Electronic Supplementary Information

An Acid-free Medium Growth of Rutile TiO_2 Nanorods Arrays and Their Application in Perovskite Solar Cells

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Experimental Section

Preparation of TiO_2 compact layer: FTO glasses were cleaned in ultrasonic bath of water, ethanol, acetone and 2-propanol in sequence, and treated in an O_2-plasma cleaner. The TiO_2 compact layer was dip-coated on an FTO substrate with a TiO_2 colloidal solution as report.[13] 1.8 mL DI water in 50 mL ethanol was added dropwise into a mixture solution containing 34 mL of tetrabutyl titanate and 8.3 ml of diethanolamine in 105 mL absolute ethanol. After dip-coating, the film was annealed at 500 °C for 30 min, providing a thickness of ~60 nm.

Hydrothermal synthesis of of TiO_2 NRs: Typically, the hydrothermal solution contains 33.0 mM (10.0 μL/ml) titanium (IV) tetraisopropoxide (TTIP), 100 mM Na_2EDTA and 2.5 vol.% glycerol in DI water. Firstly, 0.2 ml TTIP was mixed with 0.5 ml glycerol. After stirring for 5 min, 19.5 ml DI water and 0.745 g Na_2EDTA were added into the mixture, followed by heating at 70 °C for 1 hour. The mixed solution slowly turned into transparency at last, and was then transferred to a sealed container at 190 °C for several hours reaction. After cooling down to room temperature, the NR sample was rinsed with ethanol and DI water. Prior to use, the TiO_2 NR films was annealed at 450 °C for 30 min in the air. For solar cell application, the TiO_2 NRs with different length were prepared by adjusting the initial Na_2EDTA concentration in the hydrothermal solution.

Perovskite solar cell fabrication: PbI_2 (0.554 g/ml in N, N-dimethyl formamide) was spin-coated onto TiO_2 NR film at 6500 rpm. After annealing for 30 min on a 70 °C hotplate, the PbI_2-coated film was dipped into a 2-propanol solution containing 8

mg/ml CH_3NH_3I for about 80 min. During this period, the film turned from bright yellow to dark brown, indicating the formation of $CH_3NH_3PbI_3$ perovskite. Then the sample was rinsed with 2-propanol and dried on a 70 °C hotplate. A spiro-MeOTAD solution was prepared by dissolving 90 mg of spiro-MeOTAD in 1.2 ml of chlorobenzene, to which 35.9 μl of 4-tert-butyl pyridine and 27.3 μl of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 ml acetonitrile, Sigma-Aldrich, 99.8%) were added. The sprio-MeOTAD solution was spin-coated on the perovskite film at 5000 rpm for 30 s. Finally, gold electrode was thermally evaporated onto the spiro-MeOTAD-coated film to a thickness of ~60 nm.
Characterization: The morphological characterization of the TiO_2 NRs was tested by scanning electron microscopy (SEM) (FEI Quanta200F scanning electron microscope) and transmission electron microscopy (TEM) (Hitachi HF2000 and JEOL 4000EX transmission electron microscopes).

Lattice structural information was obtained on a Tecnai G2 spirit (FEI Company) instrument operated at 100 kV. The crystal phase was identified by X-ray diffraction (XRD) utilizing Rigaku MiniFlex diffractometer with a CuKα irradiation source at a scanning speed of 5 deg/min. UV–vis absorption measurement were carried out on a Varian Cary 5000UV–vis spectrophotometer. Raman spectrum of TiO_2 NRs was obtained on Renishaw inVia confocal Raman spectrometer.

The thickness of TiO_2 NR films (see Figure 3) are measured by surface profiling system DEKTAK 150.

The photocurrent density–voltage (J-V) characteristics of the solar cells were measured using a Keithley 2400 Source under illumination of a simulated sunlight (AM 1.5, 100 mW/cm2) provided by a solar simulator (Newport 69907) with an AM 1.5 filter. A black metal aperture of 0.09 cm^2 was used during the measurement to define the active area of the device and avoid light scattering through the sides. The incident photon-to-current efficiency (IPCE) was measured at DC mode with a 1/4m double monochromator (Crowntech DK242), a multimeter (Keithley 2000), and a light source (tungsten-halogen lamp, 150 W). The monochromatic light intensity for IPCE efficiency was calibrated with a reference silicon photodiode.

