Supporting Information

Hexagonal β-$NaYF_4$:Yb^{3+}, Er^{3+} Nanoprism-incorporated Upconverting Layer in Perovskite Solar Cells for Near-infrared Sunlight Harvesting

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Experimental section

Synthesis of hexagonal $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms. Hexagonal $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms were synthesized using a modified hydrothermal process.[1] Typically, 7.8 mL of yttrium(III) nitrate hexahydrate (0.2 M, 99.8%, Sigma-Aldrich), 2 mL of ytterbium(III) nitrate pentahydrate (0.2 M, 99.9%, Sigma-Aldrich) and 0.2 mL of Erbium(III) nitrate pentahydrate (0.2 M, 99.9%, Sigma-Aldrich) were added to 20 mL of aqueous sodium citrate solution (2 M, ≥99.9%, Sigma-Aldrich) and stirred for 1 h to form Ln^{3+}-citrate complex. Then, 40 mL of aqueous solution containing ammonium fluoride (2.4 M, ≥98.0%, Sigma-Aldrich) was introduced to the above solution and stirred for 1 h. pH of the mixing solution was adjusted to 3 by nitric acid. After additional stirring for 5 min, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for 2 h. White precipitates were collected by centrifugation, washed with water and ethanol, and then dried at 60 °C in a vacuum oven.

Device fabrication. TiO_2 paste was prepared by adding ethyl cellulose, lauric acid, and terpineol to an ethanol solution of TiO_2 nanoparticles, followed by stirring and sonication. TiO_2 nanoparticles were synthesized using a two-step hydrothermal method reported previously.[2] Ethanol was removed using a rotary evaporator. The paste was then mixed using a 3-roll mill to create a homogeneous mixture. The nominal composition of TiO_2/terpineol/ethyl cellulose /lauric acid was 1.25/6/0.9/0.3. The $NaYF_4:Yb^{3+}$, Er^{3+} paste was prepared in the same manner as described above. Patterned FTO glass (8 Ω/sq, Filkington) was cleaned by sonication in distilled water, acetone, and 2-propanol for 60 min each. An ethanolic solution of colloidal TiO_2 nanoparticles and titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol, Aldrich) was spin-coated on FTO glass at 5000 rpm for 30 s and heated at 150 °C for 20 min to

prepare the compact TiO_2 layer.[3] To prepare a $NaYF_4:Yb^{3+}$, Er^{3+} upconverting mesoporous layer, the TiO_2 paste was mixed with the $NaYF_4:Yb^{3+}$, Er^{3+} paste by a ratio of 1:3, 1:1 and 3:1 (25, 50 and 75 wt% $NaYF_4:Yb^{3+}$, Er^{3+} respectively). The mixed paste diluted in ethanol at a weight ratio of 1:5 were spin-coated on the compact TiO_2 layer at 3000 rpm for 30 s and annealed at 500 °C for 30 min. The upconverting mesoporous flim was post-treated with aqueous $TiCl_4$ solution (20 mM, >98%, Aldrich) at 70 °C for 20 min and sintered at 500 °C for 30 min. To fabricate methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$) film, perovskite precursor solution was prepared by mixing 461 mg of PbI_2 (99.9985%, Alpha Aesar), 159 mg of CH_3NH_3I and 78 μL of dimethyl sulfoxide (DMSO, 99.5%, Sigma-Aldrich) (molar ratio 1:1:1) in 770 μL of N, N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich) at a room temperature for 1 h. CH_3NH_3I was synthesized by the method reported elsewhere using methylamine (40 wt% in water, Sigma-Aldrich) and hydriodic acid (57 wt% in water, Sigma-Aldrich).[2] The completely dissolved solution was spin-coated on the upconverting mesoporous layer at 3000 rpm for 90 s, and 500 μL of diethyl ether was dripped at 10 s onto the rotating substrate. The precursor-coated film was heated on a hot plate at 65°C for 1 min and 100 °C for 60 min. Then the Spiro-OMeTAD solution was spin-coated on the perovskite layer at 3500 rpm for 30 s. The Spiro-OMeTAD solution was prepared by mixing 72 mg of Spiro-MeOTAD (Lumtec), 28.8 μL of tert-butylpyridine and 17.5 μL of acetonitrile solution containing 520 mg/mL lithium bis(trifluoromethylsulfonyl)imide salt in 1 mL of chlorobenzene. Finally, a 70 nm thick Au top electrode was deposited by thermal evaporation. The active area of the fabricated device was 0.09 cm^2.

