Graphical abstract

Low-Temperature Electrodeposited Crystalline SnO₂ as an Efficient Electron-Transporting Layer for Conventional Perovskite Solar Cells

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Abstract

Tin oxide (SnO₂) has recently attracted significant research interest for its role functioning as an efficient electron-transporting layer (ETL) due to its higher charge mobility than the commonly used titanium oxide (TiO₂) for realizing high-performance perovskite solar cells (PVSCs). However, it is still challenging to develop a facile, low-temperature solution-based (< 100 °C) processing method to synthesize crystalline SnO₂ with desirable charge mobility, which can facilitate its widespread applications in flexible optoelectronic devices. In this work, we utilize an electrochemical deposition technique to prepare SnO₂ films at a reduced temperature below 100 °C. The electrodeposition endows the SnO₂ film with high crystallinity and conductivity in addition to high transparency across the visible spectrum. Efficient photoluminescence (PL) quenching is observed in the bi-layered SnO₂/CH₃NH₃PbI₃ film, manifesting its efficient electron extraction capability from perovskite. Consequently, a conventional *n-i-p* PVSC using this electrodeposited SnO₂ ETL shows a high PCE of 13.88% with negligible hysteresis. This work demonstrates a low-temperature solution-based preparation route for making crystalline SnO₂ and its potential for application in large-scale PVSC production.

Keywords: Electrodeposition; tin oxide; electron-transporting materials; perovskite solar cells

1. Introduction

Recently, organic-inorganic hybrid perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{Br}^-$ or I^-) have become the most promising candidate for transformative photovoltaic technology due to its exceptional semiconducting properties, such as intense light-harvesting capability, small exciton binding energy ($\sim 20\text{-}50$ meV), and long charge carrier lifetime (> 100 ns) and diffusion length (> 1 μm), [1] and facile solution processability. [2-5] Through the deepened material- and device-level understanding of this new class of semiconductors, the power conversion efficiency (PCE) of perovskite solar cell (PVSC) has meteorically rise to over 22% in just few years. [4, 6-9]

Currently, most of the state-of-the-art PVSC are accomplished in a conventional n-i-p architecture adopting a mesoporous TiO_2 (mp- TiO_2) or/and a compact TiO_2 (c- TiO_2) layer as the electron-transporting layer (ETL). [4, 10] Such electron-transporting scaffolds have certain deficiencies that need to be further improved such as the tedious fabrication processes and defective surface. In general, the TiO_2 films require high sintering temperatures (> 500 $^\circ\text{C}$) to attain mesoporous structure and desirable crystallinity. [4, 10, 11] This high thermal process significantly limits its widespread applications in wearable electronic devices, which employs either polymer as substrate that possess a low glass transition temperature [2, 12] or stainless steel for which the high-temperature will drive the metal diffusion into the active layer [13]. In addition, the defective surface of TiO_2 ETL has been shown to incur inefficient charge transfer with perovskite. [14] Therefore, it is highly desirable to develop other n-type transition metal oxides (TMOs) that are compatible with low-temperature solution process.

Thus far, vigorous efforts have been devoted to exploring low-temperature synthetic routes for various n-type TMOs. [15-18] Among which, SnO_2 is a very promising alternative to replace the commonly used TiO_2 ETL due to its higher electron mobility (2-order magnitude) than TiO_2 in addition to its high transparency (due to its wide bandgap of

3.5 eV).[19] Various approaches have been proposed to prepare SnO₂ ETL through reduced temperature processes and applied to conventional PVSCs.[15-17, 20] For instance, Yan *et al.* have reported a low-temperature (180 °C), solution-processed route to prepare crystalline SnO₂ ETL and achieved an efficient planar PVSC with a PCE of 16.02%.[15] Efficiencies close to 21% for the planar configuration were realized by two-step low temperature (180 °C), solution processed SnO₂ (spin coating and chemical bath deposition) as ETL.[21] Soon after, Hagfeldt *et al.* have used atomic layer deposition (ALD) method to prepare a compact SnO₂ ETL at 120 °C and used it to realize a high-performance PVSC with a PCE of 18%.[17] More recently, we have successfully employed a combustion method to reduce the preparing temperature of SnO₂ ETL to 140 °C. The resultant high-quality SnO₂ ETL enables the derived conventional PVSC to show a decent PCE of ~ 15%.[16] Despite this progress, most of the developed methods still involve sophisticated preparation processes, like long gelation time[16, 22, 23], high vacuum condition,[17, 24] and high process temperature over (100 °C) which might not be compatible for mass production.