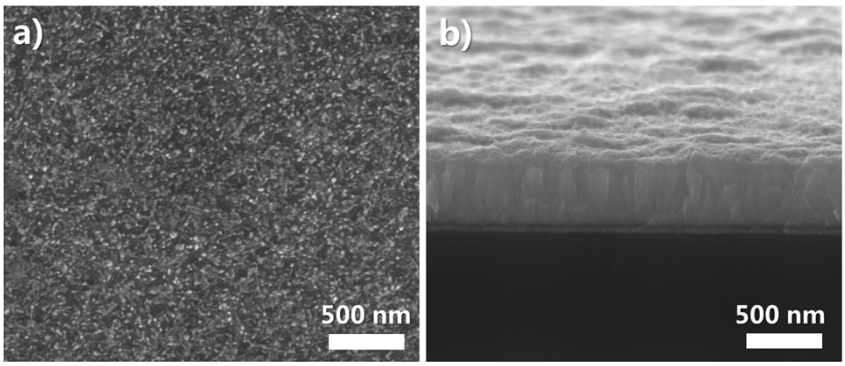

Figure S1 SEM images of TiO_2 nanoparticles synthesized with 25 mM Na_2EDTA, 33.0 mM TTIP (10.0 µl/ml aqueous solution), 2.5 vol.% glycerol in aqueous solution and growth time 3 h.

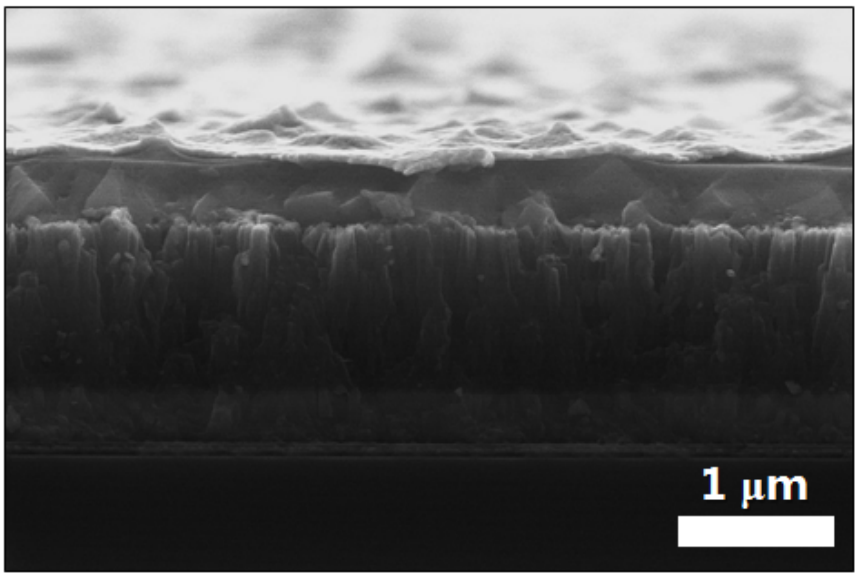

Figure S2 Cross-sectional SEM image of a perovskite solar cell device based on ~ 1.1 µm TiO_2 NR film.

