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# *In situ* one step growth of amorphous tin oxide electron transport layer for high-performance perovskite solar cells†

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Tin oxide used in electron transport layer (ETL) exhibits key role in transmitting electrons and blocking holes in perovskite solar cells (PSCs) device. However, crystal tin oxide nanoparticles (NPs) become necessary to form SnO<sub>2</sub> film by method of spin-coating, resulting in possible surface defect and cracks among SnO<sub>2</sub> NPs, corresponding to unsatisfied performance PSCs. Herein, an amorphous tin oxide thin film is creatively *in situ* grew onto Fluorine-doped Tin Oxide (FTO) substrate as ETL. The designed solar cell device with structure of FTO/SnO<sub>2</sub>/MAPbI<sub>3</sub>/Spiro-OMeTAD/Ag owns a champion photoelectric conversion efficiency (PCE) up to 17.64%, 76.20% of filling coefficient (FF), and 1.09 V of open-circuit voltage ( $V_{oc}$ ), in comparing with 16.43%, 64.35% and 1.05 V for control group (crystal tin oxide as ETL), respectively. Besides, the champion device keeps 83.33% of initial PCE under nitrogen (N<sub>2</sub>) condition for one month, in comparison with 76.09% for control group. This work provides a viable strategy for facile preparing amorphous tin oxide film based ETL in perovskite solar cells.

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## Introduction

Organic–inorganic lead halide perovskite solar cells (PSCs) with planar regular (n-i-p) structure have achieved tremendous progress with enhancement of their power conversion efficiency (PCE) from 3.8% to 25.7%.<sup>1–11</sup> Especially, the electron transport layer (ETL) is a critical component to promote the transportation of photogenerated electrons and to block hole transportation in PSC device.<sup>12–15</sup> Tin oxide (SnO<sub>2</sub>), a n-type of semiconductor, has become a desirable ETL material owing to its high optical transparency (~80%), unique band gap matching with lead-halide perovskite layer, high electron mobility up to 240 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and relatively low calcination temperature (100–500 °C) during its fabrication process.<sup>16–22</sup> Therefore, optimizing the fabrication strategy of the SnO<sub>2</sub> based ETL becomes a key factor to improve the PCE of PSCs device.

For low-temperature fabrication process, SnO<sub>2</sub> nanoparticles are often previously prepared using various ligand molecules, including tetramethylammonium hydroxide (TMAH), thiourea (CS(NH<sub>2</sub>)<sub>2</sub>), and urea (CO(NH<sub>2</sub>)<sub>2</sub>), to control the morphology of SnO<sub>2</sub> nanoparticles and to protect them from self-aggregation.<sup>23–25</sup> For instance, Fang *et al.*, designed thiourea as a capping ligand to prepare SnO<sub>2</sub> precursors with long time

stirring up to 1–2 days before a spin-coating process to form SnO<sub>2</sub> in perovskite solar cells to acquire a 19.73% of PCE.<sup>24</sup> Hou *et al.*, prepared SnO<sub>2</sub> nanoparticle precursors mixed by SnCl<sub>2</sub>·2H<sub>2</sub>O and urea in deionized water and then stirring for 4–5 days at room temperature, resulting in 16.22% of PCE.<sup>25</sup> As a result, long ripen period up to several days is essential to fully obtain the SnO<sub>2</sub> nanoparticle precursor solution and their particle size depend on the ripen time at room temperature, causing the weakly repeatable results of PCE among batch of experiments. Therefore, exploring a novel fabrication method to bypass the SnO<sub>2</sub> nanoparticles precursor becomes challengeable to optimize the surface structure of SnO<sub>2</sub> based ETL.

In comparison with crystalline metal oxide films, amorphous semi-conductive metal oxide films exhibit comparable photo-electronic properties and can keep long-time work stability at elevated temperatures, owing to that amorphous film owns fewer inter-lattice spaces and less lattice disorder effects.<sup>26</sup> Amorphous metal oxide films have become promising alternatives in solar cell field. For example, Zhang *et al.*, fabricated an electron transport layer with amorphous structure of InGaZnO<sub>4</sub> to obtain a 9.07% of PCE in device of ITO/InGaZnO<sub>4</sub>/CsPbI<sub>1.2</sub>Br<sub>1.8</sub>/C.<sup>26</sup> Kang *et al.*, modified amorphous SnO<sub>2</sub> nanoparticles onto crystalline SnO<sub>2</sub> to improve the PCE from 18.49% to 20.39%.<sup>27</sup> Especially, exploring a novel *in situ* one step growth strategy to fabricate amorphous SnO<sub>2</sub> film as ETL has rarely been explored, which may allow increased performance of lead-halide based PSCs.

Herein, this article uses SnCl<sub>2</sub>·2H<sub>2</sub>O as the tin source and N,N-dimethylformamide (DMF) as the solvent to realize *in situ*

