

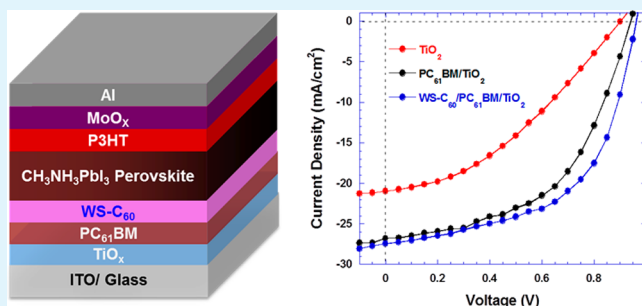
# High Performance Planar Heterojunction Perovskite Solar Cells with Fullerene Derivatives as the Electron Transport Layer

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**ABSTRACT:** In this study, we report the utilization of solution-processed high electrical conductive [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM) combined with solution-processed TiO<sub>2</sub> as the electron transport layer (ETL) to overcome extremely low electrical conductivity of solution-processed TiO<sub>2</sub> ETL in planar heterojunction (PHJ) perovskite hybrid solar cells (pero-HSCs). Due to the much more preferable electron extraction and transportation of PC<sub>61</sub>BM at the cathode side, a tremendously boosted short-circuit current density ( $J_{SC}$ ), fill factor (FF) and enhanced power conversion efficiency (PCE) are observed. To further address the wettability issues of perovskite materials on the top of PC<sub>61</sub>BM, water-soluble fullerene derivative is applied to modulate the surface of PC<sub>61</sub>BM. Consequently, further advanced FF with slightly enlarged  $J_{SC}$  and open-circuit voltage ( $V_{OC}$ ) are observed. The resulted PCE is comparable with the meso-superstructured solar cells in which high PCEs can be produced. Our studies certainly provide a simple approach to boost the efficiency of PHJ pero-HSCs.

**KEYWORDS:** high performance, perovskite solar cells, fullerene derivatives, electron transport layer, electrical conductivity, high-short circuit current



## 1. INTRODUCTION

In recent years, the organometal halide perovskite, CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, where X is a halogen atom (I, Cl, Br, or a combination of some of them) with polycrystalline structure, has been intensively developed for photovoltaic applications.<sup>1</sup> Organometal halide perovskite materials are direct bandgap semiconductors with an approximately ideal bandgap of ~1.55 eV and a high absorption extinction coefficient.<sup>2–4</sup> In addition, perovskite materials also possess ambipolar transport properties that enable both hole and electron transporting in perovskite hybrid solar cells (pero-HSCs).<sup>5,6</sup> CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> was first utilized in dye-sensitized solar cells by Miyasaka and co-workers in 2009.<sup>1</sup> Since then, CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> has been applied in a variety of other solar cell architectures.<sup>7–10</sup> On account of the long charge carrier diffusion length of perovskite materials (~1 μm in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>, ~100 nm in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>),<sup>11</sup> planar heterojunction (PHJ) pero-HSCs have been progressively developed, with a power conversion efficiency (PCE) ranging from 3% to over 15% in the past years.<sup>7–9,12–16</sup> Moreover, the simple fabrication process makes the PHJ construction appealing to large area manufacturing as compared with their meso-superstructured solar cells (MSSCs) counterparts,<sup>17,18</sup> where the high temperature sintering process of mesoporous metal oxide and the homogeneous infiltration of perovskite materials into the mesoporous electron transport material are major issues. Consequently, high efficiency PHJ pero-HSCs from low-temperature solution processing would be much more advantageous.

