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

Supplementary Information

A Large Area (70 cm^2) Monolithic Perovskite Solar Module with High Efficiency and Stability

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Table S1: Reported Data for Perovskite large scale solar device as of 15-July-2016

Title	**Size of active area**	**Efficiency**	**Architecture**
Current Manuscript work[1]	70cm^2	10.74%	FTO/TiO_2/ZrO_2/Carbon/Perovskite (Drop Casted perovskite through Carbon layer)
Perovskite solar cells and large area modules (100 cm^2) based on an air flow-assisted PbI_2 blade coating deposition process[2]	10.1cm^2 100cm^2	10.4% 4.3%	FTO/TiO_2/Perovskite/Spiro-OMeTAD/Au
Interfacial modification of hole transport layers for efficient large-area perovskite solar cells achieved via blade-coating[3]	6cm^2	10.15%	ITO/PEDOT:PSS(PSSH)/Perovskite/PCBM/Al
Large-area, high-quality organic–inorganic hybrid perovskite thin films via a controlled vapor–solid reaction[4]	1.5cm^2	6.06%	ITO/PEDOT:PSS/Perovskite /PCBM/C60/BCP/Al
Upscaling of Perovskite Solar Cells: Fully Ambient Roll Processing of Flexible Perovskite Solar Cells with Printed Back Electrodes[5]	Roll to roll	4.90%	ITO/PEDOT:PSS/Perovskite /PCBM/ZnO/Ag
Pinhole-free perovskite films for efficient solar modules[6]	4cm^2	13.6%	ITO/TiO_2/Perovskite/Spiro-OMeTAD/Au
Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers[7]	1cm^2	16.20%	FTO/NiMgLiO/Perovskite /PCBM/Ti(Nb)Ox/Ag
Toward Large Scale Roll-to-Roll Production of Fully Printed Perovskite Solar Cells[8]	Small device	11.96%	ITO/ZnO/Perovskite /P3HT/Ag
Solvent Engineering Boosts the Efficiency of Paintable Carbon-Based Perovskite Solar Cells to Beyond 14%[9]	1cm^2	9.72%	FTO/TiO_2/Perovskite/Carbon
A vacuum flash–assisted solution process for high-efficiency large-area perovskite solar cells[10]	1cm^2	19.60%	FTO/TiO_2/Perovskite/Spiro-OMeTAD/Au
Large-area hysteresis-free perovskite solar cells via temperature controlled doctor blading under ambient environment[11]	1cm^2	7.32%	ITO/PEDOT:PSS/Perovskite /PCBM/C60/BCP/Al

