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Solid-State Ligand-Capped Metal Oxide Electron-Transporting Layer for Efficient and Stable Fullerene-Free Perovskite Solar Cells

Shih-Han Huang, Yen-Chi Wang, Kai-Chi Hsiao, Pei-Huan Lee, Hsueh-Chung Liao, Yu-Xuan Huang, Yu-Ching Huang,* and Wei-Fang Su

Although perovskite solar cells (PSCs) can be prepared with excellent optoelectronic properties and solution processability, the common use of [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) as the electron-transporting layer (ETL), with its high cost and low stability, has hindered their commercialization. Metal oxides are inexpensive and highly chemically stable, making them potential alternatives to PCBM as ETLs, but requisite polar host solvents and high-temperature treatment limit the possibility of their direct deposition on perovskite layers. Herein, Ta-doped SnO2 nanoparticles (NPs) are dispersed in a nonpolar solvent and they are also directly deposited to form a Ta-SnO₂ layer on a perovskite film. Then, room-temperature solid-state ligand exchange is applied to remove insulating molecules from the Ta-SnO2 surface and thereby, enhance the band alignment between the Ta-SnO₂ layer and the Ag electrode. The highest power conversion efficiency of a PSC fabricated with Ta-SnO₂ as the ETL is 15.48%. In addition, the stability of the SnO2-based devices toward damp heat and light soaking is superior to that of corresponding PCBM-based PSCs. Therefore, this effective strategy for incorporating metal oxides as ETLs appears to be an inexpensive method for manufacturing highly efficient PSCs with longterm stability.

1. Introduction

Perovskite solar cells (PSCs) have achieved power conversion efficiencies (PCEs) of over 25%^[1] as a result of their long carrier lifetimes, long diffusion lengths, high light absorption coefficients, and tunable bandgaps. Nevertheless, the low operational

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stability and high cost of manufacturing PSCs have remained issues limiting their commercialization. The stability of a PSC depends on the quality of both the perovskite film and the interlayer between the perovskite film and the electrode. Recently, inverted p-i-n-structured PSCs have attracted much attention because of their low-temperature processing and long operating lifetimes. In such inverted PSCs, the hole-transporting layer (HTL) and electron-transporting layer (ETL) that have been employed most commonly have been $NiO_x^{[2-4]}$ and fullerene derivatives.^[5-7] Although [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) is currently the most broadly used material for deposition on the perovskite to form the ETL, it is expensive, has low chemical stability, and readily aggregates under high operating temperatures,^[8,9] thereby limiting the stability of PCBM-based PSCs.^[10,11]

N-type metal oxides (e.g., titanium dioxide $[TiO_2]$,^[12–14] tin oxide $[SnO_2]$,^[15–17] and zinc oxide $[ZnO]^{[18,19]}$ have been

applied widely as ETLs in regular n–i–p-structured PSCs. Their metal oxide films can be obtained with high crystallinity and high carrier mobility in a facile manner when annealing inexpensive precursors at temperatures above 200 °C.^[20] To deposit metal oxide films on the perovskite layers in inverted PSCs, metal oxides nanoparticles (NPs) have been prepared using low-temperature processing.^[21–24] Such metal oxide NPs, however, must often be dispersed in polar solvents, making it easy to damage the underlying perovskite layer. Although some researchers have used nonpolar solvents to prepare sol–gel metal oxide precursors for deposition on perovskite films,^[25,26] the resulting metal oxide layers require annealing at 100 °C for 10 min, potentially degrading the perovskite layer.^[27] Ideally, we would prepare highly stable PSCs incorporating ETLs fabricated from nonpolar solvents under annealing-free conditions.

