Balancing transformation and dissolution–crystallization for pure phase CH$_3$NH$_3$PbI$_3$ growth and its effect on photovoltaic performance in planar-structure perovskite solar cells

Kai Sun, Ziyang Hu*, Baihui Shen, Chunyan Lu, Cheng Yang, Can Gao, Jing Zhang, Yuejin Zhu*

Department of Microelectronic Science and Engineering, Ningbo Collaborative Innovation Center of Nonlinear Hazard System of Ocean and Atmosphere, Ningbo University, Ningbo 315211, China

ABSTRACT

In situ transformation and dissolution–crystallization mechanisms play a competing role in determining the characteristics of perovskite films **that greatly** affect the device performance of perovskite solar cells in the sequential two-step process. Herein, we develop a facile solution engineering to balance the transformation from PbI$_2$ to CH$_3$NH$_3$PbI$_3$ and dissolution–crystallization of CH$_3$NH$_3$PbI$_3$ crystal growth, producing pure phase CH$_3$NH$_3$PbI$_3$ crystals for high-efficient planar-structure solar cells. Low concentration of CH$_3$NH$_3$I in a mixed solvent of isopropanol/cyclohexane with low polarity is applied to suppress dissolution–crystallization (Ostwald ripening growth) of perovskite, while increases the transformation time from PbI$_2$ to CH$_3$NH$_3$PbI$_3$. Combination of porous PbI$_2$ and temperature-assistance effectively promote the transformation from PbI$_2$ to CH$_3$NH$_3$PbI$_3$ and reduce the time of Ostwald ripening growth of perovskite. This solution engineering reconciles the complete PbI$_2$ transformation and dissolution–crystallization of CH$_3$NH$_3$PbI$_3$, resulting in a pure phase perovskite without any residual PbI$_2$ in a short time. This strategy exemplified here can serve in the design and development of more sophisticated perovskites based on planar-structure applications without mesoporous TiO$_2$ scaffold.

1. Introduction

Organometal halide perovskite solar cells (PSCs) have attracted great attentions in the last few years owe to their high power conversion efficiency (PCE) achieved by solution process [1–4]. The latest certified PCE value over 22.1% has been achieved, which is comparable to the commercial inorganic photovoltaic devices [5]. The unique optoelectronic properties involving high absorption coefficient, long carrier diffusion length, and low exciton binding energy, accounting for such impressive achievements [6–9]. The perovskite quality greatly determines on the device performance. So far, many methods have been developed to deposit perovskite layer, which mainly include one-step and two-step processes. Although, the one-step process was first adopted [10,11], the naturally crystallized perovskite with an anisotropic growth often result in low uniformity and poor coverage [12,13], which limits the device performance. This issue was well solved by the following anti-solvent extraction strategy [14,15]. For the two-step process, PbI$_2$ layer was first deposited and followed by the conversion to perovskite. Since the deposition process and control strategy of PbI$_2$ layer are versatile, PbI$_2$ layer is easily controlled, which facilitates the improved perovskite quality [16]. PbI$_2$ converts into CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) can be realized by dip coating or spin coating MAI solution in the two-step process. In 2013, the first impressive work with a record PCE of 15% using the two-step method was reported [16]. The following modified two-step processes resulted in the better perovskite quality and enhanced device performance [17]. Combining the second spin-coating step with the optimized MAI concentration, the PCE was promoted to over 16% in 2015 [17]. By using a mixed FA/MA cation solution in the second spin-coating step, high-quality FAPbI$_3$/MAPbBr$_3$ perovskite was obtained, which boosted the PCE to ~ 20% [18–20].

However, the second spin-coating step brings in the time-consuming annealing process and downscale fabrication. The second dip-coating step is the pioneering work for the synthesis of perovskite [16], but its progress is relatively sluggish [21–23]. Since the deposited compact PbI$_2$ crystals decrease the accessibility of MAI molecules to the underlying PbI$_2$ by dip-coating step [24–26], the disfavored mesoporous TiO$_2$ is always necessary [16,27–29]. The complete transformation of PbI$_2$ to MAPbI$_3$ usually requires more than 1 h [30,31], which would lead to randomly dispersed large crystals and the dissolution and/or peeling-off of the perovskite crystals due to the Ostwald ripening growth [32–35]. Previous studies have been demonstrated that constructing mesoporous PbI$_2$ layer can promote post transformation and improve perovskite

quality [27,28].

