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Electronic Supplementary Information

Vacuum-Deposited Perovskite Photovoltaics for Highly Efficient Environmental Light Energy Harvesting

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Experimental Methods

Device preparation: The devices were prepared on cleaned and UV-ozone treated indium tin oxide (ITO) substrates. The substrates were thereafter loaded into a high vacuum chamber (base pressure < 1 × 10^{-6} Torr) to deposit MoO_3, tris[4-(5-phenylthiophen-2-yl)phenyl]amine) (TPTPA) and PbI_2 thin films layer-by-layer, and the PbI_2 layers were converted to organometallic perovskite films via sequential vacuum deposition, which was reported in another paper.[1] Subsequently, C_{60}, 1,3,5-Tri[(3-pyridyl)-phen-3-yl] benzene (TmPyPB), and Ag were deposited layer-by-layer. The thicknesses of the MoO_3, organic and PbI_2 layers were carefully calibrated in advance using a *J. A. Woollam V-VASE* ellipsometer. The devices were configured as glass substrate/ITO (145 nm)/MoO_3 (5 nm)/TPTPA (10 nm)/$CH_3NH_3PbI_3$ (≈300 nm) /C_{60} (90 nm)/TmPyPB (7 nm)/Ag (150 nm). The solution-processed perovskite devices for TPC measurements were configured as glass substrate/ITO (145 nm)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (40 nm)/$CH_3NH_3PbI_{3-x}Cl_x$ (≈250 nm)/ETL (≈120 nm)/TmPyPB (7 nm)/Ag (150 nm). Based on our previous study, spin-coated $CH_3NH_3PbI_{3-x}Cl_x$ with precursor ratio of 20% chloride exhibited the highest surface coverage and the highest power conversion efficiencies under AM 1.5G illuminaiton, hence, $CH_3NH_3PbI_{3-x}Cl_x$ rather than $CH_3NH_3PbI_3$ was used as the optimized spin-coated perovskite counterparts.[2, 3] For 1-step spin-coated [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) devices, the spin-coated perovskites were annealed at 100 °C for 10 minutes. After cooling the perovskites to room temperature, dense PCBM solutions (dissolved in chlorobenzene and chloroform (1:1, v/v), 30 mg mL^{-1}) were spin-coated on the perovskites. For 2-step spin-coated PCBM devices, the spin-coated perovskites were first annealed at 100 °C for 2 minutes. Then, dilute PCBM solutions (dissolved in chlorobenzene, 3 mg mL^{-1}) were spin-coated on the perovskite thin films, followed by thermal annealing at 100 °C for 8 minutes. After cooling the

perovskite films to room temperature, dense PCBM solutions (dissolved in chlorobenzene and chloroform (1:1, v/v), 30 mg mL^{-1}) were spin-coated on the perovskite. The device areas were defined by shadow masks when depositing cathode electrode. The overlap areas between ITOs and the top electrodes were 5.1 mm^2 and 5.68 cm^2 for small- and large-area devices, respectively. The devices were encapsulated by UV-epoxy (*EXC345*, *Everwide Chemical Co.*) and cover glasses under an anhydrous nitrogen atmosphere. Before the curing of the UV-epoxy, thin sheets of metals were placed over the active areas of the devices to keep the active areas from direct UV exposure during curing. Next, the epoxy was cured under 370 nm UV light with an intensity of ≈3 mW cm^{-2} for 20 minutes. After encapsulation, the devices were subsequently characterized in air. The vacuum-deposited and solution-processed perovskite thin films for time-resolved photoluminescence (TRPL) measurements were prepared on glass substrates and encapsulated using the same conditions as used for the device fabrication. The samples for scanning electron microscopy (SEM) measurements were prepared on glass substrates using the same conditions as used for the device fabrication. The models of crystalline and amorphous silicon photovoltaic devices are *SM-5120* (*Centenary Materials Co.*) and *SS-3111-A* (*Sinonar Corp.*), respectively.

