Modified SnO$_2$ with Alkali Carbonates as Robust Electron-Transport Layers for Inverted Organic Solar Cells

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**ABSTRACT:** We report for the first time that alkali carbonates (Li$_2$CO$_3$, K$_2$CO$_3$, and Rb$_2$CO$_3$) based on a low-temperature solution process can be used as interface modifiers for SnO$_2$ as robust electron-transport layers (ETLs) for inverted organic solar cells (iOSCs). The room-temperature photoluminescence, the electron-only devices, and the impedance studies altogether suggested the interfacial properties of the alkali carbonates–modified SnO$_2$ ETLs, which were much better than those based on the SnO$_2$ only, provided efficient charge transport, and reduced the charge recombination rates for iOSCs. The iOSCs using the polymer donor poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b′]dithiophene-2,6-diyly-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]-thiophene-2-carboxylate-2,6-diyly)] and the fullerene acceptor phenyl-C$_{70}$-butyric acid methyl ester as the active layer showed the average power-conversion efficiencies (PCEs) based on ten devices of 6.70, 6.85, and 7.35% with Li$_2$CO$_3$, K$_2$CO$_3$, and Rb$_2$CO$_3$-modified SnO$_2$ as ETLs, respectively; these are more than 22, 24, and 33% higher than those based on the SnO$_2$ only (5.49%). Moreover, these iOSC devices exhibited long-term stabilities, with over 90% PCEs remaining after the devices were stored in ambient air for 6 weeks without encapsulations. We believe that alkali carbonates–modified SnO$_2$ ETLs, which were introduced to simultaneously eliminate the use of acid and hygroscopic PETDOT:PSS will corrode the ITO, which leads to the deterioration of the anode side. To circumvent these problems, inverted organic solar cells (iOSCs) have been introduced to simultaneously eliminate the use of acid and hygroscopic PETDOT:PSS as well as the unstable low WF on both sides for OSCs. The iOSCs are normally built with a hygroscopic SnO$_2$ with Alkali Carbonates as Robust Electron-Transport Layers for Inverted Organic Solar Cells.

1. INTRODUCTION

Among various types of solar cells, bulk-heterojunction organic solar cells (OSCs) have received great attention from both academic and industrial researchers as the third generation of solar-cell technology. These types of solar cells have unique advantages, such as light weight, abundant materials, simple preparation at a low cost, and a high-throughput solution process, which is highly suitable to roll-to-roll printing technology on flexible substrates. Despite these huge advantages, however, in reality, OSCs have shown lack of stability and inferior power-conversion efficiency (PCE) compared to the counterpart dye-sensitized and commercial silicon solar cells. These are the main obstacles that prevent OSCs from entering the real photovoltaic market. Along with the development of new donor–acceptor materials and the interfacial engineering for OSCs, nowadays a PCE over 14% can be achieved with great improvement in device stability.

Conventional OSCs are usually based on an acid and hygroscopic poly[3,4-ethylenedioxythiophene]:poly(styrene sulfonate) (PEDOT:PSS) deposited on indium tin oxide (ITO) glass as a hole-collecting layer, and a metal of low work function (WF) like Al or Ca is used as the cathode. After a while, these low-WF metals in the cathode will react with oxygen and moisture in ambient air to form an insulating metal oxide like Al$_2$O$_3$, which may build a barrier against carrier transport; on the other hand, the acid and hygroscopic PEDOT:PSS will corrode the ITO, which leads to the deterioration of the anode side. To circumvent these problems, inverted organic solar cells (iOSCs) have been introduced to simultaneously eliminate the use of acid and hygroscopic PEDOT:PSS as well as the unstable low WF on both sides for OSCs. The iOSCs are normally built with a high optical transparency and stable metal oxide deposited on ITO as the top cathode side to assemble electrons, whereas an ultrastable high-WF metal like Ag or Au is used as the bottom anode side to gather holes. Thus, these iOSCs are firmly protected on both sides against the penetration of oxygen and moisture from the ambient environment.

To obtain a stable and highly efficient iOSC, one of the most effective ways is introducing a suitable electron-transport layers (ETL) between the active layer and the ITO cathodes. Ideally, an ETL should serve multiple functions, including

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tuning the energy-level alignment at the interface of the cathode and the active layer, improving charge selectivity, controlling surface properties of the cathode to alter the morphology of the active layer, increasing light absorption into the active layer, and improving interfacial engineering stability between the cathode and the active layer.16 However, a single ETL is usually not sufficient to fulfill all these requirements. Thus, interfacial engineering, like interfacial modifiers for ETLs, are receiving considerable attention as a promising way to improve both photovoltaic performance and device stability of iOSCs.17

Among various materials that have been exploited as ETLs for iOSCs, n-type metal oxides such as TiO2 and ZnO, which possess a high optical transparency and excellent charge-transport properties, are commonly used by several groups. Oxygen vacancy-related defects that usually exist on metal oxides are likely to occur during the synthesis process, leading to poor device performance. Several kinds of materials, such as conjugated polyelectrolytes (CPEs),20 nonconjugated polyelectrolytes (n-CPEs),17 small molecules,11 ionic liquids,12 alkali hydroxides,23 or cesium stearate,24 have been introduced to modified TiO2 or ZnO ETLs. Even though these iOSCs were obtained with very high PCE, an extremely high annealing temperature (∼400 to 500 °C) is usually needed to prepare TiO2 during its fabrication; also, the instability under UV light for both ZnO and TiO2 may eliminate them as choices for ideal ETLs of commercial iOSCs in the near future.25 Note that the eventually commercial iOSCs are built on flexible substrates, where a temperature higher than 200 °C is not allowed.5,6 Another serious drawback of the iOSCs using these metal oxides is “light-soaking issues” that is, a UV-light source is required for normal device operation.25 Therefore, it is crucial to develop novel ETL metal oxides with facile low-temperature solution processing; these ETLs not only need to fulfill the requirements for an ideal ETL as mentioned above, but also need extra properties, such as UV resistance and light-soaking issues free for iOSCs.

