



Article Surface Passivation of Organic-Inorganic Hybrid Perovskites with Methylhydrazine Iodide for Enhanced Photovoltaic Device Performance

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Abstract: Organic-inorganic hybrid perovskites are highly efficient in photovoltaic applications, making the commercialization of perovskite solar cells (PSCs) possible. However, the high density of defects on the surface significantly affects the performance of PSCs. To address this issue, we have demonstrated a facile post-treatment strategy utilizing methylhydrazine iodide (MHyI) to passivate the surface of the perovskite film. MHyI could co-ordinate with the dangling bonds on the surface of perovskite films, effectively passivating defects in the film and suppressing carrier non-radiative recombination. As a result, PSCs with MHyI modification exhibit a champion power conversion efficiency (PCE) of 23.19% and a high open-circuit voltage (V_{OC}) of 1.14 V (0.43 V voltage deficit). Moreover, unencapsulated solar cells maintain their initial efficiency of 88% after 30 days of exposure to ambient air with 30% humidity, and the devices with encapsulation retained 57% of their initial efficiency after 200 h of maximum power point (MPP) loading under constant light irradiation in ambient air. Overall, our results provide a facile method for improving the performance and stability of PSCs.

Keywords: post-treatment; surface defect passivation; methylhydrazine iodide; high performance; perovskite solar cell

1. Introduction

Currently, organic-inorganic hybrid perovskite (OIHP) materials are receiving significant attention due to their unique and remarkable opto-electronic properties [1–5]. As a result, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has skyrocketed from 3.8% [6] to a current record of 25.7% [7], comparable to commercial single-crystal silicon-based solar cells, indicating its emergence as the most promising contender for the next generation of photovoltaic devices. Despite these impressive achievements, the current efficiency record still falls below the theoretical limit estimated by the Shockley–Queisser (SQ) theory for single-junction solar cells [8–10]. Additionally, it is believed that achieving long-term stability, minimizing or eliminating the use of toxic solvents, and preventing lead leakage are among the most difficult parts of commercialization [11–15]. Polycrystalline perovskite materials possess an inherent ionic nature, and their low defect formation energy enables a wide variety of defects to develop at grain boundaries and on the surface while preparing perovskite films by the solution method [16–18]. These defects act as non-radiative recombination sites capable of trapping photogenerated carriers, affecting



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). carrier dynamics, compromising performance, and even the long-term stability of the device [19–22]. Significant efforts have been made toward defect passivation to reduce defects in perovskite films and further improve device efficiency and stability through various strategies, such as compositional engineering, morphology engineering, grain engineering, interface engineering, and surface passivation engineering [23–32]. In addition to efforts to passivate defects, perovskite solar cells also exhibit a massive open-circuit voltage (Voc) deficit (defined as Eg/q-Voc), which could ultimately impair efficiency.

