Low-Temperature-Processed ZnO-SnO₂ Nanocomposite for Efficient Planar Perovskite Solar Cells

Jiaxing Song^a, Enqiang Zheng^b, Xiao-Feng Wang^{b,*}, Wenjing Tian^{a,*} and Tsutomu Miyasaka^c

^a State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, PR China

^b Key Laboratory of Physics and Technology for Advanced Batteries, Ministry of Education, College of Physics, Jilin University, Changchun 130012, PR China

^c Graduate School of Engineering, Tooin University of Yokohama, 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8503, Japan

***Corresponding authors:**

E-mails: xf_wang@jlu.edu.cn (X.-F. Wang) and wjtian@jlu.edu.cn (W. Tian)

Jiaxing Song: jiaxing2199@126.com

Enqiang Zheng: 804670601@qq.com

Tsutomu Miyasaka: miyasaka@toin.ac.jp

Abstract

Electron collection layer (ECL) is one of the most important fundamentals to determine the power conversion efficiency (PCE) in organometal halide-based perovskite solar cells (PSCs). Herein, we prepared ZnO-SnO₂ nanocomposites with different Zn/Sn ratios at low temperature as ECLs for CH₃NH₃PbI₃-based planar-structured PSCs. ZnO-SnO₂ nanocomposite with the optimal ~89 mol% of the ZnO content gives higher PCE than the ZnO for the best fabricated PSC. The photoluminescence spectroscopies measured in both steady and transient states and the electrochemical impedance spectroscopy were carried out to characterize the interface of CH₃NH₃PbI₃ and different ECLs, namely ZnO, ZnO-SnO₂ composite, and SnO₂. The high PCE of PSCs based on the ZnO-SnO₂ nanocomposite ECL was thus attributed to joint contributions of the high charge extraction efficiency and large charge recombination resistance both on the CH₃NH₃PbI₃/ECL interface. The thermal stability of CH₃NH₃PbI₃ absorber and the device stability of the corresponding PSC are both dependent on the ECLs in the order: SnO₂ > ZnO-SnO₂ > ZnO, suggesting that the hydroxyl-induced degradation of CH₃NH₃PbI₃ may be predominant in the ambient air environment in the initial ~700 hours. The PCE of the optimized device was further improved to 15.2% by introducing the low-temperature processable Al₂O₃ as a capping layer to the ZnO-SnO₂ composite.

Keywords: ZnO-SnO₂; electron collection layer; low-temperature-processed; planar; perovskite solar cells

1. Introduction

As an emerging technology for next generation photovoltaics, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl, Br, I}$)-based perovskite solar cells (PSCs) have attained great success by boosting their power conversion efficiency (PCE) to over 20%, a figure that is highly competitive compared with that of other solar cell technologies developed for decades, merely within few years [1-6]. An important merit of PSCs compared with the commercially available Si-based photovoltaics is that PSCs can give high voltage output at weak illumination of light [7-8]. Therefore, PSCs are particularly useful as an energy supply for wearable and flexible electronics. The high PCE of PSCs is closely associated with the excellent photoelectrical properties of perovskite light absorbers including the appropriate band gap, the small exciton binding energy, the long and balanced ambipolar charge transport property [9-13]. In spite of the large potential of perovskite materials, numerous problems remain challenging, i.e., the reproducibility, the low-temperature processibility, the thermal/photo durability, and etc [14-20]. Needless to say, research explorations regarding any above challenges would facilitate the progress of PSCs in the real-world applications.

In the PSC device architectures, an electron collection layer (ECL) plays a significant role in suppressing recombination and rectifying photocurrent generated in the perovskite bulk films [21-30]. To date, some inorganic n-type semiconductors, such as TiO_2 , ZnO , SnO_2 , Nb_2O_5 , and WO_x , have been studied as the ECLs in PSCs [21-22,25-27,30]. Nevertheless, in order to fabricate PSCs