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[1] Current Paper

[2] Journal of Power Sources, 2015, Volume 277, Pages 286–291

3 Solar Energy Materials and Solar Cells, 2016, Volume 144, 309–315

4 J. Mater. Chem. A, 2016,4, 9124-9132

5 Advanced Energy Materials, 2015, 201500569

[6] Energy Environ. Sci.,2016, 9, 484

7 Science, 2015, 350, 944

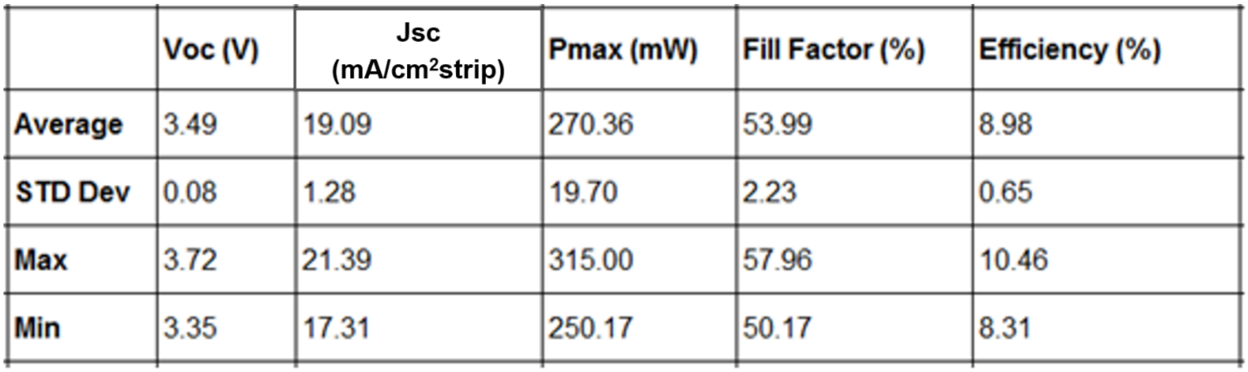
8 Advanced Material, 2015, 201404598

[9] Advanced Energy Materials, 2016,201502087

[10] Science, 2016 (DOI: 10.1126/science.aaf8060)

[11] Applied Materials Today, 2016, Volume 3, 96–102

Table S2: Statistical device analysis for eighteen modules (Fig. 5a)



	Voc (V)	Jsc (mA/cm^{2}strip)	Pmax (mW)	Fill Factor (%)	Efficiency (%)
Average	3.49	19.09	270.36	53.99	8.98
STD Dev	0.08	1.28	19.70	2.23	0.65
Max	3.72	21.39	315.00	57.96	10.46
Min	3.35	17.31	250.17	50.17	8.31

