Solar Energy Materials & Solar Cells 120 (2014) 584–590

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Direct effect of partially photooxidized poly(3-hexylthiophene) on the device characteristics of a bulk heterojunction solar cell

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ARTICLE INFO

Article history:
Received 17 August 2013
Received in revised form
26 September 2013
Accepted 27 September 2013
Available online 26 October 2013

Keywords:
MALDI-TOF mass spectroscopy
Polymer solar cells
Poly(3-hexylthiophene)
Performance degradation
Photo-induced oxidation

ABSTRACT

During the photoirreversible degradation of a polymer solar cell (PSC), it is generally assumed that the photooxidation of the organic materials (P3HT, PCBM) affects the device performance. Photooxidation of the organic materials results in a decrease in absorbance as a result of photodecomposition. However, the effect of initial photooxidation on device performance remains to be investigated. In this study, we try to establish the correlation between the initial photooxidation of the organic material and the photovoltaic performance of the PSC. Towards this aim, we investigated the device characteristics by employing a slightly degraded organic material, which had been prepared by photooxidation of the material in the solution state. UV–vis and FT-IR spectra suggest a decrease in the π-conjugation length along with the formation of ketone and sulfoxide derivatives. MALDI-TOF mass spectra indicated the partial molecular scission of P3HT even at the start of photooxidation. A deterioration in performance was observed during the device characterization, as was an increase in the resistance of the organic films. These results indicate that the fragments and oxides generated by the partial molecular scission of P3HT increase the resistance of organic films, resulting in a drop in device performance.

1. Introduction

Polymer solar cells (PSCs) have many potential advantages such as mechanical flexibility, portability, and low manufacturing costs [1,2]. Among the conducting polymers used, poly(3-hexylthiophene) (P3HT) is one of the most commonly employed material for the photoactive layer in a PSC. Recent studies on P3HT-based PSCs report a drastic improvement in the power conversion efficiency [3–7]. Furthermore, large-scale production of PSCs can be expected imminently [8]. However, it is also well known that a P3HT-based PSC degrades with long-term solar light irradiation [9,10]. In order to understand the reason for and improve on the poor long-term durability, the photo-degradation of PSCs has been investigated [11–14].

Seeman et al. reported that device degradation could be either reversible or irreversible [15]. Reversible degradation is defined as a drop in device performance that is recoverable through thermal annealing., Kawano et al. used thermally stimulated current (TSC) spectroscopy to report that reversible degradation was mainly caused by the accumulation of charge carriers at a trap site [16]. Schafferhans et al. used TSC and charge extraction from linearly increasing voltage (CELIV) measurements to report that the exposure of solar cells to synthetic air resulted in degradation, and oxygen doping increased the density of deeper charge traps [15,17].

Irreversible degradation is defined as a drop in device performance that cannot be restored using thermal annealing. Jorgensen et al. proposed that the main cause of irreversible degradation was the dramatic decomposition of organic materials such as P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) on photooxidation [9,10]. However, because it is difficult to directly evaluate an organic layer sandwiched between the transparent electrode and metal electrode of a device, the effect of the photodecomposition of organic materials on the device performance has remained undetermined [9,10]. In addition, it is not possible to exclude factors such as degradation of electrodes and interfacial buffer layers, and accumulated trapped charge while considering complete device degradation. Chang et al. recently reported on the correlation between photooxidized P3HT and the photovoltaic

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http://dx.doi.org/10.1016/j.solmat.2013.09.042

performance of PSCs by using a pre-prepared solution of photooxidized P3HT [18]. The solution of degraded P3HT was prepared by irradiating for 10 h in air at an intensity of 100 mW cm^{-2} by using a mercury light. The drastic photodecomposition of P3HT was observed by UV–vis, photoluminescence (PL), and Fourier transform- infrared (FT-IR) spectroscopy. They found that the decrease in performance could be attributed to a drop in hole mobility, light absorption, and an increase in the carrier quencher concentration upon the degradation of P3HT. Although they investigated the effect of drastic structural changes in P3HT on the device, details on the effect of initial photooxidation on the device is yet to be investigated.

In this research, we attempt to clearly correlate the effect of initial photooxidation of the organic material (P3HT, PCBM) and the photovoltaic performance of PSCs. We investigated the device characteristics in terms of the *I–V*, incident photon-to-current efficiency (IPCE), and resistance by employing a slightly oxidized organic material, which was prepared by irradiating the solution state with solar-simulated light in air for less than 1 h. We then examined the structual change using UV–vis, FT-IR, AFM, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass measurements. Degradation of the organic layer was not carried out for a complete PSC, whose mechanism might be different to that of the thin film [10]; however, the advantage of solution-based photooxidation is that it allows us to evaluate device characteristics, excluding the degradation of electrodes and interfacial buffer layers, and accumulation of trapped charge.

