Supporting Information

A General Non-CH_3NH_3X (X=I,Br)One Step Deposition of $CH_3NH_3PbX_3$ Perovskite for High Performance Solar Cells

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Experimental:

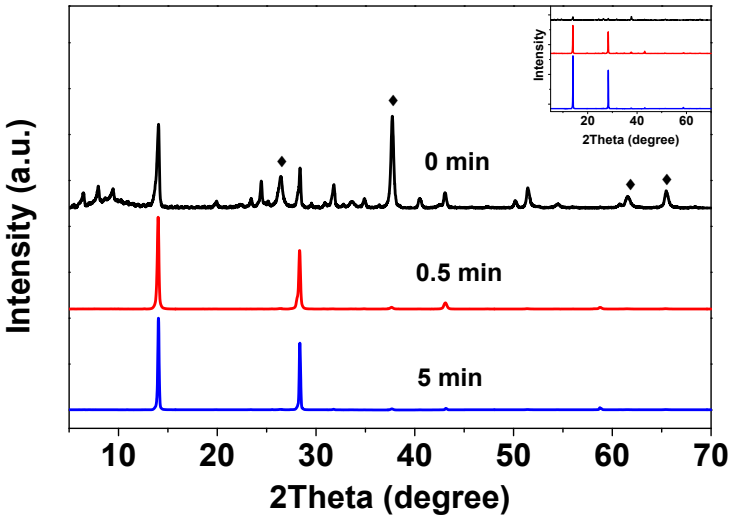
Materials. The HX+PbI_2 (X=I and Br) precursor solution were synthesized by addition stoichiometric HI/HBr using 57 wt% hydriodide acid or 47 wt% hydrobromide acid into 1.0 M 99% PbI_2 DMF solution. The cloudy PbI_2 DMF solution turn to clear after addition of HI/Br aqueous solution. This HX+PbI_2 precursor solution can be stable for at least 1 day when stored in sealed bottle. A patterned fluorine-doped tin oxide (FTO) was first spray pyrolysis deposited with a 20 nm thick compact TiO_2 layer using 0.2 M Ti(IV) bis(ethyl acetoacetate)-diisopropoxide 1-butanol solution at 450 ºC followed by one hour 450 ºC annealing. A ~100 nm thick mesoporous TiO_2 layer was spin-coated by a 20 nm TiO_2 paste as previous reported.

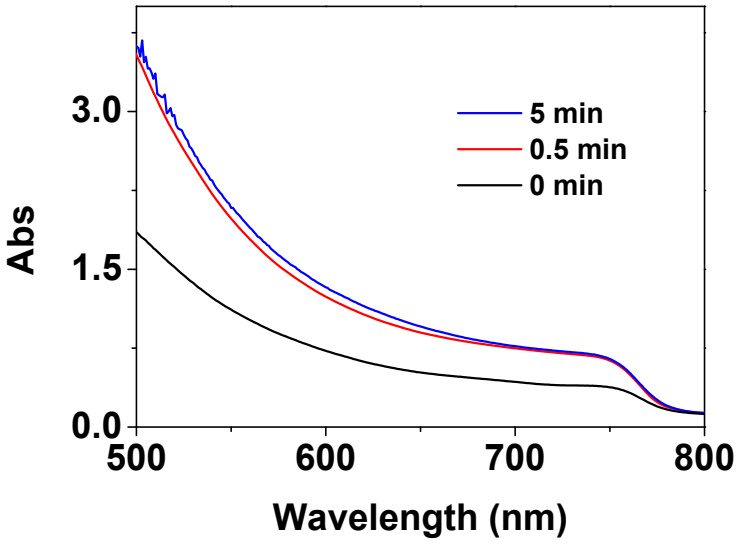
$MAPbI_2X$ (X=I, Br) perovskites deposition. A room temperature HI+PbI_2 or HBr+PbI_2 DMF precursor solution with addition of stoichiometric ratio was spin coated onto the patterned FTO at 4000 rpm for 20 sec under the CH_3NH_3 gas atmosphere (5mL CH_3NH_2 vapor was added in ~2L volumn spin coater chamber using a glass syringe). At around 10 sec, a colourless film was then turn to red brown during the spin process. The red brown film was then annealed at 100ºC for 5 min. All the process was done under drybox with less than 20% humidity.

Device fabrication. The annealed perovskite films were then immediately spin coated with a layer of hole transport material (HTM) of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane) sulfonimide lithium salt (Li-TFSi), and 0.12 M 4-*tert*-

butylpyridine (tBP) in chlorobenzene/acetonitrile (10:1, v/v) solution at 4000 rpm for 20 s. After aged in drybox for 1hr. a 120-nm-thick Ag contact layer was thermally evaporated.

