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

Supporting Information

Vapor-fumigation for record efficiency two-dimensional perovskite solar cells with superior stability

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Materials

MAI materials were synthesized according to a method previously reported. Methylammonium solution (24 mL, 33 wt.% in absolute ethanol, Aldrich) was added to a 100 mL 3-neck round-bottom flask; then hydroiodic acid (10 mL, 57 wt.% in water, Aldrich) was slowly dropped into the methylammonium solution at 0 °C. The mixture solution was stirred for 3 hours at 0 °C. Subsequently, the solvents were removed using a rotary evaporator at 60 °C, and the precipitate was obtained. The flaxen powder was dissolved in absolute ethanol; then a certain amount of diethyl ether was added into the solution. The precipitate was filtered by a Buchner funnel.

The above steps were repeated once more to obtain powder that was absolutely white. Finally, the pure MAI was dried at 60 °C in a vacuum oven for 24 hours. 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) was purchased from Yingkou OPV Tech Co., Ltd. PbI_2 (purity > 99.99%) was purchased from Alfa Aesar. The BAI and all of the solvents were purchased from Aldrich and were used without any purification.

Preparation of MA_2PbI_4 film

First, BA_2PbI_4 film was fabricated using the spin-coating method. 402 mg BAI and 462 mg PbI_2 were dissolved in 1 mL γ-butyrolactone and dimethylsulphoxide (7:3. v/v), then stirred at 60 °C overnight. The solution was filtered through a 0.22 μm filter element then spin-coated on the substrate using the anti-solvent method by a two-step spin-coating process at 1000 and 4000 rpm for 15 and 45 s, respectively. The 2.5 cm × 2.5 cm sample was treated with 200 μL chlorobenzene when the second spin-coating step had 20 s remaining. The yellowish-orange BA_2PbI_4 film (Fig. S1, left) was obtained. Then, the BA_2PbI_4 film was placed on a hot-plate at 300 °C for 30 min, and the PbI_2 film formed on the substrate (Fig. S1, middle).After cooling to room temperature, the PbI_2 sample was transferred onto a layer of MAI powder, heated to 150 °C and maintained at this temperature for 20 min. Finally, the brownish black MA_2PbI_4 thin film (Fig. S1, right) was obtained.

Calculation

In our calculations, the crystal structural parameter and electronic structure are calculated based on the plane wave method in the framework of density-functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) code. The projector augmented wave (PAW) pseudopotentials are used to describe the interaction between ion-cores and valence electrons. The generalized gradient approximation (GGA) with the Perdew Burke Ernzerhof (PBE) functional is used for the exchange-correlation effects, and an energy cutoff of 450 eV is set for the plane wave function's expansion. For the Brillouin zone intergration, a Γ-centered 3 × 3 × 1 and 3 × 3 × 2 Monkhorst-Pack k-point sampling meshes are used for monolayer structure and bulk structure, resectively. The spin-orbit coupling was also considered in the electronic structure calculations and the van der Waals (vdW) interaction between 2D layers are described by the DFT-D3 correction. The lattice parameter and atomic positions of the all structures are relaxed untill the total energy changes were less than 1.0×10^{-5} eV. Periodic boundary condition is applied along the in plane direction and a vacuum spacing >15 Å is set along the direction perpendicular to the sheet plane to avoid the interaction between period cells.

Device fabrication

Glass/FTO substrates were cleaned with acetone, isopropyl alcohol and deionized water in an ultrasonic bath for 30 min, respectively, and then dried by flowing nitrogen gas. The TiO_2 electron transport layers of ~ 60 nm-thick were deposited on FTO substrates using a chemical bath according to previous report. The FTO/TiO_2 substrates were exposed to ultraviolet light and ozone for 15 min, and then the perovskite absorbers were deposited. The 90 mg mL^{-1} spiro-OMeTAD chlorobenzene solution, mixed with dopants of 36 μL 4-tert-butylpyridine and 22 μL lithium bis(trifluoromethylsulfonyl) imide at 520 mg mL^{-1} in acetonitrile, was spin-coated onto the perovskite films at 3000 rpm for 30 s. Finally, 100-nm-thick gold layers were deposited using a thermal evaporator.

