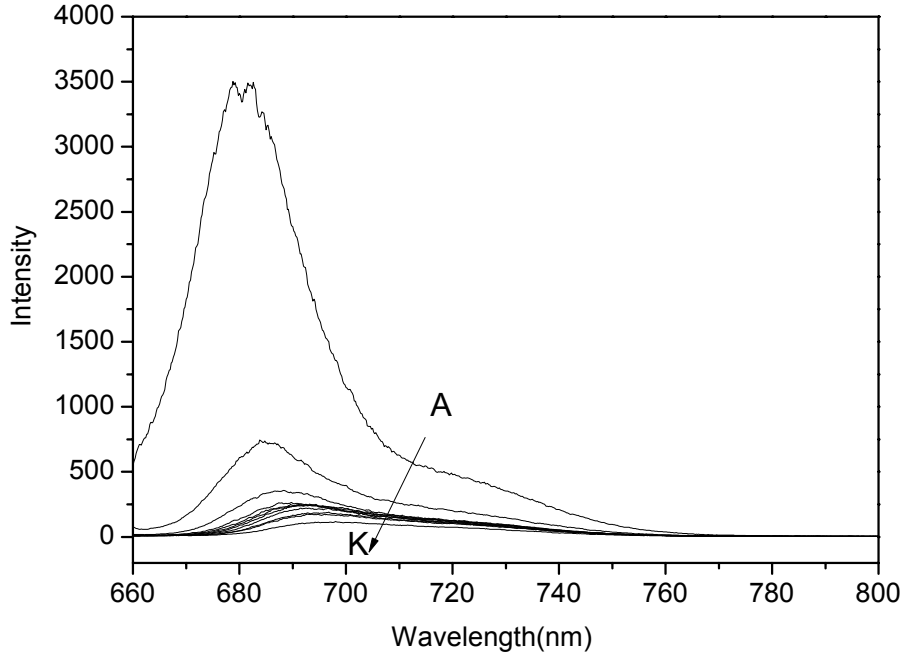

Figure S8. Room temperature fluorescent spectra of pure chlorophylls with excitation wavelength at 660 nm

Different volume of original chlorophylls was added into 1mL of pure ethanol. (A-K). 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 2000 μL.