Low-temperature processed SnO₂ compact layer by incorporating TiO₂ layer toward efficient planar heterojunction perovskite solar cells

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Abstract: Inorganic metal oxide electron-transport layers have the potential to promise perovskite solar cells with improved stability and high efficiency, but generally require high temperature to enhance conductivity and reduce defect. Here, low-temperature solution-processed inorganic SnO₂-TiO₂ composite layer for efficient planar heterojunction perovskite solar cells is demonstrated. The SnO₂-TiO₂ composite layer brings better bandgap matching at the perovskite/FTO interface that facilitates charge extraction and reduces surface recombination. Cyclic voltammetry, steady-state photoluminescence spectroscopy and electrical impedance spectroscopy were conducted to reveal the energy band alignment and charge carrier dynamics. The SnO₂-TiO₂ composite films based solar cells acquire a high power conversion efficiency (PCE) of 14.8%, which is higher than PCEs of devices based on individual SnO₂ layer and sintered TiO₂ layer.

Keywords: perovskite solar cells, low-temperature process, SnO₂-TiO₂ composite layer, charge extraction, carrier recombination

1. Introduction

Organic-inorganic perovskite solar cells (PSCs) are appearing as a hopeful new generation of photovoltaic technology due to the dramatic increase in device performance [1-5]. The outstanding absorption properties, such as high absorption

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1 coefficient and suitable band gap, make this material very appropriate for light
2 harvesting applications in photovoltaics [6, 7]. Since the first utilization of
3 organic-inorganic hybrid perovskite material in photovoltaic devices was reported, the
4 power conversion efficiency (PCE) of such PSCs has reached a remarkable value of
5 over 22% in a short span [8, 9]. In regular planar heterojunction PSCs, the perovskite
6 layer is sandwiched between an electron-selective layer (ESL) and a hole-selective
7 layer (HSL) [10]. For ESL, inorganic TiO_2 and ZnO are the two commonly used
8 materials for their suitable energy band matching and high transmittance toward the
9 visible light. However, TiO_2 usually needs high temperature sintering to better
10 transport electrons, which hinders its' further application [11]. Meanwhile, ZnO based
11 PSCs suffer from severe stability problem. Both the hydroxide constitutions and/or
12 the residual acetate ligands on synthesized ZnO lead to proton-transfer reactions at the
13 $\text{ZnO}/\text{CH}_3\text{NH}_3\text{PbI}_3$ interface and result in decomposition of the perovskite film [12,
14 13].

15 Recently, tin oxide (SnO_2) as an ESL for PSCs has attracted great attention [14-17].
16 It yields high electron mobility, long stability under UV illumination, and good
17 transmission property. However, single compact SnO_2 layer still suffers from some
18 restraints for further use in PSCs. The reports of high-efficiency PSCs for single SnO_2
19 layers are still fewer than the above two traditional metal oxides. Due to the
20 conduction band minimum of SnO_2 is low [18], this unaligned energy level is not
21 desirable for interfacial contact in planar heterojunction PSCs. Recent reports also
22 pointed out the bad quality of SnO_2 film was prepared through a simple hydrolysis
23 [19]. All of these would cause the serious recombination in the SnO_2 based PSCs.
24 Therefore, reducing the interface recombination is critically important for the high
25 efficiency. Song et al. used solvent vapor annealing method to grow the perovskite
26 film, in which the remnant wide-band-gap PbI_2 nanocrystals at the $\text{SnO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$
27 interface can block holes and reduce the interface recombination [20]. Fang et al.
28 modified SnO_2 by fullerene to promote charge transfer. The more positive conduction
29 band of fullerene and the larger band gap of SnO_2 enable the cooperative works
30 efficiently and boost the efficiency to 19.12% [21]. Bai et al. realigned the Fermi level

1 of SnO₂ by doping Sb element, which significantly enhances the open-circuit voltage
2 [22]. Depositing a thin TiO₂ layer by hydrolysis of TiCl₄ is also a very effective way
3 of energy band tuning due to the more suitable conduction band matching with the
4 perovskite absorber [23-25]. In that case, researchers built a mesoporous SnO₂
5 scaffold to load the perovskite crystals or used a colloid SnO₂ to form a compact film.
6 Then the TiCl₄ treatment followed by high temperature (500 °C) sintering was
7 adopted to reduce the recombination. Above all, combining the merits of SnO₂ and
8 TiO₂ layer may be a viable avenue to improve PCE and broaden the application for
9 PSCs.

