Supporting Information

Enhancing Dye-Sensitized Solar Cell Efficiency through Broadband Near-Infrared Upconverting Nanoparticles

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Experimental Procedures: materials, synthesis and characterization

Materials. All chemicals were of analytical grade and used without further purification. $YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $ErCl_3 \cdot 6H_2O$ (99.99%), $NdCl_3 \cdot 6H_2O$ (99.99%) were supplied by Beijing Founde Star Science and Technology Co., Ltd China. NaOH (98%), NH_4F (98%), Hexane (99.9%), 1-octadecene (ODE, 90%) and oleic acid (OA, 90%) nitrosonium tetrafluoroborate ($NOBF_4$, 95%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), were obtained from Sigma Aldrich. Chloroplatinic acid hexahydrate (H_2PtCl_6, ACS reagent), ethanol (ACS reagent, absolute), ethyl cellulose (EC), terpineol, N719 dye and IR-783 dye were purchased from the Aladdin. Fluorine-doped tin oxide (FTO) conducting glass plates (sheet resistance 10 Ω sq^{-1}) and P_{25} (TiO_2) were purchased from Qiseguang Technology Ltd. in China.

Synthesis of $NaYF_4$:10%Yb^{3+},2%Er^{3+} core nanoparticles. The core nanoparticles codoped with 2 mol% Er^{3+} and 10 mol% Yb^{3+} were synthesized using a solvothermal method adapted from our recent work. A typical procedure is as follows: a 100 mL three-necked flask containing 6 mL oleic acid (OA) and 15 mL 1-octadecene (ODE) were added given amounts of $YCl_3 \cdot 6H_2O$ (0.78 mmol), $YbCl_3 \cdot 6H_2O$ (0.2 mmol) and $ErCl_3 \cdot 6H_2O$ (0.02 mmol). The mixture was heated to 120 °C to form a pellucid solution and remove residual water and oxygen, and then cooled down to room temperature. 10 mL of methanol solution containing NaOH (2.5 mmol) and NH_4F (4 mmol) was slowly dropped into the flask and stirred for 30 min to ensure that all fluoride was completely consumed. Then the solution was heated to 70-80 °C for evaporating methanol completely from the reaction mixture. Subsequently, the solution was heated to 300 °C at a rate of about 18 °C/min, and then maintained for 1 h under argon atmosphere. After cooling down to room temperature, the resulting products were precipitated by ethanol and collected by centrifugation at 5000 rpm for 5 min. The precipitate was then purified with ethanol three times, and finally dispersed in 10ml Hexane for further uses.

Synthesis of $NaYF_4$:10%Yb^{3+},2%Er^{3+}@$NaYF_4$:X%Nd^{3+} core@shell nanoparticles. In a typical experiment, a 100 mL three-necked flask containing 6 mL oleic acid (OA) and 15 mL 1-octadecene (ODE) were added given amounts of $NdCl_3 \cdot 6H_2O$ ((X/2 mmol) X=5,10,20,30,40) and $YCl_3 \cdot 6H_2O$ ((0.5-X/2mmol) and the $NaYF_4$:10%Yb^{3+},2%Er^{3+} core NCs (0.5 mmol) in Hexane were added. The mixture was heated to 120 °C to form a pellucid solution and remove residual water and oxygen, and then cooled down to room temperature. 5 mL of methanol solution containing NaOH (1.25 mmol) and NH_4F (2 mmol) was slowly dropped into the flask and stirred for 30 min to ensure that all fluoride was completely consumed. Then the solution was heated to 70-80 °C for evaporating methanol completely from the reaction mixture. Subsequently, the solution was heated to 300 °C at a rate of about 18 °C/min, and then maintained for 1 h under argon atmosphere. After cooling down to room temperature, the resulting products were precipitated by ethanol and collected by centrifugation at 5000 rpm for

5 min. The precipitate was then purified with ethanol three times, and finally dispersed in Hexane for further measurement.

Preparation of $NOBF_4$ coated lanthanide-doped nanoparticles. The oleic acid ligands on the surface of these lanthanide-doped $NaYF_4$:10%Yb^{3+},2%Er^{3+}@$NaYF_4$:X%Nd^{3+} nanoparticles were first replaced with sub-nanometer ligands of nitrosonium tetrafluoroborate ($NOBF_4$) using an adapted procedure from literature[S1]. During this ligand exchange process, 5 mL of oleic acid coated nanoparticles dispersed in hexane (10 mg/mL) was mixed with a 5 mL N,N-dimethylformamide (DMF) solution of $NOBF_4$ (0.01 M) at room temperature. The resulting mixture was shaken gently for 10 minutes, allowing an extraction of nanoparticles from upper hexane layer into the bottom DMF layer. After disposing the hexane layer, these nanoparticles dispersed in the DMF were purified by adding a large amount of toluene and hexane (1:1 v/v) and centrifugation at 10000 rpm for 20minutes. Subsequently, the precipitated nanoparticles were weighted and re-dispersed in DMF (for NIR dye-sensitized experiments in solution). All nanoparticle solutions were stored at room temperature.

Preparation of IR783 dye solution in DMF. The IR783 dye were weighed and dissolved in DMF to produce a concentration of 1 mg/mL. After that, the bottled dye solution was purged with gentle argon gas flow and sealed with a parafilm. The dye solution was then covered with aluminum foil and stored in darkness to avoid light induced degradation.

