A sintering-free, nanocrystalline tin oxide electron selective layer for organometal perovskite solar cells

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ABSTRACT Effective electron selective layer (ESL) is critical for the power conversion efficiency in organometal halide-based perovskite solar cells (PSCs). In this work, a spin-coating process has been developed to fabricate high quality nanocrystalline SnO₂ film at 100°C without further sintering at higher temperature. When used as ESL in PSCs, such SnO₂ film shows greater electron extraction ability and higher efficiency than TiO₂ film processed under similar condition, as evidenced by the efficient time-resolved photoluminescence (TRPL) quenching SnO₂/CH₃NH₃PbI₃ film. As a result, the SnO₂-based PSCs possess higher open circuit voltage of 0.91 V, short circuit current density of 20.73 mA cm⁻², and fill factor of 64.25%, corresponding to a conversion efficiency of 12.10%, compared with 7.16% of TiO₂-based PSCs. This demonstrates the great potential of applying spin-coating sintering-free process for the low-cost and large-scale manufacturing of PSCs.

Keywords: low-temperature, sintering-free, perovskite solar cells, SnO₂, electron-selective layer

INTRODUCTION

Recent progress in perovskite solar cells (PSCs) has attracted great attention due to the rapid improvement of their power conversion efficiency (PCE) from initial 3.8% in 2009 to certified 22.1% in 2016 [1–9]. Selective extraction of photo-generated electrons and holes that inhibits charge recombination is necessary for achieving high efficiency in PSCs [10], and the exploration of the effective electron selective layer (ESL) remains a challenging scientific issue. While many semiconductors are feasible as ESL materials for PSCs, the majority of the studies focus on TiO₂ and ZnO [11–18]. Compared with TiO₂ and ZnO, SnO₂ not only has much higher electron mobility but also

a wider band gap [19–22], and thus has a smaller ESL-induced current absorption loss, and is more stable under UV illumination [23–25]. Moreover, it has been reported that improved hysteretic behaviour and high efficiencies can be achieved using SnO₂ nanocrystals in planar PSCs [22,26,27]. In such configuration, the relative energy levels of the solar cell components are shown in Fig. 1. Free charge carriers are generated in the CH₃NH₃PbI₃ layer with direct band gap and high carrier mobility, which are then extracted by the SnO₂ ESL and the spiro-OMeTAD hole transport materials (HTM), respectively. Given the highly selective properties of both SnO₂ ESL and spiro-OMeTAD HTM, high efficient devices with improved fill factors are expected.

Generally, materials processed at higher temperatures will exhibit higher charge carrier mobility due to better crystallinity, and thus in order to achieve high device performance, the solution-processed compact SnO₂ ESL normally requires a high temperature sintering procedure at 450°C [28]. In previous studies, attempts have been made to decrease the processing temperature of SnO₂ to 180°C on the fluorine doped tin oxide (FTO) glass [2,29], and to 150°C for SnO₂ nanocrystalline film with particle size of 22–43 nm [30]. Liu *et al.* [31] reported an even lower processing temperature of 140°C to achieve an effective electron selection and a high PCE greater than 15%. Nevertheless, for the facile fabrication of the low-cost and large-scale planar perovskite solar cells, it is desirable to develop a compact SnO₂ film with good crystallinity and small particle size under even lower-temperature annealing.

In this work, the highly crystalline homogeneous SnO₂

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Figure 1 (a) Device architecture of the FTO/ESL(SnO₂)/CH₃NH₃PbI₃/spiro-OMeTAD/Ag cells; (b) energy levels (relative to vacuum) of the various device components.

film was fabricated using a spin-coating and sintering-free method with film processing temperature at only 100°C. The SnO₂ film displays complete surface coverage, uniform nanocrystals size of 2–5 nm and great electron extraction ability, as evidenced by the efficient time-resolved photoluminescence (TRPL) quenching of SnO₂/CH₃NH₃PbI₃ film. Furthermore, a conversion efficiency of 12.10% is achieved in PSCs based on SnO₂ ESL processed as such, much higher than 7.16% of PSCs based on TiO₂ ESL processed in a similar manner.

