Low-temperature processed ultrathin TiO₂ for efficient planar heterojunction perovskite solar cells

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Abstract: *A compact TiO₂ (c-TiO₂) layer fabricated by spin coating or spray pyrolysis following a high-temperature sintering is a routine in high-performance planar heterojunction perovskite solar cells.* Here, we demonstrate an effective low-temperature approach to fabricate an ultrathin and discrete TiO₂ (u-TiO₂) for enhancing photovoltaic performance of perovskite solar cells. Via hydrolysis of low-concentration TiCl₄ solution at 70 °C, u-TiO₂ was grown on a fluorine doped tin oxide (FTO) substrate, forming the electron selective contact with the photoactive CH₃NH₃PbI₃ film. The perovskite solar cell using u-TiO₂ achieves an efficiency of 13.42%, which is compared to 13.56% of the device using c-TiO₂ prepared by high-temperature sintering. Cyclic voltammetry, steady-state photoluminescence spectroscopy and electrical impedance spectroscopy were conducted to study interface engineering and charge carrier dynamics. Our results suggest that u-TiO₂ functions as a bridge for electron transport between perovskite and FTO, which accelerates electron transfer and alleviates charge recombination.

Keywords: perovskite solar cells, electron selective layer, low-temperature process, ultrathin TiO₂, charge transfer

1. Introduction

Organic-inorganic perovskite solar cells (PVSCs) have encouraged the whole world's ambition toward the solar energy utilization due to the soaring increase in device performance [1-5]. Due to low-cost starting materials and simple solution procedures, organolead halide perovskites have thus revolutionized the photovoltaic field. PVSCs evolved from solid state dye sensitized solar cells (DSSCs), where compact TiO₂ (c-TiO₂) layers facilitating electron transfer and mesoporous TiO₂ (m-TiO₂) layers serving as the scaffold for perovskite growth, thus was termed as a mesoscopic PVSCs structure [6-8]. To date, the record cell efficiency has been certified at 20.1%,

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1 which was achieved with state-of the-art mesoscopic structured device [9]. Usually, the
2 photoactive perovskite layer is sandwiched between an electron-selective layer (ESL) and a
3 hole-selective layer (HSL) [10, 11]. *Due to the superior charge transfer capability of the*
4 *perovskite materials caused by high mobility and large charge diffusion length [12, 13], the*
5 *ESL-free and HSL-free PSCs with remarkable efficiency and stability have also been published*
6 *[14-16].* The interface between the ESL or HSL and perovskite film plays a key role in further
7 improving photovoltaic performance [17]. Ideally, ESL or HSL should possess a high
8 transmission, suitable energy level matching, sufficient conductivity, and excellent charge
9 extraction capacity.

10 Currently, c-TiO₂ films have been successfully used as ESLs. *Unfortunately, c-TiO₂ films are*
11 *usually deposited by spray pyrolysis or spin coating techniques [18, 19]. High-temperature*
12 *sintering (500 °C) allows the amorphous TiO₂ film transform into the crystalline anatase [20,*
13 *21].* In view of future commercialization, planar PVSCs with low-temperature (<100 °C) process
14 have attracted intense attention due to the simple device structure and compatibility with flexible
15 substrates [22, 23]. *Advanced TiO₂ deposition with low-temperature have therefore been*
16 *developed*, including atomic layer deposition [24], magnetron sputtering [25], hydrothermal
17 process [26], and TiCl₄ hydrolysis [27]. Among these, chemical bath deposition of TiO₂ from
18 TiCl₄ hydrolysis is a facile method to deposit TiO₂ film or modify the surface of the m-TiO₂ layer
19 in DSSCs, resulting in desired TiO₂ film via retarding charge recombination [28-30]. *Yella et al.*
20 *first reported a rutile nanocrystalline TiO₂ via hydrolysis of high-concentration TiCl₄ solution*
21 *at 70 °C as an efficient ESL for PVSC [27].* Cojocar et al. also suggested TiCl₄ solution
22 treatment of c-TiO₂ layers for efficient PVSCs [31]. The low-temperature c-TiO₂ film composed
23 of the interconnected anatase TiO₂ nanoparticles enhanced efficiency of mesoscopic PVSCs,
24 reported by Wojciechowski et al. [32]. In one words, previous works focused on high quality TiO₂
25 layers, *which guarantees smooth surface morphology and intimate contact with perovskite.*
26 These high-quality TiO₂ films are similar to those fabricated by the atomic layer deposition or
27 magnetron sputtering.