Due to the self-assembled growth characteristics [33,34] of perovskite films, perovskite crystal growth generally originates from the substrate and terminates on its surface, resulting in a high number of dangling bonds (especially vacancy defects) [35,36] on the perovskite film surface. The presence of these vacancy defects accelerates the infiltration of moisture and oxygen [36–38], leading to the start of perovskite decomposition, which is further accelerated due to chain reactions and may ultimately result in device malfunction. Furthermore, these defects can affect the heterojunction structure between the perovskite and hole transport layers, leading to non-ohmic contacts and significant energy level mismatch, increasing non-radiative recombination of carriers at the interface and resulting in severe energy loss. Therefore, defect passivation of the top surface of perovskite films is crucial. Considerable efforts have been devoted to passivating surface defects, including surface modification and the construction of 3D/2D heterojunctions. For instance, Jiang et al. deposited a phenethylammonium iodide (PEAI) layer on the surface of a perovskite film that efficiently suppressed non-radiative recombination by passivating surface defects, resulting in a quasi-steady-state PCE of 23.3% and a Voc of 1.18 V, which is 94.4% of the SQ limit [24]. Du et al. used a salt containing a Lewis base group called pyridinium iodide (PyI) to bind the uncoordinated Pb ions and fill iodine vacancies, thereby reducing surface defects and obtaining a Voc of 1.18 V and a PCE of 21.42% [39]. Moreover, Liang et al. spin-coated 1-naphthylmethylamine iodide (NMAI) on the perovskite film to form a passivation layer, which led to a PCE of 21.04%, an exceptionally high Voc of 1.20 V, and 98.9% of the initial efficiency after 3240 h [40]. Zhou et al. developed 3D/2D perovskite light-absorbing layers by coating a 2-(4-fluorophenyl)ethylammonium iodide (pFPEAI) capping layer on 3D perovskite, achieving a high Voc of 1.12 V and an impressive PCE of 20.54%. Additionally, the device maintained an initial efficiency of 99% after 864 h of storage [41]. Subsequently, Zhou et al. investigated the effect of the fluoride atom's position (ortho-, meso-, and para-) in fluorophenethylamine iodide salt on device performance and stability. The results show that oFPEAI-based PSCs have the best PCE of 20.60%, while *p*FPEAI-based PSCs have the best stability with only a 1% drop in their initial PCE after 1440 h of storage [42]. These studies suggest that finding alternative post-treatment salts for perovskite surface passivation to achieve high performance and larger Voc is crucial for further commercial applications of opto-electronic devices.

In this study, we synthesized an organic halide salt methylhydrazine iodide (MHyI) to passivate the surface defects of mixed-cation/halide perovskite in planar n-i-p PSCs, aiming to improve the photovoltaic performance [43]. A bulky organic salt can coordinate with the dangling halide bonds on the crystal surface and passivate defects arising from vacancies of halide ions or organic cations on the perovskite films. MHyI surface passivation significantly reduced trap density, leading to significantly improved carrier dynamics. As a result, devices with MHyI passivation demonstrated a remarkable *V*oc of 1.14 V and an outstanding PCE of 23.19%, exhibiting negligible hysteresis. The MHyI-treated devices also exhibited significantly increased stability. After 30 days of exposure to 30% relative humidity, the unencapsulated devices only degraded by 12%. Additionally, after 200 h of continuous operation, 57% of the initial power output could still be maintained under steady-state light illumination in ambient air.

2. Results and Discussion

In this work, organic-inorganic hybrid perovskite films were prepared using a two-step sequential deposition method [24]. The MHyI salt solution was spin-coated onto the

perovskite surface by a post-treatment process to introduce a passivation layer. It is worth noting that no additional annealing of the MHyI layer was required. As shown in the schematic diagram of Figure 1a, the target devices adopted a planar n-i-p architecture of Glass/FTO/SnO₂/(FAPbI₃)_{1-x}(MAPbBr₃)_x/MHyI/Spiro-OMeTAD/Au. (FTO: F-doped Tin Oxide; Spiro-OMeTAD: 2,2',7,7'-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'spirobifluorene). A representative field-emission scanning electron microscopy (FE-SEM) cross-section image of the whole device is presented in Figure S1 (Supplementary Materials). As observed, the giant longitudinal perovskite grains are sandwiched by uniform-charge transporting layers, and the thickness of the perovskite film can also be found to be 750 nm. The MHyI molecular structure and the schematic illustration of the passivation are shown in Figure 1b. We infer that the ions in MHyI are capable of filling iodine vacancies and A-site cations, maintaining the integrity of the perovskite crystal structure and providing potential benefits to device performance and stability [24].



Figure 1. (a) The device structure adopted in this study. MHyI is used for post-treatment of the perovskite surface. (b) Possible passivation mechanism of the MHyI layer for the perovskite film. (c) XRD patterns of perovskite films before and after MHyI treatment. (d) UV–vis absorption spectra, (e) Tauc Plots of the control and MHyI-treated perovskite films.

