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

Cong Li a, Qiang Guo a, Wenyuan Qiao a, Qi Chen b, Shuang Ma a, Xu Pan c, Fuzhi Wang a, Jianxi Yao a, Chunfeng Zhang b, Min Xiao b, Songyuan Dai a, **, Zhan’ao Tan a, **

a State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, Beijing Key Laboratory of Novel Thin Film Solar Cells, North China Electric Power University, Beijing 102206, China
b National Laboratory of Solid State Microstructures, School of Physics & School of Engineering and Applied Science, Nanjing University, Nanjing 210093, China
c Institute of Applied Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230088, China

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A B S T R A C T

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 and fewer pinholes. Herein, we demonstrate efficient CH3NH3PbI3/PCBM PHJ PerSCs by using lead acetate (Pb(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 Pb(Ac)2 shows enhanced surface coverage and improved photoluminescence lifetime in comparison with PbI2 sourced perovskite film. Averaged over 20 individual devices, the power conversion efficiency (PCE) of devices derived from Pb(Ac)2 reaches 14.81%, much higher than PbI2 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...
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 CH₃NH₃PbI₃/PCBM planar heterojunction perovskite solar cells by using lead acetate (Pb(Ac)₂) as lead precursor. The perovskite film derived from Pb(Ac)₂ shows enhanced surface coverage and improved photoluminescence lifetime in comparison with PbI₂ sourced perovskite film. Averaged from 20 individual devices, the power conversion efficiency (PCE) of devices derived from Pb(Ac)₂ reaches 14.81%, much higher than PbI₂ 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 Ω/sq was purchased from Wuhan Geao Instruments Science and Technology Co., Ltd (China). Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) aqueous solution (Clevios P VP AI 4083) was purchased from H. C. Stark. Methylamine solution (40 wt% in methanol) was purchased from Acros. Hydriodic acid (HI, 57 wt% in water), Pb(Ac)₂ and lead acetate (CH₃NH₃I) was synthesized according previous report with minor modification [26]. Typically, 27.86 mL of methylamine (CH₃NH₂) and 30 mL of hydroiodic 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 μm 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 CH₃NH₃PbI₃ perovskite thin films were obtained through one-step and two-step spin-coating respectively. For one-step spin-coating, mixture of CH₃NH₃I and lead source (PbI₂ or Pb(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 PbI₂:MAI is based on previous reports [27,28], where they found that by employing a large excess of organic component (CH₃NH₃I), much larger crystalline domains can be formed, and smoother films can be created than those processed from a stoichiometric mix of CH₃NH₃I and PbI₂. After spin-coating, the films were annealed at 100 °C for 2 h and 100 °C for 10 min for perovskite derived from PbI₂ and Pb(AC)₂, respectively. For two-step spin-coating, PbI₂ 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, CH₃NH₃I dissolved in isopropl alcohol with a concentration of 40 mg/mL was spin-coated on top of the dried PbI₂ 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 mm².

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 mW/cm²) 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 Cu Kα (λ = 0.15406 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°/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 PbI₂ one-step, PbI₂:two-step and Pb(AC)₂ one-step spin-coating on FTO/ PEDOT:SS 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 PbI₂ 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
from PbI₂ two-step spin-coating, there is no pin-hole can be observed from both SEM (Fig. 1(b)) and AFM (Fig. 1(e, h)) images, while the film is very coarse with an rms roughness of 38.1 nm and appears many bulgings around 700 nm. Inset of Fig. 1(b) illustrates the SEM image of PbI₂ spin-coated on the PEDOT:PSS substrate, where many pin-holes can be observed. These pin-holes in the PbI₂ film are preferential sites for the reaction of PbI₂ with CH₃NH₃I, inducing preferential growth of CH₃NH₃PbI₃ perovskite to form bulgings on the surface of the film [29]. In contrast, the perovskite film derived from Pb(Ac)₂ one-step spin-coating shows pin-hole free and very smoother surface morphology (rms, 9.9 nm) as confirmed by SEM (Fig. 1(c)) and AFM (Fig. 1(f, i)). The SEM image of perovskite obtained by Pb(Ac)₂ with the scale bar of 1 μm is shown in Fig. S1. The good morphology formation benefits from the much volatile byproducts which reduced the annealing time and temperature [13,24].

