Multifunctional Molecule Engineered SnO₂ for Perovskite Solar Cells with High Efficiency and Reduced Lead Leakage

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Outstanding performance of perovskite solar cells (PSCs) is closely linked to the optoelectrical properties of charge transporting layers. Herein, amino trimethylene phosphonic acid (ATMP) and KOH are mixed (ATMP-K) and incorporated in a SnO₂ precursor solution to significantly improve the performance of the electron transport layer (ETL) SnO₂ in PSCs. Combining density functional theory (DFT) calculations and experiments, it is demonstrated that ATMP-K effectively passivates the oxygen vacancy and reduces the hydroxyl groups on the surface of SnO₂, resulting in a larger perovskite grain size and better energy-level alignment with perovskites. ATMP-K boosts the power conversion efficiency (PCE) of the PSCs from 20.99% to 23.52%. When applying in a perovskite/silicon heterojunction tandem solar cell, the device delivers an efficiency up to 24.75% with a high V_{OC} of 1.94 V, compared with 22.67% and 1.85 V of the reference cells. Furthermore, ATMP-K-modified PSCs also show extraordinary ability to absorb Pb²⁺ ions after their degradation in water, offering a facile strategy for reducing Pb leakage.

1. Introduction

Owing to the low exciton dissociation energy, long charge carrier lifetime, high absorption coefficient, and the ease of large-area fabrication of hybrid perovskite thin films, perovskite solar cells (PSCs) have attracted extensive attention during the past decade.^[1–11] To date, the power conversion efficiency (PCE) of the state-of-the-art perovskite solar devices has been boosted from 3.8%^[12] to a certified 25.5%.^[13] Except for the composition (the types of cations and anions) and the quality of the perovskite absorber,^[7,14–19] the photoelectrical properties of the carrier transport layers (CTLs) are another important factor that determines the PCE and long-term stability of the PSCs. The optical and electrical properties of the CTLs not only affect the fill factor (FF) of the PSCs, but also the short-circuit current density (J_{SC}).^[6,8] In addition, the atomistic details of the surface of the CTLs also bring the

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inevitable impact to the following perovskite growth, which will determine the performance and long-term stability of the PSCs.^[20–22]

Due to the low cost, good chemical stability, and high electron mobility,^[23] SnO₂ is usually used as the electron transport layers (ETLs) in N–I–P-type PSCs.^[23–37] However, the relatively large gap between the Fermi level and conduction band minimum (CBM) usually produces a weak built-in field potential in the device. In addition, the poor crystallinity of SnO₂ NPs usually results in low electrical conductivity, which leads to weak electron injection/transport capabilities of SnO₂ film. Moreover, the hydroxyl on surface of SnO₂ film usually generates trap states near the valence band,^[38] which will cause nonradiative recombination at the SnO₂/perovskite interface and thus produce a low open-circuit voltage (*V*_{OC}), FF, and severe hysteresis.^[4,20,22,38–45]

Herein, the mixture of amino trimethylene phosphonic acid (ATMP) and KOH are (ATMP-K) doped in SnO₂ to overcome the aforementioned problems. First, we confirm through density functional theory (DFT) calculations that ATMP can passivate the surface of SnO₂ by replacing the surface hydroxyls and strong binding to the surface Sn atoms. Our DFT calculations also indicate strong interactions of ATMP with PbI₂. Therefore, we hypothesize that ATMP can improve the quality of the perovskite deposited on the ATMP-modified SnO₂ and of the overall interface. To examine the validity of our hypothesis, we fabricate PSCs with ATMP-modified SnO₂ as the ETL. Our experiments confirm that ATMP effectively reduces the hydroxyl groups on the surface of SnO₂ and adjusts the energy levels of SnO₂, creating a more favorable alignment with that of the perovskite absorber, as predicted from DFT.

Furthermore, we identify another advantage of the ATMP modification: due to the strong ability of PA groups to absorb Pb²⁺ ions, the ATMP-modified PSCs show much-reduced leakage of toxic Pb²⁺ during a degradation test of PSCs in water. Combining the merits of ATMP, PSCs with high PCE of

23.52% with significantly increased *V*_{OC} and FF and negligible hysteresis is achieved. Our work puts forward a simple and effective method in modifying ETL SnO₂ to achieve highly efficient and environmentally friendly PSCs.

2. Results and Discussion

2.1. DFT Calculations of ATMP-Modified SnO₂

DFT is used to explore the effects of the ATMP on SnO₂. We choose the stoichiometric (110) surface for the study as it is the most thermodynamically stable configuration.^[27,46] The calculations show that ATMP binds strongly to the SnO₂ surface by replacing the hydroxyls on the surfaces (SnO₂–(OH)_{*n*}) (Figure 1a).