EXPERIMENTAL

Raw materials

PbI₂ (99.99%) and *N,N*-dimethylformide (DMF) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. CH₃NH₃I (>99.0%) was purchased from Xi'an Polymer Light Technology Co. 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) (≥99.0%) was purchased from Shenzhen Feiming Science and Technology Co., Ltd. FTO glass with a sheet resistance of 14 ohm/square was purchased from Pilkington Glass. Pluronic F127 was purchased from Sigma-Aldrich, Inc. The purity of silver wire, purchased from Nanchang Guocai Technology Co., is 99.99%. All other materials were purchased from J&K Scientific Ltd. All of the used reagents were analytical grade.

Preparation of SnO₂ nanocrystals

Firstly, 0.1 mol L⁻¹ SnCl₄ was dissolved into 100 mL ethanol, and then 100 mL NaOH solution (1 mol L⁻¹) was dropped to the above solution. After stirring for 15 min, a white milky solution was obtained. Secondly, the white colloidal deposition was centrifuged and washed with ethanol twice, and dried at 80°C for 10 h in vacuum, and then calcined at

400°C for 1 h to obtain a snow white SnO₂ powder.

Spin-coating of SnO₂ ESL films

The prepared SnO₂ nanocrystals were spin-coated on the transparent and conductive FTO substrate as following. Firstly, FTO-coated glass substrates were cleaned by ultrasonication in an alkaline, aqueous washing solution, and rinsed with deionized water, ethanol, acetone and 2-propanol, respectively. Then the SnO₂ nanoparticles were dispersed in ethanol at a concentration of 5 mg mL⁻¹ and stirred for 24 h before use. Finally, the solution was filtered with a 0.45 μm filter and spin-coated on FTO substrates at 3000 rpm for 30 s to form a SnO₂ layer, followed by short drying at 100°C for 10 min, without further calcination or sintering.

Fabrication of TiO₂ nanocrystals and ESL films

For comparison, ESL made of TiO₂ nanoparticles was also prepared. TiO₂ nanoparticles were fabricated first as following [32]. Pluronic F127 (2.97 g) was dissolved in 36.88 g ethanol at 40°C for 30 min to form a clear solution, after which 3.4 g TiCl₄ was added to the solution. The precursor solution was then poured into a Teflon-lined stainless steel autoclave and stirred for 8 h under 40°C. The autoclave was heated in an oven at 160°C for 16 h. Subsequently, the products in autoclave were filtered, washed and dried at 80°C. The powders were then calcined at 610°C for 10 min after being kept at 300°C for 1.5 h and 500°C for 4 h. During the whole process, the heating rate was kept at 2°C min⁻¹. After sintering, the products were dispersed using deionized water and nitric acid (65%) until the pH of the solution reached about 2. Then the mixture solution was vigorously stirred at 80°C for 8 h to obtain TiO₂ nanoparticles, which were subsequently dispersed in ethanol at 5 mg mL⁻¹ and stirred for 24 h before use. Finally, the suspension

solution was filtered with a 0.45 μm filter and spin-coated on FTO substrates at 3000 rpm for 30 s to form a TiO_2 layer, followed by short drying at 100°C for 10 min, without sintering at high temperature.

Fabrication of perovskite solar cells

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was grown on ESL using a two-step solution process. To ensure the selective collection of electrons at the FTO electrodes, the perovskite layer was deposited on the n-type compact SnO_2 or TiO_2 ESL, followed by deposition of spiro-OMeTAD as the p-type hole conducting layer. Finally the Ag layer was evaporated.

The procedure for preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film on ESL was as follows: PbI_2 was dissolved in DMF at a concentration of 462 mg mL^{-1} ($\sim 1 \text{ mol L}^{-1}$) under mild stirring speed of 200 rpm at 70°C. The solution was kept at 70°C during the whole procedure. The PbI_2 film was spin-coated onto ESL at 4500 rpm for 30 s and dried. The films were then dipped in a solution of $\text{CH}_3\text{NH}_3\text{I}$ in 2-propanol (10 mg mL^{-1}) for 10 min, rinsed with 2-propanol and dried at 70°C for 30 min.