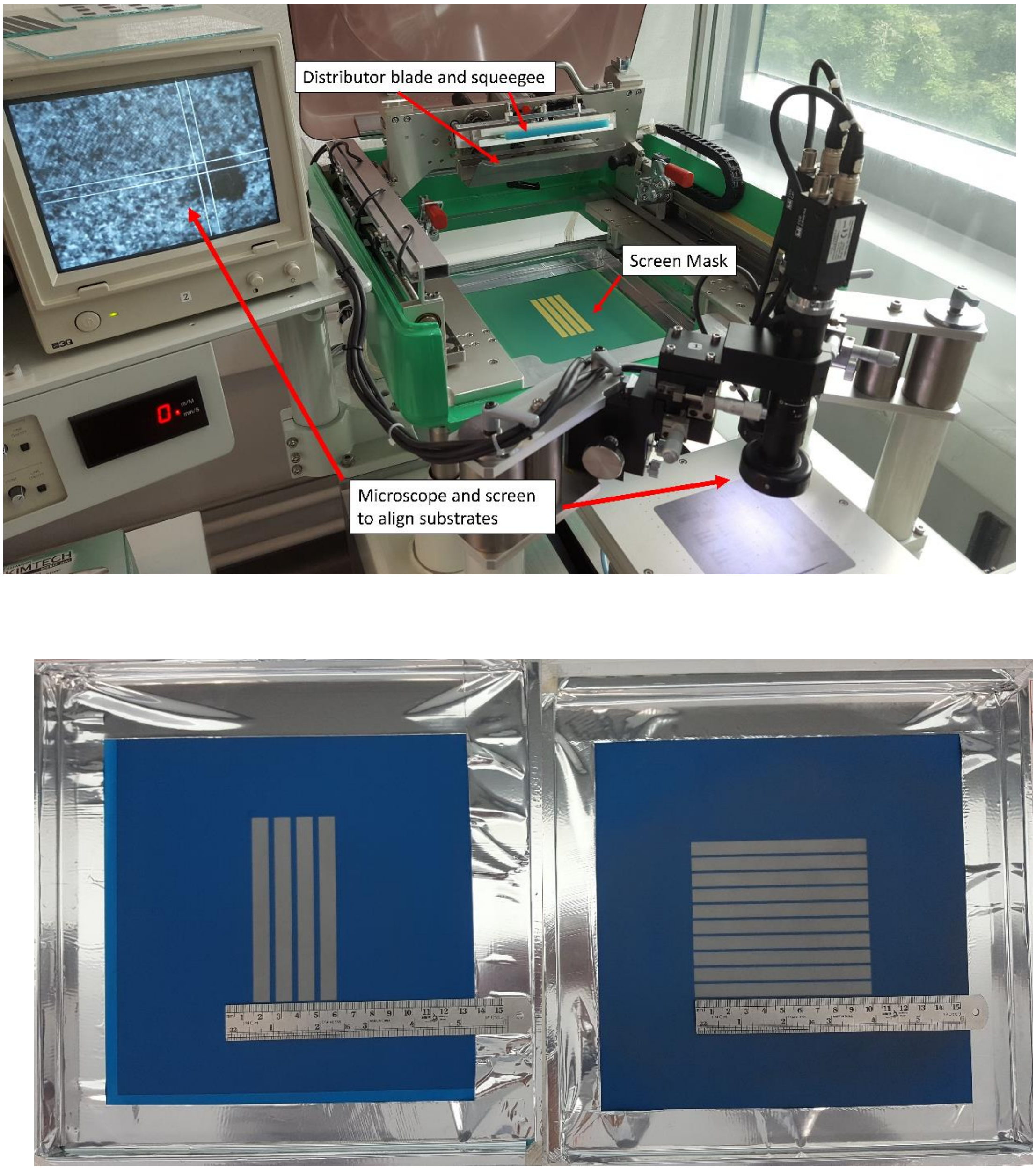


Fig S1: (a) Semi-automatic Screen Printer (MicroTec MT320TV); (b) Mask for 5cm x 10cm and 10cm x 10cm

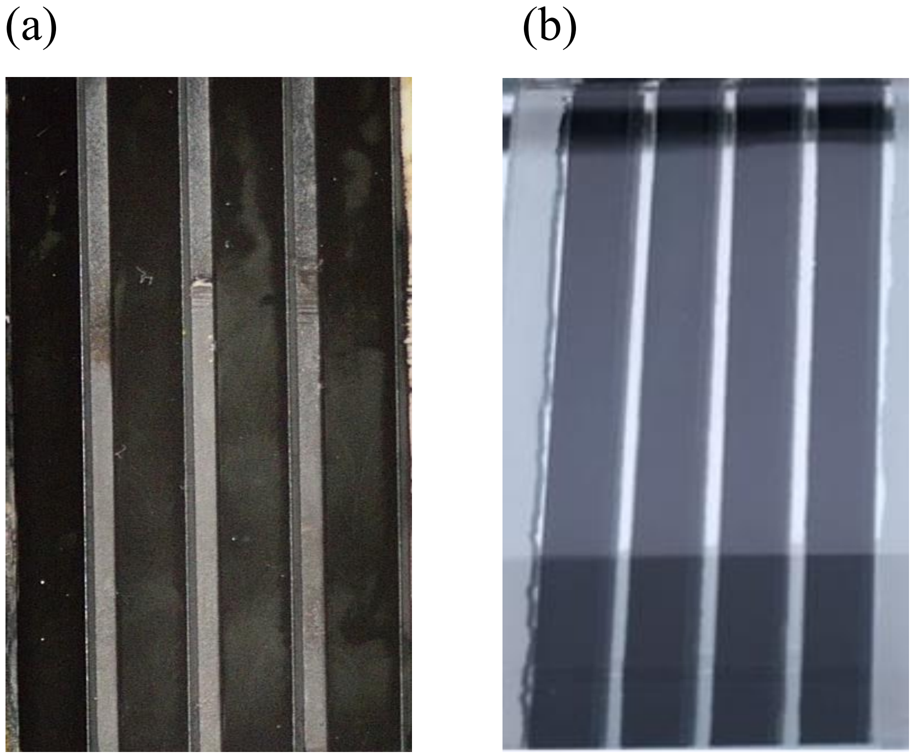


Fig. S2: Back side image of Perovskite solar module (a) unfilled or non-homogeneous mesoporous layer with perovskite crystals; (b) Uniformly filled mesoporous layers with perovskite crystals