28 In this study, we employed a facile hydrolysis of low concentration TiCl₄ solution at 70 °C to
29 modify the naked FTO substrates. As a result, we obtained an ultrathin and discrete TiO₂ (u-TiO₂)
30 by the hydrolyzed TiO₂ particles. *u-TiO₂ readily fascinates charge transport, reduce the charge*

recombination between the FTO/perovskite interface. Compared with the naked FTO based PVSCs, improved photocurrent, photovoltage, and fill factor were obtained. Planar heterojunction PVSCs based on u-TiO₂ presents the photoelectric conversion efficiency (PCE) to as much as 13.42%, which is comparable to that (13.56%) of PVSCs based c-TiO₂ layer with high-temperature sintering. It is worth noting that this type of u-TiO₂ is different from previously reported m-TiO₂ or c-TiO₂ ESLs. Our results suggest that this type of u-TiO₂ improves the adhesion between FTO/perovskite interface, in which TiCl₄ treatment may be just as the surface modifier rather than pinhole-free and uniform c-TiO₂ builder.

2. Experimental

2.1. Materials

Lead chloride (PbCl₂, 99.99%), 4-tert-Butylpyridine (4-tBP) and TiCl₄ were purchased from Sigma-Aldrich, CH₃NH₃I synthesized as reported, Li-bis (trifluoromethanesulfonyl) imide (Li-TFSI) from Acros, spiro-MeOTAD (99.0%) from Shenzhen Feiming Science and Technology Co. Ltd. All materials were used as received without any purification.

2.2 Device fabrication

FTO coated glass substrates (Nippon, 15Ω/□) were cleaned by ultrasonication in deionized water, ethanol and acetone for 10 min, respectively. And then the substrates were immersed into different concentration of aqueous TiCl₄ solution at 70 °C for various reaction times. Subsequently, the treated substrates were washed with deionized water and dried at 150 °C in air for 30 min. For c-TiO₂ substrates, the TiO₂ film was deposited onto a FTO substrate by spin coating a titanium propoxide solution and then sintered at 450 °C for 30 min. To deposit the perovskite layer, a 1:3 ratio of PbCl₂/CH₃NH₃I (0.8 M and 2.4 M) was mixed in dimethyl formamide. The blend solution was spin-coated on these substrates at 2000 rpm for 30 s and carefully heated to form a uniform perovskite film, the final annealing temperature is 95 °C for 40min. The details please refer to our previous report [33]. After that, a spiro-OMeTAD/chlorobenzene(72.3 mg mL⁻¹) solution was spin-coated on the perovskite film at 3000 rpm for 30 s. At last, ~ 100 nm thick Ag electrode was evaporated as the back contact. All the cells we measured using a non-reflective metal mask. The width and the interval space of the Ag stripes are 4 mm and 3 mm, respectively. The effective area of the cell was defined to be 0.07 cm².

