Rational design of SnO₂-based electron transport layer in mesoscopic perovskite solar cells: more kinetically favorable than traditional double-layer architecture

Qingshun Dong¹, Yuan Xue², Shi Wang², Liduo Wang^{1*}, Fan Chen², Sen Zhang², Rihan Chi², Liang Zhao² and Yantao Shi^{2*}

ABSTRACT Here, the interfacial synergism of discontinuous spot shaped SnO₂ and TiO₂ mesoporous nanocomposite as electron transfer layer (ETL) underlayer is presented in highly efficient mesoscopic perovskite solar cells (M-PSCs). Based on this new strategy, strong charge recombination observed in previous SnO₂-based ETLs is suppressed to a great extent as the pathways of charge recombination and energy loss are blocked effectively. Meanwhile, the internal series resistance of entire M-PSC is decreased remarkably. The new ETL is more kinetically favorable to electron transfer and thus results in significant photovoltaic improvement and alleviated hysteresis effect of M-PSCs.

Keywords: SnO₂, interfacial synergism, electron transfer layer, perovskite, solar cell

INTRODUCTION

Today, perovskite solar cells (PSCs) are at the frontier of research in the domain of new photovoltaics, capturing more and more attention from both academic and industrial circles. As an emerging photovoltaic material, organolead halide perovskites in PSCs have demonstrated many superiorities over the traditional ones, e.g., tunable band-gap, ultralong carrier diffusion length, as well as good solution processibility that is highly desired for future cost-effective and facile fabrication [1–4]. PSCs exhibit high flexibility in cell architectures and the ones that contain mesoporous scaffolds are usually classified to be mesoscopic PSCs (M-PSCs) which are extraordinarily representative and reliable in terms of achieving high

photoelectric conversion efficiencies (PCEs) [5,6]. In recent years, no efforts have been spared to promoting the device performance of M-PSCs and a stabilized PCE of 22.1% has been achieved recently [7]. Nowadays, with many scientific issues being explored around M-PSCs, the pursuit of further photovoltaic improvement is imperative. Electron transfer in PSCs, including both interfacial extraction and transport, is fundamental photophysical kinetic process that is implemented for electron transfer layer (ETL) and is crucial to device performance [8–11].

The configuration of routine ETL in M-PSCs consists of two layers: (i) mesoporous scaffold that affords sufficient pore filling of perovskite and favorable electron extraction and transport; (ii) compact underlayer that plays the roles of selective transfer of electrons simultaneously effective hole blocking to minimize shunt pathway. Concerning materials, TiO₂ has been widely adopted in such dual-layer structured ETL for M-PSCs so far [8,12–15]. Actually, many attempts have been performed in order to make ETL kinetically more favorable, e.g., surface modifications, nanostructure tailoring, and the utilizations of alternative materials with better optoelectronic properties [16–23]. Compared with TiO₂, SnO₂ is chemically stable as well and, more importantly, its charge mobility is almost two orders of magnitude higher than that of TiO₂ [11,24]. On the other hand, the photocatalytic activity is less pronounced due to a higher band gap of ~3.8 eV for SnO₂, which is favorable to the long-term stability of PSCs [25]. Herein, spontaneously the speculation whether

¹ Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

² State Key laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China

* Corresponding authors (emails: chldwang@mail.tsinghua.edu.cn (Wang L); shiyantao@dlut.edu.cn (Shi Y))

SnO₂-based M-PSCs is really more efficient than that based on TiO₂ is arising. However, even many efforts have been employed, utilizing SnO₂ as either mesoporous scaffold or compact underlayer in ETL did not make a contribution to the improvement of photovoltaic performance in M-PSCs as expected [26,27]. Thus, one important challenge we are facing is how to construct ETL for M-PSCs that will make the best use of SnO₂.

Herein, we illustrate our systematical investigations on the optoelectronic advantages of SnO₂ as ETL, as well as the unique photovoltaic behaviors embodied in M-PSCs. Benefitting from the cooperation with TiO₂ mesoporous scaffold, we report one rational strategy using SnO₂ as underlayer to reconstruct ETL for highly efficient M-PSCs. The concept “interfacial synergism of SnO₂/TiO₂ nanocomposite as ETL underlayer” was put forward for the first time, which perfectly explained the facilitation of charge transfer kinetic process and the passivation of strong charge recombination. To begin with, we covered the fluorine-doped tin oxide (FTO) incompletely with only a spot of SnO₂ nanocrystallites on purpose. Then, as we conducted the sequential deposition of TiO₂ colloid (for construction of mesoporous scaffold), it was inferred that a few TiO₂ nanoparticles were also capable to contact with FTO directly, through which an interfacial nanocomposite of SnO₂/TiO₂ was formed and acted as a substantial ETL underlayer. Based on this new strategy, the strong charge recombination observed in previous SnO₂-based ETLs was remarkably suppressed since the pathways of charge recombination and energy loss were blocked effectively. In the meantime, the internal series resistance of entire M-PSC was decreased remarkably. Compared with traditional ETL, this novel one was more kinetically favorable to electron transfer, thus leading to substantial photovoltaic improvement and alleviated hysteresis effect for M-PSCs. The steady-state and champion PCEs of the M-PSCs using the new ETL were 16.31% and 17.58%, respectively, higher than that (steady-state PCE=14.23%; champion PCE=16.37%) of M-PSCs with traditional ETLs.

EXPERIMENTAL SECTION

Materials and reagents

Unless stated otherwise, all materials were purchased from Sigma-Aldrich or Alfa Aesar and used as received. The TiO₂ paste was purchased from Dyesol (18NR-T). Fluorine-doped tin oxide (FTO, 15 Ω/sq) was purchased from Pilkington, in USA. Spiro-MeOTAD and CH₃NH₃I were purchased from Borun New Material Technology

Co., Ltd and Xi'an Polymer Light Technology Corp, respectively.

SnO₂ or TiO₂ underlayer precursor solution preparation

5.64 g SnCl₂·2H₂O was dissolved in 50 mL absolute ethyl alcohol, and the solution was stirred on a magnetic stirring apparatus for 3 h at the temperature of 78°C, then aged for 3 h at 30°C. After that, the solution was put in a reagent bottle for over 7 d at room temperature, and the faint yellow SnO₂ organic sol was gotten. Then, the sol of 0.5 mol L⁻¹ was diluted into different concentrations and used to prepare the SnO₂ underlayers.

