All-solid-state hybrid solar cells based on a new organometal halide perovskite sensitizer and one-dimensional TiO_2 nanowire arrays

Supporting Information

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Synthesis of TiO_2 nanowire arrays. TiO_2 nanowire arrays (NWAs) were synthesized on seeded FTO substrates by hydrothermal process.[22] FTO glasses (10 Ω/cm^2, Nippon Sheet Glass) were first cleaned ultrasonically 10 min in acetone, 10 min in ethanol and then rinsed with distilled water. After cleaning, TiO_2 seed layer (also played role as TiO_2 dense film) was deposited on FTO surface by spin coating of 100 μL 0.1 M TiO_2 sol solution with a spin coater (CAS, KW-4A) at rate of 3000 rpm for 30 s and then annealed in air at 550 °C for 30 min. The TiO_2 sol solution was obtained by dissolving equimolar tetrabutyl titanate and acetylacetone in 34 mL ethanol. Then a mixed solution composed of 0.13 mL hydrochloric acid (HCl, 37 wt%), 1.7 mL deionized water (H_2O) and 34 mL ethanol, were added dropwise to the above solution followed by stirring for 30 min at room temperature. The seeded substrates were loaded into a sealed Teflon-lined stainless steel reactor (23 mL volume), containing a mixture of 6.5 mL of deionized water, 6.5 mL of 37% HCl, and 200 μL of tetrabutyl titanate. The reactor was heated at 180 °C for 8 h to synthesize TiO_2 NWAs. To investigate the influence of film thickness, other growth time (4 and 12 h) was also employed in the hydrothermal process. The obtained TiO_2 NWAs samples were washed with ethanol and water, dried in air and annealed in air at 500 °C for 30 min.

Synthesis of organometal halide perovskite sensitizers. $CH_3NH_3PbI_3$ sensitizer was prepared according to the reported procedure with some modifications.[20,21,23,24] Typically, 0.3 mol (38 mL) methylamine (CH_3NH_2) solution (33wt% in absolute ethanol) was reacted with equimolar (40 mL) hydroiodic acid (HI) (57wt % in water) with stirring at 0 °C for about 2 h to synthesize methylammonium iodide (CH_3NH_3I). Crystallization of CH_3NH_3I was achieved using a rotary evaporator at 60 °C for 2~3 h. The obtained CH_3NH_3I power with equimolar lead(II) iodide (PbI_2) were dissolved in γ-butyrolactone with stirring at 60 °C for 6 h to produce a 2.5 mM $CH_3NH_3PbI_3$ precursor solution. Synthesis of $CH_3NH_3PbI_2Br$ was similar to $CH_3NH_3PbI_3$. First, 0.3 mol (38 mL) CH_3NH_2 solution (33wt% in absolute ethanol) was reacted with equimolar (34 mL) hydrobromic acid (HBr) (48wt % in water) with stirring at 0 °C for about 2 h to synthesize methylammonium bromine (CH_3NH_3Br). Then the as-synthesized solution was evaporated at 60 °C for 2~3 h to obtain CH_3NH_3Br power. $CH_3NH_3PbI_2Br$ precursor solution with concentration of 2.5 mM was finally obtained by dissolving equimolar CH_3NH_3Br and PbI_2 in N,N-Dimethylformamide with stirring at room temperature for 2 h.

Solar cell fabrication. The as-synthesized TiO_2 NWAs (1.5×1.5 cm) were spin-coated with 20 uL perovskite solutions at rate of 2000 rpm for 40 s and then annealed in air at 100 °C for 30 min. Before the spin coating process, the films were left stationary for 1 min for the infiltration of perovskite solutions onto the TiO_2 NWAs. After that, the hole transport material (HTM) solution (40 uL) containing 170 mM 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (*spiro*-OMeTAD), 180 mM 4-tert-butylpyridine (4-TBP), and 60 mM bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) in mixed solvent of chlorobenzene and acetonitrile (chlorobenzene: acetonitrile 20:1 v/v) was deposited onto the perovskite-sensitized TiO_2 film and left stationary for 1 min in order to penetrate the HTM solution into TiO_2 pores prior to spin coating. Then, the substrate was spun up to 2500 rpm for 40 s, followed by heating on a hot plate set at 100 °C for 20 min under N_2 atmosphere. Finally, a 50 nm Au layer was thermally evaporated on the HTM as counter electrode. The device area was defined as the overlap between the FTO anode and counter cathode (0.196 cm^2).

