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Chlorobenzene vapor assistant annealing method for fabricating high quality perovskite films

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In this study, chlorobenzene (CB) vapor assistant annealing (VAA) method is employed to make high quality perovskite films and produce high efficiency $CH_3NH_3PbI_{3-x}Cl_x$ 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.

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 heterojunction 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 $CH_3NH_3PbI_{3-x}Cl_x$ 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.

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2. Material and methods

2.1. Materials

Indium tin oxide(ITO) coated glass substrates with a sheet resistance of 10Ω/sq were purchased from CSG HOLDING CO. Poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS) and [6,6]-Phenyl-C_{61}-butyric acid methylester (PCBM) were obtained from Clevious and American Dye Source Inc., respectively. Anhydrous DMF, CB and Lead (II) chloride ($PbCl_2$) were purchased from Sigma-Aldrich and used as received without further purification.

CH_3NH_3I 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 °C to exclude the solvent. Then, the product was redissolved in ethanol and precipitated with diethy ether. After filtration, the precipitate was washed three times with diethyl ether. Finally, the solid was dried at 60 °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 °C for 10 min. The perovskite precursor solution ($PbCl_2$ and CH_3NH_3I, 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 °C for about 2 h 20 μl 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 °C to obtain black $CH_3NH_3PbI_{3-x}Cl_x$ 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 C_{60} and 100 nm of aluminum in vacuum under a base pressure of about 1×10^{-6} Torr. A shadow mask was used during thermal evaporation to define the active area of 0.09 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 Cu Kα (λ = 1.54 Å) 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 $CH_3NH_3PbI_{3-x}Cl_x$ perovskite films. Firstly, $CH_3NH_3PbI_{3-x}Cl_x$ 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 °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 peroskite 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°, 28.41° 43.3° and 58.9° which belong to the (110), (220), (314), (440) planes of $CH_3NH_3PbI_{3-x}Cl_x$ 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°, 28.41° 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

Fig. 1. Scheme of CB VAA process for fabrication of the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite films.

Fig. 2. (a) X-ray diffractions of perovskite films produced by TA method and CB VAA method. (b) Normalized X-ray diffraction of perovskite films on the (110) plane produced by TA method and CB VAA method.

Fig. 3. Top view SEM images of (a) thermal annealed perovskite film, (b) CB vapor assistant annealed perovskite film, (c) thermal annealed perovskite/PCBM bilayer, and (d) CB vapor assistant annealed perovskite/PCBM bilayer. (e) Cross-sectional SEM image of the CB vapor assistant annealed device.

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Fig. 3a, the thermal annealed perovskite film exhibits platelet-shaped crystals and possesses lots of crystal boundaries. These boundaries will be trapping centers for exciton recombination and will reduce the J_{sc} as well as the PCE of the photovoltaic devices. In contrast, when CB vapor is introduced during thermal annealing process, the as-prepared perovskite films in Fig. 3b possess large crystallites (about 2 μm) and low densities of crystal boundaries, resulting in more homogeneous surface morphology. In addition, cross-sectional SEM images of these devices shown in Fig. S1 imply that the grains along the thickness of the device in the CB vapor assistant annealed perovskite film are also larger than those of thermal annealed one. This large grain size is consistent with the higher intensity of the XRD pattern discussed above and the enhanced absorption presented in supporting information (Fig. S2). Recent reports propose that the energy loss in perovskite solar cells is derived from the nonradiative recombination of charges due to trap states on film surfaces, grain boundaries, as well as point defects (such as vacancies or interstitial defects) in the perovskite crystal lattice [34,35]. Growth of perovskite films with large crystallites and grain size would effectively remove these points, suppress energetic disorders and enable perovskite photovoltaic devices approaching higher level. These results show that the CB VAA based perovskite films possess enhanced crystallinity, lager grain size and reduced grain boundaries. So, it is expected to reduce charge recombination and achieve high short circuit current in perovskite solar cells.

In addition, the surface morphology of PCBM films on top of $CH_3NH_3PbI_{3-x}Cl_x$ were also investigated, as illustrated in Fig. 3c and d. It is observed that the morphology of PCBM is affected seriously by the morphology of perovskite below. The CB vapor assistant annealed perovskite film possesses larger grain size and more homogenous morphology, so that it is easy for PCBM to spread on it, resulting in a more uniform and transparent PCBM layer shown in Fig. 3d. Compared to CB VAA method, more PCBM aggregates and naked perovskite areas are found on the film based on thermal annealed method in Fig. 3c. The naked perovskite layer without PCBM passivation could not effectively transfer the electron and lower the energy conversion efficiency [36,37]. Besides, the CB VAA process has also change the hydrophilic-hydrophobic property of perovskite surfaces slightly (Fig. S3), improving the spreadability of PCBM on perovskite layer due to the favorable solubility of PCBM in CB. Therefore, PCBM is able to permeate into perovskite layer along grain boundaries and conformably cover perovskite film with an intimate contact. It will efficiently passivate charge trap states at perovskite surface and increase the contact areas between PCBM and perovskite layer. Thus, leakage current and interfacial charge recombination will be effectively reduced. Additionally, it is reported that trap states on the surface and grain boundaries of perovskite film is one of the origin of photocurrent hyteresis [36], so this treatment also help reduce the hysteresis.