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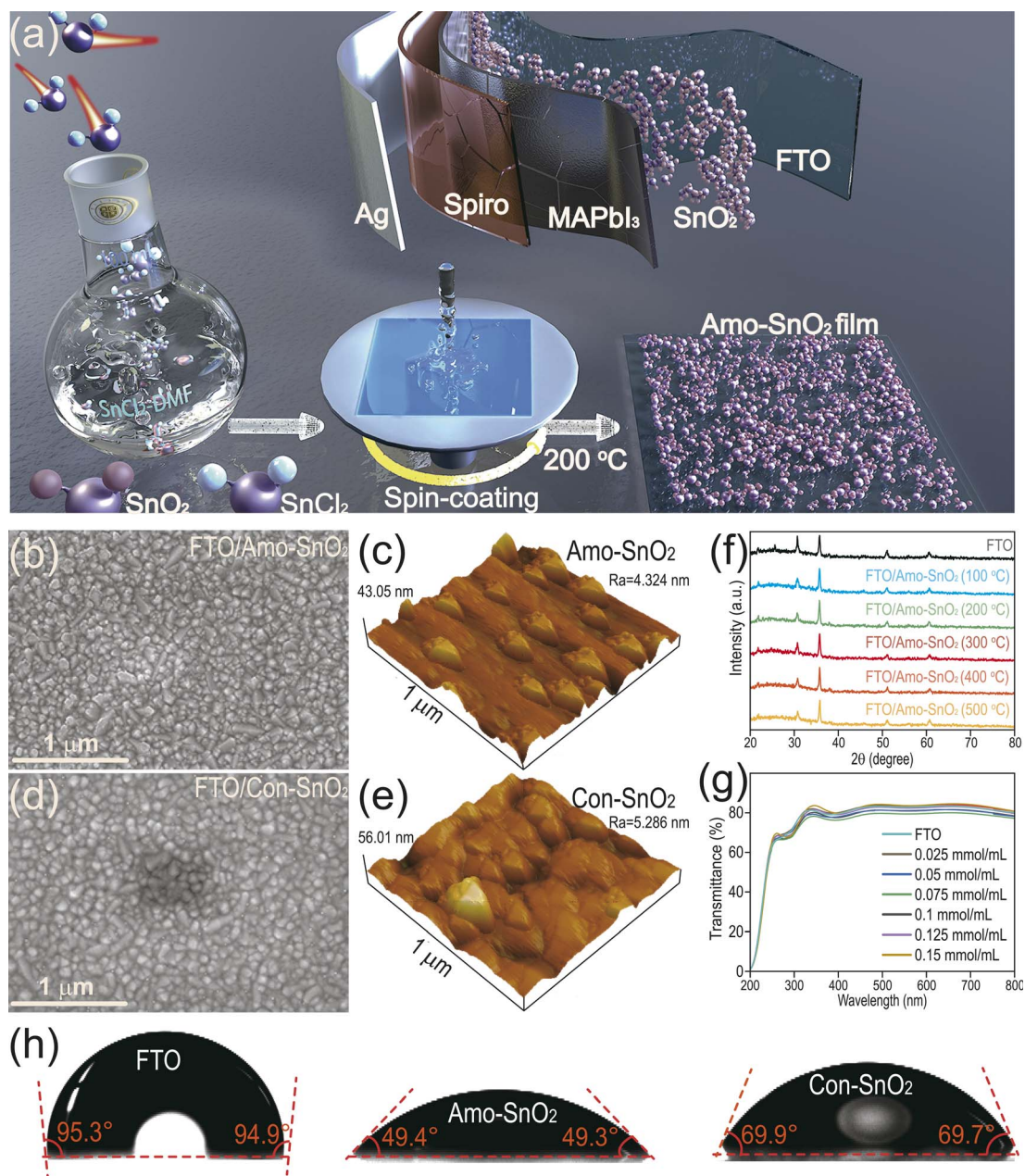
one step growth of amorphous SnO<sub>2</sub> film at relative low annealing temperature (200 °C), as shown in Fig. 1a. The designed PSCs with structure of FTO/SnO<sub>2</sub>/MAPbI<sub>3</sub>/Spiro-OMeTAD/Ag owns a champion PCE up to 17.64%, comparing with 16.43% for control group (crystal tin oxide as ETL). The amorphous and crystal SnO<sub>2</sub> electron transport layers are denoted as Amo-SnO<sub>2</sub> and Con-SnO<sub>2</sub>, respectively. The increased photo-electric efficiency and working stability of the designed PSC can be attributed to the utilization of amorphous SnO<sub>2</sub> as ETL through a facile one-step growth strategy to

modulate the separation efficiency of photogenerated carriers and the elevated structure stability of amorphous SnO<sub>2</sub>.

## Experimental section

### Experimental materials and reagents

Acetonitrile (ACN, 99.9%) and chlorobenzene (CB, 99.5%) were purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.8%), tin oxide powders (99.9%), anhydrous tin chloride (99.99%) and SnCl<sub>2</sub>·2H<sub>2</sub>O were obtained from Aladdin. Methyl iodide (MAI, 99.5%) was



**Fig. 1** (a) Schematic diagram of the proposed strategy for preparing Amo-SnO<sub>2</sub> film. SEM images of (b) Amo-SnO<sub>2</sub> and (d) Con-SnO<sub>2</sub> film by calcination at 200 °C. AFM images of (c) Amo-SnO<sub>2</sub> and (e) Con-SnO<sub>2</sub> film. (f) XRD patterns of the Amo-SnO<sub>2</sub> films at different calcination temperatures. (g) Optical Transmittance of Amo-SnO<sub>2</sub> films prepared with different concentrations of precursor solution and followed by calcination at 200 °C. (h) Contact angle images of SnO<sub>2</sub> films and FTO substrates.



purchased from Xi'an Yuri Solar Co., Ltd. Lead iodide (PbI<sub>2</sub>, 99.9%), lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI, 99.95%), 4-*tert*-butylpyridine (TBP, 96.0%) and 2,2', 7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD, 99.86%) were purchased from Advanced Election Technology Co., Ltd. Fluorine-doped tin oxide glasses (FTO, 14 Ω, 1.5 × 1.5 cm) were purchased from Advanced Election Technology Co., Ltd. Ultrapure water with 18 MΩ was obtained from device of Ultrapure Water System (Corning Technology Development Co., Ltd, PRO-3200, Chengdu). All chemicals were used as achieved without further purification process.

