Electronic Supplementary Material (ESI) for Energy & Environmental Science.
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Supporting Information for

Abnormal Crystal Growth in $CH_3NH_3PbI_{3-x}Cl_x$ Using a Multi-cycle Solution Coating Process

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1. Statistics of grain size distribution

For the statistics of grain size, SEM images with size of 17 μm×17 μm were transfer to a high contrast color mode by software of " wyddion", which is similar to the typical AFM software. The SEM images with size bars on each grain were shown in Fig. S1. These size bars were manually marked for each grain, and the grain size data was collected by software " wyddion". The grains have irregular shapes. In order to get accurate size distribution, all the size bars were aligned in the same direction, and all grains in the images were included in the statistics without selection. Fig. S1 shows the SEM images for grain size distribution statistics with size bars labeled.

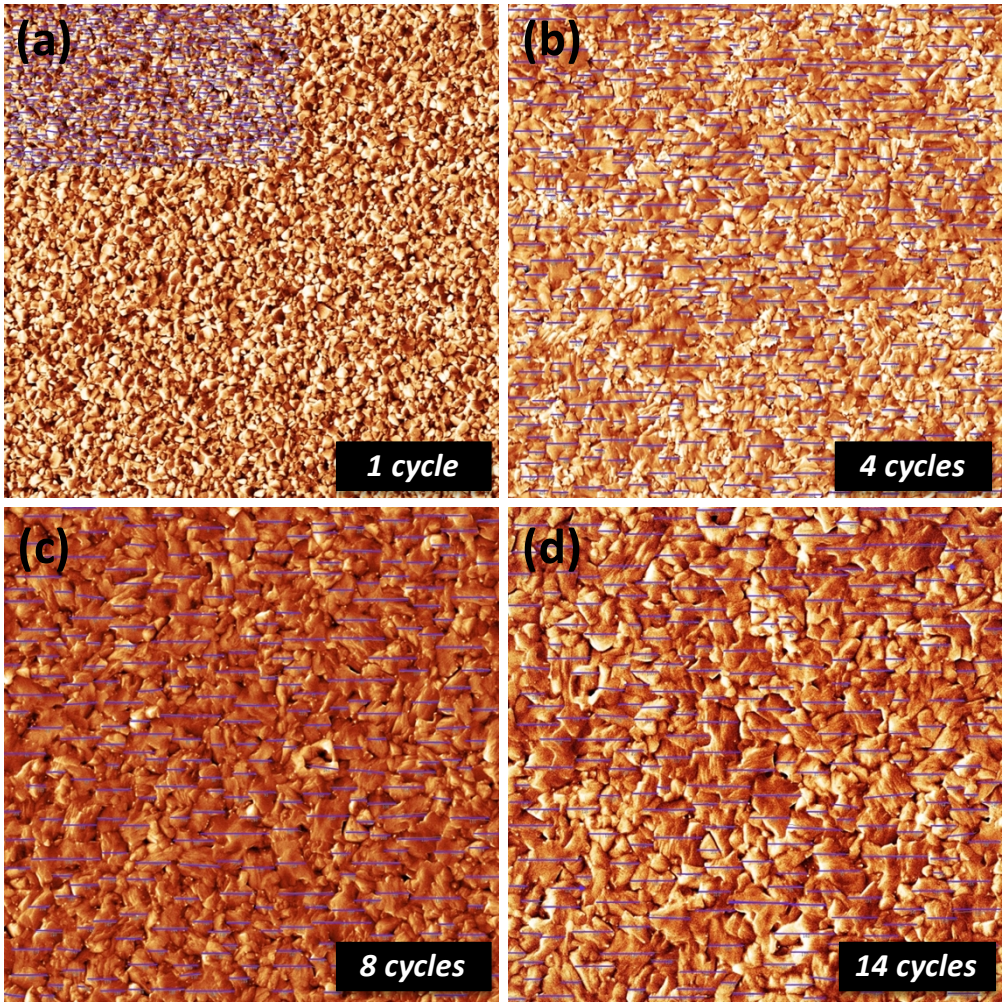

Fig. S1. *SEM images of $MAPbI_{3-x}Cl_x$ films with different coating-cycles for the statistics of grain size with high contrast color mode. Image size was 17 μm×17 μm.*

