Electronic Supplementary Information:

**Reduction of Intrinsic Defects in Hybrid Perovskite Films via Precursor Purification**

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1. Synthesis of CH$_3$NH$_3$I
The method to synthesize CH$_3$NH$_3$I (MAI) has been reported previously. In this process, 32 ml hydroiodic and (57 wt% in water, Innochem) and 22ml methylamine (30-33 wt% in alcohol, TIANJIN FUCHEN) were mixed and stirred in a 250ml round-bottomed flask at 0 $^\circ$C for 5 hours. The crude was dissolved in methylamine alcohol solution (12.5 mmol/L, TIANJIN FUCHEN), recrystallized from diethyl ether. The process of purification was repeated three times, and the product of each purification was dried at 50 $^\circ$C in a vacuum oven for 24 hours.

2. Preparation perovskite film and device fabrication
The conductive glass substrates (ITO-coated glass) were cleaned by ultrasonication in isopropanol for an hour, suds for an hour, deionized water for thirsty minutes, acetone for fifteen minutes and isopropanol for thirsty minutes, respectively. Then the cleaned ITO-coated glass were dried under a flux of nitrogen and further cleaned in the UVO$_3$ cleaner for thirty minutes. The precursor solution of electron transport layer (ETL, TiO$_2$ compact layer) was spin-coated onto ITO-coated glass at 3000rpm for 30s, then annealed at 150 $^\circ$C for thirty minutes. The perovskite precursor solution was prepared according to the reported method.$^1$To fabricate the perovskite films, the precursor solution was spin-coated onto the SnO$_2$-coated conductive glass substrates at 4000 rpm for 25s in air atmosphere and 2 mL of diethyl ether was dripped on rotating substrate in 2 s before the surface changed to be turbid. Then the prepared perovskite film was annealed at 65 $^\circ$C for one minutes and 100 $^\circ$C for two minutes. The hole-transport material (HTM) solution was prepared by dissolving 80mg of spiro-OMeTAD, 30 $\mu$l of 4-tert-butylypyridine ($>$ 96.0%, TCI), and 35ul of lithium bis (trifluoromethane-sulfonyl) imide (Li-TFSI) (99.95%, Sigma-Aldrich) solution (260 mg Li-TFSI in 1 ml acetonitrile, 99.8%, Sigma-Aldrich) in 1 ml of chlorobenzene. Then the HTM solution was spin-coated onto the perovskite layer at 3000rpm for 30s. Finally, 100nm of gold as the mental electrode on the HTM-coated film was evaporated at a metallization chamber.

3. Films and Devices Characterization
Morphology and microstructure characterization of absorber layers were investigated

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using an S-4800 High resolution field emission scanning electron microscope (FESEM) (Hitachi, Japan). The X-ray diffraction (XRD) patterns of the absorber materials were measured on PANalytical X-ray Diffractometer using Cu Kα irradiation at a scan rate \((2\theta)\) of \(3^\circ\) min\(^{-1}\). The accelerating voltage and applied current were 40KV and 40mA, respectively. The absorption spectra of perovskite precursor solution and perovskite films were measured on a UV-Vis spectrophotometer (Agilent 8453). The current density-voltage (\(J-V\)) curves were measured using a solar simulator manufactured by Enli Technology Co., Ltd with a source meter (keithley 2400) at 100 mA/cm\(^2\) illumination (AM 1.5G). The light intensity was adjusted with an NREL calibrated silicon solar cell. The active area \((0.012\ cm^2)\) was defined with a mask with aperture. Transient-state photoluminescence (PL) was measured by FLS980 (Edinburgh Instruments Ltd) with an excitation at 470 nm. The conditions of all measurement of solar cells were conducted at room temperature under ambient atmosphere without encapsulation.
**Fig. S1** UV-vis absorption spectrum of I$_2$ in DMF solution showing a peak at around 365 nm due to I$_2$ absorption.

**Fig. S2** The stabilized $J_{sc}$ for the devices of Reference, MAI-1 and MAI-2 in a nitrogen atmosphere, which the PCE are 16.03%, 17.61% and 18.20%, respectively.
Fig. S3 J-V curves for the devices of Reference, MAI-1 and MAI-2 under opposite scan direction. The lessened hysteresis of MAI-2 based device, compared with Reference and MAI-1 based device, means the defect was reduced at the MAI-2 based perovskite films.
**Fig. S4** Time resolve photoluminescence decay for perovskite films fabricated with Reference, MAI-1 and MAI-2, respectively.

**Fig. S5** Morphology of the films: (a,b,c) Top view SEM images of perovskite films fabricated with Reference, MAI-1 and MAI-2, respectively.
As shown in the Figure S3, all three samples show XRD patterns without obvious differences, which infers that using methylamine alcohol solution to purify the crude CH$_3$NH$_3$I does not affect the crystallinity of perovskite films after annealing and the films are in a desired phase with good crystallinity. From the measurement of SEM and XRD, we concluded that the improved performance of solar cells based on the CH$_3$NH$_3$I purified twice using methylamine alcohol solution is not due to the morphology of the films. The main reason of improved performance is the reduction of defect density in the perovskite films resulting from the existence of I$_2$.