High-Performance Planar Perovskite Solar Cells with Negligible Hysteresis Using 2,2,2-Trifluoroethanol-Incorporated SnO₂

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HIGHLIGHTS
An effective trifluoroethanol-incorporated SnO₂ (T-SnO₂) ETL is applied to PSCs
The T-SnO₂ ETL exhibits improved electron mobility and optimized work function
The PSC displays PCE of 20.92% and negligible hysteresis
PCE is improved to 21.68% by O₂ plasma treating the T-SnO₂ ETL

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SUMMARY
An efficient electron transport layer (ETL) between the perovskite absorber and the cathode plays a crucial role in obtaining high-performance planar perovskite solar cells (PSCs). Here, we incorporate 2,2,2-trifluoroethanol (TFE) in the commonly used tin oxide (SnO₂) ETL, and it successfully improves the power conversion efficiency (PCE) and suppresses the hysteresis of the PSCs: the PCE is increased from 19.17% to 20.92%, and the hysteresis is largely reduced to be almost negligible. The origin of the enhancement is due to the improved electron mobility and optimized work function of the ETL, together with the reduced traps in the perovskite film. In addition, O₂ plasma is employed to treat the surface of the TFE-incorporated SnO₂ film, and the PCE is further increased to 21.68%. The concept here of incorporating organic small molecules in the ETL provides a strategy for enhancing the performance of the planar PSCs.

INTRODUCTION
Lead halide perovskite solar cells (PSCs) have attracted great attention for their high efficiency, high defect tolerance, and low cost (Wang et al., 2017a; Liu et al., 2015; Stranks et al., 2013; Chen et al., 2017a; Bush et al., 2016; Ono et al., 2017). Recently, the reported efficiency has exceeded 23% by optimizing the interface, perovskite thin film, and perovskite absorber materials (Jiang et al., 2019; Yang et al., 2018a; Jeon et al., 2015). Among the PSCs, planar ones are drawing more and more interest owing to their relatively simpler fabrication (in comparison with the mesoporous PSCs) (Jiang et al., 2019; Yang et al., 2018b).

In a typical planar PSC, the perovskite absorber is usually placed between the hole transport layer (HTL) and the electron transport layer (ETL). Generally, the commonly used HTLs are 2,2',7',7''-tetrakis-(N,N-di-4-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) and poly [bis (4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA), which have been proved to be efficient HTLs with high hole mobility and remarkable electron-blocking property (Heo et al., 2015). For ETLs, TiO₂ is a typically used one, especially for high efficiency n-i-p type PSCs (Zhou et al., 2014; Jeon et al., 2018; Peng et al., 2017; Tan et al., 2017). However, the strong catalytic effect of TiO₂ can damage the stability of the PSCs under light illumination (Shin et al., 2017; Luo et al., 2018). Thereby researchers are seeking for other n-type metal oxides for better choice. SnO₂ can be processed into both compact and mesoporous films (Dong et al., 2015), and the films have high transparency in the visible region and good energy level alignment with the perovskite. Nowadays SnO₂ ETLs are widely used in PSCs to achieve high power conversation efficiencies (PCEs) (Ke et al., 2015; Wang et al., 2016; Chen et al., 2017b; Jiang et al., 2016).

However, many reports have shown that the PSCs based on the pure SnO₂ ETL still have serious hysteresis and unsatisfactory performance (Dong et al., 2017; Zhu et al., 2016; Bu et al., 2018; Wei et al., 2018). These problems are attributed to low electron mobility of the SnO₂ ETL and high trap-state density in the perovskite device (Bai et al., 2017; Schulz et al., 2019; Xiong et al., 2018; Wang et al., 2018a; Xie et al., 2017). Thereby researchers are finding efficient ways of modifying the pure SnO₂ layer to solve the problems. For examples, Ke et al. put a very thin PCBM layer on the SnO₂ layer to promote electron transport and suppress interface carrier recombination (Ke et al., 2016), Yang et al. made EDTA-complexed SnO₂ ETL to improve the electron mobility (Yang et al., 2018b), and several other groups used self-assembled monolayers (SAMs) to passivate the interfacial trap sites (Yang et al., 2017; Zuo et al., 2017). These methods all lead to enhanced performances.
Here, we made 2,2,2-trifluoroethanol (TFE)-incorporated SnO2 (T-SnO2) ETL by incorporating TFE (Meng et al., 2018), a water-soluble organic small molecule with strong electron-withdrawing group (trifluoromethyl) into the SnO2 colloidal water solution. Consequently, the electron mobility in the SnO2 ETL is largely improved and trap states in the perovskite absorber is greatly reduced. As a result, the hysteresis is obviously eliminated and a high PCE of 20.92% is achieved. Furthermore, we employed O2 plasma to treat the surface of the T-SnO2 film, and a superior PCE of 21.68% is obtained.

RESULTS AND DISCUSSION

Characterization of T-SnO2

The transmission electron microscopy images of the SnO2 and T-SnO2 nanoparticles are shown in Figure S1. For the pristine SnO2 particles, large-size clusters (50–70 nm) can be clearly seen; this is due to the aggregation of the SnO2 nanoparticles when they were in solution. For the T-SnO2 particles, the size is about 3–5 nm. The much smaller size is attributed to the strong electron-withdrawing property of the trifluoromethyl group in TFE, which greatly restricts the aggregation of the SnO2 nanoparticles in solution. X-ray photoelectron spectroscopy (XPS) was used to elucidate the state of the F and Sn in the SnO2 and T-SnO2 films coated on indium tin oxide (ITO) substrates. In Figure 1A, it is found that F 1s peak of the T-SnO2 film locates at ~684.1 eV, which is consistent with the value in the literature (Wang et al., 2017b; Kim et al., 2018). In contrast, there is no associated peak for the SnO2 film. In Figure 1B, it is found that the Sn 3d peaks of the T-SnO2 film shift to lower binding energy by about 0.36 eV in contrast to that of the SnO2 film. Fourier transform infrared (FTIR) spectrum demonstrates that the T-SnO2 nanoparticles contain the peak characteristic of both TFE and SnO2 (Figure S2). All the aforementioned tests strongly indicate that the TFE is effectively incorporated in the SnO2 film.

