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SnO₂/Perovskite Interface Engineering with Mixed-Halide Potassium Salts: A Pathway to Efficient and Stable Perovskite Solar Cells through a Combined Experimental-Density Functional Theory Approach

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combined experimental and density functional theory (DFT) analyses demonstrate that K⁺ and halide ions facilitate the removal of oxygen vacancies and extrinsic hydroxyl groups through the formation of KOH. This process effectively reduces the bond strength of surface hydroxyls and enhances interfacial ordering. This results in a smoother interface, larger perovskite grain sizes, improved adhesion, and enhanced charge extraction. The formation of Sn–Cl–Pb and Sn–I–Pb bonds, along with electrostatic interactions among interfacial K⁺, I⁻ in the perovskite structure, and O²⁻ in SnO₂, strengthens the interface and reduces ion migration. KI-modified and mixed KI+KCl devices achieved power conversion efficiencies (PCEs) of 19.86% and 19.15%, respectively, outperforming untreated SnO₂, which had a PCE of 18.41%. More importantly, the mixed KI+KCl treatment shows superior stability improvement compared to individual PHS treatments, retaining over 96% of the initial PCE after 1000 h under 40–50% relative humidity. These findings highlight the critical role of potassium salts in improving both efficiency and stability, offering an effective strategy for advancing PSC technology.

KEYWORDS: Potassium halide salts, Passivation, SnO₂/MAPbI₃ Interface, DFT, Stability

1. INTRODUCTION

The optoelectronic properties of organic—inorganic metal halide perovskites have attracted considerable attention in the field of perovskite solar cells (PSCs) and their applications.¹ These PSCs have rapidly progressed, achieving certified power conversion efficiency (PCE) in the range of 25% to 27% in recent years.^{2–4} This notable achievement makes them promising contenders for the next generation of photovoltaic technology.⁵ The exceptional performance arises from their high light absorption efficiency, superior carrier mobility, tunable direct bandgap, and cost-effective solution-based fabrication methods.^{6–9} Nonetheless, PSCs encounter persistent stability issues when subjected to environmental stresses, including moisture, heat, oxygen, and light, which hinder their commercialization.¹⁰

A standard n-i-p structure consists of an electron transport layer (ETL), a perovskite photoactive layer, and a hole transport layer (HTL), arranged sequentially. In the n-i-p structure, the ETL/perovskite interface plays a pivotal role in determining the overall efficiency and stability of the PSC.¹¹ This interface directly influences the transport and extraction of photogenerated charge carriers and facilitates the growth of the top perovskite film, with larger grains and fewer grain

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Figure 1. Side views of the optimized geometric structures of (a) the pristine $SnO_2/MAPbI_3$ perovskite interface, (b) the decomposed water molecule (H₂O) on the stoichiometric SnO_2 surface forming the terminal hydroxide (OH_T) and bridging hydroxide (OH_B) on the SnO_2 (110) surface, and (c) a distorted heterogeneous interface of the SnO_2 (110) surface with (OH_T and OH_B) stacked with the MAPbI₃ perovskite surface.

boundaries. Nonoptimized ETL/perovskite interfaces can introduce interfacial defects, energy level mismatches, dangling bonds, and charge recombination, all of which degrade PSC performance and stability.¹² Addressing these interfacial challenges is crucial to improving PSC efficiency and durability.

Among various ETL materials, including the widely used titanium dioxide (TiO₂), tin(IV) oxide (SnO_x) has emerged as one of the most promising ETLs for n-i-p structured PSCs. This is due to its outstanding properties, such as a wide bandgap with high optical transmittance, excellent charge mobility, favorable band alignment with common perovskite materials, low-temperature synthesis, and exceptional chemical stability.^{13–16} Despite its advantages, SnO₂ presents several challenges, including a high defect density, intrinsic oxygen vacancies, hydroxyl surface defects, and lattice mismatches at the SnO₂/perovskite interface.^{17,18} These challenges of the SnO₂ layer adversely affect the top perovskite surface, leading to the interfacial degradation of the crystal structure, increased nonradiative recombination, and a significant reduction in the performance and stability of PSCs.^{19,20}

To address these challenges, researchers have focused on various surface treatment strategies for SnO2 that aim to minimize crystal disorder and nonradiative recombination at the perovskite interface while simultaneously improving charge extraction through passivation techniques.¹¹ Among these, interface engineering strategies and surface treatments with potassium halide salts have garnered significant attention as facile yet efficient methods to enhance the performance and stability of PSCs. For instance, Zhu et al. employed potassium chloride (KCl) at the SnO₂/perovskite interface, which led to a notable reduction in surface defect density on the SnO₂ layer and enhanced crystallinity of the composite (FAP $bI_3)_{0.95}$ (MAPbBr)_{0.05} perovskite film.²¹ The study showed an increased open-circuit voltage (V_{oc}) of 1.137 V and, ultimately, a higher PCE of 22.2%. Liu et al. further demonstrated that incorporating a thin KCl interlayer between the SnO₂, ETL, and a triple-cation (CsFAMA) perovskite absorber effectively passivated interfacial defects, suppressed nonradiative recombination, and improved device stability, yielding a PCE of 20.5%.²² In another study, Zang et al. revealed that the doping of potassium fluoride (KF) to the SnO₂-based ETL could significantly improve the electron mobility by regulating the conduction band of the SnO₂ to match better with the (CsPbI₂Br) perovskite films, which enhanced the open circuit voltage and achieved a PCE of 15.39% of the PSCs.²³ Moreover, potassium iodine (KI) incorporation has been shown to reduce deep trap states within the bulk perovskite, effectively suppressing nonradiative recombination and minimizing hysteresis effects in PSCs.^{24,25}

Despite these numerous studies of potassium halide salts, the fundamental mechanisms underlying potassium salt treatments at the SnO₂/perovskite interface in SnO₂-based (MAPbI₃) perovskite devices remain insufficiently understood. This knowledge is essential for developing optimal passivation strategies. Previous work has shown that, when KCl is mixed into the SnO_2 precursor solution, K^+ ions predominantly accumulate at the interface rather than in the bulk.²¹ However, the specific roles of K^+ at the interface have not yet been thoroughly investigated. Preliminary density functional theory (DFT) calculations suggest that the covalent bonds anchoring hydroxyl (OH) groups to the SnO₂ surface are relatively strong, making direct ion exchange with halide ions an unlikely pathway. Instead, we hypothesize that K^+ ions contribute to healing of OH surface defects by forming KOH and enhance bonding between the SnO₂ and perovskite layers. Furthermore, most existing ab initio studies examine the effects of alkali and halide ions either in bulk²⁶ or on the SnO₂ surface²⁷ but rarely consider their roles at the SnO₂/perovskite interface. This highlights the need for ab initio models that explicitly address how potassium salt treatments influence both surfaces. Additionally, the combined effects of different potassium halide salts have yet to be systematically studied or optimized in the existing research.

In this study, potassium halide salts (KI, KCl, and their mixture KI+KCl), referred to as PHSs, are used as passivation layers at the $SnO_2/MAPbI_3$ interface in n-i-p-structured PSCs to improve interfacial quality and device stability. Scanning

electron microscopy (SEM) imaging reveals larger perovskite grains with PHS treatments, while Raman spectroscopy and DFT analyses suggest that K⁺ and halide ions play crucial roles. These ions remove surface hydroxyl groups via KOH formation, enabling halide exchange and forming a thin passivation layer with strong Sn-Cl-Pb and Sn-I-Pb bonds, which stabilize the SnO₂/perovskite interface. Interfacial K⁺ ions also enhance surface adhesion through electrostatic interactions, improving lattice matching and promoting the growth of the top perovskite with large grains and fewer grain boundaries. Characterizations, including spacecharge-limited current, photoluminescence, and electrochemical impedance spectroscopy, confirm improved charge transport, reduced trap density, and enhanced device performance. Devices treated with KI and KI+KCl achieved PCEs of 19.86% and 19.15%, respectively, outperforming the untreated devices at 18.41%. Notably, PSCs with mixed PHS treatments exhibited exceptional stability, retaining over 96% of their initial efficiency after 1000 h under 40-50% relative humidity. DFT-based interface models, including the SnO₂ surface, a PHS passivation layer, and the perovskite surface, further elucidate the chemical bonding and mechanisms underlying these improvements. This study provides key insights into the mechanisms of PHS treatments on the SnO₂ surface, contributing to the development of stable and efficient PSCs and providing information about other surface passivation approaches.

2. RESULTS AND DISCUSSION

We initiated our study by employing DFT calculations to geometrically optimize the surface and interface of the stoichiometric SnO_2 (110) surface by incorporating common surface hydroxyl defects. We constructed asymmetric SnO₂ (110) surface slab models using a supercell of $2 \times 2 \times 2$ conventional rutile SnO₂ unit cells (see the lower half of Figure 1a). The rutile SnO₂ unit cell was first geometrically relaxed using DFT, resulting in lattice parameters of a = 3.24 Å and b= c = 3.42 Å. Hence, the lattice parameters of the SnO₂ (110) surface's unit cell are a = 6.48 Å and b = 6.83 Å, which agree with previously published values.^{28,29} The lattice parameters of the cubic MAPbI₃ perovskite after DFT relaxation are a = b = c= 6.31 Å. The differences in lattice parameters while forming the $SnO_2/MAPbI_3$ interface, as shown in Figure 1a, lead to microstrain defects in which the SnO_2 (110) and perovskite (001) surfaces undergo compressive and tensile stress, respectively.³⁰ First-principles calculations presented in ref 30 reveal that these stresses cause lattice expansion in the perovskite and lattice compression in SnO2. Consequently, we adopted the lattice averaging technique using lattice parameters a = 6.35 Å and b = 6.50 Å to minimize the nonuniformity in lattice parameters at the model interface.²⁹ The lattice mismatches at the perovskite surface are 0.63% and 2.92% along *a* and *b*, and at the SnO₂ surface, they are -2.05%and -5.08% along a and b. The positive and negative values are the tensile and compressive strains, respectively.