2.3 Measurement and characterization

The top view images of the TiCl_4 treated FTO substrates and the perovskite films were studied by a scanning electron microscope (SEM, Hitachi, SU-70, Japan). X-ray diffraction patterns (XRD) of the deposited perovskite thin films were measured using a Bruker instrument (D8 advance, Bruker, German) using Cu K α radiation. Atomic force microscope (AFM) topographic images of the TiCl_4 treated FTO substrates were taken via a Bruker Dimension 5000 Scanning Probe Microscope (SPM) in tapping mode. The cyclic voltammetry (CV) was performed with the three electrode system, using Pt wire as the counter electrode, the saturated calomel electrode (SCE) as the reference electrode, and the different substrates as the working electrodes. The supporting electrolyte is 0.5 M LiClO_4 in dry acetonitrile. Steady-state photoluminescence spectroscopy (PL) (excitation at 406.2 nm) and the time-resolved photoluminescence (TRPL) (excitation at 406.2 nm and emission at 760 nm) were measured with an Edinburgh Instruments FLS 920 fluorescence spectrometer. Current-Voltage (I - V) characteristics were measured by an additional voltage from the 2400 system source meter (Keithley) together with a sunlight simulator (Newport Solar Simulator 91192, AM 1.5, 100 mW cm^{-2}) calibrated with a standard silicon reference cell. The incident photo-current conversion efficiency (IPCE) spectrum was collected by a IPCE system (Newport 2936-c power meter) in the 300–800 nm wavelength range under the irradiation of a 300 W xenon light source with an Oriel Cornerstone 260 1/4 monochromator in DC mode. Impedance spectra were measured with an electrochemical workstation (Zennium, Germany) under 1 sun illumination at 0 V bias relative to the open circuit potential. The scanning frequency was set between 10^6 Hz and 100 MHz and the amplitude of 10 mV as the sine perturbation bias.

3. Results and discussion

The device fabrication was performed on the naked FTO substrate treated by low-concentration TiCl_4 solution (40 mM) at 70 °C. This surface treatment was performed for varied times to ensure the desired surface modification. Figure 1(a) shows the device configuration of the perovskite solar cells based on FTO- TiCl_4 substrate. We performed the cross-sectional view of the device using scanning electron microscopy (SEM) in figure 1(c, d). As we can see, the obvious TiO_2 layer did not appear at the FTO/perovskite interface in figure 1(c), which is in contrast to c- TiO_2 based PVSCs in figure 1(d). The surface morphologies of FTO- TiCl_4 substrates treated with different time were then also investigated. Figure 2(a-d) compares the SEM images of FTO surfaces after being treated by TiCl_4 solution for 0 h, 0.5 h, 2 h, and 10 h. The naked FTO substrates consist of

typical tin oxide crystals as shown in figure 2(a), which have large edges and corners and present a slightly irregular morphology. From figure 2(b-d), we can see that the TiCl_4 solution treatment changed the FTO surface morphology. In figure 2(b), lots of particles were distributed on the FTO surface when the FTO substrate was treated only 0.5 h. These particles were proved to be TiO_2 by X-ray photoelectron spectroscopy (XPS) measurement (figure 2S), in which the obvious binding energy of 458.6 and 464.4 eV corresponding to Ti 2p $3/2$ and Ti 2p $1/2$ peak is the distinct characteristic of Ti^{4+} in TiO_2 , and the binding energy of 530.5 eV is attributed to the O 1s, which can be inferred as the O^{2-} state in TiO_2 . This result confirms the fact that even the low concentration TiCl_4 can hydrolyze and form TiO_2 particles. In figure 2(c), the small size of hydrolyzed TiO_2 particles aggregated onto the crystals and tiny spots emerged with the extension of time. For 10 h treatment, more and more tiny spots appeared and connected with each other, presenting the cotton-shaped structure as shown in figure 2(d). This confirms that the TiO_2 do not form a continuous compact film on the FTO substrate, and the surface morphology is significantly different with the c- TiO_2 and mesoporous TiO_2 scaffold(m- TiO_2) as given in figure 1S(a, b). The high concentration TiCl_4 solution also was used in order to compare the results. When the FTO substrate was treated by the high concentration TiCl_4 (200 mM) for 2 h, the bar and mesh structure was developed, which almost completely covers the whole naked FTO surface as shown in figure 2(e). In figure 2(f), when the FTO substrate was treated by the high concentration TiCl_4 with 400 mM for 2 h, the flower-like TiO_2 was grown on the FTO surface as the previous literature was reported [27].

