Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information for

Tunable hysteresis effect for perovskite solar cells

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Experiment

Materials

Unless stated otherwise, all materials were purchased from Sigma-Aldrich or Acros Organics and used as received. CH_3NH_3I was synthesized and purified according to literature procedures[1]. The perovskite precursor solution was prepared by dissolving 573.0 mg PbI_2, 197.5 mg CH_3NH_3I and 13.70 mg 5-AVAI in 1.0 ml γ-butyrolactone (GBL), and stirred at 70 °C for 30 min. The TiO_2, ZrO_2 and carbon pastes were prepared as previously reported[2, 3].

Device fabrication.

Unless stated otherwise, the whole device fabrication process was carried out under ambient conditions (RH25-35%). The FTO-coated glass substrates (Tec15, Pilkington) were first etched by laser and cleaned by ultrasonication with detergent, deionized water, acetone and ethanol. The c-TiO_2 layer was then deposited on the patterned substrates by aerosol spray pyrolysis as follow: The patterned FTO substrate was placed on a hotplate with a mask, as shown in Figure S1, and heated up to 450 °C. A titanium diisopropoxide bis(acetylacetonate) solution was diluted in ethanol (1:39, volume ratio), and kept in a glass sprayer which was purchased from Sigma-Aldrich. The distance between the sprayer and the hotplate was ~10 cm, and the spraying angle was 60-70 degree. The carrier gas was oxygen with a flow rate of ~10 ml/s. The sprayer moved at a speed of ~10 cm/s, along the red line marked spraying path in Figure S1. After spraying, the c-TiO_2 coated FTO substrate was sintered at 450 °C for 30 min. After cooling to room temperature (RT, 25 °C), a 1 μm-thick mesoporous TiO_2 layer, a 2 μm-thick ZrO_2 spacer layer and a 10 μm-thick carbon layer were screen-printed on the substrates layer by layer. The TiO_2 layer and ZrO_2 layer were sintered at 450 °C for 30 min, and the carbon layer was sintered at 400 °C for 30 min, forming the mesoporous triple-layer based scaffold. After cooling to room temperature, the perovskite precursor solution was infiltrated by drop casting *via* the top of the carbon layer. After drying at 50 °C for one hour, the printable mesoscopic PSCs were obtained.

Characterization

The thickness of the films was measured by a profilometer (DektakXT, Bruker). The atomic force microscope (AFM) measurements were performed on SPM9700 (Shimadzu). Photocurrent-density voltage (*J-V*) curves were characterized with a Keithley 2400 source meter and a Newport solar simulator (model 91192). The power of the simulated light was calibrated to 100 mW cm^{-2} using a Newport Oriel PV reference cell (model 91150V). The active area of the device is about 0.8 cm^2 and a black mask with a circular aperture (0.126 cm^2) was applied for *J-V* measurements. The *J–V* testing was performed with forward and backward scan directions at a scan rate of 250 mV s^{-1}, 100 mV s^{-1}, 50 mV s^{-1}, and 25 mV s^{-1} (sweep delay time of 100 ms). Before *J-V* scans, the devices were usually subjected to the simulate sun light for several minutes. All the measurements were carried out at RH25-35% and room temperature.

Table S1 Dependence of hysteresis effect on spraying cycles of c-TiO_2 and UV-Ozone treatment. The hysteresis effect has been defined as normal, free and inverted.

Condition	c-TiO_2 × 1	c-TiO_2 × 2	c-TiO_2 × 3	c-TiO_2 × 4
UV-Ozone 0 min	Normal	Normal	Normal	Normal
UV-Ozone 2.5 min	Inverted	Free	Normal	Normal
UV-Ozone 10 min	Inverted	Inverted	Normal	Normal
UV-Ozone 30 min	Inverted	Inverted	Free	Normal

Table S2. Series resistance and shunt resistance of hysteresis-normal, hysteresis-free, and hysteresis-inverted devices measured at different scan directions and scan rates (R_S: Ω cm^2; R_{SH}: kΩ cm^2).