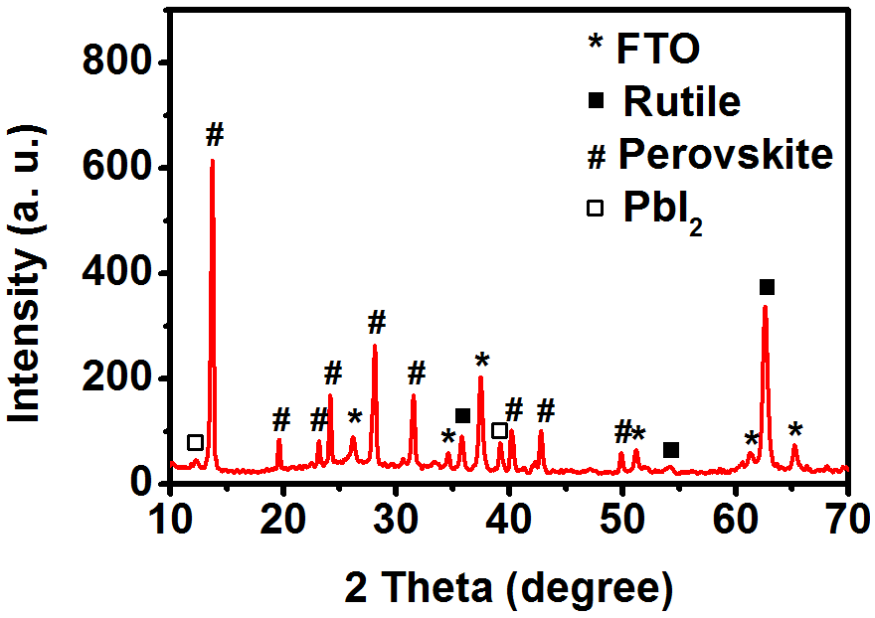

Figure S3 XRD pattern for the sample of ~1.1 μm TiO_2 NRs/ $CH_3NH_3PbI_3$

Table S1 All the J-V data for the studied devices at different NR film thicknesses (0.7~1.8 μm)

Thickness μm	J_{SC} mA/cm²	V_{OC} V	FF %	η %	Thickness μm	J_{SC} mA/cm²	V_{OC} V	FF %	η %
0.7	17.6	0.92	59.0	9.5	1.8	13.9	0.88	43.2	5.3
0.7	18.1	0.97	60.0	10.5	1.8	12.8	0.89	41.8	4.8
0.7	17.4	0.96	57.9	9.7	1.8	13.4	0.82	46.7	5.1
0.7	17.6	0.96	58.2	9.8	1.8	15.5	0.86	47.1	6.3
0.7	18.6	0.97	61.5	11.1	1.8	15.7	0.86	45.4	6.1
0.7	17.6	0.96	59.1	10.0	1.8	14.4	0.86	43.8	5.4
0.7	17.9	0.96	62.9	10.8	1.8	15.1	0.84	43.0	5.5
0.7	17.7	0.94	59.6	9.9	1.8	15.7	0.87	50.6	6.9
0.7	17.7	0.96	58.4	9.9	1.8	15.2	0.86	50.2	6.6
0.7	17.9	0.96	60.3	10.3	1.8	16.0	0.86	51.0	7.0
1.1	18.3	0.98	61.6	11.0	1.8	15.5	0.83	50.3	6.5
1.1	18.0	0.93	64.8	10.8	1.8	16.4	0.89	51.9	7.6
1.1	17.6	0.96	64.7	10.9	1.8	16.2	0.92	52.1	7.8
1.1	17.4	0.92	63.3	10.1	1.8	16.6	0.91	51.6	7.8
1.1	17.7	0.93	63.2	10.4	1.8	15.6	0.92	47.7	6.9
1.1	18.4	0.90	64.6	10.7					
1.1	18.4	0.89	62.4	10.2					
1.1	18.0	0.89	62.9	10.1					
1.1	18.1	0.88	61.9	9.9					
1.1	18.0	0.96	62.4	10.7					
1.4	16.8	0.90	52.3	7.9					
1.4	16.4	0.89	46.8	6.8					
1.4	16.9	0.95	49.0	7.9					
1.4	16.7	0.93	44.7	6.9					
1.4	16.9	0.91	56.4	8.7					
1.4	17.3	0.93	56.2	9.1					
1.4	17.7	0.86	51.9	7.9					
1.4	17.8	0.86	50.7	7.8					
1.4	17.0	0.87	49.3	7.3					
1.4	16.8	0.92	50.5	7.8					