Studies of PCBM-free PSCs, prepared using metal oxides as alternative ETLs, have been limited.^[26,28,29] Yang et al. reported that a PSC containing ZnO as the ETL exhibited a PCE of 16.1% and improving air stability.^[28] Chen et al. employed indiumdoped ZnO (IZO) as the ETL of a PSC that provided a high PCE of 16.2% and good light-soaking stability.^[29] In addition,



the use of metal oxides as ETLs, rather than organic molecules, has been demonstrated to improve the barriers to moisture and air.^[26] These studies revealed the great potential of replacing the PCBM film with a metal oxide layer to function as the ETL and, thereby, obtain highly stable PSCs. In each of the aforementioned examples. Al was used as the top metal electrode because the energy levels of the metal oxide layers and Al (\approx 4.1 eV) were well aligned. Nevertheless, Al electrodes are prone to oxidation in air, potentially decreasing the PCEs and stabilities of PSCs significantly. To avoid oxidation, inverted PSCs are often prepared with Ag instead of Al, but large energy barriers exist between these metal oxides and Ag (\approx 4.6 eV), leading to low PCEs.^[29,30] Some research groups have used interfacial engineering to minimize the energy barrier and improve charge extraction between organic materials and Ag.^[31,32] In a previous study, we revealed the importance of the energy level on the performance of PSCs; we found that an appropriate ligand (tetrabutylammonium hydroxide [TBAOH]) could modify the surface of SnO₂ NPs to adjust the energy band of the metal oxide layer to align well with that of Ag,^[33] but we still required PCBM as the ETL to obtain high-performance PSCs. Therefore, the quest remains to obtain highly efficient PCBM-free PSCs featuring Ag as the electrode.

In this study, we synthesized a stable form of n-type NPs, tantalum (Ta)-doped SnO_2 NPs, as a replacement for the organic electron transport material. This SnO_2 material exhibited improved conductivity after doping with Ta to increase the electron concentration. To obtain Ta-SnO₂ films from a nonpolar

solvent, we coated the surface of the Ta-SnO₂ NPs with insulating oleic acid (OA), which also functioned as a charge transport barrier. We then used a solid-state ligand-exchange method with 3-mercaptopropionic acid (3-MPA) to replace the OA molecules covering the SnO₂. In comparison with our previously reported TBAOH-SnO₂, the carrier transport of the 3-MPA-SnO₂ material was more effective because the 3-MPA provided a shorter alkyl chain and formed better sulfur-coordination bonds with the Ag electrode.^[34] After depositing a layer of iodopentafluorobenzene (IPFB) to passivate the perovskite layer, the PCE of the PSC device fabricated with all-oxide charge-transporting layers (AO-PSC) was 15.48%. Furthermore, the times at which the AO-PSC could still operate at 80% of its initial performance (T_{80}) during light-soaking and damp-heat (85 °C/85% relative humidity [RH]) tests were 540 and 1000 h, respectively. The excellent stability of this AO-PSC suggests a new way toward highly efficient PCBM-free PSCs.

2. Results and Discussion

The SnO₂ NPs had high crystallinity, as observed using highresolution transmission electron microscopy (HRTEM, Figure S1, Supporting Information); the (110) plane of SnO₂ featured a *d*-spacing of 0.33 nm, consistent with our previous report.^[33] According to our previous research, increasing the calcination time leads to SnO₂ with higher crystallinity and, accordingly, improved electrical properties for conventional SnO₂ films.



Figure 1. a) Schematic representation of n-type doping with Ta and Sn elements. b) Current–voltage curves and c) XRD patterns of $Sn_{1-x}Ta_xO_2$ materials prepared with various Ta doping ratios.



Unfortunately, it is difficult to modify the surfaces of highly crystalline metal oxide NPs with organic ligands (e.g., OA), making it difficult to disperse such NPs well in nonpolar solvents. As a result, highly crystalline NPs possessing good electrical properties cannot be deposited directly onto perovskite films. To allow the fabrication of PCBM-free PSCs, we used a doping method as an effective means of improving the conductivity of the NPs while also ensuring that the surfaces of these NPs could be modified. Herein, we increased the carrier concentration by doping with high-valence Ta atoms to generate additional free electrons to further improve the conductivity of SnO₂ (**Figure 1**a).^[35] The formula for doping Ta in SnO₂ is described below

$$Sn_{Sn} + O_O + Ta^{5+} \rightarrow Ta^{\bullet}_{Sn} + Sn_{Sn} + O_O + e'$$
(1)