Characterization. The crystal structures of the gas-solid reaction formed perovskite films were measured on Shimadzu XRD-6100 diffractometer with Cu K_{α} radiation. The morphologies of the $HPbI_3$ and $MAPbI_3$ films were characterized by a JSM-7800F Prime scanning electron microscope (SEM) with EDX. The absorption spectra of the $HPbI_3$ and $MAPbI_3$ films perovskite films were taken on an Cary-60 UV-vis spectrophotometer. The photocurrent density–voltage (J–V) curves of perovskite solar cells was measured by a Keithley 2401 source meter with 0.1V/sec scan rate under simulated AM 1.5G illumination (100 mW/cm^2; Enlitech Class AAA Solar Simulator), the IPCE was measured on a QE-3011 system from Enlitech.


Intensity (a.u.)
2Theta (degree)
0 min
0.5 min
5 min
Intensity
2Theta (degree)


Abs
Wavelength (nm)
5 min
0.5 min
0 min

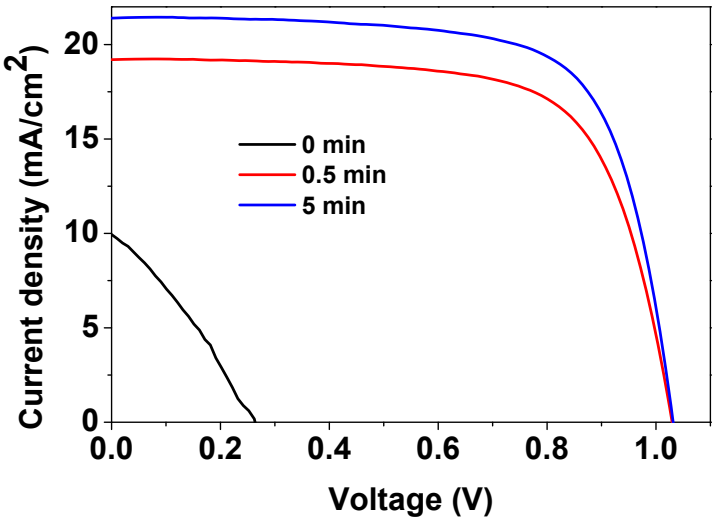

Current density (mA/cm2)
Voltage (V)
0 min
0.5 min
5 min

Figure S1. XRD patterns, UV-vis spectrums and J-V curves of perovskite films with different anneal time.

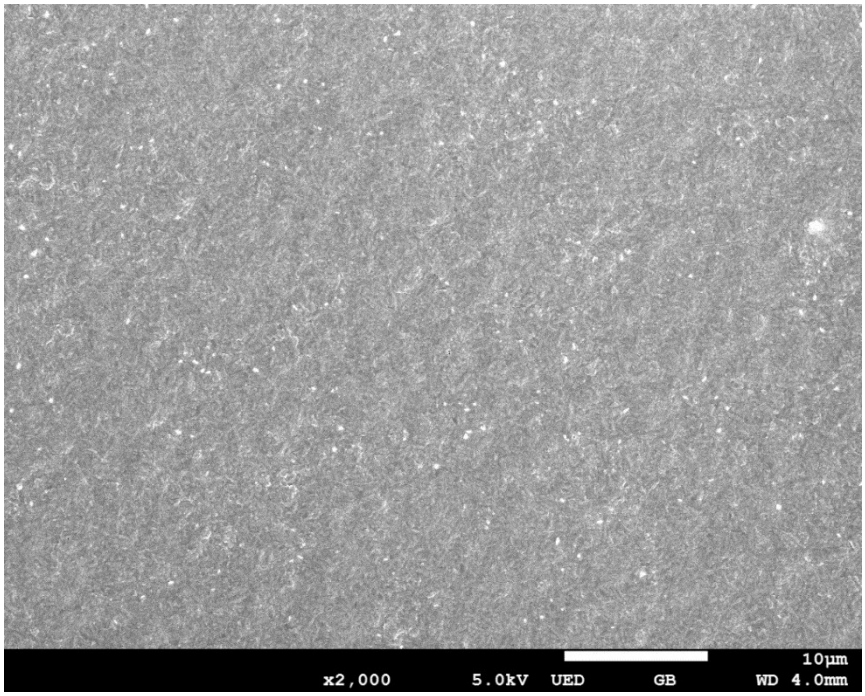


Figure S2. Typical large-scale SEM image of $MAPbI_3$ film prepared via the MA(g) +(PbI_2+ HI) reaction.