Characterization: The *J*–V characteristics of the devices were measured using a *Keithley 2636B SourceMeter* under a 6500 K color temperature *Philips T5* fluorescent lamp illumination. The irradiance and luminance of the *T5* fluorescent lamp were determined using a NIST-traceable *Ophir* radiometer (*PD300-BB-50 mW*) and a NIST-traceable *Ophir* photometer (*PD300-CIE*), respectively. The lux levels were changed by varying the distances between light source and the devices. The distances were about 124–50 cm for 200–1000 lux. After the desired lux levels were achieved, the photometer was replaced with the radiometer to get the corresponding incident light power densities, where the energy densities for 200-1000 lux illumination were 62–310 μW cm^{-2}. Subsequently, the radiometer was replaced by the devices to perform the *J*-V measurements. The scan direction was from positive to negative bias, with a step size of 10 mV and a sampling delay time of 300 ms. The power conversion efficiencies (PCEs) were calculated by dividing the maximum electrical power output densities by the incident light power densities. The external quantum efficiency (EQE) spectrum was taken by illuminating the device with chopped monochromatic light with a continuous-wave bias white light from a halogen lamp. The photocurrent signals were extracted with lock-in technique using a *Stanford Research System* current preamplifier (*SR570*) followed by an *Ametek* lock-in amplifier. The device stability test was performed with UV-epoxy encapsulated cells. The cells were stored in a normal indoor

environment (20–30 °C, 50–70% relative humidity) with ambient light intensities range from 0 (in the dark) to 600 lux (during daytime), and regularly measured under 6500 K color temperature *Philips T5* fluorescent lamp illumination. Transient photocurrent measurements were conducted in the dark using the second harmonic of a *Continuum* Nd:YAG laser (*Minilite I*, λ = 532 nm) as an excitation source. The transient signals were amplified using a *FEMTO* variable-gain high-speed current amplifier (*DHPCA-100*) and were recorded using a *Tektronix* oscilloscope (*DPO3052*). The averages of 256 traces were calculated to improve the signal-to-noise ratio. TRPL was measured by using a *PicoQuant* pulsed diode laser (*LDH-P-C-635M*, λ = 635 nm) working at a repetition rate of 0.5 MHz as an excitation source and a *Becker & Hickl GmbH* photon-counting photomultiplier tube (*PMC-100-20*) as a detector. The photon counts were accumulated using a *Becker & Hickl GmbH* time-correlated single photon counting module (*SPC-130-EM*). The SEM images were obtained using a *Hitachi SU8010* field emission scanning electron microscope.

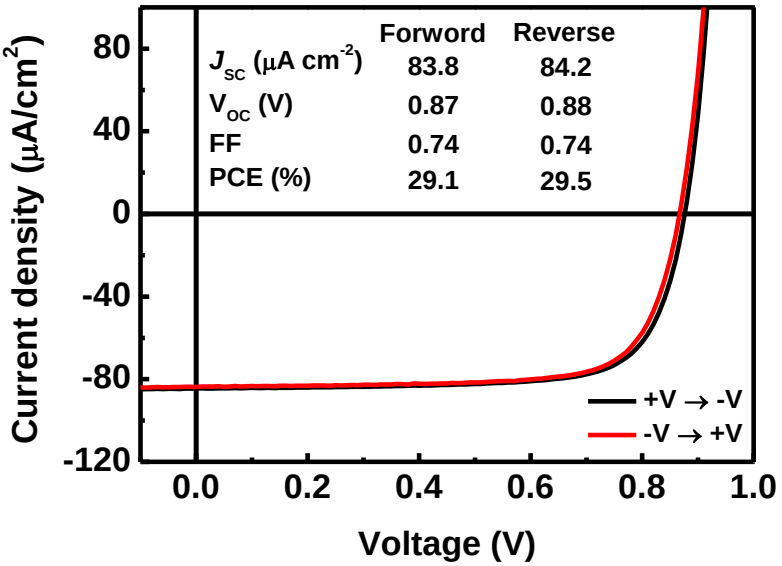

Fig. S1 The *J*–V characteristics of a vacuum-deposited perovskite photovoltaic with different scan directions under fluorescent lamp illumination of 600 lux.

