

Thick TiO₂-Based Top Electron Transport Layer on Perovskite for Highly Efficient and Stable Solar Cells

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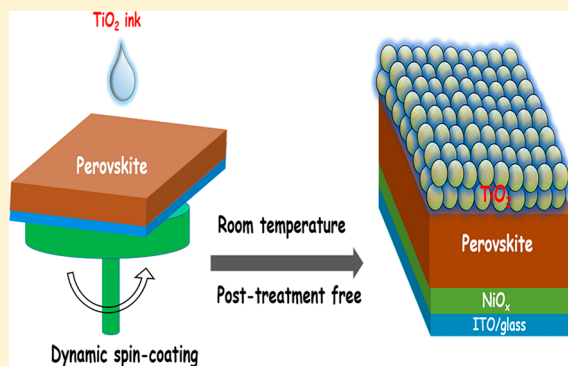
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Supporting Information

ABSTRACT: Simultaneously achieving high efficiency, long-term stability, and robust fabrication with good reproducibility in perovskite solar cells (PVSCs) is essential for their practical applications. Herein, we first demonstrate a thick TiO₂ backbone film directly on top of a perovskite film through a simple room-temperature solution process. Through the strategy of decorating the TiO₂ film with fullerene for passivating traps and filling voids, we achieve a fullerene-decorated TiO₂ electron transport layer (ETL) in inverted PVSCs. Because of the suppressed monomolecular Shockley–Read–Hall recombination and ion diffusion of the fullerene-decorated TiO₂ ETL, stabilized efficiencies of ~20% and shelf life stability remaining over 98% of initial efficiency after aging in ambient conditions or 16 months are achieved. Remarkably, the PVSCs are insensitive to TiO₂ thickness from 50 to 250 nm, which contributes significantly to the robust fabrication and high reproducibility of the PVSCs. This work provides an ETL design on top of a perovskite film for simultaneous improvement of PVSC efficiency, stability, and reproducibility.



Hybrid lead halide perovskite solar cells (PVSCs) are one of the very promising photovoltaic technologies to address the energy crisis because of their efficient conversion of sunlight to electricity with very high power conversion efficiency (PCE) exceeding 23%.^{1,2} For practical applications of PVSCs, it is critical to simultaneously achieve high PCE, long-term stability, and robust fabrication with good reproducibility. The top carrier transport layer (CTL) formed on a perovskite film plays a crucial role not only for achieving well-matched energy level alignment to obtain effective carrier extraction^{1,3} and thus high efficiency but also for suppressing ion diffusion to improve device stability.^{4–6} In particular, it has been indicated that the corrosion of the metal electrodes caused by the diffusion of ions (CH₃NH₃⁺, I[−], Pb²⁺, etc.)^{4,5,7} from perovskite films as well as the destruction of perovskite films by metal ions from electrodes (Ag or Al) or external contaminants (moisture and reactive dopants)⁶ are the main reasons for the degradation of PVSCs. Therefore, besides improving carrier extraction and thus enhancing device efficiency, the strategy of suppressing ion diffusion of the top

CTL for improving the PVSCs' stability has become a main focus of research.

Currently, some inorganic/metal oxide materials have been used as an effective CTL in PVSCs with the combined advantages of good electrical properties and stability, such as NiO,⁸ CuGaO₂,⁹ CuCrO₂,¹⁰ and CuSCN^{11,12} as the hole transport layers (HTLs) and ZnO–MgO,¹³ SnO₂,^{14,15} Zn₂SnO₄,¹⁶ and TiO₂^{17,18} as the electron transport layers (ETL). Among them, using CuSCN and CuGaO₂ as the top HTL on perovskite film and TiO₂ as the bottom ETL in normal structure PVSCs has been demonstrated to show better PCE and stability as compared to 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene (spiro-MeO-TAD).^{9,11} However, simultaneously realizing high performance, stability, and reproducibility from inverted structure PVSCs utilizing an inorganic-based top ETL has rarely been