### Preparation of SnO<sub>2</sub> film

For amorphous SnO<sub>2</sub> film, the FTO substrates were cleaned consecutively with detergent, acetone, isopropanol, ethanol, and deionized water for 50 minutes through ultrasonic cleaning, and then dried at 75 °C in an air oven for several hours before the ozone treatment for 10 minutes. Subsequently, the SnCl<sub>2</sub> precursor was prepared by dissolving 22.5 mg of SnCl<sub>2</sub>·2H<sub>2</sub>O into 1 mL of DMF and stirring for 10 minutes at room temperature to form SnCl<sub>2</sub>/DMF solution with concentration of 0.1 mmol mL<sup>-1</sup>. Then, 35 μL of the SnCl<sub>2</sub> precursor solution was spin-coated onto cleaned FTO substrate at 3000 rpm for 30 seconds and followed by annealing at various temperatures from 100 to 350 °C for 1 hour to generate amorphous SnO<sub>2</sub> electron transport layer.

For crystal SnO<sub>2</sub> film (Con-SnO<sub>2</sub>), 22.5 mg of SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in 1 mL of ethanol to form the SnCl<sub>2</sub>/ethanol solution with concentration of 0.1 mmol mL<sup>-1</sup>. Then, the precursor solution was spin-coated onto clean FTO substrate with 3000 rpm for 30 s and followed by annealing at 180 °C for 1 h to obtain the Con-SnO<sub>2</sub> film.<sup>20</sup>

### Preparation of perovskite solar cell device

The prepared SnO<sub>2</sub> electron transport layer was treated with ozone for 15 min prior to depositing perovskite precursor solution in order to remove organics on the surface of the SnO<sub>2</sub> electron transport layer. After that, 35 μL of perovskite precursor solution (containing the MAI and PbI<sub>2</sub> at 1 : 1 of stoichiometric ratio in a mixed solvent with  $V_{\text{DMF}} : V_{\text{DMSO}} = 4 : 1$  to keep the concentrations of both MAI and PbI<sub>2</sub> at 1.25 mmol mL<sup>-1</sup>) was dropped onto SnO<sub>2</sub> ETL film under conditions of 1000 rpm for 3 s and then 4000 rpm for 30 s and followed by dropping 200 μL of chlorobenzene at eighth second before annealing at 100 °C for 10 minutes. The hole transport layer (HTL) precursor solution was prepared by dissolving 17.5 μL of Li-TFSI acetonitrile (520 mg mL<sup>-1</sup>) solution, 28.8 μL of tBP and 72.3 mg of Spiro-OMeTAD solution in 1 mL of chlorobenzene into a 2 mL of flask and followed by stirring for 12 hours at nitrogen atmosphere. Then, 20 μL of HTL precursor was spin-coated onto perovskite layer at 5000 rpm for 30 s and then ripened in a drying oven at room temperature overnight in air. Finally, Ag electrode with a thickness of ~100 nm was deposited onto the surface of the hole transport layer as the top electrode under vacuum condition with  $4 \times 10^{-3}$  Pa and a current of 40 A using a heating boat for 20 minutes.

### Characterization of solar cell device

The photo-electric properties of prepared PSCs were analyzed by a standard solar cell device (San-EI Electric, XEC-300M2, Japan) equipped with a light source of atmospheric mass (AM) 1.5 G with 100 mW cm<sup>-2</sup> of incident light power density. The effective testing area of the device was kept at 0.057 cm<sup>2</sup>, and the test voltage was ranging from -0.2 to 1.2 V. Electrochemical workstation (ELS, CH Instruments, CHI 600D, China) was used for measuring the electrochemical AC impedance of PSCs, with 0.8 V of initial voltage,  $1 \times 10^6$  Hz of high frequency and 1 Hz of low frequency. Other testing parameters including the amplitude and settling time were used based on the default values of workstation. Solar cell testing system (Desai Optoelectronics, 7-SCSpec IPCE, China) was employed for external quantum efficiency (EQE) analysis of PSCs device, with testing wavelength ranging from 300 to 800 nm.

### Materials characterizations

X-ray diffraction meter (XRD, Bruker D8, Germany) was employed to analyze the crystal structure of films with scanning speed at 10° min<sup>-1</sup>, step size at 0.026°, and scanning range from 20 to 80°. The absorption and transmission spectra of films were measured by an UV-Vis spectrophotometer (UV, Shimadzu, UV-1800, Japan) in a wavelength range of 500–1100 nm at room temperature. Fluorescence spectrophotometer (PL, Hitachi, F-7100, Japan) was used for testing the photoluminescence intensity of perovskite films with an excitation wavelength of 460 nm and emission wavelength from 650 to 850 nm. Scanning Electron Microscope (SEM, Hitachi, SU8020, Japan) was employed to observe the surface morphology of films. The electronic structure of prepared films was analyzed by X-ray photoelectron spectroscopy (XPS, Escalab, 250 Xi, America). Atomic Force Microscope (AFM, Shimadzu, SPM9700, Japan) was used for testing the surface roughness of films. Fourier Transform infrared spectroscopy (FTIR, Thermo Fisher, IS55, America) was used for analyzing the organic groups in films. The hydrophilicity of the films was measured by a video optical contact angle measuring instrument (CA, Dataphysics, OCA25, Germany). Valence band of films was calculated based on formula (1), where  $E_{\text{VB}}$  is valence band,  $\phi$  is the work function of the XPS instrument ( $\phi = 4.55$  eV),  $E_{\text{VB, XPS}}$  is the valence band position *versus* XPS. Defect state density is determined from formula (2), where  $\epsilon$  is the vacuum dielectric constant,  $\epsilon_0$  is the relative dielectric constant,  $L$  is the thickness of the perovskite film,  $e$  is the elemental charge,  $V_{\text{TFL}}$  is the trap filling limit voltage at the transition point of the ohmic and trap filling limit regions,  $N_{\text{trap}}$  is the defect density of states.

