

Efficient Gradient Potential Top Electron Transport Structures Achieved by Combining an Oxide Family for Inverted Perovskite Solar Cells with High Efficiency and Stability

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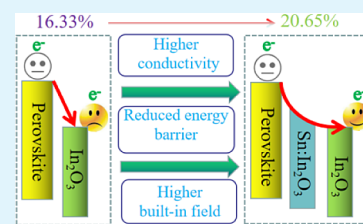
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ABSTRACT: Although inverted (p–i–n) structure perovskite solar cells (PSCs) have achieved high efficiency by commonly using fullerenes or their derivatives as electron transport layers (ETLs), the device stability and cost of fullerene materials are still of great concern. Herein, we demonstrate inorganic top ETLs simply composed from a family of metal oxides including In_2O_3 and its derivative of $\text{Sn}:\text{In}_2\text{O}_3$ with a gradient potential structure. For inverted PSCs, the typical film formation process of In_2O_3 will damage or degrade perovskite materials underneath; thus, we report a low temperature synthesis approach for obtaining In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ nanoparticles that can form effective top ETLs without any post-treatment. The one-family oxide-based top ETL features with the enhanced built-in potential, high electron extraction, and low interfacial recombination, offering a power conversion efficiency (PCE) of 20.65% in PSCs constructed from oxide-only carrier (both hole and electron) transport layers (CTLs), which is the highest efficiency in oxide-only CTL-based inverted PSCs to the best of our knowledge. Equally important, the inverted PSCs based on the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ ETL show the excellent operational stability and remain 90% of the initial value of PCE over 2000 h. Consequently, this work contributes to the robust strategy of all oxide-only CTLs in developing rigid and flexible PSCs for practical photovoltaic applications.

KEYWORDS: low temperature, solution process, inorganic metal oxides, electron transport layer, perovskite solar cells



1. INTRODUCTION

Inverted structure planar perovskite solar cells (PSCs) have been widely investigated due to their advantages such as long device stability, cost-effectiveness, low-temperature processability, and suppressed hysteresis characteristics.^{1–6} Typically, there are several requirements such as chemical compatibility,^{5,7} high electron transport ability, and low-temperature treatment^{2,5,8–10} to form electron transport layers (ETLs) on top of the perovskite layer because perovskite thin films are vulnerable to high-temperature processes and polar solvents. Besides, carrier (electron and hole) transport layers (CTLs) play an indispensable role in planar PSCs not only for effectively transporting charges and reducing carrier recombination but also for preventing the damage of devices from ambient environments, such as humidity, oxygen, and light.^{10–14} As the most commonly used ETLs, C_{60} and its derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) possess suitable energy alignment and effective charge collection ability, which resulted in a high power conversion efficiency (PCE) of about 22% in p–i–n planar PSCs.^{15–19} Although high performances were obtained for these organic ETLs, their high cost, complicated synthesis, and purification process are highly unsuitable for large-scale applications.²⁰ Additionally, there is a concern in their long-term operational and thermal instability for future commercialization.^{21,22}

Inorganic ETLs, featuring material abundance, low cost, and excellent stability, are potentially superior alternatives. Some inorganic n-type metal oxides, such as $\text{Ti}(\text{Nb})\text{O}_x$,²³ SnO_2 ,²⁴ Al-doped ZnO (AZO),²⁵ ZnO ,^{26–29} and CeO_x ,³⁰ have been reported to be a layer material as a part of the ETL structures. While most of the metal oxide-only ETLs are reported in n–i–p PSCs,^{31–36} there are no clear studies of top ETLs for inverted planar PSCs composed from simply a family of metal oxides with a gradient potential structure for improving the performance and stability of PSCs. Indeed, most of the well-performed and stable inverted PSCs are made from the ETL structure composed of organic films such as PCBM and C_{60} and the metal oxide layer.^{37–39}

In this work, we demonstrate inorganic top ETLs simply from combining one family of metal oxides including In_2O_3 and its derivative of Sn-doped In_2O_3 (hereafter named as $\text{Sn}:\text{In}_2\text{O}_3$) with a gradient potential structure in p–i–n PSCs with high efficiency and stability. To the best of our