Preparation of IR783 dye-sensitized nanoparticles solution in DMF. $NaYF_4$:10%Yb^{3+},2%Er^{3+}@$NaYF_4$:X%Nd^{3+} nanoparticles solution dispersed in DMF was mixed with an appropriate amount IR783 dye solution (1 mg/mL) to produce a defined amount NIR dye concentration in the mixture.

Fabrication of DSSC devices. Transparent fluorine-doped tin oxide (FTO) glass was used as substrate. FTO was sequentially cleaned in absolute ethanol, and deionized (DI) water for 15 minunder ultrasonic treatment. After cleaning and drying of FTO, the cleaned FTO was dried at 80 °C for further use. 1.00 g EC powder was then dissolved in 50 ml absolute ethanol, and mixed with 2.0g P_{25} (TiO_2) nanoparticles suspension, followed by sonication for 1 h at 60 °C. Terpineol (8.69 ml) was added dropwise into the as-prepared mixture. Subsequently, the ethanol in the mixture was removed on a rotary evaporator at 65 °C for 2 hours. Then, the TiO_2 films were screen-printed on FTO substrate, followed by being sintered at 450 °C for 1 h and 500 °C for 15 min in nitrogen. The sintered film was posttreated in a fresh aqueous $TiCl_4$ solution (30 mM) at 70 °C for 30min. Then, the TiO_2 film treated by $TiCl_4$ was sintered at 500 °C for 30min. After cooling down to 80 °C, the sintered photoanodes were immersed in 0.5 mM N719 dye in acetonitrile/tert-butanol mixed solution (1:1, v/v) for 24 h. The platinized counter electrodes were prepared by thermal deposition of H_2PtCl_6 solution (5 M in isopropanol) onto FTO glass at 400°C for 30 min. IR783 dye-sensitized UCNPs were deposited onto the dye sensitized films simply by immersing the films into IR783 dye-sensitized UCNPs solution (0.01 M) in hexane for 5, 10, 20 or 30 min, following by washing with hexane solution. All the immersion and washing processes were carried out under room temperature. A platinized FTO glass was used as counter electrode. TiO_2 films and counter electrode were sealed with a 25μm thick Surlyn at 120°C. There is a predrilled hole in the counter electrode, where electrolyte was introduced into the solar cells. The hole was finally sealed with a Surlyn and a thin glass. Under each condition, at least three samples were prepared for the measurements in order to obtain a medium value as the final data.

Characterization.

Transmission Electron Microscopy. The morphology and size of the resulting nanoparticles were investigated by means of transmission electron microscope (TEM, Tecnai G2 Spirit Twin 12) operating at 80 kV. High resolution transmission electron microscopic (HRTEM) images were obtained on the microscope of Spirit Twin Tecnai G2 D339 operating at 300 kV. One drop of diluted colloidal $NaYF_4$ solution dispersed in cyclohexane was allowed to be dried on the surface of the carbon-coated copper grid.

X-ray Diffraction.The powder X-Ray diffraction (XRD) pattern was carried out on a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Kα source (λ=0.15418 nm). The 2θ angle of the XRD spectra was recorded at a scanning rate of 5 °/min from 20° to 80°.

Absorption and luminescence. Absorption spectra of IR dyes, colloidal core/shell nanoparticles, as well as IR dye-sensitized core/shell nanoparticles dispersed in DMF were acquired using a Shimadzu 3600 UV–Visible-NIR spectrophotometer. The upconversion luminescence spectra (UCL) were recorded using a Fluorolog-3.11 Jobin Yvon spectrofluorometer. The UCL signal of the sample in the cuvette was collected at 90° relative to the excitation light. Near infrared (NIR). All luminescence spectra have been corrected for the spectral sensitivity of the spectroscopy system using the Fluorolog spectrofluorometer calibration curve (for UCL).

Current density-voltage (I-V) and IPCE characteristics. The current density−voltage(I−V) characteristics were measured by using a sun simulator (Oriel, AM 1.5G illumination at 100 mW/cm^2) and a computerized Keithley 2400 source meter with a voltage step of 25mV at room temperature. A black mask (6 × 6 mm) was used in the subsequent photovoltaic studies. The incident photon to current efficiency (IPCE) spectra were measured using a tungstenhalogen light source combined with a monochromator (Spectra Pro 2300, Acton Research), and a lock-in amplifier (SR-830, Stanford Research) by locking to the modulation frequency.

