# High Shunt Resistance SnO<sub>2</sub>-PbO Electron Transport Layer for Perovskite Solar Cells Used in Low Lighting Applications

Zhuoneng Bi, Shaohong Zhang, Marimuthu Thandapani, Yanqing Zhu, Yupeng Zheng, Nguyen Quang Liem, Xiudi Xiao, Gang Xu, Antonio Guerrero,\* and Xueqing Xu\*

Hybrid perovskites are promising materials for new sustainable photovoltaic applications to operate under low lighting conditions, such as the reuse of residual photons that are wasted during indoor lighting. The requirements for a perovskite solar cell (PSC) to offer maximum power conversion efficiency (PCE) under low illumination conditions are not totally clear in the literature. In this work, the PCE of the commonly used  $SnO_2$  electron transport layer (ETL) is improved by a facile method, doping the precursor nanoparticles with small concentrations of a Pb source. Under low illumination conditions (i.e.,  $0.1 \text{ mW cm}^{-2}$ ) the PCE is enhanced from 18.8% to 34.2%. From a complete analysis of the ETLs and devices using several structural and electrical techniques it is observed that the parameter that improves the most is the shunt resistance of the device which avoids the parallel leakage of the photogenerated current. The present work clearly shows that the shunt resistance is a very important parameter that needs to be optimized in PSCs for low illumination conditions.

Z. Bi, S. Zhang, Dr. M. Thandapani, Dr. Y. Zhu, Y. Zheng, Prof. X. Xiao, Prof. G. Xu, Prof. X. Xu Key Laboratory of Renewable Energy Guangdong Key Laboratory of New and Renewable Energy Research and Development Guangzhou Institute of Energy Conversion Chinese Academy of Sciences Guangzhou 510640, China E-mail: xuxq@ms.giec.ac.cn Z. Bi, S. Zhang, Y. Zheng, Prof. X. Xiao, Prof. G. Xu, Prof. X. Xu Center of Materials Science and Optoelectronics Engineering University of Chinese Academy of Sciences Beijing 100049, China Prof. N. Q. Liem Institute of Materials Science VAST, Hanoi 100803, Vietnam Prof. A. Guerrero Institute of Advanced Materials (INAM) Universitat Jaume I, Castelló 12006, Spain E-mail: aguerrer@uji.es The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adsu.202100120.

© 2021 The Authors. Advanced Sustainable Systems published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/adsu.202100120

## 1. Introduction

Perovskite solar cells (PSCs) have received much attention due to the impressive power conversion efficiencies (PCE) with record value of 25.5% under standard 1 sun illumination conditions (AM1.5G, 100 mW cm<sup>-2</sup>).<sup>[1]</sup> With these efficiencies PSCs not only find applications as solar panels installed in large solar farms that may compete with silicon technology but also show promising compatibility with light-weight and flexible devices produced at reduced costs.

A large array of new applications may be developed using PSCs which could contribute toward a sustainable energy model. $^{[2-5]}$  Due to the compatibility with light weight substrates innovative consumer applications are envisaged

including wearable photovoltaics and decorative construction elements that reuse the residual photons wasted during indoor lighting. Several photovoltaic technologies have been developed to operate under low illumination intensities, i.e., 1000 lux corresponds to ~1 mW cm<sup>-2</sup> for LED lighting. For example, dyesensitized solar cells and organic photovoltaics have demonstrated PCEs approaching ~32%<sup>[6]</sup> and ~28%,<sup>[7]</sup> respectively. Still higher PCEs have been obtained at low illumination conditions using PCSs. For example, Wang and Liao et al. achieved excellent PSCs of ~20% and ~35% under one sun illumination and under indoor condition (1000 lux), respectively.<sup>[8]</sup> The general approach has been to improve either the perovskite formulation or the extraction layers. However, the specific rules to design PSCs for low lighting conditions have not been discussed in terms of the different layers that compose a photovoltaic device.

The properties of electron transport layers (ETL) designed for operation under high illumination conditions are well stablished and these include adequate energy levels and high electron mobility. Tin oxide (SnO<sub>2</sub>) is one of the most widely used ETL due to the versatile processing conditions as it may be deposited as a compact layer, mesoporous layer or as a modifier by several techniques.<sup>[9–15]</sup> PCEs exceeding 20% have been obtained under 1 sun illumination conditions using perovskite formulations.<sup>[14]</sup> Unfortunately, under low illumination conditions (i.e., 1000 lux) devices prepared with SnO<sub>2</sub> generally provide relatively low PCE of 20.2% with  $V_{oc}$  and *FF* being the most affected parameters.<sup>[16]</sup>



Figure 1. Top-view SEM images of the SnO<sub>2</sub> with different Pb doping, the scale bar is 500 nm.