The HTM was then deposited by spin coating at 4000 rpm for 30 s. The spin-coating formulation was prepared by dissolving 72.3 mg spiro-OMeTAD, 28.8 μL 4-*tert*-butylpyridine, 17.5 μL of a stock solution of 520 mg mL^{-1} lithium bis(trifluoromethylsulphonyl) imide in acetonitrile in 1 mL chlorobenzene. In the fabrication, the perovskite film and HTM were prepared in a glove box. Finally, 150 nm Ag was thermally evaporated onto the HTM layer in vacuum to act as the cathode. The cell area is 0.09 cm^2 . While moving, the samples were placed in special boxes filled with nitrogen, and the device was stored in cabinet with flowing N_2 gas.

Characterization

X-ray diffraction (XRD) patterns were obtained using D8 advance diffractometer with Cu K α radiation (40 kV and 40 mA) and the scanning rate of 4° min^{-1} over the Bragg angle range of 10°–80°. Scanning electron microscopy (SEM) analysis was performed on a Hitachi-S-4800 electron microscope. Transmission electron microscopy (TEM) images were acquired with JEOL 200CX at 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB250 spectrometer equipped with a monochromatized Al K α source. The charge effect was calibrated using the binding energy of C 1s (284.6 eV) to reduce its effect. Atomic-force microscopy (AFM) images were recorded using asylum research MFP-3D in the AC

mode under ambient conditions. Additionally, the thicknesses of the thin films were estimated using AFM step analysis. Ultraviolet-visible (UV-vis) transmittance was recorded with a Shimadzu UV-2550 (300–600 nm: xenon lamp, 300 W; 600–900 nm: tungsten-halogen lamp, 150 W), and TRPL spectra was measured by FLS-800 spectrometers. The photocurrent-voltage (J - V) characteristics of the solar cells were measured using a Keithley 2400 source under illumination of a simulated sunlight (AM1.5, 100 mW cm^{-2}) provided by a Newport 69907 solar simulator with an AM 1.5 filter. Light intensity was adjusted with an NREL-calibrated Si solar cell using a KG-2 filter for approximating 1 sun light intensity. While measuring the current and voltage, the cell was covered by a black mask with an aperture that was close to the active device area. The incident photon-to-current efficiency (IPCE) was measured in DC mode with a 1/4 m double monochromator (CrownTech DK242), a multi-meter (Keithley 2000), and two light sources depending on the wavelength range required (300–600 nm xenon lamp, 300 W; 600–900 nm: tungsten-halogen lamp, 150 W). The monochromatic light intensity for IPCE spectra efficiency was calibrated using a reference silicon photodiode. All the measurements of the solar cells were performed under ambient atmosphere at room temperature without encapsulation.

The optimization of the perovskite solar cell device architecture can be simply illustrated by model calculation of the so-called IPCE. This quantity provides the number of electrons generated in a solar cell per one incident photon with the Equation (1)

$$\text{IPCE} = \frac{i_{\text{ph}} hc}{Pe\lambda}, \quad (1)$$

where i_{ph} is the photocurrent density, h is Planck's constant, λ is the photon wavelength, c is the velocity of light, P is the incident light power density, and e is the electron charge.

The short circuit photocurrent density for perovskite solar cell illuminated by solar light, J_{sc} , is given by the sum Equation (2) of individual contributions from IPCEs, integrated over the whole solar spectrum

$$J_{\text{sc}} = \frac{\int_{\lambda_1}^{\lambda_2} \text{IPCE}(\lambda) \cdot P_{\text{sun}}(\lambda) d\lambda}{A}, \quad (2)$$

where $P_{\text{sun}}(\lambda)$ is the solar power density at the wavelength λ . A is the area of perovskite solar cell.

