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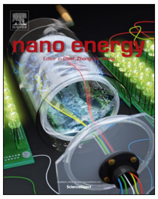

Controlled growth of textured perovskite films towards high performance solar cells

Chengbin Fei [a], Lixue Guo [a], Bo Li [b], Rong Zhang [a], Haoyu Fu [a], Jianjun Tian [b,*], Guozhong Cao [a,c,*]

[a] Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences; National Center for Nanoscience and Technology (NCNST), Beijing 100083, China
[b] Advanced Material and Technology Institute, University of Science and Technology, Beijing 100083, China
[c] Department of Materials and Engineering, University of Washington, Seattle, WA 98195-2120, USA

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ABSTRACT

Antisolvent precipitation method has been one of the favored strategies to fabricate compact, smooth and uniform perovskite films for high efficiency solar cells due to its dramatically accelerated crystallization process. However, the excessively fast crystallization restricted the further improvement of the photovoltaic performance. In this work, we introduced CH_3NH_3Cl into the pristine $CH_3NH_3PbI_3$ precursor for antisolvent precipitation at low temperature and fabricated high quality perovskite films with desired morphology, crystallinity and optical properties. The X-ray diffractometry and ultraviolent-visible spectroscopy provided ample evidence that CH_3NH_3Cl exerted significant impacts on the perovskite crystallization process by controlling the delivery speed of PbI_2 from the intermediate phase $CH_3NH_3PbI_2Cl$. The possible reactions in the perovskite formation process were first elaborated. The resultant solar cells demonstrated an average power conversion efficiency around 16.63% and a best efficiency at 17.22% under the standard light illumination condition. In addition, the ion migration was first detected in the perovskite solar cells by an ordinary impedance measurement.

1. Introduction

Owing to the suitable direct band gap (around 1.5 eV) [1], large molar extinction coefficient [2] and long electron-hole diffusion length ($>175\ \mu m$ in single crystal) [3], methylammonium lead halide ($MAPbX_3$, X=Cl, Br, I) based solar cell became a very promising device to achieve excellent performance of converting solar energy into electricity [4]. In recent four years, many researches focused on the synthesis of well crystallized perovskite for light harvesting photovoltaic device, since there was a broad understanding that the properties of perovskite solar cells (PSCs) had high correlation with the morphology and crystal structure of $MAPbX_3$ [5–7]. Generally, perovskite $MAPbX_3$ can be produced by mixing the PbX_2 and MAX precursors in organic solution or vapor phase, followed by thermal annealing to remove redundant ingredient and improve the crystallinity [8]. By applying vapor phase co-evaporation film deposition process, we could fabricate perovskite films with large scale and high repeatability, but the time consumptions and physical defect in perovskite films were still unsolved issues.[9,10] As for the solution-processing method, due to the slow crystallization procedure, the perovskite films were non-uniform, rough and incompletely covered. The high roughness increased the light diffuse reflection and further decreased the light harvesting efficiency at the range of long-wavelength (550–800 nm), while the incomplete coverage (especially pinhole) created more recombination between electron selective layer and hole transfer material [11]. To form dense and smooth perovskite films, a rapid nucleation process followed by a slow crystal growth process were requested. Therefore, antisolvent precipitation process could be a potential method to fabricate high quality perovskite film, since the crystallization process was dramatically speed up when contrasted with previous one-step solution process [12].

Antisolvent precipitation is a method for synthesizing uniform nanosized material [13]. When a solvent to which solute had none or a very low solubility was added into the initial solution, the initial solvent would be partially extracted by the new added solvent, so the concentration of solute in the initial solution raised to supersaturation in an extremely short time, thus promoted the precipitation and crystallization of solute. After the first application in the synthesis of perovskite for PSCs by Cheng et al. [12] the

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[*] Corresponding authors.
E-mail addresses: tianjianjun@mater.ustb.edu.cn (J. Tian), gzcao@u.washington.edu (G. Cao).

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significance of this process have already been demonstrated by many research groups, [6,14] but there were only few works aimed to solve the problem caused by the excessively fast crystal growth, including the time dependence of film formation (known as “the sixth second”) and the undesirable grain size and crystallinity of the resulting perovskite films. Among the few works, the standard precursor (MAI and PbI_2 in equimolar mixture) with the addition of DMSO has achieved successful synthesis of perovskite films with time dependence, but the amelioration of crystallinity was not noticed [15]. In contrast to the mixed chlorine- and iodine-containing salt precursors in planner structure solar cells, the formation of $CH_3NH_3PbI_3$ was slowed down, improving the film morphology and extending the carrier's lifetime [16–18]. Therefore, Cl-containing perovskite precursor was desirable to further improve and perfect the antisolvent precipitation process.

Herein, we present a new antisolvent precipitation process to fabricate perovskite film with a decelerated crystal growth process. By introducing MACl to pristine $CH_3NH_3PbI_3$ precursor in equivalent molar, the films' qualities were significantly improved, including relatively large grain, pin-hole-free and smooth perovskite film. With the assistant of X-ray diffractometer and ultraviolent-visible spectroscopy, the possible reaction route with the addition of MACl were studied. During the reaction process, MACl was believed to have slowed down the crystal growth process by controlling the delivery speed of PbI_2, leading to much reduced nucleation rate and near thermodynamic equilibrium subsequent growth and, thus, resulting in a large crystallites with good crystallinity. With this new method, high stability and repeatability photovoltaic devices were readily fabricated, and the solar cells obtained a 16.63% ± 0.49% average efficiency and an impressive 17.22% efficiency for the champion cell. Besides, the development on photo-to-current efficiency was proved to originate from the increased light harvesting and charge separation. Finally, an obviously ion migration behavior was first detected by a simple impedance spectrum.