2. Experimental details

2.1. Device preparation

The device structure was glass/transparent electrode/buffer layer/organic layer/Al. Indium tin oxide (ITO), poly(3-hexylthiophene) (P3HT) (Merck) (M_w=18,000 g mol^{-1}, M_w/M_n=1.60), and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (Solenne) were used as the transparent electrode, p-type organic semiconductor, and n-type organic semiconductor, respectively. ITO-coated (2 mm × 26 mm, sheet resistance= ~10 Ω/□) glass substrates were cleaned using an O_2 plasma treatment (Harrick Plasma Inc.) for 30 min. To deposit the interfacial buffer layer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (H. C. Starck Baytron PVP. AI 4083) was dropped onto the glass substrate using a 0.45 μm filter. The substrate was then spin-coated at 3000 rpm for 185 s (thickness of the PEDOT:PSS layer ~30 nm) and dried at 135 °C on a hot plate for 10 min. To prevent the adsorption of water into the PEDOT:PSS films, the substrates were immediately transferred to a glove box (N_2, 99.99%; H_2O, under 10 ppm; O_2, under 5 ppm) after annealing.

For the active layer, eight different P3HT:PCBM solutions containing different ratios of P3HT and PCBM were prepared. P3HT and PCBM were dissolved in anhydrous chlorobenzene (Sigma-Aldrich) to yield a solution of P3HT (1.8 wt%) and PCBM (1.2 wt%) in the glove box. All materials were used as recieved. The solution was stirred overnight in the glove box. The following day, half of the solution was transferred into a transparent air-filled glass bottle. The remaining half of the solution was transferred into a transparent nitrogen-filled glass bottle. The concentration of oxygen in the air and solution in the former bottle were estimated to be 3.75×10^{-5} mol and 1.63×10^{-6} mol, respectively, using Henry's law [19]. The two bottled solutions were then illuminated with AM1.5G solar-simulated light irradiation at an intensity of 100 mW cm^{-2} for 0, 20, 40, and 60 min to form eight different partially photooxidized organic solutions (0, 20, 40, 60 min in air, and 0, 20, 40, 60 min in nitrogen). We confirmed that no volatilization of the solvent occured during the irradiation. Each solution was dropped onto a PEDOT:PSS-coated ITO substrate, which was spin-coated at 2000 rpm for 120 s (thickness 110–120 nm) in the glove box. Finally, Al electrodes were deposited (thickness ~100 nm) on top of the active layers using vacuum evaporation through a shadow mask placed on each film. The active area of the cell was 0.04 cm^2. The substrates were then post-annealed at 110 °C on a hot plate for 10 min and then at 135 °C for 15 min.

2.2. Device characterization

After fabrication, each device was placed in a sample holder sealed inside the glove box, and the devices were then removed. All device characterizations were conducted at room temperature. The current density–voltage (*I–V*) curves were obtained using a source meter (Keithley Instruments Inc.) under AM1.5G solar-simulated light irradiation at an intensity of 100 mW cm^{-2}. The solar simulator was equipped with a Xe arc lamp and an AM1.5G filter (Bunkoukeiki Co., LTD.). The irradiation intensity was calibrated using a standard cell for Si solar cells (Bunkoukeiki Co., LTD.). The power conversion efficiency (η) was calculated from the *I–V* characteristics. The incident photon-to-electron conversion efficiency (IPCE) was measured under illumination with monochromatic light from a Xe lamp (1–7 mW cm^{-2} at each wavelength) (Bunkoukeiki Co., LTD.). The impedance spectra were measured using an impedance/gain-phase analyzer (Solartron Co., LTD.) The impedance response was measured in the dark over the range 1 Hz–100 kHz with an oscilation amplitude of 30 mV at different DC bias (0.0, 0.2, 0.4, 0.6, 0.8 V).

2.3. Organic film characterization

Photooxidized organic films were fabricated through spin-coating onto the CaF_2 substrates at 2000 rpm for 120 s (thickness 100–120 nm) using the organic solution created during the device preparation. These films were characterized using UV–vis–NIR (Shimadzu Co., LTD.), FT-IR (JASCO, Co.), and AFM (Seiko Instruments, Inc.). After each measurement, a sample solution was prepared by $CHCl_3$ extraction of each organic film using an ultrasonic cleaning machine. Complete extraction of the material and the absence of any effect of ultrasonication were confirmed. The solution was mixed into 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) [20]/$CHCl_3$ as a matrix solution. The samples were then characterized on a MALDI-TOF mass spectrometer (Bruker Daltonics, Inc.) using a nitrogen laser (λ=337 nm). The calibration was conducted using a peptide standard purchased from Bluker. In addition, the extracted solutions were also used to conduct gel permeation chromatography (GPC) (Waters, Co.) measurements.

3. Results and discussion

3.1. Solar cell device characteristics of the partially photooxidized P3HT: PCBM

The *I–V* curves and changes in device characteristics of photovoltaic cells are shown in Fig. 1. Prior to fabricating the organic film, a blend of P3HT and PCBM was irradiated for 0, 20, 40, and 60 min in air using simulated solar light (AM 1.5G) at an intensity of 100 mW cm^{-2}. The devices were then fabricated using this solution. The device based on the non-photooxidized organic film showed a photovoltaic behavior comparable to those previously reported [9,10,21] with an open-circuit voltage (V_{oc}) of 0.56 V, short-circuit current density (J_{sc}) of 9.13 mA cm^{-2}, fill factor (FF) of 0.48, and power conversion efficiency (η) of 2.45. However, the values of η, J_{sc}, and FF decreased, whereas that of V_{oc} and the series resistance (see Fig. S1) in the supporting information increased