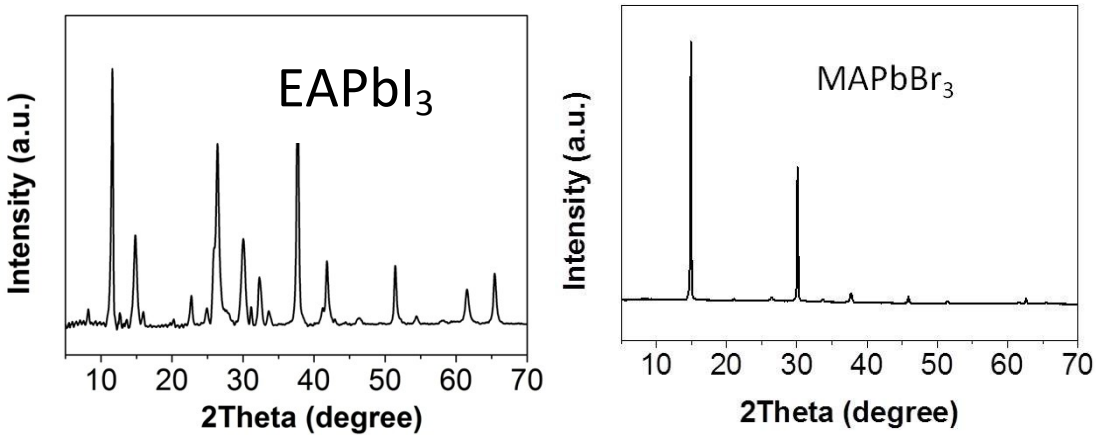


Figure S3. The XRD pattern of $EAPbI_3$ and MAPbBr3 perovskite prepared from the EA(g) + PbI_2+ HI and MA(g)+$PbBr_2$+HBr reaction.

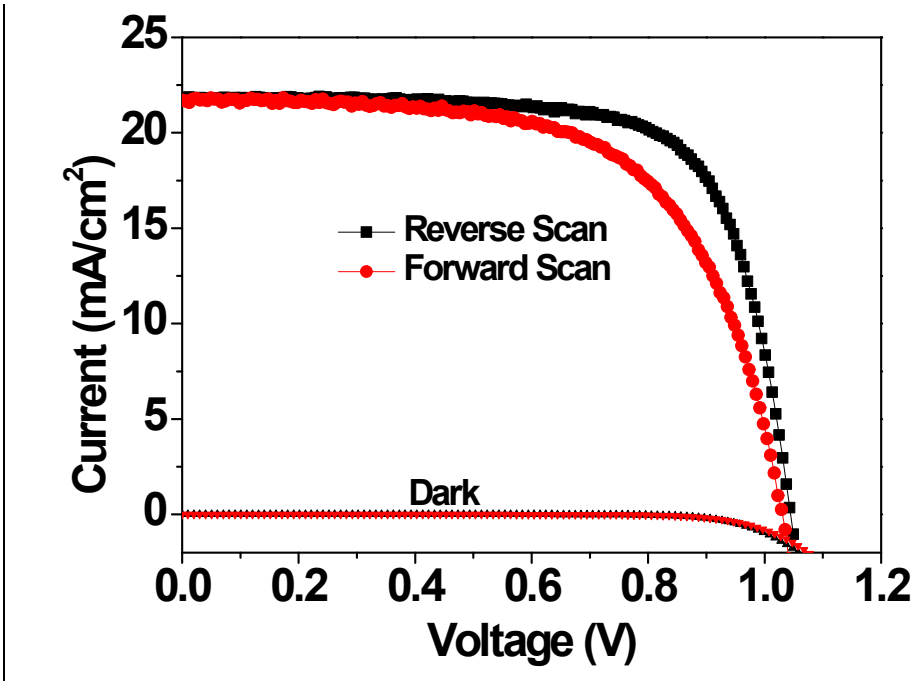


Figure S4. The typical *J–V* curve and dark *J-V* of a planar $MAPbI_3$ solar cell with the highest efficiency of 16.32% (J_{sc}=21.80 mA/cm^2, V_{oc}=1.04 V, FF=0.72) and 14.04% (J_{sc}=21. 69 mA/cm^2, V_{oc}=1.03 V, FF=0.63) under reverse/backward voltage scan at simulated one-sun illumination.