X-ray diffraction (XRD) spectroscopy is a powerful technique to investigate the crystalline quality of inorganic thin films. Fig. 2 shows the XRD spectra of the resulting perovskite films deposited on FTO/PEDOT:PSS substrate. For comparison, the XRD spectra of the CH₃NH₃I powder (Fig. 2(a)), Pb(Ac)₂ powder (Fig. 2(b)), PbI₂ powder (Fig. 2(c)) as well as FTO/PEDOT:PSS substrate (Fig. 2(d)) are also given. The diffraction peaks of CH₃NH₃I, PbI₂, and FTO/PEDOT:PSS are in good agreement with previous reports [30], and the diffraction patterns of Pb(Ac)₂ are consistent with the Powder Diffraction File (PDF Card No. 43-0743). Fig. 2(e) and (f) displays XRD patterns of the CH₃NH₃PbI₃ perovskite film grown on the FTO/PEDOT:PSS substrate derived from PbI₂ through one-step and two-step spin-coating, respectively. A series of new diffraction peaks appear in comparison with PbI₂ and CH₃NH₃I at 14.1° (110), 20.7° (112), 24.2° (211), 25.2° (202), 28.4° (220), 32.5° (312), 41.3° (224), 43.8° (330) and 59.4° (440), assigned to the tetragonal phase of the CH₃NH₃PbI₃ perovskite [15,31]. The stronger diffraction intensity of two-step spin-coated CH₃NH₃PbI₃ indicates a high level of phase purity in comparison with one-step spin-coated perovskite [32]. Fig. 2(g) shows the XRD pattern of CH₃NH₃PbI₃ perovskite derived from Pb(Ac)₂ through one-step spin-coating. Contrastingly, there are just four diffraction peaks of (110), (220), (330), and (440), indicating a very good crystallization with c axis orientation, same to the PbCl₂ derived CH₃NH₃PbI₃ perovskite [13,32].

The optical properties of the perovskite films derived from different methods are displayed in Fig. 3, and Fig. 3(a) shows the
absorption and photoluminescence (PL) spectra of perovskite films on quartz plates. The thickness of three methods obtained perovskite films are 350, 355, and 345 nm, for PbI2 one-step, PbI2 two-step, and Pb(Ac)2 one-step, respectively. Three samples demonstrate similar absorption edges at around 780 nm, while Pb(Ac)2 derived perovskite shows more stronger absorbance in the whole spectra than those of PbI2 derived films via one-step or two-step spin-coating. The enhanced absorbance should be attributed to the smooth and dense film bears higher extinction coefficient of light than that of coarse and loose film. These observations are in good agreement with the morphology results as shown in Fig. 1. Furthermore, the absorption spectra shape of perovskite film obtained from PbI2 two-step spin-coating is largely different from that of derived from PbI2 or Pb(Ac)2 one-step spin-coating due to the different perovskite growth modes. For one-step spin-coated films, the perovskite can grow freely without the restrain from the PbI2 pin-holes (Fig. 1(b) inset) in two-step spin-coated cases. The trend of the absorption spectra change for one-step and two-step spin-coated perovskite films in our experiments is in good agreement with the previous observations of perovskite grown in different sized ZnO scaffolds [33]. The full width at half maximum (FWHM) of the PL spectra for perovskite films derived from PbI2 one-step, PbI2 two-step and Pb(Ac)2 one-step spin-coating is 42, 39, and 43 nm, with the PL peak blue shifting from 776 to 767, and 764 nm, respectively. The blue-shifted emission should be attributed to the crystal strain induced or relaxed at the grain boundaries during perovskite formation [10,13,33].

