

PCBM as The Interlayer of SnO₂/Perovskite for The High Performance and Stable Perovskite Solar Cells

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Abstract. Metallic oxide and the perovskite crystals easily form the surface vacancies defects at the contact interface after the perovskite solar cells (PSCs) fabrication, which usually trap the carriers of surface of semiconductor and increase the non-radiative processes, significantly against to the PSCs performance and stability. Herein, the PCBM was employed as the interlayer between SnO₂ and perovskite interfaces. The results find that the introducing of PCBM will improve the open-circuit voltage (V_{oc}) and fill factor (FF) of devices due to the surface passivation. As a result, the n-i-p PSCs based on PCBM interlayer exhibits higher efficiency of 22.05%. Furthermore, the devices also delivered a higher light stability of 96.2% of initial performance after aging 200 h aging in atmosphere without encapsulation, meanwhile the reference PSCs exhibit 88.9% of initial performance at the same condition.

Keywords: Perovskite solar cells; PCBM; interface engineering; stability

1. Introduction

Perovskite solar cells (PSCs) have attracted vast interest in the past decade due to its excellent optical-electronic properties, such as intense absorption in visible region, long charge carrier diffusion lengths and lifetimes.^{1,2} The power conversion efficiencies (PCEs) of PSCs have achieving above 25%³, since it firstly reported by Miyasaka in 2009.⁴ It have been the most potential candidates for next generation solar cells.

For the typical n-i-p PSCs, TiO₂ and SnO₂ are the popular metallic oxide electron transportation layers (ETLs) for the most efficient PSCs fabrication. SnO₂ ETL is more popular in recently, and the devices based on chemical bath method prepared SnO₂ exhibits over 25.2% efficeincy. However, it has been found that the surface metallic oxide and the contact perovskite crystals easily form the surface vacancies⁵⁻⁸ and accumulate the defects at the contact interface of ETLs/perovskite after the PSCs fabrication. The surface vacancies will introduce the defects levels within the bandgap of ETLs and perovskite, which usually trap the carriers of surface of semiconductor and increase the non-radiative processes, significantly against to the PSCs performance and carrier collection efficiency. In addition, the metallic oxide ETLs are usually catalysed by the ultraviolet light, which also form the trap states at the contact interface with perovskite and influence the stability of the PSCs under the light. To solve these obstacles, different passivation molecules as modification layers be used in the interface of ETLs/perovskite, such as the zwitterion⁹ organic polymer and small molecules^{10, 11} which interact with the surface defects and passivating the trap defects, in addition isolate the contact of perovskite and metallic oxide ETLs markedly improving the stability of PSCs. Thus, the molecule passivation and the interface isolation is useful for the metallic oxide ETLs.

Herein, the PCBM was employed as the interlayer of SnO₂ ETLs and perovskite interfaces. The results find that the introducing of PCBM will improve the open-circuit voltage (V_{oc}) and fill factor (FF) of devices due to the surface passivation. As a result, the n-i-p PSCs based on PCBM modification exhibit excellent efficiency of 22.05% with high V_{oc} of 1.113 V, which is higher than the efficiency based on the bare SnO₂ (21.15%). Furthermore, the devices also delivered a higher light stability of 96.2% of initial performance after aging 200 h aging in atmosphere without

encapsulation, meanwhile the SnO₂ based PSCs exhibit 88.9% of initial performance at the same condition.

2. Experimental section

2.1. Materials for PSCs fabrication

4-tertbutylpyridine (tbp), bis(trifluoromethane) sulfonamide lithium salt, and FK209 [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)], chlorobenzene (CB), dimethylsulphoxide (DMSO), dimethylformamide (DMF) were supplied from Sigma-Aldrich. FAI, MAI and PbBr₂ were purchased from Great Cell Solar. Lead iodide was purchased from Alfa Aesar. Spiro-OMeTAD was purchased from Merck. PCBM was supplied from lumintac. The SnO₂ nanoparticle was supplied from Alfa Aesar.

