Additive-assisted defect passivation of perovskite with metformin hydrochloride: toward high-performance \( p-i-n \) perovskite solar cells

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Abstract

Defects at the grain boundaries and surfaces of perovskite thin films are the key factors that cause nonradiative recombination, thus restricting the performance of perovskite solar cells (Pero-SCs). By introducing foreign additives to manage the chemical environment of the precursor, perovskite films can obtain optimized morphology and reduced defects, thereby enhancing the photovoltaic performance and stability of derived Pero-SCs. Herein, we report the bifunctional molecule metformin hydrochloride (MetHCl), whose multidentate structure is capable of simultaneously passivating several sorts of defects in perovskite films. Concurrently, the strong binding ability to \( \text{Pb}^{2+} \) makes it impressive in regulating perovskite crystallization. The nonvolatile MetHCl can remain in the perovskite film, contributing to acquiring a high-quality film with denser grains and fewer pinholes. Finally, \( p-i-n \) Pero-SCs containing the MetHCl additive exhibited enhanced stability and achieved a champion power conversion efficiency of 21.59% with an open-circuit voltage of 1.17 V.

1. Introduction

Organic–inorganic hybrid perovskite materials are becoming one of the most promising photovoltaic active layers for next-generation photovoltaic technologies due to their high absorption coefficients, carrier mobility, long diffusion distances, and tunable band gaps [1–4]. In 2009, Kojima et al [5] first used perovskite in solar cells. Over a decade of development, the efficiency of perovskite solar cells (Pero-SCs) has increased from 3.8% to over 25% [6]. Pero-SCs with a \( p-i-n \) structure are readily adaptive in tandem solar cells [7]; however, their power conversion efficiency (PCE) has lagged behind that of \( n-i-p \) Pero-SCs. The nonradiative recombination of excitons is considered the main cause of the efficiency loss in \( p-i-n \) Pero-SCs [8, 9], as it can affect the quasi-Fermi level splitting, thereby reducing the open-circuit voltage (\( V_{OC} \)) of the corresponding devices. Meanwhile, the extent of nonradiative recombination is closely correlated to the defect density in perovskite [10, 11]. The ionic nature of perovskites renders them liable to generate defects associated with undercoordinated \( \text{Pb}^{2+}, \text{I}^-/\text{Br}^-, \) and \( \text{MA}^+/\text{FA}^+ \). These defects tend to accumulate at the perovskite surfaces and grain boundaries, further deteriorating the long-term stability and PCE of Pero-SCs [12–14].

Therefore, reducing defects in perovskites is the key to improving device performance. Additive engineering, which can affect the crystallization and deactivate traps in perovskites based on coordinate or ionic bonding, is a productive strategy to fabricate high-performance devices. Hence, abundant molecules are involved in the fabrication process of Pero-SCs as electron donors or acceptors [15–18]. Among them, Lewis acids [19–28], including metal ions, carboxylic acids, phosphonic acids, and ammonium groups, can neutralize undercoordinated halides and \( \text{PbI}_x^- \) anti-sites. Lewis bases [29–36], such as functional groups with...
lone pairs bearing atoms such as nitrogen (N), sulfur (S), oxygen (O), and phosphorus (P), have been reported to target Pb-interstitial and halide vacancy neutralization. Overall, various types of defects in perovskites can be reduced by specific strategies. However, seeking an efficient additive to achieve enhanced passivation effects remains a major challenge. This requires the additive to passivate multiple defects while establishing a stable bond with the perovskite. Thus, research on multifunctional molecules is of great significance for rational molecular selection.

In this work, we propose an additive-assisted defect passivation strategy based on metformin hydrochloride (MetHCl), in which MetHCl consists of an electronegative amine and imine groups alongside an electropositive ammonium group. The introduction of MetHCl can retard the crystallization of perovskite and reduce defects at the grain boundaries and surfaces of the films. The $p$-$i$-$n$ Pero-SCs based on MetHCl passivated films could achieve a champion PCE of 21.59%, with a high $V_{OC}$ of 1.17 V. Moreover, the effective passivation of MetHCl reduces the pathways for external stressors to degrade perovskite, resulting in enhanced device stability under air and heating conditions.

