



Efficient lead acetate sourced planar heterojunction perovskite solar cells with enhanced substrate coverage via one-step spin-coating



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ABSTRACT

In planar heterojunction (PHJ) perovskite solar cells (PerSCs) without mesoporous metal oxide skeleton, there is challenge of formation perovskite film with full coverage to the conductive substrate through solution-process the lead halide precursors. Selecting a lead source with more volatile byproducts is an effective approach to obtain much smoother films with smaller and fewer pinholes. Herein, we demonstrate efficient $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ PHJ PerSCs by using lead acetate ($\text{Pb}(\text{Ac})_2$) as lead precursor. The morphology of the perovskite thin films were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively, and the crystalline quality of the perovskite films were investigated by X-ray diffraction (XRD) spectroscopy. Time-resolved photoluminescence (TRPL) was used to investigate the PL lifetime of the perovskite film. The perovskite film derived from $\text{Pb}(\text{Ac})_2$ shows enhanced surface coverage and improved photoluminescence lifetime in comparison with PbI_2 sourced perovskite film. Averaged over 20 individual devices, the power conversion efficiency (PCE) of devices derived from $\text{Pb}(\text{Ac})_2$ reaches 14.81%, much higher than PbI_2 sourced devices by one-step (8.23%) or two-step (10.58%) spin-coating.

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1. Introduction

Planar heterojunction (PHJ) perovskite solar cells (PerSCs) have drawn a great attention due to their advantages of high efficiency, low-cost, light-weight, and compatible with solution-based roll-to-roll procedures [1–6]. Since the planar structure is without mesoporous metal oxide skeleton [7], there is challenge of formation perovskite film with full coverage to the conductive substrate by solution-process from lead halide due to the different surface energy between the perovskite and the substrate [8,9]. Therefore, a pin-hole-free perovskite film with optimal crystalline morphology and full coverage is essential to high performance PHJ PerSCs, since the quality of the perovskite film has greatly impact on the key

charge processes of dissociation, transportation, and recombination. To obtain a compact perovskite film with good film uniformity and big crystalline domains, several strategies have been proposed to control the crystallization processes from the aspects of precursor selection [10–14], solvent engineering [15,16], processing additive [17,18], deposition methods [8,19,20], and thermal-annealing [21–23].

In the standard solution procedure, a stoichiometric precursor of lead halide and halogenated amine was spin-coated on a substrate, followed by thermal annealing to form the crystalline perovskite. Therefore, the composition of the precursor solution, the annealing temperature, and the by-products driven out rate from the film directly influence the crystallization rate, crystal size and film morphology [24]. During the initial stages of spin-coating, solvent evaporates quickly, while the perovskite crystallization is strongly retarded by the entrapped excess organic component in the film, and the crystallization process could be accelerated by thermal-annealing of the film to drive out the excess organic component (or byproducts) [13]. If the excess organic component is not volatile

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enough, higher annealing-temperature or longer annealing-time are needed to drive it out. During this annealing, solvent evaporation and byproducts volatilization potentially induces formation of holes within the final crystalline layer. Therefore, optimal film morphology can only be achieved by successfully manipulating the nucleation and growth of the perovskite, thus the control of the crystallization and the kinetics of film formation during deposition and annealing are the keys to the optimization of film morphology. Previous study has been proven that the anions in the lead source determine the kinetics of perovskite crystal growth, which in turn affects the film morphology and device performance [10,13,25]. By choosing a lead source with more volatile byproducts, much smoother films with smaller and fewer pinholes can be obtained due to the reduced annealing temperature and shortened annealing time [13,25].

Herein, we demonstrate efficient $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ planar heterojunction perovskite solar cells by using lead acetate ($\text{Pb}(\text{Ac})_2$) as lead precursor. The perovskite film derived from $\text{Pb}(\text{Ac})_2$ shows enhanced surface coverage and improved photoluminescence lifetime in comparison with PbI_2 sourced perovskite film. Averaged from 20 individual devices, the power conversion efficiency (PCE) of devices derived from $\text{Pb}(\text{Ac})_2$ reaches 14.81%, much higher than PbI_2 sourced devices by one-step (8.23%) or two-step (10.58%) spin-coating.

2. Experimental

2.1. Materials

Patterned fluorine doped tin oxide (FTO) glass with sheet resistance of $15 \Omega/\text{sq}$ was purchased from Wuhan Geao Instruments Science & Technology Co., Ltd (China). Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) aqueous solution (Clevious P VP Al 4083) was purchased from H. C. Stark. Methylamine solution (40 wt% in methanol) was purchased from Acros. Hydriodic acid (HI, 57 wt% in water), $\text{Pb}(\text{Ac})_2$ and lead iodide (PbI_2) were purchased from Alfa Aesar [6,6].-phenyl- C_{61} -butyric acid methyl ester (PCBM) was purchased from Solarmer Materials Inc. These commercially available materials were used directly without further purification. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was synthesized according previous report with minor modification [26]. Typically, 27.86 mL of methylamine (CH_3NH_2) and 30 mL of hydriodic acid (HI) were mixed in a 100-mL round-bottomed flask at 0°C and then stirred for 2 h. The reaction mixture was rotation-evaporated at 50°C for 1 h, yielding white precipitate. The product was washed with diethyl ether three times and finally dried in a vacuum oven at 60°C for 24 h.