$$E_{\text{VB}} = \phi + E_{\text{VB, XPS}} - 0.44 \quad (1)$$

$$N_{\text{trap}} = \frac{2\epsilon_0\epsilon V_{\text{TFL}}}{eL^2} \quad (2)$$

## Results and discussion

### The surface morphology of SnO<sub>2</sub> film

The entire process from preparing precursor solution of SnCl<sub>2</sub> to generating amorphous SnO<sub>2</sub> film is described in Fig. 1a. It is



noted that the stability of precursor solution plays a key role in obtaining the SnO<sub>2</sub> film with high quality and reproducible properties among batch of experiments. The prepared SnCl<sub>2</sub> precursor exhibits acceptable chemical stability with clear and transparent state up to six months in Fig. S1.† The SnO<sub>2</sub> film is then produced by spin coating of precursor solution at different annealing temperatures. In Fig. S2,† with increasing the annealing temperature more than 200 °C, the surface of the film becomes rough and appears obvious cracks, which is not beneficial to electron transfer and the growth of perovskite layer, caused by high annealing temperature leads to more oxygen defects and pinholes in the films.<sup>28</sup> Therefore, 200 °C is optimal to obtain SnO<sub>2</sub> film with high quality (denoted as Amo-SnO<sub>2</sub>). The morphologies of Amo-SnO<sub>2</sub> and Con-SnO<sub>2</sub> films are then compared by scanning electron microscopy (SEM) and atomic force microscopy (AFM) in Fig. 1b–e and S3.† It can be seen that comparing with the Con-SnO<sub>2</sub> film, the Amo-SnO<sub>2</sub> film exhibits uniform and smooth surface covered onto FTO substrate, as demonstrated by the decreased surface roughness (*R*<sub>a</sub>) of 4.324 nm for Amo-SnO<sub>2</sub> than that of 5.286 nm for Con-SnO<sub>2</sub> films. Then, XRD pattern demonstrates the amorphous structure of prepared SnO<sub>2</sub> film in Fig. 1f. There are no detectable characteristic peaks corresponding to standard SnO<sub>2</sub> with calcination temperature from 100 to 500 °C, indicating that the formation of amorphous structure of SnO<sub>2</sub> is independent of its calcination temperature. Similar results are also obtained when SnO<sub>2</sub> is covered onto glass substrate instead of FTO in Fig. S4.† Fig. S5† shows the XRD pattern of Con-SnO<sub>2</sub> thin film, the peak of Con-SnO<sub>2</sub> corresponds to the standard SnO<sub>2</sub>: JCPDS SnO<sub>2</sub>-PDF#41-1445. The formation of SnO<sub>2</sub> using ethanol is similar with using water as solvents to provide hydroxy group to form Sn(OH)<sub>2</sub>. The function of DMF is possibly to form weak Sn–O–N bond instead of Sn–OH bond. The intermediate structure of Sn–O–N can inhibit the formation of crystal SnO<sub>2</sub>, resulting in the amorphous SnO<sub>2</sub>. For PSCs device, high optical transmittance of functional layers including HTL and ETL indicates less photons harvesting by functional layers and high photons utilization efficiency by active layers such as perovskite layer for improved performance of PSCs device. In Fig. 1g, the optical transmittance (300–800 nm) of Amo-SnO<sub>2</sub> films is optimized by modulating concentrations of SnCl<sub>2</sub> precursor. Up to 83.661% of optical transmittance is obtained with 0.1 mmol mL<sup>-1</sup> of precursor solution. Identical result is also described by replacing FTO with glass substrates to obtain 88.782% of optical transmittance in Fig. S6.† The optimal optical transmittance of SnO<sub>2</sub> film is also demonstrated up to 82.874% at 200 °C of calcination temperature in Fig. S7.† Over high temperature (>200 °C) brings some micro-cracks on the surface of film, resulting in decreased optical transmittance. It is noted that hydrophilic surface of SnO<sub>2</sub> film can facilitate the adsorption and growth of perovskite film. Therefore, the surface hydrophilicity of SnO<sub>2</sub> films is evaluated by contact angle analysis in Fig. 1h. Decreased contact angle with 49.4° for Amo-SnO<sub>2</sub> than that with 69.9° for Con-SnO<sub>2</sub> indicates the enhanced hydrophilicity of Amo-SnO<sub>2</sub>. Generally, surface roughness of film is positive correlated with its hydrophilic efficacy. However, for Amo-SnO<sub>2</sub>, hydrophilic residual including chloride ion and

DMF exist on the surface of film as demonstrated from Fig. 2c and S8,† resulting in the increased hydrophilic efficacy than that of Con-SnO<sub>2</sub>. In addition, the growth process of Amo-SnO<sub>2</sub> film is analyzed by infrared spectroscopy tests in Fig. S8.† From the magnified FTIR spectra, trace of C–H and C=O groups can be detected in Amo-SnO<sub>2</sub>-calcination, indicating the residual DMF on the surface of Amo-SnO<sub>2</sub> film. This result also demonstrates the *in situ* growth of Amo-SnO<sub>2</sub> film by converting SnCl<sub>2</sub>-DMF into amorphous SnO<sub>2</sub> film.

