Supporting information

Experimental

The synthesis process for the β-$NaYF_4$:Yb20%Er2% nanocrystals is as follows. 0.78 mmol $YCl_3{\cdot}6H_2O$, 0.2 mmol $YbCl_3{\cdot}6H_2O$, and 0.02mmol $ErCl_3{\cdot}$6H2O were added to a 100 mL three-neck round-bottom flask and dissolved in 2 mL of DI water to form a clear solution after strong stirring. Then 6 mL oleic acid (90%, technical grade) and 15 mL 1-octadecene (90%, technical grade) were subsequently added, and heated to 160 °C under argon gas flow, with constant stirring for 2 hours, and then cooled down to room temperature. 1.8 mmol NH_4F and 1.25 mmolNaOH dissolved in methanol were added and stirred at 50 °C for 30 min. After methanol was evaporated, the solution was heated to 300 °C as quickly as possible under argon gas flow with vigorous stirring for 60 min, and then cooled down to room temperature. The obtained core/shell NCs were precipitated by the addition of 15 mL acetone, collected by centrifugation at 11000 rpm for 10 min, washed with ethanol several times, and finally dispersed in 10 mL chloroform.

The TiO_2nanocrystalline film was made by using a commercial TiO_2 paste (Dyesol, 18 NR-T). After the sintering process, the transparent TiO_2 film is then immersed in the 0.35 mM Z907 acetonitrile: tert-butanol (1:1) solution for 24 hours. After the adsorption of the dye, the TiO_2 film was taken out and rinsed with methanol and dried under air. UC nanocrystals were spin coated on the TiO_2 film by dissolving it in toluene solution (0.5 wt%), and dried under air. The nanopartilce solution was firstly dropped on the TiO2 film, and let it stay on the film for 2 min (part of the solvent was evaporated). Then slow spin-coating process (500 RPM 20 sec) was applied to fully dry the film. To ensure efficient infiltration of the nanoparticles in the film, this process was repeated 10 times for each film. A thermally platinized FTO glass counter electrode and the working electrode were then sealed with a 50 μm thick hot-melt film (Surlyn) by heating the system at 120 °C. Electrolytes constitutes of 0.5 M LiI and 0.05 M I_2 in CH_3CN solution which were filled via pre-drilled holes in the counter electrodes (CEs). Finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating. The size of the cell is 5 × 5 mm^2, and a black mask (8 × 8 mm^2) was used in the subsequent photovoltaic studies under simulated sunlight AM 1.5 irradiation.

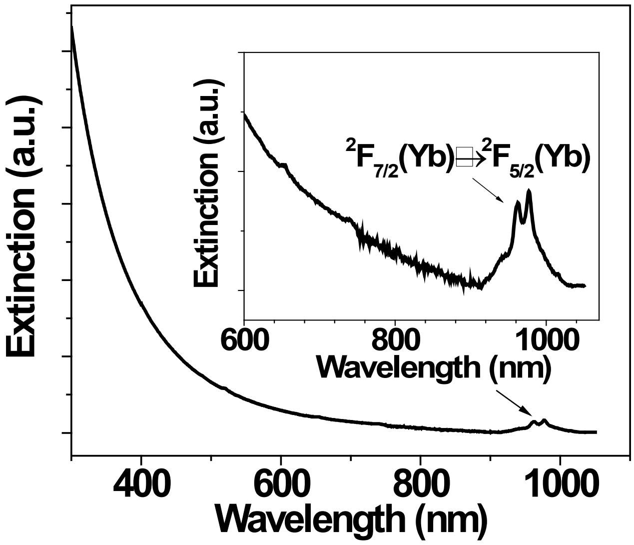

Figure S1. The absorption spectrum of **NEY-1** nanoparticles dispersed in chloroform. Inset is a magnification of the extinction in the wavelength range of 600-1050 nm.

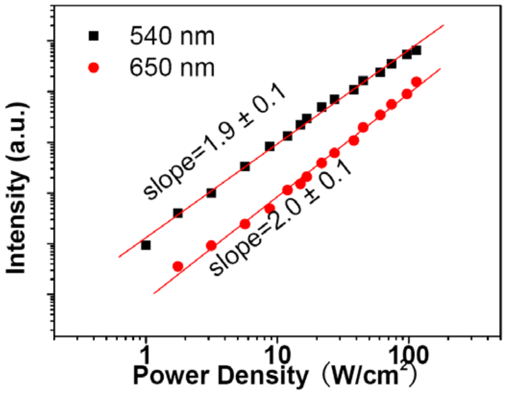

Figure S2. Dependence of the intensity of UC PL peaks at 540 and 650 nm on the power density of excitation at 980 nm for nanoparticles **NEY-1**.

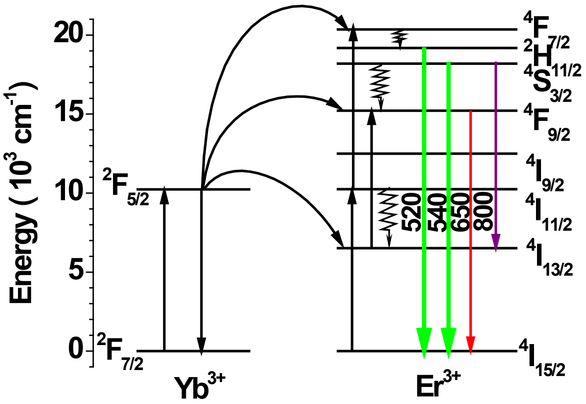

Figure S3. Mechanisms of upconversion emissions in NaYF$_4$:Yb^{3+}20%, Er^{3+}2% nanoparticles.

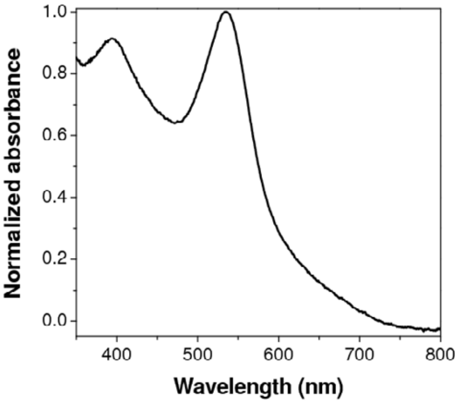

Figure S4. The absorbance spectra of Z907 dye in chloroform.

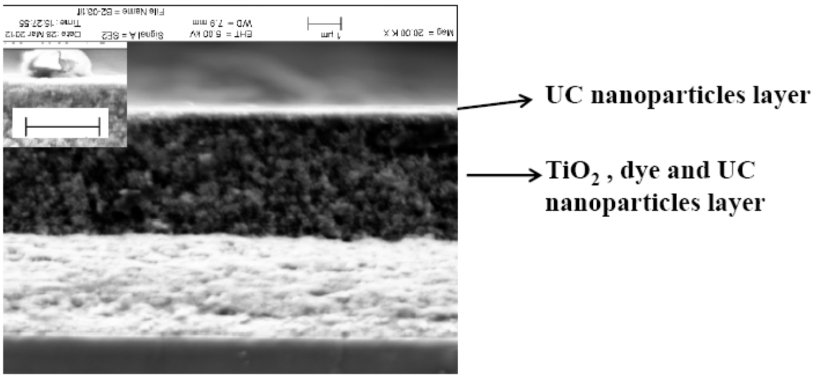

Fig. S5. SEM images of cross-section of the UC nanoparticles deposited TiO2 film (scale bar 1 μm) and UC nanoparticles aggregates on the film surface (inset, scale bar 2 μm).