



# Growth and evolution of solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ layer for highly efficient planar-heterojunction perovskite solar cells



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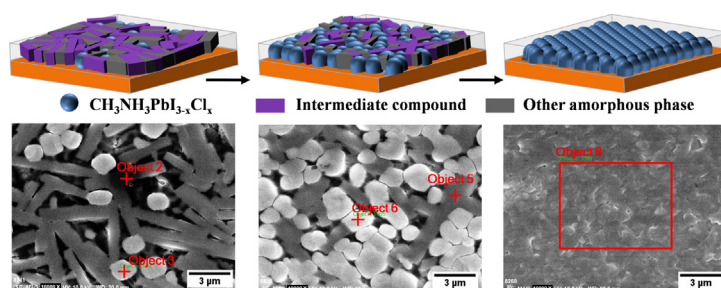
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## HIGHLIGHTS

- Phase transformation dependence of annealing time has been studied in detail.
- The effect of the  $\text{PbCl}_2$  concentrations in the precursor solution is investigated.
- $\text{PbCl}_2$  could be used to control the growth rate and morphology of perovskite films.
- The optimal device achieves a power conversion efficiency of over 15%.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Methylammonium lead iodide perovskites have attracted great attention in photovoltaic research community. In this work, we demonstrate the results of studies focusing on the chemical reaction of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  layer formation during the annealing of perovskite precursor films. We identified two kinds of grain morphologies during the formation of perovskite films grown from non-stoichiometric precursor solution. To form single-phase and high absorbance perovskite films, higher concentration of chloride in precursor solution needs longer annealing time and only a very low Cl content could be incorporated in the final  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films. Adding  $\text{PbCl}_2-3\text{CH}_3\text{NH}_3\text{I}$  to  $\text{PbI}_2-\text{CH}_3\text{NH}_3\text{I}$  precursor solution can allow a good control of the growth rate and morphology for the final perovskite film, and is beneficial to the photovoltaic performance of perovskite devices. By employing the precursor solutions of  $\text{PbCl}_2$ ,  $\text{PbI}_2$  and  $\text{CH}_3\text{NH}_3\text{I}$  with a mole ratio of 1:1:4 and inserting an ultrathin amino-functionalized polymer interlayer, we achieved planar perovskite solar cell with maximum power conversion efficiency of over 15%.

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## 1. Introduction

The emerging perovskite-based photovoltaic cells have attracted much special attention in recent years, due to their high conversion efficiency, simple preparation process, and potential

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low production cost. In 2009, Miyasaka et al. [1] first incorporated the organic-inorganic perovskite light absorbers to photovoltaic devices and reported a 3.8% power conversion efficiency of MAPbI<sub>3</sub>-based solar cell. After that, further progresses have been made on that, which is much quicker than it is on any other types of solar cells. For the past two years, several groups have demonstrated over 15% conversion efficiency for perovskite-based solar cells with both mesoporous and planar cell architectures [2–7].

Various processing techniques, which include thermal evaporation [8–11], vapor assisted solution process [12], one-step [13–16] and two-step solution process [17–19], have been used for the preparation of high quality perovskite absorbers. The solution-based process could offer a tremendous advantage in terms of cost and convenience. Snaith's group pioneered in using the precursor solutions of PbCl<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I (MAI) at 1:3 M ratio to obtain the high quality MAPbI<sub>3-x</sub>Cl<sub>x</sub> perovskite absorber by solution process [14]. Moreover, they determined that the solution-processed MAPbI<sub>3-x</sub>Cl<sub>x</sub> perovskite had a electron-hole diffusion length of over 1 μm [20]. This mixed halide perovskite precursor solution has a lead to halogen ratio Pb/(Cl+I) of 1:5, which deviates away from that of the standard stoichiometric MAPbI<sub>3-x</sub>Cl<sub>x</sub> perovskite (Pb/(Cl+I) = 1/3) and thus means some halides would sublime from the precursor film. Some authors [20–23] have reported that the Cl incorporation in perovskite film could improve the charge transport, and thus result in improved photovoltaic performance. On the other hand, highly efficient MAPbI<sub>3</sub>-based solar cells have also been prepared without the Cl doping [10,12,24–26]. In any case, the growth of perovskite film and the resulting morphology play a key role on the device performance. Recently several literature have reported that Cl inclusion, using PbCl<sub>2</sub> [27,28], MAI [23,29] or other Cl-containing compound [30] in precursor solution, would change the nucleation dynamics and have a strong effect on the morphology of perovskite thin films. Colella et al. [21] used experimental evidences and theoretical calculation to show that Cl incorporation is allowed only at low concentrations (below 3–4%) in I-based perovskite. Williams et al. [27] and Dar et al. [31] employed transmission electron microscopy to directly probe the crystallographic consequences of film growth and both concluded that Cl ion effect the growth of the MAPbI<sub>3</sub>.