TiO₂ organic sol for TiO₂ compact layer was prepared according to the reported procedure [28]. Briefly, 68 mL of tetrabutyl titanate and 16.5 mL of diethanolamine were dissolved in 210 mL absolute ethanol, and then the mixture was stirred vigorously for 1 h at room temperature (Solution A). A mixture of 3.6 mL H₂O and 100 mL ethanol (Solution B) was added dropwise into the Solution A under stirring. The resulting solution was aged for 24 h at room temperature, resulting in the TiO₂ organic sol.

Device fabrication

To fabricate the devices, the FTO coated glass was patterned by etching with Zn powder and 2 mol L⁻¹ HCl diluted in deionized water. The etched substrate was then cleaned with 2% hellmanex diluted in deionized water, rinsed with deionized water, acetone, isopropanol and deionized water and dried with clean dry air. The SnO₂ underlayer was formed through spin coating SnO₂ organic sol on the clean substrate at 4000 rpm for 30 s, followed by a sintering process in a furnace at 450°C for 2 h. A thin layer of compact anatase TiO₂ was formed through spin coating TiO₂ organic sol on the clean substrate at 3000 rpm for 30 s, followed by a sintering process in a furnace at 450°C for 2 h.

Mesoporous TiO₂ layer was prepared by spin coating a commercial TiO₂ paste diluted in ethanol (1:6, weight ratio) at 5000 rpm for 30 s. After drying at 125°C, the TiO₂ films were gradually heated to 500°C, baked at this temperature for 30 min and cooled to room temperature.

To prepare the CH₃NH₃PbI₃ layer, 462 mg of PbI₂ in 1 mL of dimethylformamide and dimethyl sulphoxide mixed precursor solution (before optimized 9:1 and after optimized 5:1, volume ratio) was heated at 60°C for 2 h under magnetic stirring, and the mixture was then spin coated on the as-prepared TiO₂ film at 3000 rpm for 30 s in glovebox. The PbI₂ films were dropped with a solution of CH₃NH₃I in 2-propanol (30 mg mL⁻¹) and spin-coated

Figure 1 Surface (top row) and cross sectional (bottom row) SEM images of SnO_2 -ETL/FTO substrates from different SnO_2 concentration colloids. (a) 0.500; (b) 0.250; (c) 0.125; (d) 0.083; (e) 0.063; (f) 0.032; (g) 0.008 mol L^{-1} . The scale bars are 500 nm.

at 5000 rpm for 30 s. Afterward, the as-prepared films were heated at 150°C for around 20 min until the color changed to dark red.

The hole transport material (HTM) was then deposited by spin coating at 3000 rpm for 30 s. The HTM was prepared by dissolving 72.3 mg spiro-MeOTAD and 28.8 μL 4-tert-butylpyridine, 17.5 μL of a stock solution of 520 mg mL^{-1} lithium bis(trifluoromethylsulfonyl)imide in acetonitrile in 1 mL chlorobenzene. Finally, 60 nm Ag was thermally evaporated on top of the device to form the back contact. The active area of this electrode was fixed at 0.105 cm^2 . All devices were fabricated in glovebox.

Characterizations

The sample morphologies were observed using scanning electron microscopy (SEM, FEI QUANTA 450). UV-vis absorption spectra were measured using a spectrophotometer equipped with an integrating sphere setup (JASCOV-570). Linear sweep voltammetry (LSV) curves of ETL underlayer/FTO substrates were measured using a Keithley 2601 source. Atomic force microscopy (AFM) was performed using BRUKER Dimension Icon. J - V curves of PSCs were measured using a Keithley 2450 source meter scanning the devices at 0.2 V s^{-1} or 0.01 V s^{-1} under simulated AM 1.5 G illumination (100 mW cm^{-2} , PEC-L15, Japan). I - V curves of devices without perovskite were measured under dark at the scan rate of 0.2 V s^{-1} . The forward bias for stability characterization of the solar cells were maintained under maximum power point. The active area was fixed at 0.105 cm^2 by attaching with a mask of 0.07 cm^2 . The electrochemical impedance spectroscopy (EIS) measurements were conducted on a

computer-controlled electrochemical workstation (Zennium Zahner, Germany) under white LED with light illumination of 10 mW cm^{-2} . The measured frequencies ranged from 100 Hz to 2 MHz at DC bias of 0 V and open-circuit voltage (V_{oc}). The amplitude was 10 mV.

RESULTS AND DISCUSSION

Considering the strong charge recombination at SnO_2 /perovskite interface as aforementioned, it is reasonable to employ TiO_2 instead of SnO_2 as mesoporous scaffold for M-PSCs in this work. Then our research concentrates on how to utilize SnO_2 as underlayer more rationally. Firstly, some essential investigations on morphology and optoelectronic features were carried out to deepen our knowledge of SnO_2 films that were prepared on FTO glass by sol-gel route [29]. Typically, an ethanol dispersion of SnO_2 sol was spread on FTO glass by spin-coating, then, the film composed of SnO_2 nanocrystallites formed after sintering at 450°C for 2 h. It was noteworthy that the control of SnO_2 film thickness was realized by changing the concentrations of SnO_2 sol. Surface and cross-sectional morphologies of the SnO_2 films were characterized by SEM as demonstrated in Fig. 1. We prepared a series of samples with the precursor concentrations from 0.500 to 0.008 mol L^{-1} . It is obviously that relatively larger concentration of SnO_2 sol results in thicker film as observed for sample SnO_2 -0.500 mol L^{-1} . Fig. 1a exhibits an average film thickness of about 100 nm for sample SnO_2 -0.500 mol L^{-1} . Despite of many pin-holes, the waved surface of FTO glass is well flattened by SnO_2 nanocrystallites. Subsequently with precursor concentration being halved, a compact layer and surface undulations can be observed

Figure 2 AFM images showing the 2D and 3D topography of (a, b) bare quartz glass and (c, d) the one with SnO_2 nanocrystallites attached as that for preparation of sample SnO_2 -0.063 mol L^{-1} .

for sample SnO_2 -0.250 mol L^{-1} , as shown in Fig. 1b. But with further decrease in precursor concentration, SEM images in Fig. 1c indicate that the surface of FTO could not be covered completely by SnO_2 nanocrystallites in sample SnO_2 -0.125 mol L^{-1} . Seen from the SEM images in Fig. 1d of sample SnO_2 -0.083 mol L^{-1} , the tendency becomes pronounced as more and more salient parts of FTO expose but the continuity of SnO_2 layer is maintained more or less. Sudden changes in surface morphology and film continuity appear when the precursor concentration is reduced to much lower levels, as in the cases of the following three samples shown in Fig. 1d–f respectively. For example, most of FTO surface in sample SnO_2 -0.083 mol L^{-1} is not covered adequately (at least apparently) and only in low-lying regions can we observe some SnO_2 nanocrystallites. Subsequent characterizations by AFM further support this fact. A relatively smooth surface of the bare quartz glass is illustrated in Fig. 2a, b. Then, a procedure which is consistent with that of the preparation of sample SnO_2 -0.063 mol L^{-1} was performed by spin-coating a dilute SnO_2 sol on quartz glass. Fig. 2c, d clearly show that the small-sized SnO_2 nanoparticles attached onto quartz glass are dispersed in the absence of good interconnectivity, indicating incomplete coverage as

observed in SEM results.