Supporting Figures

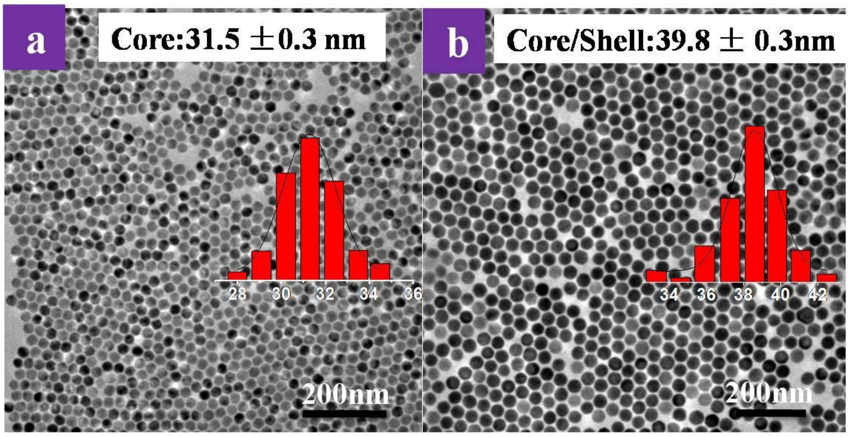


Figure S1. Transmission electron microscopy (TEM) images of (**a**) the core $NaYF_4$:10%Yb,2%Er, (**b**) the core/shell $NaYF_4$:10%Yb,2%Er@$NaYF_4$:30%Nd core/shell nanoparticles. The TEM results indicate the resulting $NaYF_4$:10%Yb,2%Er core and $NaYF_4$:10%Yb,2%Er@NaYF4:30%Nd core/shell nanoparticles have an average size of ~ 31.5 nm and ~ 38.5 nm, implying that a shell layer of 7nm is successfully coated on the core.

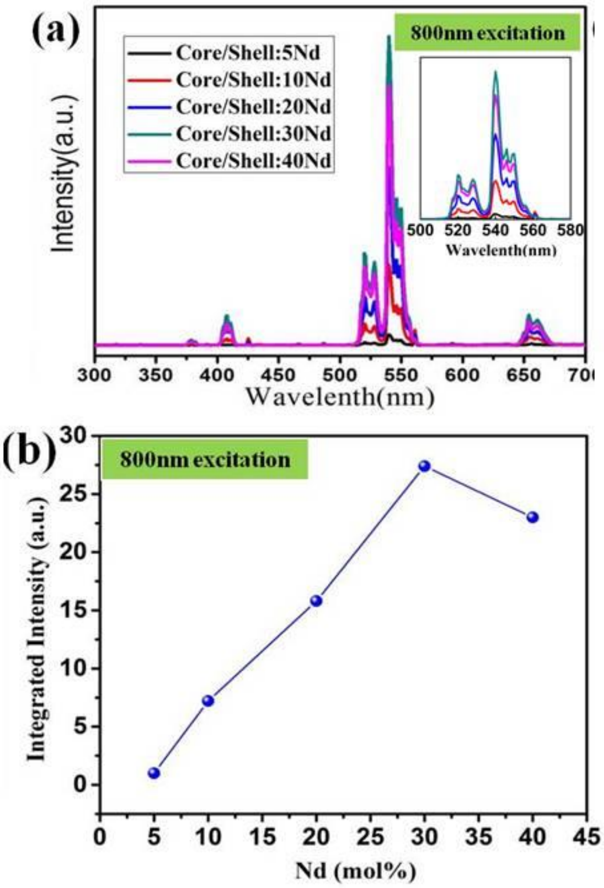


Figure S2. (a) Upconversion luminescence spectra of the colloidal ($NaYF_4$:10%Yb, 2%Er@ $NaYF_4$: x% Nd (x = 5, 10, 20, 30, 40) core/shell nanoparticles dispersed in hexane. (b) The corresponding integrated intensity of the upconversion emission shown in a. Excitation at 800 nm with a power density of 10 W/cm^2.