In order to understand the interfacial improvement from CB VAA process, steady state PL measurements of $CH_3NH_3PbI_{3-x}Cl_x$, $CH_3NH_3PbI_{3-x}Cl_x$/PCBM thin films annealed by different methods were conducted, as shown in Fig. 4a. It is found that the steady state PL spectrum of the perovskite film prepared by CB VAA method displays strikingly stronger photoluminescence than the thermal annealed one. This is because the improved crystallinity has enhanced the absorption across a broad spectral range and suppressed the nonradiative recombination channels at the same time. When PCBM layers were deposited on these perovskite films, significant quenching effects are observed in both thermal annealed and CB vapor assistant annealed $CH_3NH_3PbI_{3-x}Cl_x$/PCBM bilayer. But, it is interesting to find that the quenching effect in CB vapor assistant annealed $CH_3NH_3PbI_{3-x}Cl_x$/PCBM bilayer is more impressive than that of thermal annealed $CH_3NH_3PbI_{3-x}Cl_x$/PCBM bilayer. This demonstrates more efficient electron transport at interface between $CH_3NH_3PbI_{3-x}Cl_x$ and PCBM treated by CB VAA method than that in the thermal annealed condition. So it confirms the preferable spreadability of PCBM layer on CB vapor assistant annealed perovskite layer and the compact interfacial contact in these perovskite devices.

To further confirm the influence of CB vapor treatment on the perovskite film and PCBM layer, PL lifetime for different films such as PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$ and PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$/PCBM have been measured. The results are shown in Fig. 4b. The lifetimes of carriers were acquired by fitting the data with two exponential decay functions. For thermal annealed PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$ films, the PL lifetime is 66 ns, while the PL lifetime for CB vapor assistant annealed PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$ is 51 ns The decreased lifetime is attributed to the increased grain size and crystallinity, which facilitates the exciton dissociation and enhances the efficiency of charge transfer. Moreover, because of the stronger quenching effect of PCBM to the PL emission from the CB vapor assistant annealed perovskite layer, the PL lifetime of the film from CB VAA further decreases to 2.58 ns (the PL lifetime of thermal annealed PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$/PCBM is 4.10 ns). We propose that the PL quenching is caused by fast charge transfer at the interface. It indicates that the charge transfer from perovskite to PCBM in CB vapor assistant annealed device is more efficient than that in thermal annealed one.

The final solar cells were fabricated with a widely used inverted planar heterojunction device structure of ITO/PEDOT:PSS/perovskite/PCBM/C_{60}/Al. Table 1 lists the device parameters of the best devices produced by these two methods under AM 1.5G simulated sun light. As expected, the CB vapor assistant annealed devices display better performance than thermal annealed ones. The best device performance developed by thermal annealing displays a J_{sc} of 22.85 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.96 V, a fill factor (FF) of 63% with a PCE of 13.83%. Meanwhile the CB assistant annealed device exhibits similar V_{oc} of 0.97 V and FF of 61% and a remarkable higher J_{sc} of 24.99 mA/cm^2, yielding a PCE of 14.79%. The enhancing of J_{sc} and PCE of the best performance device was checked for reproducibility. The average device parameters and the full histogram counts of 15 devices produced under the same condition are shown in Table S2 and Fig. S4. The average J_{sc} of CB vapor assistant annealed devices can reach as high as 24.02 mA/cm^2 and a relatively higher average PCE of 13.40% is obtained under AM 1.5G simulated sun light. The average PCE is 13% higher than that of thermal annealed ones (13.40% vs 11.86%). The histogram counts shows that the devices fabricated by CB VAA process exhibit excellent performance and favorable reproducibility. These results verify the previous expection and are consistent well with the earlier measurements. It is obvious that the increased J_{sc} comes from the enhanced crystallinity of the perovskite film as well as preferable interfacial contact. Corresponding external quantum efficiency (EQE) is displayed in Fig. 5a inset. The EQE spectra for the devices annealed under CB vapor show overall enhancement in the entire absorption range, which implies that the increase of current density results from enhanced charge transfer and the reduction of exciton recombination. The improved EQE of the devices annealed with CB vapor is also consistent with the higher J_{sc} and PCE values. The asymmetry of device area and the spot size as well as the perovskite device instability contribute to the relative decrement of EQE values.