In searching a possible method to alleviate these problems, electrodeposition has been well documented in industry as an efficient approach to convert electrical energy to chemical potential and been widely utilized to prepare versatile conductive polymers and TMOs.[25] This technique has several advantages, such as operation in solutions at a lower temperature (<100 °C), precise control of nanostructures of the target materials, easy manipulation of electrical properties through electrolyte composition, and excellent adhesion between the deposited layer and the substrate. More importantly, this method is fully amenable to high throughput roll-to-roll manufacturing of large-area PVSCs.[2]

Regarding the development in this area, several groups have independently reported the utilization of electrochemical deposition technique to synthesize TMO-based ETLs for PVSCs. For example, the electrodeposited ZnO nanoparticles (NPs) and nanorods (NRs) have been exploited to realize flexible and regular conventional PVSCs with PCE of 8.90% and

10.28%, respectively.[26, 27] Electrodeposited TiO_2 has also been reported and used as a blocking layer to combine with a mesoporous TiO_2 scaffold to endow the derived PVSC with a decent PCE of 13.6%.[5] Very recently, sputtering and anodization techniques using a titanium film as the seeding layer were shown to successfully prepare single-crystalline, homogeneous TiO_2 ETLs with defect-free surface, which can enable the derived conventional PVSCs to show a respectable PCE of 15.2%.[18] However, most efficient TMO-based ETLs prepared by electrodeposition technique reported so far either needed the intermediate layer or harsh post-thermal treatment, which is probably due to their strict requirement on crystallinity as a result of inferior charge mobility.

In this study, we have utilized an electro-deposition technique to prepare crystalline SnO_2 films for functioning as efficient ETL to realize conventional PVSC. With the merit of strong interfacial electric field during electrodeposition, a crystalline SnO_2 layer consisting of single-crystalline NPs (~50 nm) can be deposited and cover the surface of ITO substrate. Compared to other deposition approaches reported for TMOs, such as sol-gel route, combustion process, and ALD method, the electro-deposition described here provides a facile low-temperature (50 °C), solution-based synthetic route that can be operated in ambient condition.

Different to the electrodeposited TiO_2 , [5, 28] the electrodeposited crystalline SnO_2 does not need additional seeding layers or post-thermal treatments. Despite the low reaction temperature at 50 °C during electrodeposition, the electrodeposited SnO_2 still shows superior conductivity than that of the commonly used TiO_2 and high transparency in the visible spectrum region across from 350 nm to 800 nm. X-ray photoelectron spectroscopy (XPS) was conducted to confirm the exact composition of the electrodeposited SnO_2 film. Its good charge extraction capability from perovskite is clearly evident in the efficient photoluminescence (PL) quenching of bi-layered $\text{SnO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ sample. Consequently, the PVSC employing this SnO_2 as ETL can yield a high PCE of 13.88% with negligible hysteresis. This work

demonstrates a low-temperature, solution-based preparation route for achieving crystalline SnO₂ and paves the way for possible application in large-scale PVSC production.

2. Experimental Section

Materials

All the chemicals, such as SnCl₂ and PbI₂, were purchased from Sigma-Aldrich without further purification. Methylammonium iodide (MAI) was synthesized by reacting 24 mL of 0.20 mol methylamine (33 wt% in absolute ethanol, Aldrich), 10 mL of 0.04 mol hydroiodic acid (57 % in water with 1.5 % hypophosphorous acid, Alfa Aesar), and 100 mL ethanol in a round bottom flask under nitrogen at 0 °C for 2h with stirring. The white powder of MAI was recovered by evaporation at 40 °C and then dissolved in ethanol by sedimentation in diethyl ether and stirring the solution for 30 min. This reaction was repeated three times and MAI powders were finally collected and dried at 50 °C in a vacuum oven for 24 h.

Preparation of SnO₂ *via* electrodeposition method

The SnO₂ films were prepared directly on indium tin oxide (ITO) coated glass substrates without using a seed layer. The ITO glass substrates (Colorado Concept Coating LLC) were cleaned via ultra-sonicated in the sequential detergent, DI water, acetone, and isopropanol for 10 min immersion, respectively, then the substrates were treated by UV-Ozone for 15 min. The electrochemical deposition was carried out in a three-electrode cell. The counter-electrode was a platinum wire and the reference electrode was a Ag/AgCl reference electrode (with a potential at +0.22 V vs standard hydrogen electrode) placed in a separate compartment. The deposition bath was a solution of 20 mM SnCl₂, 100 mM NaNO₃, and 75 mM HNO₃ dissolved in DI water. The deposition was performed at a constant applied voltage of -0.4 V vs. Ag/AgCl reference electrode for 600 s under different reaction temperature: 20, 50, and 70 °C (named as SnO₂-20, SnO₂-50 and SnO₂-70), respectively.

Preparation of TiO₂ via spin-coating method

An 20–30 nm thick TiO₂ compact layer was then deposited on the cleaned ITO substrates by spincoating an ethanol solution (1 mL) at 5000 rpm (60s) with 0.2 M titanium isopropoxide (Sigma-Aldrich, 99.999%) and 5 μ L HCl (37 wt%), followed by annealing at 500 °C for 1 h. Then, the C₆₀ electron-transporting layer (3 mg mL⁻¹ in chlorobenzene) was deposited by spin-coating at 2500 rpm for 30 s and 4000 rpm for 5 s.

