

## **Supporting Information**

### **Interstitial Mn<sup>2+</sup>-Driven High-Aspect-Ratio Grain Growth for Low-Trap-Density Microcrystalline Film for Record Efficiency Inorganic CsPbI<sub>2</sub>Br Solar Cells**

Dongliang Bai<sup>1,#</sup>, Jingru Zhang<sup>1,#</sup>, Zhiwen Jin<sup>1,\*</sup>, Hui Bian<sup>1</sup>, Kang Wang<sup>1</sup>, Haoran Wang<sup>1</sup>, Lei Liang<sup>1</sup>, Qian Wang<sup>1,\*</sup> and Shengzhong (Frank) Liu<sup>1,2,\*</sup>

<sup>#</sup>These authors contributed equally to this work

<sup>1</sup>Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology; School of Materials Science & Engineering, Shaanxi Normal University, Xi'an, 710119, P. R. China.

E-mail: jinzhiwen@snnu.edu.cn, wangqian16@snnu.edu.cn

<sup>2</sup>Dalian National Laboratory for Clean Energy; iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, P. R. China

E-mail: szliu@dicp.ac.cn

## Experimental Section

### Materials Preparation

CsPbI<sub>2</sub>Br precursor solution was prepared by dissolving CsBr:PbI<sub>2</sub> (1:1) in dimethylsulfoxide (DMSO) at 0.8 M in a N<sub>2</sub> glovebox and stirring at 55 °C for 1 h. For the Mn<sup>2+</sup>-doped precursor, different concentrations of MnCl<sub>2</sub> were immediately added into the above prepared solution. HTL solution was prepared by dissolving PTAA (90 mg), a sulfonyl imide (Li-TFSI, 22 μL) solution (520 mg Li-TFSI in 1 mL acetonitrile) and tert-butylpyridine (TBP, 36 μL) in 1 mL of CB solution. The solution was stirred at 60 °C for 24 h.

*Synthesis of CsPbI<sub>2</sub>Br QDs:* Cs<sub>2</sub>CO<sub>3</sub> (0.5 g), 1-octadecene (ODE, 50 mL) and oleic acid (OA, 2mL) were added to a round bottom flask under vacuum for 30 min at 120 °C as Cs-oleate. PbBr<sub>2</sub> (0.23 g), PbI<sub>2</sub> (0.58 g), ODE (50 mL), OA (5mL) and oleylamine (OAm, 5mL) were stirred in another round bottom flask and degassed under vacuum at 120 °C for 1 hour before filling with N<sub>2</sub>. Then, the Cs-oleate (8 mL) was swiftly injected into the reaction mixture at 170 °C and maintained 5 sec. Then, the reaction was quenched by immediate immersion of the flask into an ice bath. Finally, the synthesized CsPbI<sub>2</sub>Br QDs were precipitated by adding 200 ml ethyl acetate (EA). This process was repeated twice and the CsPbI<sub>2</sub>Br QDs were dispersed in octane with different concentrations.

### Device Fabrication

*Preparation of TiO<sub>2</sub> blocking layer:* Clean Fluorine-doped tin oxide (FTO)-coated glass with a size of 25 × 25 mm<sup>2</sup> was immersed in a 40 mM TiCl<sub>4</sub> aqueous solution for 30 min at 70 °C and washed with distilled water and ethanol, followed by annealing at 200 °C for 30 min in air to form a compact n-type blocking layer of TiO<sub>2</sub>.

