Enhanced Moisture and Water Resistance in Inverted Perovskite Solar Cells by Poly(3-hexylthiophene)

Jian Xiong, Yifang Qi, Qiqi Zhang, Dream Box, Kira Williams, James Tatum, Priyanka Das, Nihar Ranjan Pradhan, and Qilin Dai*



ABSTRACT: Poor stability of the perovskite solar cells (PSCs) under humid conditions is always an obstacle to the practical applications of PSCs. Here, a polymer-based strategy to enhance moisture and water resistance of PSCs is presented. Poly(3-hexylthiophene) (P3HT) is used as an additive to be introduced to the electron transport layer (ETL) of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) to study moisture and water resistance of the ETL film and the stability of the device under the humid conditions. The results show that a small amount of P3HT does not result in decreased power conversion efficiency (PCE), and it can improve the aggregation of PCBM, leading to enhanced moisture and water resistance of ETL. The device based on the P3HT/PCBM ratio of 1:30 exhibits a high PCE of 20.84%, with a



short-circuit current (J_{sc}) of 23.27 mA/cm², an open-circuit voltage (V_{oc}) of 1.10 V, and a fill factor of 81.47%, which is one of the high performances of the inverted PSCs based on the CH₃NH₃PbI₃ (MAPbI₃) material. The PCE of the device modified with P3HT can maintain 85.03% for 720 h [relative humidity (RH) 20%], 77.90% for 48 h (60 RH %), 44.31% for 1 h (90 RH %), and 17.43% for 30 min (in water) of its initial PCE value, while the control device can only maintain about 69.41, 47.10, 9.00, and 0.18% of its initial PCE under the same exposure conditions. This work proposes a strategy by using low-surface-energy conjugated polymers to improve the moisture and water resistance of the inverted PSCs.

KEYWORDS: inverted perovskite solar cells, moisture resistance, water resistance, stability, polymer

INTRODUCTION

Organometallic halide materials have become promising materials in the optoelectronic field because of their excellent optical and electrical properties.¹⁻³ Especially, perovskite solar cells (PSCs) have attracted great attention, and the power conversion efficiency (PCE) record is boosted to over 25%, which is comparable with that of commercial silicon (Si) solar cells.⁴ Despite the superior photovoltaic performance and the low cost of the perovskite materials, the stability of the PSCs is still the main issue to prevent it from moving forward to the practical application.^{5,6} Thus, the degradation of the PSCs has been extensively investigated, and the degradation caused by moisture,^{7,8} light,⁹ heat,¹⁰ and oxygen¹¹ has been confirmed. Among these factors, moisture is the main factor leading to device degradation.^{6,7} Moisture exposure can directly accelerate the perovskite materials to decompose to methylamine halide salt and lead halide, which may destroy the crystal structure, morphology, and optical and electrical properties of the perovskite films, resulting in poor performance of the PSCs.⁶ Therefore, it is very necessary to enhance the moisture and water resistance of PSCs toward outdoor applications, typically under harsh humidity conditions, for example, rain.¹²

Conventional structure (n-i-p) PSCs usually use a triarylamine-based hole transport layer (HTL), 2,2',7,7'-

tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD)^{13,14} and poly[bis(4-phenyl)(2,4,6-124 trimethylphenyl)amine] (PTAA),¹⁵ which directly contact with air. Some dopants, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), and tert-butylpyridine are required to enhance the mobility of the HTL because of the lower hole mobility of HTL materials.^{13,14,16} However, these dopants absorb moisture from the air and destroy the structure of the perovskite films, leading to the degradation of PSCs.¹⁷⁻¹⁹ Meanwhile, the high-temperature treatment in conventional structure PSCs is not conducive to its mass production.² Although the PCE of the inverted PSCs is not as high as those of conventional planar devices, it shows great potential in the preparation of stable PSCs without hygroscopic additives.²¹ In addition, the inverted PSCs also exhibit attractive merits of a low-temperature process and negligible hysteresis.²² Strategies to further enhance the PCE and improve the moisture stability

Received: November 23, 2020 Accepted: January 7, 2021 Published: January 15, 2021







Figure 1. (a) XRD patterns and SEM images (inset) of the MAPbI₃ films. (b) UV–vis absorption spectrum of MAPbI₃. (c) PCE of the inverted PSCs versus the concentration of PTAA. (d) J-V curve of the best inverted PSCs based on the structure of ITO/PTAA/MAPbI₃/PCBM/BCP/Ag. (e) UV–vis absorption spectra of the MAPbI₃ film at the initial state and exposure to air for 2 h (90 RH %). The inset shows the photograph of the perovskite film when the water drops on it. (f) J-V curves of the PSCs at the initial state and exposure to air (90 RH %) for 1 h.

of inverted PSCs are urgently needed for the commercial application of PSCs.