To investigate the effects of extrinsic interface defects at $SnO_2/MAPbI_3$, we introduced a water molecule (H₂O) on the stoichiometric SnO_2 (110) surface, as depicted in the inset of Figure 1b. This model will demonstrate that the presence of moisture at the interface is one of the potential contributions to the degradation of the ETL/perovskite surfaces, subsequently leading to the instability of PSCs.

From the geometry optimization, the water molecule energetically favorably breaks into OH⁻ and H⁺, which create two types of hydroxides: terminal hydroxide (OH_T) and bridging hydroxide (OH_B) .²⁷ As illustrated in Figure 1b, OH_T is the OH⁻ that bonds with a 5-fold Sn atom, while the donation of the proton to the bridging oxygen results in OH_B. Not only do these OH_T groups create deep trap states for free carriers on the SnO₂ surface,³¹ but also they can introduce extrinsic surface defects that decrease crystal quality and disrupt charge delocalization at the interface. As shown in Figure 1c, the geometric optimization results for the interface between the MAPbI₃ (001) top surface and the SnO_2 (110) substrate with OH_T and OH_B defects clearly show a lowquality heterogeneous interface, compared to the stoichiometric SnO_2 (110) without H_2O in Figure 1a. Hence, we attribute OH_T and OH_B as the primary extrinsic defects on the SnO_2 (110) surface as prepared in the laboratory (see Figure S1). The disorder at the perovskite surface, which leads to trap-assisted recombination and structural degradation, is therefore caused by the nonlinearity of the OH_T surface defects that anchor the perovskite Pb atoms to the SnO₂ 5-fold Sn atoms.³² These low-quality heterointerface ETL/perovskite interfaces further facilitate the infiltration of moisture and oxygen, accelerating the degradation of the perovskite solar cells.

The experimental results, to be discussed further below, demonstrate that treating SnO_2 with PHS can improve the device stability and efficiency. We hypothesize that the PHS passivation mechanism is directly correlated with the reduction of OH_T at the interface. However, according to our DFT calculations, due to the strong covalent bond that bonds OH_T to the SnO_2 surface and the higher nucleophilicity of OH^- on the SnO_2 substrate, direct ion exchange between the halide ions in PHSs and the OH^- of OH_T should not be the most probable pathway. We hypothesize that K^+ contributes to the healing of OH_T surface defects by forming KOH, which facilitates ion exchange, as suggested by the following characterization results.

We first examined the surface topography (Figure S2) and crystallinity (Figure S3) of FTO/SnO₂/MAPbI₃ film stacks treated with different PHSs. SEM analysis revealed that the control sample (Figure S2a) exhibited a smaller average grain size of 420 nm than the PHS-treated samples (Figure S2b-d). KCl treatment slightly increased the grain size to 426 nm, while KI and mixed KI+KCl passivation significantly enhanced the grain sizes to 466 and 517 nm, respectively. Larger grain sizes are beneficial for improving charge transport by reducing the number of grain boundaries and their defects. Since grain boundaries are susceptible to external factors like moisture and oxygen and serve as migrating channels for ion migrations,³³ the mixed KI+KCl modification should lead to the best stability improvement. The observed increase in perovskite grain size aligns with the hypothesis that PHS treatments can reduce surface OH density on SnO2, because fewer surface OH groups lead to better contact between SnO₂ and perovskite, thereby decreasing interfacial disorder and facilitating the growth of a crystalline perovskite film on top.

X-ray diffraction (XRD) patterns (Figure S3) for the control, KCl, KI, and mixed KI+KCl-treated films exhibit the perovskite phase (α -phase), which agrees with the previous studies.^{34,35} The three prominent peaks at 14.12°, 28.46°, and 31.89° correspond to crystal planes (110), (220), and (310), respectively. Zoomed-in views of these peaks in Figure S4



Figure 2. Raman spectra obtained from (a) SnO_2 nanoparticle, (b) SnO_2 treated with KOH, (c) SnO_2 treated with different PHSs, and (d) KOH Raman vibrational modes.

reveal no noticeable shifts or increases in intensity following PHS treatment, indicating that the lattice parameters and the crystallinity of the top perovskite layer remain unchanged. In contrast to the clear XRD peak shifts observed when interstitial K^+ is intentionally doped into the bulk perovskite by adding KI to the perovskite precursor solution²⁶ or during halide anion exchange within the bulk perovskite,³⁶ our unchanged XRD results suggest that K^+ and halide anions primarily influence the interface region rather than diffusing into the bulk perovskite, which justifies our DFT interface models.

Raman spectroscopy was performed on SnO₂ nanoparticles to investigate the mechanism of PHS treatment on intrinsic defects (e.g., oxygen vacancies) and extrinsic surface defects (e.g., OH_T and OH_B) in the SnO₂ film. Depending on the specific forms of SnO_x, such as rutile SnO₂ nanocrystals (see Figure S5), four active vibrational modes, A_{1g} , B_{1g} , B_{2g} , and E_{g} are typically observed.³⁷ In the Raman shift range of 400–800 cm⁻¹, which was used to identify the defects, the A_{1g} , B_{2g} , and E_{g} modes are characterized by Raman shifts at ~628, ~767, and ~470 cm⁻¹, respectively, as shown in Figure S5.

As shown in Figure 2a, the Raman spectra of rutile SnO₂ nanoparticles exhibit a broad, intense peak at ~570 cm⁻¹, referred to as the Raman A_s mode, which originates from intrinsic surface in-plane oxygen vacancies in SnO₂.³⁸ The size of the SnO₂ nanoparticle affects the Raman vibrational modes due to phonon confinement effects and surface defects, causing shifts in the Raman peaks.^{37,39} Our Raman spectra in Figure 2a are consistent with the results in ref 39; the A_{1g} peak shifts down to ~620 cm⁻¹ due to the presence of bridging oxygen vacancies and appears as a shoulder peak of A_s mode. The B_{2g} and E_g modes are observed at ~751 and ~432 cm⁻¹, respectively. The exact position of the surface OH Raman peak in SnO₂ nanoparticles remains a topic of debate.

However, ref 40 suggests that OH_T and OH_B can be indicated by the A_{1g} peak, with its intensity increasing when OH_T and OH_B are cleaved.

To investigate the role of PHS treatment in suppressing defects and to test the hypothesis that OH_T is removed through the formation of KOH prior to halide anion exchange, we compared the Raman spectra of SnO_2 nanoparticles with KOH added into the solution (Figure 2b) to those treated with PHS (Figure 2c). Comparing the relative peak intensities within the same graph, the A_s peak in Figure 2b is significantly higher than that in untreated SnO_2 nanoparticles (Figure 2a), with the peak intensity ratio increasing from 2.33 in the untreated sample to approximately 3.29 in the KOH-treated sample. This indicates increased oxygen vacancy and surface defects in the KOH-treated SnO_2 nanoparticles.

Additionally, two new peaks appear at ~1061 cm⁻¹ and ~1097 cm⁻¹. The sharp peak at ~1061 cm⁻¹, also observed in the Raman spectra of pure KOH powder (Figure 2d), is likely due to the formation of potassium carbonate (K_2CO_3) ,^{41,42} which results from the rapid reaction of KOH with atmospheric CO₂.⁴³ The broader peak centered at ~1097 cm⁻¹ in Figure 2b, however, suggests a modified local chemical environment. This feature is consistent with surface-bound K_2CO_3 or other OH-related species influenced by the interaction of K⁺ with the SnO₂ surface.

A similar broad peak near 1096 cm⁻¹ is also observed in Figure 2c, even in the absence of added KOH powder but in the presence of potassium halide salts (KI, KCl, of KI+KCl). This suggests that K^+ introduced through the treatment reacts with native OH⁻ groups on SnO₂ to form KOH in situ, which then partially converts to surface-bound K₂CO₃ under ambient conditions. These findings support the interpretation that potassium ions from PHS treatments facilitate the removal of surface OH^- via KOH formation, a process that precedes halide anion exchange.

The PHS treatments of SnO_2 nanoparticles, as shown in Figure 2c, significantly reduce the A_s peaks, with the most substantial reduction observed in the mixed PHS-treated sample, followed by the KCl-treated and KI-treated samples, respectively. In addition to the decreased A_s peak intensity, the mixed PHS treatment also exhibits the most pronounced enhancement in the A_{1g} mode. These results indicate that the mixed PHS treatment effectively reduces the number of oxygen vacancies and surface OH groups. Furthermore, a broad and intense signal corresponding to KOH vibrations appears at ~1095 cm⁻¹, supporting our hypothesis that K⁺ ions interact with OH⁻ groups on the SnO₂ surface before anion exchange, significantly weakening the bond strength of OH_T. The proposed surface models, where OH_T groups are replaced by halide ions, are illustrated in Figure S6.

