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Highly stable carbon-based perovskite solar cell with an efficiency of over 18% via hole transport engineering

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Experimental Section

Materials: Transparent patterned fluorine-doped tin oxide (FTO) on glass substrates with the sheet resistance of 15 Ω sq^{-1} and transparent patterned indium tin oxide (ITO) on flexible PEN substrates with the sheet resistance of 20 Ω sq^{-1} were scratched by laser. Dimethylformamide (DMF, 99.5%) and chlorobenzene were purchased from Aladdin Reagents. Methylammonium iodide (CH_3NH_3I, MAI, 99.5%), formamidinium iodide ($HC(NH_2)_2I$, FAI, 99.5%), lead iodide (PbI_2, 99.999%) and Poly(3-hexylthiophene-2,5-diyl) (P3HT, 90%) were purchased from Polymer Light Technology Inc. 40 wt %. $FA_{0.3}MA_{0.7}PbI_3$ precursor solution was prepared by mixing MAI, FAI and PbI_2 in a molar ratio of 7:3:10 in DMF. P3HT solution was prepared by mixing P3HT in chlorobenzene with the concentration of 15 mg/mL. For P3HT/graphene, the mixture of graphene and P3HT (15 mg P3HT and 10 mg graphene/mL) was magnetically stirred at 60 ^oC for 24 h for complete dissolution and good uniformity. We then obtained the supernatant by centrifugation for 1 h. Before preparing the P3HT/graphene film, ultrasonic dispersion was performed for 1 h. All of the reagents used in this work are of analytical grade without any further purification. The carbon paste was self-made. [1]

Device fabrication: Patterned FTO glass substrates with sheet resistance of 15 Ω sq^{-1} were cleaned by ultrasonic washing with acetone, ethanol, and deionized water in sequence for 10 min each. After being blow-dried by nitrogen, the conductive glass substrates were exposed to UV-ozone for 30 min. The clean FTO substrate was then immediately soaked in dilute 0.2 M aqueous $TiCl_4$ solution at 70 °C for 1 h, and washed with deionized water. It was then placed in a 0.04 M aqueous $SnCl_2$ solution at 70 °C for another 1 h, and washed with deionized water. Finally the substrate was annealed at 140 °C for 3h.[2] The thickness of SnO_2@TiO_2 layer is about 30 nm. $FA_{0.3}MA_{0.7}PbI_3$ precursor was then spin-coated on the SnO_2@TiO_2 layer at 2500 rpm for 10 s, and dried with the gas pump method.[3] The perovskite film with thickness of 340 nm was annealed at 100 ^oC for 20 min. For the device with graphene/P3HT as HTM, 5 mg/mL P3HT solution was first spin-coated on the perovskite film at 3000 rpm and heated at 100 ^oC for 5 min. Following this, the graphene/P3HT solution was spin-coated on the film at 2500 rpm for 30 s. For the device with P3HT as HTM, only P3HT chlorobenzene solution was spin coated on the perovskite at 2500 rpm for 30 s. The thickness of HTM layer is about 40 nm. Next the carbon paste with propylene glycol monomethyl ether acetate as solvent was coated by doctor-blade method, and annealed at 100 ^{o}C for 20 min for drying.

Characterization: The surface morphology of the perovskite films and HTL, and the cross-sectional morphologies of PSCs were analyzed by scanning electron microscopy (SEM, TESCAN MIRA 3 LMH). XRD patterns were measured by a D8 ADVANCE X-ray from Bruker at a scanning range of 10 - 70° and a scanning speed of 0.05 °/s. Absorption spectra were used to analyze optical property of the perovskite films. The steady-state PL spectra were obtained by a compact steady-state spectrophotometer (Fluoromax-4, Horiba Jobin Yvon) with an excitation wavelength of 532 nm. A LabRAM HR800 was implied to measure the time-resolved photoluminescence (TRPL) measurements of perovskite films on different substrates at 786 nm using an excitation with a 478 nm light pulse from a HORIBA Scientific DeltaPro fluorimeter. The *J-V* curves were recorded by a Keithley 2400 source-meter with an AM 1.5G filter (Sol 3A, Oriel) equipped on a 450 W Class AAA solar simulator under illumination of 100 mW/cm^2. The curves were measured with the reverse scanning from 1.2 V to -0.2 V and the forward scanning from -0.2 V to 1.2 V at a scan rate of 100 mV/s.