RESULTS AND DISCUSSION

The well-defined and uniform size of SnO_2 nanoparticles,

with an average diameter of 2–5 nm are revealed by the high-resolution TEM (HR-TEM) in Fig. 2a and Fig. S1a. The Laue electron diffraction patterns in Fig. 2a and Fig. S1b show the polycrystalline nature of SnO₂ film and the well-ordered SnO₂ crystals, as judged from dominant (110) and (101) facets. The XRD pattern of the SnO₂ nanocrystals is given in Fig. 2b. Each diffraction line is assigned to the tetragonal rutile crystalline phase of SnO₂ [33]. All of the peaks matched reasonably well with the standard pattern in JCPDS No.21-1250. The diffraction peaks at positions 26.57°, 33.87°, 37.94°, 51.75°, 57.82°, 61.87°, 65.96°, 71.28°, 78.69° correspond to (110), (101), (200), (211), (002), (310), (301), (202) and (321) as indicated by Fig. 2b, which are consistent with the selective area electron diffraction (SAED) image of SnO₂ nanocrystals in Fig. 2a. The average crystallite size of 3.5 nm is calculated from XRD patterns using the Scherrer formula, in accordance with the result from TEM image [34].

In order to further characterize the composition of SnO₂ films and the atomic valence states of SnO₂, especially of Sn, core level XPS spectrum of Sn 3d is shown in Fig. 2c, and

the full XPS spectrum survey is given in Fig. S2a, showing the presence of O and Sn. The binding energies of 487 and 495 eV in Fig. 2c correspond to the Sn 3d_{5/2} and Sn 3d_{3/2} peaks, respectively, confirming the formation of pure SnO₂ with the appearance of Sn⁴⁺ peaks [22,29]. The main binding energy of 531 eV in Fig. S2b is attributed to the O 1s, which is the O²⁻ state in SnO₂. Fig. S2c shows that there is no residual Cl observed in SnO₂ films. From the TEM, XRD and XPS data, we can see that the SnO₂ nanocrystals with uniform nanoparticle size and well-defined crystallinity have been fabricated successfully, ideal for the compact SnO₂ ESL in PSCs.

To investigate the surface morphology of SnO₂ film, SEM and AFM images are shown in Fig. 3. The surface morphology of SnO₂ films as observed from the SEM in Fig. 3a and AFM micrograph in Fig. 3b and Fig. S3 show that the grains are uniformly distributed within the scanning area, and the film is smooth with a root mean square (RMS) surface roughness of ~14.9 nm in an area of 2 μm × 2 μm, smaller than 25.76 nm reported in high-temperature processed films with large particle size [35]. This surface char-

Figure 2 Microstructure of SnO₂ nanocrystals. (a) HRTEM image (the inset is SAED image of SnO₂ film); (b) XRD pattern of SnO₂ powders; and (c) XPS spectra of Sn 3d peaks.

Figure 3 SEM image (a) and AFM height image (b) of SnO₂ film; (c) SEM image of perovskite film on SnO₂ film; (d) cross-sectional SEM image of the device.

acteristic is important for SnO₂'s applications as ESL. Cross-sectional AFM probing was used to measure the thickness of the film, as shown in Fig. S4, which is estimated to be around 10 nm for SnO₂ on FTO substrate [36]. To better illustrate the device structure, SEM images of CH₃NH₃PbI₃ perovskite films on SnO₂ and TiO₂ film are shown in Fig. 3c and Fig. S5, and a color-enhanced cross-sectional SEM image is presented in Fig. 3d. The SnO₂ films are fully compatible with the growth of CH₃NH₃PbI₃ perovskite absorbers, and the CH₃NH₃PbI₃ perovskite films have covered the SnO₂ and TiO₂ film completely with good uniformity.

TiO₂ films deposited on the FTO substrates exhibit similar morphologies as SnO₂, as shown in Fig. S6, suggesting that our low-temperature spin-coating process is ideal for fabrication of thin ESL with full surface coverage, nanoscale particle size, and uniform crystalline structure in PSCs.

