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# High-efficiency perovskite solar cells with poly(vinylpyrrolidone)-doped SnO<sub>2</sub> as an electron transport layer

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Hybrid organic–inorganic perovskites have attracted intensive attention as the absorber layer in high-performance perovskite solar cells (PSCs). The interface between the electron transport layer and the perovskite layer in perovskite solar cells has a large effect on the device performance. Herein, we report a perovskite solar cell with a cell structure of ITO/ETL/(FAPbI<sub>3</sub>)<sub>0.97</sub>(MAPbBr<sub>3</sub>)<sub>0.03</sub>/spiro-OMeTAD/MoO<sub>3</sub>/Ag, where the poly(vinylpyrrolidone) (PVP)-doped SnO<sub>2</sub> film works as the electron transport layer. We observe that the perovskite film grown on PVP-SnO<sub>2</sub> shows more uniform crystalline grains than the control sample grown on the pure SnO<sub>2</sub>, and the electron mobility of the PVP-SnO<sub>2</sub> film is higher than that of the pure SnO<sub>2</sub> film; consequently, PVP-SnO<sub>2</sub> can efficiently extract electrons from the perovskite layer. As a result, the PSCs using the PVP-doped SnO<sub>2</sub> ETL showed an increased power conversion efficiency (PCE). The optimized device using the PVP-SnO<sub>2</sub> electron transport layer shows an improved PCE of 19.55%, while the PSC using the SnO<sub>2</sub> electron transport later shows a PCE of 17.50%. Furthermore, it is feasible to add PVP into the electron transport layer of SnO<sub>2</sub> to improve the performance of the planar perovskite solar cell device.

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## Introduction

Perovskite solar cells (PSCs) with a simple planar structure have the advantages of high efficiency, low cost and facile solution processing, and have become one of the most competitive and promising next-generation photovoltaic technologies.<sup>1–4</sup> The power conversion efficiency (PCE) of PSCs swiftly increased from 3.8% to more than 25% in 10 years due to their high absorption coefficient and long carrier diffusion length.<sup>5–13</sup>

A significant amount of research effort has focused on controlling the composition and morphology of perovskites,<sup>14</sup> as well as exploring effective and promising materials for hole and electron transport layers (HTLs and ETLs).<sup>15–18</sup> Comprehensive improvements in each of these areas have led to the increased PCE records. Despite the excellent performance of PSCs, planar PSCs are normally unstable and have severe hysteresis due to ion migration and interface defects in the device.<sup>19–21</sup> Many research groups report that modifying the interface between the perovskite layer and the ETL can significantly eliminate the hysteresis in PSCs.<sup>22</sup> So far, it has been believed that an effective and promising ETL is critical to make

efficient and hysteresis-free PSCs.<sup>23</sup> A suitable ETL should meet some of the basic requirements for high equipment efficiency,<sup>24</sup> including proper optical transmission of the ETL to ensure adequate light penetration into the perovskite absorber; energy level matching with the conduction band edge of the perovskite material to produce the desired open circuit voltage ( $V_{OC}$ ); and a high electron mobility to effectively extract carriers from the active layer to minimize the charge accumulation at the interface and facilitate electron extraction in planar PSCs.<sup>25–27</sup> Therefore, developing high-quality ETLs with suitable energy levels and high electron mobility is important for high efficiency devices. SnO<sub>2</sub> exhibits exceptional attributes including excellent chemical stability, high electron mobility, and a facile and relatively low-temperature preparation process.<sup>28,29</sup> So far, SnO<sub>2</sub> is normally used as the ETL in high-performance perovskite solar cells due to its excellent photoelectric properties.<sup>30</sup> Moreover, SnO<sub>2</sub> is found to be a good ETL of perovskite solar cells, owing to the more matched energy level between SnO<sub>2</sub> and perovskites.<sup>31,32</sup> Ke *et al.* first used the SnO<sub>2</sub> ETL in conventional planar PSCs and achieved a PCE of 16.02% with no observable hysteresis.<sup>25</sup> So far, many methods have been developed to successfully prepare compact and pinhole-free SnO<sub>2</sub> films, including spin-coating, atomic layer deposition, and slot-die printing.<sup>33,34</sup> To further increase the PCE of PSCs, improvement of the open-circuit voltage ( $V_{OC}$ ) and fill factor (FF) could be more feasible than increasing the short-circuit current ( $J_{SC}$ ) because  $J_{SC}$  is

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almost close to its limit ( $\sim 26 \text{ mA cm}^{-2}$ ) for perovskite solar cells with a bandgap of around  $1.55 \text{ eV}$ .<sup>35</sup> With these factors in mind, research efforts should begin with finding ways to increase  $V_{\text{OC}}$ . To avoid charge accumulation at the ETL/perovskite interface, researchers developed several strategies to further increase the electron mobility of  $\text{SnO}_2$ , which facilitates electron extraction.<sup>36</sup> For example, the compactness and wetting property of the  $\text{SnO}_2$  layer are significantly improved by introducing polymer polyethylene glycol (PEG) into the  $\text{SnO}_2$  ETL, thereby improving the performance of the planar perovskite solar cell.<sup>37</sup> The concept of introducing a polymer into the ETL paves the way to further improve the performance of planar perovskite solar cells. As a common water-soluble polymer, poly(vinylpyrrolidone) (PVP) was successfully added into  $\text{SnO}_2$  as an ETL and improves the performance of perovskite photodetectors. PVP can inhibit the agglomeration of  $\text{SnO}_2$  nanoparticles and improve the morphology of  $\text{SnO}_2$  films.<sup>38</sup> This work provides the idea of incorporating PVP in  $\text{SnO}_2$  as an ETL in perovskite solar cells.