Fabrication of thin-film perovskite solar cells

Highly dense and homogenous perovskite film was prepared through the well-known solvent washing technique, in which non-polar solvent like toluene was *in-situ* poured to facilitate the conversion of intermediate iodoplumbate anions to perovskite.[29, 30] The precursor solution of perovskite film was made by dissolving 1 mmol PbI₂ and 1 mmol CH₃NH₃I in a binary solvent of γ -butyrolactone and dimethylsulfoxide of 700 μ L and 300 μ L, respectively. The perovskite film was spin-coated on the SnO₂-20, SnO₂-50 and SnO₂-70 by three steps: 500 rpm for 5 s, 1000 rpm for 45 s, and 5000 rpm for 40 s. Anhydrous toluene was in-situ dropped at the third stage at 20 s prior to the stop of spin-coating. Then, the deposited perovskite film was annealed at 100 °C for 10 min in glovebox. A volume of 33 μ l 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD) solution was next spin-coated on the perovskite film at the speed of 2000 rpm for 60 s, and then aging in dry air for 20 h. The spiro-MeOTAD solution was prepared by dissolving 40 mg of spiro-MeOTAD in 1 ml of chlorobenzene, to which 16 μ l of 4-tert-butyl pyridine and 33 μ l of lithium bis(trifluoromethanesulfonyl) imide (Li-TFSI) solution (175.1 mg Li-TSFI in 1 ml acetonitrile, Sigma-Aldrich, 99.8%) was added. Finally, 150 nm of silver was thermally evaporated on the spiro-MeOTAD-coated film. The device area was controlled by a shadow mask with an aperture area of 3.14 mm².

Characterization

UV-vis absorption spectra were measured by a Varian Cary5000 spectrophotometer. XRD was measured by X-ray diffractometer (Bruker D8 Discover). Scanning electron microscopy (SEM) was measured by FEI Corporation. Photoluminescence (PL) spectra were measured by Horiba Fluorolog FL-3. Transmission electron microscope (TEM) images and selected-area electron diffraction (SAED) pattern were taken using a microscope (FEI Tecnai G2 20) operated at 200 keV to observe the crystallographic orientation of electrodeposited SnO₂. For the *J-V* measurement, the light intensity had been calibrated *via* a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of the National Renewable Energy Laboratory. The *J-V* curves of the devices were measured by source-meter Keithley 2400 under AM 1.5 G of simulated solar light with the illuminating intensity of 100 mW cm⁻². The *J-V* curves were measured by reverse scan (forward bias (1.1 V) - short circuit (0 V)) or forward scan (short circuit (0 V) - forward bias (1.1 V)). The step voltage and the delay time were fixed at 6 mV and 10 ms, respectively). Then monochromatic incident photon-to-electron conversion efficiency setup equipped with a 450 W Xenon lamp (Oriel) as the incident light, a monochromator, a chopper with a frequency of 400 Hz, a lock-in amplifier (SR 830, Sanford Research Corp), and a Si-based diode (J115711-1 Si detector) for calibration was employed to obtain the external quantum efficiency spectra.

3. Results and discussion

Preparation of SnO₂ *via* electrodeposition

By taking the advantages of precise control in morphological, structural, and optoelectronic properties of the target materials, we have utilized electro-deposition technique to prepare SnO₂ layers.[19, 31] To evaluate the applied voltage for SnO₂ electrodeposition on ITO/glass substrate, the electrochemical reactions were first investigated by cyclic voltammetry (CV). In principle, in a strong oxidative environment such as nitric acid aqueous

solution, the Sn^{2+} ions will dissolve from tin dichloride (SnCl_2) and be oxidized to Sn^{4+} as follows:

Figure 1a shows a typical CV measurement of cathodic reaction mechanism for SnO_2 deposition recorded at potential between -1.0 and 0 V (vs. Ag/AgCl). When the bias first scans from 0 V to -1.0 V (vs. Ag/AgCl), a cathodic current starts to appear at ~ -0.4 V. It can be ascribed to the reduction of nitrate ions (NO_3^-) on the electrode surface *via* electron transfer step elucidated as below (the potential is relative to the Ag/AgCl electrode):

The OH^- ions are therefore generated on the cathode and induce a pH increase at the electrode vicinity. Also, the OH^- ions will further react with Sn^{4+} ions to enable the SnO_2 deposition according to the following reaction:

As can be seen in **Figure 1a**, the forward and the reverse scans show a crossover at ~ -0.4 V (vs. Ag/AgCl). The presence of this crossover can correlate with the characteristic of nucleation and crystal growth process.[32] Therefore, the applied voltage at -0.4 V was set to proceed the SnO_2 electrodeposition. In order to minimize the reaction temperature as low as possible during the electrodeposition, three temperatures ranging from 20 to 70 °C were set to conduct the SnO_2 electrodeposition, for which the deposited films are named as SnO_2 -20, SnO_2 -50 and SnO_2 -70, respectively (the number represents the reaction temperature). Shown in **Figure 1b** illustrates the current density-time transition measured at a constant bias of -0.4 V under different reaction temperatures, which can provide more insight into the initial stage of nucleation and crystal growth of SnO_2 on the ITO cathode surface. The continuous decrease in current suggests that the electrode is passivated by the deposition of a less conductive SnO_2 layer and finally reaches a steady value. As can be clearly seen, this steady-

state current increases with the reaction temperature, indicating the number of nuclei increases with increasing reaction temperatures. After being polarized for 600 s, the film thickness of the samples measured by profilometry is 23 ± 6 nm and 36 ± 8 nm for SnO₂-50 and SnO₂-70, respectively. The film thickness of SnO₂-20 is too small to be measured, suggesting that too low reaction temperature cannot facilitate the formation of uniform nucleation site.