DFT calculations of adsorption energies (E_{ads}) confirm the formation of KOH, which facilitates the removal of OH_T. The adsorption energies for direct ion exchange between halide ions (X⁻) and surface OH⁻ are calculated using the equation:

$$E_{\rm ads} = E_{\rm SnO_{2,X_{\rm T}}} + E_{\rm OH^{-}} - (E_{\rm SnO_{2},OH_{\rm T}} + E_{\rm X^{-}})$$
(1)

Here, $E_{\text{SnO}_{2,\text{Xr}}}$ and $E_{\text{SnO}_{2},\text{OH}_{T}}$ represent the total energies of the SnO₂ surface with terminal halides (Cl_T, I_T, and mixed Cl_T + I_T) and with OH_T groups, respectively. Meanwhile, $E_{\text{OH}^{-}}$ and $E_{\text{X}^{-}}$ are the total energies of isolated OH⁻ and X⁻, respectively. On the other hand, the equation of E_{ads} for the case of the KOH pathway is given by

$$E_{\rm ads} = E_{\rm SnO_2, X_T} + E_{\rm KOH} - (E_{\rm SnO_2, OH_T} + E_{\rm K^+} + E_{\rm X^-})$$
(2)

where E_{KOH} and E_{K^+} are the total energies of a single KOH molecule and isolated K⁺, respectively.

Table 1 summarizes the E_{ads} values when Cl⁻, l⁻, and mixed (Cl⁻ + l⁻) replace OH_T on the SnO₂ (110) substrate. The

Table 1. Calculated Adsorption Energies of Halides Cl⁻ and I⁻ and Mixed Halides (Cl⁻ + I⁻) Replacing OH_T on the SnO₂ (110) Substrate

	adsorption energy (Ry)		
OH _T defect replacement	direct anion exchange	anion exchange through KOH	
$OH_{\rm T}$ replaced by Cl^- ions	0.865	-0.047	
OH_T replaced by I^- ions	0.985	0.017	
OH_T replaced by mixed $(Cl^- + I^-)$ ions	0.967	-0.017	

positive and relatively large magnitudes of E_{ads} for the process of direct ion exchange indicate that this process is nonspontaneous and endothermic, making these processes less likely to occur. We noted that the SnO₂ surface does not spontaneously adsorb halide ions as the interactions between the halide ions and the surface are weak. According to Figure S7, when K⁺ is introduced near the surface with OH_T and OH_B, it is adsorbed and forms ion-dipole interactions with nearby oxygen atoms on the surface and those in the OH_T and OH_B groups. In this transition state, the coordinate covalent bonds that bind OH_T groups to the surface are much weaker, as evidenced by the significantly longer Sn–O bond length of 6.61 Å in Figure S1. This transition state facilitates ion exchange between the halide ion and weakly bound KOH. In the case of Cl⁻ and mixed Cl⁻ + l⁻ ions, the E_{ads} values become negative, indicating that these reactions are spontaneous and exothermic. These E_{ads} results are consistent with the Raman measurement (Figure 2c), which showed a great reduction in the surface hydroxyl group and oxygen vacancy defects for the case of mixed KI+KCl and KCl treatments.

Since a better interface results in fewer defects and trap states at the SnO₂/perovskite interface, the defect suppression is explored using space-charge limited current (SCLC) in an electron-only device with a configuration of FTO/SnO₂/MAPbI₃/PCBM/Ag. The SCLC results, shown in Figure 3a, reveal electron transport characteristics across three regimes: the ohmic regime, the trap-filled limited regime, and the space-charge limited regime. These regimes are distinguished by the slope $n = \frac{dlnJ}{dlnV}$, where J and V are the current density and applied voltage in the SCLC measurement, respectively. The carrier trap density (N_t) is estimated at the transition voltage from the ohmic to TFL regimes, called trap-filled-limited voltage (V_{TFL}), using the equation:⁴⁴

$$N_{\rm t} = 2 \frac{V_{\rm TFL}}{eL^2} \varepsilon \varepsilon_{\rm o} \tag{3}$$

where *e*, *L*, ε , and ε_{o} denote the elementary unit charge constant, the thickness of the perovskite active layer, the perovskite's relative dielectric constant, ^{45,46} and the permittivity of free space, respectively. The $V_{\rm TFL}$ values of the KI-treated SnO₂ ($V_{\rm TFL} = 0.16$ V) and mixed KI+KCl-treated SnO₂ ($V_{\rm TFL} = 0.25$ V) decrease significantly compared with the control device ($V_{\rm TFL} = 0.34$ V). However, the KCl-treated SnO₂ has a $V_{\rm TFL}$ of 0.35 V, which is comparable to that of the control sample. The corresponding density of the trap state, N_v is found to be 4.6×10^{15} cm⁻¹, 7.2×10^{15} cm⁻¹, 1.0×10^{16} cm⁻¹, and 9.8×10^{15} cm⁻¹ for the KI-treated, mixed PHS-treated, KCl-treated, and control samples, respectively. The results reveal that the KI and mixed KI+KCl treatments are the most effective in terms of mitigating trap states, which should also result in better device stability, which will be shown and discussed later.

The effects of PHS passivation on charge carrier dynamics, carrier lifetime, and reduction of nonradiative recombination were investigated using steady-state photoluminescence (SSPL) and time-resolved photoluminescence (TRPL). Figure 3b illustrates significant quenching of the 765 nm emission band for PHS-modified SnO_2 surfaces compared to the control SnO_2 , suggesting enhanced electron extraction from the perovskite to SnO_2 . This improvement can be attributed to reduced surface defects, improved interfacial properties, and better band alignment, which will be discussed later. The improved interface not only mitigates defects but also facilitates faster electron extraction. The SSPL quenching trend aligns with SCLC measurements, where KI-modified samples exhibit the most significant reduction in trap states, followed by mixed PHS and KCI modifications.

The TRPL decay curves shown in Figure 3c corroborate the SSPL findings, demonstrating faster decay times for the modified samples. To quantify these observations, the TRPL data were fitted using a double-exponential decay model:

$$f(t) = B_{o} + A_{1} \exp\left(-\frac{t}{\tau_{1}}\right) + A_{2} \exp\left(-\frac{t}{\tau_{2}}\right)$$
(4)



Figure 3. (a) Space-charge limited current (SCLC) measurement of the electron-only device $FTO/SnO_2/MAPbI_3/PCBM/Ag$, before and after PHS treatment. (b) Stable-state photoluminescence (SSPL) and (c) time-resolved photoluminescence (TRPL) of the deposited perovskite films on the substrate: pristine SnO_2 and SnO_2 passivated with PHS.

where B_0 is constant and τ_1 and τ_2 are the fast and slow decay time constants corresponding to their decay amplitudes A_1 and A_2 , respectively. The fitted parameters' values are shown in Table 2. The fast decay (τ_1) is attributed to electron extraction

Table 2. Fitted Parameters for the Double-Exponential Decay Model of the TRPL Spectra for Perovskite Films Deposited on Control and PHS-Treated SnO₂ Film Substrates

sample	$ au_{\mathrm{avg}} \ (\mathrm{ns})$	τ_1 (ns)	A_1	τ_2 (ns)	A_2
Control-SnO ₂	59.23	7.77	6.94	59.73	93.06
KCl-treated SnO ₂	54.41	9.29	10.84	55.33	89.16
KI-treated SnO ₂	50.66	4.01	4.75	50.84	95.25
KI+KCl-treated SnO ₂	51.07	4.74	6.71	51.38	93.29

from the perovskite active layer to the SnO₂ substrate, and the slow decay component (τ_2) corresponds to radiative recombination from the bulk perovskite. The average time constant (τ_{avg}) was calculated by using the relation: $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)^{.47}$ The fast decay times for the films treated with KI and KI+KCl mixtures significantly decreased to $\tau_1 = 4.01$ ns and $\tau_1 = 4.74$ ns, respectively, compared to the control sample ($\tau_1 = 7.77$ ns). Furthermore, the time constants τ_2 and τ_{avg} were reduced to 50.84 and 50.66 ns for the KI treatment and 51.38 and 51.07 ns for the mixed KI+KCl treatment, respectively, compared to 59.73 and 59.23 ns for the untreated case. These findings indicate an enhanced carrier transfer between the perovskite and SnO₂ layers. The

faster charge extraction is likely due to the improved interface quality achieved through PHS treatment.

Moreover, we conducted electrochemical impedance spectroscopy (EIS) in a complete PSC device configuration: FTO/ SnO₂/MAPbI₃/Spiro-OMeTAD/Ag to gain further insight into charge transfer and recombination processes. The resulting Nyquist diagram of the devices with a 0.7 V bias under one sun illumination is shown in Figure S8, along with the circuit diagram that represents the devices. The series resistance (R_s) and the charge transfer resistance (R_{ct}) reflect the charge transfer characteristics at the interface, while $R_{\rm rec}$ denotes the resistance to carrier recombination.48,49 The results presented in Table S1 show that the R_s and R_{ct} values for the KI-modified SnO_2 are 2.50 and 11.53 Ω , respectively. The values are lower than the R_s and R_{ct} of the pristine SnO₂, which are 3.37 Ω and 13.79 Ω , respectively, indicating that electrons can transfer more readily from the perovskite to the ETL following modification with PHS.⁵⁰ More importantly, the R_{rec} values for the PHS-modified devices are significantly higher than those of the control device. For instance, the resistance of KI+KCl-treated SnO₂ (94.61 Ω) exceeds that of KI-treated SnO₂ (91.46 Ω) and is significantly greater than that of untreated SnO_2 (80.21 Ω). The modified interfaces show a notable decrease in recombination, especially nonradiative recombination, suggesting enhanced quality of the heterogeneous interface and a reduction in surface defects. Our findings indicate that treatments with KI and mixed KI+KCl yield the most significant enhancements at the SnO₂/MAPbI₃ interface.



