Supporting Information

Fabrication of methylammonium bismuth iodide through interdiffusion of solution-processed BiI_3/CH_3NH_3I stacking layers

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1. Fabrication of TiO_2 film

Fluorine doped tin oxide (FTO) coated glass substrates (Nippon Sheet Glass Co., Ltd. ~15Ω sq^{-1} resistance) were etched with zinc powder and HCl (2 M) and cleaned with soap (Hellmanex) and rinsed with Milli-Q water and ethanol, respectively. Then, the sheets were sonicated for 15 minutes in a solution of acetone: isopropanol (1:1 v/v), rinsed with ethanol and dried with compressed N_2. After that, a UV/ozone treatment was performed for 15 minutes. Then, a 60 nm thick TiO_2 blocking layer was deposited onto the substrates as follows: spin coating 0.15 M titanium (diisopropoxide) *bis*(2,4-pentanedionate) dissolved in *n*-butanol, and sintering at 125 ^oC for 5 min, then spin coating the same solution with 0.3 M followed by annealing at 125 ^oC for 5 min and then heated at 500 ^oC for 30 min. After cooling down to room temperature, a mesoporous TiO_2 layer was spin coated at 3000 rpm for 30 s using commercial TiO_2 paste diluted in ethanol at weight ratio 2:7, followed by annealing at 125 ^oC for 5 min and then heated at 500 ^oC for 30 min. Finally, the cooled film was immersed in 0.02 M aqueous $TiCl_4$ solution at 70^oC for 30 min. After rinsing with DI water and ethanol, the film was heated at 500 ^oC for 30 min.

2. Fabrication of $MA_3Bi_2I_9$ film and device

Two-step spin coating process was employed for the deposition of $MA_3Bi_2I_9$ on the mesoporous TiO_2 film. First, the solution of BiI_3 was prepared by dissolving 472 mg BiI_3 powder (99%, from Energy Chemical) in 1 mL *N*,*N*-Dimethylformamide (DMF, from Sigma-Aldrich). This was mixed ultrasonically for 30 min before being filtered by PTFE syringe filter (0.22 μm). Inside a

nitrogen-filled glovebox, 20μL of the filtered solution was spread over the substrate and spin-cast at 2000 rpm for 5 s, followed by 5000 rpm for 10 s. The BiI_3 film was dried for 30 min before being annealed at 100 °C for 30 min. Subsequently, 100μL MAI solution in isopropanol with various concentrations (3mg/mL, 6mg/mL, 10mg/mL and 20mg/mL) was dropped on the top of BiI_3 film and kept for 30 s, followed by spin-coating at 4000 rpm for 20 s in a glovebox. The film was allowed to anneal at 100 °C for 60 min to form the $MA_3Bi_2I_9$ film.

One-step spin-coating method was used to deposit the $MA_3Bi_2I_9$ film on the TiO_2 mesoporous layers. A $MA_3Bi_2I_9$ solution (0.8M) was prepared by mixing 191mg of MAI, 472mg of BiI_3 in 1 mL DMF. The mixed solution was ultrasonically for 30 min and then filtered through a 0.22 μm PTFE syringe filters. 35μL of $MA_3Bi_2I_9$ solution was dropped onto the substrate and spin-coated at 4000 rpm for 30s. The film was allowed to anneal at 100 °C for 30 min to form the $MA_3Bi_2I_9$ film.

The hole transport layer was prepared by spin-coating a *spiro*-MeOTAD (2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenylamine)-9,9-spirobifluorene) solution at 4000 rpm for 30 s. The spin-coating formulation was prepared as follows: to 1 mL of chlorobenzene were added 80 mg of *spiro*-MeOTAD, 28.5 μL of 4-*tert*-butylpyridine, and 17.5 μL of a stock solution of 520 mg mL^{-1} Li-TFSI in acetonitrile. Finally, An 80 nm thick Au was thermally evaporated as a back contact under a vacuum of 5×10^{-5} Torr. The device active area was 4 mm^2, determined by the overlap of the cathode and anode.