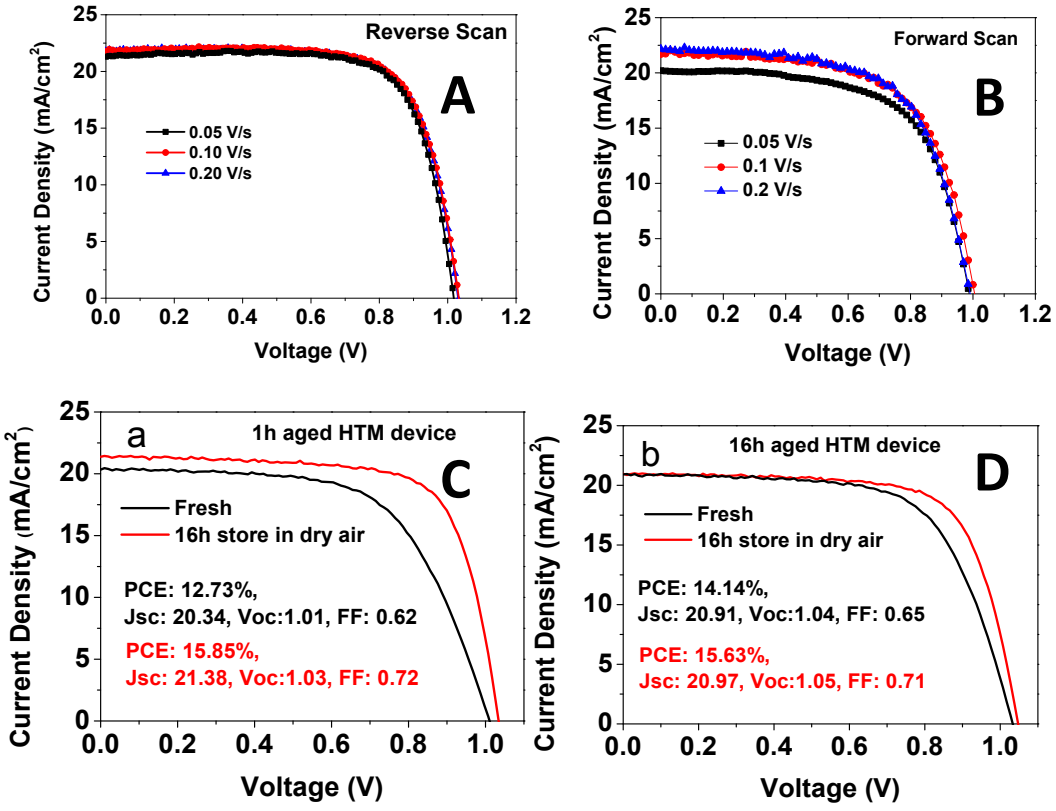


Figure S5. (A,B) The scan rate dependent J-V curves of the MAPbI3 perovskite solar cells. (C,D) The ageing effect on MAPbI3 perovskite solar cells using 1 hr and 16 hr aged HTM.

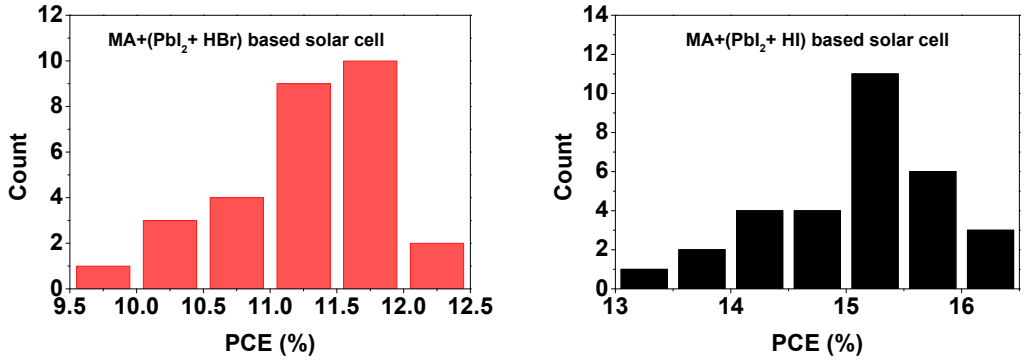


Figure S6. The PCE histogram of the $MAPbI_2Br$ and $MAPbI_3$ perovskite solar cells based on MA+(PbI_2+HBr) and MA+(PbI_2+HI) reactions.

Table S1

Device parameters of $MAPbI_3$ and $MAPbBr_2I$ perovskite solar cells. The best efficiency device's parameters and the value with deviations of each device parameters are given in parentheses (30 devices for each type)

Perovskite Type	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
$MAPbI_3$	21.80	1.04	0.72	16.32
	(20.95±0.89)	(1.00±0.04)	(0.71±0.03)	(15.08±0.74)
$MAPbI_2Br$	14.40	1.15	0.73	12.09
	14.35±0.70)	(1.09±0.05)	(0.70±0.03)	(11.18±0.66)