Improving stability and efficiency of perovskite solar cells via a cerotic acid interfacial layer

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ABSTRACT

Organic-inorganic hybrid perovskite solar cells (PSCs) are one of the most promising technologies in the field of photovoltaics due to its high-power conversion efficiency (PCE) and easy fabrication process. However, its moisture stability has posed a crucial hurdle towards its further commercialization. In this paper, we have introduced an interfacial layer, cerotic acid (CA), inspired from the honeycomb, to modify the surface of perovskite films, thus improving moisture stability. The PCE of the CA modified PSCs retained ~81% of its initial value after aging 30 days at a relative humidity of 35%, in sharp contrast with the pristine devices, only 19% retention of its initial value. In addition, the C=O group in CA was found effectively passivate the unsaturated Pb2O2 and Pb2O2−2 from entering perovskite layer. And no obvious decay was observed even as their PSCs were stored under 76% RH over 4 weeks [18]. Moreover, interface engineering could modify the physical state of the surface, such as defects and traps, to inhibit charge recombination at perovskite/charge transport layer interfaces [14].

Despite various materials having been developed as interfacial materials, the common natural materials are always the better choice due to the low-cost, highly stable as well as eco-friendly properties [9,7,19,20]. For instance, Subhabrata et al. found that titanium dioxide functionalized with the bacteriorhodopsin protein could accelerate the electron injection from excitons produced in the perovskite layer [21]. Yang et al. studied three small molecules-theophylline, caffeine, and theobromine, effective way to not only enhance stability but also tune the energetic band gap and simultaneously give a better PCE. Nevertheless, ionic crystal is the intrinsic nature of perovskite, and the degradation process has merely been delayed, not eliminated. While interface engineering is an effective way to cut off the moisture [17]. For example, Abdelmageed et al. have spin-coated oleic acid (OA) on top of CH3NH3PbI3 perovskite to prevent H2O and O2 from entering perovskite layer. And no obvious PCE decay was observed even as their PSCs were stored under 76% RH over 4 weeks [18]. Moreover, interface engineering could modify the physical state of the surface, such as defects and traps, to inhibit charge recombination at perovskite/charge transport layer interfaces [14].

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs), with the power conversion efficiency (PCE) increasing from 3.8% in 2009 to more than 25% in 2020 [1-4], have demonstrated tremendous promise for research and commercialization [5-7]. However, it still suffers critical issues in stability arising from moisture, heat, oxygen, illumination etc [8-11], and should be solved in future large-scale industrialization. Especially, when exposed to the high-humidity air, these organic-inorganic hybrid perovskites will degrade into PbI3 and PbI2, thus forming a mixed cation and anion system to stabilize the crystal structure of perovskite [16]. This has proved to be an

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and found that the interaction between oxygen atoms in caffeine and lead ions in perovskite materials could significantly improve the thermal stability of perovskite solar cells [22].

While inspired by the stable honeycomb (Fig. 1a), its one extract, cerotic acid (CA), is a 26-carbon long-chain saturated fatty acid with the chemical formula CH_{30}COOH (Fig. 1b), which is also an important hydrophobic component of beeswax [23]. Herein, we have applied CA as an interfacial layer on top of CH_{3NH2PbI3} and found that the hydrophobic CA coating significantly increased the water contact angle of halide perovskite thin films. Bare change has been observed even after 30 days of aging in a dark humid environment (RH ~35%). Furthermore, through Lewis base-acid interactions between the C=O group of CA and incoordination Pb sites in CH_{3NH2PbI3} films, CA has effectively passivated the halide perovskite films by reducing the defects. In the end, the CA modified PSCs exhibited a better photovoltaic performance, PCE of 20.57%, as well as an enhanced stability, maintained 80% of its original efficiency after storing one month at 35% RH without encapsulation. Therefore, this work has demonstrated a simple and potentially low-cost and eco-friendly approach to stabilize perovskite films, which is possibly applicable to other perovskite-based devices.