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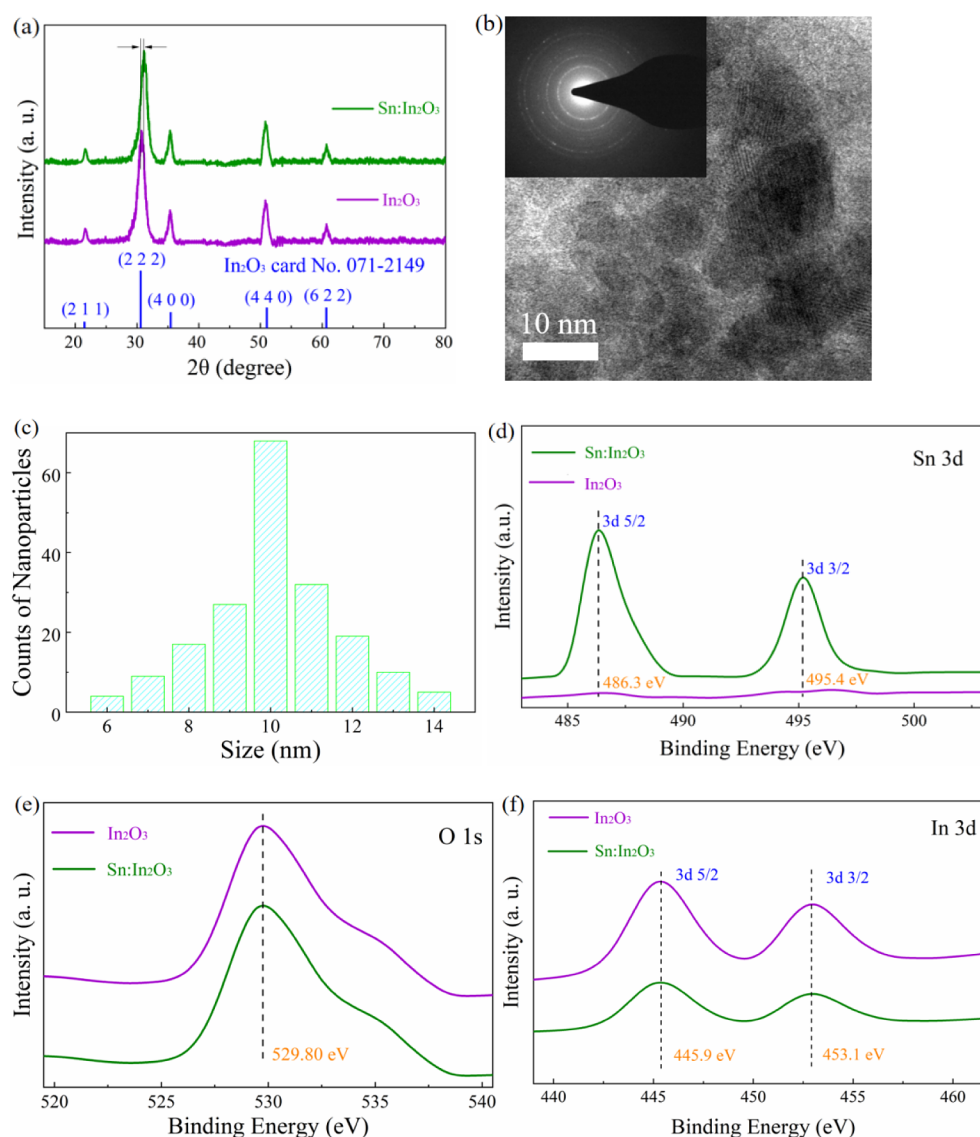


Figure 1. (a) XRD patterns. (b) TEM image and the corresponding diffraction pattern (inset) of Sn-doped In_2O_3 NPs. (c) Size distribution of Sn-doped In_2O_3 NPs. (d–f) Sn 3d, O 1s, and In 3d XPS spectra of pristine and Sn-doped In_2O_3 NPs.

knowledge, In_2O_3 and its derivatives or their combination have not been used as top ETLs in inverted PSCs since typical film formation processes of In_2O_3 ETL from indium salt precursors need annealing at 200–300 °C,⁴⁰ degrading typical perovskite materials underneath. Meanwhile, while colloidal In_2O_3 nanoparticles can potentially be used as top ETLs, such nanoparticles are mainly synthesized by hot-injection, which will involve the coating of insulative ligands such as oleyamine.⁴¹ This greatly decreases the conductivity of the In_2O_3 film as ETLs. Differently, we report a low-temperature synthesis approach to obtain In_2O_3 and Sn: In_2O_3 nanoparticles that can form effective top ETLs without any post-treatment, overcoming the above challenging issues. In addition, since our gradient potential top ETL only involves one family of In_2O_3 and its derivatives without any other kinds of oxides, we can simplify the material system, material synthesis, and device fabrication processes. Furthermore, this all-inorganic one-family oxide stepped ETL structure with the gradient carrier concentration and energy band not only displays efficient electron extracting and transporting ability but also exhibits substantially enhanced built-in potential. As a result, we

achieve remarkable suppression of nonradiative recombination losses in the device and significant improvement in both the device efficiency and stability. The optimized PSCs based on Sn: In_2O_3 / In_2O_3 ETL with the best PCE of 20.65% and ignorable hysteresis are demonstrated, which is considerably higher than that of single In_2O_3 (16.33%) and Sn: In_2O_3 ETL (19.52%). Importantly, the inverted PSCs adopted the Sn: In_2O_3 / In_2O_3 bilayer ETL and exhibit excellent thermal stability and photostability, thanks to their good intrinsic stability. Consequently, this work not only offers a new low-temperature and solution-processed metal oxide only ETL for highly efficient inverted PSCs but also provides a new strategy for designing CTLs to achieve cost-effective, stable, and high-performance photovoltaic devices.

2. RESULTS AND DISCUSSION

2.1. Properties of Pristine and Doped In_2O_3 Nanoparticles and Films. We synthesized pristine and doped In_2O_3 via our low-temperature strategy, as described in Section 4. X-ray diffraction (XRD) measurements were conducted to

