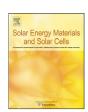
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Effect of strong base addition to hole-collecting buffer layer in polymer solar cells

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ABSTRACT

We report a brief study on the effect of strong base addition to the hole-collecting buffer layer [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)] on the performance of polymer solar cells made using blend films of poly(3-hexylthiophene) and soluble fullerene. A concentrated aqueous solution of sodium hydroxide (NaOH) was added to the PEDOT:PSS solution to decrease its acidity. The optical absorption spectra of modified buffer layers were measured to investigate the influence of NaOH addition on the spectral shape, while the surface of modified buffer layers was examined using atomic force microscopy. Results showed that the acidity of PEDOT:PSS solutions was remarkably reduced by adding the NaOH solution. However, the performance of solar cells was slightly degraded, which has been attributed to the decreased charge transportability as evidenced from the dark current–voltage characteristics.

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1. Introduction

Polymer solar cells have recently attracted keen interest as a next generation energy conversion medium from solar light to electricity [1–3]. The increasing interest can be mainly attributed to the expectations for possible low-cost manufacturing of plastic solar modules when it comes to their low temperature fabrication processes below $\sim\!150~^\circ\text{C}$ [4–6]. In particular, a sophisticated fast and large area fabrication by employing roll-to-roll process can be an additional advantage of polymer solar cells [7,8].

To date, however, the power conversion efficiency (PCE) of polymer solar cells is hardly reaching 4–6% in the case of small size cells so that their module efficiency can be lowered further [1–3,8]. Here the improvement in PCE is intrinsically dependent on the invention of new donor and acceptor materials, which can increase light-harvesting and/or open circuit voltage ($V_{\rm OC}$) [9,10]. In the meantime, the lifetime issue has been arisen because organic materials are considered as normally 'weak' materials compared to inorganic materials. Hence, a couple of studies have been reported for the reliability of polymer solar cells [11,12]. Of various issues related to the reliability of polymer solar cells, the strong acidity of hole-collecting buffer layer [poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)] was also

In this work, we have examined the performance of polymer solar cells with the PEDOT:PSS layer of which acidity was controlled by adding a strong base to its solution before coating. As a preliminary study, the equivalent molar ratio of sodium hydroxide (NaOH) to the acid part (PSS) of PEDOT:PSS was tried first and then the amount of NaOH was increased up to one and half. Results showed that the solar cell performance was slightly degraded for the device with the buffer layer modified with the equimolar concentration of NaOH to PSS, even though the acidity was considerably reduced.

2. Experimental

P3HT (Rieke metals) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁ (PCBM, nano-C) were used as received without further purification. Binary solutions of P3HT and PCBM were prepared using chlorobenzene at a solid concentration of $\sim\!60\,\text{mg/ml},$ followed by continuous stirring before use. The PEDOT:PSS solution was purchased from HC Stark (PH500) and was modified by adding a concentrated NaOH (Aldirch Chemical Co.) solution, which was prepared using high purity deionized water (18 M Ω , Millipore system). Indium-tin oxide (ITO) coated glass substrates were patterned and cleaned by acetone and isopropyl alcohol, followed by UV-ozone treatment. On top of the ITO-glass substrates, the pristine and modified PEDOT:PSS solutions were spun to make a hole-collecting buffer layer. The resulting buffer layer samples were

considered but no systematical studies have been carried out in terms of weakening the acidity.

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thermally annealed at 230 °C for 15 min. The thickness of PEDOT:PSS layer was \sim 50 nm, which was measured with a surface profiler (Alpha-step 200, Tencor). Next, the active layer (P3HT:PCBM) was spin-coated on the buffer layers, followed by soft-baking at 50 °C. Finally, these samples were loaded into a vacuum chamber system to deposit the top electrodes (Al. 100 nm thick) (see Fig. 1). The pH of PEDOT:PSS solutions with NaOH contents was measured using pH meter (Model AB15, Fisher Scientific). The dark and light current density-voltage (I-V) characteristics of devices were measured using an electrometer (Model 2400, Keithley). The photovoltaic characteristics (light *I–V* curves) of devices were measured under illumination of simulated solar light (air mass 1.5 G. 100 mW/cm²) using a solar simulator (Model 92250, Newport-Oriel). The optical properties of buffer layers were measured using UV-visible spectrophotometer (Optizen 3220UV, MECASYS Co.). The surface morphology of buffer layers was measured using atomic force microscope (AFM, Nanoscope IIIa, Digital Instrument).

