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Supporting Information

Study on Hole-Transport-Material-Free Planar $TiO_2/CH_3NH_3PbI_3$ Heterojunction Solar Cells: the Simplest Configuration of a Working Perovskite Solar Cells

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Experimental

Materials

Ethanol, acetone, diethyl ether, *N*, *N*-dimthylformamide (DMF) were purchased from Shanghai Chemical Agent Ltd., China (Analysis purity grade). Lead iodide (PbI_2), hydroiodic acid (57 wt% in water), methylamine (33 wt% in ethanol), titanium tetrachloride ($TiCl_4$) and titanium isopropoxide were purchased from Aladdin. The above agents were used without further purification.

Methods and Device Fabrication

Preparation of CH_3NH_3I. CH_3NH_3I was synthesized by reacting 25 mL methylamine (33 wt% in absolute ethanol) and 10 mL of hydroiodic acid (57 wt% in water) in 250 mL round bottomed flask at 0 °C for 2 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing solvents at 50 °C for 2 h. The product was washed with diethyl ether by stirring the solution for 30 min, which was repeated for three times, and then dried at 60 °C in vacuum oven for 24 h.

Solar Cells Fabrication. FTO glass (Nippon, sheet resistance 14 Ω/sq) was firstly patterned by etching with Zn powder and 2 M HCl. Substrates were then cleaned sequentially in deionized water, ethanol, acetone, and O_3 plasma. The cleaned substrates were spin-coated using a mildly acidic solution of titanium isopropoxide in ethanol at 2000 rpm for 30 s, and annealed at 500 °C for 30 min in air. Subsequently, the substrates were immersed in 50 mM $TiCl_4$ solutions at 70 °C for 35 min and then dried at ambient atmosphere, followed by annealing at 500 °C for 30 min in air to form a compact anatase TiO_2.

The $CH_3NH_3PbI_3$ absorber layer was grown by CH_3NH_3I vapor assisted solution method. At the beginning, solution of 400 mg/mL PbI_2 in DMF were spin coated on the TiO_2 film at a desired speed for 30 s and then heat treated at 100 °C for 10 min to remove the DMF solvent. After cooling to room temperature, the film was spin-coated with the 400 mg/mL PbI_2 in DMF for a second time to get a relatively thick and smooth film. After the spin-coating process, PbI_2 films were heat-treated at 100 °C for another 10 min. Subsequently, the PbI_2 films were reacted with CH_3NH_3I vapor at desired temperature for desired time durations in N_2 gas atmosphere in a single zone tube furnace. Finally, Au was deposited (K550X Sputter Coater) as electrode of the solar cells at an atmospheric pressure of 0.1 mbar for work functions matching.

Characterization

Scanning electron microscopy (SEM) images were obtained with an FEI-SEM (FEI Sirion 200). X-ray diffraction (XRD, X' Pert Pro MPD) was measured with a Bruker X-ray diffractometer with Cu Kα (λ= 0.154056 nm) as the radiation source. UV-vis absorption was measured with UV-vis spectrophotometer (Shimadzu SolidSpec-3700) with wavelength ranging from 300 to 900 nm. The solar cells were illuminated using a solar simulator (Oriel 3A) at one sun (AM 1.5, 100 mW cm^{-2}), and the *J*-*V* characteristics were measured by using a Keithley 2400 electrometer. The solar cells were masked with a black aperture to define the active area of 0.09 cm^{-2}. Electrochemical Impedance spectroscopy (EIS) was measured with an IM6ex electrochemical workstation under dark conditions and 1 sun illumination conditions with a sunlight simulator of 100 mW/cm^2 (AM 1.5). The scanning frequency was set between 1 Hz and 1 MHz and the amplitude of the sine perturbation bias was 10 mV. Different dc positive bias was also applied when measuring. Capacitance-voltage measurements were performed at fixed frequencies of 1 kHz in the dark. All measurements were carried out in air at room temperature.

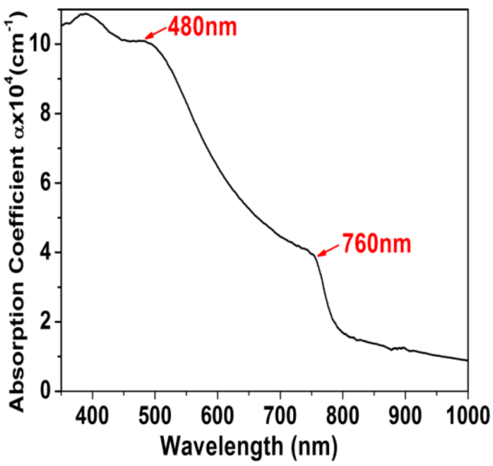

Figure S1. The absorption spectra of $CH_3NH_3PbI_3$ films prepared by reacting PbI_2 precursor films spin-coated at 2750 r/min with CH_3NH_3I at 175 °C in N_2 for 3h: absorption coefficient α vs. wavelength.