10 Here, we developed a totally low-temperature prepared SnO₂-TiO₂ composite layer.
11 The resulting device performance with an efficiency of 14.83% has been achieved.
12 The performance is higher than those of the controlled cells based on SnO₂ or TiO₂,
13 respectively. Systematic characterization and analysis were performed to study and
14 reveal the underlying mechanisms of the improvement originated from the SnO₂-TiO₂
15 composite layer. Our results suggest that a careful surface treatment of charge
16 transport layers provides a simple and effective route to facilitate charge transfer and
17 suppress the charge recombination in PSCs. More importantly, the whole low
18 temperature processing method is compatible with ITO or flexible substrate for the
19 future practical application.

20 **2. Experimental**

21 *2.1 Preparation of perovskite solar cells*

22 The SnO₂ ESLs were prepared by spin-coating the precursor solutions of 0.2 M
23 SnCl₄·5H₂O in 2-methoxyethanol with 2000 rpm for 60 s on fluorine doped tin oxide
24 (FTO) substrates. Subsequently, the substrates were heated in air at 180 °C for 1 hour.
25 For SnO₂-TiO₂ preparation, the SnO₂ films were immersed into 40 mM aqueous TiCl₄
26 solution at 70 °C for 40 min. Next, the electrodes were washed with deionized water
27 and dried at 150 °C in air for 30 min. For preparation of TiO₂ based solar cells, a
28 0.25M mildly acidic solution of titanium isopropoxide was spin coated at 3000 rpm
29 for 25 s, and annealed at 500 °C for 30 min.

To deposit the perovskite layer, a 1:3 ratio of $\text{PbCl}_2/\text{CH}_3\text{NH}_3\text{I}$ (0.8M/2.4M) was mixed in DMF. The solution was spin-coated on the substrates at 2000 rpm for 30 s and annealed on the hot plate from 60 °C to 95 °C with the ramping time for 10 min each. Then the uniform perovskite film was further baked in 95 °C for 40 min. Once the thin film grow well, a hole transport layer (HSL) solution was spin-coated at 3000 rpm for 30 s, in which spiro-OMeTAD/chlorobenzene solution was employed with addition of 18 μL Li-TFSI/acetonitrile (520mg/ml), and 29 μL 4-tert-butylpyridine. Lastly, about 90 nm thick silver layer was evaporated onto the device to form the back contact.

2.2 Characterizations and measurements

The top view images of FTO substrates, TiCl_4 treated SnO_2 substrates and the perovskite films were studied by a scanning electron microscope (SEM, Hitachi, SU-70, Japan). Atomic force microscope (AFM) topographic images were taken by a Bruker Scanning Probe Microscope in tapping mode. The cyclic voltammetry (CV) was manipulated 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 active area was controlled to be the same of 0.07 cm^2 . Meanwhile the supporting electrolyte is 0.5 M LiClO_4 in dry acetonitrile. Steady-state photo-luminescence spectroscopy (PL) measurements were acquired using Cary fluorescence spectrometer with an excitation wavelength of 532 nm. Current-Voltage (I-V) characteristics were measured by Keithley 2400 source meter together with a sunlight simulator (Newport AM 1.5, 100mW/ cm^2) calibrated with a standard silicon reference cell. ***The scanning direction is from 1.2 V to -0.2 V, with the scanning speed of 0.15 V/s.*** The solar cells were masked with a black aperture to define the active area of 0.07 cm^2 . The incident photo-current conversion efficiency (IPCE) spectrum was collected by Newport IPCE system in the wavelength of 300–800 nm range in DC mode. Impedance spectra were measured with an electrochemical workstation (Zennium, Germany) under dark at a bias voltage of 0.7 V in 0.1-10⁶ Hz and 10mV as the sine perturbation bias.