Fig. 4 shows the current-voltage characteristics (*J-V*) measured under simulated solar AM1.5G irradiation (100 mW cm⁻²) and in dark for PSCs comprised of FTO/ESL/CH₃NH₃PbI₃/Spiro-OMETAD/Ag. Typical *J-V* curves under reverse and forward scan directions for SnO₂-based device are shown in Fig. 4a, in which a small

Figure 4 (a) *J-V* curves of perovskite solar cells with SnO₂ and TiO₂ ESL; (b) dark current measurements for perovskite solar cells. All *J-V* curves were measured under 100 mW cm⁻² air mass (AM 1.5G) illumination.

Table 1 Photovoltaic performance parameters of SnO₂- and TiO₂-based solar cells with forward and reverse scans

Device	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
SnO ₂ -reverse	0.91±0.02	20.73±0.2	64.26±0.5	12.10±0.3
SnO ₂ -forward	0.93±0.02	20.22±0.2	63.53±0.5	11.92±0.3
TiO ₂ -reverse	0.81±0.02	19.36±0.2	45.55±0.5	7.16±0.3
TiO ₂ -forward	0.61±0.02	18.18±0.2	42.92±0.5	5.77±0.3

hysteresis is observed. The hysteresis is mostly dependent on the device architecture [8,37,38]. A reference cell with TiO₂ ESL is also presented for comparison, showing much larger hysteresis. The PSCs with SnO₂ ESL displayed an open-circuit voltage (V_{oc}) of 0.91±0.02 V, a short circuit current density (J_{sc}) of 20.73±0.2 mA cm⁻² and a fill factor (FF) of 64.26%±0.5%, resulting in a PCE of 12.10%±0.3% in the reverse scan. With TiO₂ ESL, the PSCs in the reverse scan show a lower PCE of 7.16%±0.3%, with a significant reduction in the average FF (from 64.26% to 45.55%), V_{oc} (from 0.91 to 0.81 V) and J_{sc} (from 20.73 to 19.36 mA cm⁻²). The PSCs with SnO₂ ESL exhibit a high V_{oc} , J_{sc} and FF largely due to the effective charge dissociation between CH₃NH₃PbI₃ and SnO₂, followed by fast electrons transport through SnO₂ to the FTO. As a result, the charge recombination in the SnO₂-based PSCs could be suppressed much more effectively compared with the TiO₂-based PSCs, leading to a rather lower back current density in SnO₂-based PSCs, as exhibited by the dark J - V characteristics in Fig. 4b [39]. Apparently, all the dark current-voltage characteristics display very similar trends, and the saturation current density of the SnO₂-based device is lower than that of the TiO₂-based cell, thereby resulting in a larger V_{oc} [39,40]. The stability of the perovskite devices with SnO₂ as the ESL was tested without encapsulation in air at room temperature (Fig. S7). After 45,000 s (12.5 h), the PCE, J_{sc} and V_{oc} of SnO₂-based solar cell devices were stabilized at about 10%, 18 mA cm⁻² and 0.9 V, compared with 6%, 17 mA cm⁻² and 0.7 V of TiO₂-based solar cell devices, respectively.

To verify that SnO₂ and TiO₂ are effective quenching materials for electrons, the steady-state photoluminescence (PL) spectra of perovskite films with these quenchers in the middle of FTO and perovskite layer were measured. As shown in Fig. 5a, compared with the perovskite on glass, the PL peak decrease for both SnO₂ and TiO₂, whereas the SnO₂ shows much better quenching efficiency. Electrons or holes are dissociated at the interfaces between CH₃NH₃PbI₃ perovskite and the SnO₂ or TiO₂ quencher, which are then transferred to the quencher and can no longer contribute to PL. In order to extract quantitative