Characterization

The *J-V* curves were performed using a Keithley 2400 SourceMeter under ambient temperature and air conditions. The light source was a 450 W Xenon lamp (Oriel solar simulator) equipped with a SchottK113 Tempax sunlight filter (Praezisions Glas & OptikGmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the illumination intensity was 100 mWcm^{-2} calibrated by an NREL-traceable KG5-filtered silicon reference cell. The scan rate was 0.1 V s^{-1}, the scan step was 0.02 V, and the scan delay time was 10 ms. A non-reflective black mask with an aperture area of 0.09052 cm^{2} was covered part of the active area (0.1134 cm^{2}) to avoid light scattering through the sides during the measurement. The aperture area was determined by the MICRO VUE sol 161 instrument. The EQE was acquired using a Crowntech QTest Station 2000ADI system. The light source was a 300 W xenon lamp, and the monochromatic light intensity for the EQE measurement was calibrated with a reference silicon photodiode. GIWAXS measurements were performed in the D-line at the Cornell High Energy Synchrotron Source (CHESS). The x-rays wavelength was 1.166 Å with a bandwidth $\Delta\lambda/\lambda$ of 1.5%. The scattering 10 signal was collected using a Pilatus 200K detector. The incident angle of the x-ray beam was at 0.25°, and the integration time was 1 s. Steady-state PL (excitation at 532 nm) measurements were carried out using an Edinburgh Instruments Ltd (FLS980). The TRPL spectra were acquired on an Edinburgh Instruments FLS980 fluorescence spectrometer with the time-correlated single-photon counting method. SEM images were obtained by a field emission scanning electron microscope (SU8020) with an accelerating voltage of 3 keV. XRD patterns were acquired on a SmartLab x-ray diffraction system. The UV-Vis spectra were acquired by a PerkinElmer 10 UV-Lambda 950 instrument. XPS data were measured on a Thermo Fisher Scientific (K-Alpha system) using Al Kα as the exciting x-ray source at a pressure of 1×10^{-8} Pa.

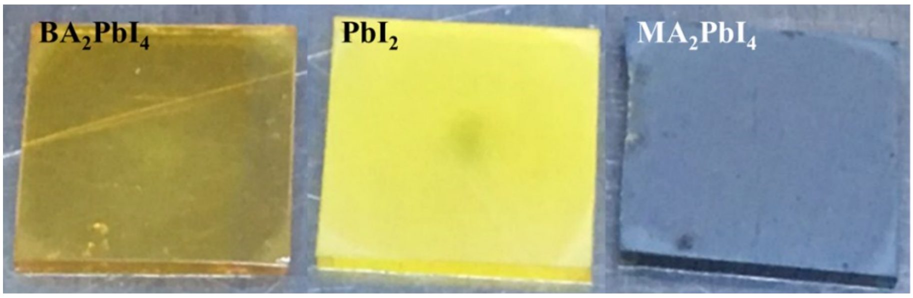


Fig. S1. Photograph of BA_2PbI_4, PbI_2, and MA_2PbI_4 films.