Atomic force microscopy (AFM) was performed to compare the roughness of the T-SnO2 and SnO2 films. As shown in Figure 1C, the roughness of the T-SnO2 film (root mean square [RMS]: 1.70 nm) is less than that of the SnO2 film (RMS: 2.17 nm). The smoother surface is beneficial for later perovskite film growth and a better contact with the T-SnO2 ETL. In addition, UV photoelectron spectroscopy (UPS) measurement was carried out to estimate the work function (WF) of the SnO2 and T-SnO2 films (Figure S3). Figure 1D shows the energy levels of the perovskite film and the two ETLs. It is seen that the WF of the T-SnO2 film is closer to the conduction band of the perovskite film (Figure 1E) in comparison with that of the SnO2 film, which is beneficial for increasing Voc (Wang et al., 2018b; Yang et al., 2016; Yu et al., 2018).

Figure 1E compares the optical transmission spectra of the SnO2 and T-SnO2 films. It is seen that all the samples display good transparency in the visible region. In addition, the T-SnO2 film exhibits a higher electron mobility (6.17 × 10−3 cm2 V−1 s−1) than that of the SnO2 film (2.10 × 10−3 cm2 V−1 s−1), as measured by the space charge limited current (SCLC) method (Figure S5) (Jiang et al., 2016; Yu et al., 2018).

Structure and Performance of PSCs

We then fabricated planar PSCs with the T-SnO2 and the SnO2 ETLs in an architecture of glass/ITO/ETL/perovskite/Spiro-OMeTAD/Au. The cross-sectional scanning electron microscopy (SEM) of the T-SnO2 device is shown in Figure 2A, in which each layer is clearly seen. The ~680-nm-thick perovskite layer is coated on the ETL substrates using the widely adopted two-step method (more details are shown in Transparent Methods) (Jiang et al., 2016; Wang et al., 2018b). SEM top view of the perovskite films grown on the two ETLs are provided in Figure S6; it is seen that both films are pinhole-free and uniform and contain similar crystal grains. The grain sizes are ~750 nm. X-ray diffraction (XRD) measurements (Figure S7) also give very similar results for the two perovskite films (Wang et al., 2018b; Jiang et al., 2017; Chen et al., 2014; Kim et al., 2016). These studies confirm that TFE has a negligible effect on the perovskite crystallization.

The device performance is optimized by varying the TFE volume and the annealing temperature for the ETL. The PCE reaches a maximum when the TFE volume increases to 350 µL (Figure S8 and Table S1). The optimal annealing temperature is 130 °C for the T-SnO2 film (Figure S9). Figure 2B indicates the J–V curves of the best SnO2 and T-SnO2 devices, and the device parameters are shown in Table 1. The SnO2 device displays quite obvious hysteresis: under reverse scan direction, it has a PCE of 19.17% (Voc: 1.10 V, Jsc: 23.12 mA cm−2, and FF: 0.755); under forward scan direction, it has a PCE of 16.47% (Voc: 1.06 V, Jsc: 23.03 mA cm−2 and FF: 0.674). In contrast, the T-SnO2 device presents negligible hysteresis: under reverse scan, it has a PCE of 20.92% (Voc: 1.12 V, Jsc: 23.91 mA cm−2 and FF: 0.780); under forward scan, it has a PCE of 20.62% (Voc: 1.11 V, Jsc: 23.87 mA cm−2 and FF: 0.777). We conducted statistical studies for the SnO2 and T-SnO2 devices. Fifty PSCs were made for each, and the results are given in Figure S10.
For the 50 SnO₂ devices, the average PCE, \( V_{oc} \), \( J_{sc} \), and FF are 18.38%, 1.09 V, 22.91 mA cm\(^{-2}\), and 0.734, respectively, whereas for the 50 T-SnO₂ devices, the corresponding values are 20.12%, 1.11 V, 23.66 mA cm\(^{-2}\), and 0.764. The larger \( V_{oc} \) can be attributed to the better-aligned energy levels of the T-SnO₂ and perovskite layers. The higher FF and \( J_{sc} \) are likely due to the improved electron mobility. In addition, the T-SnO₂ devices exhibit a narrower distribution of PCE (19%–21% versus 17%–20%), indicating their excellent reproducibility (Figure 2C). All the above-mentioned statistical results confirm the advantage of the T-SnO₂ ETL. The external quantum efficiency (EQE) spectra of the T-SnO₂ device is exhibited in Figure 2D, and the integrated \( J_{sc} \) for the T-SnO₂ device is 23.48 mA cm\(^{-2}\), which is consistent with the \( J_{sc} \) of 23.91 mA cm\(^{-2}\) obtained from the J-V result (within 2% deviation).

