

Supplementary Materials

Highly reproducible, efficient hysteresis-less $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ planar hybrid solar cells without requiring heat-treatment

Jin Hyuck Heo, Sang Hyuk Im*

Functional Crystallization Center (FCC), Department of Chemical Engineering, Kyung Hee University, 1732 Deogyong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, Republic of Korea

* To whom correspondence should be addressed. E-mail: imromy@khu.ac.kr

Method:

Preparation of $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed halide perovskite solution

To prepare $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed halide perovskite, we first synthesized MAI (methylammonium iodide) by reacting 50 mL hydriodic acid (HI: 57% in water, Aldrich) and 50 mL methylamine (40% in methanol, Junsei Chemical Co. Ltd.) in a 250 mL round-bottom flask at 0 °C for 2 h with magnetically stirring. The white precipitates were recovered by evaporation at 50 °C for 1 h with a rotary evaporator. The products were dissolved in ethanol and recrystallized from diethyl ether to purify MAI. Finally the products were dried at room temperature in a vacuum oven at room temperature for 24 h. Then, we mixed 3:1 molar ratio of MAI:PbCl₂ (Junsei Chemical Co. Ltd.) powder (3 g : 1.76g) in 20 mL vial by hand shaking, added 15 mL anhydrous isopropanol (IPA: Aldrich), and reacted them for 30 min at 60 °C under magnetically stirring. After reaction, we recovered the precipitate by centrifuge and washed it to remove the excess MAI and MAI using absolute IPA. We named the washing with IPA and centrifugation process to 1 cycle. To completely remove the unreacted MAI and MAI byproduct, we repeated the washing and centrifugation process (8000 rpm for 10 min) to 1, 2, 3, 4, and 5 cycles. Then, we dried the centrifuged powder in vacuum oven at 50 °C for 5 h to get the $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed

halide perovskite powder. For spin-coating, we prepared 40 wt% MAPbI_{3-x}Cl_x mixed halide perovskite solution with 10 vol% HI (57% in water, Aldrich) additive by mixing 0.1 mL HI additive and MAPbI_{3-x}Cl_x powder in 1 mL DMF (N,N-dimethylformamide: Adrich) at 60 °C.

Device fabrication

For planar type MAPbI_{3-x}Cl_x mixed halide perovskite solar cells, a ~50 nm-thick dense TiO₂ electron conductor was deposited on a cleaned F-doped SnO₂ (FTO, Pilkington, TEC8) glass substrate by spray pyrolysis deposition (SPD) method with 40 mL of 20 mM of titanium diisopropoxide bis(acetylacetonate) (Aldrich)/iso-propanol solution at 450 °C. A 0.1 mL of 40 wt% MAPbI_{3-x}Cl_x/DMF solution with HI additive (40 wt% MAPbI_{3-x}Cl_x solution in DMF/HI = 1 mL/0.1 mL) was then spin-coated on the TiO₂/FTO substrate at a specific spin speed (500, 1000, 1500, 2000, 2500, and 3000 rpm) for 200 s and the resulting film was dried on a hot plate at 100 °C for 2 min in air under 35 % relative humidity. A poly(triaryl amine) (PTAA, EM index) hole conductor was deposited on the MAPbI_{3-x}Cl_x/TiO₂/FTO substrate by spin-coating PTAA/toluene (15 mg/mL) solution with 7.5 μL Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI)/acetonitrile (170 mg/mL) and 7.5 μL tert-butylpyrrolidine (t-BP)/acetonitrile (1 mL/1 mL) additives at 3000 rpm for 30 s. Finally, ~60 nm-thick Au counter electrode was deposited by thermal evaporation. We used all chemicals as received. All experiments were conducted at ambient atmosphere under controlled relative humidity below 35 %. The active area was fixed to 0.16 cm².

