

Supporting Information

Guarding the heterogeneous interface of perovskite solar cells by anion-barrier synthesized using residual PbI_2

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Experimental section

Materials: The SnO₂ colloid precursor solution was purchased from Alfa Aesar (tin (IV) oxide, 15% in H₂O colloidal dispersion). Iodine (I₂, >99.99%) was bought from Yuexiang Chemical Technology Co., Ltd. Cesium acetate (CsAc, >99%) was purchased from Chaoyou Biotechnology Co., Ltd. Methylamine hydrochloride (MAcI, 99.5%), lead(II) iodide (PbI₂, >99.99%), lead(II) bromide (PbBr₂, 99.99%), methylammonium iodide (MAI, >99.99%), formamidinium hydroiodide (FAI, >99.9%), as well as the solvents including isopropyl alcohol dimethyl (IPA, 99.5%), N,N-dimethylformamide (DMF, 99.8%) and dimethyl sulfoxide (DMSO, 99.5%) were bought from Alfa Aesar. The anti-solvent of chlorobenzene (CB, 99.5%) and the hole transport layer material of Spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp (China).

Solution Preparation: To generate Cs-I precursor solution, iodine was added into the IPA solvent, which was stirred by a magnetic stirrer at a rotational speed of 4000 rpm and temperature of 80 °C for 7 days to obtain the required iodine solution. Subsequently, CsAc was blended with equal weight iodine solution to form mixed solution. Then the mixed solution was stirred again for another 15 min at room temperature before filtering to obtain the required Cs-I precursor solution. The required different concentrations (0.05, 0.15, 0.25, 0.5 mg/mL) were achieved by adding IPA.

The 1.5 M perovskite precursor solution was prepared by dissolving 34 mg MAcI, 12.21 mg MABr, 656.9 mg PbI₂, 40.37 mg PbBr₂, and 240.52 mg FAI in the mixed solvents of DMF (800 μL) and DMSO (200 μL). For Spiro-OMeTAD solution, 72.5 mg of Spiro-OMeTAD was dissolved in 1 mL of CB. Then 28.8 μL of tBP and 17.5 μL of Li-TFSI stock solution (520 mg Li-TFSI in 1 mL of acetonitrile) were added in it.

Device fabrication: The ITO substrates were firstly cleaned by using plasma, then ultrasonic machine (KQ3200DV) in a mixed detergent of deionized water and Decon was used to continue washing at 60 °C. Subsequently, they were washed in deionized water for five times. The tin oxide colloidal precursor was prepared by diluting as received solution three times with deionized water. The tin oxide colloidal precursor was spin coated on ITO at 4000 rpm for 40 s and then annealed at 150 °C for 30 min. Next, they were treated with UV-ozone for 15 min. The perovskite precursor solution was spin-coated at 3500 rpm for 30 s. The anti-solvent was dropped 20 s after the begin of the spin coating, followed by annealing at 150 °C in the air for 10 min. Cs-I precursor solution was

spin-coated on the perovskite film through one-step method which consists of two successive spin-speeds, that is, 400 rpm for 3 s and 6000 rpm for 30 s, followed by annealing at 60 °C for 10 min. The Spiro-OMeTAD solution was spin-coated at 5500 rpm for 30 s. Finally, a 120 nm thick silver film was formed on the top electrode by thermal evaporation to complete device fabrication.

Characterization: XRD measurements using the XRD-7000 X-ray diffractometer from Shimadzu were performed. The SEM images and EDS spectroscopy were obtained using a JSM6700F scanning electron microscope. J–V measurements were conducted by using a Keithley 2400 source meter. The simulated sunlight of illumination of 100 mW/cm² (AM 1.5 G) was produced by using a Newport simulator (model 94043A). A Shimadzu UV2550 spectrophotometer was used to collect UV-vis absorption and transmission spectra. The EQE measurements were conducted on an EQE measurement system. The XPS was measured using a Thermo Fisher ESCALAB 250Xi instrument with Al K α X-ray radiation. The AFM images were taken using CSPM5500 SPM. PL and TRPL were obtained using FluoroMax-4P from Horiba Jobin Yvon (France). TPV and TPC measurements were performed with an oscilloscope. After shining a laser pulse (532 nm, 6 ns width from an Nd:YAG laser) on the sample, the decay of signals was recorded. EIS measurements were recorded with the electrochemical workstation model 660D from Shanghai Chen Hua Instrument Co., Ltd.

