Electronic Supplementary Material (ESI) for Nanoscale
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Electronic Supplementary Information:

Upconversion induced enhancement of dye sensitized solar cell based on core-shell structured β-$NaYF_4$: Er^{3+}, Yb^{3+}@SiO_2 nanoparticles

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Experimental section

Reagents.: Y_2O_3 (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%), oleic acid (90%) and 1-octadecene (90%) were purchased from Aladdin. HCl (37+%), NaOH (96+%), NH4F (95+%), ammonia (26%), cyclohexane (99.5+%), methanol (99.5+%), ethanol (99.7+%), isopropanol (99.7+%), polyvinyl pyrrolidone (PVP, K-30), tetraethyl orthosilicate (TEOS, 28.4+%)were purchased from SCRC. All the reagents were used without any further purification.

Synthesis of β-$NaYF_4$:Er^{3+}, Yb^{3+} nanoparticles: β-$NaYF_4$:Er^{3+}, Yb^{3+} upconversion nanoparticles (β-NYEY UCNPs) were synthesized by solvothermal technology. The reaction precursor was mixed by 5ml $RECl_3$ (0.2M, RE = Y, Yb, and Er (molar ratio is 39:10:1) in methanol, 8 ml oleic acid and 15 ml 1-octadecene. The solution was heated to 160□ under argon and maintained at this temperature to evaporate the methanol and then cooled down to 65□. After10ml of NH_4F (1.6M) and NaOH (1.2M) in methanol was added in the flask by funnel , the solution was heated to 300□ under argon for 90 min and then cooled down to room temperature. The resulting products were collected by centrifugation , then washed by methanol and cyclohexane for several times and dried at 60□ finally.

Sythesis of core-shell structured β-$NaYF_4$:Er^{3+}, Yb^{3+}@SiO_2 nanoparticles: 0.2g of dried β-NYEY UCNPs were dispersed in the compounded solvent mixed by 20ml cyclohexane ,20ml isopropanol and 0.02 g polyvinyl pyrrolidone (PVP) ,then mixed with 4ml water and 0.06ml tetraethyl orthosilicate (TEOS). 0.5ml ammonia was added slowly into the solution under continuous stirring. The product was collected by centrifugation and washed twice with ethanol.

Fabrication of DSCs: The photoelectrode was prepared by doctorblading the paste of TiO_2 particles (40-60nm). TiO_2 paste was obtained by hydrothermal method according to the reported procedure and added with different concentration of β-NYEY@SiO_2 UCNPs. The thickness of membrane was constant owing to the number of tapes was the same for each sample. The thickness of the film was about 10μm. Then photoelectrode was annealed under 500℃ .And then cooled down to room temperature and washed by acetonitrile. After dyed for 12h, the photoelectrode was washed by acetonitrile again to remove the accumulated dye molecules on the surface of nanocrystalline TiO_2 membrane. A DSC of sandwich-type configuration was the composite of photoelectrode, platinum plate counter electrode and electrolyte. An electrolyte was composed of 0.1mol 1-propy-3-methylimidazolium iodide (PMII), 0.05mol LiI, 0.1mol GNCS, 0.03mol I_2, 0.5M 4-tert-butylpridine (TBP) in mixed solvent of acetonitrile and propylene carbonate (PC) (volume ratio:1/1).

Characterization: Power X-ray diffraction (XRD) measurements was carried out by a Bruker diffractometer (D8 Advance, Bruker). The surface morphology images of the photoelectrode were obtained by field emission scanning electron microscopy equipped with energy dispersive X-ray analyzing system (FESEM/EDX, JEOL 6700F, JEOL) and atomic force microscopy (AFM, SPM-9500J3, Shimadzu). UV-Vis spectrum were measured by Lambda 650S (Perkin Elmer, UK). High solution transmission electron microscope (HRTEM, JEOL, 2010) was applied to investigate the core-shell structure. The values of square average roughness were measured with a profilometer (Taly Form S4C-3D). The J-V characteristics and electrochemical impedance spectroscopy (EIS) measurement of the DSCs were carried out under AM 1.5 illumination of 78.8 mW cm^{-2} produced by Newport 91192 light simulated solar light source with 0.25 cm^2 active area. The upconversion emission spectra were obtained under excitation of a 975 nm continuous-wave (CW) diode laser and recorded by a spectrometer (Spectrapro 2500i, Acton). The image of membrane under excited was recorded by using an ordinary camera (EOS40D, Canon) equipped with two 300–750 nm band-pass filters (FSR-KG3, Newport).