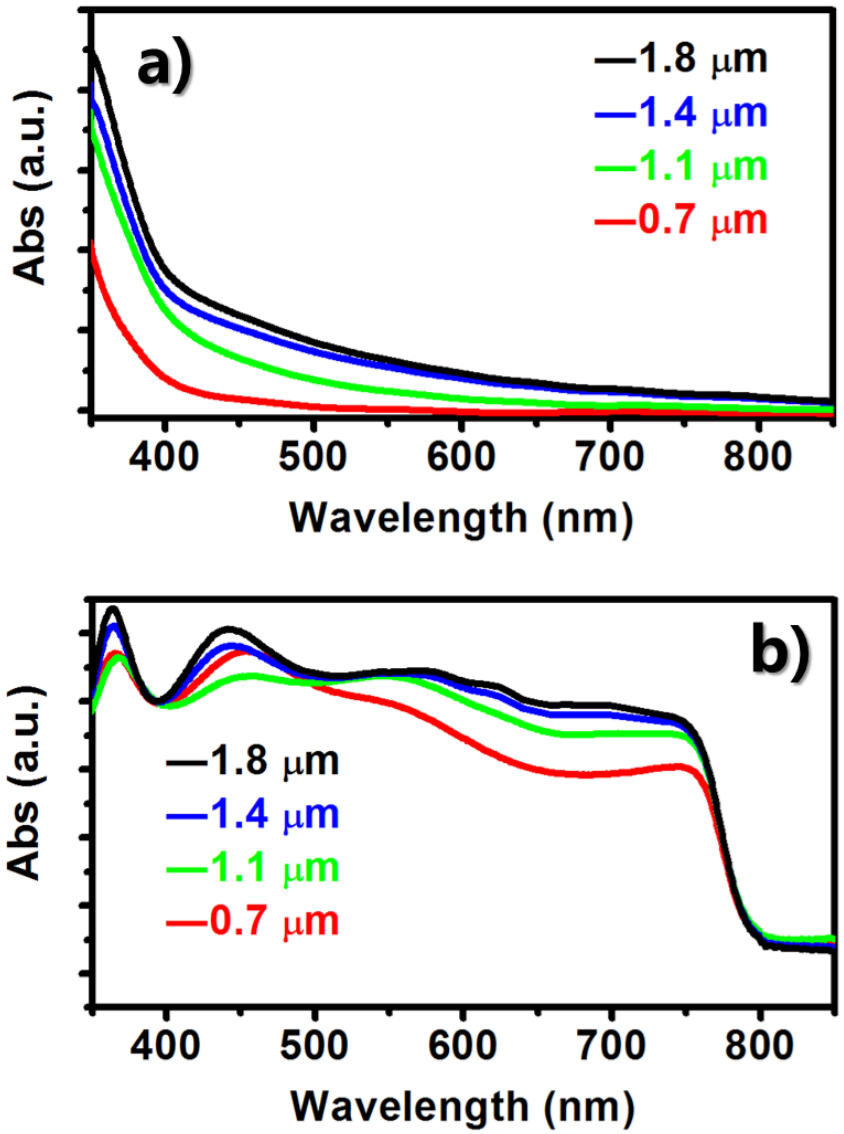

Figure S4 UV-vis absorption spectra for a) FTO/TiO_2 NRs and b) FTO/TiO_2 NRs/$CH_3NH_3PbI_3$ with different NR film thickness.