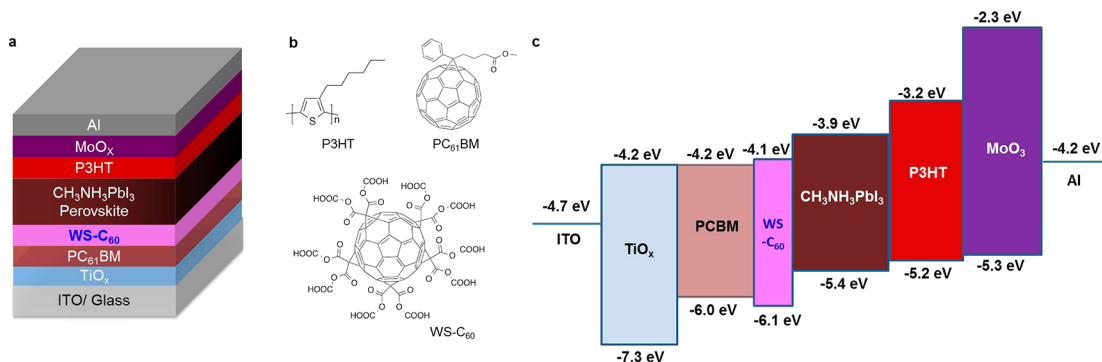
However, a severe limitation of the PHJ architecture that restricts the solar cell performance is the extremely low electrical conductivity of the compact TiO<sub>2</sub> layer (~10<sup>-11</sup> S/cm).<sup>19</sup> Charge carriers transport from perovskite materials to the cathode electrode would be drastically suppressed, insinuating the moderate short-circuit current density ( $J_{SC}$ ) and fill factor (FF). Furthermore, due to the shorter diffusion length of electrons than that of holes in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite material ( $L_{eff,e-}/L_{eff,h+} < 1$ ),<sup>20,21</sup> a more efficient electron transport layer (ETL) and electron extraction layer (EEL) would be favorable for balancing the electron and hole transport in pero-HSCs, resulting in both enhanced  $J_{SC}$  and FF. In addition, the low-temperature sol-gel processed TiO<sub>2</sub> layer showed less conformity, which generates high probability of direct contact between perovskite materials and the indium tin oxide (ITO) cathode, giving rise to massive charge carrier recombination and large leakage current.<sup>22</sup> Therefore, addressing the electron transporting issues between a perovskite material and the ETL becomes one of the top priorities for advancing the efficiency of PHJ pero-HSCs.

Herein, we report high performance PHJ pero-HSCs employing [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM) as the ETL. Due to the much higher electrical conductivity of PC<sub>61</sub>BM (~10<sup>-7</sup> S/cm)<sup>23</sup> than that (~10<sup>-11</sup> S/cm) of TiO<sub>2</sub>,<sup>19</sup> the charge transfer from CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> to the

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**Figure 1.** (a) Device structure of perovskite hybrid solar cells incorporated with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the electron extraction layer, (b) molecular structures of PC<sub>61</sub>BM, water-soluble fullerene derivative (C<sub>60</sub>-Ac<sub>10</sub>) and poly(3-hexylthiophene-2,5-diyl) (P3HT) and (c) LUMO and HOMO energy levels of the materials and the work functions of ITO and Al electrodes used to fabricate perovskite hybrid solar cells.

ETL would be much more effective, which is expected to bring about decreased electron/hole recombination at the ETL/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface. As a result, a super high  $J_{SC}$  of 26.7 mA/cm<sup>2</sup> was observed, with a FF of 52.1%, open-circuit voltage ( $V_{OC}$ ) of 0.93 V and corresponding PCE of 13.2%. However, insufficient coverage of perovskite materials arising from the poor wettability of PbI<sub>2</sub> on top of PC<sub>61</sub>BM emerged as the prime issue that sacrifices the efficiency of pero-HSCs. Thus, to address this problem, a water-soluble fullerene derivative (WS-C<sub>60</sub>) was applied to re-engineer the surface of the PC<sub>61</sub>BM layer, which not only serves to improve the wettability of PbI<sub>2</sub> on the top of PC<sub>61</sub>BM but also occludes the back transfer of holes into the cathode electrode. A high PCE of 14.6% was consequently achieved, with an enhanced  $J_{SC}$  of 27.4 mA/cm<sup>2</sup>,  $V_{OC}$  of 0.95 V and FF of 56.3%.

## 2. EXPERIMENTAL DETAILS

**2.1. Materials.** TiO<sub>2</sub> precursor, tetrabutyl titanate (TBT) and PC<sub>61</sub>BM were purchased from Sigma-Aldrich and Nano-C Inc., respectively, and used as received without further purification. Water-soluble fullerene derivative (WS-C<sub>60</sub>) was synthesized in our lab by a method reported elsewhere.<sup>24</sup> Lead iodine (PbI<sub>2</sub>) was purchased from Alfa-Aesar. Methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I, MAI) was synthesized in our lab using a method reported in the literature.<sup>25</sup> The perovskite precursor solution was prepared as the following: PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I were dissolved in dimethylformamide (DMF) and ethanol with concentrations of 400 mg/mL for PbI<sub>2</sub> and 35 mg/mL for CH<sub>3</sub>NH<sub>3</sub>I, respectively. All the solutions were heated at 100 °C for around 10 min to make sure both MAI and PbI<sub>2</sub> were fully dissolved.