3. Results and discussion

It is remarkable that the generated TiO_2 via the hydrolysis of TiCl_4 at low temperature is amorphous (am- TiO_2) [26]. We measured X-ray photoelectron spectroscopy to analysis the composition of the coated film. The binding energies of 486.83 and 495.26 eV correspond to the Sn 3d 3/2 and Sn 3d 5/2 peaks respectively (figure 1(a)), suggesting the formation of SnO_2 . The obvious binding energies of 458.6 and 464.4 eV in figure 2b corresponding to Ti 2p 3/2 and Ti 2p 1/2 peaks are the distinct characteristics of Ti^{4+} in TiO_2 , further indicating the generated TiO_2 thin layer by TiCl_4 solution treatment. The main binding energy of 530.5 eV is attributed to the O 1s, which can be concluded as the O^{2-} state in SnO_2 and TiO_2 (figure 1(c)). The higher binding energy at 531.1eV can be assigned to the chemisorbed oxygen atoms or hydroxyl groups [27]. There is no residual Cl observed in the SnO_2 films in figure 1(d), which means the $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ precursor can fully hydrolyze to generate SnO_2 particles at this low temperature and the TiCl_4 solution has fully converted to TiO_2 on the SnO_2 substrates.

We studied the morphologies of the SnO_2 layer with and without TiCl_4 treatment. In figure 2(b), the SEM image of the SnO_2 coated FTO sample exhibits uniform cloudy surface, indicating that the SnO_2 films almost completely cover the conductive substrates. As we can see, the SnO_2 surface morphology basically replicates the homogeneous morphology of the underlying FTO layer (figure 2(a)). In the case of full coverage, the SnO_2 layer should act as an effective blocking layer that physically separates the photovoltaic active layer and metallic electrode. When the SnO_2 layer was treated by TiCl_4 solution, the small size of hydrolyzed TiO_2 particles appear on the crystals and form a discrete ultrathin film as presented in figure 2(c). These discrete TiO_2 particles enhance the interfacial contact area between perovskite and SnO_2 film. The AFM images in figure 2(d-e) show the deposition of SnO_2 film reduces the surface roughness of the FTO substrate from 11.0 nm to 7.69 nm. Besides, when treated by TiCl_4 , the roughness of the SnO_2 layer (RMS: 7.69 nm) is continued to reduce to 6.26 nm. From the above we concluded that the SnO_2 - TiO_2 composite layer owns the more uniform surface.

Cyclic voltammetry (CV) of the SnO₂, SnO₂-TiO₂, TiO₂ substrates was used to check the conduction band edges of the semiconductors [28, 29]. During the negative scan as the long arrow indicated in figure 3(a), the onset potential of the current, which can be used to estimate the conduction band edge of the three semiconductor substrates, moves negatively for SnO₂-TiO₂ films compared with SnO₂. This indicates the raising of the conduction band of SnO₂-TiO₂ composite layer. These short arrows in figure 3(a) indicate the onset potential, which can be evaluated as the potential where an inflection is observed in the charge-discharge curve. The obtained onset potential is -0.067 V, -0.163 V and -0.226 V (vs. SCE) for SnO₂, SnO₂-TiO₂, and TiO₂, respectively. It should be noted that the conduction band edge of the am-TiO₂ is still a little bit more negative than compact anatase TiO₂ (an-TiO₂), which is not deviate from the literature [30], given that the mildly downshift of the conduction band for the anode will be more attractive to charge transfer. Figure 3(b) shows the UV-vis absorption spectra of the three films. The treatment of the SnO₂ layer doesn't affect the transmittance due to the very small thickness of TiO₂. The band-to-band excitation wavelength of SnO₂-TiO₂ film is a litter blue shift compared with SnO₂ film, indicating the enlarged band gap. Combined with the CV results, the SnO₂-TiO₂ ESL maintains the moderate conduction band edge, which presents the preferable energy band matching as the electron-selective contact.