2.2. Device fabrication.

The chemically etched FTO glass was cleaned with detergent solution, acetone, and ethanol. SnO₂ nanoparticle was diluted at deionized water with a ratio of 1:4 and coated on FTO substrate at a speed of 3000 rpm for 20 s with a ramp-up of 2000 rpm s⁻¹ finally heating at 150 °C for 10 min. The PCBM layer was dissolved in chlorobenzene at various concentration of 1, 3, 5mg/mL and spin-coating on the SnO₂ layer at a speed of 4000 rpm for 20 s with a ramp-up of 2000 rpm s⁻¹ finally heating at 100 °C for 10 min. Next, the perovskite solutions (the ratio of PbI₂, MAI, FAI, PbBr₂ was 1: 0.16: 0.84: 0.11, the molar of PbI₂ was 1.38 mmol/mL, the MACl was 0.305 mmol/mL which added to the perovskite solution. The solvent was composed of DMSO and DMF (1:4) and was successively spin-coated on the substrates at 1000 rpm for 10 s and 5000 rpm for 30 s, respectively. 200 µL of chlorobenzene was dropped over 10 s at 5000 rpm. The perovskite films were annealed at 150 °C for 10 min. The HTM solution was prepared by dissolving 75 mg of Spiro-OMeTAD (Merck) with additives in 1 mL of chlorobenzene, for the new HTMs, it was prepared by dissolving 50 mg into 1 mL chlorobenzene. The following additives: 18 µL of Li-bis(trifluoromethanesulfonyl) imide from the stock solution (520 mg in 1 mL of acetonitrile), 13 µL of FK209 [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt (III) tris (bis (trifluoromethylsulfonyl)imide) (375 mg in 1 mL of acetonitrile), and 30 µL of 4-tert-butylpyridine, were added. The HTMs layers were formed by spin-coating the solution at 4000 rpm for 20 s and then deposition of the Au electrode to complete the device. All the preparative work to deposit PCBM, perovskite and Spiro-OMeTAD was performed inside the glove box filled with nitrogen.

2.3. Film and device characterization.

SEM of film was investigated using a high-resolution scanning electron microscope (Merlin, Zeiss) equipped with a GEMINI II column and a Schottky Field Emission gun. Images were acquired with an In-Lens Secondary Electron Detector. Current-voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450 W xenon lamp (Oriel) equipped with a SchottK113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cutoff filter (KG-3, Schott). The cells were masked with the active area of 0.09 cm² to fix the active area.

3. Results and discussion

We fabricated n-i-p structure PSCs consisting of FTO/ SnO₂/PCBM (3mg/mL)/perovskite/Spiro-OMeTAD/Au as illustrated schematically in Figure 1a. The Figure 1b is the corresponding cross-sectional scanning electron microscopy (SEM) of the devices. It can be found that the SnO₂/PCBM layer is very thin and nearly can not see at the SEM. For the perovskite layer, the crystal is dense and

with a high thickness of about 700 nm, which may benefit for the high performance PSCs fabrication. From the interface between perovskite and ETL, the contact seems very well, it indicates the employing of PCBM is hardly affect the contact of perovskite to ETL even the PCBM is hydrophobic.

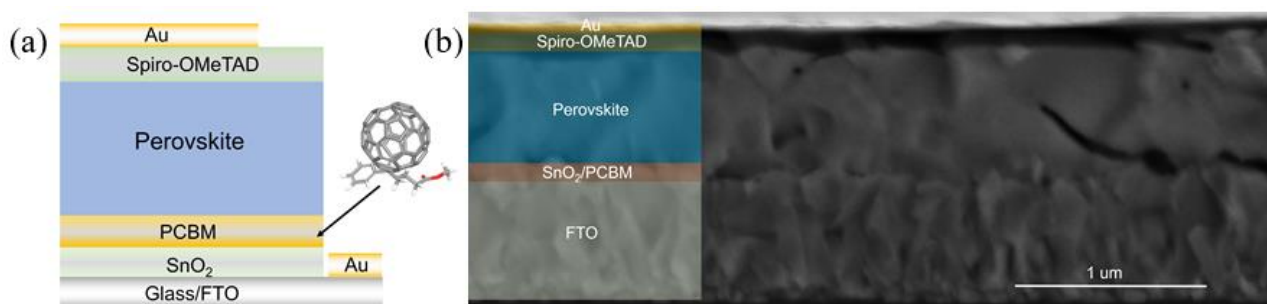


Figure 1. (a) Device structure of the PSCs with the PCBM modification; (b) the corresponding cross-sectional SEM of the devices.

To study the performance influence of PCBM on the PSCs, the current-voltage (J - V) curves were measured under AM1.5G standard light. The J - V curves of the champion devices based on various PCBM concentrations are presented in Figure 2a and their corresponding photovoltaic parameters are summarized in Table 1, as well as the statistical results of devices based on different concentrations of PCBM exhibits in Figure 2d. It can be seen that the employing of PCBM with 1, 3, 5 mg on the SnO_2 surface will enhance the efficiency of the PSCs (Figure 2d). From the champion J - V curves (Figure 2a), the reference devices exhibit a PCE of 21.15% with the low open-circuit voltage (V_{oc}) of 1.086 V, when 1 mg PCBM is spin-coated on the SnO_2 film, the V_{oc} enhance over 1.1 V without obvious change in short-circuit current (J_{sc}) and fill factor (FF). With the increasing the concentration to 3 mg, the PCE boosting to 22.05% with higher V_{oc} (1.113 V) and FF (79.4%), however, there is a little decreasing of PCE when the concentration increase to 5 mg. Thus, the enhancement of PCE certified the useful of the interlayer of PCBM which may passivate the surface trap states. Furthermore, the steady efficiency of champion device based on PCBM modification is also studied (Figure 2c), The device based on PCBM (3 mg) exhibits a stabilized PCE of 21.81% after 130 s light soaking, which is agree well with PCE from the J - V curve (22.05%). The J - V hysteresis is also important for the PSCs and it is estimated based on the hysteresis index (HI) which is given by the equation, $HI = (PCE_{RS} - PCE_{FS}) / PCE_{RS}$, where PCE_{RS} and PCE_{FS} represent the efficiency of devices for the reverse scan and forward scan in respectively (Figure 1b and Table 1). As a results, the PSCs employing PCBM presents lower HI values of 1.17% as compared to the reference devices (3.4%).