3. Film characterization

XRD patterns were recorded by using an X-ray diffractometer (Rigaku, D/MAX RINT-2500) with a CuK radiation source. The surface morphology of the films as well as cross-section was analyzed by using a JEM-7500F field-emission scanning electron microscope (SEM). Absorption spectra of the film samples were recorded by using a Shimadzu UV-vis 1800 spectrophotometer. Steady-state photoluminescence (PL) spectra were acquired using a FLS980 (Edinburgh Instruments,United Kingdom).

4. Device characterization

Current–voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a Keithley model 2400 digital source meter. The light source was a 300 W collimated xenon lamp (Newport) calibrated with the light intensity to

100 mW cm^{-2} under AM 1.5G solar light conditions by a certified silicon solar cell. The *J–V* curve was recorded by the reverse scans with a rate of 200 mV s^{-1}. The external quantum efficiency (EQE) for solar cells was performed using a commercial setup (PV-25 DYE, JASCO). A 300 W Xenon lamp was employed as a light source for the generation of a monochromatic beam. Electrochemical impedance spectroscopy (EIS) was carried out by an electrochemical workstation (Zennium, IM6, Germany) over the frequency from 10 mHz to 2 MHz under simulated AM 1.5G (100 mW cm^{-2} irradiance).

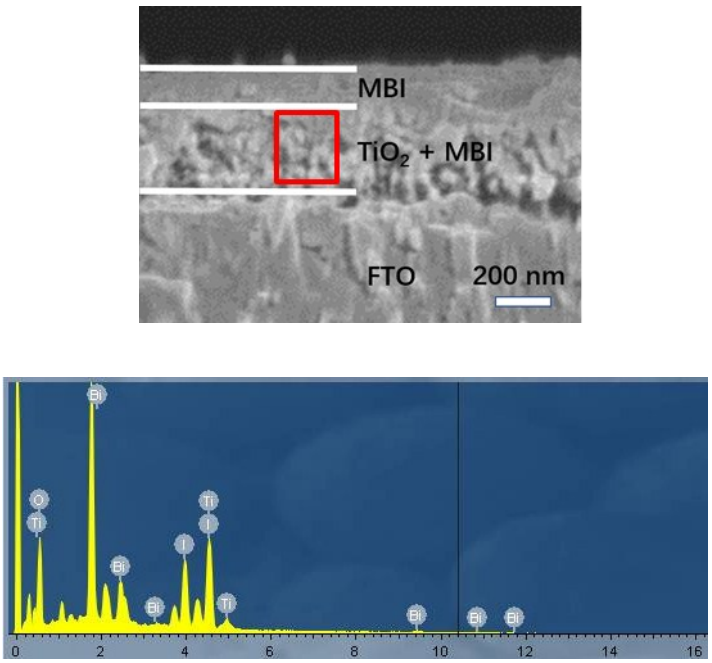

Fig. S1 SEM-EDX elemental analysis of $MA_3Bi_2I_9$ perovskite film.

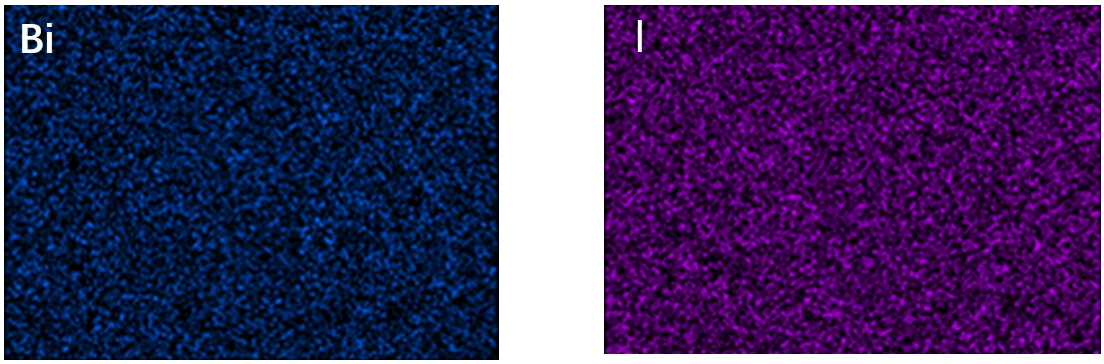

Fig. S2 EDX elemental mapping of Bi and I in $MA_3Bi_2I_9$ perovskite film.