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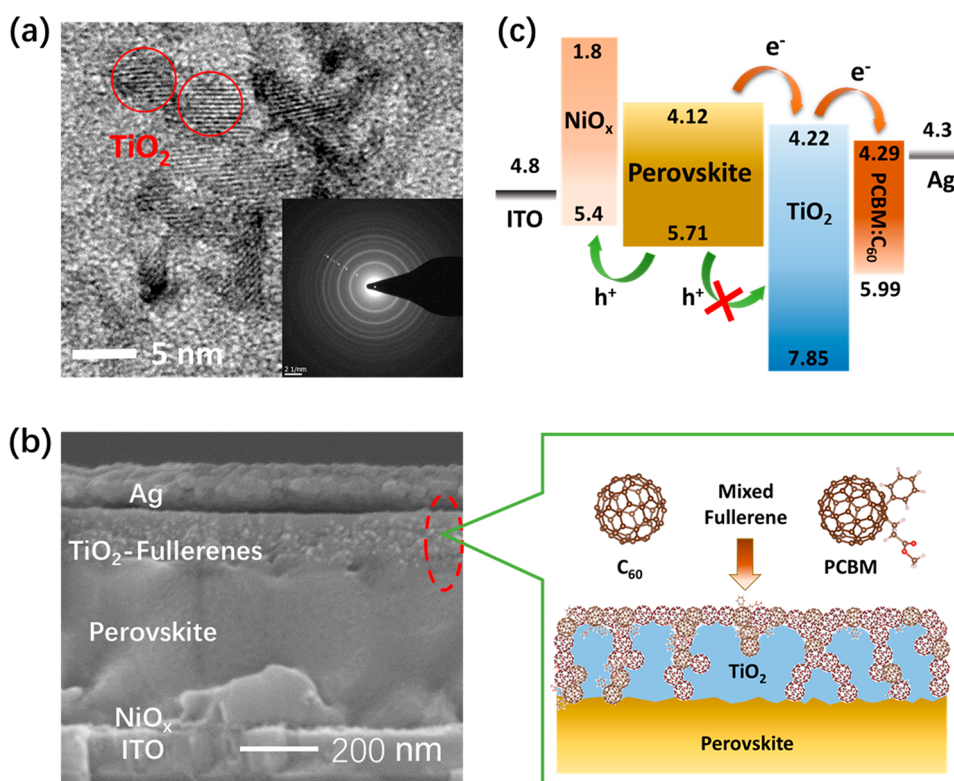


Figure 1. (a) TEM image and the corresponding diffraction pattern of TiO₂ nanocrystals. (b) High-resolution cross-sectional SEM image and the relevant schematic diagram of a complete solar cell with fullerene-decorated TiO₂ as the top ETL. (c) Corresponding energy band diagram of the TiO₂-fullerene-based PVSCs.

reported. For inverted PVSCs, the most-used PCBM and C₆₀ top ETLs with thin thickness of about 20–80 nm cannot effectively resist the inherent ion diffusion between perovskite and electrode⁴ and the attack of H₂O from air.⁶ As a result, the inverted device degradation usually starts from these top ETLs, especially at the interface of the perovskite/ETL^{4,19} or the ETL/metal electrode caused by inherent ion diffusion from layer to layer.⁵ Although the introduction of an ion-blocking layer (e.g., carbon quantum dots,⁴ amine-mediated titanium suboxide (TiO_x),⁵ and atomic layer deposition (ALD)-based SnO_x^{6,20,21}) at the perovskite/organic ETL interface or organic ETL/electrode interface can suppress the ion diffusion, it can result in sacrificing PCE because of the energy level misalignment and inefficient carrier transport of ion-blocking layer as well as increasing fabrication complexity and cost. Increasing the thickness of the top ETL is an effective method to temporarily suppress the diffusion of ions or molecules but will have the trade-off of reducing the device PCE especially in the PCBM-based PVSCs because of its low conductivity.⁴ A recent work demonstrated that device performance and stability of inverted PVSCs can be simultaneously improved by using solution-processed ZnO nanoparticles to modify the interface between PCBM and the metal electrode.²² However, the performance of low-temperature processed inverted PVSCs is still lower than that of the normal structure.^{11,17} To address this issue, it is highly desirable to develop a stable and thick top ETL with appropriate energy level, high electrical conductivity, and effective ion diffusion suppression.

Besides high PCE and long-term stability, high reproducibility is also vital for the practical application of PVSCs. The thick CTL film offers high tolerance to unexpected and inherent variations during the fabrication process, especially on

rough perovskite film, which is essential to enable highly reproducible PVSCs. To deposit a thick, effective CTL with the above-mentioned excellent properties on perovskite film, several fundamental factors including fabrication compatibility with perovskites (e.g., low temperature and compatible solvents), intrinsic stability, electrical conductivity, and energy level properties should be considered comprehensively in choosing the best practical materials. Titanium dioxide (TiO₂) as one of the most widely used ETL materials in normal PVSCs, which is cheap, stable, and safe, has yielded high and stabilized PCEs^{23,24} in normal structure PVSCs, suggesting its excellent properties for optoelectronics application. However, the severe preparation of most TiO₂ films involves high temperature (~500 °C or higher)^{9,11,18} or polar solvents, making the fabrication of a thick TiO₂ ETL directly on susceptible perovskite films challenging.

In this work, we propose and demonstrate the approach to form a thick TiO₂ film on top of perovskite by a simple room-temperature solution process as the backbone of the top ETL in inverted PVSCs. Our results show that the fullerene-decorated TiO₂ films are uniform and void-free, which can effectively suppress the diffusion of ions or molecules from both the perovskite layer and electrode into each other. In addition, the well-matched energy level alignment of NiO_x/perovskite/TiO₂ and excellent electrical conductivity of the fullerene-decorated TiO₂ film remarkably facilitate carrier extraction and transport. Benefiting from these excellent properties of the TiO₂-based top ETL, the inverted PVSCs simultaneously achieved stabilized efficiencies of ~20% and good long-term stability (maintaining >98% and 90% of their initial efficiency after being exposed to ambient air for 16 months and maximum power point (MPP) tracking test under

