Supporting Information

20.7% Highly Reproducible Inverted Planar Perovskite Solar Cells with Enhanced Fill Factor and Eliminated Hysteresis

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Experimental Details

Materials and Chemicals

Patterned indium tin oxide (half etched ITO) glass substrates (10 ohm \Box^{-1}) were purchased from Ying Kou You Xuan Trade Co., Ltd (China). Poly [bis (4-phenyl) (2,4,6trimethylphenyl)amine] (PTAA) were supplied by Xi'an Polymer Light Technology Corp (China). Lead (II) iodide (PbI₂, 99.999%, beads), lead (II) bromide (PbBr₂, 99.999%, powder), CsI (<=100%, beads), C60 (98%), bathocuproine (BCP, 99.99%), silver (Ag shot, \geq 99.99%), chlorobenzene (anhydrous, 99.9%, CB) and toluene (anhydrous, 99.5%), acetonitrile (\geq =99.5%) and SigmaClean water (30-60%) were purchased from Sigma-Aldrich (Singapore). Tetrafluorotetracyanoquinodimethane (purified by sublimation, F4-TCNQ, \geq 98%) and dimethyl sulfoxide (DMSO, anhydrous, 99.9%) and N, N-Dimethylformamide (DMF, \geq 99.5%) were received from Tokyo Chemical Industry Co. (TCI, Singapore). methylammonium bromide (MABr, \geq =99%) and formamidinium iodide (FAI, \geq = 99%) were purchased from the GreatCell Solar (Australia). All chemicals and reagents were used as received without further purification unless particular illustration in this work.

Materials Preparations

Substrates preparation: patterned ITO and glass with the size of $(1.5 \text{ cm} \times 1.5 \text{ cm})$ were cleaned successively in Sigmaclean water (6 mL in 1L deionized (DI) water), DI water, Acetone, isopropanol (IPA) for 30 min in a ultrasonic cleaner with the temperate of water lower than 40°C. All substrates were further treated in an ultraviolet Ozone cleaner for 10 min before use.

Preparation of PTAA solutions: F4-TCNQ stock solution was first dissolved in CB (0.43 mg ml⁻¹) and stirred at 60 °C for an overnight. Each time prior to use, the F4-TCNQ solution was added into PTAA solution (5 mg ml⁻¹ in toluene) with a weight ratio of 1%, following a

previous report.¹ The pure PTAA (1.5 mg/ml) is also being used as HTL to reveal the chemical reactive sites. If no special illustration in this work, the device and characterization results are obtained using F4-TCNQ doped PTAA. The mixed solution was stirred at 60 °C for half an hour before deposition.

Preparation of PMMA solutions: 0.45 mg/ml PMMA dissolved in acetonitrile was realized through diluting 3 mg/ml PMMA solution. The prepared solution was also stirred at 60 °C for half an hour before deposition. Previous reports using ethyl acetate, CB as selected solvents to dissolve PMMA.² However, those solvents will either dissolve PTAA (ethyl acetate and CB) or F4-TCNQ (DMSO) and ultimately lead to undesirable PTAA/PMMA film.

Preparation of Perovskite solutions: The preparation of the triple cation mixed perovskite $(Cs_{0.05}(FA_{0.85}MA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3, (CsFAM))$ was prepared by dissolving the precursors of CsI, FAI, MABr, PbI₂ and PbBr₂ in mixed solvents of DMF and DMSO based on the actual molarity by following a previous report.³ The perovskite solution was stirred at 75°C for 1 hour for a homogeneous mixture of three perovskite compositions. A 0.45 µm PTFE filter was used to filter the perovskite precursor solution.

Device Fabrications

The perovskite solar cell devices were fabricated based on the inverted planar architecture (PIN) ⁴ with the specific steps as follows:

As-cleaned substrates were transferred into a glovebox with N₂ newly filled, in which O₂ and H₂O concentrations were lower than 0.1 ppm. The glovebox was purchased half year ago and fully circulated for a whole day to eliminate possible organic vapour, *i. e.* DMSO, CB, DMF, IPA. We found that the organic vapour atmosphere, if not eliminated, would also affect the film quality of perovskite layer as compared with the films prepared in the old glove box (more than 5 year). 80 μ l of 1 wt% F4-TCNQ doped PTAA solution was spin-coated onto the ITO substrates at 6000 rpm (with a ramping rate of 3000 rpm) for 35 s and then annealed at