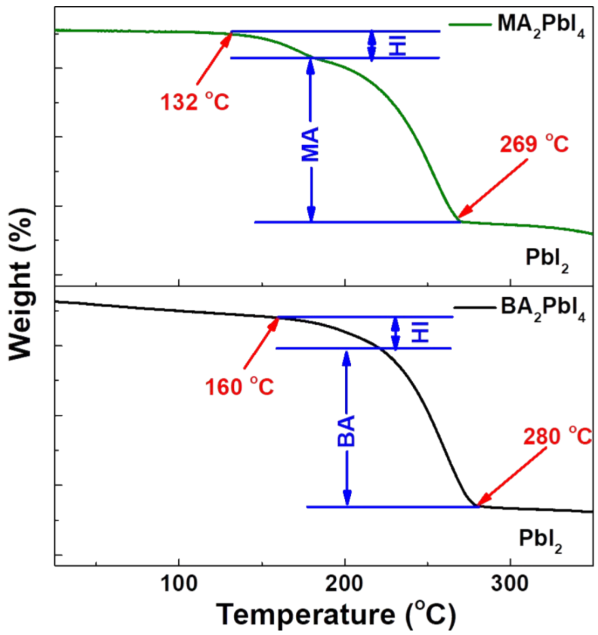


Fig. S2. Decomposition analysis of BA$_2$PbI$_4$ and MA$_2$PbI$_4$ powder. TGA was performed from room temperature to 350 °C under active nitrogen gas flow. There is weight loss observed below 160 °C caused by the removal of other impurities adsorbed on the BA$_2$PbI$_4$ powder. When the temperature exceeded 160 °C, the TGA curve sharp declined, indicating that the BA$_2$PbI$_4$ started decomposition into BA, HI and PbI$_2$. As the temperature continuously increased, BA and HI completely sublimated. This decomposition ended at 280 °C, and the weight of the residual is approximately 56% of its initial total value, which is very close to the mass proportion of PbI$_2$ in BA$_2$PbI$_4$, meaning that PbI$_2$ template is successfully generated by BA$_2$PbI$_4$ decomposition. In addition, TGA of MA$_2$PbI$_4$ powder was measured. When it is heated to beyond 132 °C, the TGA curve drops sharply, indicating that the MA$_2$PbI$_4$ starts to decompose into MA, HI and PbI$_2$. When the temperature overs 269 °C, the net mass hits a plateau, indicating that the volatile MA and HI are completely gone. It is clear that the thermal decomposition of MA$_2$PbI$_4$ starts at 132 °C, lower than that of BA$_2$PbI$_4$.

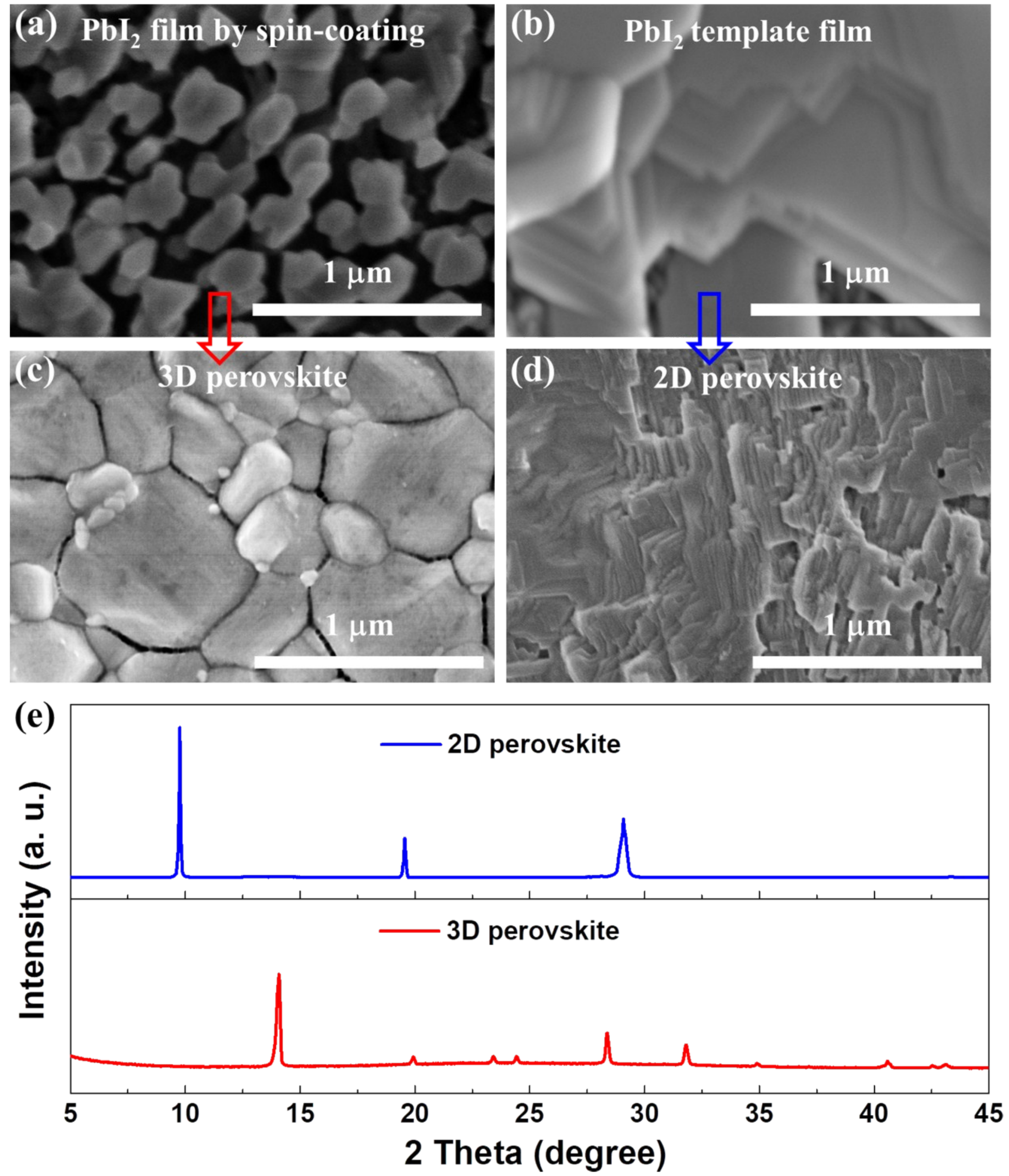


Fig. S3 SEM images of (a) PbI_2 film fabricated by spin-coating, and (b) PbI_2 template film. Corresponding top-view SEM images of (c) 3D perovskite film, and (d) 2D perovskite film. (e) XRD patterns of films based on various PbI_2 films.