Time-resolved photoluminescence (TRPL) is widely used in PerSCs to investigate the charge processes of transfer, transport and recombination [28,34,35]. Fig. 3(b) shows the TRPL spectra of the perovskite films derived from PbI2 one-step, PbI2 two-step and Pb(Ac)2 one-step spin-coated on quartz glasses; (b) The time-resolved photoluminescence of the corresponding perovskite films spin-coated on FTO substrates, inset shows the three-component exponential fitted carrier lifetimes.
Pb(Ac)₂ one-step spin-coated on FTO substrates. All the curves are fitted with three-component exponential decay according to previous report [36], as summarized in the inset of Fig. 3(b). The fast decay component $t_1$ and the long decay component $t_2$ could be attributed to bimolecular recombination and free carriers recombination, respectively [28,34–36]. The average PL lifetime $\tau_{avg}$ for perovskite derived from PbI₂ one-step spin-coating is 3.99 ns, while this value increases to 15.21 ns for perovskite derived from PbI₂ two-step spin-coating, indicating less recombination occurs within the film. Interestingly, the perovskite film derived from Pb(Ac)₂ one-step spin-coating demonstrates much longer bimolecular recombination lifetime (13.81 ns) and free carriers recombination lifetime (118.85 ns), inducing prolonged average PL lifetime $\tau_{avg}$ of 52.75 ns. These observations are in good agreement with the XRD and morphology findings since uniform and pinhole-free film with higher crystallinity hares less trap sites, which benefit the carriers travel longer length before recombination [35].

To investigate the photovoltaic performance of PerSCs with difference sourced lead precursors, a planar heterojunction structure was designed as shown in Fig. 4(a), where CH₃NH₃PbI₃ perovskite photo absorption layer is sandwiched between PEDOT:PSS hole transportation layer and PCBM electron transportation layer. With light irradiation from FTO side, the photons will be absorbed by CH₃NH₃PbI₃ perovskite layer to yield excitons and free carriers, photovoltaics devices based on simple thin-film planar-heterojunction architectures are possible for materials with charge-carrier diffusion pathways that are sufficiently long to allow for charge migration through a whole absorber layer [37]. The multilayered sandwich structure of Pb(Ac)₂ derived PerSC was further confirmed by cross-section scanning electron microscopy (SEM) as illustrated in Fig. 4(b). The cross section SEM images of perovskite fabricated by PbI₂ one-step and two-step are given in Fig. 52. The optimal thickness for PEDOT:PSS, CH₃NH₃PbI₃ and PCBM is 30, 350, and 30 nm, respectively.

Fig. 5(a) displays the current density-voltage ($J$-$V$) curves of the PerSCs derived from PbI₂ one-step, PbI₂ two-step and Pb(Ac)₂ one-step spin-coating in the dark and under the illumination of standard one sun, and the characteristic parameters (averaged over 20 individual devices) of open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), filling factor (FF) and PCE are summarized in Table 1. From the dark J-V curves illustrated in Fig. 5(a), the rectification ratio of the device derived from PbI₂ one-step spin-coating is only 55 at $\pm$1.5 V. The low rectification ratio should be ascribed to the bad morphology of pin-holes with a diameter varied from tens of nanometers to one micron, and those large-sized pinholes are difficult to be fully covered by the following PCBM thus inducing large leakage current [38]. However, the rectification ratio for the device derived from PbI₂ two-step spin-coating increases to 309, and this value is further increased to $1.2 \times 10^{4}$ for Pb(Ac)₂ derived devices (Fig. 53), much higher than those of PbI₂ derived PerSCs.