on flexible substrates for potential applications in flexible and wearable electronics, the ECL must be processed at a low temperature. In view of this, many investigations into low-temperature processed PSCs with TiO_2 or ZnO as ECL have been carried out, and have shown high PCEs of 14~19% [18,23]. However, the low-temperature-processed PSCs based on either TiO_2 or ZnO are environmentally unstable [18,23], probably owing to the remaining $-\text{OH}$ residues on the ECL surface to cause the decomposition of perovskite absorbers, as suggested by a recent investigation [34]. Besides TiO_2 and ZnO , SnO_2 was also employed as ECL in PSCs [27-29], due to its high transparency, superior electron mobility and low-temperature processability [29,31-32]. Moreover, PSCs based on SnO_2 show excellent durability in the ambient environment [29]. On the other hand, the PCE of SnO_2 -based PSCs is lower than that of ZnO -based PSCs, owing to inherent lower conduction band edge and low current rectification property of SnO_2 compared with that of ZnO resulting in more severe charge recombination between the ECL and perovskite in the former than the latter [27,33]. Thus, the insufficiency of each ECL material investigated in PSCs so far strongly encourages further development of ECL by either exploring other n-type semiconductor that outperforms current ECL semiconductors or by combining two semiconductors into one so that they can compensate each other.

Semiconductor nanocomposites are a large group of nanomaterials that their chemical, physical and opto-electrical properties are tuned by varying the

composition of each semiconductor in a mixture to fulfill some particular requirements of semiconductor devices. The nanocomposites of ZnO–TiO₂, SnO₂–MgO, TiO₂–Nb₂O₃, SnO₂–TiO₂ and SnO₂–ZnO under this concept have been very successfully applied in dye-sensitized solar cells to result in enhanced photovoltaic performance [35–37]. Similarly, the use of nanocomposite ECLs in PSCs will also be of considerable interests and provide an important piece of information in further development of this photovoltaic field. However, to the best of our knowledge, there is no report on inorganic semiconductors nanocomposite as ECL for PSCs so far.

In this investigation, we prepared ZnO-SnO₂ nanocomposite thin films by spin-coating of mixed nanoparticles as ECLs to fabricate low-temperature-processed PSCs. We employed a previously reported two-step sequential deposition technique to grow CH₃NH₃PbI₃ active layer [29]. We observed clear dependence of short-circuit current (J_{sc}) and fill factor (FF) on the component content in the composite films despite almost unchanged open-circuit voltage (V_{oc}). With planar layered structures, the PSCs exhibited relatively high PCE of $14.0 \pm 0.3\%$ under the standard AM 1.5G ($100 \text{ mW} \cdot \text{cm}^{-2}$) simulated sunlight illumination with an optimal weight ratio of 2:1 for ZnO/SnO₂ in solution. Most importantly, the CH₃NH₃PbI₃ layer and device based on ZnO-SnO₂ nanocomposite thin film exhibited improved thermal stability and device stability in comparison with that based on ZnO, respectively. This study will contribute to both the progress of the

low-temperature planar-heterojunction PSCs and the real-world applications of the PSC technology.

2. Experimental

2.1 Materials

The ZnO (ZnO-350, Sumitomo Osaka Cement Co.) [38] and SnO₂ nanoparticles (ca. 22~43 nm, Wako chemicals) were used as received. Al₂O₃ paste was purchased from Sigma-Aldrich. The lead iodide (beads, -10 mesh, 99.999% trace metals basis) and lithium salts (>99.0%) were purchased from Aldrich. The CH₃NH₃I (>99.0%) was purchased from Xi'an Polymer Light Technology Co. (PLT). The Spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene, >99.0%) was purchased from Merck. Ultradry solvent of N, N-dimethyl formamide (DMF, >99.9%) and isopropanol (>99.9%) were obtained from J&K and Acros, respectively. All the chemicals and solvents were kept in the glove-box before starting our experiment.

2.2 Device fabrication

The pre-patterned ITO substrates were cleaned with detergent, deionized water, acetone, and 2-propanol in sequence. The ZnO and SnO₂ nanoparticles were dispersed in butanol in different blending proportion with a total concentration of 6 mg/ml and stirred for 3 hours before use. The solution was filtered with a PVDF hydrophobic 0.45μm filter and spin-coated on ITO substrates at 2500 rpm for 30s to form a relatively compact ZnO-SnO₂ thin layer, and followed by short baking at 150°C for 5 min. This procedure was repeated for three times before finally baking at 200°C for 1 hour. A 460 mg/mL solution of PbI₂ in DMF was then spin-coated on the top of the