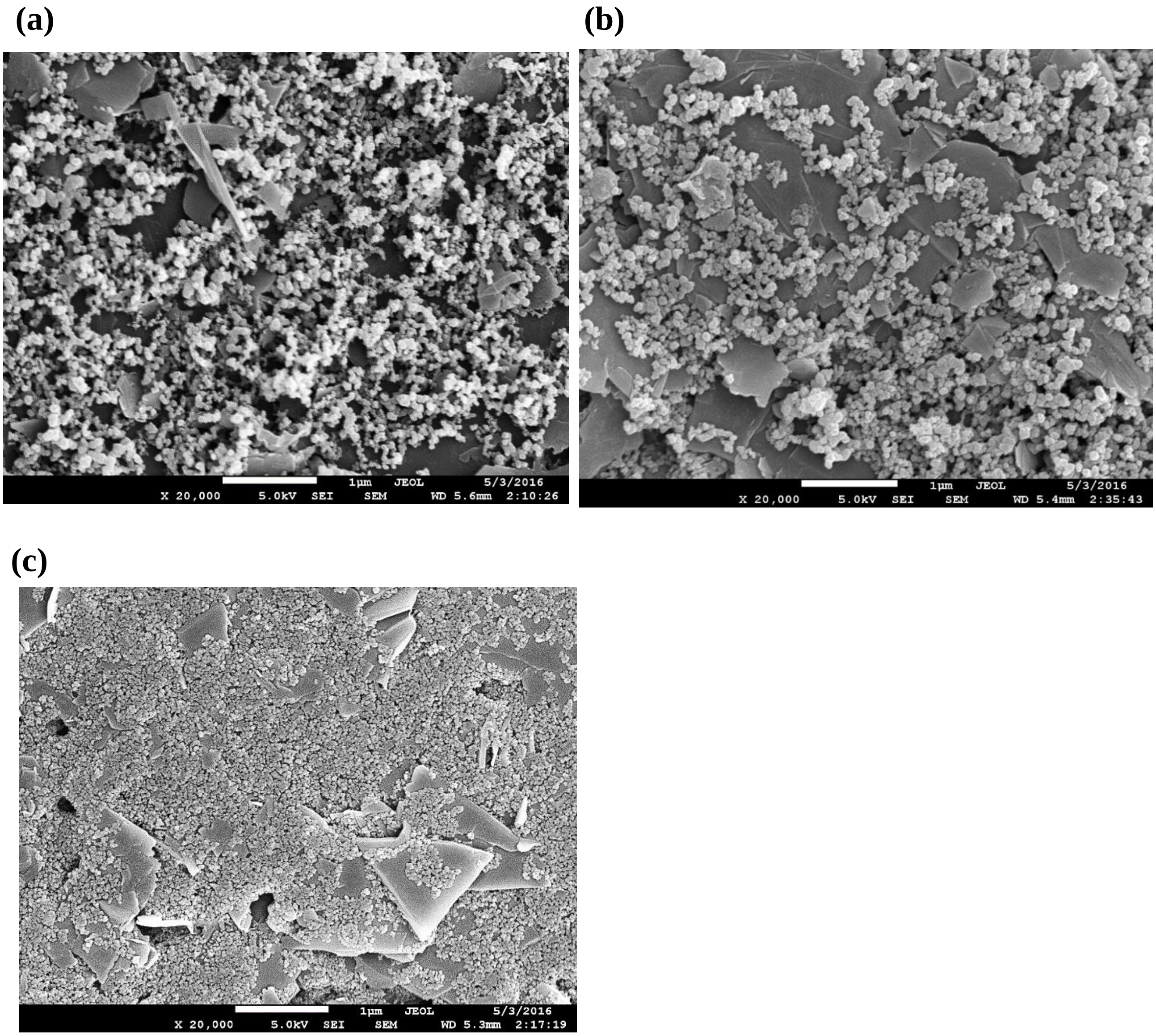


Fig. S3: High Resolution SEM image of carbon Film (a) Carbon 1 (b) Carbon 2 and (c) Carbon 3

