Morphology Tuning and Its Role in Optimization of Perovskite Films Fabricated from A Novel Nonhalide Lead Source

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1. Introduction

Organic–inorganic lead halide perovskite solar cells (PSCs) have recently attracted increasing attention due to their excellent photovoltaic performance. To date, the power conversion efficiency (PCE) of PSCs has soared to a verified value of 25.2%,[1] rapidly approaching the Shockley–Queisser limit for single junction solar cells. Perovskite materials, constituting the key component in PSCs—the light absorbing layer, possess superior optical and electronic properties ideally suited for photovoltaic devices, including high absorption coefficient,[2,3] high carrier mobility,[4–6] long minority carrier lifetimes,[7,8] long charge diffusion lengths,[8] and have been a key focus in PSC researches. Perovskite materials are generally characterized by their ABX3 structure. Inorganic–inorganic perovskites, typically A=organic cation (CH3NH3, NH2CHNH2, etc.), B=bivalent metal (Pb or Sn), and X=halide (Cl, Br, I, etc.).[9–11] As an archetypical perovskite, CH3NH3PbI3 (methylammonium lead triiodide, MAPbI3) is renowned for its excellent photovoltaic performance, relatively simple crystal structure and facile production methods,[12,13] and has thus been the focus of PSC research from the beginning, while also providing the starting point to study its many derivatives (e.g., via doping) and variations (e.g., via substitution).[14–17]

For synthesizing MAPbI3, typical process involves dissolving lead halide source (e.g., PbI2) and alkyl ammonium halide in an organic solvent.[15,18–20] Recently, usage of nonhalide lead sources has attracted increasing attention[21–25] due to resultant improvements in fabrication process and film quality, such as fast crystallization at low temperature,[23] superior stability,[22] and ultrasmooth surface,[25] all of which are key toward successful manufacturing of commercial-grade PSC products. Although nonhalide lead sources have been investigated for a few years, the correlation between optoelectronic properties of these films and the corresponding device performance are still lack of understanding. Toward its broad adoption, a number of important issues remain yet to be addressed. For example, study on the effects of morphology tuning for PSCs derived from nonhalide lead sources remains elusive. In particular, it has been known that grain boundaries (GBs) plays a vital role in PSC...
performance as it determines a series of key factors, such as carrier lifetime,\textsuperscript{[24]} trap density,\textsuperscript{[26]} current hysteresis,\textsuperscript{[25,27]} and photovoltaic (PV) performance.\textsuperscript{[25,28,29]} While a number of methods have been proposed to suppress the defects at the perovskite GBs, such as Lewis bases treatment,\textsuperscript{[30]} adding fullerene,\textsuperscript{[27]} constructing “patches,”\textsuperscript{[31]} introduction of CH$_3$NH$_3$I (MAI) healing layer,\textsuperscript{[32]} or PbI$_2$ materials,\textsuperscript{[33]} such effort has been limited to perovskite derived from conventional halide lead sources. Further, a systematic understanding has remained elusive for the functions of the nonhalide lead sources in the film morphology and optoelectronic response of PSC devices, such as their effect on the defect states and carrier transport in the resulting perovskite film. Hence, it is of both practical and fundamental importance to explore novel strategies that can both leverage the benefits associated with the usage of nonhalide lead sources and achieve PSCs with high PCE values, while performing systematic characterization on the film formation and carrier dynamics toward better understanding of the underlying mechanisms.