To probe the influence of PCBM interlayer on the stability of PSCs, the light stability of devices was measured under the atmosphere without encapsulation (Figure 2e). As the results, the devices based on SnO_2 exhibits lower than 90% of the initial PCE after 200 h light aging. However, when the PCBM as the interlayer between SnO_2 and perovskite, the device retains 96.2% of the initial efficiency at the same condition. It indicates the introduce of PCBM will improve the light stability which may attribute to the reduce of contact of perovskite and SnO_2 .

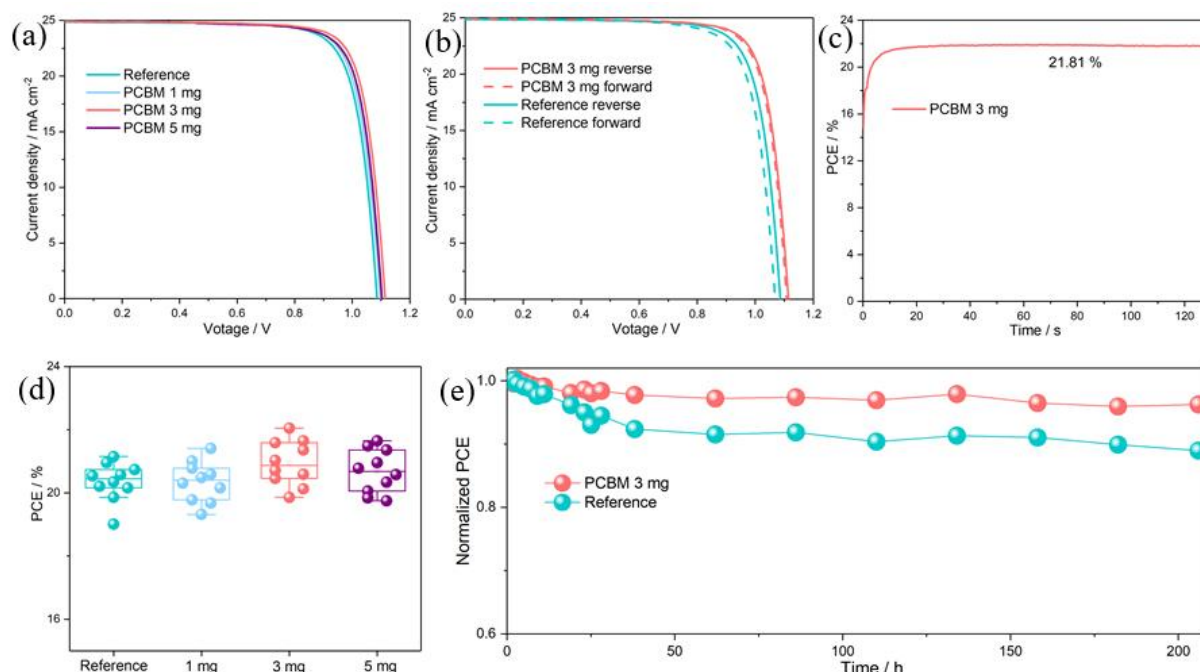


Figure 2. (a) the champion J - V curves of devices based on different concentrations of PCBM; (b) the champion J - V curves of devices based on PCBM and reference with the reverse and forward scan; (c) the steady efficiency of devices based on PCBM modification; (d) the statistical results of devices based on different concentrations of PCBM; (e) the light stability of devices based on reference and PCBM modification.

Table 1. Photovoltaic parameters of devices based on various concentrations of PCBM modification.

HTMs	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
Control Reverse	24.85	1.086	78.4	21.15
Control Forward	24.90	1.067	76.9	20.43
1 mg Reverse	24.89	1.096	78.5	21.41
3 mg Reverse	24.93	1.114	79.4	22.05
3 mg Forward	24.95	1.107	78.9	21.79
5 mg Reverse	24.91	1.103	78.8	21.65

4. Conclusions

In summary, the PCBM was successfully employed as the interlayer between SnO_2 ETLs and perovskite interfaces which significantly improved the efficiency to 22.05% due to the possible passivation of surface trap states. Furthermore, the devices also delivered a higher light stability of 96.2% of initial performance after aging 200 h aging in atmosphere without encapsulation, meanwhile the reference PSCs exhibit 88.9% of initial performance at the same condition. The improvement of the stability maybe attribute to the isolation of SnO_2 and perovskite interface.

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