For the certification, a new testing protocol from Newport Corporation PV Lab, MT, USA is applied. Firstly, spectral response is measured under both dark and light bias conditions to verify linearity of operation and determine spectral correction factor. Secondly, IV sweeps are performed both in the forward and reverse directions, at a rapid sweep rate (~100 mV/s) and then at a much slower sweep rate (~10 mV/s). Thirdly, a stabilized IV sweep is performed wherein each bias voltage (0A current for V_{OC}) is applied and held until the measured current (voltage for V_{OC}) has stabilized. The criterion for this determination is that successive current (voltage for V_{OC}) values agree to within 0.05%. The time interval between current readings is approximately 20 seconds, and 13 voltage points are used, including V_{OC} and I_{SC}. Finally, the performance parameters to be certified are the stabilized values.

Space charge limited current (SCLC) method

To measure the hole mobility of the HTMs, the devices with a structure of FTO/HTM/Au were fabricated. For the P3HT HTM devices, the P3HT solution was spin-coated on FTO/glass substrate at 1000 rpm for 30 s. For the P3HT/graphene

HTM devices, P3HT solution was spin-coated on FTO/glass substrate at 1000 rpm for 30 s, followed by the P3HT/graphene solution at 1000 rpm for 30 s. After depositing the HTM, an 80 nm Au layer was vacuum-deposited on the HTM. The hole mobility μ was calculated by fitting the dark current to the model of a single carrier SCLC. The Equation was descripted as:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V}{d^3}$$

Wherein J is the current density, ε_0 is the free-space permittivity, ε_r is the relative permittivity, V is the effective voltage, d is the thickness of the HTL (90 nm). ε_0 = 8. 854187817 × 10^{-12} F/ m, ε_r =3.

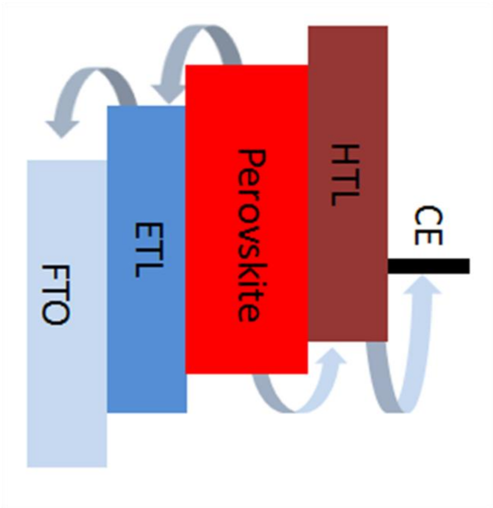

Figure S1. Schematic of the structure and the charge transport of the carbon-based perovskite solar cells studied in this work.

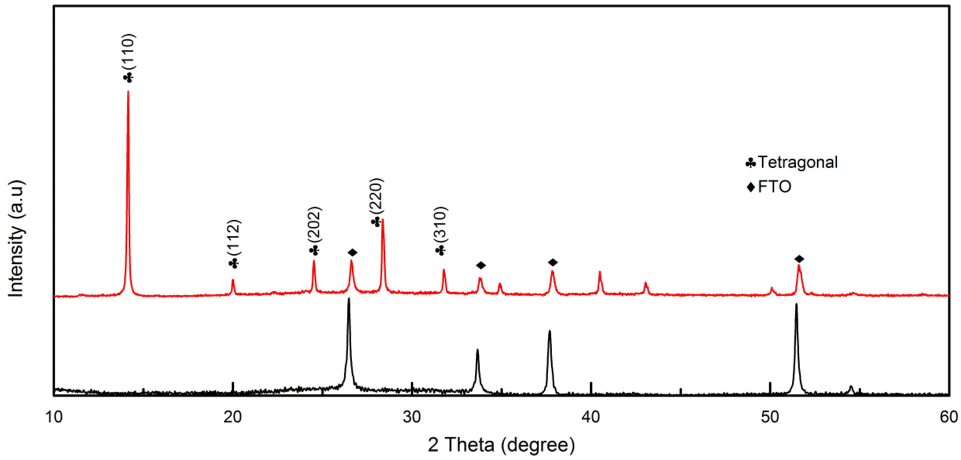

Figure S2. XRD patterns of the bare FTO substrate and that coated with $FA_{0.3}MA_{0.7}PbI_3$ layer.