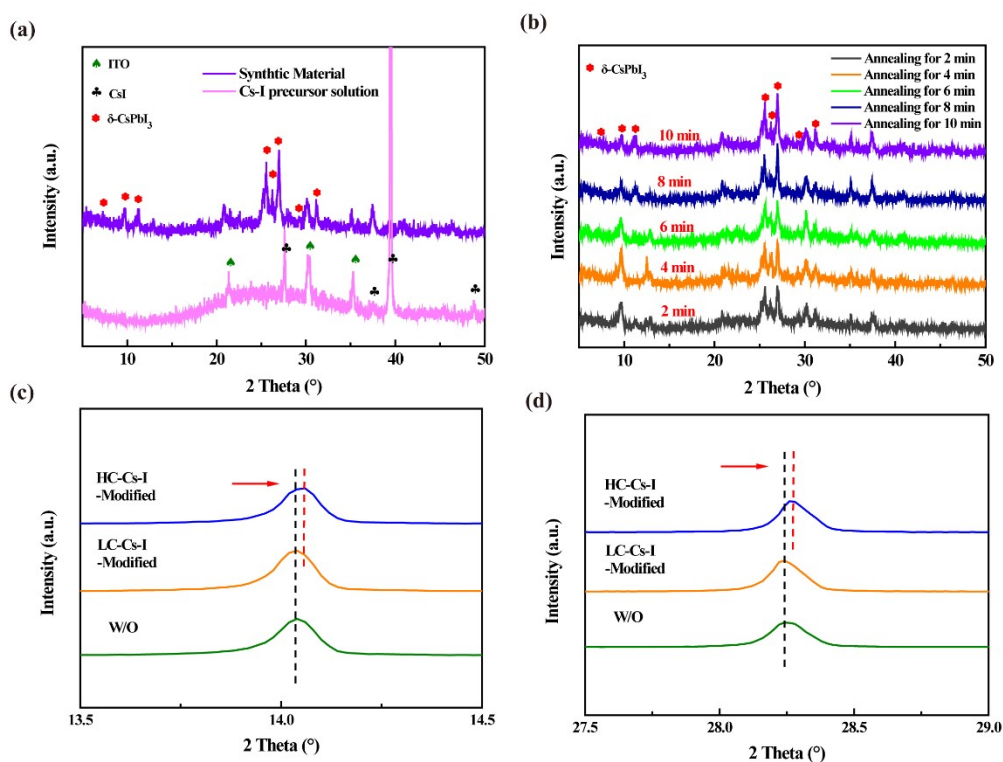


Fig. S1. (a) The XRD of the films was obtained before and after Cs-I precursor solution reacted with lead iodide. (b) XRD patterns of the samples by reacting PbI₂ with equal molar Cs-I precursor solution for difference annealing time. Magnification of the (c) (001) and (d) (022) peaks of the reference and perovskite films treated with low and high concentrations of Cs-I precursors.

