Multifunctional molecule engineered SnO2 for perovskite solar cells with high efficiency and reduced lead leakage

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

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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...
inevitable impact to the following perovskite growth, which will determine the performance and long-term stability of the PSCs.\cite{20–22}

Due to the low cost, good chemical stability, and high electron mobility,\cite{23} SnO$_2$ is usually used as the electron transport layers (ETLs) in N–I–P-type PSCs.\cite{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 SnO$_2$ NPs usually results in low electrical conductivity, which leads to weak electron injection/transport capabilities of SnO$_2$ film. Moreover, the hydroxyl on surface of SnO$_2$ film usually generates trap states near the valence band,\cite{38} which will cause nonradiative recombination at the SnO$_2$/perovskite interface and thus produce a low open-circuit voltage ($V_{OC}$), FF, and severe hysteresis.\cite{4,20,22,38–45}

Herein, the mixture of amino trimethylene phosphonic acid (ATMP) and KOH are (ATMP-K) doped in SnO$_2$ to overcome the aforementioned problems. First, we confirm through density functional theory (DFT) calculations that ATMP can passivate the surface of SnO$_2$ by replacing the surface hydroxyls and strong binding to the surface Sn atoms. Our DFT calculations also indicate strong interactions of ATMP with PbI$_2$. Therefore, we hypothesize that ATMP can improve the quality of the perovskite deposited on the ATMP-modified SnO$_2$ and of the overall interface. To examine the validity of our hypothesis, we fabricate PSCs with ATMP-modified SnO$_2$ as the ETL. Our experiments confirm that ATMP effectively reduces the hydroxyl groups on the surface of SnO$_2$ and adjusts the energy levels of SnO$_2$, 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 Pb$^{2+}$ ions, the ATMP-modified PSCs show much-reduced leakage of toxic Pb$^{2+}$ 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 SnO$_2$ to achieve highly efficient and environmentally friendly PSCs.

2. Results and Discussion

2.1. DFT Calculations of ATMP-Modified SnO$_2$

DFT is used to explore the effects of the ATMP on SnO$_2$. We choose the stoichiometric (110) surface for the study as it is the most thermodynamically stable configuration.\cite{27,46} The calculations show that ATMP binds strongly to the SnO$_2$ surface by replacing the hydroxyls on the surfaces (SnO$_2$/C$_0$(OH)$_n$) (Figure 1a).

According to the following equation

$$\text{SnO}_2 - (\text{OH})_n + \text{ATMP} \rightarrow \text{SnO}_2(\text{OH})_{n-x} - \text{ATMP} + x\text{H}_2\text{O}$$

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 $\text{P}=\text{O}–\text{Sn}$ bonds. Apart from the hydroxyl removal from the SnO$_2$ 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 SnO$_2$ is 0.6 eV higher than that of the fully hydroxylated SnO$_2$ (Figure S1, Supporting Information).

The quality of the perovskite deposited on the ATMP optimized SnO$_2$ is also expected to be superior to that of a film deposited on reference SnO$_2$ 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 SnO$_2$ surface. b) Reaction energies of ATMP removing $x$ hydroxyl on SnO$_2$ surface for $x = 1$, 2, and 3, respectively. c) The schematic of mechanisms of the perovskite growth on SnO$_2$ and ATMP optimized SnO$_2$. 

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The molecule’s geometry does not seem to facilitate the creation of more than three bonds with SnO2; however, we speculate the remaining dangling phosphate groups can interact with the perovskite species (in the formation of PbI3 and the subsequent formation of perovskites) and further affect its morphology (Figure 1c). The calculated interaction energy between a PbI2 molecule with the ATMP optimized SnO2 surface is $-1.25$ eV compared with $-0.66$ eV for the fully hydroxylated SnO2 (Figure S2, Supporting Information). This means that at the crystallization stage, the stronger interaction between ATMP and PbI2 could slow down the nucleation process, resulting in an improved perovskite morphology. Moreover, ATMP is found to bind the surface of FAPbI3 through $\equiv P=O$ bonds, with a binding energy of $-1.58$ eV, implying a potential strong adhesion of the perovskite to the optimized SnO2 (Figure S3, Supporting Information). Interestingly, such $\equiv P=O$ bonds have been previously suggested to stabilize the perovskite deposited on SnO2 by blocking environmental O2 and H2O.

