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Electrodeposition of SnO₂ on FTO and its Application in Planar Heterojunction Perovskite Solar Cells as an Electron Transport Layer

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Abstract

We report the performance of perovskite solar cells (PSCs) with an electron transport layer (ETL) consisting of a SnO₂ thin film obtained by electrochemical deposition. The surface morphology and thickness of the electrodeposited SnO₂ films were closely related to electrochemical process conditions, i.e., the applied voltage, bath temperature, and deposition time. We investigated the performance of PSCs based on the SnO₂ films. Remarkably, the experimental factors that are closely associated with the photovoltaic performance were strongly affected by the SnO₂ ETLs. Finally, to enhance the photovoltaic performance, the surfaces of the SnO₂ films were modified slightly by TiCl₄ hydrolysis. This process improves charge extraction and suppresses charge recombination.

Keywords: SnO₂, Electrodeposition, Perovskite solar cell, Electrochemistry

Background

Solar cell devices based on organometallic halide perovskite materials have exhibited unprecedented performance over the brief span of 6 years, and organometallic halide perovskite solar cells (PSCs) show promise as affordable alternative solar cells with high power conversion efficiency (PCE) [1–3]. The huge interest in this new class of solar cells is due to their high absorption coefficient, ambipolar charge transport, small exciton binding energy, and long diffusion length [4–6]. Despite these excellent properties, PSCs possess several drawbacks. The most important of these are the sensitivity of perovskite materials to moisture, heat, and UV irradiation. To address these drawbacks, it has been found that adding formamidinium and/or an inorganic cation (Cs or Rb) to a methylammonium cation improves the stability against these environmental factors [3], and the durability of PSCs thus depends on both the device configuration (n-i-p, p-i-n) and the metal oxide semiconductors [7]. Generally, TiO₂ materials are widely used in

PSCs as electron transport layers (ETLs) in the n-i-p device configuration because of their large band gap and band alignment, and highly efficient PSCs are realized using TiO₂ ETLs [8]. Although PSCs with TiO₂ ETLs exhibit remarkable efficiency, the UV sensitivity and electronic properties of TiO₂ have been suggested as targets for improvement to reduce the hysteresis and obtain durable PSCs [9]. Specifically, Heo et al. reported that Li doping can enhance the carrier mobility and conductivity of TiO₂ and thus yield PSCs without significant hysteresis [10]. Ito et al. reported that when TiO₂ in a PSC is exposed to UV irradiation, electrons are extracted at the TiO₂/perovskite interface, degrading the perovskite material [11].

Stannic oxide (SnO₂) has been widely studied for diverse applications such as batteries, gas sensors [12], solar cells [13], and catalysts. It is regarded as a promising candidate for use as a transparent conducting material and photoelectrode in photovoltaic devices. Considerable attention has been drawn recently to its application in PSCs as an alternative ETL with the goal of enhancing device performance and light stability, as it has a larger band gap (~3.6 eV at 300 K), higher electrical conductivity, and greater chemical stability than

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TiO₂ semiconductors [2]. Various synthetic routes to SnO₂, including sol-gel methods [14], molten-salt synthesis [15], microwave techniques [16], atomic layer deposition (ALD), and electrochemical deposition (ED) [17–20] have been developed. ALD and spin-coating solution processes are the dominant methods for fabricating SnO₂ ETLs in PSCs [21–23]. The fabrication of ETLs in photovoltaic devices is paramount for limiting production costs because of the requirements for its production, such as thermal treatment, multiple processing steps, operation control, and scalable processing.

Here, we report on the synthesis and ETL application of SnO₂ thin films on fluorine-doped tin oxide (FTO) by ED. Among the available methods, electrodeposition has the advantages of reduced production cost and large-scale manufacturing because it does not require a vacuum environment or complex operation control. Considering that perovskite materials are suitable for roll-to-roll manufacturing, the application of electrodeposition to obtain SnO₂ ETLs will demonstrate not only a simple, cost-effective, and scalable strategy for alternative ETLs but also facilitate development of a continuous roll-to-roll process for industrial application of PSCs.