	F-R scan		R-F scan		F-R scan		R-F scan		F-R scan		R-F scan		F-R scan		R-F scan	
	25 mV s^{-1}				50 mV s^{-1}				100 mV s^{-1}				250 mV s^{-1}			
	R_S	R_{SH}	R_S	R_{SH}	R_S	R_{SH}	R_S	R_{SH}	R_S	R_{SH}	R_S	R_{SH}	R_S	R_{SH}	R_S	R_{SH}
Normal	6.27±0.24	0.59±0.16	6.49±0.30	0.53±0.40	6.15±0.21	0.71±0.21	5.87±0.19	0.28±0.10	5.95±0.14	0.71±0.34	5.48±0.12	0.49±0.26	5.46±0.20	0.45±0.27	5.53±0.15	0.20±0.07
Free	6.60±0.13	0.50±0.27	7.24±0.26	0.66±0.4	6.24±0.21	0.36±0.22	7.02±0.18	1.22±0.48	6.19±0.1	0.51±0.23	6.62±0.16	0.4±0.24	6.42±0.21	0.51±0.27	6.53±0.02	0.43±0.21
Inverted	6.25±0.22	0.58±0.13	6.49±0.26	0.36±0.14	6.15±0.19	0.69±0.19	5.88±0.17	0.38±0.25	5.95±0.14	0.71±0.34	5.48±0.12	0.49±0.26	5.51±0.20	0.56±0.35	5.52±0.13	0.29±0.20

Table S3 Fitting decay times of time-resolved photoluminescence (TRPL) spectra. The semi-devices were fabricated as FTO/c-TiO_2/m-TiO_2/ZrO_2/Perovskite, and the c-TiO_2 layers were sprayed with 1-4 cycles.

c-TiO_2 cycle	**τ_1 (ns)**	**τ_2 (ns)**
1	1.12	33.91
	1.16	36.48
	1.10	36.89
2	2.16	51.29
	1.29	37.90
	1.11	38.39
3	1.23	39.95
	1.19	37.68
	1.18	37.58
4	1.46	40.05
	1.39	39.57
	1.21	40.66

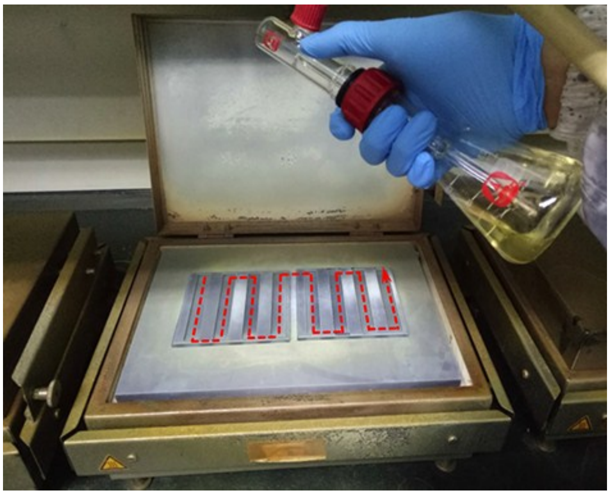

Fig. S1 The spraying deposition process of the compact-TiO_2 (c-TiO_2) layer. The sprayer is purchased from Sigma-Aldrich, and the carrier gas is N_2 with a flow rate of ~10 ml/s.

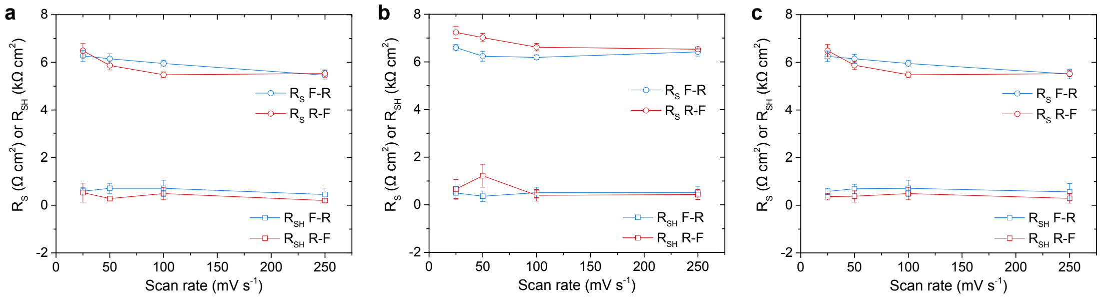

Fig. S2 The dependence of R_S and R_{SH} on scan rates for hysteresis-normal, hysteresis-free and hysteresis-inverted devices.