Recently, SnO2 has been recognized as a highly promising candidate for the electron-transport layer because of its merits, such as abundant n-type material with high transparency, high conductivity, a suitable conduction band minimum, excellent chemical stability, and UV resistance.25,27,28,33 Interestingly, it has been reported that iOSCs based on SnO2 are not only of free light-soaking issues29 but also excellent in terms of device stability.30 Additionally, SnO2 possesses higher electron mobility up to 240 cm2 V−1 s−1 (which is more than 2 orders of magnitude higher than TiO2),27,31 and a wider band gap (3.6–4.0 eV),27,31 as well as low trap density compared with ZnO and TiO2.52 Moreover, SnO2 has a very suitable conduction-band minimum (CBM) for efficient charge transport, and a deeper valence-band maximum (VBM), which is helpful for hole blocking in iOSCs.33,34

In the past, SnO2 has been noted for an excellent ETL for optoelectronic devices35 however, the preparation of SnO2 is usually based on a high-cost process like thermal evaporation, which is conducted at a high vacuum pressure.30 Note that SnO2 can be prepared by a solution process, but a high annealing temperature (above 450 °C) is usually required to form crystallized SnO2.30 In 2015, with huge progress in solution processing, SnO2 can be prepared at a much lower temperature (∼180 °C) with high transparency and uniform substrate coverage.33 Note that a low temperature of about 180 °C is possible for a low-cost, high-throughput roll-to-roll printing technique on flexible substrates for eventually commercial iOSCs.25 To date, there are reports for low-temperature solution-processed SnO2 as ETLs,25,27,28,33 however, most of them are applied to perovskite solar cells. To our knowledge, so far, there are few reports on SnO2 ETLs, and in most cases, these iOSCs are based on a normal well-studied P3HT:PC61BM active layer.37–39 Besides, very recently, Shen et al. reported that a poly(9,9-n-diethyl-2,7-fluorene-alt-9-phenyl-3,6-carbazole (PFN) can modify SnO2 as ETLs for polymer solar cells (PSCs) based poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2,6-diyl] (PTB7-Th):phenyl-C61-butyric acid methyl ester (PC70BM). An impressive PCE of 11.05% was achieved; however, their PSC devices based on SnO2 only revealed a humble PCE of 4.31% due to trap-induced recombination at the interface between the SnO2 and the active layer.40 Moreover, Shen et al. have not studied the device stability of PSCs.40

Among several materials in the past, alkali carbonates have been used as independent ETLs for iOSCs because of their effective electron-transport properties.41,42 However, because of their weak hole-blocking properties, alkali carbonates eliminated themselves as candidates for ideal ETLs of iOSCs.43 Recently, alkali carbonates have emerged as a doping source or modifiers for ETLs and have shown good improvements in device performance, ranging from iOSCs to perovskite solar cells.44,45 However, to our knowledge, so far there is no published work on using any kind of alkali carbonates—modified SnO2 for polymer-based iOSCs (e.g., PTB7-Th:PC70BM).

In this contribution, we first report on the use of alkali carbonates (Li2CO3, K2CO3, and Rb2CO3) as efficient modifiers for SnO2 as ETLs for improving the device performance of iOSCs based on a facile low-temperature solution process (our annealing temperature was 185 °C for SnO2 and 120 °C for alkali carbonates). In our work, SnO2–alkali carbonates were achieved simply by spin-coating alkali carbonate solutions with a concentration of 1 mg mL−1 in deionized (DI) water onto the prepared SnO2. The room-temperature photoluminescence (PL), the electron-only devices, and the impedance studies were employed as effective tools for demonstrating the excellent interfacial properties of the alkali carbonates–modified SnO2–ETLs as compared to those based on SnO2 only. The iOSCs using the polymer donor PTB7-Th and the fullerene acceptor PC70BM as the active layer show average PCEs based on ten devices of 6.70, 6.85, and 7.35% with Li2CO3-, K2CO3-, and Rb2CO3-modified SnO2 as ETLs, respectively; these values are more than 22, 24, and 33% higher than those based SnO2 only (5.49%). Furthermore, our iOSC devices also exhibited long-term stabilities, with over 90% of PCEs remaining after storing the devices in ambient air for 6 weeks without encapsulations. To our knowledge, the excellent chemical stability of SnO2, the inverted-geometry type of devices, and, more importantly, the better interfacial engineering stability between SnO2 and the active layer with alkali carbonate modifiers are the compelling reasons for our iOSC device stabilities. We believe that the alkali–carbonates-modified SnO2 approach can be an effective way to obtain stable and highly efficient iOSCs. Its applications may be extended to other optoelectronic devices where an ETL is necessary, such as perovskite solar cells or organic light-emitting diodes.
2. RESULTS AND DISCUSSION

2.1. Optical Properties of SnO$_2$ and SnO$_2$/Alkali Carbonate Films.
In general, the optical properties of the ETLs in the wavelengths ranging from 380 to 750 nm (visible wavelength range) play a very important role in the performance of the iOSCs. A higher transparency of the ETLs will help a greater ratio of photons reach the active layer, resulting in better photocurrents, which will help achieve a higher PCE of the iOSCs. It is self-evident that, to ensure that enough photons reach the active layer, the transparency of an ideal ETL should be over 85% in the visible wavelength range. To evaluate the optical properties of SnO$_2$ and SnO$_2$/alkali carbonate films, we conducted UV−vis absorption and transmittance measurements on these samples. Figure 1a,b shows the UV−vis absorption and optical transmission spectra of SnO$_2$ and SnO$_2$/alkali carbonate films on glass substrates. It is interesting that all the SnO$_2$ or SnO$_2$/alkali carbonate samples exhibit excellent optical properties, with average transmittance over 97% in the visible wavelength range. To evaluate the optical properties of SnO$_2$ and SnO$_2$/alkali carbonate films, we conducted UV−vis absorption and transmittance measurements on these samples. Figure 1a,b shows the UV−vis absorption and optical transmission spectra of SnO$_2$ and SnO$_2$/alkali carbonate films on glass substrates. It is interesting that all the SnO$_2$ or SnO$_2$/alkali carbonate samples exhibit excellent optical properties, with average transmittance over 97% in the visible range. Compared to SnO$_2$, the SnO$_2$/alkali carbonate samples show a slightly better transmittance, perhaps because of the reduced reflection. The excellent optical properties of SnO$_2$ and SnO$_2$/alkali carbonate samples make them ideal candidates for ETLs for the eventual commercialization of organic solar-cell technology.

2.2. Photoluminescence Studies for SnO$_2$ and SnO$_2$/Alkali Carbonate Films. Photoluminescence (PL) studies are an effective tool for evaluating the merits of ideal ETLs in terms of the charge recombination in iOSCs. In general, the oxygen-vacancy-related defects that usually exist on metal oxides are likely to occur during the synthesis process. These defects act as recombination centers that lead to poor performance for iOSC devices. A proper topography of ETLs will help to build a good physical contact with the active layer, allowing an efficient charge extraction and carrier transport at the interface from the active layer to the ETL of iOSC devices. Thus, good morphology with suitable surface roughness values is desirable for achieving highly efficient iOscs. Figure 1d−g presents the AFM height images of SnO$_2$ and alkali carbonates modified SnO$_2$ films on the ITO glass substrates. The surface roughness root-mean-square (RMS) values of SnO$_2$, SnO$_2$/Li$_2$CO$_3$, SnO$_2$/K$_2$CO$_3$, and SnO$_2$/Rb$_2$CO$_3$ as shown in Figure 1d−g are 1.34, 1.21, 1.45, and 1.18 nm, respectively. Obviously, all these RMS values are significantly lower than that of a bare ITO glass substrate (1.94 nm) (Figure S2), demonstrating the excellent morphol-
ogy of our ETL samples. Compared to those based on SnO$_2$ only, all alkali carbonates–modified SnO$_2$ samples exhibit slight differences in RMS surface roughness values. However, the best surface roughness value was obtained for the Rb$_2$CO$_3$–modified SnO$_2$ samples. Generally speaking, a lower RMS surface roughness value is needed to guarantee an intimate contact between the ETLs and the active layers, contributing to reducing the series resistances of iOSCs to increase PCE.53