Characterization. The morphology of the hexagonal $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms, upconverting mesoporous layer and cross sectional view of perovskite solar cell was observed by

Field-emission scanning electron microscopy (FE-SEM) a JEOL 6700. X-ray diffraction (XRD) was performed using a Bruker New D8 Advance with a Cu-Kα radiation source (λ: 1.5406 Å) at 40 kV and 300 mA (12 kW). The Upconversion photoluminescence (PL) spectrum of the hexagonal $NaYF_4$:Yb^{3+}, Er^{3+} nanoprisms was measured by a homemade spectrometer equipped with a 980 nm laser (SDL-980LM-500T, Shanghai Dream Lasers Technology), a monochromator (HoloSpec f/ 1.8i, Kaiser Optical Systems), and a charge-coupled device (CCD) camera (PIXIS 400BR, Princeton Instruments). The photocurrent–voltage (J−V) characteristics of the fabricated perovskite solar cells were evaluated using a 530 W xenon lamp (XIL model 05A50KS source units; AM 1.5 solar irradiance; intensity: 100 mW cm^{-2}). The incident photon-to-current conversion efficiency (IPCE, PV Measurements, Inc.) was measured from 300 to 900 nm under short-circuit conditions. Electrochemical Impedance Spectroscopy (EIS) measurement was performed using a Zahner Electrik IM6 analyzer under a dark condition.

References

(1) Liang, L.; Liu, Y.; Zhao, X.-Z., Double-shell β-$NaYF_4$:Yb^{3+}, Er^{3+}/SiO_2/TiO_2 Submicroplates as a Scattering and Upconverting Layer for Efficient Dye-sensitized Solar Cells. *Chem. Commun.* **2013**, 49, 3958-3960.

(2) Im, J.-H.; Jang, I.-H.; Pellet, N.; Grätzel, M.; Park, N.-G., Growth of $CH_3NH_3PbI_3$ Cuboids with Controlled Size for High-Efficiency Perovskite Solar Cells. *Nat. Nanotechnol.* **2014**, 9, 927-932.

(3) Wojciechowski, K.; Saliba, M.; Leijtens, T.; Abate, A.; Snaith, H. J., Sub-150 °C Processed Meso-superstructured Perovskite Solar Cells with Enhanced Efficiency. *Energy Environ. Sci.* **2014**, 7, 1142-1147.