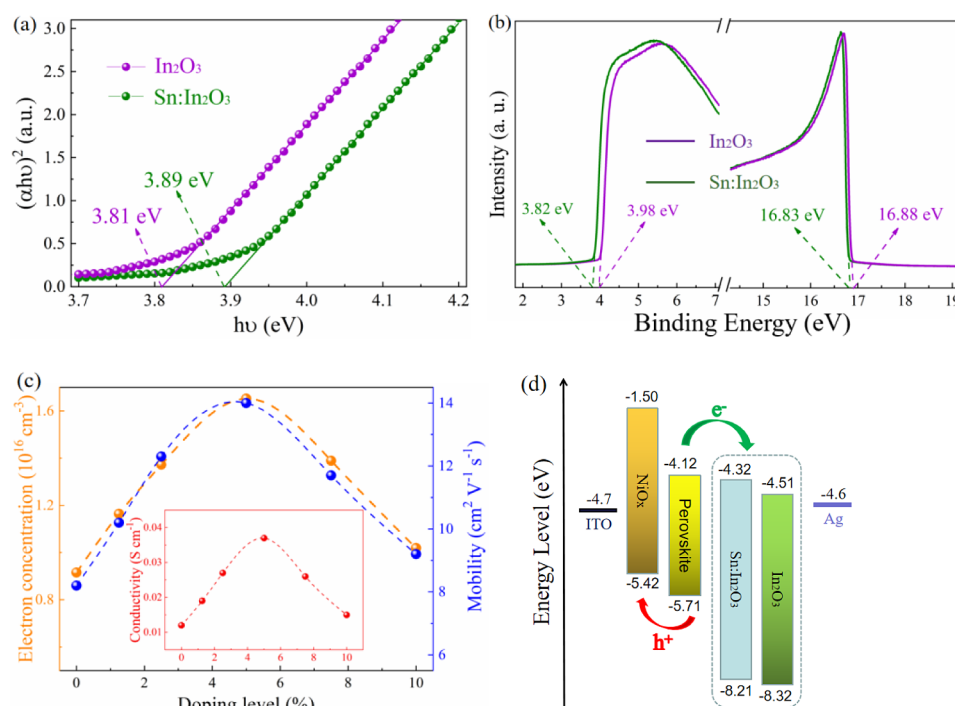


Figure 2. (a) Band gap evaluated by the Tauc plots. (b) UPS spectra of In_2O_3 and $\text{Sn:In}_2\text{O}_3$. (c) Electron concentration and mobility of $\text{Sn:In}_2\text{O}_3$ with different Sn concentrations. The inset shows the calculated conductivity according to the equation $\sigma = en\mu$. (d) Band diagram of the inverted PSC.

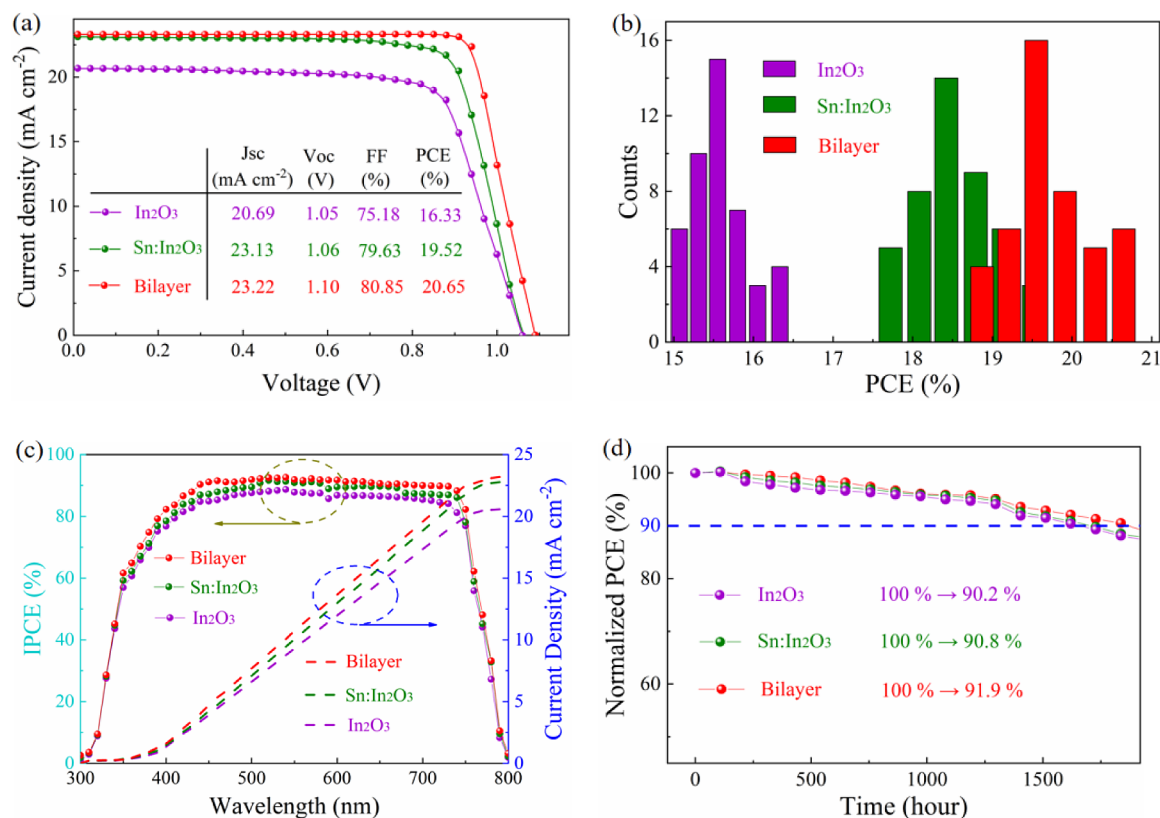


Figure 3. (a) J - V curves of the champion PSCs based on In_2O_3 , $\text{Sn:In}_2\text{O}_3$, and bilayer ($\text{Sn:In}_2\text{O}_3/\text{In}_2\text{O}_3$). (b) Histograms of PCEs for PSCs based on different ETLs. (c) IPCE and integrated current of the devices based on different ETLs. (d) Time-related variation of the normalized PCE under simulated working conditions between day (85°C) and night (room temperature) intervals.

confirm the component of the as-synthesized pristine In_2O_3 and Sn-doped In_2O_3 ($\text{Sn:In}_2\text{O}_3$) NPs films. As shown in Figure

1a, the XRD patterns of the pristine and Sn-doped In_2O_3 are similar. Their XRD peaks of 21.7° , 30.8° , 35.4° , 50.9° , and

60.8° correspond to (211), (222), (400), (440), and (622) planes, respectively, which are in good agreement with that of In_2O_3 (PDF no. 071-2194). No other peaks appear except In_2O_3 peaks. The results indicate that no other oxides are formed in the synthesis process and Sn only acts as a dopant in In_2O_3 . Notably, the strong diffraction peak of $\text{Sn}:\text{In}_2\text{O}_3$ located at 30° shifts toward the larger 2θ angle slightly. This shift can be explained by the reduced lattice distance when In^{3+} (0.81 Å) is substituted with the smaller radius Sn^{4+} (0.71 Å), demonstrating that Sn is successfully doped into In_2O_3 .

