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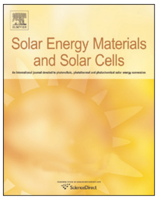

Zinc oxide: Conjugated polymer nanocomposite as cathode buffer layer for solution processed inverted organic solar cells

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ABSTRACT

Cathode buffer layer (CBL) is one of the key issues influencing the performance of organic solar cells. In this article, a nanocomposite of zinc oxide nanoparticles (ZnO) together with a conjugated polymer, poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctyl)-fluorene] (PFN) was developed, and used as the CBL for solution processed inverted organic solar cells (OSC). In comparison with the bare ZnO, PFN or ZnO/PFN stacked layer, the ZnO:PFN nanocomposite CBL employing device showed superior device performance, in particular significantly improved fill factor. Optimized power conversion efficiency (PCE) of P3HT:$PC_{61}BM$ and PTB7:$PC_{61}BM$ device using ZnO:PFN composite CBLs reached to 3.56% and 7.17%, respectively. Influences of the mixing ratio and the layer thickness of the ZnO:PFN nanocomposite CBL on solar cell performance were carefully studied, and results indicated that ZnO:PFN CBL showed a wide tolerance of blend ratio and layer thickness. In particular, no obvious thickness dependent-device performance was found, even when the CBL layer thickness was higher than 125 nm, providing a good printing processibility of the nanocomposite. Photoelectron spectroscopy, photoluminescence, as well as electric conductivity of the ZnO:PFN films were studied, and the results were compared with that of the other three reference CBLs. Results demonstrated that the interaction between ZnO and PFN decreases the work function of the blended film, leading to a more favorable energy level alignment for electron injection at the interface. Analysis on the dark J–V curves of the solar cells revealed that device using ZnO:PFN CBL had the best diode characteristics including lowest reverse saturated current density (J_0), ideal factor (n), and series resistance (R_s), and highest shunt resistance (R_{sh}). Such an improvement was ascribed to the defect passivation by the conjugated polymer, which led to an improved charge carrier selectivity of the CBL and consequently enhanced the FF of the solar cells. In addition, long-term stability of organic solar cells was also improved by using ZnO:PFN nanocomposite as the CBL. The current work provides a valuable guideline for the development of high performance cathode buffer layer material for printable organic solar cells.

1. Introduction

Organic solar cells have attracted wide research attentions owing to their advantages of flexibility, light-weight, low cost and ease of large-area fabrication relative to conventional inorganic solar cells. Nowadays, large scale roll-to-roll fabrication of organic solar cells has achieved rapid development both for single and tandem model devices [1–5]. It was proved that organic solar cells with an inverted architecture, where ITO electrode is used as cathode, are more ambient stable and more suitable for large-scale printing process [6–8]. However, the work function of ITO is about 4.8 eV, which is unfavorable for electron extraction. ITO electrode is therefore usually modified by a cathode buffer layer (CBL) to decrease the work function in inverted organic solar cells [9]. Commonly used CBLs include transparent metal oxides [10], water/alcohol soluble polyetherimide (PEI) derivatives [11], and conjugated polymer electrolytes (CPE) [12]. Among various metal oxides, ZnO is one of the most widely used CBL materials in organic solar cells because of its high electron mobility, high visible transparency, easy of fabrication, as well as environment friendly and excellent stability [13]. A variety of low temperature solution processable ZnO colloidal inks have been developed to realize solution-processing of organic solar cells. However, ZnO

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colloidal films often presented rough surface morphology with large aggregations, which led to un-favorable interface between CBL and the photoactive layer [14]. In addition, the solution-processed ZnO colloidal is general un-stoichiometry with high densities of surface defects, which would cause increased charge recombination rate at the intra-gap state and consequently decrease the device performance [15]. In the meanwhile, the conductivity of ZnO was found to be highly dependent on the absorption and desorption of surface oxygen [16], and UV illumination soaking was often applied to achieve the best device performance [16,17].

Aiming to further improve the performance of ZnO CBLs-based organic solar cell devices, various surface treatments on ZnO film have been tested. As examples, the PEI derivatives or CPEs, which have been used as the CBL alone in organic solar cells, were proved to be able to improve the solar cell performances when they were coated on the top of ZnO layer [7,15,18,19]. However, such a layer treatment with polymeric materials can only modify the top surface of the ZnO film, while the internal defects are far away to be passivated. Furthermore, due to the low conductivity of the polymer, device performances were found to be highly dependent on the thickness of the polymer layer, and the optimized layer thickness was mostly limited to several tens of nanometers, featuring an incompatibility with large area printing process [20]. Treating the ZnO layer with self-assembled small organic molecule (e.g. C_{60} derivatives) is another successful way to passivate the surface defects of ZnO [21]. However, such a strategy can only passivate the defects of the ZnO top surface as well. Recently, Jin et al. reported a new modification method of treating ZnO with ethanedithiol (EDT). Results indicated that ethanedithiol could effectively remove the surface defects of the ZnO nanocrystal films by forming zinc ethanedithiolates [22]. Nevertheless, a post-annealing step at 150 °C for 30 min was required to remove excess of EDT molecules, and thus might limit the application of this method in flexible substrates. So there is still an urgent need to develop novel cathode buffer layer materials that is compatible with future printing processing.

