Efficient electron extraction of SnO2 electron transport layer for lead halide perovskite solar cell

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SnO2 electron transport layer (ETL) has been spotlighted with its excellent electron extraction and stability over TiO2 ETL for perovskite solar cells (PSCs), rapidly approaching the highest power conversion efficiency. Thus, how to boost the performance of ETL is of utmost importance and of urgent need in developing more efficient PSCs. Here we elucidate the atomic origin of efficient electron extraction and long stability of SnO2-based PSCs through the analysis of band alignment, carrier injection, and interfacial defects in the SnO2/MAPbI3(MA = CH3NH3+) interface using unprecedentedly high level of first-principles calculations at the PBE0 + spin-orbit-coupling + dispersion-correction level for all possible terminations and MA directions. We find that Sn-s orbitals play a crucial role in carrier injection and defect tolerance. SnO2/MAPbI3 shows favorable conduction band alignments at both MAI- and PbI2-terminations, which makes the solar cell performance of SnO2/MAPbI3 excel that of TiO2/MAPbI3. Different electron transfer mechanisms of dipole interaction and orbital hybridization at the MAI- and PbI2-terminations indicate that post-transition metal (sp valence) oxide ETLs would outperform transition metal (d valence) oxide ETLs for PSCs.

INTRODUCTION

Recently, lead halide perovskite (LHP) solar cells (PSCs) based on ABX3 [A = Cs+, CH3NH3+, (MA+), CHN2H4+, (FA+), B = Pb2+, Sn2+, Ge2+, X = I−, Br−, Cl−] have become one of the most promising large-scale photovoltaic materials by achieving the power conversion efficiency over 25%.1–7 The electron transport layer (ETL) plays a crucial role in extracting and transporting photo-generated electron carriers and serves as a hole-blocking layer by suppressing charge recombination as one of the most important components for photovoltaic devices.8 The physical properties of the ETL, including charge mobility, energy level alignment, defect states, morphology, and related interfacial properties, are significant for the photovoltaic performance.9 Until now, TiO2 has been widely used as the ETL material for organic/inorganic PSCs.10,11 However, TiO2 shows some limitations as a stable and efficient ETL for PSCs12–16. The conduction band minimum (CBM) of TiO2 is slightly higher than that of MAPbI3,17 which hinders the electron extraction from TiO2.18 TiO2 decomposes under the exposure to ultraviolet (UV) for a long time, which is not suitable for commercialization of PSCs.12–14 High temperature annealing for processing TiO2 also hampers elaborate device fabrication.15 In addition, the bulk electron mobility in SnO2 is two orders of magnitude higher than that of TiO2.22 SnO2 is easily processed at low-temperature, which is suitable for large-scale commercialization.24,29 Although SnO2 has been used as an alternative ETL for PSCs till now, the electron extraction mechanism of SnO2-based PSCs has not been studied yet. Here, we show a comparative study of rutile SnO2/MAPbI3 and rutile TiO2/MAPbI3 interfaces to uncover the mechanism behind the superior SnO2-based PSCs by employing first-principles calculations at the hybrid Perdew–Burke–Ernzerhof (PBE0) + spin-orbit-coupling (SOC) dispersion correction (PBE0-SOC-TS) level. Because the electronic structure of the interface is largely affected by the termination type and the alignment of organic A-site cation MA+, we investigate various directions of MA (001), (011), and (111) and termination types for MAPbI3 (MAI- and PbI2-terminations) at the SnO2/MAPbI3 and TiO2/MAPbI3 interfaces. The SnO2/MAPbI3 shows superior features to TiO2/MAPbI3, including CBM band alignments, large electron carrier injection, and the suppression of mid-gap defect states. In addition, we discuss a fundamental difference in electron extraction mechanisms between MAI-terminated (dipole polarization) and PbI2-terminated (orbital hybridization) MAPbI3.

