Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Recombination Reduction on Lead Halide Perovskite Solar Cells based on Low Temperature Synthesized Hierarchical TiO_2 Nanorods

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Experimental section

FTO substrates pretreatment

Firstly, the FTO layer (Pilkington TEC15, 15 Ω/sq resistance) was partially etched with zinc powder and HCl (2 M) to prevent short circuit, cleaned by hand with soap and deionized water, followed by sonication in a mixture 2-propanol/acetone/ethanol (1:1:1 v/v) for 15 min. The cleaned FTO substrates were further treated with UV-O_3 for 20 min.

TiO_2 nanorod films

TiO_2 NRs were prepared using hydrothermal method as reported elsewhere.[1] Briefly, 1 mL of titanium (IV) isopropoxide was added drop by drop into a mixture of DI water (25 mL) and HCl (25 mL), kept under vigorously stirring to obtain a transparent solution. The solution was transferred to a Teflon liner of an autoclave where the FTO substrates have been positioned. The hydrothermal method was conducted at 180 °C for different growth time 110, 120, 125 and 130 min to obtain TiO_2 NR lengths of 380, 540, 700 and 1100 nm, respectively. After the synthesis, the FTO substrate was taken out, rinsed with DI water and dried in air at 50 °C.

3D TiO_2 hierarchical nanorod films

3D TiO_2 hierarchical nanostructures were synthesized by a second hydrothermal method using the as prepared TiO_2 NR films as seeds. Typically, 2.4 mL of deionized water was slowly dropped into a mixture of dichloromethane (20 mL) and $TiCl_4$ (0.4 mL) at 0°C. Again, the solution was placed in a Teflon liner with the as prepared TiO_2 NR on the FTO substrate and set in an electric oven at 180 °C for 2 h. After the hydrothermal reaction, the TiO_2 3D HNR on FTO substrate was finally washed with ethanol and DI water, respectively, and then dried in an oven at 60 °C.

TiO_2 compact layer films

TiO_2 compact layer films were used in control devices. It was deposited on the FTO substrates by spray pyrolysis at 450 °C using a diluted solution of titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol) in ethanol (1:39 v/v) and compressed oxygen as carrier gas. After spraying the precursor solution, the substrates were sintered on a hot plate for 30 min at 450 °C and then cooled down to ambient temperature.

Perovskite solar cells fabrication

$CH_3NH_3PbI_3$ (Sing-MAICl) was synthesized using two different methods broadly extended in the literature. On one hand, single step method using $PbCl_2$ precursor. Following the most used literature nomenclature we have call this perovskite $CH_3NH_3PbI_{3-x}Cl_x$, despites the amount of Cl is significantly low under the detection limit in many cases. For this synthesis, 100 μL of precursor solution prepared by adding 1 mL of anhydrous DMF into a mixture of CH_3NH_3I (0.423 g) and $PbCl_2$ (0.246 g), was spin-coated through one-step deposition route onto the three TiO_2 structures films inside the glove box at different spin rates (from 1000 to 4000 r.p.m.) for 60 s. Then, the films were putted on a hot plate for 30 min at 100 °C, followed by annealing at 100 °C for an additional hour in an oven under air flow. The CH_3NH_3I was prepared in our laboratory by following standard procedures.[2]

On the other hand, $CH_3NH_3PbI_3$ perovskite layer (Seq-MAI) was deposited by two-steps sequential method.[3] In brief, 20 μL of PbI_2 solution prepared by dissolving PbI_2 (462 mg) in 1 mL of anhydrous DMF under stirring at 70 °C, was spin-coated on the different TiO_2 films at 3000 r.p.m. for 5 s and 6000 r.p.m. for 5 s. After spinning, the film was dried at 40 °C for 3 min and 100 °C for 5 min, and cooled down to ambient temperature. Then, the film was immersed in a 2-propanol solution containing CH_3NH_3I (0.04 M) and dried at 100 °C for 5 min. All deposition steps were carried out inside the glove box.