### Characterizations of electronic structure

X-ray photoelectron spectroscopy (XPS) is used to analyze the surface electronic structure of Amo-SnO<sub>2</sub> and Con-SnO<sub>2</sub> films. In Fig. S9,† detectable elements including Sn and O in both two kinds of films indicate the successful preparation of SnO<sub>2</sub> films without impurities. In Fig. 2a, it is found that there are peaks at 486.83 and 495.23 eV (corresponding to Sn 3d<sub>5/2</sub>) for Amo-SnO<sub>2</sub> and SnO<sub>2</sub> powder, respectively, indicating the existence of Sn<sup>4+</sup> on the surface of Amo-SnO<sub>2</sub> film. Absence of Sn<sup>2+</sup> is also demonstrated by the disappearance of peak at 486.0 eV for Amo-SnO<sub>2</sub>. For SnO<sub>2</sub> film, the O 1s XPS (Fig. 2b) peaks at ~530.4 eV and ~531.8 eV can be attributed to Sn–O bond and hydroxyl (–OH) adsorbed on the surface of film, respectively.<sup>21,22,29,30</sup> The peak area ratio of Sn–O to hydroxyl for Amo-SnO<sub>2</sub> and Con-SnO<sub>2</sub> are calculated as 0.95 and 0.87, respectively, indicating the increased absorption of hydroxyl for Amo-SnO<sub>2</sub> than that for Con-SnO<sub>2</sub>. Owing to the increased hydrophilic capability of Amo-SnO<sub>2</sub> over Con-SnO<sub>2</sub> (Fig. 1h), Amo-SnO<sub>2</sub> tends to absorb water molecule from air before XPS analysis. Increased hydrophilic surface of Amo-SnO<sub>2</sub> film exhibits advantage in depositing perovskite film toward high-performance PSCs. Compared with SnO<sub>2</sub> powder, the characteristic peaks of Sn 3d and O 1s of Amo-SnO<sub>2</sub> films exhibit minor shifts to high binding energy, which is caused by the residual chloride ions on its surface to passivate the vacancy of oxygen.<sup>25,31</sup> Besides, there exists Cl 2p peak for the Amo-SnO<sub>2</sub> (Fig. S9† and 2c), indicating the less amount of chloride ions on its surface. Comparing with SnCl<sub>2</sub> powder, the binding energy of Cl<sup>-</sup> moves towards higher energy for Amo-SnO<sub>2</sub> film in Fig. 2c, which can be attributed to the formation of Sn–Cl bond, resulting in some oxygen vacancies existing on the surface.<sup>31</sup> Therefore, replacing the ethanol with DMF solvent can introduce less amounts of chloride ions on the surface of amorphous SnO<sub>2</sub> film. The presence of Cl<sup>-</sup> contributes to growing perovskite films, passivating the defects at the interface of Amo-SnO<sub>2</sub> and perovskite, and inhibiting the non-radiative recombination of carriers.<sup>32,33</sup> It is noted that negligible difference for Sn 3d and O 1s spectra is found between Con-SnO<sub>2</sub> and SnO<sub>2</sub> powder, demonstrating that there is almost no Cl<sup>-</sup> in Con-SnO<sub>2</sub> (Fig. 2a and b). Then, semiconductive properties of SnO<sub>2</sub> films are analyzed in Fig. 2d. Valence band is calculated based on formula (1) described in experimental sections. Similar valence bands are obtained for the Amo-SnO<sub>2</sub> (7.43 eV) and SnO<sub>2</sub> powder (7.23 eV). In contrast, higher band gap up to 3.63 eV is observed for Amo-SnO<sub>2</sub> than that for SnO<sub>2</sub> powder with 3.58 eV (Fig. 2e), possibly caused by the special amorphous structure of SnO<sub>2</sub>. Besides, ultraviolet



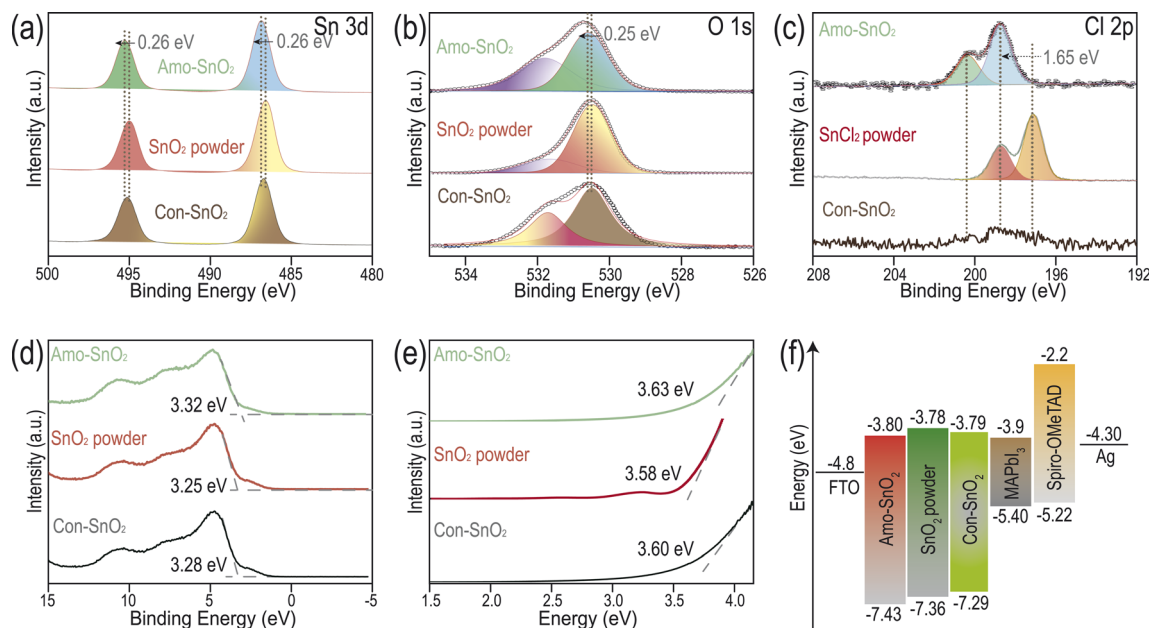


Fig. 2 High-resolution XPS spectra of  $\text{SnO}_2$  based films: (a) Sn 3d, (b) O 1s, (c) Cl 2p. (d) Valence band spectra of films. (e) Bandgap diagram of films. (f) Energy level diagram of each layer in PSCs.