According to the following equation

the calculated reaction energies are –0.90, –0.47, and –0.25 eV for *x* = 1, 2, and 3, respectively (Figure 1b). In other words, a single ATMP molecule can replace at least three –OH surface groups with P=O–Sn bonds. Apart from the hydroxyl removal from the SnO₂ surface, ATMP also gives rise to a favorable shift of the work function, ultimately leading to the improved device performance (will be discussed in sections of materials characterization and device performance). Specifically, the calculated work function for the ATMP optimized SnO₂ is 0.6 eV higher than that of the fully hydroxylated SnO₂ (Figure S1, Supporting Information).

The quality of the perovskite deposited on the ATMP optimized SnO₂ is also expected to be superior to that of a film deposited on reference SnO₂ because ATMP can passivate reactive sites, such as hydroxyls and dangling Sn bonds created by oxygen vacancies, and create a smooth surface for the perovskite growth.

Figure 1. DFT calculations and structural models. a) Schematic diagram of ATMP removing the hydroxyls on SnO₂ surface. b) Reaction energies of ATMP removing *x* hydroxyl on SnO₂ surface for *x* = 1, 2, and 3, respectively. c) The schematic of mechanisms of the perovskite growth on SnO₂ and ATMP optimized SnO₂.

The molecule's geometry does not seem to facilitate the creation of more than three bonds with SnO_2 ; however, we speculate the remaining dangling phosphate groups can interact with the perovskite species (in the formation of PbI_2 and the subsequent formation of perovskites) and further affect its morphology (Figure 1c). The calculated interaction energy between a PbI_2 molecule with the ATMP optimized SnO_2 surface is -1.25 eV compared with -0.66 eV for the fully hydroxylated SnO_2 (Figure S2, Supporting Information). This means that at the crystallization stage, the stronger interaction between ATMP and PbI_2 could slow down the nucleation process, resulting in an improved perovskite morphology. Moreover, ATMP is found to bind the surface of FAPbI_3 through $\text{P}=\text{O}-\text{Pb}$ bonds, with a binding energy of -1.58 eV, implying a potential strong adhesion of the perovskite to the optimized SnO_2 (Figure S3, Supporting Information). Interestingly, such $\text{P}=\text{O}-\text{Pb}$ bonds have been previously suggested to stabilize the perovskite deposited on SnO_2 by blocking environmental O_2 and H_2O .

2.2. Characterization of ETLs

We further proceed with experiments to investigate the validity of our hypothesis regarding the influence of ATMP on SnO_2 . When ATMP alone is doped into the SnO_2 colloidal solution, as shown in Figure S4, Supporting Information, the nanoparticles in the SnO_2 solution agglomerate and the SnO_2 film cannot be formed,

probably because of the strong acidity nature of ATMP. Therefore, we used a mixed solution of KOH and ATMP (denoted as $\text{SnO}_2 + \text{ATMP-K}$), where KOH is used to reduce the acidity of ATMP and then stabilize the SnO_2 colloidal dispersion. SnO_2 precursor solutions with and without ATMP-K are spin-coated on the ITO substrate, and then annealed at 150°C for 30 min.

The surface morphology of SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ is examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM), and it appears to be very uniform, similar to that of pristine SnO_2 (Figure S5 and S6, Supporting Information). The presence of element phosphorus (P) in the doped SnO_2 is confirmed by a small peak at 134 eV in the X-ray photoelectron spectroscopy (XPS) spectrum of $\text{SnO}_2 + \text{ATMP-K}$ films (Figure S7a,b, Supporting Information). Sn 3d peaks in $\text{SnO}_2 + \text{ATMP-K}$ has moved to higher binding energies (Figure 2a), which can be attributed to the strong binding of the $\text{P}=\text{O}$ groups of ATMP to the surface Sn atoms.^[43] This is further supported by the absence of such a shift, when SnO_2 is doped with KOH only (Figure S7c, Supporting Information). In Figure 2b,c, the XPS results for O 1s for both samples are presented, where the red and blue regions correspond to the oxygen in bulk SnO_2 and the oxygen from hydroxyl ($-\text{OH}$), respectively. It can be seen that the area of hydroxyl oxygen decreases upon ATMP-K doping. In contrast, the proportion of hydroxyl groups on the surface of the

Figure 2. Characterization of SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ Film. a) XPS core-level spectra of Sn 3d on SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ film. b) XPS spectra of O 1s on SnO_2 film, O₁ and O₂ correspond to the oxygen in bulk SnO_2 and the oxygen from hydroxyl ($-\text{OH}$), respectively. c) XPS spectra of O 1s on $\text{SnO}_2 + \text{ATMP-K}$ film, O₁ and O₂ correspond to the oxygen in bulk SnO_2 and the oxygen from hydroxyl ($-\text{OH}$), respectively. d) The tail of UPS spectra of SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$, respectively, where their work functions and VBMs can be derived. e) The band-level diagram of SnO_2 before and after doping of ATMP-K, respectively. f) The conductivity of SnO_2 before and after doping of ATMP-K, respectively.