Here, we report on the use of PVP-doped  $\text{SnO}_2$  (PVP- $\text{SnO}_2$ ) as an ETL for PSCs to increase the efficiency and reduce hysteresis compared to  $\text{SnO}_2$ -based control devices. It is also demonstrated that the ETL with the PVP-doped  $\text{SnO}_2$  can improve the crystallinity of the perovskite and extract electrons more effectively. Therefore, the best-performance device of perovskite solar cells using PVP- $\text{SnO}_2$  as the ETL achieved a PCE of 19.55%, with a  $V_{\text{OC}}$  of 1.120 V, a  $J_{\text{SC}}$  of  $23.83 \text{ mA cm}^{-2}$ , and a FF of 73.27%. More importantly, the device with the PVP- $\text{SnO}_2$  ETL showed better stability than the control device.

## Results and discussion

The device structure of the perovskite solar cells we used in this study is shown in Fig. 1a. The full device structure is ITO/ETL/(FAPbI<sub>3</sub>)<sub>0.97</sub>(MAPbBr<sub>3</sub>)<sub>0.03</sub>/spiro-OMeTAD/MoO<sub>3</sub>/Ag, in which the  $\text{SnO}_2$  film or PVP- $\text{SnO}_2$  film is the ETL for the reference and test devices, respectively.

We optimized the performance of the PVP- $\text{SnO}_2$ -based solar cells by varying the content of PVP in the PVP- $\text{SnO}_2$  precursor. As the PVP content increased from  $2 \text{ mg mL}^{-1}$  to  $3 \text{ mg mL}^{-1}$ ,

the PCE of the corresponding PSCs was improved from 18.22% to 19.55%. When the concentration of PVP increased to  $5 \text{ mg mL}^{-1}$ , the PCE was decreased to 17.80%. The conductivity of PVP is poor, so the higher concentration of PVP in  $\text{SnO}_2$  can damage the charge carrier mobility of the  $\text{SnO}_2$  layer. Accordingly, excessive PVP polymer cannot improve the performance of perovskite solar cells. The  $J$ - $V$  curves for the PVP- $\text{SnO}_2$ -based devices with different PVP contents are provided in Fig. 1b, and the device performance parameters are summarized in Table 1.

Fig. 2a shows the optical transmission spectra of the bare indium tin oxide (ITO), ITO/ $\text{SnO}_2$  and ITO/PVP- $\text{SnO}_2$  ( $3 \text{ mg mL}^{-1}$  PVP in  $\text{SnO}_2$  solution) films. It is found that the transmittances of the ITO/ $\text{SnO}_2$  and ITO/PVP- $\text{SnO}_2$  films in the wavelength range of 300–500 nm are higher than the ITO without a coating. The ITO/PVP- $\text{SnO}_2$  film has the best transmittance, thereby permitting more light to be absorbed by the perovskite layer. Therefore it proves that ITO/PVP- $\text{SnO}_2$  has good optical quality. The introduction of  $\text{SnO}_2$  may change the reflectance over the entire wavelength region. Hence, the transmittances of the ITO/ $\text{SnO}_2$  and ITO/PVP- $\text{SnO}_2$  films in the wavelength range of 300–500 nm are higher than the ITO without a coating, while the transmittances of the ITO/ $\text{SnO}_2$  and ITO/PVP- $\text{SnO}_2$  films in the wavelength range of 500–900 nm are lower than the ITO without a coating.<sup>36</sup> It is known that the electron mobility is a key parameter of ETLs in PSCs, so it is necessary to know the electron mobility of ETLs. The electron mobilities of different ETLs were measured using the space charge-limited current (SCLC) method,<sup>39</sup> as shown in Fig. 2b. It is found that the electron mobility of PVP- $\text{SnO}_2$  is  $2.75 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , higher than that of  $\text{SnO}_2$  ( $2.24 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). The high electron mobility of the PVP- $\text{SnO}_2$  based PSCs effectively promotes electron transfer and reduces charge accumulation at the ETL/perovskite interface, which improves the efficiency and suppresses hysteresis.<sup>27,36</sup>

The X-ray photoelectron spectra (XPS) of the  $\text{SnO}_2$  and PVP- $\text{SnO}_2$  films deposited on ITO glass substrates were measured to confirm the existence of PVP, and the corresponding results are shown in Fig. 2c. All XPS measurements of binding energy data have been calibrated through the carbon 1s line at 284.8 eV. It is clear from these measurements that  $\text{SnO}_2$  shows distinct

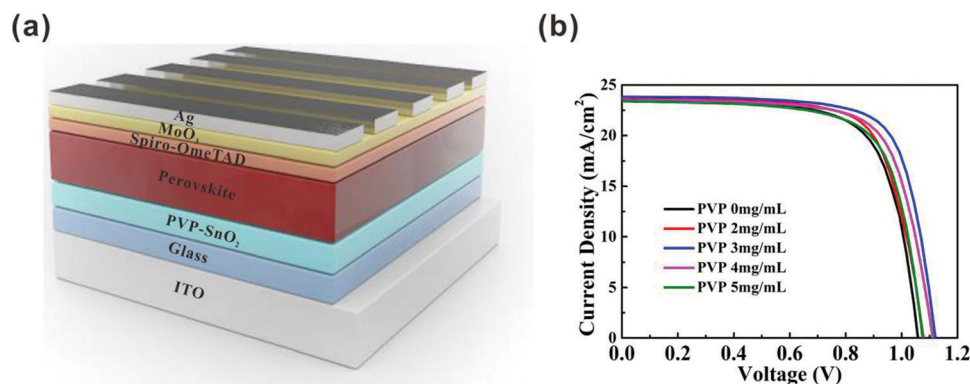


Fig. 1 (a) Schematic view of the device structure in this work. (b)  $J$ - $V$  characteristics of PSCs with PVP- $\text{SnO}_2$  ETLs with various amounts of PVP.