2.2. Device fabrication

FTO coated glass substrates were ultrasonic cleaned twice with detergent, deionized water, acetone and isopropanol in sequence for 15 min. The pre-cleaned FTO substrates were then cleaned by UV-ozone (Shanghai Guoda UV Equipment Co., Ltd) for 15 min to remove the residual organic contaminant. The hole collection layer of PEDOT:PSS was spin-coated from its aqueous solution filtered with a $0.45 \mu\text{m}$ filter on the cleaned FTO substrate at 2000 rpm for 35 s, and then thermal annealed at 150°C for 15 min in air. The thickness of the PEDOT:PSS layer is around 35 nm. The modified substrates were transferred into a nitrogen-filled glove-box for following procedures. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin films were obtained through one-step and two-step spin-coating respectively. For one-step spin-coating, mixture of $\text{CH}_3\text{NH}_3\text{I}$ and lead source (PbI_2 or $\text{Pb}(\text{Ac})_2$) dissolved in anhydrous N,N-Dimethylformamide (DMF) at a molar ratio of 1:3 with final concentration of 40 wt%

was spin-coated on FTO/PEDOT:PSS substrate at 6000 rpm for 30s. We choosing the 1:3 M ratio of PbI_2 :MAI is based on previous reports [27,28], where they found that by employing a large excess of organic component ($\text{CH}_3\text{NH}_3\text{I}$), much larger crystalline domains can be formed, and smoother films can be created than those processed from a stoichiometric mix of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 . After spin-coating, the films were annealed at 100°C for 2 h and 100°C for 10 min for perovskite derived from PbI_2 and $\text{Pb}(\text{Ac})_2$, respectively. For two-step spin-coating, PbI_2 dissolved in DMF with a concentrations of 400 mg/mL was spin-coated on the FTO/PEDOT:PSS substrate at 2000 rpm for 30 s, and then thermal annealed at 80°C for 10 min. After that, $\text{CH}_3\text{NH}_3\text{I}$ dissolved in isopropyl alcohol with a concentration of 40 mg/mL was spin-coated on top of the dried PbI_2 layer at 6000 rpm for 30 s, followed by thermal annealing at 100°C for 2 h to formation perovskite. Then the electron collection layer of PCBM was obtained by spin-coating its chlorobenzene solution (20 mg/mL) onto the perovskite layer at 1000 rpm for 30 s. Finally, the devices were transferred to a vacuum chamber for Al (100 nm) electrode evaporation. The active area of the device was fixed at 4 mm^2 .

2.3. Device characterization

The current density–voltage (J – V) measurements of the devices were conducted on a computer-controlled Keithley 2400 Source Measure Unit (SMU) in a nitrogen-filled glove-box under simulated AM1.5G irradiation ($100 \text{ mW}/\text{cm}^2$) with a xenon-lamp-based solar simulator (SAN-EI, AAA grade). The incident photon to current efficiency (IPCE) was measured by QE-R systems (Enli Tech.), and the light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The IPCE measurements were performed under ambient conditions at room temperature.

2.4. Instrumentation

Lambda 950 UV/Vis/NIR spectrophotometer was used to measure the absorption of the thin film and the reflection of the devices. An AC Mode III (Agilent) atomic force microscopy (AFM) was used to measure the surface morphologies of the thin films operated in the tapping mode. The surface and the cross-section morphology of the samples were observed by Scanning electron microscopy (SEM) of FEI Quanta 200F at an accelerating voltage of 30 kV. X-ray diffraction (XRD) patterns were recorded with a diffractometer (Shimadzu XRD 6000) using $\text{Cu K}\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation with a Nickel filter operating at 40 kV and 10 mA in the 2θ range of 5 – 60° at a scanning rate of $3^\circ/\text{min}$. Dektak XT (Bruker) surface profilometer was used to measure the thickness of the films involved in the devices. All the measurements were carried out under ambient conditions at room temperature.

3. Results and discussion

The morphology of the perovskite thin film derived from PbI_2 one-step, PbI_2 two-step and $\text{Pb}(\text{Ac})_2$ one-step spin-coating on FTO/PEDOT:PSS substrates were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) as shown in Fig. 1. Observing the SEM image (Fig. 1(a)) of perovskite derived from PbI_2 one-step spin-coating, there are many pin-holes with a diameter varied from tens of nanometers to one micron. These pin-holes are also plainly visible from AFM images as shown in Fig. 1(d) and (g), and the film shows a root-mean-square (rms) roughness of 50.4 nm. The formation of these pin-holes should be attributed to slow byproducts volatilization, inducing longer annealing time and higher annealing temperature needed to form stoichiometric perovskite crystal thin film [22,24]. For perovskite thin film derived

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