ZnO-SnO₂ layer at 3000 rpm for 30s in the glove-box. The PbI₂-coated ZnO-SnO₂ thin film was kept in a petri dish for about 5 minutes allowing a slow growth of PbI₂ nanocrystals, and was followed by annealing at 70°C for 30 min. After cooling to room temperature, the films was dipped into a CH₃NH₃I 2-propanol solution (10 mg/mL) for 50 s, and was followed by annealing at 70°C for 20 min to give a desired crystallite formation. As hole-transporting material (HTM), a Spiro-OMeTAD solution (80 mg of Spiro-OMeTAD, 10.5μL of 4-tert-butylpyridine (tBP), and 46.5μL of a lithium-bis(tri-fluoromethanesulfonyl)imide (Li-TFSI) solution (170 mg Li-TFSI/1 mL acetonitrile) in 1 mL chlorobenzene) was spin-coated at 4000 rpm for 30s on the CH₃NH₃PbI₃. The substrates with HTM were left overnight in the dry air in dark at room temperature. Finally, 60 nm thick Ag electrode was thermally evaporated on the top of HTM to produce a completed PSC device.

2.3 Device characterization

The current-voltage characteristics of solar cells were measured by a computer-controlled Keithley 2400 source meter measurement system with an AM1.5G filter at a calibrated intensity 100mWcm⁻² illumination, as determined by a standard silicon reference cell (91150V Oriel Instruments). The effective area of the cell was defined to be 0.04 cm² using a non-reflective metal mask. IPCE spectra was measured in air under short-circuit conditions using a commercial IPCE setup (CrownTech QTest Station 1000AD), which was equipped with a 100W Xe arc lamp, filter wheel, and monochromator. Monochromated light was chopped at a frequency of 80 Hz and photocurrents were measured using a lock-in amplifier. The setup was

calibrated against a certified silicon reference diode. The impedance spectroscopy measurement was carried out by a VSP multichannel potentiostatic-galvanostatic system (Biologic, France), under dark conditions by applying a 5 mV voltage perturbation with the frequency ranging between 1 MHz and 1 Hz. Z-View Analyst software was used to model the Nyquist plots obtained from the impedance measurements.

2.4 Thin film characterization

Film thicknesses were measured using a Veeco Dektak 150 surface profilometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5301PC spectrophotometer. Time-resolved photoluminescence (TPL) spectra were obtained on a PL spectrometer (Edinburgh Instruments, FLS 980), excited with a picosecond pulsed diode laser (EPL-375). A Hamamatsu C5680-04 streak camera was used for TPL. The X-ray diffraction (XRD) patterns were recorded on Rigaku SmartLab X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 25°C. The data were collected with a 0.01° step size (2θ). A field emission scanning electron microscope (Hitachi SU8020) was used to acquire SEM images. The energy band values were measured with an integrated ultrahigh vacuum system equipped with multi-technique surface analysis system (VG Scienta R3000) UPS.

3. Results and discussion

3.1 Sequential deposition of CH₃NH₃PbI₃ on ZnO-SnO₂ ECL

The ZnO-SnO₂ nanocomposite films were prepared by spin coating the mixed nanoparticles through a PVDF filter with average pore size of 0.45 μm . The

nanoparticles are both commercially available. We simply confirmed the nanoparticles by measuring their X-ray diffraction (XRD) patterns. Fig.S1 in the Supplementary Material shows the XRD patterns of both ZnO and SnO₂ nanoparticles used in this investigation. Each of these diffraction lines is commonly assigned to the hexagonal crystalline phases of ZnO and to the tetragonal rutile crystalline phases of SnO₂ as reported before [29]. Fig. S2 shows the high magnification scanning electron microscope (SEM) surface images of the ZnO-SnO₂ thin film prepared by spin-coating the ZnO-SnO₂ nanoparticle solution containing ZnO and SnO₂ nanoparticles with different weight ratios of 5:1, 2:1, 1:1 and 1:2. The morphologies for the ZnO-SnO₂ composite thin films are basically identical with the SEM images taken for each ZnO and SnO₂ in our previous investigations [26,29]. In addition, these composite films are very flat suggesting the corresponding PSCs are likely based on the planar-heterojunction configuration. Given that the mixture of nanoparticles was spin coated from a PVDF filter, the exact ratios of ZnO and SnO₂ on the resultant films must be different from their mixed ratios. We performed energy-dispersive X-ray spectroscopy (EDX) to analyze the real mole ratio of ZnO (Zn mol%) in the composite films as a function of the mixed weight ratio in the solution. As shown in Fig. 1, the exact amount of ZnO in the composite films is basically dependent on the amount of ZnO in the mixed solution. The Zn mol% of 97%, 89%, 77%, and 60% in the composite films corresponds to the mixed weight ratios of ZnO/SnO₂ of 5:1, 2:1, 1:1 and 1:2 in the mixed solution, respectively. In addition, the weight ratios for ZnO in the composite films calculated from the mole ratios are also provided in Fig. 1. The

