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Highly conductive PEDOT:PSS transparent electrode prepared by a post-spin-rinsing method for efficient ITO-free polymer solar cells

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ABSTRACT

We have proposed a post-spin-rinsing method (PSRM) with polar organic solvent dimethyl sulfoxide (DMSO) to prepare highly conductive and transparent PEDOT:PSS films. The PSRM-prepared PEDOT:PSS film exhibits a conductivity of 1335 S cm^{-1}, much higher than 776 S cm^{-1} of the PEDOT:PSS film prepared with the conventional pre-adding method (PAM). In contrast to the PAM, the PSRM with DMSO is more effective to remove the insulating PSS and push the PEDOT chains from coiled to a linear/extended-coil alignment with conformation change from a benzoid structure to a more conductive quinoid structure, leading to an enhanced conductivity of the PEDOT:PSS film. The highly conductive PEDOT:PSS film is used as transparent electrode to fabricate indium tin oxide-free polymer solar cells and a power conversion efficiency of 4.82% is achieved for polymer solar cells based on PCDTBT:$PC_{71}BM$ blend.

1. Introduction

As a cheap alternative of renewable energy sources, polymer solar cells (PSCs) have received widespread attention because of their mechanical flexibility, lightweight and compatibility with low-cost roll-to-roll large scale manufacturing [1–3]. Indium tin oxide (ITO) is a commonly used transparent electrode material due to its excellent optoelectronic properties such as high conductivity and high transparency [4]. However, the high vacuum and high temperature requirement for sputtering fabrication of ITO and its mechanical brittleness render it not an ideal transparent electrode choice for flexible PSCs [5–7]. Thus, some promising ITO alternatives including metal nanowires [8–11], metal grids [12–14], conducting polymers [15–19], carbon nanotubes and graphenes [20–25], have been investigated as transparent electrodes for flexible PSCs. Among them, the conductive poly(3,4-ethylenedioxy-thiophene):poly(styrene sulfonate)(PEDOT:PSS) is considered as a promising candidate owing to its predominant advantages involving mechanical flexibility and solution processibility. PEDOT:PSS is a complex of conductive PEDOT and insulating PSS, in which PSS acts as both a stabilizer and a soluble template for PEDOT. The as-prepared PEDOT:PSS films coated from its aqueous dispersion consist of core–shell structures, in which hydrophobic and conductive PEDOT-rich grains are encapsulated by hydrophilic and insulating PSS-rich grains [26–28]. A pre-adding method (PAM) has been commonly employed to enhance the conductivity of PEDOT:PSS film. With this method, some additives including ethylene glycol, glycerol, sorbitol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), as well as surfactants were introduced into the PEDOT:PSS solution and the conductivity of the resulted PEDOT:PSS films were enhanced [29–34]. Post-treatment to the PEDOT:PSS films with polar solvents or sulfuric acids is another effective approach to increase its conductivity [15–17,35–40]. More recently, the PEDOT:PSS films subject to an immersing process in concentrated sulfuric acid have achieved a conductivity higher than 4000 S cm^{-1}, close to that of ITO [41]. However, the process is difficult to control due to strong corrosive feature of sulfuric acid. The post-treatment of PEDOT:PSS films with organic solvents is mild and less environmentally hazardous, drawing more research interest. The post-treatment of organic solvents includes to dip in a polar solvent bath [19], to anneal in polar solvent vapor or to drop low boiling point organic solvents onto the PEDOT:PSS films at a relatively high temperature [16,40].

In this work, we have proposed a post-spin-rinsing method (PSRM) to prepare highly conductive PEDOT:PSS films by spin-rinsing the PEDOT:PSS films with high-boiling polar solvent DMSO. The PSRM is more effective to enhance the conductivity of

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the PEDOT:PSS films than the PAM with the same DMSO solvent. The PSRM-prepared PEDOT:PSS films achieve an average conductivity of 1335 S cm^{-1}, much higher than 776 S cm^{-1} of the PEDOT:PSS films prepared with DMSO PAM method. Further studies have disclosed that the PSRM with DMSO is more effective to remove the insulating PSS and push the PEDOT chains from coiled to a linear/extended-coil alignment with conformation change from a benzoid structure to a more conductive quinoid structure, leading to an enhanced conductivity of the PEDOT:PSS film. The PCDTBT:$PC_{71}BM$ PSCs with PSRM-modified PEDOT:PSS film or ITO as transparent anodes have been fabricated. The PSC based on PSRM-modified PEDOT:PSS anode achieves a power conversion efficiency (PCE) of 4.82%, only 16% lower than that of the ITO-based control device.

2. Experimental

2.1. Materials

Aqueous PEDOT:PSS solution (Clevios™ PH1000) was purchased from Heraeus having a PEDOT:PSS concentration of 1.3% by weight and the weight ratio of PSS to PEDOT was 2.5:1. The poly [*N*-9′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) with a weight-average molecular weight of 28,000 and a polydispersity index (PDI) of 1.8 was synthesized in our laboratory. [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$, $>99\%$) was purchased from American Dye Source Inc. Other chemicals, including DMSO (ACS reagent, $\geq 99.9\%$) and Zonyl FS-300 were obtained from Sigma-Aldrich. All the materials were used as received.