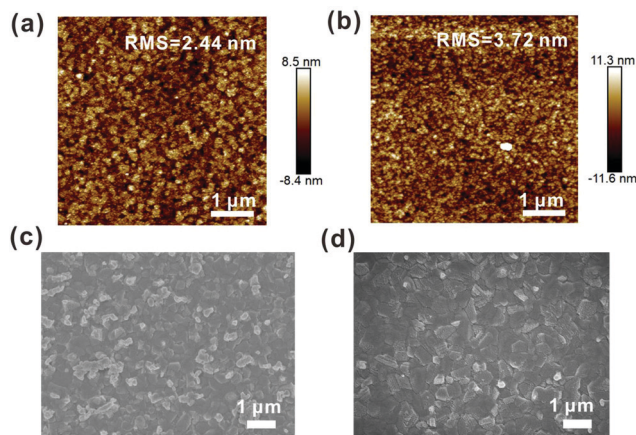


**Table 1** Photovoltaic performance of perovskite solar cells based on the SnO<sub>2</sub> ETL with various amounts of PVP

ETLs	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PVP-SnO <sub>2</sub> (2 mg mL <sup>-1</sup> )	1.084	23.66	71.03	18.22
PVP-SnO <sub>2</sub> (3 mg mL <sup>-1</sup> )	1.120	23.83	73.27	19.55
PVP-SnO <sub>2</sub> (4 mg mL <sup>-1</sup> )	1.111	23.52	71.44	18.67
PVP-SnO <sub>2</sub> (5 mg mL <sup>-1</sup> )	1.074	23.40	70.76	17.80

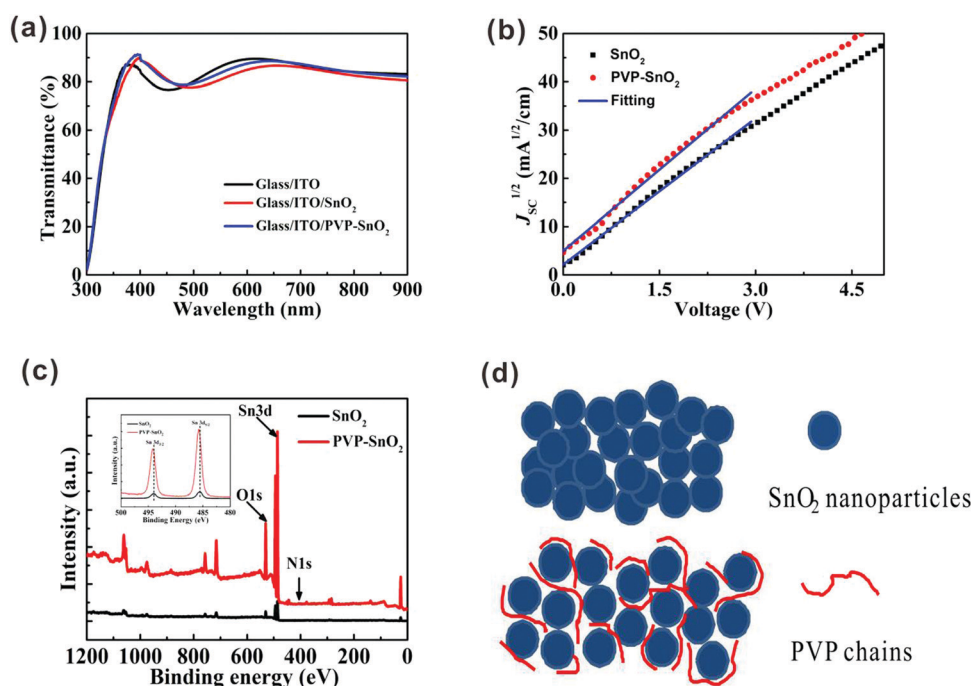
peaks of Sn and O. After the PVP treatment, the PVP-SnO<sub>2</sub> film shows not only peaks of Sn and O, but also an additional peak located at 400 eV ascribed to N, which indicates the successful incorporation of PVP into SnO<sub>2</sub>. Meanwhile, the inset gives specific XPS spectra at Sn 3d peaks of the SnO<sub>2</sub> and the PVP-SnO<sub>2</sub> films. It is obvious that the Sn 3d peak of the PVP-SnO<sub>2</sub> film was shifted to higher binding energy by 0.2 eV in contrast to that of the pristine SnO<sub>2</sub>, indicating that PVP is bound to SnO<sub>2</sub>.<sup>36</sup> PVP can inhibit the agglomeration of SnO<sub>2</sub> nanoparticles and improve the morphology of the SnO<sub>2</sub> film,<sup>38</sup> as shown in Fig. 2d. PVP can suppress the defects between the ETL layer and the perovskite and decrease the leakage current of the interface, thus improving the performance of perovskite solar cells. If the concentration of PVP is too large, the transportation of charge carriers will be damaged because of the poor conductivity of PVP. Therefore, a 2 mg mL<sup>-1</sup> concentration of PVP is optimal for achieving the highest PCE and larger concentrations of PVP will inhibit the properties of perovskite solar cells.

The interface between the perovskite layer and the ETL layer has a significant effect on the device performance. Therefore, it is critical to examine the morphology of ETLs. We use atomic



**Fig. 3** AFM images of the SnO<sub>2</sub> (a) and the PVP-SnO<sub>2</sub> (b) films deposited on ITO. SEM images of the perovskites coated on the SnO<sub>2</sub> film (c) and the PVP-SnO<sub>2</sub> film (d).

force microscopy (AFM) images to study the roughnesses of the pristine SnO<sub>2</sub> and PVP-SnO<sub>2</sub> films (3 mg mL<sup>-1</sup> in SnO<sub>2</sub> solution) deposited on ITO glass substrates as shown in Fig. 3a and b. It is also found that the roughness of the PVP-SnO<sub>2</sub> film is higher (RMS: 3.72 nm) than that of the pristine SnO<sub>2</sub> film without PVP (RMS: 2.44 nm). The surface roughness of the ETL compact layer could affect electron transport as it affects the contact area between the perovskite active layers and the ETL layer.<sup>40</sup> An appropriately high roughness of PVP-SnO<sub>2</sub> could lead to an increase in the contact area between the active layer and the ETL layer, thereby leading to improved charge transport.<sup>41,42</sup>



**Fig. 2** (a) Transmission spectra of ITO, ITO with SnO<sub>2</sub>, and ITO with PVP-SnO<sub>2</sub> substrates. (b)  $J^{1/2}$ - $V$  plots for obtaining the electron mobilities of the SnO<sub>2</sub> and PVP-SnO<sub>2</sub> films using the SCLC model. (c) XPS spectra for the SnO<sub>2</sub> and PVP-SnO<sub>2</sub> films deposited on ITO substrates. The inset gives the XPS spectra of Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> of the SnO<sub>2</sub> and PVP-SnO<sub>2</sub> films. (d) Schematic images of the SnO<sub>2</sub> and PVP-SnO<sub>2</sub> films.