The electrical behaviors of the SnO_2 samples were evaluated by comparisons with conventional TiO_2 compact layer and bare FTO, through which the fact of incomplete coverage of SnO_2 on FTO surface in some samples can be further confirmed. LSV curves in Fig. 3a show the current *versus* applied bias voltage, which can be used to qualitatively compare and evaluate the conductive feature of film samples. Evidently, the conventional TiO_2 compact film of ca. 60 nm in thickness [30] has an inferior conductivity as indicated by the curve slope. In contrast, a better conductive feature of SnO_2 is well reflected by the sample of SnO_2 -0.500 mol L^{-1} since it outputs larger current under the same bias voltage. Moreover, the decrease in thickness results in further enhancement in conductivity for sample SnO_2 -0.250 mol L^{-1} . Speaking of the above three samples with FTO glass completely covered, the slopes of their LSV curves change more or less along with the bias voltage especially within the range between -1 and 1 V, suggesting that the current-voltage feature shown in LSV curves arises from the intrinsic properties of TiO_2 and SnO_2 . Remarkable enhancement in conductivity is observed as the FTO surface is not completely covered by SnO_2 nanocryst-

Figure 3 Electrical and optical properties demonstrated by LSV curves (a) and transmittance spectra of different film samples (b), respectively.

Table 1 Average photovoltaic parameters of M-PSCs using SnO_2 as underlayer in ETL

Underlayer in ETL ^{a)}	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
SnO_2 -0.500 mol L ⁻¹	0.81±0.05	22.43±1.54	0.55±0.03	9.97±1.14
SnO_2 -0.125 mol L ⁻¹	0.96±0.02	22.14±0.37	0.66±0.01	13.99±0.55
SnO_2 -0.063 mol L ⁻¹	0.99±0.02	21.28±0.84	0.71±0.02	14.87±0.63
SnO_2 -0.032 mol L ⁻¹	1.01±0.02	20.45±0.50	0.73±0.01	15.13±0.48
SnO_2 -0.016 mol L ⁻¹	1.00±0.02	20.03±0.74	0.73±0.03	14.76±0.74
SnO_2 -0.008 mol L ⁻¹	0.98±0.02	20.56±0.87	0.71±0.02	14.17±0.65
W/O underlayer	0.93±0.03	20.30±0.30	0.69±0.02	13.07±0.88

a) Cell configuration: FTO/underlayer/M-TiO₂ scaffold and perovskite/spiro-MeOTAD/Ag

tallites. For instance, a linear response of current under bias voltage is output for the sample of SnO_2 -0.125 mol L⁻¹. Further with more FTO surface being exposed as in the cases of SnO_2 -0.032 mol L⁻¹ and SnO_2 -0.008 mol L⁻¹, the two LSV curves nearly coincide with that of bare FTO. Hence, we could draw the conclusion that the sudden change as reflected in the samples of SnO_2 -0.125 mol L⁻¹, SnO_2 -0.032 mol L⁻¹ and SnO_2 -0.008 mol L⁻¹ stems from the intrinsic conductive behavior of FTO. The results of LSV measurement are well consistent with SEM images and further elucidate that the FTO surfaces in the above three samples are not covered completely by SnO_2 . It is verified that the properties in light transmission of SnO_2 also surpass that of TiO_2 . Fig. 3b shows the transmittance spectra obtained by adopting the substrate glass of FTO as reference. It is clearly revealed that, compared with conventional TiO_2 compact film (sample FTO/ TiO_2), SnO_2 -based films have shown higher transmittance from 350 to 850 nm. In particular, the light transmittance of sample SnO_2 -0.500 mol L⁻¹ (with the largest film thickness among SnO_2 -based samples) even exceeds 100% in a very wide range better than bare FTO, which is of great significance. This finding suggests that SnO_2 is competent to

perform as an anti-reflection layer on FTO, in turn allowing more photons to be collected for subsequent conversion into photocurrent [31,32]. Through the series of parallel comparisons, it can be inferred that SnO_2 as ETL material possesses both electrical and optical advantages.

In principle, the underlayer of ETL in M-PSCs ought to be compact and pin-hole free so as to retard charge recombination and play the role of hole-blocking effectively [33]. If so, some samples with FTO being covered incompletely by SnO_2 in this work are supposed to be undesirable. For this reason, our subsequent results are contradictory to the “universal” principle. However, sample SnO_2 -0.500 mol L⁻¹ realized full coverage of FTO by SnO_2 underlayer while Table 1 shows that the relevant M-PSCs delivered unsatisfied average PCE of 9.97% as a result of lower V_{OC} (0.81 V) and fill factor (FF) (0.55), respectively. With no doubt, strong charge recombination derived from the trap states of SnO_2 remains responsible to this issue, as reported in the literatures from our team and others. Nevertheless, when the decrease in thickness of SnO_2 underlayer leads to exposure of FTO, the promotion in photovoltaic performance is achieved.

