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Enhanced polymer solar cells efficiency by surface coating of the PEDOT: PSS with polar solvent

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Abstract

Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) films were post-treated with polar solvent dimethylsulfoxide (DMSO) by spin-coating method and polymer solar cells (PSCs) based on poly [N-9″]-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT) : [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) were fabricated to investigate the effect of the treatment. By post-modifying the PEDOT: PSS layer, the conductivity of the PEDOT: PSS film was largely improved. Using electrochemical impedance spectroscopy (IS) we observed that the series resistance of the device decreased greatly after the treatment. With DMSO-treated PEDOT: PSS transport layer, the power conversion efficiency (PCE) of the PSC based on PCDTBT: $PC_{71}BM$ raised from 5.95% to 6.52% with both increase in Jsc and FF. We systematically studied charge transport property via space-charge-limited-current (SCLC) and our results suggest that the increment in device efficiency can be attributed to the increased hole-mobility and thus more balanced charge transport benefits the enhancement of polymer solar cell efficiency. We also noted that if measured without a shadow mask much more overestimation will take place in the DMSO-treated device as a result of lateral electrical conduction. We suggest that when we apply the highly conductive PEDOT: PSS layer in the PSCs, careful measurement should be carried out to avoid inaccuracy.

Keywords: Polymer solar cell; PEDOT: PSS; Dimethylsulfoxide; Charge transport

1. Introduction

Over the past decades, polymer solar cells have attracted remarkable attention due to their advantages of low cost, light weight and good mechanical flexibility as well as easy processability (Hoppe and Sariciftci, 2004; Dennler et al., 2009; Li et al., 2012). And extensive efforts have been directed toward this field from designing and synthesizing novel polymers (Chen and Cao, 2009; Cheng et al., 2009; Gunes et al., 2007; Scharber et al., 2006) to optimizing the fabrication of the devices (Krebs, 2009; Kim et al., 2006). Hitherto, power conversion efficiency of PSCs in laboratory scale has exceeded 10% paving a promising way for future commercialization (You et al., 2013). PEDOT: PSS, an electro-conductive polymer solution, has been widely used as a hole transport layer (HTL) in solar cell devices because of its high transparency in the visible region, good thermal stability, high mechanical

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stability, strong hole affinity and high work function (Lim et al., 2014). However, the PEDOT: PSS naturally suffers from low conductivity (less than 1 S/cm) and thus inevitably limits the performance of the PSCs (Kim et al., 2011). Several methods have been implemented to promote its conductivity including: the addition of a suitable percentage of solvents such as surfactant (Fang et al., 2011), glycerol (Lee et al., 2009), ethylene glycol (Li et al., 2015), dimethyl sulfoxide (Thomas et al., 2014), acids (Song et al., 2013; Xia and Ouyang, 2012), graphene oxide (Yang et al., 2015) and isopropanol (Zhang et al., 2014); immersing the films in a polar organic solvent like ethylene glycol (Kim et al., 2012) and DMSO (Unsworth et al., 2014). Through these approaches, the conductivity of PEDOT: PSS was successfully increased by up to 2 or 3 orders of magnitude. It is well accepted that PEDOT: PSS aqueous dispersions are of low conductivity because the PSS chains are rather insulating (Lim, 2013). Special attention has been paid to the variation of the PEDOT: PSS, but rare of the literature discuss about charge transport property in detail and the mechanism about how each method affects the device is still under debate.

In this article, we adapted the polar organic solvent DMSO to modify the prepared PEDOT: PSS films by spin-coating and successfully improved their conductivity. As a consequence, we obtained enhanced power conversion efficiency of PCDTBT: $PC_{71}BM$ based solar cells from 5.95% to 6.52%, with simultaneous increase in short current density (Jsc) and fill factor (FF). We also measured charge carriers' mobility via SCLC and systematically investigated the transporting mechanism with this treatment.