2.2. Characterization of ETLs

We further proceed with experiments to investigate the validity of our hypothesis regarding the influence of ATMP on SnO2. When ATMP alone is doped into the SnO2 colloidal solution, as shown in Figure S4, Supporting Information, the nanoparticles in the SnO2 solution agglomerate and the SnO2 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 SnO2 + ATMP-K), where KOH is used to reduce the acidity of ATMP and then stabilize the SnO2 colloidal dispersion. SnO2 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 SnO2 and SnO2 + 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 SnO2 (Figure S5 and S6, Supporting Information). The presence of element phosphorus (P) in the doped SnO2 is confirmed by a small peak at 134 eV in the X-ray photoelectron spectroscopy (XPS) spectrum of SnO2 + ATMP-K films (Figure S7a,b, Supporting Information). Sn 3d peaks in SnO2 + ATMP-K has moved to higher binding energies (Figure 2a), which can be attributed to the strong binding of the $\equiv P=O$ groups of ATMP to the surface Sn atoms. This is further supported by the absence of such a shift, when SnO2 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 SnO2 and the oxygen from hydroxyl (–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...
SnO$_2$ + 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 SnO$_2$ + 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 $E_F - E_{VBM}$ value of ETL increases from 3.48 to 3.68 eV after ATMP doping, and the band structures of SnO$_2$ + 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 SnO$_2$ + 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 SnO$_2$ + ATMP-K is calculated as $6.32 \times 10^{-5}$ S cm$^{-1}$ and $6.50 \times 10^{-3}$ 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 of the perovskite films deposited on different ETLs is displayed (Figure S13, Supporting Information). The top-view SEM of the perovskite films spin-coated on the pristine SnO$_2$ and SnO$_2$ + ATMP-K both shows a continuous and uniform film without apparent pinholes. Moreover, the perovskite deposited on SnO$_2$ + 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 SnO$_2$ + ATMP-K is 870 nm and 1 μm, respectively. In addition, the perovskite on SnO$_2$ + 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
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 PbI₂. The proportions of PbI₂ decrease from 7.06% to 6.17% after ATMP-K doping, indicating the conversion of the PbI₂ to perovskites in the two-step procedure is facilitated by the ATMP-K doping on SnO₂ (Table S2, Supporting Information). We speculate that the strong interaction between ATMP and PbI₂, 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 SnO₂ and SnO₂ + 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 SnO₂ + 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 (τ₁) and slow decay (τ₂) component (Figure 3g and Table S3, Supporting Information). The τ₁ and τ₂ of the SnO₂ + ATMP-K sample are 45 and 170 ns, respectively, while the control sample showed a larger τ₁ of 57 ns and a comparable τ₂ of 147 ns. PL and TRPL both show that SnO₂ + 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 nₑ is 4.85 × 10¹⁵ cm⁻³ and 2.26 × 10¹⁵ cm⁻³ (described in the Experimental Section), respectively. Therefore, after ATMP-K doping, the trap density of the perovskite film decreases dramatically, by ≤53%, compared with the perovskite based on the pristine SnO₂ 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 SnO₂ 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 SnO₂ 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, Vₑ, Jₑ, FF, and PCE increase at first and then decrease (Figure S16, Supporting Information). Steady-state PL of the SnO₂ films with different concentrations of ATMP-K doping was measured, and the results are shown in Figure S17, Supporting Information.ITO/SnO₂ + (10:4) 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 SnO₂ causes nanocrystal agglomeration, which reduces the dispersion of SnO₂ nanocrystals and inhibits the transfer and transportation of charges. From Figure 4a, the SnO₂ + ATMP-K-based devices exhibit negligible hysteresis, in contrast to the undoped SnO₂-based devices (Table S5, Supporting Information). An optimized device with a PCE of 23.52% with Vₑ of 1.15 V, Jₑ of 25.50 mA cm⁻², and FF of 80.21% was successfully fabricated (Figure S18a, Supporting Information). Different from the wide distribution of SnO₂-based PSCs (Vₑ from 1.07 to 1.13 V, FF from 72% to 80%), the Vₑ and FF of SnO₂ + 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 Vₑ and FF. We attribute the increase in FF to the elevated electron mobility because of the doping of ATMP, while the increase in Vₑ stems from the optimized energy-level position of SnO₂ 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 Jₑ 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 SnO₂ + 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 SnO₂ + 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 Vₑ of 1.942 V, Jₑ of 16.66 mA cm⁻², and FF of 76.50%, compared with pristine SnO₂-based TSC of 22.67%, with Vₑ of 1.854 V, Jₑ 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—I—I–P-type perovskite/silicon heterojunction TSC. The increased device efficiency is attributed to the enhanced Vₑ and FF, and the Vₑ is the highest voltages demonstrated by N—I—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