The current density–voltage (J – V) characteristics (figure 4) of the PSCs with SnO₂, SnO₂-TiO₂, TiO₂ layers were measured in dark and under simulated one sun illumination (AM 1.5G), and the detail parameters are given in table1. The SnO₂ based PSC exhibits an open circuit voltage (V_{oc}) of 0.651 V, a short-circuit current (J_{sc}) of 18.49 mA/cm², a fill factor (FF) of 52.9% and a low efficiency of 6.2%. However, after TiCl₄ treatment, the SnO₂-TiO₂ based PSC presents the desired PCE of 14.8% with a V_{oc} of 0.918 V, a J_{sc} of 21.84 mA/cm² and a FF of 74.0%, which surpasses PSC (12.4%) using the TiO₂ ESL. It is found that the three parameters have been significantly improved, thus the enhanced PCE. Figure 4 (b) presents the IPCE spectra, showing the same tendency for the different J_{sc} of the three PSCs.

As we all know, the incomplete perovskite coverage will lead to direct contact

1 property, thus the current leakage [31, 32]. However, the top view SEM images of the
2 formed $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ films all present a high coverage, due to relative hydrophilic
3 surfaces of the metal oxides as the contact angles of deionized water measured in
4 figure 1S. It is worth noting that the static contact angle of the SnO_2 - TiO_2 surface is
5 about three times reduced in comparison with SnO_2 and the perovskite films exhibit
6 the smoothest and pin-hole less shape. The TiCl_4 treatment enhances the wettability of
7 the metal oxide. Because the V_{oc} of the ‘p-i-n’ PSCs is commonly determined by the
8 energy-level offset between the quasi Fermi levels of the ESL and the HSL adjacent
9 to the perovskite absorber [33, 34], it is expected that the enlarged V_{oc} can be well
10 explained by altering the electronic structure of SnO_2 using the ultrathin am- TiO_2
11 surface modifier. Also, the increase V_{oc} can be due to reduced non-radiative
12 recombination at the interface. Besides, we consider the improvements of J_{sc} and FF
13 owing to the improved adhesion between perovskite layer and the composite layer
14 due to the facilitating charge extraction and reducing carrier recombination as
15 discussed below [35].

16 The photoluminescence (PL) measurements were performed to evaluate the
17 charge transport ability of the three electron selective contacts. In figure 5(a), the
18 samples of the independent perovskite film, SnO_2 /perovskite, SnO_2 - TiO_2 /perovskite,
19 and TiO_2 /perovskite were prepared on FTO substrates. It is found that the three films
20 exhibit the obvious PL quenching, indicating the charge extraction ability of the ESLs.
21 However, the distinct larger degree of PL quenching was detected in the SnO_2
22 substrates compared with TiO_2 , suggesting the more efficient electron extraction, due
23 to the deeper conduction band edge of SnO_2 . Interestingly, the SnO_2 - TiO_2 films
24 present further degree of PL quenching, indicating the most impactful electron
25 picking up. These discrete TiO_2 particles enhance the interface area between
26 perovskite and ESL, which accelerates electron extraction from the absorber layer.

27 To evaluate the recombination in the three different devices, electrochemistry
28 impedance spectroscopy (EIS) was applied to track the interface charge behavior in
29 perovskite solar cells [36, 37]. Figure 5(b) shows Nyquist plots of the perovskite solar

cells using the three different ESLs. The upper-right corner of figure 5(b) shows the equivalent circuit for the cells. As we can see, the right semicircle in the low frequency range in figure 5(b) can be mainly attributed to the recombination resistance (R_{rec}) between the perovskite film and the ESL. The main semicircle in the inset corresponding to the high-frequency part is mainly assigned to the contact resistance (R_{co}) at ESL/absorber interface (since the absorber/HSL interface is identical in both cases) [38]. PSC using the SnO_2 ESL gives the smallest R_{rec} , suggesting the strong recombination in these cells. By contrast, the larger R_{rec} of the SnO_2 - TiO_2 based PSCs compared with both TiO_2 and SnO_2 in the low frequency part indicates the recombination in these PSCs has been sharply suppressed, which accounts for the enhanced V_{oc} and FF. The cells measured in dark exhibit extremely smaller current compared with the SnO_2 based PSCs under the same bias voltage in figure 4(a), which also indicates this change. *We also found reduced photocurrent hysteresis in the SnO_2 - TiO_2 based devices (figure 4S). The improved injection and transfer of electrons lead to reduced interface recombination. It also suppresses charge accumulation at the SnO_2 - TiO_2 /perovskite interface. All these results lead to reduced hysteresis [39, 40].* Furthermore, the inset of figure 5(b) shows that our SnO_2 film has a largest R_{co} , while the R_{co} of the TiO_2 film is the smallest. Based on the CV results, the energy gap between SnO_2 and the absorber is the largest, which may cause the biggest energy barrier that results the largest R_{co} . While coating the ultrathin TiO_2 layer on SnO_2 substrates, the conduction band edge is upshifted although still lower than TiO_2 , which contributes to the smaller R_{co} than SnO_2 but still larger than TiO_2 .