$\text{SnO}_2 + \text{KOH}$ is the same as that of the reference SnO_2 (Figure S7d, Supporting Information). This suggests that the observed reduction of hydroxyl on the surface of SnO_2 is a result of the ATMP treatment, consistent with our DFT calculations.

Both the original SnO_2 and the $\text{SnO}_2 + \text{ATMP-K}$ films coated on the glass show good transmittance in the visible light range (Figure S8, Supporting Information). The work function of SnO_2 shifts from -4.22 to -3.72 eV after doping with ATMP-K as can be seen from the ultraviolet photoelectron spectroscopy (UPS) results in Figure 2d and S9, Supporting Information, but doping with KOH alone does not affect the work function (Figure S10, Supporting Information). The observed work function shift, which is in agreement with the DFT calculated shift, improves the energy-level alignment between the ETL and the perovskite layer, facilitating charge transport and decreasing charge recombination at the interface. Figure S9, Supporting Information, shows that the $E_F - E_{\text{VBM}}$ value of ETL increases from 3.48 to 3.68 eV after ATMP doping, and the band structures of $\text{SnO}_2 + \text{ATMP-K}$ and SnO_2 were measured by UPS (Figure S12a, Supporting Information). The calculated CBM (E_{CBM}) is -3.90 eV for SnO_2 and -3.60 eV for $\text{SnO}_2 + \text{ATMP-K}$. UPS and absorption spectra were conducted to identify the energy band structure of the two types of films as the ETL, and the results are shown in Figure 2e. Notably, the Fermi level moves closer to the CBM after the ATMP-K doping (Figure 2e), which indicates that ATMP-K increases the electron density in the SnO_2 and thus improves the n-type properties of the SnO_2 film. To clearly illustrate the role of ATMP-K in charge transfer,

the electrical conductivity of SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ is calculated as $6.32 \times 10^{-5} \text{ S cm}^{-1}$ and $6.50 \times 10^{-3} \text{ S cm}^{-1}$ (described in the Experimental Section), respectively (Figure 2f and Table S1, Supporting Information). The aforementioned analysis points to the fact that doping ATMP-K significantly improves the conductivity of SnO_2 .

2.3. Morphological, Structural, and Optical Properties of Perovskites

Next, we study the influence of ATMP on perovskite films deposited on ETLs. All the functional layers of the device are highlighted using different colors in the cross-sectional SEM image of the PSCs (Figure 3a). The top-view topographic SEM image of the perovskite films deposited on different ETLs is displayed (Figure 3b,c). The top-view SEM of the perovskite films spin-coated on the pristine SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ both shows a continuous and uniform film without apparent pinholes. Moreover, the perovskite deposited on $\text{SnO}_2 + \text{ATMP-K}$ shows a larger grain size than that deposited on SnO_2 . The average grain size of perovskite films grown on the original SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ is 870 nm and 1 μm , respectively. In addition the perovskite on $\text{SnO}_2 + \text{ATMP-K}$ is smoother with a root mean square of 20.58 nm, whereas the reference is 21.18 nm (see also Figure S11, Supporting Information).

Figure 3d shows the X-ray diffraction (XRD) patterns of the films deposited on different ETLs. The stronger intensity of the XRD peaks indicates better crystallization. The typical

Figure 3. Morphological, structural, and optical properties of perovskite films deposited on SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$. a) The cross-sectional SEM and schematic structure of the device based on $\text{SnO}_2 + \text{ATMP-K}$. b) The surface SEM images of the perovskite deposited on $\text{SnO}_2 + \text{ATMP-K}$. c) The surface SEM images of the perovskite deposited on SnO_2 . d) X-ray diffraction (XRD) patterns for perovskite deposited on $\text{SnO}_2 + \text{ATMP-K}$ and SnO_2 . e) UV-vis absorption spectra of perovskite films deposited on SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$. f) Steady-state PL spectrum of perovskite films on glass, SnO_2 , and $\text{SnO}_2 + \text{ATMP-K}$ substrates. g) TRPL decay curves of perovskite films on glass, SnO_2 , and $\text{SnO}_2 + \text{ATMP-K}$ substrates.

patterns of the black perovskite crystal with the main diffraction peak at 14.1° for the (110) phase can be seen, along with a peak at 12.7° corresponding to the (001) plane of the hexagonal PbI_2 . The proportions of PbI_2 decrease from 7.06% to 6.17% after ATMP-K doping, indicating the conversion of the PbI_2 to perovskites in the two-step procedure is facilitated by the ATMP-K doping on SnO_2 (Table S2, Supporting Information). We speculate that the strong interaction between ATMP and PbI_2 , as predicted by our DFT calculations, may slow down the nucleation process, contributing to the observed increase in the average perovskite grain size. The optical characteristics of perovskite films are studied by UV-vis absorption spectra in Figure 3e. The presence of ATMP does not affect the absorption edge of perovskite films while slightly increasing the absorption intensity. The bandgap of both films extracted from Tauc plots shows an identical value of 1.52 eV (Figure S12b, Supporting Information). In addition, the XPS spectra of the perovskite films deposited on SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ are the same, indicating that the composition of the perovskite remains the same after the ATMP-K doping (Figure S13, Supporting Information).