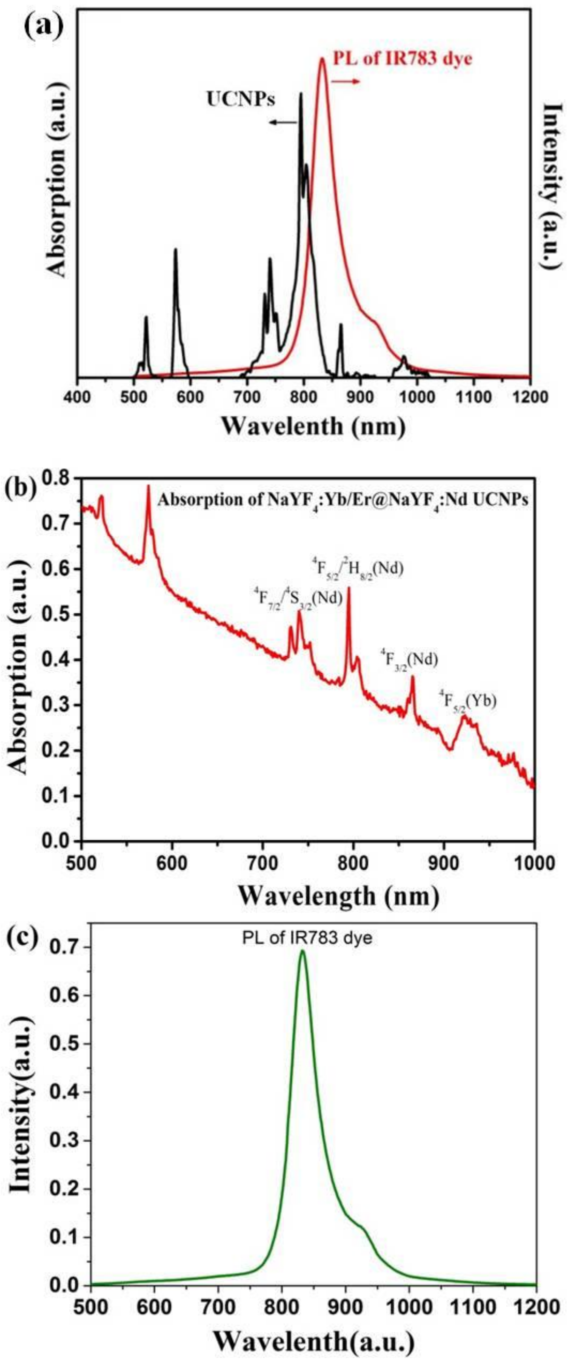


Figure S3. (a) Normalized absorption spectrum of the $NaYF_4$:10%Yb,2%Er@$NaYF_4$:30%Nd core/shell UCNPs and the emission spectrum of IR783 dye. The un-normalized spectrum of (b) absorption of the $NaYF_4$:10%Yb,2%Er@$NaYF_4$:30%Nd core/shell UCNPs, and (c) the emission of IR783 dye.

Molecular weight estimate of $NaYF_4$: 10%Yb,2%Er@$NaYF_4$:30%Nd UCNPs. We follow the same protocol reported in our previous work to calculate the mass percentage of OA ligand coated on the UCNPs,[2] and the mass loss was determined to be ~20% compared with the initially OA coated UCNPs.

A hexagonal-phase $NaYF_4$ unit cell has the following parameters: a=b=0.596 nm, c=0.353 nm. The density is 4.23g/cm^3. The average diameter (d) of sphere-like core@shell $NaYF_4$: 10%Yb,2%Er@$NaYF_4$:30%Nd UCNPs is ~39.8 nm, and the volume of an UCNP was determined by a spherical approximation. The density of $NaYF_4$: 10%Yb,2%Er@$NaYF_4$:30%Nd is taken to be the same as for $NaYF_4$, and the molecular weight of the UCNPs can be calculated as follows:

The volume of a single UCNP (ligand free) is $V_{UCNP} = 4/3\times(d/2)^3\times\pi = 4/3\times(39.8/2)^3\times3.14 = 3.299\times10^4$ nm^3, while the average mass of a single UCNP (ligand free) is $m_{UCNP} = \rho_{NaYF4}\times V_{UCNP} = 4.23\times10^{-21}\times3.299\times10^4 = 1.395\times10^{-16}$g. Considering the mass loss of OA ligands, the average mass of initial OA-coated single UCNP is $m_{UCNP\text{-}OA} = 1.395\times10^{-16} \div 80\% = 1.743\times10^{-16}$g. As a result, the “molecular weight” of initial OA-coated single UCNP is $M_{UCNP\text{-}OA} = m_{UCNP\text{-}OA}\times N_A = 1.743\times10^{-16}\times6.02\times10^{23} = 1.049\times10^8$g/mol. In terms of the dye sensitized $NaYF_4$: 10%Yb,2%Er@$NaYF_4$:30%Nd UCNPs experiment, the mass of initial OA-coated UCNPs used was 8.3 mg in each sample. So the number of $NaYF_4$: 10%Yb,2%Er@$NaYF_4$:30%Nd UCNPs in each sample is $N_{UCNP\text{-}OA} = 0.0083/1.049\times10^8 = 0.079$ nmol

Number of IR783 dyes per UCNPs.

The number of dye molecules at the lowest concentration of IR783 dye used

$N_{IR783} = 36.7\times10^{-6}$ g / 749.36g/mol = 48.975 nmol

The number of IR783 per $NaYF_4$: 10%Yb,2%Er@$NaYF_4$:30%Nd

$N_{IR783/UCNP} = 48.975\div0.079 = 620$

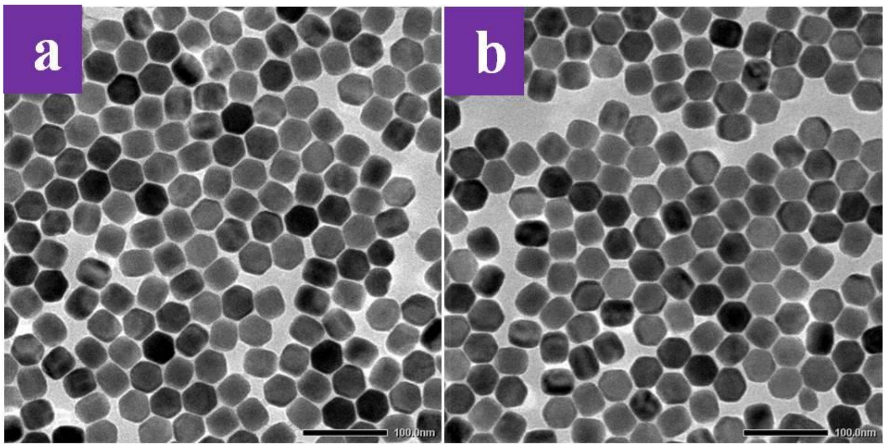


Figure S4. Transmission electron microscopy (TEM) images of (a) $NaYF_4$:10%Yb,2%Er@$NaYF_4$:30%Nd core/shell nanoparticles (without IR783 dye treatment). (b) $NaYF_4$:10%Yb,2%Er@$NaYF_4$:30%Nd core/shell nanoparticles treated with IR783 dye.