Figure 4. Photovoltaic performance parameters of 42 devices with various SnO_2 modifications, presented as box plots for (a) V_{oc} (b) J_{sc} (c) fill factor (FF), and (d) power conversion efficiency (PCE). The step-like appearance of the V_{oc} box plots in panel (a) arises from the use of three significant digits in the J-V analysis software and the finer *y*-axis scale (0.01 V), which reflects the last reported digit of the data. (e) Forward scan (FS) and reverse scan (RS) current density–voltage (J-V) curves of fresh champion perovskite solar cells deposited on untreated SnO_2 and SnO_2 passivated with KI, KCl, and KI+KCl under A.M. 1.5G illumination. (f) Long-term stability of devices tested under 40–50% relative humidity.

The photovoltaic parameters presented in this study are based on 42 devices fabricated from two independent batches. The first batch consisted of 24 devices and the second batch consisted of 18 devices, each derived from (2.5 cm \times 2.5 cm) FTO substrates (six devices per substrate, active area of 0.16 cm² per device) The photovoltaic properties of 42 fabricated devices are presented in Figure 4a-d, demonstrating reproducibility across both control and PHS-treated devices. The box plots in Figure 4 illustrate the variations in (a) the open-circuit voltage (V_{oc}) , (b) short-circuit current density (J_{sc}) , (c) fill factor (FF), and (d) power conversion efficiency (PCE) for fresh PSCs with and without PHS treatment. In Figure 4e, the dashed and solid lines represent the forward scan (FS) and reverse scan (RS) J-V curves of the champion device for each case, respectively. Table S2 provides a statistical summary, detailing average values, standard deviation, and 95% confidence intervals for reverse-scan photovoltaic parameters (J_{sc} , V_{oc} , FF, and PCE) across 42 devices featuring various SnO₂ surface treatments.

Notably, KCl-treated devices exhibit the lowest standard deviation values for (J_{sc}) and PCE, indicating superior deviceto-device reproducibility. This may be attributed to the high electronegativity of Cl⁻, which facilitates efficient ion exchange with the surface-bound hydroxyl group during PHS treatment, as supported by our DFT calculations. The high consistency in J_{sc} is likely related to the most negative conduction band offset (CBO), which will be discussed later in Figures S10–S11. However, this more negative CBO may also enhance back-injection and interfacial recombination, resulting in greater variation in the fill factor (FF) and ultimately a lower overall PCE compared to those of the KI- and mixed KI+KCl-treated devices.

The efficiency parameters of the fresh champion PSCs are summarized in Table S3. For all cases, devices with PHS treatments have higher efficiency than the untreated devices. Devices with KI modification produce the best PCE of 19.86% due to the higher $J_{\rm sc}$ (22.64 mAcm⁻²) and $V_{\rm oc}$ (1.11 V). The devices with mixed KI+KCl passivation exhibited the second-best PCE of 19.15%. However, the champion KCl-treated sample has a lower $J_{\rm sc}$ than the control sample but a higher FF. These JV results align with previous characterization findings, demonstrating that PHS treatment, particularly with KI and mixed KI+KCl, enhances charge extraction and transport while reducing recombination losses at the SnO₂/perovskite interface, as evidenced by the increased $J_{\rm sc}$ and FF.

To investigate the origin of the improved PCE in PHStreated devices, photoelectron spectroscopy (PES) was used to quantitatively evaluate the valence band edge and work function, as shown in Figure S10. Combined with photoluminescence-derived bandgap values, this enabled the construction of the energy band alignment diagrams presented in Figure S11. Upon treatment with KCl, KI, and mixed KI +KCl, the conduction band minimum (CBM) of SnO₂ shifts upward from -4.38 eV (bare SnO₂) to -4.37, -4.18, and -4.31 eV, respectively. Compared to the perovskite CBM at -3.94 eV, the corresponding conduction band offset (CBO), defined as $CBO = CBM_{SnO_2} - CBM_{perovskite}$ changes from -0.44 eV (bare SnO₂) to -0.43, -0.24, and -0.37 eV for the KCl-, KI-, and mixed KI+KCl-treated samples, respectively. All CBO values remain negative, indicating cliff-type band alignment, $^{51-53}$ where the SnO₂ CBM lies below that of the perovskite. While this alignment facilitates electron extraction, more negative CBO values can promote interfacial recombination by reducing the energy barrier for back-injection of electrons from the ETL to the perovskite. This leads to increased recombination losses and can reduce J_{sc} , V_{oc} , and fill factor (FF).^{51–53}

As the CBO becomes less negative (shallower cliff), interfacial recombination is suppressed without significantly impeding electron extraction, resulting in improved charge collection and enhanced photovoltaic performance. Moreover, excessively negative CBO can cause the electron quasi-Fermi level to pin at the ETL's CBM, contributing to more V_{oc} deficiency.⁵⁴ Therefore, a less negative or slightly positive CBO (0.0–0.3 eV) is generally considered optimal for achieving high PCE.⁵⁵ This trend is consistent with our findings. As shown in Figure S11, the order of increasing SnO₂ CBM—and thus increasing CBO—is: bare SnO₂ < KCI-treated < mixed KI +KCI-treated < KI-treated. This progression correlates well with the improvements in J_{sc} , V_{oc} , FF, and PCE of the fresh devices observed in the box plots in Figure 4.

The hysteresis index (HI) of a J-V curve is an important metric that reflects ion accumulation and migration at the interface, which leads to unstable and poor charge extraction at the SnO₂/perovskite interface and device degradation. By using the RS and FS curves in Figure 4e, we calculated the HI values as follows: The control device exhibits significant J-Vhysteresis with a PCE of 14.30% under FS compared to 18.41% under RS, resulting in a high HI of 0.223. Introducing PHS at the interface significantly improved the HI, resulting in the HI values of the champion mixed KI+KCl, KI, and KCltreated devices of 0.149, 0.17, and 0.17, respectively. These results suggest that the mixed KI+KCl treatment is the most effective in lowering mobile ions.

Figure 4f presents the long-term operational stability measurements conducted at room temperature and 40-50% relative humidity (RH), with devices periodically tested while being stored in a drybox (20-30% RH, dark conditions) between measurements. Compared with the control device, all PHS-treated devices exhibit enhanced stability. Notably, the mixed KI+KCl-treated device demonstrates the highest stability, retaining over 96% of its initial PCE after 1000 h under testing conditions, followed by the KI-treated, KCltreated, and control devices, which retain 91%, 90%, and 85%, respectively. Although the KI-treated devices show the highest initial PCE among fresh samples, they degrade fastest among the PHS-treated devices. The PSCs in Figure 4 exhibited notable stability, as they were not subjected to continuous bias. However, when PCE was evaluated over time through repeated voltage sweeps from -1.2 to 0.2 V under continuous AM 1.5G illumination during maximum power point tracking (MPPT) (Figure S12), a rapid decline in PCE was observed in all cases, with the mixed KI+KCl-treated devices showing the least degradation. This suggests that the mixed KI+KCl treatment most effectively enhances device stability, likely due to reduced ion migration, as evidenced by the hysteresis index (HI) values. In contrast, KCl-treated devices exhibited inferior stability, performing similarly to the control samples in both the stability test (Figure 4f) and MPPT results (Figure S12).

To further assess long-term trap-assisted recombination behavior, we extracted the ideality factor (n_{id}) by fitting the J-V curves of the best-performing devices at various aging intervals using the Shockley diode equation.⁵⁶ Theoretically, an n_{id} value of 1 indicates bimolecular (radiative) recombination, while a value of 2 suggests dominant trap-assisted recombination. In practice, however, n_{id} can exceed 2 as the extent of trap-assisted or interfacial recombination increases.⁵⁷ Figure S9 presents the evolution of n_{id} values over 1000 h. The fitting methodology is described in the Supporting Information. The control and KCl-treated devices exhibit a noticeable increase in $n_{\rm id}$ over time, indicating progressive interfacial recombination likely due to defect formation. In contrast, the KI+KCl-treated devices maintain the lowest and most stable $n_{\rm id}$ values throughout the aging period, suggesting the effective suppression of trap-assisted recombination and enhanced long-term interfacial stability. These findings align with the PCE trends observed in the stability test and further demonstrate the effectiveness of mixed halide passivation in improving device durability.

The results thus far indicate that SnO₂ surface treatment with KI yields the highest efficiency in newly fabricated devices, whereas the combination of KI and KCl provides optimal stability. Since the device structures of our PSCs are identical except for the ETL/perovskite interface, we speculate that this specific interface plays a crucial role in determining the stability of the devices over time. To elucidate the functions of mixed PHSs in stability enhancement, we further employed DFT to calculate the surface adhesion energy (E_{adhs}) and charge density difference (CDD).