To further study the charge transfer at ETL/perovskite interface, steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopy measurements are performed. Figure 3f shows that the quenching efficiency of the $\text{SnO}_2 + \text{ATMP-K}$ samples is higher, which indicates that the ATMP-K doping can facilitate the extraction of electrons from the perovskite film. To quantify this process, TRPL spectra are collected and fitted by biexponential decay function producing a fast decay (τ_1) and slow decay (τ_2) component (Figure 3g and Table S3, Supporting Information). The τ_1 and τ_2 of the $\text{SnO}_2 + \text{ATMP-K}$ sample are 45 and 170 ns, respectively, while the control sample showed a larger τ_1 of 57 ns and a comparable τ_2 of 147 ns. PL and TRPL both show that $\text{SnO}_2 + \text{ATMP-K}$ exhibits faster electron extraction. As determined from the dark current J - V curve of electron-only device (Figure S14, Supporting Information), the calculated n_t is $4.85 \times 10^{15} \text{ cm}^{-3}$ and $2.26 \times 10^{15} \text{ cm}^{-3}$ (described in the Experimental Section), respectively. Therefore, after ATMP-K doping, the trap density of the perovskite film decreases dramatically, by $\approx 53\%$, compared with the perovskite based on the pristine SnO_2 layer. This can be related to the increased grain size of the perovskite film with the doping of ATMP (Figure 3b).

2.4. Device Performance

To determine the optimal mixing ratio of ATMP and KOH for fabricating efficient devices, from 100 to 600 μL ATMP is mixed with 1000 μL KOH (KOH has a fixed concentration, see the Experimental Section for more details) and the mixture is added to the SnO_2 dispersions. It is worth mentioning that the aforementioned characterizations are all based on the best ratio. Figure S15, Supporting Information, shows the J - V curves of PSCs with SnO_2 doped with KOH and different concentrations of ATMP-K. The device performance is shown in Table 1 and Table S4, Supporting Information. All devices exhibit good reproducibility. With the increased amount of ATMP, V_{OC} , J_{SC} , FF, and PCE increase at first and then decrease (Figure S16, Supporting Information). Steady-state PL of the SnO_2 films with different

Table 1. The device performance obtained with SnO_2 dispersions containing ATMP-K with different concentrations.

	V_{OC} [V]	FF [%]	J_{SC} [mA cm^{-2}]	PCE [%]
SnO_2	1.11	78.84	23.69	20.73
$\text{SnO}_2 + (10:1) \text{ ATMP-K}$	1.13	78.67	24.05	21.38
$\text{SnO}_2 + (10:2) \text{ ATMP-K}$	1.14	79.36	24.07	21.78
$\text{SnO}_2 + (10:4) \text{ ATMP-K}$	1.15	80.59	24.42	22.63
$\text{SnO}_2 + (10:6) \text{ ATMP-K}$	1.13	80.54	23.76	21.62

concentrations of ATMP-K doping was measured, and the results are shown in Figure S17, Supporting Information. ITO/ $\text{SnO}_2 + (10:4) \text{ ATMP-K}$ /perovskite yields a stronger PL quenching effect, indicating faster electron extraction capacity for ETLS. When the volume of ATMP doping is too high (600 μL), the device performance drops to 21.22%. Excessive ATMP in SnO_2 causes nanocrystal agglomeration, which reduces the dispersion of SnO_2 nanocrystals and inhibits the transfer and transportation of charges. From Figure 4a, the $\text{SnO}_2 + \text{ATMP-K}$ -based devices exhibit negligible hysteresis, in contrast to the undoped SnO_2 -based devices (Table S5, Supporting Information). An optimized device with a PCE of 23.52% with V_{OC} of 1.15 V, J_{SC} of 25.50 mA cm^{-2} , and FF of 80.21% was successfully fabricated (Figure S18a, Supporting Information). Different from the wide distribution of SnO_2 -based PSCs (V_{OC} from 1.07 to 1.13 V, FF from 72% to 80%), the V_{OC} and FF of $\text{SnO}_2 + \text{ATMP-K}$ -based PSCs range between 1.12–1.16 V and 78–83%, respectively (see also Figure S18b, Supporting Information). According to the aforementioned discussion, the enhanced performance is mainly attributed to the increased V_{OC} and FF. We attribute the increase in FF to the elevated electron mobility because of the doping of ATMP, while the increase in V_{OC} stems from the optimized energy-level position of SnO_2 relative to that of perovskite absorber and the improved quality of the perovskite film. The light response of the devices was investigated by external quantum efficiency (EQE) spectra (Figure 4b). From 400 to 750 nm, EQE values are higher than 90%. The integrated J_{SC} from the EQE reaches 24.80 mA cm^{-2} , which is close to that from the J - V measurement. The steady-state efficiency at maximum power point (MPP) tracking of the optimized PSC was also measured, and the $\text{SnO}_2 + \text{ATMP-K}$ based devices exhibit stable output for over 2000 s with a PCE of 22.37% (Figure 4c).