corresponding ZnO weight ratios are 95%, 81%, 64% and 45%. For the convenience of discussion, however, we simply refer to the mixed ratios in the following investigation.

A previously reported two-step sequential deposition method [29] was employed to prepare $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on ZnO-SnO₂ thin films as detailed in the experimental section. With this method, PbI_2 with high crystallinity remains in the perovskite layer to give a passivation effect [29]. The XRD pattern of the perovskite films in Fig. S3a is basically consistent with previous results [29]. The XRD signals appearing at each 14.0° , 24.3° , 28.4° , 31.7° and 50.3° correspond to the (110), (202), (220), (310) and (404) planes of the tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$, respectively [40]. Fig. S3b also shows the SEM surface image of the perovskite films used in this investigation.

3.2 *J-V* characteristics of the solar cells

PSCs were then fabricated with the above perovskite layer as the absorber and with ZnO, SnO₂, and ZnO-SnO₂ (5:1, 2:1, 1:1, 1:2) nanocomposite as the ECLs. In each PSC, an ~18 nm thick ECL and a ~210 nm thick perovskite layer was commonly employed. Fig. 2a shows the PSC device configuration based on the ZnO-SnO₂ ECL. Fig. 2b shows the energy level diagram of the PSC devices based on ZnO or SnO₂ ECL [23,29]. The conduction band edge (CBE) of either ZnO (-4.2 V) or SnO₂ (-4.5 V) is sufficiently lower than the lowest occupied molecular orbital (LUMO) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite absorber ensuring efficient extraction (or dissociation) of free charge carriers (or excitons) at the ECL/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface [23]. The spectra of the ultraviolet photoelectron spectroscopy (UPS) and UV-vis absorption spectroscopy of

the ZnO-SnO₂ nanocomposite with the best blend ratio (2:1 in solution) are shown in Fig. S4. The band edges of the valence and conduction bands were thus estimated to be -7.55 eV and -4.25 eV, respectively with these UPS and absorption spectra, and are shown in Fig. 2b. For the ZnO-SnO₂ nanocomposites, their CBEs are located between that of ZnO and SnO₂, as widely studied in the previous investigations [35,39]. Noticeably, in the heterojunction structure, there may be some interfacial trap states between ZnO-SnO₂ and CH₃NH₃PbI₃ interface owing to the imperfection from both the materials and from lattice mismatch-induced defects between them. The poor screening of the surface charge-induced electric field by the low concentration of free carrier density in the semiconductor can lead to the band bending that has an effect on the charge transfer [44]. In the energy level diagram of Fig. 2b, the interface state effect is put aside temporarily and we regard the heterojunction as an ideal condition.

Fig. 3 shows the current-voltage (J - V) characteristics measured from the reversed voltage scan of PSCs with each ZnO, SnO₂, and ZnO-SnO₂ nanocomposites (5:1, 2:1, 1:1, 1:2) as ECL, and the detailed parameters are summarized in Table 1. Interestingly, no significant change in the V_{oc} value was observed, despite the CBE of SnO₂ is significantly below that of ZnO. This insensitivity of the V_{oc} value to the CBE level of the ECL could be attributed to both the passivation effect of the remnant PbI₂ and the effective charge collection by both ZnO and SnO₂ ECL layers [29]. For the FF and J_{sc} values, however, they exhibit clear dependence on the ZnO/SnO₂ ratio, i.e., with increased SnO₂ component, the J_{sc} value increases whereas the FF value

decreases. For the SnO₂-based device, it gives the highest J_{sc} , which may be due to the most efficient interfacial charge-transfer, the smallest current loss derived from the wide band gap, and the best antireflection effect [28,41]. In contrast, the highest FF value obtained for the ZnO-based device is the consequence of the higher electron mobility and carrier selectivity (rectification) by ZnO [23]. As the result of the varied J_{sc} and FF values, the highest PCE of 14.3%, determined by a J_{sc} =19.6 mA cm⁻², a V_{oc} = 1.06 V, and a FF =0.688, was achieved for the best fabricated device with ZnO/SnO₂= 2:1. Fig. S5 in the Supplementary Material shows the dependence of each photovoltaic parameter on the ZnO/SnO₂ ratios.

