



Pure- or mixed-solvent assisted treatment for crystallization dynamics of planar lead halide perovskite solar cells



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ARTICLE INFO

Article history:

Received 14 March 2016

Received in revised form

5 May 2016

Accepted 7 June 2016

Available online 15 June 2016

Keywords:

Perovskites

Mixed-solvent

Morphology

Crystallinity

ABSTRACT

Pure chlorobenzene (CBZ) and 2-propanol (IPA) or mixed-solvent assisted spin-coating have been applied to one-step fabricate $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films, respectively. However, with the treatment of pure- or mixed solvent, there are obvious differences in the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films with full coverage and large crystal grain size, as well as the role in the photovoltaic performance. Furthermore, the nucleation and growth dynamics of perovskite crystals have been taken into consideration with the activation energy of transporting crystallizing segments across the crystal interface and the formation free energy of a critical-sized nucleus. Planar heterojunction (PHJ) perovskite solar cells (PSCs) based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ by mixed-solvent treatment exhibit a poor power conversion efficiency (PCE) owing to the formation little amount of perovskite crystals with low crystallinity. While pure CBZ treatment renders the corresponding device get efficiency of 8.1%, which is due to the formation of uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with higher surface coverage and crystallinity. Inversely, PSCs based on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ with mixed-solvent shows the highest PCE of 9.2%, short-circuit current density (J_{sc}) of 16.06 mA/cm² and fill factor (FF) of 63.6% with high device reproducibility and low photocurrent hysteresis, because of possessing higher light absorption ascribed from bigger crystal size and better surface morphology with no pin-holes. These results will provide significant guidance for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite device performance optimization and large-scale application by pure- and mixed-solvent treatment.

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1. Introduction

Solar cells based on organolead halide perovskites as light absorbers have rapidly developed in recent years and may prospectively become new generation photovoltaic technology for solar energy conversion because of possessing high absorption coefficient, excellent ambipolar charge mobility, small exciton binding energy and low-cost [1–4]. Over the past five years, the power conversion efficiencies (PCEs) of the perovskite solar cells (PSCs) with mesoporous structure or planar structure have reached 20.1% and 19.3%, which shows the bright future for the organic-inorganic hybrid perovskite solar cells [5,6].

However, the device performance strongly depends on the morphology of the perovskite film and crystallinity of perovskite

layer [7–9]. Generally, “island” like perovskite with poor crystallinity leads to current leaking and negative influence on the charge dynamics of PSCs [10–13]. The growth process of perovskite crystallites differs greatly in the structure of perovskite devices. The meso-structured PSCs generally employs a scaffold layer of mesoporous TiO_2 [14,15] or Al_2O_3 [16,17] with the thickness of hundred nanometers, so that the crystallization of the perovskite greatly benefits from the enhanced nucleation at the meso-structure surface. However, the planar heterojunction (PHJ) PSCs has a p-i-n junction, in which the perovskite is directly deposited on a compact n-type inorganic oxide or p-type poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) layer, then covered by a solid organic hole transport layer or fullerene electron transport layer,[8,18] respectively [19]. Owing to the simpler device structure and a high-temperature (500 °C) sinter process becoming no longer necessary, the planar PSCs should be more attractive for practical application. Generally, a fully covered dense layer of perovskite with large crystal grain size is important for further PHJ PSCs to gain efficient light absorption, and reduce the energy loss in the charge transport and collection process.

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Moreover, the uniform morphology with full coverage and high crystallinity are controlled by the fabrication process and further optimization of perovskite films.

To date, the fabrication of perovskite thin film includes one-step spin-coating [20], sequential deposition method [21–23], two-step spin-coating deposition [24] and vapor deposition [10,25]. In consideration of the future large-scale application, one-step spin-coating is one of the most candidate for industry manufacture for its relative low-cost and simple solution process. The strategies including adding additives, varying the composition, solvent washing and controlling annealing time, temperature, or atmosphere, etc. are applied to control the perovskite morphology prepared by one-step spin-coating, which all focuses on the crystallization kinetics. Zuo et al. has reported an innovative approach by using chloride additives to slow down the crystallization rate and cause crystallization coarsen. The light-absorbing perovskite layer fabricated using NH_4Cl additive shows higher crystallinity and better morphology [26]. Also N-cyclohexyl-2-pyrrolidone (CHP) additive could also be employed to control the morphology [27]. Furthermore, Xiao et al. has utilized a fast deposition-crystallization (FDC) procedure by adding the second solvent for preparing a flat and uniform perovskite thin film with induced crystallization, in which an instant darkening of the perovskite film could be regarded as the formation of the desired perovskite crystals [28]. Also, photocurrent hysteresis can be reduced to a certain extent by introducing 2-propanol (IPA) treatment, which improves the perovskite crystals purity by washing residual methylamine iodide ($\text{CH}_3\text{NH}_3\text{I}$, MAI) on the surface, for its excellent solubility of MAI as well as low boiling point.[15,25] All these demonstrate the control of morphology and crystallization is an important part of enhancing the performance of PHJ PSCs.