The use of SnO/ZnO bilayers as ETLs are effective to improve PCE to values of 37.2% and improves the stability using the same conditions. The PCE improvement of the bilayers was ascribed to a suppression of the trap-assisted recombination. However, the role of the leakage current and shunt resistance have not been clarified which should be one of the most important parameters for low illumination conditions as discussed by Proctor et al. in the field of organic photovoltaics.<sup>[17]</sup> In particular, the  $V_{\rm oc}$  and FF should be strongly affected by a variation in the shunt resistance.

In this work, we introduce a PbO precursor into SnO<sub>2</sub> nanoparticles that forms an ETL layer that greatly enhance the PCEs of photovoltaic devices measured under low illumination conditions. The ETL narrows the bandgap of pure SnO<sub>2</sub> and increases the shunt resistance of devices that avoids the leakage of photogenerated current. It is found that ETLs containing SnO<sub>2</sub>/PbO shows excellent performance with perovskite formulation prepared by blade-coating (compatible with roll-to-roll production methods),<sup>[18]</sup> best PCE of 18.8% (1 sun) and 34.2% (0.1 mW cm<sup>-2</sup>) under white-light LED illumination. Very importantly, we highlight the effect of the shunt resistance on the V<sub>OC</sub> and *FF* of the devices used under low illumination intensity.

## 2. Results and Discussion

## 2.1. Characterization of Layers Containing $SnO_2$ -PbO on Fluorine-doped Tin Oxide (FTO)

Layers of SnO<sub>2</sub> nanoparticles containing PbO were prepared by a simple method, such as spin coating of mixtures of SnO<sub>2</sub> nanoparticles with lead acetate. A detailed synthesis is explained in the experimental section and incorporation of PbO into the nanoparticles are confirmed by a range of techniques as described next. The molar ratio of Pb to Sn was varied from 0.5% to 6%. The top-view scanning electron microscope (SEM) images (**Figure 1**) shows reference samples containing bare FTO and FTO/SnO<sub>2</sub>. As can be observed, SnO<sub>2</sub> covers homogeneously the FTO and aggregates slightly. Alternatively, in the presence of Pb the morphology of the thin film is modified with relevant aggregation of particles increasing with the proportion of lead acetate in the precursor solution. With the highest Pb concentration of 6% the FTO film cannot be fully covered due to the severe aggregation of the nanoparticles.

X-ray diffraction (XRD) was measured (**Figure 2a**) on films deposited on glass using the conditions described above. As expected, the SnO<sub>2</sub> shows a tetragonal structure (JCPDS No. 01-072-1147) with most relevant peaks appearing at  $2\theta = 26.6$ , 33.8, and 52.1 that can be associated with (110), (101), (211) planes, respectively. The Pb precursor does not greatly modify the SnO<sub>2</sub> tetragonal structure.<sup>[19]</sup> However, the structure gets distorted as the Pb concentration increases as noted by the decrease in the intensity of (110) planes and by the shift of the peaks to lower  $2\theta$  values. The second observation indicates that introduction of Pb into the lattice increases the interplanar crystal spacing as expected by the replacement of some Sn atoms by the larger Pb atom. Further supporting the incorporation of Pb into the SnO<sub>2</sub> lattice we show transmission electron microscopy analysis as Supporting Information.

X-ray photoelectron spectroscopy (XPS) shows the surface composition of the layers and helps to determine the oxidation state of Sn, Pb, and O. Figure 2b displays the Sn3d<sub>5/2</sub> and Sn3d<sub>3/2</sub> spectra of SnO<sub>2</sub> and samples containing Pb. The binding energies (BE) of the Sn3d<sub>5/2</sub> and Sn3d<sub>3/2</sub> are very similar in all samples except sample containing Pb-6% which was shown in the SEM images to show an anomaly behavior. Figure 2c shows the Pb4f<sub>5/2</sub> and Pb4f<sub>7/2</sub> and Sn4s spectra of all samples. The Sn4s peaks overlap with Pb4f7/2 at BE of 138.4 for the Pb doped samples. When the Pb-doping concentration increases from 0.5% to 6%, the Pb4f7/2 fitting peak shifts from BE 138.3 to 138.6, respectively. As the BE of the  $Pb4f_{7/2}$  of Pb native oxide (PbO) is 138.4 we confirm that PbO is present in all samples as observed in Figure 2d.<sup>[20]</sup> As expected, the intensity of the signal increases with the increased Pb concentration. The quantitative analysis of Pb:Sn ratio and each Atomic-% is shown in the Table S1 (Supporting Information). As can be observed in Figure 2e, there is a small variation in the valence band edge position decreasing from 3.32 to 2.95 eV when comparing SnO<sub>2</sub> with increasing amounts of Pb concentration.<sup>[21]</sup> The current results suggests that Pb introduction into the nanoparticles leads to a reduction in valence band edge, further XPS analysis





