Thiamine additive engineering enables improved film formation towards high efficiency and moisture stability in perovskite solar cells

Peng Zhang, Fengren Cao^{*}, Wei Tian and Liang Li^{*}

ABSTRACT Perovskite solar cells (PSCs) attract widespread research interest due to their exceptional properties. However, the instability of the perovskite layer, especially the moisture instability, and existing defects seriously restrict the performance and limit the development of PSCs towards commercialization. Herein, we fabricate moisture-stable and efficient PSCs by incorporating a thiamine (THM) additive into a lead iodide (PbI₂) precursor using a two-step spin-coating method. This strategy enables a better interaction between the THM additive and PbI₂. Then, a higher energy barrier is produced when the material reacts with A-site cations to form perovskite crystals, resulting in larger grains and better-quality perovskite films. Through optimization of the concentration of the THM additive, the optimal perovskite achieves improved moisture stability and decreased trap states; thus, the corresponding unencapsulated devices achieve a remarkable power conversion efficiency (PCE) of 21.40% and maintain >92% of their initial PCE after 180 h in ambient air (~50% humidity). The excellent performance is mainly attributed to the fact that THM promotes crystal growth and passivates defects in perovskite films.

Keywords: perovskite, moisture stability, solar cell, passivation

INTRODUCTION

Metal halide perovskite solar cells (PSCs) are promising candidates for photoelectric conversion devices due to their optoelectronic characteristics. Currently, the highest certified power conversion efficiency (PCE) of devices has reached 25.5% [1]. However, the instability of the perovskite layer in the ambient environment (light illumination, heat treatment or moisture erosion) [2–5], and the existing defects seriously restrict the performance and limit its development towards practical applications and commercialization [6–10]. Among the various environmental factors that cause instability, moisture instability is a major obstacle because of its severe harmfulness, which causes hydrate formation, promoting the irreversible decomposition of perovskite accompanied by a sharp decline in optical absorption and severe electron-hole recombination [11,12]. Moreover, moisture is also the most difficult to control in the actual working environment due to the large humidity range. Thus, it is desirable to explore an appropriate strategy to passivate film defects and improve the moisture stability.

To date, tremendous efforts have been dedicated to improving

the moisture stability and reducing intrinsic defects [13–18]. For instance, many different kinds of polymers have been added to perovskite precursor solutions to tune the crystallinity and morphology of perovskite layers [16,19–23]. The polymerization-assisted grain growth strategy can effectively passivate the uncoordinated lead ions when the polymers are anchored on the boundaries after perovskite film formation or make the energy level of the perovskite and transport layer match better [19,21]. In addition, some molecules containing cross-linked and hydrophobic functional groups were post-treated on the surface of perovskite to form chemical bonds or hydrogen bonds with perovskite to impede the penetration of water molecules into the perovskite layer and improve the moisture resistance stability of the film [24–28]. These interfacial materials could not only defend against water infiltration but also improve the device performance with excellent charge transfer properties at the same time [24]. However, the addition of polymer materials most likely affects the crystallization of perovskite or hinders the transmission efficiency of the carrier due to their poor conductivity. Interfacial treatment with molecules may form a dense, poorly conductive layer, and commonly used solvents (such as isopropanol (IPA)) will inevitably affect the quality of the underlying perovskite film [22]. Recently, Yang's group [7,19] found that adding a polymer or molecule to the lead iodide (PbI₂) precursor through a two-step preparation method can enable a more sufficient interaction between the additives and PbI₂. The interaction produces a higher energy barrier when the PbI₂ crystals react with A-site cations to form perovskite crystals, which helps to form larger grains and better-quality perovskite films. However, the additives currently used to passivate perovskite defects will either redissolve in IPA in the second step or only have a limited variety and number of functional groups so that it is difficult to interact with different types of solvated Pb²⁺ atoms. Therefore, it is necessary to select more suitable additives for this novel monomer additive strategy.