Meanwhile, the transmission electron microscopy (TEM) and selected area electron diffraction characterization were conducted, and the results are shown in Figure 1b, the Sn-doped In_2O_3 NPs synthesized by our low-temperature strategy show a high crystallinity and small size distribution. The average size of $\text{Sn}:\text{In}_2\text{O}_3$ NPs is about 10 nm, as shown in Figure 1c, which is beneficial to form high-quality top ETLs with good physical contact on the perovskite surface, thereby efficiently promoting charge collection in PSCs.^{10,13} Remarkably, through simple room-temperature spin-coating methods, compact and uniform $\text{Sn}:\text{In}_2\text{O}_3$ and In_2O_3 films are formed on the perovskite surface, as confirmed from the top-view scanning electron microscopy (SEM) image of the structure indium tin oxide (ITO)/hole transport layer (HTL)/perovskite/ $\text{Sn}:\text{In}_2\text{O}_3$ in Figure S1. Consequently, In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ NPs are successfully synthesized and both of them can form high-quality oxide films on perovskite films by a simple room-temperature solution approach.

X-ray photoelectron spectroscopy (XPS) was utilized to further verify the presence of Sn^{4+} within the In_2O_3 NPs and the corresponding chemical states and the results are displayed in Figure 1d–f. The characteristic XPS signals in both In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ are observed at binding energies of 529.8 eV shown in Figure 1e and 445.9 eV and 453.1 eV shown in Figure 1f, which are ascribed to O 1s, In $3d_{3/2}$, and In $3d_{5/2}$, respectively. Importantly, the XPS peaks of Sn $3d_{5/2}$ at 486.3 eV and Sn $3d_{3/2}$ at 495.4 eV are clearly observed from $\text{Sn}:\text{In}_2\text{O}_3$ NPs, as shown in Figure 1d, which are not present in pristine In_2O_3 NPs. This further demonstrates the successful doping of Sn. It is estimated from the XPS results that the Sn content in $\text{Sn}:\text{In}_2\text{O}_3$ is 5%, which is very close to the Sn molar ratio used in the precursor. This result also indicates a good incorporation of Sn in In_2O_3 . In addition, the corresponding doping concentration is confirmed by the measurement of inductively coupled plasma atomic emission spectroscopy (ICP-OES), and the results are shown in Table S1.

To assess the energy band alignment of the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer, we analyze the Tauc plots and ultraviolet electron spectroscopy (UPS) of pristine In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$. From the Tauc plots (Figure 2a) and absorbance spectra (Figure S2), the band gap energy increases from 3.81 eV (In_2O_3) to 3.89 eV ($\text{Sn}:\text{In}_2\text{O}_3$) after Sn doping. As discussed previously, partly substituting In^{3+} by smaller size Sn^{4+} will reduce the lattice size and enhance the crystal field due to stronger coupling of In–O, resulting in the broadened band gap of the $\text{Sn}:\text{In}_2\text{O}_3$ film. The valance band energies (E_{VB}) of In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ calculated from UPS spectra shown in Figure 2b are –8.32 and –8.21 eV, respectively. Then, the conduction band energy (E_{CB}) is calculated by combining the band gap and E_{VB} , where the E_{CB} (–4.51 eV) of $\text{Sn}:\text{In}_2\text{O}_3$ decreases from –4.32 eV of In_2O_3 after doping with Sn into In_2O_3 . Figure 3d shows the band alignment diagram of In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ and materials used in p–i–n structure PSCs. Notably, the small energy offset of

0.2 eV between the $\text{Sn}:\text{In}_2\text{O}_3$ layer (–4.32 eV) and perovskite film (–4.12 eV)¹² is beneficial for electron extraction from the perovskite layer.

The electrical properties of $\text{Sn}:\text{In}_2\text{O}_3$ ETLs, including carrier concentration (n), mobility (μ), and conductivity (σ), are investigated and calculated from the Hall effect measurements as a function of Sn doping concentration, as shown in Figure 2c. The electrical properties all show an increase at first and then decrease with increasing the doping concentration. It should be noted that conductivity is calculated from the equation $\sigma = ne\mu$, where e is an electron charge. As shown in Figure 2a, the maximum of carrier concentration, mobility, and conductivity are $1.65 \times 10^{16} \text{ cm}^{-3}$, $14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and 0.037 S cm^{-1} , respectively at 5% doping concentration. Notably, the higher conductivity of $\text{Sn}:\text{In}_2\text{O}_3$ compared to In_2O_3 contribute to enhancing the charge transport and collection at the interface. Moreover, as shown in Figure 2d, the designed $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL with a layer of In_2O_3 contacting directly with the Ag electrode, where the Schottky barrier (0.09 eV) between the conduction band minimum of In_2O_3 and work function of the Ag electrode is very small, which can promote electron extraction from ETL to the cathode efficiently. Consequently, the gradient energy band alignments in the ETL region and at the cathode formed by the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer structure can (1) contribute to the carrier separation by offering a higher built-in voltage, which comes from the higher carrier concentration and (2) benefit the carrier extraction by the cascade energy alignment structure, which suppresses the recombination loss and contributes to the higher fill factor (FF) and V_{OC} .