Hole transport material solution consisting of 72.3 mg Spiro-OMeTAD (2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) in 1 mL of chlorobenzene was prepared. Then, the solution was mixed with 28.8 μl of 4-tert-butylpyridine and 17.5 μL of a stock solution of 520 mg/mL bis(trifluoromethylsulfonyl)amine lithium salt and spin-coated onto the perovskite layers at 4000 r.p.m. for 30 s under air conditions. Finally, the PSCs were completed by thermal evaporation of 60 nm of gold counter electrode.

Characterization of nanorods, hierarchical nanorods and perovskite solar cells

The film morphologies, TiO_2 NR and HNR branches lengths and layer thicknesses were examined with a Field Emission Scanning Electron Microscopy using a Hitachi S4800

(FEG-SEM). The film structure was characterized by X-ray diffraction (XRD) at a grazing angle of 0.5° with a Rigaku Diffractometer (D/MAX 2200) using the CuKα ($\lambda = 1.54$ Å) radiation source.

PSCs current density–voltage (*J–V*) curves were recorded by a Keithley 2400 digital source meter and xenon arc lamp simulator (Sun 2000, ABET Technologies) with an AM 1.5G spectral filter. The power density was calibrated to 1 sun illumination (100 mW.cm^{-2}) with an NREL-calibrated Si solar cell. All the measurements were performed with a dark mask of 0.11 cm^2 and without encapsulation. The incident-photon-to-current-efficiency (IPCE) spectra were determined using a xenon lamp power source coupled with a monochromator controlled by a computer. The photocurrent was measured using an Oriel Instruments 70310 optical power meter and a Si photodiode to calibrate the system. Impedance spectroscopy measurements were carried out under illumination conditions and at different applied voltages by means of a FRA equipped PGSTAT-30 from Autolab, by applying a 20 mV voltage perturbation over the constant applied bias with the frequency ranging between 1 MHz and 0.1 Hz.

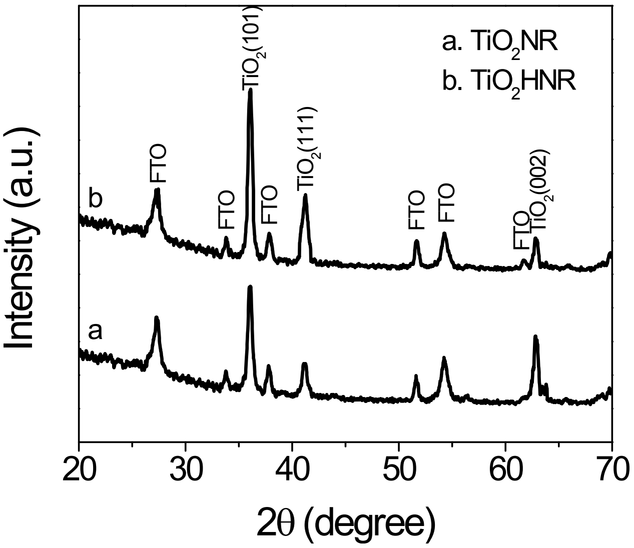

Figure S1: XRD patterns of TiO_2 films grown on FTO glass. (a) TiO_2 nanorods film. (b) TiO_2 hierarchical based on nanorods.