Compared with the M-PSC based on sample $\text{SnO}_2\text{-}0.50$ mol L^{-1} , the average V_{OC} and FF of that based on sample $\text{SnO}_2\text{-}0.125$ mol L^{-1} increase remarkably to 0.96 V and 0.66, respectively, achieving an average PCE of 13.99% as a consequence. Data listed in Table 1 distinctly indicate that the photovoltaic improvement of M-PSCs in this work is ascribed to the increases in V_{OC} and FF, which are sensitive to charge recombination and cell internal resistance. We further diluted the SnO_2 sol gradually and the FTO surface was exposed to a greater degree, while the average PCEs of M-PSCs rise all the same until an optimized value of 15.13% is attained based on sample $\text{SnO}_2\text{-}0.032$ mol L^{-1} . Although a spot of SnO_2 nanocrystallites are attached to FTO surface in the cases of samples $\text{SnO}_2\text{-}0.016$ mol L^{-1} and $\text{SnO}_2\text{-}0.008$ mol L^{-1} , only slight decrease is observed in photovoltaic performance. Our results demonstrate the peculiar behaviors of SnO_2 as underlayer in ETL for M-PSCs, which is quite different from that of TiO_2 . Evidently, using SnO_2 film of ~ 100 nm in thickness as underlayer is not that appropriate, because the average PCE of M-PSCs is even lower than that in the absence of any underlayer. It can be certified from Table 1 that M-PSCs containing only mesoporous TiO_2 scaffold in ETL deliver an average PCE of 13.07%, much higher than that without TiO_2 compact underlayer as reported previously [34]. Above findings interest us and we decide to go deep into the researches on the underlayer in ETL, by which further developments of device performance in M-PSCs are expected.

A practice we widely adopt during J - V (photocurrent-voltage) measurement is to mask the active area of one solar cell. Concerning M-PSCs with SnO_2 as underlayer in ETL, another unique phenomenon we can observe is the pseudo photocurrent and PCE when the active area is un-masked, which is more striking especially in the case of thicker SnO_2 films. Fig. 4 shows the J - V curves of M-PSCs with active area masked or un-masked. Detailed photovoltaic parameters are summarized in Table 2. Device based on sample $\text{SnO}_2\text{-}0.500$ mol L^{-1} gives a pseudo photocurrent density (J_{sc}) of 41.87 mA cm^{-2} (a pseudo

Figure 4 J - V characteristics curves of M-PSCs using SnO_2 as underlayers, the suffix “M” in line tab represents the masked active area, while the “UM” means un-masked during measurement.

PCE of 14.67%), much larger than the veritable value of 23.97 mA cm^{-2} . Despite alleviated by the decrease in the thickness of SnO_2 underlayer, the pseudo J_{sc} and PCE are still notable as exhibited in the case of sample $\text{SnO}_2\text{-}0.250$ mol L^{-1} that covers FTO completely. However, the pseudo J_{sc} and PCE become negligible when sample $\text{SnO}_2\text{-}0.063$ mol L^{-1} is applied, which cannot realize the full coverage of FTO. Likewise for M-PSCs using TiO_2 underlayer, it has been reported that the critical parameters would not be affected whether a mask was used in J - V measurement or not. Actually, it is the highly conductive carrier transport materials such as SnO_2 in this work that should be responsible to the pseudo photocurrent as observed in bulk heterojunction and other hybrid solar cells. Hence, the high conductivity of the SnO_2 together with better interparticle connectivity facilitates the formation of 2D transport channels. If no mask is applied in J - V measurement, the 2D transport channels enable the collection of photogenerated electrons from adjacent “inactive areas” under illumination. TiO_2 as underlayer is unlikely to be able to form 2D transport channels available because of its poor conductivity, and in the meantime, it is also

Table 2 Photovoltaic parameters of M-PSCs measured with or without masking the active area

Underlayer in ETL (mol L^{-1})	Condition	V_{OC} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
$\text{SnO}_2\text{-}0.500$	Un-masked	0.86	41.87	0.41	14.67
	Masked	0.79	23.97	0.48	8.99
$\text{SnO}_2\text{-}0.250$	Un-masked	0.91	31.84	0.47	13.75
	Masked	0.85	21.61	0.48	8.86
$\text{SnO}_2\text{-}0.063$	Un-masked	0.95	19.92	0.66	12.44
	Masked	0.95	19.72	0.66	12.32

Scheme 1 Schematic diagram illustrating M-PSCs architecture and ETL that consists of two layers, $\text{SnO}_2/\text{TiO}_2$ composite underlayer and TiO_2 mesoporous layer, respectively.

unachievable for some SnO_2 samples in this work (such as $\text{SnO}_2\text{-}0.063\text{ mol L}^{-1}$) due to the discontinuities. Therefore, it is acceptable that pseudo photocurrent appears in M-PSCs based on samples $\text{SnO}_2\text{-}0.500\text{ mol L}^{-1}$ and $\text{SnO}_2\text{-}0.250\text{ mol L}^{-1}$, in which the V_{OC} and FF are also affected under different measuring conditions as shown in Table 2. As active sites for charge recombination, the SnO_2 surface states can be passivated by photogenerated electrons, and then, it is very clear why higher V_{OC} and FF can be obtained for M-PSCs if measured with all area illuminated.

The architecture of M-PSCs is shown in Scheme 1, in which the ETL is extracted for a close-up illustration. Despite the incomplete covering of FTO by SnO_2 nanocrystallites, we never deny the significance of full coverage of FTO in terms of hole-blocking and electron transfer. Therefore, a new perspective is put forward: interfacial synergism of $\text{SnO}_2/\text{TiO}_2$ nanocomposite. Taking the sample of $\text{SnO}_2\text{-}0.032\text{ mol L}^{-1}$ as example, the largely diluted SnO_2 sol is spreaded onto FTO but fails to fully cover the substrate. After the sequential spin-coating of TiO_2 sol (to prepare mesoporous scaffold), some of the TiO_2 nanocrystallites are inferred to fill the interspace where FTO is exposed. Under this synergism, an interfacial layer of $\text{SnO}_2/\text{TiO}_2$ nanocomposite is achieved (see the top-view image in Scheme 1) which is tightly attached to FTO surface acting as effective underlayer in ETL for M-PSCs actually.

Herein, two types of devices are designed to evaluate the capability of hole-blocking, as depicted by Fig. 5a, c, respectively. The difference between the two architectures is the incorporation of TiO_2 mesoporous scaffold in the second one. As observed in Fig. 5b, d, these two types of devices both generate larger dark current in the absence of

any underlayer, suggesting that this process is governed by the direct contact of Spiro-MeOTAD with FTO. In terms of the first device, the dark current can be effectively reduced even with a spot of SnO_2 nanocrystallites attached to FTO for the samples like $\text{SnO}_2\text{-}0.016\text{ mol L}^{-1}$ and $\text{SnO}_2\text{-}0.032\text{ mol L}^{-1}$. However, full coverage of FTO by sample $\text{SnO}_2\text{-}0.250\text{ mol L}^{-1}$ does not bring about further improvement, and the decrease of dark current is not as much as another two samples ($\text{SnO}_2\text{-}0.125\text{ mol L}^{-1}$ and $\text{SnO}_2\text{-}0.063\text{ mol L}^{-1}$) instead. What we can deduce from the findings above is that the surface trap states of SnO_2 probably provide another route for dark current in addition to direct contact. The second type of testing device is more equivalent to the real architecture of M-PSCs and the regularity demonstrated in Fig. 5d is distinct from that based on the first one. It can be acknowledged that the dark current decreases regularly in the order of dilutions of the SnO_2 sol concentrations, from sample $\text{SnO}_2\text{-}0.250\text{ mol L}^{-1}$ to $\text{SnO}_2\text{-}0.032\text{ mol L}^{-1}$. This evidence powerfully supports our viewpoint on the interfacial synergism based on which the incontinuous SnO_2 underlayer together with TiO_2 mesoporous scaffold can cooperate well to effectively play the role of hole-blocking.