Table S2 SEM-EDX elemental analysis of $MA_3Bi_2I_9$ perovskite film

Element	Weight %	Atomic %
I	33.88	9.44
Bi	12.95	2.19

Note: experimental I:Bi ratio: 4.31:1. (For carefully checking the ratio of I:Bi, we do not include atomic% elements such as C, O, N, Ti, Si.)

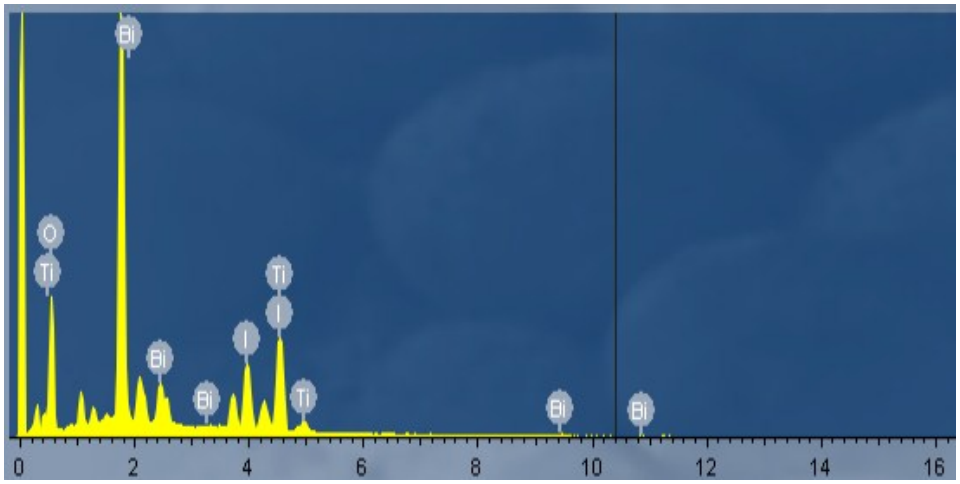

Fig. S3 SEM-EDX elemental analysis of BiI_3 film.

Table S2 SEM-EDX elemental analysis of BiI_3 film

Element	Weight %	Atomic %
I	17.72	3.30
Bi	11.09	2.25

Note: experimental I:Bi ratio: 2.64:1 (For carefully checking the ratio of I:Bi, we do not include atomic% elements such as C, O, N, Ti, Si.).

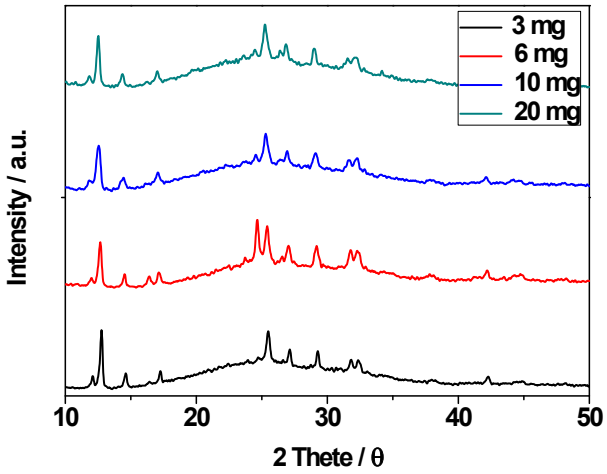

Fig. S4 XRD patterns of MBI films deposited by the two-step method with different concentrations of MAI on TiO2 substrate.