To highlight the benefit of ATMP, we also apply $\text{SnO}_2 + \text{ATMP-K}$ to perovskite/silicon heterojunction tandem solar cell (TSC) (Figure S19, Supporting Information). The device with ATMP-K delivers a PCE of 24.75% with V_{OC} of 1.942 V, J_{SC} of 16.66 mA cm^{-2} , and FF of 76.50%, compared with pristine SnO_2 -based TSC of 22.67%, with V_{OC} of 1.854 V, J_{SC} of 16.58 mA cm^{-2} , and FF of 73.75% (Figure 4d and Table S6, Supporting Information), which is state of the art in N-I-P-type perovskite/silicon heterojunction TSC. The increased device efficiency is attributed to the enhanced V_{OC} and FF, and the V_{OC} is the highest voltages demonstrated by N-I-P-type perovskite/silicon heterojunction TSC (Table S7, Supporting Information). The integrated current of top/bottom cells from the EQE spectra of perovskite/silicon heterojunction TSC is

Figure 4. Performance of device with SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$. a) Forward and reverse scanned J - V curves of the best device measured under AM1.5G solar irradiation at 100 mW cm^{-2} (the effective area of PSCs is 0.089 cm^2). b) The corresponding EQE spectra of the device based on SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$. c) The corresponding steady-state PCE of the device based on $\text{SnO}_2 + \text{ATMP-K}$ under continuous illumination. d) J - V curves of perovskite/silicon heterojunction TSC with $\text{SnO}_2 + \text{ATMP-K}$ and pristine SnO_2 (the effective area of TSCs is 0.5091 cm^2). e) The EQE of the top and bottom cells for the tandem device with $\text{SnO}_2 + \text{ATMP-K}$. f) The corresponding steady-state PCE of perovskite/silicon heterojunction TSC with $\text{SnO}_2 + \text{ATMP-K}$ under continuous illumination. g) Long-term stability measurements of devices based on different ETLs without encapsulation under N_2 atmosphere at room temperature.

16.9 and 16.9 mA cm^{-2} , respectively (Figure 4e). The stabilized PCE outputs of the devices are further monitored at MPP bias voltages, as shown in Figure 4f. Stabilized PCEs of 24.4% are shown for perovskite/silicon heterojunction TSC with the $\text{SnO}_2 + \text{ATMP-K}$. Finally, we performed long-term operational stability tests to determine the benefit of ATMP. The stability of the device with SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ stored in N_2 atmosphere for 50 days is shown in Figure 4g. The devices based on SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$ are stored for 50 days at room temperature in a N_2 atmosphere without any light during the storage period except for measurement. The efficiency of the devices based on SnO_2 decreases rapidly, while the efficiency of the devices based on $\text{SnO}_2 + \text{ATMP-K}$ decreases only slightly, retaining 93% of the initial efficiency after 1000 h. Figure S20, Supporting Information, shows the stability of the unencapsulated PSCs stored in an ambient environment with 30–50% RH. The PCE of PSCs based on $\text{SnO}_2 + \text{ATMP-K}$ remained at 90% of its initial

value after 1200 h storage, whereas the PCE of PSCs based on SnO_2 decreased to 20% of its initial value. These stability tests indicated that perovskite films grown on the $\text{SnO}_2 + \text{ATMP-K}$ were more robust against the erosion of moisture and oxygen.