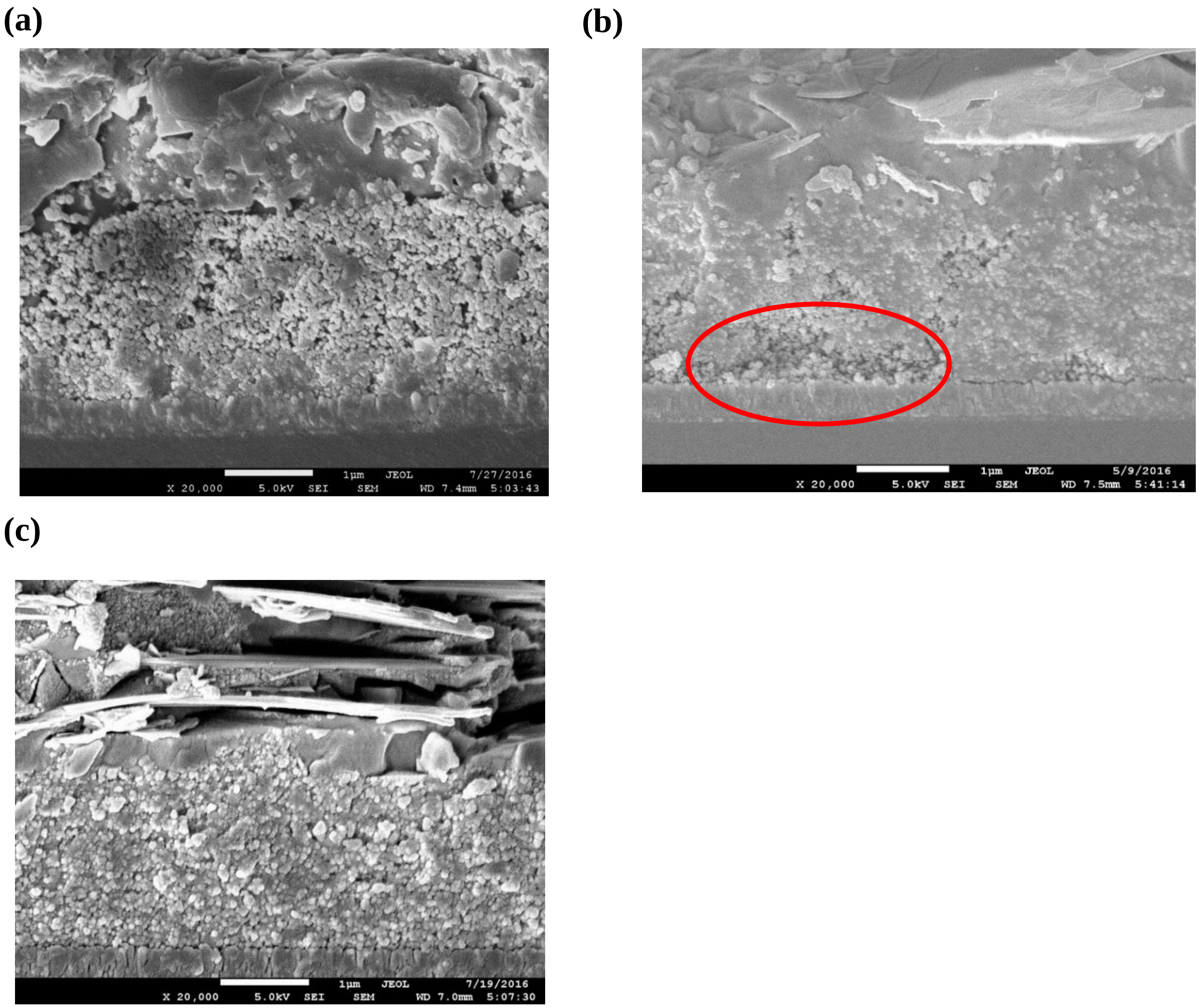