Device characterization

The current density-voltage (J-V) curves were measured by a solar simulator (Pecell, PEC-L01) with a potentiostat (IVIUM, IviumStat) at under illumination of 1 sun (100 mW/cm² AM 1.5G) and a calibrated Si-reference cell certificated by JIS (Japanese Industrial Standards). The J-V curves of all devices were measured by masking the active area with metal mask of 0.096 cm². To measure the hysteresis of J-V curves, the forward and reverse scan rate was set to 10 mV/0.2s

as a standard condition and was varied from 10 mV/0.1 s to 10 mV/1 s. The external quantum efficiency (EQE) was measured by a power source (ABET, 150W Xenon lamp, 13014) with a monochromator (DONGWOO OPTRON Co., Ltd., MonoRa-500i) and potentiostat (IVIUM, IviumStat). Intensity-modulated photocurrent and photovoltage were measured by potentiostat (IVIUM, IviumStat) with light emitting diode (LED) (IVIUM, IM1225).

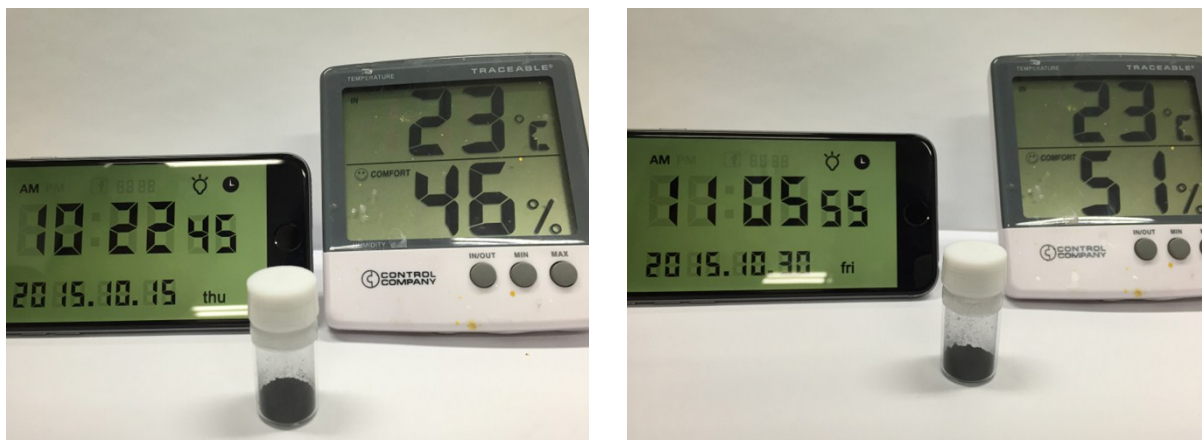


Fig. S1. Long term storage stability of $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed halide perovskite powder.

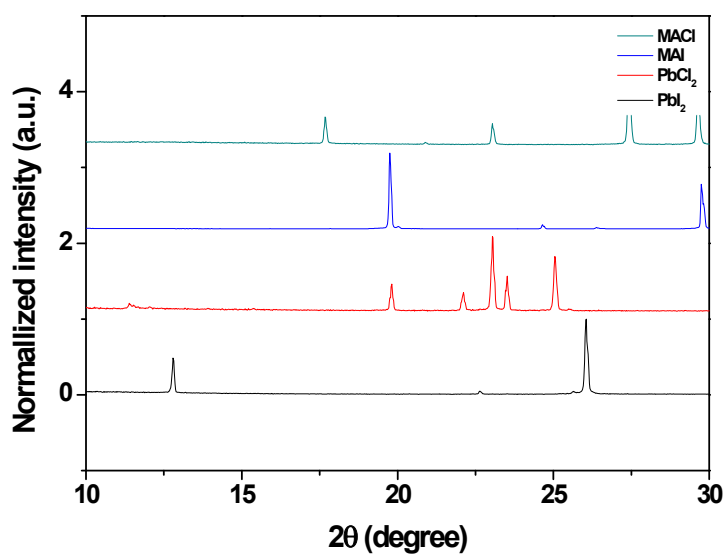


Fig. S2. XRD patterns of MACl , MAI , PbCl_2 , and PbI_2 powder.