In inverted PSCs, phenyl-C₆₁-butyric acid methyl ester (PCBM) is widely used as an acceptor and a high PCE of over 20% has been achieved based on the MAPbI₃/PCBM heterojunction because of its high electron mobility and good solubility in the non-polar solvent.²³⁻²⁵ Unfortunately, it is difficult for PCBM to form a flat and dense film upon perovskite films due to its low viscosity and solubility in the organic solvents.^{23,26} The perovskite films cannot be fully covered due to the poor film-forming properties of PCBM, leading to the direct contact between Ag and perovskite films, which may result in recombination loss and quick interface degradation.^{23,27} Furthermore, the rough film with pinholes may provide pathways for moisture to erode the perovskite films. In order to overcome this issue, C₆₀ and bathocuproine (BCP) are usually inserted between PCBM and Ag to reduce the recombination loss and prevent direct contact between Ag and perovskite films.²⁸⁻³⁰ Recently, Tan et al. confirmed that this strategy cannot efficiently solve this problem.³¹ Except this, some additives are also introduced to improve the morphology of PCBM, such as Triton X-100,²³ poly(methyl methacrylate),³² and 1,8-diiodooctane,³³ while the impact of most of the additives on the stability of the devices is still unclear.

Although the traditional encapsulation technologies using glass plates can efficiently protect the moisture, it cannot be compatible with the flexible devices.³⁴ Recently, the Al₂O₃ packing layer prepared by an atom-layer-deposition strategy has been compatible with flexible devices, and it has achieved great progress in improving the moisture resistance of the perovskite films.^{35,36} However, the high cost will limit its commercial applications.³⁴ Moreover, there are also major challenges for the complete isolation of water and oxygen packaging,³⁷ and the traditional encapsulation technologies cannot completely overcome the interface degradation due to ion migration or element diffusion between layers. Thus, enhancing the moisture resistance of the device by interlayers is of great significance to the production and application of PSCs. Here, the efficient inverted PSCs based on the structure

of ITO/PTAA/MAPbI₃/PCBM/BCP/Ag are fabricated by optimizing the thickness of undoped PTAA. The PCE of 20.10% is achieved for the control devices. A strategy to enhance moisture and water resistance by the polymer poly(3hexylthiophene) (P3HT) is presented. P3HT is used as an additive to be doped into PCBM films. The moisture resistance of the electron transport layer (ETL) film and the stability of the device in the different humid environments are both improved. The inverted PSCs based on P3HT exhibit a high PCE of 20.84%, which is slightly higher than that of the control devices. The PCE can maintain 85.03% [20 relative humidity (RH) % for 720 h], 77.90% (60 RH % for 48 h), 44.31% (90 RH % for 1 h), and 17.43% (in water for 30 min), while the control devices only can maintain about 69.41, 47.10, 9.00, and 0.18%. This work provides a facile way by using low-surfaceenergy conjugated polymers to improve the moisture and water resistance of the inverted PSCs.

EXPERIMENT

Materials. Lead(II)iodide (PbI₂, 98%) and BCP (>98%) were purchased from TCI America. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl) amine] (PTAA, >99%) was obtained from Solaris Chem. (Canada). Methylammonium iodide (99.5%) was purchased from Xi'an Polymer Light Technology Corp. (China). P3HT (4002-E) was purchased from Rieke Metals Inc. (USA). PCBM (>99%), *N*,*N*-dimethylformamide (Super Dry, DMF), chlorobenzene (anhydrous, CB), and isopropyl alcohol (anhydrous, IPA) were obtained from Sigma-Aldrich (USA). Dimethyl sulfoxide (DMSO) and Ag wires (99.9%) were purchased from Alfa Aesar (USA).

Device Fabrication. In this work, the inverted PSCs with the structure of ITO/PTAA/MAPbI₃/P3HT/PCBM/BCP/Ag were fabricated. For the preparation of the devices, the ITO glasses were used as the substrates and ultrasonically cleaned in acetone, detergents, distilled water, and IPA for 15 min sequentially. After that, they were dried with hot air and treated with UV-ozone for 15 min. Then, the ITO substrates were transferred into the glovebox (both H_2O and $O_2 < 0.1$ ppm). The HTL was prepared by spin-coating of the PTAA solution (1-5 mg/mL in CB) onto the patterned ITO substrates and dried on a hot plate at 100 °C for 10 min. The thickness of HTL is controlled by the concentration of the PTAA solution. Then, the perovskite films are prepared by the anti-solvent method. First, the perovskite precursor (154 mg of CH₃NH₃I, 446 mg of PbI₂, 1 mL of DMF, and 71 µL of DMSO) was spin-coated on the ITO/PTAA substrate at 4000 rpm for 30 s. A CB solvent (100 μ L) was quickly dropped onto the center of the substrate at the proper time. After that, the film was immediately transferred to a hotplate and annealed at 100 °C for 10 min. In order to prepare the ETL, the P3HT/ PCBM (weight ratio of P3HT/PCBM = 30:1) solution (2 wt % in CB) was spin-coated onto the MAPbI₃ layer at 1500 rpm for 30 s. Then, the PCBM films were annealed at 90 °C for 30 min. For the control devices, the PCBM (2 wt % in CB) was also prepared with the same procedure. Then, the BCP solution (0.5 mg/mL in IPA) was spin-coated on PCBM at 4000 rpm for 30 s. Finally, a bar-like defined Ag electrode (100 nm) by mask was deposited by thermal evaporation under a vacuum of $\sim 4 \times 10^{-4}$ Pa.