**2.2. Pero-HSCs Fabrication and Characterization.** A compact TiO<sub>2</sub> layer was deposited on pre-cleaned ITO substrates from tetrabutyl titanate (TBT) isopropyl alcohol solution (concentration 3 vol %), with various thicknesses ranging from 28 to 65 nm, followed by thermal annealing at 90 °C for 60 min in ambient atmosphere. After that, a PC<sub>61</sub>BM layer of different thickness was casted on the top of the compact TiO<sub>2</sub> layer from dichlorobenzene (*o*-DCB) solution. For the pero-HSCs incorporated with the water-soluble fullerene derivative, WS-C<sub>60</sub>, ~3 nm of WS-C<sub>60</sub> was spin-coated on the top of the PC<sub>61</sub>BM layer from WS-C<sub>60</sub>/ethanol solution with a concentration of 1 mg/mL, at a spin-speed of 1000 rpm. For the PHJ pero-HSCs fabrication, the PbI<sub>2</sub> layer was spin-coated from 400 mg/mL DMF solution at 3000 rpm for 35 s, on the top of the PC<sub>61</sub>BM or PC<sub>61</sub>BM/WS-C<sub>60</sub> layer, and then the film was dried at 70 °C for 5 min. After the film cooled to room temperature, the MAI layer was spin-coated on the top of the PbI<sub>2</sub> layer from 35 mg/mL ethanol solution at 3000 rpm for 35 s, followed by transferring to a hotplate (100 °C) immediately. After thermal annealing at 100 °C for 2 h, the poly(3-hexylthiophene-2,5-diyl) P3HT layer was deposited from 20 mg/mL *o*-DCB solution at 1000 rpm for 55 s. Lastly, the pero-HSCs was finished by thermal

evaporating MoO<sub>3</sub> (8 nm) and aluminum (Al) (100 nm). The device area is defined to be 0.045 cm<sup>2</sup>.

Pero-HSCs were characterized under an AM 1.5 G calibrated solar simulator (Newport model 91160-1000) with the light intensity of 100 mW/cm<sup>2</sup>, which was calibrated by utilizing a monosilicon detector (with a KG-5 visible color filter) of National Renewable Energy Laboratory (NREL) to reduce spectral mismatch. The  $J$ - $V$  characteristics of pero-HSCs were recorded using a Keithley 2400 source meter.

The impedance spectroscopy (IS) was obtained using a HP 4194A impedance/gain-phase analyzer, under the illumination of white light with the light intensity of 100 mW/cm<sup>2</sup>, with an oscillating voltage of 50 mV and frequency of 5 Hz to 13 MHz.

**2.3. Thin Film Characterizations.** Thicknesses of TiO<sub>2</sub>, PC<sub>61</sub>BM and WS-C<sub>60</sub> were measured by tapping-mode atomic force microscopy (AFM) images using a NanoScope NS3A system (Digital Instrument), as were the surface morphologies of TiO<sub>2</sub>, PC<sub>61</sub>BM and WS-C<sub>60</sub>. It is noteworthy that measuring the thickness of WS-C<sub>60</sub>, which is under 10 nm, is difficult for direct measurement from AFM images. We prepared 20 mg/mL WS-C<sub>60</sub>/ethanol solution and spin-coated the film at 1000 rpm, whose thickness was measured to be ~60 nm by AFM images. Therefore, the film thickness from 1 mg/mL WS-C<sub>60</sub> solution was estimated to be ~3 nm. Contact angles of PbI<sub>2</sub> on the top of PC<sub>61</sub>BM and the top of WS-C<sub>60</sub>/PC<sub>61</sub>BM were measured by a KRUSS DSA100 instrument. Photoluminescence (PL) spectra were obtained with a 532 nm pulsed laser as the excitation source at a frequency of 9.743 MHz.