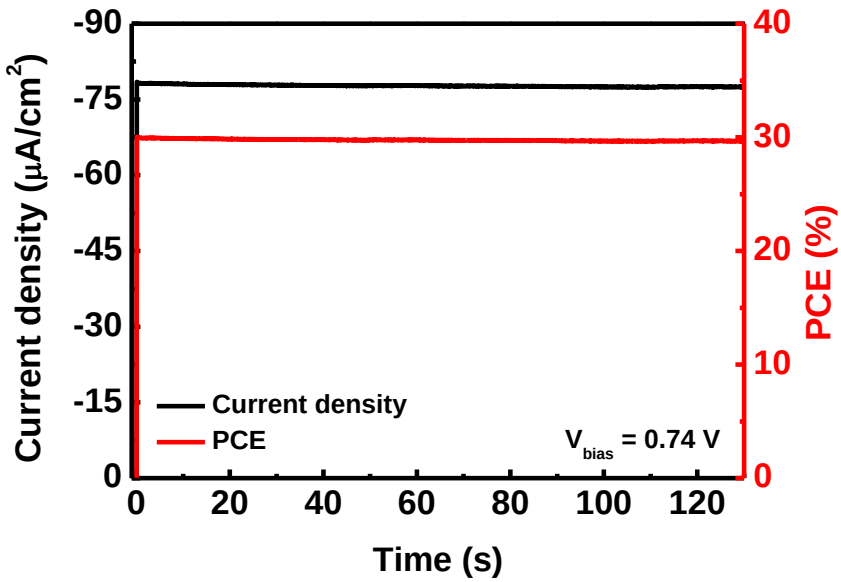

Fig. S2 Photocurrent density and power conversion efficiency as functions of time of the vacuum-deposited perovskite photovoltaic under fluorescent lamp illumination of 600 lux.

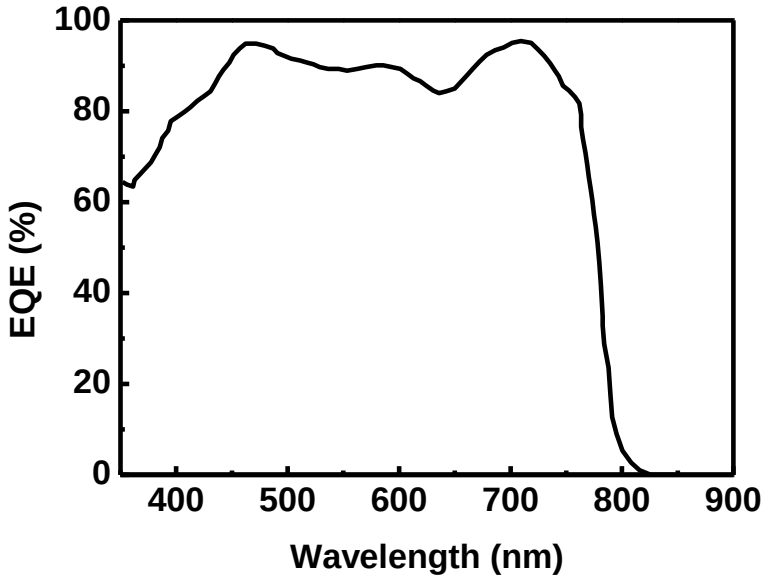

Fig. S3 The EQE spectrum of a vacuum-deposited perovskite photovoltaic.

