Electronic Supplementary Information

Rutile TiO_2 Nanowires Perovskite Solar Cells

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Experimental

Synthesis of TiO_2 blocking layer on FTO glass

FTO glass substrates were ultrasonicated in 7x detergent-water solution (1V:10V), isopropanol, acetone and ethanol sequentially. Distilled deionized water was used to rinse the substrates between each step. The washed FTO glass substrates were further cleaned with oxygen plasma for 15 mins before use. 0.2 M Ti(IV) bis(ethyl acetoacetate)-diisopropoxide in 1-butanol solution was sprayed onto the FTO substrates at 450°C on a hot plate, followed by annealing at 450 ℃ for 1 hour in air.

Synthesis of Different length of TiO_2 nanowire arrays on FTO:

Solvothermal method was used to synthesize rutile TiO_2 nanowire. FTO substrates coated with a blocking layer of TiO_2 thin film were loaded into a sealed Teflon-lined stainless steel reactor filled with 6 mL 2-butanone, 6 mL 37% hydrochloric acid and 0.5 mL tetrabutyltitanate, followed by keeping mixture at 200 °C for 40 minutes. The obtained substrates with nanowire arrays were cleaned by dipping in a H_2O_2 (30 wt%) /NH_4OH(25 wt%) (10:1 of volume ratio) solution for 10 min, followed by annealing at 450 °C for 30 min under O_2 atmosphere. The synthesize TiO_2 nanowire were soaked in 40mM $TiCl_4$ solution at 65 °C for 1 hour and then rinsed with DI water. After $TiCl_4$ treatment, TiO_2 nano-wires were annealed at 500 °C for 30 minutes.

Synthesis of TiO_2 mesoporous on FTO:

Analytical-grade reagents were used as supplied without further purification. Titanium isopropoxide 12 ml ($Ti(O^iPr)_4$, Aldrich, 97%) and 3ml propanediol were added dropwise into mixture of 80 ml water and 25ml acetic acid at 0 ℃. The mixture was heated to 78℃ over 1 h and held at this temperature with stirring for another 3.5 h. The resulting colloidal solution was concentrated to 100 ml via rotary evaporation. The mixture was and loaded into a Teflon insert titanium autoclave, heated to 200 ℃ over 1 h and held for 12h. 0.8g of the resulting mixture, 0.1ml terpineol and 0.025g methylcellulose were mixed under stirring for 2 hrs. The resulting paste was spread on FTO glass substrates by doctor blade and keep at 550 ℃ for 2 hrs.

Synthesis of CH_3NH_3I

Methylamine (19.5ml, 40 wt % aqueous solution, Aldrich) was added to hydroiodic acid (32.3ml, 57 wt % aqueous solution, Aldrich) slowly in an ice bath with stirring for 2 hrs. After extracted in a rotary evaporator at 50 °C, the brown product was filtered and washed by diethyl ether to yield white powders. Purification was conducted by recrystallization in ethanol and diethyl ether[1].

Synthesis of precursory perovskite $CH_3NH_3PbI_3$

0.289g of PbI_2 and 0.1g CH_3NH_3I (1:1 molar ratio) were dissolved in 0.52 ml γ-butyrolactone at 60 °C to produce precursory perovskite solution[2].

Hole transport material (HTM)

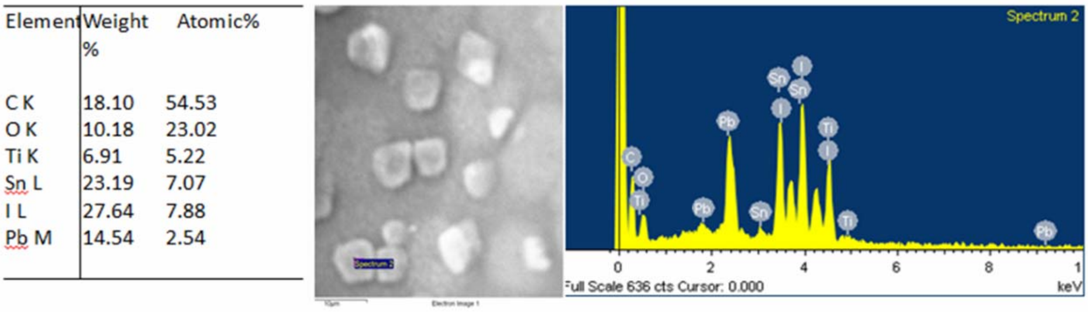
The HTM was prepared according to literature[3]. 92 mg 2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9’-spiro-bifluorene (spiro-MeOTAD), 7.2 mg Lithium bis-trifluoromethane sulfonimide, and 12 mg 4-tert-butylpyridine were dissolved in 1 ml chlorobenzene.