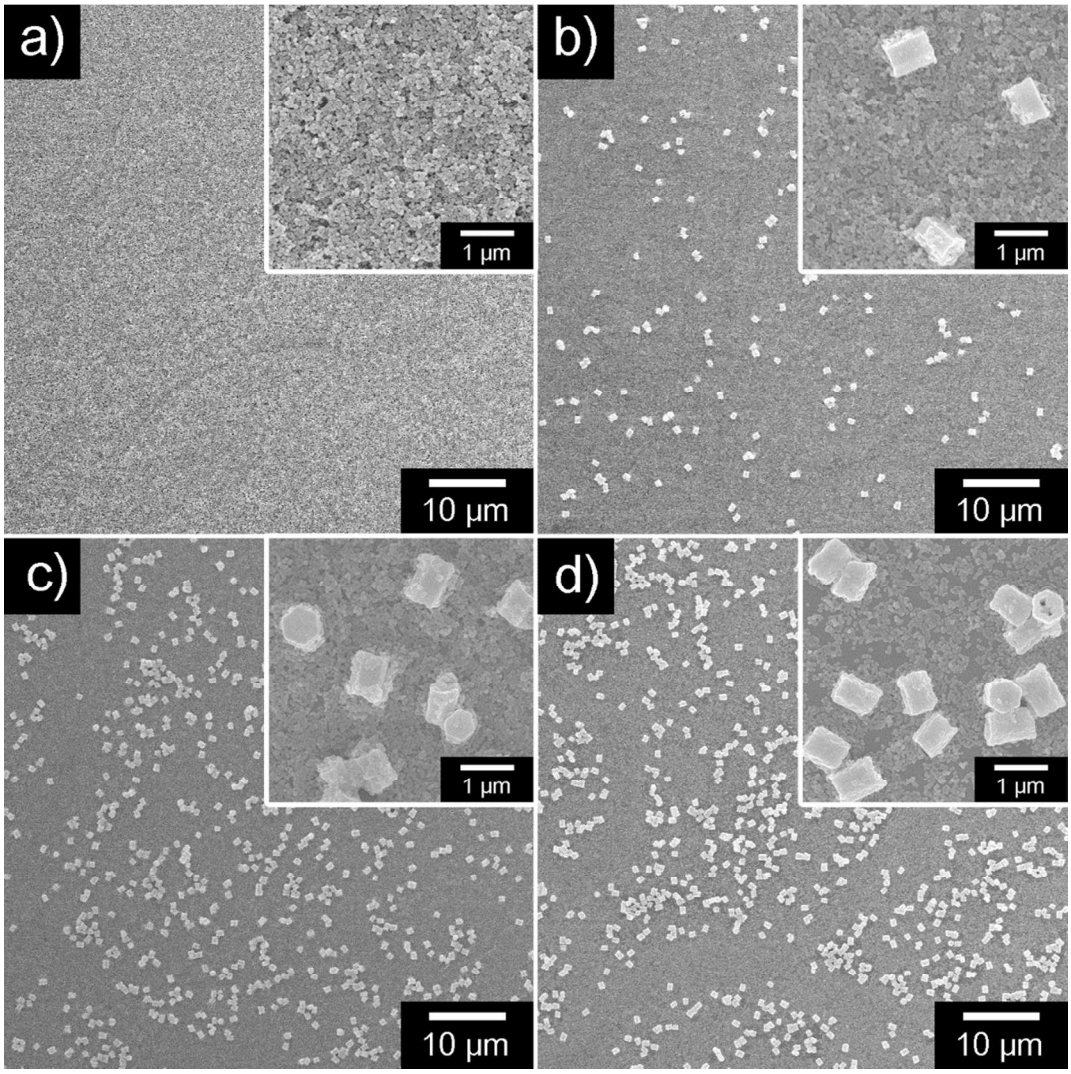

Figure S1. Scanning electron microscopy (SEM) images of the TiO_2 mesoporous layer with various $NaYF_4:Yb^{3+}$, Er^{3+} nanoprism concentrations: a) only TiO_2 nanoparticles (reference), b) TiO_2 nanoparticles with 25 wt% $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms, c) TiO_2 nanoparticles with 50 wt% $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms, and d) TiO_2 nanoparticles with 75 wt% $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms.