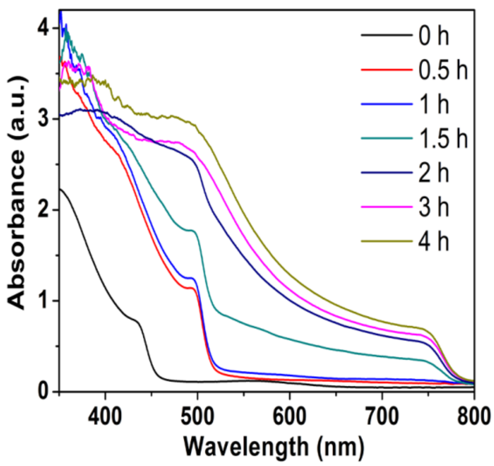

Figure S2. UV-visible absorption spectra of $CH_3NH_3PbI_3$ films prepared by reacting PbI_2 precursor films spin-coated at 2750 r/min with CH_3NH_3I at 175 °C in N_2 for different annealing time: 0h, 0.5h, 1h, 1.5h, 2h, 3h, and 4h, respectively.

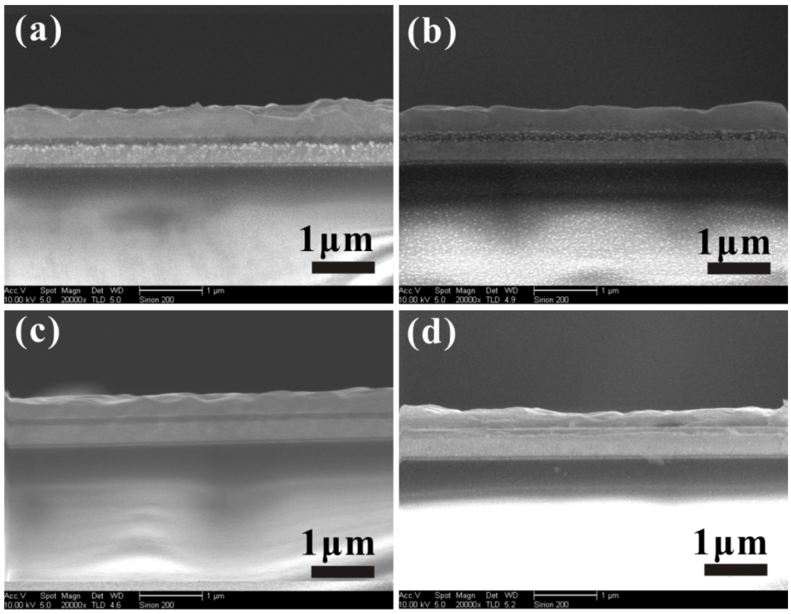

Figure S3. Cross-sectional SEM images of $CH_3NH_3PbI_3$ films of different thickness prepared by reacting PbI_2 precursor films with CH_3NH_3I at 175 °C in N_2 atmosphere for 3 h via changing spin-coating speed: (a) 2000 r/min, (b) 2500 r/min, (c) 2750 r/min, and (d) 3000 r/min.

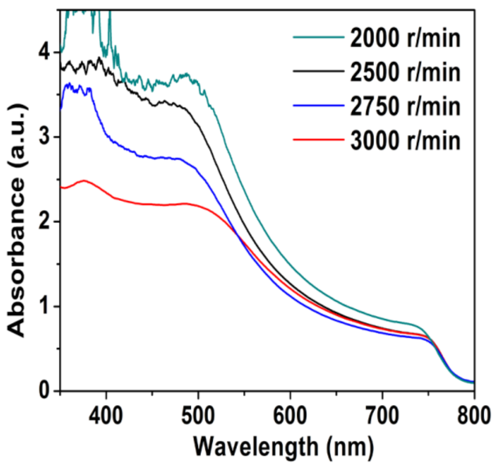

Figure S4. UV-Visible absorption spectra of $CH_3NH_3PbI_3$ films prepared by reacting PbI_2 precursor films with CH_3NH_3I at 175 °C in N_2 atmosphere for 3 h via changing spin-coating speed: (a) 2000 r/min, (b) 2500 r/min, (c) 2750 r/min, and (d) 3000 r/min.