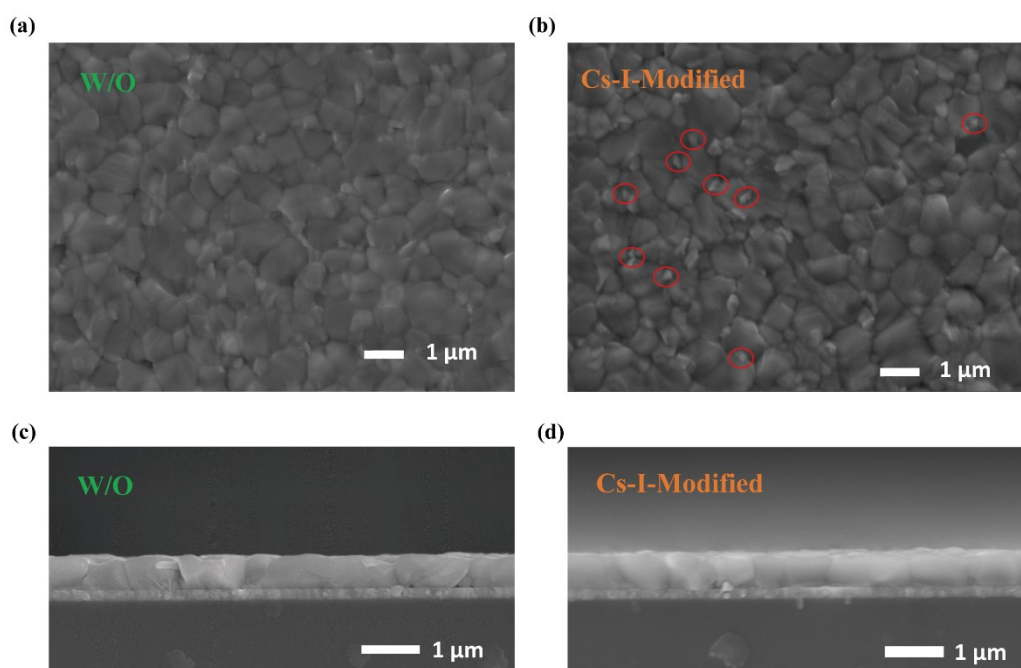


Fig. S2. (a, b) Top view and (c, d) cross sectional SEM images of the perovskite films of the reference and Cs-I modified films. The scale bar is 1 μm.

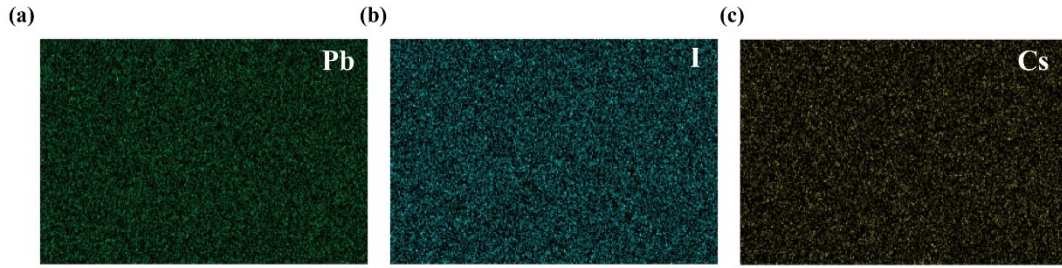


Fig. S3. Top-view EDS images of perovskite films with Cs-I modification. Element mapping analysis of (a) Pb, (b) I, (c) Cs of the films, respectively.

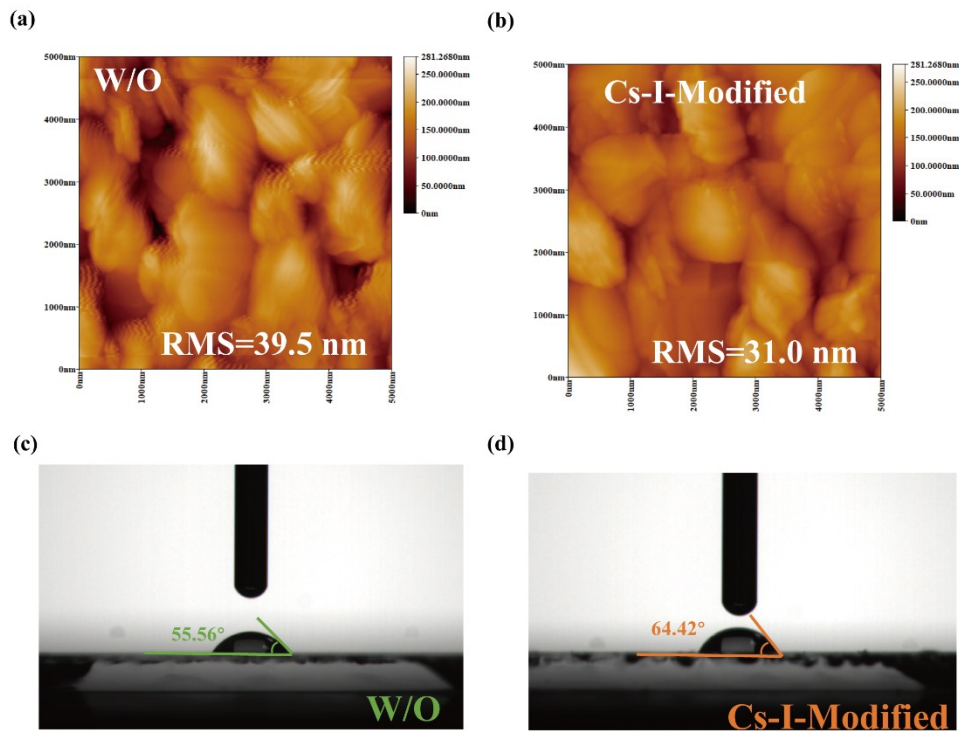


Fig. S4. The AFM images of perovskite films (a) without (W/O) and (b) with Cs-I modification. The contact angles of the perovskite films (c) without (W/O) and (d) with Cs-I modification.