The Ta⁵⁺ species could replace Sn⁴⁺ species in the crystal lattice because the ionic radius of Ta⁵⁺ is similar to that of Sn⁴⁺ (64 and 69 pm, respectively). We explored the effect of the Ta doping amount on the conductivity and lattice structure. Figure 1b displays the current-voltage characteristics of $Sn_{1-x}Ta_xO_2$ species prepared with various Ta doping ratios, allowing us to determine the conductivities and resistivities of the metal oxide thin films (Table S1, Supporting Information). The conductivity of the $Sn_{1-x}Ta_xO_2$ films increased initially upon increasing the Ta doping ratio, reaching a maximum of $3.06 \times 10^{-4} \,\mathrm{S \, cm^{-1}}$ when the Ta doping ratio was 7.5 mol% (cf., 1.59×10^{-4} S cm⁻¹ for the pristine SnO₂ film). The conductivity of the $Sn_{1-x}Ta_xO_2$ film decreased, however, upon increasing Ta doping ratio to 10 mol%; we suspect that the $Sn_0 Ta_0 Ta_0 O_2$ film underwent ionized impurity scattering, a phenomenon of localized charge disorder caused by overdoping that can lead

to low charge mobility of metal oxides.^[36] Figure 1c presents X-ray diffraction (XRD) patterns of the various $Sn_{1-x}Ta_xO_2$ films, with characteristic peaks at 26.5°, 33.9°, and 51.5° representing the (110), (101), and (211) crystal planes, respectively, of the SnO_2 .^[27,28] Even when the content of doped Ta was 10 mol%, these characteristic peaks of SnO_2 had not shifted. Table S1, Supporting Information, lists the grain sizes of the $Sn_{1-x}Ta_xO_2$ films, calculated using the Scherrer equation, as well as the average particle sizes determined using TEM (Figure S2, Supporting Information). Thus, doping with Ta cations maintained the crystal structure and high crystallinity of SnO_2 .

We used X-ray photoelectron spectroscopy (XPS) to measure the actual doping ratios of Ta in these materials. Figure 2a displays the binding energy peaks of the Ta and Sn elements in the pristine SnO_2 and $Ta-SnO_2$ ($Sn_{0.925}Ta_{0.075}O_2$). Compared with those of the pristine SnO₂, the Sn 3d peaks of Ta-SnO₂ had shifted slightly to higher binding energy, implying that the Ta atoms were interacting with the Sn atoms. In addition, peaks appeared for the Ta $4d_{3/2}$ and Ta $4d_{5/2}$ binding energies at 241.74 and 230.72 eV, respectively; we determined the atomic ratio of Ta (Ta 4d) to be 6.75%, guite similar to the doping ratio of 7.5 mol% in the solution. The charge mobility and the energy level of any ETL are critical to the performance of its resulting PSC. We used Hall effect measurements to obtain the charge mobility of the Ta-SnO2 materials. Table S2, Supporting Information, lists the carrier concentrations and carrier mobilities of the pristine SnO₂ and Ta-SnO₂. Compared with the pristine SnO₂, the carrier concentration of Ta-SnO₂ had increased from 4.80×10^{12} to 5.74×10^{12} cm⁻³. Thus, the carrier mobility of Ta-SnO₂ had improved from 21.92 to $29.17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, consistent with the results of the conductivity measurements.



Figure 2. a) XPS spectra revealing the binding energy peaks of Ta and Sn elements. b) UPS spectra of SnO_2 and $Ta-SnO_2$ ($Sn_{0.925}Ta_{0.075}O_2$). c) Energy band diagram of the various layers.



In addition, an ideal ETL should have the ability to facilitate rapid separation and effective transport of the carriers generated by the perovskite layer, processes dominated by the energy-level alignment of the ETL and the perovskite layer. Therefore, we used ultraviolet photoelectron spectroscopy (UPS) to characterize the energy band structures; Figure S3, Supporting Information and Figure 2b present the UPS spectra. Figure 2c and Table S2, Supporting Information, present the energy band diagram of the perovskite layer and the various ETLs. After doping with Ta, the conduction band of SnO₂ shifted from -3.92 to -4.01 eV, implying that the perovskite and PCBM. Moreover, the valence band of Ta-SnO₂ (-7.66 eV) was deeper than that of PCBM (-6.00 eV), suggesting that the hole-blocking ability of Ta-SnO₂ would be a better than that of PCBM.

