Effects of Preheating Treatments on the Performance of Perovskite Solar Cells

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Abstract. Perovskite solar cells (PSCs) have fascinated widespread focus for prominent performances recently. The processing parameters in spin-coating have great influence on the efficiency of PSCs. Herein, we have researched the influence of different preheating treatments on the performance of PSCs. The power conversion efficiency (PCE) has a significant enhancement to 15.89% through preheating the substrate together with precursor solution simultaneously. This work promotes the development of high performance PSCs and their industrialization.

1. Introduction

Lead halide perovskite (CH$_3$NH$_3$PbX$_3$, X=Cl, Br, I) based solar cells have been rapidly developed thanks to their superior photovoltaic characteristics (PCE) and plain preparation approaches [1-5]. Characteristics of perovskite solar cells (PSCs) are highly influenced by device fabrication details, including the preparation of precursors, annealing temperature and time, annealing approach, preheating substrate, preheating perovskite precursors and so on [6-12]. For example, the solvent engineering method has been proved useful for improving PCE and stability. Burschka et al. reported that the PCE of approximately 15% by a two-step sequential deposition method with good reproducibility [6]. The enhanced PCE is ascribed to the superior crystallization kinetics through the two-step sequential deposition method. Liu et al. fabricated a planar heterojunction PSC using vapor deposition method and a PCE of 15.4% was demonstrated ascribed to the uniform and compact morphology of film [7]. The morphology and crystallization of the perovskite film are crucial for high efficiency PSCs. Trap state density, non-radiative recombination, charge transport efficiency and charge extraction velocity are all affected by the morphology and crystallization. The influence of annealing temperature on the film quality was also studied and suitable annealing temperature and heating time promoted film to form distinct islands of materials with a PCE up to 11.66% [8]. By controlling the annealing temperature, heating time and the film thickness, Eperon et al. observed various forms of CH$_3$NH$_3$PbI$_3$-Cl, capping layer and obtained a best PCE of 11.4% [10]. These capping layers can effectively cover the perovskite surface leading to high-quality films. Ko et al. reported preheating substrate to promote the compactness between the TiO$_2$ and PbI$_2$ films. Preheating substrate could conduct to pinholes filling and trap state suppressing. Finally, the PCE of device was enhanced to 15.76% [12]. Therefore, preheating treatment is an effective way to prepare PSCs with high PCE. In this work, preheating treatment is adopted to improve CH$_3$NH$_3$PbI$_3$ based device performance. A PCE of 15.89% was demonstrated through a method of preheating the substrate together with precursor solution simultaneously. The trap state density and non-radiative recombination are effectively suppressed by this preheating method.
2. Material and Methods

The perovskite devices with the structure of ITO/PVK/Perovskite/PC61BM/Ag were adopted in our study, as shown in Figure 1, along with the energy level diagram. ITO glass substrates (20 × 20 mm²) were cleaned and dried with N₂ flow. PVK solution was prepared by dissolving 2.5 mg PVK into 1 mL chlorobenzene (CB). The hole transporting layer of PVK was fabricated by spin-coating at 4500 rpm for 30 s, then annealed at 100 °C for 10 min. 650 mg PbI₂ and 220 mg CH₃NH₃I were dissolved in 900 μL N,N-Dimethylformamide (DMF) and 100 μL Dimethyl sulfoxide (DMSO) to form perovskite precursor solution. The perovskite films were spin-coated at 4000 rpm for 30 s and 70 μl of CB solution was dripped on the absorber layer at the last 24 s during the spin-coating process. Then, the films were annealed at 65 °C for 3 min followed by 100 °C for 5 min. PC61BM layer was deposited on CH₃NH₃PbI₃ film at 2000 rpm for 45 s using 20 mg/ml solution dissolved in CB. Ultimately, 120 nm Ag cathode was fabricated through transferring the devices into a vacuum chamber by thermal evaporation. The device area is about 4 mm². To reveal the effect of preheating treatment on the characteristics of PSCs, we fabricated four kinds of devices, named D1 (without any preheating treatment), D2 (only ITO/PVK substrate was preheated at 80 °C on the hot plate during the deposition of CH₃NH₃PbI₃ film), D3 (only the perovskite precursor was preheated at 80 °C before the deposition of CH₃NH₃PbI₃ film), and D4 (both ITO/PVK substrate and perovskite precursor solution were preheated at 80 °C), respectively.

![Figure 1. PSC device structure with the energy levels of each functional layer](image)

3. Result and Discussion

In order to correlate the preheating treatments to performance of perovskite solar cells, the corresponding J-V characteristics were studied. The J-V characteristic of PSCs with various preheating treatments is depicted in Figure 2, which indicates that preheating treatments influence the performances of solar cells. Each photovoltaic parameters are gathered in Table 1. For sample D1, the average values of open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF) and PCE are 0.986 V, 20.65 mA/cm², 62% and 14.75%, respectively. The sample D2 exhibits Voc, Jsc, FF and PCE of 0.996 V, 21.14 mA/cm², 64% and 15.48%, showing the photocurrent of preheating the ITO/PVK substrate during preparing the perovskite film was slightly higher than that of sample D1 without preheating treatment. For sample D4 with preheating the perovskite precursor solution, a PCE
of 15.83% is achieved. Sample D₂ and D₃ have the significant improvement on J_{sc} and FF, which can be ascribe to the reduction of trap state density and suppressed non-radiative recombination by preheating the ITO/PVK substrate or the perovskite precursor solution. The preheating operation can effectively optimize the quality of film formation and crystallization process. Furthermore, by preheating the ITO/PVK substrate and the perovskite precursor solution simultaneously for device preparation, there is a further increase in J_{sc}, V_{oc}, and FF for sample D₄ compared with sample D₂ and D₃. Especially the V_{oc} has a larger enhancement compared with sample D₂ and D₃ versus sample D₁, which might due to the adjustment of band energy leading to a suitable band matching. A PCE of 15.89% is obtained finally for sample D₄, which is improved about 8% compared to the sample D₁ without any preheating treatment. All the parameters exhibit obviously promotion versus sample D₁. The performance of devices with preheating treatments should be much higher because we only chose 80 °C as the preheating temperature. Further optimization to find the most suitable concentration is of great assistant to further enhance the performance of the device. The performance of PSCs with preheating treatments are enhanced probably due to the enlarged grain size and reduced grain boundary of perovskites, which will be studied by scanning electron microscopy measurement. The crystallinity could also be improved, which will be measured by X-ray diffraction.

![Figure 2. J-V curves of PSCs treated by different preheating process](image)

| Devices | D₁ | D₂ | D₃ | D₄ |
|---------|----|----|----|----|
| V_{oc}(V) | 0.986 | 0.996 | 0.999 | 1.039 |
| J_{sc}(mA/cm²) | 20.65 | 21.14 | 21.90 | 23.27 |
| Fill Factor(%) | 61.61 | 64.34 | 63.57 | 64.35 |
| Efficiency(%) | 14.75 | 15.48 | 15.83 | 15.89 |

4. Conclusions
In summary, the function of preheating treatments on the performance of PSCs has been demonstrated. We have achieved a remarkable PCE of 15.89% through a method of preheating the substrate together with precursor solution simultaneously, which is improved about 8% compared to that of the device without any preheating treatment. It is worth pointing out that all the parameters exhibit obviously
This research work has greatly promoted the efficiency and the development of PSCs and proved the effectiveness of preheating treatment on performance improvement, which can provide the guidance for preparation of superior PSCs.

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6. References
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