ECL	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
SnO ₂	1.06 ± 0.01	19.9 ± 0.3	58.2 ± 0.8	12.1 ± 0.3
ZnO:SnO ₂ =1:2	1.07 ± 0.01	19.7 ± 0.2	61.3 ± 0.7	12.7 ± 0.3
ZnO:SnO ₂ =1:1	1.06 ± 0.01	19.5 ± 0.2	64.3 ± 0.9	13.2 ± 0.2
ZnO:SnO ₂ =2:1	1.06 ± 0.01	19.4 ± 0.3	68.7 ± 0.6	14.0 ± 0.3
ZnO:SnO ₂ =5:1	1.05 ± 0.01	18.8 ± 0.4	69.7 ± 0.6	13.7 ± 0.2
ZnO	1.06 ± 0.01	18.5 ± 0.3	70.2 ± 0.8	13.6 ± 0.3

Table 1. The corresponding photovoltaic performance parameters for PSCs based on different ECLs. **Data are derived from the measurements on 10 separate devices.**

3.3 Steady state and time-resolved photoluminescence measurements

As discussed previously, the 2:1 ratio of ZnO/SnO₂ in solution actually

corresponds to a real proportion of 89% for ZnO in the nanocomposite film. This means that ZnO content tends to be predominant in the composite film. Fig. S6 in the Supplementary Material shows the XRD pattern of nanocomposite obtained from ZnO/SnO₂=2:1 mixed solution. The fact that the XRD signal of SnO₂ is much weaker than that of ZnO again proves that SnO₂ is a minor component in this nanocomposite film. To verify the effect of SnO₂ in the composite ECL, we investigated the opto-electrical properties of ZnO, SnO₂ and their 2:1 nanocomposite. Fig. 4 shows the steady state photoluminescence (PL) spectra of the CH₃NH₃PbI₃ films on following different substrates: bare glass, glass/ZnO, glass/ZnO-SnO₂ (2:1), and glass/SnO₂. The PL signal at 760 nm is assigned to the emission from CH₃NH₃PbI₃ [42]. Obviously, the intensity of PL signal is substantially weakened with the presence of ECL; the PL intensity for different ECLs is in the order: ZnO> ZnO-SnO₂> SnO₂. Based on that the PL quenching is originated from the carrier extraction across the interface between CH₃NH₃PbI₃ and ECLs [42-43], the efficiency of carrier extraction by these ECLs is in the order: SnO₂> ZnO-SnO₂> ZnO. This is because that the deeper CBE of SnO₂ compared with that of ZnO provides a large potential for electron transfer between the perovskite layer and the ECL following the energy gap law.

Carrier extraction behavior of different ECLs was further dynamically verified by the time-resolved photoluminescence (TPL) spectroscopy. Fig. 5 shows the decay dynamics of PL intensity for perovskite on different ECLs. The lifetime (τ) of PL signals was thus obtained by exponentially fitting the dynamic curves. As the result of the fitting, the τ value for SnO₂, ZnO-SnO₂, ZnO, and no ECL is 16.1 ns, 19.6 ns, 22.5

ns, and 34.2 ns, respectively, being consistent with the steady state PL result. The shortest PL lifetime with SnO₂ as the ECL confirms that the photoinduced electron transfer between perovskite and SnO₂ is faster than that between perovskite and other investigated ECLs [27,30]. The charge extraction efficiency which is controlled by the material property of ECLs is one of the factors to determine the J_{sc} value in PSCs [27], thus the rank order of PL quenching efficiency, i.e., SnO₂ > ZnO-SnO₂ > ZnO, is coincident with the rank order of J_{sc} value of the corresponding PSCs.