The study of the perovskite film quality, including the grain size, crystallinity, surface coverage, *etc.*, is very important for high-performance perovskite solar cells. Top-view SEM was used to study the surface morphology of perovskite films deposited on different ETLs, which is provided in Fig. 3c and d. It is apparent from these images that continuous pinhole-free films were obtained, which indicates films with full surface coverage. The crystal grain sizes of the perovskite film on PVP-SnO<sub>2</sub> are more uniform and larger than those of the perovskite film deposited on SnO<sub>2</sub>. Moreover, the perovskite films deposited on both SnO<sub>2</sub> and PVP-SnO<sub>2</sub> have a white phase, which was confirmed to be PbI<sub>2</sub>.<sup>43</sup> PVP can help the growth of the SnO<sub>2</sub> layer, thus improving the morphology of the perovskite layer. As the SEM shows, the crystal grain size of the perovskite based on PVP-SnO<sub>2</sub> is larger than that on SnO<sub>2</sub>, which can reduce the carrier recombination between the grain boundaries of the perovskite. As a result, the reverse saturation current is decreased and the open circuit voltage is increased. As we know, the growth of a perovskite is highly dependent on the substrate, and especially depends on the wetting properties of the substrate.<sup>44</sup> The different growth behavior of SnO<sub>2</sub> and PVP-SnO<sub>2</sub> could be explained by two possible reasons: the different hydrophilic properties between SnO<sub>2</sub> and PVP-SnO<sub>2</sub> could be one reason; when the perovskite precursor was spin coated on the SnO<sub>2</sub> layer, it wetted very well with SnO<sub>2</sub> and nucleated everywhere due to the highly hydrophilic properties of SnO<sub>2</sub>, while the perovskite could only nucleate on some places of the PVP-SnO<sub>2</sub> surface due to inferior hydrophilic properties compared with SnO<sub>2</sub>. On the other hand, the PVP-SnO<sub>2</sub> film is dense and consists of particles; the PVP-SnO<sub>2</sub> particles could provide effective nucleation sites to initiate perovskite crystal growth. Both of these could lead to larger perovskite crystals on PVP-SnO<sub>2</sub> than on the SnO<sub>2</sub> layer. As a result, the larger perovskite crystal grains are beneficial for electron transfer and then improve the photoelectric performance. The perovskite film on PVP-SnO<sub>2</sub> has less PbI<sub>2</sub> phase than the perovskite film on SnO<sub>2</sub>. According to the literature,<sup>45,46</sup> an appropriate PbI<sub>2</sub> amount is beneficial to the performance of PSCs.

XRD analysis of perovskite films deposited on different ETLs is also performed. The XRD patterns of the perovskite films spin-coated on the ITO/SnO<sub>2</sub> and ITO/PVP-SnO<sub>2</sub> substrates

are shown in Fig. 4a. It is found that the perovskite film on PVP-SnO<sub>2</sub> has almost the same diffraction peaks as the perovskite on the pure SnO<sub>2</sub>. A typical perovskite peak was found in perovskite films deposited on both ITO/SnO<sub>2</sub> and ITO/PVP-SnO<sub>2</sub> at 14.2°. At the same time, a peak at 12.7° corresponding to PbI<sub>2</sub> was observed, which has a negative impact on the performance of perovskite solar cells. The perovskite on PVP-SnO<sub>2</sub> has less PbI<sub>2</sub> than the perovskite on SnO<sub>2</sub>, which is consistent with the conclusion of SEM in Fig. 3c and d.

Photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectra can be used to effectively analyze the interface charge transfer of PSCs. As shown in Fig. 4b, the PL spectra of the perovskites on ITO, SnO<sub>2</sub> and PVP-SnO<sub>2</sub> were measured to evaluate the interface charge transfer between the perovskite and the ETL. It can be clearly found that the PL peaks of the perovskite film spin-coated on ITO, ITO/SnO<sub>2</sub> and ITO/PVP-SnO<sub>2</sub> at 780 nm were quenched effectively when the SnO<sub>2</sub> or PVP-SnO<sub>2</sub> ETL was used, which demonstrated that the SnO<sub>2</sub> ETL can help the electron extraction from the perovskite to the electrode. The perovskite on PVP-SnO<sub>2</sub> exhibits more quenched PL than on SnO<sub>2</sub>, which is related to the more efficient electron transfer from the perovskite to the ETL. The results of TRPL show that the lifetime of the perovskite layer was significantly reduced when it was deposited on PVP-SnO<sub>2</sub> compared to the one on SnO<sub>2</sub>, which indicates that efficient electron transfer occurred from the perovskite to PVP-SnO<sub>2</sub> as shown in Fig. 4c. From all of the above analyses, we conclude that PVP-SnO<sub>2</sub> as the ETL might improve the performance of perovskite solar cells.

We have proven that the performance of the device is improved by adding a small amount of PVP to the SnO<sub>2</sub> solution. To confirm the positive effect of the PVP doping on the photovoltaic performance of PSCs, the performance of the devices based on SnO<sub>2</sub> and PVP-SnO<sub>2</sub> (3 mg mL<sup>-1</sup> PVP) with the same device structure was compared, and the corresponding results are shown in Fig. 5a. For the PVP-SnO<sub>2</sub> device, the best device shows an efficiency of 19.55% with  $V_{OC} = 1.120$  V,  $J_{SC} = 23.83$  mA cm<sup>-2</sup> and FF = 73.27%. The highest efficiency of the device without the PVP additive is only 17.50%.