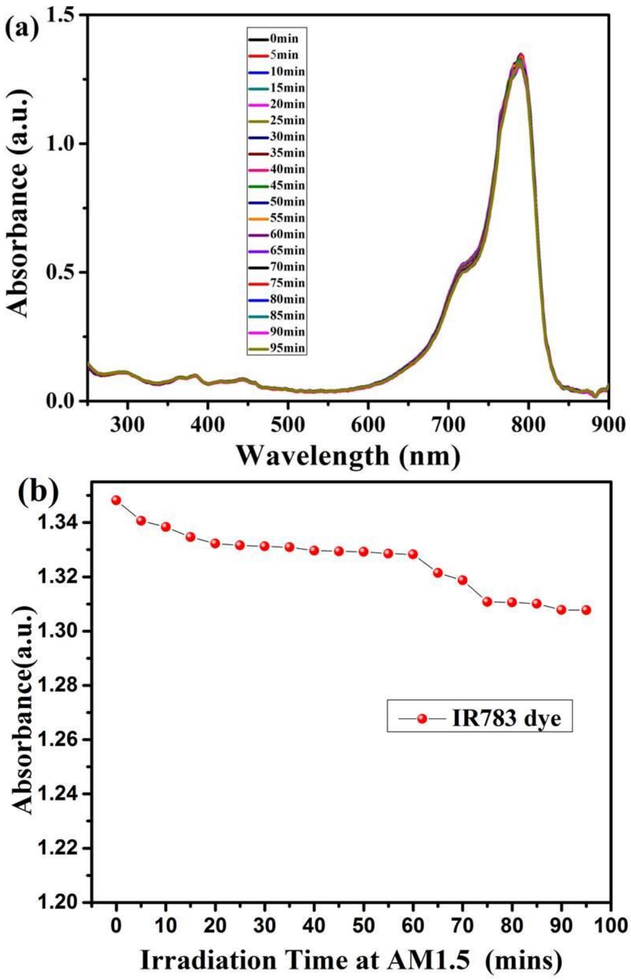


Figure S5. Evaluation of the photostability of IR783 dye (dissolved in DMF) under AM1.5 G simulated sunlight irradiation.

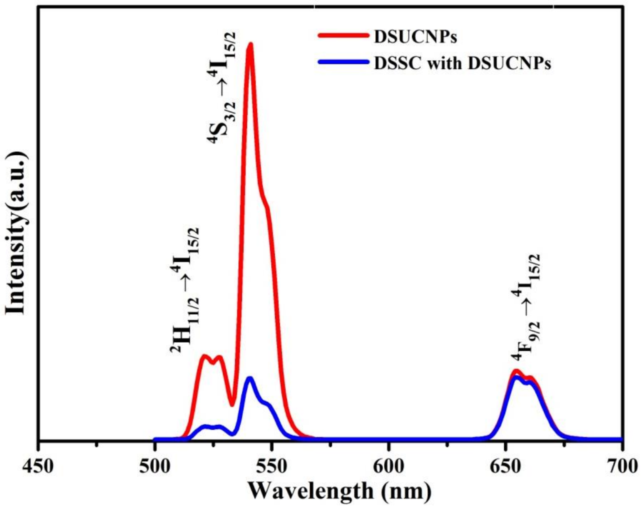


Figure S6. The upconversion luminescence spectra of DSUCNPs depositing on the TiO_2 photoanode with (blue line) and without (red line) N719 dye. The emission bands at 655 nm were normalized, which correspond to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of the Er^{3+} ions.

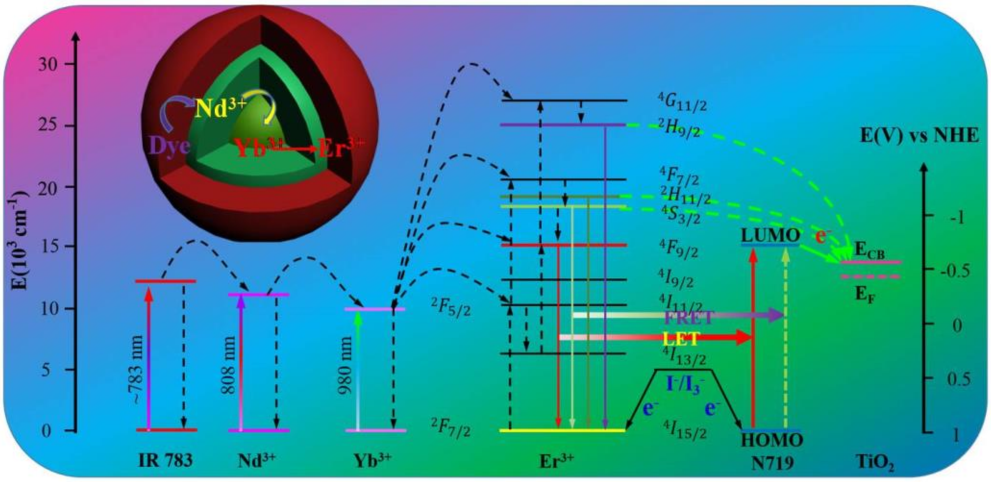


Figure S7. Energy level illustration of the IR783 dye sensitized-UCNPs treated DSSCs, where the NIR energy is converted into the visible spectrum energy via the internal energy transfer (ET) of IR783 dye sensitized-UCNP, and the upconverted energy from the IR783 dye sensitized-UCNP is transferred to the photosensitizer, N719 dye, via the processes of fluorescence resonance energy transfer (FRET) and Luminescence-mediated energy transfer (LET) under solar illumination.