To examine the crystal structure and crystallinity of the perovskite films before and after MHyI passivation, X-ray diffraction (XRD) plots were carried out. As shown in Figure 1c, full width at half maximum (FWHM) values for the control and MHyI-treated films at (110) crystal planes were 0.144 and 0.149, respectively, suggesting almost the same crystallinity. Post-treatment with MHyI resulted in a slight decrease in the peak at 12.7° for lead iodide and a slight increase in the peak at 14.04° for perovskite (110) crystal plane, demonstrating that MHyI could react with PbI₂. Notably, no additional peaks were found at low reflecting angles ($2\theta < 10^\circ$) in the passivated films, implying our post-treatment approach does not form low-dimensional perovskite. UV–vis spectra of these perovskite films were collected in Figure 1d to explore the role of the MHyI layer on light absorption. We observed similar absorbance behavior for films without and with a passivation layer. The passivation layer with a negligible thickness affords a minimal effect on the light

absorption. The corresponding Tauc plots (Figure 1e) show that the band-gap of two perovskite films seems almost identical, equal to 1.57 eV, indicating that the post-treatment of MHyI does not noticeably affect the band-gap of the perovskite.

The surface morphology of the perovskite films, with and without MHyI post-treatment, was investigated using top-view SEM. Figure 2a,b revealed dense grains and zero pinholes in the perovskite films. Moreover, we determined that the impact of MHyI surface passivators on grain size and surface morphology was negligible. According to the atomic force microscopy (AFM) pictures (Figure 2c,d), the root-mean-square (RMS) roughness values of the MHyI-treated films were 41.82 nm, lower than those of the control film (47.84 nm). A lower RMS suggests that MHyI fills the perovskite's grain boundaries to some extent [44], producing a smoother surface. Furthermore, a smoother surface enables effective hole extraction by improving contact between the perovskite film and the hole transport layer.



Figure 2. Top-view SEM images of perovskite films (**a**) before and (**b**) after MHyI-treated. (**c**,**d**) AFM images of control and MHyI-treated perovskite films. (**e**) Steady-state PL. (**f**) TRPL spectra of the control and target perovskite films deposited on glass substrates.

To study the non-radiative recombination behavior and charge carrier dynamics in the perovskite films without and with MHyI treatment, we monitored the steady-state photoluminescence (PL) and time-resolved PL (TRPL) decay of the perovskite films. As shown in Figure 2e, the PL intensity of MHyI-treated perovskite film is significantly enhanced compared with the control film, indicating very suppressed non-radiative recombination centers due to the effective passivation by MHyI molecules on the surface. The impact of defect passivation was further confirmed by the PL peak of the perovskite film, which blue-shifted from 794 to 788 nm after being treated with MHyI [45]. Moreover, as shown in Figure 2f, the TRPL data were fitted with a bi-exponential decay function (see the detailed fitted parameters in Table S1, Supplementary Material) as Equation (1):

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + I_0,$$
(1)

where I_0 is the decay constant; A_1 and A_2 are decay amplitudes; τ_1 is the fast decay process caused by photogenerated free-carrier bimolecular recombination; and τ_2 is the slow decay process caused by the trap-assisted recombination [46]. The average lifetime

increased remarkably from 118.09 ns (control) to 346.37 ns (MHyI-treated). This indicates that the defect-assisted recombination is significantly reduced, which reduces charge carrier trapping in the MHyI-treated perovskite film [47]. PL and TRPL results suggest that the defects on the surface of perovskite films are greatly diminished, contributing to the opto-electronic performance and long-term stability of the devices.

We further performed space charge-limited current (SCLC) measurements to quantitatively estimate the trap density (N_t) of the films. For this purpose, we fabricated electrondominated devices (FTO/SnO₂/perovskite/MHyI/PCBM/BCP/Ag) and characterized them in the dark (Figure 3a). The N_t was calculated by Equation (2) [48]:

$$N_{\rm t} = \frac{2\varepsilon\varepsilon_0 V_{\rm TFL}}{{\rm e}L^2},\tag{2}$$

where ε is the relative dielectric constant of the perovskite layer (46.9 is used here) [49]; ε_0 is the vacuum permittivity; e is the elementary charge; V_{TFL} is the trap-filled limit voltage; and L is the thickness of the perovskite layer (750 nm is used here according to the cross-section SEM in Figure S1). The V_{TFL} of the MHyI-treated sample was slightly reduced to 0.14 V, compared to a relatively high V_{TFL} of 0.22 V for the control sample. The corresponding trap density values were calculated to be 2.03×10^{15} and 1.28×10^{15} cm⁻³, respectively. The reduction in trap density suggests that MHyI can effectively passivate existing surface defects, thereby suppressing non-radiative carrier recombination. Subsequently, the dependence of Voc on light intensity was further investigated. When the ideal factor of n is close to 1, Shockley–Read–Hall (SRH) recombination is substantially suppressed [50]. From the curves in Figure 3b, the ideality factor of the optimized device decreases from 2.15 to 1.68 $K_{\rm B}T/q$. Obviously, optimized devices show effective trap-state passivation, suggesting that the charge recombination is successfully suppressed and consequently improves the Voc [51]. In addition, the capacitance–voltage response (C–V) and Mott–Schottky analysis of control and MHyI-treated devices were performed in Figure 3c. The built-in electric field can be estimated by Equation (3):

$$\frac{1}{C^2} = \frac{2(V_{\rm bi} - V)}{\varepsilon_0 \varepsilon N A^2 q},$$
(3)

where *A*, ε , ε_0 , *V*, *C*, and *N* correspond to the device area, the relative dielectric constant of perovskite, vacuum permittivity, the applied bias, the capacitance, and the carrier concentration, respectively [52,53]. The V_{bi} value for the control device was determined to be 0.88 V, increasing to 0.94 V for the MHyI-treated device. The significantly improved V_{bi} value implies that the driving force for the charge separation is enhanced, and carrier recombination is inhibited, which is favorable for achieving a higher Voc.

To elucidate the carrier transport dynamics and recombination process in PSCs, electrochemical impedance spectroscopy (EIS) was conducted further to unravel the passivation effect of MHyI on perovskite films. Figure 3d shows the Nyquist plots of devices taken with devices in the dark. The fitted parameters from the equivalent circuit are summarized in Table S2. The higher recombination resistance of the optimized device corresponds to more efficient hole transport and extraction and reflects a lower interfacial recombination rate, which is better for improving the performance of PSCs, especially Voc and FF [54]. In the case of MhyI-treated devices, the charge recombination resistance (R_{rec}) of 39.32 K Ω is greater than that of the control device (21.89 K Ω), providing strong evidence of reduced non-radiative recombination losses at the perovskite/Spiro-OMeTAD interface. For a more detailed investigation of the charge-carrier behavior in the PSCs with MhyI, transient photovoltage (TPV) and transient photocurrent (TPC) measurements were fitted using a single exponential decay model. As shown in Figure 3e, the charge recombination times (τ_r) of the control and MHyI-treated devices were 9.98 µs and 23.52 µs, respectively. A much longer τ_r occurred, indicating the efficiently suppressed charge recombination after MHyI passivation [42]. In addition, as shown in Figure 3f, the charge collection times (τ_c) of the device decreased from 4.75 µs (control) and 3.62 µs (MHyI), indicating a facilitated

charge collection process in the MHyI-treated device [27]. The EIS results and the TPV and TPC measurements show good agreement. Hence, it could be suggested that a suitably thin MHyI passivation layer can efficiently inhibit interfacial charge recombination while enhancing interfacial contacts and thereby facilitating the ability to transport photogenerated carriers from the perovskite layer.



Figure 3. (a) SCLC measurements for the electron-only devices. (b) V_{OC} versus light intensity for the PSCs with and without MhyI. (c) Mott–Schottky curves for different PSCs. (d) EIS measurements of PSCs and the corresponding equivalent circuits. Normalized TPV (e) and TPC (f) decay curves for the solar cells with and without MHyI.