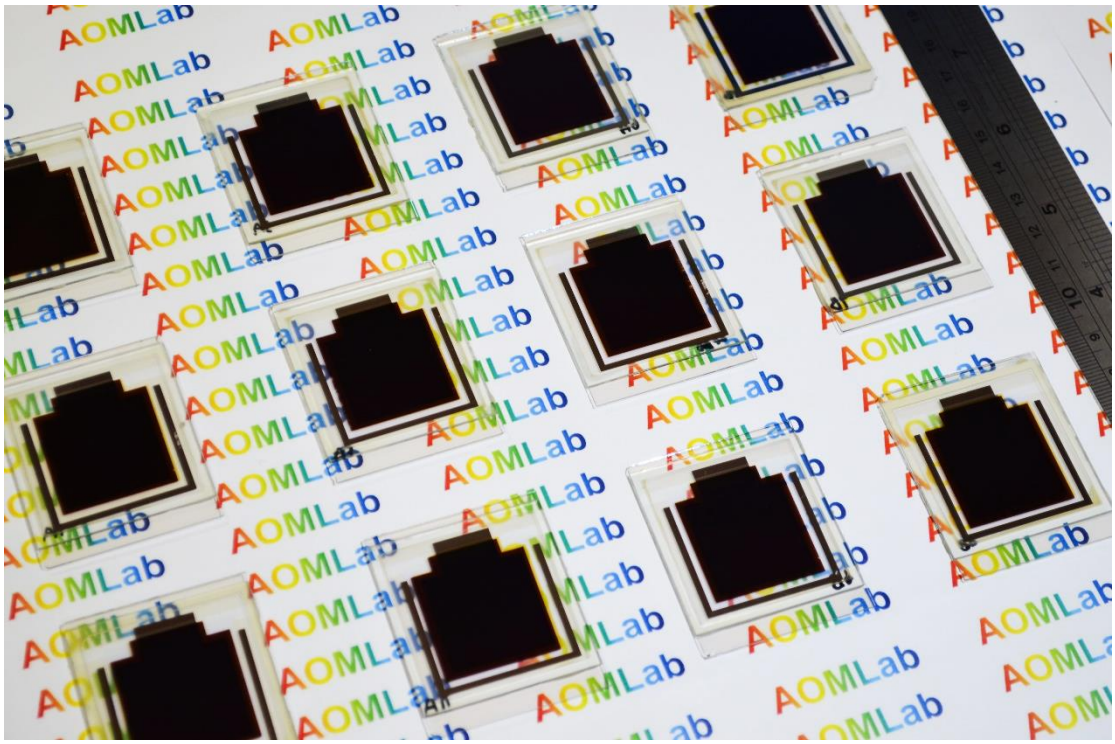

Fig. S4 Photograph of the large-area vacuum-deposited perovskite devices.

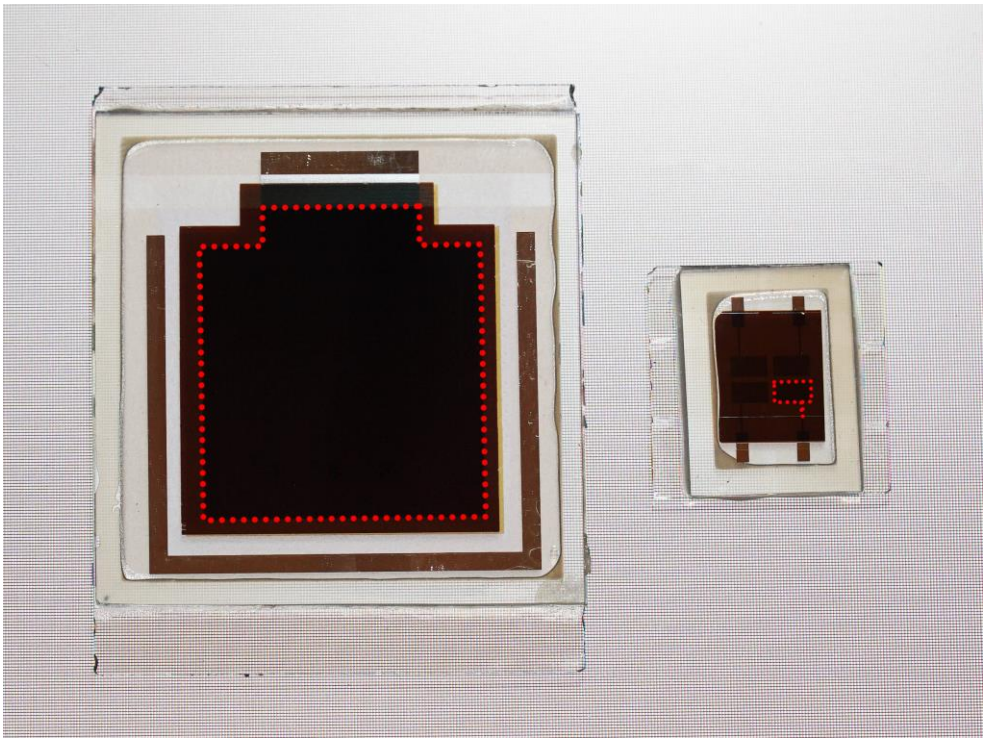

Fig. S5 A close-up photograph of the small- and large-area vacuum-deposited perovskite devices placed on a LCD screen displaying white light. The dashed lines enclosed the overlap areas between ITOs and the top electrodes, which were 5.1 mm^2 and 5.68 cm^2 for small- and large-area devices, respectively.