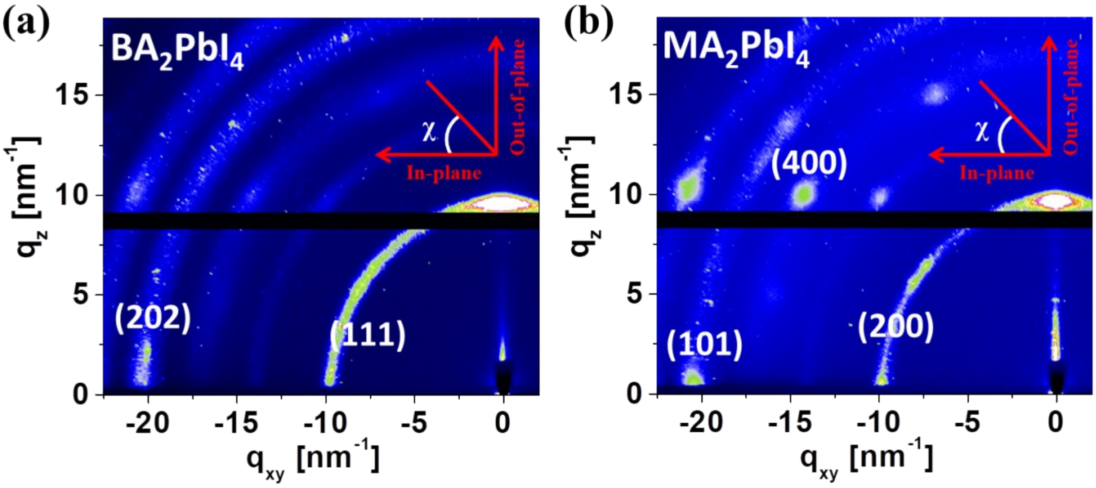


Fig. S4. GIWAXS images for (a) BA_2PbI_4 and (b) MA_2PbI_4.

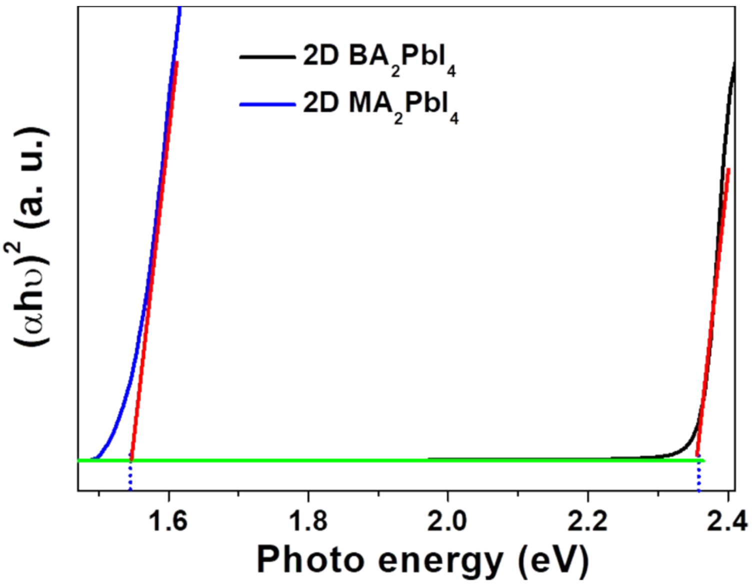


Fig. S5. The band gap (E_g) of BA_2PbI_4 and MA_2PbI_4 films established from the corresponding absorbance spectra.

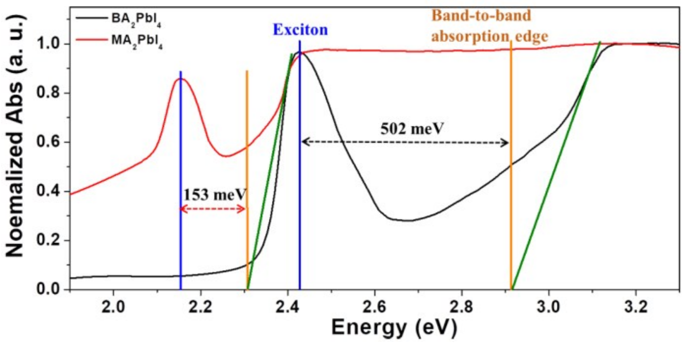


Fig. S6. Estimated exciton binding energy by absorption spectra. The 2D perovskites show a typical exciton peak and a step-like band-to-band absorption. The exciton binding energy of BA$_2$PbI$_4$ and MA$_2$PbI$_4$ are 502 meV and 153 meV, respectively.