We performed the schematic diagrams of charge transport and recombination in these three cells for a better comprehension in figure 6. For SnO_2 based PSCs in figure 6(a), we attribute that the transferred free electrons will easily re-inject into the valence band of the perovskite absorber due to a low interfacial energy offset, causing serious front surface recombination. Meanwhile, we think that trap states will exist in SnO_2 film for this low-temperature hydrolysis making process, resulting in electron trapping. All the above bring about the inferior V_{oc} and FF. For TiO_2 based PSCs, the shallower conduction band affects the charge extraction rate and leads to bulk

1 recombination as presented in figure 6(b). Impressively, the SnO₂-TiO₂ composite
2 layer in figure 6(c) not only facilitates charge transfer but also improves electron
3 transport efficiency, resulting in reduced electron recombination. Besides, TiCl₄
4 treatment can reduce the surface defect of SnO₂ [41], thus inhibits the surface trapping.
5 Additionally, the upshifted conduction band also suppresses the front surface
6 recombination. Hence, combining the high-mobility SnO₂ and efficient
7 electron-extraction TiO₂, the SnO₂-TiO₂ composite layer works efficaciously and
8 achieves the optimized matching.

9 **4. Conclusions**

10 In summary, we demonstrate a simple TiCl₄ treatment to obtain a versatile
11 SnO₂-TiO₂ composite layer via low-temperature processing for planar heterojunction
12 PSCs. A modified interface after TiCl₄ treatment facilitates charge extraction and
13 suppresses charge recombination. This kind of composite layer can combine the
14 merits of both SnO₂ and TiO₂ thus exhibiting superior application in photovoltaic
15 devices. As a result, the device based on SnO₂-TiO₂ composite layer shows
16 significantly enhanced V_{oc} and FF, achieving a PCE of ~15%. Our results suggest that
17 the SnO₂-TiO₂ composite layer may be a viable avenue to efficient flexible PSCs.

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25 **References**

- 26 [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal Halide Perovskites as Visible-Light
27 Sensitizers for Photovoltaic Cells, *Journal of the American Chemical Society*, 131 (2009) 6050-6051.
28 [2] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, N.-G. Park, 6.5% efficient perovskite
29 quantum-dot-sensitized solar cell, *Nanoscale*, 3 (2011) 4088-4093.
30 [3] J. Burschka, N. Pellet, S.J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, M. Gratzel,
31 Sequential deposition as a route to high-performance perovskite-sensitized solar cells, *Nature*, 499

(2013) 316-+.

[4] M.Z. Liu, M.B. Johnston, H.J. Snaith, Efficient planar heterojunction perovskite solar cells by vapour deposition, *Nature*, 501 (2013) 395-+.

[5] H.P. Zhou, Q. Chen, G. Li, S. Luo, T.B. Song, H.S. Duan, Z.R. Hong, J.B. You, Y.S. Liu, Y. Yang, Interface engineering of highly efficient perovskite solar cells, *Science*, 345 (2014) 542-546.

[6] C. Zuo, H.J. Bolink, H. Han, J. Huang, D. Cahen, L. Ding, *Advances in Perovskite Solar Cells*, *Advanced Science*, 3 (2016).

[7] Z. Song, M.J. Heben, Pathways toward high-performance perovskite solar cells: review of recent advances in organo-metal halide perovskites for photovoltaic applications, *Journal of Photonics for Energy*, 6 (2016).