In a previous study,^[33] we found that the surface of SnO₂ could be modified with work-function-tunable ligands and dispersed in a polar solvent (e.g., ethanol). We deposited those SnO₂ NPs on top of the PCBM layer to function as a protective layer and workfunction-modified layer for inverted PSCs. Nevertheless, these SnO₂ NPs could not be deposited directly on the perovskite layer because the polar solvent decomposed the perovskite layer. For deposition as the ETL on the surface of perovskite layer, it was necessary for the Ta-SnO₂ NPs to be dissolved in a nonpolar solvent to avoid damage to the perovskite layer. We determined that long alkyl chain ligands, such as that of OA, could modify the surface of SnO₂ to form NPs that could be dispersed well in nonpolar solvents. Nevertheless, the long and insulating hydrocarbon chains of the OA units enhanced the interfacial resistivity of Ta-SnO₂ and hindered its carrier transport. Therefore, to improve the electron extraction capability of the Ta-SnO₂ layer, OA was replaced with ligands having shorter carbon chains,



namely, TBAOH, 3-mercaptobenzoic acid (3-MBA), and 3-MPA (molecular structures provided in Figure 3a). Sizes of the Ta-SnO₂ NPs prepared with the various ligands by using dynamic light scattering (Figure S4, Supporting Information). The size distributions of the modified Ta-SnO₂ NPs in nonpolar solvents were larger than that of the Ta-SnO₂ capped with OA, indicating the poor dispersivity of the Ta-SnO₂ NPs presenting the new ligands, due to the high polarity of those ligands. Figure S5, Supporting Information, presents SEM images of the Ta-SnO₂ films deposited from the various Ta-SnO₂ NP solutions. Compared with the uniform Ta-SnO₂-OA film, many aggregates appeared on the ligand-exchanged Ta-SnO₂ films, confirming that these Ta-SnO₂ NPs possessed poor dispersibility in nonpolar solvents. Thus, we fabricated PCBM-free PSCs by dispersing Ta-SnO₂ NPs in a nonpolar solvent, depositing the Ta-SnO₂ laver on the perovskite film directly, and then performing room-temperature solid-state ligand exchange to remove the insulating molecules (OA units) from the Ta-SnO₂ and replace them with various other ligands, thereby optimizing the band alignment between Ta-SnO₂ and the Ag electrode in PCBM-free PSCs. The weak van der Waals forces between the OA ligands and SnO₂ were replaced by dipole-dipole interactions with the small polar molecules. We used Fourier transform infrared (FTIR) spectroscopy to verify the concentration effect of the various ligands on the surficial modification through solid-state ligand exchange (Figure S6, Supporting Information). The characteristic peaks of the Ta-SnO₂ NPs at 540-660 cm⁻¹ represent the stretching vibrations of their O-Sn-O and Sn-O bonds.^[37] In addition, the C-H, C=O, and COO⁻ stretching vibrations of OA appeared as characteristic peaks at 2800-3000, 1701, and 1400–1550 cm⁻¹, respectively.^[38] Figure 3b presents the FTIR spectra of the Ta-SnO₂ NPs modified with the various ligands,



Figure 3. a) Molecular structures of the ligands. b) FTIR spectra and c) conductivities of Ta-SnO₂ NPs capped with the various ligands.



