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## Performance enhancement of inverted polymer solar cells with fullerene ester derivant-modified ZnO film as cathode buffer layer

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## ABSTRACT

In this paper, we reported that ZnO nanoparticles (NPs) film modified with C<sub>60</sub> pyrrolidine tris-acid ethyl ester (PyC<sub>60</sub>) was used as cathode buffer layer in inverted polymer solar cells. The resultant device with a blend of PTB7:PC<sub>71</sub>BM as photoactive materials exhibited an open-circuit voltage ( $V_{oc}$ ) of 0.753 V, a short-circuit current ( $J_{sc}$ ) of 16.04 mA cm<sup>-2</sup>, a fill factor ( $FF$ ) of 72.5%, and an overall power conversion efficiency (PCE) of 8.76%. It was higher than the control devices based on sole ZnO NPs film or ZnO: PyC<sub>60</sub> hybrid film as cathode buffer layer. It was found that the morphology improvement of ZnO/PyC<sub>60</sub> film contributed to reducing series loss and interfacial charge recombination. In addition, it improved the interfacial contact with photoactive layer. The results increased electron injection and collection efficiency, and improved  $FF$ .

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## 1. Introduction

Recently, the polymer solar cells (PSCs) have been extensively studied due to their mechanical flexibility, lightness, and ease of large-area fabrication [1–3]. The power conversion efficiency (PCE) of polymer solar cells has surpassed 10%, which demonstrates their significant applicable potential in the future [4]. It is well known that two main structures of organic solar cells (OSCs) have been developed for single junction device, including the conventional forward device structure and the inverted device structure. Compared to the forward structure which has been widely investigated, the inverted device structure gradually received more attentions in recent years since it makes the PSCs long-term stable [5–9].

To restrain charge recombination and enhance electron collection in inverted PSCs, the key point is to find the favorable cathode buffer layer materials on top of ITO electrode. Among many n-type metal oxides, the solution-processed ZnO NPs are promising candidate for cathode buffer layer due to its relatively high electron mobility, favorable environmental friendliness and stability and high transparency. Therefore ZnO has been intensively exploited in the inverted device [10,11]. However, ZnO buffer layer has several

problematic issues such as surface roughness, leakage currents, interfacial recombination and so on. The major concerns with ZnO buffer layer lie in the surface defects and the aggregation of ZnO NPs, which result in relatively low photovoltaic performance [12,13]. So more efforts should be made to modify the ZnO buffer layer and develop low-defect and uniform ZnO film so as to realize high-efficiency inverted PSCs.

In recent literatures, many methods have been applied to modify the ZnO film in the PSCs. In addition to doping metal nanoparticles into ZnO film to improve charge carrier mobility [14,15], one method is adding the polymers or organic small molecules into the ZnO solution to prepare hybrid film [13,16,17]. By this means, the voids of ZnO film can be filled in and the defects of ZnO NPs are passivated. But the incompatible nature of organic molecule with metal oxides limits these applications. Therefore, one modified strategy is implemented by coating a thin self-assembled layer on the surface of ZnO layer such as carboxylic acid-functionalized fullerene [18,19] or conjugated polyelectrolyte [5]. It can fill the surface traps to improve electronic coupling of the ZnO/organic layer, so as to improve  $J_{sc}$  and  $FF$ .

The fullerene derivatives are commonly used as electron-accepting materials in OSCs due to their high electron mobility, good solubility and the preferable compatibility with the electron-donating materials [20–23]. Meanwhile, when the fullerene derivatives are used as cathode buffer layers, they could reduce the series resistance ( $R_s$ ) of device and improve electron injection and collection. This eventually improves the  $FF$  and the  $J_{sc}$  [8,24,25] by

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decreasing the electron injection barrier between photoactive layer and electrode. Furthermore,  $C_{60}$ -based self-assembled monolayer (SAM) formed onto ZnO NPs film has been systematically investigated in the OSCs [26]. These modifiers serve multiple advantages, such as passivating surface charge traps to improve forward charge transfer, tuning the energy level offset and making up the upper organic layer morphology [27,28]. However, due to the acidic nature of the phosphonic anchoring group, the erosion of the ZnO surface could induce potential device degradation, resulting in poor device performance. So the  $C_{60}$ -based modifiers with less-acidic binding units have been explored [12,29,30]. In addition, the modifiers with ester units possess much weaker acidity and have affinity to metal oxide surfaces [26]. Moreover, the fullerenes with ester units have non-covalent interaction with the other  $\pi$ -conjugated molecules and retain the high electron mobility [22,31,32].

Herein, we demonstrate high-efficiency inverted PSCs with ZnO NPs modified by  $PyC_{60}$  as the cathode buffer layer. The inverted device achieves the PCE of 8.76% based on a blend of Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo-[1,2-b:4,5-b'] dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)-carbonyl]-thieno-[3,4-b]thiophenedi-yl]] (PTB7) and (6,6)-phenyl C71-butyric acid methyl ester ( $PC_{71}BM$ ). It is higher than those of the devices based on sole ZnO buffer layer and ZnO:  $PyC_{60}$  hybrid buffer layer. To figure out the reason of PCE improvement, the energy level property, optoelectronic properties, surface morphology of the ZnO/ $PyC_{60}$  film have been fully investigated. It is found that the film morphology of ZnO/ $PyC_{60}$  and the contact quality between ZnO/ $PyC_{60}$  and photoactive layer are improved. It leads to the increment in both  $V_{oc}$  and  $FF$ , giving the high photovoltaic performance.