The photovoltaic performances of PSCs were measured under standard AM 1.5G solar illumination, and the current density-voltage (J-V) curves, including both the reverse and forward scans for the champion devices, were recorded in Figure 4a. Meanwhile, the corresponding photovoltaic parameters for the devices are summarized in Table 1. It can be seen that the Jsc remains almost the same, while the Voc substantially increases compared with the control device. Our results demonstrate a promising performance based on the comprehensive data collected from devices treated with various ammonium salts (Figure S6, Supplementary Material). Furthermore, the hysteresis index (HI = ($PCE_{Reverse}$ -PCE_{Forward})/PCE_{Reverse}) decreased from 6.29% for the control device to 0.94% for the MHyItreated device. These improvements in photovoltaic performance are inextricably linked to a reduction in surface defects due to the coordination between the MHyI and the dangling bonds at the crystal surface, which could suppress charge recombination and reduce interface charge accumulation [55]. The concentration of MHyI in the isopropanol solution was optimized in advance (Figure S2, Supplementary Material). The PCEs of devices increased when gradually increasing the concentration of MHyI (from 0 to 1 mg/mL) in an isopropanol solution. Then, the lessening of PCEs could be seen beyond the concentration of 1 mg/mL, which may be due to excessive molecular accumulation on the surface hindering carrier transport. Thus, optimized results were obtained when the concentration of MHyI was 1 mg/mL. To evaluate the reproducibility of MHyI treatment on the performance of devices, we counted the PCE values of 20 devices (Figure 4b). The MHyI-treated devices showed higher PCEs and narrower distributions, indicating better performance

and reproducibility. The external quantum efficiency (EQE) spectrum of the device is shown in Figure 4c. The combined Jsc values of control and MHyI-treated devices were 24.21 and 24.39 mA/cm², respectively, which matched well with the Jsc values measured by the J-V curve. Meanwhile, the band-gap of two absorber types was determined to be 1.57 eV by the dEQE/d λ [56] (Figure S3, Supplementary Material), consistent with the results from the Tauc plots.



Figure 4. (a) The typical *J*–*V* curve of the devices with MHyI and without MHyI treatment under one-sun (100 mW/cm²) conditions. The reverse and forward scans are both included. (b) Histogram of solar cell efficiencies for 20 samples. (c) EQE and integrated *J*sc of control and MHyI-modified devices. (d) Long-term stability of the unencapsulated devices aged under room temperature and 30% relative humidity. (e) Continuous MPP tracking for the encapsulated control and MHyI-treated cells under 1 sun in ambient air.

Device	Scanning Mode	Jsc (mA/cm ²)	Voc (V)	FF (%)	PCE (%)
Control	Reverse	25.47	1.09	78.95	21.91
	Forward	25.42	1.05	76.94	20.53
MHyI-treated	Reverse	25.36	1.14	80.24	23.19
	Forward	25.48	1.12	80.51	22.97

Table 1. Static figures of merit for the control and MHyI-treated devices.

Then, we tested and compared the long-term storage and light stability of the control and MHyI-treated devices. As shown in Figure 4d, we tested the shelf stability of corresponding PSCs in an ambient environment of 30% relative humidity without encapsulation. It was found that the PSCs with MHyI remained above 88% of their initial efficiency, whereas the control devices fell below 56% of their initial efficiency. The steady-state power outputs (SPO) of the control and MHyI-treated devices were measured under the bias at the maximum power point (*V*max). As shown in Figure S4, the stabilized PCEs were recorded as 20.26% and 21.58% for control and MHyI-treated devices, respectively, with an active area of 0.1 cm² for 300 s. Moreover, we checked the operational stability of encapsulated PSCs by performing maximum power point (MPP) tracking in the ambient (25 $^{\circ}$ C and 30–40% relative humidity) for 200 h (Figure 4e). It was observed that the MHyI-treated devices retained 57% of their initial PCE, while the control devices retained only 39% of their initial PCE. This also indicates that the MHyI-treated devices have better stability than the control devices. Obviously, employing MHyI is an effective way to passivate trap defects and enhance device stability because the positively charged cations (MHy+) coordinate with the dangling halide bonds on the crystal surface and passivates defects arising from vacancies of halide ions or organic cations on the perovskite films.