2.2. Device Performances and Detailed Understanding. The p–i–n PSCs using pristine In_2O_3 only, $\text{Sn}:\text{In}_2\text{O}_3$ only, and $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer structures as the top ETL are fabricated, and the J – V curves are plotted in Figure 3a. Furthermore, Figure 3b shows the reproducibility of the PSC efficiency based on different ETLs, suggesting the PSCs based on the bilayer ETL have good reproducibility. To the best of our knowledge, this work has the best performance among the reported p–i–n planar PSCs with all metal-oxide top ETL.^{23,24} The cross-sectional SEM image in Figure S3 shows the all oxide electron and HTL-based device structure of ITO/ NiO_x /perovskite/ $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$. It is important to note that by introducing the combined approaches of purifying ethanol solvent from residue water (before being used for the dispersion of the metal oxide NPs) and the dynamic spin coating process in metal oxide film formation, we address the common issue of ethanol solvent induced damage on the perovskite film, as further described in Section 4. This facilitates the formation of the top metal oxide only ETL structure for highly efficient and stable PSCs. Compared to PSCs based on the pristine In_2O_3 ETL (PCE = 16.33%), those with a $\text{Sn}:\text{In}_2\text{O}_3$ ETL show better performances with PCE reaching 19.52% due the increase of both the short circuit current (J_{SC}) and the FF, which is attributed to the enhanced electrical properties of the $\text{Sn}:\text{In}_2\text{O}_3$ ETL. The detailed optimization of PSCs based on $\text{Sn}:\text{In}_2\text{O}_3$ with different doping concentrations and thicknesses are summarized in Tables S2 and S3, respectively. Interestingly, by introducing the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL, we can further boost the PCE to 20.65% ($J_{\text{SC}} = 23.22 \text{ mA cm}^{-2}$, open-circuit voltage ($V_{\text{OC}} = 1.10 \text{ V}$ and FF = 80.85%) and all device parameters improve as compared to those of PSCs with either the pristine In_2O_3 (20.69 mA cm^{-2} , 1.05 V, and 75.18%) or $\text{Sn}:\text{In}_2\text{O}_3$ ETL (23.13