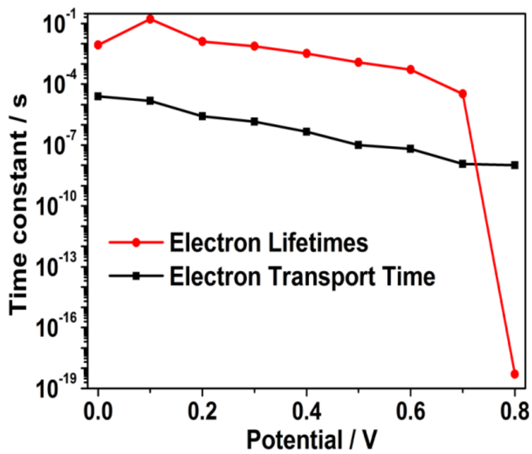

Figure S5. Electron transport time, τ_{trans} (black squares) and lifetime, τ_n (red circles) of the planar HTM-free $CH_3NH_3PbI_3$ solar cells in the dark based on $CH_3NH_3PbI_3$ films prepared by reacting PbI_2 precursor films with CH_3NH_3I at 175 °C in N_2 atmosphere for 3 h with spin-coating speed of 2750 r/min.

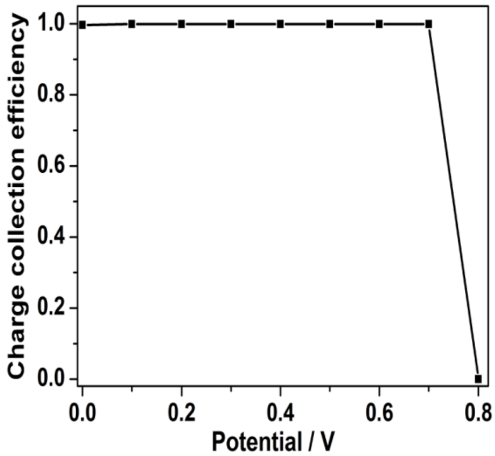

Figure S6. Charge collection efficiency calculated from the R_{trans} and R_{ct} of the planar HTM-free $CH_3NH_3PbI_3$ solar cells in the dark based on $CH_3NH_3PbI_3$ films prepared by reacting PbI_2 precursor films with spin-coated speed of 2750 r/min with CH_3NH_3I at 175 °C in N_2 atmosphere for 3 h.

Table S1. Summary of photovoltaic parameters, V_{oc}, J_{sc}, FF, η, R_s, and R_{sh} for planar HTM-free $CH_3NH_3PbI_3$ solar cells based on $CH_3NH_3PbI_3$ thin films prepared by reacting PbI_2 precursor films spin-coated at 2750 r/min with CH_3NH_3I at 175 °C in N_2 atmosphere for different reaction time duration.

Time (h)	V_{oc} （V）	J_{sc} (mA/cm^2)	**FF** (%)	η (%)	R_s (Ω)	R_{sh} (Ω)
4	0.70	14.70	37.13	3.80	256	1117
3	0.76	21.57	58.18	9.52	80	5554
2	0.73	10.44	52.41	3.97	279	2092
1.5	0.66	4.50	35.48	1.05	726	37766
1	0.056	1.78	19.01	0.019	308	317
0.5	0.27	0.0003	31.77	0	7752985	283145

Table S2. Summary of parameters, film thickness, V_{oc}, J_{sc}, FF, η, R_s, and R_{sh} for planar HTM-free $CH_3NH_3PbI_3$ solar cells based on different thickness $CH_3NH_3PbI_3$ thin films being prepared by reacting PbI_2 precursor film with CH_3NH_3I at 175 °C in N_2 atmosphere for 3 h via changing spin-coating speed.

Speed (r/min)	**Thickness (nm)**	V_{oc} (V)	J_{sc} (mA/cm^2)	**FF (%)**	η (%)	R_s (Ω)	R_{sh} (Ω)
2000	500±5	0.72	12.39	42.96	3.82	203	2850
2500	400±5	0.74	18.0	58.0	7.74	125	2198
2750	330±5	0.76	21.57	58.18	9.52	80	5554
3000	280±5	0.73	16.32	33.41	4.00	216	855

Table S3. Stability of planar HTM-free $CH_3NH_3PbI_3$ solar cells based on $CH_3NH_3PbI_3$ films being prepared by reacting PbI_2 precursor film with spin-coated speed of 2750 r/min with CH_3NH_3I at 175 °C in N_2 atmosphere for 3 h. Summary of solar cell performance parameters, V_{oc}, J_{sc}, FF, η, R_s, and R_{sh} stored under ambient conditions for different days.

Time (Days)	V_{oc} (V)	J_{sc} (mA/cm^2)	**FF (%)**	η (%)	R_s (Ω)	R_{sh} (Ω)
0	0.76	21.57	58.18	9.52	80	5554
2	0.75	21.24	59.61	9.54	79	6586
7	0.76	20.5	55.06	8.6	99	7023
31	0.72	20.25	51.34	7.74	163	3267
91	0.71	17.72	46.29	5.81	142	2917