revealing decreases in the intensities of the peaks of OA after modification. Thus, solid-state ligand exchange could indeed effectively remove the OA units capping the surface of the Ta-SnO₂ layer. XPS confirmed the presence of the new ligands on the Ta-SnO₂ surface. Figure S7, Supporting Information, provides the N 1s (401.45 eV) and S 2p (163.92 eV) spectra of the Ta-SnO₂ samples modified with TBAOH, 3-MBA, and 3-MPA, revealing that these ligands had replaced the OA unit on the surface of the Ta-SnO2 NPs. Figure S8, Supporting Information, displays SEM images of the ligand-exchanged Ta-SnO₂ films fabricated through solid-state ligand exchange; the morphologies of the Ta-SnO₂ films presenting the various ligands were as smooth as that of the Ta-SnO₂-OA film. The resistivity and conductivity of the modified Ta-SnO₂ samples had both improved (Figure 3c and Table S3, Supporting Information), especially for the 3-MPA-modified Ta-SnO₂ $(2.81 \times 10^3 \,\Omega \,\text{cm}$ and $3.56 \times 10^4 \,\Omega^{-1} \,\text{cm}^{-1}$, respectively). In addition, Table S3, Supporting Information, reveals that the carrier densities and mobilities of these modified Ta-SnO₂ samples were greatly enhanced relative to those of the unmodified Ta-SnO₂. We used UPS to measure the energy band diagram of the Ag (Figure S9, Supporting Information); the calculated work functions of Ag, Ag/TBAOH, Ag/3-MBA, and Ag/3-MPA were -4.51, -4.18, -4.02, and -4.19, respectively (Table S4, Supporting Information). Thus, TBAOH, 3-MBA, and 3-MPA could all be used as work function modifiers, due to their strong molecular dipole-induced shifting of the vacuum level. In addition, the thiol functional groups of 3-MBA and 3-MPA favorably react with Ag atoms to form covalent Ag-S bonds, potentially further minimizing contact resistance between the active layers and the Ag electrodes.^[34] Steady-state PL spectra of the perovskite films treated with the various Ta-SnO₂ films are provided in Figure S10, Supporting Information. Because of the presence of its insulting OA ligands, the PL intensity of the perovskite/ Ta-SnO₂–OA film had decreased only slightly from that of the unmodified perovskite film. After the Ta-SnO₂–OA film had been subjected to solid-state ligand exchange, the PL intensities of the perovskite/Ta-SnO₂ films decreased significantly, depending on the type of ligand exchanged. Because it contained the ligand with the shortest alkyl chain, the PL intensity of the perovskite/Ta-SnO₂–3MPA film exhibited the highest degree of PL quenching, consistent with the electrical measurements.

Next, we applied the Ta-SnO₂ NPs to form the ETLs of PSCs having a p-i-n architecture. Figure 4a and Table 1 display the I-V curves and detailed photovoltaic characteristics of these devices. The PSC incorporating PCBM/PEI (the reference PSC) exhibited a high PCE of 17.10%, with an open-circuit voltage (V_{oc}) of 1.04 V, a short-circuit current density (J_{sc}) of 21.79 mA cm⁻², and a fill factor (FF) of 75.63%. When replacing the PCBM and PEI layers with the Ta-SnO₂ NPs, the PCEs of the PSCs were lower than that of the reference device, the result of lower values of V_{oc} , J_{sc} , and FF. Among them, the PSC featuring the 3-MPA-modified Ta-SnO₂ had the highest PCE (13.01%), with a value of $V_{\rm oc}$ of 0.94 V, a value of $J_{\rm sc}$ of 20.52 mA cm⁻², and an FF of 67.21%. Figure 4b presents the maximum power point tracking (MPPT) profiles of these PSCs; the reference PSC displayed lower efficiency and faster degradation under MPPT conditions, relative to those of the PSCs incorporating the Ta-SnO₂ materials. After 100 s of MPPT, the PCEs of the



Figure 4. a) *J*–V curves and b) MPPT profiles of PSCs incorporating various ligand-capped Ta-SnO₂ ETLs. c) Damp-heat and d) light-soaking stability tests of PSCs incorporating PCBM and 3-MPA-modified Ta-SnO₂ as ETLs.

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| ETL ^{a)} | V _{oc} [V] | $J_{\rm sc} [{\rm mA cm^{-2}}]$ | FF [%] | PCE [%] | PCE _{MPP} [%] |
|----------------------------|--------------------------------|-----------------------------------|----------------------------------|--------------------------------|------------------------|
| PCBM/PEI | 1.02 ± 0.02 (1.04) | 21.94 ± 0.53 (21.79) | 69.39 ± 4.05 (75.63) | 15.51 ± 1.22 (17.10) | 16.53 |
| Ta-SnO ₂ –OA | 0.86 ± 0.02 (0.86) | 20.18 ± 1.01 (21.57) | 57.71 ± 1.78 (57.34) | 9.99 ± 0.72 (10.63) | 8.42 |
| Ta-SnO ₂ –TBAOH | 0.91 ± 0.05 (0.91) | 20.01 ± 0.89 (20.20) | 62.14 ± 6.29 (63.46) | 11.25 ± 0.40 (11.65) | 12.11 |
| Ta-SnO ₂ –3-MBA | 0.91 ± 0.03 (0.95) | 20.75 ± 1.12 (21.80) | 64.30 ± 4.19 (60.65) | 12.15 ± 0.25 (12.52) | 12.69 |
| Ta-SnO ₂ 3-MPA | 0.92 ± 0.02 (0.94) | 21.85 ± 0.80 (20.52) | 62.83 ± 1.27 (67.21) | 12.57 ± 0.52 (13.01) | 13.12 |

Table 1. Performance of PSCs incorporating various ligand-capped Ta-SnO₂ materials as ETLs.