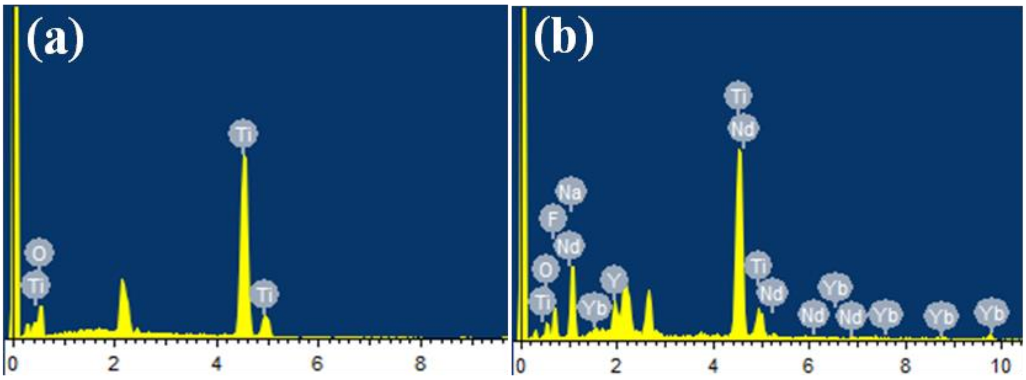


Figure S8. EDS spectra of: (a) TiO_2 photoanode; (d) TiO_2 photoanode with DSUCNPs.

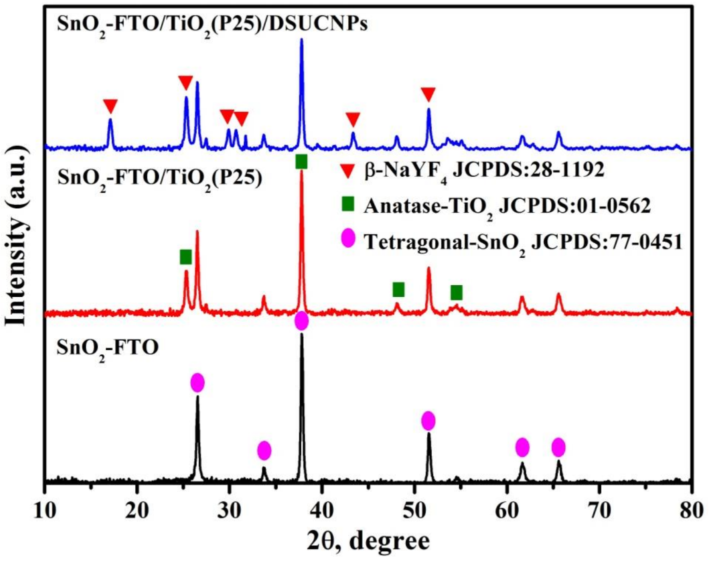


Figure S9. XRD patterns of FTO substrate purchased TiO_2 deposited on FTO substrate and TiO_2 photoanode with core/shell DSUCNPs.

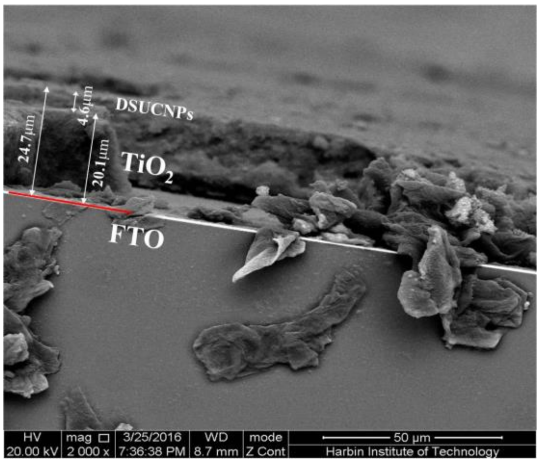
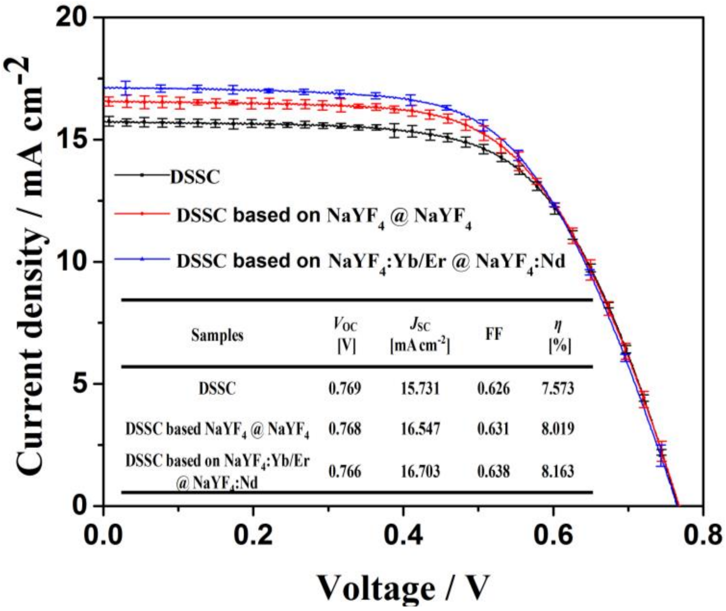
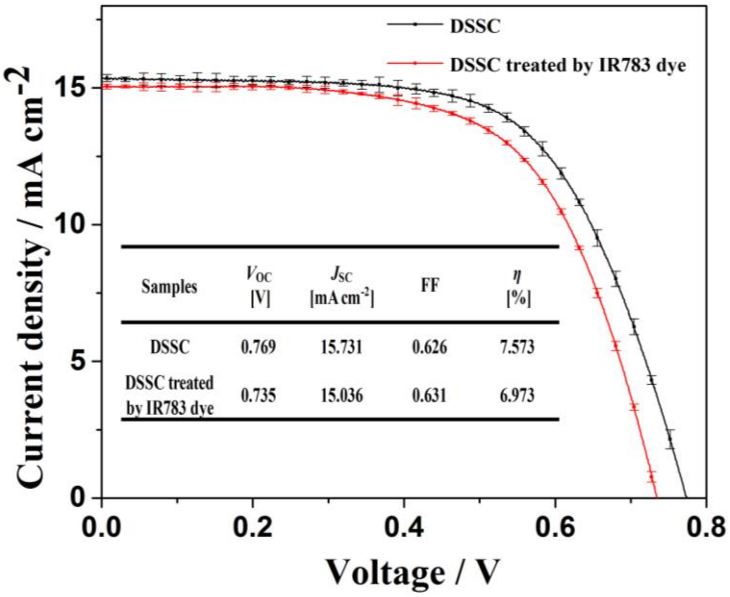