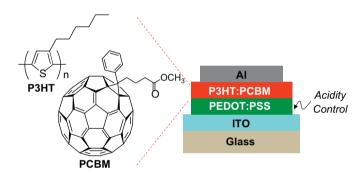


Fig. 1. Schematic illustration of polymer solar cell and chemical structure of materials used in this work.

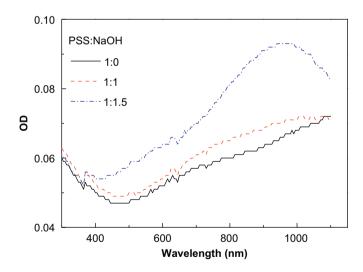


Fig. 2. UV–visible absorption spectra of PEDOT:PSS layers modified with NaOH (PSS:NaOH is in molar ratio).

3. Results and discussion

As shown in Fig. 2, the optical density (OD) of buffer layer modified with PSS:NaOH=1:1 ratio was very slightly increased up to the wavelength of $\sim\!1050\,\mathrm{nm}$. In particular, the pronounced increase was observed at the wavelengths between 700 and 1000 nm. This indicates that the added NaOH molecules influenced the interaction environment between PEDOT and PSS. Moreover, furthermore addition of NaOH (PSS:NaOH=1:1.5) resulted in relatively huge increase in the optical density at the wavelengths between 700 and 1000 nm in the presence of an obvious peak at around 950 nm. This result may reflect the dedoping of PEDOT:PSS by the addition of NaOH, as evidenced from the drastic ($\sim\!5$ times) increase in the sheet resistance for the modified buffer layer (PSS:NaOH=1:1.5) (data are not shown here).

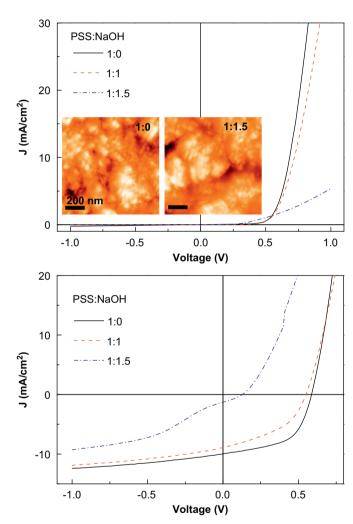


Fig. 3. Dark (top) and light (bottom) *J–V* characteristics of polymer solar cells with the buffer (PEDOT:PSS) layers modified with NaOH (PSS:NaOH is in molar ratio). The inset images (top panel) show the AFM images of the pristine PEDOT:PSS layer and the modified PEDOT:PSS layer (1:1.5).

Table 1 Summary of solar cell performances (AM1.5G, 100 mW/cm²).

PSS:NaOH (molar ratio)	$\alpha (10^5 \text{cm}^{-1})$		рН	J _{SC} (mA/cm ²)	$V_{\rm OC}\left({\sf V}\right)$	FF (%)	PCE (%)	$R_{\rm S}$ (k Ω /cm ²)	R_{SH} (k Ω /cm ²)
	530 nm	965 nm						() -)	() ,
1:0	0.22	0.30	1.64	9.99	0.58	0.56	3.24	10.63	280.16
1:1 1:1.5	0.24 0.28	0.33 0.44	2.71 11.66	8.91 1.28	0.55 0.12	0.43 0.34	2.13 0.05	15.08 54.43	184.06 111.83

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