(b) (a) (c) Pb4f7/2 SnO<sub>2</sub> Sn3d<sub>5/2</sub> Pb 0.5% Relative intensity (a.u.) Pb 6% Pb 2% Pb4f<sub>5/2</sub> Pb 3% Pb 3% ntensity Intensity Pb 6% SnO<sub>2</sub> Sn3d<sub>3/2</sub> Pb 2% Pb 0.5% Pb 2% Pb 0.5% Pb 3% SnO<sub>2</sub> Pb 6% 101 (211 202) (321) Sn4s 002) 112 148 146 144 142 140 138 136 150 20 30 40 50 60 70 80 480482484486488490492494496498500 **Binding Energy** 2-Theta (deg.) **Binding Energy** (d) (e) (f) 01s SnO<sub>2</sub> Pb 0.5% Vormalized  $(\alpha h \nu)^2$ Pb 2% Pb 3% Counts / s ntensity SnO-Pb 6% SnO<sub>2</sub> Pb 0.5% Pb 0.5% Pb 2% Pb 2% Pb 3% Pb 3% Pb 6% Ph 6% 540 538 536 534 532 530 528 526 10 6 4 2 8 0 3.5 3.7 3.8 3.9 3.2 3.3 3.4 3.6 **Binding Energy** Binding Energy (eV) hv(eV)

**Figure 2.** a) XRD patterns. b) XPS spectra depicting the Sn 3d3/2, Sn 3d5/2 peaks. c) XPS spectra depicting the Pb4f5/2, Pb4f7/2 peaks, d) XPS spectra depicting the O Is peaks. e) The valence spectrum. f) Normalized  $(\alpha h v)^2$  versus hv plot of pure and Pb doped SnO<sub>2</sub> layer on glass. All the binding energies are referenced to the CIs peak at 284.8 eV.

is shown as the Supporting Information. The work function and valence band maximum (VBM) measurements were carried out by ultraviolet photoelectron spectroscopy (UPS) and the results are shown in Figure S5 (Supporting Information).<sup>[22]</sup> Finally, the optical energy bandgap (Eg) was evaluated from the UV–vis absorption spectra by using the direct interband absorption gap, as shown in Figure 2f. The bandgap of samples can be calculated by extrapolating the linear portion of the  $(\alpha hv)^2$  versus hv curve to zero where hv is the photon energy.<sup>[19]</sup> Importantly, it is found that the bandgap is slightly reduced from 3.67 to 3.53 eV with the increase in Pb concentration up to 3%. The energy levels of the prepared ETL are shown in **Figure 3**a which shows adequate values to extract electrons from the perovskite layer.

## 2.2. Device Fabrication and Characterization of Photovoltaic Devices Using MAPbl<sub>3</sub> Formulation Deposited on SnO<sub>2</sub>-PbO

High quality MAPbI<sub>3</sub> perovskite was deposited by doctor blade onto the SnO<sub>2</sub> ETL layer containing 3% of PbO,<sup>[23]</sup> a deposition method compatible with industrially relevant methods such as roll-to-roll. Complete optimization conditions of the deposition process and characterization of the layers are shown as the Supporting Information. As previously reported the MAPbI<sub>3</sub> film shows spherulitic morphology and fully covers the surface of the ETL. Photovoltaic devices have been prepared in the configuration shown in Figure 3, Glass/FTO/SnO<sub>2</sub>-PbO/MAPbI<sub>3</sub>/ Spiro-OMeTAD/Au. Cross-section SEM images clearly show



Figure 3. a) Schematic energy level diagram of the complete device including the  $SnO_2$ -PbO ETL. b) Cross-section SEM image of the  $SnO_2$ -PbO ETLs based PSCs, the scale bar is 1  $\mu$ m.



SUST AINABLE SYSTEMS www.advsustainsys.com



**Figure 4.** a)  $J_{SC}$ ,  $V_{OC}$ , and FF versus light intensity using a solar simulator (AM 1.5 G). b) J–V curves measured at 100 mW cm<sup>-2</sup>. c) Statistics of 20 controls (SnO<sub>2</sub>) and 20 bilayer SnO<sub>2</sub>-PbO ETLs-based devices under AM 1.5. d)  $J_{SC}$ ,  $V_{OC}$ , and FF versus light intensity under white-light LED. e) J–V curves under 0.1 mW cm<sup>-2</sup> white-light LED. f) Statistics of 20 controls (SnO<sub>2</sub>) and 20 bilayer SnO<sub>2</sub>-PbO ETLs-based devices under AM 1.5. d)  $J_{SC}$ ,  $V_{OC}$ , and FF versus light intensity under white-light LED. e) J–V curves under 0.1 mW cm<sup>-2</sup> white-light LED. f) Statistics of 20 controls (SnO<sub>2</sub>) and 20 bilayer SnO<sub>2</sub>-PbO ETLs-based devices under 0.1 mW cm<sup>-2</sup> white-light LED.

that  $MAPbI_3$  films benefit from very large grains without the presence of any pin holes. In addition, the ETL thickness is measured to be in the range between 30 and 50 nm.

between SnO<sub>2</sub> and SnO<sub>2</sub>-PbO with average PCE of 10.1% and 30.3%, respectively. The origin of this remarkable improvement in performance will be analyzed below.