**Charge Transport Studies**

To study the trap density, the SCLC model was adopted with the electron-only devices (ITO/ETL/perovskite/PCBM/Ag) (Chen et al., 2017b). Figure 3A shows the dark I-V curves of the two devices. Generally,
at low bias voltage, the $I-V$ curve shows linear ohmic-type response. With the increase of the bias voltage, the current starts to increase nonlinearly, indicating the trap filling process is triggered. The kink point between the linear region and the nonlinear region is defined as trap-filled limit voltage ($V_{TFL}$), and the trap density ($N_t$) can be calculated using the following Equation 1:

$$N_t = \frac{2\varepsilon_0 e V_{TFL}}{eL^2}$$  (Equation 1)

where $\varepsilon_0$, $\varepsilon$, $e$, and $L$ are permittivity of vacuum, relative dielectric constant, elementary charge, and perovskite film thickness, respectively. The calculated trap density of the perovskite film on the T-SnO$_2$ ETL is about $8.94 \times 10^{15}$ cm$^{-3}$, much lower than that of the perovskite film deposited on the SnO$_2$ ETL ($1.95 \times 10^{16}$ cm$^{-3}$).

Figure 3B shows the steady-state photoluminescence (PL) spectra of the perovskite films coated on bare glass and the SnO$_2$ and T-SnO$_2$ ETLs. It is seen that the perovskite film on the T-SnO$_2$ ETL gives most significant PL quenching, indicating very efficient electron transfer from the perovskite film to the T-SnO$_2$ ETL. This is due to the reduced trap density in the perovskite film and enhanced electron mobility in the T-SnO$_2$ ETL. Time-resolved photoluminescence (TRPL) of the three samples are given in Figure 3C, from which carrier lifetime can be calculated. The carrier lifetime of the Glass/perovskite, SnO$_2$/perovskite, and T-SnO$_2$/perovskite samples are $\sim 763$, 147, and 52 ns, respectively (Table S2). The significantly reduced carrier lifetime of the perovskite/T-SnO$_2$ sample strongly indicates a fast electron transfer from the perovskite film into the T-SnO$_2$ film, hence carrier recombination can be greatly suppressed (Zhu et al., 2014; Liang et al., 2014).

| ETL     | Scan Direction | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (-) | PCE (%) |
|---------|----------------|-------------|--------------------------|--------|---------|
| SnO$_2$ | Reverse        | 1.10        | 23.12                    | 0.755  | 19.17   |
|         | Forward        | 1.06        | 23.03                    | 0.674  | 16.47   |
| T-SnO$_2$| Reverse     | 1.12        | 23.91                    | 0.780  | 20.92   |
|         | Forward        | 1.11        | 23.87                    | 0.777  | 20.62   |

Table 1. Performances of the SnO$_2$ and T-SnO$_2$ Devices
Figure 3. Charge Transport Properties Studies
(A) Dark I-V measurement of the electron-only devices based on SnO2 and T-SnO2 ETLs (inserted picture).
(B and C) PL (B) and TRPL (C) spectra of the perovskite films coated on Glass, SnO2, and T-SnO2, respectively.
(D) EIS spectra of the SnO2 and T-SnO2 devices in dark with a bias of ~1 V.

Figure 3D shows the Nyquist plots of the impedance spectroscopy (EIS) for the SnO2 and T-SnO2 devices; the equivalent circuit is also shown. $R_{tr}$ is charge transfer resistance; $R_{rec}$ is recombination resistance (Yang et al., 2015; Li et al., 2015; Jin et al., 2016). The extracted $R_{tr}$ and $R_{rec}$ are listed in Table S3. It is seen that the T-SnO2 device has larger $R_{rec}$ (650.5 vs 294.2), meaning a weaker carrier recombination in the perovskite film. The T-SnO2 device has a smaller $R_{tr}$ (36.8 vs 56.4), meaning a more efficient electron transfer process from the perovskite film to the ETL. The EIS results are consistent with the above-mentioned trap density, PL, and TRPL analysis. All the results presented in Figure 3 are in good agreement with the enhanced PCE and the remarkable negligible hysteresis of the T-SnO2 device.

Oxygen Plasma Treatment
Oxygen plasma is usually used to treat the ITO or (FTO) surface in fabrication of planar PSCs (Minarik and Vana, 2015; Dao et al., 2015; Tang et al., 2018; Huang et al., 2017). Here, we use O2 plasma to treat the surface of the T-SnO2 ETL. The O2 gas flow rate is fixed at 0.05 L h$^{-1}$, and the power varies. The treated ETL is named p-T-SnO2 ETL. Figure 4A shows the structure of the p-T-SnO2 device (ITO/p-T-SnO2/Perovskite/Spiro-OMeTAD/Au), and a cross-section SEM is exhibited in Figure S11. The FTIR and XPS results show that the F mainly exists in TFE state in the p-T-SnO2 ETL (Figure S12). Figure 4B shows the J-V curves of the p-T-SnO2 devices (with different plasma powers); the device parameters are shown in Table S4. The champion device exhibits a PCE of 21.68% ($V_{oc}$: 1.12 V, $J_{sc}$: 24.06 mA cm$^{-2}$, and FF: 0.802), which is higher than the best T-SnO2 device. The improvement can be attributed to the smoother surface of the p-T-SnO2 film, which is indicated by AFM measurements (Figure S13 and Table S5): the roughness of the p-T-SnO2 ETL is 1.13 nm and that of the T-SnO2 ETL is 1.67 nm. The very high FF of larger than 0.80 should have resulted from the improved interface between the p-T-SnO2 ETL and the perovskite film. As depicted in Figure 4B, $V_{oc}$ decreases from 1.12 to 1.07 V as the power increases from 60 to 140 W; this can be explained by the plasma-caused WF change of the T-SnO2 ETL (Figure S14 and Table S6): the WF is going down (from 4.21 to 4.40 eV) away from the conduction band of the perovskite film (4.18 eV). Figure 4C shows the EQE and integrated $J_{ac}$ (23.61 mA cm$^{-2}$) of the p-T-SnO2 device, which is consistent with the $J_{ac}$ of 24.06 mA cm$^{-2}$ obtained from $J$-$V$ measurement (with 2% deviation). Statistical study was conducted for 50 p-T-SnO2 devices, and the PCE distribution is shown in Figure 4D. The PCE ranges from 20% to 22%, and most of the devices are among the >21% range, indicating very good reproducibility of the p-T-SnO2 devices.
Stability Tests