[8] M. Saliba, T. Matsui, K. Domanski, J.Y. Seo, A. Ummadisingu, S.M. Zakeeruddin, J.P. Correa-Baena, W.R. Tress, A. Abate, A. Hagfeldt, Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance, *Science*, 354 (2016).

[9] D. Bi, C. Yi, J. Luo, J.-D. Décoppet, F. Zhang, Shaik M. Zakeeruddin, X. Li, A. Hagfeldt, M. Grätzel, Polymer-templated nucleation and crystal growth of perovskite films for solar cells with efficiency greater than 21%, *Nature Energy*, 1 (2016) 16142.

[10] G. Hodes, D. Cahen, Photovoltaics: Perovskite cells roll forward, *Nat Photon*, 8 (2014) 87-88.

[11] M.A. Green, A. Ho-Baillie, H.J. Snaith, The emergence of perovskite solar cells, *Nat Photon*, 8 (2014) 506-514.

[12] Y. Cheng, Q.-D. Yang, J. Xiao, Q. Xue, H.-W. Li, Z. Guan, H.-L. Yip, S.-W. Tsang, Decomposition of Organometal Halide Perovskite Films on Zinc Oxide Nanoparticles, *ACS Applied Materials & Interfaces*, 7 (2015) 19986-19993.

[13] J. Yang, B.D. Siempelkamp, E. Mosconi, F. De Angelis, T.L. Kelly, Origin of the Thermal Instability in CH₃NH₃PbI₃ Thin Films Deposited on ZnO, *Chemistry of Materials*, 27 (2015) 4229-4236.

[14] W. Ke, G. Fang, Q. Liu, L. Xiong, P. Qin, H. Tao, J. Wang, H. Lei, B. Li, J. Wan, G. Yang, Y. Yan, Low-Temperature Solution-Processed Tin Oxide as an Alternative Electron Transporting Layer for Efficient Perovskite Solar Cells, *Journal of the American Chemical Society*, 137 (2015) 6730-6733.

[15] Z. Zhu, Y. Bai, X. Liu, C.-C. Chueh, S. Yang, A.K.Y. Jen, Enhanced Efficiency and Stability of Inverted Perovskite Solar Cells Using Highly Crystalline SnO₂ Nanocrystals as the Robust Electron-Transporting Layer, *Advanced Materials*, 28 (2016) 6478-6484.

[16] Q. Liu, M.-C. Qin, W.-J. Ke, X.-L. Zheng, Z. Chen, P.-L. Qin, L.-B. Xiong, H.-W. Lei, J.-W. Wan, J. Wen, G. Yang, J.-J. Ma, Z.-Y. Zhang, G.-J. Fang, Enhanced Stability of Perovskite Solar Cells with Low-Temperature Hydrothermally Grown SnO₂ Electron Transport Layers, *Advanced Functional Materials*, 26 (2016) 6069-6075.

[17] E.H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A. Abate, M. Gratzel, A. Hagfeldt, J.-P. Correa-Baena, Highly efficient and stable planar perovskite solar cells by solution-processed tin oxide, *Energy & Environmental Science*, (2016).

[18] J.P.C. Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T.J. Jacobsson, A.R.S. Kandada, S.M. Zakeeruddin, A. Petrozza, A. Abate, M.K. Nazeeruddin, M. Gratzel, A. Hagfeldt, Highly efficient planar perovskite solar cells through band alignment engineering, *Energy & Environmental Science*, 8 (2015) 2928-2934.

[19] G. Murugadoss, H. Kanda, S. Tanaka, H. Nishino, S. Ito, H. Imahori, T. Umeyama, An efficient electron transport material of tin oxide for planar structure perovskite solar cells, *Journal of Power Sources*, 307 (2016) 891-897.