2. Results and discussion

Figure 1(a) shows a schematic diagram of the passivation of defects in perovskite with MetHCl. Multiple functional sites in MetHCl can interact with defects such as undercoordinated Pb$^{2+}$ and halide vacancies caused by the rapid crystallization of perovskite. To explore the passivation effect of MetHCl, $^1$H NMR measurements were carried out to prove the interaction between MetHCl and PbI$_2$. The $^1$H NMR spectra of neat MetHCl and MetHCl + PbI$_2$ solution in deuterated dimethyl sulfoxide-$d_6$ (DMSO-$d_6$) are shown in figure 1(b). The chemical shift located at 6.70 ppm should be assigned to the amino group of MetHCl. After mixing with PbI$_2$, the NMR signal shifted to 6.55 ppm, which should be attributed to the enhanced shielding effect due to the transition from N–H···Cl$^-$ to N–H···I$^-$. The interaction between MetHCl and Pb$^{2+}$ was further verified by Fourier transform infrared (FTIR) spectroscopy. As shown in figure 1(c), the peaks at 1628 and 1570 cm$^{-1}$ are assigned to the stretching vibration of C=N and the deformation vibration of N–H, respectively. The vibration peaks of C=N and N–H shifted to 1622 and 1576 cm$^{-1}$, respectively, which should be ascribed to the interaction between MetHCl and PbI$_2$. Since the vibrational frequency is proportional to the square root of the force constant in the harmonic motion of the diatomic model, the frequency decrease of C=N implies a weaker bond strength, corresponding to a stronger interaction between imine and Pb$^{2+}$. The frequency increase of the N–H bond should be attributed to the bonding transition from N–H···Cl$^-$ to N–H···I$^-$. X-ray photoelectron spectroscopy (XPS) was employed to further investigate the interaction between MetHCl and perovskite. As shown in figure 1(d), the binding energies at 143.4 and 138.5 eV are respectively assigned to 4f$^{5/2}$ and 4f$^{7/2}$ of Pb$^{2+}$ in the control group (perovskite film without MetHCl). These peaks shifted to lower binding energies when doped with MetHCl because the combination between electron-rich N and the undercoordinated Pb$^{2+}$ led to electron-rich Pb. Meanwhile, the decreased binding energy of Pb core-level electrons implies a reduction in the oxidation state of Pb, which could lead to a lower oxidation state of iodide. This can also be reflected in the shift of the characteristic signal of I 3d$_{5/2}$ from 619.2 to 618.8 eV as shown in figure S1 in supporting information (SI).

Next, the effect of MetHCl on the morphology and structure of perovskite films was investigated. As shown by the atomic force microscopy (AFM) images in figure 2, nano-flakes appeared on the perovskite surfaces upon the addition of MetHCl, and amount of the nano-flakes increased with MetHCl. The scanning electron microscope (SEM) images showed similar results (figure S2 in SI). According to the morphology, the nano-flakes might be a kind of 2D perovskite. However, an overdose (0.2 wt%) of MetHCl led to a decrease in the crystallinity of the perovskite film (figure S3 in SI). Excessive MetHCl may hinder the reaction between PbI$_2$ and methylamine. The addition of MetHCl did not cause any peak shift or appearance of new peaks, which suggests that MetHCl had little effect on the crystal lattice of perovskite films.

UV–vis spectra were used to characterize the effect of MetHCl on the optical properties of perovskite thin films. As shown in figure 3(b), MetHCl has little effect on the absorption edge and a slight enhancement effect on the absorbance (note that the film thickness was controlled the same). The unchanged absorption...
Figure 1. (a) Schematic diagram of passivation of defects in perovskite with MetHCl; (b) $^1$H NMR spectra and (c) FTIR of MetHCl in the presence/absence of PbI$_2$; (d) XPS of perovskite films with and without MetHCl.