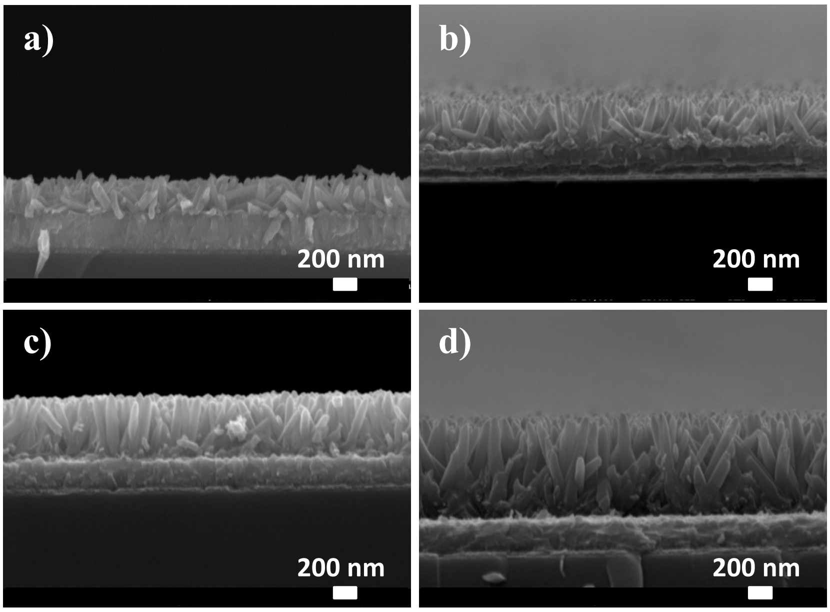

Figure S2: FESEM images of the TiO_2 nanorods grown by hydrothermal synthesis, using 25 ml of DI water, 25 ml of HCl and 1 ml of TTIP, at 180 °C for different growth time. a) 110 min (380 nm). b) 120 min (500 nm). c) 125 min (700 nm). d) 130 min (1100 nm).