Fig. 5b shows the external quantum efficiency (EQE) spectra and the corresponding integrated currents of the PSCs with different ETLs. The devices exhibit a broad peak above 80% in



Fig. 4 (a) X-ray diffraction (XRD) patterns of the perovskites deposited on different ETLs. (b) Photoluminescence (PL) spectra of the perovskite films deposited on ITO, SnO<sub>2</sub> and PVP-SnO<sub>2</sub> substrates. (c) Normalized time-resolved photoluminescence (TRPL) spectra of the perovskite films deposited on ITO, SnO<sub>2</sub> and PVP-SnO<sub>2</sub> substrates.





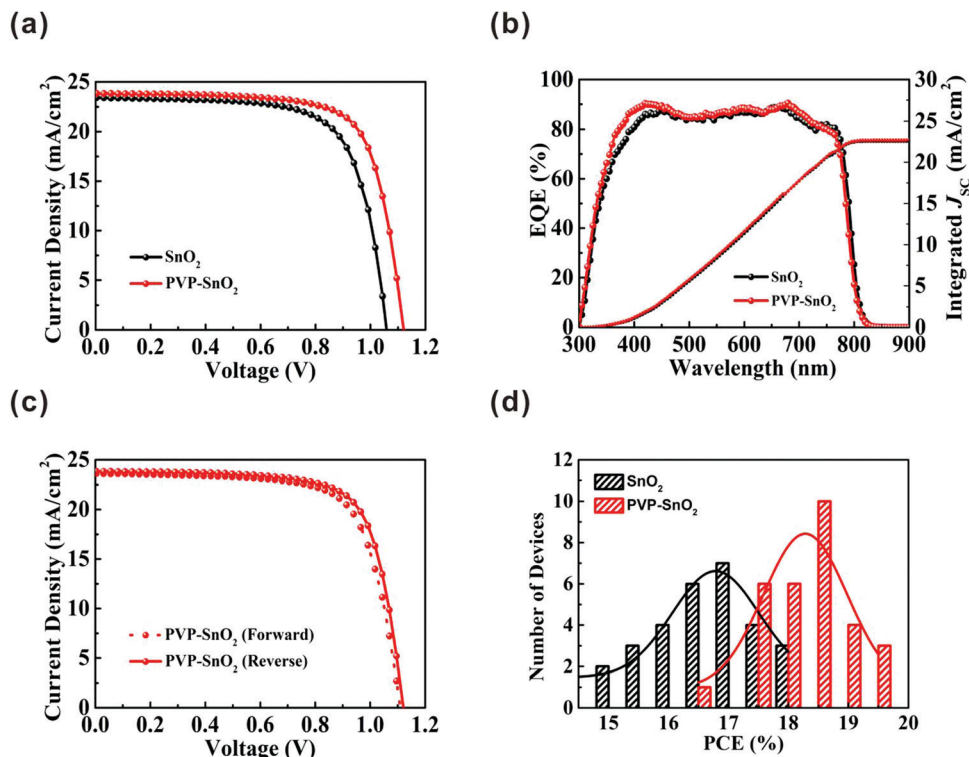


Fig. 5 (a)  $J$ - $V$  curves of the best-performing perovskite solar cells using the  $\text{SnO}_2$  and PVP- $\text{SnO}_2$  ETLs measured under reverse scans. (b) The external quantum efficiency (EQE) spectra and the corresponding integrated  $J_{\text{SC}}$  curves for the best-performance PSCs with different ETLs. (c)  $J$ - $V$  curves of devices using the PVP- $\text{SnO}_2$  ETL under reverse and forward scans. (d) The PCE distribution histogram of the planar type PSCs with different ETLs.

Table 2 Photovoltaic performance of perovskite solar cells based on  $\text{SnO}_2$  and PVP- $\text{SnO}_2$  with forward and reverse scans

ETLs	Scanning direction	$V_{\text{OC}}$ (V)	$J_{\text{SC}}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)	Average PCE (%)
$\text{SnO}_2$	Forward scan	1.045	23.41	68.19	16.68	$16.21 \pm 3.03$
	Reverse scan	1.057	23.39	70.75	17.50	
PVP- $\text{SnO}_2$ ( $3 \text{ mg mL}^{-1}$ )	Forward scan	1.109	23.61	71.59	18.76	$17.74 \pm 3.01$
	Reverse scan	1.120	23.83	73.27	19.55	

the range of 400 to 760 nm. The integrated current values calculated from the EQE spectra are  $22.55$  and  $22.67 \text{ mA cm}^{-2}$  for the devices with  $\text{SnO}_2$  and PVP- $\text{SnO}_2$  as the ETL, respectively, which are close to the  $J$ - $V$  measurements (within the error range). For the hysteresis test,<sup>47</sup> Fig. 5c shows the  $J$ - $V$  curves of devices using the PVP- $\text{SnO}_2$  ETL under reverse and forward scans. The PVP- $\text{SnO}_2$ -based device yielded a PCE of 19.55% from a reverse current-voltage scan, with  $V_{\text{OC}} = 1.120 \text{ V}$ ,  $J_{\text{SC}} = 23.83 \text{ mA cm}^{-2}$  and FF = 73.27%. A small amount of hysteresis was observed with a forward scan yielding PCE = 18.76%. The detailed parameters of the reverse scan and forward scan of the two devices with the pure  $\text{SnO}_2$  and the optimized PVP- $\text{SnO}_2$  are summarized in Table 2. The results show that the PVP- $\text{SnO}_2$ -based device has reduced hysteresis in comparison with the control device with  $\text{SnO}_2$ .

Fig. 5d shows the PCE distribution histogram for devices with different ETLs. It is apparent that the devices with the PVP- $\text{SnO}_2$  ETL show better repeatability and smaller standard deviations than those with the  $\text{SnO}_2$  ETL. This result indicates that PVP- $\text{SnO}_2$  can be used as a good candidate for the ETL in planar PSCs.