X-ray photoelectron spectroscopy (XPS) is then used to study the composition of the electrodeposited SnO₂ film. As clearly shown in **Figure 2a**, the survey of full XPS spectra show that only Sn and O related core levels are detectable. The binding energies of 487.0 eV, 496.0 eV, and 531.4 eV shown in **Figure 2b** correspond to Sn 3d_{5/2}, Sn 3d_{3/2}, and O 1s peaks, respectively. The quantitative analysis based on the area estimation of O 1s and Sn 3d_{5/2} spectral lines (using the atomic sensitivity factor analytical procedure)[33] shows a [O]/[Sn] relative concentration of the electrodeposited SnO₂ thin films equals to 1.9, 1.8 and 1.4 for SnO₂-20, SnO₂-50 and SnO₂-70, respectively. The SnO₂-70 thin film exhibiting evident non-stoichiometry corresponds to the mixture of SnO and SnO₂, which may result from the rapid reaction rate or uncompleted dehydration of formed Sn(OH)₄ at higher temperatures.[33] Therefore, based on the results of profilometry and XPS, the optimized temperature for electrodepositing SnO₂ film is set to 50 °C.

Illustrated in **Figure 2c** is the corresponding UV-Vis absorption of the prepared SnO₂ films, wherein high transparency in the region from 350 nm to near-infrared (NIR) is clearly observed. Such high transparency is important to avoid the parasitic absorption loss of perovskite absorber in the derived device for achieving optimal photocurrent. **Figure 2d** presents the Kubelka-Munk-transformed diffuse reflectance spectrum of the SnO₂-50 film. The calculated E_g of SnO₂ is around 3.67 eV which agrees well with that of the reported value.[34] The absorption spectrum of SnO₂-70 film and its corresponding Kubelka-Munk-transformed diffuse reflectance spectrum were displayed in **Figure S1**. The relatively low E_g

(~2.43 eV) compared to SnO₂-50 film might result from the existence of SnO.[35] The PL spectrum of SnO₂-50 shows a maximum emission at 400 nm, which arises from the oxygen vacancies and associated traps (**Figure S2**).

Characteristics of SnO₂ films and the grown perovskite

The morphology of the electro-deposited SnO₂ films is characterized by using SEM as presented in **Figure 3a-c**. As shown, the SnO₂-20 reveals a poor morphology with the formation of island-like structures (**Figure 3a**). While increasing the deposition temperature to 50 °C and 70 °C, showing better coverage of SnO₂ films on ITO substrate with the formation of densely packed domains consisting of 50 nm and 85 nm sized crystalline NPs, respectively (**Figure 3b** and **3c**). The larger NPs observed in SnO₂-70 film relative to SnO₂-50 film can be attributed to the higher reaction rate during electrodeposition as a result of its reaction current. Note that we also investigated the optimized reaction time for the electrodeposited SnO₂ at 50 °C as shown in **Figure S3**. The film was only poorly covered with separated clusters consisting of 50 nm sized NPs if the deposition time was decreased to 120s. This non-uniformity of SnO₂ layer will inevitably cause direct contact between perovskite and ITO to short the devices. This clearly suggests that it is critical to carefully control the depositing time for electro-deposited SnO₂ in order to achieve homogenous films.

The crystal structure and orientation of SnO₂ was further confirmed by the bright-field TEM (BF-TEM) and selected area electron diffraction (SAED). The TEM image shown in **Figure 4a** reveals the SnO₂-50 NPs are randomly oriented and highly crystalline. The inset SAED pattern can be indexed to the tetragonal (rutile) SnO₂ structure, wherein the 3.3, 2.6, and 1.8 Å, corresponds to the (1 1 0), (1 0 1) and (2 0 0) reflections of the SnO₂ structure.[36] The corresponding high-resolution TEM (HR-TEM) image and fast Fourier transform (FFT) pattern also indicate the formation of SnO₂. The HR-TEM image (**Figure 4b**) shows a 3.30 Å spacing of (1 1 0) SnO₂ lattice fringes, corroborating well with the SAED analysis. All

1 reflections in the FFT pattern fit well with the tetragonal SnO₂ structure imaged along the [0
2 0 1] zone axis orientation. It is important to point out that there is no need to use any
3 additional seeding layers or post-thermal treatments for the electro-deposition of crystalline
4 SnO₂. Such simplified process offers promising merits for the large-scale, roll-to-roll
5 processing of PVSCs.
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11 We next evaluate the conductivity of electrodeposited SnO₂-50 layer by measuring the
12 current-voltage (*I-V*) characteristics of a simple device of ITO/SnO₂-50/Ag (**Figure S4**). From
13 the *I-V* slope, the corresponding conductivity (σ) can be calculated to be $\sim 3.47 \times 10^{-6}$ S/cm
14 according to the formula of $I = \sigma AV/d$, wherein *A* is the area (3.14 mm²) and *d* is the
15 thickness (23 nm). The conductivity of electro-deposited SnO₂-50 layer obtained here
16 significantly exceeds the value (6.0×10^{-8} S/cm) of TiO₂ measured by the same condition,
17 manifesting its advantage as an efficient ETL for PVSC.[37]
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29 For PVSCs, the quality and morphology of perovskite layer is one of the most pivotal
30 factors in influencing the resultant photovoltaic performance.[38, 39] To understand the
31 quality of perovskite film formed on the electrodeposited SnO₂ layer, the surface morphology
32 and crystallinity of perovskites have been examined by using SEM and XRD. Noting that the
33 CH₃NH₃PbI₃ deposition performed in this study adopts the one-step, spin-coating method
34 modified with toluene solvent-washing procedure.[16, 40] Detailed processing information of
35 perovskite film is described in the experiment section. As shown in **Figure 5a**, the
36 CH₃NH₃PbI₃ grown on electrodeposited SnO₂ film exhibits a fully covered surface
37 morphology with densely packed grains (with size around 100-300 nm). The corresponding
38 XRD spectrum presented in **Figure 5b** exhibits the diffraction signals at $2\theta = 13.95^\circ$ and
39 28.35° in all cases, corresponding to the (110) and (220) planes of tetragonal CH₃NH₃PbI₃
40 phase, affirming the formation of crystalline CH₃NH₃PbI₃ films.
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59 Photovoltaic Performance of PVSCs