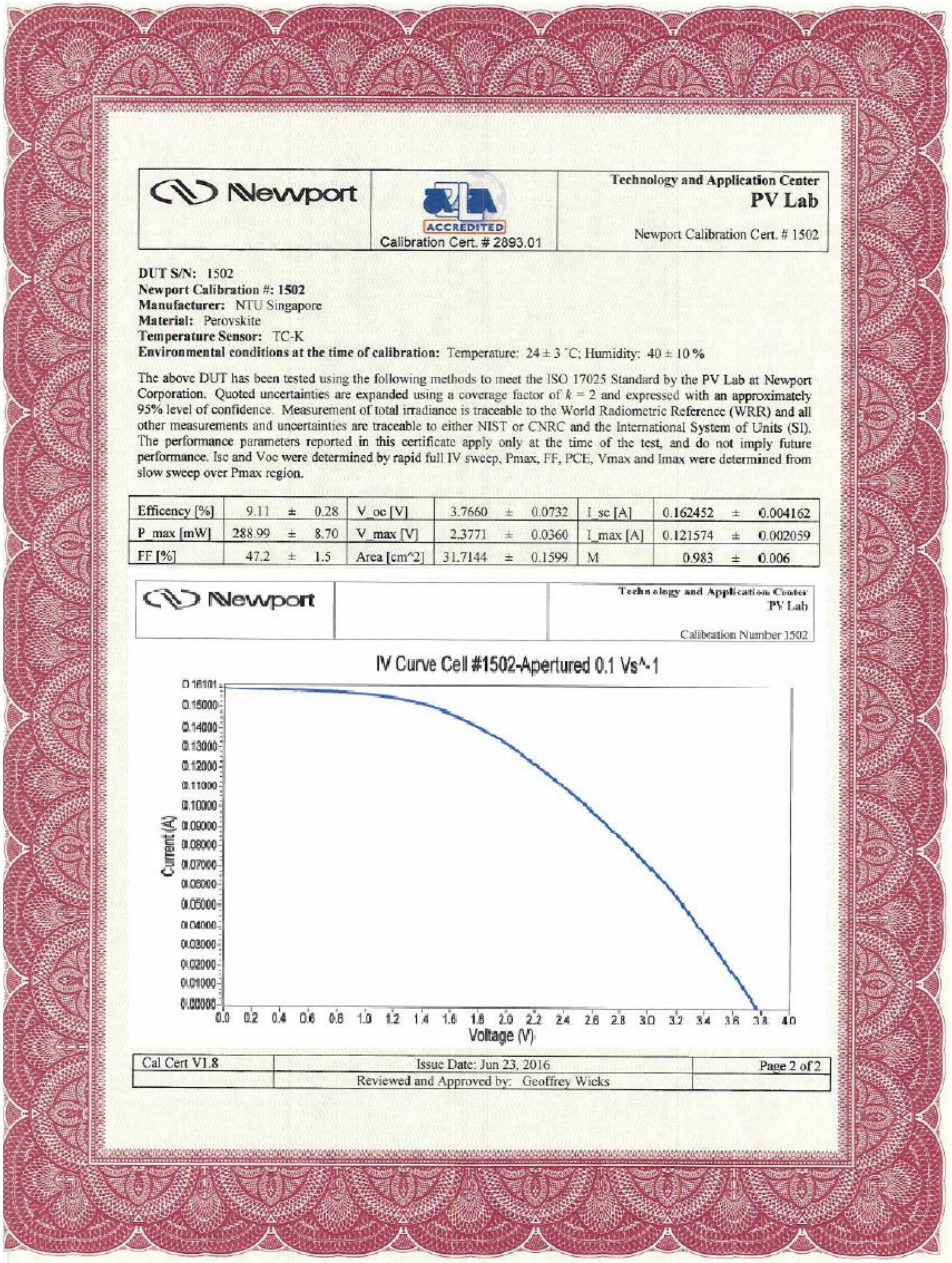