Here we demonstrate a facile solution process for fabricating high-quality, high-efficiency PSCs based on a nonhalide lead source, Pb(HCOO)$_2$ (lead formate), and systematically study the effects of its morphological controlling. In particular, we focus on the formation and role of PbI$_2$ at the GBs in such perovskite films. We find that the growth of PbI$_2$ crystals can be controlled to embed in the GBs by tuning the ratio between Pb(HCOO)$_2$ and MAI, and that PbI$_2$ can form domain “walls” at GBs between individual perovskite crystal domains and help passivate defect states, thereby improving the performance of perovskites. Benefitting from the suppressed lateral carriers diffusion from the “walls,” the perovskite films exhibit an impressive minority carrier lifetime on the microsecond scale ($\tau_e = 1714$ ns), rivaling MAPbI$_3$ single crystal.\textsuperscript{[4,34,35]} Using this nonhalide lead source, we achieve an optimized PSC with a PCE value of 20.3%. Furthermore, through systematic comparison of perovskites formed from different lead sources, we find that the usage of lead formate shows significant advantages in controlling PbI$_2$ walls at GBs and leading to superior device performance. Our findings can help pave the pathways toward facile production of high-quality PSCs, and advance the understanding of film formation that can be further leveraged to enhance the device performance.

2. Results and Discussion

2.1. Fabrication Process of the Perovskite Films

We employ a nonhalide lead source, Pb(HCOO)$_2$, with orthorhombic crystal structure (space group: Pnma)\textsuperscript{[36]} in fabricating perovskite films (Figure 1a). The X-ray diffraction (XRD) of the Pb(HCOO)$_2$ powder well matches that from the Crystallography Open Database (COD 2018763) (Figure 1b). Thermogravimetry (TG) analysis (Figure 1c) confirms that the Pb(HCOO)$_2$ powder shows sudden and steep weight loss at from 228 to 330 °C (generation of PbO), and remains 79.6% of original weight at 330 °C, further confirming the composition of the Pb(HCOO)$_2$ source.\textsuperscript{[37]} The perovskite films are prepared by dissolving the nonhalide lead source, Pb(HCOO)$_2$, and the alkyl ammonium halide source, CH$_3$NH$_3$I (MAI) in organic solvent, such as N,N-dimethylformamide (DMF) (Figure S1. Supporting Information). We optimize the process by varying a number of conditions, including adding dimethyl sulfoxide (DMSO) in the precursor (to control the crystal growth rate),\textsuperscript{[38]} introducing nitrogen flow during spinning (to adjust the nucleation density),\textsuperscript{[39]} and using thermal annealing as a post processing (to tune the crystallization of the perovskite films). Upon examining the resultant films using scanning electron microscope (SEM), Fourier-transform infrared spectroscopy, and XRD (Figures S2–S5, Supporting Information), we determine that the optimal processing condition involves applying 10% DMSO additive into the solution followed by nitrogen flowing and thermal annealing. The resultant films exhibit typical absorption and emission spectra for high-quality perovskites (Figure 1e).\textsuperscript{[40,41]}