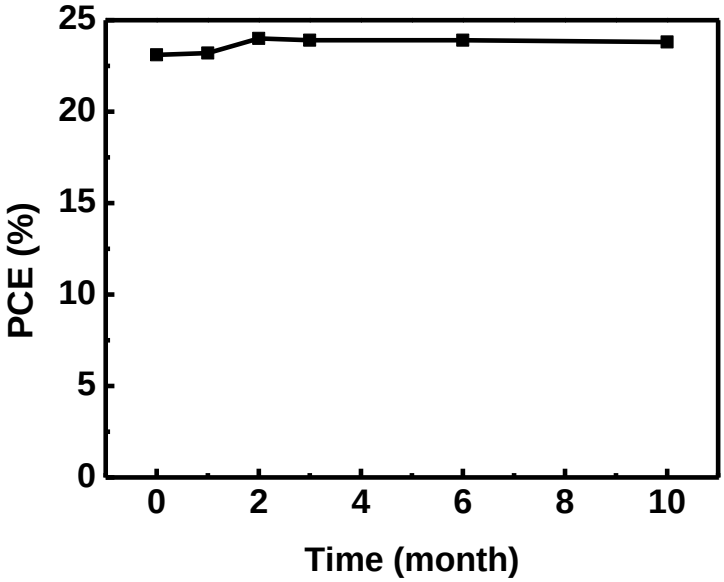

Fig. S6 Long-term PCE stability under illumination of 1000 lux of a large-area vacuum-deposited perovskite photovoltaic. The device was placed in normal in-door envirnoment with irregular 200 to 1000 lux illumination between the measurement points.

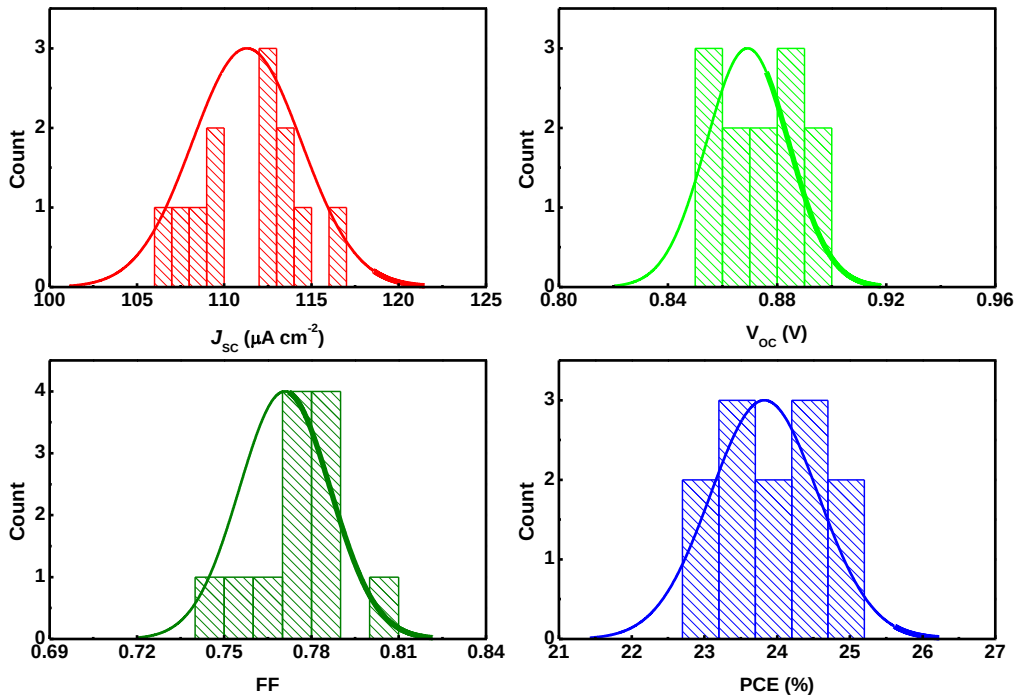

Fig. S7 Histograms of the performance parameters of 12 large-area vacuum-deposited perovskite devices under fluorescent lamp illumination of 1000 lux. The Gaussian fits are presented as a guide to the eye.

科技部 Ministry of Science and Technology

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Research Center for New Generation Photovoltaics (RCNPV)
科技部有機太陽能電池研究量測實驗室
Advanced Laboratory of Accommodation & Research for Organic Photovoltaics (AROPV)

I-V Characterization under Indoor Lighting (Evaluation Activity of MOST)

Report No.: SSC00350020170503

Date of Issue: May 22, 2017

Tested Samples

Manufacturer: Laboratory-G

Sample Type and Identification: Perovskite Solar Cell and LG-S1～LG-S3 (3 Samples)

Sample Receipt and I-V Measurement Dates: May 4, 2017 and May 8, 2017

Test Conditions

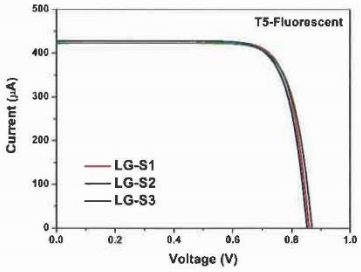
Light Source: T5-Fluorescent or YILS-P150 (LED) with an Illuminance of 1000 lx