Figure 2. AFM images of perovskite films (a) with 0, (b) 0.05, (c) 0.1, and (d) 0.2 wt% MetHCl.

dge was confirmed by the similar band gap of perovskite extrapolated from Tauc plots (figure S4 in SI). The slight enhanced absorbance could be attributed to denser grains and stronger crystallinity caused by MetHCl doping [54]. These results indicate that MetHCl can help improve the crystal growth and passivate the defects in the perovskite films, but it is not involved in the crystal lattice. These results are consistent with the XRD results.

The quality of the perovskite films was evaluated by steady-state photoluminescence (PL). As shown in figure 3(c), the emission of the perovskite film was greatly enhanced upon the addition of MetHCl, indicating that the nonradiative recombination was effectively suppressed due to the improvement of the film quality [55–58]. Time-resolved PL (TRPL) was carried out to shed light on the transient evolution of the
photogenerated carriers. As shown in figure 3(d), the TRPL decay curves were fitted with a biexponential function, and the detailed parameters are summarized in table S1. The fast decay \((\tau_1, f_1)\) is related to the charge-trapping process, and the slower decay \((\tau_2, f_2)\) represents the radiative recombination in the bulk of perovskite films [59]. Upon the addition of MetHCl, \(\tau_1\) increased from 7.72 to 15.63 ns, and \(f_1\) decreased from 44% to 17%. In addition, \(\tau_2\) increased from 17.89 to 46.25 ns, and \(f_2\) increased from 56% to 83%. These results indicate that the addition of MetHCl suppressed the nonradiative recombination, which can also be reflected by the notable elongation of the average lifetime from 15.34 to 44.28 ns. The improvement should be attributed to the reduced defects, e.g. undercoordinated Pb and halide vacancies [60]. Confocal laser scanning fluorescence microscopy (CLSM) images provide an emission property evaluation on the whole film instead of a spot such as that provided by fluorescence spectra. As shown in figure 3(e), the CLSM image of the perovskite film with MetHCl was much brighter, which was further confirmed by the intensity distribution shown in the insets. The improved quality of the perovskite film is thus further verified by the CLSM images, and such a result promises reduced energy loss in Pero-SCs.

Pero-SCs with a configuration of ITO/PTAA/MAPbI\(_{3-x}\)Cl\(_x\)/C\(_{60}\)/BCP/Ag were fabricated. The device configuration is shown in figure 4(a), and the cross-sectional SEM images of the devices with and without MetHCl are shown in figure S5 in SI. The detailed fabrication process of the device is described in the experimental section. The photovoltaic performance of the Pero-SCs was measured under the illumination of an AM 1.5G solar simulator with an intensity of 100 mW cm\(^{-2}\). The amount of MetHCl added to the perovskite precursor was optimized according to the performance of the devices. The \(J–V\) curves are shown in figure S6, and the photovoltaic parameters are summarized in table S2 in SI. The PCE increased as the amount of MetHCl increased from 0 to 0.1 wt%. However, further increasing the amount of MetHCl to 0.2 wt% resulted in a decrease in PCE, as well as the fill factor (FF) and short-circuit current density (\(J_{SC}\)). We assume that the decrease in the PCE should be attributed to the formation of craggly grains due to the overdosed addition of MetHCl. Figure 4(b) shows the \(J–V\) curves of the champion device with and without MetHCl. The pristine device without passivation showed a PCE of 19.71%, with a \(V_{OC}\) of 1.08 V, a \(J_{SC}\) of 22.36 mA cm\(^{-2}\), and an FF of 81.2%. The device treated with MetHCl achieves a considerably enhanced PCE.
of 21.59%, with a $V_{OC}$ of 1.17 V, a $J_{SC}$ of 22.57 mA cm$^{-2}$, and an FF of 81.9%. We summarized the recent reports on $p$-$i$-$n$ solar cells based on MAPbI$_3$, the data are listed in table S3 in SI. Compared with the currently published results, both the PCE and $V_{OC}$ presented in this study are quite competitive. The most probable PCEs were 19.28% and 20.93% for Pero-SCs without and with MetHCl, respectively, as shown in figure 4(c).