analysis on the yield of light induced charge carrier separation, we performed the TRPL measurements in Fig. 5b. Excitons emerged by light excitation of perovskite were extracted into free charge carriers within 1 ps [41]. The hole-carrier through thin SnO₂ and TiO₂ nanocrystals layer was measured by the PL decay. The PL decay at the interface of CH₃NH₃PbI₃ perovskite and SnO₂ films displays an average time constant of τ_e =(5.1±0.4) ns, whereas for the TiO₂, τ_e is (5.5±0.4) ns, both of which are shorter than the perovskite layer on glass (78±0.5) ns, indicating that charge carriers within the CH₃NH₃PbI₃ perovskite layer can be dissociated effectively by these inorganic oxides [42]. The shorter exciton (electron hole pair) lifetime observed with SnO₂ ESL suggests a faster charge-transfer kinetics, and it is an indicator of lower defect concentration and good crystalline quality [9,22,43]. The efficient carrier dissociation in SnO₂-based solar cells results from the high carrier mobility or lower conduction band level of SnO₂ electron selective layer. This advantage can be regarded as a factor that results in +1.37 mA cm⁻² higher J_{sc} of SnO₂ than that of TiO₂-based solar cell device.

Fig. 5c, d show the UV-vis transmission spectra and IPCE for the SnO₂ and TiO₂ ESL, respectively. Generally, the trends of the IPCE spectra of the CH₃NH₃PbI₃ devices in Fig. 5d agree with that of the UV-vis transmission spectrum in Fig. 5c: the shapes of the IPCE spectrum match excellently with that of the UV-vis transmission spectrum, and the IPCE is enlarged upon improving the light transmission intensity. The onset of the UV-vis transmittance at ~340 nm for SnO₂ corresponds to the band gap of 3.64 eV. For TiO₂ nanoparticles, the UV-vis absorption band at 370 nm corresponds to the band gap 3.2 eV. The IPCE spectrum with SnO₂ ESL shows a broad peak value of about 90%, while TiO₂ as the ESL displays a broad peak value below 80% in the range from 400 to 780 nm. The photocurrents of 21.0 mA cm⁻² integrated from area of the SnO₂-based IPCE spectra is consistent with the J_{sc} values gained from the J - V . The onset of IPCE photocurrent is at ~780 nm, consistent with the reported band gap [6,44]. The ultrathin SnO₂ ESL can put ~80% light through, and this potentially increases

Figure 5 (a) Steady-state PL of perovskite deposited on SnO₂ film, TiO₂ film and glass; (b) TRPL (excitation wavelength at 507 nm) of the perovskites on SnO₂ film, TiO₂ film and glass; (c) transmission spectra of TiO₂/FTO and SnO₂/FTO films; (d) IPCE spectra of perovskite devices with SnO₂ and TiO₂ as ESL.

the amount of light absorption in perovskite layer above SnO₂ ESL. The simple planar structure and the production of such high-performance cells with low-temperature spin-coating of ESL confirm the good potential of SnO₂ in photovoltaic applications [29,45,46].

CONCLUSIONS

The well-crystallized SnO₂ ESL is successfully spin-coated on FTO glass at 100°C without further high-temperature sintering process. The low-temperature spin-coated SnO₂ film displays uniform particle size of 2–5 nm, ultrathin thickness of 10 nm, complete surface coverage and fast charge-transfer kinetics of 5.1 ns, and the resulting efficiency of 12.10% is notable compared with 7.16% in TiO₂ based PSCs. The stabilized efficiency of SnO₂-based PSCs is ascribed to the crystallized compact/thin SnO₂ ESL suppressing the electron recombination. We believe that this sintering-free nanocrystalline SnO₂ ESL film will find applications in large-scale and low-cost PSCs.

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- 1 Kojima A, Teshima K, Shirai Y, *et al.* Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J Am Chem Soc*, 2009, 131: 6050–6051
- 2 Park M, Kim JY, Son HJ, *et al.* Low-temperature solution-processed Li-doped SnO₂ as an effective electron transporting layer for high-performance flexible and wearable perovskite solar cells. *Nano Energy*, 2016, 26: 208–215
- 3 Lee MM, Teuscher J, Miyasaka T, *et al.* Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*, 2012, 338: 643–647
- 4 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
- 5 Chen W, Wu Y, Yue Y, *et al.* Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science*, 2015, 350: 944–948
- 6 Zhou H, Chen Q, Li G, *et al.* Interface engineering of highly efficient perovskite solar cells. *Science*, 2014, 345: 542–546
- 7 Zhao Z, Chen X, Wu H, *et al.* Probing the photovoltage and photocurrent in perovskite solar cells with nanoscale resolution. *Adv Funct Mater*, 2016, 26: 3048–3058
- 8 Yang WS, Noh JH, Jeon NJ, *et al.* High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 2015, 348: 1234–1237
- 9 Wang Q, Chen H, Liu G, *et al.* Control of organic-inorganic halide perovskites in solid-state solar cells: a perspective. *Sci Bull*, 2015, 60: 405–418
- 10 Ke W, Fang G, Wan J, *et al.* Efficient hole-blocking layer-free planar