Recently, polymer:metal oxide nanocomposite films were reported as effective electrode buffer layer in organic solar cells, which possessed advantages of easy of fabrication, good film forming ability and less thin film defects [14,23–25]. For example, Barth et al. reported the use of ZnO:PVP composite in organic solar cell [14]. By using this ZnO:PVP nanocomposite CBL, high device performance was achieved without post-UV illumination, whereas such a post-UV treatment was necessarily for device using bare ZnO as the CBL to remove the "S-shape" kink. Another example is ZnO:poly(ethylene oxide) (PEO) composite. By using ZnO:PEO nanocomposite, charge carrier recombination rate was decreased in solar cells, and the short circuit current (J_{SC}) and fill factor (FF) were considerably improved consequently [26]. More recently, Xie et al. reported an excellent ZnO based nanocomposite incorporating phosphonate-functionalized polyfluorene (PFEP) for use as the CBL in organic solar cells. High device performance and less layer thickness sensitivity were found for ZnO:PFEP based solar cells [24]. During the submission of this article, nano composites of fullerene-end-capped poly(ethylene glycol) (PEG-C_{60}) with ZnO [27], and polyethylenimine (PEI) with ZnO [28] were also reported as the cathode interfacial layers for use in organic solar cells. Interestingly, although poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctyl)-fluorene] (PFN) has been widely used as the cathode buffer layer or metal oxide surface modifier in organic electronic devices [12], there was only one paper that reported the use of ZnO and PFN composite as the CBL in organic solar cells [25], where the "kinked" current density–voltage (*J*–*V*) curve found in PFN-based device was eliminated by using such a blended interfacial layer. However, neither deep insight in the properties of such a composite film, nor the mechanism for the enhanced device performance was reported.

In this contribution, the ZnO:PFN nanocomposite was developed by simply mixing these two components together. Inverted organic solar cells using the composite CBLs exhibit superior device performance when compared with devices using bare ZnO, PFN or ZnO/PFN stacked layer. High device performance was achieved using this ZnO:PFN nanocomposite as the CBL without high temperature post-thermal annealing. In particular, the device performance was found to be less CBL thickness dependence for the ZnO:PFN based devices. In the meanwhile, photoelectron spectroscopy, photoluminescence, as well as electric properties of the ZnO:PFN composite films were systematically studied to get a full view of this kind of blended materials.

2. Experimental sections

2.1. Materials

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS Clevios PVP AI 4083) was purchased from Heraeus Precious Metals GmbH & Co. KG. Regioregular poly(3-hexylthiophene) (SMI-P3HT, $Mn=5.0\times10^4$ g/mol, PDI=1.7, regioregularity Rr=95%) was purchased from Solarmer Energy, Inc. (Beijing). Poly[[4,8-bis[(2-ethylhexyl]oxy]-benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexl)-carbonyl]thieno [3,4-b]thiophenediyl]] (PTB7) was purchased from 1-Material. Phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) was purchased from Solenne B.V. Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctyl)-fluorene] (PFN, Mn=9300 g/mol, PDI=1.4) was provided by Sunatech Inc.

2.2. The preparation of ZnO:PFN composite inks

ZnO colloidal particles were synthesized through the reaction of KOH and $Zn(OAc)_2$ in methanol solvent as reported by Beek et al. [29]. The ZnO colloidal particles were precipitated 3 times in methanol by centrifugation and finally dispersed in a mixture solvent of methanol, n-butanol, and chloroform with a concentration of 10–60 mg/mL. PFN was dissolved in methanol in 1–4 mg/mL with addition of 0.07% volume ratio of acetic acid. The ZnO:PFN composite inks were prepared through mixing the ZnO and PFN inks with different volume ratios, and the weight ratios between these two components reported herein were calculated accordingly.

2.3. Films characterization

The film thickness of the solution-processed ZnO-based CBLs (ZnO, ZnO:PFN) was measured using an AlphaStep profilometer (Veeo, Dektak 150). An average thickness error of 3 nm was taken into account since the surface was not totally homogenous. The thickness of the PFN layer was calculated from the absorbance of the thin film according to a linear relationship between layer thickness and the absorbance. The transmittance and UV–vis absorption spectra were recorded by the Lamada 750 UV/vis/NIR spectrophotometer (PerkinElmer). Steady state photoluminescence spectra of the different CBLs were recorded by the F 4600 fluorescence spectrophotometer (Hitachi), under the excitation of 390 nm. Atomic Force Microscopy (AFM) images were recorded by Dimension 3100.