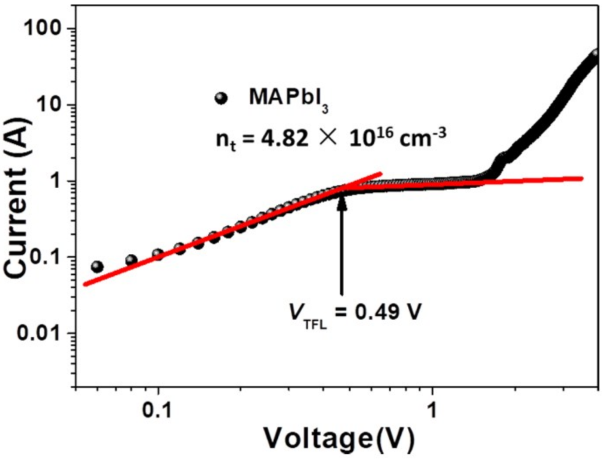


Fig. S7. Dark *I*-*V* curves of the $MAPbI_3$ devices.

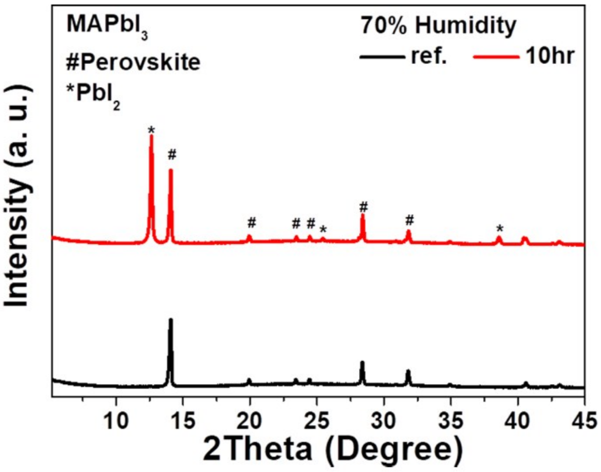
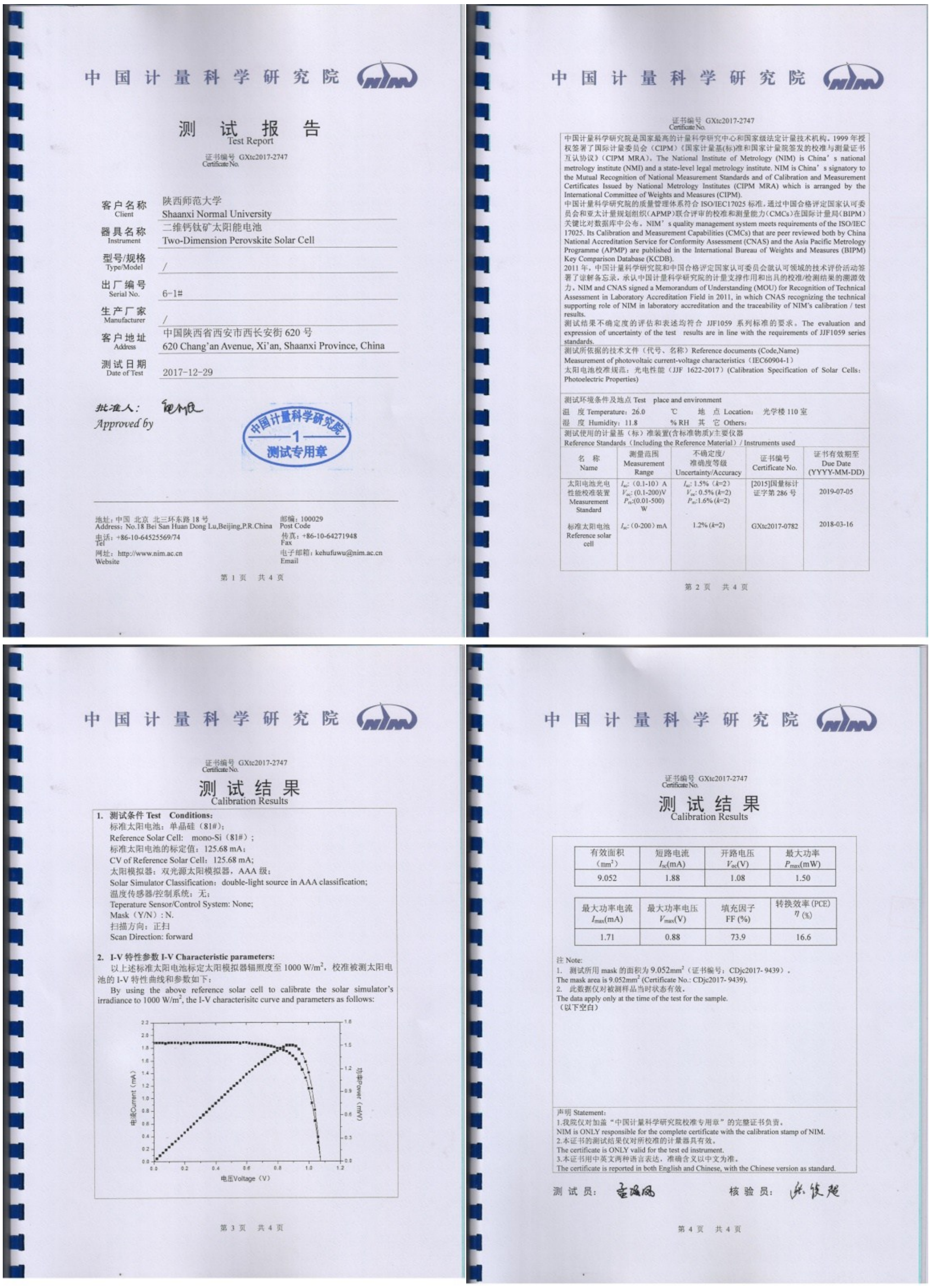