RESULTS AND DISCUSSION

We employ 2√2 x 2√2 supercell of (001) plane rutile SnO2, rutile TiO2, and unit cell of (001) plane cubic MAPbI3 surfaces for the study. The slab consists of symmetric SnO2 or TiO2 (5 layers, 22 Sn/ Ti atoms and 44 O atoms) and MAPbI3 (001) (3 layers, MAI-termination: 4 MA molecules, 3 Pb atoms, and 10 I atoms, TiO2-termination: 4 MA molecules, 3 Pb atoms, and 10 I atoms) have become one of the most promising large-scale photovoltaic materials by achieving the power conversion efficiency over 25%.1–7 The electron transport layer (ETL) plays a crucial role in extracting and transporting photo-generated electron carriers and serves as a hole-blocking layer by suppressing charge recombination as one of the most important components for photovoltaic devices.8 The physical properties of the ETL, including charge mobility, energy level alignment, defect states, morphology, and related interfacial properties, are significant for the photovoltaic performance.9 Until now, TiO2 has been widely used as the ETL material for organic/inorganic PSCs.10,11 However, TiO2 shows some limitations as a stable and efficient ETL for PSCs12–16. The conduction band minimum (CBM) of TiO2 is slightly higher than that of MAPbI3,17 which hinders the electron extraction from TiO2.18 TiO2 decomposes under the exposure to ultraviolet (UV) for a long time, which is not suitable for commercialization of PSCs.12–14 High temperature annealing for processing TiO2 also hampers elaborate device fabrication.15 In addition, the bulk electron mobility in SnO2 is two orders of magnitude higher than that of TiO2.22 SnO2 is easily processed at low-temperature, which is suitable for large-scale commercialization.24,29 Although SnO2 has been used as an alternative ETL for PSCs till now, the electron extraction mechanism of SnO2-based PSCs has not been studied yet. Here, we show a comparative study of rutile SnO2/MAPbI3 and rutile TiO2/MAPbI3 interfaces to uncover the mechanism behind the superior SnO2-based PSCs by employing first-principles calculations at the hybrid Perdew–Burke–Ernzerhof (PBE0) + spin-orbit-coupling (SOC) dispersion correction (PBE0-SOC-TS) level. Because the electronic structure of the interface is largely affected by the termination type and the alignment of organic A-site cation MA+1, we investigate various directions of MA (001), (011), and (111) and termination types for MAPbI3 (MAI- and PbI2-terminations) at the SnO2/MAPbI3 and TiO2/MAPbI3 interfaces. The SnO2/MAPbI3 shows superior features to TiO2/MAPbI3, including CBM band alignments, large electron carrier injection, and the suppression of mid-gap defect states. In addition, we discuss a fundamental difference in electron extraction mechanisms between MAI-terminated (dipole polarization) and PbI2-terminated (orbital hybridization) MAPbI3.

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PbI₂-termination: 3 MA molecules, 4 Pb atoms, and 11 I atoms), where the lattice mismatches between MAPbI₃ and SnO₂ or TiO₂ are as small as ~3% with a vacuum size of ~40 Å. Considering the lattice parameter of pristine SnO₂ ($\sqrt{2} \times \sqrt{2}$ supercell) and MAPbI₃ is about 6.7 and 6.3 Å, respectively, we choose the average lattice parameter of 6.5 Å which makes the lattice mismatch of both sides being 3%. With combinations of MAI- and PbI₂-terminations with [001], [011], and [111] directions of MA in MAPbI₃, six types of SnO₂/MAPbI₃ (Fig. 1a–c, Supplementary Figs. 1 and 2) and TiO₂/MAPbI₃ (Fig. 1d–f, Supplementary Figs. 3 and 4) interfaces are investigated. We mainly focused on the SnO₂/MAPbI₃ (Fig. 1a) and TiO₂/MAPbI₃ (Fig. 1d) interfaces with the [111] MA direction where the short strong hydrogen bonding (SSHB) exists after the geometry optimization being the lowest energy configuration¹.

Because the PbI₂-terminated SnO₂/MAPbI₃ has stronger binding energy along the [001] MA direction than either [011] or [111] (Supplementary Table 1), we focus on SnO₂/MAPbI₃ (Fig. 1c) and TiO₂/MAPbI₃ (Fig. 1f) interfaces with the [001] MA direction. Before the relaxation, each interface with [001], [011], and [111] MA orientation does not contain the SSHB. However, in the case of interface with [111] MA orientation, the MA molecule at the interface rotates during the relaxation so that the SSHB forms between the nitrogen atom of MA molecule and the oxygen atom of interfacial SnO₂. In contrast, in the case of interface with [001] and [011] MA orientation, MA molecules at the interface cannot rotate enough to form the SSHB during the relaxation. Supplementary Figs. 1 and 2 are SnO₂/MAPbI₃ and TiO₂/MAPbI₃ interfaces before the relaxation, all of which do not contain the SSHB. Supplementary Figs. 3 and 4 are SnO₂/MAPbI₃ and TiO₂/MAPbI₃ interface after the relaxation and only Supplementary Figs. 3c and 4c contain the SSHB.