The long-term stabilities of the SnO$_2$, T-SnO$_2$, and p-T-SnO$_2$ devices were measured without any encapsulation. Figure 5A shows PCE vs time in 720-h dark condition storage (RH 30%–40%); it is seen that the SnO$_2$ device maintains only 76% of its initial PCE, whereas the T-SnO$_2$ and p-T-SnO$_2$ devices retain over 90% of their initial PCEs. The enhanced stability is due to improved interface binding strength induced by the TFE modification and plasma treatment (Tress et al., 2016; Tan et al., 2017). Figure 5B shows the steady-state efficiency of the devices under MPP (maximum power point) conditions. It is seen that the SnO$_2$ device takes about 50 s to reach the maximum photocurrent, likely owing to a trap-filling process or ion migration (Wei et al., 2018; deQuilettes et al., 2016). Its PCE then stabilizes at about 18.6%, whereas the PCEs of the T-SnO$_2$ and p-T-SnO$_2$ devices immediately stabilize at about 20.1% and 21.0%, respectively. The stability test clearly indicates the advantage of the T-SnO$_2$ and p-T-SnO$_2$ ETLs.

Figure 5. Stability Tests for the SnO$_2$, T-SnO$_2$, p-T-SnO$_2$ Devices without any Encapsulation

(A) Air stability (30%–40% RH).
(B) Maximum power point tracking.
Conclusion
In conclusion, we present a simple, low-cost method by introducing TFE in the SnO₂ colloidal solution and achieved an effective ETL. The T-SnO₂ ETL exhibits improved electron mobility, suitable energy levels that aligned well with that of the perovskite film. The ETL also shows a very smooth surface, which allows high-quality perovskite film growth and ensures a good ETL/perovskite interface. As a result, the device displays an improved PCE of 20.92% with negligible hysteresis. In addition, the surface of T-SnO₂ film is further optimized by O₂ plasma treatment, and a higher PCE of 21.68% is obtained, together with a very high FF of larger than 0.80. Moreover, the devices with T-SnO₂ ETLs exhibit excellent stability. The simple and economical method provides an insightful strategy for preparing efficient ETLs for future PSCs.

Limitations of the Study
In this study, we found that the fluorine was incorporated into the perovskite crystal at T-SnO₂/perovskite interface (Figure S15), which might contribute to the defects passivation. However, we do not have convincing evidence for this. More studies are needed to reveal the role of fluorine at the ETL/perovskite interface.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.06.004.

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AUTHOR CONTRIBUTIONS
Y.L., P.M., Y.W., J.Z., T.L., and J.W. conceived the idea. Y.L., X.Y., and J.W. designed the experiments. Y.L. fabricated the devices and carried out the majority of measurements. J.Z. conducted the SEM and PL experiments. Y.W. conducted the AFM experiments. N.C. conducted the EIS experiments. X.Y., C.L., P.M., and T.L. assisted in data analysis. Y.L. and J.W. wrote the manuscript and interpreted the data.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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REFERENCES
Bai, Y., Meng, X., and Yang, S. (2017). Interface engineering for highly efficient and stable planar p-i-n perovskite solar cells. Adv. Energy Mater. 8, 1701883.

Bu, T., Li, J., Zheng, F., Chen, W., Wen, X., Xu, Z., Peng, Y., Zhong, J., Cheng, Y.-B., and Huang, F. (2018). Universal passivation strategy to slot-die printed SnO₂ for hysteresis-free efficient flexible perovskite solar module. Nat. Commun. 9, 4609.

Bush, K.A., Bailie, C.D., Chen, Y., Bowring, A.R., Wang, W., Ma, W., Leijtens, T., Moghadam, F., and McGhee, M.D. (2016). Thermal and environmental stability of semi-transparent perovskite solar cells for tandems enabled by a solution-processed nanoparticle buffer layer and sputtered ito electrode. Adv. Mater. 28, 3937–3943.

Chen, Q., Zhou, H., Song, T.-B., Luo, S., Hong, Z., Duan, H.-S., Dou, L., Liu, Y., and Yang, Y. (2014). Controllable self-induced passivation of hybrid lead iodide perovskites toward high performance solar cells. Nano Lett. 14, 4158–4163.

Chen, H., Ye, F., Tang, W., He, J., Yin, M., Wang, Y., Xie, F., Bi, E., Yang, X., Grätzel, M., et al. (2017a). A solvent- and vacuum-free route to large-area perovskite films for efficient solar modules. Nature 550, 92–95.

Chen, H., Liu, D., Wang, Y., Wang, C., Zhang, T., Zhang, P., Sarvari, H., Chen, Z., and Li, S. (2017b). Enhanced performance of planar perovskite solar cells using low-temperature solution-processed Al-doped SnO₂ as electron transport layers. Nanoscale Res. Lett. 12, 6.

Dao, V.-D., Larina, L.L., and Choi, H.-S. (2015). Minimizing energy losses in perovskite solar cells using plasma-treated transparent conducting layers. Thin Solid Films 593, 10–16.

deQuilettes, D.W., Zhang, W., Burlakov, V.M., Graham, D.J., Leijtens, T., Osterov, A., Bulović, V., Snaith, H.J., Ginger, D.S., and Stranks, S.D. (2016). Photo-induced halide redistribution in...
organic-inorganic perovskite films. Nat. Commun. 7, 11683.