Finally, we investigated the water contact angle of control and MHyI-treated perovskite films to obtain more direct evidence of enhanced device stability. As shown in Figure S5, the MHyI-treated film shows a larger water contact angle of 57.37° compared to 53.46° for the control sample, so the more hydrophobic surface efficiently prevents water penetration into the perovskite, thus suppressing the perovskite degradation.

3. Materials and Methods

3.1. Materials

The SnO₂ colloid precursor (tin (IV) oxide, 15% in H₂O colloidal dispersion) was purchased from Alfa Aesar, Shanghai, China. Lead iodide (PbI₂) was purchased from TCI, Shanghai, China. Bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), isopropanol (IPA), chlorobenzene (CB) and acetonitrile (ACN) were purchased from Sigma–Aldrich, Shanghai, China. Methylhydrazine (MHy, 40% in water, Shanxi Yulong Chemical Co., Ltd.), Shuozhou, China. Formamidinium iodide (FAI) and methylammonium bromide (MABr) were synthesized by reacting formamidine acetate (Aladdin, Shanghai, China) and hydroiodic acid (55.0–58.0 wt% in H₂O, Aladdin, Shanghai, China), methylamine (30–33 wt% in ethanol, Aladdin, Shanghai, China), and hydrobromic acid (48 wt% in H₂O, Aladdin, Shanghai, China), respectively. Methylammonium chloride (MACI) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. Spiro-OMeTAD was purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd., Shenzhen, China.

3.2. Synthesis of MHyI

The synthesis procedure was based on our previously reported method [43]. First, 20 mL of the MHy solution in the round bottom flask was cooled to 0 $^{\circ}$ C in an ice bath. Next, 26.5 mL of HI solution was slowly added, and the reaction mixture was allowed to warm up to room temperature for over 2 h. After removing all volatiles with a rotary evaporator, the solid was recrystallized and washed with ethanol and diethyl ether until the color turned white. Finally, the MHyI precipitate was dried in a vacuum oven at 50 $^{\circ}$ C for 24 h.

3.3. Device Fabrication

The laser-patterned FTO substrates were cleaned with detergent solution, deionized water, acetone, and anhydrous ethanol in sequence, each with ultrasonication for 15 min. Then, after plasma treatment of the substrate for 10 min, a thin layer of SnO₂ nanoparticle film (diluted to 2.67% from a 15% stock solution) was spin-coated on the FTO substrate at 3000 rpm for 30 s and annealed at 150 °C in ambient air for 30 min. The films were then treated with plasma for 10 min before being transferred to a glove box. To prepare the precursor solution for the perovskite layer, a 1.45 M solution of PbI₂ (DMF/DMSO, v:v = 9:1) and an organic ammonium salt solution (FAI: MABr: MACl = 75 mg: 7.5 mg: 9 mg in 1 mL IPA) were stirred for 6 h at room temperature. After filtering through a 0.22 µm filter, 50 µL of the PbI₂ solution was spin-coated onto the deposited SnO₂ layer at 1500 rpm for 30 s and immediately transferred to a hot plate and annealed at 60 °C for 1 min. After cooling, another 100 µL of the organic ammonium salt solution was transferred to a hot plate in ambient air (35–40% relative humidity) and annealed at 150 °C for 15 min. For

surface passivation treatment, 50 μ L of the MHyI solution (1 mg/mL in IPA) was deposited on the cooled perovskite film at 4000 rpm for 30 s without further annealing in an N₂-filled glove box. A stock solution of 72.3 mg Spiro-OMeTAD in 1 mL CB with 28.8 μ L tBP and 17.5 μ L Li-TFSI solution (520 mg Li-TFSI powder in 1 mL ACN) was then loaded onto the perovskite films at 3000 rpm for 30 s. Finally, the gold electrode (80 nm) was thermally evaporated in a high vacuum to complete the fabrication of the device.