Figure S10. FESEM image of cross-section of DSUCNPs deposited on N719-dyed TiO_2 film.



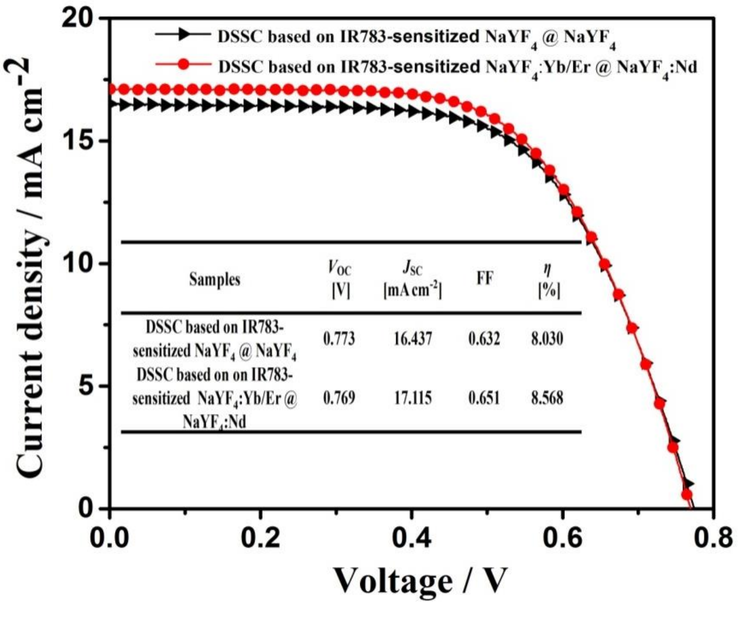
Samples	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
DSSC	0.769	15.731	0.626	7.573
DSSC based $NaYF_4$ @ $NaYF_4$	0.768	16.547	0.631	8.019
DSSC based on $NaYF_4$:Yb/Er @ $NaYF_4$:Nd	0.766	16.703	0.638	8.163

Figure S11. Photovoltaic performance of DSSCs, DSSCs based on $NaYF_4$@$NaYF_4$ treated photoanodes and DSSCs based on $NaYF_4$:Yb/Er@$NaYF_4$:Nd (UCNPs) treated photoanodes. The photovoltaic parameters measured for three times.



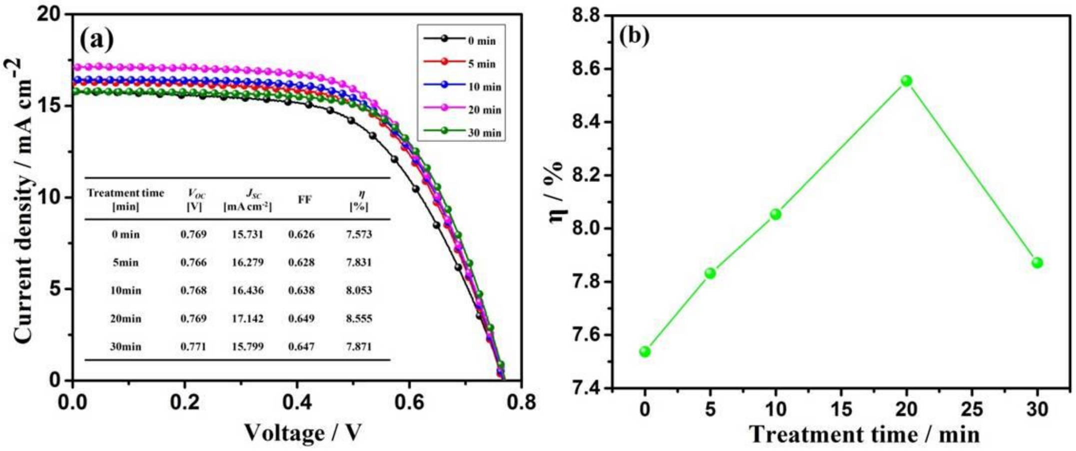
Samples	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
DSSC	0.769	15.731	0.626	7.573
DSSC treated by IR783 dye	0.735	15.036	0.631	6.973

Figure S12. Photovoltaic performance of DSSCs and DSSCs based on only IR783-treated photoanodes. The photovoltaic parameters measured for three times.