Methods

Preparation of SnO₂ Film

A chronopotentiometry technique (VSP 200, Biologic) was used for ED of Sn nanospheres onto an FTO substrate using a standard three-electrode system in a deionized water solution (50 mL) containing 0.05 M SnCl₂·2H₂O [tin chloride (II), Sigma Aldrich] and 1 mL of nitric acid (HNO₃, Samchun Chemical). The nanospheres were then thermally treated in air at 400 °C for 30 min to obtain SnO₂. The aqueous solution was stirred for 1 h at 60 °C on a hot plate. After N₂ purging for 10 min, the solution was used for electrodeposition. In the standard three-electrode system, FTO was used as the working electrode, and a platinum plate was used as the counter electrode. The reference electrode was a Ag/AgCl electrode (CHI111) in 1 M KCl solution.

Device Fabrication

The prepared SnO₂ thin films on FTO (TEC 8) were used in the fabrication of PSCs. The perovskite layer was processed in two steps. A mixture of PbI₂ (99.999%, Aldrich) and PbCl₂ (99.999%, Aldrich) was dissolved in *N,N*-dimethylformamide and stirred at 60 °C. The molar ratio of the precursor solution (PbI₂:PbCl₂) was 1:1 (1 M). The PbI₂/PbCl₂ solution was spin-coated on the SnO₂-coated FTO at 5000 rpm for 30 s in a glove box and dried on a hotplate at 70 °C. To convert it to a perovskite material, 120 μL of methylammonium iodide solution (40 mg/mL) was loaded at 0 rpm for 35 s and then spin-coated at 3500 rpm for

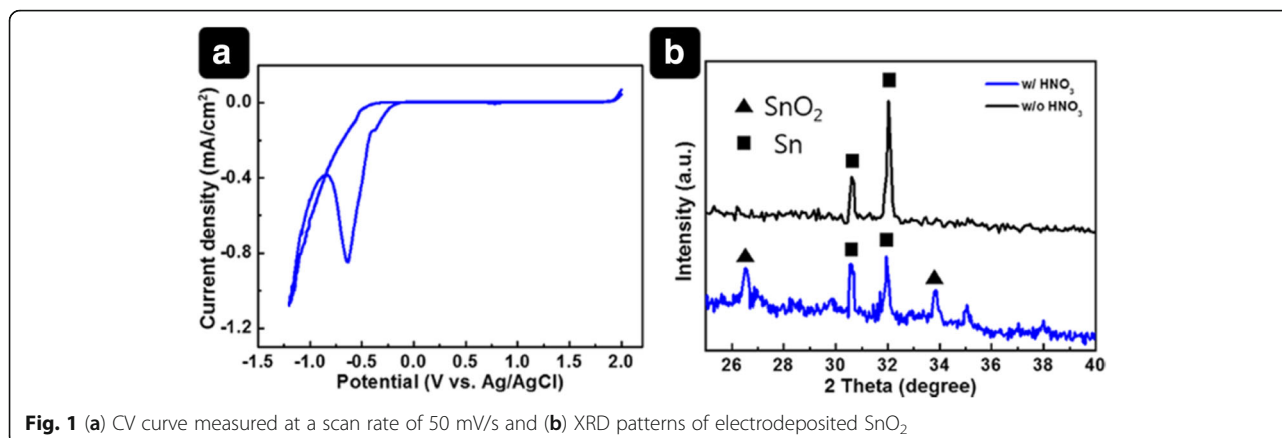
20 s; the sample was then annealed isothermally at 105 °C for 75 min in the ambient environment. After annealing, the films were moved into the glove box in N₂ atmosphere, and a hole-transporting material (HTM) was spin-coated on the MAPbI_{3-x}Cl_x/SnO₂/FTO film at 3000 rpm for 30 s. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (EM Index) solution (20 mg/1 mL) was used as the HTM with 15 μL of Li-bis(trifluoromethanesulfonyl)imide/ acetonitrile (170 mg/1 mL) and 15 μL of tert-butylpyrrolidine. Finally, Au was deposited via thermal evaporation. TiCl₄ hydrolysis treatment was applied by immersing the electrodeposited SnO₂ films in a 40 mM TiCl₄ solution at 70 °C for 30 min and drying them at 150 °C in air.

