Supporting Information

Integration of Upconverting β-$NaYF_4$:Yb^{3+},Er^{3+}@TiO_2 Nanocomposites as Light Harvesting Layer in Dye-Sensitized Solar Cells

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The annealing profile is as follows: the electrode was heated from room temperature to 150 °C at a rate of 120 °C/hr and held for 15 min, then to 325 °C at a rate of 240 °C/hr and held for 5 min, then to 375 °C at a rate of 120 °C/hr and held for 5 min, and finally to 450 °C at a rate of 60 °C/hr and held for 30 min. After this, was cooled to room temperature at a rate of 60 °C/hr. The profile is shown in Figure S1.

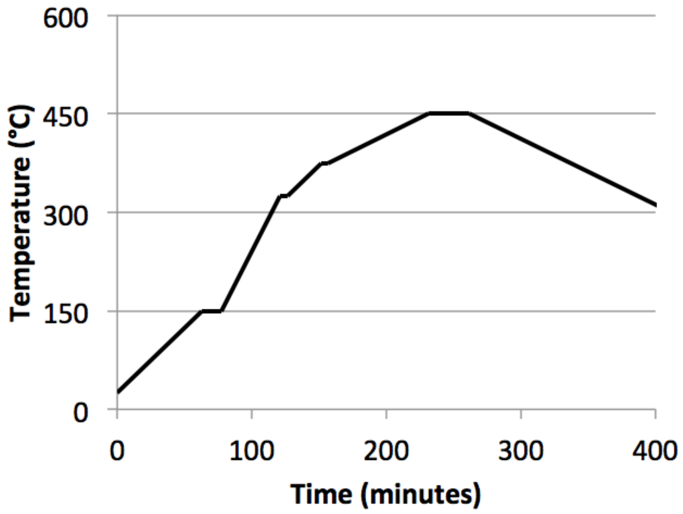

Figure S1. Heating profile for the DSSC annealing process

Upconverter Characterization: Powders were characterized before and after annealing by powder x-ray diffraction (XRD), transmission electron microscopy, and upconversion luminescence.

XRD analysis was done using a Bruker Discover D8 diffractometer with λCu,Kα=1.5406 Å radiation operated at 40 kV and 20 mA. A VANTEC 2000 2D x-ray area detector was used with a 2θ frame width of 23° and angular scanning resolution of 0.05°. Four frames were collected for each sample at 50 seconds/frame. Analysis was done using the Eva software package provided by Bruker. TEM analysis was done using a Philips CM200 TEM operated at 200 kV.

Upconversion spectra were collected from 450 nm to 700 nm with 0.5 nm step size and 2 nm emission slit using a Fluoromax-2 spectrophotometer with a 980 nm IR laser diode (100 mW, Startech) as excitation source. The fluorescence was measured using the solid powder; the laser spot size was kept the same when comparing samples, ensuring that the interaction volume and laser intensity was the same from sample to sample. The measurement spectra of all samples were recorded under the same conditions. The position of the laser relative to the samples was identical during all measurements. Each sample was immobilized and pressed between two glass slides to ensure a flat surface and uniform packing, and fixed using a metallic sample holder. All annealed samples were ground using a mortar and pestle prior to measurement to minimize soft agglomeration.

Dye-Sensitized Solar Cell Characterization: All DSSCs were characterized using a solar simulator (Class ABA, PV Measurements) calibrated using a silicon reference photodiode. The solar cell characteristics were calculated as an average of the forward and backward voltage sweeps with a voltage settling time of 100 ms for each voltage point in order to properly account for the slow response typical in DSSCs.[1] Cells were properly masked in order to eliminate extra scattered light and edge effects.[2] The active area of all cells measured was 0.25 cm^2.

Incident photon to electron conversion efficiency (IPCE) was measured using a QEX10 measurement system (PV Measurements) from 300 nm to 1400 nm using silicon and germanium photodiodes with known photoresponse for calibration. Monochromated light was chopped at a frequency of 4 Hz to account for the slow response of DSSCs. In order to roughly simulate 1 sun conditions in the IPCE, a light bias was used, biasing each cell to its short-circuit current obtained from the I-V curve under solar simulation.