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**Fig. 4.** (a) Device structure of the planar heterojunction perovskite solar cells, and (b) cross-section SEM image of Pb(Ac)₂ based PerSCs. **Fig. 5.** (a) $J$-$V$ and (b) EQE curves of the perovskite solar cells based on perovskite films derived from PbI₂ one-step, PbI₂ two-step and Pb(Ac)₂ one-step spin-coating. Inset shows the logarithmic scaled dark $J$-$V$ curves of the devices.
The higher rectification ratio of the Pb(II) derived PerSCs benefit from the higher injection current at the positive bias voltage and lower leakage current at the negative bias voltage, and this should be attributed to the PbI2 one-step spin-coated film demonstrate uniform and pin-hole-free morphology as shown in Figs. S1 in Supporting Information. The device based on a molar ratio of 1:1 only shows a Voc of 0.76 V, a Jsc of 12.96 mA/cm2, an FF of 56%, and a PCE of 5.50%. In contrast, the device with perovskite film derived from PbI2 two-step spin-coating shows enhanced Voc, Jsc, FF, and the overall PCE, which is 0.97 V, 16.50 mA/cm2, 66%, and 10.58%, respectively, and 9.78% improvement in the literature so far for perovskite/fullerene based solar cells. The higher rectification ratio of the PbI2:MAI) have shown as Fig. S1 in Supporting Information. The device based on a molar ratio of 1:1 only shows a Voc of 0.76 V, a Jsc of 12.96 mA/cm2, an FF of 56%, and a PCE of 5.50%. In contrast, the device with perovskite film derived from PbI2 two-step spin-coating shows enhanced Voc, Jsc, FF, and the overall PCE, which is 0.97 V, 16.50 mA/cm2, 66%, and 10.58%, respectively, and 9.78% improvement in the literature so far for perovskite/fullerene based solar cells. The improvement in Voc and FF for PbI2-derived PerSCs should attribute to the uniform and pin-hole free morphology with high crystalinity which enhanced the carrier lifetime and extended the carrier diffusion length [13,35].

To investigated the light response of the PerSCs, external quantum efficiency (EQE) measurements were conducted as shown in Fig. 5(b). All devices demonstrate strong light response within the absorption band (300–800 nm), indicating most of the absorbed photons are converted into free charge carriers. The EQE curves of devices based on perovskite derived from PbI2 one-step and two-step spin-coating display similar shapes, while that of PbAc2 derived device gives much stronger light response, and this is in good agreement with the absorption spectra as shown in Fig. 3(a). Integrating the EQE curve with a standard AM 1.5G solar spectrum, we can obtain the integrated photocurrent density (Jint) of the devices, and the Jsc for devices derived from PbI2 one-step, PbI2 two-step and PbAc2 one-step spin-coating is 15.74, 15.85, and 19.32 mA/cm2, respectively. Considering the test condition of Jsc in (a) (in nitrogen-filled glove-box) and EQE (in ambient atmosphere) measurements, the Jsc are in good agreement with the measured Jsc from J-V curves.

4. Conclusion

In conclusion, efficient CH3NH3PbI3/PCBM planar heterojunction perovskite solar cells were demonstrated by using lead acetate as lead precursor through one-step spin-coating. The obtained perovskite film shows enhanced substrate coverage, uniform and pin-hole free morphology, high crystalinity, and prolonged PL lifetime. The power conversion efficiency (PCE, averaged over 20) of devices derived from PbAc2 reaches 14.81%, much higher than PbI2 sourced devices by one-step (8.23%) or two-step (10.58%) spin-coating. Our findings suggest that PbAc2 is a promising lead precursor for high performance PerSCs.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2016.03.017.

Table 1

<table>
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<tr>
<th>Deposition method</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm2)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
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<tr>
<td>PbI2 one-step</td>
<td>0.85 ± 0.03</td>
<td>16.23 ± 0.15</td>
<td>60 ± 0.01</td>
<td>8.23 ± 0.11</td>
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<tr>
<td>PbI2 two-step</td>
<td>0.87 ± 0.02</td>
<td>16.50 ± 0.21</td>
<td>66 ± 0.22</td>
<td>10.58 ± 0.20</td>
</tr>
<tr>
<td>PbAc2 one-step</td>
<td>1.01 ± 0.01</td>
<td>20.60 ± 0.21</td>
<td>71 ± 0.11</td>
<td>14.81 ± 0.11</td>
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References