Without any encapsulation, the long-term stability of the PSCs with  $\text{SnO}_2$  and PVP- $\text{SnO}_2$  was investigated in a nitrogen environment. The shelf-stability of PSCs with different ETLs as a function of storage time is shown in Fig. 6. The device with the PVP- $\text{SnO}_2$  ETL retains 88% of its initial PCE after 41 days of storage, while the device with the  $\text{SnO}_2$  ETL dropped to 80% of its initial PCE after 41 days. It indicates that the device with the PVP- $\text{SnO}_2$  ETL is more stable than that with the  $\text{SnO}_2$  ETL, which is ascribed to the improved contact between the perovskite and the PVP- $\text{SnO}_2$  ETL. It is known that the instability of perovskite solar cells is related to the degradation of the perovskite layer and the charge transport layer. Because of the improved contact between the PVP- $\text{SnO}_2$  ETL and the perovskite layer, the PVP- $\text{SnO}_2$  based devices are more stable than the  $\text{SnO}_2$  based devices.

## Conclusion

In summary, the incorporation of PVP into  $\text{SnO}_2$  improves the performance of planar perovskite solar cells. The characterization



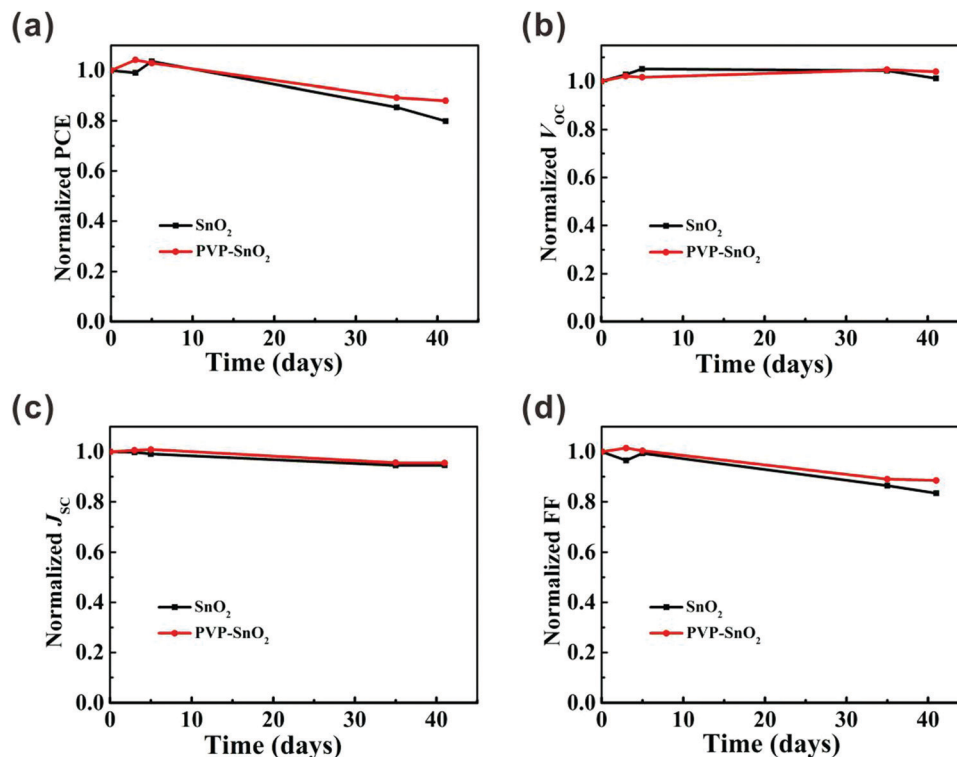


Fig. 6 The shelf-stability of perovskite solar cells in a glove box without any encapsulation. Normalized (a) PCE, (b)  $V_{oc}$ , (c)  $J_{sc}$  and (d) FF.

and analysis show that the PVP-SnO<sub>2</sub> ETL promotes electron collection and transfer, which inhibits charge accumulation at the interface between the ETL and the perovskite, resulting in a high efficiency. In addition the crystal grain sizes of the perovskite film on PVP-SnO<sub>2</sub> are more uniform and larger than the perovskite film deposited on SnO<sub>2</sub>. As a result, the PCE of the planar PSCs has increased to 19.55% from with the baseline of 17.50% from the control PSC with the SnO<sub>2</sub> ETL, and the  $J$ - $V$  hysteresis is alleviated. Therefore, we conclude that SnO<sub>2</sub> with a suitable PVP content is a promising electron transport material for high-performance PSCs, and provides a viable method for improving the performance of perovskite solar cells.

## Experimental section

### Materials

FAI, MABr, MACl, and spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp. PbI<sub>2</sub> was purchased from Sigma-Aldrich Company. The SnO<sub>2</sub> colloid precursor was obtained from Alfa Aesar (tin(IV) oxide, 15% in H<sub>2</sub>O colloidal dispersion). Polyvinylpyrrolidone (PVP) was purchased from Shanghai Aladdin.

### Solar cell fabrication

ITO patterned glass substrates (1.5 cm × 1.5 cm) were ultrasonically cleaned by using detergent solution, deionized water, propanol and isopropanol for 15 minutes in each step. The ITO glass substrates were further cleaned by an ultraviolet ozone

treatment for 20 minutes before depositing the ETL. In the process of preparing the device, two ETL solutions are mainly used, namely the SnO<sub>2</sub> precursor solution and the PVP-SnO<sub>2</sub> precursor solution. The SnO<sub>2</sub> precursor solution was obtained by mixing 1 mL of the aqueous SnO<sub>2</sub> solution with 3 mL of H<sub>2</sub>O. For the PVP-SnO<sub>2</sub> precursor solution, first 1 mL of aqueous SnO<sub>2</sub> solution was mixed with 3 mL of water, and then PVP (2–5 mg mL<sup>-1</sup>) was added to the SnO<sub>2</sub> solution. The SnO<sub>2</sub> and PVP-SnO<sub>2</sub> precursors were stirred at room temperature for five hours. The different ETLs were deposited onto the treated ITO glass substrate by spin-coating at 4000 rpm for 40 s, and the samples were immediately annealed on a hotplate at 180 °C for 20 min. The preparation of the different ETLs is carried out in air. After cooling, the substrates were subjected to UV ozone treatment for 15 min, and transferred into a glove box for the deposition of the perovskite layer. The lead iodide solution was prepared as follows: 599.3 mg of PbI<sub>2</sub> was dissolved in a mixed solvent of 1 mL of dimethylformamide (DMF) and anhydrous dimethyl sulfoxide (DMSO) at a temperature of 70 °C for one hour, wherein the volume ratio of DMF to DMSO was 9:1. The mixture solution was synthesized by dissolving FAI (60 mg), MABr (60 mg) and MACl (6 mg) in 1 mL isopropanol and stirred for one hour. The perovskite films were deposited using a two-step spin coating method. First, the PbI<sub>2</sub> solution was deposited onto different ETLs by spin-coating at 1500 rpm for 30 s, and then the substrates were annealed at 70 °C for 7 s to form PbI<sub>2</sub> films. After spin-coating with the mixed solution, the substrates were annealed at 135 °C for 15 min to form a dark perovskite layer in air. After deposition of the perovskite layer,