Dong, Q., Shi, Y., Wang, K., Li, Y., Wang, S., Zhang, H., Xing, Y., Du, Y., Bai, X., and Ma, T. (2013). Insight into perovskite solar cells based on SnO2 compact electron-selective layer. J. Phys. Chem. C 119, 10212–10217.

Dong, Q., Shi, Y., Zhang, C., Wu, Y., and Wang, J. (2017). Energetically favored formation of SnO2 nanocrystals as electron transfer layer in perovskite solar cells with high efficiency exceeding 19%. Nano Energy 40, 336–344.

Heo, J. H., Han, H. J., Kim, D., Ahn, T. K., and Im, S. H. (2013). Hysteresis-less inverted CH3NH3PbI3 nanocrystals as efficient planar perovskite solar cells. J. Phys. Chem. Lett. 4, 1844–1851.

Jeon, N. J., Noh, J. H., Yang, W. S., Kim, Y. C., Ryu, S., Seo, J., and Seok, S. I. (2015). Compositional engineering of perovskite materials for high-performance solar cells. Nature 517, 476–480.

Jeon, N. J., Na, H., Jung, E. H., Yang, T. Y., Lee, Y. G., Kim, G., Kim, H. W., Seok, S. I., Lee, J., and Jeo, J. (2018). A fluorene-terminated hole-transporting layer for efficient perovskite solar cells. Adv. Energy Mater. 28, 1703852.

Jiang, Q., Zhao, Y., Zhang, X., Yang, X., Chen, Y., Chu, Z., Ye, Q., Li, X., Yin, Z., and You, J. (2019). Surface passivation of perovskite film for efficient perovskite solar cells. Nat. Photon. https://doi.org/10.1038/s41566-019-0398-2.

Jin, Z., Wang, A., Zhou, Q., Wang, Y., and Wang, J. (2016). Detecting trap states in planar perovskite solar cells. Adv. Energy Mater. 7, 1602104.

Kim, J. H., Yonezawa, S., and Okada, T. (2018). Effects of surface fluorination on the dispersion stability and the electrical conductivity of SnO2 particles using fluorine gas. Chem. Lett. 47, 393–395.

Li, H., Cao, J., Zhou, Q., Ding, L., and Wang, L. (2015). High-performance inverted P3HTPT:PC70BM solar cells. Nano Energy 15, 125–134.

Liu, Y., Yang, Z., Cui, D., Ren, X., Sun, J., Liu, X., Zhang, J., Wei, Q., Fan, H., Yu, F., et al. (2015). Two-inch-sized perovskite CH3NH3PbI3Br:K (X = Cl, Br) crystals: growth and characterization. Adv. Mater. 27, 5176–5183.

Luo, J., Chen, J., Wu, B., Goh, T.W., Qiao, W., Ku, Z., Yang, H.B., Zhang, L., Sum, T.C., and Liu, B. (2018). Surface reutilization of anatase TiO2 for efficient electron extraction and stable Pmax output of perovskite solar cells. Chem. 4, 911–923.

Meng, X., Ho, C.H.Y., Xiao, S., Bai, Y., Zhang, T., Hu, C., Lin, H., Yang, Y., So, S.K., and Yang, S. (2018). Molecular design enabled reduction of interface trap density affords highly efficient and stable perovskite solar cells with over 83% fill factor. Nano Energy 52, 300–306.

Minarik, S., and Vana, D. (2015). Applicability of random sequential adsorption algorithm for simulation of surface plasma polishing kinetics. Appl. Surf. Sci. 355, 364–368.

Ono, L. K., Park, N.-G., Zhu, K., Huang, W., and Qi, Y. (2017). Perovskite solar cells towards commercialization. ACS Energy Lett. 2, 1749–1751.

Peng, J., Duong, T., Zhou, X., Shen, H., Wu, Y., Mulmudi, H.K., Wan, Y., Zhong, D., Li, J., Tszuiki, T., et al. (2017). Efficient Indium-doped TiO2 electron transport layers for high-performance perovskite solar cells and perovskite-silicon tandem. Adv. Mater. 29, 1601768.

Schulz, P., Cahan, D., and Kahn, A. (2019). Halide perovskites: is it all about the interfaces? Chem. Rev. 119, 3349–3417.

Shin, S.S., Yeom, E.J., Yang, W.S., Hur, S., Kim, M.G., Im, J., Jeo, S., Noh, J.H., and Seok, S.I. (2017). Colloidal prepared La-doped BaSnO3 electrodes for efficient, photostable perovskite solar cells. Science 356, 167–171.

Stranks, S.D., Eperon, G.E., Grancini, G., Menelaou, C., Alcocer, M.J.P., Stranks, S.D., Eperon, G.E., Grancini, G., Menelaou, C., Alcocer, M.J.P., Leijtens, T., Herz, L.M., Petrozza, A., and Smith, H.J. (2013). Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. Science 342, 341–344.

Tan, H., Jain, A., Voznyy, O., Lan, X., García de Arquer, F.P., Fan, J.Z., Quintero-Bermúdez, R., Yuan, M., Zhang, B., Zhao, Y., et al. (2017). Efficient and stable solution-processed planar perovskite solar cells via contact passivation. Science 355, 722–726.

Tang, P., Liu, C., Zhang, J., Wu, L., Wei, L., Feng, L., Zeng, G., and Wang, W. (2018). Surface modification effects of fluorine-doped tin dioxide by oxygen plasma ionimplantation. Appl. Surf. Sci. 436, 134–140.

Tress, W., Correa Baena, J.P., Saliba, M., Abate, A., and Graetzel, M. (2016). Inverted current-voltage hysteresis in mixed perovskite solar cells: polarization, energy barriers, and defect recombination. Adv. Energy Mater. 6, 1600396.