The feasible method to suppress Ostwald ripening growth shortens the transformation time from PbI_2 to $MAPbI_3$. Herein, we first utilized a mixed solvent with ultralow concentration MAI solution to suppress the Ostwald ripening process. Further, combination of porous PbI_2- and temperature-assistance readily facilitates the transformation from PbI_2 to $MAPbI_3$ and reduces the time of Ostwald ripening growth of perovskite. This solution engineering reconciles the complete PbI_2 transformation and dissolution–crystallization of $CH_3NH_3PbI_3$, resulting in a pure phase perovskite without any residual PbI_2 in a short time. Our results demonstrate that the two-step dip coating process was still promising for large-scale and rapid process in planar-structure PSCs.

2. Experimental

2.1. Device fabrication

The FTO glass substrates (Nippon, 15 Ω/□) were selectively etched with Zn powder and diluted HCl. After patterned, the substrates were completely cleaned and further treated with ultraviolet ozone. The compact TiO_2 films were deposited onto the FTO substrates by spin coating. After spin coating, the coated substrates were heated on a hot plate at 120 °C for 5 min, and then sintered at 450 °C for 30 min. Finally, the films were treated with $TiCl_4$ aqueous solution (25 mM) at 70 °C for 30 min and sintered at 500 °C for 30 min again. The $MAPbI_3$ layer was prepared by a two-step method. For a compact PbI_2 film, 1.3 M PbI_2 solution in DMF was spun on TiO_2 films, then heated at 90 °C for 5 min. For mesoporous PbI_2, 1.3 M PbI_2 solution in mixed DMF:DMSO (V:V = 3:7) solution was used. CH_3NH_3I was prepared by dissolving 10, 20, and 30 mg/ml MAI in isopropanol(IPA) or 1 mg/ml MAI in IPA/cyclohexane(CHex). For temperature-assisted transformation from PbI_2 to $MAPbI_3$, PbI_2 films were immersed into MAI solution (1 mg/ml IPA/CHex) kept at 20 °C, 35 °C, 50 °C,and 70 °C for different time. These films were subsequently washed with isopropanol and dried. The hole transport layer spiroMeOTAD was spin coated on the perovskite layer. Finally, a Ag electrode ~ 90 nm in thickness was deposited.

2.2. Measurements and characterizations

$MAPbI_3$ crystals were investigated by X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu Kα radiation, 40 kV). The morphology and structure were characterized by field emission scanning electron microscopy (SEM, Hitachi, SU-70, Japan). The optical absorption spectra were measured by using a Cary 500 Spectrophotometer. Steady-state photoluminescence spectroscopy (PL) was measured with an Edinburgh Instruments FLS 920 fluorescence spectrometer. Electrical impedance spectra were measured with an electrochemical workstation (Zennium, Germany) under dark at a bias voltage of 0.6 V. Current-Voltage (J-V) characteristics were measured by a 4200 system source meter (Keithley) together with a sunlight simulator (Newport Solar Simulator 91192, AM 1.5, 100 mW cm^{-2}) calibrated with a standard silicon reference cell. All J-V measurements were conducted using a nonreflective metal aperture of 0.10 cm^2 to define the active area of the device. The scan directions of the forward and reverse voltage scans were from −0.2 V to 1.2 V and from 1.2 V to −0.2 V, respectively. The scan rate was 0.03 V s^{-1}.