We note that the interfacial binding energy at the SnO₂/MAPbI₃ interface (Fig. 1a–c) is larger than that at TiO₂/MAPbI₃ (Fig. 1d–f) for both MAI- and PbI₂-terminations (Table 1). For the MAI-termination, the larger binding energy of SnO₂/MAPbI₃ interface can be explained with the stronger SSHB at the interface. The binding energy of the interface A/B is calculated by the formula $E_{b}(A/B) = E(A/B) - E(A) - E(B)$. The binding energy $E_{b}(\text{SnO}_2/\text{MAPbI}_3)$ = $E(\text{SnO}_2/\text{MAPbI}_3) - E(\text{SnO}_2) - E(\text{MAPbI}_3) = 1.53$ eV/unit-cell which surpasses $E_{b}(\text{TiO}_2/\text{MAPbI}_3) = E(\text{TiO}_2/\text{MAPbI}_3) - E(\text{TiO}_2)$.

**Fig. 1** Optimized geometry of SnO₂/MAPbI₃ and TiO₂/MAPbI₃ interfaces. SnO₂/MAPbI₃ interfaces of a MAI-termination with the SSHB, b MAI-termination without the SSHB, and c PbI₂-termination. TiO₂/MAPbI₃ interfaces of d MAI-termination with the SSHB, e MAI-termination without the SSHB, and f PbI₂-termination [Pb (black), I (purple), C (brown), N (light blue), H (white), Sn (dark blue), Ti (blue), and O (red)]. Dotted gray line between H and O at the interface represents the short strong hydrogen bonding (SSHB).
−E(MAPbI3) = 1.26 eV/unit-cell indicates the high stability of SnO2/MAPbI3 interface (Table 1). The SSHB distance between hydrogen and oxygen atoms at the interface is shorter at the SnO2/MAPbI3 interface (d(O − HN) = 1.54 Å) than at the TiO2/MAPbI3 interface (d(O − HN) = 1.60 Å). Accordingly, the interaction energy of the SSHB, defined as the energy difference between the structure with and without HB between MA and interfacial O at SnO2/MAPbI3 (ΔE = 0.52 eV/unit-cell) is almost twice stronger than that at TiO2/MAPbI3 (ΔE = 0.27 eV/unit-cell). The SSHB stabilizes the oxygen dangling bond and enhances the binding energy of interface. For the PbI2-termination, Eb(SnO2/MAPbI3) is 3.00 eV/unit-cell, much stronger than Eb(TiO2/MAPbI3) = 2.40 eV/unit-cell.

Table 1. Binding energy (BE), SSHB distance (d(O − HN)), and interaction energy (ΔE) of the SSHB in the (a) SnO2/MAPbI3 and (b) TiO2/MAPbI3 interfaces. The unit of d(O − HN) is given in Å and that of ΔE and BE is given in eV/unit-cell.

| Termination/MA orientation | d(O − HN) | ΔE  | BE     |
|----------------------------|-----------|------|--------|
| MAI-(111)                  | 1.54 (SSHB) | 0.52 | 1.53   |
| MAI-(011)                  | –         | –    | 0.87   |
| PbI2-(001)                 | –         | –    | 3.00   |
| MAI-(111)                  | 1.60 (SSHB) | 0.27 | 1.26   |
| MAI-(011)                  | –         | –    | 0.96   |
| MAI-(001)                  | –         | –    | 2.40   |