To demonstrate our rational conception in designing the present ETL adequately, parallel comparisons are conducted among three groups of M-PSCs classified according to the difference in underlayers of TiO_2 , SnO_2 or free. Meanwhile TiO_2 mesoporous scaffold is employed in all M-PSCs. It is worth noting that in this section, the photovoltaic performance of M-PSCs has been improved a lot through optimizing the deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ by DMSO-assistant “two-step” route as reported previously (Fig. S1, Supplementary information) [35]. The sample $\text{SnO}_2\text{-}0.032\text{ mol L}^{-1}$ based M-PSCs delivering

Figure 5 Schematic architectures of the devices (a, c) for the dark-current measurements (b, d).

Table 3 Average photovoltaic parameters and internal resistance of M-PSCs using different underlayers in ETL

Underlayer	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
Free	1.00±0.02	20.26±0.57	0.72±0.03	14.63±0.71	2.51±0.42	3372±1281
TiO ₂	1.02±0.02	20.56±0.65	0.70±0.02	14.70±0.57	2.91±0.62	1570±502
SnO ₂	1.03±0.02	21.05±0.41	0.74±0.02	16.08±0.42	2.49±0.24	2213±717

higher PCE is selected for comparison with conventional TiO₂ underlayer with an optimized thickness of ~60 nm. Table 3 shows the average photovoltaic parameters obtained from 60–70 devices for each group of M-PSCs. Detailed data distributions are shown in Fig. S2. It can be found that M-PSCs without using any underlayer can still yield an average PCE of 14.63%, comparable to that of 14.70% based on conventional TiO₂ underlayer. Comparing the parameters of the two groups, only little difference in V_{OC} and J_{SC} are observed in the absence of TiO₂ underlayer. It is widely acknowledged that FF of solar cells is seriously affected by the internal resistance that includes both series resistance (R_s) and shunt resistance (R_{sh}). We can conclude from the above comparison that the introduction of one TiO₂ underlayer into M-PSCs will lead to increased R_s and decreased R_{sh} due to more surface trap states which aggravate charge recombination and current leakage. Thus, it can be easily understood that,

due to lower R_s and larger R_{sh} , the average FF of underlayer-free M-PSCs is relative higher than that of the group using TiO₂ underlayer. On the other hand, the unfavorable electron transfer between FTO and perovskite that infiltrates in TiO₂ scaffold dominates another important route for charge recombination. Thus, even possessing a larger R_{sh} , the underlayer-free M-PSCs still yield an average V_{OC} slightly lower than the ones using TiO₂ underlayer. By contrast, the introduction of the “ultrathin” SnO₂ underlayer into M-PSCs does not increase average R_s , while the average R_{sh} (2213 Ω cm²) is much higher than that (1570 Ω cm²) of those based on TiO₂ underlayer. Our present strategy for using SnO₂ as underlayer in ETL is more feasible because it can enhance the conductivity of M-PSCs and simultaneously avoid the introduction of additional trap states. Corresponding M-PSCs thereby achieve further improvement in all photovoltaic parameters, and finally an average PCE of 16.08% with better

Figure 6 EIS characterization of M-PSCs under constant light illumination of 10 mW cm^{-2} . (a) Nyquist plots of M-PSCs measured at a DC bias of 0 V, inset: equivalent circuit for the cells; (b) Nyquist plots of M-PSCs measured at DC bias of V_{OC} , inset: zoom at high-frequency region.

Figure 7 (a) J - V curves (scan mode: backward, from 1.2 to 0 V) and photovoltaic parameters of the champion cells of three groups; (b) the steady-state output of PCE obtained under applied voltages of 0.85 V for “free” and “TiO₂”, and 0.90 V for “SnO₂”, respectively; (c) normalized characteristics of perovskite collar cells using different underlayers in ETLs *versus* time of storage in ambient air (at 25°C and 60% rH).

reproducibility is obtained.

EIS characterization was used to elucidate the charge transfer dynamics within M-PSCs [36,37]. Nyquist plots in Fig. 6 were measured under light illumination of 10 mW cm^{-2} at DC bias of 0 V and V_{OC} , respectively. The fitted equivalent circuit model is composed of series resistance (R_s), two components for transfer resistance (R_{trans}) at the ETL/perovskite and the perovskite/HTL interfaces, and recombination resistance (R_{rec}) forming a parallel circuit with capacitors. The R_{trans} is ascribed to high-frequency arc and the R_{rec} is assigned to low-frequency arc [31,38,39]. Since the only difference among the three devices lies in the microstructure between TiO₂ mesoporous scaffold and FTO, we believe the difference of impedance spectra is in direct relevance to different charge transfer behaviors at the interface. In the case of short circuit (under a bias of 0 V), M-PSCs based on SnO₂ show a much higher R_{rec} (12,613 Ω) than that of the free-based device (3301 Ω), indicating that the SnO₂/TiO₂ in-

terfacial nanocomposite ETL underlayer could effectively block electrons transfer from FTO to perovskite and in turn minimize energy loss. In addition, the R_{trans} and R_s of SnO₂-based device, either at the bias of 0 V or V_{OC} (Fig. 6a, b), are similar with the one without underlayer, but lower than the TiO₂ devices, implying that the photo-generated electrons can transfer from perovskite to FTO more conveniently when using our SnO₂-based ETL architecture. Thus, it can be concluded that SnO₂-based ETL could decrease electron transfer resistance and meanwhile effectively suppress charge recombination, which endows M-PSCs with more superior photovoltaic performance.