the substrates were transferred from the air to the glove box for the deposition of the HTL. The spiro-OMeTAD precursor solution was prepared by dissolving 72.3 mg spiro-OMeTAD, 35  $\mu\text{L}$  of bis (trifluoromethane) sulfonimide lithium salt in acetonitrile ( $260 \text{ mg mL}^{-1}$ ) and 30  $\mu\text{L}$  of *tert*-butylpyridine in 1 mL chlorobenzene. The spiro-OMeTAD precursor solution was subsequently coated on the top of the perovskite film at 2500 rpm for 30 s. Note that after spin-coating the spiro-OMeTAD layer, the substrates were placed in air in a humidity-control box for 12 hours to ensure sufficient oxidation of the spiro-OMeTAD film. Finally, 7.5 nm of  $\text{MoO}_3$  and 100 nm of Ag were deposited by thermal evaporation at a vacuum condition of  $9 \times 10^{-5}$  Torr. The effective area of the perovskite cells reported in this work is  $1.8 \text{ mm} \times 4.8 \text{ mm}$  ( $0.0864 \text{ cm}^2$ ).

### Device characterization

The power conversion efficiencies of the perovskite solar cells were measured from current density–voltage ( $J$ – $V$ ) curves using a Keithley 2400 source under a simulated AM 1.5G spectrum with an intensity of  $100 \text{ mW cm}^{-2}$  (450 W Newport 94023A solar simulator). The devices were tested in an  $\text{N}_2$  glove box with the reverse scan ( $1.2 \rightarrow 0 \text{ V}$ , step 0.02 V, delay time 30 ms) and the forward scan ( $0 \rightarrow 1.2 \text{ V}$ , step 0.02 V, delay time 30 ms). The scanning electron microscopy (SEM) images of the perovskite surfaces and the cross-sections of the devices were measured using an S-4800 SEM setup. The external quantum efficiency (EQE) was measured using an Oriel LPCE-66894 in air. The transmission spectra of the films were measured by using a UV/vis spectrophotometer (PerkinElmer, Lambda 365). X-ray diffraction analysis was performed with a Bruker D8 Advance diffractometer operated at 30 kV and 10 mA at  $2\theta$  in the range of  $10$ – $60^\circ$ , step  $0.02^\circ$  and scan speed  $2.3^\circ \text{ min}^{-1}$ .

### Conflicts of interest

There are no conflicts to declare.

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### References

- M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643.
- P. Luo, Z. Liu, W. Xia, C. Yuan, J. Cheng and Y. Lu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2708.
- F. Zhang, X. Yang, H. Wang, M. Cheng, J. Zhao and L. Sun, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16140.
- J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.
- H. Zhang, J. Cheng, D. Li, F. Lin, J. Mao, C. Liang, A. K. Y. Jen, M. Grätzel and W. C. Choy, *Adv. Mater.*, 2017, **29**, 1604695.
- E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T. Y. Yang, J. H. Noh and J. Seo, *Nature*, 2019, **567**, 511.
- F. Fu, S. Pisoni, T. P. Weiss, T. Feurer, A. Wäckerlin, P. Fuchs, S. Nishiwaki, L. Zortea, A. N. Tiwari and S. Buecheler, *Adv. Sci.*, 2018, **5**, 1700675.
- A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050.
- M. He, B. Li, X. Cui, B. Jiang, Y. He, Y. Chen, D. O'Neil, P. Szymanski, M. A. El-Sayed, J. Huang and Z. Lin, *Nat. Commun.*, 2017, **8**, 16045.
- J. Qi, H. Xiong, C. Hou, Q. Zhang, Y. Li and H. Wang, *Nanoscale*, 2020, **12**, 3646–3656.
- J. Qi, L. Li, H. Xiong, A. C. Wang, C. Hou, Q. Zhang, Y. Li and H. Wang, *J. Mater. Chem. A*, 2019, **7**, 26154–26161.
- J. Qi, H. Xiong, G. Wang, H. Xie, W. Jia, Q. Zhang, Y. Li and H. Wang, *J. Power Sources*, 2018, **376**, 46–54.
- B. Wang, J. Iocozzia, M. Zhang, M. Ye, S. Yan, H. Jin, S. Wang, Z. Zou and Z. Lin, *Chem. Soc. Rev.*, 2019, **48**, 4854–4891.
- H. Tsai, W. Nie, P. Cheruku, N. H. Mack, P. Xu, G. Gupta, A. D. Mohite and H. L. Wang, *Chem. Mater.*, 2015, **27**, 5570.
- R. Singh, A. Giri, M. Pal, K. Thiyagarajan, J. Kwak, J. J. Lee, U. Jeong and K. Cho, *J. Mater. Chem. A*, 2019, **7**, 7151.
- B. Wang, M. Zhang, X. Cui, Z. Wang, M. Rager, Y. Yang, Z. Zou, Z. L. Wang and Z. Lin, *Angew. Chem., Int. Ed.*, 2020, **59**, 1611–1618.
- W. Hu, W. Zhou, X. Lei, P. Zhou, M. Zhang, T. Chen, H. Zeng, J. Zhu, S. Dai, S. Yang and S. Yang, *Adv. Mater.*, 2019, **31**, 1806095.
- B. Wang, J. Iocozzia, M. Zhang, M. Ye, S. Yan, H. Jin, S. Wang, Z. Zou and Z. Lin, *Chem. Soc. Rev.*, 2019, **48**, 4854–4891.
- K. Domanski, E. A. Alharbi, A. Hagfeldt, M. Grätzel and W. Tress, *Nat. Energy*, 2018, **3**, 61.
- H. J. Snaith, A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, S. D. Stranks, J. T. Wang, K. Wojciechowski and W. Zhang, *J. Phys. Chem. Lett.*, 2014, **5**, 1511.
- J. Wei, H. Li, Y. Zhao, W. Zhou, R. Fu, Y. L. Wang, D. Yu and Q. Zhao, *Nano Energy*, 2016, **26**, 139.
- J. Cao, B. Wu, R. Chen, Y. Wu, Y. Hui, B. W. Mao and N. Zheng, *Adv. Mater.*, 2018, **30**, 1705596.
- Y. C. Wang, X. Li, L. Zhu, X. Liu, W. Zhang and J. Fang, *Adv. Energy Mater.*, 2017, **7**, 1701144.
- P. Zhang, J. Wu, T. Zhang, Y. Wang, D. Liu, H. Chen, L. Ji, C. Liu, W. Ahmad, Z. D. Chen and S. Li, *Adv. Mater.*, 2018, **30**, 1703737.
- W. Ke, G. Fang, Q. Liu, L. Xiong, P. Qin, H. Tao, J. Wang, H. Lei, B. Li, J. Wan, G. Yang and Y. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 6730.
- T. Bu, J. Li, F. Zheng, W. Chen, X. Wen, Z. Ku, Y. Peng, J. Zhong, Y. B. Cheng and F. Huang, *Nat. Commun.*, 2018, **9**, 4609.
- Q. Jiang, L. Zhang, H. Wang, X. Yang, J. Meng, H. Liu, Z. Yin, J. Wu, X. Zhang and J. You, *Nat. Energy*, 2016, **2**, 1.
- W. Ke, G. Fang, Q. Liu, L. Xiong, P. Qin, H. Tao, J. Wang, H. Lei, B. Li, J. Wan, G. Yang and Y. Yan, *J. Am. Chem. Soc.*, 2015, **137**, 6730.