2. Experimental procedures

2.1. Device fabrication

SnO_2 electron selective layer was prepared by spin-coating precursor solutions of $SnCl_4 \cdot 5\,H_2O$ in ethanol on clean FTO substrates. The SnO_2 thin films were finally heated in air at 180 °C for 1 h. Afterwards, 0.02 M $TiCl_4$ aqueous solution was used to treat the surface of SnO_2 as the previously reported method [19]. The perovskite $CH_3NH_3PbI_3$ films were prepared through the following method: firstly, 159 mg CH_3NH_3I and 461 mg PbI_2 were dissolved in 1 mL dimethylformamide (DMF) at the ambient temperature, then 69 mg CH_3NH_3Cl was added into the solution to form the precursor. 30 μl perovskite precursor solution was dropped onto the prepared electron selective layer. After the substrate was spun at 4000 r/min for 4–15 s, ethyl acetate (100 μl, three big drops) was dropped on the center of the substrate continuously to induce quick crystallization of the perovskite. The pristine film was prepared according to the literature [12]. The obtained films were heated in air at 100 °C for 1.5 h. The hole transfer layer was spin-coated by the chlorobenzene solution including 72.3 mg/mL Spiro-MeOTAD, 28.8 μl/mL tertbutylpyridine and 17.5 μL/mL li-TFSI solution at 4000 r/min for 30 s. Finally, an Au counter electrode was formed by thermal evaporation. The active area was 0.07 cm^2.

2.2. Characterization

The morphologies of the perovskite films and completed devices were imaged by a high-resolution field emission SEM (SU-8020, Hitachi). The absorption and transmission spectra were characterized by an ultraviolet–visible (UV–vis) spectrophotometer (UV-3600, Shimadzu) at ambient temperature. The X-ray diffraction pattern was recorded on X-ray diffractometer (PANalytical, Netherlands) using Cu Kα radiation. The photovoltaic characteristics and the electrochemical impedance spectroscopy (EIS) of the devices were performed using an electrochemical workstation (Zahner, Zennium) under simulated standard one sun illumination (AM 1.5, 100 mW/cm^2) provided by a solar simulator (SOL02 series, Crowntech). The intensity-modulated photovoltage/photocurrent spectroscopy (IMVS/IMPS) were also characterized on electrochemical workstation with the assistant from light source Zahner (PP211). The photoluminescence (PL) spectra and fluorescence decay curve were taken out with combined steady state and time resolved fluorescence spectrometer (FLS980, Endinbergh). The incident photon-to-current conversion efficiency (IPCE) spectra was measured from an accessory kit of the electrochemical workstation.

3. Results and discussion

In the new antisolvent precipitation method, dimethylformamide (DMF) was used as the initial solution to dissolve MAI, MACl and PbI_2, while ethyl acetate (EA) was used as antisolvent to make the solute precipitation and crystallization from the initial solution rapidly. With a spinning-coating and low temperature heating processing, the perovskite film with TiO_2 treated SnO_2 compact layer and FTO substance were developed. The morphology of films produced from the precursor with and without MACl were shown as Fig. 1. The films were both compact and well covered (100% coverage) which efficiently block the charge leakage between SnO_2 compact layer and Spiro-OMeTAD. With a MACl additive, the average grain size increased from 200 to 300 nm to above 500 nm, which provided a potential of promoted light harvesting in all wavelength below the absorption edge (commonly around 800 nm) [20]. Besides, the textured surface was very important in eliminating the shunting path and diffuse reflectance loss which has been proved harmful to the photon capture and electron collection in such a nanoscaled film [21]. The cross-section image was shown as Fig. 1e, the thickness of perovskite $MAPbI_3$ layer in the planar junction structure is around 400 nm, which ensure enough light harvesting efficiency and electron collection efficiency [22].

To reveal the variation of crystal structure in perovskite films, the X-Ray diffractograms (XRD) were investigated. As shown in Fig. 2 and Table S1, the perovskite films both identical to the one obtained with solution-process method, exhibiting a preferential orientation accompanied by the appearance of two diffraction peaks at the angels 14.2° and 28.4°, corresponding to the (110) and (220) lattice planes [23]. Notably, the peak intensity of the perovskite film fabricated from MACl containing precursor was 2 orders of magnitudes higher than that from the common precursor (pristine sample), while the full width at half maxima (FWHM) of (110) plane was reduced from 0.14° to 0.08°, which directly confirmed the improvement of crystallinity [24]. This improvement was mainly due to the slow crystallization rate and increased grain size which strengthen the long-range order in the film. Besides the two prominent peaks, several weak peaks were also found in $MAPbI_3$ diffraction pattern. However, those peaks reduced to almost invisible after the introduction of MACl, thus suggested that the presence of MACl in the precursors also impacted the crystallographic orientation in the resultant films. In this consideration, the introduction of MACl in $MAPbI_3$ precursors played a predominant role in the lattice orientation selection and crystallinity optimization in perovskite formation process.

Optical properties were always very powerful criterion for