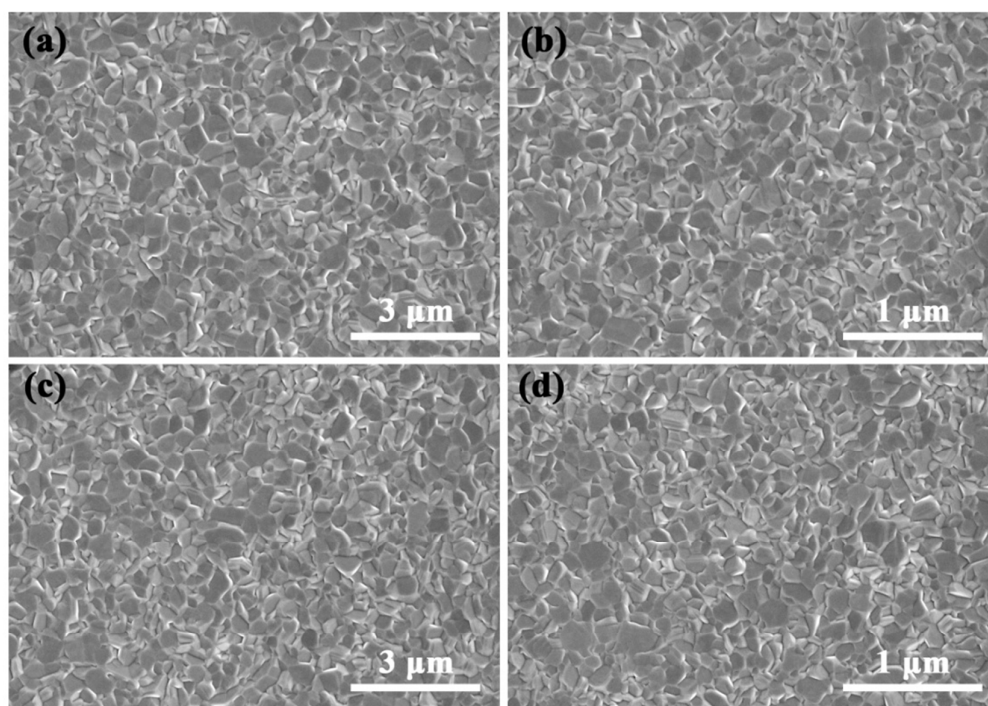
*Growth of the CsPbI<sub>2</sub>Br film:* The CsPbI<sub>2</sub>Br layer was fabricated by spin-coating the prepared solution onto the O<sub>2</sub>-plasma-treated above-prepared substrate at 4000 rpm for 30 s. Immediately after, the films were sintered at 260 °C for 10 min. Then, the CsPbI<sub>2</sub>Br QDs solution was dropped onto the prepared film, maintained a moment, and spin-dried at 2000 rpm for 30 s in turn with the film quickly dipped in neat ethyl acetate solution and dried with a stream of air.

*Assembly of the solar cells:* An HTL film was prepared onto the above CsPbI<sub>2</sub>Br film at 4000 rpm for 30 s. Finally, a gold electrode with a thickness of ~70 nm was thermally evaporated onto the HTL-coated film to finish the device fabrication.

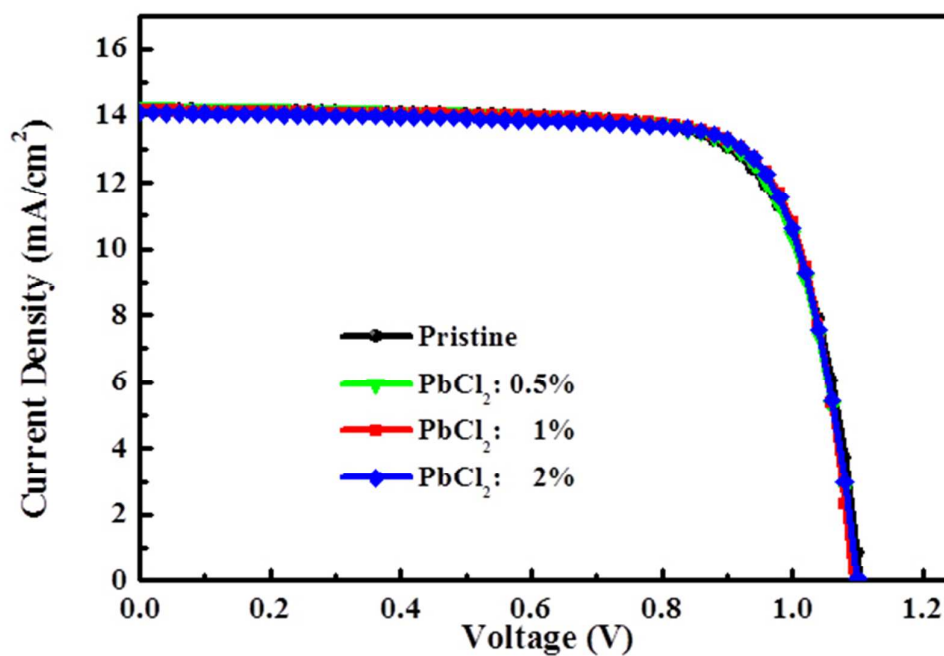
### Characterization

The film surface morphology was characterized by SEM and EDS (Jeol SU-8020). Absorbance spectra were collected using a Shimadzu UV-3600 double beam spectrometer. PL spectra were measured using an HORIBA Jobin Yvon Fluoro Log2 spectrofluorometer. TRPL spectra were acquired according to a time-correlated single photon counting method using an Edinburgh Instruments FluoTime 300 fluorescence spectrometer. The XPS measurements were performed in a VG ESCALAB MK2