Fig. 7a, b illustrates the J - V curves and detailed parameters of the champion cells from each group, as well as their steady-state PCE output under maximum power point. It can be found that, based on reverse scan, a considerable PCE of 15.77% is achieved by the champion cell of the underlayer-free group, only slightly lower than

that (16.37%) of the one using conventional TiO₂ underlayer. Whereas, the two champion cells behave differently in their steady-state outputs (10.78% *versus* 14.23%) under an identical applied voltage of 0.85 V, as shown in Fig. 7b. This experimental fact convincingly supports the necessity of underlayer for efficient electron collection in M-PSCs of working status. As we can see, PSC with the best photovoltaic performance is the one based on SnO₂ underlayer that endows M-PSCs with the highest PCE of 17.58% in this work. High values of V_{OC} (1.08 V) and FF (0.78) both benefit from the major roles that SnO₂ underlayer plays in hole-blocking and reducing internal series resistance, due to which one steady-state PCE of 16.31% is output under an applied voltage of 0.90 V. We then tested the long term stability of three kinds M-PSCs based on different ETLs. These devices were stored at ambient air of high relative humidity (rH) (at 25°C and 60% rH) in the dark, and the photovoltaic parameters were tracked each day. From Fig. 7c, we can find that the M-PSCs based on SnO₂ underlayer shows a better stability than the other two devices. After 6 d, the M-PSCs on TiO₂ compact layer and the one free of underlayer demonstrated a notable decrease to ca. 25% of their initial PCEs. By comparison, the performance of the one using SnO₂ underlayer shows no degradation. This might be attributed to the unfavorable electron extraction property of ETL with TiO₂ compact layer or without compact layer, which leave many electrons accumulated near the ETL to decompose the perovskite [40]. On the contrary, the fast extraction of electrons through the SnO₂/TiO₂ synergistic ETL would hardly accumulate electrons at the interface near underlayer and thus construct a more stable device. In addition, it has been reported previously that TiO₂ is easy to be excited by UV light to accelerate the decomposition of perovskite [41]. As aforementioned, the photocatalytic activity of SnO₂ is less pronounced due to a higher band gap of ~3.8 eV, which is favorable to the device's stability when exposed to UV light.

In planar or mesoporous PSCs, hysteresis effect in current-voltage characterizations is a common phenomenon observed under different conditions including scan directions and rates, as well as applying bias voltage and light soaking prior to measurement [42,43]. To date, many reasons have been indicated to be the causes of hysteresis behavior, such as ion migration and transient ferroelectric polarization [44]. On the other hand, any factor disadvantageous to charge transfer kinetic processes can also result in pronounced hysteresis, like serious charge recombination, slow transport, and less

efficient interfacial charge extraction [45,46]. Herein we focus specifically on revealing the influence of ETL underlayer on the hysteresis behavior. Fig. 8 illustrates the J - V curves of M-PSCs under two different scan rates, and detailed parameters are summarized in Table 4. In the absence of underlayer, it is confirmed that the hysteresis behavior of M-PSCs is very obvious where the gap between the parameters obtained under is sizeable. Here, we adopt a modified hysteresis index (HI) defined by Equation (1) as follows to demonstrate the hysteresis effect quantitatively:

$$HI = \frac{J_{RS}(0.8V_{OC}) - J_{FS}(0.8V_{OC})}{J_{RS}(0.8V_{OC})}, \quad (1)$$

where J_{RS} ($0.8V_{OC}$) and J_{FS} ($0.8V_{OC}$) stand for the photocurrent density at 80% of V_{OC} for the reverse scan and forward scan, respectively. At a faster scan rate of 0.20 V s^{-1} , the V_{OC} , FF and PCE taken from the forward J - V curve are only 0.84 V, 0.39 and 6.82%, respectively, much lower than that ($V_{OC} = 1.10 \text{ V}$, FF = 0.75, PCE = 15.56%) under reverse scan at the same rate yielding a very high HI of 0.475 consequently. At a slower scan rate of 0.01 V s^{-1} , HI is reduced remarkably to 0.202, in accordance with that reported previously. By comparison, the hysteresis effect is suppressed a lot for the M-PSCs with TiO₂ underlayer, with relevant HIs decreased to 0.220 and 0.165 at the two scan rates of 0.20 and 0.01 V s^{-1} . The improvement obviously stems from the significant effect of underlayer on electron transfer dynamics, in particular on the retardation of charge recombination through hole-blocking. As mentioned above, the synergism of SnO₂/TiO₂ makes the underlayer more favorable to electron transfer. Thus, it is easy to understand why SnO₂ based M-PSCs present the slightest hysteresis behavior, with a very small HI of 0.082 at the scan rate of 0.01 V s^{-1} shown in Fig. 8f.

CONCLUSION

In summary, in this work we demonstrated comprehensive investigations on the optoelectronic properties of SnO₂. Moreover, one rational strategy for using SnO₂ combined with TiO₂ mesoporous scaffold as ETL underlayer in M-PSCs was presented. Very different from traditional ETLs in which we always necessitated one compact underlayer, it was found that only a spot of SnO₂ nanocrystallites attached to FTO, pitifully inadequate to cover FTO completely, were sufficient to play the roles of hole-blocking and electron transfer. Subsequently, one mechanism was put forward to explain this finding: the

Figure 8 *J-V* curves of M-PSCs with underlayer of free (a, b), TiO_2 (c, d), and SnO_2 (e, f), obtained under reverse and forward scan and at two different rates.

Table 4 Photovoltaic parameters from *J-V* curves obtained at different scan rates and directions

Underlayer	Scan rate and direction	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)	HI
Free	0.20 V s^{-1} reverse	1.01	20.49	0.75	15.56	0.475
	0.20 V s^{-1} forward	0.84	21.08	0.39	6.82	
	0.01 V s^{-1} reverse	1.03	17.95	0.77	14.30	
	0.01 V s^{-1} forward	1.01	21.06	0.52	11.08	
TiO_2	0.20 V s^{-1} reverse	1.04	21.62	0.71	15.86	0.220
	0.20 V s^{-1} forward	0.99	21.64	0.57	12.24	
	0.01 V s^{-1} reverse	1.04	20.51	0.70	14.94	
	0.01 V s^{-1} forward	1.03	20.94	0.58	12.45	
SnO_2	0.20 V s^{-1} reverse	1.08	21.00	0.76	17.26	0.254
	0.20 V s^{-1} forward	1.03	20.92	0.59	12.80	
	0.01 V s^{-1} reverse	1.09	19.55	0.77	16.46	
	0.01 V s^{-1} forward	1.09	21.20	0.69	16.01	