Characterization

Cyclic voltammetry (CV, scan rate 50 mV/s) measurements were made to confirm the electrochemical behavior of the SnCl₂·2H₂O solution from -1.5 to 2 V. The crystalline structure of the samples was characterized by X-ray diffraction (XRD, Rigaku, Dmax 2200, Cu Kα) and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI 5000, VersaProbe II). The morphologies of the samples were observed by field emission scanning electron microscopy (SEM, Hitachi S4800). The *J*-*V* curves of the PSCs were obtained using an electrochemical station (VSP200, Bio-Logic) under 100 mW/cm² AM 1.5G light (Sun 3000 class AAA, ABET Technology) with a metal mask 0.098 cm² in area. Devices were scanned at a 20 mV/s scan rate. CV measurements of the blocking layer effect were performed using a three-electrode setup after nitrogen purging for 10 min. The aqueous electrolyte contained 0.5 M KCl and the electron redox couple K₄[Fe(II)(CN)₆]/K₃[Fe(III)(CN)₆] at a concentration of 5 mM. A Ag/AgCl electrode was used for the reference electrode, and a Pt wire was used for the counter electrode; the scan rate was 50 mV/s. An Oriel-calibrated Si solar cell (SRC-1000-TC-KG5-N) was used to adjust the light intensity to one-sun illumination. The external quantum efficiency (EQE) was measured using an Ivium potentiostat and a monochromator (DongWoo Optron Co., Ltd.) under a light support (ABET 150 W xenon lamp, ABET Technology). EQE data were acquired in DC mode. Photoluminescence (PL) spectra were measured using a luminescence spectrometer (LS 55, PerkinElmer) with excitation at 530 nm. The intensity-modulated photocurrent and photovoltage were measured by an Ivium potentiostat with a Modulight LED (Ivium).

Results and Discussion

We performed CV measurements of the SnCl₂·2H₂O solution to identify suitable potential values. Figure 1a shows the CV curve, which was scanned from 2.0 to



–1.2 V. All potential values were recorded with respect to the reference electrode (Ag/AgCl). As shown in Fig. 1a, an increase in the cathodic current was observed from –0.5 to –1.2 V. Generally, when the voltage is swept in a CV experiment from positive to negative voltage, the current first increases because of an electrochemical reaction on the working electrode surface and then decreases owing to local depletion of the chemical species close to the working electrode.

On the basis of the CV result, we performed ED using a chronovoltammetry technique. Note that the phase of the deposits depends on the concentration ratio of [HNO₃] to [Sn²⁺] because nitric acid acts as an oxygen source in the phase [24]. The presence of HNO₃ (as identified in the XRD pattern, Fig. 1b) facilitated generation of a SnO₂–Sn co-phase. This will be referred to as SnO₂–Sn nanospheres to distinguish it from pure SnO₂. Figure 2 shows SEM images of the SnO₂–Sn nanospheres deposited on FTO substrates at different potential values (–0.5, –0.6, –0.7, –0.8, –0.9, and –1 V). We found that the applied voltage is a very important

parameter in the electrodeposition process, as the morphologies of the deposits were dramatically different. For relatively low absolute potentials (–0.5 and –0.6 V), few SnO₂–Sn nanospheres formed. On the other hand, the FTO was overlaid with Sn having irregular shapes at –0.9 and –1 V. Even though comparable SnO₂–Sn nanosphere formation occurred at –0.7 and –0.8 V, the uniformity was better at –0.7 V. As a result of these observations, –0.7 V was chosen as a suitable potential for electrodeposition of SnO₂–Sn nanospheres.