Supplementary Figure

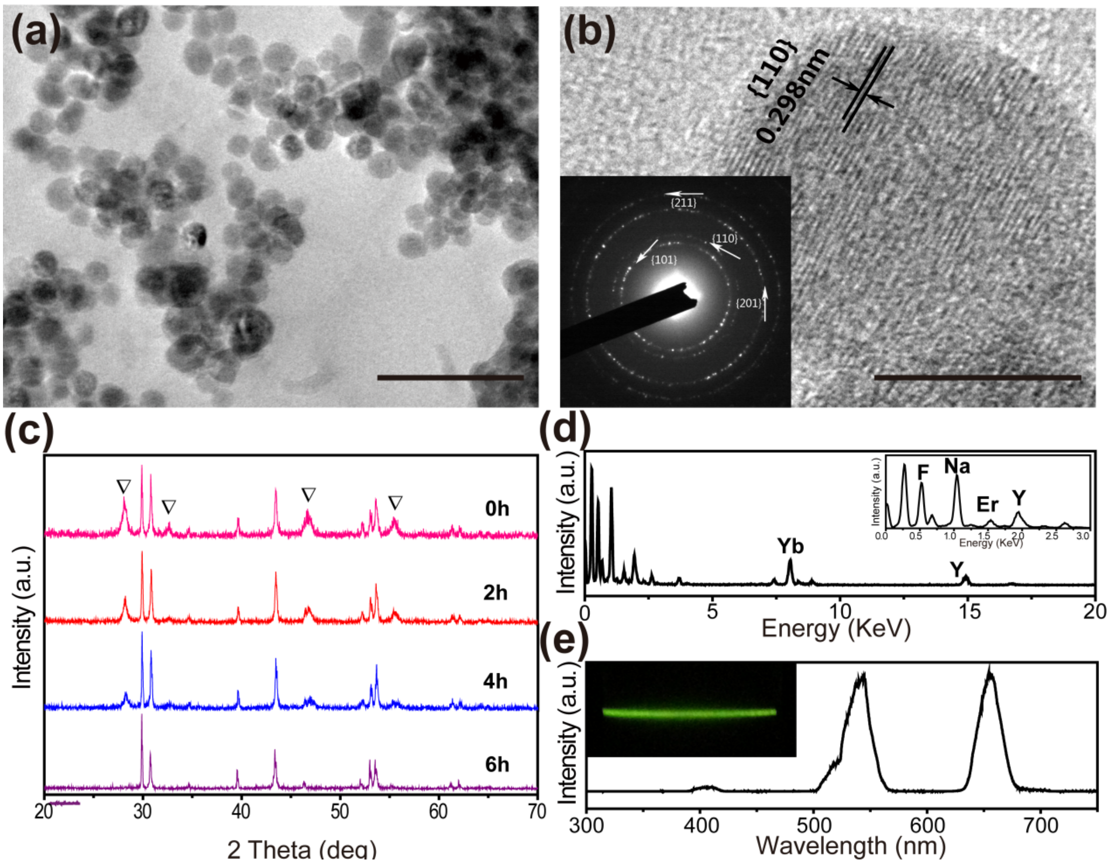


Fig S1. (**a**) TEM image of bared β-NYEY UCNPs. (**b**) High-resolution TEM image of β-NYEY. The inset is corresponding selected area electron diffraction pattern of the β-NYEY. (**c**) Corresponding XRD measurement of the core-shell structured β-NYEY@SiO$_2$ annealed under 400℃ for 0, 2, 4, 6 hours are showed from above to bottom. The demonstration proved the α-NaYF$_4$:Er^{3+}, Yb^{3+} could be convert into β-NYEY in the annealing process of photoelectrode. (peaks of α-NaYF$_4$: Er^{3+}, Yb^{3+} were marked by inverted triangle) (**d**) Corresponding EDX measurements of the bared β-NYEY. The inset is zoomed-in EDX spectrum ranging from 0 to 3 KeV. (**e**) Upconversion emission spectrum of bared β-NYEY in ethanol. The inset is optical image of upconversion emission in ethanol. The area bars in **a** and **b** are 100 and 10 nm, respectively.