Herein, we introduce for the first time the small-molecule thiamine (THM), which has a thiazole ring, a pyrimidine carbon ring and an amino group (–NH₂), into the PbI₂ precursor to form a high-quality perovskite film, thereby improving the performance and moisture stability of PSCs. The C=N in the thiazole ring and pyrimidine carbon can interact with lead ions, and –NH₂ can interact with iodide ions in perovskite [29–35], which will delay the crystallization rate and guide the crystal growth and passivate defects caused by undercoordinated lead

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and iodide ions. Through optimizing the concentration of the THM additive, a high-quality perovskite film with improved crystallinity, larger grain size, fewer defects, and improved moisture stability (remaining in black phase for 12 h at a relative humidity of 99%) was obtained. Finally, the optimal device obtained an enhanced PCE of 21.40% compared with 19.60% for the control device, and the corresponding unencapsulated devices retained >92% of the initial PCE after 180 h in air with a humidity of ~50%. These results provide a promising strategy for constructing high-performance perovskite devices with high-quality perovskite films and moisture stability.

RESULTS AND DISCUSSION

The fabrication process of the perovskite devices is presented in Fig. 1a. In brief, a SnO_2 thin film was coated on indium tin oxide (ITO) substrates by a spin-coating and annealing process. Then, a $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ (FA = $\text{CH}(\text{NH}_2)_2$, MA = CH_3NH_3) film was covered on the SnO_2 /ITO substrates by a conventional two-step deposition strategy [25]. In this process, different concentrations (0, 0.05, 0.1 and 0.15 mg mL^{-1}) of THM within the PbI_2 precursor solution were spin-coated on the SnO_2 /ITO substrate and annealed at an optimized temperature (Fig. S1). The corresponding final perovskite films are labeled as $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$, where X represents the concentration of THM. Finally, a spiro-OMTAD layer and 90-nm-thick Ag were deposited on the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$ film to obtain the final device. The architecture of the device is shown in Fig. 1b, and the detailed preparation process is presented in the experimental section (see Supplementary information).

Fig. 2a displays the molecular structure of THM, and the probable interaction between two neighboring grains with THM is illustrated in Fig. 2b. The C=N probably interacts with lead ions in perovskite, and the ammonium ion interacts with iodide ions. To prove the interaction between THM and $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ and determine the exact mechanism of the reaction, Fourier transform infrared (FTIR) spectra of pure THM and THM- PbI_2 hybrid films were measured. As shown in Fig. 2c, the C=N vibration peak of molecular THM is 1658.74 cm^{-1} and moves to 1641.38 cm^{-1} after the reaction with PbI_2 . This indicates a strong interaction between THM and PbI_2 , and the reaction sites are between the C=N and uncoordinated Pb^{2+} . To further confirm

the conclusion drawn from the FTIR results, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements were adopted as the supplementary information. For the pure perovskite film (Fig. 2d), the peaks at 143.28 and 138.38 eV are indexed to Pb^{2+} [36–39]. The two weak satellite peaks at 136.68 and 141.58 eV are assigned to metallic Pb (Pb^0), which is caused by unsaturated lead. After introducing the THM additive, the peaks of Pb^{2+} shift to lower binding energy, and the two peaks of Pb^0 disappear compared with the pristine perovskite film, indicating increased electron density on the Pb nucleus and decreased defect density due to coordination of THM with undercoordinated Pb^{2+} ions. Correspondingly, the peaks of I 3d in the perovskite film with THM additive shifted to higher binding energies (Fig. 2e), which should be attributed to the strong electronic interactions produced by the hydrogen bond between the $-\text{NH}_2$ of THM and I^- in the perovskite film. These results further confirmed the passivation effect of THM on the perovskite film. Fig. 2f, g show the XRD patterns of the PbI_2 and PbI_2 -THM hybrid films before and after annealing treatments. The peak at 9.8° of the unannealed films corresponds to the PbI_2 -dimethyl sulfoxide (DMSO) intermediate phase. After annealing, the pristine PbI_2 film has a strong lead iodide crystal phase, while the emergence of crystallinity is suppressed by the hybrid film [40]. This indicates that the sufficient interaction between the THM and PbI_2 and Pb^{2+} probably locked in the crystal lattice. Moreover, the corresponding XRD patterns of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$ illustrate that the intensity ratio between the PbI_2 peak at 12.8° and the (100) peak of perovskite at 14.0° decreases from 1.9 to 1.2 as the THM doping concentration increases from 0 to 0.15 mg mL^{-1} (Fig. 2h), indicating that the excess lead iodide can be neutralized after the formation of THM-treated perovskite.