Fig. S4: Cross Section image of full device with infiltration of perovskite crystals (a) Carbon 1 (b) Carbon 2 and (c) Carbon3 as counter electrode



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ACCREDITED
Calibration Cert. # 2893.01

Technology and Application Center
PV Lab
Newport Calibration Cert. # 1502

DUT S/N: 1502
Newport Calibration #: 1502
Manufacturer: NTU Singapore
Material: Perovskite
Temperature Sensor: TC-K
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. Isc and Voc were determined by rapid full IV sweep, Pmax, FF, PCE, Vmax and Imax were determined from slow sweep over Pmax region.

Efficency [%]	9.11	±	0.28	V_oc [V]	3.7660	±	0.0732	I_sc [A]	0.162452	±	0.004162
P_max [mW]	288.99	±	8.70	V_max [V]	2.3771	±	0.0360	I_max [A]	0.121574	±	0.002059
FF [%]	47.2	±	1.5	Area [cm^2]	31.7144	±	0.1599	M	0.983	±	0.006

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Technology and Application Center
PV Lab
Calibration Number 1502

IV Curve Cell #1502-Apertured 0.1 Vs^-1

Cal Cert V1.8	Issue Date: Jun 23, 2016	Page 2 of 2
	Reviewed and Approved by: Geoffrey Wicks	

Fig. S5: Independent certification from Newport Corporation, confirming a PCE of 9.11 %.

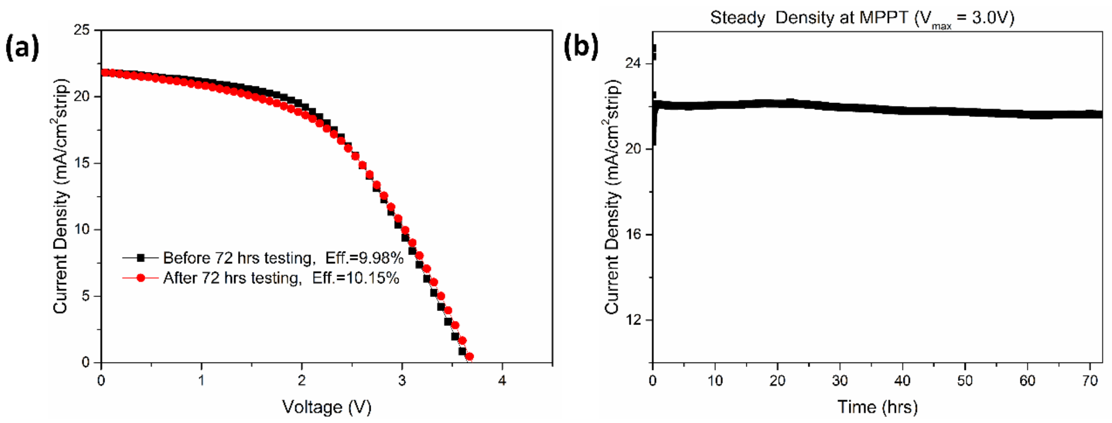

Fig. S6 (a) IV data measured under solar simulator before and after the steady state measurement tests; (b) Steady state current measurement at 2.3V for 3 days using a white light LED light source.

Experimental Section:

Fluorine doped tin oxide (FTO, ~14 ohm per square, 2.2 mm thick) substrates were first etched with CO_2 laser to form the desired pattern, which was cleaned with an ultrasonicator twice with decon soap solution, followed by deionized water (DI water) and finally ethanol. Each sonication process is held at 40°C for 30 mins. These substrates were then immersed in 50 mM of $TiCl_4$ solution (Wako Pure Chemical Industries, Ltd) for 30 min at 70°C, followed by rinsing with DI water. The substrates are held at 500°C for 30 mins to allow formation of TiO_2 crystals to serve as the seed layer. Using a screen-printer (MicroTec MT320TV, Fig s5a), a layer of compact TiO_2 paste (Dyesol BL-1) is printed onto the substrate using screen mask (Fig s5b). The printed film is allowed to relax for 20 mins before calcined at 500°C for 30 mins. These substrates were finally immersed in 100 mM of $TiCl_4$ solution (Wako Pure Chemical Industries, Ltd) for 30 min at 70°C to fill up the defective "pin-holes", followed by rinsing with DI water. A final heat treatment of 500°C completes the formation of the blocking layer.

A 500nm thick layer of mesoporous TiO_2 film is printed onto the substrate with a TiO_2 paste (Dyesol NRD-30, diluted with terpineol (Sigma, FG) in weight ratio 1:1.4). Then, the substrates are sintered for 30 mins at 500°C to improve the crystallinity. Subsequently, a ZrO_2 (Solaronix, Zr-Nanoxide ZT/SP) spacer layer is printed on top of the meso-TiO_2 layer and heated to 500°C for 30 mins to remove the binders. Finally, carbon paste was printed on top of ZrO_2 to complete the device stack. The substrates were heated at 400°C for 30 mins.