3.4 Electrochemical impedance spectroscopy and electron mobility measurements

Although the charge extraction efficiency and J_{sc} of SnO₂ is higher than those of ZnO and their nanocomposite, the FF value of the SnO₂-based PSC is lower than that of other ECL-based PSCs. This means the charge collection and current rectifying efficiency, determined by the interfacial charge-transfer, the charge-transport and the recombination dynamics, is the lowest for SnO₂ among all investigated ECLs. Thus, we carried out electrochemical impedance spectroscopy (EIS) measurements in the dark at 0 V relative to the open circuit potential on the devices with the configuration of ITO/ECL/CH₃NH₃PbI₃/Spiro-OMeTAD/Ag, in which ECL is SnO₂, ZnO-SnO₂, and ZnO, respectively. Fig. 6a shows the Nyquist plots of PSC devices with these ECLs. The Nyquist plot is composed of two irregular arcs, i.e., a small arc at high frequency and a large arc at low frequency [30]. We fitted the experimental data with a relatively simple equivalent circuit model from the previous investigation [42] as shown in Fig. 6b. Here, the high-frequency feature

is ascribed to contact resistance (R_{co}) associated with the ECL/perovskite interface (the perovskite/Spiro-OMeTAD interface is identical), while the lower frequency element is associated with the recombination resistance (R_{rec}) and chemical capacitance (C_{μ}) of the system [42]. In addition, the value of the starting point at the real part of the Nyquist plot corresponds to the series resistance R_s [30]. The values fitted to the equivalent circuit are tabulated in Table S1. For each of these R_s , R_{co} , and R_{rec} parameter obtained from different ECLs, the resistance values always follow the same order, i.e., $ZnO > ZnO-SnO_2 > SnO_2$. The SnO_2 -based device gives the lowest R_{co} value indicating that charge extraction is most efficient at the $SnO_2/CH_3NH_3PbI_3$ interface among all the investigated ECL/ $CH_3NH_3PbI_3$ interfaces, a fact that is consistent with the (T)PL results [42]. Moreover, the lower R_s and R_{co} values must jointly contribute to the high J_{sc} value of SnO_2 -based PSCs [27-28,42]. By contrast, the R_{rec} value is the highest for ZnO among the three ECLs, suggesting the charge recombination is unfavorable between $ZnO/CH_3NH_3PbI_3$ [42]. Thus, the high FF value of the ZnO-based PSC could be attributed to the suppressed charge recombination between ZnO and $CH_3NH_3PbI_3$. For the ZnO- SnO_2 nanocomposite, it gives medium values of R_s , R_{co} , and R_{rec} . This property of ZnO- SnO_2 nanocomposite led to similar PCE values in the ZnO- SnO_2 -based PSCs with moderately high values of J_{sc} (electron extraction) and FF (charge collection).

Electron mobilities of the three devices were then evaluated by the space charge-limited current (SCLC) method with the architecture: ITO/Al/ECL/CH₃NH₃PbI₃/Spiro-OMeTAD/Al as shown in Fig. S7. The carrier mobility was calculated with eq. (1) [45]:

$$J=9\varepsilon_0\varepsilon_r\mu(V-V_{bi}-V_r)^2/8L^3 \quad (1)$$

The electron mobilities of the three devices determined by this method are $5.9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ (ZnO), $4.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ (ZnO-SnO₂) and $2.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ (SnO₂). ZnO ECL exhibits relatively higher electrical conductivity among the three ECLs, indicating that the transport and collection of electrons must be equally favorable in ZnO ECL among the three ECLs. The mobility results nicely explain the variation in FF values in the corresponding PSCs.

3.5 Thermal stability of CH₃NH₃PbI₃ and device stability

It was previously reported that CH₃NH₃PbI₃ absorber underwent fast thermal degradation on the ZnO ECL surface [19,31]. We certainly wonder if the presence of minor SnO₂ component in the ZnO-SnO₂ composite film can suppress the thermal degradation of CH₃NH₃PbI₃. Fig.7 shows the photographs of CH₃NH₃PbI₃ films on ZnO, ZnO-SnO₂ (2:1) and SnO₂ before and after the thermal treatment. Before the thermal treatment, all perovskite films showed the same black color. As the thermal treatment was carried out at 110°C for 6 min, the perovskite film on ZnO partially turned to yellow, whereas that on ZnO-SnO₂ and SnO₂ remained black. As the temperature of the thermal treatment was further elevated to 120°C, the CH₃NH₃PbI₃ film on ZnO became purely yellow in 6 min, reflecting a complete decomposition of perovskite into

