



Simultaneous enhancement of the efficiency and stability of organic solar cells using PEDOT:PSS grafted with a PEGME buffer layer



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ABSTRACT

We report a simple processing method to simultaneously improve the efficiency and stability of organic solar cells (OSCs). Poly(4-styrene sulfonate)-doped poly(3,4-ethylenedioxy-thiophene (PEDOT:PSS), widely used as hole transport layer (HTL) in OSCs, tends to accelerate the degradation of devices because of its hygroscopic and acidic properties. In this regard, we have modified PEDOT:PSS to reduce its hygroscopic and acidic properties through a condensation reaction between PEDOT:PSS and poly(ethylene glycol) methyl ether (PEGME) in order to improve the efficiency and stability of OSCs. As a result, the power conversion efficiency (PCE) increased by 21%, from 2.57% up to 3.11%. A better energy level alignment by the reduced work function of the modified PEDOT:PSS with a highest occupied molecular orbital (HOMO) level of poly(3-hexylthiophene-2,5-diyl) (P3HT) is considered the origin of the improved efficiency. The half-life of OSCs with PEDOT:PSS modified with PEGME buffer layer also increased up to 3.5 times compared to that of devices with pristine PEDOT:PSS buffer layer.

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1. Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) have attracted considerable attention as next generation green energy sources because of their low-cost, flexibility, low weight, and easy fabrication [1–6]. In OSCs, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is widely used as the hole transport layer (HTL) for the following reasons: hole-only transport (electron blocking) [7], improved smoothness of the indium-tin oxide (ITO) anode surface [8,9], and the appropriate energy level alignment of the work function of PEDOT:PSS between the anode and active layer. However, the acidic property of PEDOT:PSS leads to corrosion of the ITO layer and results in diffusion of In and Sn from the corroded ITO into the active layer, which induces the degradation of OSCs [10,11]. In addition, PEDOT:PSS films are hygroscopic; thus, the absorption of atmospheric water accelerates cathode oxidation and increases the resistivity of the PEDOT:PSS/active layer interface resulting in the degradation of OSCs [10,11]. To solve these problems, other conducting materials [12], reduced graphene oxide [13,14], and the metal oxides [15–18] such as NiO, MoO₃, V₂O₅, and WO₃ have been introduced as HTLs in OSCs. The majority of studies on metal oxides used vacuum

based thermal evaporation, sputtering, and pulsed laser deposition, which is a high-cost and time-consuming fabrication process. To circumvent these limitations, solution-based processes for some metal oxides have been developed [19–21]. Nevertheless, PEDOT:PSS is still widely used as an HTL to achieve a high power conversion efficiency (PCE) of OSCs. Additionally, the aqueous solubility of PEDOT:PSS facilitates easy and mass handling in the device fabrication process. Although many studies have focused on improving the PCE of OSCs by modifying PEDOT:PSS, few studies have investigated the improvement of OSC stability by modifying PEDOT:PSS. Kim et al. reported a 25% increase in the lifetime of OSCs by adding 0.2 M NaOH to adjust the pH of the PEDOT:PSS solution [22]. While the PCE of the device was almost unchanged by small addition of NaOH (0.2 M ratio), further NaOH addition to improve the device's lifetime degraded its PCE. The removal of PSS from PEDOT:PSS film is one way to improve the OSC stability because PSS is the prime reason for the degradation of OSCs. Alemu et al. reported a method to remove PSS from PEDOT:PSS film by immersing the film in a methanol solution, dropping methanol on the film, or both [23]. However, this method did not completely remove PSS from PEDOT:PSS films, and dark lines of segregated PSS were formed by dropping methanol on the PEDOT:PSS film. In addition, multiple process steps including repeated annealing were required. Furthermore, the effect of PSS removal on the OSC lifetime was not confirmed because the

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lifetime of OSCs with treated PEDOT:PSS anode or ITO anode was compared. Another method to remove PSS from PEDOT:PSS film, reported by Xia et al., involves dropping H_2SO_4 on the film [24]. While this method largely removed PSS from the PEDOT:PSS film, it has a considerable safety limitation for mass production because H_2SO_4 is a strong acid.

In this study, PEDOT:PSS was modified to reduce its hygroscopic and acidic properties through a condensation reaction between PSS and PEGME. The condensation reaction between the $-\text{OH}$ and $-\text{SO}_3\text{H}$ groups from two polymers is well known. Gu et al. successfully cross-linked sulfonated poly(phthalazinone ether sulfone ketone) (PPESK) with poly(vinyl alcohol) (PVA) via a condensation reaction between the $-\text{OH}$ groups in PVA and the $-\text{SO}_3\text{H}$ groups in sulfonated PPESK [25]. Mikhailenko et al. cross-linked sulfonated poly(ether ether ketone) (SPEEK) with polyatomic alcohols through a condensation reaction with the sulfonic acid groups [26]. Furthermore, Subramanian et al. suggested cross-linking sulfonated polystyrene (SPS) electrospun fibers in the presence of poly(ethylene oxide) (PEO) via a condensation reaction between the $-\text{OH}$ groups in PEO and the $-\text{SO}_3\text{H}$ groups in SPS [27]. Since the condensation reactions can proceed in a typical annealing condition of PEDOT:PSS layer ($>120^\circ\text{C}$), no further processing except mixing is required for fabrication of OSCs with the modified PEDOT:PSS buffer layer. To our knowledge, this is the first report investigating the effect of the condensation reaction between PEGME and PSS in the PEDOT:PSS buffer layer on the stability of OSCs. This work shows that the efficiency and stability of OSCs can be improved through the simple modification of PEDOT:PSS without replacing the PEDOT:PSS layer for other materials.