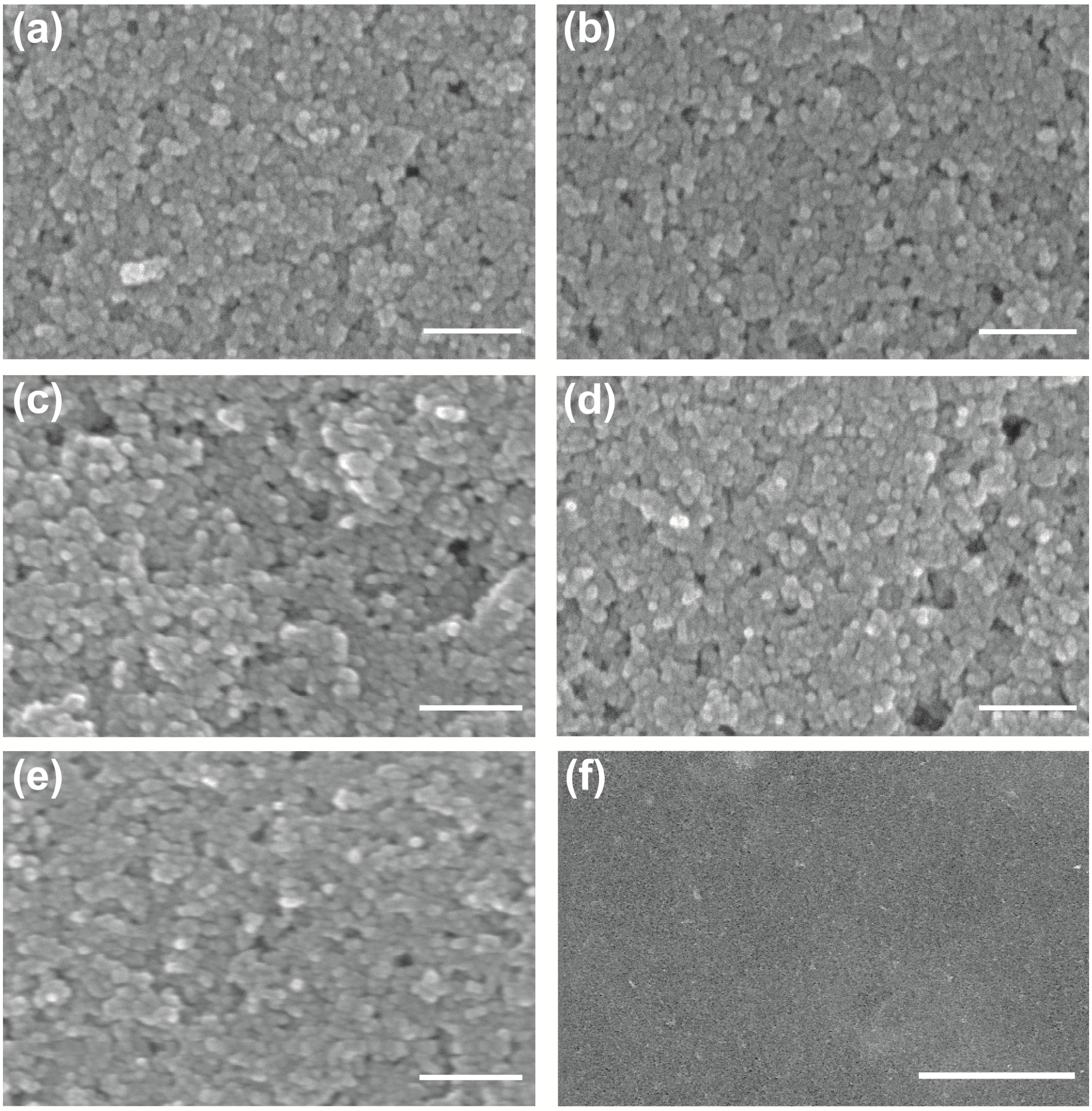


Fig S2. SEM surface morphology image of TiO_2 photoelectorde added core-shell structured β-NYEY@SiO_2 UCNPs varying the concentration of (**a**) 0% (no β-NYEY@SiO_2 used), (**b**) 2%, (**c**) 4%, (d) 6% and (**e**) 10%. (**f**) Low-resolution SEM surface morphology image of hybrid TiO_2 photoelectrode with 4% of core-shell structured β-NYEY@SiO_2 , which performed as the best one. The area bars are 200 nm for **a** to **e** , while 1μm for **f**