The photovoltaic properties have been analyzed under different light sources. The results of measurements under high light intensity conditions using a solar simulator (AM 1.5 G) are shown in Figure 4a-c as a function of the light intensity, from 100 to 10 mW cm<sup>-2</sup>. At these relatively high illumination conditions the response of the devices show expected results with a direct relationship between light intensity (photogeneration) and extracted current density, a small decrease in  $V_{oc}$  and similar FF at the different lighting conditions. Figure 4b shows *I*–V curves at 1 sun light intensity (100 mW cm<sup>-2</sup>) for both samples where it can be observed that there is a modest improvement in the J-V response for SnO<sub>2</sub>-PbO as compared to the reference SnO<sub>2</sub> sample. Statistics over 20 devices (Figure 4c) measured at 100 mW cm<sup>-2</sup> show a modest improvement in PCE from 16.2% to 17.7% when PbO is incorporated into the SnO<sub>2</sub> layer. Reduced FF and photocurrents are observed for the sample which does not contain PbO. Analogous measurements were carried out using a white-light LED at still lower light intensities from 0.1 to 10 mW cm<sup>-2</sup> (Figure 4d-f). Figure 4d shows a large variation in the performance parameters as a function of the light intensity between the two samples. Whilst the SnO<sub>2</sub>-PbO follows a similar behavior to results measured under high illumination conditions the reference  $SnO_2$  sample shows inferior  $V_{oc}$  and FF. The *I*-V curves of representative solar cells at 0.1 mW cm<sup>-2</sup> (≈285 Lux) under a white-light LED are displayed in Figure 4e. Results, clearly highlight the poor performance of the SnO<sub>2</sub> sample with a  $V_{\rm oc}$  of only 0.4 V, with results similar to those reported by other authors.<sup>[16]</sup> Statistics over 20 devices measured at 0.1 mW cm<sup>-2</sup> (Figure 4f) highlights a marked difference

## 2.3. Origin of Improved Performance of Devices Containing $SnO_2$ -PbO

We believe that the improved performance observed under low illumination conditions for ETLs containing  $\text{SnO}_2$ -PbO is related to formation of PbO at the interface with the perovskite that increases the shunt resistance of the device. PbO is known to be highly resistive with bulk resistance values of about 10<sup>7</sup>  $\Omega$ .<sup>[24]</sup> In our work, generation of a thin layer of PbO should be sufficient to increase the shunt resistance and block the extraction of undesired leakage current. In order to test this hypothesis, we have completed a set of electrical measurements.

First, devices in the configuration FTO/ETL/Au have been prepared and *J*–*V* curves (**Figure 5**a) and impedance spectroscopy (Figure 5b) have been measured in the dark at voltages close to 0 V. The introduction of PbO increases the series resistance of the device reducing the current that can be driven through the SnO<sub>2</sub>/PbO layer. The shunt resistance ( $R_{\rm sh}$ ) cannot be measured by impedance spectroscopy itself as  $R_{\rm sh}$  belongs to a parallel subcircuit. However, the measurement provides two pieces of valuable information: 1) The series resistance increases, as directly observed from the intercept with the *x*axis, when PbO is present in the layer with values of  $\approx 6 \Omega$  as compared to with values of  $\approx 5 \Omega$  for SnO<sub>2</sub>. 2) The observed arc provides information on the charge transfer resistance from the electrode to the ETL with values of  $\approx 5 \Omega$  for the SnO<sub>2</sub>/PbO and  $\approx 2 \Omega$  for the SnO<sub>2</sub>. This increased charge transfer resistance www.advancedsciencenews.com

DVANCED



**Figure 5.** a) J-V curves and b) Impedance spectroscopy measured in the dark of devices in the configuration of FTO/ETL/Au. c) Open-circuit voltage decay of SnO<sub>2</sub> and SnO<sub>2</sub>-PbO ETLs based PSCs. d) Dark J-V curves of electron-only device with a configuration of FTO/SnO<sub>2</sub> or SnO<sub>2</sub>-PbO ETLs / perovskite/PCBM/Au. e) J-V curves measured in the dark and extraction of  $R_{sh}$ .

observed for  $SnO_2/PbO$  will be the origin of the increased shunt resistance in photovoltaic devices which avoids the leakage of current.