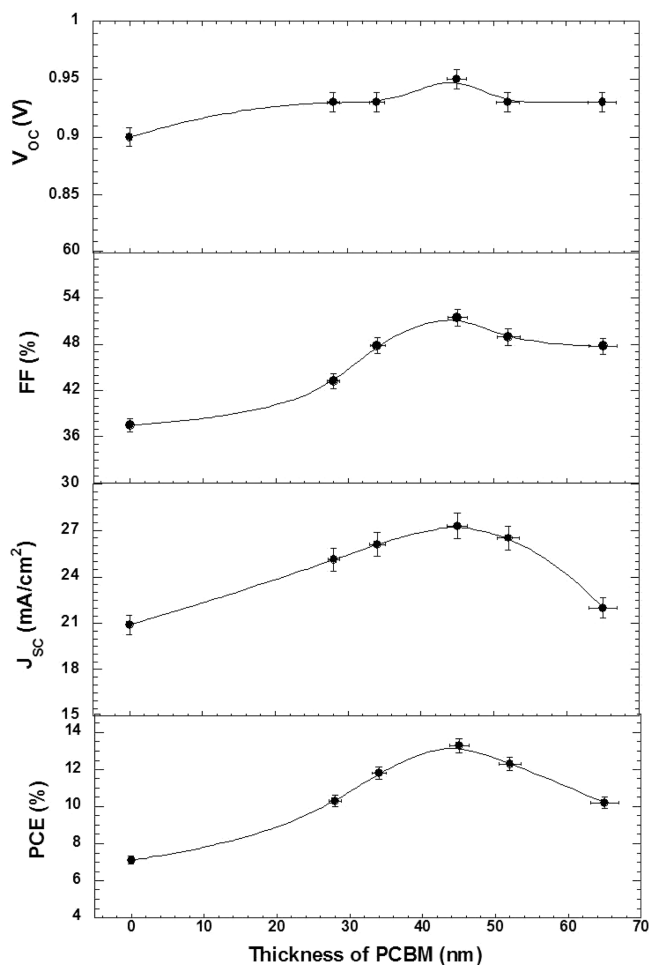
## 3. RESULTS AND DISCUSSION

Figure 1a,b presents the device structure of pero-HSCs and molecular structures of PC<sub>61</sub>BM, WS-C<sub>60</sub> and P3HT; Figure 1c displays the energy levels of the materials and workfunctions of ITO and Al electrodes used for fabrication of pero-HSCs. The tremendously increased electrical conductivity of PC<sub>61</sub>BM (~10<sup>-7</sup> S/cm)<sup>23</sup> over that of TiO<sub>2</sub> (~10<sup>-11</sup> S/cm)<sup>19</sup> combined with efficient ~0.3 eV lowest unoccupied molecular orbital (LUMO) offset between CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and PC<sub>61</sub>BM,<sup>26</sup> is expected to bring about both improved  $J_{SC}$  and FF. For the hole transport layer (HTL), considering the widely used hole-transporting material 2,2',7,7'-tetrakis(*N,N*-dip-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) needs to be dried in air,<sup>27</sup> which will sacrifice the performance of pero-HSCs, we utilize solution-processed P3HT and thermal-evaporated MoO<sub>3</sub> as the HTL and the electron-blocking layer (EBL), respectively.

We note that during the measurement of all pero-HSCs, a light-soaking effect on enhancing PCEs was observed.<sup>28-31</sup> As compared with the  $J_{SC}$  from the pero-HSCs without any illumination, we found that the  $J_{SC}$  was enhanced over 30% from the pero-HSCs with a "conventional" device structure of

ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (Figure 1a) after the pero-HSCs was illuminated about 5–10 min; under the same illumination condition, however, the  $J_{SC}$  kept a constant for the pero-HSCs with a “inverted” device structure of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/Al. Thus, we conduct the  $J$ – $V$  characteristics of pero-HSCs after the pero-HSCs was illuminated about 10 min.<sup>28–31</sup>

The performance of pero-HSCs was optimized by tuning the thickness of the PC<sub>61</sub>BM layer. The dependencies of PCE,  $J_{SC}$ ,  $V_{OC}$  and FF on the thickness of PC<sub>61</sub>BM are shown in Figure 2.

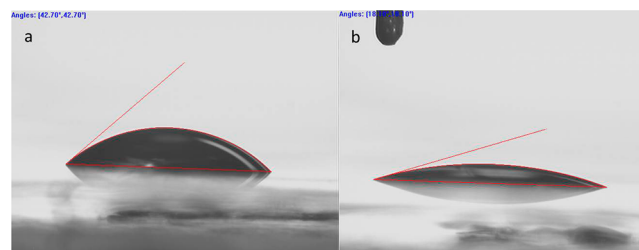


**Figure 2.** Device performance ( $J_{SC}$ ,  $V_{OC}$ , FF and PCE) of perovskite hybrid solar cells with a structure of ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al versus the thickness of PC<sub>61</sub>BM layer.