2.5. Lead Detection of PSCs

According to our DFT calculation, there is a strong interaction between ATMP and PbI_2 . We speculate that the doping of ATMP may reduce the lead leakage in the perovskite. To verify the feasibility of doping ATMP in minimizing the Pb^{2+} leakage in the degraded perovskite, research is conducted on the perovskite in water. In Figure 5a, the positions of $\text{Pb } 4f_{7/2}$ and $\text{Pb } 4f_{5/2}$ peaks at 138.7 and 142.8 eV remain unchanged, while the peak intensity is slightly reduced after the ATMP-K doping, which is consistent with the XRD pattern result. To investigate the effect of ATMP on the degradation of PSCs, SnO_2 and $\text{SnO}_2 + \text{ATMP-K}$

Figure 5. Lead detection of PSCs. a) Schematic diagram of Pb detection on the surface of ETLs. Before and after the decomposition of the perovskite, XPS is performed to detect the Pb concentration on the surface of SnO₂ and SnO₂ + ATMP-K (Figure 5a). The Pb content on the surface of SnO₂ + ATMP-K was found to be 11.3 times higher than that on the surface of SnO₂. Perovskites tend to decompose into lead iodide in the presence of water; however, our DFT calculations show the PA groups of ATMP form a strong and stable bond with Pb²⁺, explaining the fact that a larger amount of Pb²⁺ species are found on the surface of ATMP-doped SnO₂ than the reference SnO₂. Furthermore, to further verify the ability of absorbing Pb²⁺ ions of ATMP, the devices were washed by deionized water many times after perovskite decomposed. XPS was performed to compare the concentration of Pb on different ETLs (Figure 5b, Figure S21 and Table S8, Supporting Information). It can be seen that the lead on SnO₂ + ATMP-K changes little with the increase in washing times, while the lead on SnO₂ decreases, especially after washing eight times, no lead being found on SnO₂. All the aforementioned results indicate that the ATMP forms a strong and stable bond to Pb²⁺ and captures Pb²⁺ leaked from degraded perovskite.

K with the perovskite layer are immersed in 10 mL deionized water with a pH value of ≈ 6.2 for 5 days. Then XPS is used to measure the Pb concentration on the surface of SnO₂ and SnO₂ + ATMP-K (Figure 5a). The Pb content on the surface of SnO₂ + ATMP-K was found to be 11.3 times higher than that on the surface of SnO₂. Perovskites tend to decompose into lead iodide in the presence of water; however, our DFT calculations show the PA groups of ATMP form a strong and stable bond with Pb²⁺, explaining the fact that a larger amount of Pb²⁺ species are found on the surface of ATMP-doped SnO₂ than the reference SnO₂. Furthermore, to further verify the ability of absorbing Pb²⁺ ions of ATMP, the devices were washed by deionized water many times after perovskite decomposed. XPS was performed to compare the concentration of Pb on different ETLs (Figure 5b, Figure S21 and Table S8, Supporting Information). It can be seen that the lead on SnO₂ + ATMP-K changes little with the increase in washing times, while the lead on SnO₂ decreases, especially after washing eight times, no lead being found on SnO₂. All the aforementioned results indicate that the ATMP forms a strong and stable bond to Pb²⁺ and captures Pb²⁺ leaked from degraded perovskite.

To investigate the lead leakage that occurred in the degraded PSCs and quantify the adsorption ability of ATMP for Pb²⁺ ions, SnO₂ + ATMP-K and reference SnO₂ samples were put in the aforementioned contaminated water with Pb²⁺ (Figure 5a) for 5 days. Then 0.22 μm membrane was used to filter the water in the petri dish, and inductively coupled plasma optical emission spectrometer (ICP-OES) was used to quantify the Pb²⁺ concentrations. In Figure 5c, the Pb²⁺ concentrations in the sample with SnO₂ + ATMP-K dropped sharply to 50% of the original concentration, while that with SnO₂ was 86% of the original concentration (94.49 $\mu\text{g mL}^{-1}$), indicating ATMP can capture Pb²⁺ ions leaked from the degraded PSCs.

3. Conclusion

In summary, the molecule ATMP was introduced as an additive to modify S in PSCs. Combining DFT calculations and experimental testing, the ATMP is found to passivate oxygen vacancies and to reduce the surface hydroxyl groups, providing an

optimized interface for the growth of larger grains and improved quality of perovskite film. Such surface modification also enhances the photoelectrical properties of SnO_2 in the PSCs by shifting the work function upward to achieve better energy alignments with the perovskite absorber layer. PSCs based on SnO_2 + ATMP-K produce an excellent PCE of 23.52%, with a V_{oc} of 1.15 V and a J_{sc} of 25.50 mA cm^{-2} , and FF of 80.21%. The PSCs retain 93% of their initial performance (PCE > 22%) after being stored in the glove box for 1000 h. In addition, the PCE of PSCs based on SnO_2 + ATMP-K remained at 90% of its initial value after 1200 h storage in an ambient environment with 30–50% RH. Further degradation testing confirms that the ATMP can effectively combine with Pb^{2+} via forming strong $\text{Pb}=\text{O}=\text{P}$ bonding, improving the stability of PSCs and reducing lead leakage during their degradation in water. Furthermore, the employment of the SnO_2 + ATMP-K layer also lifted the PCE of the perovskite/silicon TSC from 22.67% to 24.75%, which was mainly attributed to the improvements in both V_{oc} and FF. Our strategy of using ATMP to optimize the atomistic details of the surface/interfaces of SnO_2 for improved efficiency and stability as well as preventing Pb leakages during the degradation of PSCs paves the way for the large-scale deployment PSCs.