At the MAI-termination, the energy shift is governed by the MA dipolar polarization via the SSHB at the interface, largely affecting the band alignment. The interfacial CBM of SnO2 is slightly lower (by 0.23 eV) than that of MAPbI3 when the interfacial SSHB exists (Fig. 2a and Supplementary Fig. 9a). Without the SSHB, the band alignment of CBMs becomes unfavorable, as the interfacial CBM of SnO2 is 0.65 eV higher than that of MAPbI3 (Fig. 2b and Supplementary Fig. 9b), indicating a crucial role of the SSHB for CBM energy shift at the interface. On the contrary, the CBM of TiO2 alignments. For example, at the MAI-terminated SnO2/MAPbI3 interface with the SSHB (Supplementary Fig. 3c), the CBM of Sn is much lower than the CBM of Pb, indicating a significant open circuit voltage loss of the device. Also, the charge transfer cannot be described accurately within the PBE-SOC-TS level, which results in a fictitious vacuum level shift because of wrong band alignments. Because we need to use the same level of theory to compare two interfaces, we investigated the band gap errors under various DFT functionals (PBE, PBE0, and HSE06) and GW approximation (Supplementary Tables 2, 3, and Methods). We find that the PBE0-SOC-TS shows the lowest average band gap error for the SnO2(TiO2)/MAPbI3 interface system.

Quarti et al. showed that the band alignment is significantly influenced by the surface termination type30. We find that the band alignment mechanisms are related to the dipole polarization and orbital hybridization31–34 at MAI-termination and PbI2-termination, respectively. In order to analyze the band alignment of SnO2/MAPbI3 and TiO2/MAPbI3 at each termination, we plot the partial density of states (PDOS) of the SnO2/MAPbI3 and TiO2/MAPbI3 interfaces at MAI-termination and PbI2-termination (Fig. 2).

Fig. 2 Partial density of states (PDOS) of SnO2/MAPbI3 and TiO2/MAPbI3 interfaces at the PBE0-SOC-TS level. SnO2/MAPbI3 interface: a MAI-termination with the SSHB, b MAI-termination without the SSHB, and c PbI2-termination. TiO2/MAPbI3 interface: d MAI-termination with the SSHB, e MAI-termination without the SSHB, and f PbI2-termination. The fermi level is set to 0 eV. The SnO2/MAPbI3 has favorable band alignments for all MA orientations and terminations [Sn (red), Ti (orange), Pb (black), O (blue), and I (green)].
at the interface is always unfavorable regardless of the SSHB (Figs. 2d, e and Supplementary Fig. 9d, e). The CBM of TiO$_2$ is 0.37 eV (Fig. 2d and Supplementary Fig. 9d) and 1.00 eV (Fig. 2e and Supplementary Fig. 9e) higher than that of MAPbI$_3$. At the PbI$_2$-termination, SnO$_2$/MAPbI$_3$ shows 0.17 eV of CBM misalignment (Fig. 2c and Supplementary Fig. 9c). However, such a small misalignment still allows the electron extraction$^{11,21}$. The CBM misalignment at the TiO$_2$/MAPbI$_3$ interface (Fig. 2f and Supplementary Fig. 9f) is 0.33 eV, which is approximately twice higher than that of the SnO$_2$/MAPbI$_3$. However, we emphasize that this large misalignment still allows the electron extraction$^{11,21}$. The CBM misalignment at the TiO$_2$/MAPbI$_3$ interface (Fig. 2f and Supplementary Fig. 9f) is 0.33 eV, which is approximately twice higher than that of the SnO$_2$/MAPbI$_3$. However, we emphasize that this large misalignment still allows the electron extraction$^{11,21}$. The CBM misalignment at the TiO$_2$/MAPbI$_3$ interface (Fig. 2f and Supplementary Fig. 9f) is 0.33 eV, which is approximately twice higher than that of the SnO$_2$/MAPbI$_3$. However, we emphasize that this large misalignment still allows the electron extraction$^{11,21}$.

The band gap of bulk SnO$_2$ and (001) surface has a significant difference (Supplementary Table 5). The calculated band gap (at PBE0-SOC-TS level) of the (001) surface of SnO$_2$ is 2.92 eV which is much lower than that of bulk SnO$_2$ (3.58 eV). In contrast, the calculated band gap (at PBE0-SOC-TS level) of the (001) surface of TiO$_2$ is 3.96 eV which is similar with that of bulk TiO$_2$ (4.09 eV). This is because of the multivalent property of Sn atom. The surface Sn atoms are reduced from Sn$^{4+}$ to Sn$^{2+}$, resulting in SnO$_2$-like environment at the surface. This reduction makes the Sn-5s state filled with electrons near the valence band edge, which reduces the band gap (Supplementary Fig. 13)$^{36,37}$. Thus, a band gap of 2.68 eV (2.65 eV) for SnO$_2$ (in Supplementary Fig. 9a, c) is not so