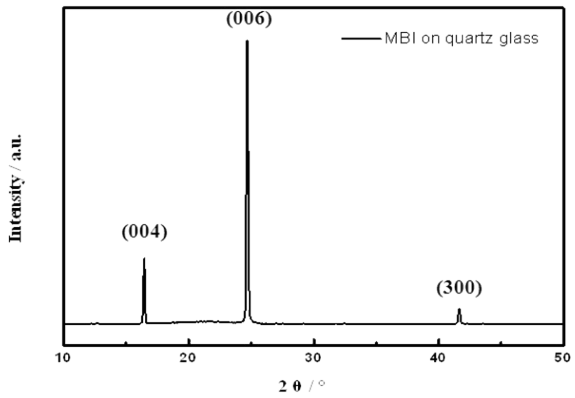

Fig.S5 XRD pattern of MBI on quartz glass substrate.

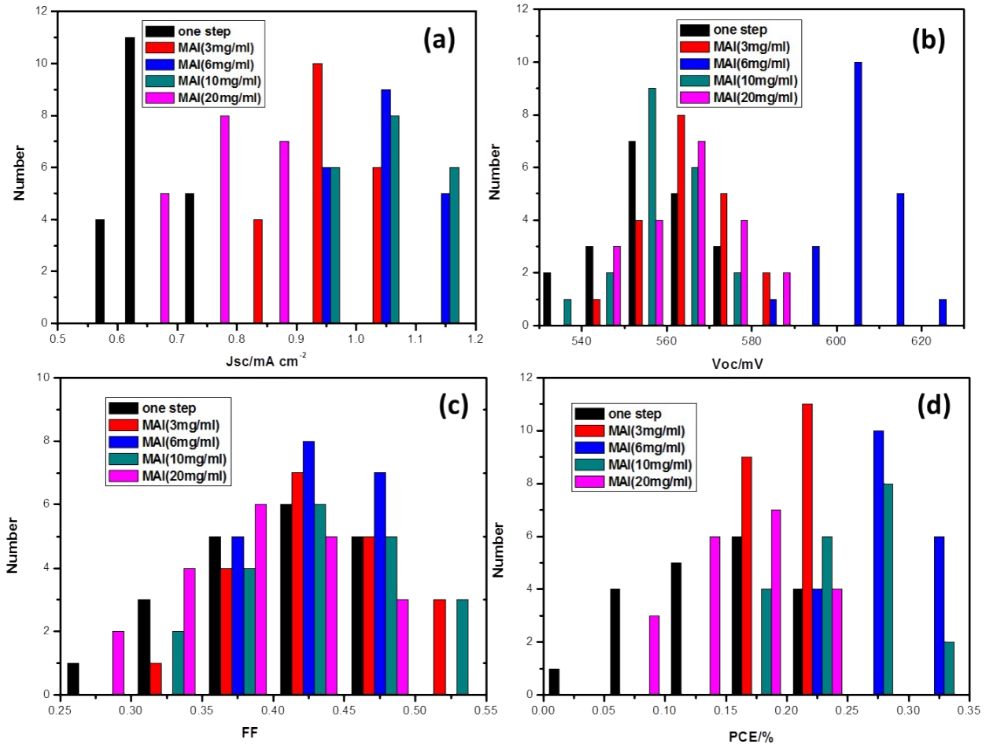

Fig.S6 The statistics of photovoltaic performance for devices by one step method and two step method with different concentrations of MBI.