2.2. GBs and Its Forming Mechanism

In order to gain insight into the role that Pb(HCOO)$_2$ plays in governing the morphological properties of perovskite films, we systematically vary the molar ratio between Pb(HCOO)$_2$ and MAI in the DMF solution (1:3.00, 1:3.15, 1:3.30, and 1:3.45). SEM images show that PbI$_2$ can form at the GBs (bright particles in SEM images\textsuperscript{[42,43]} outlined by red circles in Figure 2a,b), and its formation can be effectively tuned by adjusting the starting materials. The density of PbI$_2$ decreases as the amount of MAI increases (Figure 2a–d), and completely disappears at 1:3.45 (Figure 2d), consistent with the known fact that residual PbI$_2$ can easily react with excessive MAI. In particular, at the ratio of 1:3.15, PbI$_2$ is mostly formed at the GBs between perovskite crystalline domains, demonstrating good control over its density and morphology. XRD results (Figure 2e) confirm this trend in the evolution of the diffusion peak of PbI$_2$ crystal at $2\theta = 12.6^\circ$ (Figure S6, Supporting Information), and show that the perovskite films are highly crystallized in the (110) and (220) directions. Femtosecond Transient Absorption (fs-TA) spectroscopy further confirms the above observation: at the ratio of 1:3.15, the PbI$_2$ feature (bleaching at 490 nm and induced absorption at 520 nm, Figure 2f inset)\textsuperscript{44,45} is present in the TA spectrum; while at higher MAI ratio, the PbI$_2$ feature vanishes, and only the band-edge transitions in the perovskite (strong bleaching at 760 nm) remains visible (Figure S7, Supporting Information). Importantly, we find that PbI$_2$ forms not only on the film surface, but also continue to controllable formation of PbI$_2$ crystals at the perovskite GBs. Further, we observe significant domain walls formed by PbI$_2$. All the above observations show that using Pb(HCOO)$_2$ and MAI with carefully-tuned ratio as the starting materials can lead to controllable formation of PbI$_2$ crystals at the perovskite GBs. It is important to note that this is only observed for perovskite films made from Pb(HCOO)$_2$/MAI; other organic acid-based lead sources, such as lead acetate ((PbCH$_3$COO)$_2$, i.e., Pb(Ac)$_2$), has less control over the formation of PbI$_2$ at the GBs (Figure S9a–d, Supporting Information).
To understand the unique role of HCOO\(^-\) in the formation of perovskite films, we employ density functional theory to evaluate the Gibbs free energy (\(\Delta G\)) of all possible octahedral structures [Pb\(_{6-x}\)(HCOO)\(_x\)]\(^{4-}\) (0 \(\leq x \leq 6\)) in the precursor (Figure 3a).\([46]\) We find \(\Delta G < 0\) for structures with \(x \leq 4\), suggesting they can be spontaneously formed in perovskite precursors.\([22]\) In contrast, structures with \(x = 5, 6\) do not converge in calculation and thus cannot form.\([47]\) These observations are further confirmed by the absorption spectra of the precursor (Figure S10, Supporting Information), and consistent with observation in other nonhalide lead sources.\([22,48]\)

When MAI and Pb(HCOO)\(_2\) react in the precursor (Figure 3b), [PbI\(_4\)]\(^{2-}\) (\(x = 0\)) octahedral first self-assemble with MA\(^+\) and crystallize into MAPbI\(_3\) (reaction b). Other octahedral (1 \(\leq x \leq 4\)) also gradually convert to [PbI\(_4\)]\(^{2-}\) through anion exchange (HCOO\(^-\) to I\(^-\), reaction a)\([49]\) before forming perovskites, while the remaining HCOO\(^-\) is vaporized during heating. Such delayed process could contribute to better crystallization of the film. Interestingly, new reaction product arises when there is insufficient MAI: the I\(^-\) deficiencies lead to incomplete exchange of HCOO\(^-\) (reaction c), thus cause point sharing [PbI\(_{6-x}\)(HCOO)\(_x\)]\(^{4-}\) octahedral to transform into face sharing [PbI\(_{6}\)]\(^{14-}\) octahedral, eventually forming PbI\(_2\) upon loss of MA\(^+\) (reaction d) at the perovskite GBs, as the sample shown in Figure 2b.

To confirm the absence of HCOO\(^-\) in the resulting films, we use X-ray photoelectron spectroscopy (XPS) to examine the presence of oxygen (i.e., O 1s) and iodine (i.e., I 3d) inside films etched by Ar\(^+\) plasma (Figure 3c,d). The results confirm that oxygen signal only exists on the surface of perovskite, likely due to surface adsorbrates (Figure S11, Supporting Information).\([50,51]\) The complete absence of O element inside the perovskite confirms that no HCOO\(^-\) is left in the final product, consistent with the picture that all [PbI\(_{6-x}\)(HCOO)\(_x\)]\(^{4-}\) loose HCOO\(^-\) through ion exchange before forming perovskite crystal and GBs. It further confirms that the GBs do not contain any HCOO\(^-\) or PbO. With good understanding of the formation of PbI\(_2\) at the GBs, we now focus on systematically analyzing their effects on passivating the defect states and improving device performance.
2.3. Tuning of Carrier Dynamics