As previously discussed, anion exchange occurs on the SnO₂ (110) surface, replacing OH_T with terminal chloride (Cl_T), iodide (I_T), or mixed metal (Cl_T + I_T). To reveal the role of PHS at the SnO₂/perovskite interface, two DFT calculation models were used to create the heterointerface between the perovskite film and the SnO₂ substrate. The first model introduced terminal halides (Cl_T, I_T, and mixed Cl_T + I_T) as an interlayer between the ETL and the perovskite film. This is to indicate the effect of excess/different halides without considering K⁺ ions at the interface, as illustrated in Figure 5a-c. Based on the findings of Cao et al.,²⁶ which identified



Figure 5. Side views of geometrically optimized models of passivated $SnO_2/MAPbI_3$ interfaces with (a) terminal chloride (Cl_T), (b) terminal iodine (I_T), (c) mixed $Cl_T + I_T$, (d) potassium chloride (KCl), (e) potassium iodide (KI), and (f) mixed KI+KCl.

the influence of interstitial alkali ions on the bulk perovskite's ion migration energy barrier, we propose that interstitial K^+ at the $SnO_2/MAPbI_3$ interface may similarly enhance adhesion and ion migration activation energy due to the supplementary Coulombic forces exerted by K^+ . Consequently, we propose a second model in which K^+ ions are positioned on the surface of SnO_2 , as illustrated in Figure 5d–f.

Figure 6 presents the CDD calculations, illustrating the redistribution of electron density upon contact between SnO_2 and the perovskite of the structures in Figure 5. These visualizations offer insights into the bonding properties at the interface. In the CDD results, blue regions indicate electron



Figure 6. Side views of charge density differences (CDDs) from DFT calculations for the SnO₂/MAPbI₃ interface passivated with (a) terminal chloride ions (Cl_T), (b) terminal iodide ions (I_T), (c) mixed Cl_T + I_T, (d) K⁺ and Cl_T, (e) K⁺ and I_T, and (f) K⁺ and mixed Cl_T + I_T. Yellow regions indicate electron accumulation, while blue regions indicate electron depletion.

depletion, while yellow regions represent electron accumulation. The results presented in Figures 5 and 6 are discussed along with the adhesion energy findings.

The adhesion energy (E_{adhs}) , which is defined as the energy per unit area required to separate two layers into distinct surfaces, was computed using eq 5.

$$E_{\rm adhs} = \frac{E_{\rm s1} + E_{\rm s2} - E_{\rm sys}}{A}$$
(5)

where E_{s1} and E_{s2} represent the energies associated with separate SnO₂ surface with PHS treatment and the perovskite surface, respectively, E_{sys} denotes the total energy of the interface model, and A is the surface area.⁵⁸ A higher value of E_{adhs} indicates stronger surface adhesion, which is directly related to the long-term stability. Conversely, lower or negative E_{adhs} values correspond to thermodynamically unstable interfaces that are prone to delamination between the top and bottom layers. Such separation increases the interfacial distance, reducing electron transfer efficiency across the interface and thereby promoting trap-assisted recombination and accelerating device degradation. The E_{adhs} values and corresponding interfacial separation distance (*d*) for each case are presented in Table 3.

The DFT calculation results in Table 3 indicate that SnO_2 surface passivation with PHS, both with and without K⁺(Figure 5a-f), enhances adhesion compared to the control sample (Figure 1c). The comparison of Figures 5 and 6 with Figure 1c

Table 3. Adhesion Energy (E_{adhs}) and Interfacial Separation Distance for the SnO₂/MAPbI₃ Interfaces with Different Surface Treatments

interface models	ionic species	$adhesion \\ energy (E_{adhs}) \\ [Jm^{-2}]$	interfacial separation distance [Å]
Control (Figure 1c)		-8.450	N/A
Without interfacial K ⁺ (Figure 5a- c)	Cl_T	0.248	0.124
	I _T	-0.158	0.130
	$I_T + Cl_T$	-0.227	0.141
With interfacial K ⁺ (Figure 5d-f)	K^{+} and Cl_{T}	-1.104	0.130
	$\mathrm{K}^{\scriptscriptstyle +}$ and I_{T}	-0.132	0.126
	K^+ and $I_T + Cl_T$	0.375	0.121

highlights that the elimination of surface OH_T on the SnO_2 surface is crucial to achieve a highly ordered SnO_2 /perovskite heterointerface. For passivation without K⁺, the top panels of Figures 5 and 6 show that the CI_T and I_T ions, which replace OH_T groups on the SnO_2 surface, form bonds with Sn atoms in the SnO_2 plane and Pb atoms in the PbI₂ plane of the MAPbI₃ surface, respectively, through a combination of ionic and covalent interactions.⁵⁹ As a result, the strength of surface adhesion largely depends on the electronegativity of the terminal halide.⁶⁰ The larger electron accumulation region around CI_T (Figure 6a) compared to I_T (Figure 6b) suggests that the Sn–Cl–Pb bond has more ionic character and is stronger than the Sn–I–Pb bond due to the higher electronegativity of Cl relative to I.

However, when Cl_T and I_T are mixed, the larger ionic radius of I⁻ (0.220 nm) compared to Cl⁻ (0.181 nm) leads to greater interfacial plane separation and weakens the Sn–Cl–Pb bonds, as evidenced by the significantly reduced electron accumulation region around Cl_T in Figure 6c. Consequently, for passivation without K⁺, the Cl_T-passivated interface exhibits the highest E_{adhs} value, followed by I_T and mixed $Cl_T + I_T$ passivation, consistent with the trend in interfacial separation distances. However, these trends contradict the experimental stability results shown in Figure 4f, indicating the presence of additional mechanisms besides surface anion exchange.

When K⁺ is incorporated into the interface (lower panels of Figures 5 and 6), significant changes occur in the interface atomic configurations. In the case of KCl passivation (Figures 5d and 6d), Cl_T ions that were originally bonded to Sn atoms are pulled toward K⁺ due to the strong Coulombic interaction between K⁺ and Cl⁻. The CDD results in Figure 6d show large regions of electron density accumulation and depletion between K⁺ and Cl⁻, indicating the formation of ionic KCl bonds at the interface. This reconfiguration disrupts the Sn–Cl–Pb bond, resulting in the lowest E_{adhs} value among the PHS passivation cases.

For the mixed KI+KCl case (Figures 5f and 6f), similar ionic KCl molecules with Cl_T closer to the SnO₂ surface are observed alongside Sn-I-Pb bonds. However, the CDD results in Figure 6f show no electron accumulation or depletion between Cl_T and K⁺, suggesting that the KCl ionic bond forms on the SnO₂ surface prior to contact with the perovskite. Conversely, more pronounced and ordered CDD regions are observed around the Sn-I-Pb bonds and K⁺ ions. When Figure 6f is compared to Figure 6d,e, the bottommost atomic layer of the perovskite appears smoother, indicating a more uniform interface that supports the growth of a highly crystalline perovskite layer. This is likely due to reorganization of the interfacial ionic layer to minimize lattice strain. The interactions between Cl⁻, I⁻, and K⁺ allow for a more gradual transition of the surface roughness that is caused by the size mismatch between small Cl⁻ (0.181 nm) and larger I⁻ (0.220 nm). This redistribution reduces abrupt strain at the SnO₂perovskite interface, leading to a more stable and energetically favorable configuration.

Moreover, all of the CDD results in Figure 6 suggest that K⁺ ions interact with I⁻ ions in the perovskite structure and with O^{2-} ions in SnO₂ through Coulombic forces, in addition to the Sn–I–Pb or Sn–Cl–Pb bonds. These additional attractive forces strengthen interface adhesion, reduce I⁻ ion migration,²⁶ and suppress the formation of oxygen vacancies on the SnO₂ surface, aligning with the Raman results in Figure 2 and the hysteresis and stability results in Figure 4d,f. Consequently,

when K^+ is incorporated into the surface (Figures 5d–f and 6d–f), the calculated E_{adhs} and interfacial separation distance trends align with the experimental data, particularly for the mixed KI+KCl treatment, which is the only case yielding a positive E_{adhs} . These DFT calculations elucidate the mechanisms behind the enhanced stability achieved with mixed KI+KCl passivation and highlight the critical role of interstitial K⁺ ions at the interface.

Based on the combined experimental and computational results, the KI-treated devices exhibit the highest initial PCE, primarily due to a more favorable conduction band minimum (CBM) alignment with the perovskite absorber. This is supported by photoelectron spectroscopy data in Figures S10 and S11, which show the smallest conduction band offset (CBO) in the KI-treated case. Additionally, SCLC analysis reveals lower initial trap densities, and PL-based measurement (steady-state and time-resolved) indicates more efficient charge extraction compared to other treatments.

However, iodide ions alone interact more weakly with the SnO₂ surface, as indicated by the lower adsorption energy in Table 1. Furthermore, the SnO₂/perovskite interface in the KItreated system exhibits weaker surface adhesion than that of the mixed KI+KCl case, as shown in Table 3. In contrast, the mixed KI+KCl treatment offers stronger surface binding, more favorable interfacial energy, and a smoother interface. Our DFT results suggest that the presence of both I⁻ and Cl⁻ enables better atomic packing and reduces local lattice strain, contributing to enhanced interfacial stability. This is further supported by SEM images (Figure S2), where the mixed-salt treatment results in larger grain sizes and more uniform perovskite films. These combined effects explain why the KItreated devices achieve the highest initial efficiency, while the mixed KI+KCl-treated device exhibits the most robust longterm stability.