Characterization. The micromorphology of films was characterized by atomic force microscopy (AFM) (Veeco Dimension 3100 AFM) and using a field emission scanning electron microscope (LYR3 XMH, Tescan). The crystallinity

of the perovskite film was examined using an X-ray diffraction (XRD) system (Rigaku, MiniFlex 600). UV–visible (UV–vis) absorption spectra were recorded using a UV–vis spectrophotometer (Cary 60, Agilent, USA). The current–voltage characteristics were measured using a Keithley 2400 sourcemeter (Keithley Instruments Inc.) under AM 1.5G simulated sunlight (100 mW/cm²) (Newport). The light intensity was calibrated using a Si solar cell (91150V, Newport). The incident photon-to-current efficiency (IPCE) spectrum was recorded using the quantum efficiency measurement system (IQE-200B, Newport). To test the stability of the PSC exposure on a special humidity environment, the environmental chamber (Electro-Tech Systems, 503, USA) was used to control the moisture and atmosphere of the devices.

RESULTS AND DISCUSSION

Figure 1a is the XRD pattern of the MAPbI₃ film. Three main XRD peaks located at 14.06, 28.40, and 31.79° and other small peaks at 19.94, 23.45, 2.44, 34.96, 40.58, and 43.21° are observed, which correspond to the different crystalline planes of the cubic perovskite structure as labeled in the figure.³⁸ The dense and continuous film with stone-like perovskite grains is formed upon the PTAA layer (inset of Figure 1a), which is similar to the results reported by Tang et al.³⁹ The UV-vis absorption spectrum of the MAPbI₃ film upon the ITO/PTAA substrate shows an absorption onset at 780 nm (Figure 1b), indicating that the MAPbI₃ band gap is 1.59 eV, which is consistent with our previous report.¹⁷ The investigations of the corresponding inverted PSCs with different thicknesses of PTAA are carried out. The thickness of PTAA is very difficult to measure because of a very thin thickness; thus, we directly label the concentration of the PTAA solution to distinguish the thickness of the PTAA layer.

The performance of the PSCs is significantly influenced by the concentration of PTAA. The typical J-V curves of the inverted PSCs with different PTAA concentrations are shown in Figure S1, and all parameters are summarized in Table S1. The PCE values are summarized in Figure 1c. All parameters $[V_{oc}$ fill factor (FF), J_{sc} and PCE] increase as the PTAA concentration increases from 1 to 3 mg/mL and then decrease as the PTAA concentration further increases to 5 mg/mL. The PSCs based on 3 mg/mL PTAA exhibits the highest average PCE of 19.52%, with a J_{sc} of 23.23 mA/cm², a V_{oc} of 1.08 V, and an FF of 78.16%. The champion device shows a PCE of 20.10%, with a J_{sc} of 23.50 mA/cm², a V_{oc} of 1.08 V, and an FF of 79.34% (Figure 1d).

It is known that MAPbI₃ is very sensitive to water. When the water is dropped onto the surface of the films, the color of MAPbI₃ immediately changes to yellow, which indicates that MAPbI₃ decomposes to PbI₂ and some other compositions.⁴⁰ Figure 1e shows the UV-vis absorption spectra of the MAPbI₃ films at the initial state and exposure to air (90 RH %) for 2 h. It is clear that the absorption intensity between 350 nm and 545 nm decreases after film exposure to air (90 RH %), which is attributed to the MAPbI₃ film decomposition after the moisture exposure. The decomposed film absorption baseline is slightly higher than the initial film, suggesting the high roughness of the decomposed film. According to previous reports, the perovskite material decomposition leads to serious interface degradation and zero PCE.^{8,41} Figure 1f shows the *J*-V curves of the device at the initial state and exposure to air (90 RH %) for 1 h. The PCE quickly decays from 19.46 to

1817



Figure 2. (a) Photographs of ITO/PTAA/MAPbI₃/PCBM/BCP and ITO/PTAA/MAPbI₃/P3HT:PCBM/BCP films with a water drop aging for 1 min. (b) UV–vis absorption spectra of the MAPbI₃ films with different coating layers at the initial state and exposure to air (90 RH %) for 2 h. (c.d) AFM images of the surface of ITO/PTAA/MAPbI₃/PCBM and ITO/PTAA/MAPbI₃/P3HT/PCBM films, respectively. (e) Schematic diagram of the improved moisture resistance of the perovskite films by P3HT.



Figure 3. (a) Summary of the PCE of the devices based on different P3HT/PCBM ratios. (b) J-V curves of the best device with P3HT under reverse and forward scan directions.

3.15%, and all the photovoltaic parameters decrease when exposed to air (90 RH %) for 1 h. In addition, even though PCBM/BCP is coated upon MAPbI₃, the water can still easily penetrate the entire perovskite film (left of Figure 2a). Thus, it is urgently needed to develop a method to improve the stability of the inverted PSCs by preventing the devices from moisture.