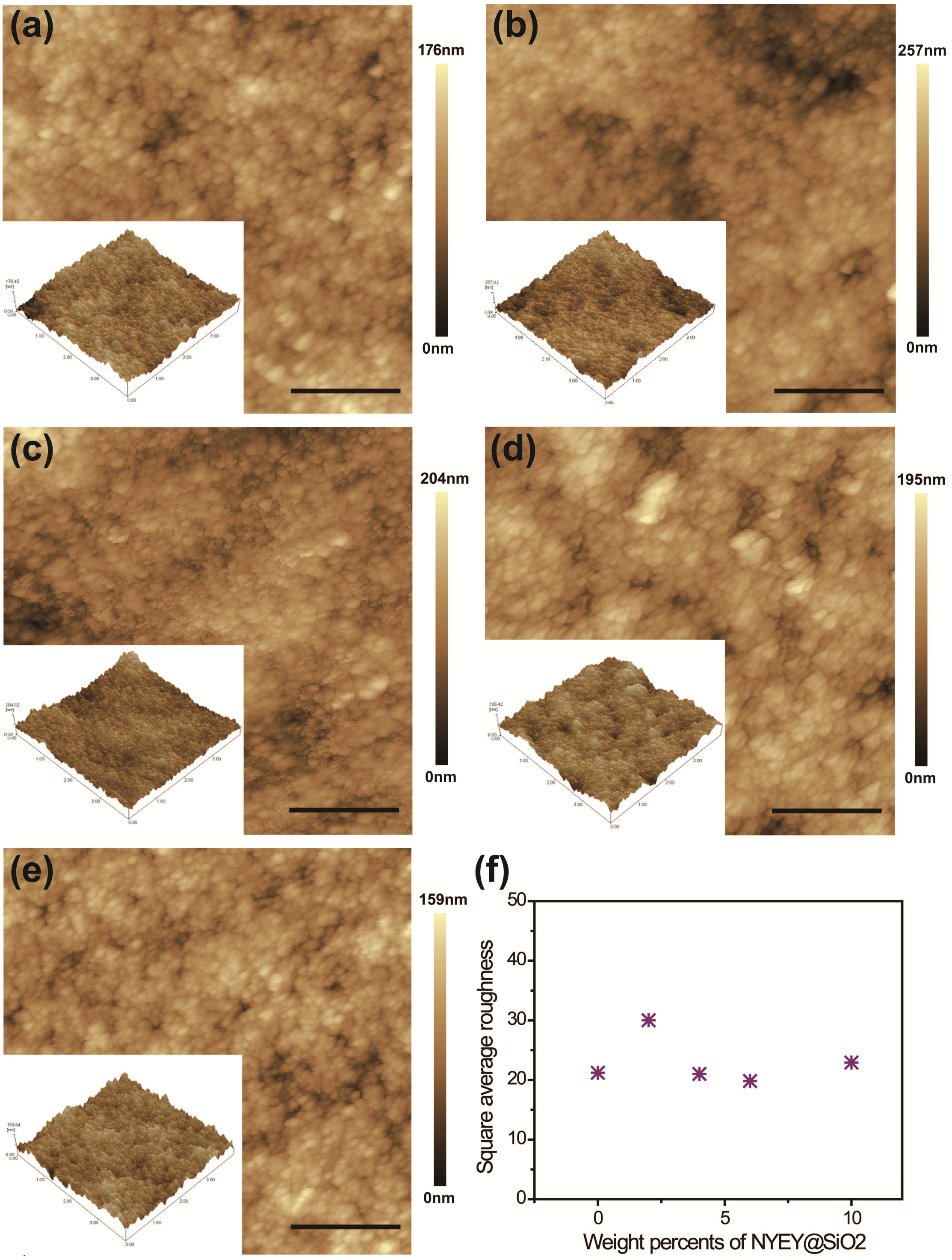


Fig S3. Corresponding AFM morphology measurement of the photoelectrode in **Fig S2** were showed in (**a**) to (**e**). The inset is three-dimensional AFM images of each photoelectrode. (**f**) Square average roughness of each photoelectrode. The area bar are 1μm for **a** to **e**.