- [20] J. Song, E. Zheng, J. Bian, X.-F. Wang, W. Tian, Y. Sanehira, T. Miyasaka, Low-temperature SnO₂-based electron selective contact for efficient and stable perovskite solar cells, *Journal of Materials Chemistry A*, 3 (2015) 10837-10844.
- [21] W. Ke, D. Zhao, C. Xiao, C. Wang, A.J. Cimaroli, C.R. Grice, M. Yang, Z. Li, C.-S. Jiang, M. Al-Jassim, K. Zhu, M.G. Kanatzidis, G. Fang, Y. Yan, Cooperative tin oxide fullerene electron selective layers for high-performance planar perovskite solar cells, *Journal of Materials Chemistry A*, 4 (2016) 14276-14283.
- [22] Y. Bai, Y. Fang, Y. Deng, Q. Wang, J. Zhao, X. Zheng, Y. Zhang, J. Huang, Low Temperature Solution-Processed Sb:SnO₂ Nanocrystals for Efficient Planar Perovskite Solar Cells, *ChemSusChem*, 9 (2016) 2686-2691.
- [23] Z. Zhu, X. Zheng, Y. Bai, T. Zhang, Z. Wang, S. Xiao, S. Yang, Mesoporous SnO₂ single crystals as an effective electron collector for perovskite solar cells, *Physical Chemistry Chemical Physics*, 17 (2015) 18265-18268.
- [24] Y. Li, J. Zhu, Y. Huang, F. Liu, M. Lv, S. Chen, L. Hu, J. Tang, J. Yao, S. Dai, Mesoporous SnO₂ nanoparticle films as electron-transporting material in perovskite solar cells, *RSC Advances*, 5 (2015) 28424-28429.
- [25] H.-S. Rao, B.-X. Chen, W.-G. Li, Y.-F. Xu, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, Improving the Extraction of Photogenerated Electrons with SnO₂ Nanocolloids for Efficient Planar Perovskite Solar Cells, *Advanced Functional Materials*, 25 (2015) 7200-7207.
- [26] Z. Ren, J. Wang, Z. Pan, K. Zhao, H. Zhang, Y. Li, Y. Zhao, I. Mora-Sero, J. Bisquert, X. Zhong, Amorphous TiO₂ Buffer Layer Boosts Efficiency of Quantum Dot Sensitized Solar Cells to over 9%, *Chemistry of Materials*, 27 (2015) 8398-8405.
- [27] B. Bob, T.-B. Song, C.-C. Chen, Z. Xu, Y. Yang, Nanoscale Dispersions of Gelled SnO₂: Material Properties and Device Applications, *Chemistry of Materials*, 25 (2013) 4725-4730.
- [28] A. Kay, R. Humphry-Baker, M. Graetzel, Artificial Photosynthesis. 2. Investigations on the Mechanism of Photosensitization of Nanocrystalline TiO₂ Solar Cells by Chlorophyll Derivatives, *The Journal of Physical Chemistry*, 98 (1994) 952-959.
- [29] N. Sakai, Y. Ebina, K. Takada, T. Sasaki, Electronic Band Structure of Titania Semiconductor Nanosheets Revealed by Electrochemical and Photoelectrochemical Studies, *Journal of the American Chemical Society*, 126 (2004) 5851-5858.
- [30] D. Yang, R. Yang, J. Zhang, Z. Yang, S. Liu, C. Li, High efficiency flexible perovskite solar cells using superior low temperature TiO₂, *Energy & Environmental Science*, 8 (2015) 3208-3214.
- [31] G.E. Eperon, V.M. Burlakov, P. Docampo, A. Goriely, H.J. Snaith, Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells, *Advanced Functional Materials*, 24 (2014) 151-157.
- [32] A. Dualeh, N. Tétreault, T. Moehl, P. Gao, M.K. Nazeeruddin, M. Grätzel, Effect of Annealing Temperature on Film Morphology of Organic-Inorganic Hybrid Perovskite Solid-State Solar Cells, *Advanced Functional Materials*, 24 (2014) 3250-3258.
- [33] M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites, *Science*, 338 (2012) 643-647.
- [34] S. Ryu, J.H. Noh, N.J. Jeon, Y. Chan Kim, W.S. Yang, J. Seo, S.I. Seok, Voltage output of efficient perovskite solar cells with high open-circuit voltage and fill factor, *Energy & Environmental Science*, 7 (2014) 2614-2618.
- [35] C. Ludmila, U. Satoshi, S. Yoshitaka, N. Jotaro, K. Takaya, S. Hiroshi, Surface Treatment of the

Compact TiO₂ Layer for Efficient Planar Heterojunction Perovskite Solar Cells, *Chemistry Letters*, 44 (2015) 674-676.