The surface morphologies were further investigated by AFM. Figure 3S shows the surface topographical images comparing the FTO surfaces before and after TiCl_4 treatment. For the naked FTO surface, the surface roughness value of the root mean square (RMS) is 11.0 nm for the whole scanned area. After TiCl_4 treatment for 0.5 h, the nanoscale TiO_2 particles formed on the FTO surface, and the RMS was slightly increased to 12.3 nm. Along with the increased treated time, the aggregation of the nanoscale TiO_2 particles result in a reduced RMS (11.5 nm). While for 10 h treatment, more and more tiny TiO_2 spots appeared and lead to the increased RMS (12.4 nm). These results were consistent with the SEM images in figure 2.

The transmission spectra of different FTO substrates were presented in figure 3. As we can see, the naked FTO substrates exhibit the considerable transmission, which presents the transmittance

of about 85% during the whole visible spectrum. The FTO-TiCl₄ substrates present slightly reduced transmittance, indicating the morphology change of the FTO substrates. However, the FTO-TiO₂ substrates exhibit the obviously reduced transmission due to the absorption to TiO₂. Therefore, we can conclude that the high transmission allows maximum photonflux to reach the absorber layer for photon-generated carriers.

The device performance was investigated when the different FTO substrates were used. In figure 4(a), the *J-V* curves of PVSCs based on different TiO₂ layers under simulated AM 1.5G solar irradiation (100 mW/cm²) are given. PVSCs based on the naked FTO substrate without any treatment exhibited an open circuit voltage (*V_{oc}*) of 0.902 V, a short-circuit current (*J_{sc}*) of 11.63 mA/cm², a fill factor (FF) of 48.3% and a low PCE of 5.07%. The best device base on FTO-TiCl₄ substrate for 2 h provides a PCE of 13.42% with a *V_{oc}* of 1.04 V, a *J_{sc}* of 22.10 mA cm⁻² and an FF of 58.4%, which is compared with that (13.56%) of the device based on FTO-TiO₂ substrate via a high-temperature sintering. Detailed photovoltaic parameters of the devices based on different substrates are shown in table 1. In figure 4S, the devices based on treated substrates by high concentration of TiCl₄ solution(200 mM and 400 mM) present PCEs over 10% as shown in table 1S, which is similar to the previous results [27]. In resemble to the other planar device based on TiO₂/perovskite/Spiro-OMeTAD structure, the present structure also showed hysteresis (figure 5S), depending on the scanning direction, which needs further and deeper investigation. Figure 4 (b) shows the incident photon-to-current conversion efficiency (IPCE) spectrum of this cell. The IPCE spectra shows efficiencies of about 80% in the wavelength range of 400-760 nm, giving an integrated *J_{sc}* of 21.08 mA cm⁻², which is close to the value derived from the *J-V* measurement. Obviously, the devices based on FTO-TiCl₄ substrates improve the *J_{sc}*, *V_{oc}*, FF and thus the enhanced PCE.

The improved device performance originates from the photoactive morphology and interface due to the incorporation of u-TiO₂. To investigate the impact of TiCl₄ treatment on the morphology of perovskite film, the CH₃NH₃PbI_{3-x}Cl_x films was developed on naked FTO and treated FTO substrates via a one-step method. Figure 5(a) shows the surface morphology of perovskite films without TiCl₄ treatment. It is found that several pinholes with the size of ~ 900 nm appear in the perovskite film, and the bare tin oxides underneath, as is determined by the SEM images. These distinct pinholes suggest the incomplete coverage of perovskite film, which can

1 lead to low-resistance shunting paths thus affecting the performance of final devices. However,
2 figure 5(b) shows the greatly improved quality of perovskite films, in which few pinholes were
3 observed, suggesting the complete coverage of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films.