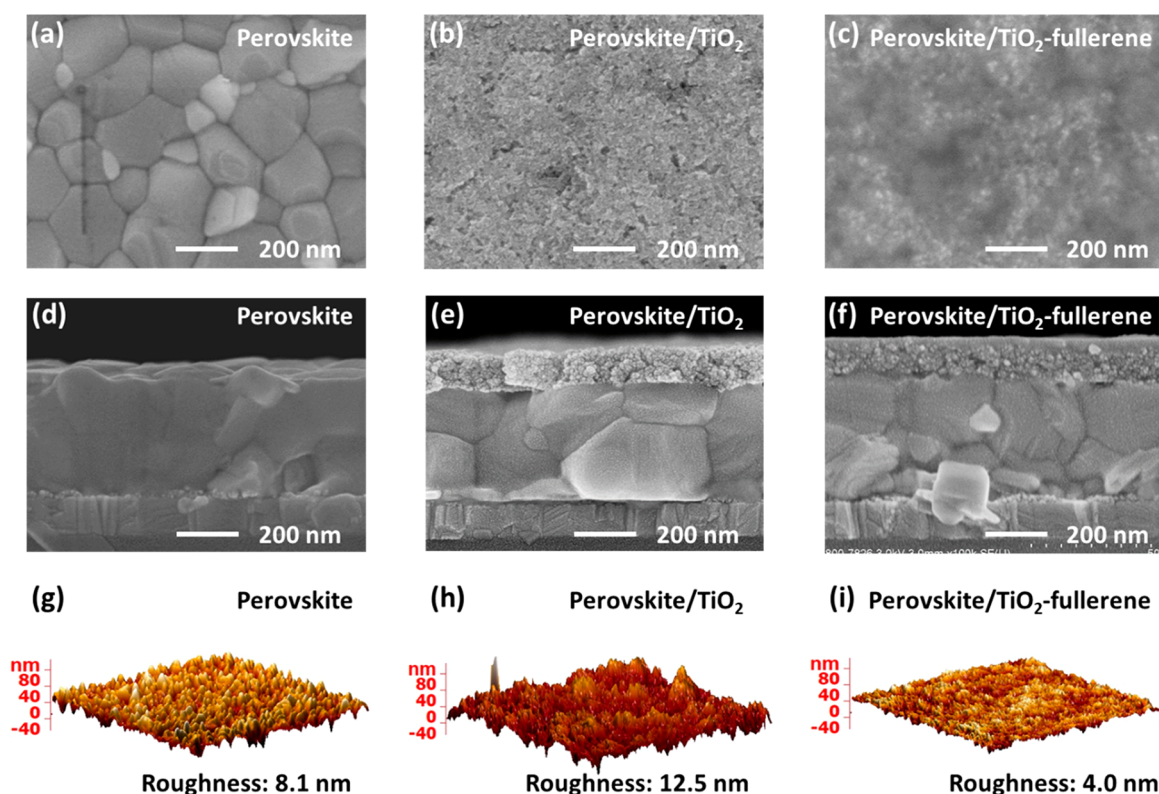


Figure 2. Top-view SEM, cross-sectional SEM, and three-dimensional AFM images. Top-view high-resolution SEM images ($\times 100k$) of (a) perovskite film, (b) TiO_2 film on perovskite, and (c) fullerene-decorated TiO_2 film on perovskite. Cross-sectional SEM images ($\times 100k$) of (d) perovskite film, (e) TiO_2 film on perovskite, and (f) fullerene-decorated TiO_2 film on perovskite. Three-dimensional AFM images of (g) perovskite film, (h) TiO_2 film on perovskite, and (i) fullerene-decorated TiO_2 film on perovskite.

continuous light soaking for 350 h, respectively). Remarkably, the performance of the PVSCs has no clear sensitivity to the TiO_2 film thickness (ranging from about 50 to 250 nm), which significantly contributes to the robust fabrication and high reproducibility of PVSCs for industrial application.

The ligand-free TiO_2 nanocrystals were synthesized by a nonaqueous method^{25,26} as described in the [Supporting Information](#). As shown in [Figure 1a](#), the transmission electron microscopy (TEM) image and its corresponding diffraction pattern show that the diameter of TiO_2 nanocrystals is about 4 nm. The ligand-free feature of the TiO_2 nanocrystals contributes to the formation of the film at room temperature with good electrical properties using a low-boiling-point solvent as described below. To form a thick TiO_2 backbone film on the perovskite layer without destroying the perovskite and perovskite/ TiO_2 layered structure with very good electrical contact in between, we disperse the TiO_2 nanocrystals in ethanol without adding any other ligands to avoid the subsequent annealing or other special treatments (for ligand removal during the film formation). In addition, because of the low surface tension and viscosity of ethanol, the TiO_2 -ethanol solution can form good contact with the perovskite and spread uniformly on the surface of the perovskite film immediately to form a uniform and well-packed film. To effectively prevent the damage of the perovskite (as shown in [Figure S1](#)), the dynamic spin-coating process was adopted to reduce the exposure time of perovskite film to ethanol. Consequently, through the three sequential steps of ligand-free TiO_2 nanocrystals, the use of the low-boiling-point solvent of ethanol, and the introduction of dynamic spin-coating method, we successfully form a TiO_2 ETL backbone with controllable thickness (by changing spin

coating speed) directly on perovskites through a simple room-temperature solution process.