A potential of –0.7 V was also used to optimize the deposition time in the range of 150 to 210 s. Figure 3 shows SEM images of samples obtained at various deposition times and the corresponding device performance. Fewer particles formed at 150 s than at 180 s. For a longer deposition time (210 s), aggregation of SnO₂–Sn nanospheres was confirmed. To evaluate the photovoltaic performance of PSCs with the electrodeposited SnO₂ films, the SnO₂–Sn nanosphere films were thermally treated in air at 450 °C for 30 min to obtain fully converted SnO₂ films. A CH₃NH₃PbI_{3-x}Cl_x perovskite

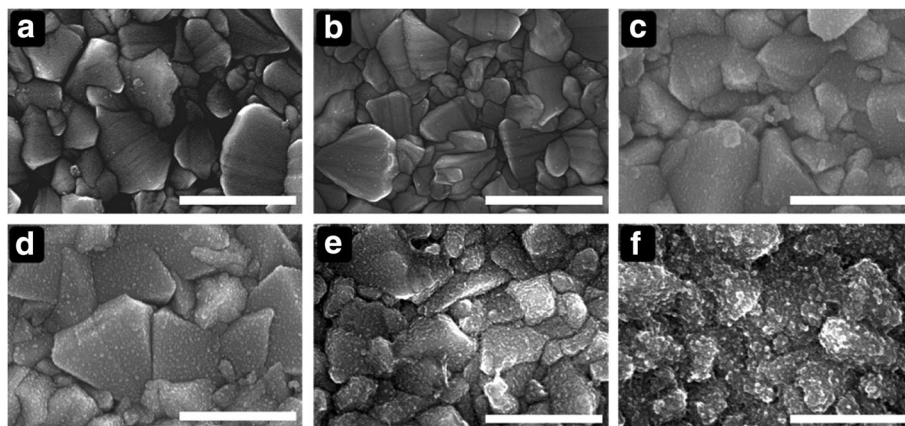


Fig. 2 Top-view SEM images of SnO₂ films electrodeposited at various applied voltages. (a) –0.5 V, (b) –0.6 V, (c) –0.7 V, (d) –0.8 V, (e) –0.9 V, and (f) –1.0 V vs. Ag/AgCl. Scale bar is 1 μm

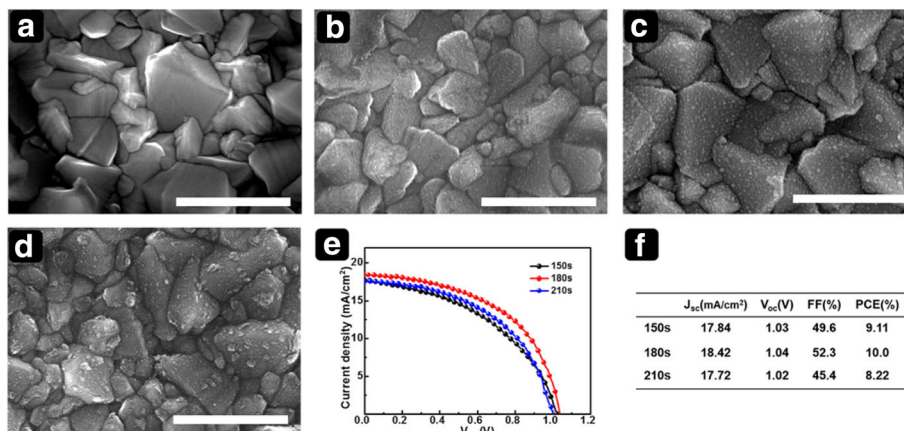


Fig. 3 Top-view SEM images of substrates for different deposition time. (a) Bare FTO and SnO₂ films deposited for (b) 150 s, (c) 180 s, and (d) 210 s. Corresponding photovoltaic performance: (e) J - V curves and (f) photovoltaic parameters of PSCs with electrodeposited SnO₂ ETL. Scale bar is 1 μ m