2. Optimization the efficiency of the $MAPbI_{3-x}Cl_x$ and $MAPbI_3$ solar cells

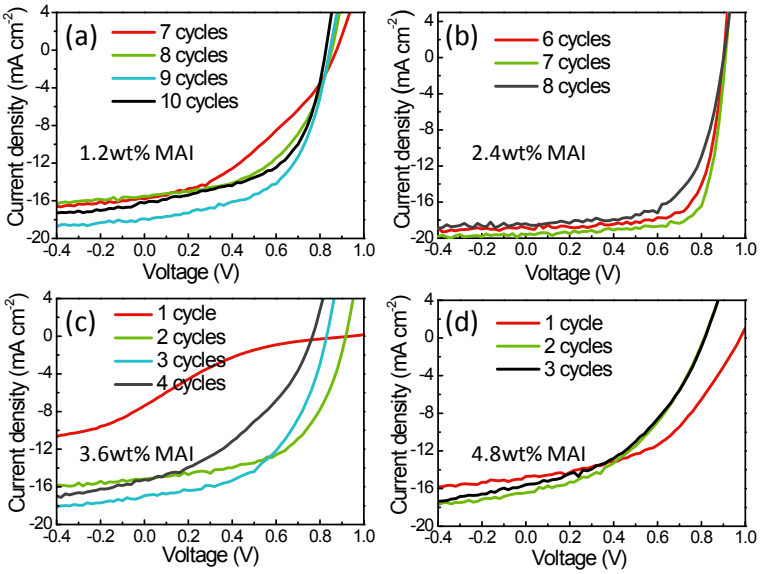

Fig. S2. *Coating-cycle dependent J-V curves of coating interdiffusion processed perovskite solar cells based on PbI_2 and MAI precursor with different concentration.*

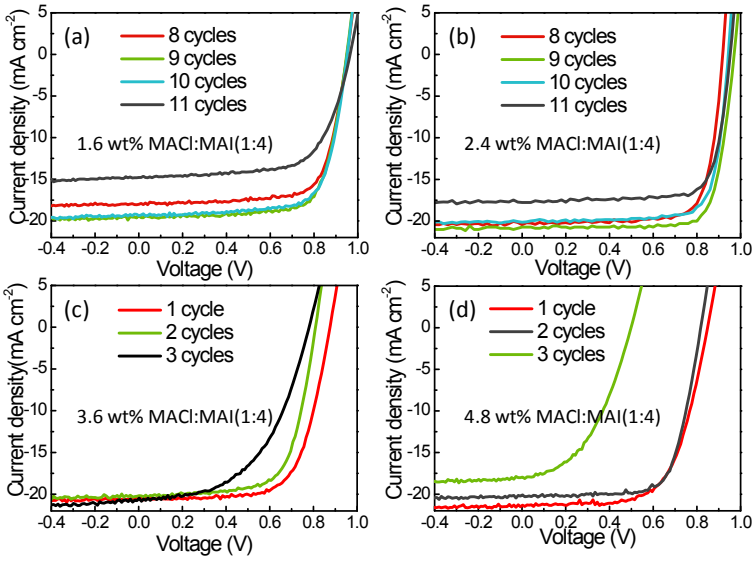

Fig. S3. *Coating-cycle dependent J-V curves of coating interdiffusion processed perovskite solar cells based on PbI_2 and MACl:MAI precursor with different concentration.*

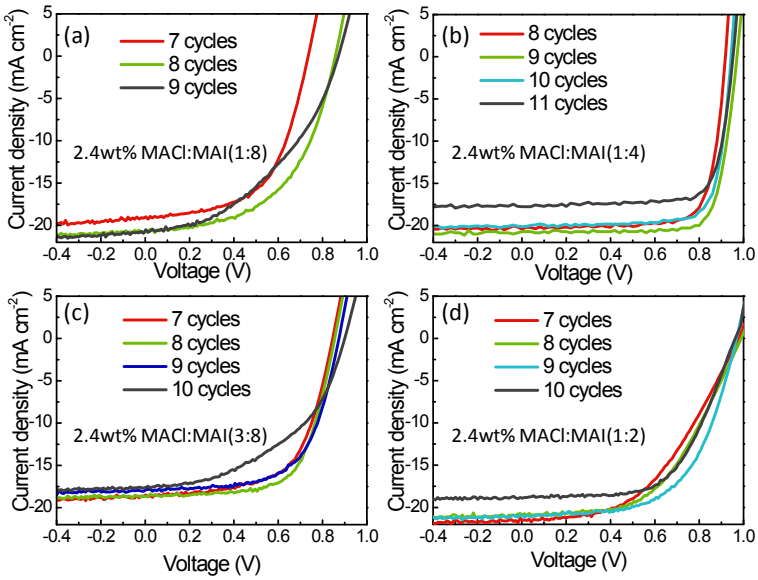

Fig. S4. *Coating-cycle dependent J-V curves of coating interdiffusion processed perovskite solar cells based on different MACl:MAI ratio.*