To obtain more insight into the role of Pb(HCOO)$_2$ in enhancing the optoelectronic properties of perovskite films, and to evaluate carrier diffusion kinetics properties of perovskite films with PbI$_2$ walls at GBs, we perform both steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements (Figure 4b,d) on the films prepared with varying ratio of Pb(HCOO)$_2$ : MAI. All samples exhibit PL features at 768 nm, consistent with expected optical properties of MAPbI$_3$ films (Figure 4b). Importantly, the measured PL intensity show clear correlation with the morphology of the perovskite films (Figures 4c, and 2a–d), with peak PL value found at the ratio of Pb(HCOO)$_2$ : MAI = 1:3.15, in which the perovskite crystalline domains are nicely bordered by PbI$_2$ (Figure 2b; and Figure S12, Supporting Information). Furthermore, TRPL measurements (Figure 4d) show that carrier lifetime follows the exactly same trend (Figure 4e), with the film prepared with Pb(HCOO)$_2$ : MAI = 1:3.15 exhibiting an impressively long carrier lifetime ($\tau$) in the microsecond range (Table S1, Supporting Information), $\tau_2 = 1714$ ns (with A$_2 = 61\%$; $\tau_1 = 460$ ns, A$_1 = 39\%$; $\tau_{avg} = 1224$ ns). This remarkably long carrier lifetime of our sample is even tantamount to that of most MAPbI$_3$ single crystals.$^{[4,34,35]}$ We note that the usage of Pb(HCOO)$_2$ is advantageous for achieving such long lifetime; as a comparison, perovskite made from Pb(AC)$_2$ produces a much shorter lifetime ($\tau_2 = 437$ ns, shorter by one order of magnitude; see Figure S9–f.
Figure 3. Formation mechanism of perovskite films via Pb(HCOO)$_2$ route. a) Calculated values of $\Delta G$ versus the different octahedral structure, [PbI$_{6-x}$(HCOO)$_x$]$^{4-}$ ($0 \leq x \leq 4$). b) Schematic representation of the main stages that transition from precursor to perovskite. (For the [PbI$_{6-x}$(HCOO)$_x$]$^{4-}$ ($1 \leq x \leq 4$) octahedral, take $x = 1$ as example). c,d) XPS spectra of perovskite films via Pb(HCOO)$_2$ route, the sample was etched using the Ar$^+$ plasma for 0s, 100s, 200s. Narrow scanning XPS spectra of O 1s c) and I 3d d).

and Table S2, Supporting Information). Here we again find clear correlation between carrier lifetime and film morphology. Specifically, even in the Pb(Ac)$_2$ derived films with longest lifetime (1:3.15 ratio), the PbI$_2$ only loosely decorates the perovskite GBs (Figure S9b, Supporting Information), while in the films made from Pb(HCOO)$_2$ the PbI$_2$ form a complete boundary around the perovskite crystalline domains (Figure 2b). Besides, TRPL decay measurements provide a direct insight into the trap-state induced carrier dynamics. We applied a simulation model based on our previous work$^{[52]}$ to build a clear connection between defect recombination and carrier lifetime (Figure S13 and Table S3, Supporting Information) and indicate that the reduced defect density in 1:3.15 sample leads to its increased carrier lifetime. This suggests that by carefully choosing and tuning the starting materials, PbI$_2$ can effective form domain “walls” that segregate the individual perovskite crystal domains, thus effectively passivating the defects at the perovskite GBs and suppressing lateral diffusion and recombination of the carriers (Figure 4a).$^{[33]}$
To further evaluate such passivation effects, we quantify the density of defects in these MAPbI$_3$ films using space-charge-limited current (SCLC) measurements. We fabricate electron-only devices with the structure of fluorine-doped tin-oxide (FTO)/TiO$_2$/MAPbI$_3$/[6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM)/Au and characterize their dark current–voltage response (Figure 4f–g; and Figure S14, Supporting Information). The trap states density ($N_{\text{defects}}$) is estimated by:

$$N_{\text{defects}} = \frac{2e\varepsilon_0}{\varepsilon L^2} V_{\text{TFL}}$$

where $V_{\text{TFL}}$ represents the trap-filled limit voltage, $e$ is the electronic charge, $L$ is the thickness of the perovskite film, $\varepsilon$ is the relative dielectric constant of MAPbI$_3$ ($\varepsilon = 32$),$^{[35]}$ and $\varepsilon_0$ is the vacuum permittivity. As expected, lower defect density corresponds to longer carrier lifetime, with the best value ($1.31 \times 10^{16}$ cm$^{-3}$) achieved again for the Pb(HCOO)$_2$/MAI = 1:3.15 film (Figure 4h), in which the PbI$_2$ nicely filling the perovskite GBs (Figure 2b). These results confirm that the trap densities can be significantly reduced by controlling the density and morphology of PbI$_2$ crystal at perovskite GBs, which lead to long carrier lifetimes.

### 2.4. Photovoltaic Performance

To confirm that the optimized embedded PbI$_2$ crystals at the GBs and long carrier lifetime can help achieve better PCE, we...
assess the photovoltaic performance of resulting PSCs (Figure 5a). As expected, a similar trend (PCE dependence on the molar ratio) is observed (Figure S15, Supporting Information), with the best-performing devices achieved for films made with the molar ratio of 1:3.15. The champion device exhibits an optimized PCE of 19.2%, yielding short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), and fill factor (FF) of 22.1 mA cm$^{-2}$, 1.12 V and 77.5%, respectively (Figure 5b). We also show that the PCE can be further enhanced through simple additive engineering which has been known as an effectively way to enhance PCE in MAPbI$_3$ PSCs.$^{[54,55]}$ As a demonstration, we introduce MACl as additive in the precursor to assist the crystal growth (see the experimental procedures for details).$^{[56]}$ The resulting devices show clearly improved PCE values up to 20.3% (Figure 5c), by far surpassing all PSCs made from pure nonhalide sources (Tables S4 and S5, Supporting Information), with a stabilized value of 19.1% (Figure 5d). We also measure its external quantum efficiency (EQE), from which we obtain an integrated $J_{sc}$ value of 21.9 mA cm$^{-2}$ (Figure 5e), in good agreement with the $J$–$V$ scan result (Figure 5c). The slight mismatch is likely due to the spectral mismatch between the light sources of the EQE and solar simulator, as commonly found in literature.$^{[55,57]}$ In addition, the device exhibits remarkable stability, with measured PCE retaining at 89% of initial value after 1000 h without any encapsulation (Figure 5f). The testing of photo and humidity stability further demonstrated that devices with optimized amount of PbI$_2$ GBs (1:3.15) show obvious better stability than those with minor PbI$_2$ GBs (1:3.30) under all conditions (Figure S16, Supporting Information), certifying the role of these GBs in protecting perovskite grains. The above examples demonstrate that by using Pb(HCOO)$_2$ as the starting material, and by carefully controlling the molar ratio, one can achieve optimized film morphology with PbI$_2$ filling the perovskite GBs leading to high-quality PSCs.

3. Conclusion

In conclusion, we report a new nonhalide lead source, lead formate Pb(HCOO)$_2$, for fabricating high-quality perovskite films, which offers a unique pathway for controlling the decoration of PbI$_2$ at the perovskite GBs. In perovskite films fabricated with the optimized Pb(HCOO)$_2$:MAI ratio, the PbI$_2$ crystals filling the MAPbI$_3$ GBs can effectively passivate the defects, consistent with the SCLC measurements, and lead to a significant enhancement in the carrier lifetime, reaching an impressively value of $\tau_2 = 1714$ ns. This allows us to achieve PSCs with an optimal PCE of 20.3%, surpassing all PSCs made from nonhalide sources. Our work demonstrates a strategy for optimizing device performance through careful control of film morphology, revealing great potentials of Pb(HCOO)$_2$ as the starting material for pushing PSCs into industrial application due to its low cost and facile fabrication method while retaining the superior performance of devices.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carrier lifetime, grain boundaries, lead formate, nonhalide lead source

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