In addition, open-circuit voltage decay (OCVD) measurements were carried out by illumination at 1 sun light intensity, the illumination is turned off within 100 ms by using a shutter and results are shown in Figure 5c. In agreement with previously reported results for the reference SnO<sub>2</sub> the device polarization leads to accumulation of charge and depolarization process is around  $\approx 10-100 \text{ s.}^{[25,26]}$  Alternatively, the SnO<sub>2</sub>-PbO shows that depolarization occurs significantly slower in the range of 500-1000 s. This result points to depolarization of the device via a slow leakage of the charge due to a reduced parallel current pathway related shunt resistance  $(R_{\rm sh})$ as discussed below. While devices containing  $SnO_2$  suffer from a low  $R_{\rm sh}$  (increased parallel pathways) the SnO<sub>2</sub>-PbO benefit from high  $R_{\rm sh}$ . To rule out effects of charge transport inside the ETL the electron mobility was measured using the space charge-limited current (SCLC) method,<sup>[27]</sup> as shown in Figure 5d. In trap-free Child' s region, forming space charge limited current, the dark current was well fitted by the Mott-Gurney law

$$J_{\rm D} = \frac{9\varepsilon\varepsilon_0 \mu V_{\rm b}^2}{8L^3} \tag{1}$$

Where  $J_D$  is the dark current density of devices,  $V_b$  is applied voltage, L ( $\approx$ 500 nm) is the thickness between two electrodes,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon$  (= 32) is relative dielectric constant of MAPbI<sub>3</sub>,  $\mu$  is the carrier mobility. Using this technique, it is found that electron mobility is only slightly improved from of 6.52 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for SnO<sub>2</sub> as compared to 1.07 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for SnO<sub>2</sub>-PbO samples. Similar conclusions are obtained using steady state photoluminescence (PL) and time-resolved photoluminiscence (TRPL) as discussed in supporting information with charge lifetimes of 12.44 and 8.74 ns for SnO<sub>2</sub> and SnO<sub>2</sub>-PbO, respectively. The shorter PL lifetime and

significant PL quenching for the SnO<sub>2</sub>-PbO confirms its slightly superior electron extraction ability but does not account for the significant difference in  $V_{oc}$  observed under low illumination conditions. Alternatively, the shunt resistance can be extracted from the J-V measured in dark (Figure 5e) using the single diode model as explained in the Supporting Information.<sup>[28]</sup> This parameters offer straight forward information on parallel charge pathways which do not contribute to the photocurrent. Results clearly show differences in  $R_{\rm sh}$  of more than one order of magnitude with values of 22.3 and 671.1 k $\Omega$  cm<sup>2</sup> for SnO<sub>2</sub> and SnO<sub>2</sub>-PbO, respectively.

We recall here that results using perovskite solar cells used for low illumination conditions ascribed efficiency improvement to reduced trap-assisted recombination but the current results point to a great enhancement in the  $R_{\rm sh}$  similar to results observed in organic photovoltaic by Proctor.<sup>[17]</sup> For this reason, we next simulated J-V using the single diode model (Figure 6a) with the basic parameters defined as the reverse saturated current density  $(J_0)$ , junction ideality factor (A), shunt resistance  $(R_{\rm sh})$ , and series resistance  $(R_{\rm s})$ .<sup>[29,30]</sup> Parameters are extracted from the devices and electrical measurements obtained in this work. As it can be observed, the *FF* and  $V_{oc}$  of the device is greatly affected by the shunt resistance under lowlight conditions. This is because the photovoltage is a function of the light intensity (and photogenerated current) and in the extreme case at open circuit conditions the difference in potential between the two terminals cannot be maintained if there is a shunt current that shorts the device. At high light intensity there is still sufficient photogenerated current to maintain the photovoltage of the device but at low illumination conditions the shunt current and photogenerated current are comparable. The shunt loss rate can be defined as  $J_{\rm sh}/J_{\rm ph}$  and the shunting loss is more obvious under low-light condition. Hence, high  $R_{\rm sh}$ is necessary for solar cells to work under low-light condition. If we use parameters extracted from the devices actually prepared in this work the model can be used to simulate different conditions in which  $R_{\rm sh}$  changes significantly. Here, we used fixed parameters of  $J_0 = 1 \times 10^{-11}$  mA cm<sup>-2</sup>, A = 1.5, T = 310 K and



**Figure 6.** a) Equivalent circuit of solar cell. b,c) Simulated  $V_{OC}$ - $J_{ph}$  and FF- $J_{ph}$  curves as a function of the  $R_{sh}$  for different shunt resistances using the parameters shown in the panels.