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The conventional n-i-p PVSC with a device configuration of ITO/electrodeposited $\text{SnO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Spiro-OMeTAD}/\text{Ag}$ (**Figure 6a**) was then fabricated and the corresponding energy level diagram is illustrated in **Figure 6b**. **Figure 6c** displays the cross-sectional SEM image of the fabricated device, where the thickness of SnO_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$, and Spiro-OMeTAD layers is estimated to be ~ 30 nm, ~ 140 nm and ~ 150 nm, respectively. All of the studied PVSCs were measured at 1 sun intensity (100 mW cm^{-2}) under simulated AM 1.5G illumination. The photovoltaic performance measured under both reverse (open-circuit condition to short-circuit condition) and forward (short-circuit condition to open-circuit condition) directions with a scan rate of 600 mV s^{-1} were examined as shown in **Figure 7** and the resultant photovoltaic parameters were summarized in **Table 1**.

As shown, the SnO_2 -20 PVSC only showed an inconspicuous performance (PCE: 3.82%; open circuit voltage (V_{oc}): 0.72 V; J_{sc} : 12.45 mA cm^{-2} ; fill factor (FF): 0.43) accompanied with large hysteresis. Such poor performance, especially for the low V_{oc} and FF , can be clearly ascribed to the inferior coverage of SnO_2 -20 film on ITO substrate as portrayed in **Figure 3(a)**, which not only introduces severe interfacial defects to trap charges but also causes the direct contact of perovskite and ITO to induce short circuit. Whereas, the SnO_2 -50 PVSC produces a decent PCE of 13.88%, with a V_{oc} of 1.08 V, a J_{sc} of 19.75 mA cm^{-2} , and a FF of 0.65 when measured under a reverse scan. While measured under a forward scan, the photovoltaic performance is 13.39 %, with a V_{oc} of 1.07 V, a J_{sc} of 19.58 mA cm^{-2} , and a FF of 0.64. This negligible hysteresis can be attributed to the high crystallinity of SnO_2 -50 ETL, which affords respectable charge transport and extraction from perovskite independent of voltage to result in low carrier recombination loss. The SnO_2 -70 PVSC showed a slightly decreased PCE (11.63%) compared to the SnO_2 -50 based device, which may result from the reason that the existence of impurity p -type SnO hider the electron injection to ITO side.[29]

It is important to mention that the top-performing SnO_2 -50 PVSC showed a comparable performance to that of a conventional TiO_2 -based PVSC (**Figure S5** and **Table S1**), wherein

the TiO₂ ETL was prepared through a high-temperature annealing procedure and passivated by a thin C₆₀ layer to facilitate the electron transport between perovskite and itself.

The hysteresis-free behavior of the SnO₂-50 based PVSC is further confirmed by the transient photocurrents recorded at 0.87 V, resembling the operation of device at the maximum power point. As exhibited in **Figure 8a**, a steady photocurrent is reached after switching from V_{oc} to 0.87 V for 10 min. The stabilized current is in a good agreement with the current obtained in the J - V curve at 0.87 V, which is found to be 15.8 mA cm⁻². In order to examine the charge collection efficiency of SnO₂ in device, we have performed J - V scans of SnO₂-50 based PVSC at various voltage sweep rates as shown in **Figure 8b**, where only the performance measured under a reverse scan is plotted. As shown, no significant variation is observed when increasing the scan rate from 10 to 2000 mV s⁻¹, suggesting the defect-free surface of electrodeposited SnO₂-50 ETL as a result of its high crystallinity.[41, 42]

It is worthwhile to note that we have previously adapted a simple spin-coating method to prepare the SnO₂ ETL.[16] Our previous results manifested the difficulty in obtaining an efficient SnO₂ ETL through a low-temperature annealing procedure. Besides, additional surface passivation onto SnO₂ film was strictly required to yield decent performance and alleviate the J - V hysteresis. The results from other groups [15, 20] have also revealed the similar situation, wherein a relatively high annealing temperature above 180 °C is essential to afford respectable performance of the derived PVSCs. As compared to these spin-cast SnO₂ films, the electrodeposition technique revealed herein indeed highlights an effective low-temperature (50 °C) procedure endowed with scalable capability and exemption from additional post-treatments to prepare a sufficient SnO₂ ETL for realizing efficient and hysteresis-free PVSCs compatible to the roll-to-roll printing technique.