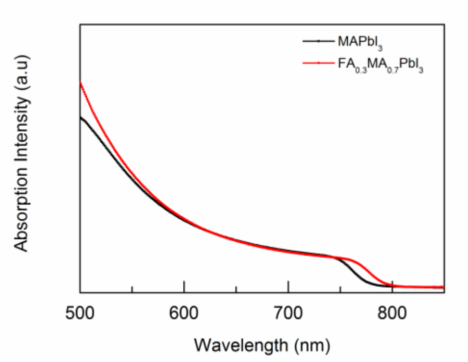

Figure S3. Comparison of the absorption spectra of $MAPbI_3$ and $FA_{0.3}MA_{0.7}PbI_3$ film.

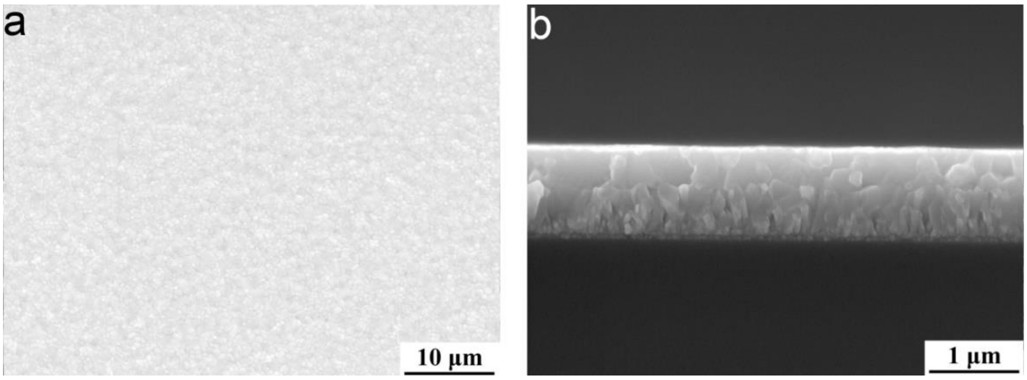

Figure S4. a) The surface morphology of the $FA_{0.3}MA_{0.7}PbI_3$ layer, b) the cross-section morphology of the $FA_{0.3}MA_{0.7}PbI_3$ layer coated on FTO