Top-view scanning electron microscopy (SEM) images of the pure $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ and $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$ films are presented in Fig. 3a, b and Fig. S2. The grain size gradually increases from 1400 to 1700 nm as the doping concentration increases from 0 to 0.1 mg mL^{-1} , while the grain size begins to decrease when the doping concentration further reaches 0.15 mg mL^{-1} . This trend is attributed to the presence of a strong interaction between PbI_2 and THM, which leads to a higher activation energy and then reduces the reaction rate of the PbI_2 and

Figure 1 (a) Schematic of the fabrication process of the perovskite devices. (b) Schematic architecture of the final device.

Figure 2 (a) Molecular structure of THM. (b) Schematic illustration of the interaction between two neighboring grains and THM. (c) FTIR spectra of pure THM and PbI₂/THM hybrid film. XPS spectra of FAMAPbI₃ and FAMAPbI₃-0.1: (d) Pb 4f and (e) I 3d orbitals. XRD patterns of the pure PbI₂ film and PbI₂-THM film: (f) before and (g) after annealing. (h) XRD of perovskite films with different concentrations of THM.

Figure 3 Top-view SEM images of perovskite films with (a) 0 and (b) 0.1 mg mL⁻¹ THM additives, (c, d) cross-sectional SEM images of the corresponding perovskite devices.

FAI/MAI/MACl solutions in the second step of the two-step preparation process [19]. However, when the doping concentration is further increased, more nucleation rapidly occurs at the unformed complex as the interaction force between THM and PbI_2 increases. The corresponding cross-sectional SEM images (Fig. 3c, d) demonstrate that the introduction of THM helps to improve the surface flatness of the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ film. In addition, the steady-state photoluminescence (PL) spectra and the corresponding time-resolved PL (TRPL) decay with a structure of ITO/ SnO_2 /perovskite were measured to clarify the beneficial effect of the THM additive on defect passivation (Fig. 4). Fig. 4a displays the PL spectra of the perovskite films with different THM concentrations, and the intensities of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$, $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-}0.05$, $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-}0.1$, and $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-}0.15$ are 6.72×10^5 , 4.14×10^5 , 3.39×10^5 and 4.84×10^5 (a.u.), respectively. The weaker strength of the PL intensity indicates the more efficient charge extraction efficiency of the interface between the perovskite and electron transport layer, which can be interpreted as the quenching of more carriers due to interface transmission rather than radiative recombination. Moreover, the blueshift of the peak for the THM-treated perovskite film further indicates a reduction in defect states compared with the pristine film [8]. The corresponding TRPL

decay is presented in Fig. 4b, and the fitting parameters are summarized in Table S1. The smallest PL decay (179.19 ns) suggests a more efficient electron extraction process between $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-}0.1$ and SnO_2 . In addition, the PL and TRPL spectra with a structure of glass/perovskite are provided in Fig. S3 and the fitting parameters are summarized in Table S2. The results show that the perovskite film treated with THM has more carriers and longer life than the control film, indicating that the THM-treated perovskite film has better quality. The results are consistent with the conclusion obtained from the perovskite film on SnO_2 /ITO substrate. Moreover, we utilized the space-charge-limited-current (SCLC) technique to quantitatively study the defect density in the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-}X$ films. The associated current-voltage curves for both pristine and THM-treated perovskite films are displayed in Fig. 4c. The trap filled limit voltage (V_{TFL}) is 0.76 V for the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ -based device and 0.51 V for the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-}0.1$ -based device. The defect density (N_{defects}) is calculated from the equation $N_{\text{defects}} = 2\epsilon\epsilon_0 V_{\text{TFL}}/eL^2$, where ϵ and L are the dielectric constant and thickness of the perovskite, respectively; ϵ_0 , V_{TFL} , and e are the vacuum permittivity, trap filled limit voltage, and electron charge, respectively. A lower defect state density was obtained by the optimized device ($2.09 \times 10^{16} \text{ cm}^{-3}$) compared with the