The inverted planar heterojunction PVSCs in this study were fabricated with the structure of glass/ITO/ NiO_x / $\text{Cs}_{0.05}(\text{MA}_{0.15}\text{FA}_{0.85})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3/\text{TiO}_2$ -fullerene/Ag. (The fullerene-decorated TiO_2 film is abbreviated as TiO_2 -fullerene in device structure descriptions and all figures and tables.). The thick TiO_2 ETL (from about 50 to 250 nm) was deposited onto $\text{Cs}_{0.05}(\text{MA}_{0.15}\text{FA}_{0.85})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ perovskite film directly by spin coating the TiO_2 nanocrystal solution and then decorating the as-formed TiO_2 film with mixed fullerene C_{60} and PCBM. Meanwhile, the PVSCs use p-type NiO_x as the bottom HTL on ITO glass. Both of these metal-oxide CTLs were processed at room temperature by spin coating without involving any annealing process. The cross-sectional scanning electron microscopy (SEM) image and the relevant schematic diagram of this device architecture are shown in [Figure 1b](#); the thickness of fullerene-decorated TiO_2 film is around 150 nm. [Figure 1c](#) shows the corresponding energy band diagram of the fullerene-decorated TiO_2 -based perovskite solar cells. The relevant energy levels of each layer are determined by ultraviolet photoelectron spectroscopy ([Figure S2](#)) and ultraviolet–visible absorption spectra ([Figure S3](#)). The corresponding parameters are summarized in [Table S1](#). Because the conductive band (CB) of TiO_2 (about -4.22 eV) is between those of $\text{Cs}_{0.05}(\text{MA}_{0.15}\text{FA}_{0.85})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ perovskite (-4.12 eV) and fullerene mixture PCBM: C_{60} (-4.29 eV), photoexcited electrons in the CB of perovskite can effectively cascade into fullerene mixture via TiO_2 . Simultaneously, TiO_2 has a deeper valence band (-7.85 eV) than that of fullerene mixture (-5.99 eV), which would

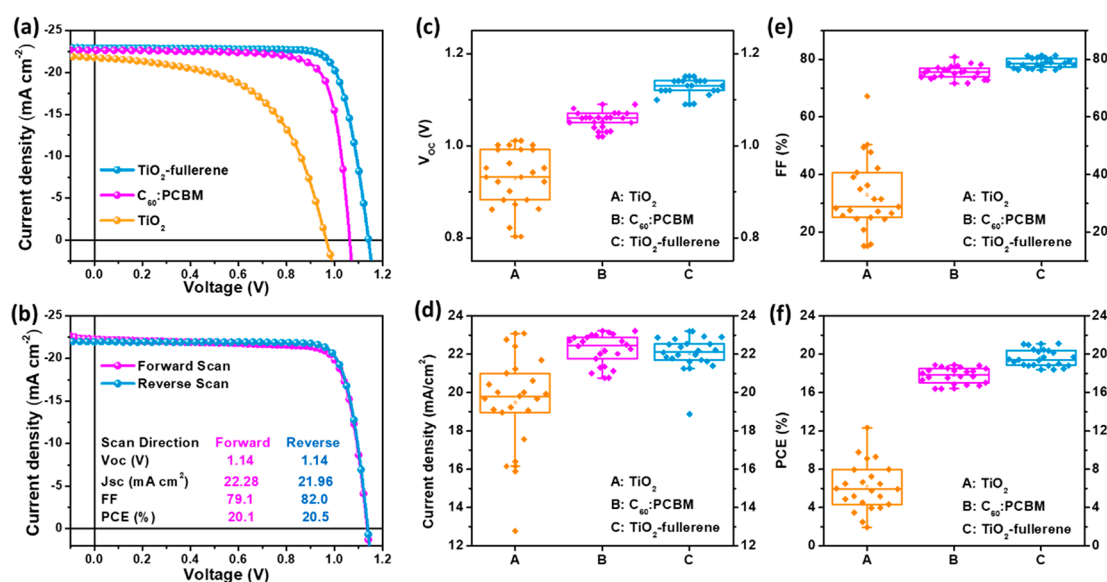


Figure 3. Device performance. (a) J - V curves of PVSCs with the structure of ITO/NiO_x/perovskite/TiO₂/Ag, ITO/NiO_x/perovskite/C₆₀:PCBM/Ag, and ITO/NiO_x/perovskite/TiO₂-fullerene/Ag. (b) J - V curves of fullerene-decorated TiO₂-based PVSCs measured in both reverse and forward scanning directions under AM 1.5G illumination at 100 mW cm⁻². Statistics of device performance V_{oc} (c), J_{sc} (d), FF (e), and PCE (f) of PVSCs with TiO₂, C₆₀:PCBM, and fullerene-decorated TiO₂ as ETLs.

effectively block hole transport and inhibit the carrier recombination at the perovskite/ETL interface and thus enhance the V_{oc} . Therefore, we expect that fullerene-decorated TiO₂ ETL could suppress the interfacial recombination and thus improve the PVSC performance.