PbI₂. At 120°C, compared with the perovskite layer on SnO₂ that still showed excellent thermal stability, the perovskite layer on ZnO-SnO₂ composite film also started decomposition. The *J*_{sc} and PCE values of the PSC devices prepared with these annealed perovskite layers are shown in Fig. S8. The photovoltaic performance of the PSCs is consistent with the degree of decomposition upon thermal treatment of the perovskite films. It was found that the thermal decomposition of perovskite on ZnO was originated from the hydroxyl residues and/or residual acetate ligands on ZnO [34]. Fig. 8 shows the FT-IR spectra of the ZnO, ZnO-SnO₂ (2:1) and SnO₂ films obtained without high temperature sintering. Remarkably, the fact that the IR shift around 3440 cm⁻¹ from the stretching of hydroxyl residues and around 1580 cm⁻¹, 1440 cm⁻¹ from that of residual acetate ligands [34] could be clearly observed not for SnO₂ but for ZnO, strongly suggesting that the high thermal stability of perovskite on SnO₂ is an indication of absence of hydroxyl and/or acetate ligands-induced degradation. For ZnO-SnO₂, IR shift from the stretching of hydroxyl residues and residual acetate ligands remarkably reduced compared to the ZnO. We therefore attribute the improved thermal stability by compositing SnO₂ into ZnO to the reduced number of surface hydroxyl groups and/or residual acetate ligands.

To gain some understanding of the stabilized power output under working conditions, we measured the photocurrent of the devices held at the forward bias as a function of time in Fig. S9. The measured photocurrent generally slightly

increased from an initial value to a stabilized value after tens of second illumination, resulting in an increased stabilized PCE of the devices. The quick turning on the photocurrent confirms the absence of large density charge traps, while the slow climbing of the J_{SC} to the maximum value indicates there may be a relatively small density of deep traps in the devices [46]. Importantly, all three devices show short ON-OFF relaxation time and repeatable ON-OFF performance reflecting excellent device stabilities.

As discussed above, the different thermal stability of perovskite on ZnO, ZnO-SnO₂ composite, and SnO₂ is attributable to the different number of hydroxyl residues on the ECL films. This suggests that PSCs based on these ECLs may exhibit similar trend in the device stability during the storage, because hydroxyl-induced chemical degradation can slowly occur even at the room temperature and is likely predominant over other degradation pathways during the device storage in dark. Fig. 9 shows the stability result of PSCs based on ZnO, ZnO-SnO₂ (2:1) and SnO₂ as ECLs during the storage in ambient air environment in room temperature. Despite the three PSCs exhibited similar stability in the initial 240 hours of storage time, further increasing the storage time reduced the PCE of ZnO-based PSC more significantly than that of SnO₂-based PSC. Importantly, the fact that the stability of PSC based on ZnO-SnO₂ composite is between that of PSCs based on ZnO and SnO₂ strongly support the conjecture that the hydroxyl and/or acetate ligands-induced

degradation is a main mechanism to cause reduction of PCEs during the storage time within ~700 hours.

3.6 Introduction of mesoporous Al₂O₃ capping layer

Finally, we examined further improvement of the photovoltaic performance of the ZnO-SnO₂ composite based PSC by incorporating mesoporous Al₂O₃, because Al₂O₃ layer is also high-temperature sintering-free and can retard the charge recombination between the ECL and perovskite absorber [2,14]. Therefore, we fabricated PSCs with Al₂O₃ as insulator between perovskite and nanocomposite ZnO-SnO₂ (2:1), the SEM image for the cross section of the Al₂O₃-based PSC is shown in Fig. S10 in the Supplementary Material. Fig. 10 shows (a) the *J*-*V* characteristics and (b) the IPCE profiles of PSCs with and without the presence of mesoporous Al₂O₃. With the Al₂O₃ layer, an improved PCE of 15.2% was achieved as determined with a *J*_{sc} = 19.5 mA cm⁻², a *V*_{oc} = 1.07 V, and a FF = 0.728. This improvement in the PCE is mainly attributed to the improved FF value in combination of high *V*_{oc}, indicating the charge-recombination process between CH₃NH₃PbI₃ and ZnO-SnO₂ ECL is further suppressed by Al₂O₃. The photocurrents as integrated area under the IPCE spectra reach 18.53 mAcm⁻² and 18.70 mAcm⁻² for PSCs with and without the presence of mesoporous Al₂O₃, which are in good agreement with the corresponding measured *J*_{sc} values (19.5 mAcm⁻² and 19.6 mAcm⁻²) with below 5% mismatches. The IPCE values of both devices reach more than 70% across a

broad range of wavelength proving excellent light-harvesting and quantum conversion by the devices [26].