Based on the AFM results, we think the best performance of iOSCs may be by those using SnO$_2$/Rb$_2$CO$_3$ as ETLs. The three-dimensional (3D) AFM images of SnO$_2$ and alkali carbonate–modified SnO$_2$ samples are also given in Figure S3. Besides the AFM measurements, the surface of SnO$_2$ and SnO$_2$/alkali carbonate samples were also investigated using the top-view scanning electron microscopy (SEM) characterization. The detailed observations from the SEM images of our ETL samples (Figure S4) seem to be strongly consistent with their AFM results. The coexistence and uniform distribution of SnO$_2$ and SnO$_2$/alkali carbonate films on ITO glass substrates can be further demonstrated via energy-dispersive X-ray (EDX) spectrum and elemental mapping analysis (Figures S5–S8). Note that, from Figure S6, presenting the EDX spectrum and elemental mapping analysis for SnO$_2$/Li$_2$CO$_3$, the Li elements were not seen because of the limits of detection of EDX analysis in our SEM measurement systems (the first three elements, H, He, and Li, of the periodic table are not detectable by normal EDX analysis because of the very low energy of their characteristic radiation). The presence of Li in SnO$_2$/Li$_2$CO$_3$ can be proved using X-ray photoelectron spectroscopy (XPS) measurements, presented in the next section.

2.4. Structural Properties and Chemical States of SnO$_2$ and SnO$_2$/Alkali Carbonate Films. The structural properties of SnO$_2$ and SnO$_2$/alkali carbonate samples were first investigated using X-ray diffraction (XRD) analysis. Figure S9 presents the XRD spectra of SnO$_2$ and of SnO$_2$/alkali carbonate ETLs coated on glass substrates. Obviously, no clear dominant peaks of SnO$_2$ or SnO$_2$/alkali carbonate ETLs can be clearly seen in the XRD pattern for SnO$_2$ (JCPDS card no. 41-1445), perhaps because of the amorphous structure of SnO$_2$ and SnO$_2$/alkali ETLs caused by the low-temperature annealing (∼185 °C), reported by several groups.54,55

Because we could not obtain enough information to firmly confirm the component and chemical states of the SnO$_2$ and SnO$_2$/alkali carbonate samples via XRD, we further conducted XPS measurements on our ETL samples to demonstrate their chemical states. Figure 2a–c gives the XPS spectra surveys along with XPS spectra profiles of the Sn 3d and O 1s regions of the SnO$_2$ and SnO$_2$/alkali carbonate ETL samples. To our knowledge, in general, the Sn 3d$_{5/2}$ peaks in SnO$_x$ consisted of three peak components: Sn$^{4+}$ is located at 486.58 eV, Sn$^{2+}$ at 485.88 eV (the Sn$^{2+}$ shifted to a lower binding energy by 0.7 eV compared to Sn$^{4+}$), and Sn$^{0+}$ at 484.38 eV (the Sn$^{0+}$ shifted to a much lower binding energy by 2.2 eV compared to Sn$^{4+}$).56,57 On the other hand, the O 1s peaks in SnO$_x$ are known to be constructed by two binding components: O$^{-}$Sn$^{4+}$ and O$^{-}$Sn$^{2+}$, which have binding energies of 530.37 and 529.77 eV, respectively (O$^{-}$Sn$^{2+}$ shifted to a lower binding energy by 0.6 eV compared to O$^{-}$Sn$^{4+}$).56,57 As displayed in Figure 2a,b, the binding energy values of the Sn 3d$_{5/2}$ and the O 1s peaks of our SnO$_2$ ETL samples are 486.98 and 530.54 eV, which correspond to Sn$^{4+}$ constituent and O$^{-}$Sn$^{4+}$, respectively. Note that in our SnO$_2$ ETL samples, the peaks related to the Sn$^{2+}$ constituent and O$^{-}$Sn$^{2+}$ were not seen, which is compelling evidence that confirmed the pure SnO$_2$ component states in our ETL samples. Interestingly, SnO$_2$ modified with the alkali carbonates revealed the same dominant peaks for Sn$^{4+}$ and O$^{-}$Sn$^{4+}$ binding energies at...
486.58 and 530.27 eV, respectively. Compared to the SnO\textsubscript{2} only, the positions of these dominant peaks were shifted to a bit lower binding energy that may be ascribed to the electronegative anion component (CO\textsubscript{3})\textsuperscript{2−} of alkali carbonates.

Figure 2d−f shows the XPS spectra of the Li, K, and Rb regions for SnO\textsubscript{2}/Li\textsubscript{2}CO\textsubscript{3}, SnO\textsubscript{2}/K\textsubscript{2}CO\textsubscript{3}, and SnO\textsubscript{2}/Rb\textsubscript{2}CO\textsubscript{3} samples, respectively. As can be seen from Figure 2d−f, the dominant peaks are located at 55.90, 292.70, and 110.60 eV, which can be assigned to Li 1s of Li\textsubscript{2}CO\textsubscript{3}, K 2p\textsubscript{3/2} of K\textsubscript{2}CO\textsubscript{3}, and Rb 3d\textsubscript{5/2} of Rb\textsubscript{2}CO\textsubscript{3}, respectively.58 Thus, we may conclude that our XPS results are strong evidence that confirms the coexistence of the alkali carbonates (Li\textsubscript{2}CO\textsubscript{3}, K\textsubscript{2}CO\textsubscript{3}, and Rb\textsubscript{2}CO\textsubscript{3}) in our SnO\textsubscript{2}/alkali carbonate ETL samples.

2.5. Calculation of Band Gaps and Energy Levels of ETLs. Based on the UV−absorption profiles of SnO\textsubscript{2} and SnO\textsubscript{2}/alkali carbonate ETLs (Figure 1a), the band gaps (E\textsubscript{g}) of these ETLs were then calculated via the Tauc plot method with the following equation: \((\alpha h\nu)^2 = A(h\nu − E_g)^\delta,\) where \(h\nu\) is stands for the photo energy, \(A\) is a constant, and \(\alpha\) is the absorption coefficient. Figure S1 presents the Tauc plots of \((\alpha h\nu)^2\) versus \(h\nu\) of SnO\textsubscript{2} and SnO\textsubscript{2}/alkali carbonate ETLs. By executing the linear extrapolation for these curves, as can be seen in Figure S1, the band gaps were found to be 3.87, 3.89, 3.90, and 3.96 eV for SnO\textsubscript{2}, SnO\textsubscript{2}/Li\textsubscript{2}CO\textsubscript{3}, SnO\textsubscript{2}/K\textsubscript{2}CO\textsubscript{3}, and SnO\textsubscript{2}/Rb\textsubscript{2}CO\textsubscript{3} ETLs, respectively. It appears that the band gaps of SnO\textsubscript{2}/alkali carbonate ETLs show a slight increase compared to the SnO\textsubscript{2} only; this may be ascribed to a slight
shift up of the conduction band edges of these ETLs caused by the presence of alkali carbonates on SnO$_2$.

