



Effect of excessive Pb content in the precursor solutions on the properties of the lead acetate derived $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells



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ABSTRACT

Organic–inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) inverted structured perovskite films were prepared using Pb (CH_3COO)₂ ($\text{Pb}(\text{OAc})_2$) and $\text{CH}_3\text{NH}_3\text{I}$ (MAI) as source materials. The structural, optical and photoelectronic properties of the MAPbI₃ films varied with the $\text{Pb}(\text{OAc})_2$ /MAI molar ratio. It was found that the $\text{Pb}(\text{OAc})_2$ /MAI molar ratio greatly influenced the structure and morphology of the MAPbI₃ films. A suitable amount of excessive $\text{Pb}(\text{OAc})_2$ (about 5 mol% excessive Pb) in the solution made the film smoother with improved film crystallinity. This resulted in enhanced power conversion efficiency (PCE). However, for films derived from solution with low $\text{Pb}(\text{OAc})_2$ /MAI or high $\text{Pb}(\text{OAc})_2$ /MAI ratio, defects such as pits or pinholes were easily formed with low crystallinity, and hence decreased the lifetime of the carriers and photoelectrical properties of the final solar cells. Using a solution with 5% excessive Pb, inverted structured $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with PCE of nearly 14% were obtained.

1. Introduction

Organic–inorganic lead halide perovskites have attracted great attention during the past several years as a renewable energy source due to their technological advantages of cost-effective and low temperature synthesis process [1–4]. Power conversion efficiencies (PCE) of photovoltaic devices that contain these materials have increased from around 4% to more than 20% [5–10]. To successfully fabricate reproducible high performance solar cells, the perovskite crystallization process needs to be controlled either by the appropriate choice of processing parameters, techniques and/or by materials selection. The perovskites $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ are normally prepared by the reaction in a solution of $\text{CH}_3\text{NH}_3\text{I}$ (MAI) and PbI_2 in a 1:1 ratio or MAI and PbCl_2 in a 3:1 ratio. However, it is more difficult to control the film surface quality when PbI_2 or PbCl_2 are used as starting materials. For this case, the perovskite solar cells (PSCs) are always discontinuous, with pinholes of different sizes and no clear grain boundaries [11].

Recently, Zhang et al. prepared PSCs with the lead acetate Pb (CH_3COO)₂ ($\text{Pb}(\text{OAc})_2$) as precursor and obtained smooth, pinhole-free perovskite films on TiO_2 /FTO/glass substrates; from which, it resulted in devices with a champion power conversion efficiency (PCE) of 15.2% [12]. Moreover, the annealing time was much shorter for the films prepared from $\text{Pb}(\text{OAc})_2$ (5 min at 100 °C), as compared to perovskite

films prepared from PbCl_2 and PbI_2 (which needed to be annealed for 2 h and 40 min, respectively) [13,14]. Due to these advantages, the Pb (OAc)₂ derived MAPbI₃ perovskite solar cells showed potential in future applications.

Improvement of the photovoltaic performance and reduction of the hysteresis is another critical issue. A recent investigation by Yang et al. illustrated that the introduction of excessive PbI_2 (as second phase into the perovskite matrix) improved the performance of the solar cells. It was reported that PbI_2 formed at the grain boundaries (GBs) could reduce the carrier recombination near GBs [15]. Nazeeruddin and co-workers observed improvements in both the photovoltaic efficiency and stability when PbI_2 and MAI at a non-stoichiometric ratio were used in the precursor solution [16]. On the contrary, some groups believed that the introduction of PbI_2 into the perovskite matrix brought about adverse effects on the device properties. Wang et al. reported that the excessive PbI_2 deteriorated the photovoltaic performances [17]. Liu et al. reported that a small amount of excess PbI_2 had detrimental effects on the perovskite film stability, although perovskite devices with excess PbI_2 exhibited high initial efficiency [18]. They also reported that the presence of a small amount of excessive PbI_2 resulted in the degradation of the perovskite layer under illumination even when stored in an inert atmosphere [18].