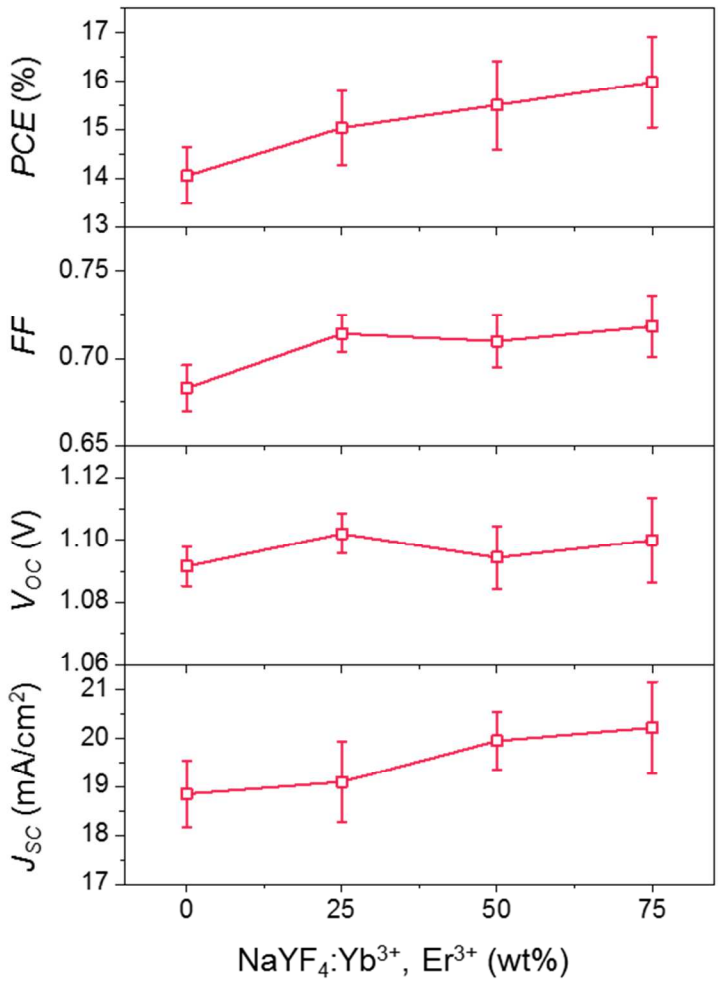

Figure S2. Photovoltaic performance of PSCs using an upconverting mesoporous layer with an increasing concentration of hexagonal $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms.

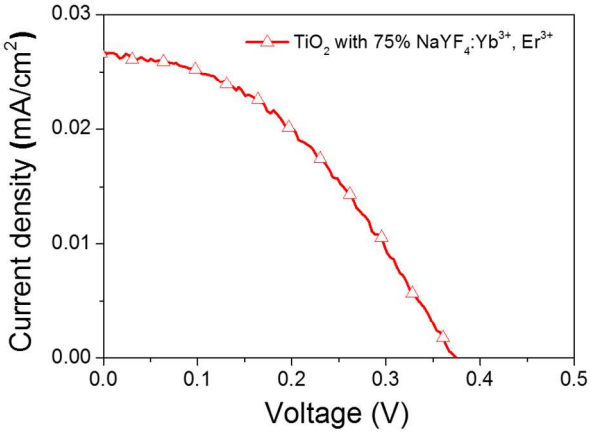

Figure S3. Current density-voltage curve obtained from PSC having a TiO_2 NP-based mesoporous layer with 75 wt% of $NaYF_4:Yb^{3+}$, Er^{3+} under 980 nm NIR laser with laser power of 1W.

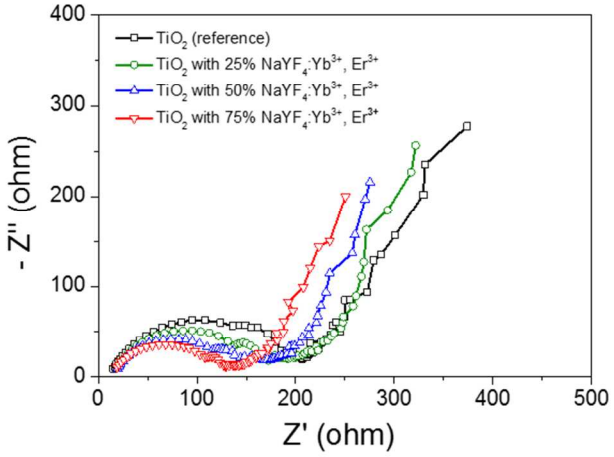

Figure S4. Electrochemical impedance spectroscopy (EIS) measurements performed under a light illumination of 100 mW cm^{-2} condition.

Table S1. Average photovoltaic parameters of perovskite solar cells (PSCs) containing hexagonal $NaYF_4:Yb^{3+}$, Er^{3+} nanoprisms (0, 25, 50, and 75 wt%). Average values of all parameters were obtained for 15 devices.

Devices	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)
TiO_2 (Reference)	18.85 ± 0.69	1.09 ± 0.01	0.68 ± 0.01	14.05 ± 0.59
TiO_2 with 25% $NaYF_4:Yb^{3+}$, Er^{3+}	19.10 ± 0.84	1.10 ± 0.01	0.71 ± 0.01	15.04 ± 0.76
TiO_2 with 50% $NaYF_4:Yb^{3+}$, Er^{3+}	19.95 ± 0.60	1.09 ± 0.01	0.71 ± 0.02	15.51 ± 0.92
TiO_2 with 75% $NaYF_4:Yb^{3+}$, Er^{3+}	20.23 ± 0.94	1.10 ± 0.01	0.72 ± 0.02	15.98 ± 0.93

Table S2. Summary of the photovoltaic properties of PSC having a TiO_2 NP-based mesoporous layer with 75 wt% of $NaYF_4:Yb^{3+}$, Er^3 nanoprisms.

Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	η (%)
TiO_2 with 75% $NaYF_4:Yb^{3+}$, Er^{3+}	0.027	0.374	0.41	0.01