interfacial synergism of $\text{SnO}_2/\text{TiO}_2$ nanocomposite as underlayer, where TiO_2 nanoparticles came from TiO_2 mesoporous scaffold and contacted with FTO directly. Based on this new strategy, strong charge recombination observed in previous SnO_2 -based ETLs is suppressed remarkably, as the pathways of charge recombination and energy loss were blocked effectively, and meanwhile, the internal series resistance of entire M-PSCs was minimized as much as possible. Compared with traditional ETL, the new one was more kinetically favorable to electron transfer and thus resulted in substantial photovoltaic improvement and alleviated hysteresis effect for M-PSCs. Finally, the steady-state and champion PCEs of the M-PSCs using the new ETL were 16.31% and 17.58%, respectively, higher than that (steady-state PCE=14.23%; champion PCE=16.37%) of M-PSCs with traditional ETL. We believe that our strategy to re-construct ETLs is meaningful and it paves a new way for further developments in device performance.

Received 29 June 2017; accepted 11 August 2017;
published online 14 September 2017

- Stranks SD, Eperon GE, Grancini G, *et al.* Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science*, 2013, 342: 341–344
- Burschka J, Pellet N, Moon SJ, *et al.* Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, 2013, 499: 316–319
- Liu T, Zhou Y, Hu Q, *et al.* Fabrication of compact and stable perovskite films with optimized precursor composition in the fast-growing procedure. *Sci China Mater*, 2017, 60: 608–616
- Noh JH, Im SH, Heo JH, *et al.* Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett*, 2013, 13: 1764–1769
- Niu G, Yu H, Li J, *et al.* Controlled orientation of perovskite films through mixed cations toward high performance perovskite solar cells. *Nano Energy*, 2016, 27: 87–94
- Yang WS, Noh JH, Jeon NJ, *et al.* High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 2015, 348: 1234–1237
- Yang WS, Park BW, Jung EH, *et al.* Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science*, 2017, 356: 1376–1379
- Liu H, Huang Z, Wei S, *et al.* Nano-structured electron transporting materials for perovskite solar cells. *Nanoscale*, 2016, 8: 6209–6221
- Shin SS, Yeom EJ, Yang WS, *et al.* Colloidally prepared La-doped BaSnO_3 electrodes for efficient, photostable perovskite solar cells. *Science*, 2017, 356: 167–171
- Tan H, Jain A, Voznyy O, *et al.* Efficient and stable solution-processed planar perovskite solar cells via contact passivation. *Science*, 2017, 355: 722–726
- Zhao J, Wei L, Liu J, *et al.* A sintering-free, nanocrystalline tin oxide electron selective layer for organometal perovskite solar cells. *Sci China Mater*, 2017, 60: 208–216
- Kazim S, Nazeeruddin MK, Grätzel M, *et al.* Perovskite as light harvester: a game changer in photovoltaics. *Angew Chem Int Ed*, 2014, 53: 2812–2824
- Jeong I, Jung H, Park M, *et al.* A tailored TiO_2 electron selective layer for high-performance flexible perovskite solar cells via low temperature UV process. *Nano Energy*, 2016, 28: 380–389
- Wu WQ, Chen D, Caruso RA, *et al.* Recent progress in hybrid perovskite solar cells based on n-type materials. *J Mater Chem A*, 2017, 5: 10092–10109
- Yin X, Guo Y, Xue Z, *et al.* Performance enhancement of perovskite-sensitized mesoscopic solar cells using Nb-doped TiO_2 compact layer. *Nano Res*, 2015, 8: 1997–2003
- Fakharuddin A, Di Giacomo F, Palma AL, *et al.* Vertical TiO_2 nanorods as a medium for stable and high-efficiency perovskite solar modules. *ACS Nano*, 2015, 9: 8420–8429
- Ke W, Fang G, Liu Q, *et al.* Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells. *J Am Chem Soc*, 2015, 137: 6730–6733
- Wang K, Shi Y, Li B, *et al.* Amorphous inorganic electron-selective layers for efficient perovskite solar cells: feasible strategy towards room-temperature fabrication. *Adv Mater*, 2016, 28: 1891–1897
- Zhou H, Shi Y, Wang K, *et al.* Low-temperature processed and carbon-based $\text{ZnO}/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{C}$ planar heterojunction perovskite solar cells. *J Phys Chem C*, 2015, 119: 4600–4605
- Ren X, Yang D, Yang Z, *et al.* Solution-processed Nb: SnO_2 electron transport layer for efficient planar perovskite solar cells. *ACS Appl Mater Interfaces*, 2017, 9: 2421–2429
- Li X, Dai SM, Zhu P, *et al.* Efficient perovskite solar cells depending on TiO_2 nanorod arrays. *ACS Appl Mater Interfaces*, 2016, 8: 21358–21365
- Niu G, Li W, Li J, *et al.* Progress of interface engineering in perovskite solar cells. *Sci China Mater*, 2016, 59: 728–742
- Da P, Zheng G. Tailoring interface of lead-halide perovskite solar cells. *Nano Res*, 2017, 10: 1471–1497
- Fonstad CG, Rediker RH. Electrical properties of high-quality stannic oxide crystals. *J Appl Phys*, 1971, 42: 2911–2918
- Tiwana P, Docampo P, Johnston MB, *et al.* Electron mobility and injection dynamics in mesoporous ZnO , SnO_2 , and TiO_2 films used in dye-sensitized solar cells. *ACS Nano*, 2011, 5: 5158–5166
- Roose B, Baena JPC, Gödel KC, *et al.* Mesoporous SnO_2 electron selective contact enables UV-stable perovskite solar cells. *Nano Energy*, 2016, 30: 517–522
- Li Y, Zhu J, Huang Y, *et al.* Mesoporous SnO_2 nanoparticle films as electron-transporting material in perovskite solar cells. *RSC Adv*, 2015, 5: 28424–28429
- Yu H, Zhang S, Zhao H, *et al.* An efficient and low-cost TiO_2 compact layer for performance improvement of dye-sensitized solar cells. *Electrochim Acta*, 2009, 54: 1319–1324
- Dong Q, Shi Y, Wang K, *et al.* Insight into perovskite solar cells based on SnO_2 compact electron-selective layer. *J Phys Chem C*, 2015, 119: 10212–10217
- Shi Y, Hou K, Wang Y, *et al.* Two methoxyaniline-substituted dibenzofuran derivatives as hole-transport materials for perovskite solar cells. *J Mater Chem A*, 2016, 4: 5415–5422
- Xiong L, Qin M, Yang G, *et al.* Performance enhancement of high temperature SnO_2 -based planar perovskite solar cells: electrical characterization and understanding of the mechanism. *J Mater Chem A*, 2016, 4: 8374–8383
- Shin SS, Yang WS, Noh JH, *et al.* High-performance flexible per-