Despite the controversy mentioned above, perusal of the literature

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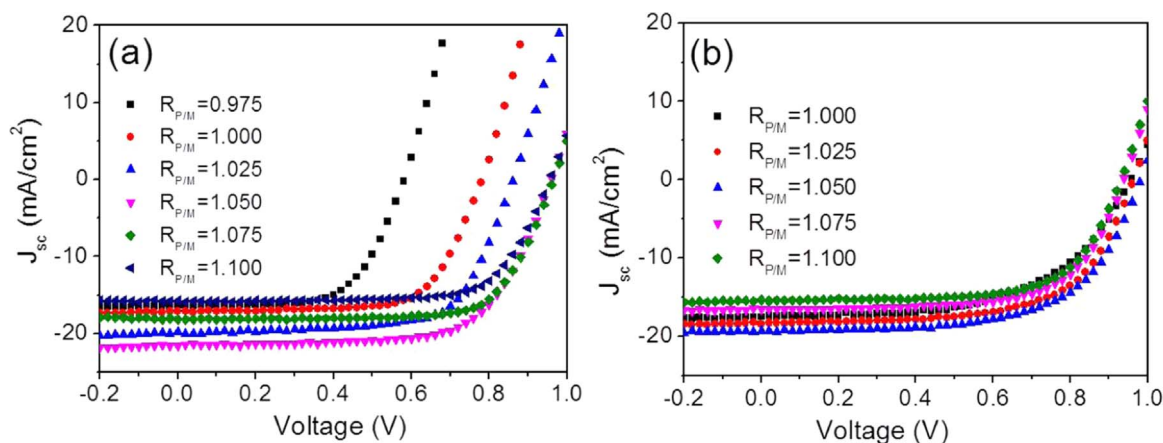
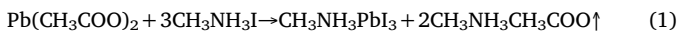


Fig. 1. J-V curves of the samples derived from solutions with different $R_{P/M}$ ratios. Samples in (a) were annealed at 80 °C for 15 min, and samples in (b) were annealed at 90 °C for 5 min.

that reported the effect of the PbI_2 on the performance of PSCs reveals that the perovskite layers were basically prepared from the source materials of PbI_2 and MAI. There are few reports of the effect of excessive Pb on the properties of the perovskite derived from $Pb(OAc)_2$. When $Pb(OAc)_2$ is used to synthesize the $MAPbI_3$, the formation of $MAPbI_3$ is expressed by formula (1) which has a different formation mechanism than the case when PbI_2 and MAI are used as source materials, as expressed by formula (2) [12]:



Therefore, when $MAPbI_3$ is formed by reaction of MAI with excessive $Pb(OAc)_2$, a large amount of the $CH_3NH_3^+$ (MA) species and I^- voids are formed in the films as the main defects. Note these defects are different from the defects in the samples derived from excessive PbI_2 . Therefore, a new phenomenon is expected. Triggered by this expectation, we reported on the effect of the excessive Pb ions in the precursor solutions on the properties of $Pb(OAc)_2$ derived $MAPbI_3$ PSCs. Considering that the standard n-i-p device configuration requires a high temperature annealing treatment for the TiO_2 layer and always show a pronounced hysteresis during the J-V characterization, the inverted planar perovskite heterojunction using $Pb(OAc)_2$ as starting materials are prepared in this paper. Results show that suitable amounts of excessive $Pb(OAc)_2$ in the solution can improve the film crystallinity and surface quality, both of which enhance the PCE of the perovskite layers. However, excessive amount of PbI_2 formed in the film degrades the film properties.

2. Experimental

Methylammonium iodide was purchased from Dyesol, lead acetate trihydrate ($Pb(OAc)_2 \cdot 3H_2O$) was purchased from Alfa Aesar, and both materials were used as received. To prepare the perovskite precursor solution, 3.0 mmol MAI and 1 mmol $Pb(OAc)_2 \cdot 3H_2O$ were dissolved in 1 mL anhydrous DMF solution. To investigate the influence of the content of Pb on the film properties, a total of six solutions with different $Pb(OAc)_2$:MAI ratios ($R_{P/M}$) of 0.975:3, 1.000:3, 1.025:3, 1.050:3, 1.075:3, and 1.100:3 (for short, $R_{P/M} = 0.975, 1.000, 1.025, 1.050, 1.075$ and 1.100, respectively).