- halide perovskite thin-film solar cells. *Nat Commun*, 2015, 6: 6700
- 11 Wojciechowski K, Saliba M, Leijtens T, *et al.* Sub-150°C processed meso-superstructured perovskite solar cells with enhanced efficiency. *Energy Environ Sci*, 2014, 7: 1142–1147
 - 12 Zhao JJ, Wang P, Liu ZH, *et al.* Controlled reaction for improved $\text{CH}_3\text{NH}_3\text{PbI}_3$ transition in perovskite solar cells. *Dalton Trans*, 2015, 44: 17841–17849
 - 13 Zhong D, Cai B, Wang X, *et al.* Synthesis of oriented TiO_2 nanocones with fast charge transfer for perovskite solar cells. *Nano Energy*, 2015, 11: 409–418
 - 14 Zhao J, Wang P, Wei L, *et al.* Efficient charge-transport in hybrid lead iodide perovskite solar cells. *Dalton Trans*, 2015, 44: 16914–16922
 - 15 Liu D, Kelly TL. Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. *Nat Photon*, 2013, 8: 133–138
 - 16 Gonzalez-Pedro V, Juarez-Perez EJ, Arsyad WS, *et al.* General working principles of $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite solar cells. *Nano Lett*, 2014, 14: 888–893
 - 17 Xu X, Zhang H, Shi J, *et al.* Highly efficient planar perovskite solar cells with a TiO_2/ZnO electron transport bilayer. *J Mater Chem A*, 2015, 3: 19288–19293
 - 18 Son DY, Bae KH, Kim HS, *et al.* Effects of seed layer on growth of ZnO nanorod and performance of perovskite solar cell. *J Phys Chem C*, 2015, 119: 10321–10328
 - 19 Han GS, Chung HS, Kim DH, *et al.* Epitaxial 1D electron transport layers for high-performance perovskite solar cells. *Nanoscale*, 2015, 7: 15284–15290
 - 20 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
 - 21 Zhu Z, Zheng X, Bai Y, *et al.* Mesoporous SnO_2 single crystals as an effective electron collector for perovskite solar cells. *Phys Chem Chem Phys*, 2015, 17: 18265–18268
 - 22 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
 - 23 Grätzel M. Photoelectrochemical cells. *Nature*, 2001, 414: 338–344
 - 24 Snaith HJ, Ducati C. SnO_2 -based dye-sensitized hybrid solar cells exhibiting near unity absorbed photon-to-electron conversion efficiency. *Nano Lett*, 2010, 10: 1259–1265
 - 25 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
 - 26 Sadoughi G, Sivaram V, Gunning R, *et al.* Enhanced electronic contacts in SnO_2 -dye-P3HT based solid state dye sensitized solar cells. *Phys Chem Chem Phys*, 2013, 15: 2075–2080
 - 27 Kranz L, Abate A, Feurer T, *et al.* High-efficiency polycrystalline thin film tandem solar cells. *J Phys Chem Lett*, 2015, 6: 2676–2681
 - 28 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
 - 29 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
 - 30 Song J, Zheng E, Bian J, *et al.* Low-temperature SnO_2 -based electron selective contact for efficient and stable perovskite solar cells. *J Mater Chem A*, 2015, 3: 10837–10844
 - 31 Liu X, Tsai KW, Zhu Z, *et al.* A low-temperature, solution processable tin oxide electron-transporting layer prepared by the dual-fuel combustion method for efficient perovskite solar cells. *Adv Mater Interfaces*, 2016, 3: 1600122