105°C for 10 min. 60 µl of PMMA solution was spin-coated on the cooled down PTAA layer at 6000 rpm (with a ramping rate of 3000 rpm) for 30 s and then heated at 100 °C for 5 min. 60 µl DMF solvent was spin-coated at a speed of 5000 rpm for 30s (with a ramping rate of 3000 rpm s⁻¹) to pre-wet the PTAA film for the case of our control device, following a previous report.⁵ In another case, the deposited PTAA or PMMA/PTAA film was treated by a homemade Ozone plasma generator for the hydrophilic groups grafting (HGG). It should be noted that the optimal treatment should be adjusted according to the power of UV light, the distance between the sample, the UV source and the chamber size that will influence the concentration of ozone plasma. 90 µl of perovskite solution was spin-coated on the treated PTAA or PMMA/PTAA film immediately by a two-consecutive step program at 3800 rpm (with a ramping rate of 3000 rpm s⁻¹) for 5s and 5000 rpm (with a ramping rate of 3000 rpm s⁻¹) for 35s. 120 µl of CB was dripped to the centre of the spinning substrates 10s prior to the end of the whole spinning program. The spin coating processes with the dripping of antisolvents are extremely significant for a high-quality film, which were carefully optimized based on previous reports^{3, 5, 6}, according to the atmosphere in the spin-coater and glove box, the concentration and types of solvents and perovskites. For the dripping of CB on spinning films, it should be dript in the middle part of films within a time period of 1-2s. After the spin-coating process, the perovskite film was heated at 100 °C for half an hour. Then the devices were completed by consecutive deposition of C60 (30 nm, 0.2-0.3 Å/s), BCP (8 nm, 0.1-0.2 Å/s) and Ag (100 nm, < 1 Å/s) at a vacuum condition of $\sim 10^{-7}$ Torr using a thermal evaporator. A mask with the active area of 0.105 cm^2 was utilized during thermal evaporation. All samples were stored in a N₂ filled box during transport.

Solar Cell Test

J-V curves of the PSCs were recorded using a Keithley 2400 source/meter unit under ambient conditions. The photocurrent was measured under AM1.5 illustration (100 mW cm⁻²), which

was calibrated using a standard Si photodiode detector. For the photovoltaic performance stability measurement, devices were stored in the dry box where the humidity and temperature were controlled in the range of 45-55% RH and 20-30°C, respectively. The external quantum efficiency (EQE) measurements were performed using a commercial QEPVSI-b set-up (Newport). Before the EQE measurement, the intensity of the light source was calibrated with a standard silicon detector (ThorLabs).

Characterizations

X-ray diffraction (XRD) characterizations were performed using a Bruker D8 Advance X-ray diffractometer with Cu_{Ka} radiation (λ =0.15406 nm). A Si wafer with strong (400) peak was used as substrates for the calibration of XRD peaks. UV/Vis measurements were achieved with a Shimadzu UV-1800 UV/Vis spectrophotometer. Scanning electron microscopy (SEM) was performed with a Zeiss Supra 40 FESEM. Atomic force microscopy (AFM) images were obtained with a Veeco NanoScope IV Multi-Mode AFM operated in the tapping mode. Steady state photo-luminescence (PL) spectra were acquired using a LS 55 Fluorescence Spectrometer (PerkinElmer) with an excitation wavelength of 550 nm. The time-resolved photo-luminescence (Tr-PL) was conducted on LifeSpec II (Edinburgh Instruments). The perovskite layers deposited on the HTM substrates with and without hydrophilic groups grafting buffer layer are used to perform the transient photoluminescence measurement. The perovskite samples were deposited on quartz and excited by a 475 nm laser beam and the signal was at 760 nm. High resolution XPS and UPS were obtained with a Kratos Axis Ultra DLD XP spectrometer. The XPS and UPS spectra were calibrated with the adventitious carbon C 1s peak (284.8 eV) and Ag foil, respectively. The work function and HOMO values were derived from the UPS following previous reports.7, 8 Electrochemical impedance spectroscopy (EIS) and Capirance-Frequency (C-F) curves measurements were performed using an electrochemical workstation (PARSTAT MC) in the dark. In specific, the EIS was

conducted with an applied bias of 0.1 V in the range of 3 MHz to 1 Hz with an amplitude voltage of 400 mV, and the C-F was measured with an applied bias of 10 mV in the range of 1 MHz to 1 Hz for an individual perovskite cell. The Contact angle was measured using surface tension measurer (AST Products, VCA-Optima).

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using an Agilent 660 spectrophotometer with a KBr plate as the blank sample. The samples for FTIR measurement were prepared by using the method reported by Peng *et. al.*² In specific, PMMA or PTAA (treated with and without Ozone plasma for 10 min for the convenience of observation) were mixed with CsFAMA and diluted by 1 mL DMSO. 80 µl of the transparent solution (PMMA mixed with CsFAM), and spin-coated on the KBr plate at 500 rpm (ramping rate of 500 rpm s⁻¹) for 60 s. For the PTAA mixed with CsFAMA case, 80 µl of the suspension solution was spin coated at 3000 rpm (ramping rate of 1500 rpm s⁻¹) for 60 s. All prepared samples were heated at 150 °C for 2 hours for intensive drying purpose.