4 The residual organic species absorbed on FTO substrates can result in somewhat hydrophobic
5 and this has detrimental effect on the formation of perovskite films [16]. As a result, rough
6 perovskite film with pin-holes can be easily obtained. Ultra-violet/ozone (UVO) treatment is
7 widely used to clean surface and can significantly reduce the contact angle of the polar solvents.
8 We found that low concentration TiCl_4 treatment also enhance the wettability of metal oxides. We
9 measured the contact angle of the different surface as shown in figure 6. The static contact angles
10 of deionized water is 70.9° on the naked FTO substrates, while the static contact angles is only
11 26.8° on the FTO- TiCl_4 substrates, which is compared to the value of the UVO treated FTO
12 substrates and FTO- TiO_2 substrates. Improved hydrophilicity allows the perovskite precursor
13 solution to well spread on the substrate and favor the growth of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films, both of
14 which improved the film quality, as shown in figure 5. To further compare the impact of TiCl_4
15 treatment on the property of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films, XRD patterns of the two films were studied
16 in figure 6S. It was observed that all these perovskite diffraction peaks became significantly
17 enhanced with the treatment of TiCl_4 , indicative of the improvements in the crystalline property of
18 the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film.

19 Interface or surface engineering is often utilized for performance optimization in optoelectronic
20 devices, such as organic solar cells, solid-state DSSCs, etc. Recent reports also demonstrated the
21 importance of interfaces in perovskite solar cells [17, 34]. A compact electron-selective contact,
22 such as TiO_2 or ZnO , is believed to be a necessary layer for highly efficient perovskite-based solar
23 cells [35]. In the present work, the efficient electron-selective contact was achieved by modifying
24 the FTO surface with low-concentration TiCl_4 solution. Modification of FTO could tune the
25 surface work function and establish better ohmic contacts between the active layer and FTO.
26 Cyclic voltammetry (CV) is a useful tool to investigate the energy states of the semiconductor [36,
27 37]. In this work, CV was employed to study the surface potential changes for FTO before and
28 after TiCl_4 treatment. As we all know, the onset potential can be used to estimate the conduction
29 band edge of the semiconductor during the reverse scan. *From figure 7(a), we can see upon*
30 *increasing the negative applied potential as the arrow indicated, the onset potential of the*

1 *treated FTO-TiCl₄ substrates moves much negatively compared with the untreated ones, and*
2 *nearly the same with c-TiO₂ film indicating the much improved ability of accepting electrons.*
3 *The obtained onset potentials are 0,093 V, -0.226 V, and -0.16 V (V vs SCE) for FTO,*
4 *FTO-TiO₂, and FTO-TiCl₄ substrate, respectively. We can conclude that the conduction band*
5 *edge of FTO-TiCl₄ surface is upshifted compared with FTO, which better aligns with the*
6 *perovskite absorber. Thus this FTO-TiCl₄ interface could facilitate the electron collection from*
7 *the perovskite layer to the FTO substrate. Although TiCl₄ treatment do not form a continuous*
8 *and compact layer, the function of electron selection is achieved, which is different from the*
9 *conventional compact metal oxide contacts.* In other words, FTO is fluorine doped tin oxide,
10 which is also a compact metal oxide film like TiO₂ or ZnO [35]. FTO film provides the metallic
11 property. Thus, the FTO-TiCl₄ substrate could be acted as the compact n-doped FTO in the
12 surface of bulk FTO film, resulting in the improved ohmic contact between perovskite materials
13 and an FTO conducting substrate.

14 The impact of TiCl₄ treatment on charge transfer properties of the perovskite film was further
15 discussed by steady-state photo-luminescence (PL) spectroscopy. Figure 7(b) shows the PL
16 spectra of the FTO/perovskite, FTO-TiO₂/perovskite and FTO-TiCl₄/perovskite films. Compared
17 with the FTO/perovskite interface, *substantial PL quenching was occurred within*
18 *FTO-TiO₂/perovskite and FTO-TiCl₄/perovskite interface.* This result indicates that the electron
19 injection from perovskite to FTO is slower than the electron injection from perovskite to TiO₂.
20 Interestingly, PL quenching was greatly degraded when the perovskite was deposited on
21 FTO-TiCl₄ substrate, which is lower than that of the perovskite deposited on FTO-TiO₂ layer. This
22 means that the charge transfer between perovskite and u-TiO₂ film is more efficient, indicating the
23 suppression of charge recombination within the perovskite film. *The discrete TiO₂ spots*
24 *contribute to the increased interface area between perovskite and TiO₂ particles, which*
25 *facilitates the electron transfer from perovskite to TiO₂.* Meanwhile, the suitable energy level
26 alignment between the perovskite absorber and FTO by incorporation of u-TiO₂ accelerates
27 electron extraction from the absorber layer. Time-resolved photoluminescence curves were
28 simultaneously meteraged as shown in figure 7(c), of which the fitted time constants τ_e (associate
29 with the electron-hole lifetime of perovskite) are 14.74, 3.52, and 2.36 ns for CH₃NH₃PbI_{3-x}Cl_x
30 films deposited on FTO, FTO-TiO₂ and FTO-TiCl₄ substrates respectively, further confirming the