Characterization. The morphologies of the TiO_2 NWAs were characterized by field emission scanning electron microscope (FE-SEM; JEOL 6700F) operated at 5 kV. Further structural analysis of TiO_2 nanowire was carried out using transmission electron microscope (TEM; JEOL 2010F) operated at 200 kV. X-ray diffraction (XRD) patterns of the samples were obtained using a diffractometer (Philips, PW-1830) with Cu Kα radiation at scan rate of 4°/min under operation condition of 30 kV and 40 mA. Elemental composition of the perovskite sensitizers on TiO_2 NWAs film was investigated by energy dispersive X-ray spectroscope (EDS; Oxford INCA Energy) attached to the SEM and the distribution of the perovskites in TiO_2 NWAs was analyzed by mapping technique. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed on the perovskite-sensitized TiO_2 film using a photoelectron spectrometer (Kratos Analytical, AXIS-ultra-DLD) with He (I) excitation of 21.22 eV and pass energy of 5 eV. Fabricated photovoltaic cells were characterized by current-voltage (*J*-*V*) characteristics and incident photon-to-current conversion efficiency (IPCE). Photocurrent and voltage were measured by a solar simulator (Oriel, 450 W Xe lamp, AM 1.5 global filter) equipped with an electrochemical workstation (Zahner, Zennium). The light source was calibrated to 1 sun (100 mW/cm^2) using an optical power meter (Newport, model 1916-C) equipped with a Newport 818P thermopile detector. IPCE measurements were carried out with Zahner Zennium CIMPS-PCS system established with the tunable light source (TLS).

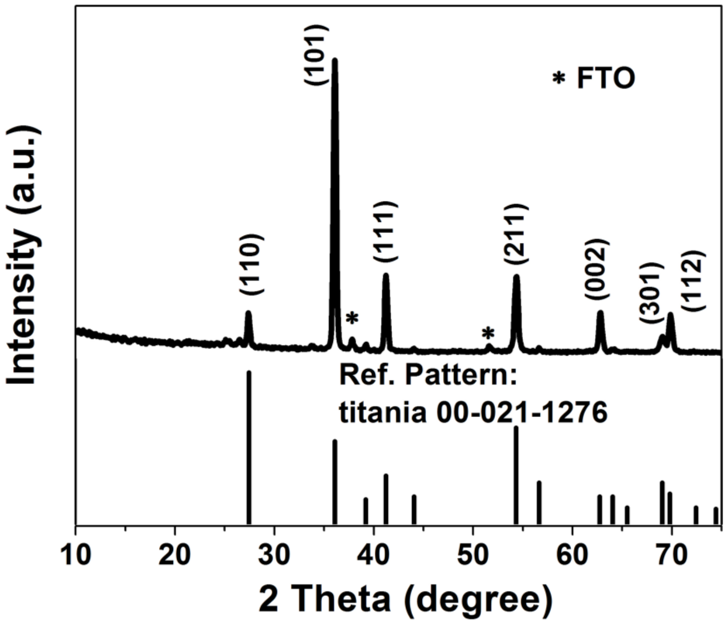


Fig. S1 XRD pattern of TiO_2 NWAs grown on FTO substrate (asterisks stands for FTO).