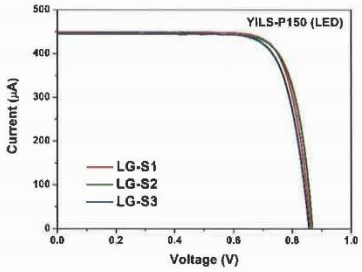
Irradiance (380～780 nm): 325.2 μW cm^{-2} (T5-Fluorescent) or 338.2 μW cm^{-2} (YILS-P150 (LED))

Sample Temperature: 25 ± 1 °C (T-type Thermocouple)

I-V Measurement: Forward Direction (from Isc to Voc) with the Sampling Delay Time of 10000 ms

Characterization Results





Light Source	T5-Fluorescent			YILS-P150 (LED)		
Sample	LG-S1	LG-S2	LG-S3	LG-S1	LG-S2	LG-S3
Isc (μA)	426.98	422.61	427.85	449.00	444.42	445.40
Voc (V)	0.860	0.870	0.853	0.862	0.869	0.857
FF (%)	78.94	77.92	78.11	79.07	78.94	77.69
Pmax (μW)	289.87	286.49	285.07	306.03	304.87	296.55
Area (cm^2)	3.999	4.000	4.000	3.999	4.000	4.000
Jsc (μA cm^{-2})	106.77	105.65	106.96	112.28	111.11	111.35
Eff. (%)	22.3	22.0	21.9	22.6	22.5	21.9

Note 1. The report without seal is invalid.
Note 2. The measurement results are only responsible to the samples tested.
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Traceability of Results

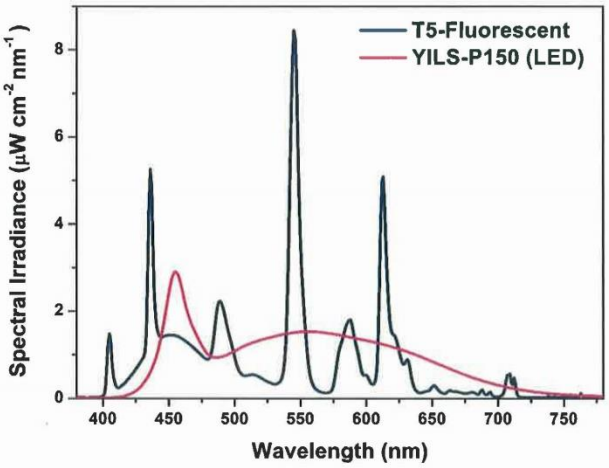
Illuminance: NML (No. O150080A) and JEMIC (No. 011-158653-100)
Irradiance: Otsuka Electronics Co., Ltd. (No. CC43-074-0)
Sample Temperature: Keysight Tech. (No. 1-8415368244-1) and Pink Tech. Co. (No. P611083-C)
Current and Voltage: ETC (No. 16-08-BAC-605-04-L)

Responsible Institute for Issuing Report

Name: PV Efficiency Verification Laboratory (PVEVL) of Research Center for New Generation Photovoltaics (RCNPV), National Central University (NCU), Taiwan
Address: No. 300, Zhongda Rd., Zhongli City, Taoyuan County 32001, Taiwan (R.O.C.)
Website: http://ncu.rcnpv.com.tw/03-6-ev-intro.php
Telephone: 886-3-4227151 ext. 25365 or 25351

Appendix

Output spectra of T5-Fluorescent and YILS-P150 (LED) with an illuminance of 1000 lx



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科技部 Ministry of Science and Technology

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Advanced Laboratory of Accommodation & Research for Organic Photovoltaics (AROPV)

I-V Characterization under Indoor Lighting (Evaluation Activity of MOST)

Report No.: SSC00350020170503-S (Supplementary Results)