| Table 1. The device performance obtained with SnO₂ dispersions containing ATMP-K with different concentrations. |
|-------------------------------------------------|----------|----------|----------|----------|
| Vₑ [V] | FF [%] | Jₑ [mA cm⁻²] | PCE [%] |
| SnO₂ | 1.11 | 78.84 | 23.69 | 20.73 |
| SnO₂ + (10:1) ATMP-K | 1.13 | 78.67 | 24.05 | 21.38 |
| SnO₂ + (10:2) ATMP-K | 1.14 | 79.36 | 24.07 | 21.78 |
| SnO₂ + (10:4) ATMP-K | 1.15 | 80.59 | 24.42 | 22.63 |
| SnO₂ + (10:6) ATMP-K | 1.13 | 80.54 | 23.76 | 21.62 |
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 SnO$_2$ + 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 SnO$_2$ + ATMP-K stored in N$_2$ atmosphere for 50 days is shown in Figure 4g. The devices based on SnO$_2$ and SnO$_2$ + 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 SnO$_2$ + 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 SnO$_2$ + 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 SnO$_2$ + 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 Pb 4f$_{7/2}$ and 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 SnO$_2$ + ATMP-
K with the perovskite layer are immersed in 10 mL deionized water with a pH value of \(
\approx 6.2\) for 5 days. Then XPS is used to measure the Pb concentration on the surface of SnO\(_2\) and SnO\(_2\) + ATMP-K (Figure 5a). The Pb content on the surface of SnO\(_2\) + ATMP-K was found to be 11.3 times higher than that on the surface of SnO\(_2\). 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 Pb\(^{2+}\), explaining the fact that a larger amount of Pb\(^{2+}\) species are found on the surface of ATMP-doped SnO\(_2\) than the reference SnO\(_2\). Furthermore, to further verify the ability of absorbing Pb\(^{2+}\) 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 SnO\(_2\) + ATMP-K changes little with the increase in washing times, while the lead on SnO\(_2\) decreases, especially after washing eight times, no lead being found on SnO\(_2\). All the aforementioned results indicate that the ATMP forms a strong and stable bond to Pb\(^{2+}\) and captures Pb\(^{2+}\) leaked from degraded perovskite.

To investigate the lead leakage that occurred in the degraded PSCs and quantify the adsorption ability of ATMP for Pb\(^{2+}\) ions, SnO\(_2\) + ATMP-K and reference SnO\(_2\) samples were put in the aforementioned contaminated water with Pb\(^{2+}\) (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 sued to quantify the Pb\(^{2+}\) concentrations. In Figure 5c, the Pb\(^{2+}\) concentrations in the sample with SnO\(_2\) + ATMP-K dropped sharply to 50% of the original concentration, while that with SnO\(_2\) was 86% of the original concentration (94.49 μg mL\(^{-1}\)), indicating ATMP can capture Pb\(^{2+}\) 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 SnO₂ in the PSCs by shifting the work function upward to achieve better energy alignments with the perovskite absorber layer. PSCs based on SnO₂ + 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 SnO₂ + 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 Pb²⁺ via forming strong Pb-O=Sn bonding, improving the stability of PSCs and reducing lead leakage during their degradation in water. Furthermore, the employment of the SnO₂ + 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 atomic details of the surface/interfaces of SnO₂ for improved efficiency and stability as well as preventing Pb leakages during the degradation of PSCs paves the way for the large-scale deployment of PSCs.

4. Experimental Section

Materials: Lead iodide (PbI₂), bis(trifluoromethylsulfonyl)imide lithium salt (LiTFSI), 4-tert-butylpyridine (TBP) chlorobenzene, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), and isopropyl alcohol (IPA) were purchased from Sigma-Aldrich. Formamidinium iodide (FAI), methylvammonium iodide (MAI), and methylammonium chloride (MACI), 2,2′,7,7′-tetakis(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 Shanghai Titan Technology Corp. 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. SnO₂ 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, Pbl₂ (0.6915 g) precursor solution was spin-coated onto SnO₂ at the speed of 1500 rpm for 30 s and annealed at 70 °C for 1 min. Then the top contact was formed by using ATMP-K. The space-charge-limited-current (SCLC) method based on the electron-only devices with the structure of ITO/SnO₂(+)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 ($V_{tf}$), which is linearly proportional to the density of trap states ($n_t$) of the perovskite layer according to the following equation: $n_t = 2V_{tf}e_d/e_f^2$, where $e$ is the dielectric constant of perovskite, $e_d$ is the vacuum permittivity, $d$ is the thickness of perovskite film, and $e_f$ 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).

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Ernzerhof (PBE) within the spin-polarized generalized gradient approximation, (GGA)[21] Energy and force convergence criteria of $10^{-3}$ eV and $10^{-2}$ eV Å$^{-1}$, respectively, were used in all calculations. For the geometry optimization of bulk SnO$_2$, 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.[22] To model the (110) SnO$_2$ surface, symmetric three-trilayer slabs were used, with a $4 \times 2$ surface supercell and a vacuum region of $\approx 28$ 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 SnO$_2$ slab calculations, as well as a dipole correction to prevent the interaction between periodic images.[3] For the calculation of the ATMP binding energy on FAPbI$_3$, an 11-layer PbI$_2$ terminated slab was used with a $2 \times 2$ 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 SnO$_2$ 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 calculations. 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.

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