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Supplementary Information

Laser-assisted crystallization of CH₃NH₃PbI₃ film for efficient perovskite solar cell with high open-circuit voltage

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Experimental details:

Materials

Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. Specific details of all materials can refer to our previous work.^{1,2} 2,2',7,7'-tetrakis (N,N-di-pmethoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD, 99.68%) was purchased from Shenzhen Feiming Science and Technology Co., Ltd. (China). The methyl ammonium iodide (CH₃NH₃I) was synthesized according to the previous reports.³ All chemicals used were analytic grade reagents without further purification.

Preparation of CH₃NH₃Pbl₃ films

The pristine film of CH₃NH₃I•Pbl₂•DMSO was synthesized according to method reported elsewhere.⁴ 461mg of Pbl₂, 159 mg of CH₃NH₃I and 78 mg of dimethylsulfoxide (DMSO) were mixed in 600 mg of *N*,*N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich). The precursor solution was spin-coated on the TiO₂ hole-blocking layer at 4000 rpm for 20 second, and 0.5 ml of diethyl ether was dripped on the rotating substrate in 5 second before the surface changed to be turbid caused by rapid vaporization of DMF. The pristine films were crystallized by laser irradiation. The wavelength of continuous wave laser is 450 nm, and the laser beam by the shaping system was homogenized to a spot of 5 mm×8 mm. The pristine films was irradiated by

different laser power density (1.38 W/cm², 1.58 W/cm², 2.01 W/cm², 2.70 W/cm², 3.10 W/cm² and 4.20 W/cm²), and the scanning speed of laser beam is 0.5 mm/s. In order to make film crystallization more uniform, laser irradiation was carried out by one repeated scanning. So the laser expose time is about 20 s. As a comparison, the CH₃NH₃I•PbI₂•DMSO pristine film was also crystallized by thermal annealing at 100 °C for 5 min.

Fabrication of devices

The device fabrication process was descripted as follows. The patterned FTO substrate was coated with a TiO₂ hole-blocking layer (~60 nm), followed by the CH₃NH₃PbI₃ light absorption layer (~400 nm). Then, the HTM layer consisted of 90 mg Spiro-MeOTAD, 17.5 μ L lithium Li-TFSI in acetonitrile (500 mg/mL) and 28.8 μ L TBP mixed in 1mL chlorobenzene, was spin-coated on CH₃NH₃PbI₃ layer. Finally, a thermally evaporated silver layer (~100 nm) was coated to form the back contact of the device.

Characterizations

X-Ray diffraction (XRD) patterns were collected on a Rigaku Ultima III X-ray diffractometer (Cu K α). A FEI NOVA NanoSEM230 scanning electron microscopy (SEM) was employed to characterize the morphological properties of the samples. Electrochemical impedance spectroscopy (EIS) analysis was conducted with an electrochemical test station (PAR2273, Princeton Applied Research, USA). EIS test was scanned from 10 Hz to 100 kHz at 0-1.0 V bias without illumination. The simulated parameters of the impedance spectra were obtained using ZView software. A Shimadzu UV-2550 UV-vis spectrometer fitted with an integrating sphere was used to investigate the absorption properties of the samples. The atomic concentration and the atomic ratio of I/Pb was analyzed by X-ray photoelectron spectroscopy (XPS; PHI-5000C ESCA system). The performance measurements of the as-fabricated solar cells were carried on a Keithley 2400 source measurement unit under AM1.5 illumination (standard 100 mW/cm²) cast by an Oriel 92251A-1000 sunlight simulator calibrated by the standard reference of a Newport silicon solar cell. A black mask with a circular aperture (0.09 cm²) was applied on top of the solar cells to define the active area. The J-V curves were measured via reverse scanning at scan rate of 45 mV/s.

LPD	J _{sc}	V _{oc}	CC	PCE
(W/cm²)	(mA/cm²)	(∨)		(%)
1.36	16.42	0.923	0.56	8.5
1.58	19.59	1.035	0.54	10.9
2.01	20.44	1.067	0.64	14.0
2.70	21.45	1.140	0.68	16.5
3.10	22.20	1.014	0.69	15.5
4.20	18.23	0.907	0.56	9.2

Table S1 Summarizes the photovoltaic parameters of the laser irradiation $CH_3NH_3PbI_3$ devices under different Laser power density (LPD).



Fig. S1 The surficial and cross-sectional SEM images of CH₃NH₃PbI₃ films fabricated by thermal annealing (a, c) and laser irradiation (b, d), respectively.



Fig. S2 Influence of scanning conditions on planar heterojunction PSCs J-V characteristics. The PSCs based on AT-CH₃NH₃PbI₃ and LI-CH₃NH₃PbI₃ devices measured under simulated AM1.5 100 mW/cm² sun light at a range of scan rates from 10 to 150 mV/s (a, c), and J-V data depending on scan direction at scan rate of 45 mV/s (b, d).



Fig. S3 The narrow-scan spectra of X-ray Photoelectron Spectroscopy for Pb 4f (a) and I 3d regions (b) on the surface of $CH_3NH_3PbI_3$ films prepared by thermal annealing and laser irradiation.

Table S2 The atomic concentratior	n and the atomic ratio of I/Pb
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	C 1s	I 3d	Pb 4f	I/Pb
Thermal annealing	49.65	36.08	14.27	2.53
Laser irradiation	56.09	29.57	14.34	2.06





Fig. S4 Electrochemical impedance spectroscopy (EIS) characterizations. The impedance plots for LI-CH₃NH₃PbI₃ (a-e) and TA-CH₃NH₃PbI₃ (f-j) based solar cells at different forward applied bias, which were fitted by ZView software. Inset graphs are zooms. Symbols are the experimental results correspond to the fit using the equivalent circuit.

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