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Amphiphilic fullerene derivative as effective interfacial layer for inverted polymer solar cells

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ABSTRACT

Amphiphilic fullerene derivative with poly(ethylene glycol) chain (C60-PEG) was applied as effective interfacial layer to improve the performance of inverted polymer solar cells. C60-PEG could not only be used as cathode buffer layer alone by replacing ZnO, but also be used as a self-assembled monolayer to modify ZnO. C60-PEG can tune energy level alignment and improve the interfacial compatibility between active layer and ITO or ZnO. Moreover, due to the strong interaction between ZnO nanoparticles and PEG chain, C60-PEG can passivate the surface defects and traps of ZnO, and facilitate the charge selective and dissociation. Consequently, inverted polymer solar cells based on thieno[3,4-*b*]thiophene/benzodithiophene (PTB7):[6,6]- phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) present a PCE of 6.6% by incorporating C60-PEG into as cathode buffer layer. Moreover, an improved PCE of 7.4% with good long-term stability in air were further achieved by using C60-PEG/ZnO interlayer. In this work, C60-PEG could be prepared by solution process at room temperature without additional annealing, which shows the potential in large-scale printed polymer solar cells.

1. Introduction

The polymer solar cells (PSCs) have been researched as a promising alternative to conventional silicon-based solar cells in the past decade owing to their mechanical flexibility and large area roll-to-roll manufacturing at low temperatures [1–4]. Nowadays, the highest power conversion efficiency (PCE) of PSCs exceeds 11% [5]. It is believable that PSCs could be applied in our lives widely. In order to further improve the performance of PSCs, various efforts were adopted, such as designing efficient active materials [6–8], developing effective processing technique [5,9,10], and using suitable device structure [11,12]. Meanwhile, interface engineering is crucially important in improving the performance of PSCs. Interfacial layers possess multiple functions, for example, tuning the energy level alignment [13,14], adjusting the light absorbing [15,16] and improving the interfacial stability [17]. Generally, interfacial materials contain conducting polymer [4,18], metal oxides [19–21], conjugated polymer electrolytes [12,22], carbon nanomaterials [23–25] and crosslinkable materials [26].

Among them, fullerene-based interfacial materials were used widely as good cathode buffer layer (CBL) due to their special chemical compatibility to active layer. Some fullerene derivatives are blended with active layer, then forming a buffer layer on the top of active layer spontaneously, like fullerene derivative with a fluorocarbon chain [27], fullerene with poly(ethylene glycol) chain [28] and amine-based fullerene [29]. However, the drawback of the fullerene-based CBL is the relatively low inherent conductivity. Therefore most of fullerene-based interfacial materials are applied as self-assembled molecular layer (SAM) to modify the zinc oxide (ZnO) but used alone, such as phosphonic acid-anchored C60 [30], carboxylic acid-anchored C60 [25], phenyl-C61-butyric acid·(PCBA) [31] and so on. Although ZnO is a potential CBL with relatively high electron mobility, the compatibility between organic polymer and inorganic metal oxide should not be ignored. In this case, a good solubility is particularly important for fullerene interfacial materials to be used as SAM.

Herein, amphiphilic fullerene derivative C60-PEG was synthesized by modifying $PC_{61}BM$ with hydrophilic poly(ethylene glycol) side chain. C60-PEG could not only be used as CBL alone to show a comparable performance to ZnO, but also act as a layer of SAM to modify ZnO with a better performance. C60-PEG can tune energy

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level alignment and improve the interfacial compatibility between active layer and ITO or ZnO. Moreover, C60-PEG can passivate the surface defects and traps of ZnO, and facilitate the charge selective and dissociation. As a result, inverted polymer solar cells based on thieno[3,4-b]thiophene/benzodithiophene (PTB7) [6,6]:- phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) with C60-PEG as CBL presented a comparable PCE of 6.6% to ZnO. Meanwhile, a further enhanced PCE of 7.4% with good long-term stability in air was achieved when C60-PEG was employed as modification layer. In addition, C60-PEG could be prepared by spin coating at room temperature without annealing, which provides the possibility for large-area printed PSCs.

2. Experimental

2.1. Synthesis of C60-PEG

C60-PEG was synthesize by Steglich esterification according to the literature [32]. At first, PCBM was hydrolyzed to get [6,6]-phenyl-C_{61}-butyric acid (PCBA) [33]. Then, a blend solution was obtained by dissolving PCBA (0.1 g, 0.112 mmol) and PEG (0.456 g, 0.076 mmol) in the mixed solvent of 1,2-dichlorobenzene and methylbenzene (V:V = 1:1), and the solution was sonicated for 1 h to dissolve PCBA completely. Triphenylphosphine (0.08 g, 0.290 mmol) and the diethyl azodicarboxylate (0.055 g, 0.290 mmol) was added dropwise to the solution. The reaction was held at room temperature for two days. At last, the products were purified by column chromatography with ethyl acetate and methyl alcohol.