P3HT with lower surface energy has been confirmed with excellent hydrophobic properties.⁴² The excellent moisture resistance of the PSCs using P3HT as HTL has been reported in conventional planar PSCs.⁴³ Here, we introduce P3HT in inverted PSCs via doping in the PCBM ETL to further study the influence of P3HT on the device performance under severe humidity conditions, such as 90 RH % and even soaking in water. Figure 2a shows the photographs of ITO/PTAA/MAPbI₃/PCBM/BCP and ITO/PTAA/MAPbI₃/P3HT/PCBM/BCP films with a water drop on the surface of the films aging for 1 min. The color of MAPbI₃ coated by P3HT/PCBM/BCP does not show any obvious change (right of Figure 2a) compared to the yellow color of ITO/PTAA/MAPbI₃/PCBM/BCP (left of Figure 2a). The results show

that the P3HT introduction can efficiently prevent water diffusion into the perovskite layer.

To investigate the impact of P3HT on the moisture resistance of the ETL, the MAPbI₃/PCBM and MAPbI₃/ P3HT/PCBM films are exposed to air (90 RH %) for 2 h to test their absorption properties (Figure 2b). The absorption intensity between 400 and 545 nm decreases for both films. The film without P3HT shows more decrease compared to the film with P3HT, indicating the improved moisture resistance. AFM measurements are carried out to further investigate the reasons for this improvement. Figure 2c shows the AFM images of the ITO/PTAA/MAPbI₃/PCBM surface. From Figure 2c, some large aggregation clusters are formed in the PCBM film because of its low viscosity and solubility in a nonpolar solvent, CB, which results in a poor film formation upon the MAPbI₃ film. After P3HT introduction, the root-meansquare (rms) value of the ETL reduces from 6.14 to 1.59 nm, and the aggregation clusters are eliminated. Therefore, the P3HT molecules distribute throughout the PCBM film as well as the ETL layer, which prevents the perovskite film from water diffusion (Figure 2e).

In order to explore the influence of P3HT on device performance, the inverted PSCs based on the structure of ITO/PTAA/MAPbI₃/P3HT/PCBM/BCP/Ag are fabricated with different weight ratios of P3HT/PCBM. Figure 3a shows the PCE as a function of weight ratio of P3HT/PCBM, and the average performance parameters derived from six devices are listed in Table 1. The average values of PCE of the devices

Table 1. he Summary of the Performance Parameters of the Inverted PSCs Based on Different Weight Ratios of P3HT/ PCBM

P3HT/PCBM	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
1:10	22.62	1.04	70.20	16.46
1:20	22.88	1.06	73.71	17.78
1:30	23.63	1.07	76.78	19.43
1:40	23.53	1.07	76.74	19.43
1:50	23.41	1.08	76.36	19.31
0:100	23.23	1.08	78.16	19.52

do not show evident vibration when the ratio of P3HT/PCBM is below 1:30 and the PCE values maintain over 19%. However, when the P3HT/PCBM is over 1:20, the decreased PCE is observed. Excess P3HT in ETL may change the electrical properties of the ETL, leading to a decreased PCE. Thus, we fix the P3HT/PCBM ratio to be 1:30 to maintain the high performance of the devices. Figure 3b shows the J-V curves of the best device with P3HT measured with different scan directions. The high PCE of 20.84%, with a J_{sc} of 23.27 mA/cm², a V_{oc} of 1.10 V, and an FF of 81.47%, is achieved under the reverse scan. The PCE of 20.56% can be achieved based on the forward scan, which shows very negligible hysteresis. The IPCE spectrum of the best device is shown in Figure S2, and the maximum value of 92% is achieved. The

PCE can maintain about 93% of its initial value after continuous light illumination under 100 mW/cm² for 1000 s (Figure S3). The above results show that the device with P3HT shows good photovoltaic performance.

To evaluate the impact of P3HT doping on the moisture resistance of PSCs, the stability of the devices exposed to air is investigated. The PCE of the devices with P3HT shows slow decay when exposed to air at the humidity of 20 RH %. The average PCE can maintain about 85.03% of its initial value, while the control devices can only maintain 69.41% of its initial value (Figure 4a) after 720 h exposure. The control devices show faster decay after 360 h exposure compared to the devices with P3HT. This may result from the fact that the H_2O molecules are completely diffused into the perovskite layer after 360 h exposure, leading to serious damage to the perovskite materials in control devices. The $V_{\rm oc}$ and FF of the control devices show evident degradation after 720 h exposure and decrease by 8.80 and 14.39%, respectively, while the $V_{\rm oc}$ and FF of the devices with P3HT decrease by 1.69 and 5.35%, respectively. In addition, the J_{sc} of the control devices quickly decays after 120 h exposure and can only maintain 86.94% of its initial value after 720 h. After P3HT introduction, the J_{sc} almost exhibits no degradation at first 360 h exposure and can maintain 91.41% of its initial value after 720 h exposure. These results show that P3HT can efficiently act as a shield layer to protect the perovskite from moisture-induced decay. The improved device stability may also be related to the more stable interface of PCBM/perovskite due to P3HT introduction.44