2. Results and discussion

Fig. 1c illustrates the deposition process of CA interfacial layer. Due to the poor solubility, a hot dynamic spin-coating of CA solution was conducted, followed by thermal annealing at 100°C for 1 min. And from Fig. 1d, an obvious increase of the water contact angle was observed on CA modified perovskite (~110°) compared with that of bare perovskite (~56°), exhibiting the possible function of CA as moisture resisting layer. The concentration of the CA solution was then optimized from 1 to 1.2 and 4 mg mL\(^{-1}\) in chlorobenzene (CB). Their morphologies on top of perovskite films were studied by scanning electron microscope (SEM) and atomic force microscopy (AFM). As shown in Fig. 1e-h, when 2 mg mL\(^{-1}\) CA was introduced, the modified sample shows a compact and uniform morphology with a lowest root-mean-square (RMS), ca 10.58 nm (Fig. S1). This will be beneficial for a better charge transport efficiency along with the confirmation in Fig. S2 [24]. And as indicated in the UV–vis absorption spectra in Fig. S3, the introduction of CA has no influence on the absorption of the perovskite films.

Fig. 2a shows the current density-voltage (J-V) characteristics of the PSCs with (w/) and without (w/o) CA interfacial layer. The corresponding photovoltaic parameters are listed in Table S1. With CA interfacial layer, the optimal device exhibits a PCE of 20.57% under reverse scan with an open circuit voltage (V\(_{OC}\)) of 1.14 V, short circuit current density (J\(_{SC}\)) of 23.2 mA cm\(^{-2}\), and fill factor (FF) of 0.77. Compared with the control device (PCE of 19.65%, V\(_{OC}\) of 1.13 V, J\(_{SC}\) of 22.29 mA cm\(^{-2}\), and FF of 0.78), it can be seen that the slightly improved PCE was mainly coming from the improved J\(_{SC}\). The external quantum efficiency (EQE) and integrated current density as a function of wavelength are shown in Fig. 2b, where no prominent difference was observed. The calculated integrated current density was 20.71 and 21.28 mA cm\(^{-2}\), agreeing well with the J\(_{SC}\) from J-V curves. Further, we have ascertained these values by tracking the PCE and J\(_{SC}\) at the maximum power point, giving a steady state PCE of 19.91% and 20.01% and J\(_{SC}\) of 21.85 and 22.10 mA cm\(^{-2}\) for the control and CA modified PSCs, respectively (Fig. 2c).

Besides, the reproducibility of the devices was examined by fabricating 13 independent devices. The statistical distributions are summarized in Fig. 2d and Table S2. The average V\(_{OC}\)-J\(_{SC}\)-FF and PCE based on PSCs w/o CA are 1.126 ± 0.013 V, 22.682 ± 0.901 mA cm\(^{-2}\), 0.751 ± 0.029 and 19.373 ± 0.773 %, respectively. While after inserting CA, the corresponding values are slightly improved to 1.126 ± 0.010 V, 22.827 ± 0.655 mA cm\(^{-2}\), 0.754 ± 0.020 and 19.607 ± 0.748 %, accordingly. The smaller standard deviation also illustrates an enhanced reproducibility of PSCs.

The charge transport efficiency was then characterized by the steady-state and time-resolved photoluminescence (PL and TRPL). In Fig. 3a, the PL intensity of perovskite film (peak at ~780 nm) is slightly higher when CA was deposited, which could possibly be due to the reduced non-radiative decay rate induced by the CA mitigated trap density [9]. This is also confirmed by the TRPL in Fig. 3b, where a biexponential decay was found, and the fast decay time (τ\(_f\)) standing for the trap-assisted recombination was determined to be 53.88 and 167.82 ns for bare and CA modified perovskite film, respectively. Thus, it is considered that the deposition of CA is beneficial for the trap passivation. In addition, the charge transfer efficiency at the perovskite/spiro-OMeTAD interfaces was also compared by conducting the electrochemical impedance spectroscopy (EIS) as shown in Fig. 3c [25]. From Nyquist plots as well as the equivalent circuit, the insertion of CA was found to impart a smaller charge transfer resistance (R\(_t\)) on
the devices, 27.0 vs 29.9 Ω, suggesting a more efficient hole extraction and suppressed charge recombination processes.