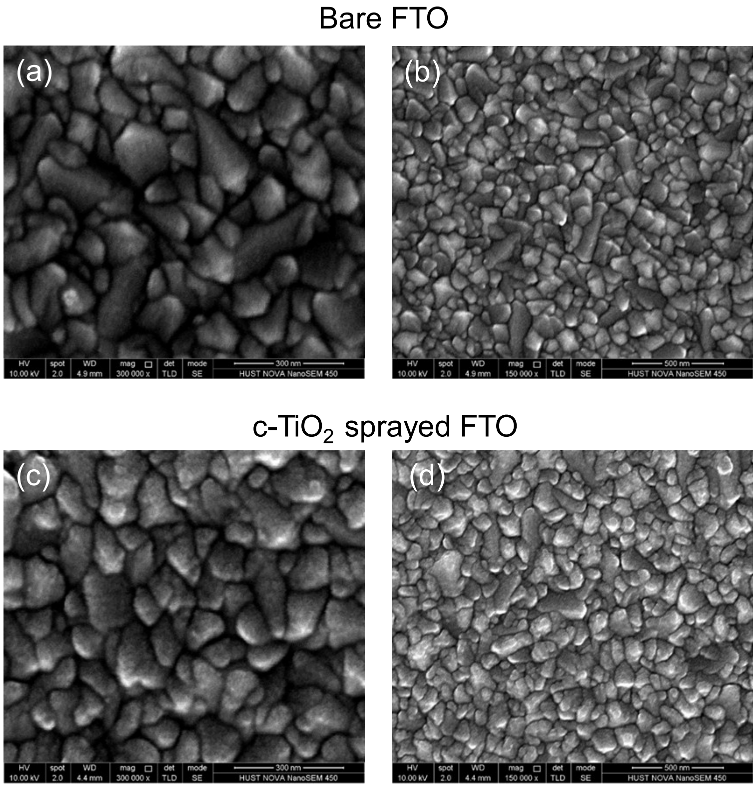

Fig. S3 Surface morphology characterizations. The SEM images of the bare FTO substrate (a, b) and c-TiO_2 sprayed (two cycles) FTO substrate (c, d).

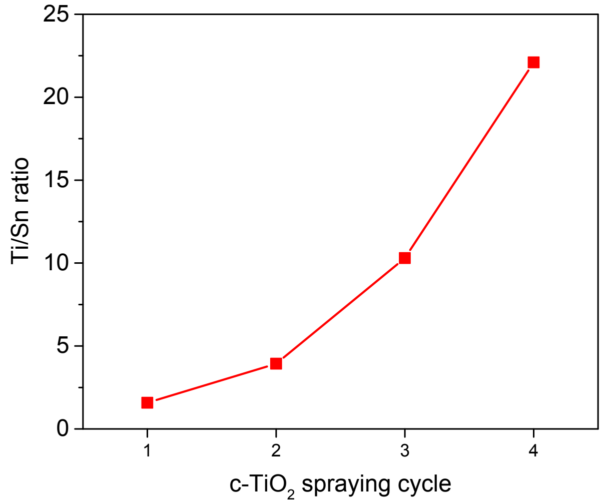

Fig. S4 XPS results of FTO substrates sprayed with 1-4 cycles of c-TiO_2 layer. The measurements were performed using the same accumulation time, and the Ti and Sn peak areas are compared.