- 29 Y. Huang, S. Li, C. Wu, S. Wang, C. Wang and R. Ma, *Chem. Phys. Lett.*, 2020, 137220.
- 30 W. Zhang, Y. Li, X. Liu, D. Tang, X. Li and X. Yuan, *Chem. Eng. J.*, 2020, 379, 122298.
- 31 Z. Zhu, Y. Bai, X. Liu, C. C. Chueh, S. Yang and A. K. Y. Jen, *Adv. Mater.*, 2016, 28, 6478.
- 32 W. Q. Wu, D. Chen, Y. B. Cheng and R. A. Caruso, *Sol. RRL*, 2017, 1, 1700117.
- 33 S. Jeong, S. Seo, H. Park and H. Shin, *Chem. Commun.*, 2019, 55, 2433.
- 34 J. Zhang, T. Zhang, L. Jiang, U. Bach and Y. B. Cheng, *ACS Energy Lett.*, 2018, 3, 1677.
- 35 F. Qi, X. Deng, X. Wu, L. Huo, Y. Xiao, X. Lu, Z. Zhu and A. K. Y. Jen, *Adv. Energy Mater.*, 2019, 9, 1902600.
- 36 D. Yang, R. Yang, K. Wang, C. Wu, X. Zhu, J. Feng, X. Ren, G. Fang, S. Priya and S. F. Liu, *Nat. Commun.*, 2018, 9, 3239.
- 37 J. Wei, F. Guo, X. Wang, K. Xu, M. Lei, Y. Liang, Y. Zhao and D. Xu, *Adv. Mater.*, 2018, 30, 1805153.
- 38 C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S. W. Tsang, T. H. Lai, J. R. Reynolds and F. So, *Nat. Photonics*, 2012, 6, 115–120.
- 39 L. La Notte, P. Cataldi, L. Ceseracciu, I. S. Bayer, A. Athanassiou, S. Marras, E. Villari, F. Brunetti and A. Reale, *Mater. Today Energy*, 2018, 7, 105.
- 40 Z. Ma, Z. Tang, E. Wang, M. R. Andersson, O. Inganäs and F. Zhang, *J. Phys. Chem. C*, 2012, 116, 24462.
- 41 Q. Liu, X. Zhang, C. Li, H. Lu, Z. Weng, Y. Pan, W. Chen, X. C. Hang, Z. Sun and Y. Zhan, *Appl. Phys. Lett.*, 2019, 115, 143903.
- 42 R. Ranjan, A. Prakash, A. Singh, A. Singh, A. Garg and R. K. Gupta, *J. Mater. Chem. A*, 2018, 6, 1037.
- 43 Q. Jiang, Z. Chu, P. Wang, X. Yang, H. Liu, Y. Wang, Z. Yin, J. Wu, X. Zhang and J. You, *Adv. Mater.*, 2017, 29, 1703852.
- 44 C. Bi, Q. Wang, Y. Shao, Y. Yuan, Z. Xiao and J. Huang, *Nat. Commun.*, 2015, 6, 7747.
- 45 Y. C. Kim, N. J. Jeon, J. H. Noh, W. S. Yang, J. Seo, J. S. Yun, A. Ho-Baillie, S. Huang, M. A. Green, J. Seidel, T. K. Ahn and S. I. Seok, *Adv. Energy Mater.*, 2015, 6, 1502104.
- 46 B. Shi, X. Yao, F. Hou, S. Guo, Y. Li, C. Wei, Y. Ding, Y. Li, Y. Zhao and X. Zhang, *J. Phys. Chem. C*, 2018, 122, 21269–21276.
- 47 P. Liu, W. Wang, S. Liu, H. Yang and Z. Shao, *Adv. Energy Mater.*, 2019, 9, 1803017.