In this manuscript, a chemical reaction analysis of the annealing of perovskite precursor film to form high-quality perovskite absorber is presented. The perovskite films were subjected to annealing at different time and analyzed by scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) to identify the composition of each grain. As far as we know, this is the first work that the composition change of the grains during the annealing was clearly presented at the grain scale using EDX analysis. On the basis of detailed investigation of the growth and properties of MAPbI<sub>3-x</sub>Cl<sub>x</sub> film by one-step solution process, we have derived a model to explain the role of Cl in thin film formation. Furthermore, we carry out the study on device performance for planar-heterojunction perovskite solar cells. In contrast to the devices employing PbI<sub>2</sub> (or PbCl<sub>2</sub>) and MAI precursor materials, the use of the precursor mixture of PbCl<sub>2</sub>, PbI<sub>2</sub> and MAI with moderate precursor ratios can significantly improve the power conversion efficiency. This study offers insights into the chemical reaction of perovskite precursor film at the grain scale and provides an effective way for obtaining high-quality smooth perovskite films by one-step mixed halide solution. With the addition of an amino-functionalized polymer interlayer (PN4N), the device performance increased further, reaching 15.7% for the optimized device.

## 2. Experimental section

### 2.1. MAI synthesis

The material CH<sub>3</sub>NH<sub>3</sub>I (MAI) was synthesized based on the literature [14]. In short, to prepare MAI, hydroiodic acid (10 mL, 57 wt % in water, Sigma–Aldrich) and methylamine (10 mL, 33 wt% in absolute ethanol, Sigma–Aldrich) were reacted in a round bottomed flask in ice-cold water with stirring for 60 min. Raw MAI was obtained by removing the solvent at 50 °C on a rotary evaporator. The material was then washed in diethyl ether and filtered several times. The precipitate was then dried in vacuum oven overnight at 50 °C and kept in nitrogen-filled glove box.

### 2.2. Solar cell fabrication

ITO-coated glasses (7 Ω/□ sheet resistivity) were patterned by etching with a laser to remove 1/3 electrode area, which aims to prevent the short circuit between underlying ITO electrode and the contact point for current–voltage measurement. Before deposition of other films, the ITO-coated glass substrates were ultrasonically cleaned with detergent, deionized water, acetone and ethanol sequentially, and then were blow-dried in nitrogen. After that, PEDOT:PSS solution (Clevious AI 4083) was spin-coated on ITO-coated substrates at 2000 r.p.m for 45 s, and then the PEDOT:PSS films were annealed at 150 °C for 20 min. After cooling down, perovskite precursor solutions were spin-coated on PEDOT:PSS films at 3000 r.p.m for 45 s. The precursor solutions were prepared by mixing PbCl<sub>2</sub> (or/and PbI<sub>2</sub>) (Alfa Aesar) and MAI in N,N-dimethylformamide (DMF, Sigma–Aldrich). Note that the weighing and dissolution of MAI and lead halide materials were both done in the nitrogen-filled glove box. The spin-coated perovskite films were then annealed at 100 °C for 90 min on a hot plate. 20 mg ml<sup>-1</sup> PCBM (FEM. Inc.) solution in chlorobenzene (Sigma–Aldrich) was then spin-coated at 1000 r.p.m for 45 s. Finally, Ag metal layer was deposited by evaporation through an aperture mask to complete the devices with ITO/PEDOT:PSS/Perovskite/PCBM/Ag planar structure. The active device area is about 0.12 cm<sup>2</sup>. This device structure can provide significant advantage of low-temperature processing, which enables the application of perovskite solar cells in a broader range of substrates [32,33]. Steady-state photoluminescence (PL) measurement was carried out to study the compatibility of the PEDOT:PSS and PCBM with perovskite film. A considerable decrease in PL intensities (Fig. S1) could be found when perovskite film contacts with PEDOT:PSS or PCBM film, indicating PEDOT:PSS and PCBM can act as exceptional hole and electron acceptors, respectively, to collect photogenerated species in MAPbI<sub>3-x</sub>Cl<sub>x</sub> absorber.

### 2.3. Measurement and characterization

X-ray diffraction (XRD) analysis was performed on a D/max-RB diffractometer (Rigaku) using Cu Kα radiation at a scan rate of 6° min<sup>-1</sup>. Steady-state photoluminescence (PL) spectra were measured using an excitation wavelength of 600 nm in an Edinburgh FLS 920 spectrophotometer equipped with a Xe lamp and monochromator. The energy-dispersive X-ray (EDX) compositions and spectra were performed using energy-dispersive spectroscopy (EDS) combined with a field-emission scanning electron microscope (SEM, Hitachi S4500). SEM images were obtained using Hitachi S4500 and Hitachi S5200. Film absorbance spectra were measured by Shanghai UV–vis SP-752 spectrometer. Current–voltage measurements and power conversion efficiencies were obtained using Keithley 2400 at room temperature under AM 1.5G

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