## 2. Experimental section

### 2.1. Reagent and materials

Indium tin oxide (ITO) coated glass substrates were bought from CSG HOLDING CO., LTD (China) ( $R_s \leq 10 \Omega/\square$  and  $T_r \geq 83\%$ ). Electron acceptor material  $PC_{71}BM$  was purchased from ADS. And electron donor material PTB7 was purchased from 1-material Chemsitech.  $PyC_{60}$  and chlorobenzene were obtained from Sigma-Aldrich.

### 2.2. Preparation of the ZnO NPs and $PyC_{60}$ solution

ZnO nanoparticles were synthesized according to the procedures [33,34]. We used the mixed solvent (methanol:chloroform = 2:1 V/V) to disperse the nanoparticles to obtain a sol with, on average,  $15 \text{ mg mL}^{-1}$  ZnO. The  $PyC_{60}$  solutions with different concentrations were prepared by dissolving the  $PyC_{60}$  with the chloroform. The hybrid buffer layer was obtained from spin-coating blend solution (ZnO NPs and  $PyC_{60}$ ) with weight ratio (10:2  $\text{mg mL}^{-1}$ ). The blend solution was prepared by mixing the respective solutions of ZnO NPs ( $15 \text{ mg mL}^{-1}$ ) and  $PyC_{60}$  ( $10 \text{ mg mL}^{-1}$ ).

### 2.3. Device fabrication and characterization

The inverted PSCs herein have a structure of ITO/(ZnO/ $PyC_{60}$  or ZnO NPs or ZnO:  $PyC_{60}$ )/PTB7: $PC_{71}BM$ /MoO<sub>3</sub>/Al. The devices were fabricated on ITO-coated glass substrates which were cleaned by sequential ultrasonic baths of detergent, deionized water, acetone and isopropanol. The substrates were dried with nitrogen stream and then exposed to UV-ozone for 30 min. The ZnO film annealed at 80 °C for 10 min, giving the thickness of 25 nm. To modify ZnO film, the  $PyC_{60}$  solutions were spin-coated on ZnO film at 2500 rpm for 60 s and the resultant ZnO/ $PyC_{60}$  film was placed

under the vacuum for 10 min. The photoactive layer of PTB7: $PC_{71}BM$  (10:8 in weight ratio) was prepared via spin-coating from chlorobenzene solution at 2000 rpm for 120 s. Finally the device fabrication was completed by thermal evaporation of 10 nm of MoO<sub>3</sub> and 100 nm of Al under vacuum with a base pressure of  $1 \times 10^{-6}$  mbar. The device area was  $0.04 \text{ cm}^2$ . The  $J$ - $V$  characteristics were measured with a Keithley 2400 source measure unit under AM 1.5G irradiation ( $100 \text{ mW cm}^{-2}$ ).

### 2.4. Cathode buffer layers characterization

Optical transmittance spectra were measured in a UV-3300 spectrophotometer. The surface morphology and the film roughness of the specimens were characterized by scanning electron microscopy (SEM) operated at an acceleration voltage of 8 kV (S-4800). Atomic force microscope (AFM) measurements were operated in tapping mode using a Veeco dimension V atomic microscope. Scanning Kelvin probe microscopy (SKPM) measurements were carried out on an AFM equipment with the standard SKPM mode. The external quantum efficiency (EQE) was performed by the IQE200TM data acquisition system.

## 3. Results and discussion

### 3.1. Photovoltaic device structure and energy level diagram

The inverted device structure is shown in Fig. 1a along with the chemical structure of  $PyC_{60}$  which has three ester groups. To visualize the energy level relationship of photoactive materials as well as ZnO/ $PyC_{60}$  film, cyclic voltammetry (CV) was carried out to investigate the electrochemical properties of  $PyC_{60}$  and  $PC_{71}BM$  (see Fig. S1 in the Supporting information). The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of  $PyC_{60}$  are  $-4.14 \text{ eV}$  and  $-5.83 \text{ eV}$ , respectively. The energy levels of  $PC_{71}BM$  are also determined as  $-4.04 \text{ eV}$  and  $-5.74 \text{ eV}$ , respectively. The electronic energy levels of PTB7 and MoO<sub>3</sub> were obtained from the literatures [9,35]. Fig. 1b displays the corresponding energy level diagram of the components in the device. It is obvious that the LUMO level of  $PyC_{60}$  is just in between

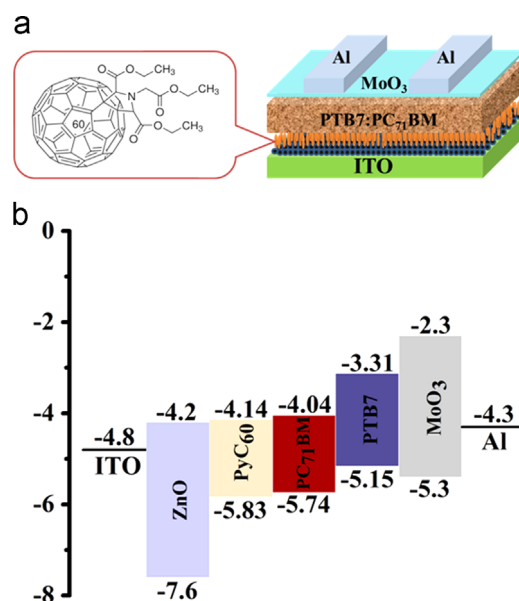


Fig. 1. (a) Device structure of the inverted PSCs with the bilayer film of ZnO/ $PyC_{60}$  as cathode buffer layer. (b) The corresponding energy level diagram of the components of the device.

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