



# Chlorobenzene vapor assistant annealing method for fabricating high quality perovskite films



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## ABSTRACT

In this study, chlorobenzene (CB) vapor assistant annealing (VAA) method is employed to make high quality perovskite films and produce high efficiency  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite solar cells. The perovskite films made by this method present several advantages such as increased crystallinity, large grain size and reduced crystal boundaries compared with those prepared by thermal annealing (TA) method, which is beneficial to charge dissociation and transport in hybrid photovoltaic device. In addition, it is found that the CB VAA method could improve the surface property of perovskite film, resulting in a preferable coverage of PCBM layer and a better interfacial contact between perovskite film and upper PCBM film. Consequently, the short circuit current density ( $J_{sc}$ ) of the devices is significantly increased, yielding a high efficiency of 14.79% and an average efficiency of 13.40%, which is 13% higher than that of thermal annealed ones. This work not only put forward a simple and efficient approach to prepare highly efficient perovskite solar cells but also provide a new idea to improve the morphology and interfacial contact in one integration step.

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## 1. Introduction

Organic-inorganic hybrid perovskite solar cells have attracted tremendous attentions due to their advantages of large absorption coefficient, broad absorption range, high charge carrier mobility, long electron diffusion length, low-cost and easy fabrication. The power conversion efficiency (PCE) of the devices has obtained remarkable increment exceeding 20% from 3.8% among 6 years [1–6]. To date, perovskite solar cells are widely investigated in two configurations, i.e. mesoporous structure [7,8] and planar hetero-junction architecture [9–11]. For both of mesoporous and planar structure, the high-quality of perovskite films with high crystallization and favorable morphology is essential to achieve high-performance perovskite device [12–15]. This is because perovskite films in poor quality containing trap states at grain boundaries and surfaces as well as point defects in the perovskite crystal lattice will cause electrical shorting and extremely impact charge

transport in the devices.

Many efforts have been devoted to achieve perovskite films in high quality by optimizing the fabrication process, such as varying precursor concentrations [16] or ratio [17], using mixed solvent [18], adding additive [19–24], controlling vapour deposition [15], optimizing annealing condition [25,26]. Besides, solvent or vapor assistant process has been proven as an effective method to optimize the quality of the perovskite films [8,10,27–29]. Dissolving solvent such as N, N-dimethylformamide (DMF) has been successfully applied in solvent annealing process [10,30]. Introducing DMF vapor during the annealing process provides the wet environment for the precursor ions and molecules to diffuse in a long distance, resulting in large size grain growth. In addition to dissolving solvent, dropping non-dissolving solvent (such as toluene, diethyl ether etc.) into perovskite precursor film during spin-coating process has been also developed to produce high crystallinity and uniform perovskite films [8,31,32]. Dropping non-dissolving solvent can help wash out the residue solvent to form a supersaturated precursor solution, which can preferably control the crystallization of the perovskite film and form uniform film with large crystalline grains. However these methods are difficult

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to control accurately. The perovskite film will be eroded if excessive solvent is added in. Similarly the homogeneous perovskite film will not be obtained if the non-dissolving solvent is not dropped at the accurate time [32]. In addition it is proved to be hard to extend these operations to large area production. Therefore, exploring a simple and effective method to produce high quality perovskite film is highly demanded.

In this study, we develop a simple method to prepare  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite films in high quality by using chlorobenzene (CB) vapor assistant annealing (VAA) method. Moreover, it is found that this method have a positive effect on the interfacial contact between perovskite film and upper PCBM film. Hybrid perovskite solar cells with planar heterojunction fabricated by this method demonstrate a reproducible optimal PCE of 14.79% and an average PCE of 13.40%, which are better than thermal annealed ones. Characterizations such as X-ray diffraction (XRD), scanning electron microscopy (SEM), steady state photoluminescence (PL) and PL lifetime are conducted to investigate the influence of CB VAA method on the perovskite films and interface property of the hybrid devices. These results indicated that CB VAA method is an effective method to fabricate high efficiency perovskite solar cells.

## 2. Material and methods

### 2.1. Materials

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of  $10\Omega/\text{sq}$  were purchased from CSG HOLDING CO. Poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS) and [6,6]-Phenyl- $\text{C}_{61}$ -butyric acid methylester (PCBM) were obtained from Clevis and American Dye Source Inc., respectively. Anhydrous DMF, CB and Lead (II) chloride ( $\text{PbCl}_2$ ) were purchased from Sigma-Aldrich and used as received without further purification.

$\text{CH}_3\text{NH}_3\text{I}$  was synthesized according to the literature reported by Lee et al. [7] with slight modification. 20 mL hydroiodic acid (57 wt % in water, Aladdin, China) was dropwise added to 48 ml methylamine (33 wt % in ethanol, Aldrich) in a 250 ml round-bottom flask. After stirring for 2 h, the precipitate was dried with a rotary evaporator at  $50^\circ\text{C}$  to exclude the solvent. Then, the product was redissolved in ethanol and precipitated with diethyl ether. After filtration, the precipitate was washed three times with diethyl ether. Finally, the solid was dried at  $60^\circ\text{C}$  in a vacuum for about 24 h.