The detailed photovoltaic parameters of the devices with and without MetHCl are shown in table 1, and the distribution of the detailed photovoltaic parameters is shown in figure S7. The average efficiency of the devices with MetHCl is 20.86%, which is significantly higher than the average efficiency of the pristine devices of 19.13%. The improved PCE and $V_{OC}$ of the device could be attributed to the effective passivation of the defects by MetHCl and thus suppressed the nonradiative recombination of the charge carriers.

As shown in figure 4(d), the devices exhibit negligible hysteresis, and the detailed parameters are listed in table S4. Figure 4(e) exhibits the stable power output at the maximum power point of the MetHCl-doped device under AM 1.5G continuous illumination. The stabilized PCE is 21.15%, which is in good agreement with the results obtained from the $J$–$V$ curves. The external quantum efficiency (EQE) was measured as shown in figure 4(f). The integrated current densities ($J_{int}$) of the device with and without MetHCl were 22.30 mA cm$^{-2}$ and 21.93 mA cm$^{-2}$, respectively, which matched well with the results obtained from the corresponding $J$–$V$ curves.

To gain insight into the improved performance of devices, the space charge confined current (SCLC) method was performed to characterize the trap density ($n_t$) of the perovskite films. The dark $J$–$V$ curves of hole-only and electron-only devices with and without MetHCl are shown in figures 5(a) and S8. The ohmic region at low bias exhibits a linear relation between the current and electric field, and the trap-filled limited region at intermediate bias shows a marked increase in the current injection until reaching the trap-filled limit voltage ($V_{TFL}$) [61]. $n_t$ was calculated by the equation $n_t = \frac{2\varepsilon_0 V_{TFL}}{\varepsilon L^2}$, where $\varepsilon$ and $\varepsilon_0$ are the relative and vacuum permittivity, respectively, and $L$ is the thickness of the perovskite film. The calculated $n_t$s were $2.41 \times 10^{15}$ $(2.15 \times 10^{15})$ and $1.66 \times 10^{15}$ $(1.36 \times 10^{15})$ cm$^{-3}$ for the hole-only (electron-only) devices without and with MetHCl. These results indicate that the defects in the perovskite film should be effectively passivated by MetHCl. The semilogarithmic dark-light $J$–$V$ curves of the champion Pero-SCs with and without MetHCl are shown in figure 5(b), where all devices showed good rectifying behavior, and a smaller
leakage current is shown for the device with MetHCl, providing further evidence for the facilitated charge transportation induced by the addition of MetHCl.

To further elucidate the charge recombination behavior of the Pero-SCs, $V_{OC}$ under different light intensities was determined, as shown in figure 5(c). The ideal factor ($n$) was determined by the equation $V_{OC} = \frac{n k_B T}{e} \ln(I)$, where $k_B$ is the Boltzmann constant, $T$ is the Kelvin temperature, and $e$ is the elementary charge [62]. An $n$ closer to 1 corresponds to less nonradiative recombination of the charge carriers [63]. The $n$ values for the control and MetHCl-doped devices were 1.64 and 1.52, respectively, indicating that defect-assisted recombination is effectively suppressed due to the reduced defect density by the incorporation of MetHCl.

Alternating current impedance spectroscopy (ACIS) was carried out to study the carrier transfer and recombination dynamics of Pero-SCs. Figure 5(d) shows the Nyquist plot of the devices measured at the bias voltage of $V_{OC}$ in the dark, in which the inset is the equivalent circuit used for data fitting. The detailed parameters are shown in table 2, where $R_s$ represents the internal series resistance related to the sheet resistance of the electrode, and $R_{tr}$ represents the charge transport resistance at the interface, such as the resistance between the perovskite layer and the interface transport layer [64]. For the two groups of Pero-SCs, the $R_s$ values are comparable, while the $R_{tr}$ values are quite different. The $R_{tr}$ values were 48.65 and 36.84 Ω for the control and the device based on MetHCl, respectively. The decreased $R_{tr}$ implies that charge carrier recombination was significantly reduced due to the defect passivation induced by the addition of MetHCl.