All pero-HSCs possess similar  $V_{OC}$ 's, but with different  $J_{SC}$ 's and FFs, and consequently different PCEs. Both  $J_{SC}$  and FF are dramatically enhanced along with increased thickness of PC<sub>61</sub>BM at first, reaching the highest PCE of 13.3% with a super high  $J_{SC}$  of 27.3 mA/cm<sup>2</sup>, but then dropped with further raising the thickness of the PC<sub>61</sub>BM layer. The first rising stage for both  $J_{SC}$  and FF from thickness values of ~28 to ~45 nm was attributed to the drastically augmented electrical conductivity of PC<sub>61</sub>BM than that of TiO<sub>2</sub>, leading to more efficient electron transportation from perovskite material to the cathode electrode. However, further enhancing the thickness of PC<sub>61</sub>BM layer will increase the optical interference between the incident light and the reflected light, in which the destructive interference will weaken the incident light and consequently results in diminished light reached at the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer.

Therefore, we can observe a largely decreased  $J_{SC}$  and slightly decreased FF. In addition, given that PC<sub>61</sub>BM also serves as a passivating layer on the top of TiO<sub>2</sub> (as can be elucidated by AFM images in the later context), the dark current is expected to be reduced owing to the diminished leakage current. Therefore, a slightly increased  $V_{OC}$  from 0.90 to 0.95 V can be observed from pero-HSCs incorporating with PC<sub>61</sub>BM with different thicknesses.

Even though the PCEs of pero-HSCs are dramatically improved with the incorporation of PC<sub>61</sub>BM as the ETL, the poor wettability of PbI<sub>2</sub> on the top of PC<sub>61</sub>BM would be another issue for further improvement of PCEs. As it is evidenced from Figure 3a, a large contact angle of 42.7°

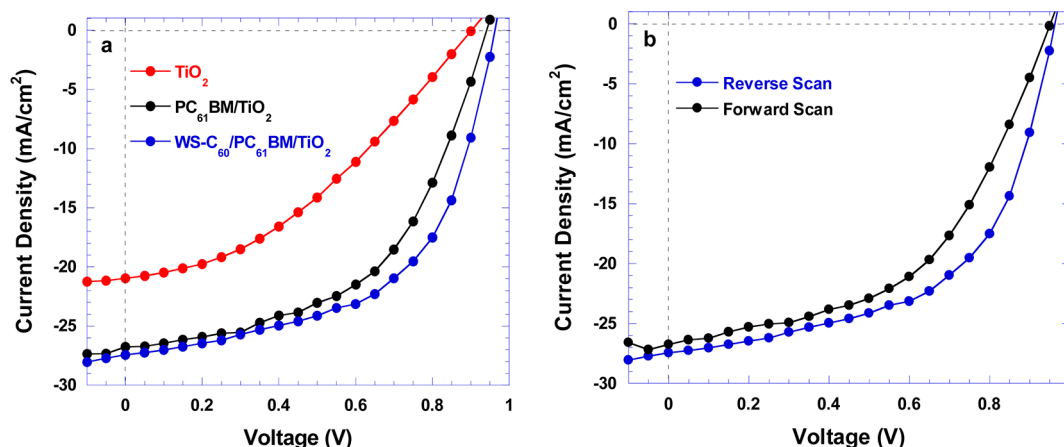


**Figure 3.** Contact angles of PbI<sub>2</sub> on the top of (a) PC<sub>61</sub>BM layer and (b) WS-C<sub>60</sub>/PC<sub>61</sub>BM layer.

observed at the PC<sub>61</sub>BM/PbI<sub>2</sub> interface would lead to insufficient coverage of perovskite materials on the top of the PC<sub>61</sub>BM layer, which generates a large leakage current and consequently results in an inferior FF. To overcome this problem, the water-soluble fullerene derivative WS-C<sub>60</sub> is used to re-engineer the surface of the PC<sub>61</sub>BM layer. It can be seen clearly in Figure 3b that full coverage of perovskite materials is expected due to the much reduced contact angle of 18.1° at the WS-C<sub>60</sub>/PbI<sub>2</sub> interface. In addition, WS-C<sub>60</sub> also acts as the hole blocking layer (HBL) to occlude the holes to be back transferred to PC<sub>61</sub>BM, reducing the electron–hole recombination at perovskite/PC<sub>61</sub>BM interface,<sup>32</sup> which contributes to higher  $J_{SC}$  and FF as well.