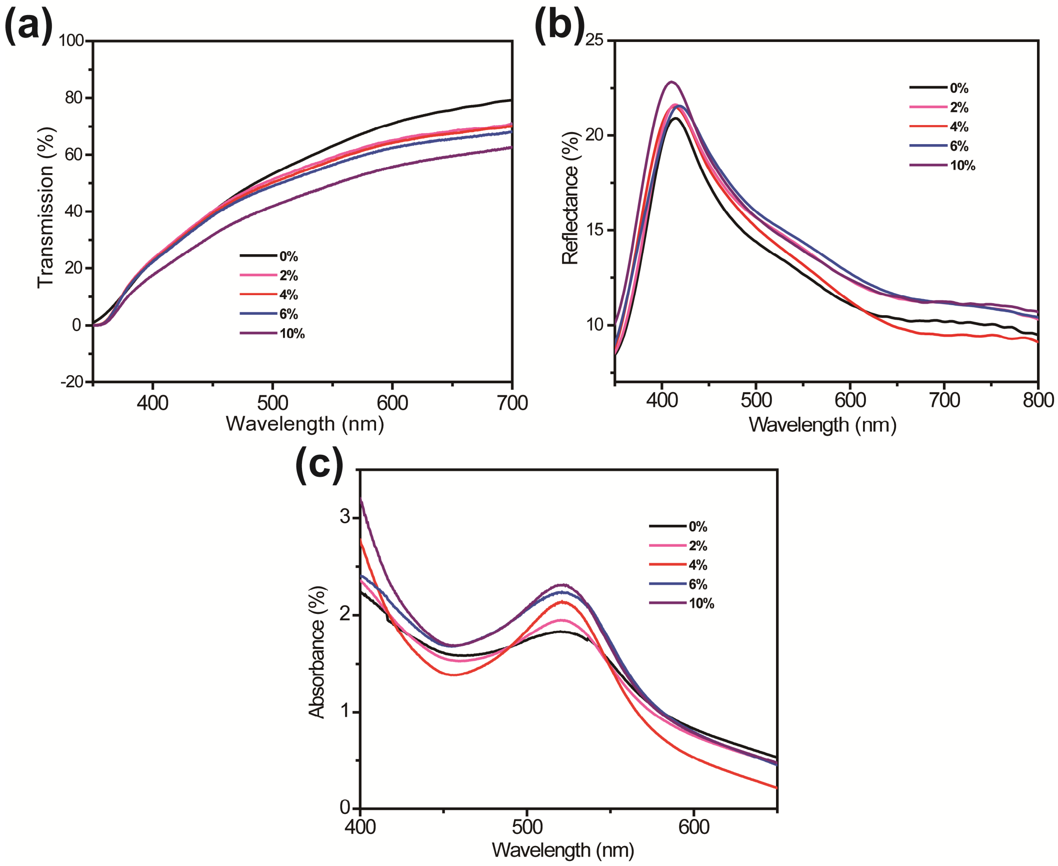
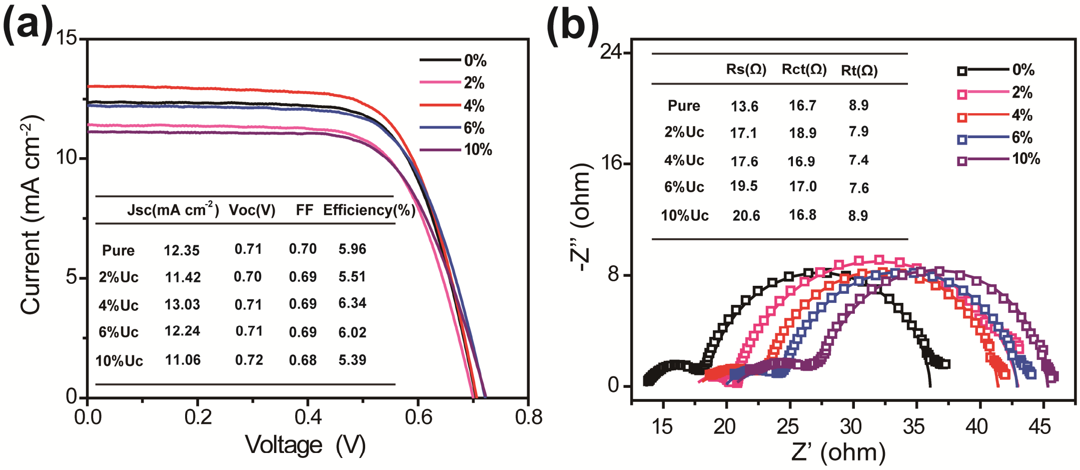