Fig. S8. XRD spectra of MAPbI$_3$ stored at 70% humidity for different time.



中国计量科学研究院

测 试 报 告
Test Report

证书编号 GXtc2017-2747
Certificate No.

客户名称 Client: 陕西师范大学 Shaanxi Normal University
器具名称 Instrument: 二维钙钛矿太阳能电池 Two-Dimension Perovskite Solar Cell
型号/规格 Type/Model: /
出厂编号 Serial No.: 6-1#
生产厂家 Manufacturer: /
客户地址 Address: 中国陕西省西安市西长安街 620 号 620 Chang'an Avenue, Xi'an, Shaanxi Province, China
测试日期 Date of Test: 2017-12-29

批准人:
Approved by

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中国计量科学研究院

证书编号 GXtc2017-2747
Certificate No.

中国计量科学研究院是国家最高的计量科学研究中心和国家级法定计量技术机构。1999 年授权签署了国际计量委员会（CIPM）《国家计量基(标)准和国家计量院签发的校准与测量证书互认协议》（CIPM MRA）。The National Institute of Metrology (NIM) is China's national metrology institute (NMI) and a state-level legal metrology institute. NIM is China's signatory to the Mutual Recognition of National Measurement Standards and of Calibration and Measurement Certificates Issued by National Metrology Institutes (CIPM MRA) which is arranged by the International Committee of Weights and Measures (CIPM).

中国计量科学研究院的质量管理体系符合 ISO/IEC17025 标准，通过中国合格评定国家认可委员会和亚太计量规划组织(APMP)联合评审的校准和测量能力(CMCs)在国际计量局(BIPM)关键比对数据库中公布。NIM's quality management system meets requirements of the ISO/IEC 17025. Its Calibration and Measurement Capabilities (CMCs) that are peer reviewed both by China National Accreditation Service for Conformity Assessment (CNAS) and the Asia Pacific Metrology Programme (APMP) are published in the International Bureau of Weights and Measures (BIPM) Key Comparison Database (KCDB).

2011 年，中国计量科学研究院和中国合格评定国家认可委员会就认可领域的技术评价活动签署了谅解备忘录，承认中国计量科学研究院的计量支撑作用和出具的校准/检测结果的溯源效力。NIM and CNAS signed a Memorandum of Understanding (MOU) for Recognition of Technical Assessment in Laboratory Accreditation Field in 2011, in which CNAS recognizing the technical supporting role of NIM in laboratory accreditation and the traceability of NIM's calibration / test results.