The steady state photocurrent represents the actual power output and has been used to characterize the device efficiency [10]. In order to verify the enhanced efficiency, we recorded the photocurrent of these cells held at their maximum power point voltage (0.735 V for CB vapour assistant annealed device and 0.719 V for thermal annealed device) under AM 1.5G 100 mW/cm^2

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Fig. 4. (a) Steady state PL spectra of various films: TA perovskite, CB VAA perovskite, TA perovskite/PCBM, and CB VAA perovskite/PCBM. (b) PL lifetime of various films: PEDOT:PSS/TA perovskite, PEDOT:PSS/CB VAA Perovskite, PEDOT:PSS/TA Perovskite/PCBM, PEDOT:PSS/CB VAA Perovskite/PCBM.

Table 1
Photovoltaic parameters of the perovskite solar cells produced by TA method and CB VAA method under AM 1.5G simulated solar light.

Number	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)		R_s (Ω cm^2)	R_{sh} (Ω cm^2)
				Best	Average		
T A	0.96	22.85	0.63	13.83	11.86	6.44	328.9
CB VAA	0.97	24.99	0.61	14.79	13.40	5.88	251.3

R_s is the series resistance, and R_{sh} is the shunt resistance.

Fig. 5. (a) The current density-voltage (J-V) curves of the devices fabricated by TA method and CB VAA method measured under AM 1.5G 100 mW/cm^2 simulated solar light. Inset is the corresponding EQE of these devices. (b) Steady-state efficiency with the photocurrent density of thermal annealed and CB vapor assistant annealed devices as a function of time applied at a forward bias of 0.719 V and 0.735 V.

simulated solar light. As shown in Fig. 5b, the photocurrent of CB assistant annealed device stabilizes at 19 mA cm^{-2} and a stable-state PCE of 13.96% is obtained (PCE = 0.735 V × 19.0 mA/100 mW = 13.96%). Meanwhile, the thermal annealed device shows a photocurrent density of 16.2 mA cm^{-2} with a PCE of 11.6% (PCE = 0.719 V × 16.2 mA/100 mW = 11.65%). It indicates that the stabilized power output of the CB vapor assistant annealed device is higher than that of thermal annealed one. This suggests that the optimized PCE by using CB assistant annealing method are reliable.

An anomalous hysteresis in *J-V* curves has been observed in many perovskite solar cells [38,39]. It has been reported that the hysteresis is originated from the traps, ferroelectric properties and electromigration of ions in the perovskite films. By optimizing perovskite films, some groups successfully fabricated planar perovskite solar cells without hysteresis [5,40,41]. Therefore, *J-V* curves of these devices with different scanning direction and different scanning rates are tested in our study. As shown in Fig. 6b, the CB vapor assistant annealed device exhibits a PEC of 14.79% from the forward bias to short circuit (FB to SC) and a PCE of 14.26% under an opposite scan direction (SC to FB). Whereas, the thermal annealed device shows a PCE of 13.83% (FB to SC) and 13.03% (SC to FB) for each scanning direction (Fig. 6a). The difference of PCE between the forward bias scanning and the reverse bias scanning in CB vapor assistant annealed perovskite solar cell is less than that of thermal annealed ones (0.53% vs 0.8%). Moreover, the *J-V* curves of CB vapor assistant annealed devices at different scanning rates (0.21 V/s, 0.15 V/s, 0.10 V/s) have little difference with each other compared with the thermal annealed ones (Fig. 6c and d). The results indicated that the quality of perovskite film annealed under CB vapor is much better than thermal annealed films and CB VAA method is an effective method to enhance the efficiency of perovskite solar cell.

4. Conclusions

In conclusion, the CB vapor assistant annealing method is introduced to fabricate $CH_3NH_3PbI_{3-x}Cl_x$ perovskite film in high quality. High performance planar perovskite solar cells with efficiency of 14.79% are obtained based on this absorber layer. An enhanced J_{sc} is observed compared to the common thermal

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Fig. 6. *J-V* characteristic curves of devices obtained from forward bias to short circuit (FB-SC) and from short circuit to forward bias (SC-FB): (a) thermal annealed device, (b) CB vapor assistant annealed device. *J-V* characteristic curves of devices obtained at forward scan direction and different scanning rate: (c) thermal annealed device, (d) CB vapor assistant annealed device.

annealed devices. This is ascribed to the enhanced crystallinity, grain size and reduced crystal boundaries of the perovskite films proved by the XRD and SEM measurement. In addition, the CB VAA process also improves the spreadability of the upper PCBM layer, resulting in preferable PCBM layer verified by SEM measurement, contact angle measurements and better interfacial contact for electron transfer. The steady-state PL quenching and PL lifetime measurement indicates that the CB vapor assistant annealed devices are in favour of charge transport so as to verify the better interfacial contact between perovskite layer and PCBM layer. To summarize, this method may offer a simple but effective way in cooperation of solvent vapor annealing and thermal annealing to produce high efficient perovksite solar cells. Furthermore, this method can be extended into other photoelectronic system to achieve high film quality and better interfacial contact so as to enhance the device performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2016.04.024.

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