Figure 4 (a) PL and (b) TRPL spectra of perovskite films treated with different concentrations of THM. (c) SCLC measurements of electron-only devices based on FAMAPbI_3 and $\text{FAMAPbI}_3\text{-}0.1$ films. (d) UV-visible absorption spectra of perovskite films with different THM concentrations. Absorption spectra of (e) pristine and (f) THM-treated perovskite films exposed to ambient air with an RH of ~50% for different days. WCA with time based on (g) pristine and (h) THM-treated perovskite films.

pristine perovskite film ($3.12 \times 10^{16} \text{ cm}^{-1}$), and the result is consistent with the PL and TRPL results. In addition, the initial ultraviolet (UV) absorption spectra of the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$ film are presented in Fig. 4d. All perovskite films have an identical absorption edge of 805 nm and the same absorption intensity, indicating that the THM additive has negligible effects on the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ phase and light utilization capacity. However, the absorption of the control film declines gradually from 0 to 5 days and exhibits a sharp drop for ten days during storage under ambient conditions with a humidity of $\sim 50\%$, while the film with THM treatment only exhibits a slight decrease during storage for 15 days (Fig. 4e, f). Moreover, the water resistance is also important for perovskite films and greatly improved with the THM additive. As seen in the water contact angle (WCA) characterization in Fig. 4g, h, with addition of THM, the WCA of the perovskite film becomes larger, indicating enhanced hydrophobicity of the hybrid film. Meanwhile, the WCA of the control film decreases sharply from 58.4° to 41.3° after 10 min, while the optimized film with THM only has a very small variation from 66.7° to 62.0° . This result indicates that the addition of THM to perovskite films can prevent further reaction between the surface of the film and water, which should be attributed to the formation of a dense film due to the interaction of THM molecules and perovskite. Furthermore, to test the limit of the moisture resistance of the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$ film, the control film and THM-treated film were placed in an airtight and low-pressure container with humidity of 99%. The

pristine perovskite film decomposes into large amounts of lead iodide after 6 h and almost completely decomposes after 12 h, while the THM-treated film (1 mg mL^{-1}) remains unchanged within 9 h and only decomposes slightly after 12 h (Fig. S4). These results indicate that moisture stability is greatly enhanced with the THM additive integrated with the perovskite film.

Fig. 5a displays the current density-voltage (J - V) characteristics of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-X}$ -based devices. The detailed photovoltaic parameters are summarized in Table 1. In addition, the corresponding statistical distributions are summarized in Fig. S5. The devices based on the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ film with a suitable THM additive exhibit enhanced PCE, open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) compared with the control device, and the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3\text{-0.1}$ -based device delivers the highest PCE of 21.40% with an enhanced V_{oc} of 1.10 V, J_{sc} of 24.83 mA cm^{-2} , and FF of 78.64%.

The integrated current of the external quantum efficiency (EQE) (Fig. S6) is 23.6 mA cm^{-2} . The slight reduction is caused by the different effects of the factors, such as surface defect states, light intensity and frequency. Note that although a slightly large concentration of THM cannot improve the efficiency of the device, it does not cause substantial damage either (Fig. S7). The improvement of V_{oc} and FF is due to the better quality of the perovskite film and good defect passivation impact with the introduction of THM. Repeatability and hysteresis are also critical parameters of PSCs; thus, Fig. 5b summarizes the efficiency distribution of thirty devices, and Fig. S8 compares the J - V

Figure 5 (a) J - V curves of the hybrid PSCs with different concentrations of THM additive. (b) Histogram of the efficiency distribution of 30 devices based on the pristine and THM-treated perovskites. (c) Nyquist plot of PSCs based on the control and optimized hybrid perovskite devices. (d) The air stability of FAMAPbI_3 - and $\text{FAMAPbI}_3\text{-0.1}$ -based devices.