KPFM characterization was performed by using an Asylum Research AFM using a MFP-3D template. During measurement, alternating contact mode (AC) was operated, *i.e.* alternating in contact with the sample and above the sample surface. An AC voltage of 3V with drive amplitude voltage of 630 mV and drive frequency of 75 kHZ was applied on the cantilever during operation. The tip began at a height of 35 nm from the sample and the lift height was kept as 35 nm in all measurements. To better present the KPFM results, the surface potential images were unified to the same scale range.

PL mapping was performed by an integrated system of a Nikon inverted microscope (with x50 objectives), cooperated with PI XY Piezo transition stage, which is controlled by commercial software SymPho Time. A coherent Ti: sapphire laser (Chameleon Ultra II, 680-1080 nm, 140 fs, repetition frequency 80 MHz) was used as light source. The selected laser light wavelength was 1060 nm (~300 mW) and focused into BBO crystal to produce SHG

signal (530 nm) as excitation source. In order to narrow the spectral line width, a 530/10 nm band-pass filter was used during operation. In measurement, the optical signal was collected by Princeton Instruments, Acton Spectra Pro 2300i spectrometer (grating 150 g/mm), which combined with a PicoQuant PMA series PMT (for PL mapping, monitor wavelength at 750 nm), and Acton Pixis 100 CCD (for collection of steady spectra). A 633 nm long pass filter was used to block the excitation signals. The characterization results might be varied sample-to-sample, thus the best results are utilized for illustration and comparison for each condition in this work.



Fig. S1 (a) Device architecture and (b) energy-level diagram of the fabricated cell.



Fig. S2 J-V curves of the best-performing devices with UVO treated PTAA as HTM.

aHTMs.				
Conditions	$J_{sc}(\mathbf{mA}/cm^2)$	Voc (V)	FF	PCE (%)
Contrl-Best	21.753	1.080	0.741	17.417
Contrl-Aver	21.87±0.70	1.07±0.02	0.67±0.03	15.53±0.99
UVO10-Best	22.543	1.050	0.769	18.222
UVO10-Aver	22.19±0.30	1.02 ± 0.04	0.72 ± 0.03	16.23±1.24
UVO20-Best	22.771	0.990	0.612	13.805
UVO20-Aver	22.64±0.30	0.93 ± 0.07	0.57±0.10	11.83±1.92
* The Statistical analysis is based on 33 devices for control devices and 10 devices for UVO treated devices.				

Table S1. Photovoltaic Performance of PSCs with UVO treated PTAA aHTMs.

Figure S2 compares champion efficiencies achieved by PSCs with UVO treated PTAA as HTMs. The specific photovoltaic parameters of the best PCE and average PCE are summarized in Table S1. The control device with the use of DMF pre-wetting method exhibit a best PCE of 17.417% with a short-circuit current density (J_{sc}) of 21.753 mA/cm², an opencircuit voltage (V_{oc}) of 1.080 V and a fill factor (FF) of 0.741, which is comparable to previous reports.^{9, 10} For the UVO treated PTAA based PSCs, 10s treatment exhibits the best PCE of 18.222% with J_{sc} of 22.543 mA/cm², V_{oc} of 1.050 V and FF of 0.769. With the UVO treatment duration increases to 20s, the PCE of the resultant PSCs drops to 13.805% with the J_{sc} of 22.771 mA/cm², V_{oc} of 0.990V and FF of 0.612. Compared with the control device, it is found that the V_{oc} values for UVO treated devices all show decreased tendency. Since the V_{oc} highly relies on the energetic alignment between the perovskite and HTM ^{7, 11}, we can speculate that the decrease of V_{oc} is due to the structural damage of PTAA caused by UVO treatment, which is supported by the XPS characterization shown in Figure S3. However, the J_{sc} and FF of PSCs with 10s UVO treatment are improved, indicating more electron-hole carriers generation and balanced transport. ^{12, 13} This is related to a better perovskite growth on PTAA due to the reduced surface tension force, as presented in Figure S4. ^{14, 15}



Fig. S3 XPS spectra of element C of PTAA treated with and without 20s UVO.