To identify the energy-level alignment between the ETLs and the active layers, the ultraviolet photoelectron spectroscopy (UPS) measurements were carried out on SnO$_2$ and SnO$_2$/alkali carbonate samples. Figure 3 shows the UPS spectra on the valance-band regions ($E_{\text{valence}}$), survey, and secondary electron cutoffs ($E_{\text{cutoff}}$) of SnO$_2$ and alkali carbonates—modified SnO$_2$ coatings on ITO glass substrates. As displayed in Figure 3a, the $E_{\text{cutoff}}$ were found to be 3.85, 3.83, 3.72, and 3.69 eV and the $E_{\text{valence}}$ were 16.81, 17.13, 17.19, and 17.14 eV for SnO$_2$, SnO$_2$/Li$_2$CO$_3$, SnO$_2$/K$_2$CO$_3$, and SnO$_2$/Rb$_2$CO$_3$ ETLs, respectively. The valence-band maximums (VBM) of these ETLs can be computed using the following formulation:

$$VBM = h\nu - (E_{\text{cutoff}} - E_{\text{cutoff}})$$

where $h\nu = 21.22$ eV is the incident photo energy from a He(I) source of UPS measurement systems. The VBM were calculated and found to be $-8.26$, $-7.92$, $-7.77$, and $-7.75$ eV for SnO$_2$, SnO$_2$/Li$_2$CO$_3$, SnO$_2$/K$_2$CO$_3$, and SnO$_2$/Rb$_2$CO$_3$ ETLs, respectively. The conduction-band minimums (CBM) of SnO$_2$, SnO$_2$/Li$_2$CO$_3$, SnO$_2$/K$_2$CO$_3$, and SnO$_2$/Rb$_2$CO$_3$ ETLs were deduced from their $E_g$ and VBM, as $-4.39$, $-4.03$, $-3.85$, and $-3.81$ eV, respectively. Note that these CBM and VBM values of SnO$_2$ and SnO$_2$/alkali carbonates will be used to build an energy-level diagram of the ETL components of the iOSCs in the next section (Figure 4c). Because the lowest unoccupied molecular orbital (LUMO) of PC$_{70}$BM is about $-3.9$ eV, the reduction of CBMs of ETLs can help to build a favorable energy alignment between the ETLs and the active layers. For SnO$_2$/K$_2$CO$_3$ and SnO$_2$/Rb$_2$CO$_3$, the VBM were shifted up to $-3.85$, and $-3.81$ eV, respectively, which is higher than that of PC$_{70}$BM ($-3.9$ eV), and switches the electric contact between the ETL and the active layer from a Schottky to an Ohmic contact, as a salient feature for an ideal ETL. Given no energy barrier between PC$_{70}$BM and SnO$_2$/alkali carbonate ETLs, the electrons can easily be extracted and transported through PC$_{70}$BM through these ETLs to the cathodes in iOSCs.

It is well known that the WF of the cathode can be used as an effective tool to evaluate the charge-transport properties of the ETLs and the $V_{oc}$ in IOSCs. We have calculated the WF for our ETL samples using the following expression:

$$WF = h\nu - (E_{\text{cutoff}} - E_{\text{vac}} - E_F)$$

The WF of SnO$_2$, SnO$_2$/Li$_2$CO$_3$, SnO$_2$/K$_2$CO$_3$, and SnO$_2$/Rb$_2$CO$_3$ ETLs were then figured out to be 4.41, 4.03, and 4.08 eV, respectively. Evidently, all SnO$_2$/alkali carbonate samples had shown a significant WF reduction in comparison to the SnO$_2$, suggesting that efficient charge transport in OSCs can be obtained by using SnO$_2$/alkali carbonates as ETLs. To our knowledge, the reduction of the WF with alkali carbonates—modified SnO$_2$ might originate from the formation of an interface dipole between the alkali atoms and the metal oxides (M–O–A) in SnO$_2$/alkali carbonate samples, where M, O, and A stand for metal, oxygen, and alkali metal species, respectively.

2.6. Device Performance of iOSCs Using SnO$_2$ and SnO$_2$/Alkali Carbonates as ETLs. Figure 4a presents the chemical structures of the polymer donor PTB7-Th and the fullerene acceptor PC$_{70}$BM. The device structure and energy-level diagram of the iOSCs using SnO$_2$ or SnO$_2$/carbonates as ETLs are given in Figure 4b,c, respectively. Cross-sectional SEM images of these complete IOSC devices can be seen in Figure S10.

Figure 4d shows typical characteristics of iOSCs using SnO$_2$ and SnO$_2$/alkali carbonates as ETLs under one-sun illumination (100 mW cm$^{-2}$ AM 1.5G). The iOSCs based on the SnO$_2$ only as ETLs show an average in ten iOSC devices with a $V_{oc}$ of 0.69 V, a $J_{sc}$ of 16.71 mA cm$^{-2}$, an fill factor (FF) of 47.68%, and an overall PCE of 5.49%. When using alkali carbonates (Li$_2$CO$_3$, K$_2$CO$_3$, and Rb$_2$CO$_3$) as interfacial modifiers for SnO$_2$ as ETLs, the performance of these iOSCs was greatly improved, with average PCEs of 6.70% ($J_{sc}$ = 16.95 mA cm$^{-2}$, $V_{oc}$ = 0.77 V, and FF = 54.83%), 6.85% ($J_{sc}$ = 16.85 mA cm$^{-2}$, $V_{oc}$ = 0.77 V, and FF = 52.91%), and 7.33% ($J_{sc}$ = 16.89 mA cm$^{-2}$, $V_{oc}$ = 0.78 V, and FF = 55.55%) for SnO$_2$/Li$_2$CO$_3$, SnO$_2$/K$_2$CO$_3$, and SnO$_2$/Rb$_2$CO$_3$ ETLs, respectively, as summarized in Table 1; these are more than 22, 24, and 33% higher than the PCE of those based on the SnO$_2$ only (5.49%). Note that the detailed photovoltaic parameters of all those iOSCs devices are recorded and given in Tables S1–S4; the PCE distribution of these devices is presented in Figure S11. Evidently, all the iOSCs using SnO$_2$/alkali carbonate ETLs show a much better performance than those based on the SnO$_2$-only ETLs. It appears that the improved performance of the iOSC devices could be attributed to the improvement of $J_{sc}$, $V_{oc}$, and FF. Although the improvements of $J_{sc}$ are not obvious, the improvement of $V_{oc}$ and FF are clearly seen. To our knowledge, the $V_{oc}$ of those iOSCs using SnO$_2$/alkali carbonates as ETLs are improved mainly because of a significant reduction of WF of these ETLs in comparison to those based on SnO$_2$ only, although the great suppression of charge recombination in those iOSCs might be another reason.