photoelectron spectroscopy (UPS) is performed to analyze the conduction bands of films in Fig. S10.† Combined with the band gap in Fig. 2e, the conduction band of the Amo- $\text{SnO}_2$  and Con- $\text{SnO}_2$  are determined as 3.8 and 3.79 eV. Finally, the energy levels of the Amo- $\text{SnO}_2$ ,  $\text{SnO}_2$  powder, Con- $\text{SnO}_2$  and the perovskite active layer are described in Fig. 2f. This diagram indicates the appropriate conduction match between Amo- $\text{SnO}_2$  and perovskite active layer, promoting the extraction and transport of photo-generated electrons by active layer.

### Characterizations of perovskite solar cell device

The morphologies of perovskite solar cell devices are characterized by SEM in Fig. 3a–d. Smooth and dense surface with larger grain size is observed for perovskite layer coated onto Amo- $\text{SnO}_2$  than that coating onto Con- $\text{SnO}_2$ , which can promote the transfer of photo-generated electrons and reduce recombination of non-radiative charges. Cross-sections of PSCs are then explored in Fig. 3b and d. Dense contact between ETL and perovskite layers is obtained for Amo- $\text{SnO}_2$  and the thickness of each layer of the PSCs are determined as  $\sim 23$  nm for Amo- $\text{SnO}_2$  (ETL),  $\sim 290$  nm for  $\text{MAPbI}_3$  (active layer),  $\sim 100$  nm for Spiro-OMeTAD (HTL), and  $\sim 100$  nm for Ag electrode, respectively. Besides, crystal structure of perovskite layers coated separately onto Amo- $\text{SnO}_2$  and Con- $\text{SnO}_2$  films are analyzed in Fig. S11.† The intensity of diffraction peak at  $14.65^\circ$  (corresponding to (110) plane) for Amo- $\text{SnO}_2$  is 1.45 times higher than that for Con- $\text{SnO}_2$  (Fig. S11†). Moreover, for Amo- $\text{SnO}_2$  films prepared at different annealing temperatures, 200 °C of annealing temperature results in higher crystallinity of  $\text{MAPbI}_3$  in Fig. S12,† which is possibly caused by over high annealing temperature can deteriorate the surface structure of  $\text{SnO}_2$ . In Fig. 3e and f, increased optical absorption (380–760 nm) and decreased fluorescence emission intensity at 700 nm for perovskite layer

coated onto Amo- $\text{SnO}_2$  layer are obtained than that onto Con- $\text{SnO}_2$  layer. Above results indicate that comparing with Con- $\text{SnO}_2$  layer, the Amo- $\text{SnO}_2$  layer is more suitable for growing perovskite with dense contact and high quality to provide higher electron extraction and transport efficacy with less non-radiation loss for high-performance device.

### Performance of perovskite solar cell device

In order to further study the function of Amo- $\text{SnO}_2$  as an electron transport layer in perovskite solar cells, the n-i-p type of PSCs with structure of FTO/Amo- $\text{SnO}_2$ /MAPbI<sub>3</sub>/Spiro-MeOTAD/Ag are prepared. For Amo- $\text{SnO}_2$ , the performance of PSCs is optimized by modulating the concentrations of precursor solutions of  $\text{SnCl}_2$  and calcination temperature in Fig. S13 and S14.† The optimal parameters are kept at 0.1 mmol mL<sup>-1</sup> of concentration and 200 °C of calcination temperature. Champion device with corresponding parameters including open circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (FF) and photovoltaic conversion efficiency (PCE) are summarized in Tables S1 and S2.† In Fig. 4a, the photoelectric conversion efficiency (PCE) of using Amo- $\text{SnO}_2$  as ETL reaches up to 17.64%, which is significantly higher than that of using Con- $\text{SnO}_2$  as ETL PSCs (16.43% of PCE). This result is further demonstrated using batch of PSCs with twenty samples for PCE analysis by reverse scan in Fig. S15.† Average PCE for Amo- $\text{SnO}_2$  and Con- $\text{SnO}_2$  are  $16.59 \pm 0.59$  and  $15.34 \pm 0.74$ , respectively. Forward and reverse scan of  $J-V$  curves are provided in Fig. S16.† For Amo- $\text{SnO}_2$ , 15.44% and 17.38% of PCE are obtained for forward and reverse scan, respectively, comparing with the 13.87% and 16.19% for Con- $\text{SnO}_2$ . Therefore, less hysteresis effect is obtained by Amo- $\text{SnO}_2$  than by Con- $\text{SnO}_2$  used as ETL in PSCs. To exploring the recombination of charge carriers occurring on the surface and inside of perovskite thin films, the