3. Results and discuss

We first attempt to discover the reality of perovskite transformed by the compact PbI_2 (c- PbI_2) and compared with the porous PbI_2 (p- PbI_2. As shown in Fig. 1(a), scanning electron microscopy (SEM) results show that the c- PbI_2 film has a rough surface with tiny holes due to the self-organization of $[PbI_6]^{4-}$ units and growth of PbI_2 crystals during annealing [36]. The c-PbI_2 crystals decrease the accessibility of MAI to the underlying PbI_2 and prevent their complete conversion to perovskite

[37,38]. When the mixed solvent with DMF and DMSO is used for PbI_2 solution, the resulted PbI_2 annealed film shows a porous morphology with large and deep holes, as shown in Fig. 1(b). Before annealing, the DMSO molecules strong coordinated with Pb atoms by Lewis base reaction [19,20], remaining in the wetted PbI_2 film. During the annealing process, DMSO molecules escaped from the wetted PbI_2 film, leaving the porous structure. Therefore, the content of DMSO is determined on the size and magnitude of the porous. This porous structure is advantageous compared to that of the compact one because an enlarged surface area assures the fast conversion of PbI_2 into $CH_3NH_3PbI_3$ [27,39]. As expected, we found that it take a long time for c-PbI_2 complete conversion into perovskite. Therefore, the effect of MAI concentration on crystal growth based on c- and p- PbI_2 layers was further investigated.

The experiments were carried out at room temperature for the fixed time of 10 min Fig. 2(a)−(f) display the SEM images of $MAPbI_3$ perovskite reacted with MAI concentrations of 10, 20, and 30 mg/ml, respectively. For a concentration of 10 mg/ml, the morphology of two $MAPbI_3$ films exhibits many crystalline cubic-like grains but with different size, large (~ 300 nm) for p- PbI_2 film (Fig. 2(d)), small (~ 100 nm) for c- PbI_2 film (Fig. 2(a)). This result demonstrates that the porous structure is advantage for large-size perovskite growth. For 20 mg/ml, obvious nanowires have grown from the surface (Fig. 2(b)) especially for the c-PbI_2 sample. The background surface of two **perovskites** becomes smooth, and the corner angles of the cubic perovskite particles are erased. The size of these $MAPbI_3$ nanowires continues to increase and dangled cubic grains were appeared for the p-PbI_2 sample. The nanowires are ~ 1 μm in length and are several tens of nanometers in diameter. The size and shape of the cubic grains are different, while the thickness is usually about a few hundred nanometers. The growth of nanowires and dangled micro-cubic grains indicate the different mode of crystallization, also suggesting the additional Pb source from the solution. Compared with the previous reports [30,33], we found that the increased concentrations of MAI have the same effects similar to the prolonged reaction time between PbI_2 and MAI. Here, it is apparent that p-PbI_2 not only suppresses the dissolution of $MAPbI_3$ but also facilitated the transformation from PbI_2 to $MAPbI_3$. For a low concentration MAI solution, the large cubic perovskite particles were obtained, the high concentration for the small particles. Different from the drop-coating of MAI solution, the dip coating would suffer from the long reaction atmosphere in solution, therefore, the dissolution–crystallization (Ostwald ripening growth) of perovskite is more obvious [33].

In Fig. S1, the corresponding XRD patterns of the $MAPbI_3$ show that the diffraction peak intensity increases dramatically as the reaction concentration increases, indicating a significant enhancement in the crystallinity of $MAPbI_3$. Meantime, the observed PbI_2 diffraction peak is gradually weak but still presented in all $MAPbI_3$ films, which suggests that the PbI_2 not completely reacted with MAI and convert into $MAPbI_3$ even the high concentration MAI and p- PbI_2 were synchronously used. The ideal way to complete transformation is to prolong the reaction time. Generally, perovskite nuclei are created as a result of the following spontaneous reactions [33]:

$$PbI_2 + CH_3NH_3I \rightarrow MAPbI_3 \tag{1}$$

This reaction is reversible. PbI_2 is not soluble in the IPA solution, but the perovskite nucleus can be dissolved in IPA solution, as shown below.

$$MAPbI_3 + I^- \longleftrightarrow CH_3NH_3 + PbI_4^{2-} \tag{2}$$
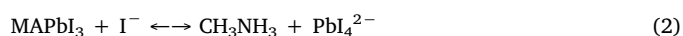
Since IPA is a polar solvent, the MAI solubility is high. For a low MAI concentration, the forward reaction (1) is not preferable, hence, few perovskite nucleus are formed in situ at first. To push the reaction (1) forward, one can increase the MAI concentration, but then the reaction (2) also initiates correspondingly. The dissolution-crystallization process called d as Ostwald ripening growth not only results in large