On the other hand, the significant improvements in FF for those iOSCs might originate from surface passivation, which reduces oxygen-vacancy-related defects in SnO$_2$ with alkali carbonate modifiers.

To better understand charge-transport properties of ETLs in our IOSC system, we have further fabricated IOSC devices.

| ETL Configuration | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|-------------------|--------------------------|-------------|--------|---------|
| Bare ITO          | 12.18 ± 0.13             | 0.21 ± 0.001| 36.94 ± 0.39| 0.95 ± 0.02 |
| Li$_2$CO$_3$      | 14.02 ± 0.15             | 0.43 ± 0.011| 50.57 ± 0.50| 3.08 ± 0.13 |
| K$_2$CO$_3$       | 14.37 ± 0.17             | 0.68 ± 0.010| 52.82 ± 2.72| 5.13 ± 0.30 |
| Rb$_2$CO$_3$      | 14.62 ± 0.32             | 0.64 ± 0.010| 56.68 ± 1.06| 5.27 ± 0.15 |
| SnO$_2$           | 16.71 ± 0.45             | 0.69 ± 0.004| 47.68 ± 1.97| 5.49 ± 0.21 |
| SnO$_2$/Li$_2$CO$_3$| 16.88 ± 0.36             | 0.77 ± 0.002| 51.48 ± 2.05| 6.70 ± 0.15 |
| SnO$_2$/K$_2$CO$_3$| 16.85 ± 0.62             | 0.77 ± 0.002| 52.91 ± 2.34| 6.85 ± 0.11 |
| SnO$_2$/Rb$_2$CO$_3$| 16.89 ± 0.75             | 0.78 ± 0.003| 55.55 ± 3.28| 7.35 ± 0.15 |
| SnO$_2$/Li$_2$CO$_3$| 16.88 ± 0.36             | 0.77 ± 0.002| 51.48 ± 2.05| 6.70 ± 0.15 |
| SnO$_2$/K$_2$CO$_3$| 16.85 ± 0.62             | 0.77 ± 0.002| 52.91 ± 2.34| 6.85 ± 0.11 |
| SnO$_2$/Rb$_2$CO$_3$| 16.89 ± 0.75             | 0.78 ± 0.003| 55.55 ± 3.28| 7.35 ± 0.15 |

Table 1. Photovoltaic Performance of the PTB7-Th:PC$_{70}$BM-Based iOSCs Using Bare ITO, Alkali Carbonates Only, SnO$_2$, and SnO$_2$/Alkali Carbonates as ETLs
using alkali carbonates only without SnO2 ETLs (based on the bare ITO glass only). The device characteristics of iOCS devices with bare ITO and alkali carbonates only as ETLs are embellished in Figure 4d–f, whereas their photovoltaic parameters are given in Tables 1 and S5. It is revealed that the average PCEs of the iOCS devices using bare ITO, Li2CO3, K2CO3, and Rb2CO3 as ETLs are 0.95, 3.08, 5.13, and 5.27%, respectively. Obviously, the PCEs of iOCSs using alkali carbonates only as ETLs are inferior to iOCS devices based on the SnO2 or alkali carbonates−modified SnO2, demonstrating the more powerful electron-transport properties of SnO2 or alkali carbonates−modified SnO2 in comparison to the alkali carbonates only.

Figure 4e shows the dark current of iOCSs using SnO2 and SnO2/alkali carbonates as ETLs; their EQEs are given in Figure 4f. A lower leakage current (Figure 4e) along with a higher EQE (Figure 4f) for those using SnO2/alkali carbonate ETLS are compelling evidence for improvements in Jsc to higher PCEs of those iOCSs. Note that, in general, a higher electron-collection ratio from the active layer to the cathode will benefit from a lower leakage current, which results in a higher Jsc whereas a higher light–to–photons conversion ratio in those iOCS devices benefits from their higher EQE, which leads to the increased Jsc. Interestingly, we observe the trend in improving iOCS device performance with alkali carbonates−modified SnO2 from Li2CO3 to Rb2CO3. To our knowledge, this might originate from the increased dipole moments at the interface between the active layers and the ETLs because of the increased electronegativity of the alkali metals, from Li to Rb.23 It has been reported that the counter anions of electron-transport materials showed different behaviors in OSCs. Embellished in Figure 5. (a) UV absorption and (b, c) room-temperature PL spectra of the active layers deposited on SnO2 and SnO2/alkali carbonate ETLs on bare glass substrates. (d–g) AFM images of the active layers deposited on SnO2 and SnO2/alkali carbonate ETLs on ITO glass substrates.

which is a clear evidence which elucidates that the performance of iOCS using SnO2/Rb2CO3 showed the best average PCEs (7.35%). Meanwhile, the average PCEs of the iOCS devices based on SnO2/K2CO3 (6.85%) appear slightly higher than that of SnO2/Li2CO3 (6.70%), which is consistent with the weaker interaction (M−O−A) in SnO2/Li2CO3 compared to the SnO2/K2CO3 (due to the size of Li ions is less than that of K ions). It has been noted that the trend in improvement in iOCS device performance with alkali carbonates−modified SnO2, from Li2CO3 to Rb2CO3, is well consistent with the increased size of metal ions from Li to Rb in alkali carbonates.