测试结果不确定度的评估和表述均符合 JJF1059 系列标准的要求。The evaluation and expression of uncertainty of the test results are in line with the requirements of JJF1059 series standards.

测试所依据的技术文件（代号、名称）Reference documents (Code,Name)
Measurement of photovoltaic current-voltage characteristics（IEC60904-1）
太阳电池校准规范：光电性能（JJF 1622-2017）(Calibration Specification of Solar Cells: Photoelectric Properties)

测试环境条件及地点 Test place and environment
温 度 Temperature：26.0 ℃ 地 点 Location： 光学楼 110 室
湿 度 Humidity：11.8 %RH 其 它 Others：

测试使用的计量基（标）准装置(含标准物质)/主要仪器
Reference Standards（Including the Reference Material）/ Instruments used

名 称 Name	测量范围 Measurement Range	不确定度/ 准确度等级 Uncertainty/Accuracy	证书编号 Certificate No.	证书有效期至 Due Date (YYYY-MM-DD)
太阳电池光电性能校准装置 Measurement Standard	I_{sc}:（0.1-10）A V_{oc}: (0.1-200)V P_m:(0.01-500) W	I_{sc}: 1.5%（k=2） V_{oc}: 0.5% (k=2) P_m:1.6% (k=2)	[2015]国量标计证字第 286 号	2019-07-05
标准太阳电池 Reference solar cell	I_{sc}:（0-200）mA	1.2% (k=2)	GXtc2017-0782	2018-03-16

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证书编号 GXtc2017-2747
Certificate No.

测 试 结 果
Calibration Results

1. 测试条件 Test Conditions:
标准太阳电池：单晶硅（81#）;
Reference Solar Cell: mono-Si（81#）;
标准太阳电池的标定值：125.68 mA;
CV of Reference Solar Cell：125.68 mA;
太阳模拟器：双光源太阳模拟器，AAA 级;
Solar Simulator Classification：double-light source in AAA classification;
温度传感器/控制系统：无;
Teperature Sensor/Control System: None;
Mask（Y/N）: N.
扫描方向：正扫
Scan Direction: forward

2. I-V 特性参数 I-V Characteristic parameters:

以上述标准太阳电池标定太阳模拟器辐照度至 1000 W/m^2，校准被测太阳电池的 I-V 特性曲线和参数如下：

By using the above reference solar cell to calibrate the solar simulator's irradiance to 1000 W/m^2, the I-V characterisitc curve and parameters as follows:

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Certificate No.

测 试 结 果
Calibration Results

有效面积（mm^2）	短路电流 I_{sc}(mA)	开路电压 V_{oc}(V)	最大功率 P_{max}(mW)
9.052	1.88	1.08	1.50

最大功率电流 I_{max}(mA)	最大功率电压 V_{max}(V)	填充因子 FF (%)	转换效率 (PCE) η (%)
1.71	0.88	73.9	16.6

注 Note:
1. 测试所用 mask 的面积为 9.052mm^2（证书编号：CDjc2017- 9439）。
The mask area is 9.052mm^2 (Certificate No.: CDjc2017- 9439).
2. 此数据仅对被测样品当时状态有效。
The data apply only at the time of the test for the sample.
（以下空白）

声明 Statement:
1.我院仅对加盖“中国计量科学研究院校准专用章”的完整证书负责。
NIM is ONLY responsible for the complete certificate with the calibration stamp of NIM.
2.本证书的测试结果仅对所校准的计量器具有效。
The certificate is ONLY valid for the test ed instrument.
3.本证书用中英文两种语言表达，准确含义以中文为准。
The certificate is reported in both English and Chinese, with the Chinese version as standard.

测 试 员： 核 验 员：

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Fig. S9. Certificated results of 2D MA_2PbI_4 PSC from the National Institute of Metrology (NIM) of China. The certificated efficiency is 16.6% with J_{sc} = 20.77 mA cm^{-2}, V_{oc} = 1.08 V and FF = 73.9%. A mask area of 9.052 mm^2 has been used when certification.

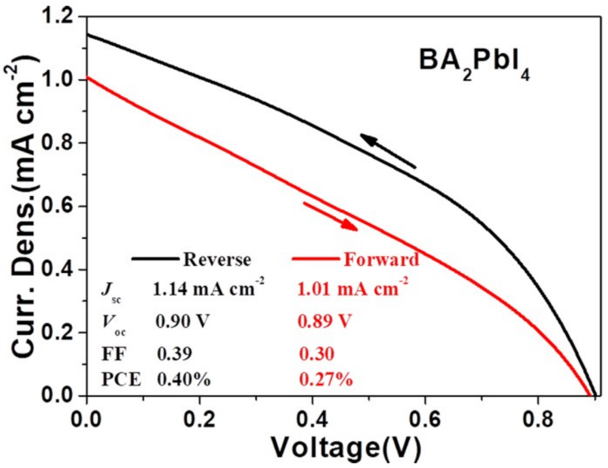

Fig. S10. *J*-*V* characterizations of BA$_2$PbI$_4$ PSCs scanned at the reverse and forward directions.