### 2.2. Device fabrication

The patterned ITO substrate was cleaned with a sequence of detergent, deionized water, acetone, isopropanol for 15 min in an ultrasonic bath. Then the precleaned ITO-coated glasses were dried with a nitrogen stream and treated with oxygen plasma for 20 min. A thin layer of PEDOT:PSS was made on the substrate with spin speed of 4000 rpm for 60 s, and then dried on a hotplate at  $140^\circ\text{C}$  for 10 min. The perovskite precursor solution ( $\text{PbCl}_2$  and  $\text{CH}_3\text{NH}_3\text{I}$ , 1:3 molar ratio, in DMF 40 wt%) was spin-coated on top of the PEDOT:PSS layer at 2000 rpm for 45 s. Then, the films were put on a hotplate and covered by a petri dish annealed at  $100^\circ\text{C}$  for about 2 h. 20  $\mu\text{l}$  CB solvent was dropped at the edge of the petri dish so that CB vapor could go into the petri dish and form the CB vapor atmosphere. The perovskite films were kept at this CB vapor condition at  $100^\circ\text{C}$  to obtain black  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films. PCBM solution (20 mg/ml) was spin-coated on top of the perovskite layer at 2000 rpm for 60 s. Finally, devices were completed by thermally depositing 50 nm of  $\text{C}_{60}$  and 100 nm of aluminum in vacuum under a base pressure of about  $1 \times 10^{-6}$  Torr. A shadow mask was used

during thermal evaporation to define the active area of  $0.09\text{ cm}^2$ .

### 2.3. Device characterization

The current density-voltage characteristics of the perovskite solar cells were carried out by using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5G simulated solar light. External quantum efficiency (EQE) was performed using a Newport IQE-200 Measurement System. XRD measurements were performed using a D8 Advance (Bruker AXS) with a  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation source. SEM imaging was conducted on S-4800 scanning electron microscope operated at an acceleration voltage of 4 kV. Steady state PL spectra were acquired using a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Tokyo, Japan) with a 150 W Xe lamp as an excitation source at room temperature. The PL lifetimes were obtained from a single photon counting spectrometer on Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER337) as the excitation light source. Droplet images were recorded on a contact-angle system, model OCA20.

## 3. Results and discussion

Fig. 1 illustrates the CB VAA process for the formation of the  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite films. Firstly,  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  precursor was spun onto the PEDOT:PSS covered indium tin oxide (ITO) glass to form a uniform yellow (in the web version) film. Then, the film was annealed at  $100^\circ\text{C}$  for crystal growth. During the heating process, CB vapor was introduced to assist the formation of perovskite crystal. It can be observed that the thermal annealed film without CB VAA process turned to dark brown (in the web version) slowly and then light yellow and finally turned to black. In contrast, the CB assistant annealed ones turned to light yellow immediately when the CB vapor was introduced and then turned to black gradually in 2 h. It seems that the CB vapor help DMF evaporate and accelerate the crystallization. The acceleration process has been proved by the effect of anti-solvent during the spin-coating (ADSC) process used in one step fabrication method. In the dropping ADSC process, the anti-solvent must be dropped at the accurate time to form super saturation of perovskite precursor solution so as to form a high quality film with large crystalline grains [31,32]. If not, the homogeneous perovskite film is hard to be achieved. Our method provides CB vapor atmosphere during the thermal annealing process which is easy to control and does not require a rigid time window.

In order to understand the influence of CB VAA on the crystallization, the resultant films produced by TA and CB VAA methods were characterized by XRD. As shown in Fig. 2a, both films show major diffraction peaks at  $14.08^\circ$ ,  $28.41^\circ$ ,  $43.3^\circ$  and  $58.9^\circ$  which belong to the (110), (220), (314), (440) planes of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  crystal. These peaks are consistent with the results in the earlier reports [15, 26, 33]. This indicates that both perovskite films have a tetragonal crystal structure with high crystallinity. It can be observed that the intensity of the peaks at  $14.08^\circ$ ,  $28.41^\circ$  of CB vapor assistant annealed perovskite films increased which reveals the as-prepared perovskite film possesses enhanced crystallinity and larger grain size. Besides, after normalization on the (110) plane, it is found that the peaks for some planes such as (112), (202), (310), (224) are weaker than those of thermal annealed one (in Fig. 2b), especially for (202) plane. This suggests slightly increased (110) orientation made by CB VAA method. (110) plane preferentially orients parallel to the surface of substrate which could achieve high performance perovskite devices [19,29].

SEM measurements were performed to characterize the surface morphology of the perovskite films and further investigate the influence of CB VAA effect on the resultant films. As shown in

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