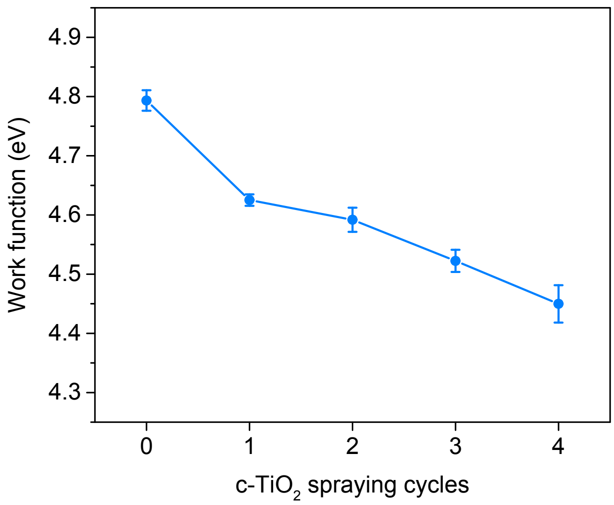

Fig. S5 Work function of FTO substrates sprayed with 0-4 cycle of c-TiO_2 layer (Error bars represent *s.d.* calculated from five values obtained with the same testing parameters).

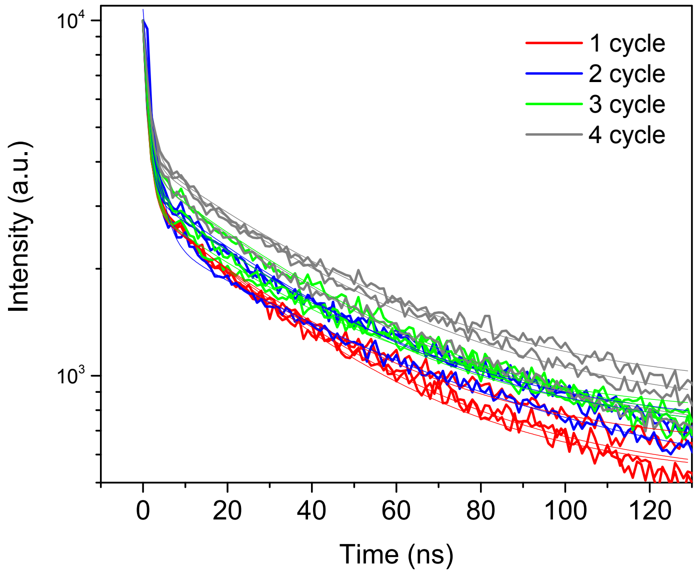

Fig. S6 Time-resolved photoluminescence (TRPL) spectra of FTO/c-TiO_2/m-TiO_2 /ZrO_2/Perovskite semi-devices. The c-TiO_2 layers were sprayed with 1-4 cycles. For each spraying cycle, three samples were prepared and characterized.

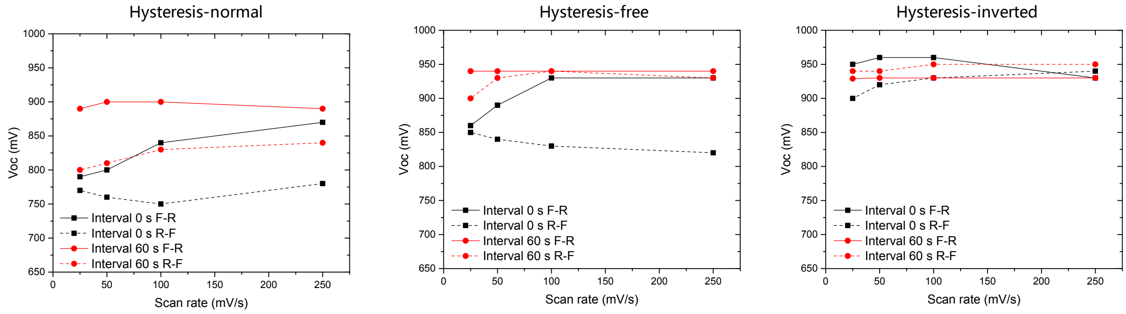

Fig. S7 Dependence of V_{OC} on scanning rates. The hysteresis-normal, -free and -inverted devices were continuously scanned with an interval of 0 s or discontinuously scanned with an interval of 60 s at 250 mV s^{-1}, 100 mV s^{-1}, 50 mV s^{-1} and 25 mV s^{-1} firstly in F-R direction, and then in R-F direction.

Reference

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3. A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Grätzel and H. Han, *Science*, 2014, **345**, 295-298.