Fig S4. (**a**) Corresponding UV-Vis transmission spectroscopy of unsensitized TiO_2 porous membrane in **Fig S2**. (**b**) UV-Vis reflection spectroscopy of the unsensitized TiO_2 porous membrane. (**c**) UV-Vis absorption spectroscopy of the sensitized TiO_2 porous membrane. The slight fluctuations were caused by the absorption of β-NYEY in visible light region. (1)



	Jsc(mA cm^{-2})	Voc(V)	FF	Efficiency(%)
Pure	12.35	0.71	0.70	5.96
2%Uc	11.42	0.70	0.69	5.51
4%Uc	13.03	0.71	0.69	6.34
6%Uc	12.24	0.71	0.69	6.02
10%Uc	11.06	0.72	0.68	5.39

	Rs(Ω)	Rct(Ω)	Rt(Ω)
Pure	13.6	16.7	8.9
2%Uc	17.1	18.9	7.9
4%Uc	17.6	16.9	7.4
6%Uc	19.5	17.0	7.6
10%Uc	20.6	16.8	8.9

Fig S5. (**a**) Corresponding J-V curves of devices assemble based on TiO_2 porous membrane in **Fig S2**. (**b**) EIS spectra of the devices in **a**. Results showed inside the figure **a** and **b** were obtained under 100 mW cm^{-2}, AM1.5 simulated sunlight irradiation with active area of 0.25 cm^{2} .

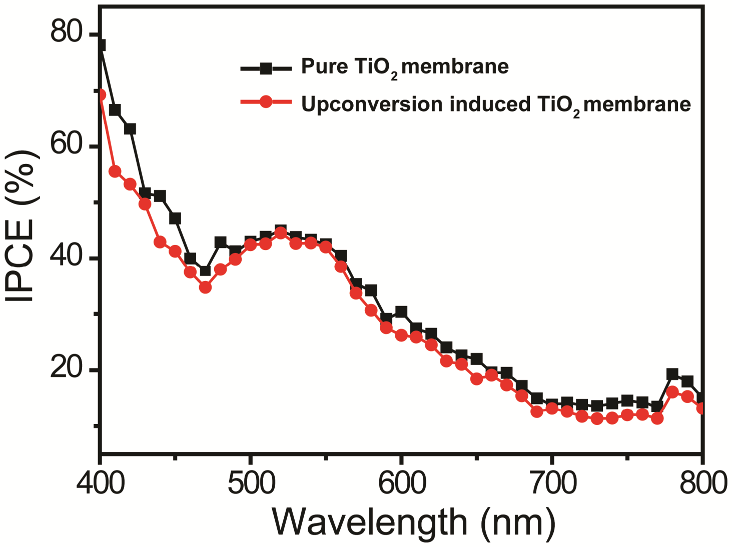


Fig S6. Incident photon-to-current conversion efficiency of devices composed of pure TiO_2 porous membrane and upconversion induced TiO_2 porous membrane (4% of UCNPs). The slight decrease of upconversion induced one in visible region was the result from reduction of dye loading.$^{(2)}$ The dye loading of each membrane were separately 1.89×10^{-7} and $1.77\times10\text{E}^{-7}$ mol cm^{-2}. This observation would further prove the enhancement of efficiency was caused by upconversion effect in NIR region.

References for Supporting Information

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2. P. M. Sommeling, B. C. O'Regan, R. R. Haswell, H. J. P. Smit, N. J. Bakker, J. J. T. Smits, J. M. Kroon and J. A. M. van Roosmalen, *The Journal of Physical Chemistry B*, 2006, **110**, 19191-19197,