4. Experimental Section

Materials: Lead iodide (PbI_2), bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI), 4-tert-butylpyridine (tBP) chlorobenzene, dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and isopropyl alcohol (IPA) were purchased from Sigma-Aldrich. Formamidinium iodide (FAI), methylammonium iodide (MAI), and methylammonium chloride (MACl), 2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) were purchased from Xi'an Polymer Light Technology Corp. Tin (IV) oxide colloid precursor was purchased from Alfa Aesar. ATMP was purchased from Shanghai Titan Technology Corp.

Single-Junction PSCs: First, the ITO substrates were cleaned by detergent, deionized water, and isopropyl alcohol, respectively. The as-cleaned substrates were treated by UV-ozone for 20 min. KOH (0.22 mg) is added into deionized water (10 mL), taking KOH (1000 μL) mix with different volumes of ATMP. SnO_2 with ATMP-KOH was spin-coated at 4000 rpm for 30 s, and annealed at 150°C for 30 min in ambient air. After that, PbI_2 (0.6915 g) precursor solution was spin-coated onto SnO_2 at the speed of 1500 rpm for 30 s and annealed at 70°C for 1 min. When the PbI_2 film was cooled down to room temperature, a mixture solution of organic salt (FAI:MAI:MACl = 90:6.39:9) was spin-coated onto the PbI_2 film at a speed of 2000 rpm for 30 s followed by annealing at 150°C for 15 min in ambient air (about 30–40% humidity).^[47] After perovskite formation, the samples were transferred to a nitrogen-filled glove box for further processing. The PEAI (0.005 M) solution was dissolved in IPA and spin-coated onto the perovskite surface at a spin rate of 5000 rpm without any further processing. Then the hole transporting layer was deposited on top of the perovskite layer at a spin rate of 3000 rpm for 30 s using spiro-OMeTAD (72.3 mg spiro-OMeTAD, 35 μL bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) stock solution (260 mg Li-TFSI in 1 mL acetonitrile), 30 μL 4-tertbutylpyridine and 1 mL chlorobenzene). Finally, 80 nm of Au top electrode was thermally evaporated under vacuum with a shadow mask. The area of the cells was 0.12 cm^2 ; when measuring, a 0.089 cm^2 mask was used to define the accurate aperture area for the cells.

Perovskite/Silicon Heterojunction TSCs: Silicon heterojunction (SHJ)-bottom cell was treated with UV-O_3 for 15 min. SnO_2 (+ATMP-K) is used as the electron transport layer. The $\text{Cs}_{0.22}\text{FA}_{0.78}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ (50 μL) with the concentration of 1.4 M was spread on the substrate and spun at 5000 rpm with a ramp rate of 1000 rpm s^{-1} for 50 s. The methyl acetate (200 μL) was

dripped onto the substrate with 20 s remaining in the spin cycle. The perovskite layer was then annealed at 100°C for 30 min. Spiro-OMeTAD on the perovskite film was fabricated at 5000 rpm for 20 s. Furthermore, the 9 nm-thick MoO_x was thermally evaporated on the substrate in a vacuum chamber at a base pressure around 4×10^{-5} mbar and deposition rates of $0.1 \text{ \AA s}^{-1}$. Then the top contact was formed by 110 nm-thick ITO deposited by DC magnetron sputter deposition at room temperature and without further annealing of the sample. The TSCs with home-made PDMS antireflection film.^[48] Finally, a gold electrode was thermally evaporated on the top through a shadow mask, defining a frame around the transparent cell area.