3. CONCLUSION

In summary, potassium salts (KI, KCl, and their mixture KI +KCl) are utilized as a passivation layer at the $SnO_2/MAPbI_3$ interface in n-i-p device configuration PSCs. This approach enhances the quality and adhesion of the interface, leading to efficient and long-term stable PSC devices. Our combined experiment and DFT studies indicate that K⁺ and halide ions in PHS serve several significant functions. First, they remove the extrinsic terminal hydroxyl group (OH_T) from moisture on the SnO₂ surface, which causes distortion in the crystal structure at the interface. The mechanism involves the formation of KOH, which weakens the OH_T bonds and subsequently facilitates the exchange of anion with halide ions in the PHSs. SEM and Raman analyses confirmed the enhanced quality of the perovskite film and the reduction of surface defects. Additionally, K⁺, I⁻, and Cl⁻ play an important part in the formation of a thin passivation layer that facilitates the binding of SnO₂ and perovskite surfaces. This is achieved through the formation of Sn-Cl-Pb and Sn-I-Pb bonds, along with additional electrostatic attractive forces between K⁺ and I^- in the perovskite and O^{2-} in the SnO₂. The KI-modified and mixed KI+KCl-modified devices achieved PCEs of 198.6% and 19.15%, respectively, surpassing those of untreated SnO_{2} , which exhibited an efficiency of 18.41%. The enhancements in PCEs result from improved energy band alignments, as verified by PES measurements. The synergistic interactions of K⁺ and mixed Cl_T + I_T, along with their more coherent ionic radii, result in superior surface adhesion compared with individual

PHS treatment. The electrostatic interactions between K^+ and adjacent anions diminish ion migration, as evidenced by the reduced hysteresis index. The synergies create PSCs with mixed KI+KCl changes that can keep their original power conversion efficiency (PCE) of over 96% for 1000 h at 40– 50% relative humidity (RH). This indicates that the mixed KI +KCl-modified devices exhibit enhanced moisture resistance and improved stability. While KI-treated devices exhibited the highest initial PCE due to an optimal band alignment and charge extraction, the mixed KI+KCl treatment provided superior long-term stability, attributed to stronger interfacial adhesion and reduced strain at the SnO₂/perovskite interface.

4. EXPERIMENTAL SECTION

4.1. Materials. All of the materials utilized for this study are procured from the manufacturers and used exactly as received, without further purification. The transparent glass of fluorine-doped tin oxide (FTO) was procured from Bangkok Solar Thailand. Methylammonium iodide (MAI) was purchased from Great Cell Solar. Potassium iodide (KI), potassium chloride (KCl), potassium hydroxide (KOH), N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), acetonitrile (99.8%), bis-trifluoromethane sulfonimide lithium salt (Li TFSI), FK 209 Co (III) tris-2-1Hpyrazol-1-yl-4-tetra-butylpyradine cobalt(III) tribis (trifluoromethane) sulfonimide Co (III) TFSI, 4-tetra-butylpyridine (TBP, 96%), and phenyl C61-butyric acid methyl ester were all procured from Sigma-Aldrich. Tin(IV) oxide (SnO₂, 15% in H₂O) was purchased from Alfa Aesar. Lead iodide (PbI₂) and spiro-OMeTAD were purchased from New Material, China. Finally, silver pellets (99.99%) were purchased from the Kurt J. Lesker Company.

4.2. Device Preparation. The glass substrate coated with FTO was carefully etched with zinc powder, diluted hydrochloric acid (HCl), cleaned through various stages involving detergent, and then rinsed in deionized water and eventually immersed in acetone and finally IPA, each for 15 min. After the cleaning process, the FTO substrate was blow-dried with nitrogen. Before the deposition of the SnO₂ as an ETL, the precleaned substrates were treated with UV-zone cleaning for 30 min to enhance their wetting properties. ETL was prepared by spin-coating a diluted SnO₂ colloidal solution at 3000 rpm for 30 s onto the cleaned FTO substrate, followed by annealing at 150 °C for 60 min in ambient air. KI (0.03 M) and KCl (0.03 M) solutions were individually prepared by dissolving the salts in deionized (DI) water for PHS treatment. For the mixed solution, 0.015 M KI and 0.015 M KCl were separately dissolved in DI water and then combined, resulting in the same total salt concentration as the individual solutions. Each solution of KI, KCl, and the mixed KI +KCl was stirred at room temperature for 45 min. Subsequently, the potassium halide salt solutions were spin-coated onto the prepared SnO₂ films at 2000 rpm for 30 s, followed by annealing at 100 °C for 15 min. PbI₂ (1.2 M) and MAI (1.2 M) were dissolved in 1 mL of a mixed solution of DMF and DMSO with a volume ratio of 4:1 solvent to form a single-cation perovskite solution. The 70 μ L perovskite precursor solution was deposited onto the FTO/SnO2 substrate and spun at 3000 rpm for 30 s. At first, during the spin-coating process, 200 μ L of CB antisolvent was introduced into the perovskite film. The resulting active layer of the MAPbI₃ perovskite was annealed at 120 °C for 10 min. A hole transporting layer (HTL) solution was prepared by dissolving 0.091 g of Spiro-OMeTAD (70 mM) in 1 mM chlorobenzene (CB), followed by the addition of 35.9 µL of 4-tertbutylpyridine (TBP), 20.6 μ L of lithium bis(trifluoromethanesulfony) imide (Li-TFSI) solution (1.8 M, prepared by dissolving 520 mg of Li-TFSI in 1 mL of acetonitrile), and 8.9 μ L of cobalt(III) TFSI solution (0.25 M, prepared by dissolving 375 mg of Co (III) TFSI in 1 mL of acetonitrile). The resulting HTL solution was spin-coated onto the perovskite layer at 3000 rpm for 30 s. Lastly, a shadow mask was thermally evaporated and deposited an 80 nm Ag layer electrode onto the spiro-OMeTAD layer, resulting in a device with an active area of 0.16 cm^2 .

4.3. Characterization. Using the Rigaku (SmartLab) diffractometer with Cu K $\alpha \sim 1.5406$ Å radiation, the XRD patterns determine the crystallography of all the crystal films in scan steps of 0.01° , ranging from 10° to 60° . The photoelectron spectroscopy (PES) of the samples was measured in Thai Synchrotron National Lab (Beamline 3.2U) with a radiation energy of 60.0 eV, a takeoff angle fixed at 70°, and a negative bias of -10.0 V. Morphology images of all the samples were obtained using SEM (Quanta 450 FEI) with an accelerated voltage of 30 kV. The steady-state PL measurement excitation was 405 nm with an operating pulse of 10 kHz, whereas the TRPL pulse was 500 kHz using a DeltraFlex spectrometer, Horiba. The SCLC measurements based on Mott Gurney were employed to extract the electronic defect states using an electron-only device in the FTO/SnO₂/perovskite/PCBM/Ag structure. Raman spectra were analyzed by using a Raman spectrometer (Horiba-LabRAM-HR-Evolution) using a 532 nm excitation laser with a beam spot diameter of ~1 μ m. The Raman shifts were received within a 100–3000 cm⁻¹ range at a resolution of 1.5 cm⁻¹. The modulated electrochemical impedance spectroscopy (EIS) curves were measured in the dark using a PAIOS system, covering a frequency range of 10 Hz to 1 MHz.

4.4. Computational Methods. All computational calculations were conducted within the framework of DFT using the Quantum Espresso (QE) simulation package,⁶¹ with the exchange-correlation potential generated within the generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhop (PBE).⁶² A plane wave projected augmented wave (PAW) pseudopotential defined the core orbital and valence orbital electron configurations of each as follows: $5s^2 5p^2 4d^{10}$ for Sn, $2s^2 2p^4 3d^{-2}$ for O, $3s^2 3p^5 3d^{-1}$ for Cl, $1s^1 2p^{-1}$ for H, $5s^2 5p^5 4d^{10}$ for I, $4s^1 4p^0 3d^{-1}$ for K, $4f^{14} 6s^2 6p^2 5d^{10}$ for Pb, $2s^2 2p^2 3d^{-2}$ for C, and $2s^2 2p^3 3d^{-2}$ for N atoms. A model of a slab with three layers of PbI₂ terminations on the perovskite surface for the study was obtained from the bulk cubic unit cell of MAPbI_3 perovskite. Moreover, we built a supercell of a symmetric slab from the conventional rutile of the stoichiometric SnO_2 (110) surface²⁷ of $2 \times 2 \times 4$ with four Sn atomic layers. The two bottom layers were fixed throughout the calculations to maintain the bulk properties. We performed geometry optimizations with a vacuum space of 20 Å through the ion dynamics of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm⁶ and a tolerance convergence force of $0.001/\text{\AA}$. The convergence test sufficiently adopted the energy cutoff and electron charge density of 70 and 630 Ry, respectively. Additionally, for the 3D models of stoichiometric SnO₂ (110) and cubic MAPbI₃ perovskite supercells, the Monkhorst-Park Scheme K-point meshes⁶⁴ of $(2 \times 2 \times 1)$ and (4 \times 4 \times 1), respectively, were adopted with an electron convergence threshold of 1.0×10^{-6} and mixing a beta of 0.5.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.5c04415.

Geometrically optimized SnO_2 structures; morphology of MAPbI₃ films; XRD patterns; Raman spectra; Nyquist plots; values of recombination resistance, charge transfer resistance, and series resistance from the EIS equivalent circuit models for samples of untreated SnO_2 and different SnO_2 treatments; photovoltaic performance parameters of devices with the control and different SnO_2 surface modifications; method for Shockley diode fitting and ideality factor extraction; evolution of the ideality factor; energy onset data; energy level diagram; maximum power point tracking results (PDF)

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Notes

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REFERENCES

(1) Zhao, Y.; Zhu, K. Organic-Inorganic Hybrid Lead Halide Perovskites for Optoelectronic and Electronic Applications. *Chem. Soc. Rev.* **2016**, *45* (3), 655–689.