Figure 4a illustrates the  $J$ – $V$  characteristics of pero-HSCs with the structures of ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al, ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al and ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al. All the devices are measured under reverse scan (from  $V_{OC}$  to  $J_{SC}$ ). The pristine pero-HSCs show a  $V_{OC}$  of 0.90 V,  $J_{SC}$  of 20.9 mA/cm<sup>2</sup>, FF of 37.5% and a corresponding PCE of 7.1%. The pero-HSCs incorporated with PC<sub>61</sub>BM exhibit slightly enhanced  $V_{OC}$  of 0.93 V, dramatically enhanced  $J_{SC}$  of 26.7 mA/cm<sup>2</sup>, FF of 52.1% and consequently an enhanced PCE of 13.2%. For the pero-HSCs incorporating WS-C<sub>60</sub> re-engineered PC<sub>61</sub>BM, the most remarkable enhancement is embodied by FF, rising to 56.3%, with a slightly increased  $J_{SC}$  (27.4 mA/cm<sup>2</sup>) and  $V_{OC}$  (0.95 V); as a result, a high PCE of 14.6% is obtained. It is noteworthy that the slightly enhanced  $V_{OC}$  is in agreement with the lower highest occupied molecular orbital (HOMO) level of WS-C<sub>60</sub> than that of PC<sub>61</sub>BM (as shown in Figure 1c). A larger energy offset between the HOMO of ETL and the LUMO of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is consequently formed, which is proportional to  $V_{OC}$ . Such a high PCE is comparable to that observed from pero-HSCs with a MSSCs structure, in which high PCEs can be generated.<sup>17,18</sup>

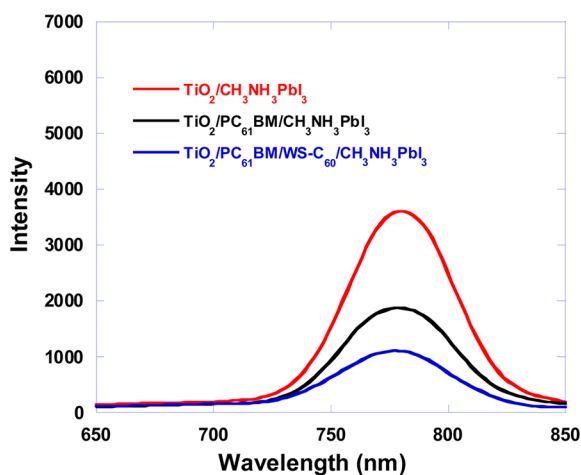
To study the hysteresis effects of devices with the structure ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al,



**Figure 4.** (a) Current–voltage characteristics of perovskite hybrid solar cells with the structures of pero-HSCs with device structures: ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (represented as TiO<sub>2</sub>), ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (represented as PC<sub>61</sub>BM/TiO<sub>2</sub>), and ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (represented as WS-C<sub>60</sub>/PC<sub>61</sub>BM/TiO<sub>2</sub>); (b) *J*–*V* characteristics under forward and reverse scan directions for the pero-HSCs with a device structure of ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al.

both forward (from  $J_{SC}$  to  $V_{OC}$ ) and reverse scan directions were conducted (as shown in Figure 4b). As shown above, pero-HSCs incorporating WS-C<sub>60</sub> re-engineered PC<sub>61</sub>BM exhibited PCE of 14.6%, with  $V_{OC}$  0.95 V,  $J_{SC}$  27.4 mA/cm<sup>2</sup> and FF 56.3%. Under forward scan, the same device showed  $V_{OC}$  0.94 V,  $J_{SC}$  26.7 mA/cm<sup>2</sup>, FF 51.3% and consequently PCE 12.9%. These are relatively consistent PCEs under different scan directions, which indicates a comparatively small hysteresis effect in the pero-HSCs incorporating WS-C<sub>60</sub> re-engineered PC<sub>61</sub>BM and consequently a decent device performance.