Table 1 Summary of the photovoltaic parameters of PSCs with different concentrations of THM additive

Concentration (mg mL ⁻¹)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
0	1.07	24.62	74.43	19.60
0.05	1.09	24.92	75.94	20.66
0.1	1.10	24.83	78.64	21.40
0.15	1.07	24.70	74.98	19.82

curves under reverse and forward scan directions of the FA_{0.85}MA_{0.15}PbI₃ and optimal FA_{0.85}MA_{0.15}PbI₃-0.1-based devices. Good normal distribution and improved median efficiency prove the good repeatability of the FA_{0.85}MA_{0.15}PbI₃-0.1-based device. The notable reduction in the hysteresis benefits from the synergetic effect of the grain size increase and defect passivation after doping with THM. In addition, electrochemical impedance spectroscopy (EIS) measurements are used as a supplement to the investigation of charge transport. As shown in Fig. 5c, the related equivalent circuit model for EIS fitting includes the device series resistance (R_s), charge transport resistance (R_{ct}), and recombination resistance (R_{rec}). The R_{ct} is systematically reduced from 110 Ω of the control device to 95.8 Ω of the optimized device. A lower R_{ct} indicates a higher charge transport capability, and this result further confirms the better film morphology and defect passivation produced by THM treatment. For confirmation, we adopt long-term stability tests for unencapsulated devices under ambient conditions with humidity of ~50% and a temperature of ~25°C (Fig. 5d). After 180 h of exposure to air, the device with THM additive retains >92% of its initial PCE, while the pure perovskite-based device drops rapidly to 45% of its initial PCE during the same aging time. The results obtained with the final devices are consistent with the results obtained during the film research process and further indicate that proper THM addition can improve the film morphology and passivate defects in the perovskite film, thereby improving the performance of the corresponding device.

CONCLUSIONS

In summary, we have successfully improved the quality of the FA_{0.85}MA_{0.15}PbI₃ film by introducing a THM molecule additive. After the introduction of THM, the defects at the perovskite grain boundaries are passivated, the perovskite film becomes flattened, and the hydrophobicity of the perovskite film is improved. Hence, the best performing device with the optimal THM additive attained an efficiency of 21.40% and improved stability. These results suggest that integrating cross-linked materials with perovskites by a novel additive use strategy is a promising strategy for fabricating high-performance perovskite devices with high-quality stable perovskite films.

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- 1 National Renewable Energy Laboratory. Best Research-Cell Efficiencies Chart, <https://www.nrel.gov/pv/cell-efficiency.html>
- 2 Dong Q, Zhu C, Chen M, *et al.* Interpenetrating interfaces for efficient perovskite solar cells with high operational stability and mechanical robustness. *Nat Commun*, 2021, 12: 973
- 3 Wang R, Mujahid M, Duan Y, *et al.* A review of perovskites solar cell