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**Fig. 3** Averaged crystal orbital Hamiltonian population analysis of interfacial atomic pairs of TiO$_2$/MAPbI$_3$ (red) and SnO$_2$/MAPbI$_3$ (blue). **a** MAI-terminated and **b** PbI$_2$-terminated interfaces at the PBE0-TS level. Both in **a** MAI-termination and **b** PbI$_2$-terminations, the off-diagonal elements of COHP of SnO$_2$/MAPbI$_3$ are almost twice of TiO$_2$/MAPbI$_3$. The larger orbital hybridizations in SnO$_2$/MAPbI$_3$ at both terminations indicate the superior electron injection to the TiO$_2$/MAPbI$_3$ interface. **c** Schematic illustration which shows better orbital hybridization between Sn and Pb atoms than Ti and Pb atoms. Left and right geometry indicates MAI-terminated SnO$_2$/MAPbI$_3$ and TiO$_2$/MAPbI$_3$, respectively. The larger orbital hybridizations in SnO$_2$/MAPbI$_3$ at both terminations indicate the superior electron injection to the SnO$_2$/MAPbI$_3$ interface.
much underestimated as that of the (001) surface of SnO2 (2.92 eV).

The band gap difference between MAPbI3 for MAI-termination with the SSHB (1.95 eV, Supplementary Fig. 9a) and without the SSHB (1.55 eV, Supplementary Fig. 9b) is explained by the presence of the SSHB that significantly affects the band alignments of MAI-terminated interface. The SSHB (between interfacial O of SnO2 and H of MA) stabilizes the dangling bond of interfacial O of SnO2, which in turn lowers the CBM of SnO2. While this interfacial SSHB stabilizes SnO2, it destabilizes MAPbI3, even though the interface is stabilized overall. The interfacial MAPbI3 has three pairs of hydrogen bonding between I and H of MA. However, these hydrogen bonds inside MAPbI3 are broken in the favor of the SSHB between O of SnO2 and H of MA. And, this enhances the CBM level of MAPbI3 and increases the band gap (Supplementary Table 6).88

The COHP elements at the SnO2(TiO2)/MAI-terminated MAPbI3 and SnO2(TiO2)/PbI2-terminated MAPbI3 interfaces show that the interfacial atom-pairs form dominant antibonding states at both interfaces at the conduction bands (Fig. 3). The off-diagonal elements of COHP spanned by local orbital pairs can provide the covalent contributions (orbital hybridization) of the bonds and in turn the carrier injections between interfacial atoms. As mentioned, the hybridization is an order of magnitude larger at the PbI2-termination than the MAI-termination (Figs. 3a, b). This affirms that the orbital hybridization is a dominant mechanism for the band alignment in the PbI2-termination. Though the hybridization at the MAI-termination is weaker than at the PbI2-termination, we observe a trend where the off-diagonal COHP elements of conduction bands of SnO2/MAPbI3 interfacial atoms are larger than those of TiO2/MAPbI3 by averaging 14 atom-pairs within 2.0–9.0 Å (Fig. 3a). In the PbI2-terminated MAPbI3 interface, the COHP elements of the conduction bands at SnO2/MAPbI3 interface are twice larger than those of TiO2/MAPbI3 interface by averaging 19 atom-pairs within 2.0–5.0 Å. The result clearly indicates the larger orbital hybridization of interfacial atoms and larger electron carrier injection at the SnO2/MAPbI3 interface (Fig. 3b). The CBMs of SnO2, TiO2, and MAPbI3 are mostly composed of Sn-5s, Ti-3d, and Pb-6p, respectively. Thus, the CBM orbital hybridizations occur between Sn-5s and Pb-6p orbitals at the SnO2/MAPbI3 interface and between Ti-3d and Pb-6p at the TiO2/MAPbI3 interface. This large orbital hybridization could be also verified by the atomic orbital PDOS (Supplementary Fig. 12) in that behavior of Sn-5s orbital and Pb-6p orbital at the CBM is similar. In general, d-orbitals do not strongly hybridize with s- or p-orbitals and the COHP results show that the orbital hybridizations in the SnO2/MAPbI3 interface are larger than in the TiO2/MAPbI3 interface (Fig. 3c and Supplementary Fig. 14). Since the orbital hybridization is directly related to the carrier injection at the interface, this can qualitatively explain the reason for the superior carrier injection in SnO2/MAPbI3 interface which contributes to the high efficiency of PSCs.