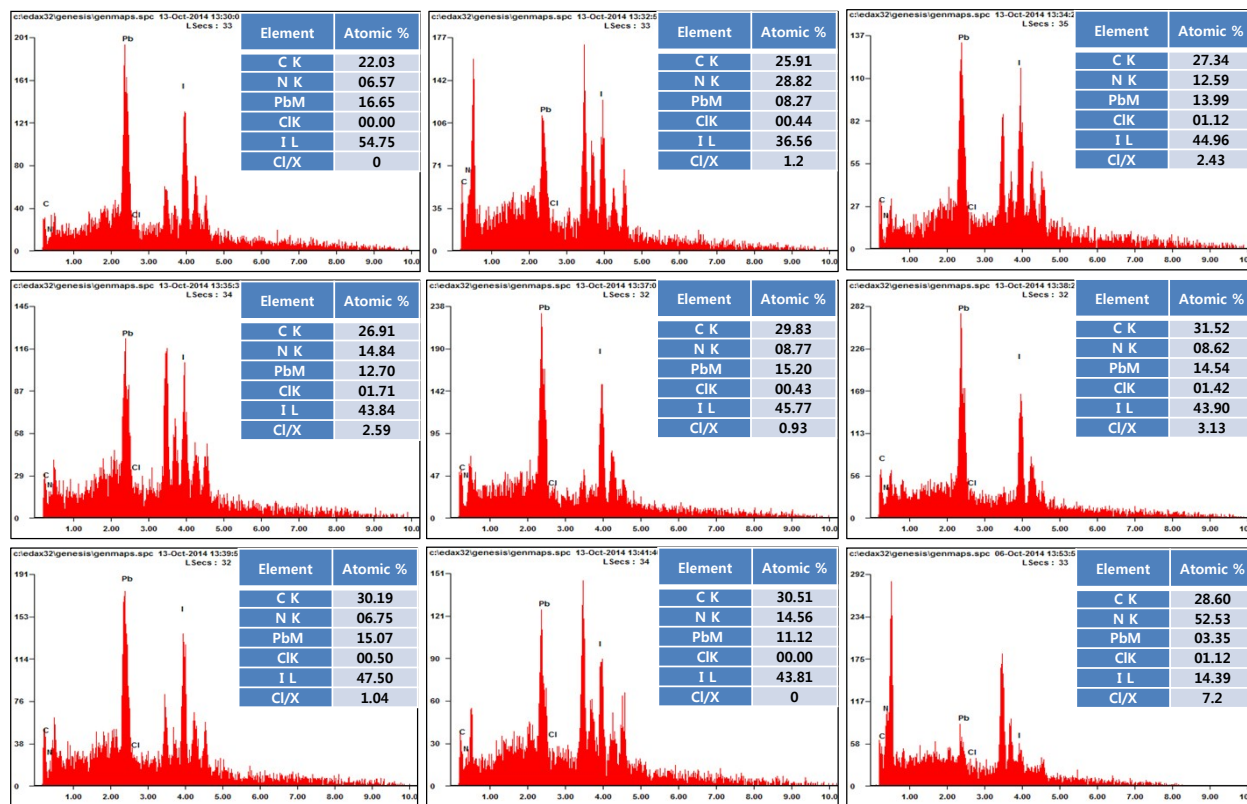


Fig. S3. EDS spectra of the conventional $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed halide perovskite film prepared by heat-treatment process of 3:1 MAI:PbCl₂ film at 100 °C for 40 min under air condition.