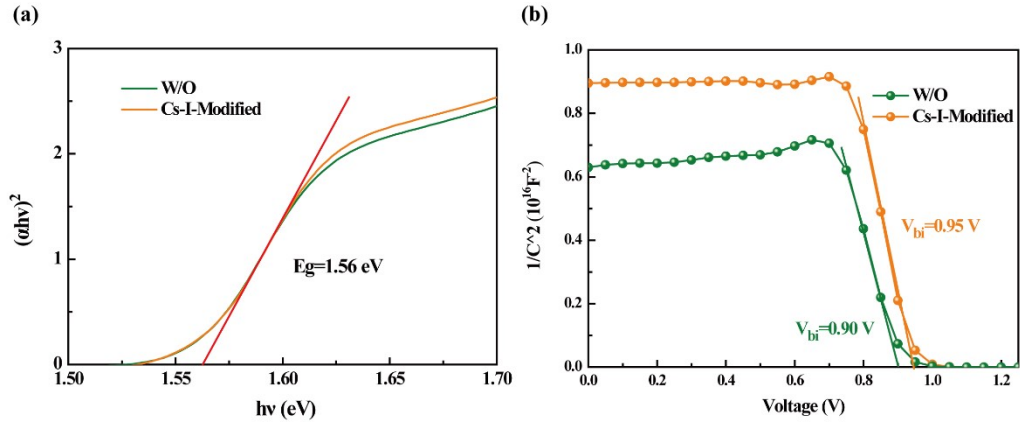


Fig. S5. (a) $(\alpha h\nu)^2$ as a function of photon energy of W/O- and Cs-I-Modified perovskite films. The band gap (E_g) obtained by extrapolating is 1.56 eV. (b) The Mott-Schottky measurements.