Defects are one of the main setbacks for an efficient photovoltaic device, which generate shallow donor/acceptor levels and deep recombination centers around the gap.85,86 The defect in the ETL hampers the performance of PSC devices because of generation of trap states. Although, defects in the LHP only generates the shallow defect levels close to the band edges which does not damage the electron extraction from LHP to ETL.81 Azpiroz et al. showed that defect migration can hamper the electron extraction at the interface which contributes to the hysteresis of PSC devices.42

In this work, we mainly focus on how defect states in ETL affect the SnO2/MAPbI3 and TiO2/MAPbI3 interface. We study the neutral oxygen vacancy V0 and the Sn(Ti) interstitial Sn1(Ti1) at the surface or interface, which are known to be dominant defects in rutile SnO2,43,44 and TiO2,45,46 by employing the supercell layers of SnO2/TiO2 (Supplementary Figs. 15 and 16). In pristine TiO2, both V0, Ti0 generate deep levels below the CBM (Supplementary Fig. 16e, f), which is consistent with bulk TiO2.47–49. For pristine SnO2, the V0 (bridging) and Sn0 levels are different in the surface and the bulk. For the bulk SnO2, the V0 creates a shallow level below the CBM in the bulk.50,51 We find that the interfacial bridging V0 defect forms a SnO-like defect states near the VBM in SnO2 surface (Supplementary Fig. 16b) by a strong 5s–5p hybridization, which is consistent with the previous experiment.51 We confirm this hypothesis by observing a significant reduction of Sn+ → Sn0 from the Bader charge analysis (Supplementary Tables 7 and 8).52 For both MAI- and PbI2-termination, the charge difference of Sn2 atom is the most significant among tin atoms near V0 (Sn1–Sn4), indicating that charge is localized on Sn2 atom due to V0.53 Since both surface tin (and Sn2) oxygen have threefold coordination, their charge should be equal with opposite sign. From this, we can confirm the surface is reduced to SnO composition (Sn2+O2−), which means the charge of surface tin atom near V0 is reduced from Sn2+ to Sn2+. This reduction makes the Sn-Ss state filled with electrons and results in strong 5s–5p hybridization. This unique interfacial defect property, derived from the multi-valency of Sn, creates a favorable electronic environment for the electron transfer between MAPbI3 and SnO2. While Sn0 forms a shallow level below the CBM (Supplementary Fig. 16c) at SnO2 surface, bulk Sn0 is a shallow donor inside the CBM in bulk SnO2.54

The interfacial V0 at SnO2/MAPbI3 interface shows the consistent defect states near VBM for MAI- (Fig. 4a) and PbI2-terminations (Fig. 4c). The band structure of these configurations (Fig. 4a, c) are also calculated (Supplementary Fig. 17a, b), indicating that the occupied Ss state of Sn at the surface lies slightly above the top of the valence band. This state does not show any flat dispersion, indicating that this state is due to the multivalence of Sn. Therefore, these SnO-like defect states near the VBM in the SnO2/MAPbI3 interface (Fig. 4a, c and Supplementary Fig. 17) does not affect the electron extraction process at the CBM. The interfacial Sn0 generates a shallow level near VBM at both MAI- and PbI2-termination (Fig. 4b, d). On the contrary, the interfacial V0 and Ti0 of TiO2 create the Ti mid-gap deep level trap states at the MAI- and PbI2-terminated TiO2/MAPbI3 interfaces (Fig. 4h). Therefore, the SnO2/MAPbI3 interface has the superior defect tolerance to the TiO2/MAPbI3 interface at both terminations for all dominant defect types.

In summary, we studied the theoretical origin of high electron extraction of SnO2 ETL for PSCs at the PBE0-SOC-TS level by comparing the SnO2/MAPbI3 and TiO2/MAPbI3 interfaces. We calculated the binding energy, band alignment, carrier injection, and the interfacial defect levels at various terminations with different MA directions. We unveil crucial distinction of the conduction band electron transfer mechanisms at the MAI-termination (dipole polarization) and the PbI2-termination (orbital hybridization) in the SnO2(TiO2)/MAPbI3 interface. We explicitly showed that SnO2 exhibits favorable band alignments to MAPbI3 at both MAI- and PbI2- terminations over conventional TiO2 ETL. The carrier injection of the SnO2/MAPbI3 is larger than that of the TiO2/ MAPbI3 because of strong Sn-Ss and Pb-Sp/Si-Ss orbital hybridizations. Also, the interfacial V0 and Sn0 defect levels in SnO2 do not form deep recombination centers unlike TiO2 interface. Given that one of the crucial parts of PSC device is ETL, this understanding of electron transfer mechanism in the SnO2/MAPbI3 interface can pave a way to design better ETL materials for PSCs.