2. Experimental

2.1. Materials and reagents

PEDOT: PSS aqueous solution (Clevious P VP AI 4083) was purchased from H. C. Starck. (Germany). $PC_{71}BM$ (purity 99.5%) was acquired from American Dye Inc. and used as received. PCDTBT ($M_n = 95$ kDa; $M_w = 152$ kDa; PDI = 1.6) was synthesized ourselves according to the literature (Blouin et al., 2007). All other reagents and chemicals were bought from Sigma–Aldrich and used without further purification. Patterned Indium Tin Oxide (ITO) glass (15 mm × 15 mm, 10 Ω/sq) substrates were received from Nanbo Co. Ltd. (China).

2.2. Preparation and characterization of the PEDOT: PSS films

First, ITO substrates were sequential ultrasonic cleaned in detergent, acetone, isopropanol, deionized water and alcohol. And they were dried under nitrogen followed by an ultraviolet-ozone treatment to remove residual organics. PEDOT: PSS solution was filtered through a 0.45 μm PTFE filter and spin coated on the ITO glass at 3500 rpm for 40 s with a thickness of 45 nm approximately. These substrates were then annealed at 150 °C for 30 min on a hot plate in ambient atmosphere. The samples were transferred to a glove box for subsequent procedures. Solvent treatment was performed by spin-casting 25 μl DMSO onto the prepared PEDOT: PSS film at 3000 rpm for 40 s. The films were dried at 100 °C for 15 min. All films were allowed to cool down to room temperature before following processes were performed.

The surface roughness and morphology images of the films were characterized using atomic force microscopic (AFM; Veeco Dimension 3100) by tapping mode. The thickness of the PEDOT: PSS films was estimated with an Alpha D-120 stylus profilometer (KLA, Tencor, USA)

2.3. Fabrication and characterization of polymer solar cells

The mixture of PCDTBT:$PC_{71}BM$ (1:4, wt%) at a concentration of 7 mg/ml for polymer in ortho-dichlorobenzene (o-DCB) pre-stirred at 50 °C for eight hours was spin coated at 1500 rpm for 60 s both onto the treated and untreated PEDOT: PSS layer, respectively. The prepared films were thermal annealed at 70 °C for 10 min in the glove box. Two narrow sides (about 1 mm) on both edge of the film were wiped off using methanol-wetted swab to allow the contact of ITO and Ca/Al electrodes. The samples were brought into an evaporate chamber afterwards and a 20 nm calcium (Ca) layer followed by a 100 nm aluminum (Al) electrode was deposited on top of the photoactive layer at a base pressure of 10^{-6} mbar. The evaporation thickness was controlled by SQC-310C deposition controller (INFICON, Germany). Four devices were fabricated on one substrate and the effective area of each device was 4 mm^2 defined by a shadow mask.

The current–voltage (J–V) curves were measured with a Keithley 2400 Source-measure unit under the illumination of AM 1.5 G irradiation (100 mW/cm^2) using a 150 W solar simulator (Oriel 91159A, Newport, USA) in ambient air. The light intensity was calibrated by a standardized monosilicon cell (Oriel PN 91150V, Newport, USA) prior to the measurements. A 2 mm × 2 mm shadow mask was utilized to cover the active area to avoid interference from scattering light and adjacent current leakage. The monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra was obtained using a 500 W Xe lamp-based solar simulator (Oriel lamp 74001) with a lock-in amplifier under short-circuit conditions. A calibrated silicon (Si) photodiode (PRL-12, Newport, USA) was used as a reference. The transmittance spectra of the PEDOT: PSS films were taken with a lambda-950 (Perkin Elmer, USA) spectrophotometer. The impedance spectroscopy (IS) measurement was performed using a Zahner Zennium 40562 electrochemical workstation. X-ray photoelectron spectroscopy (XPS) (Model. ESCALAB250Xi) was applied to measure the sulfur S2p core-level spectra of the PEDOT: PSS films coated on Si/SiO_2 substrates.