To have a better understanding of the largely increased  $J_{SC}$  from the pero-HSCs incorporating with PC<sub>61</sub>BM as the ETL, photoluminescent (PL) properties of three different thin films, TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> are studied. Figure 5 shows the PL spectra of TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. It was found that a more strikingly quenching effect was in TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> than in TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. This indicates a much more efficient electron transport at the PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface over that at the TiO<sub>2</sub>/



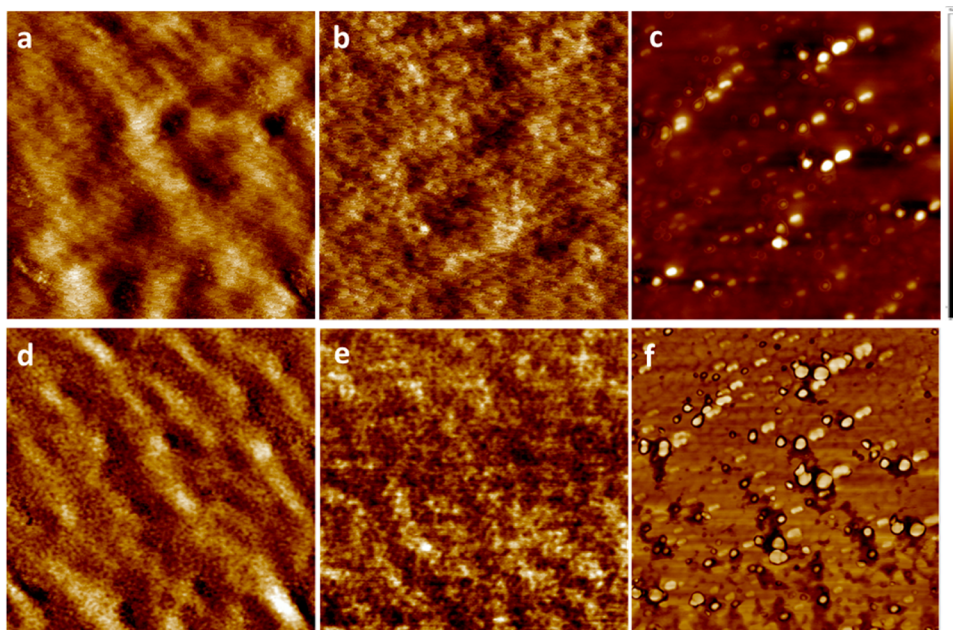
**Figure 5.** Photoluminescence (PL) spectra of TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films.

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface, confirming the role of higher electrical conductive PC<sub>61</sub>BM for favoring the electron extraction at the ETL/perovskite material interface. Remarkably, an even greater quenching effect is observed in the TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film, which demonstrates that the more homogeneous perovskite film formation ensures larger interface between the fullerene derivatives and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.

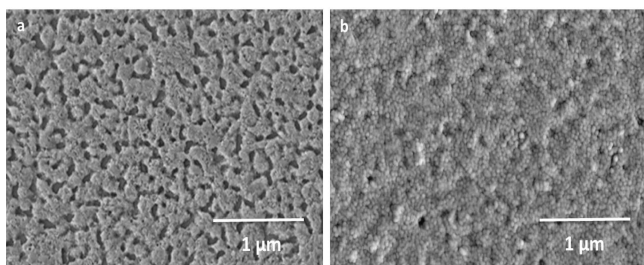
To verify the hypothesis that the TiO<sub>2</sub> surface is passivated by the PC<sub>61</sub>BM layer, AFM was used to study the surface morphology of the TiO<sub>2</sub> film, TiO<sub>2</sub>/PC<sub>61</sub>BM film and TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub> film. The height AFM images are shown in Figure 6a–c, and phase images are shown in Figure 6e–g. It is obviously that sol–gel processed TiO<sub>2</sub> showed rather uneven surface with a relatively large root-mean-square roughness (RMS) of 3.5 nm. Upon the passivation with PC<sub>61</sub>BM, the surface becomes quite smoother, with remarkably reduced RMS of 0.25 nm. Outcome of the ameliorated surface morphology was the much lessened leakage current, which consequently results in drastically boosted  $J_{SC}$ , FF and minor increased  $V_{OC}$ .<sup>33</sup> Through further modification of PC<sub>61</sub>BM surface with WS-C<sub>60</sub>, very smooth film can be observed, which is also beneficial for enhancement in solar cell performance.

Scanning electron microscopy (SEM) images were carried out to study the thin film morphology of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer influenced by the WS-C<sub>60</sub> re-engineered PC<sub>61</sub>BM layer. The PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> thin film demonstrated clearly incomplete coverage of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> on the top of the PC<sub>61</sub>BM layer (shown in Figure 7a), which is due to the poor wettability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> on PC<sub>61</sub>BM. In clear contrast, upon the surface re-engineering with WS-C<sub>60</sub>, the wettability dramatically improved, leading to a complete coverage of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> on the top of PC<sub>61</sub>BM layer. Consequently, Figure 7b exhibits a much denser and more homogeneous film for the PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer, which results in the slightly improved  $J_{SC}$  and largely enhanced FF.