 $R_{\rm s} = 1.2 \ \Omega \ {\rm cm}^2$ . Figure 6b,c shows the results of the simulations where photogenerated current is plot with either  $V_{\rm oc}$  or *FF*. If we consider the actual values of  $R_{\rm sh}$  calculated from devices in this work,  $R_{\rm sh} = 22 \ {\rm k}\Omega \ {\rm cm}^2$  for SnO<sub>2</sub> and 671 k $\Omega \ {\rm cm}^2$  for SnO<sub>2</sub>-PbO, each device would correspond to blue and orange traces in the plots. Under these conditions it is clear that both the  $V_{\rm oc}$  and *FF* are very sensitive to the  $R_{\rm sh}$  and SnO<sub>2</sub>-PbO ETL is well suited for photovoltaic devices used for low illumination conditions.

#### 3. Conclusions

In summary, we presented a simple method to incorporate PbO into SnO<sub>2</sub> nanoparticles under low processing temperatures to form an ETL well suited for low illumination conditions photovoltaic devices. Doping the nanoparticles with Pb slightly improves the performance under 1 sun light illumination as compared to a reference device that only contains SnO<sub>2</sub>. The performance of optimized devices approaches the maximum PCE obtained using the simple perovskite formulation based on MAPbI<sub>3</sub> (≈19%). Alternatively, the performance improvement under low illumination conditions (i.e.,  $0.1 \text{ mW cm}^{-2}$ ) is remarkable with PCE improving from 10.1% to 30.3% when the ETL layer is doped with a PbO precursor. Characterization of the ETLs and corresponding devices points that such a remarkable improvement is related to a large increase in the shunt resistance when PbO is incorporated. Simulation results clearly show the large impact of the  $R_{\rm sh}$  for applications under low illumination conditions on the V<sub>OC</sub> and FF. Therefore, Pb-doped SnO<sub>2</sub> nanoparticles are presented as a very promising ETL layer for low illumination conditions.

#### 4. Experimental Section

*Materials*: PbI<sub>2</sub> (99.99%) and 4-tert-butylpyridine (TBP) were purchased from TCI. CH<sub>3</sub>NH<sub>3</sub>I (MAI) and Spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp. The SnO<sub>2</sub> solution (tin (IV) oxide, 15 wt% in H<sub>2</sub>O colloidal dispersion) was obtained from Alfa Aesar. Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O (99.99%) was obtained from Aladdin. dimethyl sulfoxide (DMSO), gamma-Butyrolactone (GBL) and lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI) (99.95%) were purchased from Sigma-Aldrich Inc. Other materials were purchased from Aladdin.

*Precursor Solutions*: For ETL layers containing only  $SnO_2$  the commercially available aqueous nanoparticle colloidal dispersion (15 wt%) was diluted to 2.5 wt% using deionized water. The solution was stirred at room temperature for 2 h. For ETLs containing PbO the

Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O was dissolved in deionized water followed by addition of the SnO<sub>2</sub> aqueous colloidal dispersion (15 wt%), the Pb: Sn molar ratio was varied from 0.5% to 6%. These solutions were stirred in the atmosphere at room temperature for 12 h. The perovskite precursor solution was prepared by mixing GBL and DMSO solvents with PbI<sub>2</sub> and MAI (1.05: 1 mol%). The GBL: DMSO ratio was modified as required for optimization. In the best condition, the concentration of 1.2 M and 3: 2 volume ratio corresponding to PbI<sub>2</sub> 580.9 mg, MAI 190.8 mg, GBL 600  $\mu$ L, and DMSO 400  $\mu$ L.

Device Fabrication: FTO-coated glass substrates (14  $\Omega/\Box$ ) were patterned by etching with zinc powder and HCl (2 M). The etched substrates were ultrasonically cleaned with soap solution, deionized water, ethanol, and isopropanol, respectively, and then dried under a stream of nitrogen. The SnO<sub>2</sub> layer was spin coated onto the precleaned FTO substrate using SnO<sub>2</sub> solution at 4000 rpm for 30 s, then, annealed on a hot plate at 90 °C for 10 min followed by 150 °C for 30 min. The SnO<sub>2</sub>-PbO layer were deposited by two different methods, both display similar PCEs and behavior with light intensity. A single layer of SnO<sub>2</sub>-PbO was prepared by deposition on FTO of the SnO<sub>2</sub> nanoparticles doped with lead acetate solution at 4000 rpm for 30 s followed by a thermal treatment at 150 °C during 1 h. A bilayer approach was also attempted. First, depositing and thermally treating Pb-doped SnO<sub>2</sub> solution as before, UV-O<sub>3</sub> treated for 15 min and followed by deposition of a second layer using the same conditions with the SnO<sub>2</sub> solution. Both methodologies show similar results. The ETLs-coated substrates were then treated in a UV-O3 cleaner for 15 min before bladecoating perovskite film. The perovskite precursor solution (20 µL) was coated by using doctor blade coater at the substrate temperature of 155 °C. The gap between the blade and the substrate was 150  $\mu$ m and the blade speed was 1 mm/s. The perovskite dark phase was formed within the first few seconds. Perovskite precursor deposition was performed in ambient conditions (R.H. 30% ~ 40%). The hole-transport material (HTM) solution was spin-coated onto the perovskite layer at 4000 rpm for 30 s, which was prepared by dissolving 72.3 mg of Spiro-OMeTAD, 28.8 µl of TBP, and 17.5 µl of Li-TFSI solution (520 mg Li-TFSI in 1 ml acetonitrile) in 1 ml of chlorobenzene. Finally, 50 nm thickness of gold layer was thermally evaporated on top of the Spiro-OMeTAD-coated film as a back contact.