The characterization of the morphology of the perovskite film, TiO₂-only, and fullerene-decorated TiO₂ films coated on top of the perovskite film was conducted via top-view SEM, cross-sectional SEM, and three-dimensional atomic force microscopy (AFM), as shown in Figure 2. It can be seen from the cross-sectional SEM image that the thickness of only the TiO₂ film is around 150 nm (in Figure 2e). After fullerene decoration, there is no clear variation of the thickness of the obtained fullerene-decorated TiO₂ film, which is still around 150 nm (in Figure 2f) (i.e., the top ETL is dominated by the TiO₂ material). The surface morphology of the film of only TiO₂ is rough with voids, as shown in Figure 2b,e,h, making it difficult to form good ohmic contact at the interface of TiO₂/silver electrode. Although the perovskite/TiO₂ carrier transport structure possesses the advantage of well-matched energy alignment to achieve higher V_{oc} , the performance of TiO₂-only based PVSCs is extremely poor, as shown in Figure 3. This poor performance is mainly due to imperfect contact and the energy barrier at the interface of TiO₂/silver electrode and the inherent localized trap states in TiO₂ film,^{27,28} which hide the full advantages and potential of the top TiO₂ ETL for inverted PVSCs.

To resolve this interface issue, the TiO₂ film was modified with mixed fullerene C₆₀ and PCBM electron transport materials by spin coating. After this surface modification, the obtained fullerene-decorated TiO₂ film exhibits a uniform and void-free morphology (Figure 2c,f,i). The surface average roughness was reduced significantly from 12.5 nm in TiO₂-only film (Figure 2h) to 4.0 nm in fullerene-decorated TiO₂ film (Figure 2i). The surface modification with fullerene not only fills the inner voids of the TiO₂ backbone but also passivates the inherent localized trap states of TiO₂ film,^{27,29}

which will benefit the device performance and stability (will be discussed later).

Based on the identical perovskite film and device structure, the inverted PVSCs with fullerene-decorated TiO₂ ETL produce an impressive V_{oc} (1.13 ± 0.03 V), fill factor (FF) ($78.73 \pm 1.60\%$), and short-circuit current (J_{sc}) (22.05 ± 0.89 mA cm⁻²), resulting in an overall device PCE of $19.7 \pm 0.85\%$ with improved reproducibility (and less performance deviation, Figure 3c-f) and negligible current hysteresis (Figure S4) in comparison with those with only TiO₂ ($V_{oc} = 0.93 \pm 0.06$ V, FF = $33.09 \pm 12.28\%$, $J_{sc} = 19.46 \pm 2.42$ mA cm⁻², and PCE = $6.13 \pm 2.48\%$) and C₆₀:PCBM ($V_{oc} = 1.05 \pm 0.03$ V, FF = $75.56 \pm 2.22\%$, $J_{sc} = 22.26 \pm 0.75$ mA cm⁻², and PCE = $17.8 \pm 0.81\%$). The current density-voltage (J - V) curves of the optimized fullerene-decorated TiO₂ PVSCs without obvious J - V hysteresis are presented in Figure 3b. The V_{oc} of 1.14 V, FF of 82%, and J_{sc} of 21.96 mA cm⁻² were achieved, resulting in an overall device efficiency of 20.5% for reverse scan direction (from 1.2 V to -0.1 V with the scan rate of 0.1 V/s). For the forward scan direction (from -0.1 V to 1.2 V with the scan rate of 0.1 V/s), an overall device efficiency of 20.1% was achieved with the V_{oc} of 1.14 V, FF of 79.1%, and J_{sc} of 22.28 mA cm⁻². The integration of the incident-photon-to-current efficiency (IPCE) over the AM 1.5 solar emission spectrum produces photocurrent (21.10 mA cm⁻²) that is in close agreement (within 5%) with the J_{sc} derived from the corresponding J - V curve (see Figure S5), showing negligible spectral mismatch of our solar simulator with the standard solar light. We also monitored the power output with time (Figure S6). The photocurrent of fullerene-decorated TiO₂ PVSCs stabilizes within seconds to approximately 20.65 mA cm⁻², yielding a stabilized PCE of $\sim 20\%$, measured after 60 s. More importantly, the PCE of fullerene-decorated TiO₂-based PVSCs is insensitive to the thickness variation, remaining around 19.0% when the thickness of TiO₂ ETL is changed from about 50 nm to 250 nm as shown in Figure S7. The relatively higher V_{oc} and FF and the insensitive efficiency to the ETL thickness mainly arise from the synergetic effects of the