3.4. Characterizations

X-ray diffraction (XRD) patterns were collected using an X-ray diffractometer (Rigaku Miniflex 600, Rigaku, Tokyo, Japan) with Cu K α radiation. The absorption spectra were measured with a UV-vis spectrometer (Agilent Cary 5000, Agilent, Santa Clara, CA, USA). The surface morphology was characterized by field-emission scanning electron microscopy (FE-SEM, Apreo S, Thermo Fisher, Franklin, MA, USA) and atomic force microscopy (AFM, Multi-mode-8 J, Bruker, Billerica, MA, USA). Steady-state photoluminescence (PL) spectral emission was measured using a monochromatized Xe lamp excited by a 460 nm light source. At the same time, time-resolved photoluminescence (TRPL) decay was performed using a fluorescence spectrophotometer (FLS980, Edinburgh Instruments, Edinburgh, Livingston, UK) with a picosecond pulsed diode laser excitation source at a wavelength of 460 nm. Space charge-limited current (SCLC) measurement was performed on a Keithley 2401 (Keithley, Salem, OR, USA) source meter ranging from 0 to 3 V. Voc vs. light intensity, Mott–Schottky, electrochemical impedance spectroscopy (EIS), transient photovoltage (TPV), and transient photocurrent (TPC) decay measurements were carried out using an electrochemical workstation (Zennium Zahner, Kronach, Germany). The photovoltaic performance of the devices was measured with a Keithley 2401 source meter using a solar simulator (SS-F5-3A, Enlitech, Taiwan) at 100 mW/cm² illumination (AM 1.5 G) equipped with a calibrated Si reference cell (SRC-2020, Enlitech, Taiwan). The J–V curves of the PSCs were measured in reverse scan (from 1.2 to -0.1 V) or forward scan (from -0.1 to 1.2 V) modes at a scan rate of 100 mV/s. External quantum efficiencies (EQE) were measured by an Enli Technology EQE measurement system (Enlitech, Taiwan). Maximum power point (MPP) tracking was measured under a white light-emitting diode lamp and was performed in ambient air. Contact angle measurements were performed on a DataPhysics OCA-20 (DataPhysics, Filderstadt, Germany) with a drop of ultrapure water (0.05 mL).

4. Conclusions

To sum up, we have demonstrated the effectiveness of small molecular ammonium salt in passivating the perovskite surface, significantly reducing defects and suppressing non-radiative recombination losses. This may be ascribed to the interaction between MHyI and the dangling bonds on the crystal surface. This passivation strategy has led to an impressive power conversion efficiency (PCE) of 23.19% and an improved open-circuit voltage (*V*oc) from 1.09 to 1.14 V. Additionally, the hydrophobic MHyI layer has served as a water-resistant layer on the perovskite films, successfully protecting them from water damage and enhancing the long-term operation stability of PSCs. Overall, this study provides an efficient method, utilizing small molecular ammonium salt to improve the efficiency and stability of PSCs.

Supplementary Materials: The following supporting information can be downloaded at https:// www.mdpi.com/article/10.3390/inorganics11040168/s1: Figure S1: Cross-sectional SEM image of the target device; Figure S2: *J–V* curves of the PSCs treated with different concentrations of MHyI solution; Figure S3: Determination of the absorption of the perovskite absorber by the differential of EQE curves; Figure S4: The SPO of the control and MHyI-treated devices. Figure S5: The static water contact angle of the standard film and MHyI-treated film. Figure S6: Comparative performance of devices with different post-treatment ammonium salts; Table S1: Fitted results of TRPL curves of perovskite films with and without MHyI-modified using a bi-exponential decay equation; Table S2: Fitting parameters of the EIS measurement based on control and MHyI-treated perovskite solar cells. **Author Contributions:** Conceptualization, C.H., J.C. and P.G.; data collection, C.H. and Z.Z.; data interpretation, C.H., Z.Z., J.C. and P.G.; writing—original draft preparation, C.H.; writing—review and editing, J.C. and P.G.; supervision, J.C. and P.G. All authors have read and agreed to the published version of the manuscript.

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