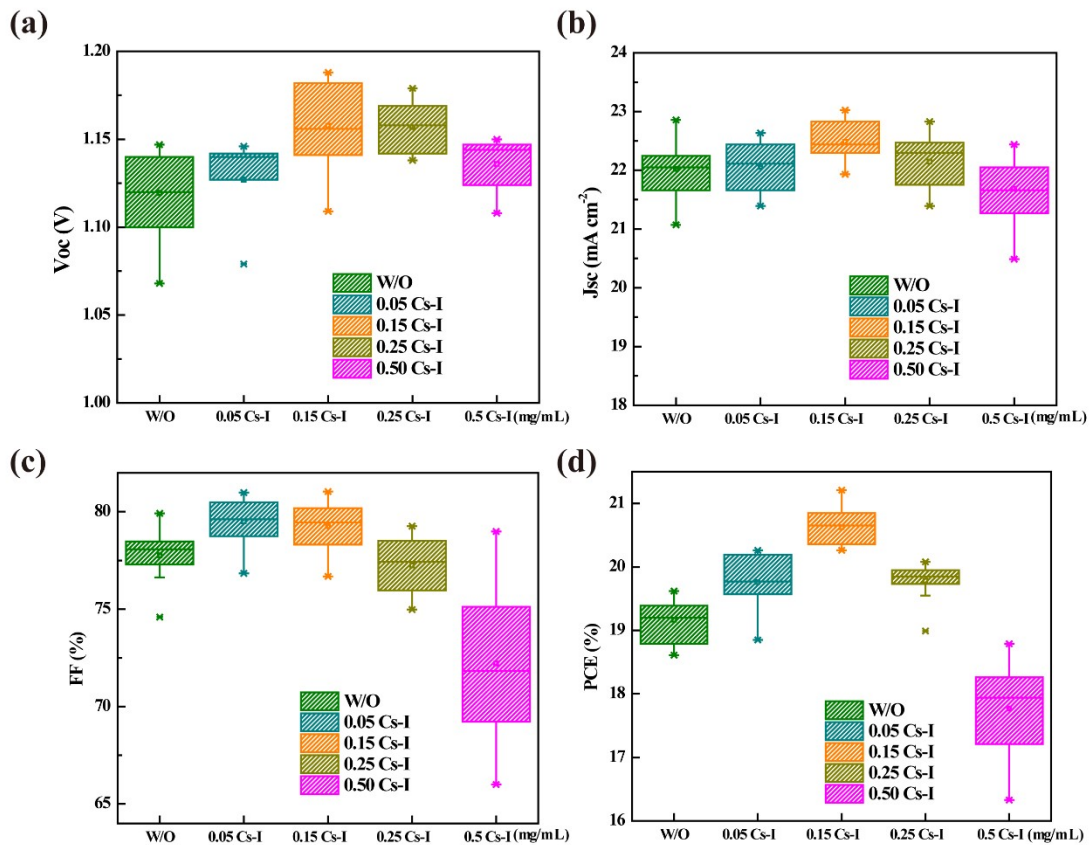


Fig. S6. Statistical box charts for the photovoltaic parameters of PSCs modified with different concentrations of Cs-I precursor solutions.

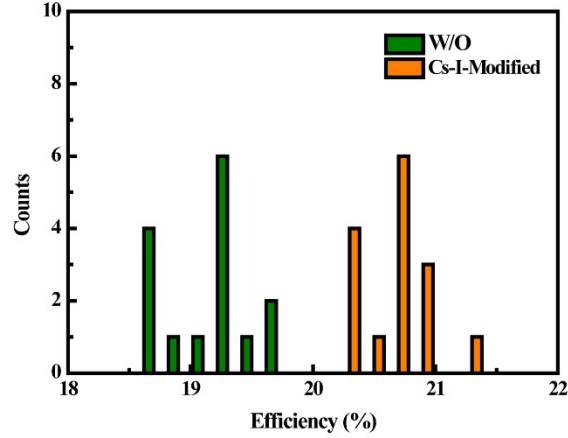


Fig. S7. Statistical PCE of the W/O- and Cs-I-Modified PSCs.

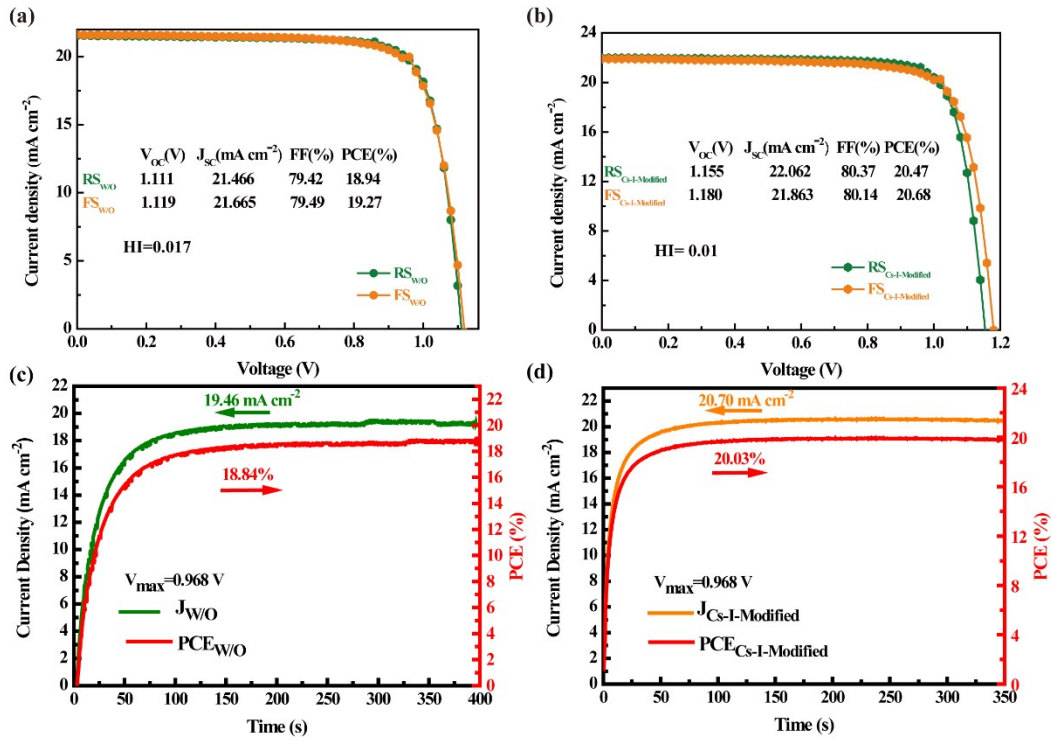


Fig. S8. J-V curves measured by reverse scan (RS) and forward scan (FS) for (a) W/O and (b) Cs-I-Modified perovskites. Steady-state current density and PCE versus time for the devices employing (c) W/O and (d) Cs-I-Modified perovskites measured at the maximum power points.