2.2. Preparation of highly conductive PEDOT:PSS films

Blank glass substrates were cleaned successively with detergent, de-ionized water, acetone and isopropyl alcohol (IPA) each for 15 min, and then dried in an oven. 0.1% Zonyl FS-300 in volume was firstly added into the PEDOT:PSS solution (Clevios PH1000) to improve its wetting property. For the PAM-modified PEDOT:PSS, a 5% DMSO in weight was added into the PEDOT:PSS solution. The prepared PEDOT:PSS solution was filtered through a 0.45 μm syringe filter and was spin coated on the pre-cleaned glass substrates at 1000 rpm for 60 s. The spin-coated PEDOT:PSS films were then annealed on a hot plate in ambient atmosphere at 130 °C for 30 min. For the PSRM-modified PEDOT:PSS film, the DMSO treatment was carried out by dropping 100 uL DMSO on the dried pristine PEDOT:PSS films and standing for different times, and then spin-coated at 4000 rpm for 60 s. The obtained films were dried at 120 °C for 10 min. For the fabrication of a multilayer of PEDOT:PSS film, the above preparation process was repeated.

2.3. Thin film characterization

The thicknesses of various films were measured using a Dektak 6M surface profilometer. The conductivity of the PEDOT:PSS films was measured by a KDY-1 four-point probe instrument. Transmittance and absorption spectra of the films were measured using a PU-1901 spectrophotometer. The films were prepared on the quartz substrates for absorption measurement. The atomic force microscopy (AFM) images were obtained using a SPI3800N AFM instrument (Seiko Instrument Inc.) in a tapping mode with a 2 N m^{-1} probe and at a scan rate of 1 Hz under ambient condition. The X-ray photoelectron spectroscopy (XPS) spectra were collected on Thermo ESCALAB 250 equipped with a monochromatized Al Kα source ($hv=1486.8$ eV). X-ray diffraction (XRD) patterns were obtained using a Bruker D8 grazing incident X-ray diffraction (GIXRD) in a conventional theta/2theta geometry with Cu Kα radiation ($\lambda=1.5406$ Å). The Raman spectra of the films were taken using a Horiba Jobin Yvon LabRam HR800 Raman system with a 632.8 nm HeNe laser as an excitation source.

2.4. PSCs fabrication and testing

The PEDOT:PSS (Clevios PH1000) films prepared with PAM and PSRM approaches were patterned to serve as the anode. The PSCs were fabricated on the PEDOT:PSS-coated glass substrates, and the PSCs on the ITO glass substrate with a sheet resistance of 10 Ω/□ were also fabricated for comparison. The PSCs were prepared as the following process. A 40 nm-thick less conductive PEDOT:PSS layer (Clevios P VP AI 4083) was firstly spin-coated on the ITO or

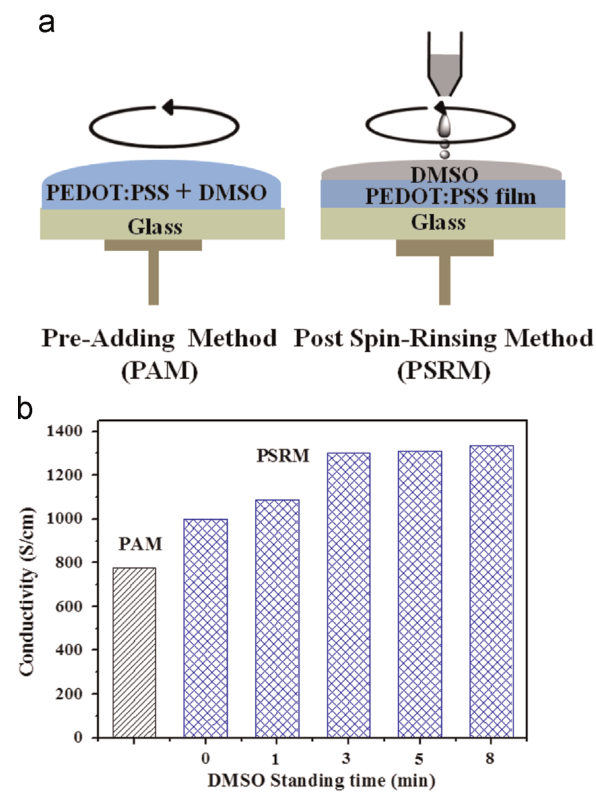

Fig.1. (a) Schematic illustration of the PAM and PSRM approaches to modify the PEDOT:PSS films. (b) Average conductivity of the PEDOT:PSS films modified by PAM or PSRM with different standing time.

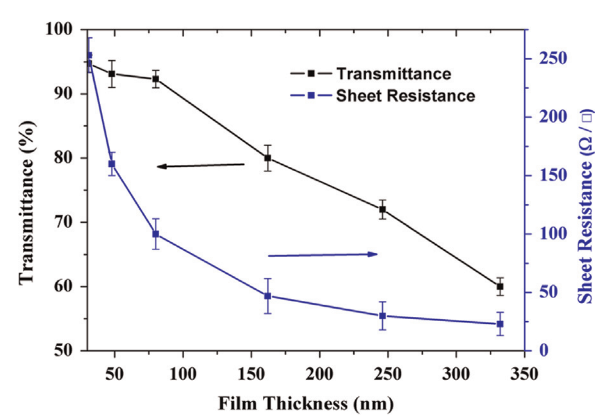

Fig. 2. Dependence of the transmittance (at 550 nm) and sheet resistance on the film thickness for the PEDOT:PSS films treated with DMSO by PSRM method. The error bars represent the standard deviation from several measurements.