Three different types of carbon paste are being prepared. For carbon paste (1), 1.5g of graphite (Sigma Aldrich, Part number: 282863) is mixed with 4.4g of ethyl cellulose (Sigma, mixed with ethanol in a 1:10 weight ratio), 0.5g of Super P carbon (TimCal Ltd, part number: H30253) in 10ml of α-terpineol (Sigma, FG). This mixture was then ball milled for 2 hours through 8 cycle repetitions of 10 mins ball milling at 300rpm and resting for 5 mins.

A micropipette (of maximum capacity 10µl) is used to control the amount of perovskite solution. For a width of 7.75mm, 7.5µl of solution is dispensed from the micropipette. The volume is dispensed as 5 drops, making each drop approximately 1.5µl. This amount of solution is sufficient to wet approximately 2.5 to 3cm of an individual strip length. The same process is repeated 16 times to ensure complete coverage of the whole 5cm x 10cm module (4 strips) by perovskite solution. The amount of perovskite solution and corresponding droplet size is adjusted accordingly to the change in strip width.

For carbon paste (2), 1.5g of graphite (Sigma Aldrich, Part number: 282863) is mixed with 1.3g of ethyl cellulose (Sigma, mixed with ethanol in a 1:10 weight ratio), 0.5g of meso-carbon (Sigma, part number:699624) in 5ml of α-terpineol (Sigma, FG). This mixture was then ball milled for 4 hours through 16 cycle repetitions of 10 mins ball milling at 350rpm and resting for 5 mins.

Rotary Evaporation is used to remove ethanol from both pastes.

Perovskite solution is obtained by mixing equimolar ratio of PbI_2 andCH_3HN_3I (Tokyo Chemical Limited) in γ-Butyrolactone (Sigma, ≥99%). 5 AVA-I prepared by reacting 5-aminovaleric acid (Sigma) with hyrdiodic acid (Sigma) in equimolar ratio, followed by filtering and purification. 5 AVA-I was added to the perovskite solutions in molar ratio of 1:20 (AVA-I to MAI). The solutions are kept stirring overnight on a 50^{o}C hotplate for complete dissolution of the precursors. Perovskite solution is dropped on the carbon layer using a micropipette.

The FE-SEM (Jeol JSM-7600F Field Emission Scanning Electron Microscope) is used to obtain the morphology and cross-section imageries of the devices. I-V characteristics of the devices are measured using the solar simulator (San-EI Electric, XEC-301S), which is connected to a Keithley 2612A SourceMeter. The Quantachrome NOVA 3200 BET setup is used to determine the surface area of the printed film. Carbon films were prepared by printing on a glass substrate, annealed, and scrapped off to measure the surface area of the printed film.

A four-probe tester (Advanced Instrument Technologies CMT-SR2000N) was used to carry out experiments on a printed carbon film of dimensions 3cm×5cm for their conductivity measurement. Pin type is an in-line 4 probe electrode with spacing of 1mm between each pin. Current limit is set to be automatic, while current direction is set to flow in both directions. The average film thickness was input into the software for the measurement of sheet resistance of the carbon film, and the reported values are averaged results of 8 data points. FTO measured in a similar manner had a sheet resistance of 14.23 Ω/sq.

Steady state power tracking was done for 3 days on a 5cmx10cm perovskite module. The current was monitored using Autolab machine (PGSTAT302N, Software version- NOVA 1.11) with a white light LED light source (Model number: ALFL-100, rated @ 100W, CCT of 6000K, Manufactured by Arianetech Pte Ltd, Singapore). The intensity of the light received by the solar module is adjusted by varying the distance of the module and the light source. The distance and the applied voltage (2.3V) were fixed to yield similar currents as the maximum power point current measured under the solar simulator. All measurement was done in ambient (Temperature ≈ 25^{o}C, and humidity ≈ 65%RH).