(2) National Renewable Energy Laboratory (NREL). *Best Research-Cell PV Efficiency Chart*; https://www.nrel.gov/pv/pvdpc/ (accessed 2025–04–27).

(3) Wang, S.; Yang, T.; Yang, Y.; Du, Y.; Huang, W.; Cheng, L.; Li, H.; Wang, P.; Wang, Y.; Zhang, Y.; Ma, C.; Liu, P.; Zhao, G.; Ding, Z.; Liu, S.; Zhao, K. In Situ Self-Elimination of Defects via Controlled Perovskite Crystallization Dynamics for High-Performance Solar Cells. *Adv. Mater.* **2023**, *35* (42), No. 2305314.

(4) Tan, H.; Yu, X.; Ren, W.; Yin, T.; Wen, H.; Guo, Y.; Zhang, Z.; Liu, C.; Zhou, G.; Li, H.; Qiu, X.; Wu, H.; Yang, Z.; Huang, S. A Versatile Bridging Molecule Managed the Buried SnO2/Perovskite Interface for Efficient and Stable Perovskite Solar Cells. *Small* **2025**, No. 2500978.

(5) Webb, T.; Sweeney, S. J.; Zhang, W. Device Architecture Engineering: Progress toward Next Generation Perovskite Solar Cells. *Adv. Funct. Mater.* **2021**, *31* (35), No. 2103121.

(6) Huang, J.; Yuan, Y.; Shao, Y.; Yan, Y. Understanding the Physical Properties of Hybrid Perovskites for Photovoltaic Applications. *Nat. Rev. Mater.* **2017**, *2* (7), 1–19.

(7) Lim, J.; Hörantner, M. T.; Sakai, N.; Ball, J. M.; Mahesh, S.; Noel, N. K.; Lin, Y. H.; Patel, J. B.; McMeekin, D. P.; Johnston, M. B.; Wenger, B.; Snaith, H. J. Elucidating the Long-Range Charge Carrier Mobility in Metal Halide Perovskite Thin Films. *Energy Environ. Sci.* **2019**, *12* (1), 169–176.

(8) Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörantner, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snaith, H. J. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Adv. Energy Mater.* **2016**, *6* (8), No. 1502458.

(9) Wang, P.; Wu, Y.; Cai, B.; Ma, Q.; Zheng, X.; Zhang, W. H. Solution-Processable Perovskite Solar Cells toward Commercialization: Progress and Challenges. *Advanced Functional Materials.* **2019**, 29 (47), No. 1807661.

(10) Zhou, W.; Pan, T.; Ning, Z. Strategies for Enhancing the Stability of Metal Halide Perovskite towards Robust Solar Cells. *Science China Materials* **2022**, *65* (12), 3190–3201.

(11) Park, S. Y.; Zhu, K. Advances in SnO2 for Efficient and Stable n-i-p Perovskite Solar Cells. *Adv. Mater.* **2022**, *34* (27), No. 2110438.

(12) Rajagopal, A.; Yao, K.; Jen, A. K. Y. Toward Perovskite Solar Cell Commercialization: A Perspective and Research Roadmap Based on Interfacial Engineering. *Adv. Mater.* **2018**, *30* (32), No. 1800455. (13) Han, J.; Kwon, H.; Kim, E.; Kim, D. W.; Son, H. J.; Kim, D. H. Interfacial Engineering of a ZnO Electron Transporting Layer Using Self-Assembled Monolayers for High Performance and Stable Perovskite Solar Cells. *J. Mater. Chem. A Mater.* **2020**, *8* (4), 2105– 2113.

(14) Yang, G.; Chen, C.; Yao, F.; Chen, Z.; Zhang, Q.; Zheng, X.; Ma, J.; Lei, H.; Qin, P.; Xiong, L.; Ke, W.; Li, G.; Yan, Y.; Fang, G. Effective Carrier-Concentration Tuning of SnO2 Quantum Dot Electron-Selective Layers for High-Performance Planar Perovskite Solar Cells. *Adv. Mater.* **2018**, *30* (14), No. 1706023.

(15) Zhu, P.; Gu, S.; Luo, X.; Gao, Y.; Li, S.; Zhu, J.; Tan, H. Simultaneous Contact and Grain-Boundary Passivation in Planar Perovskite Solar Cells Using SnO2-KCl Composite Electron Transport Layer. *Adv. Energy Mater.* **2020**, *10* (3), No. 1903083.

(16) Huang, L.; Zhou, X.; Xue, R.; Xu, P.; Wang, S.; Xu, C.; Zeng, W.; Xiong, Y.; Sang, H.; Liang, D. Low-Temperature Growing Anatase TiO2/SnO2Multi-Dimensional Heterojunctions at MXene Conductive Network for High-Efficient Perovskite Solar Cells. *Nanomicro Lett.* **2020**, *12* (1), 1–19.

(17) Banihashemi, M.; Kashani Nia, A. Effects of Negative Hydroxyl Ions at the SnO2/Perovskite Layer Interface on the Performance of Perovskite Solar Cells. J. Comput. Electron **2024**, 23 (6), 1162–1169. (18) Adnan, M.; Lee, W.; Irshad, Z.; Kim, S.; Yun, S.; Han, H.; Chang, H. S.; Lim, J. Managing Interfacial Defects and Charge-Carriers Dynamics by a Cesium-Doped SnO2 for Air Stable Perovskite Solar Cells. Small **2024**, 20 (37), No. 2402268.

(19) Aydin, E.; De Bastiani, M.; De Wolf, S. Defect and Contact Passivation for Perovskite Solar Cells. *Adv. Mater.* **2019**, *31* (25), No. 1900428.

(20) Boehm, H. P. Acidic and Basic Properties of Hydroxylated Metal Oxide Surfaces. *Discuss. Faraday Soc.* **1971**, *52*, 264–275.

(21) Zhu, P.; Gu, S.; Luo, X.; Gao, Y.; Li, S.; Zhu, J.; Tan, H. Simultaneous Contact and Grain-Boundary Passivation in Planar Perovskite Solar Cells Using SnO2-KCl Composite Electron Transport Layer. *Adv. Energy Mater.* **2020**, *10* (3), No. 1903083.

(22) Liu, X.; Zhang, Y.; Shi, L.; Liu, Z.; Huang, J.; Yun, J. S.; Zeng, Y.; Pu, A.; Sun, K.; Hameiri, Z.; Stride, J. A.; Seidel, J.; Green, M. A.; Hao, X. Exploring Inorganic Binary Alkaline Halide to Passivate Defects in Low-Temperature-Processed Planar-Structure Hybrid Perovskite Solar Cells. *Adv. Energy Mater.* **2018**, *8* (20), No. 1800138.

(23) Zhang, S.; Gu, H.; Chen, S. C.; Zheng, Q. KF-Doped SnO2as an Electron Transport Layer for Efficient Inorganic CsPbI2Br Perovskite Solar Cells with Enhanced Open-Circuit Voltages. J. Mater. Chem. C Mater. 2021, 9 (12), 4240–4247.

(24) Son, D. Y.; Kim, S. G.; Seo, J. Y.; Lee, S. H.; Shin, H.; Lee, D.; Park, N. G. Universal Approach toward Hysteresis-Free Perovskite Solar Cell via Defect Engineering. *J. Am. Chem. Soc.* **2018**, *140* (4), 1358–1364.

(25) Alanazi, T. I.; Game, O. S.; Smith, J. A.; Kilbride, R. C.; Greenland, C.; Jayaprakash, R.; Georgiou, K.; Terrill, N. J.; Lidzey, D. G. Potassium Iodide Reduces the Stability of Triple-Cation Perovskite Solar Cells. *RSC Adv.* **2020**, *10* (66), 40341–40350.

(26) Cao, J.; Tao, S. X.; Bobbert, P. A.; Wong, C. P.; Zhao, N. Interstitial Occupancy by Extrinsic Alkali Cations in Perovskites and Its Impact on Ion Migration. *Adv. Mater.* **2018**, *30* (26), No. 1707350.

(27) Jung, E. H.; Chen, B.; Bertens, K.; Vafaie, M.; Teale, S.; Proppe, A.; Hou, Y.; Zhu, T.; Zheng, C.; Sargent, E. H. Bifunctional Surface Engineering on SnO2reduces Energy Loss in Perovskite Solar Cells. ACS Energy Lett. **2020**, 5 (9), 2796–2801.

(28) Batzill, M.; Kim, J.; Beck, D. E.; Koel, B. E. Epitaxial Growth of Tin Oxide on Pt(111): Structure and Properties of Wetting Layers and SnO2 Crystallites. *Phys. Rev. B* **2004**, *69* (16), No. 165403.

(29) Kim, J.; Kim, K. S.; Myung, C. W. Efficient Electron Extraction of SnO2 Electron Transport Layer for Lead Halide Perovskite Solar Cell. *NPJ. Comput. Mater.* **2020**, *6* (1), 100.

(30) Pu, W.; Xiao, W.; Wang, J.; Li, X. W.; Wang, L. Stress and Defect Effects on Electron Transport Properties at SnO2/Perovskite Interfaces: A First-Principles Insight. *ACS Omega* **2022**, 7 (18), 16187–16196.

(31) Kim, J.; Park, J.; Kim, Y. H.; Jo, W. Improvement of Open-Circuit Voltage Deficit via Pre-Treated NH4+ Ion Modification of Interface between SnO2 and Perovskite Solar Cells. *Small* **2022**, *18* (44), No. 2204173.