layer was fabricated via a PbCl₂-seed-layer-assisted interdiffusion process. Details are provided in the experimental section. As shown in Fig. 3e, f, for a deposition time of 150 s, the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE (%) were 17.84 mA/cm², 1.03, 0.496, and 9.11%, respectively. As the deposition time increased from 150 to 180 s, J_{sc} improved, and a higher PCE of 10.0 was obtained. The use of a deposition time of 210 s mainly affected the J_{sc} and FF value, leading to a lower PCE of 8.22. To gain further insight into parasitic resistances, we calculated series resistance (R_s) and shunt resistance (R_{sh}) from the J - V curves. R_s values are 10.4, 5.2, and 12.5 (ohm cm²); R_{sh} values are 194.9, 558.5, and 167.1 (ohm cm²) for the time of 150, 180, and 210 s, respectively. The calculated parasitic resistances explain device performances in operation obtained from different electrochemical deposition condition. As shown in the SEM image in

Fig. 3d, the poor morphology of the SnO₂ film at a deposition time of 210 s is expected to impede charge transfer between CH₃NH₃PbI_{3-x}Cl_x and FTO, resulting in a reduced J_{sc} .

Considering that the electrodeposition process depends on the ion mobility in an electrolyte solution, we also explored the effect of temperature on the morphology of the films. Figure 4 shows top-view SEM images of films deposited at different bath temperatures with -0.7 V for 180 s. As expected, the surface morphology of the SnO₂-Sn nanospheres prepared at different bath temperatures varies. The nanosphere size, roughness, and thickness seem to be affected, as the migration of Sn²⁺ ions was enhanced at higher temperature. The photovoltaic efficiency of PSCs fabricated using these films is compared in Fig. 4e, f. A finer SnO₂ film yields better performance, and the optimum efficiency was obtained for the film deposited at 60 °C. The SnO₂ film

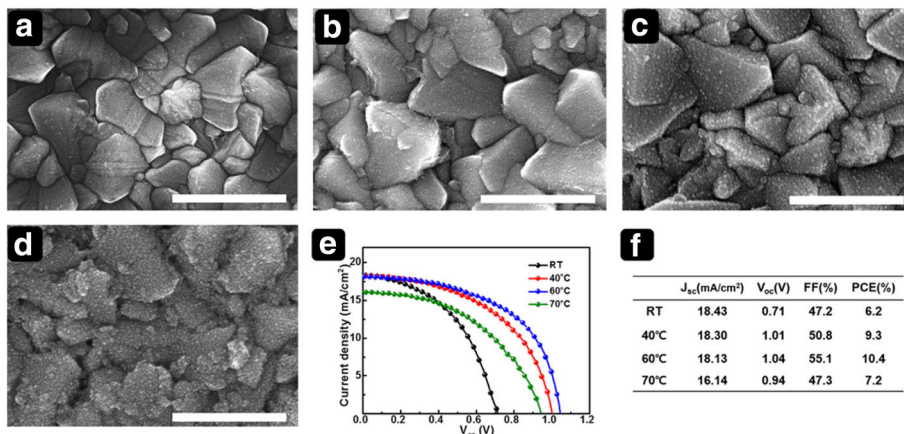


Fig. 4 Top-view SEM images of SnO₂ films electrodeposited at various bath temperatures. (a) RT, (b) 40 °C, (c) 60 °C, and (d) 70 °C. Corresponding photovoltaic performance: (e) J - V curves and (f) photovoltaic parameters of PSCs with electrodeposited SnO₂ ETL. Scale bar is 1 μ m

morphology is expected to significantly affect the PSC performance because planar PSCs have a direct interface between the ETL and the perovskite layer. The improved conformality could result in good contact that affords enhanced electron transport [25]. The SEM images of perovskite layer fabricated from varied ETLs were provided in supporting information (SI) Additional file 1: Figure S1.