Fig. S4 Water contact angles of PTAA (a) without and (b) with 20s UVO treatment.



ozone plushu treuthent duluton.					
Conditions	$J_{sc}(\mathbf{mA}/cm^2)$	Voc(V)	FF	PCE (%)	
Contl-Best	21.753	1.080	0.741	17.417	
Contl-Aver	21.88±0.69	1.07 ± 0.01	0.66 ± 0.04	15.47±1.05	
Ozone10-Best	22.625	1.070	0.778	18.839	
Ozone10-Aver	22.43±0.91	1.06 ± 0.02	0.72 ± 0.04	16.23±1.08	
Ozone20-Best	22.910	1.080	0.795	19.671	
Ozone20-Aver	22.84±0.63	1.07 ± 0.01	0.77 ± 0.02	18.83±0.66	
Ozone30-Best	22.403	1.061	0.784	18.636	
Ozone30-Aver	21.92±0.58	1.05 ± 0.01	0.73±0.04	16.83±0.90	
Ozone1m-Best	22.814	0.972	0.666	14.768	
Ozone1m-Aver	21.96±0.81	0.99±0.03	0.58±0.06	12.67±1.04	
Ozone2m-Best	22.540	0.919	0.585	12.118	
Ozone2m-Aver	22.18±0.57	0.91±0.05	0.55±0.06	10.98±1.44	
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Table S2. Device metrics of inverted plana	ar PSCs with HGG through van	rying
ozone plasma treatment duration.		

* The Statistical analysis is based on 33 devices for control and 20s Ozone plasma treated devices and 18 devices for other conditions.



Fig. S6 Power output of devices for Control #1 and Target #1, pointing out the maximum power point (MPP)





Fig. S7 Power output of devices for Control #2 and Target #2, pointing out the maximum power point (MPP) values (0.919 V and 0.946 V for Control #1 and Target #1, respectively).



Fig. S9 J-V curves of (a) device without HGG (Control #1), (b) device with HGG (Target #1), (c) device with buffer layer without HGG (Control #2) and (d) device with buffer layer and HGG (Target #2). All devices are fabricated using the HTL of PTAA without doping with F4-TCNQ.



Fig. S10 Contact angle measurement images of (e) Control #1 HTM (90.3°), (b) Target #1 HTM (83.3°), (c) Control #2 HTM (86.2°) and (d) Target #2 HTM (76.3°).



Fig. S11 Full XPS spectra of PMMA-coated PTAA (top) and PTAA (bottom) treated with and without HGG.



Fig. S12 (a) J-V plots of the hole-only devices with the use of pristine, HGG 20s and HGG 120s treated PTAA. (b) Logarithmic plot of the J-V curves in (a) with only positive applied voltage.



Fig. S13 UPS spectra of PTAA with/without buffer layer and with/without HGG and the CsFAMA perovskite.



Fig. S14 UV-Vis spectra of PTAA and PMMA-coated PTAA treated with different treatment and duration.



Fig. S15 AFM images of PTAA (a) without HGG and (b) with HGG; buffer layer PMMA-coated PTAA (c) without HGG and (d) with HGG.



Fig. S16 Photograph of perovskite films grown on (a) PTAA, (b) DMF pre-wetted PTAA (Control perovskites) and (c) PTAA with HGG (Target perovskites). Right images show the coverage of perovskite, and the left images display the light pass uniformity of perovskite films. The size of perovskite film is 1.5 cm×1.5cm.



Fig. S17 SEM images of (a) Control #1 perovskite, (b) Target #1 perovskite, (c) Control #2 perovskite and (d)

Target #2 perovskite. The scale bar is 200 nm.



Fig. S18 (a) XRD curves and (b) summarized FWHM and intensity of characteristic peaks of Control #1, Target

#1, Control #2 and Target #2 CsFAMA perovskite.





Fig. S20 3D PL mapping of (a) Control #1, (b) Target #1, (c) Control #2 and (d) Target #2 perovskite films.

Conditions	Series	Recombination	Capacitance (C)
	Resistance (R _s) (ohm)	Resistance (R _{rec}) (ohm)	(F)
Control #1	79.7	3733	2.28E-9
Target #1	54.61	4535	5.29E-9
Control #2	167.8	32550	1.92 E-9
Target #2	91.2	83260	1.48E-9

Table S3. Fitted parameters of EIS Nyquist plots of solar cell devices.



Fig. S21 XRD curves of Control #1, Target #1, Control #2 and Target #2 perovskite films put in air with relative

humidity of $50 \pm 5\%$.



Fig. S22 KPFM images of (a) Control #1, (b) Target #1, (c) Control #2 and (d) Target #2 perovskite films.



Fig. S23 Contac Angle measurement of (a) Control #1, (b) Target #1, (c) Control #2 and (d) Target #2

perovskite films.

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