Wang, C., Zhao, D., Grice, C.R., Liao, W., Yu, Y., Cimaroli, A., Shrestha, N., Roland, P.J., Chen, J., Yu, Z., et al. (2016). Low-temperature plasma-enhanced atomic layer deposition of tin oxide for efficient selective layers for efficient planar perovskite solar cells. J. Mater. Chem. A 4, 12080–12087.

Wang, Z., Lin, Q., Chmiel, F.P., Sakai, N., Herz, L.M., and Henny, J.S. (2017a). Efficient ambient-air-stable solar cells with 2D-3D heterostructured butylammonium-cadmium-formamidinum lead halide perovskites. Nat. Energy 2, 17135.

Wang, X., Wang, X., Di, Q., Zhao, H., Liang, B., and Yang, J. (2017b). Mutual effects of fluorine dopant and oxygen vacancies on structural and luminescence characteristics of F doped SnO2 nanoparticles. Materials (Basel) 10, 1398.

Wang, Y., Duan, C., Li, J., Han, W., Zhao, M., Yao, L., Wang, Y., Yan, C., and Jiu, T. (2018a). Performance enhancement of inverted perovskite solar cells based on smooth and compact PC61BM: SnO2 electron transport layers. ACS Appl. Mater. Interfaces 10, 12026–12035.

Wang, C., Zhang, C., Wang, S., Liu, G., Xia, H., Tong, S., He, J., Niu, D., Zhou, C., Ding, K., et al. (2018b). Low-temperature processed, efficient, and highly reproducible cesium-doped triple-cation perovskite planar heterojunction solar cells. Sol. RRL 2, 1700209.

Wei, J., Guo, F., Wang, X., Xu, K., Lei, M., Liang, Y., Zhao, Y., and Xu, D. (2018). SnO2-in-polymer-matrix for high-efficiency perovskite solar cells with improved reproducibility and stability. Adv. Mater. 30, 1805153.

Xie, J., Huang, K., Yu, Y., Yang, Z., Xiao, K., Qiang, Y., Zhu, X., Xu, L., Wang, P., Cui, C., et al. (2017). Enhanced electronic properties of SnO2 via electron transfer from graphene quantum dots for efficient perovskite solar cells. ACS Nano 11, 9176–9182.

Xiong, L., Guo, Y., Wen, J., Liu, H., Yang, G., Qin, P., and Fang, G. (2018). Review on the application of SnO2 in perovskite solar cells. Adv. Funct. Mater. 28, 1802757.

Yang, D., Yang, R., Zhang, J., Yang, Z., Liu, S., and Li, C. (2015). High efficiency flexible perovskite solar cells using superior low temperature TiO2. Energy Environ. Sci. 8, 3208–3214.

Yang, D., Zhou, X., Yang, R., Yang, Z., Wu, W., Wang, X., Li, C., Liu, S., and Chang, R.P.H. (2016). Surface optimization to eliminate hysteresis for record efficiency planar perovskite solar cells. Energy Environ. Sci. 9, 3071–3078.
Yang, G., Wang, C., Lei, H., Zheng, X., Qin, P., Xiong, L., Zhao, X., Yan, Y., and Fang, G. (2017). Interface engineering in planar perovskite solar cells: energy level alignment, perovskite morphology control and high performance achievement. J. Mater. Chem. A 5, 1658–1666.

Yang, Z., Dou, J., and Wang, M. (2018a). Interface engineering in n-i-p metal halide perovskite solar cells. Sol. RRL 2, 1800177.

Yang, D., Yang, R., Wang, K., Wu, C., Zhu, X., Feng, J., Ren, X., Fang, G., Priya, S., and Liu, S. (2018b). High efficiency planar-type perovskite solar cells with negligible hysteresis using EDTA-complexed SnO2. Nat. Commun. 9, 3239.

Yu, H., Yeom, H.-I., Lee, J.W., Lee, K., Hwang, D., Yun, J., Ryu, J., Lee, J., Bae, S., Kim, S.K., et al. (2018). Superfast room-temperature activation of SnO2 thin films via atmospheric plasma oxidation and their application in planar perovskite photovoltaics. Adv. Mater. 30, 1704825.

Zhou, H., Chen, Q., Li, G., Luo, S., Song, T.-b., Duan, H.-S., Hong, Z., You, J., Liu, Y., and Yang, Y. (2014). Interface engineering of highly efficient perovskite solar cells. Science 345, 542–546.

Zhu, Z., Ma, J., Wang, Z., Mu, C., Fan, Z., Du, L., Bai, Y., Fan, L., Yan, H., Phillips, D.L., et al. (2014). Efficiency enhancement of perovskite solar cells through fast electron extraction: the role of graphene quantum dots. J. Am. Chem. Soc. 136, 3760–3763.

Zhu, Z., Bai, Y., Liu, X., Chueh, C.-C., Yang, S., and Jen, A.K.-Y. (2016). Enhanced efficiency and stability of inverted perovskite solar cells using highly crystalline SnO2 nanocrystals as the robust electron-transporting layer. Adv. Mater. 28, 6478–6484.