Indium-doped tin-oxide (ITO) coated glass substrates were subsequently cleaned with a detergent solution, deionized water, acetone, and isopropyl alcohol, and UV-ozone treated for 10 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevious PVP Al4083 filtered through a 0.45 μm filter) was spin-coated onto the ITO substrates at 4000 rpm followed by a thermal anneal at 130 °C for 15 min in glovebox. The $Pb(OAc)_2$:MAI solutions were then spin-coated for 60 s on the PEDOT layers at 4000 rpm followed by thermal

annealing at 80 °C for 15 min or 90 °C for 5 min, resulting in perovskite films with thickness of about 250 nm (as indicated by Fig. S1(a)). After that, phenyl-C₆₁-butyric acid methyl ester (PCBM, Aldrich) dissolved in chlorobenzene with a concentration of 22 mg/mL was spin-coated on top of the perovskite layer at 2000 rpm for 60 s. Finally, the devices were finished with the thermal evaporation of an 80 nm thick Al electrode. This resulted in the inverted planar heterojunction solar cells, as indicated by Fig. S1(b). The size of the substrate is 2.5 cm \times 2.5 cm, and the active device area (defined by the overlapping of ITO and Al electrode) is 0.2 cm².

The as-prepared samples were characterized with scanning electron microscopy (SEM-XL30 Environmental FEG (FEI)). X-ray diffraction (XRD) measurements were done with an X-ray Diffractometer using Cu K α radiation at a step of 0.01°. Surface morphologies and roughness images of the samples were analyzed using Veeco Dimension 3100 atomic force microscopy in tapping mode. Absorption spectra were recorded using Cary 5000 UV/VIS spectrometer. Current density-voltage (J-V) characteristics of the solar cells were measured with simulated AM 1.5 global solar irradiation (100 mW/cm²) using a xenon-lamp solar simulator (Spectra Physics, Oriel Instruments, USA). The steady state photoluminescence (PL) spectra of the samples were tested by a Renishaw InVia spectroscopy system with a $\times 100$ objective lens using a laser source with 488 nm wavelength. The lifetime of charge carriers were detected by a Picosecond Time-Correlated Single Photon Counting (TCSPC) Spectrofluorometer. The PL decay time for perovskite films was monitored at 775 nm with a femtosecond Ti:S laser (Spectra Physics) with a frequency doubler and a pulse selector. The excitation wavelength was fixed at 425 nm. The photoluminescence decay kinetics was fitted to a bi-exponential decay function.

3. Results and discussion

Different $R_{P/M}$ solutions are used to fabricate solar cells with a typical device structure of glass/ITO/PEDOT/perovskite/PCMB/Al. Typical J-V curves of samples annealed at 80 °C and 90 °C are shown in Fig. 1. Results from Fig. 1 show that for samples derived from $R_{P/M} = 0.975$ or 1.000 solutions, the PCE is basically not more than 11%. For samples annealed at 80 °C, the PCE value increases to 13.82% with the $R_{P/M}$ increase from 1.000 to 1.100, and then decreases to 10.83% at $P/M = 1.100$. The highest PCE value at $R_{P/M} = 1.050$ is obtained by simultaneously improving two factors: J_{sc} of 21.620 mA cm⁻², V_{oc} of 0.958 V. Although the PCE of samples annealed at 90 °C is lower than that of the 80 °C-annealed samples, the similar trend is obtained for both groups of samples. From the data listed in Table 1, it shows that for both groups of samples, samples derived from $P/M = 1.05$ solution show the highest PCE, J_{sc} , and V_{oc} . The FF, however, basically increases with $R_{P/M}$, which is same to the results reported by Nazeeruddin et al.

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