2.2. Device fabrication

ITO conductive glass (35 Ω cm^{-2}) were cleaned by alcohol, detergent, deionized water and isopropyl, then dried by N_2 flow in sequence. Before the spin-coating of cathode buffer layers, ITO substrates were treated by plasma 15 min. In this work, ZnO was synthesized by the hydrolysis of precursor at 200 °C for 40 min [34]. C60-PEG was dissolved in $CH_3OCH_2CH_2OH$ (10 mg/ml), and was spin-coated on top of ITO (2000 rpm) or ZnO (6000 rpm) without annealing. After that, the blended solution P3HT:$PC_{61}BM$ or PTB7:$PC_{71}BM$ was spin coated on top. Finally, anode buffer layer MoO_3 (7 nm) and anode Ag (90 nm) was prepared by thermal evaporation. Current-voltage (*J-V*) characteristics were tested using Keithley 2400 Source Meter in the dark and under simulated AM 1.5 G (100 mW cm^{-2}) irradiation (Abet Solar Simulator Sun2000). Incident photon-to-current efficiency (IPCE) were measured under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode.

2.3. Characterizations

PerkinElmer Lambda 750 spectrophotometer was performed to research the ultraviolet–visible (UV–vis) absorption spectra. Hitachi F-7000 spectrofluorophotometer was carried out to study photoluminescence (PL). The morphology images of ZnO, C60-PEG and ZnO/C60-PEG were obtained from atomic force microscope (AFM) (Digital Instrument Nanoscope 31) test. Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurements were realized by employing AXIS-ULTRA DLD spectrometer (Kratos Analytical Ltd.) under monochromatic light source of He (I) (21.2 eV). The thicknesses of all the layers were measured by surface profilometry (Alpha-Step-IQ). JC2000A contact angle instrument was used to measure the water contact angle.

3. Results and discussion

The chemical structures of active materials and C60-PEG employed for device preparation and the inverted device architecture with the schematic diagram of cathode buffer layer are presented in Fig. 1. The synthetic details of C60-PEG are described in experimental section. As we reported previously [35], C60-PEG has a good air stability and a good solubility in alcohols and organic solvents. Due to the hydrophilic PEG side chain, the water contact angle of ZnO/C60-PEG decreased in contrast with that of bare ZnO (Fig. S1). In this paper, ZnO modified by C60-PEG is noted as ZnO/C60-PEG for easily describing.

UV/Vis absorption profiles of the samples are shown in Fig. S2. C60-PEG CBL has an extremely low absorption in the Vis-NIR wavelengths. The same absorption around 378 nm for ZnO and ZnO/C60-PEG is assigned to the usual band-edge emission in the UV. At the same time, the transmittance of C60-PEG and ZnO/C60-PEG CBLs are comparable to that of ITO (Fig. S3). It is proved that C60-PEG has a suitable optical property to be used as CBL for inverted PSCs.

Atomic force microscopy (AFM) was used to look into the morphology of different CBL and the height images are displayed in Fig. 2. Compared to ZnO (Fig. 2a), bare C60-PEG shows a different morphology with an increased root-mean-square (RMS) roughness value of 3.8 nm (Fig. 2b). When the surface of ZnO was modified by C60-PEG, the morphology changed to homogeneous network structure (Fig. 2c). There is a strong interaction between ZnO nanoparticles and PEG molecular chain [36], which drives the hydrophilic and oxygen-rich PEG side chain to the ZnO surface. In this sense, C60-PEG molecular moved and formed the homogeneous network film spontaneously. Further spin coating the active layer on the top of C60-PEG or ZnO/C60-PEG, the P3HT:$PC_{61}BM$ represented a smooth film.

To research the origin of the different morphology for C60-PEG on ZnO and ITO, X-ray photoelectron spectroscopy (XPS) was carried out on three CBLs. The O 1s XPS spectrum of bare ZnO exhibits two typical peaks, located at about 530.0 eV and 531.4 eV (Fig. 3a). The peak at lower binding energy corresponds to the Zn–O bonds [37]. The other peak at higher binding energy is ascribed to oxygen atoms from hydroxyl oxygen [37,38]. Besides the two peaks from ZnO, an additional peak (~532.5 eV) from C60-PEG appears for O 1s XPS spectrum of the ZnO modified by C60-PEG, which associated with O-C-O. Due to the long PEG side chain, the main peak for O 1s XPS spectrum of C60-PEG is originated from O-C-O. The O 1s peak from carboxyl groups (COO-) [39] may be included in the wide peak of O-C-O, so it cannot be distinguished in the O 1s spectrum. Due to the C60-PEG on top, the peak at 530.0 eV for Zn-O of ZnO/C60-PEG is weaker than that of pristine ZnO. Fig. 3b presents the C 1s XPS spectra of ZnO, C60-PEG and ZnO/C60-PEG. It is found that all the samples have two peaks ~285 eV (C–OR, R = C_2H_5) and ~288.5 eV (COOR), which is assigned to the C atoms of carbonyl groups [40]. Compared to ZnO, the different peak at ~286.2 eV of C60-PEG and ZnO/C60-PEG for O-C-O is attributed to aromatic carbons from C60-PEG [40,41]. The atomic concentrations of carbon, oxygen and zinc in all the samples based on the C 1s, Zn 2p and O 1s XPS spectra are summarized in Fig. 3c. C60-PEG possesses the highest atomic concentrations of carbon, oxygen because of its chemical structure. The atomic concentrations of carbon for ZnO/C60-PEG is higher than that for bare ZnO, but the atomic concentrations of oxygen is lower. When C60-PEG was spin coated on the top of ZnO, the hydrophilic and oxygen-rich PEG side chain tend to the ZnO surface, leaving the hydrophobic and carbon-rich fullerene cage facing toward the opposite direction. In that case, more carbon and less oxygen were detected. Meanwhile, the photoluminescence (PL) was performed to study the function of C60-PEG on the surface