system with monochromatized Al K $\alpha$  radiation. XRD patterns were performed on a DX-2700 with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). J-V curves were measured at 25 °C under AM1.5G (100 mW/cm<sup>2</sup>) illumination (scan rate: 0.5 V/s, both forward (from I<sub>SC</sub> to V<sub>OC</sub>) and reverse (from V<sub>OC</sub> to I<sub>SC</sub>) scan modes). Here, the bare devices without any encapsulation were stored and tested upon exposure to the ambient environment (in air at relative humidity of 25%~35% at 25 °C). A black cardboard mask with a window area of 0.09 cm<sup>2</sup> was clipped onto the glass side to define the active area of the cell. The spectral response was taken by an EQE measurement system (QEX10, PV Measurement), which was equipped with a monochromator, a lock-in amplifier, a Xe lamp, and a current-voltage amplifier. Prior to the use of the light, the spectral response and the light intensity were calibrated using a mono-silicon detector. The capacitance-voltage (CV) measurements were performed using a Zahner Zennium electrochemical workstation. The CV measurements were recorded at a frequency of 1 kHz for extracting V<sub>b</sub>.



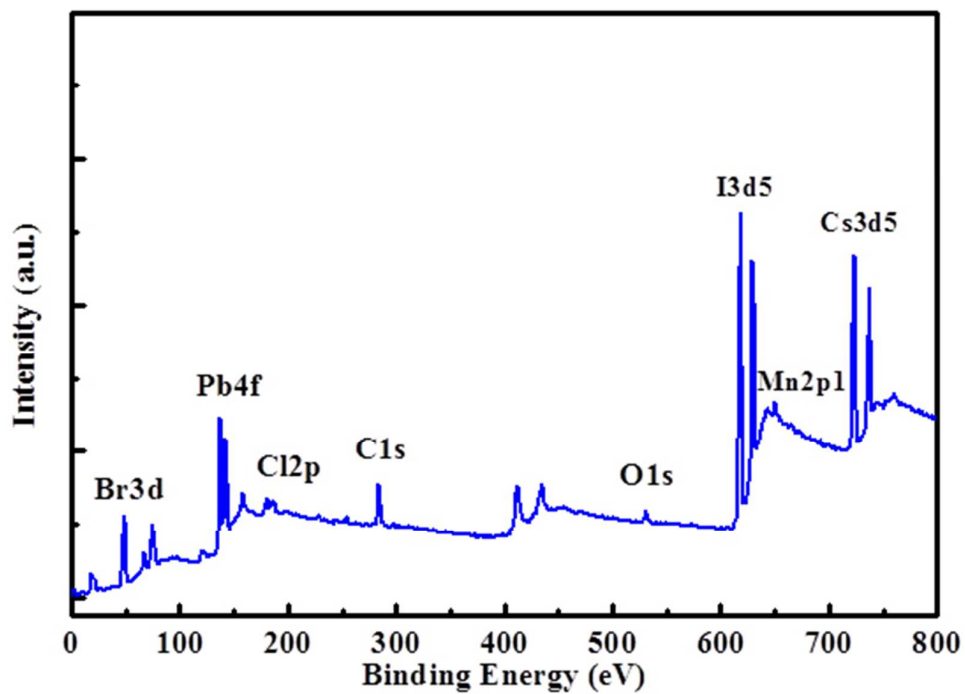
**Figure S1.** SEM images for CsPbBr<sub>2</sub> films formed using different PbCl<sub>2</sub> concentrations: (a) pristine, (b) 0.5% PbCl<sub>2</sub>, (c) 1% PbCl<sub>2</sub>, (d) 2% PbCl<sub>2</sub>.