At this point, it can be anticipated that alkali carbonate with bigger sizes of metal ions might exhibit a better device performance in iOCSs. To confirm this behavior of alkali carbonates in device performance of iOCSs, we have further fabricated iOCSs using another alkali carbonate like Cs2CO3, which possess a bigger size of metal ions of Cs than Rb in Rb2CO3 to modified SnO2 as ETLs. Besides, to compare electron-transport properties of SnO2 with those of alkali carbonates−modified SnO2, we have also fabricated iOCSs based on Cs2CO3 only (without SnO2) as ETLs. As expected, it revealed that the average PCEs of the iOCS devices using Cs2CO3-modified SnO2 as ETLs are 7.52% (Table S6, or Figure S12), which is slightly higher than that of the devices based on Rb2CO3-modified SnO2 (7.35%). To our knowledge, the reason behind this interesting result of iOCSs using SnO2/ Cs2CO3 might originate from a stronger interaction (M−O−A) in SnO2/Cs2CO3 compared to the SnO2/Rb2CO3 due to the bigger size of metal ions of Cs in comparison to Rb. Moreover, it has been shown that the average PCEs of iOCSs using Cs2CO3 only without SnO2 ETLs are 5.40% (Table S6, or Figure S12), which is inferior to iOCS devices based on the SnO2 or alkali carbonates−modified SnO2, thus firmly confirming the more powerful electron-transport properties of SnO2 or alkali carbonates−modified SnO2 in comparison to the alkali carbonates only.
examining the recombination rates in iOSCs. Figure 5b,c gives values are 6.86, 5.39, 6.79, and 5.42 nm for PTB7-Th:PC70BM respectively. Evidently, all RMS surface roughness values of SnO2/Rb2CO3 show the maximum quenching in a wide EQE measurements (Figure 4f), which have shown better light that these UV absorption results are strongly consistent with higher PCE can be accomplished. It is worth mentioning here total light-to-photons conversion ratio in iOSCs; as a result, a better light harvesting of the active layers can directly a above in PL studies for ETLs (Figure 1c), the signi was clearly seen, as compared to Figure 1c. As we discussed 350 nm. Interestingly, the same PL quenching at ETL regions the PTB7-Th region, respectively, with a wavelength excitation of related defects of SnO2 with alkali carbonate modi surface passivation, which helps to reduce the oxygen-vacancy-coatings on SnO2, SnO2/Li2CO3, K2CO3, and SnO2/Rb2CO3, samples as visualized by a schematic diagram as the inset of S13. As seen in Figure 5d, the RMS surface roughness values of those based on SnO2/alkali carbonates are lower than those based on SnO2 only. Moreover, it is likely that the PTB7-Th:PC70BM coatings on SnO2/alkali carbonate ETLs show good phase separation together with favorable domain size, which are considered as main factors for an effective charge-separation process in iOSCs. In general, a lower RMS surface roughness of an active layer not only helps to form an intimate contact between the active layer and the hole-transporting layer but also reduces series resistances in iOSC devices to improve PCE. It is clear that, besides the PL results, the AFM measurements for our active layers are other compelling evidence to explain our iOSC device performance.

2.7. UV Absorption, PL Quenching, and Morphology Studies of the Active Layers. To elucidate the performance of iOSCs using SnO2 and SnO2/alkali carbonates as ETLs, we first studied the UV absorption and PL quenching of the active layers with a configuration of glass/ETLs/PTB7-Th:PC70BM samples as visualized by a schematic diagram as the inset of Figure 5a, which displays the UV absorption of the active layers with different ETLs; it appears that all alkali carbonates—modified SnO2 exhibited some increase in the 380–760 nm range. Among these alkali carbonate samples, the active layers deposited on SnO2/Rb2CO3 show a maximum absorption improvement relative to the SnO2 only. General speaking, the better light harvesting of the active layers can directly affect the total light-to-photons conversion ratio in iOSCs; as a result, a higher PCE can be accomplished. It is worth mentioning here that these UV absorption results are strongly consistent with EQE measurements (Figure 4f), which have shown better light absorption in the 380–760 nm range.

The PL quenching of the active layer is an effective tool for examining the recombination rates in iOSCs. Figure 5b,c gives the survey PL in the whole wavelength range and the PL at the PTB7-Th region, respectively, with a wavelength excitation of 350 nm. Interestingly, the same PL quenching at ETL regions was clearly seen, as compared to Figure 1c. As we discussed above in PL studies for ETLs (Figure 1c), the significant quenching at these regions (350–600 nm) likely results from surface passivation, which helps to reduce the oxygen-vacancy-related defects of SnO2 with alkali carbonate modifiers, whereas the PL quenching in the PTB7-Th region suggests the suppression of recombination processes and encourages charge transfer from the active layer to the SnO2/alkali carbonate ETLs. In comparison to the others, samples based on SnO2/Rb2CO3 show the maximum quenching in a wide wavelength range (300–900 nm). Our PL results are clear evidence to that can be used to explain our iOSC device performance.

Apart from PL-quenching studies, the surface morphology of the active layers also greatly affects their iOSC device performance. Figure 5d–g presents the two-dimensional height AFM images of the PTB7-Th:PC70BM active layers coated on SnO2 and SnO2/alkali carbonate ETLs on ITO glass substrates; their 3D AFM images are also given in Figure S13. As seen in Figure 5d–g, the RMS surface roughness values are 6.86, 5.39, 6.79, and 5.42 nm for PTB7-Th:PC70BM coatings on SnO2, SnO2/Li2CO3, K2CO3, and SnO2/Rb2CO3, respectively. Evidently, all RMS surface roughness values of these based on SnO2/alkali carbonates are lower than those based on SnO2 only. Moreover, it is likely that the PTB7-Th:PC70BM coatings on SnO2/alkali carbonate ETLs show good phase separation together with favorable domain size, which are considered as main factors for an effective charge-separation process in iOSCs. In general, a lower RMS surface roughness of an active layer not only helps to form an intimate contact between the active layer and the hole-transporting layer but also reduces series resistances in iOSC devices to improve PCE. It is clear that, besides the PL results, the AFM measurements for our active layers are other compelling evidence to explain our iOSC device performance.

2.8. Electron-Only Devices. To gain a deeper understanding of how alkali carbonates—modified SnO2 affects the electron-transport properties of these ETLs in devices, the electron-only devices with a configuration of ITO/ETLs/PTB7-Th:PC70BM/LiF/Al were fabricated to calculate their electron mobility (\(\mu_e\)). The space-charge-limitation-current (SCLC) method, which is well known as the Mott–Gurney law, was chosen as a standard model for the calculation of the electron mobility. Figure 6a presents the \(J–V\) characteristics measured in the dark for these electron-only devices. The linear fittings for \(J^2–V\) curves of these devices are also given in Figure 6b. The \(\mu_e\) of these electron-only devices can be calculated using the Mott–Gurney formulation\(^{60–62}\)

\[
J_{SCLC} = \frac{9e_0}{8} \mu_e \epsilon_0 \frac{V^2}{L^2}
\]

where \(J_{SCLC}\) is the current density obtained by measuring the electron-only devices in the dark with the applied voltage potential (\(V\)), \(L\) is the thickness of the active layer of the electron-only device, \(e_0 = 8.854 \times 10^{-12} \, \text{C} \, \text{V}^{-1} \, \text{m}^{-1}\) is the electric or permittivity of free space constant, and \(e_e\) stands for the relative dielectric constant of the active layer (PTB7-Th:PC70BM), which is normally assumed to be 3.5.\(^{67,68}\) The \(\mu_e\) was found to be 5.78 \times 10^{-4}, 1.17 \times 10^{-3}, 1.26 \times 10^{-3},\) and 1.52 \times 10^{-3} cm² V⁻¹ s⁻¹ for SnO2, SnO2/Li2CO3, SnO2/K2CO3, and SnO2/Rb2CO3 ETLs, respectively. Obviously, the \(\mu_e\) values of all the electron-only devices with SnO2/alkali carbonates as ETLs are greater than twice those based on the SnO2 only. These \(\mu_e\) values are self-evident in explaining the improvements of device performance for those using alkali carbonates—modified SnO2 as ETLs.