Figure 8c illustrates the external quantum efficiency (EQE) curve of the top-performing SnO₂-50 PVSC. A broad EQE plateau at 70 % across 400 to 700 nm is clearly shown, which affirms the efficient photo-response of perovskite absorber. The calculated J_{SC} (17.6 mA cm⁻²)

from the EQE spectra is consistent with the measured value. Steady-state photoluminescence (PL) measurement shown in **Figure 8d** clearly corroborates the efficient charge transfer between electrodeposited SnO₂ and perovskite. The significant PL quenching of CH₃NH₃PbI₃ in the bi-layered SnO₂/CH₃NH₃PbI₃ sample suggests the good charge-collecting ability of the electrodeposited SnO₂.

4. Conclusion

We have successfully employed electrodeposition technique to prepare crystalline SnO₂ ETLs to yield efficient PVSCs. We revealed that the deposition temperature and time could be modulated to manipulate the morphology and chemical composition of the electrodeposited SnO₂ films. Aided by the strong interfacial electric field during electrodeposition, the single crystalline SnO₂ NPs with size of ~50 nm can be formed and fully deposited over the ITO substrate at a low temperature of 50 °C. The electrodeposition endows the SnO₂ film with high crystallinity and high conductivity. The relatively efficient PL quenching of CH₃NH₃PbI₃ on the bi-layered SnO₂/CH₃NH₃PbI₃ film suggests its good charge-extracting capability from perovskite. Combining with its high transparency, a PVSC derived from this SnO₂ ETL shows a quite high PCE of 13.88% with negligible hysteresis. It is important to point out that there is no need to use any additional seeding layers or post-thermal treatments for the electrodeposition of crystalline SnO₂. Such simplified process offers promising merits for the large-scale, roll-to-roll processing of PVSCs.

Acknowledgements

This work is supported by the Office of Naval Research (N00014-14-1-0246), the Asian Office of Aerospace R&D (FA2386-15-1-4106), and the Department of Energy SunShot (DE-EE0006710). Alex K.-Y. Jen thanks the Boeing-Johnson Foundation for their financial support. J.-Y. Chen thanks the Ministry of Science and Technology, R.O.C. for financial support (104-2917-I-002-019).

References

- [1] M.B. Johnston, L.M. Herz, Hybrid Perovskites for Photovoltaics: Charge-Carrier Recombination, Diffusion, and Radiative Efficiencies, *Acc. Chem. Res.*, 49 (2016) 146-154.
- [2] S.T. Williams, A. Rajagopal, C.-C. Chueh, A.K.Y. Jen, Current Challenges and Prospective Research for Upscaling Hybrid Perovskite Photovoltaics, *J. Phys. Chem. Lett.*, 7 (2016) 811-819.
- [3] N.J. Jeon, J.H. Noh, Y.C. Kim, W.S. Yang, S. Ryu, S.I. Seok, Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells, *Nat Mater*, 13 (2014) 897-903.
- [4] W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, High-performance photovoltaic perovskite layers fabricated through intramolecular exchange, *Science*, 348 (2015) 1234-1237.
- [5] T.-S. Su, T.-Y. Hsieh, C.-Y. Hong, T.-C. Wei, Electrodeposited Ultrathin TiO₂ Blocking Layers for Efficient Perovskite Solar Cells, *Sci. Rep.*, 5 (2015) 16098.
- [6] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells, *J. Am. Chem. Soc.*, 131 (2009) 6050-6051.
- [7] H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, Interface engineering of highly efficient perovskite solar cells, *Science*, 345 (2014) 542-546.
- [8] Research Cell Efficiency Records, NREL, http://www.nrel.gov/ncpv/images/efficiency_chart.jpg, in, 2016.
- [9] J. Berry, T. Buonassisi, D.A. Egger, G. Hodes, L. Kronik, Y.-L. Loo, I. Lubomirsky, S.R. Marder, Y. Mastai, J.S. Miller, D.B. Mitzi, Y. Paz, A.M. Rappe, I. Riess, B. Rybtchinski, O. Stafsudd, V. Stevanovic, M.F. Toney, D. Zitoun, A. Kahn, D. Ginley, D. Cahen, Hybrid Organic–Inorganic Perovskites (HOIPs): Opportunities and Challenges, *Adv. Mater.*, 27 (2015) 5102-5112.

- [10] D. Bi, W. Tress, M.I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel, A. Hagfeldt, Efficient luminescent solar cells based on tailored mixed-cation perovskites, *Sci. Adv.*, 2 (2016).
- [11] M.-C. Wu, S.-H. Chan, M.-H. Jao, W.-F. Su, Enhanced short-circuit current density of perovskite solar cells using Zn-doped TiO₂ as electron transport layer, *Sol. Energy Mater. Sol. Cells*, 157 (2016) 447-453.
- [12] X. Liu, X. Xia, Q. Cai, F. Cai, L. Yang, Y. Yan, T. Wang, Efficient planar heterojunction perovskite solar cells with weak hysteresis fabricated via bar coating, *Sol. Energy Mater. Sol. Cells*, 159 (2017) 412-417.
- [13] D. Bae, S. Kwon, J. Oh, W.K. Kim, H. Park, Investigation of Al₂O₃ diffusion barrier layer fabricated by atomic layer deposition for flexible Cu(In,Ga)Se₂ solar cells, *Renew Energy*, 55 (2013) 62-68.
- [14] E. Hendry, M. Koeberg, B. O'Regan, M. Bonn, Local Field Effects on Electron Transport in Nanostructured TiO₂ Revealed by Terahertz Spectroscopy, *Nano Lett.*, 6 (2006) 755-759.
- [15] 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, *J. Am. Chem. Soc.*, 137 (2015) 6730-6733.
- [16] X. Liu, K.-W. Tsai, Z. Zhu, Y. Sun, C.-C. Chueh, A.K.Y. Jen, 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) n/a-n/a.
- [17] J.P. Correa Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T.J. Jacobsson, A.R. Srimath Kandada, S.M. Zakeeruddin, A. Petrozza, A. Abate, M.K.