Characterization: SEM (FEI NanoSEM650) was used to characterize the morphology of the In_2O_3 , SnO_2 , and perovskite films and also the cross-sectional image of the full device. The XRD patterns of the perovskite films were performed by Mini Flex 600 (Rigaku D/MAX-2500, Japan). The AFM images were characterized by AFM (NanoNavi-SPA400, Japan). The PL and TRPL spectra were conducted via a fluorescence spectrophotometer (FLS980, Edinburgh Instruments, UK). The current–voltage characteristics of the devices were measured by a Keithley 2400 Source meter under AM1.5G illumination with a xenon-lamp-based solar simulator (SS-F5-3A, Enli. Tec., Taiwan). The intensity of the light was calibrated with a KG-5 filter Si photodiode. And the cells were measured with a metal mask (0.0887 cm^2) to reduce the influence of the scattered light. The measuring condition was forward scan (0–1.2 V, scan rate 20 mV s^{-1} , delay time 20 ms) and reverse scan (1.2–0 V, scan rate 20 mV s^{-1} , delay time 20 ms) at 25°C in N_2 -filled glove box. The EQE spectra were conducted in the air without encapsulation by the Enli Tec (Taiwan) measurement system. For TSCs, photocurrent density–voltage (J – V) curves of solar cells were measured at 25°C in N_2 -filled glove box under the AM1.5G (100 mW cm^{-2}) illumination with a xenon-lamp-based solar simulator (SS-F5-3A, Enli. Tec., Taiwan). The monolithic tandem cell has an active area of 0.5091 cm^2 defined by the overlapping area of the top and bottom subcell, and a 0.5091 cm^2 aperture was used during J – V measurement. Unless specified, a bias scan was operated first from 2.0 to 0 V (the so-called reverse scan) with a voltage step of 20 mV and delay time 20 ms. A reverse curve is mainly adopted to evaluate the device performance. The current–voltage characteristics of the devices were measured by a Keithley 2400 Source meter under AM1.5G illumination with a xenon-lamp-based solar simulator (SS-F5-3A, Enli. Tec., Taiwan). The intensity of the light was calibrated with a KG-5 filter Si photodiode. The steady-state photocurrent density and efficiencies were obtained by tracking the maximum output power point, following the method described in reference. The spectral response was taken by EQE measurement system (QEX10, PV Measurement) in the wavelength range from 300 to 1200 nm with a scanning step of 10 nm. Xenon arc lamp was used as the monochromatic light excitation source and filtered by a double grating. The frequency of monochromatic light was around 80 Hz. Each individual subcell in the tandem must be electrically isolated to obtain an EQE spectrum. The top cell was measured by saturating the bottom cell with infrared light ($>800 \text{ nm}$), whereas the bottom cell was measured by saturating the top cell with blue light (400–500 nm). No white-light bias was used during the EQE measurement. The conductivity σ of SnO_2 and SnO_2 + ATMP-K is determined by the slope of the J – V curve according to the equation $J = \sigma AV/d$, where A is the detection area and d represents the average thickness of SnO_2 and SnO_2 + ATMP-K. The space-charge-limited-current (SCLC) method based on the electron-only devices with the structure of ITO/ SnO_2 (+ATMP-K)/perovskite/PCBM/Cu is used to measure the trap-state density within the perovskite film. In addition, the applied voltage at the kink-point voltage is defined as the trap-filled limit voltage (V_{TFL}), which is linearly proportional to the density of trap states (n_t) of the perovskite layer according to the following equation: $n_t = 2V_{\text{TFL}}\epsilon_0/ed^2$, where ϵ is the dielectric constant of perovskite, ϵ_0 is the vacuum permittivity, d is the thickness of perovskite film, and e is the electronic charge.

DFT Calculation: DFT calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP).^[49–52] The electronic exchange–correlation interaction was described by the functional of Perdew, Burke, and

Ernzerhof (PBE) within the spin-polarized generalized gradient approximation (GGA).^[53] Energy and force convergence criteria of 10^{-5} eV and 10^{-2} eV Å⁻¹, respectively, were used in all calculations. For the geometry optimization of bulk SnO₂ a rutile unit cell of six atoms was used, along with a kinetic energy cutoff of 500 eV and a $4 \times 4 \times 4$ *k*-point grid. The calculated lattice parameters were $a = 4.83$ Å and $c = 3.24$ Å, in good agreement with the experimental values $a = 4.74$ Å and $c = 3.19$ Å.^[54] To model the (110) SnO₂ surface, symmetric three-trilayer slabs were used, with a 4×2 surface supercell and a vacuum region of ≈ 28 Å separating the slabs. The bottom trilayer was kept fixed, while the ion positions of the top layers were allowed to relax. A kinetic energy cutoff of 400 eV and a $2 \times 2 \times 1$ *k*-point grid were used for the SnO₂ slab calculations, as well as a dipole correction to prevent the interaction between periodic images.^[55] For the calculation of the ATMP binding energy on FAPbI₃, an 11-layer PbI₂ terminated slab was used with a 2×2 cubic supercell and a vacuum region of 20 Å. Only the top three layers were allowed to relax. The same energy cutoff and *k*-point grid were used, as in the case of the SnO₂ slab calculations. Still, the D3 correction was used to account for the van der Waals interactions due to the presence of the organic cations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

X.Z., J.Z., and R.L. proposed the research and designed the experiments. J.Z. and R.L. conducted the experiments. S.A. and J.J. contributed to the density functional theory calculations under the guidance of G.B. and S.T. R.L., N.R., and W.H. fabricated the perovskite/silicon heterojunction tandem solar cell. P.W., B.S., N.R., W.H., Q.H., G.B., and Y.Z. helped the analysis. J.Z., R.L., and S.A. wrote the first version of the manuscript. X.Z. and S.T. revised the manuscript. All authors commented on the manuscript. X.Z. directed the overall project.

Data Availability Statement

Research data are not shared.

Keywords

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