2. Experimental

2.1. Preparation and characterization of PEDOT:PSS films

An aqueous dispersion of PEDOT:PSS (Clevios PH) was purchased from Heraeus Ltd. with the solid content of 1.2–1.4% by weight and a PEDOT:PSS weight ratio of 1:2.5. The stock dispersion was blended with PEGME, obtained from Sigma–Aldrich (average M_n 550, to various concentrations (PSS:PEGME weight ratio = 1:0, 1:0.25, 1:0.50, 1:0.75, 1:1.00, 1:1.25, 1:1.50, 1:1.75, 1:2.00) and stirred for 2 h at 60°C . The blends were filtered through a $0.45\ \mu\text{m}$ PTFE syringe filter before use. Thin films of the PEDOT:PSS samples were deposited onto a pre-cleaned glass substrate by spin-coating and annealed on a hot plate at 150°C for 30 min in air.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were measured with a Spectrum 100 (PerkinElmer) for PEDOT:PSS and poly(styrene sulfonic acid) (PSS) films deposited on glass or by dropping PEGME on the IR cell. The thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA instruments). X-ray photoelectron spectroscopy (XPS) analysis was carried out using K-alpha, Thermo U. K. equipped with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV). For measurement of the indium concentration at the surface of PEDOT:PSS films, PEDOT:PSS samples were deposited onto a pre-cleaned ITO substrate. The electrical conductivity of the PEDOT:PSS films were calculated from the sheet resistance and thickness, measured using a four-point probe meter (Napson, RT-70V/RG-5) and a surface profiler (Alpha step IQ, KLA-Tencor), respectively. The work function was measured using a Kelvin Probe (Scanning Kelvin probe 5050, KP Technology). The surface morphology was investigated by atomic force microscopy (AFM; JPK instruments) in the tapping mode. For measurement of the highest occupied molecular orbital (HOMO) energy level of poly(3-hexylthiophene-2,5-diyl) (P3HT) (Rieke Metals, 4002-EE),

cyclic voltammetry (CV) was performed by using a ITO-coated glass slide which had a thin film of the P3HT polymer as working electrode, a platinum wire as a counter electrode and an Ag/AgCl reference electrode in a 0.1 M LiClO_4 acetonitrile solution. The half-wave potential of ferrocene was estimated to be 400 mV against an Ag/AgCl reference electrode [28].

2.2. Fabrication and characterization of organic solar cells

The OSCs were fabricated as described below. Glass coated with ITO ($150\ \text{nm}$ thick, $10\ \Omega/\square$) was cleaned by sequential ultrasonic treatment in acetone and isopropanol. The cleaned ITO glass was dried at 100°C under vacuum for 1 h, and then treated in an ultraviolet-ozone cleaner for 15 min. The PEDOT:PSS solutions mixed with various concentration of PEGME were individually spin-coated at 2000 rpm for 40 s onto the cleaned ITO glass. The PEDOT:PSS-coated ITO glass samples were then thermally annealed at 150°C for 30 min in air, and transferred to a nitrogen-filled glove box. P3HT (Rieke Metals, 4002-EE) and C61-butyric acid methyl ester (PCBM) (Nano-C, 99%) with weight ratio of 1:0.6 were dissolved in chlorobenzene. The solution containing P3HT and PCBM was stirred for 1 d at 50°C , filtered through a $0.2\ \mu\text{m}$ PTFE syringe filter, and spin-coated onto the PEDOT:PSS-coated ITO glass at 600 rpm for 40 s. The thin films were then thermally annealed on a hot plate at 120°C for 10 min. To complete the structure of the device, the top contact was formed through sequential thermal evaporation of lithium fluoride ($0.6\ \text{nm}$) and aluminum ($100\ \text{nm}$) through a shadow mask under vacuum (pressure: 2×10^{-6} Torr).

The photovoltaic performance was measured by illumination of the devices in air with a solar simulator (1000 W xenon lamp, Oriel, 91193), which provided a simulated AM 1.5 spectrum ($100\ \text{mW}/\text{cm}^2$). The simulated light was calibrated with a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si + KG filter, Certificate No. C-ISE269) to a sun light intensity of 1 ($100\ \text{mW}/\text{cm}^2$). The active area of each device was $4.84\ \text{mm}^2$. When the device was illuminated, a metal mask was used to define the exposed area and eliminate any unwanted extra current. To analyze the effect of PEGME-modified PEDOT:PSS buffer layer on the stability of the devices, their performances were recorded as a function of exposure time to air in dark without encapsulation. The devices were stored in a box filled with a silica gel, while testing was performed without any control of air.

3. Results and discussion

3.1. Condensation reaction between PEDOT:PSS and PEGME

The condensation reaction between the $-\text{SO}_3\text{H}$ groups in sulfonated polymers and the $-\text{OH}$ groups in polyols to afford sulfonic acid esters is well known [25–27]. We also reported a complex including a PEDOT:PSS grafted with PEGME copolymer with excellent water, chemical and weather resistance by the condensation reaction [29]. While many reports describe the addition of various alcohol derivatives such as ethylene glycol (EG), poly(ethylene glycol) (PEG) and glycerol as dopants to PEDOT:PSS, these studies mainly focused on enhancing the conductivity of PEDOT:PSS films to improve the PCE of OSCs [30–32]. However, the effects of condensation reactions on the device stability have not been reported. Herein, we investigated the effect of condensation reaction by PEGME on the hygroscopic and acidic properties of PEDOT:PSS to increase the lifetime of OSCs.

Fig. 1 illustrates condensation reaction between PEDOT:PSS and PEGME. The sulfonate ester ($\text{S}-\text{O}-\text{C}$) linkage and a water molecule are formed in the condensation reaction at annealing temperature

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