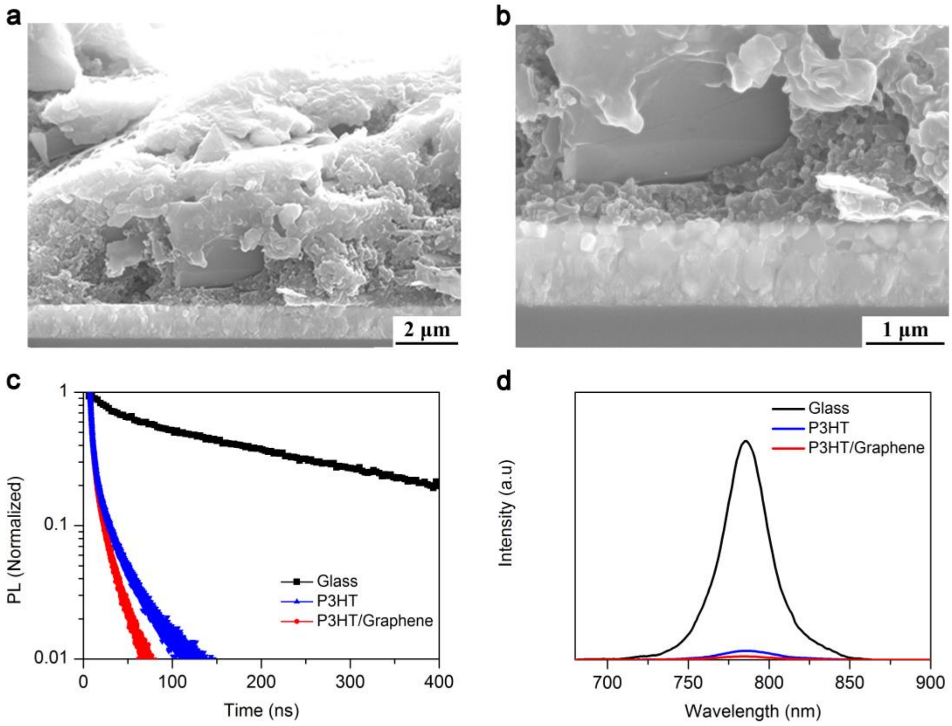

Figure S5. a) The cross-section SEM image and b) magnified image of the planar carbon-based PSC using P3HT as HTM c) The steady-state and (d) time-resolved photoluminescence spectra of pure perovskite film on glass, perovskite film covered by P3HT, perovskite film covered by P3HT/graphene.

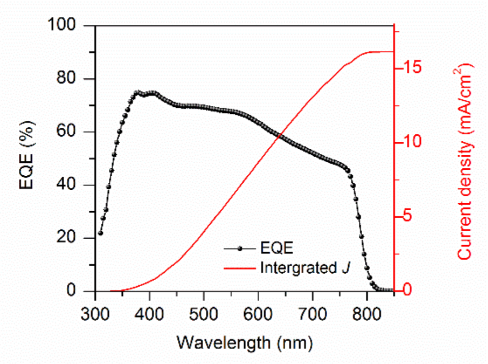

Figure S6. IPCE and integrated current density of the planar carbon based perovskite solar cell based P3HT as HTM

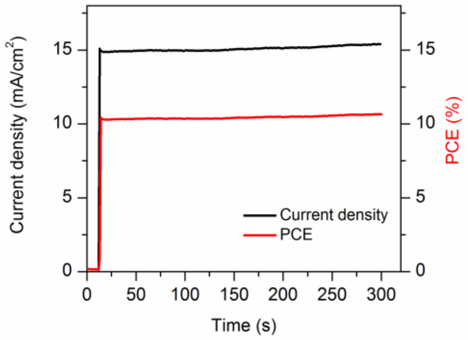

Figure S7. The steady-state output of champion device with P3HT as HTM at the max power point (V =0.69 V) under 1-sun illumination

Newport	ACCREDITED Calibration Cert. # 2893.01	**Technology and Application Center** **PV Lab** Newport Calibration Cert. # 1829

DUT S/N: 7160264 A1
Newport Calibration #: 1829
Manufacturer: Xi'an Jiaotong University
Material: Planar Carbon-Based Perovskite Solar Cell
Measurement Date: 13-Dec-2017
Temperature Sensor: TC-K, DUT Temperature: 24.9 ± 0.8 °C
Environmental conditions at the time of calibration: Temperature: 24 ± 3 °C; Humidity: 40 ± 10 %

The above DUT has been tested using the following methods to meet the ISO 17025 Standard by the PV Lab at Newport Corporation. Quoted uncertainties are expanded using a coverage factor of $k = 2$ and expressed with an approximately 95% level of confidence. Measurement of total irradiance is traceable to the World Radiometric Reference (WRR) and all other measurements and uncertainties are traceable to either NIST or CNRC and the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test, and do not imply future performance.

Reported performance parameters were measured under a 13 point IV sweep configuration wherein the bias voltage (current for Voc determination) is held constant until the measured current (voltage for Voc) is determined to be unchanging at the 0.05% level. This is intended to represent the stabilized performance of the device. Total IV measurement time under these conditions was 42 minutes, 10 seconds.