Date of Issue: May 22, 2017

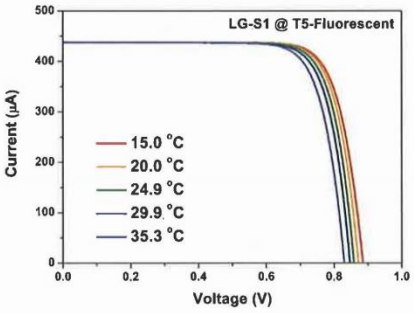
Tested Sample

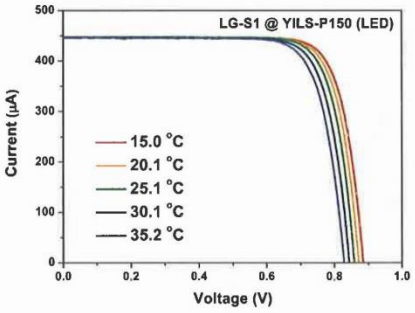
Manufacturer: Laboratory-G
Sample Type and Identification: Perovskite Solar Cell and LG-S1
Sample Receipt Date: May 4, 2017

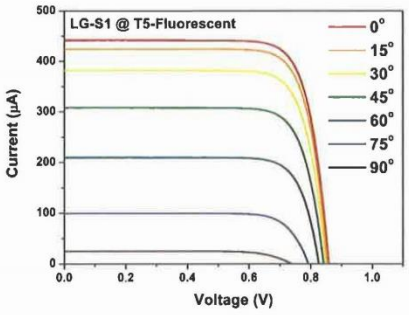
Test Conditions

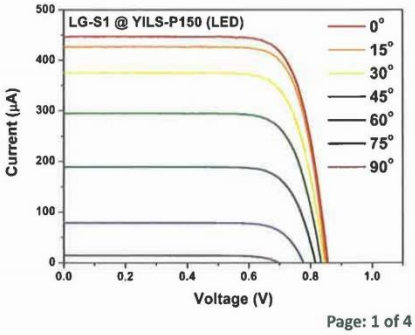
I-V Measurement Dates: May 9, 2017～May 11, 2017
Light Source: T5-Fluorescent or YILS-P150 (LED)
Sample Temperature: 15～35 °C (Tabulated; T-type Thermocouple)
Incident Angle: 0～90 Degree (Tabulated)
I-V measurement: Forward Direction (from Isc to Voc) with the Sampling Delay Time of 5000 ms

Characterization Results









Sample	LG-S1				
Area	3.999 cm^2				
Light Source	T5-Fluorescent				
Illuminance	1038 lx				
Irradiance	337.4 μW cm^{-2} (380～780 nm)				
Tilt Angle	0 Degree				
Temperature (°C)	15.0	20.0	24.9	29.9	35.3
Isc (μA)	438.64	438.27	437.92	437.60	437.27
Voc (V)	0.885	0.872	0.859	0.844	0.830
FF (%)	78.78	79.18	79.26	79.16	78.34
Pmax (μW)	305.82	302.60	298.15	292.37	284.32
Jsc (μA cm^{-2})	109.69	109.59	109.51	109.43	109.34
Eff. (%)	22.7	22.4	22.1	21.7	21.1

Sample	LG-S1				
Area	3.999 cm^2				
Light Source	YILS-P150 (LED)				
Illuminance	1006 lx				
Irradiance	340.4 μW cm^{-2} (380～780 nm)				
Tilt Angle	0 Degree				
Temperature (°C)	15.0	20.1	25.1	30.1	35.2
Isc (μA)	447.94	447.38	446.89	446.44	446.10
Voc (V)	0.885	0.872	0.859	0.844	0.829
FF (%)	79.78	79.73	79.62	78.84	78.11
Pmax (μW)	316.27	311.04	305.64	297.07	288.86
Jsc (μA cm^{-2})	112.01	111.87	111.75	111.64	111.55
Eff. (%)	23.2	22.8	22.5	21.8	21.2

Sample	LG-S1						
Light Source	T5-Fluorescent						
Illuminance	1039 lx (Normal)						
Temperature (°C)	25 ± 1 °C (T-type Thermocouple)						
Tilt Angle (°)	0	15	30	45	60	75	90
Isc (μA)	441.72	424.46	382.30	308.08	209.80	99.44	24.93
Voc (V)	0.858	0.855	0.850	0.842	0.826	0.792	0.738
FF (%)	78.66	78.58	78.27	78.52	79.05	78.05	74.32
Pmax (μW)	298.12	285.18	254.34	203.68	136.99	61.47	13.67

Sample	LG-S1						
Light Source	YILS-P150 (LED)						
Illuminance	1004 lx (Normal)						
Temperature (°C)	25 ± 1 °C (T-type Thermocouple)						
Tilt Angle (°)	0	15	30	45	60	75	90
Isc (μA)	446.81	426.83	375.44	295.00	189.01	78.60	14.33
Voc (V)	0.856	0.849	0.844	0.835	0.816	0.778	0.698
FF (%)	76.48	77.22	75.87	76.30	76.99	78.42	78.47
Pmax (μW)	292.51	279.83	240.41	187.95	118.74	47.95	7.85