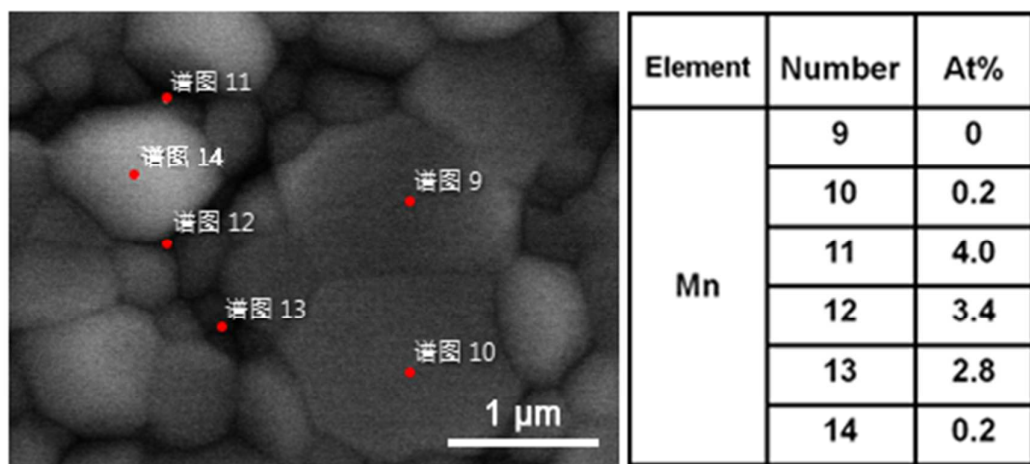
**Figure S2.** Comparison of the  $J$ - $V$  characteristics for CsPbBr<sub>2</sub> PSCs doped with PbCl<sub>2</sub> at different concentrations.

**Table S1.** Comparison of performance of devices based on different CsPbBr<sub>2</sub> films (extracted from **Figure S2**).

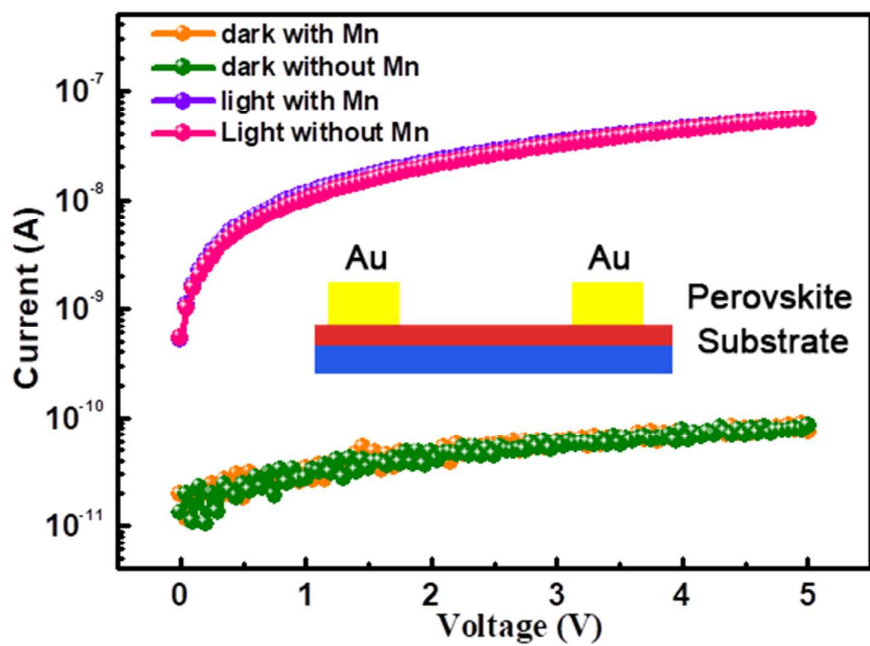
Film	$J_{sc}$ (mAcm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)
Pristine	14.15	1.115	75.3	11.88
PbCl <sub>2</sub> 0.5%	14.22	1.099	76.0	11.88
PbCl <sub>2</sub> 1%	14.13	1.093	77.8	12.02
PbCl <sub>2</sub> 2%	14.06	1.100	77.6	12.00



**Figure S3.** XPS spectrum for 2% MnCl<sub>2</sub> doped CsPbBrI<sub>2</sub> film.



**Figure S4.** The SEM image of CsPbBrI<sub>2</sub> film and the EDX elemental distribution of Mn in the CsPbBrI<sub>2</sub> film at different locations labeled by red dots.



**Figure S5.** Comparison of I-V curves of the CsPbBrI<sub>2</sub> device with and without Mn doping as measured in the dark, and under 525 nm light irradiation at 5 mW/cm<sup>2</sup>. The inset is a schematic for the device configuration.