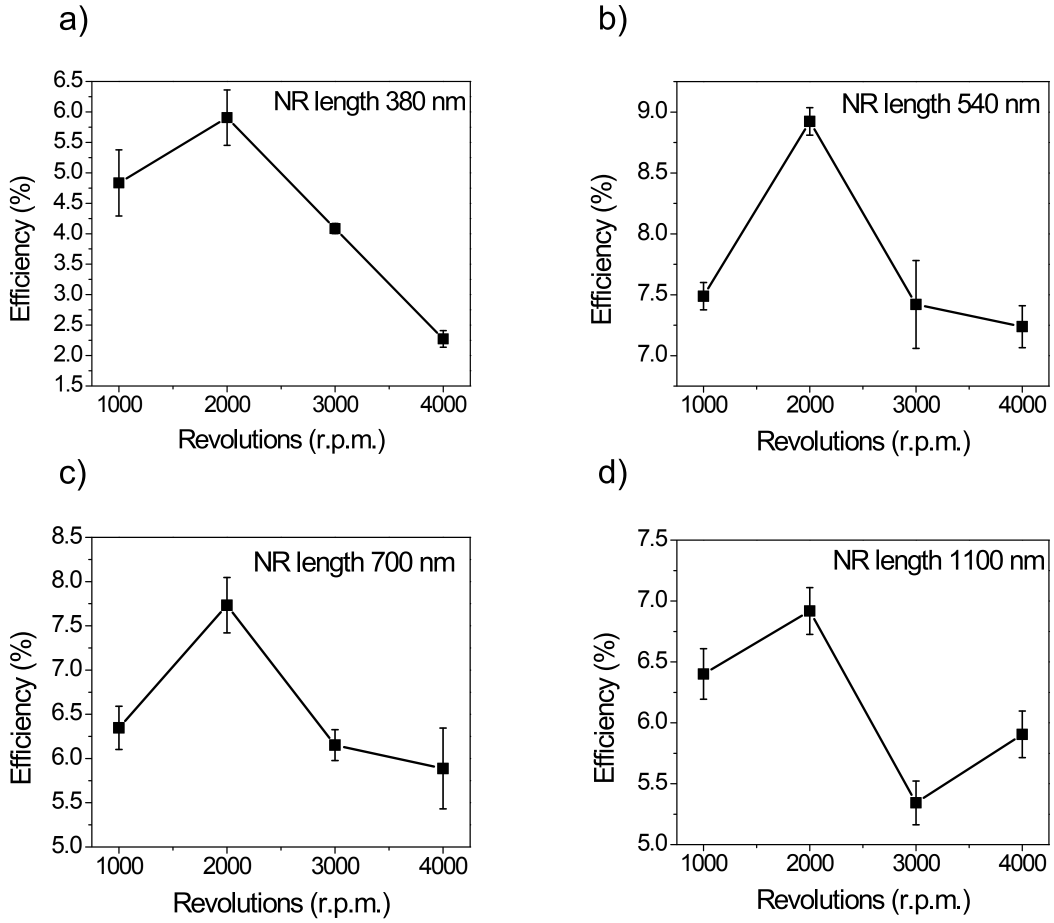

Figure S3: PCE values vs. spin rates at a different TiO_2 NR lengths. Error bars correspond to the standard distribution taking into account 10 devices prepared at each condition. (a) 380 nm. (b) 540 nm. (c) 700 nm. (d)1100 nm.

Table S1: Average *J/V* curves parameters and standard deviation based on ten NR PSCs at different NR lengths.

Length (nm)	**Jsc (mA/cm^2)**	**Voc (mV)**	**FF (%)**	**Efficiency (%)**
380	13.35 ± 0.79	807.95 ± 11.19	50.98 ± 0.63	5.91 ± 0.45
540	17.34 ± 0.15	803.91 ± 18.72	62.45 ± 0.95	8.92 ± 0.18
700	16.48 ± 0.86	797.67 ± 19.53	58.87 ± 1.51	7.73 ± 0.31
1100	15.31 ± 0.11	791.31 ± 15.73	57.11 ± 0.63	6.92 ± 0.22

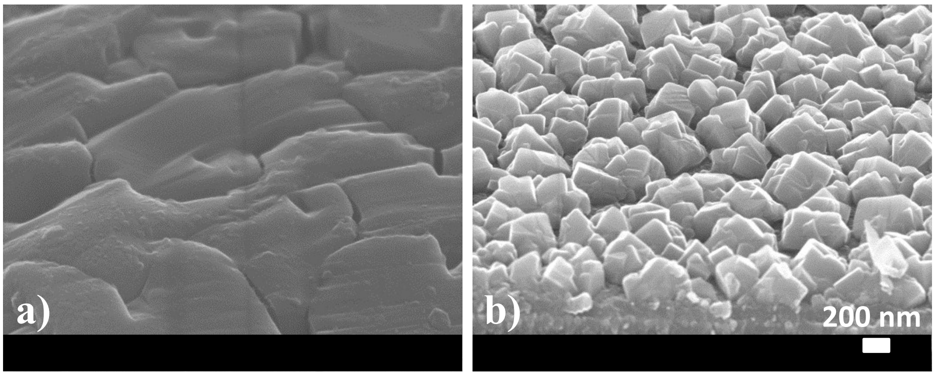

Figure S4: FESEM images of TiO_2 surface coverage using a different perovskite layer. a) Sing-MAICl b) Seq-MAI.

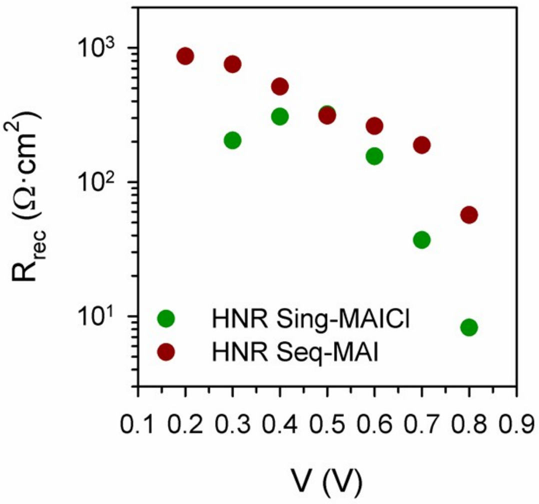

Figure S5: Comparison of R_{rec} for HNR samples using Seq-MAI and Sing-MAICl as light harvester.

References

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