[36] V. Gonzalez-Pedro, E.J. Juarez-Perez, W.-S. Arsyad, E.M. Barea, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, General Working Principles of CH₃NH₃PbX₃ Perovskite Solar Cells, *Nano Letters*, 14 (2014) 888-893.

[37] H.-S. Kim, I. Mora-Sero, V. Gonzalez-Pedro, F. Fabregat-Santiago, E.J. Juarez-Perez, N.-G. Park, J. Bisquert, Mechanism of carrier accumulation in perovskite thin-absorber solar cells, *Nat Commun*, 4 (2013).

[38] D. Liu, J. Yang, T.L. Kelly, Compact Layer Free Perovskite Solar Cells with 13.5% Efficiency, *Journal of the American Chemical Society*, 136 (2014) 17116-17122.

[39] J.H. Heo, M.S. You, M.H. Chang, W. Yin, T.K. Ahn, S.-J. Lee, S.-J. Sung, D.H. Kim, S.H. Im, Hysteresis-less mesoscopic CH₃NH₃PbI₃ perovskite hybrid solar cells by introduction of Li-treated TiO₂ electrode, *Nano Energy*, 15 (2015) 530-539.

[40] K. Mahmood, B.S. Swain, A. Amassian, Highly Efficient Hybrid Photovoltaics Based on Hyperbranched Three-Dimensional TiO₂ Electron Transporting Materials, *Advanced Materials*, 27 (2015) 2859-2865.

[41] H.J. Snaith, C. Ducati, SnO₂-Based Dye-Sensitized Hybrid Solar Cells Exhibiting Near Unity Absorbed Photon-to-Electron Conversion Efficiency, *Nano Letters*, 10 (2010) 1259-1265.

Figure captions

Figure 1. High-resolution XPS spectra of Sn 3d (a), O 1s (b), Ti 2p (c) and Cl 2p (d) for the low temperature TiCl₄ treated SnO₂ films.

Figure 2. Top-view SEM images of FTO (a), SnO₂ without (b) and with TiCl₄ treatment (c), AFM images of FTO (d), SnO₂ without (e) and with TiCl₄ treatment (f).

Figure 3. Cyclic voltammograms (a), UV-vis spectra (b) of the SnO₂, SnO₂-TiO₂ and TiO₂ substrates.

Figure 4. *J-V* curves for the SnO₂, SnO₂-TiO₂, TiO₂ based PSCs (a), IPCE spectral of the corresponding cells (b).

Figure 5. (a) Steady-state photoluminescence spectroscopy of the CH₃NH₃PbI_{3-x}Cl_x films deposited on different substrates. (b) Nyquist plots of the PSCs using the three different ESLs. Inset: Nyquist plots in the high frequency range.

Figure 6. Schematic diagrams illustrate the band alignment and charge recombination in the cells with SnO₂(a), TiO₂(b) and SnO₂-TiO₂(c) as the electron-selective layers. The digital 1, 2, 3 represent electron trapping, front surface recombination and bulk recombination, respectively.

1 **Table caption**

2 Table1. *The best performing device from each category.*

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2 Table1. Performance of the SnO₂, SnO₂-TiO₂, TiO₂ based PSCs. Characteristic
3 parameters of all fabricated PSC samples.

Cells	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF	PCE (%)
SnO ₂	18.49	0.651	0.529	6.2
SnO ₂ -TiO ₂	21.84	0.918	0.740	14.8
TiO ₂	20.17	1.012	0.611	12.4

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2 Low-temperature solution-processed inorganic SnO_2 - TiO_2 composite layer brings
 3 perfect band-gap matching and closes interface-contact between perovskite layer and
 4 FTO substrate, which contributes to facilitating charge extraction and reducing carrier
 5 recombination, leading to device efficiency as high as 15%.

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