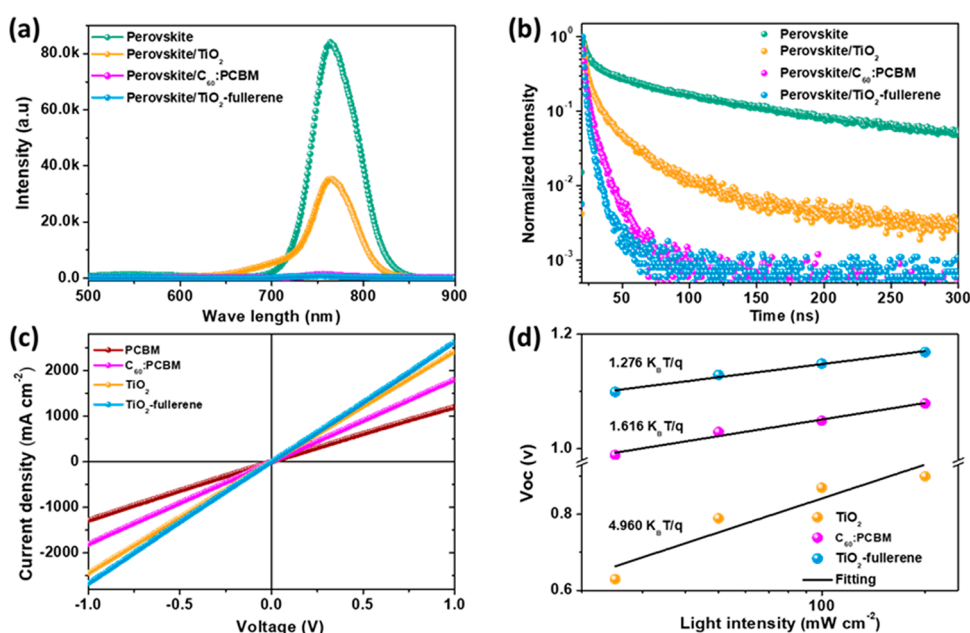


Figure 4. Charge transport properties. (a) Photoluminescence of perovskite film and perovskite film in contact with different ETLs: TiO_2 , C_{60} :PCBM, and fullerene-decorated TiO_2 . (b) TRPL characteristics of those structure devices of quartz/perovskite, quartz/perovskite/ TiO_2 , quartz/perovskite/ C_{60} :PCBM, and quartz/perovskite/ TiO_2 -fullerene. (c) Dark J - V characteristics of glass/ITO/PCBM/Ag, glass/ITO/ C_{60} :PCBM/Ag, glass/ITO/ TiO_2 /Ag, and glass/ITO/ TiO_2 -fullerene/Ag. (d) Open-circuit voltage dependent on the light intensity of the TiO_2 -based PSCs, C_{60} :PCBM-based PVSCs, and fullerene-decorated TiO_2 -based PVSCs.

fullerene-decorated TiO_2 film, e.g., suitable energy level, high conductivity, smooth surface, etc., which allows more efficient electron extraction and transport from the perovskite film to silver electrode.

To evaluate the electron extraction dynamics, the steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) of quartz/perovskite with different top ETLs were studied (Figures 4a,b). On contact with the ETL, perovskite films typically exhibit strong PL quenching as evidence of efficient carrier transfer from the perovskite photoactive layer to the ETL. Figure 4a shows the steady-state PL of quartz/perovskite, quartz/perovskite/ TiO_2 , quartz/perovskite/ C_{60} :PCBM, and quartz/perovskite/ TiO_2 -fullerene. A clear decrement of PL intensity in the quartz/perovskite/ETL film is observed compared to that of quartz/perovskite, especially in quartz/perovskite/ C_{60} :PCBM and quartz/perovskite/ TiO_2 -fullerene films. The corresponding TRPL measurements of these films are shown in Figure 4b. Fitting the data with biexponential decay yields a fast decay (τ_1) component and a slow decay (τ_2) component, and the detailed parameters are summarized in Table S2. The fast decay is originated from the quenching of charge carriers by the ETL contact, and the slow decay component could be attributed to the radiative recombination of free charge carriers before the carrier collection.^{30,31}

In the case of quartz/perovskite, the fast decay lifetime was $\tau_1 = 15.03$ ns with the ratio of 27.88% and the slow decay lifetime was $\tau_2 = 144.46$ ns with the ratio of 72.12%, suggesting that the depopulation of photogenerated carriers was dominated by radiative recombination in the perovskite film. In contrast, for quartz/perovskite/ TiO_2 , both τ_1 and τ_2 were shortened to 7.24 and 41.64 ns with the ratio of 80.18% and 19.82%, respectively, and τ_1 dominated the PL decay, which can be interpreted as a fast carrier transfer from perovskite to TiO_2 film. Notably, the films based on quartz/perovskite/

C_{60} :PCBM and quartz/perovskite/ TiO_2 -fullerene reveal a faster carrier transfer and more efficient collection. Particularly, for quartz/perovskite/ TiO_2 -fullerene, both τ_1 and τ_2 were shortened to 2.40 and 11.10 ns with the ratios of 91.07% and 8.93%, respectively, which are attributed to high conductivity and small interfacial recombination of fullerene-decorated TiO_2 film as compared to that of C_{60} :PCBM and TiO_2 . Consequently, our results show that the fullerene-decorated TiO_2 can extract photogenerated carriers from the perovskite layer more effectively.