To further confirm the effect of P3HT introduction on the enhancement of the moisture resistance of PSCs, the devices are exposed to air with severe humid environments (60 and 90 RH %). In the 60 RH % environment, the PCE of the control devices drops by 52.90% after exposure for 48 h, while the



Figure 4. Degradation of normalized performance parameters of (a) PCE, (b) J_{sc} (c) V_{oc} and (d) FF during 720 h in the air (20 RH %) for the PSC devices without and with P3HT. Each average performance parameter point is derived from six devices.

www.acsaem.org



Figure 5. Degradation of normalized performance parameters of (a) PCE, (b) J_{scr} (c) V_{ocr} and (d) FF during 48 h in the air (60 RH %) for the PSC devices without and with P3HT introduction. Each average performance parameter point is derived from six devices. (e,f) PCE of PSCs with and without P3HT at the initial state and exposed in the air (90 RH %) for 1 h, respectively. The PCE is derived from six devices.



Figure 6. J-V curves of (a) control devices and (b) devices with P3HT in water.

PCE drops by 22.10% of its initial value with P3HT introduction (Figure 5a). The quick decay of control devices can be attributed to all the quick decreased parameters during exposure (Figure 5b-d). When P3HT is doped into PCBM, the V_{oc} , J_{sc} and FF decrease by 2.34, 9.85, and 11.29%, respectively, and the V_{oc} , J_{sc} and FF of the control devices decrease by 16.85, 15.99, and 32.53%, respectively. Furthermore, the attenuation behavior of the device in a humidity environment of 90 RH % is also studied. Figure 5e,f shows the

PCE of the PSCs with and without P3HT at the initial state and exposed to air (90 RH %) for 1 h, and the detailed performance parameters are listed in Table S2. The PCE of the control device drops quickly in just 1 h. The average PCE decreases by 91.00% from 18.01 to 1.62%, while the J_{sc} , V_{oc} , and FF decrease by 55.92, 75.00, and 48.57%, respectively. P3HT can slow down this decay, and the PCE, J_{sc} , V_{oc} , and FF decrease by 55.69, 10.28, 22.94, and 36.54%, respectively.

These results further confirm that the introduction of P3HT enhances the moisture resistance of the devices.

In order to test the water resistance of the devices, the devices with and without P3HT are soaked in water directly. The attenuation video of the two devices in water is shown in the Supporting Information (Movie S1). From Movie S1, the backside of the control devices immediately shows a color change when the devices are put in water for 1 min. This result confirms that the water can easily penetrate the device through the PCBM/BCP layer, leading to the decomposition of the perovskite active layer. In the device with P3HT, there are no visible color changes in water for 1 min. Figure 6 shows the evolution of the I-V curves of the control device and the device with P3HT in water for 30 min, and the performance parameters are summarized in Table S3. The PCE of the control device decreases by 43.25% (from 17.11 to 9.71%) after 1 min in water and completely loses its efficiency after 30 min (Figure 6a and Table S3). For the device with P3HT, the PCE exhibits a slower decay rate with the PCE decay by 39.96% (from 18.77 to 11.27%) after 1 min in water (Figure 6b and Table S3). After 30 min in water, the PCE of devices with P3HT is 3.26%.

According to the above statements, P3HT introduction can improve the moisture and water resistance of the inverted PSCs due to its lower surface energy and improved PCBM film-forming properties. This work confirms the feasibility of the donor polymer doping PCBM to improve the moisture and water resistance of the inverted PSCs. More suitable materials and related mechanisms need to be investigated in the future.

CONCLUSIONS

In summary, P3HT is doped into the PCBM film to enhance the moisture and water resistance of the ETL and the corresponding devices. P3HT introduction can improve the surface morphology of PCBM and improve the moisture and water resistance of the ETL. The performance and stability of the device with P3HT under various humid conditions are investigated. The devices with P3HT/PCBM (30:1) exhibit a PCE of 20.84%, which belongs to high PCE in the inverted PSCs based on MAPbI₃ as an active layer. The PCE of the devices with P3HT can maintain 85.03% (20 RH % for 720 h), 77.90% (60 RH % for 48 h), 44.31% (90 RH % for 1 h), and 17.43% (in water for 30 min) of their initial values, while the control devices can only maintain about 69.41, 47.10, 9.00, and 0.18% of their initial values under the same exposure conditions, respectively. This research provides a facile way to use low-surface-energy conjugated polymers to improve the moisture and water resistance of the inverted PSCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c02941.

Typical J-V curves of the inverted PSCs based on different PTAA concentrations; summary of the performance parameters of the inverted PSCs based on different PTAA concentrations; summary of the performance parameters of PSCs with and without P3HT at the initial state and exposed to air (90 RH %) for 1 h; and performance parameters of the control PSCs and the devices with P3HT in water for 30 min (PDF) Stability of the inverted PSCs in water (MP4)

AUTHOR INFORMATION

Corresponding Author

Qilin Dai – Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States; orcid.org/0000-0001-8680-4306; Email: qilin.dai@jsums.edu

Authors

- Jian Xiong Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- Yifang Qi Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- Qiqi Zhang Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- **Dream Box** Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- Kira Williams Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- James Tatum Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- Priyanka Das Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States
- Nihar Ranjan Pradhan Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, Mississippi 39217, United States; Orcid.org/0000-0002-3912-4233

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.0c02941

Author Contributions

J.X. conceived the experiments and wrote the original draft. Y.Q., Q.Z., D.B., K.W., J.M.T., P.D., and N.P. characterized the performance of the films and materials. Q.D. contributed to writing, review, and editing of the manuscript.