Efficency [%]	17.83 ± 0.57	V_oc [V]	1.0924 ± 0.0084	I_sc [A]	0.002204 ± 0.000047
P_max [mW]	1.772 ± 0.052	V_max [V]	0.896 ± 0.013	I_max [A]	0.001978 ± 0.000045
FF [%]	73.6 ± 1.4	Area [cm^2]	0.0994 ± 0.0005	M	0.994 ± 0.015

Methods:

I-V: ASTM E948-16 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-15 *Standard Test Method for Spectral Responsivity Measurements of Photovoltaic Devices*

Standard Reporting Conditions:

Spectrum: AM1.5-G (ASTM G173-03/IEC 60904-3 ed. 2)
1000.0 W/m ^{2} at 25.0°C

Secondary Reference Cell:

Device S/N: 10510-0054 KG5
Device Material: mono-Si
Window Material: KG5
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 1938
Certified short circuit current (I_{sc}) under standard reporting conditions (SRC): 47.93mA
Calibration due date: 29-Sep-19

Solar Simulator:

Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer_Scan_0197.xls*
Total irradiance: 1000 W/m^2 based on I_{sc} of the above Secondary Reference Cell

Quantum Efficiency for DUT:

Newport Corporation filename *QE 1829, 7160264 A1, 0.4 mA WLB.log*
Spectral mismatch correction factor: M = 0.994 ± 0.015

DUT Calibration Procedures:

Newport Corporation document WI1 (EQE).docx
Newport Corporation document Area Measurement WI2 (Area).docx
Newport Corporation document WI3 (IV.Sweep).docx