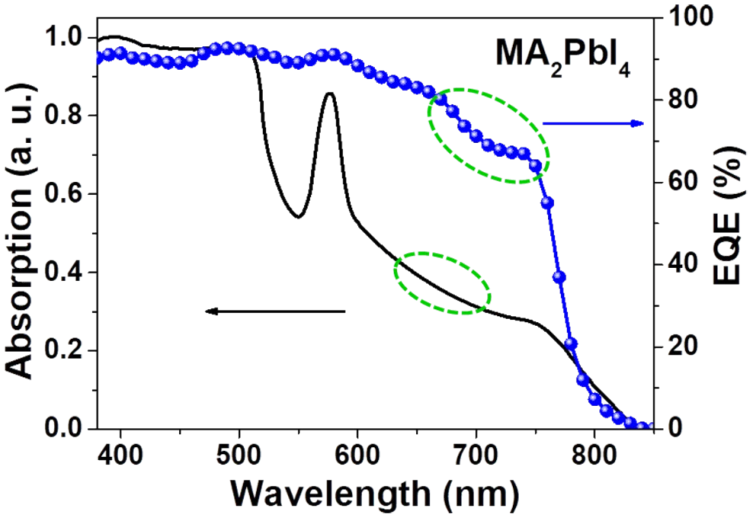

Fig. S11. EQE and absorbance curves of MA$_2$PbI$_4$. EQE curve of a PSC based on MA$_2$PbI$_4$ absorber and absorbance spectra of 2D MA$_2$PbI$_4$ film. Both edge lines cut off at ca. 800 nm. The EQE shows a fast decline from 650 to 750 nm, which indicates weak absorption in this range due to the thinness of the 179 nm-thick MA$_2$PbI$_4$ absorber (Fig. 4b).

Table S1. The optimized lattice parameters of BA_2PbI_4 and MA_2PbI_4.

BA_2PI_4			MA_2PbI_4		
Triclinic	a	8.46	Triclinic	a	8.57
	b	8.69		b	8.71
	c	28.62		c	19.31
	α	83.91		α	101.38
	β	90.77		β	100.96
	γ	90.12		γ	91.65
Layer spacing	d	14.2	Layer spacing	d	9.2

Table S2. The electrical conductivity of BA_2PbI_4 and MA_2PbI_4 films.

Sample	σ_0 (mS cm^{-1})
BA_2PbI_4	1.53×10^{-3}
MA_2PbI_4	2.96×10^{-3}

Table S3. The parameters of MA_2PbI_4 solar cells.

Device	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	19.17	1.00	0.70	13.42
2	19.65	0.98	0.71	13.67
3	21.05	0.96	0.71	14.35
4	20.68	0.98	0.75	15.20
5	19.17	0.96	0.75	13.80
6	20.49	0.96	0.75	14.75
7	20.50	0.98	0.76	15.27
8	19.75	0.98	0.76	14.71
9	21.66	0.98	0.76	16.13
10	21.18	0.98	0.76	15.77
11	18.02	1.00	0.77	13.88
12	19.33	0.96	0.77	14.29
13	19.31	0.98	0.78	14.76
14	21.00	1.06	0.76	16.91
15	21.40	0.96	0.60	12.33
16	19.79	0.90	0.61	10.86
17	20.53	0.90	0.61	11.27
18	22.07	0.96	0.62	13.14
19	20.35	0.96	0.62	12.11
20	21.34	0.96	0.62	12.70
21	20.44	0.96	0.62	12.17
22	22.83	0.94	0.63	13.52
23	22.71	0.92	0.63	13.16
24	19.51	0.96	0.65	12.17
25	23.12	0.92	0.65	13.83
26	23.22	0.90	0.66	13.79
27	22.47	0.90	0.66	13.35
28	20.68	0.90	0.66	12.28
29	22.65	0.92	0.68	14.17

30	22.39	0.92	0.68	14.01
Average	20.88 ± 1.36	0.98 ± 0.04	0.73 ± 0.06	14.18 ± 1.40

References

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