To identify the species of trap state, we have conducted the X-ray photoelectron spectra (XPS). In Fig. 3d, the peaks of Pb 4f$^{7/2}$ and Pb 4f$^{5/2}$ in pristine perovskite were located at binding energy of 138.43 and 143.25 eV. While with the help of CA, their binding energies moved to 138.13 and 142.98 eV. Such a negative shift (~0.3 eV) is probably attributed to the coordinating interaction between the under-coordinated Pb$^{2+}$ within the perovskite and the lone pair electrons within the electron-rich carboxyl (C=O) groups in CA [26]. The trap density was then evaluated by the space-charge-limited current (SCLC) based on a device structure of ITO/PEDOT:PSS/perovskite/spiro-OMeTAD/Au in dark (Fig. 3e). The density of trap states ($n_t$) is calculated from the equation $n_t = \frac{2\varepsilon\varepsilon_0L}{eL^2}$, where $L$, $\varepsilon$, $\varepsilon_0$, and $e$ are the device thickness, permittivity, vacuum permittivity, and electron charge, respectively.

Fig. 2. Photovoltaic performances. (a) Current-density–voltage ($J$–$V$) curves of the optimal device based on perovskite w/o or w/ CA modification. (b) EQE spectra of the PSCs. (c) Stabilized maximum power point current density and PCE. (d) The statistic PCEs of PSCs w/o and w/ CA modified.

Fig. 3. (a) Steady-state PL spectra of perovskite films ($\lambda_{ex} = 460$ nm). (b) Time-resolved PL spectra (TRPL) of perovskite films. All films were deposited on FTO glass substrates. (c) Nyquist plot of PSCs based on pristine and CA modified perovskite. (d) X-ray photoelectron spectroscopy (XPS) spectra of Pb 4f orbital of CH$_3$NH$_3$PbI$_3$ and CA modified CH$_3$NH$_3$PbI$_3$. (e) SCLC measurement of hole-only devices, inset shows the device structure. (f) Light intensity dependence of $V_{OC}$ for PSCs w/ or w/o CA.
\[ \varepsilon, \epsilon_0, \text{ and } \epsilon \text{ are the thickness of the perovskite film, dielectric constant of the material, permittivity of vacuum, and electronic charge, respectively [27,28]. The determined } n, \text{ for the devices based on CH}_3\text{NH}_3\text{PbI}_3 \text{ w/o and w/ CA are } 2.16 \times 10^{16} \text{ and } 1.57 \times 10^{16} \text{, separately. And the relationship between } V_{OC} \text{ and light intensity was also examined. In the formula: } V_{OC} = n k T \ln(T)/q + C, C \text{ is a constant, } k \text{ represents the Boltzmann constant, } T \text{ is absolute temperature, } q \text{ is the elementary charge, } n \text{ is an ideal factor related to monomolecular recombination [29]. As illustrated in Fig. 3f, the ideal factor } n \text{ was determined to be } -1.35 \text{ and } 0.91 \text{ for perovskite films w/o and w/ CA, respectively, suggesting the less trap-assisted recombination when modified with CA. Hence, it is concluded that CA passivated the Pb defects at the perovskite surface, and facilitated the charge transport and charge transfer processes, leading to an enhanced photovoltaic performance [30].}

Due to the hydrophobicity of CA, we have further investigated the moisture stability of the perovskite films. By comparing the X-ray diffraction (XRD) pattern of the fresh and aged perovskite films stored at relative humidity (RH) of 85% over one day, except the characteristic peaks of orthorhombic crystal structure at 2\(\theta\) = 14.15\(^\circ\), 24.47\(^\circ\), 28.50\(^\circ\), 31.90\(^\circ\), and 43.05\(^\circ\), assigned to the (110), (202), (220), (310), and (330) lattice planes, respectively [31], a hexagonal PbI\(_2\) peak (20 = 12.6\(^\circ\)) was observed for the CA-free perovskite film (Fig. 4a). By contrast, the CA modified perovskite thin film maintained its original XRD pattern with dark brownish color [28].