 - 32 Zhao J, Zhang J, Wang W, *et al.* Facile synthesis of CuInGaS_2 quantum dot nanoparticles for bilayer-sensitized solar cells. *Dalton Trans*, 2014, 43: 16588–16592
 - 33 Gu F, Fen Wang S, Feng Song C, *et al.* Synthesis and luminescence properties of SnO_2 nanoparticles. *Chem Phys Lett*, 2003, 372: 451–454
 - 34 Patterson AL. The Scherrer formula for X-ray particle size determination. *Phys Rev*, 1939, 56: 978–982
 - 35 Khan AF, Mehmood M, Rana AM, *et al.* Effect of annealing on electrical resistivity of rf-magnetron sputtered nanostructured SnO_2 thin films. *Appl Surface Sci*, 2009, 255: 8562–8565
 - 36 Chen Z, Lin YM, Rooks MJ, *et al.* Graphene nano-ribbon electronics. *Physica E*, 2007, 40: 228–232
 - 37 Snaith HJ, Abate A, Ball JM, *et al.* Anomalous hysteresis in perovskite solar cells. *J Phys Chem Lett*, 2014, 5: 1511–1515
 - 38 Frost JM, Butler KT, Brivio F, *et al.* Atomistic origins of high-performance in hybrid halide perovskite solar cells. *Nano Lett*, 2014, 14: 2584–2590
 - 39 Cai B, Xing Y, Yang Z, *et al.* High performance hybrid solar cells sensitized by organolead halide perovskites. *Energy Environ Sci*, 2013, 6: 1480–1485
 - 40 He Z, Xiao B, Liu F, *et al.* Single-junction polymer solar cells with high efficiency and photovoltage. *Nat Photon*, 2015, 9: 174–179
 - 41 Ponseca Jr CS, Savenije TJ, Abdellah M, *et al.* Organometal halide perovskite solar cell materials rationalized: ultrafast charge generation, high and microsecond-long balanced mobilities, and slow recombination. *J Am Chem Soc*, 2014, 136: 5189–5192
 - 42 You J, Meng L, Song TB, *et al.* Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. *Nat Nanotech*, 2015, 11: 75–81
 - 43 Mei A, Li X, Liu L, *et al.* A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science*, 2014, 345: 295–298
 - 44 Docampo P, Ball JM, Darwich M, *et al.* Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates. *Nat Commun*, 2013, 4: 2761
 - 45 Seo J, Park S, Chan Kim Y, *et al.* Benefits of very thin PCBM and LiF layers for solution-processed p-i-n perovskite solar cells. *Energy Environ Sci*, 2014, 7: 2642–2646
 - 46 Edri E, Kirmayer S, Henning A, *et al.* Why lead methylammonium tri-iodide perovskite-based solar cells require a mesoporous electron transporting scaffold (but not necessarily a hole conductor)? *Nano Lett*, 2014, 14: 1000–1004

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基于氧化锡纳米晶的低温电子传输层型钙钛矿太阳能电池的研究

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摘要 高效的电子选择层对提高有机金属卤化物基钙钛矿太阳能电池的能量转换效率起着至关重要的作用。本文采用低温100°C旋转涂膜和后续高温烧结的方法制备了高结晶度的纳米氧化锡薄膜,利用瞬态时间分辨荧光光谱测试对SnO₂/CH₃NH₃PbI₃薄膜进行分析发现,这种低温氧化锡薄膜与相同条件下制备的低温氧化钛薄膜相比,具有更高的荧光淬灭和电子抽取能力。电流-电压曲线表明,低温氧化锡基钙钛矿太阳能电池具有优异的光电转换性能,其开路电压为0.91 V,短路电流密度为20.73 mA cm⁻²,填充因子为64.25%,其器件光电转换效率达到12.10%,高于低温二氧化钛基器件的光电转换效率7.16%。上述无高温烧结的旋转涂膜方法为制备低温大面积钙钛矿太阳能电池提供了一种研究思路。