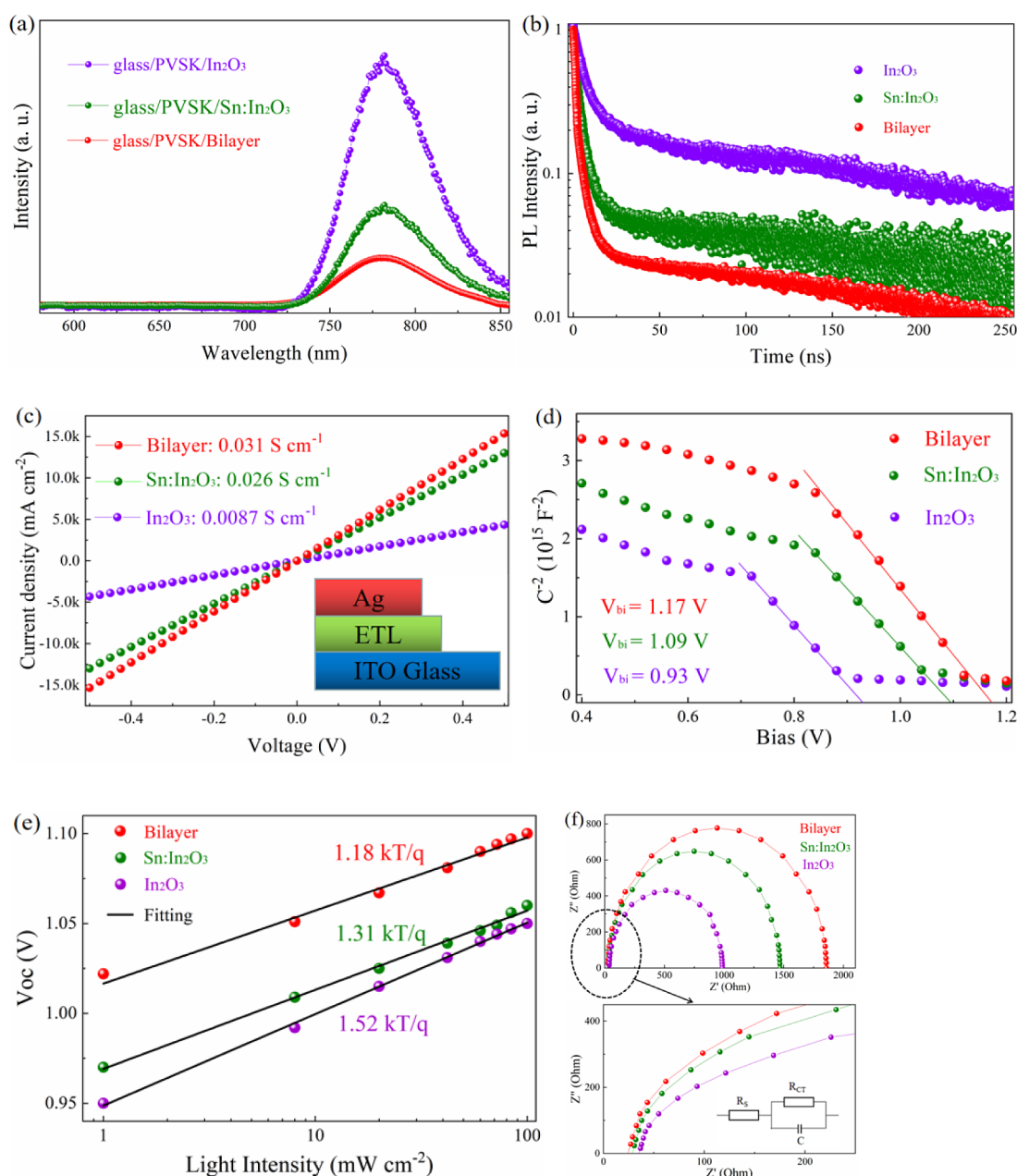


Figure 4. (a) Steady-state and (b) time-resolved PL spectra of the perovskite coated on glass, In_2O_3 , $\text{Sn:In}_2\text{O}_3$, and bilayer of $\text{Sn:In}_2\text{O}_3/\text{In}_2\text{O}_3$. (c) Current–voltage curves of ITO/ETL/Au under dark conditions; ETL = In_2O_3 , $\text{Sn:In}_2\text{O}_3$, and bilayer ($\text{Sn:In}_2\text{O}_3/\text{In}_2\text{O}_3$). (d) C^{-2} – V dependence of PSCs based on different ETLs. (e) V_{OC} as a function of light intensity for PSCs with different ETLs. (f) EIS spectra of the devices based on different ETLs.

mA cm^{-2} , 1.06 V, and 79.63%). Previous reports about PSCs based on oxide-only CTL are summarized in Table S4. To the best of our knowledge, the PCE of our PSCs is the highest among those reported values. The incident photon-to-electron conversion efficiency (IPCE) spectra of PSCs based on different ETLs together with the corresponding integrated current densities are displayed in Figure 3c, which is consistent with the values from J – V curves with an error less than 5%. Regarding the hysteresis properties of PSCs, we study J – V curves with the different scan directions as shown in Figure S4, and the corresponding photovoltaic parameters are listed in Table S5. The results show that all PSCs with the oxide-based ETLs show very small hysteresis particularly the bilayer ETL-based PSCs with the hysteresis index of 0.7%. To understand

the improved performances of $\text{Sn:In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL-based PSCs, we will study the carrier separation and extraction ability, energy band alignment, and built-in field, which will affect the electron transport from the perovskite layer to the electrode and charge recombination at the ETL/perovskite interface. When light is irradiated onto the photoactive layer, the photogenerated carriers will be extracted to charge transport layers under short-circuit conditions because of the intrinsic V_{bi} . A high V_{bi} can provide a driving force to promote the separation of electrons and holes.⁴² By combining the as-synthesized $\text{Sn:In}_2\text{O}_3$ with pristine In_2O_3 , we demonstrate the $\text{Sn:In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer as the ETL offering high V_{bi} for the device and gradient carrier concentrations and energy bands, thereby improving device performances especially V_{OC} , which

will be discussed further in later sections with more detailed results provided.

The most critical issue that limits the commercialization of PSCs is their long-term stability. It is confirmed that the poor device stability resulting from the moisture- or O₂-induced perovskite decomposition can be controlled by good encapsulation. However, under realistic operating conditions, the stability of the PSC is inevitably affected by light and high temperature, which is the focus of this work. As shown in Figure 3d, the time-related variation of the device performance is collected by testing the devices at 85 °C for 12 h and then at room temperature in the dark for another 12 h, which is similar to the realistic operational condition with day and night alternates. Notably, in terms of the temperature stability test, the PSC is transferred in an oven rather than being placed on a hot plate in a N₂ glove box for characterization. This arrangement ensures that the whole device is in a high-temperature atmosphere (85 °C) rather than only one side of the device being heated by the hot plate. After 69 days (1656 h), all PSC PCEs maintain >90% of their initial values, but PSCs based on the Sn:In₂O₃/In₂O₃ bilayer ETL show a slightly higher remaining PCE (91.9%), which is attributed to the excellent chemical inactivity of inorganic charge transport layers sandwiching the perovskite layer. Meanwhile, the advantages of more efficient charge extract and transport ability as well as enhanced built-in field of the used Sn:In₂O₃/In₂O₃ bilayer ETL are beneficial for separating photoexcited charges and then impeding the degradation of the perovskite. Furthermore, the time-related variation of the device performance under 12 h continuous 1 sun illumination and then 12 h interval in the dark is shown in Figure S5. Obviously, after 2000 h operation, the devices with the Sn:In₂O₃/In₂O₃ bilayer ETL remain 91.8% PCEs of their initial values, preceding that of In₂O₃, Sn:In₂O₃. The improved photostability is considered to be resulted from less recombination due to more efficient electron extraction.

To investigate the improved performance of PSCs, especially for the Sn:In₂O₃/In₂O₃ bilayer ETL, dynamics and device physics are discussed. To evaluate charge extraction from the devices, the steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) are measured and presented in Figure 4a,b. By inserting one layer of the In₂O₃ ETL on top of perovskite layers, the PL intensity is significantly quenched due to the charge transfer from perovskite layers to the In₂O₃ ETL. The charge transfer in the Sn:In₂O₃/perovskite interface is more efficient than that of the In₂O₃-based interface, and the Sn:In₂O₃/In₂O₃ bilayer has the most efficient charge extraction. As shown in Figure 4b, TRPL spectra are collected for better understanding of the charge extraction process. As expected, we can observe that the PL decay lifetime (fitted with a biexponential decays model) is reduced from 9.6 ns of the pristine In₂O₃/perovskite sample to 7.4 ns of for the Sn:In₂O₃/perovskite sample and 5.8 ns of the Sn:In₂O₃/In₂O₃/perovskite sample. The results indicate a more efficient charge transfer for Sn:In₂O₃/In₂O₃ bilayer ETL-based PSCs,^{44,45} agreeing well with the PL spectra and the favorable energy band level. Charge extraction and recombination information can also be derived from the transient photocurrent and photovoltage (Figure S6a,b). It can be calculated that the charge-extraction lifetimes (CELs) are 0.52, 0.44, and 0.31 μs, while the charge-recombination lifetimes (CRLs) are 1.2, 1.8, and 2.1 μs for In₂O₃, Sn:In₂O₃, Sn:In₂O₃/In₂O₃-based devices, respectively. Importantly, the shortest