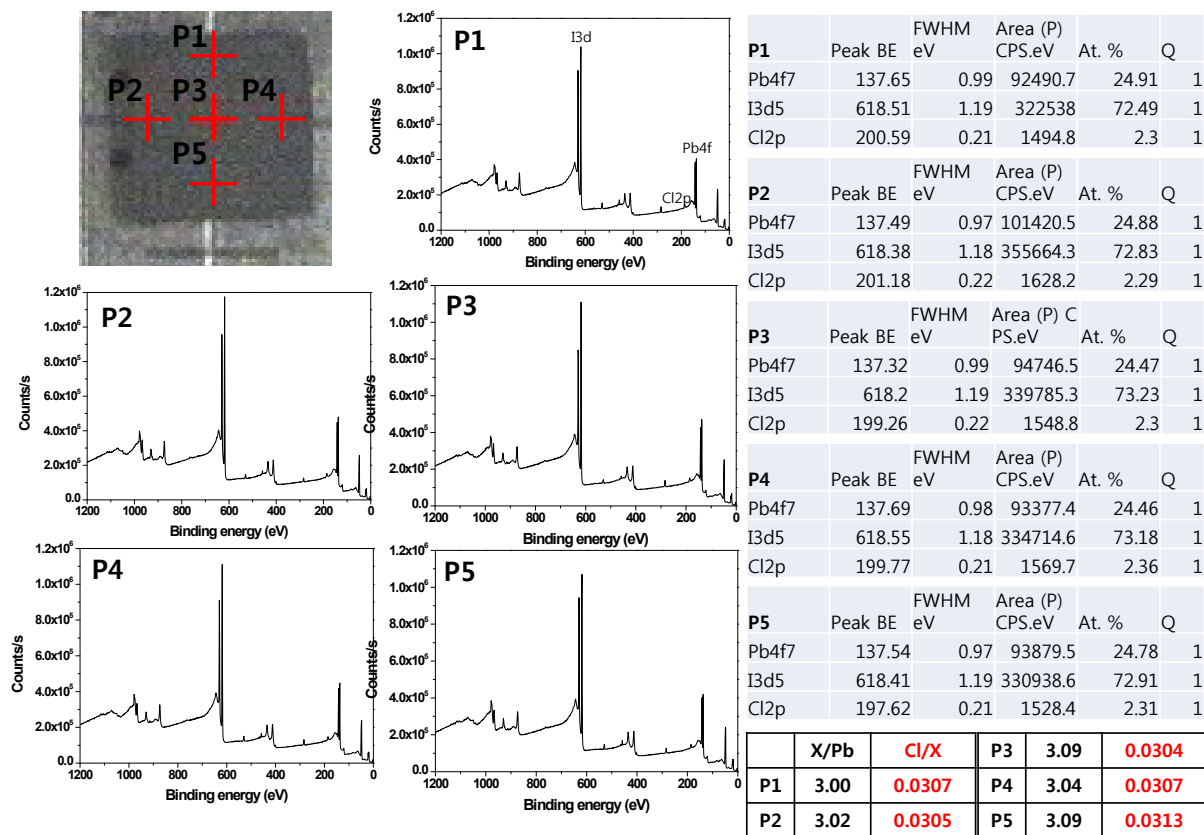


Fig. S4. XPS (X-ray photoelectron spectroscopy) spectra of $\text{MAPbI}_{3-x}\text{Cl}_x$ film at 5 different points (P1~P5), $X = \text{Cl} + \text{I}$.

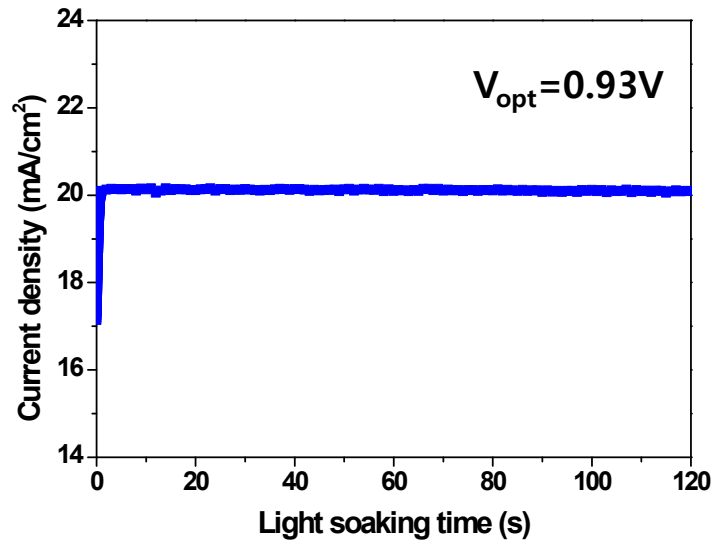


Fig. S5. Current density variation of MAPbI_{3-x}Cl_x planar perovskite solar cell with light soaking time under applied bias voltage (V_{opt}) at maximum power (P_{max})