^{a)}Average values obtained from ten devices; champion values listed in parentheses.

PSCs fabricated using the modified Ta-SnO₂ remained unchanged. Accordingly, we conducted damp-heat (85 °C/85% RH) and light-soaking tests to determine the stabilities of the AO-PSC featuring the 3-MPA-modified Ta-SnO₂ (Figure 4c,d). In the damp-heat tests performed over 1000 h, the PCEs of the AO-PSC and reference PSC decreased to 85% and 31% of their initial values, respectively, indicating that the water and heat resistance of the Ta-SnO₂ was superior to that of PCBM. In the light-soaking tests, the T_{80} lifetimes of the AO-PSC and reference PSC were 540 and 420 h, respectively. In addition, the color of the reference PSC became yellow, while the AO-PSC remained brown (Figure S11, Supporting Information). This color change was caused by the reaction of the perovskite layer with the Ag; thus, the 3-MPA-modified Ta-SnO₂ also prevented Ag-induced decomposition of the perovskite layer, thereby improving the long-term operational stability of it PSC. To the best of our knowledge, this stability is the best ever reported for a PCBM-free PSC fabricated at room temperature in air (Table S5, Supporting Information).

Although the AO-PSCs exhibited impressive stability, their PCEs remained far below that of the fullerene-based PSC, presumably because of charge extraction loss at the interface between the hot-cast perovskite layer and the Ta-SnO₂ layer.^[39] If charge accumulated at the interface, due to poor interfacial contact between the perovskite and Ta-SnO₂ layers, it would be readily trapped by defects and also increase the recombination loss. Therefore, to improve the PCEs of the AO-PSCs, we employed iodopentafluorobenzene (IPFB, a Lewis acid and strong acceptor) to modify the interface, improve the charge extraction efficiency, and stabilize the I- ions of the perovskite.^[40] Figure S12, Supporting Information, displays the photoluminescence (PL) spectra of the perovskite films prepared with and without an IPFB layer. Compared with the spectrum of the pristine perovskite film, the spectrum of the perovskite film prepared with the IPFB layer exhibited greater PL intensity, consistent with a lower content of defects in the latter. Figure 5a displays the PCE distribution of the PSCs; Figure S13 and Table S6, Supporting Information, present the related J–V curves and photovoltaic characteristics, respectively. The average PCE of the PSC modified with IPFB was higher than that of the PSC prepared without IPFB treatment, with the highest PCE

increasing from 13.47% to 15.48%. This enhancement in PCE arose mainly from the value of $V_{\rm oc}$ improving from 0.93 to 1.03 V; thus, modification with IPFB did, indeed, passivate the defects in the perovskite layer and minimize extraction loss at the perovskite-Ta-SnO2 interface. The improvements in the PCEs of the fullerene-PSC and AO-PSC devices were 4.4% and 14.9%, respectively, indicating that treatment IPFB had a greater effect on the all-oxide PSC. This result points that the surface passivation by IPFB is essential to improve the performance of all-oxide PSCs. Moreover, we used electrochemical impedance spectroscopy (EIS) and the space charge limited current (SCLC) method to obtain insights into the interfacial modification of the perovskite layer (Figure 5b). We measured the charge-transfer resistance (R_{CT}) according to the equivalent circuit and impedance curve fitting (Table S7, Supporting Information); the value of $R_{\rm CT}$ decreased from 253.60 Ω for the PSC prepared without IPFB treatment to 238.30Ω for the IPFB-modified PSC. In addition, we obtained the trap-filled limit voltage ($V_{\rm TFL}$) and trap density (N_t) by fitting the slope of the SCLC curves in the trapfilled limit (TFL) region (Table S7, Supporting Information).^[5] The calculated values of N_t for the perovskite layers prepared without and with IPFB modification were 3.07×10^{16} and $1.44 \times 10^{16} \,\mathrm{cm^{-3}}$, respectively. This decrease in trap density indicates that modification with IPFB could effectively passivate defects and facilitate charge extraction at the perovskite-Ta-SnO₂ interface.