1 Nazeeruddin, M. Gratzel, A. Hagfeldt, Highly efficient planar perovskite solar cells through
2 band alignment engineering, *Energ. Environ. Sci.*, 8 (2015) 2928-2934.
3

4 [18] J. Choi, S. Song, M.T. Hörantner, H.J. Snaith, T. Park, Well-Defined Nanostructured,
5 Single-Crystalline TiO₂ Electron Transport Layer for Efficient Planar Perovskite Solar Cells,
6 ACS Nano, (2016).
7

8 [19] M. Batzill, U. Diebold, The surface and materials science of tin oxide, *Prog. Surf. Sci.*,
9 79 (2005) 47-154.
10

11 [20] M. Park, J.-Y. Kim, H.J. Son, C.-H. Lee, S.S. Jang, M.J. Ko, Low-temperature solution-
12 processed Li-doped SnO₂ as an effective electron transporting layer for high-performance
13 flexible and wearable perovskite solar cells, *Nano Energy*, 26 (2016) 208-215.
14

15 [21] E.H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A.
16 Abate, M. Gratzel, A. Hagfeldt, J.-P. Correa-Baena, Highly efficient and stable planar
17 perovskite solar cells by solution-processed tin oxide, *Energ. Environ. Sci.*, 9 (2016) 3128-
18 3134.
19

20 [22] Z. Zhu, Y. Bai, T. Zhang, Z. Liu, X. Long, Z. Wei, Z. Wang, L. Zhang, J. Wang, F. Yan,
21 S. Yang, High-Performance Hole-Extraction Layer of Sol–Gel-Processed NiO Nanocrystals
22 for Inverted Planar Perovskite Solar Cells, *Angew. Chem. Int. Ed.*, 53 (2014) 12571-12575.
23

24 [23] J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. Yang, W.-H. Chang, Z. Hong, H. Chen, H.
25 Zhou, Q. Chen, Y. Liu, N. De Marco, Y. Yang, Improved air stability of perovskite solar cells
26 via solution-processed metal oxide transport layers, *Nat Nano*, 11 (2016) 75-81.
27

28 [24] C.-Y. Chang, K.-T. Lee, W.-K. Huang, H.-Y. Siao, Y.-C. Chang, High-Performance,
29 Air-Stable, Low-Temperature Processed Semitransparent Perovskite Solar Cells Enabled by
30 Atomic Layer Deposition, *Chem. Mater.*, 27 (2015) 5122-5130.
31

32 [25] L.P. Bicelli, B. Bozzini, C. Mele, L. D'Urzo, A Review of Nanostructural Aspects of
33 Metal Electrodeposition, *Int. J. Electrochem. Sc.*, (2008).
34

- [26] M.H. Kumar, N. Yantara, S. Dharani, M. Graetzel, S. Mhaisalkar, P.P. Boix, N. Mathews, Flexible, low-temperature, solution processed ZnO-based perovskite solid state solar cells, Chem. Commun., 49 (2013) 11089-11091.
- [27] J. Zhang, P. Barboux, T. Pauporté, Electrochemical Design of Nanostructured ZnO Charge Carrier Layers for Efficient Solid-State Perovskite-Sensitized Solar Cells, Adv. Energy Mater., 4 (2014) n/a-n/a.
- [28] J. Choi, S. Song, M.T. Hörantner, H.J. Snaith, T. Park, Well-Defined Nanostructured, Single-Crystalline TiO₂ Electron Transport Layer for Efficient Planar Perovskite Solar Cells, ACS Nano, 10 (2016) 6029-6036.
- [29] D. Bae, A. Palmstrom, K. Roelofs, B. Mei, I. Chorkendorff, S.F. Bent, P.C.K. Vesborg, Tailoring Mixed-Halide, Wide-Gap Perovskites via Multistep Conversion Process, ACS Appl. Mat. Interfaces, 8 (2016) 14301-14306.
- [30] D.-Y.S. Namyoungh Ahn, In-Hyuk Jang, Seong Min Kang, Mansoo Choi, Nam-Gyu Park, Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated via Lewis Base Adduct of Lead(II) Iodide, J. Am. Chem. Soc., 137 (2015) 8696-8699.
- [31] T. Ishizaki, N. Saito, O. Takai, Surfactant-Assisted Fabrication of Tin Oxide Nanowires Through One-Step Electrochemically Induced Chemical Deposition, J. Electrochem. Soc., 156 (2009) D413-D417.
- [32] S.B. Sadale, P.S. Patil, Nucleation and growth of bismuth thin films onto fluorine-doped tin oxide-coated conducting glass substrates from nitrate solutions, Solid State Ionics, 167 (2004) 273-283.
- [33] M. Kwoka, L. Ottaviano, M. Passacantando, S. Santucci, G. Czempik, J. Szuber, XPS study of the surface chemistry of L-CVD SnO₂ thin films after oxidation, Thin Solid Films, 490 (2005) 36-42.