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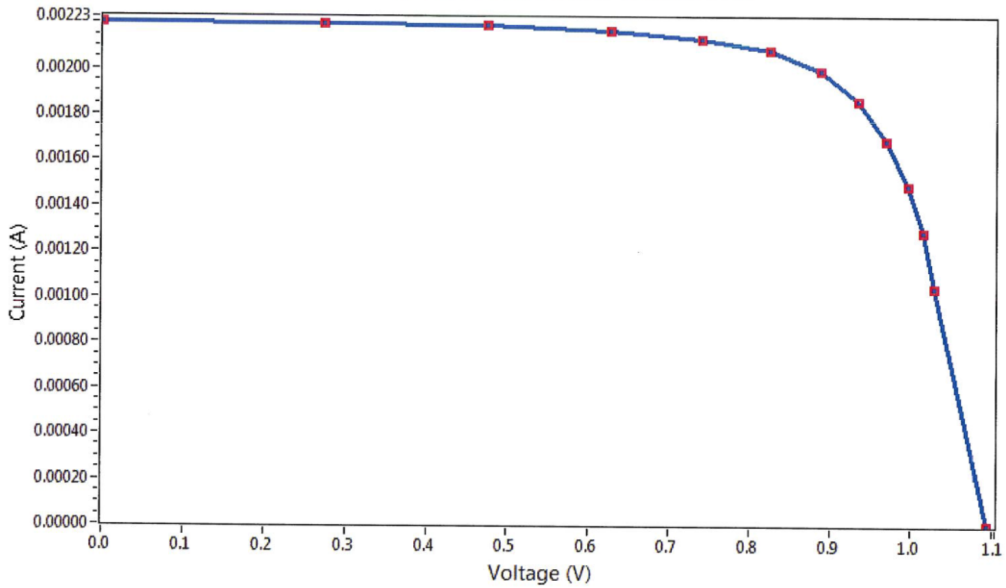
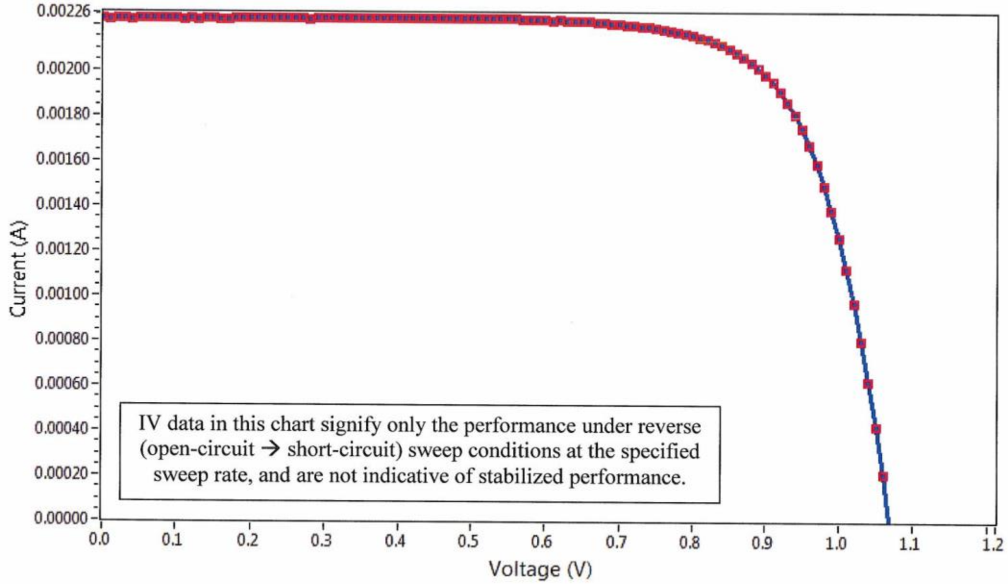
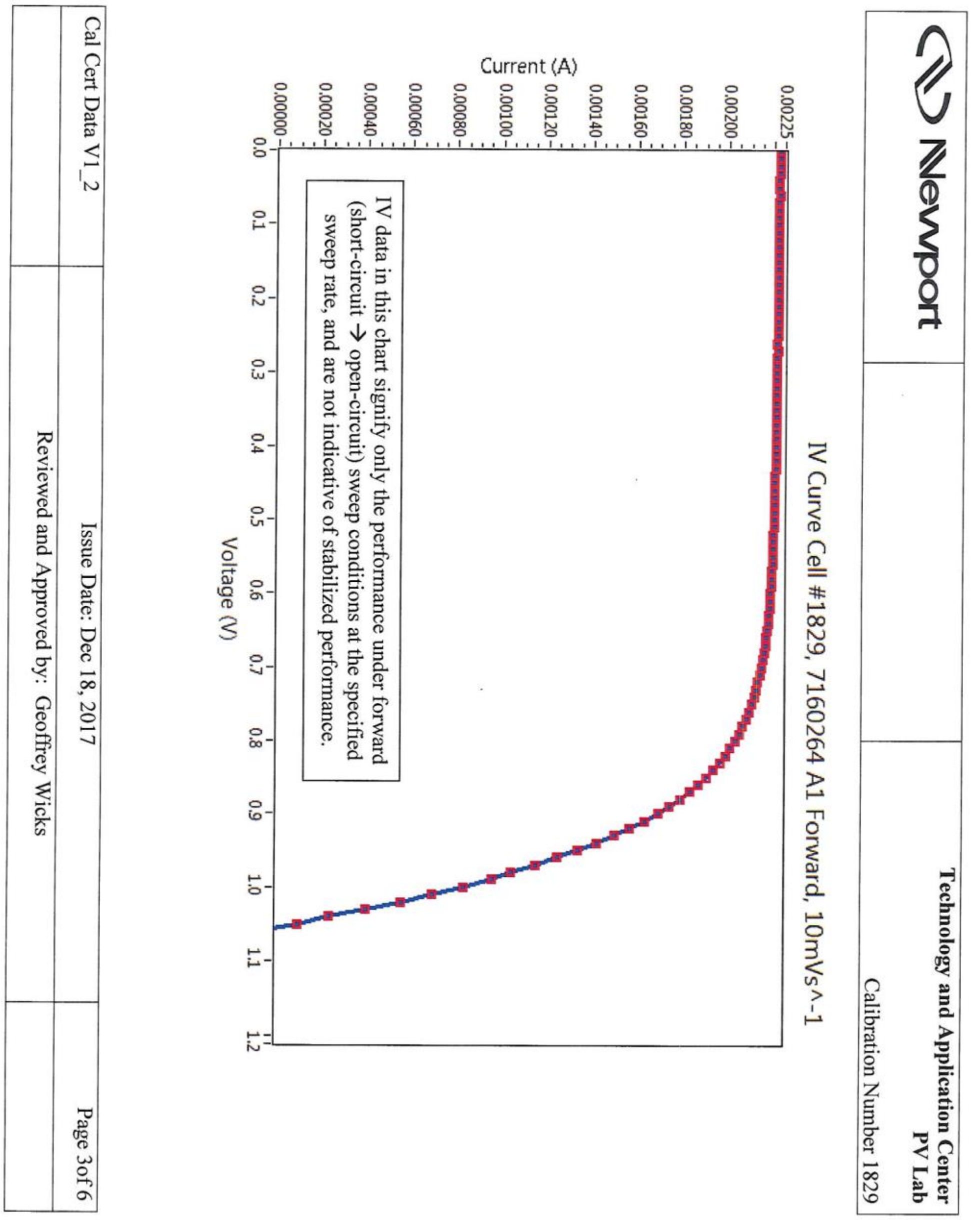
IV Curve Cell #1829, 7160264 A1