Device fabrication

Spin coating of Perovskite $CH_3NH_3PbI_3$ precursor was done with 2000 rmp for 1 min in dry air, followed by annealing in Ar at 105 °C for 10 minutes HTM layer was spin coated at 2500 rpm. Thermal coating of 80 nm Au film was conducted in an Edward 306A thermal evaporator.

Characterization

Scanning electron microscope (SEM) images were taken on Tescan SEM (model Vega II SBH). Potentiostat (Gamry Reference 600) and solar simulator (Photo Emission Inc. CA, model SS50B) were used to acquire the current density-voltage (*J*-*V*) curves at 200mV/s with step of 2 mV from low to high. The light harvesting spectrums, namely, diffusive reflectance of the devices, were taken on a Filmetrics F20-ExR thin film analyzer with a integrating sphere. Energy Dispersive Spectrometer (EDS) was taken on the SEM equipped with an INCAx-act Analytical Standard EDS Detector (Oxford Instruments). The open-circuit photovoltage transient was measured on Gamry Reference 600 at a resolution of 10 μs per data point. An ultrafast optical shutter is used (UniBlitz model LS6, 700 μs from full closure to full open, aperture is 6mm in diameter with a shutter driver model D 122) to control the incident sunlight. A commercial solid-state silicon photodiode (OSRAM Opto Semiconductor, BPX 61, response time 20ns, spectral range 400nm-1100nm, and active area 2.65mmx2.65mm=7mm^2) is used as a reference to verify the measurement limit of our setup. XRD was taken on X-ray powder diffractmeter (X'Pert PRO, PANalytical, Almelo, The Netherlands).



Element	Weight %	Atomic%
C K	18.10	54.53
O K	10.18	23.02
Ti K	6.91	5.22
Sn L	23.19	7.07
I L	27.64	7.88
Pb M	14.54	2.54

Figure S1. EDS analysis of $CH_3NH_3PbI_3$.

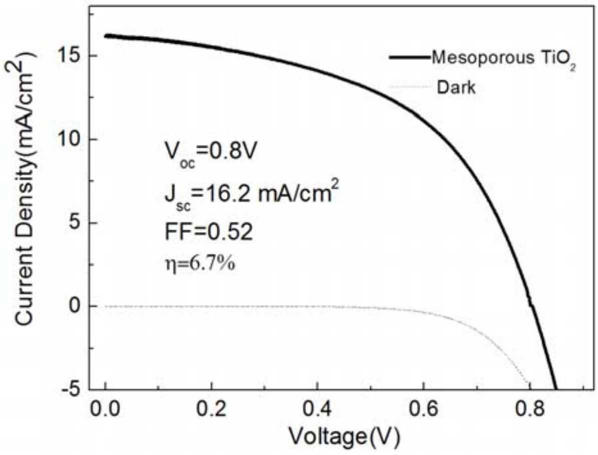


Figure S 2. J-V curves of perovskite solar cell with mesoporous TiO_2 as photoanode.