Film and Device Characterization: Morphology and microstructural characterization were performed using an SU-70 High resolution analytical SEM (Hitachi, Japan). The X-ray diffraction (XRD) measurements were carried out on X'Pert PRO MPD X-ray diffractometer using Cu K $\alpha$  irradiation at a scan rate (2 $\theta$ ) of 0.0167° S<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was performed on Thermo Scientific ESCALAB 250Xi instrument with Al K $\alpha$  as the X-ray source. UPS was also carried out on a Thermo Scientific ESCALAB 250Xi, with the HeI (21.22 eV) emission line employed for excitation. The data were acquired at a bias of 0V to-25V. High-resolution transmission electron microscope (HRTEM) images were obtained using a JEOL-2100F TEM. Absorption spectra were recorded using a Perkin-Elmer Lambda 750 spectrophotometer. The PL spectrum and lifetime measurements of perovskite films were conducted on Edinburgh fluorescence spectrometers (FLS980). The current density-voltage (I-V) curves were measured using an Autolab TYPE II electrochemical work station. The ADVANCED SCIENCE NEWS \_\_\_\_\_

cells were illuminated using the ABET Sun 3000 solar simulator with a source meter (Keithley 2420) at 100 mA/cm<sup>2</sup> illumination (AM 1.5 G), where the light intensity was adjusted with an NREL calibrated silicon solar cell. The white light LED and indoor condition light intensity were measured using TENMARS TM-208. The devices and white light LED were placed in dark box at fixed distance. The light intensity was adjusted by changing the input current of LED using a calibrated photodiode. The solar cells were masked with an aperture to define the active area of 0.24 cm<sup>2</sup>. All the measurements of the solar cells were performed under ambient atmosphere at room temperature without any encapsulation.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

This work was supported by the Project on Collaborative Innovation and Environmental Construction Platform of Guangdong Province (No. 2018A050506067). The authors also thank the financial support from the Key Laboratory of Renewable Energy, Chinese Academy of Sciences (No. y807j71001), Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development (Grant No. Y909kp1001), and the Key Project on Synergy Collaborative Innovation of Guangzhou City (No. 201704030069). University Jaume I is also acknowledged for financial support (No. UJI-B2020-49).

## **Conflict of Interest**

The authors declare no conflict of interest.

### **Data Availability Statement**

Research data are not shared.

### Keywords

indoor applications, low illumination, perovskite solar cells, shunt resistance  $% \left( {{\left[ {{{\rm{s}}_{\rm{s}}} \right]}_{\rm{s}}} \right)$ 

Received: April 19, 2021 Revised: June 2, 2021

Published online:

- NREL, B. R.-C. E., https://www.nrel.gov/pv/cell-efficiency.html (accessed: 13 April 2021).
- [2] H. J. Snaith, J. Phys. Chem. Lett. 2013, 4, 3623.
- [3] M. A. Green, A. Ho-Baillie, H. J. Snaith, Nat. Photonics 2014, 8, 506.
- [4] X. T. Hu, Z. Q. Huang, F. Y. Li, M. Su, Z. D. Huang, Z. P. Zhao, Z. R. Cai, X. Yang, X. C. Meng, P. W. Li, Y. Wang, M. Z. Li, Y. W. Chen, Y. L. Song, *Energy Environ. Sci.* **2019**, *12*, 979.