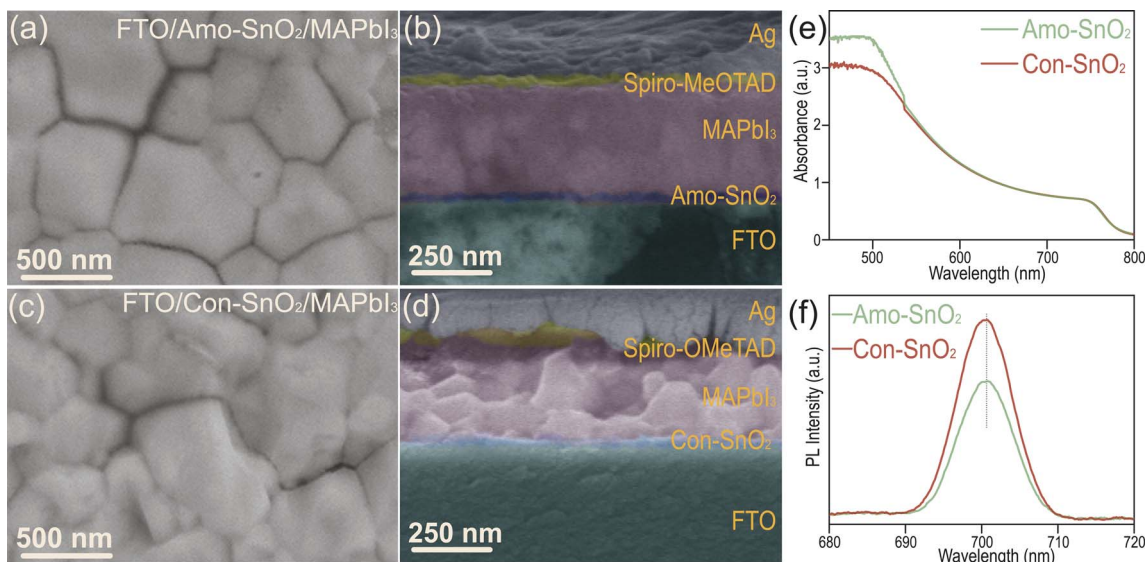


Fig. 3 SEM images of MAPbI<sub>3</sub> film coated onto (a) Amo-SnO<sub>2</sub> and (c) Con-SnO<sub>2</sub> films. Cross sections of PSCs using (b) Amo-SnO<sub>2</sub> and (d) Con-SnO<sub>2</sub> as ETL. (e) Ultraviolet visible absorbance and (f) PL spectra of perovskite films deposited separately onto Con-SnO<sub>2</sub> and Amo-SnO<sub>2</sub> layers.

external quantum efficiency (EQE) analysis is performed using the champion device. In Fig. 4b, the device of using Amo-SnO<sub>2</sub> as ETL owns higher optical response than that using Con-SnO<sub>2</sub>

as ETL, resulting in increased  $J_{sc}$  of device using Amo-SnO<sub>2</sub> as ETL. The surface and internal defects of devices are evaluated by dark current density analysis. In Fig. 4c, dark current curve of