Funding

This material is based on work supported by the National Science Foundation under grant no. 1757220. K.W. and J.T. are supported by National Science Foundation Research Initiation Award: Novel Perovskite Solar Cells Based on Interface Manipulation (award #1900047). Q.Z. is supported by NSF-PREM grant #DMR-1826886.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation under grant no. 1757220. K.W. and J.T. are supported by National Science Foundation Research Initiation Award: Novel Perovskite Solar Cells Based on Interface Manipulation (award #1900047). Q.Z. is supported by NSF-PREM grant #DMR-1826886.

www.acsaem.org

REFERENCES

(1) He, Z.; Xiong, J.; Dai, Q.; Yang, B.; Zhang, J.; Xiao, S. Highperformance inverted perovskite solar cells using 4-diaminomethylbenzoic as a passivant. *Nanoscale* **2020**, *12*, 6767–6775.

(2) Miao, J.; Zhang, F. Recent progress on highly sensitive perovskite photodetectors. J. Mater. Chem. C 2019, 7, 1741–1791.

(3) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical management for colorful, efficient, and stable inorganic organic hybrid nanostructured solar cells. *Nano Lett.* **2013**, *13*, 1764–1769.

(4) NREL. Best research-cell efficiencies. 2020, https://www.nrel.gov/pv/cell-efficiency.html.

(5) Ji, G.; Wang, Y.; Luo, Q.; Han, K.; Xie, M.; Zhang, L.; Wu, N.; Lin, J.; Xiao, S.; Li, Y.-Q.; Luo, L.-Q.; Ma, C.-Q. Fully coated semitransparent organic solar cells with a doctor-blade-coated composite anode buffer layer of phosphomolybdic acid and PEDOT:PSS and a spray-coated silver nanowire top electrode. ACS Appl. Mater. Interfaces 2018, 10, 943–954.

(6) Kim, G.-W.; Kang, G.; Malekshahi Byranvand, M.; Lee, G.-Y.; Park, T. Gradated mixed hole transport layer in a perovskite solar cell: improving moisture stability and efficiency. *ACS Appl. Mater. Interfaces* **201**7, *9*, 27720–27726.

(7) Wang, Q.; Chen, B.; Liu, Y.; Deng, Y.; Bai, Y.; Dong, Q.; Huang, J. Scaling behavior of moisture-induced grain degradation in polycrystalline hybrid perovskite thin films. *Energy Environ. Sci.* **2017**, *10*, 516–522.

(8) Xiong, J.; Yang, B.; Cao, C.; Wu, R.; Huang, Y.; Sun, J.; Zhang, J.; Liu, C.; Tao, S.; Gao, Y.; Yang, J. Interface degradation of perovskite solar cells and its modification using an annealing-free TiO_2 NPs layer. Org. Electron. **2016**, 30, 30–35.

(9) Leijtens, T.; Eperon, G. E.; Pathak, S.; Abate, A.; Lee, M. M.; Snaith, H. J. Overcoming ultraviolet light instability of sensitized TiO_2 with meso-superstructured organometal tri-halide perovskite solar cells. *Nat. Commun.* **2013**, *4*, 2885.

(10) Dualeh, A.; Gao, P.; Seok, S. I.; Nazeeruddin, M. K.; Grätzel, M. Thermal behavior of methylammonium lead-trihalide perovskite photovoltaic light harvesters. *Chem. Mater.* **2014**, *26*, 6160–6164.

(11) Pearson, A. J.; Eperon, G. E.; Hopkinson, P. E.; Habisreutinger, S. N.; Wang, J. T. W.; Snaith, H. J.; Greenham, N. C. Oxygen degradation in mesoporous Al₂O₃/CH₃NH₃PbI_{3-x}Cl_x perovskite solar cells: kinetics and mechanisms. *Adv. Energy Mater.* **2016**, *6*, 1600014.

(12) Idígoras, J.; Aparicio, F. J.; Contreras-Bernal, L.; Ramos-Terrón, S.; Alcaire, M.; Sánchez-Valencia, J. R.; Borras, A.; Barranco, Á.; Anta, J. A. Enhancing moisture and water resistance in perovskite solar cells by encapsulation with ultrathin plasma polymers. *ACS Appl. Mater. Interfaces* **2018**, *10*, 11587–11594.

(13) Qin, P.-L.; Yang, G.; Ren, Z.-w.; Cheung, S. H.; So, S. K.; Chen, L.; Hao, J.; Hou, J.; Li, G. Stable and efficient organo-metal halide hybrid perovskite solar cells via π -conjugated lewis base polymer induced trap passivation and charge extraction. *Adv. Mater.* **2018**, *30*, 1706126.