CEL and the longest CRL indicate a better charge extraction and lower recombination at the Sn:In₂O₃/In₂O₃/perovskite interface than that of the In₂O₃/perovskite and Sn:In₂O₃/perovskite interfaces. The result is well consistent with the PL and TRPL measurements as well as PSC performances. The conductivity of the single In₂O₃ and Sn:In₂O₃ ETLs and Sn:In₂O₃/In₂O₃ bilayer ETL is also confirmed by characterizing the current density (*J*) voltage (*V*) characteristics of ITO/ETL/Au under dark conditions (as illustrated in Figure 4c). It is clear that the conductivity of the bilayer is much higher than that of the monolayer of In₂O₃ and Sn:In₂O₃. Notably, all the thickness of ETL is 60 nm, where the Sn:In₂O₃/In₂O₃ bilayer ETL consists of 30 nm In₂O₃ and 30 nm Sn:In₂O₃.

Capacitance–voltage (*C–V*) measurements are performed to further understand the effect of different ETLs on *V*_{OC}. The built-in potential of the device can be obtained from the *x*-intercept of the linear regime in the Mott–Schottky plot (Figure 4d) by fitting the experiments with the Mott–Schottky equation:⁴³ $1/C^2 = (2/\epsilon\epsilon_0 eN)(V - V_{bi})$, where ϵ is the dielectric constant of the material, ϵ_0 is the permittivity of the vacuum, e is the element charge, and N is the carrier concentration in the device. The *V*_{bi} of the device with the Sn:In₂O₃/In₂O₃ bilayer ETL is 1.17 V, which is 0.08 and 0.24 V higher than that of Sn:In₂O₃ (1.09 V) and In₂O₃ (0.93 V), respectively. Typically, the high *V*_{bi} not only offers a strong driving force to carrier separation and transport in PSCs and promotes *V*_{OC} of the device but also contributes to the effectively suppressed recombination as well as improved device performance. The enhancement of *V*_{bi} of the device with the Sn:In₂O₃/In₂O₃ bilayer contributes to an increase in *V*_{OC} in PSCs, which results from the large difference of charge concentration between In₂O₃ and Sn:In₂O₃.

To obtain more information about charge transport and recombination mechanisms, the dependence of the *J*_{SC} and *V*_{OC} on the light power intensity is determined; as plotted in Figures S7 and 4c, *J*_{SC} has a power-law relationship with the light intensity (*J*_{SC} = *kI*^{*n*}). When the perovskite film is trap-free, the recombination in the perovskite film is the bimolecular recombination and *n* is equal to 1. The slope based on the bilayer ETL is 0.93, the closest value to 1, indicating the low nonradiative recombination. In addition, from the *V*_{OC} versus light intensity as shown in Figure 4e, the ideality factor is estimated by the formula $n = \frac{q}{kT} \frac{dV_{OC}}{d \ln(\phi)}$, which also provides information about the recombination process in PSCs. Since the slope of *V*_{OC} versus the light intensity is greater than 1, it indicates the presence of additional trap-assisted Shockley–Read–Hall (SRH) recombination.^{46–48} As shown in Figure 4e, the slopes of 1.52 *KT*/*q*, 1.31 *KT*/*q*, and 1.18 *KT*/*q* correspond to the devices based on In₂O₃, Sn:In₂O₃, and Sn:In₂O₃/In₂O₃ bilayer ETL, respectively. The decreased slope indicates a significant reduction in the trap-assisted SRH recombination in devices with the Sn:In₂O₃/In₂O₃ bilayer ETL, which is consistent with the increment of *V*_{OC} and FF. Furthermore, the charge recombination in PSCs based on different ETLs is also compared by their dark *J–V* curves. As shown in Figure S8, the Sn:In₂O₃/In₂O₃ bilayer ETL-based PSCs exhibit the smallest dark current density compared to the single In₂O₃ and Sn:In₂O₃ ETL-based PSCs, which corresponds to the lowest recombination loss in devices. The lowest SRH recombination of the Sn:In₂O₃/In₂O₃ bilayer ETL-based devices should be ascribed to (1) the improved charge

transport ability by using Sn-doped In_2O_3 and the appropriate energy band level of the designed bilayer ETL as well as (2) the enhanced built-in field in the whole devices.