**METHODS**

We performed the noncollinear density functional theory (DFT) calculations with the hybrid PBE0 functional44 including TS dispersion corrections53 using Vienna Ab initio Simulation Package56 with dipole corrections. This is because the PBE0 functional can describe the band alignment of our system very well.

In order to choose a suitable exchange-correlations, we performed band gap calculation for bulk SnO2, TiO2, and MAPbI3 with different exchange-
correlations, such as PBE, PBE0, and HSE06, including spin-orbit coupling (Supplementary Table 2). For SnO2, the PBE0-SOC-TS gives the most similar band gap to experiment, whereas the HSE06-SOC-TS gives similar results for TiO2. For MAPbI3, both the PBE and the PBE-SOC-TS give similar band gaps to experiment. We noted that regardless of exchange-correlation, theoretical band gap is larger in TiO2, whereas experimental band gap is larger in SnO2. The same trend is also noted in the GW calculation of bulk SnO2 and TiO2 (Supplementary Table 3). Therefore, instead of choosing different exchange-correlation for SnO2/MAPbI3 and TiO2/MAPbI3 interfaces, we selected only one potential for the whole interface calculations which can minimize the average band gap error. Since the PBE0-SOC-TS gives the minimum band gap error compared with the experimental band gap, we choose the PBE0-SOC-TS exchange-correlation. In order to check surface properties, we also calculated the band gap of (001) surface of SnO2 and TiO2 at the PBE0-SOC-TS level (Supplementary Table 4). We used PAW pseudopotentials of Ti(3d
\text{p}^{2}), Sn(4d
\text{p}^{2}), O(2\text{s}^{2}\text{p}^{4})$, Pb$5\text{d}^{6}\text{f}^{2}$, and I(5s^25p^2). We employed $\Gamma$-centered $(4 \times 4 \times 1)$ $k$-mesh for sampling the Brillouin zone and $560$ eV energy cutoff for the planewave basis. Structural geometry optimization was performed with energy convergence and force convergence of $10^{-6}$ eV and $0.02$ eV/Å, respectively (Fig. 1 and Supplementary Table 9). The COHP analysis was done using LOBSTER v.3.1.057. COHP is a theoretical bond-detecting tool for solids, which partitions the band-structure energy into orbital-pair interactions.

In order to obtain the quantitative band alignments (Supplementary Fig. 9), we extracted the band alignment from the PDOS of bulk-like regions of the respective layers (L3 for SnO2 (TiO2) and L2 for MAPbI3 in Supplementary Figs. 7 and 8). Also, in order to show the PDOS method is reliable, we calculated the CBO for MAI-termination with SSHB and PbI2-termination of SnO2/MAPbI3 interface (Supplementary Fig. 18) by using an alternative method called Hartree potential alignment. In order to obtain the CBO of the interface A/B by using Hartree potential alignment, we need the Hartree potentials (VH) of the interface (A/B) and its corresponding A and B structure with the lattice parameter of the interface (or constrained bulk systems from the geometry of the interface). Then, the Hartree potentials of A and B are vertically shifted to be overlapped with the Hartree potential of the interface (A/B), where A and B are SnO2 and MAPbI3 in our system, respectively. Here, we obtain the shifts of the Hartree potential VH\text{A,B} (energy shift between the interface A/B and A) and VH\text{A,B} (energy shift between the interface A/B and B) (Supplementary Fig. 18a, b). The CBO is calculated by CBO = (CBO\text{A} + VH\text{A,B} - VH\text{A,B} - CBO\text{B}).

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AUTHOR CONTRIBUTIONS
C.W.M. and J.K. conceived the idea and devised the theory. J.K. and C.W.M. performed all calculations. All authors wrote the manuscript. K.S.K. and C.W.M. supervised the project.

COMPETING INTERESTS
The authors declare no competing interests.

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