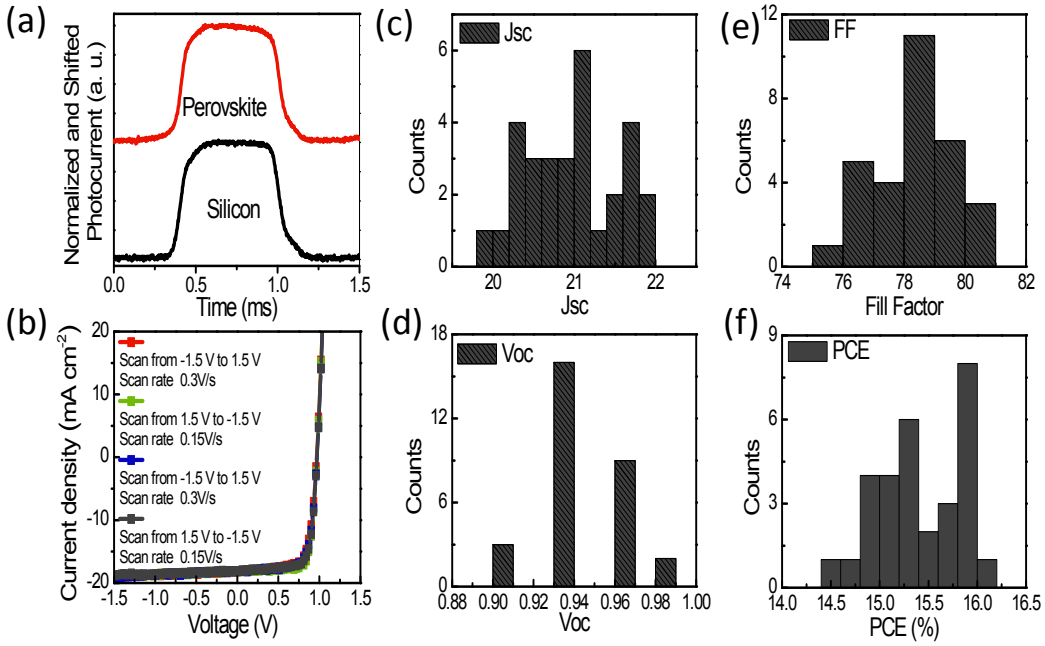

Fig. S5. *(a) Transient response of the optimized $MAPbI_{3-x}Cl_x$ devices and Silicon diode, and (b) photocurrents scan with increasing or decreasing voltage at varied scan rate. (c-f) The statistics of the FF, V_{OC}, J_{SC} and PCE based on 30 mixed halide PPVs.*

3. Impedance spectroscopy measurement

We applied the impedance spectroscopy measurement developed by J. Bisquert [2] to evaluate the charge recombination lifetime in the solar cell devices under illumination. The equivalent circuit we used is shown in the Fig. S6. The charge collection events and charge recombination events are represented by two separate time constants: $\tau_1=R_1 \cdot C_1$ and $\tau_2=R_2 \cdot C_\mu$. The R_1 and C_1 is the bulk resistance, and the capacitance includes both the geometry and photo- excitation component, respectively. The time constant τ_1 is related to the electron transit time through the bulk of the perovskite layer. [3] The R_2 and constant phase element (C_μ) corresponds to the recombination resistance and chemical capacitance. The time constant τ_2 determined by the product of the R_2 and C_μ is the recombination lifetime which is related to the recombination events in the device [4].

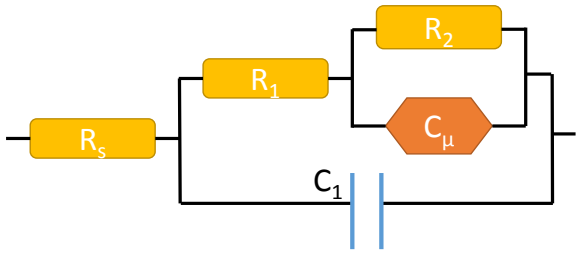

Fig. S6. *The equivalent circuit for fitting the impedance spectroscopy results*

The chemical capacitance reflects the capability of a solar cell device to accept or release additional charge carriers, i. e. the variation of density of states N_i with respect to a change of their chemical potential, μ_i, and can be defined as

$$C_\mu = e^2 \frac{\partial N_i}{\partial \mu_i}$$

The chemical capacitance is caused by the accumulation of photogenerated charges in the devices which do not recombine immediately.

The recombination resistance is defined as

$$R_{rec} = \frac{1}{A}\left(\frac{\partial j_{rec}}{\partial V}\right)^{-1}$$

where j_{rec} is the recombination current, A is the device area and V is the splitting of the Fermi level. The recombination resistance is inversely proportional to the recombination rate. Thus the recombination resistance is an indicator whether the photogenerated charge carriers will be extracted to the electrodes or recombine in the perovskites. When the recombination resistance is larger than the bulk resistance, the charge carriers are more likely to be collected than to recombine.

A constant phase element connected in parallel to a recombination resistance is often used in many optoelectronic devices such as organic solar cells [4], organic light emitting diodes [5] and photoelectrochemical cells [6] to describe materials or interfaces which exhibit a distribution of relaxation times.

Reference

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