3. Conclusions

We have prepared a highly efficient PSC incorporating a metal oxide (Ta-SnO₂) ETL that had been deposited onto the perovskite layer under ambient conditions. We greatly improved the conductivity of the Ta-SnO₂ and adjusted its band alignment with Ag by applying solid-state ligand exchange at room temperature. We further modified the interfacial contact between the perovskite layer and the Ta-SnO₂ by incorporating IPFB. The PCEs of the PSCs fabricated from the 3-MPA-modified Ta-SnO₂ reached 15.48%. In addition, the optimized AO-PSC exhibited excellent stability, with T_{80} lifetimes in damp-heat and light-soaking tests of 1000 and 540 h, respectively. Furthermore,





Figure 5. a) Statistical distributions of the photovoltaic characteristics and b) EIS and SCLC data of PSCs incorporating perovskite films fabricated with and without IPFB treatment.

compared with the corresponding organic ETL, the Ta-SnO₂ ETL provided an improved barrier toward moisture and air ingress.

4. Experimental Section

Materials: Acetone (99.0%) and boron trifluoride etherate (BF₃·OEt₂, 98.0+%) were purchased from Alfa Aesar. Benzyl alcohol (99.0%), chlorobenzene (99.0+%), chloroform (99.0+%), dichloromethane (99.8+%), dimethyl sulfoxide (DMSO, 99.9+%), γ -butyrolactone (GBL, 99+%), hexane (99+%), isopropyl alcohol (IPA, 99.8%), and toluene (99.8+%) were purchased from Acros Organics. Butylamine (BA, 99.5%), OA (90%), 1-octadecene (90%), oleylamine (98%), tetrabutylammonium hydroxide 30-hydrate (TBAOH, 95+%), SnCl₄, cesium iodide (CsI), IPFB, 3-MBA, 3-MPA, multiwalled carbon nanotubes, tantalum(V) ethoxide [(CH₃CH₂O)₅Ta], and polyethyleneimine (PEI, branched; average M_n : 10 k) were purchased from Sigma-Aldrich. Diethyl ether (99.0%) and ethanol (99.99%) were purchased from Fisher Chemical. Formamidinium lead iodide (FAI) was obtained from Starek Scientific. Fluorine-doped tin oxide (FTO) glass and PCBM (99.0%) were purchased from Front Materials. All chemicals were used as received, without any further purification. 2-Thiophene ethylammonium chloride (TEACl) was prepared according to the synthesis procedure reported in the literature.^[41]

OA-Capped SnO₂ NPs: SnO₂ NPs were synthesized using a chemical and solvothermal method, as discussed previously.^[33] A precursor solution of 0.3 M SnCl₄ was prepared in benzyl alcohol and toluene (volume ratio, 3:1; 20 mL). This precursor solution was heated to 180 °C in an oven for 12 h. The precipitate was collected by centrifugation and washed with diethyl ether and ethanol. To prepare the SnO₂-OA suspension, the collected SnO₂ NPs were redispersed in chloroform (5 mL) and excess OA (1 mL). BA (1 mL) was added to obtain a colorless transparent suspension. The SnO₂-OA suspension was purified by adding acetone to wash off the excess OA and BA; the sample was then centrifuged and redispersed in chloroform at a concentration of 200 mg mL⁻¹. To obtain the Ta-doped SnO₂ samples, tantalum(V) ethoxide was added to the precursor solution at a specific concentration prior to synthesizing the ${\rm SnO}_2~{\rm NPs}.$