(14) Xiong, J.; Eedugurala, N.; Qi, Y.; Liu, W.; Benasco, A. R.; Zhang, Q.; Morgan, S. E.; Blanton, M. D.; Azoulay, J. D.; Dai, Q. Efficient and stable perovskite solar cells via shortwave infrared polymer passivation. *Sol. Energy Mater. Sol. Cells* **2021**, *220*, 110862.

(15) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. Compositional engineering of perovskite materials for highperformance solar cells. *Nature* **2015**, *517*, 476–480.

(16) Jiang, J.; Wang, Q.; Jin, Z.; Zhang, X.; Lei, J.; Bin, H.; Zhang, Z.-G.; Li, Y.; Liu, S. F. Polymer doping for high-efficiency perovskite solar cells with improved moisture stability. *Adv. Energy Mater.* **2017**, *8*, 1701757.

(17) Zhao, Q.; Wu, R.; Zhang, Z.; Xiong, J.; He, Z.; Fan, B.; Dai, Z.; Yang, B.; Xue, X.; Cai, P.; Zhan, S.; Zhang, X.; Zhang, J. Achieving efficient inverted planar perovskite solar cells with nondoped PTAA as a hole transport layer. *Org. Electron.* **2019**, *71*, 106–112.

(18) Kim, G.-W.; Kang, G.; Kim, J.; Lee, G.-Y.; Kim, H. I.; Pyeon, L.; Lee, J.; Park, T. Dopant-free polymeric hole transport materials for highly efficient and stable perovskite solar cells. *Energy Environ. Sci.* **2016**, 9, 2326–2333.

(19) Yang, S.; Zhao, H.; Wu, M.; Yuan, S.; Han, Y.; Liu, Z.; Guo, K.; Liu, S.; Yang, S.; Zhao, H.; Yuan, S.; Han, Y.; Liu, Z.; Liu, S.; Wu, M.; Guo, K. Highly efficient and stable planar CsPbI₂Br perovskite solar cell with a new sensitive-dopant-free hole transport layer obtained via an effective surface passivation. *Sol. Energy Mater. Sol. Cells* **2019**, *201*, 110052.

(20) Yin, G.; Ma, J.; Jiang, H.; Li, J.; Yang, D.; Gao, F.; Zeng, J.; Liu, Z.; Liu, S. F. Enhancing efficiency and stability of perovskite solar cells through Nb-doping of TiO_2 at low temperature. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10752–10758.

(21) Wu, S.; Zhang, J.; Li, Z.; Liu, D.; Qin, M.; Cheung, S. H.; Lu, X.; Lei, D.; So, S. K.; Zhu, Z.; Jen, A. K.-Y. Modulation of defects and interfaces through alkylammonium interlayer for efficient inverted perovskite solar cells. *Joule* **2020**, *4*, 1248–1262.

(22) Luo, D.; Yang, W.; Wang, Z.; Sadhanala, A.; Hu, Q.; Su, R.; Shivanna, R.; Trindade, G. F.; Watts, J. F.; Xu, Z.; Liu, T.; Chen, K.; Ye, F.; Wu, P.; Zhao, L.; Wu, J.; Tu, Y.; Zhang, Y.; Yang, X.; Zhang, W.; Friend, R. H.; Gong, Q.; Snaith, H. J.; Zhu, R. Enhanced photovoltage for inverted planar heterojunction perovskite solar cells. *Science* **2018**, *360*, 1442–1446.

(23) Lee, K.; Ryu, J.; Yu, H.; Yun, J.; Lee, J.; Jang, J. Enhanced efficiency and air-stability of NiO_X based perovskite solar cells via PCBM electron transport layer modification with Triton X-100. *Nanoscale* **2017**, *9*, 16249.

(24) Yang, S.; Dai, J.; Yu, Z.; Shao, Y.; Zhou, Y.; Xiao, X.; Zeng, X. C.; Huang, J. Tailoring passivation molecular structures for extremely small open-circuit voltage loss in perovskite solar cells. *J. Am. Chem. Soc.* **2019**, *141*, 5781–5787.

(25) Chen, W.; Wang, Y.; Pang, G.; Koh, C. W.; Djurišić, A. B.; Wu, Y.; Tu, B.; Liu, F. z.; Chen, R.; Woo, H. Y.; Guo, X.; He, Z. Conjugated polymer-assisted grainboundary passivation for efficient inverted planar perovskite solar cells. *Adv. Funct. Mater.* **2019**, *29*, 1808855.

(26) Xia, F.; Wu, Q.; Zhou, P.; Li, Y.; Chen, X.; Liu, Q.; Zhu, J.; Dai, S.; Lu, Y.; Yang, S. Efficiency enhancement of inverted structure perovskite solar cells via oleamide doping of PCBM electron transport layer. *ACS Appl. Mater. Interfaces* **2015**, *7*, 13659–13665.

(27) Fan, B.; He, Z.; Xiong, J.; Zhao, Q.; Dai, Z.; Yang, B.; Xue, X.; Cai, P.; Zhan, S.; Tong, S.; Yang, J.; Zhang, J. The efficient and non-hysteresis inverted non-fullerenes/CH₃NH₃PbI₃ planar solar cells. *Sol. Energy* **2019**, *189*, 307.