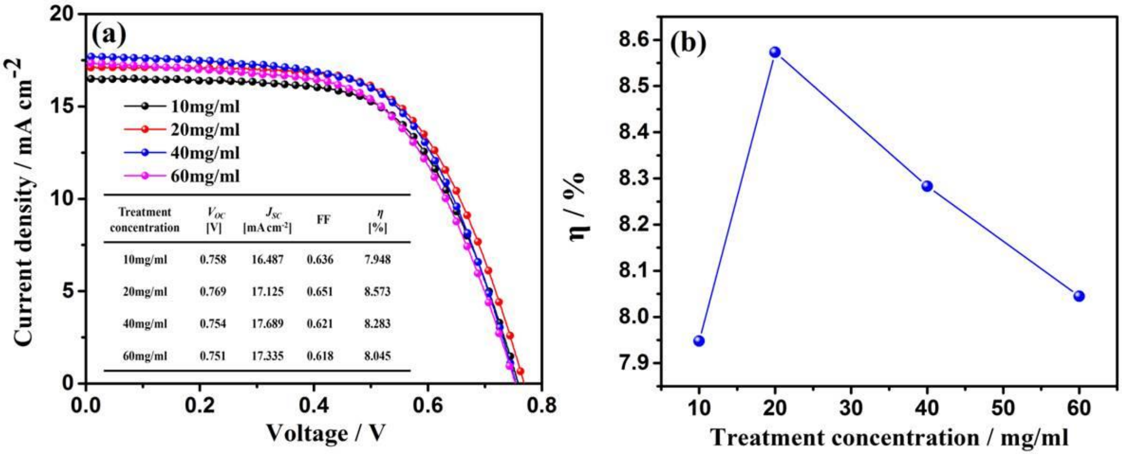
Samples	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
DSSC based on IR783-sensitized NaYF$_4$ @ NaYF$_4$	0.773	16.437	0.632	8.030
DSSC based on on IR783-sensitized NaYF$_4$:Yb/Er @ NaYF$_4$:Nd	0.769	17.115	0.651	8.568

Figure S13. Photovoltaic performance of DSSCs based on IR783-sensitized NaYF$_4$@NaYF$_4$ treated photoanodes and DSSCs based on IR783-sensitized NaYF$_4$:Yb/Er@NaYF$_4$:Nd NPs (DSUCNPs) treated photoanodes.



Treatment time [min]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
0 min	0.769	15.731	0.626	7.573
5min	0.766	16.279	0.628	7.831
10min	0.768	16.436	0.638	8.053
20min	0.769	17.142	0.649	8.555
30min	0.771	15.799	0.647	7.871

Figure S14. (a) *J*-*V* curves of DSSC based on untreated and dyed photoanodes with various soaking times in a 40mg/ml DSUCNPs solution under AM1.5 G simulated sunlight irradiation (100 mWcm^{-2}); (b) The corresponding conversion efficiency of DSSC device with various soaking times in a 40mg/ml DSUCNPs solution. The efficiency was significantly enhanced due to the prolonged treatment times of IR783-sensitized core@shell NPs; the maximum efficiency reaches 8.555% at an optimal treatment time of ~20 min. This result verifies the IR783-sensitized core@shell NPs treatment is beneficial to NIR photon harvest.



Treatment concentration	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
10mg/ml	0.758	16.487	0.636	7.948
20mg/ml	0.769	17.125	0.651	8.573
40mg/ml	0.754	17.689	0.621	8.283
60mg/ml	0.751	17.335	0.618	8.045

Figure S15. (a) *J*-*V* curves of DSSC based on dyed photoanodes treated with DSUCNPs solution of various concentrations under AM1.5 G simulated sunlight irradiation (100 mWcm^{-2}). The soaking time was fixed in 20mins. (b) The corresponding conversion efficiency of DSSC device treated with DSUCNPs of various concentrations solution. The efficiency was significantly enhanced due to the increase of IR783-sensitized core@shell NPs; the maximum efficiency reaches 8.573% at an optimal treatment concentration of ~20mg/ml. This result verifies the DSUCNPs (IR783-sensitized core@shell NPs) treatment is beneficial to NIR photon harvest.

References

S1. Dong, A. G.; Ye, X. C.; Chen, J.; Kang, Y. J.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. *J. Am. Chem. Soc.*, **2011**, *133*, 998-1006.

S2 G. Y. Chen, J. A. Damasco, H. L. Qiu, W. Shao, T. Y. Ohulchanskyy, R. R. Valiev, X. Wu, G. Han, Y. Wang, C. H. Y ang, H. Ågren, P. N. Prasad, Nano Lett., 2015, 15, 7400.