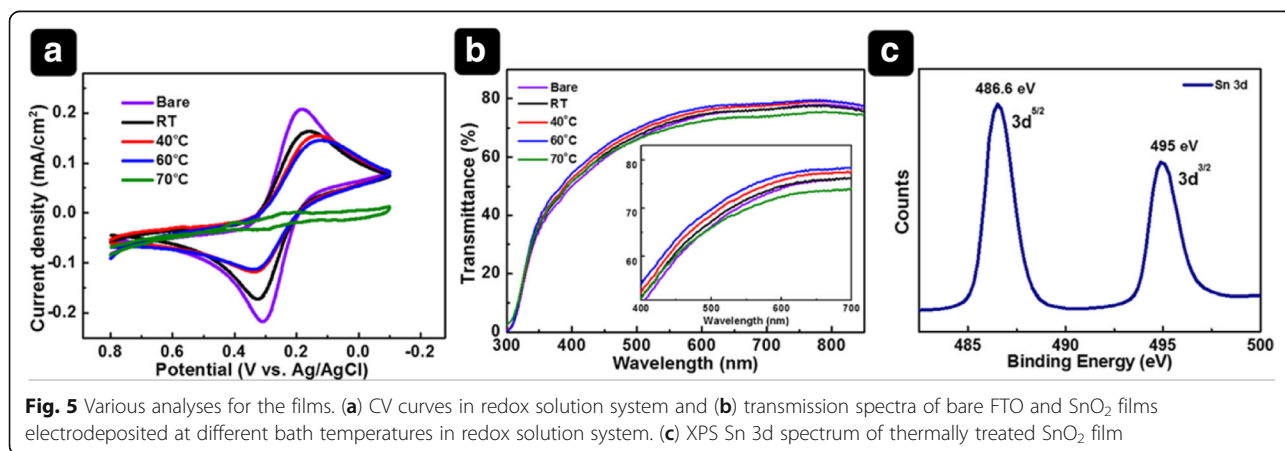
To further examine the effect of temperature on the morphology with respect to the blocking effect of the electrodeposited SnO₂ films, we conducted CV measurements in an aqueous electrolyte containing [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ because the redox reaction depends on charge transfer between the FTO and the electrolyte [26]. The electron transfer kinetics can be interpreted by extracting the separation of the peak potentials and peak current of a redox system from the CV curves. If the redox reaction between [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ ions is hampered by the SnO₂ layer, the oxidized and reduced forms of the redox couple exhibit peak potentials that are shifted away from the control on bare FTO and become semireversible; consequently, the peak current density will be reduced [27]. Figure 5a shows the CV curves of bare FTO and the SnO₂ films. The CV curve of bare FTO clearly shows a reversible redox reaction, indicating a lower barrier to electron transfer. In contrast, the FTO with electrodeposited SnO₂ exhibits a larger peak-to-peak separation (ΔE_p) of the cathodic and anodic peak potentials compared to that of bare FTO. The ΔE_p values of films deposited at room temperature (RT), 40, 60, and 70 °C are 125, 175, 207, and 230 mV, respectively. This indicates that the kinetics of the redox reaction are changed by the blocking effect of the SnO₂ films. In contrast, charge transfer at the FTO is highly suppressed by the film deposited at 70 °C, implying that the SnO₂ is densely deposited onto the FTO. The thick SnO₂ film could result in less effective and slower electron transport, negatively affecting the photovoltaic performance. The cathodic peak current (I_p) of the films