2.9. Electrochemical Impedance Spectroscopy (EIS) Studies. Apart from the electron mobility of the electron-only devices, EIS is an effective tool for characterizing the charge-
transport and the recombination processes in an inner iOSC. To understand the carrier-transport and carrier-transfer processes at the interface between the active layer and the ETLs, impedance was measured on our iOSC devices. Figure 7 presents the Nyquist plots of the iOSC devices measured in the dark with zero applied bias. The corresponding circuit that fit these Nyquist plots is displayed in the inset of Figure 7. It is clear from the Nyquist plots that the inner series resistances (the sheet resistance ($R_S$) and the charge transfer resistance ($R_{CT}$)) at the interface of the active layer and ETLs as well as between the ETLs and the electrode) of our iOSC devices were in the order of $SnO_2/Rb_2CO_3 < SnO_2/K_2CO_3 < SnO_2/Li_2CO_3 < SnO_2$. In general, an efficient charge extraction and charge transportation will benefit from a lower contact resistance between the interfaces of the active layer and ETLs, as well as between the ETLs and the electrode. Thus, the Nyquist plots for our iOSC devices are clear evidence that explains the improvements in device performance for those using alkali carbonates-modified SnO$_2$ as ETLs.

2.10. Device Stability Studies. Aside from high efficiency, the long-term lifetime of iOSCs has become a great obstacle in commercializing the eventual product of the iOSC technology. In general, the lifetime of iOSCs depends on the time at which the PCE retains 80% of the initial value. In this respect, we studied the stability of iOSCs using SnO$_2$ or SnO$_2$/alkali carbonates as ETLs. The performance of iOSC devices derived from SnO$_2$ or SnO$_2$/alkali carbonates as ETLs was recorded for their storage in ambient air without encapsulations; the detailed photovoltaic parameters of these devices are summarized in Tables S7–S10. Figure 8 shows the device stability results of our iOSC devices. It appears that all our iOSC devices had good long-term lifetime stability, with PCEs retaining more than 90% of their initial values after 6 weeks. To our knowledge, the excellent long-term lifetime stability of our iOSC devices may have first originated from the inverted device structure types with an air-stable high WF metal (Ag), and more importantly due to the ultrastability of our ETLs based on SnO$_2$. It appears that the stability of the iOSCs using alkali carbonates-modified SnO$_2$ was significantly improved because of the enhanced interfacial property between SnO$_2$ and the active layer by inserting alkali carbonate modifiers. More interestingly, among these alkali carbonates, Rb$_2$CO$_3$-modified SnO$_2$ gives the best long-term stability to iOSC devices. According to our results, Rb$_2$CO$_3$ modifier plays the best role in interfacial engineering improvements (the best

Figure 7. Impedance spectra (Nyquist plot) of the iOSC devices using SnO$_2$ or SnO$_2$/alkali carbonates as ETLs, measured in the dark with zero applied bias.

Figure 8. Stability of the PTB7-Th:PC$_{70}$BM iOSC devices using SnO$_2$ and SnO$_2$/alkali carbonates as ETLs: (a) PCE, (b) $V_{oc}$, (c) FF, and (d) $J_{sc}$.
WF reduction, morphological improvement, and surface passivation effects) between SnO₂ and the active layer.

3. CONCLUSIONS

We demonstrated that alkali carbonates (Li₂CO₃, K₂CO₃, and Rb₂CO₃) based on a facile low-temperature solution process are excellent modifiers for SnO₂ in applications as ETLs for iOSC. A significant reduction of the WF of the cathode, efficient charge transport and extraction at the interface between the ETL and the active layer, and a higher electron mobility can be achieved with alkali carbonates—modified SnO₂. These alkali carbonates can also help to greatly passivate oxygen-vacancy-related defects that usually exist on SnO₂. The iOSC using the donor polymer PTB7-Th and the acceptor polymer PC70BM were used to prepare the active layer. The donor polymer poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethyl-hexyl)-3-fluorothieno[3,4-b′]thiophene-2-carboxylate-2,6-diyl)] (PTB7-Th) and the acceptor polymer phenyl-C₇₀-butyric acid methyl ester (PC70BM) were used to prepare the active layer. These alkali carbonates can also help to greatly passivate oxygen-vacancy-related defects that usually exist on SnO₂. These alkali carbonates can help to greatly passivate oxygen-vacancy-related defects that usually exist on SnO₂. Furthermore, our iOSC show long-term stability, with more than 90% PCEs retained after storage in ambient air for 6 weeks without encapsulations. Our findings offer an effective way to achieve highly efficient and stable iOSC by using low-temperature solution processed alkali carbonates—modified SnO₂ as ETLs. In addition, its application may be extended to other optical devices that required an ETL, such as organic light-emitting diodes or perovskite solar cells.

4. EXPERIMENTAL SECTION

4.1. Materials. Chemicals used to prepare SnO₂ and SnO₂/alkali carbonate films were as follows. Precursor tin(II) chloride dihydrate (SnCl₂·2H₂O, 98%) was purchased from Alfa Aesar, and ethanol (C₂H₅OH, 99.9%) was received from EMD Millipore Corporation. Alkali carbonates [(Li₂CO₃, 99.997%), (K₂CO₃, 99.995%), and (Rb₂CO₃, 99.8%)] were obtained from Sigma-Aldrich (St. Louis, MO).

The donor polymer poly[4,8-bis(S-2-ethylhexyl)thiophen-2-yl]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethyl-hexyl)-3-fluorothieno[3,4-b′]thiophene-2-carboxylate-2,6-diyl)] (PTB7-Th) and the acceptor polymer phenyl-C₇₀-butyric acid methyl ester (PC₇₀BM) were used to prepare the active layer; these materials were purchased from Solarmer Energy, Inc., and Nano Holding, respectively. 1,2-Dichlorobenzene (ODCB, 99%) and 1,8-diodooctane (DIO, 98%, contains copper as stabilizer) purchased from Sigma-Aldrich (St. Louis, MO), were used as solvent and additive for preparing the active layer. Note that all these chemicals were used as received, without any further purification.

4.2. Preparation of SnO₂ and Alkali Carbonate Solutions. The precursor solution of SnO₂ (0.1 M) was obtained by dissolving 1.128 g precursor of tin (SnCl₂·2H₂O) in 50 mL absolute ethanol using a 100 mL round-bottom flask. The SnO₂ solution was then stirred for approximately 8 h at 80 °C in an oil bath. After this step, the solution was removed from the oil bath and kept at room temperature for at least 1 day, allowing the aging process. Afterward, we used this solution for preparing SnO₂ films by spin-coating without any purification. It is worth mentioning here that the precursor solution of SnO₂ revealed very long-term stability. We can use these solutions to prepare SnO₂ ETLs up to 6 months later. In our case, we experienced the same device performance using the fresh solution of SnO₂ or the aging solution, which was kept at room temperature in a clear glass vial without any encapsulation for up to 6 months.