IV Curve Cell #1829, 7160264 A1 Reverse, 10mVs^-1




Newport

Technology and Application Center
PV Lab
Calibration Number 1829

IV Curve Cell #1829, 7160264 A1 Forward, 10mVs^-1

IV data in this chart signify only the performance under forward (short-circuit → open-circuit) sweep conditions at the specified sweep rate, and are not indicative of stabilized performance.

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Figure S8. The certificate of the planar carbon-based perovskite solar cell with P3HT/graphene as HTM in this work

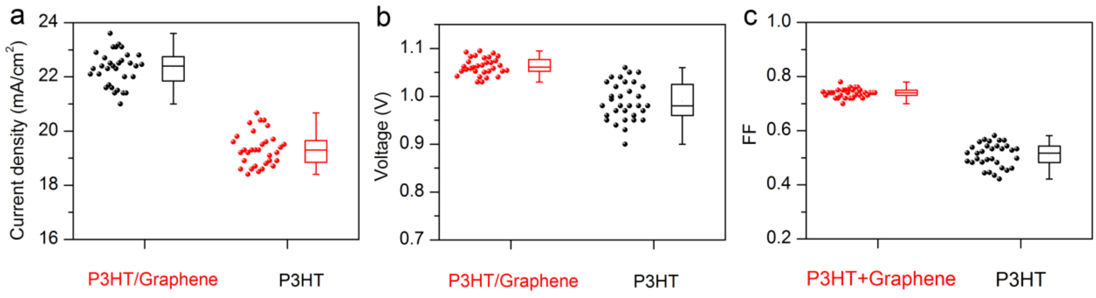

Figure S9. Statistics of a) V_{oc}, b) J_{sc} and c) FF of 32 planar carbon-based perovskite cells based P3HT or P3HT/graphene as HTM

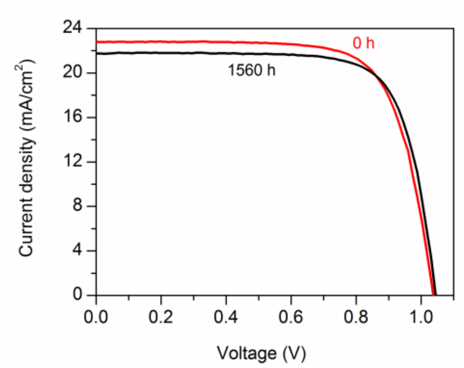

Figure S10. *J-V* curves of the non-encapsulated planar carbon-based perovskite solar cell using P3HT/graphene as HTM as fresh and after aging for 1560 h in the ambient condition (without illumination).

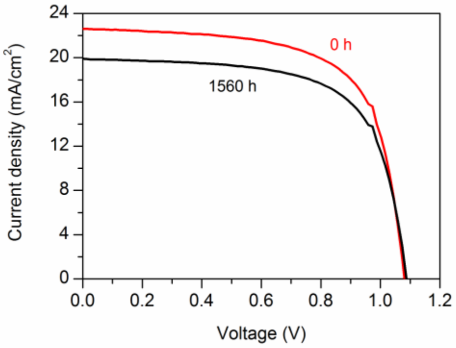

Figure S11. *J*-*V* curves of the encapsulated planar carbon-based perovskite solar cell using P3HT/graphene as HTM as fresh and after constant 1-sun illumination for 600 h.