1 u-TiO₂ improves the electron collection efficiency.

2 To obtain a deeper insight of the role of the u-TiO₂ film in the performance of PVSCs, electrical
3 impedance spectroscopy (EIS) was used to study the interface charge transport [38-40]. A
4 simplified circuit model reported previously was used to fit these Nyquist curves (see the inset of
5 figure 8), in which the left semicircle in the high-frequency series resistance (R_s) element is
6 mainly assigned to the contact resistance (R_{co}) at ESL/absorber interface (since the absorber/HTL
7 interface is identical in both cases). While the right incomplete semicircle in the low frequency
8 range is a transmission line, which is mainly attributed to recombination resistance (R_{rec}) at the
9 perovskite/ESL interface. The data analyzed by the Z-view software are summarized in table 2S. It
10 shows that the both cells with FTO-TiCl₄ and FTO-TiO₂ substrates have lower R_{co} compared with
11 the FTO substrates, which is mainly due to the more favorable energy level alignment. This allows
12 for more efficient extraction of the electrons, which is in accordance with the results of the CV
13 and PL measurements. The R_{co} of the FTO-TiCl₄ substrates is the lowest, indicating the fastest
14 extraction of the photon-generated electrons. We attribute this to the formation of an intimate
15 junction of large interfacial area between u-TiO₂ and CH₃NH₃PbI₃ film, which is much more
16 effective in extracting photogenerated electrons. Moreover, the left part shows the PVSC with the
17 FTO-TiCl₄ film has a highest R_{rec} , leading to a lower carrier recombination rate, so the V_{OC} is also
18 improved. The reduced R_{co} and increased R_{rec} imply more efficient extraction/transport of the
19 electrons resulting in increased J_{sc} for the FTO-TiCl₄ film based solar cells.

20 It should be noted that the conducted XRD measurements proves that the TiO₂ film hydrolyzed
21 by low concentration TiCl₄ is amorphous [41], as shown in figure 7S. Compared with the rutile or
22 anatase TiO₂, the conductivity of the amorphous TiO₂ is lower, therefore, the c-TiO₂ layer is often
23 subject to sintering for obtaining excellent electrical conductivity. ***Further, c-TiO₂ films doped***
24 ***with other elements were applied to improve electron transport [17, 36].*** When the FTO-TiCl₄
25 substrate was sintered at 500 °C, however, the resulting device did not show improved
26 photovoltaic performance compared with the pristine devices. Thus, we infer that the increased
27 electrical conductivity for u-TiO₂ film does not give rise to the enhanced performance. To explain
28 this reason, we need to consider the operational mode of these devices with different substrates
29 [42]. We would expect for sensitized TiO₂ devices, after light absorption in the perovskite,
30 electrons would be transferred to the TiO₂ with subsequent electron transport to the FTO electrode