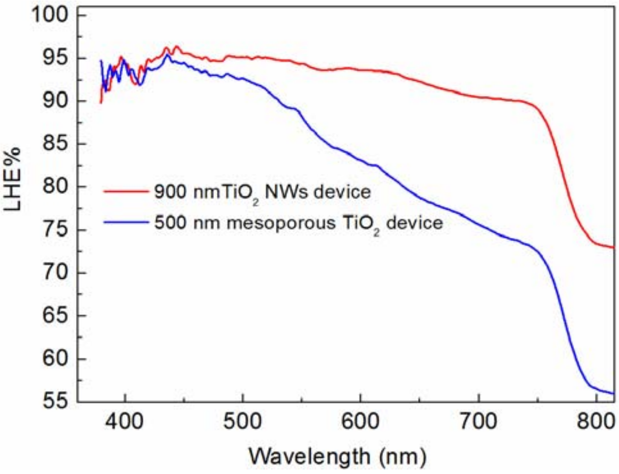


Figure S3. Light harvesting efficiency of devices with TiO_2 NWs and mesoporous TiO_2 as photoanodes.

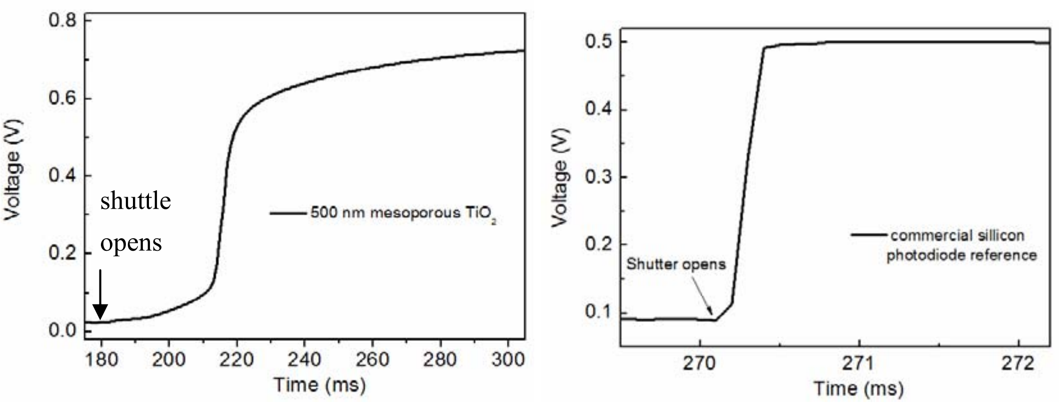


Figure S 4. Photovoltage rising transients of (a) a perovskite solar cell with mesoporous TiO_2 as photoanode with rising time of 110 ms and (b) a commercial Si-based photodiode (response time = 20ns) as reference.

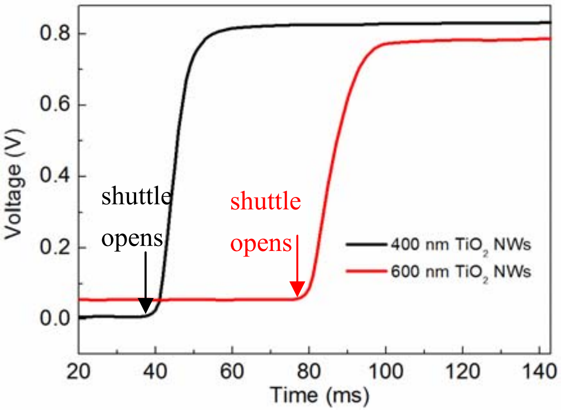


Figure S 5. Photovoltage rising transients of (a) a perovskite solar cell with 400 nm TiO_2 NWs as photoanode with 16.7ms rising time (b) 600 nm TiO_2 NWs as photoanode with 16.9 ms rising time.

It can be clearly seen that the response time of the photovoltage rising transient of the Si-based photodiode is approximately 0.70 ms, which is approximately the time needed for the shutter to go across the area of the Si photodiode. This value is much faster than that of the measured photovoltage rising kinetics of the perovskite solar cells, indicating that the kinetic limitation of our measurement system (e.g. shuttle speed) is far faster than the kinetics of the photovoltage rising transient of the perovskite solar cells studied herein. Thus, the measured photovoltage rising kinetics of the perovskite solar cells by our measurement system is warranted to be valid.

References

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