The electrical conductivity of different ETL films was also analyzed by measuring the J - V curve of glass/ITO/PCBM/Ag, glass/ITO/ C_{60} :PCBM/Ag, glass/ITO/ TiO_2 /Ag, and glass/ITO/ TiO_2 -fullerene/Ag devices in dark conditions as shown in Figure 4c. The direct current (DC) conductivity (σ_0) is extracted from the J - V plot using the equation $J = \sigma_0 A d^{-1} V$, where A is the active area and d is the thickness of the sample. The extracted results (in Figure S8) show that the fullerene-decorated TiO_2 film exhibits a conductivity (3.11×10^{-4} S/cm) higher than that of PCBM (0.85×10^{-4} S/cm), C_{60} :PCBM (1.51×10^{-4} S/cm), and TiO_2 (2.44×10^{-4} S/cm), which is a benefit of the better quality of the fullerene-decorated TiO_2 film and improved TiO_2 /silver contact in the glass/ITO/ TiO_2 -fullerene/Ag device. As shown in Figure S7, benefiting from the higher electrical conductivity of fullerene-decorated TiO_2 film (about 3.7 times higher than that of PCBM film), the efficiencies of fullerene-decorated TiO_2 -based PVSCs (maintained around 19.0%) were almost insensitive to the changing TiO_2 film thickness (from about 50 to 250 nm), implying a better charge transport within the fullerene-decorated TiO_2 layer. This thickness-insensitive property also contributes to the improvement of device reproducibility.

To better understand the recombination mechanism of photogenerated carriers during device operation, the dependence of the V_{oc} on light intensity was studied.^{32–34} In principle,

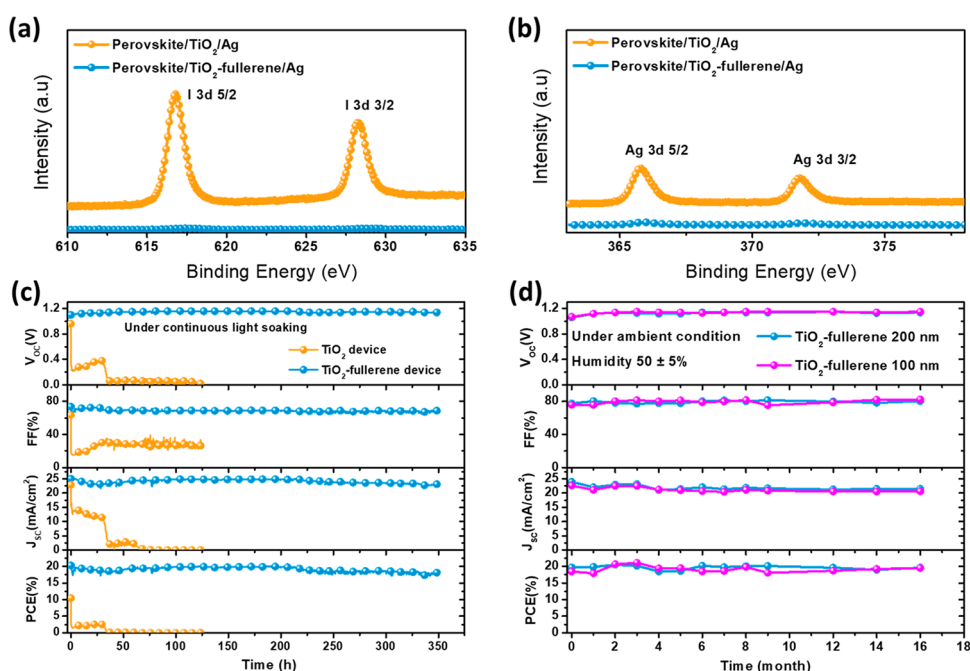


Figure 5. X-ray photoelectron spectroscopy (XPS) spectra in TiO_2 and fullerene-decorated TiO_2 charge transport layer and the device stability. (a) High-resolution XPS spectra of iodide (I). (b) High-resolution XPS spectra of silver (Ag). (c) Maximum power point tracking of the TiO_2 -based PVSCs and fullerene-decorated TiO_2 -based PVSCs aged under continuous 1 sun illumination soaking. The illumination source was a white LED lamp. (d) Shelf life stability results of PVSCs with 100 and 200 nm fullerene-decorated TiO_2 -based aged under ambient conditions, measured under AM 1.5G illumination at 100 mW cm^{-2} .

the slope of V_{oc} versus light intensity close to $1 K_B T/q$ indicates that the main recombination mechanism is monomolecular recombination (i.e., Shockley–Read–Hall (SRH) recombination), while a factor of 2 indicates a bimolecular recombination (band to band recombination).³⁴ As shown in Figure 4d, the slopes of the linearly fitting V_{oc} versus log-scaled light intensity in the PVSCs based on TiO_2 , C_{60} :PCBM, and fullerene-decorated TiO_2 were calculated to be $4.960 K_B T/q$, $1.616 K_B T/q$ and $1.276 K_B T/q$, respectively. The lower slope value of $1.276 K_B T/q$ in fullerene-decorated TiO_2 -based PVSCs suggests that the monomolecular recombination is dominated in this device, which means the fullerene-decorated TiO_2 can effectively reduce trap-mediated recombination compared with C_{60} :PCBM and TiO_2 , especially compared with the TiO_2 -only based PVSCs with $4.96 K_B T/q$. Consequently, the efficient collection of the electrons by fullerene-decorated TiO_2 contributes to the enhanced V_{oc} and FF. This agrees well with the observed trends in device performances described previously (see Figure 3a,c,e).