- [34] L. Xiao, H. Shen, R. von Hagen, J. Pan, L. Belkoura, S. Mathur, Microwave assisted fast and facile synthesis of SnO₂ quantum dots and their printing applications, *Chem. Commun.*, 46 (2010) 6509-6511.
- [35] Y. Ogo, H. Hiramatsu, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, p-channel thin-film transistor using p-type oxide semiconductor, SnO, *Appl. Phys. Lett.*, 93 (2008) 3.
- [36] H. Lorenz, Q. Zhao, S. Turner, O.I. Lebedev, G. Van Tendeloo, B. Klötzer, C. Rameshan, S. Penner, Preparation and structural characterization of SnO₂ and GeO₂ methanol steam reforming thin film model catalysts by (HR)TEM, *Mater. Chem. Phys.*, 122 (2010) 623-629.
- [37] J.H. Heo, H.J. Han, D. Kim, T.K. Ahn, S.H. Im, Hysteresis-less inverted CH₃NH₃PbI₃ planar perovskite hybrid solar cells with 18.1% power conversion efficiency, *Energ. Environ. Sci.*, 8 (2015) 1602-1608.
- [38] S.T. Williams, C.-C. Chueh, A.K.Y. Jen, Navigating Organo-Lead Halide Perovskite Phase Space via Nucleation Kinetics toward a Deeper Understanding of Perovskite Phase Transformations and Structure–Property Relationships, *Small*, 11 (2015) 3088-3096.
- [39] S.D. Stranks, P.K. Nayak, W. Zhang, T. Stergiopoulos, H.J. Snaith, Formation of Thin Films of Organic–Inorganic Perovskites for High-Efficiency Solar Cells, *Angew. Chem. Int. Ed.*, 54 (2015) 3240-3248.
- [40] 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, *Adv. Mater.*, 28 (2016) 6478-6484.
- [41] H.-S. Kim, I.-H. Jang, N. Ahn, M. Choi, A. Guerrero, J. Bisquert, N.-G. Park, Control of I–V Hysteresis in CH₃NH₃PbI₃ Perovskite Solar Cell, *J. Phys. Chem. Lett.*, 6 (2015) 4633-4639.
- [42] S. Meloni, T. Moehl, W. Tress, M. Frankevičius, M. Saliba, Y.H. Lee, P. Gao, M.K. Nazeeruddin, S.M. Zakeeruddin, U. Rothlisberger, M. Graetzel, Ionic polarization-induced

current–voltage hysteresis in CH₃NH₃PbX₃ perovskite solar cells, Nat. Commun., 7 (2016)
10334.

Figure 1. (a) Typical CV curve obtained at ITO/glass electrode in 20 mM SnCl_2 , 100 mM NaNO_3 and 75 mM HNO_3 . The insert figure is the setup of electrochemical cell where WE, RE and CE is the short for working electrode, reference electrode and counter electrode, respectively. (b) Variation of the current density with deposition time at applied voltage of -0.4 V vs. Ag/AgCl.

Figure 2. XPS spectra of (a) survey (b) Sn 3d and O 1s, (c) optical transmittance and (d) Kubelka-Munk-transformed diffuse reflectance spectrum of the electrodeposited SnO₂ thin film.

Figure 3. SEM images of (a) SnO₂-20, (b) SnO₂-50 and (c) SnO₂-70 films.

Figure 4. (a) BF-TEM image of SnO₂-50 with corresponding insert SAED pattern. (b) HR-TEM micrograph of SnO₂-50 with corresponding insert FFT pattern.

Figure 5. SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film grown on (a) SnO_2 -50 and (b) the corresponding XRD patterns for SnO_2 -20, SnO_2 -50 and SnO_2 -70 films, respectively.

Figure 6. PVSCs using electrodeposited SnO₂ films as ETL. (a) Device structure, (b) the corresponding energy level diagram, and (c) the cross-sectional SEM image.

Figure 7. *J-V* curves of the studied PVSCs using (a) SnO_2 -20, (b) SnO_2 -50 and (c) SnO_2 -70 film as the ETL.

Figure 8. (a) Current density variation of SnO₂-50 derived cell with light soaking time under the applied bias voltage at maximum power. (b) J - V curve of SnO₂-50 derived cell under different scan rate. (c) EQE of the top-performing PVSC using SnO₂-50 as ETL. (d) PL spectra of glass/CH₃NH₃PbI₃ and the SnO₂-50/CH₃NH₃PbI₃ film.

Table 1. Device parameters of the PVSCs using electrodeposited SnO₂ as ETLs

Film	Scan direction	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
SnO ₂ -20	Forward	0.59	12.58	0.37	2.71
	Reverse	0.72	12.45	0.43	3.82
SnO ₂ -50	Forward	1.07	19.58	0.64	13.39
	Reverse	1.08	19.75	0.65	13.88
SnO ₂ -70	Forward	1.04	19.26	0.58	11.62
	Reverse	1.04	19.49	0.57	11.63