The relative external quantum efficiency (EQE) spectrum and tabulated results of the measured sample are normalized to unity for the response at the peak wavelength

Tested Sample

Manufacturer: Laboratory-G

Sample Type and Identification: Perovskite Solar Cell and LG-S1

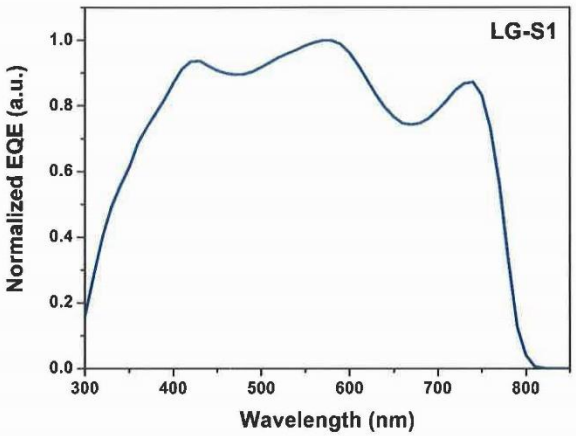
Sample Receipt and EQE Measurement Dates: May 4, 2017 and May 14, 2017

Traceability of EQE Spectrum

Reference Detector: AROPV-RC-10

Calibration Traceability: PTB (No. 47030-PTB-16)

Normalized EQE Spectrum and Data Sheet



Wavelength (nm)	EQE (a.u.)	Wavelength (nm)	EQE (a.u.)	Wavelength (nm)	EQE (a.u.)	Wavelength (nm)	EQE (a.u.)
300	0.1618	440	0.9219	580	0.9993	720	0.8466
310	0.2866	450	0.9088	590	0.9887	730	0.8683
320	0.4021	460	0.9001	600	0.9619	740	0.8724
330	0.4900	470	0.8958	610	0.9225	750	0.8318
340	0.5560	480	0.8968	620	0.8792	760	0.7307
350	0.6132	490	0.9047	630	0.8350	770	0.5613
360	0.6863	500	0.9173	640	0.7958	780	0.3278
370	0.7334	510	0.9324	650	0.7661	790	0.1256
380	0.7764	520	0.9481	660	0.7467	800	0.0402
390	0.8208	530	0.9600	670	0.7425	810	0.0070
400	0.8701	540	0.9708	680	0.7467	820	0.0011
410	0.9127	550	0.9836	690	0.7619	830	0.0002
420	0.9350	560	0.9935	700	0.7874	840	0.0000
430	0.9373	570	1.0000	710	0.8153	850	0.0000

Fig. S8 Independent certification from AROPV.

Table S1. Fitted parameters of the PL decay curves for the vacuum-deposited perovskite thin film (abbreviated as v. per.) and solution-processed perovskite thin film (abbreviated as s. per.) deposited on glass. The relative intensity ratio for each fraction is also shown in the table.

sample	τ_1 [ns]	τ_2 [ns]	τ_3 [ns]	$\tau_{average}$[a)] [ns]
v. per.	4.1 (48%)	51.4 (28%)	503.7 (24%)	137.2
s. per.	2.1 (74%)	19.8 (23%)	557.4 (3%)	22.8

a) $\tau_{average} = \sum_i \alpha_i \tau_i$

Reference

1. S.-Y. Hsiao, H.-L. Lin, W.-H. Lee, W.-L. Tsai, K.-M. Chiang, W.-Y. Liao, C.-Z. Ren-Wu, C.-Y. Chen and H.-W. Lin, *Adv. Mater.*, 2016, **28**, 7013-7019.
2. Y.-C. Huang, C.-S. Tsao, Y.-J. Cho, K.-C. Chen, K.-M. Chiang, S.-Y. Hsiao, C.-W. Chen, C.-J. Su, U. S. Jeng and H.-W. Lin, *Sci. Rep.*, 2015, **5**, 13657.
3. C.-Y. Chen, J.-H. Chang, K.-M. Chiang, H.-L. Lin, S.-Y. Hsiao and H.-W. Lin, *Adv. Funct. Mater.*, 2015, **25**, 7064-7070.