www.advsustainsys.com

- [5] X. T. Hu, F. Y. Li, Y. L. Song, ACS Energy Lett. 2019, 4, 1065.
- [6] Y. M. Cao, Y. H. Liu, S. M. Zakeeruddin, A. Hagfeldt, M. Gratzel, *Joule* 2018, 2, 1108.
- [7] H. K. H. Lee, J. Y. Wu, J. Barbe, S. M. Jain, S. Wood, E. M. Speller, Z. Li, F. A. Castro, J. R. Durrant, W. C. Tsoi, *J. Mater. Chem. A* 2018, 6, 5618.
- [8] C. Dong, M. Li, Y. Zhang, K.-L. Wang, S. Yuan, F. Igbari, Y. Yang, X. Gao, Z.-K. Wang, L.-S. Liao, ACS Appl. Mater. Interfaces 2020, 12, 836.
- [9] L. B. Xiong, Y. X. Guo, J. Wen, H. R. Liu, G. Yang, P. L. Qin, G. J. Fang, Adv. Funct. Mater. 2018, 28, 1802757.
- [10] E. H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A. Abate, M. Gratzel, A. Hagfeldt, J. P. Correa-Baena, *Energy Environ. Sci.* **2016**, *9*, 3128.
- [11] Q. Jiang, L. Q. Zhang, H. L. Wang, X. L. Yang, J. H. Meng, H. Liu, Z. G. Yin, J. L. Wu, X. W. Zhang, J. B. You, *Nat. Energy* **2017**, *2*, 16177.
- [12] J. P. C. Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T. J. Jacobsson, A. R. S. Kandada, S. M. Zakeeruddin, A. Petrozza, A. Abate, M. K. Nazeeruddin, M. Gratzel, A. Hagfeldt, *Energy Environ. Sci.* 2015, *8*, 2928.
- [13] K. Liu, S. Chen, J. H. Wu, H. Y. Zhang, M. C. Qin, X. H. Lu, Y. F. Tu, Q. B. Meng, X. W. Zhan, *Energy Environ. Sci.* 2018, *11*, 3463.
- [14] M. M. Tavakoli, F. Giordano, S. M. Zakeeruddin, M. Gratzel, Nano Lett. 2018, 18, 2428.
- [15] X. Gong, Q. Sun, S. S. Liu, P. Z. Liao, Y. Shen, C. Gratzel, S. M. Zakeeruddin, M. Gratzel, M. K. Wang, *Nano Lett.* **2018**, *18*, 3969.
- [16] Y. W. Noh, I. S. Jin, K. S. Kim, S. H. Park, J. W. Jung, J. Mater. Chem. A 2020, 8, 17163.
- [17] C. M. Proctor, T. Q. Nguyen, Appl. Phys. Lett. 2015, 106, 083301.
- [18] F. Huang, M. J. Li, P. Siffalovic, G. Z. Cao, J. J. Tian, Energy Environ. Sci. 2019, 12, 518.
- [19] S. N. Sarangi, G. K. Pradhan, D. Samal, J. Alloy Compd. 2018, 762, 16.
- [20] D. J. Payne, R. G. Egdell, W. Hao, J. S. Foord, A. Walsh, G. W. Watson, Chem. Phys. Lett. 2005, 411, 181.
- [21] H. K. Wang, K. P. Dou, W. Y. Teoh, Y. W. Zhan, T. F. Hung, F. H. Zhang, J. Q. Xu, R. Q. Zhang, A. L. Rogach, *Adv. Funct. Mater.* 2013, 23, 4847.
- [22] W. J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J. N. Kondo, M. Hara, M. Kawai, Y. Matsumoto, K. Domen, J. Phys. Chem. B 2003, 107, 1798.
- [23] Z. N. Bi, X. Rodriguez-Martinez, C. Aranda, E. Pascual-San-Jose, A. R. Goni, M. Campoy-Quiles, X. Q. Xu, A. Guerrero, J. Mater. Chem. A 2018, 6, 19085.
- [24] A. A. A. Darwish, E. F. M. El-Zaidia, M. M. El-Nahass, T. A. Hanafy, A. A. Al-Zubaidi, J. Alloy Compd. 2014, 589, 393.
- [25] N. E. Courtier, J. M. Cave, J. M. Foster, A. B. Walker, G. Richardson, Energy Environ. Sci. 2019, 12, 396.
- [26] L. Bertoluzzi, R. S. Sanchez, L. F. Liu, J. W. Lee, E. Mas-Marza, H. W. Han, N. G. Park, I. Mora-Sero, J. Bisquert, *Energy Environ. Sci.* 2015, *8*, 910.
- [27] Q. F. Dong, Y. J. Fang, Y. C. Shao, P. Mulligan, J. Qiu, L. Cao, J. S. Huang, *Science* **2015**, 347, 967.
- [28] D. S. H. Chan, J. C. H. Phang, IEEE Trans. Electron. Dev. 1984, 31, 381.
- [29] A. Jain, A. Kapoor, Sol. Energy Mater. Sol. Cells 2004, 81, 269.
- [30] R. Steim, T. Ameri, P. Schilinsky, C. Waldauf, G. Dennler, M. Scharber, C. J. Brabec, Sol. Energy Mater. Sol. Cells 2011, 95, 3256.