Zuo, L., Chen, Q., De Marco, N., Hsieh, Y.-T., Chen, H., Sun, P., Chang, S.-Y., Zhao, H., Dong, S., and Yang, Y. (2017). Tailoring the interfacial chemical interaction for high-efficiency perovskite solar cells. Nano Lett. 17, 269–275.
Supplemental Information

High-Performance Planar Perovskite Solar Cells with Negligible Hysteresis Using 2,2,2-Trifluoroethanol-Incorporated SnO₂

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Supplemental Information

Figure S1 TEM images of the a) SnO$_2$ and b,c) T-SnO$_2$ nanoparticles. Related to figure 1.
Figure S2 FTIR spectra of the TFE, SnO$_2$ and T-SnO$_2$ films. Related to figure 1A and 1B.
Figure S3 The UPS cut-off edge of the SnO$_2$ and T-SnO$_2$ films. Relate to figure 1D.
Figure S4 The UPS data of the perovskite film. a) the cut-off edge. b) Valence band. c) Bandgap. d) band structure. It can be calculated that the conduction band ($E_c$) of the perovskite is 4.18 eV. Relate to figure 1D.
**Figure S5** The electron mobility for the SnO$_2$ and T-SnO$_2$ films calculated by the SCLC model with the device structure of Glass/ITO/Al/ETL/Al. Related to figure 1.
Figure S6 The morphology of perovskite deposited on the SnO$_2$ and T-SnO$_2$ substrates. Top-view SEM images and the grain size distribution of perovskite coated on a,c) SnO$_2$ and b,d) T-SnO$_2$. Related to figure 2.
Figure S7 XRD spectra of the perovskite film grown on the SnO$_2$ and T-SnO$_2$ ETLs. Related to figure 2.
Figure S8. J-V curves of the PSCs based on the T-SnO₂ ETLs. T-SnO₂ ETLs with various TFE contents in the SnO₂ solution. The solar cells show the optimum performance at the TFE volume of 350 μl. Related to figure 2B.
Figure S9  $J$-$V$ curves of the PSCs based on the T-SnO₂ ETLs. T-SnO₂ ETLs with various annealing temperatures. The solar cells show the best performance at the annealing temperature of 130°C. Related to figure 2B.
Figure S10 Comparison of photovoltaic parameters for the SnO$_2$ and T-SnO$_2$ devices. There were 50 cells for each counted from 10 different batches. All the data are from reverse scan. Related to figure 2C.
Figure S11 SEM cross-sectional image of the p-T-SnO$_2$ device. Related to figure 4A.
Figure S12  a) FTIR spectra of the SnO$_2$, T-SnO$_2$ and p-T-SnO$_2$ films. b) XPS spectra of the F 1s peaks for the T-SnO$_2$ and p-T-SnO$_2$ films. Related to figure 4.
**Figure S13** The AFM images of the T-SnO$_2$ films (with different plasma powers). Note that the 0 W condition is T-SnO$_2$ without any plasma treated. Related to figure 4B.
Figure S14 The UPS cut-off edge of the T-SnO$_2$ films (with different plasma powers). Related to figure 4B.
**Figure S15** The XPS spectra of F 1s peaks of T-SnO₂ films without any treatment, with DMSO washed and washed with DMSO after depositing perovskite on the T-SnO₂ films. And once fluorine entered into the perovskite lattice from the T-SnO₂/perovskite interface, it could be dissolved in DMSO. Related to figure 1A.
**Table S1** Photovoltaic parameters of the PSCs with different ETLs. Related to figure 2B.

| ETL      | Scan direction | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE (%) |
|----------|----------------|--------------|--------------------------|----|----------|
| SnO$_2$  | Reverse        | 1.10         | 23.12                    | 0.755 | 19.17    |
|          | Forward        | 1.06         | 23.03                    | 0.674 | 16.47    |
| 100-T-SnO$_2$ | Reverse   | 1.10         | 23.51                    | 0.756 | 19.55    |
|          | Forward        | 1.06         | 23.43                    | 0.703 | 17.49    |
| 250-T-SnO$_2$ | Reverse   | 1.11         | 23.74                    | 0.779 | 20.57    |
|          | Forward        | 1.08         | 23.69                    | 0.757 | 19.33    |
| 350-T-SnO$_2$ | Reverse   | 1.12         | 23.91                    | 0.780 | 20.92    |
|          | Forward        | 1.11         | 23.87                    | 0.777 | 20.62    |
| 380-T-SnO$_2$ | Reverse   | 1.10         | 23.55                    | 0.767 | 19.88    |
|          | Forward        | 1.09         | 23.54                    | 0.766 | 19.71    |

**Table S2** Parameters of the TRPL spectra of perovskite deposited on different substrates. Related to figure 3C.

| Sample                  | $\tau_{ave}$/ns | $\tau_1$/ns | $A_1$ | $\tau_2$/ns | $A_2$ |
|-------------------------|-----------------|-------------|-------|-------------|-------|
| Glass/perovskite        | 763.36          | 303.56      | 41.68 | 890.16      | 51.54 |
| SnO$_2$/perovskite      | 146.89          | 61.73       | 34.74 | 164.11      | 64.60 |
| T-SnO$_2$/perovskite    | 52.39           | 10.65       | 35.60 | 56.64       | 65.74 |

**Table S3** EIS parameters of the SnO$_2$ and T-SnO$_2$ devices. Related to figure 3D.

| Substrates | $R_s$ (Ω) | $R_{tr}$ (Ω) | $C_{tr}$ (Ω) | $R_{rec}$ (Ω) | $C_{rec}$ (Ω) |
|------------|-----------|--------------|--------------|---------------|---------------|
| SnO$_2$    | 29.9      | 56.4         | 5.781E-8     | 294.2         | 1.056E-8      |
| T-SnO$_2$  | 27.6      | 36.8         | 8.419E-8     | 650.5         | 4.480E-8      |
Table S4 Photovoltaic parameters of the p-T-SnO$_2$ devices with different plasma powers at fixed O$_2$ gas flow rate of 0.05 L h$^{-1}$. Related to figure 4B.