- stability. *Adv Funct Mater*, 2019, 29: 1808843
- 4 Li N, Niu X, Chen Q, *et al.* Towards commercialization: The operational stability of perovskite solar cells. *Chem Soc Rev*, 2020, 49: 8235–8286
- 5 Zhang S, Liu Z, Zhang W, *et al.* Barrier designs in perovskite solar cells for long-term stability. *Adv Energy Mater*, 2020, 10: 2001610
- 6 Gao F, Zhao Y, Zhang X, *et al.* Recent progresses on defect passivation toward efficient perovskite solar cells. *Adv Energy Mater*, 2019, 10: 1902650
- 7 Zhao Y, Zhu P, Huang S, *et al.* Molecular interaction regulates the performance and longevity of defect passivation for metal halide perovskite solar cells. *J Am Chem Soc*, 2020, 142: 20071–20079
- 8 Mai CL, Zhou Q, Xiong Q, *et al.* Donor- π -acceptor type porphyrin derivatives assisted defect passivation for efficient hybrid perovskite solar cells. *Adv Funct Mater*, 2021, 31: 2007762
- 9 Wang R, Xue J, Wang KL, *et al.* Constructive molecular configurations for surface-defect passivation of perovskite photovoltaics. *Science*, 2019, 366: 1509–1513
- 10 Liu Z, Cao F, Wang M, *et al.* Observing defect passivation of the grain boundary with 2-aminoterephthalic acid for efficient and stable perovskite solar cells. *Angew Chem Int Ed*, 2020, 59: 4161–4167
- 11 Christians JA, Miranda Herrera PA, Kamat PV. Transformation of the excited state and photovoltaic efficiency of CH₃NH₃PbI₃ perovskite upon controlled exposure to humidified air. *J Am Chem Soc*, 2015, 137: 1530–1538
- 12 Mohamad Noh MF, Arzaee NA, Nawas Mumthas IN, *et al.* High-humidity processed perovskite solar cells. *J Mater Chem A*, 2020, 8: 10481–10518
- 13 Hui W, Chao L, Lu H, *et al.* Stabilizing black-phase formamidinium perovskite formation at room temperature and high humidity. *Science*, 2021, 371: 1359–1364
- 14 Jeong M, Choi IW, Go EM, *et al.* Stable perovskite solar cells with efficiency exceeding 24.8% and 0.3-V voltage loss. *Science*, 2020, 369: 1615–1620
- 15 Zhang F, Xiao C, Chen X, *et al.* Self-seeding growth for perovskite solar cells with enhanced stability. *Joule*, 2019, 3: 1452–1463
- 16 Kim B, Kim M, Lee JH, *et al.* Enhanced moisture stability by butyldimethylsulfonium cation in perovskite solar cells. *Adv Sci*, 2020, 7: 1901840
- 17 Ahmad S, Fu P, Yu S, *et al.* Dion-Jacobson phase 2D layered perovskites for solar cells with ultrahigh stability. *Joule*, 2019, 3: 794–806
- 18 Wang S, Chen H, Zhang J, *et al.* Targeted therapy for interfacial engineering toward stable and efficient perovskite solar cells. *Adv Mater*, 2019, 31: 1903691
- 19 Zhao Y, Zhu P, Wang M, *et al.* A polymerization-assisted grain growth strategy for efficient and stable perovskite solar cells. *Adv Mater*, 2020, 32: 1907769
- 20 Han TH, Lee JW, Choi C, *et al.* Perovskite-polymer composite cross-linker approach for highly-stable and efficient perovskite solar cells. *Nat Commun*, 2019, 10: 520
- 21 Jiang J, Wang Q, Jin Z, *et al.* Polymer doping for high-efficiency perovskite solar cells with improved moisture stability. *Adv Energy Mater*, 2018, 8: 1701757
- 22 Kim M, Motti SG, Sorrentino R, *et al.* Enhanced solar cell stability by hygroscopic polymer passivation of metal halide perovskite thin film. *Energy Environ Sci*, 2018, 11: 2609–2619
- 23 Li X, Zhang W, Wang YC, *et al.* In-situ cross-linking strategy for efficient and operationally stable methylammonium lead iodide solar cells. *Nat Commun*, 2018, 9: 3806
- 24 Akman E, Akin S. Poly(*N,N'*-bis-4-butylphenyl-*N,N'*-bisphenyl)benzidine-based interfacial passivation strategy promoting efficiency and operational stability of perovskite solar cells in regular architecture. *Adv Mater*, 2021, 33: 2006087
- 25 Guo P, Ye Q, Liu C, *et al.* Double barriers for moisture degradation: Assembly of hydrolysable hydrophobic molecules for stable perovskite solar cells with high open-circuit voltage. *Adv Funct Mater*, 2020, 30: 2002639
- 26 Jiang Q, Zhao Y, Zhang X, *et al.* Surface passivation of perovskite film