The electrical conductivities of all pero-HSCs are further investigated by AC impedance spectroscopy (IS), which can provide detailed electrical properties of pero-HSCs that cannot be determined in direct current measurement.<sup>34</sup> Figure 8 presents the IS spectra of ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al, ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al and ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/



**Figure 6.** AFM height images of (a) TiO<sub>2</sub> film, (b) TiO<sub>2</sub>/PC<sub>61</sub>BM film and (c) TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub> film; AFM phase images of (d) TiO<sub>2</sub> film, (e) TiO<sub>2</sub>/PC<sub>61</sub>BM film and (f) TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub> film.

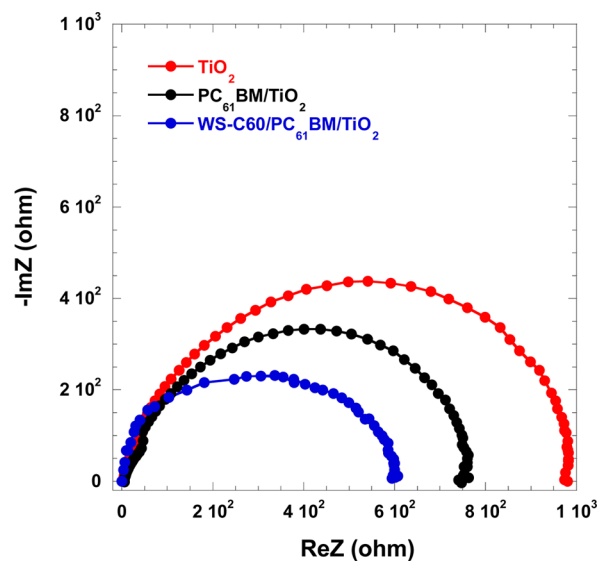


**Figure 7.** SEM images of (a) TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film and (b) TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film.

MoO<sub>3</sub>/Al. The internal series resistance ( $R_S$ ) is composed of the sheet resistance ( $R_{SH}$ ) of the electrodes, the charge-transfer resistance ( $R_{CT}$ ) inside the perovskite thin film and at perovskite material/ETL (HTL) interfaces. Because all perovskite solar cells possess the same device structure, the  $R_{SH}$  was assumed to be the same. The only difference is the  $R_{CT}$ , which arises from the different electron transport at ETL/perovskite interface. The  $R_S$  of ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al is 976 Ω, which is lowered to 750 Ω from ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al, and further reduced to 600 Ω from ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al. These results confirm the role of PC<sub>61</sub>BM as a much more efficient ETL than that of TiO<sub>2</sub>. The efficient ETL would benefit electron extraction and transporting from perovskite materials to the cathode electrode. The reduced  $R_S$  from ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al is attributed to the improved wettability of PbI<sub>2</sub> on the top of PC<sub>61</sub>BM by WS-C<sub>60</sub>, which brings about full coverage of the perovskite material and consequently better contact between perovskite materials and PC<sub>61</sub>BM ETL, resulting in high PCE.

#### 4. CONCLUSION

In conclusion, we reported the utilization of high electrical conductive PC<sub>61</sub>BM as the electron transport layer in PHJ



**Figure 8.** Nyquist plots at  $V \approx V_{OC}$  for perovskite hybrid solar cells with the structures of ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (represented as TiO<sub>2</sub>), ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (represented as PC<sub>61</sub>BM/TiO<sub>2</sub>) and ITO/TiO<sub>2</sub>/PC<sub>61</sub>BM/WS-C<sub>60</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Al (represented as WS-C<sub>60</sub>/PC<sub>61</sub>BM/TiO<sub>2</sub>).

perovskite solar cells. Through tremendously boosted  $J_{SC}$  and FF values, enhanced PCEs are obtained. By utilizing the water-soluble fullerene derivative, WS-C<sub>60</sub>, to settle the wettability issues of PbI<sub>2</sub> on the top of PC<sub>61</sub>BM, further enlarged FF values, with minor enhanced  $J_{SC}$  and  $V_{OC}$  values and a high PCE of 14.6%, are obtained. Such a high PCE is comparable to that observed from perovskite solar cells with meso-superstructures, whereas a high PCE is typically noticed. Our studies certainly provide a simple approach to boost the efficiency of PHJ perovskite solar cells.

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## Notes

The authors declare no competing financial interest.

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