4. Conclusions

In summary, we successfully developed ZnO-SnO₂ nanocomposites as electron collection layer for CH₃NH₃PbI₃-based perovskite solar cells. The composition of the nanocomposites was optimized by adjusting ZnO and SnO₂ nanoparticles in the mixed solution. The relatively high power conversion efficiency of $14.0 \pm 0.3\%$ was achieved with ZnO-SnO₂ (2:1 weight ratio in solution) nanocomposite as the ECL. This high efficiency was originated from an excellent charge extraction efficiency of the ZnO-SnO₂ composite and a large recombination resistance between CH₃NH₃PbI₃ and ZnO-SnO₂, as revealed by the steady state photoluminescence spectroscopy, the time-resolved photoluminescence spectroscopy and the electrochemical impedance spectroscopy measurements. Moreover, the ZnO-SnO₂ nanocomposite thin films exhibit better thermal stability of CH₃NH₃PbI₃ and resultant PSC device stability, as compared to ZnO. The development of ZnO-SnO₂ nanocomposite as electron collection layer for perovskite solar cells provides a new choice for the further advances of the novel photovoltaic technology for perovskite.

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Figure Captions:

Figure 1. EDX analysis of the Zn mol% and corresponding weight ratio of ZnO in the nonocomposite ZnO–SnO₂ thin films vs. ZnO mass relative to the total mass of solute in the solution (the Zn mol% is based on the total mol% of metal ions in the film). The Gaussian fits provided as a guide to the eye.

Figure 2. Device architecture (a) and energy level diagram (b) of the ITO/ECL/CH₃NH₃PbI₃/spiro-OMeTAD/Ag PSCs based on ZnO, SnO₂ or ZnO/SnO₂ (2:1).

Figure 3. *J*-*V* characteristic for the PSC devices based on ZnO-SnO₂ ECL prepared from different mass ratio for ZnO and SnO₂ in the solution.

Figure 4. Steady state photoluminescence (PL) spectra of perovskite films: Glass/CH₃NH₃PbI₃ (blue line), Glass/ZnO/CH₃NH₃PbI₃ (black line), Glass/ZnO-SnO₂/CH₃NH₃PbI₃ (green line), and Glass/SnO₂/CH₃NH₃PbI₃ (red line).

Figure 5. Time resolved photoluminescence (TPL) spectra of perovskite films: Glass/CH₃NH₃PbI₃ (blue line), Glass/ZnO/CH₃NH₃PbI₃ (black line), Glass/ZnO-SnO₂/CH₃NH₃PbI₃ (green line), and Glass/SnO₂/CH₃NH₃PbI₃ (red line).

Figure 6. (a) Nyquist plots for the perovskite solar cells with SnO₂ (pink circles), ZnO-SnO₂ (red circles) and ZnO (blue circles) ECLs, respectively. The inset is an expanded view of the Nyquist plots at high frequency. Experimental data are shown as solid circles; the theoretical fits are shown as solid lines. (b) Equivalent circuit employed to fit the Nyquist plots.

Figure 7. The thermal stability test for (a) ITO/ZnO/CH₃NH₃PbI₃ (b)

ITO/ZnO-SnO₂/CH₃NH₃PbI₃ (C) ITO/ SnO₂/CH₃NH₃PbI₃. (1) initial condition (2) 110°C, 6 min (3) 120°C, 6 min.

Figure 8. The FT-IR spectra of the ZnO, SnO₂ and ZnO-SnO₂ films processed at low temperature.

Figure 9. Durability of the ZnO-based, ZnO-SnO₂-based and SnO₂-based PSC devices exposed to ambient air. The test was on the devices without encapsulation.

Figure 10. *J-V* characteristic (a) and IPCE spectra (b) for the highest-performing PSC devices based on ZnO-SnO₂ with (red line) and without (blue line) mp-Al₂O₃, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

Figure 7

Figure 8

Figure 9

Figure 10