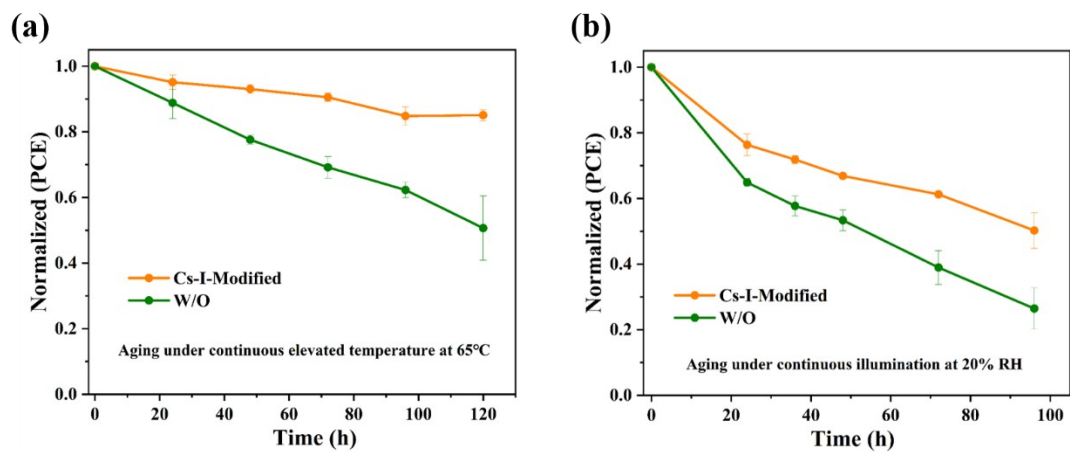


Fig. S9. (a) Thermal stability of the PSCs monitored under continuous elevated temperature at 65°C, (b) Photostability of the PSCs monitored under continuous illumination.

Table S1. FWHM of different XRD diffraction peaks of W/O- and Cs-I-Modified perovskite films.

Samples	Peak position (degree)	Plane	FWHM (degree)
W/O	14.03	(001)	0.128
	28.25	(022)	0.173
Cs-I-Modified	14.03	(001)	0.124
	28.24	(022)	0.158

Table S2. XPS results of Pb 4f and I 3d signals of W/O- and Cs-I-Modified perovskite films.

Samples	Pb 4f _{7/2} (eV)	Pb 4f _{5/2} (eV)	I 3d _{5/2} (eV)	I 3d _{3/2} (eV)
W/O	136.82	141.72	617.61	629.06
Cs-I-Modified	136.92	141.82	617.59	629.04

Table S3. Fitted results of TRPL curves of the Spiro-OMeTAD films deposited on the perovskite substrates without and with Cs-I precursor solution modification.

Sample	A ₁	τ_1 (ns)	A ₂	τ_2 (ns)	τ_{ave} (ns)
Quartz/pristine PVSK/Spiro-OMeTAD	0.51	73.73	0.49	282.73	238.11
Quartz/Cs-I-Modified PVSK/Spiro-OMeTAD	0.68	50.11	0.32	195.17	143.96

Table S4. The fitted EIS parameters of planar perovskite solar cells devices based on W/O and Cs-I-Modified perovskites.

Samples	R_s (Ω)	R_{ct} (Ω)	R_{rec} (Ω)
W/O	37.18	587.6	943.3
Cs-I-Modified	44.92	524.3	1273

Table S5. Hysteresis index (HI) of PSCs based on W/O or Cs-I-Modified perovskite films.

Samples	Scan directions	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	HI
W/O	Reverse	1.111	21.466	79.42	18.94	0.017
	Forward	1.119	21.665	79.49	19.27	
Cs-I-Modified	Reverse	1.155	22.062	80.37	20.47	0.010
	Forward	1.137	21.863	80.14	20.68	