(32) Sinner-Hettenbach, M. SnO2 (110) and Nano-SnO2: Characterization by Surface Analytical Techniques. Ph.D. dissertation, Eberhard Karls University of Tubingen, 2000.

(33) Yuan, Y.; Huang, J. Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability. *Acc. Chem. Res.* **2016**, *49* (2), 286–293.

(34) Zuo, L.; Gu, Z.; Ye, T.; Fu, W.; Wu, G.; Li, H.; Chen, H. Enhanced Photovoltaic Performance of CH3NH3PbI3 Perovskite Solar Cells through Interfacial Engineering Using Self-Assembling Monolayer Enhanced Photovoltaic Performance of CH3NH3PbI3 Perovskite Solar Cells through Interfacial Engineering Using Self-Assembling Monolayer. J. Am. Chem. Soc. 2015, 137 (7), 2674–2679.

(35) Zuo, L.; Guo, H.; Dequilettes, D. W.; Jariwala, S.; De Marco, N.; Dong, S.; Deblock, R.; Ginger, D. S.; Dunn, B.; Wang, M.; Yang, Y. Polymer-Modified Halide Perovskite Films for Efficient and Stable Planar Heterojunction Solar Cells. Science advances **2017**, 3 (8), No. e1700106.

(36) Nedelcu, G.; Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Grotevent, M. J.; Kovalenko, M. V. Fast Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, I). *Nano Lett.* **2015**, *15* (8), 5635–5640.

(37) Diéguez, A.; Romano-Rodríguez, A.; Vilà, A.; Morante, J. R. The Complete Raman Spectrum of Nanometric SnO2 Particles. *J. Appl. Phys.* **2001**, *90* (3), 1550–1557.

(38) Liu, L. Z.; Wu, X. L.; Gao, F.; Shen, J. C.; Li, T. H.; Chu, P. K. Determination of Surface Oxygen Vacancy Position in SnO2 Nanocrystals by Raman Spectroscopy. *Solid State Commun.* **2011**, *151* (11), 811–814.

(39) Liu, L. Z.; Li, T. H.; Wu, X. L.; Shen, J. C.; Chu, P. K. Identification of Oxygen Vacancy Types from Raman Spectra of SnO 2 Nanocrystals. J. Raman Spectrosc. **2012**, 43 (10), 1423–1426.

(40) Chai, N.; Chen, X.; Zeng, Z.; Yu, R.; Yue, Y.; Mai, B.; Wu, J.; Mai, L.; Cheng, Y. B.; Wang, X. Photoexcitation-Induced Passivation of SnO2thin Film for Efficient Perovskite Solar Cells. *Natl. Sci. Rev.* **2023**, *10* (11), No. nwad245.

(41) Ma, Y.; Yan, W.; Sun, Q.; Liu, X. Raman and Infrared Spectroscopic Quantification of the Carbonate Concentration in

K2CO3 Aqueous Solutions with Water as an Internal Standard. *Geoscience Frontiers* **2021**, *12* (2), 1018–1030.

(42) Buzgar, N.; Apopei, A. I. The Raman study of certain carbonates. *Geologie Tomul L.* **2009**, 2 (2), 97–112.

(43) Fan, X.; Syu, Y.; Juangsa, F. B.; Nozaki, T. Integration of KOH-Based CO2 Absorption and Ca(OH)2-Triggered Mineralization: Process Tracking and Kinetic Analysis. *International Journal of Greenhouse Gas Control* **2025**, *143*, No. 104339.

(44) Huang, Y.; Li, L.; Liu, Z.; Jiao, H.; He, Y.; Wang, X.; Zhu, R.; Wang, D.; Sun, J.; Chen, Q.; Zhou, H. The Intrinsic Properties of FA (1- X) MA x PbI 3 Perovskite Single Crystals. *J. Mater. Chem. A Mater.* **2017**, 5 (18), 8537–8544.

(45) Bi, H.; Zuo, X.; Liu, B.; He, D.; Bai, L.; Wang, W.; Li, X.; Xiao, Z.; Sun, K.; Song, Q.; Zang, Z.; Chen, J. Multifunctional Organic Ammonium Salt-Modified SnO2nanoparticles toward Efficient and Stable Planar Perovskite Solar Cells. *J. Mater. Chem. A Mater.* **2021**, *9* (7), 3940–3951.

(46) Chen, J.; Zhao, X.; Kim, S. G.; Park, N. G. Multifunctional Chemical Linker Imidazoleacetic Acid Hydrochloride for 21% Efficient and Stable Planar Perovskite Solar Cells. *Adv. Mater.* 2019, 31 (39), No. 1902902.

(47) Chen, J.; Dong, H.; Li, J.; Zhu, X.; Xu, J.; Pan, F.; Xu, R.; Xi, J.; Jiao, B.; Hou, X.; Wei Ng, K.; Wang, S. P.; Wu, Z. Solar Cell Efficiency Exceeding 25% through Rb-Based Perovskitoid Scaffold Stabilizing the Buried Perovskite Surface. *ACS Energy Lett.* **2022**, 7 (10), 3685–3694.

(48) Liu, X.; Zhang, Y.; Shi, L.; Liu, Z.; Huang, J.; Yun, J. S.; Zeng, Y.; Pu, A.; Sun, K.; Hameiri, Z.; Stride, J. A.; Seidel, J.; Green, M. A.; Hao, X. Exploring Inorganic Binary Alkaline Halide to Passivate Defects in Low-Temperature-Processed Planar-Structure Hybrid Perovskite Solar Cells. *Adv. Energy Mater.* **2018**, *8* (20), No. 1800138.

(49) Ma, Y.; Wei, N.; Wang, Q.; Wu, C.; Zeng, W.; Gao, Y.; Xu, C.; Huang, L.; Zhao, J. Ultrathin PEDOT:PSS/RGO Aerogel Providing Tape-Like Self-Healable Electrode for Sensing Space Electric Field with Electrochemical Mechanism. *Adv. Electron Mater.* **2019**, 5 (12), No. 1900637.

(50) Duan, J.; Wang, Y.; Yang, X.; Tang, Q. Alkyl-Chain-Regulated Charge Transfer in Fluorescent Inorganic CsPbBr3 Perovskite Solar Cells. *Angewandte Chemie - International Edition* **2020**, *59* (11), 4391– 4395.

(51) Ding, C.; Zhang, Y.; Liu, F.; Kitabatake, Y.; Hayase, S.; Toyoda, T.; Yoshino, K.; Minemoto, T.; Katayama, K.; Shen, Q. Effect of the Conduction Band Offset on Interfacial Recombination Behavior of the Planar Perovskite Solar Cells. *Nano Energy* **2018**, *53*, 17–26.

(52) Minemoto, T.; Murata, M. Theoretical Analysis on Effect of Band Offsets in Perovskite Solar Cells. *Sol. Energy Mater. Sol. Cells* **2015**, *133*, 8–14.

(53) Bagade, S. S.; Barik, S. B.; Malik, M. M.; Patel, P. K. Impact of Band Alignment at Interfaces in Perovskite-Based Solar Cell Devices. *Mater. Today Proc.*, in press; DOI: 10.1016/j.matpr.2023.02.117.

(54) Chen, N.; Luo, D.; Chen, P.; Li, S.; Hu, J.; Wang, D.; Zhu, R.; Lu, Z. H. Universal Band Alignment Rule for Perovskite/Organic Heterojunction Interfaces. ACS Energy Lett. **2023**, 8 (3), 1313–1321. (55) Minemoto, T.; Murata, M. Theoretical Analysis on Effect of Band Offsets in Perovskite Solar Cells. Sol. Energy Mater. Sol. Cells **2015**, 133, 8–14.

(56) Diantoro, M.; Suprayogi, T.; Hidayat, A.; Taufiq, A.; Fuad, A.; Suryana, R. Shockley's Equation Fit Analyses for Solar Cell Parameters from I-V Curves. *Int. J. Photoenergy* **2018**, *2018* (1), No. 9214820.

(57) Thongprong, N.; Supasai, T.; Li, Y.; Tang, I. M.; Rujisamphan, N. Insights into Recombination Processes from Light Intensity– Dependent Open-Circuit Voltages and Ideality Factors in Planar Perovskite Solar Cells. *Energy Technology* **2020**, *8* (5), No. 1901196. (58) Han, Y.; Lai, K. C.; Lii-Rosales, A.; Tringides, M. C.; Evans, J. W.; Thiel, P. A. Surface Energies, Adhesion Energies, and Exfoliation Energies Relevant to Copper-Graphene and Copper-Graphite Systems. *Surf. Sci.* **2019**, *685*, 48–58. (59) Walsh, A. Principles of Chemical Bonding and Band Gap Engineering in Hybrid Organic-Inorganic Halide Perovskites. J. Phys. Chem. C 2015, 119 (11), 5755–5760.

(60) Deng, J.; Wei, K.; Yang, L.; Lin, L.; Xiao, Y.; Cai, X.; Zhang, C.; Wu, D.; Zhang, X.; Zhang, J. Halides-Enhanced Buried Interfaces for Stable and Extremely Low-Voltage-Deficit Perovskite Solar Cells. *Adv. Mater.* **2023**, *35* (28), No. 2300233.

(61) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; De Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21* (39), No. 395502.

(62) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865.

(63) Head, J. D.; Zerner, M. C. A Broyden—Fletcher—Goldfarb— Shanno optimization procedure for molecular geometries. *Chemical physics letters* **1985**, *122* (3), 264–270.

(64) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13* (12), 5188.