Despite the high PCE, one major concern is PVSC stability for practical applications. Current research results show that suppressing the diffusion of ions or molecules through the ETL is essential to inhibit the corrosion of the metal electrode and the destruction of the perovskite film for preventing device degradation.^{4–7} To scrutinize the ionic suppressing capability of the fullerene-decorated TiO_2 film, we compared the X-ray photoelectron spectroscopy (XPS) spectra from the films of TiO_2 and fullerene-decorated TiO_2 which were deposited on top of perovskite film followed by deposition of around 5 nm of silver on top. These films were soaked under continuous light for 100 h to accelerate the diffusion of ions or molecules. To get a fair comparison, the TiO_2 -only and fullerene-decorated TiO_2 films are the same thickness ($\sim 150 \text{ nm}$), and the XPS signal was obtained from the same sputtering

depth ($\sim 70 \text{ nm}$) in both films. The signal from the ions or molecules of perovskite, especially the signal of iodide (I) (in Figure 5a), in the TiO_2 -only film is obvious. In contrast, there was no clear signal of these ions or molecules in fullerene-decorated TiO_2 film, which indicates that the fullerene-decorated TiO_2 layer blocked the diffusion of ions or molecules from perovskite effectively. In addition, the obvious signal from silver (Ag) in the TiO_2 -only layer was also observed from the XPS result in Figure 5b, which will accelerate the device degradation because of the formation of an insulating Ag–I bond.⁵ However, there is only a weak silver signal in fullerene-decorated TiO_2 film, suggesting that the silver ion diffusion from the silver electrode to fullerene-decorated TiO_2 was also suppressed effectively.

To further identify the relationships between the ion-blocking capability of top ETL and device stability, the long-term stability of TiO_2 -only based and fullerene-decorated TiO_2 -based PVSCs with encapsulation was monitored. The encapsulated devices were tested by maximum power point (MPP) tracking under continuous light soaking in ambient conditions at $\sim 30^\circ \text{C}$ with $50 \pm 5\%$ humidity. As shown in Figure 5c, the TiO_2 -only based devices degraded dramatically with a rapid drop in PCE to almost zero after only 30 h. Encouragingly, the fullerene-decorated TiO_2 -based device remains $\sim 90\%$ of its initial PCE (18.1% vs 20.3%) after 350 h MPP tracking test, which benefits from the passivation and filling of the fullerene mixture. As shown in Figure S9, the fullerene mixture-based devices also show good stability. As a result, the fullerene-decorated TiO_2 -based PVSCs achieve excellent efficiency retention of high PCE of $\sim 19.7\%$ after 16 months of storage in ambient conditions (Figure 5d), which is 98.5% of its initial PCE ($\sim 20.0\%$). Evolution of other device parameters (V_{oc} , FF, and J_{sc}) during the aging process are also presented in Figure 5c,d. When the ion diffusion results from

XPS are combined with the stability monitoring during the device aging process, the fullerene-decorated TiO₂-based PVSCs are seen to be much more stable with negligible degradation as compared with TiO₂-only based devices after the same aging tests. Consequently, our results strongly suggest that the thick TiO₂ layer decorated with fullerene can very effectively suppress ion diffusion for achieving long-term stable PVSCs.

In summary, we demonstrate room-temperature solution-processed TiO₂ as the backbone of an efficient top ETL on perovskite for inverted PVSCs. Together with the decoration of the TiO₂ film with fullerene for passivating its trap and filling its voids, we demonstrate a fullerene-decorated TiO₂ ETL for achieving high PCE, stability, and reproducibility simultaneously in inverted PVSCs. The well-matched energy level alignment of NiO_x/perovskite/TiO₂ charge transport structure and good conductivity of the fullerene-decorated TiO₂ film improves carrier transport and reduces interface recombination to enable a high V_{oc} of 1.13 ± 0.03 V and FF of $78.73 \pm 1.60\%$ and finally achieve stabilized PCE of $\sim 20\%$. In addition, the XPS analysis and device stability testing show that the suppressed diffusion of ions or molecules from both the perovskite layer and metal electrode by the fullerene-decorated TiO₂ film significantly improves device stability. Meanwhile, the insensitive dependence of the device efficiency to TiO₂ layer thickness is very beneficial to large-scale robust industrial production (i.e., roll-to-roll manufacturing). To achieve large-area perovskite modules for practical applications, selection of suitable solvents for dispersing TiO₂ nanoparticles and modification of the surface of perovskite films with solvent resistance shall be further investigated. Consequently, this work contributes an important foundation for utilizing an inorganic material-based ETL directly on perovskite to realize high efficiency, stability, and reproducibility in PVSCs for promoting their practical applications.

EXPERIMENTAL METHODS

See the [Supporting Information](#).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsenergylett.8b01507](https://doi.org/10.1021/acsenergylett.8b01507).

Experimental details and additional results ([PDF](#))

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Notes

The authors declare no competing financial interest.

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