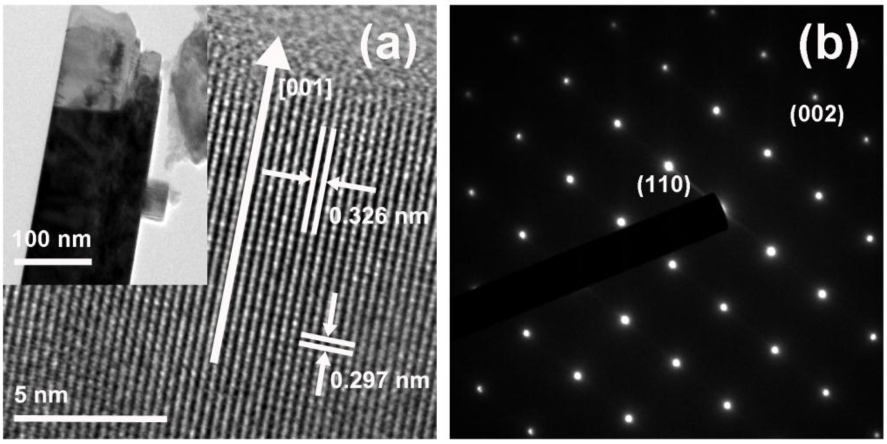


Fig. S2 (a) TEM (insert) and HRTEM images of TiO_2 nanowire. (b) Selected area electron diffraction (SAED) of TiO_2 nanowire.

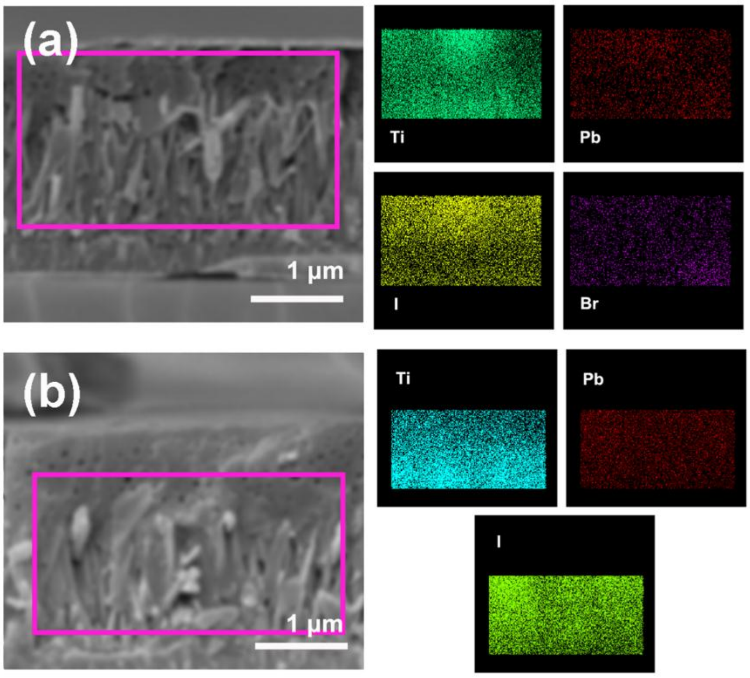
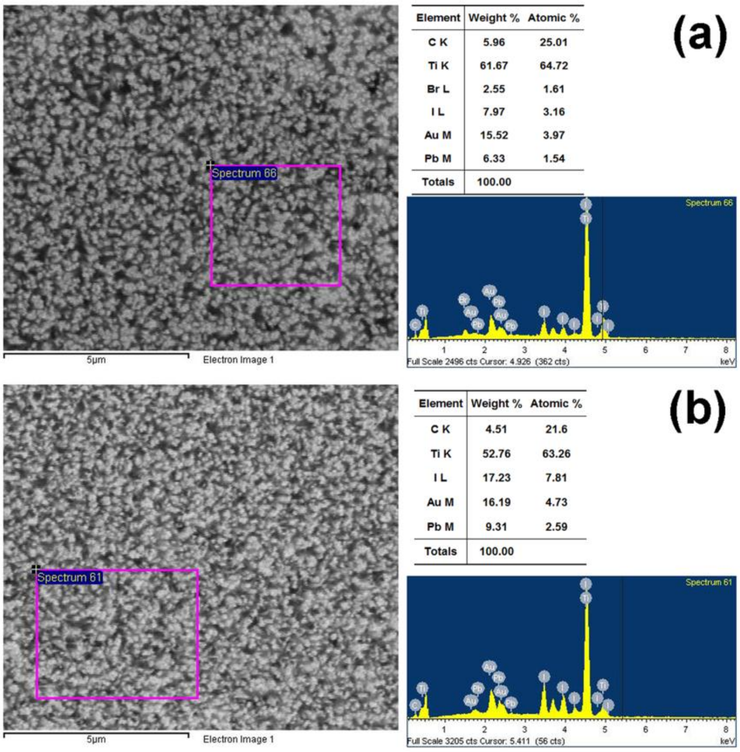


Fig. S3 EDS with elemental mapping results from the cross-sectional SEM of the photovoltaic cells based on (a) $CH_3NH_3PbI_2Br$ and (b) $CH_3NH_3PbI_3$ sensitizers.