Figure 4f shows the Nyquist plots collected from electrochemical impedance spectroscopy (EIS). The largest charge recombination resistances fitted by an equivalent circuit model is obtained, as shown in the inset of Figure 4d, for $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL based devices. The results reflect the efficiently suppressed recombination at the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer/perovskite interface, which agrees with the previous discussion. Meanwhile, the smallest series resistance for $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL based devices proves the improved interfacial contact between the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL and perovskite and also the enhanced charge transport due to the increased conductivity contributing to the enhancement of J_{SC} and FF in PSCs. To further demonstrate the mechanism of reduced charge recombination, the capacitance (C) of In_2O_3 , $\text{Sn}:\text{In}_2\text{O}_3$, and bilayer are detected according to previous reports.^{4,49} The capacitances are shown in Figure S9 and the values are 31.6, 36.2, and 39.7 nF, respectively, from which we can determine the respective ϵ_r (relative permittivity) as 4.86, 5.58, and 6.11, thus resulting in the reduced critical radius (R_C) of the electron capture regions of 11.94, 10.40, and 9.50 nm, respectively. Therefore, the electron capture region is 7.13×10^{-18} , 4.71×10^{-18} , and $3.59 \times 10^{-18} \text{ cm}^{-3}$, demonstrating only a half room for electron capture. The reduced electron capture region can result in an obvious suppression of the trap-assisted recombination and lead to a higher FF in the solar cells (which is shown in the latter results of the device parameters). This approach has also been adopted previously for studying the recombination loss.^{4,49}

3. CONCLUSIONS

In conclusion, $\text{Sn}:\text{In}_2\text{O}_3$ NPs are synthesized through a low-temperature solution process method, and a post-treatment-free $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ stepped structure of the top bilayer ETL is proposed and demonstrated for achieving high-efficiency and stable p-i-n PSCs. Electrical properties are improved by doping Sn in In_2O_3 , and the formation of gradient carrier structure and their energy bands with enhanced built-in electric field is proposed. After optimization, PSCs based on the $\text{Sn}:\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ bilayer ETL exhibit a high PCE of 20.65% with improved J_{SC} , V_{OC} , and FF on account of the enhanced charge separation, extraction and transfer, and suppressed recombination. PSCs with this all-oxide ETL structure also show high thermal stability and photostability. Consequently, the PSCs constructed from the oxide-only HTL and ETLs achieve high efficiency, stability, and completely ambient condition process, which promotes the development of inverted PSCs for practical applications.

4. EXPERIMENTAL DETAILS

4.1. Material Synthesis and Device Fabrication. Indium(III) acetate monohydrate ($\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$, 99.99%) and tin(IV) chloride (SnCl_4) were purchased from Sigma-Aldrich and Macklin Reagent, respectively. Ethanol absolute, methanol, chlorobenzene (CB, 99.8%, extra dry), hydrochloric acid (37%), dimethylformamide (DMF, 99%, extra dry), dimethyl sulfoxide (DMSO, 99%, extra dry), 1,2-dichlorobenzene (DCB, 98+%, extra dry), isopropanol (99.8%, extra dry), and ammonium hydroxide solution (28% in water) were purchased from Acros Organics. Methylammonium iodide and formamidinium iodide were purchased from Dyesol. Lead(II) iodide (PbI_2 , 99%) was purchased from TCI. All chemicals were used as

received unless otherwise noted. In_2O_3 and $\text{Sn}:\text{In}_2\text{O}_3$ NPs are synthesized via a modified hydrothermal approach, which is similar to our previously reported method.¹² Typically, 0.62 g of $\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$ was dissolved in 12 mL of absolute ethanol and then 0.4 mL of NaOH (1 g) aqueous solution was added. After stirring for 15 min, the mixed solution was transferred into an 18 mL Teflon-lined autoclave, which was sealed and kept at 140 °C for 5 h. In terms of the synthesis of $\text{Sn}:\text{In}_2\text{O}_3$, a different amount of SnCl_4 was added with $\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$ together, and the other process was the same as In_2O_3 synthesis. The NPs were dried and kept in a glovebox for further use.

According to our previous work,¹⁰ the perovskite film is fabricated first. Subsequently, the ethanol solution of In_2O_3 or/and $\text{Sn}:\text{In}_2\text{O}_3$ NPs with different concentrations (20, 30, and 40 mg/mL) is dynamically spin-coated on top of the perovskite layers through different speeds (800–2000 rpm). Importantly, before the formation of the ETL films, the well-dispersed metal oxide NP solution was prepared from the purified ethanol by removing possibly residual water. The purified ethanol was obtained through vacuum distillation and cooling in the glovebox. This combined processes could impede the damage of the perovskite film by its direct contact with water. Additionally, it prevents the contact between the perovskite film and water after the volatilization of ethanol due to its lower boiling point than water. Different amounts of NPs were added in the evaporated ethanol in a glovebox and then ultrasonic treatment was performed. Finally, 100 nm thick Ag electrodes are directly deposited on the top ETL.

4.2. Characterization. Elemental analysis was carried out by ICP-OES. Photocurrent and photovoltage decay curves were measured using a 450 W Xenon lamp and a Keithley 2400 source meter. For Hall effect measurements, Sn-doped In_2O_3 films with different concentrations were spin-coated on a glass substrate, and the Au electrode in the Van der Pauw configuration was thermally evaporated. TPV and TPC decays were recorded using a digital oscilloscope (Tektronix TBS 1202B). To obtain the TPV data, 530 nm laser pulse was used and the PSCs were exposed to 0.3 sun background illumination. To obtain TPC measurements, the short-circuited PSCs were illuminated by a 530 nm laser pulse with a pulse width of 120 fs. The capacitance measurements were processed according to the previous report⁴ based on the capacitors with the structure of $\text{ITO}/\text{NiO}_x/\text{ETL}/\text{Ag}$. The details of other characterization methods have been described in our previous work.¹²

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c05284>.

Elemental composition; parameters of the PSCs; top SEM images; absorption spectra; section-cross SEM; J - V curves; PCE summary; parameters of the best PSCs; normalized PCE; photocurrent and photovoltage decay; J_{SC} vs light intensity; dark current; and capacitance vs frequency (PDF)

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Notes

The authors declare no competing financial interest.

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