Subsequently, the stability of PSCs against the high-humidity moisture was evaluated by aging the prepared devices in dark at relative humidity (RH) of 85%. After one day, the device with CA modifier has maintained 80% of the original performance, in sharp contrast with the CA-free devices, decreased to merely 50%, as demonstrated by the PCE distribution in Fig. 4b.

Besides, the drip test on the surface of these two kinds of perovskite films was also recorded. As shown in Fig. 4c, the pristine perovskite immediately degraded to PbI\(_2\) when contacted with water, while the water drop slip off the surface of CA-modified perovskite film without obvious damage. Consequently, the introduction of CA on top of perovskite films may induce the formation of a moisture-proof layer and facilitate the inner encapsulation [26], leading to a long-term preservation of the perovskite film even in high-humidity environment.

While at a comparably low RH 35% condition, the control film degraded to PbI\(_2\) within the first week (Fig. 5a). However, the CA modified perovskite film shows bare degradation even after 4 weeks (Fig. 5b). These phenomena further ascertain the enhanced stability of perovskite films by CA treatment. Afterwards, Fig. 5c shows the corresponding long-term stability of the PSCs without encapsulation. Similarly, the devices with CA treatment maintain 81% of their initial efficiency after aging in a humid environment for 30 days, from 19.72% to 15.94%, whereas the PCE of devices based on pristine perovskite films drop to 3.87%.

Furthermore, Fig. S4 shows the thermal stability of the corresponding perovskite solar cells under heating stress (80\(^\circ\)C) at N\(_2\) atmosphere. The PCE of the devices without any encapsulation shows a 26% loss for the CA modified devices exhibiting slightly better thermal stability, while a31% loss was observed for the control device. We thereby attribute this improvement to the suppression of MA\(^+\) motion with intermolecular interactions, i.e., Lewis adducts and hydrogen bonding between CA and MA\(^+\).

3. Conclusion

In summary, we have demonstrated a moisture-stability strategy for perovskite films by introducing a natural material CA from honeycomb as an interfacial layer. The moisture stability of the device has been greatly improved, that the CA-modified device retained 80.83% of its original PCE when exposed to atmosphere at RH 35% over 30 days. Meanwhile, the carboxyl group of CA can interact with the perovskite and passivate the unsaturated Pb sites, thus exhibiting a lower defect density and increased carrier lifetime than pristine perovskite thin films. Thereby, CA as an easily obtainable natural material presents its potential application for the highly efficient and stable perovskite solar cells.
4. Experimental section

4.1. Material

Methylammonium iodide (MAI, 99.5%) was purchased from Xi’an Polymer Light Technology Co. Ltd. Lead iodide (PbI₂, 99.9%) and 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) were purchased from Yingkou Libra New Energy Technology Co., Ltd. Cerotic acid (CA, 98%) was purchased from Yua-nye Bio-Technology Co., Ltd. Bis(trifluoromethanesulfonyl)imide (Li-TFSI), tert-butylpyridine (t-BP), dimethyl formamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.8%), acetonitrile and butanol were purchased from Sigma–Aldrich. SnCl₂ • 2H₂O was purchased from Alfa Aesar. Besides, fluorine-doped tin oxide glasses (FTO, 7 Ω/sq) were purchased from Yingkou Libra New Energy Technology Co. Ltd, and silver (Ag) were obtained from commercial sources with high purity (>99.9%). All materials were stored under inert nitrogen atmosphere inside a glovebox.

4.2. Preparation of colloidal SnO₂ nanocrystalline solution

SnO₂ nanocrystalline solution was prepared by our previous method [31].