Table S1. The photovoltaic parameters of the champion planar carbon-based perovskite solar cells with P3HT or P3HT/graphene as HTM

HTM		**PCE**	V_{oc} **(V)**	J_{sc} **(mA/cm^2)**	**FF**
P3HT/Graphene	Reverse Scan	18.22	1.09	22.45	0.74
	Forward Scan	16.70	1.08	22.39	0.69
P3HT	Reverse Scan	11.12	0.99	20.67	0.54
	Forward Scan	9.20	0.96	19.69	0.49

Table S2. Photovoltaic metrics evolution of the non-encapsulated planar carbon-based perovskite solar cells with P3HT/graphene as HTM stored in the air (average humidity of ~50%)

Time (day)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	Norm. PCE
0	22.78195	1.03622	0.7276	17.17653	1
2	22.26146	1.03461	0.74471	17.15211	0.998578
4	22.688	1.03749	0.74321	17.4941	1.018489
6	22.83266	1.01689	0.7461	17.32318	1.008538
8	22.37952	1.02375	0.75262	17.2433	1.003887
10	22.9232	1.00544	0.7543	17.38503	1.012139
15	22.93175	1.01047	0.75029	17.3856	1.012172
20	22.71357	1.03238	0.75344	17.66744	1.02858
25	22.54292	1.03732	0.7464	17.45398	1.016153
30	22.27871	1.03324	0.75203	17.31117	1.007839
35	21.70668	1.048166	0.753847	17.15167	0.998553
40	22.12383	1.032785	0.754192	17.23265	1.003267
45	21.65896	1.030531	0.743036	16.58473	0.965546
50	21.45051	1.032111	0.757743	16.7759	0.976676
55	21.3925	1.039337	0.754368	16.77263	0.976485
60	21.6239	1.0434	0.7442	16.7922	0.977625
65	21.8165	1.0382	0.7429	16.8266	0.979627
70	21.3683	1.0443	0.7485	16.70271	0.972415

Table S3. The photovoltaic metrics evolution of the encapsulated planar carbon-based perovskite solar cells with P3HT as HTM under continuous 1-sun light illumination

Time (day)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	Norm. PCE
0	22.5493	1.0805	0.6687	16.29255	1
1	22.678	1.1018	0.6627	16.55863	1.016331
2	22.566	1.0948	0.6671	16.48088	1.011559
3	22.585	1.092	0.6662	16.43037	1.008459
4	22.5889	1.0919	0.66693	16.44971	1.009646
5	22.6239	1.0935	0.66688	16.4981	1.012616
10	21.961	1.089	0.66819	15.98012	0.980824
15	20.8579	1.0867	0.66693	15.11682	0.927836
20	20.3923	1.0856	0.66711	14.7684	0.906451
25	19.9236	1.0873	0.66654	14.4392	0.884912

Reference:

1. Q.-Q. Chu, B. Ding, Q. Qiu, Y. Liu, C.-X. Li, C.-J. Li, G.-J. Yang, Cost effective perovskite solar cells with a high efficiency and open-circuit voltage based on a perovskite-friendly carbon electrode, *J. Mater. Chem. A*, 2018, **6**, 8271.
2. B. Ding, S.-Y. Huang, Q.-Q. Chu, Y. Li, C.-X. Li, C.-J. Li, G.-J. Yang, Low-temperature SnO2-modified TiO2 yields record efficiency for normal planar perovskite solar modules, *J. Mater. Chem. A*, 2018, DOI:10.1039/C8TA01192C
3. B. Ding, Y. Li, S.-Y. Huang, Q.-Q. Chu, C.-X. Li, C.-J. Li, G.-J. Yang, Material nucleation/growth competition tuning towards highly reproducible planar perovskite solar cells with efficiency exceeding 20%, *J. Mater. Chem. A*, 2017, **5**, 6840.