Dye loading was calculated by immersing sensitized films in 0.1 M aqueous NaOH dye-desorption for 10 minutes. The UV-visible absorption was measured (Cary 5000), and the concentration calculated using a 0.01 mM dye solution in 0.1 M aqueous NaOH as reference.

Electrochemical impedance spectroscopy was measured using a VSP-potentiostat system (BioLogic) using a Mott-Schottky staircase potential measurement sweep under 1 sun illumination with 12 steps between -0.35 and -0.9 V applied to the photoanode with an additional AC bias of 10 mV applied over a frequency range from 100 kHz to 1 Hz with 6 points per decade. The data was fit using the commercially available Z-View software.

The scattering efficacy of the various UC@TiO_2 devices is demonstrated by the degree of transparency as illustrated in the digital photographs shown in Figure S2. The degree of transparency decreases as the amount of TiO_2 increases (i.e. UC to UC@T1 to UC@T2) demonstrating higher degrees of light scattering in the films with higher amounts of TiO_2.

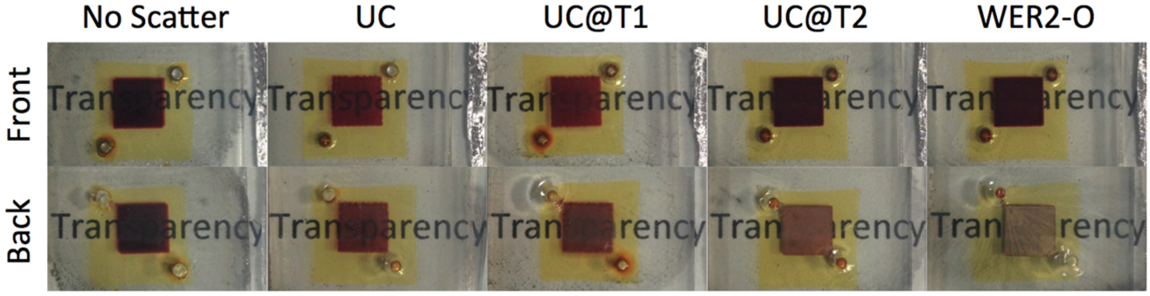

Figure S2. Digital photographs illustrating the effect of scattering on the transparency of the DSSCs as observed from the front (photoanode) side and the back (counter electrode) side

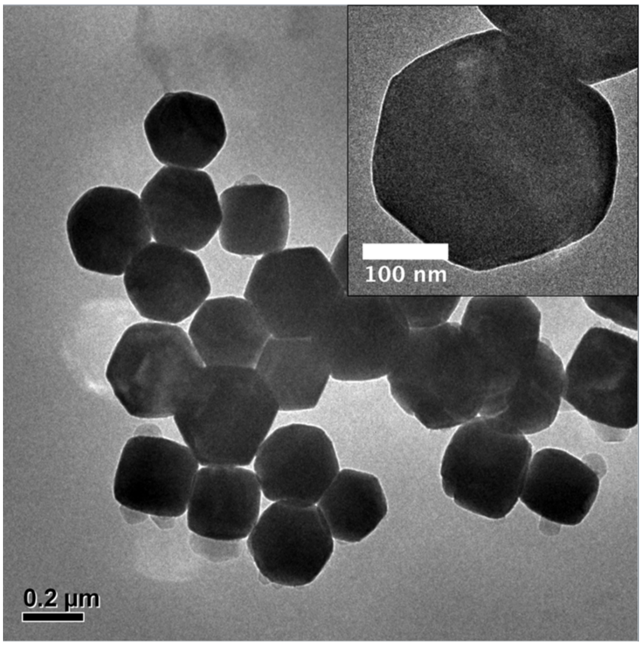

Figure S3. TEM images showing the morphology of the as-produced $NaYF_4:Yb^{3+},Er^{3+}$ particles following hydrothermal synthesis

[1] Yang X, M Yanagida, L Han. Reliable evaluation of dye-sensitized solar cells. *Energy & Environmental Science* 2013; **6**: 54.

[2] Snaith H. The perils of solar cell efficiency measurements. *Nature Photonics* 2012; **6**: 337–340.