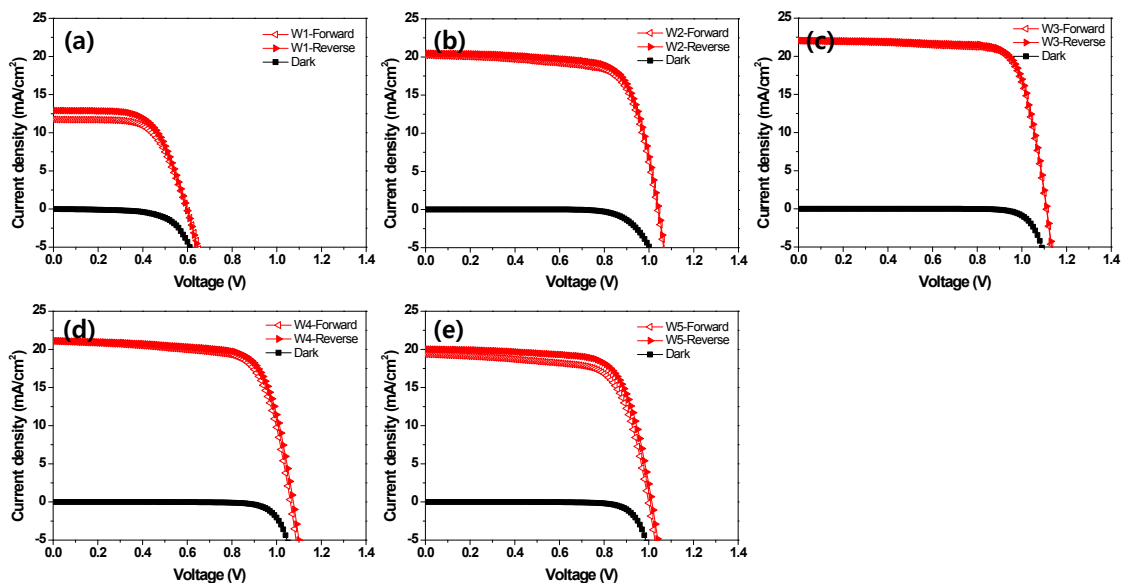


Fig. S6. J-V curves of perovskite devices with different washing times.

| Washing time | Scan Direction | V_{oc} (V) | J_{sc} (mA/cm ²) | F.F (%) | η (%) |
|--------------|----------------|--------------|--------------------------------|---------|------------|
| 1 | Forward | 0.59 | 11.7 | 63 | 4.3 |
| | Reverse | 0.59 | 12.9 | 64 | 4.9 |
| 2 | Forward | 1.03 | 20.3 | 71 | 14.8 |
| | Reverse | 1.04 | 20.3 | 72 | 15.2 |
| 3 | Forward | 1.10 | 22.1 | 77 | 18.7 |
| | Reverse | 1.10 | 22.1 | 78 | 19.0 |
| 4 | Forward | 1.06 | 21.1 | 71 | 15.9 |
| | Reverse | 1.07 | 21.1 | 72 | 16.3 |
| 5 | Forward | 0.99 | 19.4 | 70 | 13.4 |
| | Reverse | 1.01 | 20.0 | 71 | 14.1 |

Table S1. Summary of photovoltaic properties of perovskite devices with different washing times.

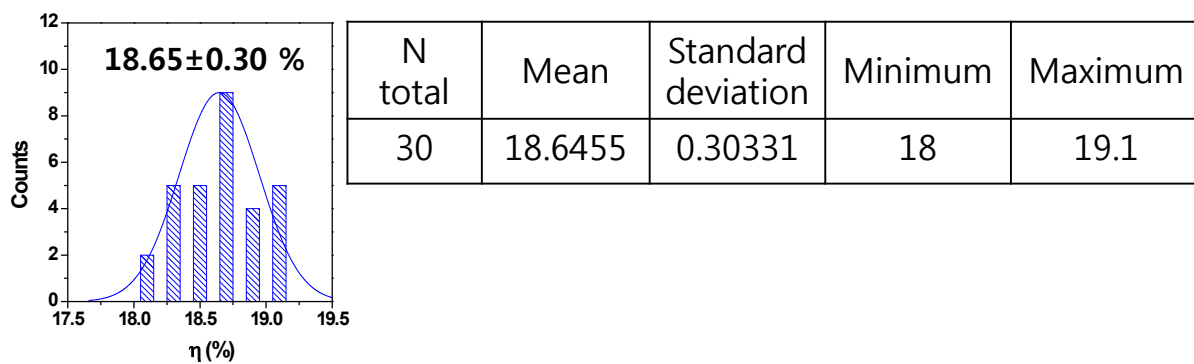


Table S2. Statistical data for 30 MAPbI_{3-x}Cl_x mixed halide perovskite solar cells.