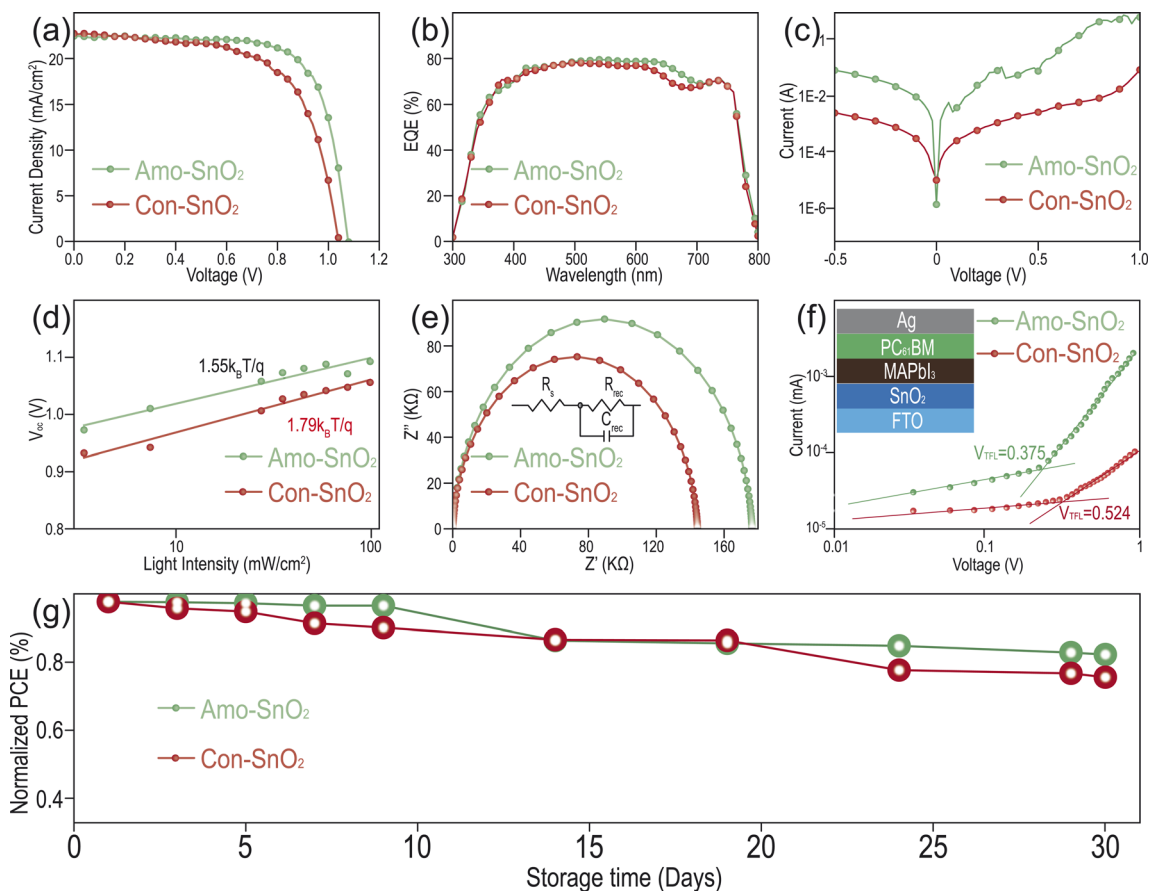


Fig. 4 (a)  $J$ - $V$ , (b) EQE, (c) dark current density, (d) voltage changing with light intensity, (e) EIS in dark conditions at 0.8 V bias, (f) SCLC and (g) working stability curves of the devices using different electron transport layers.



device using Amo-SnO<sub>2</sub> as ETL indicates the decreased leakage current at the low-voltage scale, which suggests the dense interfacial contact between Amo-SnO<sub>2</sub> ETL and the active layer. Furthermore, photo-generated carrier recombination efficiency of device using various ETL can be illustrated by the light intensity and open circuit voltage curve in Fig. 4d. For PSCs with structure of FTO/SnO<sub>2</sub>/MAPbI<sub>3</sub>/Spiro-MeOTAD/Ag, Amo-SnO<sub>2</sub> exhibits smaller ideal factor (1.55) than Con-SnO<sub>2</sub> (1.79), indicating the suppression of non-radiative recombination, reduction and inhibition of V<sub>oc</sub> losses and leakage current of PSCs using Amo-SnO<sub>2</sub> as ETL. Besides, the recombination of charge carriers in devices are analyzed using electrochemical impedance spectroscopy (EIS) in Fig. 4e. In the Nyquist plots, both devices using Amo-SnO<sub>2</sub> and Con-SnO<sub>2</sub> as ETL exhibit obvious semi-circular curves. Comparing with Con-SnO<sub>2</sub>, device using Amo-SnO<sub>2</sub> as ETL obtains a larger semi-circular diameter, indicating higher composite resistance, larger composite resistance and lower probability of carrier recombination, which is beneficial for PSCs. To verify the carrier recombination of the device under light conditions, EIS map under light conditions are conducted in Fig. S17.† The composite resistance (R<sub>rec</sub> = 52.48 kΩ) of Amo-SnO<sub>2</sub> is significantly higher than that of Con-SnO<sub>2</sub> (R<sub>rec</sub> = 41.09 kΩ). In PSCs, higher R<sub>rec</sub> and smaller R<sub>s</sub> indicate lower carrier recombination and higher efficiency of extracting electrons, which is conducive to the performance of the PSCs. Combined EIS results under both light and dark conditions demonstrate weak carrier recombination efficiency when Amo-SnO<sub>2</sub> film is employed as ETL. In addition, the space charge limited current method (SCLC) is used to quantitatively characterize the defect state density of the PSCs. Defect densities of electrons are analyzed using the device without hole transport layer (FTO/SnO<sub>2</sub>/MAPbI<sub>3</sub>/PC<sub>61</sub>BM/Ag). In Fig. 4f, the V<sub>TFL</sub> of the champion device using Con-SnO<sub>2</sub> and Amo-SnO<sub>2</sub> as electron transport layers are 0.524 V and 0.375 V, respectively. The corresponding electrons trap densities (N<sub>trap</sub>) using Amo-SnO<sub>2</sub> as ETL is obtained with 4.839 × 10<sup>15</sup> cm<sup>-3</sup>, which is significantly lower than that using Con-SnO<sub>2</sub> as ETL (6.762 × 10<sup>15</sup> cm<sup>-3</sup>). Finally, the long-term stability of the device is evaluated in Fig. 4g. After 30 days of storage, the device using Amo-SnO<sub>2</sub> as ETL still maintains 83.33% of the initial PCE in the glove box, in contrast with only 76.09% for Con-SnO<sub>2</sub>, indicating the excellent stability of device using Amo-SnO<sub>2</sub> as ETL. Moreover, the prepared SnCl<sub>2</sub>/DMF precursor also demonstrates long-time of stability over conventional SnCl<sub>2</sub>/EtOH solution. In Fig. S18,† only 0.63% of PCE is reduced for Amo-SnO<sub>2</sub> after nine months of storage of SnCl<sub>2</sub>/DMF solution at room temperature, in contrast with 1.85% of PCE reduction for Con-SnO<sub>2</sub> with identical treating process. Long time stability of PSCs using Amo-SnO<sub>2</sub> as ETL can be attributed to the special amorphous structure of SnO<sub>2</sub> favoring to maintain the long-time structure stability and keep dense contact between Amo-SnO<sub>2</sub> ETL and the active layer.

## Conclusions

In summary, a facile *in situ* one step method is proposed for preparing amorphous SnO<sub>2</sub> film as the ETL. The as-synthesized

Amo-SnO<sub>2</sub> film owns superior electrical conductivity, optimized band gap, and lower trap density compared with Con-SnO<sub>2</sub>. The proposed method simplifies the preparation process of ETL in n-i-p type of device and extends the application of amorphous materials in PSCs. The device based on the Amo-SnO<sub>2</sub> thin film attains champion PCE up to 17.64% and 1.09 V of V<sub>oc</sub>. In addition, the device using Amo-SnO<sub>2</sub> as ETL presents excellent stability up to 30 days with only 83.33% of reduction of initial PCE. Finally, this work provides a viable method for the application of amorphous electron transport layers in perovskite solar cells.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

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