4.3. Perovskite solar cells fabrication

Substrate preparation. FTO-coated glasses were ultrasonically cleaned with detergent, deionized water, and isopropanol in sequence for 15 minutes. All substrates were further cleaned by UV-Ozone for 10 min before depositing SnO₂. The SnO₂ were prepared by spin-coating SnO₂ NCs solution on FTO substrates at 3000 rpm for 30 s, followed by thermal annealing at 150°C for 30 minutes. After cooling down, the substrates were immediately transferred in a nitrogen atmosphere glove box for the deposition of the perovskite films after cleaned by UV-Ozone for 10 minutes.

4.3.1. Perovskite precursor solution and film preparation

Typically, 922 mg of PbI₂ and 320 mg of MAI were dissolved in 1.6 ml mixed solvent of DMF and DMSO (7:3 V/V), stirring for 12 h before use. The MAPbI₃ precursor solution was spin-coated on FTO/SnO₂ substrates at 500 rpm for 3 s and 4000 rpm for 30 s, with dripping of 420 µL chlorobenzene onto the rotating perovskite film at the beginning of 8th s of the second spin-coating step. Then the films were annealed at 100 °C for 10 minutes. For CA treatment, 50 µL of CA in chlorobenzene with various concentrations were dynamic spin-coated on to the as-prepared perovskite films at 5000 rpm for 30 s. Then, the treated perovskite films were heated at 100°C for 1 min.

4.3.2. Hole transporting layer and the top electrode

After the perovskite annealing the substrates were cooled down for few minutes and the HTM solution was spun at 3000 rpm for 30 s. The solutions were prepared as follows: 72.3 mg spiro-OMeTAD, 17.5 µL Li-TFSI solution (520 mg in 1 ml acetonitrile), 30 µL t-BP was dissolved in 1 ml chlorobenzene. Finally, 100 nm of Ag electrode was thermally evaporated on top of the device at a speed of 0.8 Å.

4.4. Characterisation

Morphology: The morphology and microstructures were investigated by scanning electron microscope (SEM) (ZEISS Ultra-55) and

Fig. 5. Ambient stability. XRD patterns of the aged perovskite films (a) w/o and (b) w/ CA stored in a desiccator with RH of 35% ± 5%. (c) Ambient stability of the devices without encapsulation.
atomic force microscopy (AFM) (Asylum Research, Cypher).

PL and TRPL: Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were measured by fluorescence spectrometer (HTACHF F-5000) exited at 530 nm and PLS980 with excitation wavelength of 450 nm.

UV-Vis: The absorption spectra of ESLs deposited on quartz and the transmittance of glass/perovskite were measured by UV-vis spectrometer (Shanghai Jinhua Technology Instrument Co., Ltd. UV-759) in a wavelength range at 300-800 nm.

J-V characteristics: The current–voltage (J-V) curves of the non-encapsulated solar cells were measured by Keithley 2400 in a glovebox. The transmittance of glass/perovskite were measured by UV-vis spectrom with a xenon light source. A potentiostat.

External Quantum Efficiency (EQE) measurement: The EQE measurements of solar photovoltaic devices were carried out using EQE system (Newport 66902), consist of a xenon light source, a monochromator, and a potentiostat.

EIS characterization: The electrochemical impedance spectroscopy (EIS) measurements were performed on the Zahner Zennium electrochemical workstation with an illumination of 300 W m\(^{-2}\) light source. A 5 mV ac-sinusoidal signal source was employed over a frequency range of 0.1 Hz to 1.0 MHz in dark.

SCLC measurement: Space charge limited current (SCLC) characteristics of the devices were measured using a Keithley 2400 in the dark. The devices configuration follows: FTO/SnO\(_2\)/Perovskite/PCBM/Au for electron-only devices. The perovskite films were made by the same protocols used in solar cell fabrication. PCBM films were prepared by spin-coated PCBM solution on perovskite at 3000 rpm for 30 s.

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Supplementary materials


References

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