Transient photovoltage (TPV) was also used to investigate the charge recombination for Pero-SCs with and without MetHCl. As shown in figure 5(e), the carrier recombination lifetime in the device shows an increase from 5.43 µs to 11.83 µs with the addition of MetHCl, indicating that MetHCl treatment suppresses charge carrier recombination. This result is in good agreement with the higher $V_{OC}$ in MetHCl-doped devices. Figure S9 shows the transient photocurrent (TPC) curves of Pero-SCs measured under short-circuit conditions. The time constants for the control and the Pero-SC based on MetHCl were 193.6 and 58.6 ns, respectively. The relatively fast decay of Pero-SC based on MetHCl suggests that efficient charge carrier extraction and favorable charge transport were achieved due to the addition of MetHCl.

The storage stability of the unencapsulated Pero-SCs was investigated in ambient air under controlled humidity (RH = 20 ± 10%) and high humidity (RH = 65 ± 10%) at room temperature. As shown in

|             | $R_s$ (Ω) | $R_{tr}$ (Ω) | $C_{tr}$ (F) |
|-------------|-----------|--------------|--------------|
| Control     | 11.75     | 48.65        | $1.34 \times 10^{-8}$ |
| w MetHCl    | 13.23     | 36.84        | $1.30 \times 10^{-8}$ |
figure 5(f), the control decreased to 50% of its initial PCE after 400 h in air, whereas the Pero-SC based on MetHCl retained approximately 80% of its initial PCE after 800 h. Similarly, Pero-SC with MetHCl also exhibited better stability than the control device under high humidity, as shown in figure S10(a) in SI. Last, the thermal stability of the Pero-SCs with and without MetHCl was evaluated at 70 °C inside a glove box filled with N₂. As shown in figure S10(b) in SI, there is no significant PCE decay for the MetHCl passivated device after being heated for 200 h, while the PCE of the control device started to fall off after 100 h of heating. The enhanced ambient and thermal stability could be attributed to the synergistic functions of MetHCl. On the one hand, the improved film quality of the perovskites caused by MetHCl could help defend against attacks from foreign species. On the other hand, the reduced defects and the robust binding of MetHCl to perovskite could inhibit ion migration and slow down the degradation process of perovskite.

3. Conclusions

In summary, MetHCl bearing multifunctional groups was introduced into the perovskite precursor as an additive to passivate the defects caused by undercoordinated Pb²⁺ and I⁻ ions. The quality of the perovskite films was remarkably improved in terms of grain size, defect density, and crystallinity, and thereby both the performance and stability of the corresponding Pero-SCs were notably improved. After the treatment, the PCE increased from 19.71% to 21.59%. These improvements should be attributed to the facilitated charge extraction/transportation and suppressed charge recombination induced by the addition of MetHCl. This study presents a potential additive for improving the quality of perovskite toward highly efficient and resilient Pero-SCs.

4. Experimental section

4.1. Reagents and materials

Unless stated otherwise, all reagents and materials were commercially available and used without further purification. N,N-dimethylformamide (99.8%), isopropanol (99.5%), and toluene (99.9%) were purchased from J&K. ITO glass was purchased from China Southern Glass Group, and poly(triarylamine) (PTAA), MAI, MACl, PbI₂, BCP, PCBM and C₆₀ were purchased from Xi'an Polymerlight Optoelectronics Co., Ltd. SnO₂ Nanoparticle Solutions (tin (IV) oxide, 15 wt% in H₂O colloidal dispersion) were purchased from Alfa Aesar Ltd. Metformin hydrochloride was purchased from Across. Except for SnO₂, all the materials are stored in the glove box filled with N₂.

