Supporting Information for

Abnormal Crystal Growth in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ Using a Multi-cycle Solution Coating Process

Qingfeng Dong, Yongbo Yuan, Yuchuan Shao, Yanjun Fang, Qi Wang and Jinsong Huang*

Department of Mechanical and Materials Engineering and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0656

1. Statistics of grain size distribution

For the statistics of grain size, SEM images with size of 17 $\mu$m×17 $\mu$m were transferred 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 x 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 PbI₂ and MAI precursor with different concentration.

Fig. S3. Coating-cycle dependent J-V curves of coating interdiffusion processed perovskite solar cells
based on PbI₂ 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 MACI: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 $\tau_1$ is related to the electron transit time through the bulk of the perovskite layer.$^3$ The $R_2$ and constant phase element ($C_{\mu}$) corresponds to the recombination resistance and chemical capacitance. The time constant $\tau_2$ determined by the product of the $R_2$ and $C_{\mu}$ 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, \( \mu_i \), 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

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

where \( j_{\text{rec}} \) 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, organic light emitting diodes and photoelectrochemical cells to describe materials or interfaces which exhibit a distribution of relaxation times.
Reference