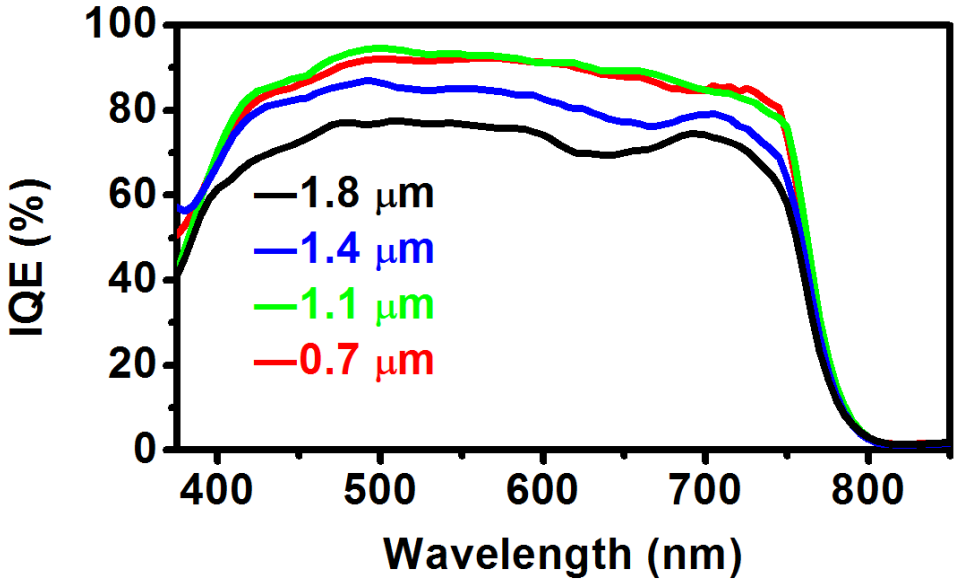

Figure S5 Internal quantum efficiency (IQE) spectrum for the perovskite solar cells base on different NR film thickness.

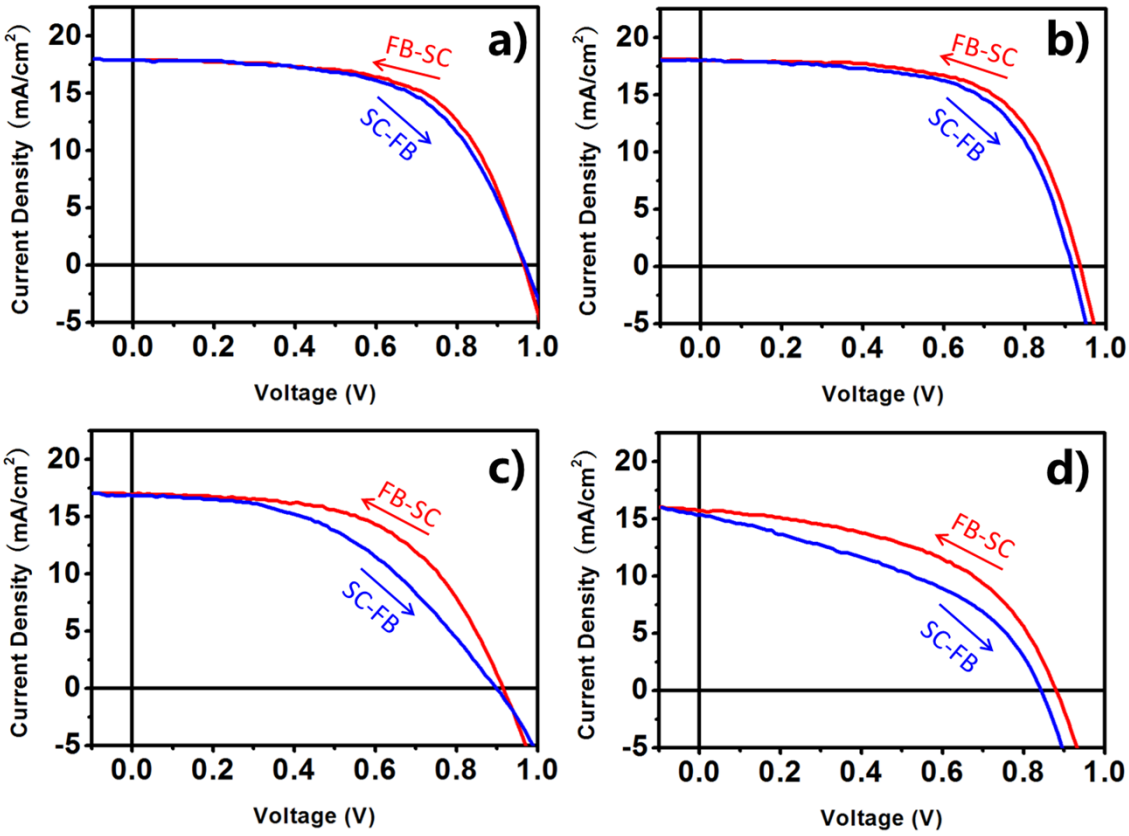

Figure S6 The J-V hysteresis depending on NR thickness: a) 0.7 μm, b) 1.1 μm, c) 1.4 μm and d) 1.8 μm. The device was scanned from forward bias to short circuit (FB-SC, red) and from short circuit to forward (SC-FB, blue) under simulated AM1.5G solar irradiation of 100 mW/cm^2 with a scan rate of ~0.1 V/s.