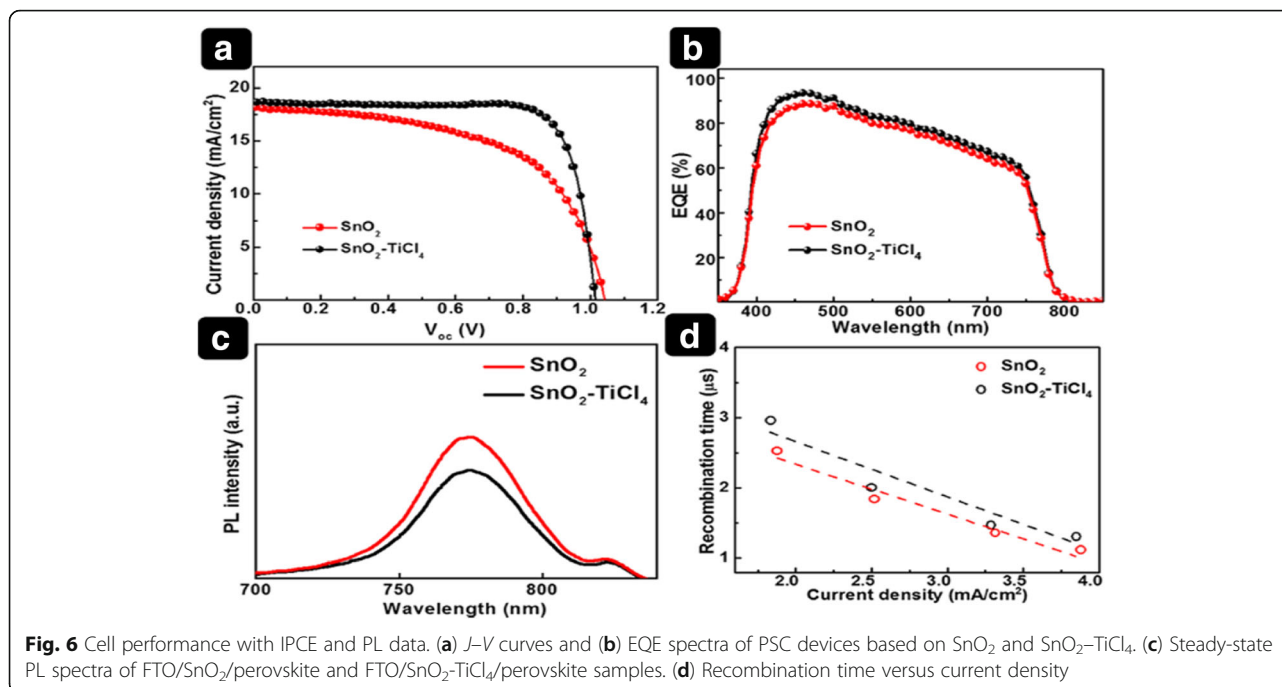
decreased with increasing bath temperature, indicating that the FTO coverage was improved.

On the basis of the CV results and SEM images, we could speculate that the FTO electrode at low temperature is covered with fewer nanoparticles; therefore, we conclude that the SnO₂ film fabricated at 60 °C has a suitable thickness and morphology for use in PSCs and has a dominant effect on the device performance. The optical transmission of the SnO₂ films is also compared (Fig. 5b). As the bath temperature increases from RT to 60 °C, the transmittance of the SnO₂ films is enhanced compared to that of FTO. At a high bath temperature of 70 °C, the transmittance is inferior to that of FTO, which is attributed to the increased film thickness, as evidenced by the SEM image.

XPS was performed to measure the composition of the electrodeposited films. The XPS spectrum of the thermally treated SnO₂ film is shown in Fig. 5c. Sn 3d_{5/2} and Sn 3d_{3/2} peaks at binding energies of 486.6 and 495 eV, respectively, were observed, whereas the film without heat treatment showed Sn 3d_{5/2} and Sn 3d_{3/2} peaks at 484.8 and 493.2 eV, respectively (SI, Additional file 1: Figure S2) [21]. The SnO₂ film is clearly obtained through heat treatment.

On the other hand, although SnO₂ electrodeposition provides a versatile and low-cost route toward scalable manufacturing systems [28], the demonstrated photovoltaic performance of the electrodeposited SnO₂ films is not impressive. To improve the device performance, TiCl₄ treatment was used to modify the SnO₂ surface. As shown in Fig. 6a, the device based on SnO₂ without TiCl₄ treatment shows a J_{sc} value of 18.12 mA/cm², a V_{oc} value of 1.04 V, a FF of 57.3%, and a PCE of 10.83%. In comparison, the device based on SnO₂ with TiCl₄ treatment (SnO₂-TiCl₄) exhibits a J_{sc} value of 18.65 mA/cm², a V_{oc} value of 1.02 V, a FF of 79.1%, and a PCE of 14.97% (a 38% enhancement). The efficiency improvement is attributed mainly to the improved J_{sc} and FF.