(28) Wang, Q.; Shao, Y.; Dong, Q.; Xiao, Z.; Yuan, Y.; Huang, J. Large fill-factor bilayer iodine perovskite solar cells fabricated by a low-temperature solution-process. *Energy Environ. Sci.* **2014**, *7*, 2359–2365.

(29) Shao, Y.; Xiao, Z.; Bi, C.; Yuan, Y.; Huang, J. Origin and elimination of photocurrent hysteresis by fullerene passivation in CH₃NH₃PbI₃ planar heterojunction solar cells. *Nat. Commun.* **2014**, *5*, 5784.

(30) Lin, Y.; Shen, L.; Dai, J.; Deng, Y.; Wu, Y.; Bai, Y.; Zheng, X.; Wang, J.; Fang, Y.; Wei, H.; Ma, W.; Zeng, X. C.; Zhan, X.; Huang, J. π -conjugated lewis base: efficient trap-passivation and charge-extraction for hybrid perovskite solar cells. *Adv. Mater.* **2017**, *29*, 1604545.

(31) Tan, D.; Zhang, X.; Liu, X.; Zhang, H.; Ma, D. Stability enhancement of inverted perovskite solar cells using LiF in electron transport layer. *Org. Electron.* **2020**, *80*, 105613.

(32) Chen, K.; Hu, Q.; Liu, T.; Zhao, L.; Luo, D.; Wu, J.; Zhang, Y.; Zhang, W.; Liu, F.; Russell, T. P.; Zhu, R.; Gong, Q. Charge-carrier balance for highly efficient inverted planar heterojunction perovskite solar cells. *Adv. Mater.* **2016**, *28*, 10718–10724.

(33) Liu, Z.; Lee, E.-C. Solvent engineering of the electron transport layer using 1,8-diiodooctane for improving the performance of perovskite solar cells. *Org. Electron.* **2015**, *24*, 101–105.

(34) Corsini, F.; Griffini, G. Recent progress in encapsulation strategies to enhance the stability of organometal halide perovskite solar cells. *J. Phys. Energy* **2020**, *2*, 031002.

Article

(35) Lv, Y.; Xu, P.; Ren, G.; Chen, F.; Nan, H.; Liu, R.; Wang, D.; Tan, X.; Liu, X.; Zhang, H.; Chen, Z.-K. Low-temperature atomic layer deposition of metal oxide layers for perovskite solar cells with high efficiency and stability under harsh environmental conditions. *ACS Appl. Mater. Interfaces* **2018**, *10*, 23928–23937.

(36) Seo, S.; Jeong, S.; Park, H.; Shin, H.; Park, N.-G. Atomic layer deposition for efficient and stable perovskite solar cells. *Chem. Commun.* **2019**, *55*, 2403–2416.

(37) Han, Y.; Meyer, S.; Dkhissi, Y.; Weber, K.; Pringle, J. M.; Bach, U.; Spiccia, L.; Cheng, Y.-B. Degradation observations of encapsulated planar CH₃NH₃PbI₃ perovskite solar cells at high temperatures and humidity. *J. Mater. Chem. A* **2015**, *3*, 8139–8147.

(38) Xu, G.; Xue, R.; Chen, W.; Zhang, J.; Zhang, M.; Chen, H.; Cui, C.; Li, H.; Li, Y.; Li, Y. New strategy for two-step sequential deposition: incorporation of hydrophilic fullerene in second precursor for high-performance p-i-n planar perovskite solar cells. *Adv. Energy Mater.* **2018**, *8*, 1703054.

(39) Tang, G.; You, P.; Tai, Q.; Wu, R.; Yan, F. Performance enhancement of perovskite solar cells induced by lead acetate as an additive. *Sol. RRL* **2018**, *2*, 180006.

(40) Huang, J.; Tan, S.; Lund, P. D.; Zhou, H. Impact of H_2O on organic–inorganic hybrid perovskite solar cells. *Energy Environ. Sci.* 2017, 10, 2284–2311.

(41) Li, J.; Dong, Q.; Li, N.; Wang, L. Direct evidence of ion diffusion for the silver-electrode-induced thermal degradation of inverted perovskite solar cells. *Adv. Energy Mater.* **2017**, *7*, 1602922.

(42) Widjonarko, N. E.; Schulz, P.; Parilla, P. A.; Perkins, C. L.; Ndione, P. F.; Sigdel, A. K.; Olson, D. C.; Ginley, D. S.; Kahn, A.; Toney, M. F.; Berry, J. J. Impact of hole transport layer surface properties on the morphology of a polymer-fullerene bulk heterojunction. *Adv. Energy Mater.* **2014**, *4*, 1301879.

(43) Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T.-Y.; Noh, J. H.; Seo, J. Efficient, stable and scalable perovskite solar cells using poly(3-hexylthiophene). *Nature* **2019**, *567*, 511–515. (44) Turak, A. Interfacial degradation in organic optoelectronics. *RSC Adv.* **2013**, *3*, 6188–6225.