| Style              | Power (W) | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF  | PCE (%) |
|--------------------|-----------|--------------|--------------------------|-----|--------|
| Oxygen plasma      | 0         | 1.12         | 23.91                    | 0.780 | 20.92  |
|                    | 60        | 1.12         | 24.06                    | 0.802 | 21.68  |
|                    | 100       | 1.10         | 24.00                    | 0.795 | 21.07  |
|                    | 140       | 1.07         | 23.92                    | 0.796 | 20.35  |

Table S5 Roughnesses of the p-T-SnO$_2$ films with different plasma powers at fixed O$_2$ gas flow rate of 0.05 L h$^{-1}$. The scan size of all the films is 3 um. The roughness is almost 32% lower than original one (pure T-SnO2), and when the power increased from 60 W to 140 W, the variation in roughness is negligible. Related to figure 4.

| Plasma power (W) | $R_q$ (nm) | $R_a$ (nm) | $R_{max}$ (nm) |
|------------------|------------|------------|----------------|
| 0 W              | 1.67       | 1.27       | 14.2           |
| 60 W             | 1.13       | 0.89       | 12.1           |
| 100 W            | 1.09       | 0.86       | 12.6           |
| 160 W            | 1.08       | 0.86       | 11.2           |

Table S6 Work functions of the p-T-SnO$_2$ films with different plasma powers at fixed O$_2$ gas flow rate of 0.05 L h$^{-1}$. Related to figure 4.

| Plasma power (W) | 0 | 60 | 100 | 140 |
|------------------|---|----|-----|-----|
| Work function (eV) | 4.19 | 4.21 | 4.34 | 4.40 |
Transparent Methods

Precursor SnO₂ and T-SnO₂ Solution

The SnO₂ precursor solution was obtained by diluting the SnO₂ colloidal solution (the concentration is 2.67%). For T-SnO₂ solution, the 2,2,2-Trifluoroethanol (aladdin) was added into the distilled water and fully stirred (the total volume is 650 μl). After that, the SnO₂ colloidal solution (100 μl) was added into the mixed solution. The solution was then heated to 32°C and stirred about 30 min to form T-SnO₂ solution.

Fabrication of Solar Cells

The glass/ITO was washed in the order of cleanser essence, distilled water, acetone and isopropyl alcohol for 30 min. For the SnO₂ ETL, the precursor solution was spin-coated onto the ITO at 3500 rpm for 35 s, and then annealed at 150 °C for 30 min. For the T-SnO₂ ETL, the precursor solution was spin-coated onto the ITO at 3500 rpm for 35 s, and then annealed at 130 °C for 30 min. For the p-T-SnO₂ ETL, the T-SnO₂ ETL surface was treated by O₂ plasma for 5 min with various powers at a fixed O₂ flow rate of 0.05 L h⁻¹. The perovskite film was made by two-step method. For the first step, 760 mg PbI₂ was added into 1 ml DMF and 160 μl DMSO mixed solution, then was stirred over night at 25°C. The as-prepared solution was used as PbI₂ layer by spin-coating at 1600 rpm for 23 s and then 4000 rpm for 27 s, Then annealed at 70°C for 2 min. For the second step, the FAI: MACl: MABr mixed solution (110: 11: 11.5 mg in 1.5 ml isopropyl alcohol) was spin-coated onto the PbI₂ layer at 2000 rpm for 23 s, then the sample was taken out of the glove box and annealed at 140 °C for 20 min (ambient air, ~40% humidity). After annealing, the sample was rapidly transferred to the glove box for HTL coating. The Spiro-OMeTAD (72.3 mg) in chlorobenzene (CB) solution (1 ml), adding 17.5 μl Li-TFSI/acetonitrile mixed solution (170 mg ml⁻¹) and 28.8 μl 4-tBP, which was coated at 4000 rpm for 27 s. After that, the sample was stored in the drying cabinet (ambient air, ~1% humidity) for 20 h. Finally, 90 nm Au electrode was deposited by vacuum evaporation at the pressure of 3×10⁻⁶ Torr.

Thin Film Characterization

UPS and XPS tests were performed on XPS machine (ESCALAB250XI, Thermo Fisher Scientific). The XRD patterns were obtained to research the crystallographic characteristics of perovskite, which was measured by using Rigaku-2500 X-ray diffractometer with CuKα radiation, λ =1.5406 Å. The surface morphology and cross section of the devices are investigated by SEM (S-4800, Japan). The surface roughness of the electron transfer layers were obtained by using atomic force microscope (AFM, Bruker MultiMode 8 SPM system).

Electron Mobility Calculation

The electron mobilities of SnO₂ and T-SnO₂ films were calculated by the SCLC method. The Equation is below:

\[ J = \frac{9}{8} \mu_e \varepsilon_0 \varepsilon_r \frac{V^2}{L^2} \]

Where \( \mu_e, \varepsilon_0, \varepsilon_r \) and L are electron mobility, free space permittivity, dielectric constant and the thickness of electron transport layer.

Average Carrier Lifetime Calculation

The carrier lifetime (\( \tau_{ave} \)) can be calculated using the Equation:
\[ \tau_{\text{ave}} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \]

where \( A_i \) and \( \tau_i \) are the decay amplitude and decay time.

**Device Characterization**

All J-V curves were measured using the Keithley 2420, and the solar cell was illuminated by a solar simulator (Newport 94043A, AM 1.5G, USA). The light intensity was calibrated by the monocrystalline silicon reference cell with a standard value 100 mW cm\(^{-2}\). The device area was 0.044 cm\(^2\). The external quantum efficiency (EQE) spectra was obtained with Newport 300 W Xenon Light Source (Newport IQE 200, USA). The electrical impedance spectroscopy (EIS) was measured by Zennium (Zahner).