Element	Weight %	Atomic %
C K	5.96	25.01
Ti K	61.67	64.72
Br L	2.55	1.61
I L	7.97	3.16
Au M	15.52	3.97
Pb M	6.33	1.54
Totals	100.00	

Element	Weight %	Atomic %
C K	4.51	21.6
Ti K	52.76	63.26
I L	17.23	7.81
Au M	16.19	4.73
Pb M	9.31	2.59
Totals	100.00	

Fig. S4 EDS spectra for the (a) $CH_3NH_3PbI_2Br$ and (b) $CH_3NH_3PbI_3$ sensitized TiO_2 NWAs.

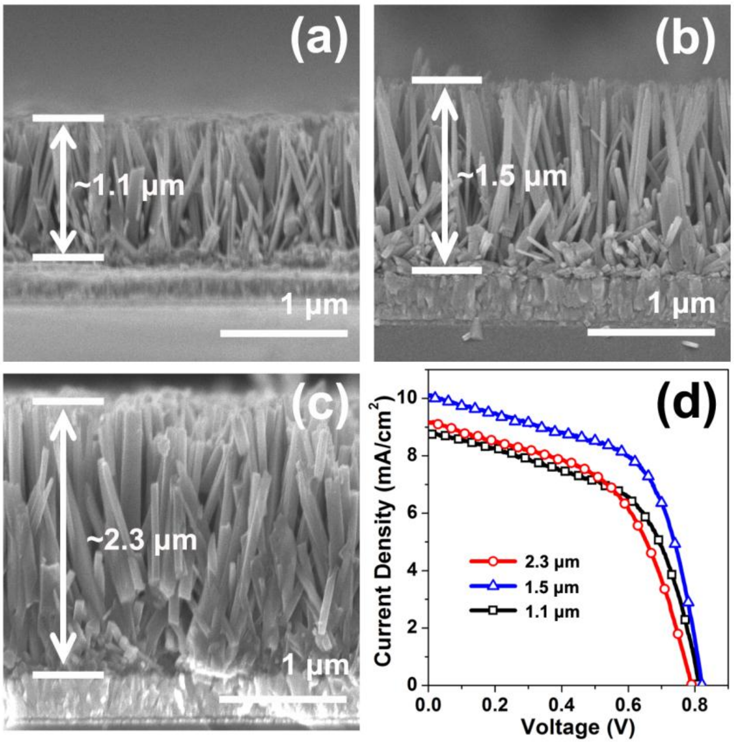


Fig. S5 Cross-sectional SEM images of TiO_2 NWAs with different film thickness obtained at different growth time: (a) 4 h, (b) 8 h and (c) 12 h. (d) Photovoltaic properties of hybrid solar cells based on $CH_3NH_3PbI_2Br$ and TiO_2 NWAs with different film thickness.

Table S1 Photovoltaic properties of the hybrid solar cells based on the $CH_3NH_3PbI_2Br$ perovskite sensitizer and 1D TiO_2 NWAs with different film thickness

Film thickness	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
Sample (a) (~1.1 μm)	8.82	0.81	0.55	3.95
Sample (b) (~1.5 μm)	10.12	0.82	0.59	4.87
Sample (c) (~2.3 μm)	9.30	0.79	0.52	3.78

[a] The estimated error is ±5%. 1D TiO_2 NWAs with different film thickness were obtained by varying the hydrothermal growth time (t): Sample (a) 4 h, Sample (b) 8 h, Sample (c) 12 h; Growth temperature: T = 180 °C.