4.2. Device fabrication

The ITO glass was ultrasonically cleaned sequentially with detergent, Milli-Q water, acetone, ethanol, and isopropanol, using each solvent twice for 20 min each. The cleaned ITO glass was treated with UV ozone for 20 min before use. Then the ITO glass was transfer to a glove box filled with N₂ for the next steps. PTAA (2 mg ml⁻¹ in toluene) was first spin-coated on ITO at 6000 rpm for 30 s, then annealed at 100 °C for 10 min. After the substrate cooled to room temperature, the perovskite films were prepared by a two-step method. The mixture of 461 mg ml⁻¹ PbI₂ in DMF was stirred at 70 °C for 12 h. MAI and MACl were mixed in isopropanol with final concentrations of 50 mg ml⁻¹ and 5 mg ml⁻¹, respectively. All perovskite precursor solutions were filtered with 0.45 μm polytetrafluoroethylene filters before use. The PbI₂ solution was first spin-coated on PTAA at 3500 rpm for 20 s, and the mixed solution of MAI and MACl was added dropwise to the center of the spinning PbI₂ film for 30 s. The resulting films were annealed at 70 °C for 3 min and 100 °C for 3 min in a glove box filled with N₂. Finally, 20 nm of C₆₀, 8 nm of BCP, and 80 nm of Ag electrodes were sequentially evaporated using a shadow mask under vacuum. The active area of the Ag electrode is 0.15 cm², and the devices were masked with a metal aperture mask (0.0757 cm²) during the J–V measurement.

For the MetHCl-doped samples, a given amount of MetHCl was added to the PbI₂ solution. 0.05, 0.1, and 0.2 wt% refer to the mass ratio of MetHCl/PbI₂. Specifically, MetHCl was first dissolved in DMF at a concentration of 0.25–1 mg ml⁻¹ and then added to the PbI₂ precursor (461 mg ml⁻¹). Unless stated otherwise, the ‘with MetHCl’ described in the manuscript suggests that 0.1 wt% MetHCl was added to the PbI₂ precursor in the experiment. This is the optimal doping concentration according to the performance of the Pero-SCs.

4.3. Characterization

FTIR was measured with a Bruker VERTEX 70v spectrometer. XPS was performed on an Axis Ultra HAS instrument (KRATOS, Japan). NMR was measured on a Bruker 400 MHz Avance NEO spectrometer. AFM images were obtained using a MultiMode 8 microscope (Bruker, Santa Barbara, CA). SEM images were collected using a SU8010 (Hitachi, Japan) instrument. XRD was performed on a D2 PHASER diffractometer.
(Bruker, Germany) with Cu Kα radiation. Absorption spectra were measured with a UV spectrometer (Agilent Technologies Cary 5000 UV–vis–NIR). Fluorescence distribution spectra were measured using a JMAT-S confocal laser scanning microscope (SouthPort Co., Ltd, Taiwan) with an excitation wavelength of 445 nm, a confocal aperture size of 50 µm, and an objective lens of ten times. PL spectra were measured on an FLS 980 (Edinburgh Instrument, UK). The J–V curves of the Pero-SCs were measured using a Keithley 2400 source meter (Keithley Instruments, USA) in a glove box filled with N2 under AM 1.5G sunlight with a power of 100 mW cm−2. The sweep speed was 10 mV s−1. EQE curves were measured in air by a solar cell spectral response system QE-R3011 (Enli Technology Co., Ltd, Taiwan). Nyquist plots were measured on an IM6 electrochemical workstation (Zahner Zennium, Germany) in the dark, with biases set at the Voc. Transient fluorescence measurements were performed on a Lifespec II (Edinburgh Instrument, UK) with an excitation light source of 477 nm (2 MHz). TPV and TPC spectra were obtained from TPVC-1G (SouthPort Co., Ltd, Taiwan).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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