Alkali carbonate solutions (Li₂CO₃, K₂CO₃, and Rb₂CO₃) were prepared with 10 mg of each alkali carbonate in a volume 20 mL clear glass vial. Then, 10 mL of DI water was added to each vial to achieve three alkali carbonate solutions with the same concentration of 1 mg mL⁻¹. Prior to the spin-coating of alkali carbonate layers on SnO₂, these vials were stirred at room temperature for about 3 h to form uniform and homogeneous alkali carbonate solutions.

4.3. Preparation and Characterization of SnO₂ and SnO₂/Alkali Carbonate Films. SnO₂ films with a thickness of ~20 to 25 nm on the bare glass or ITO glass were first achieved by using the prepared precursor solution of SnO₂ via the spin-coating technique on these substrates in air, at 3000 rpm for 40 s. These samples were then annealed on a hot plate at 185 °C for about 1 h. The SnO₂/alkali carbonate films (SnO₂/Li₂CO₃, SnO₂/K₂CO₃, and SnO₂/Rb₂CO₃) were obtained by spin-coating each alkali carbonate on the prepared SnO₂ samples, at a speed of 4000 rpm for 40 s in air, to form a thickness of about 7–10 nm. After spin-coating, the SnO₂/alkali carbonate samples were dried at 120 °C for 20 min. Note that, in making iOSC devices, the SnO₂ or SnO₂/alkali carbonate ETL samples were first prepared as above and then transferred to a N₂-filled glovebox while waiting to deposit the active layer.

The optical properties (UV–vis absorption and transmittance) of SnO₂ and SnO₂/alkali carbonate films on glass substrates were measured using the Shimadzu UV-2550 spectrophotometer. Room-temperature photoluminescence (PL) spectra of SnO₂ and SnO₂/alkali carbonate films coated on glass substrates and of the active layer deposited on the ETLs glass/SnO₂/alkali carbonate/PTB7-Th:PC₇₀BM were recorded using a Jasco FP-6500 spectrophotometer with an excitation wavelength of 350 nm. Scanning electron microscopy (SEM, Hitachi S-4800) and atomic force microscopy (AFM, tapping mode, Bruker) were used to characterize the morphologies of the ETLs and the active layers. The elemental mappings of SnO₂ along with SnO₂/alkali carbonate samples were done with the energy-dispersive X-ray spectroscopy (EDX) tool equipped with the SEM system. The cross-sectional SEM image of the complete iOSC devices using SnO₂ or SnO₂/alkali carbonates as ETLs were also obtained with the SEM measurement system (Hitachi S-4800). The amorphous structure states of SnO₂ as well as SnO₂/alkali carbonate films on the glass substrates caused by low-temperature annealing (~185 °C) were measured by X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was used to confirm the chemical states and surface compositions of SnO₂ and alkali carbonates—modified SnO₂ samples. Finally, to obtain detailed information on the work functions and on the energy level of condition bands of SnO₂ and SnO₂/alkali carbonate samples, we used ultraviolet photoelectron spectroscopy (UPS, He I source, 21.2 eV, AXIS-ULTRA DLD spectrometer system, Kratos Analytical, Ltd.) on these ETL samples.

4.4. Device Fabrication and Characterizations. 4.4.1. Device Fabrication. ITO glass substrates received from Korea Electronics Technology Institute (a sheet resistance of 12 Ω/sq, 2.5 × 2.5 cm²) were first cleaned with deionized (DI) water in a beaker in ultrasonic bath for 30 min; then, the cleaning of the ITO glass substrates was continued with acetone and isopropanol (IPA) source. Prior to coating...
the ETL, the ITO glass substrates were dried using a heat gun. After coating SnO₂ and SnO₂/alkali carbonate (Li₂CO₃, K₂CO₃, and Rb₂CO₃) ETL films, these samples were moved to a N₂-filled glovebox to deposit the active layer. The thick active layer PTB7-Th:PC70BM (a thickness of ~200 nm) was obtained by spin-coating PTB7-Th:PC70BM (1:1.5 wt %) in mixed solvent ODCB:DIO (97:3 vol %) at a speed of 500 rpm for 40 s. Note that, before spin-coating, these mixing solutions of PTB7-Th:PC70BM were vigorously stirred at room temperature overnight to make sure of a homogeneous and well-mixed active solution. After spin-coating the active layers, the samples were initially dried for about 5 min inside the glovebox before being transferred to a vacuum chamber for thermal evaporation. To obtain complete drying and to remove the additive (DIO), the samples were kept inside the vacuum chamber for approximately 3 h before the electrode-deposition processes. To complete the device fabrication, a 10 nm MoO₃ hole-transporting layer and 100 nm Ag were subsequently thermally evaporated onto active layers through a shadow mask to form the top anode of the iOSC devices under a high vacuum at a pressure less than 1 × 10⁻⁶ Torr. Here, the thermal evaporation rates of MoO₃ and Ag were controlled at 0.1 and 2 Å s⁻¹, respectively. A LiF (0.6 nm)/Al (100 nm) electrode were used for the electron-only device fabrication. The thermal evaporation rates of LiF and Al were also controlled at 0.1 and 2 Å s⁻¹, respectively. Note that all the devices had an effective area of 0.11 cm², as determined by the shadow masks.

4.4.2. Characterization. Device performance of all iOSCs was measured using the solar cell I–V system with a source Keithley 2400, conducted in ambient conditions. To obtain the dark current and the normal J–V characteristics, iOSC devices were measured in the dark or under standard conditions (100 mW cm⁻² AM 1.5 G), respectively. For normal testing, prior to the measurements, the light illumination of the system was calibrated with a monocrystalline silicon solar cell (2 cm², calibrated at NREL, CO) to set the standard conditions (100 mW cm⁻² AM 1.5 G), respectively. All the iOSC devices were scanned in the reverse direction, from −1 to 1 V, at a scan speed of 0.2 V s⁻¹; the scan step was 0.02 V and the delay time was 10 ms. The J–V characteristics of the electron-only devices were also obtained with the Keithley 2400 equipment, measured in the dark with an applied voltage ranging from 0 to 3.5 V, at a scan speed of 0.2 V s⁻¹, a scan step of 0.05 V, and a delay time of 100 ms. A Polaronix K3100 spectrometer system was used to record the external quantum efficiency (EQE) of the iOSC devices. The impedance studies for the iOSC devices were conducted via a VersaSTAT3 (METEK) system; the frequency was set between 10 kHz and 0.1 Hz measured in the dark with zero applied bias.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02773.

Tauc plots, AFM and SEM images, XRD, EDX spectra, and elemental mapping analysis of SnO₂ as well as SnO₂/alkali carbonate samples, the cross-sectional SEM image of complete iOSC devices. The PCE distribution and detailed photovoltaic parameters of iOSC devices (PDF)

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Notes
The authors declare no competing financial interest.

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