Precursor Solutions: To obtain the NiO_x sol–gel solution, nickel acetate tetrahydrate was dissolved in ethanol at a concentration of 0.12 wt% and stirred at 60 °C for 20 min. Ethanolamine (30 μ L) was added to the NiO_x precursor solution and the resulting solution was filtered through a 0.2 μ m PTFE filter for purification. To obtain the perovskite precursor solution, a mixture of DMSO and GBL (volume ratio, 4:6) was used to dissolve the perovskite precursor powder. Cs_{0.2}FA_{0.8}PbI₃ was prepared by dissolving FAI, CsI, and PbI₂ in a glove box at a concentration of 0.6 m. TEACI was dissolved in IPA at a concentration of 2.5 mM. To obtain the electron transport layer, PCBM was dissolved in chlorobenzene at a concentration of 20 wt% and stirred at room temperature for 1 h. PEI was dissolved in IPA at a concentration of 0.01 wt% and stirred in a glove box overnight.

Device Fabrication: The device structure of the PSCs was FTO/HTL/ perovskite/ETL/Ag. FTO glass was washed ultrasonically in sequence with base solution, methanol, and isopropanol. A UV-ozone cleaner was then used to remove the organics. The HTL layer was prepared by spin coating (4000 rpm, 30 s) the NiO_x precursor onto the FTO glass and then annealing in air (350 °C, 30 min). The perovskite precursor solution was preheated at 75 °C; the FTO/NiO, sample was preheated at 180 °C for 15 min. The perovskite precursor was spin-coated (4000 rpm, 15 s) onto the as-prepared NiO_x film in a dry box (<10% RH). The TEACI solution was spin-coated (3000 rpm, 20 s) onto the perovskite layer and then thermally annealed (70 °C, 15 min). For the devices treated with IPFB, IPFB was spin-coated (3000 rpm, 20 s) onto perovskite layer. Two kinds of PSCs featuring different ETLs, PCBM and SnO2, were fabricated in this study. For the PCBM-based PSCs, the PCBM layer was spin-coated (1000 rpm, 30 s) onto the perovskite layer and then the PEI layer was deposited (3000 rpm, 30 s) on the PCBM layer. For the SnO₂-based PSCs (PCBM-free PSCs), the various SnO₂ precursors were spin-coated (1500 rpm, 30 s) onto the perovskite layer. The solid-state ligand exchange involved placing chloroform solution of TBAOH, 3-MBA, and 3-MPA on the SnO₂ film for a period of time (5 s), and then spinning (3000 rpm, 30 s). Finally, a Ag electrode (100 nm) was deposited through thermal evaporation. The device area was 0.09 cm². The encapsulation procedure was performed in a glove box.

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After the device had been coated with UV-curable resin, it was covered with an upper-glass substrate and treated under a UV lamp (365 nm, 1.5 W) for 45 min. A polyisobutylene (PIB) tape was pasted around the device to form an edge seal, and then the system was heated at 140 °C for 15 min for thermal curing.

Characterization: TEM images of the SnO₂ NPs were obtained using an FEI transmission electron microscope (JEOL 2010F). The crystal structures of the various metal oxides were determined using XRD (Rigaku, TTRAXIII, Japan) with Cu K α radiation at 50 kV. XPS was performed using a PHI 5000 Versa Probe system (ULVAC-PHI, Chigasaki) and a microfocused (100 μ m, 25 W) Al X-ray beam. The work functions of the materials were determined through UPS (PHI 5000 VersaProbe, ULVAC-PHI) with a UV light source of He I emission (21.2 eV, B50 W), calculated using the equation

$$\Phi = h\nu - (E_0 - E_F) \tag{2}$$

FTIR spectra were measured using a Spectrum 100 spectrometer (PerkinElmer). The *J*–V curves of the devices were measured using a voltage source meter (Keithley 2410) and an AM1.5G solar simulator (Yamashita Denso YSS-50A-400A) with irradiation of 100 mW cm⁻². The resistances were recorded using EIS (Solartron Analytical). For trap density measurements, electron-only devices were fabricated having the structure FTO/TiO₂/perovskite/SnO₂/Ag. The measured *I*–V curves were fitted with the SCLC. For stability tests, the encapsulated PSCs were placed in an environmental chamber (Terchy HRMB-80) for the damp-heat (85% RH, 85 °C) tests and illuminated under a Xe lamp (100 mW cm⁻²) with a UV filter for the light-soaking tests.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

electron-transporting layer, ligand exchange, metal oxide nanoparticles, perovskite solar cells, stability

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