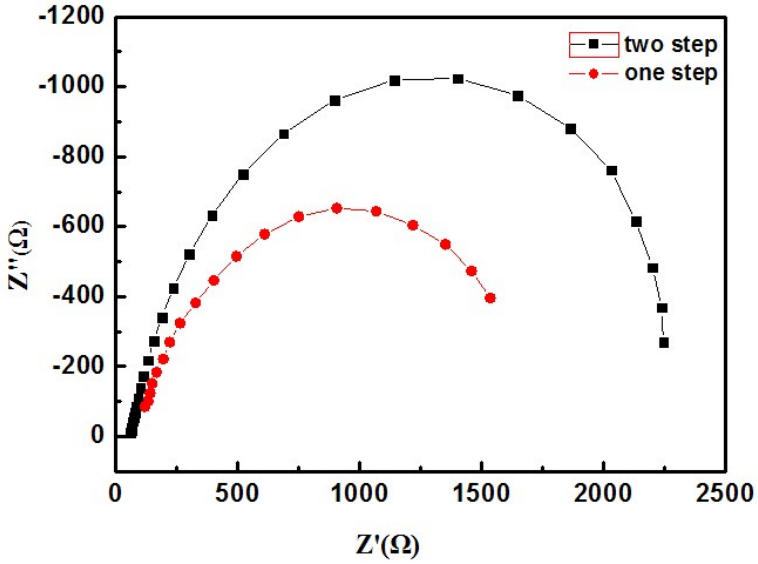

Fig. S7 Nyquist curves of the devices with MBI film from one-step method and two-step method (MAI, 6 mg/ml) over the frequency range of 10 mHz to 2 MHz under simulated AM 1.5G (100 mW cm^2 irradiance).

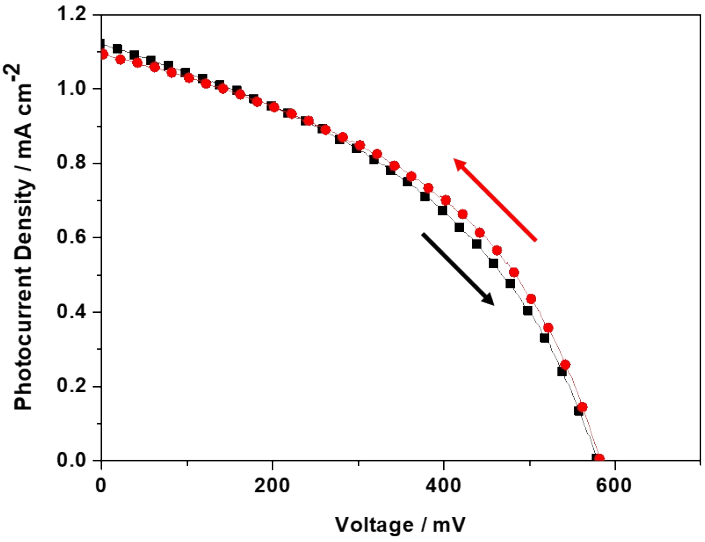

Fig. S8 *I-V* curves with forward and reverse scanning at a rate of 100 mV/s.

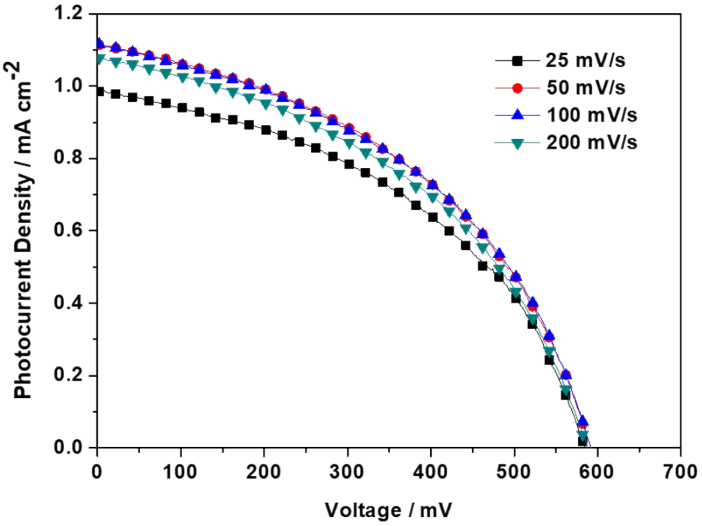

Fig.S9 *I-V* curves with reverse scanning at various rates of 25 to 200 mV/s.