- for efficient solar cells. *Nat Photonics*, 2019, 13: 460–466
- 27 Chen J, Park NG. Materials and methods for interface engineering toward stable and efficient perovskite solar cells. *ACS Energy Lett*, 2020, 5: 2742–2786
  - 28 Chen H, Liu T, Zhou P, *et al.* Efficient bifacial passivation with crosslinked thioctic acid for high-performance methylammonium lead iodide perovskite solar cells. *Adv Mater*, 2020, 32: 1905661
  - 29 Cai Y, Cui J, Chen M, *et al.* Multifunctional enhancement for highly stable and efficient perovskite solar cells. *Adv Funct Mater*, 2020, 31: 2005776
  - 30 Chen H, Wei Q, Saidaminov MI, *et al.* Efficient and stable inverted perovskite solar cells incorporating secondary amines. *Adv Mater*, 2019, 31: 1903559
  - 31 Yao Q, Xue Q, Li Z, *et al.* Graded 2D/3D perovskite heterostructure for efficient and operationally stable MA-free perovskite solar cells. *Adv Mater*, 2020, 32: 2000571
  - 32 Yoo JJ, Wieghold S, Sponseller MC, *et al.* An interface stabilized perovskite solar cell with high stabilized efficiency and low voltage loss. *Energy Environ Sci*, 2019, 12: 2192–2199
  - 33 Wu X, Jiang Y, Chen C, *et al.* Stable triple cation perovskite precursor for highly efficient perovskite solar cells enabled by interaction with 18C6 stabilizer. *Adv Funct Mater*, 2019, 30: 1908613
  - 34 Yang S, Chen S, Mosconi E, *et al.* Stabilizing halide perovskite surfaces for solar cell operation with wide-bandgap lead oxysalts. *Science*, 2019, 365: 473–478
  - 35 Xue J, Wang R, Chen X, *et al.* Reconfiguring the band-edge states of photovoltaic perovskites by conjugated organic cations. *Science*, 2021, 371: 636–640
  - 36 Wu T, Wang Y, Li X, *et al.* Efficient defect passivation for perovskite solar cells by controlling the electron density distribution of donor- π -acceptor molecules. *Adv Energy Mater*, 2019, 9: 1803766
  - 37 Wu Z, Jiang M, Liu Z, *et al.* Highly efficient perovskite solar cells enabled by multiple ligand passivation. *Adv Energy Mater*, 2020, 10: 1903696
  - 38 Gao XX, Luo W, Zhang Y, *et al.* Stable and high-efficiency methylammonium-free perovskite solar cells. *Adv Mater*, 2020, 32: 1905502
  - 39 Song S, Park EY, Ma BS, *et al.* Selective defect passivation and topographical control of 4-dimethylaminopyridine at grain boundary for efficient and stable planar perovskite solar cells. *Adv Energy Mater*, 2021, 11: 2003382
  - 40 Bai S, Da P, Li C, *et al.* Planar perovskite solar cells with long-term stability using ionic liquid additives. *Nature*, 2019, 571: 245–250

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Author contributions Zhang P and Cao F conducted the experiment and wrote the paper. Cao F and Li L designed this study and analyzed the data. Tian W offered some helpful suggestions. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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盐酸硫胺添加剂改善钙钛矿的成膜质量以制备高效的、湿度稳定的钙钛矿太阳能电池

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摘要 钙钛矿太阳能电池由于其特殊的性质引起了广泛关注. 然而, 钙钛矿层的不稳定性, 尤其是水分不稳定性以及存在的缺陷, 严重制约了钙钛矿电池的性能并限制了其商业化发展. 在此, 我们将盐酸硫胺 (THM) 添加剂掺入碘化铅 (PbI₂) 前驱体中, 使用两步旋涂方法制备出了耐湿且高效的钙钛矿电池. 这一策略可以使 THM 添加剂和 PbI₂ 之间产生更好的相互作用, 当与 A 位阳离子反应形成钙钛矿晶体时会产生能量势垒, 从而形成更大的晶粒和质量更好的钙钛矿薄膜. 通过优化 THM 添加剂的浓度, 最佳的钙钛矿薄膜实现了湿度稳定性的提高以及缺陷态密度的降低. 因此, 相应的未封装器件实现了 21.40% 的能量转换效率, 并在 ~50% 湿度的空气环境中 180 小时后依旧保持其初始效率的 92% 以上. 其优异性能主要归因于 THM 促进了晶体生长并钝化了钙钛矿薄膜中的缺陷.