In this paper, we report a method to control perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) morphology and crystallinity prepared by one-step fabrication process with pure- or mixed-solvent assisted spin-coating. For pure IPA solvent treatment, residual MAI and byproduct methylamine chloride ($\text{CH}_3\text{NH}_3\text{Cl}$, MACl) can be washed away due to its good solubility, which is beneficial for the formation of perfect perovskite films. Although chlorobenzene (CBZ) is a poor solvent for its insolubility of perovskite precursor, it plays an important role in accelerating the crystallization rate of perovskite crystals because of the reduced solubility of perovskite rapidly promoting fast nucleation and growth of the crystals in the film. Furthermore, it has also been found that there are obvious differences in the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films with pure- and mixed- solvent treatment. In order to analysis the effect of the pure- and mixed-solvent treatment on the morphology and crystallinity of the perovskite films, several measurements such as scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been conducted to give the evidence. Furthermore, the detail nucleation and growth dynamics of perovskite crystals have been taken into consideration. Planar heterojunction PSCs based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ by mixed-solvent process exhibit a poor power conversion efficiency (PCE) owing to perovskite with low crystallinity. While pure CBZ treatment renders the corresponding device get superior efficiency of 8.1%, which is due to the formation uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with higher surface coverage and crystallinity. Inversely, PSCs based on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ with mixed-solvent process shows the highest efficiency of 9.2% with superior short-circuit current density (J_{sc}) of 16.06 mA/cm^2 and fill factor (FF) of 63.6%, because of possessing higher light absorption ascribed from bigger crystal size and more good surface morphology with no pin-holes. The results indicate that the pure- and mixed-solvent treatment will be an effective strategy for enhancing PHJ PSCs device performance based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, respectively.

2. Results and discussion

Scheme 1 shows the structure of perovskite device based on ITO/PEDOT:PSS/Perovskite/ $\text{PC}_{61}\text{BM}/\text{Al}$ and one-step fabrication process for perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) films prepared by pure- or mixed-solvent assisted spin-coating. As shown, PEDOT:PSS was first spin-coated on the ITO substrate for about 40 nm. $\text{CH}_3\text{NH}_3\text{PbI}_3$ (45 wt%) and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (40 wt%) precursor solutions in N,N-dimethylformamide (DMF) were then spin-coated on the PEDOT:PSS layer at 5500 rpm and 3000 rpm, respectively. Then a second pure 2-propanol (IPA) or pure chlorobenzene (CBZ), or mixed-solvent (with different volume ratio including CBZ:IPA = 1:3, CBZ:IPA = 2:2, CBZ:IPA = 3:1) was added to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer substrates after a specific delay time for 6 s and 25 s, respectively. For evaporating the residual solvent and further promoting a well crystallization, the perovskite films were then transferred to a hot-plate annealing at 100 °C for 10 min and 1 h, respectively. From the photographs of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite samples in Fig. 1, films treated by pure-solvent were bright black and fully covered, while yellow films with surface defect were obtained after mixed-solvent treatment. As seen from the photographs for $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ samples in Fig. 2, reddish brown films were obtained after mixed-solvent treatment, especially for CBZ: IPA = 2:2 processing, while pure IPA treated film was colorless and transparent. For pure IPA solvent treatment, residual $\text{CH}_3\text{NH}_3\text{I}$ (MAI) and byproduct $\text{CH}_3\text{NH}_3\text{Cl}$ (MACl) can be washed away due to its good solubility, which is beneficial for the formation of perovskite films. CBZ plays an important role in accelerating the crystallization rate of perovskite crystals because of the reduced solubility of perovskite rapidly promoting fast nucleation and growth of the crystals in the film [28]. It is good for $\text{CH}_3\text{NH}_3\text{PbI}_3$ achieving perfect crystallinity without impure phases by pure-solvent treatment. However, the phenomenon with mixed-solvent treatment is unsatisfactory. For $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, there are defects and pin-holes free perovskite films with mixed-solvent treatment, especially for CBZ:IPA = 2:2. However, IPA treatment results in the formation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite with big pin-holes. CBZ treatment leads to generate large number of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite crystals with small grain size, which is adverse to the formation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite with good surface coverage and high crystallinity. It is crucial to explore why there are obvious differences in the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films with pure- and mixed- solvent treatment.

First, the effect of the pure- and mixed-solvent treatment on the morphologies of the perovskite films formed on PEDOT:PSS have been investigated by scanning electron microscopy (SEM). The typical crystalline morphology of the perovskite is visible. As shown in Fig. 1, an opaque gray film obtained by conventional spin-coating contains rod-like grains with an incomplete coverage on the substrate, which is in accordance with previous observations. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ films produced by mixed-solvent treatment shows a low surface coverage with little crystal in the selected area. While the perovskite films with the addition of pure CBZ or IPA exhibit full surface coverage with micron-sized crystalline grains. It has been noted that crystallization regulation by manipulating the perovskite nucleation and growth can improve the film morphology and coverage effectively. In order to investigate the effect of different solvent treatment on the nucleation and growth of perovskite crystals, the following Turnbull-Fisher equation [29–31] has been utilized to analyze the detail dynamics.

$$I = I_0 \exp\left(-\frac{E_d}{kT} - \frac{\Delta G^*}{kT}\right) \quad (1)$$

Where I represents the formation of crystal nucleus number on unit area per second, I_0 is pre-exponential factor (a constant under

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