through the TiO_2 , and holes to the spiro-OMeTAD with subsequent transport to the Ag electrode. During the process of electron transport from perovskite to FTO cathode, the electron conduction must depend on the TiO_2 , so the conductivity and thickness of compact TiO_2 determine the efficiency of electron transport. For the naked FTO based cells, the electrons can directly inject into FTO cathode, so the electron transport only depend on the injection efficiency from perovskite to FTO. The CV and PL results suggest that the low injection efficiency is always existed due to the improper energy level alignment and high carrier recombination between perovskite and FTO. For the FTO- TiCl_4 based cells, the discrete TiO_2 spots provide the enhanced interfacial area between perovskite and TiO_2 , which improves the electron injection efficiency from perovskite to TiO_2 . Meanwhile, the u- TiO_2 allows the transferred elections to be collected quickly by FTO for the short conduction distance. The u- TiO_2 acts as a bridge for electron transport between perovskite and FTO cathode, which accelerates the electron transfer and alleviates the charge recombination. The cartoon illustrating the charge transfer and transport in a FTO- TiCl_4 based solar cell was shown in figure 1(b). Therefore, we suggest that the low conductivity of amorphous TiO_2 also can be functioned as efficient ESL by minimizing the thickness. Thus, exploring of optimal morphology of amorphous TiO_2 film would be a viable way to fabricate low-temperature high efficient PVSCs.

4. Conclusions

In summary, the FTO surface modified by low concentration TiCl_4 solution to achieve the efficient electron-selective contacts for efficient PVSCs was realized. A u- TiO_2 film can function as c- TiO_2 layer, which promises the enhanced photovoltaic performance of PVSCs. CV, PL and EIS measurements confirm that the low-concentration TiCl_4 treatment improves the energy level alignment between the FTO/perovskite interface, facilitating charge extraction and suppressing charge recombination. Exploring of optimal morphology of amorphous TiO_2 film would be a viable way to fabricate low-temperature high efficient PVSCs in the future. These results imply that interface engineering provides a promising approach to simplify device configuration and reduce the fabrication cost for PVSCs.

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Figure captions

Fig. 1 (a) Schematic of the device structure, (b) Cartoon illustrating the charge transfer and transport in a FTO-TiCl₄ based solar cell. Cross-sectional SEM images of the u-TiO₂ (c) and c-TiO₂ (d) based PVSCs.

Fig. 2 Top-view SEM images of FTO substrates treated by TiCl₄ solutions with low concentrations (40 mM) at different time (a) 0 h, (b) 0.5 h, (c) 2 h, (d) 10 h. The top-view SEM images of FTO substrates treated by high concentration TiCl₄ solutions (200 mM (e), 400 mM (f)) for 2 h.

Fig. 3 Transmission spectra of different FTO substrates.

Fig. 4 (a) $J-V$ curves obtained from the devices based on different substrates, (b) IPCE spectral of the corresponding cells.

Fig. 5 Top-view SEM images of the CH₃NH₃PbI_{3-x}Cl_x films deposited on FTO without (a) and (b) with TiCl₄ treatment for 2 h. Insets are the high magnification top-view SEM images of the CH₃NH₃PbI_{3-x}Cl_x films.

Fig. 6 The static contact angles of deionized water is 70.9° on naked FTO substrates (a), 26.8° on FTO-TiCl₄ substrates (b), and 31.9° on UVO treated FTO substrates (c).

Fig. 7 (a) Cyclic voltammetry of the FTO, FTO-TiCl₄, FTO-TiO₂ substrates, (b) Steady-state PL spectroscopy of the CH₃NH₃PbI_{3-x}Cl_x films deposited on FTO, FTO-TiCl₄ and FTO-TiO₂ substrates.

Fig. 8 Electrical impedance spectroscopy (EIS) of the PVSCs based on three different substrates.

Table captions

Table 1 Detailed photovoltaic parameters of the devices based on different substrates.

Table 1

Substrates	$J_{sc}(\text{mAcm}^{-2})$	$V_{oc}(\text{V})$	FF	PCE (%)
FTO-TiCl ₄ (0 h)	11.63	0.902	0.483	5.07
FTO-TiCl ₄ (0.5 h)	21.29	0.918	0.532	10.40
FTO-TiCl ₄ (2 h)	22.10	1.040	0.584	13.42
FTO-TiCl ₄ (10 h)	21.95	0.882	0.625	12.10
FTO-TiO ₂	20.94	1.012	0.640	13.56

Figure(s)

(a)

(b)

(c)

(d)

Figure(s)

Figure(s)

Figure(s)

(a)

(b)

Figure(s)

Figure(s)