To understand the mechanism by which TiCl_4 treatment improves the J_{sc} value, we measured the EQE (Fig. 6b). The EQE of the $\text{SnO}_2\text{-TiCl}_4$ device shows an increase from 17.8 to 18.6 mA/cm^2 in the entire wavelength spectral region. The enhancement in the EQE after TiCl_4 treatment is in good agreement with the improved J_{sc} in the J - V curves, which implies efficient charge collection. The EQE enhancement is expected to be originated from a better injection of electrons at the ETLs/perovskite interface [29, 30]. To further investigate the electron injection, the steady-state PL was measured for substrates with both ETLs. Figure 6c shows the PL spectra of the FTO/ SnO_2 /perovskite and FTO/ $\text{SnO}_2\text{-TiCl}_4$ /perovskite samples. Compared to the SnO_2 -based film, the $\text{SnO}_2\text{-TiCl}_4$ -based film exhibited reduced PL intensity, indicating that electron transfer from the perovskite to the ETL was enhanced by TiCl_4 treatment since the PL emission of perovskite layer is quenched by contact. Possibly, the enhanced electron injection in ETLs with TiCl_4 treatment improved the EQE. To further examine the improved performance of the $\text{SnO}_2\text{-TiCl}_4$ -based device, intensity-modulated photovoltage spectroscopy (IMVS, Additional file 1: Figure S3) was performed to characterize the recombination time (τ_r) (Fig. 6d). The recombination lifetime depends on the concentration of charge carriers in the solar cell. Thus, the recombination time is influenced by the current density, which is modulated by varying the light intensity. The carrier recombination time for the $\text{SnO}_2\text{-TiCl}_4$ -based device was 1.17 times longer than that of the SnO_2 -based devices. The longer time

constant for recombination is expected to afford an increase in J_{sc} , FF, and better device performance [31, 32]. The device statistics (30 samples for each) were provided in Additional file 1: Figure S4.

Conclusions

In summary, we demonstrated a versatile and scalable electrodeposition technique to obtain a SnO_2 ETL for planar heterojunction PSCs. The properties of the electrodeposited SnO_2 depended strongly on the deposition time, electrolyte bath temperature, and applied voltage. Moreover, devices based on SnO_2 treated with TiCl_4 showed significantly enhanced V_{oc} and J_{sc} , leading to a PCE enhancement of 42%.

Additional file

Additional file 1: Figure S1. SEM images of perovskite layer prepared from varied ETLs. (a) RT of SnO_2 , (b) 40°C of SnO_2 , (c) 60°C of SnO_2 , (d) 70°C of SnO_2 , and (e) 60°C of $\text{SnO}_2\text{-TiCl}_4$. Figure S2 XPS spectrum of SnO_2 film without thermal treatment. Figure S3 IMVS curves of (a) SnO_2 -based and (b) $\text{SnO}_2\text{-TiCl}_4$ -based devices. Figure S4 Performance statistic of devices based on different ETLs. (DOCX 3379 kb)

Abbreviations

ALD: Atomic layer deposition; CV: Cyclic voltammetry; ED: Electrochemical deposition; EQE: External quantum efficiency; ETL: Electron transport layer; FF: Fill factor; FTO: Fluorine-doped tin oxide; HTM: Hole-transporting material; IMVS: Intensity-modulated photovoltage spectroscopy; PCE: Power conversion efficiency; PL: Photoluminescence; PSC: Perovskite solar cell; RT: Room temperature; SEM: Scanning electron microscopy; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

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Authors' Contributions

YK, YRK conducted electrochemical experiments to prepare main electrodes with corresponding analyses, and HJ, MK carried out IMVS to understand lifetimes after perovskite solar cell applications, and YJ designed the whole experimental processes and corresponding supervising. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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