- ovskite solar cells exploiting Zn_2SnO_4 prepared in solution below 100 °C. *Nat Commun*, 2015, 6: 7410
- 33 Peng B, Jungmann G, Jäger C, *et al.* Systematic investigation of the role of compact TiO_2 layer in solid state dye-sensitized TiO_2 solar cells. *Coord Chem Rev*, 2004, 248: 1479–1489
- 34 Chandiran AK, Yella A, Mayer MT, *et al.* Sub-nanometer conformal TiO_2 blocking layer for high efficiency solid-state perovskite absorber solar cells. *Adv Mater*, 2014, 26: 4309–4312
- 35 Li W, Fan J, Li J, *et al.* Controllable grain morphology of perovskite absorber film by molecular self-assembly toward efficient solar cell exceeding 17%. *J Am Chem Soc*, 2015, 137: 10399–10405
- 36 Kim HS, Mora-Sero I, Gonzalez-Pedro V, *et al.* Mechanism of carrier accumulation in perovskite thin-absorber solar cells. *Nat Commun*, 2013, 4: 2242
- 37 Guerrero A, Garcia-Belmonte G, Mora-Sero I, *et al.* Properties of contact and bulk impedances in hybrid lead halide perovskite solar cells including inductive loop elements. *J Phys Chem C*, 2016, 120: 8023–8032
- 38 Shih YC, Wang LY, Hsieh HC, *et al.* Enhancing the photocurrent of perovskite solar cells *via* modification of the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ heterojunction interface with amino acid. *J Mater Chem A*, 2015, 3: 9133–9136
- 39 Yang D, Yang R, Zhang J, *et al.* High efficiency flexible perovskite solar cells using superior low temperature TiO_2 . *Energy Environ Sci*, 2015, 8: 3208–3214
- 40 Ahn N, Kwak K, Jang MS, *et al.* Trapped charge-driven degradation of perovskite solar cells. *Nat Commun*, 2016, 7: 13422
- 41 Niu G, Guo X, Wang L. Review of recent progress in chemical stability of perovskite solar cells. *J Mater Chem A*, 2015, 3: 8970–8980
- 42 Zhao C, Chen B, Qiao X, *et al.* Revealing underlying processes involved in light soaking effects and hysteresis phenomena in perovskite solar cells. *Adv Energy Mater*, 2015, 5: 1500279
- 43 Correa Baena JP, Steier L, Tress W, *et al.* Highly efficient planar perovskite solar cells through band alignment engineering. *Energy Environ Sci*, 2015, 8: 2928–2934
- 44 Snaith HJ, Abate A, Ball JM, *et al.* Anomalous hysteresis in perovskite solar cells. *J Phys Chem Lett*, 2014, 5: 1511–1515
- 45 Tress W, Marinova N, Moehl T, *et al.* Understanding the rate-dependent *J-V* hysteresis, slow time component, and aging in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells: the role of a compensated electric field. *Energy Environ Sci*, 2015, 8: 995–1004
- 46 Heo JH, Song DH, Han HJ, *et al.* Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with constant 17.2% average power conversion efficiency irrespective of the scan rate. *Adv Mater*, 2015, 27: 3424–3430

Acknowledgements This work was supported by the National Natural Science Foundation of China (51402036, 51273104 and 91433205), and the International Science & Technology Cooperation Program of China (2013DFA51000).

Author contributions Shi Y, Dong Q and Xue Y developed the SnO_2 -based ETLs for M-PSCs. Dong Q prepared the SnO_2 and TiO_2 underlayer precursor solution and the ETL films, characterized the SEM, AFM, SLV and UV-vis absorption of ETL underlayers. Xue Y fabricated the PSCs. Chen F and Zhan S tested the *J-V* curves. Chi R designed the scheme of PSCs. Zhao L helped the EIS measurement. Shi Y and Dong Q prepared the manuscript. Wang L and Wang S helped to revised the manuscript. The final version of the manuscript was approved by all authors.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Qingshun Dong received the Master's degree from Dalian University of Technology (DUT), China, in 2012. Currently, he is a PhD candidate at Tsinghua University. His research interest focuses on charge transfer materials and stability of perovskite solar cells.

Liduo Wang is a professor of the Department of Chemistry at Tsinghua University. He received his PhD degree from Nagoya University of Japan in 1995. Dr. Wang has once worked as a visiting scholar in the Department of Chemistry and as a research associate in the Department of Electrical and Electronic Engineering at Hong Kong University of Science and Technology, and as a postdoctoral researcher in the Department of Materials Science and Engineering, Tsinghua University. His current research interests include perovskite solar cells, organic-inorganic semiconductor multilayer, and its optoelectronic properties.

Yantao Shi graduated from Lanzhou University in 2005 with a Bachelor's degree, then studied at Tsinghua University for his Master's degree and PhD from 2005 to 2010. As a visiting scholar, he worked at the Department of Physics, Hong Kong University of Science and Technology in the following two years. In 2012, he joined Dalian University of Technology with focus on the third generation thin film solar cells, e.g., dye-sensitized solar cells and perovskite solar cells. His contributions include synthesizing novel photoelectric materials, revealing the effects of nanostructures on cell performance, improving long-term durability, and so on.

介孔钙钛矿太阳能电池中二氧化锡基电子传输层的合理设计: 比传统双层结构更具动力学优势

董庆顺¹, 薛源², 王适², 王立铎^{1*}, 陈凡², 张森², 迟日涵², 赵亮², 史彦涛^{2*}

摘要 本文采用点分布 SnO_2 和 TiO_2 介孔层中的纳米粒子组成的“协同层”作为高效介孔钙钛矿太阳能电池的电子传输层衬层。基于该新策略, 电荷复合和能量损失路径被有效阻隔, 使得之前报道的 SnO_2 基电子传输层介孔钙钛矿太阳能电池中的强烈电荷复合被有效抑制。同时, 整个介孔钙钛矿太阳能电池的串联电阻显著降低。新型的电子传输层动力学上更有利的电子传输有效提升了介孔钙钛矿太阳能电池的光伏性能, 并明显抑制了电池的回滞。