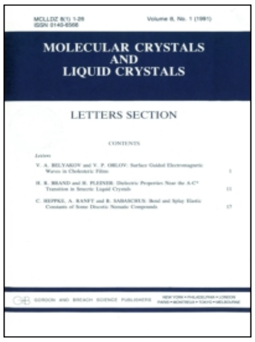

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Cathode modification of polymer solar cells by ultrahydrophobic polyelectrolyte

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ABSTRACT
A ultrahydrophobic polylectrolyte (PVPy-F) based on poly(4-vinylpyridine) is applied to polymer solar cell (PSC) as a cathode buffer layer. The Kelvin probe microscopy measurement support the formation of favorable interface dipole between the active layer and the cathode. PSC with the PVPy-F as a cathode buffer layer demonstrate the power conversion efficiency (PCE) of 3.46% (open circuit voltage (V_{oc}) = 0.62 V, short circuit current (J_{sc}) = 10.8 mA/cm^2, fill factor (FF) = 51.7%), which is better than the device without interlayer (PCE = 2.88%, V_{oc} = 0.61 V, J_{sc} = 9.15 mA/cm^2, FF = 51.6%). This is due to that the reduction of a Schottky barrier at the cathode interface. Most increase in the PCE of the devices with interlayer is resulted from enhancement of the J_{sc}.

KEYWORDS
polymer solar cell; cathode buffer layer; electron collection layer; ultrahydrophobic polyelectrolyte

1. Introduction

Polymer solar cells (PSCs) have been a attracting research field due to their readily tailoring materials and application in flexible devices [1–3]. Interfacial property at the cathode and anode is strongly related with the charge collection property, which is very important parameter to get high performance PSCs through enhancement of the short circuit current (J_{sc}) of the devices. π-Conjugated oligo- or polymer electrolytes [4–13] have been mainly used for cathode buffer layer to achieve high performance opto-electronic devices. Also, non-conjugated polymers such as poly(4-vinylpyrirolidone), poly(4-vinylalcohol), poly(sodium 4-styrenesulfonate), and polyviologen [14–19] have been applied to PSCs to improve the efficiency. By the formation of interface dipole at the cathode interface through introducing the thin layer of these materials, the J_{sc} of the devices is mainly enhanced by the reduction of a Schottky barrier at the interface. In addition, the fill factor (FF) and the open circuit voltage (V_{oc}) could be improved by interfacial layer.

In this research, we synthesize a non-conjugated ultrahydrophobic polyelectrolyte based on poly(4-vinylpyridine), which is simply prepared by the reaction between poly(4-vinylpyridine) and perfluorooctyl iodide (PVPy-F) (Scheme 1). Even though PVPy-F is very

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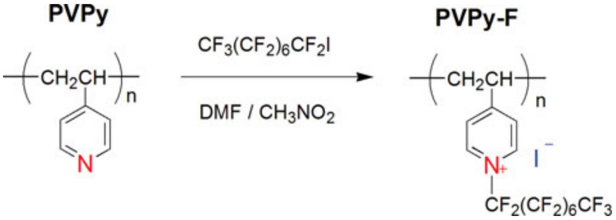

Scheme 1. Synthesis of poly(4-vinyl *N*-heptadecafluorooctyl pyridinium iodide) (PVPy-F).

polar, which is soluble in methanol and ethanol, the film forming property of PVPy-F will be excellent on the hydrophobic active layer surface because PVPy-F has an ultrahydrophic property.[20] We introduce PVPy-F as a cathode buffer layer at the cathode interface. The interface dipole at the cathode will be generated by the thin layer of PVPy-F. This lowers the electron injection barrier at the cathode interface. Thus, the PCE of PSC based on PVPy-F is improved from 2.88% ($J_{sc} = 9.15$ mA/cm^2, open circuit voltage (V_{oc}) = 0.61 V, fill factor (FF) = 51.6%) to 3.46% ($J_{sc} = 10.8$ mA/cm^2, $V_{oc} = 0.62$ V, FF = 51.7%).

2. Experimental

Chemicals were purchased from Aldrich Chemical Co. and Alfa Aesar and were used as received unless otherwise described. Poly(4-vinylpyridine) (average Mw ~ 60000, Cat. No. 472344) was purchased from Aldrich. Regioregular poly(3-hexylthiophene) (P3HT) (Cat. No. 4002-EE) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) (Cat No. nano-cPCBM-BF) were purchased from Rieke Metals Inc. and nano-C, Inc., respectively.

2.1. Measurements

X-ray photoelectron spectroscopy (XPS) are recorded using Al Kα X-ray line (15 kV, 300 W) (Thermo Electron Co., MultiLab 2000). Kelvin probe microscopy (KPM) measurements (KP technology Ltd. Model KP020) were performed to investigate the direction of interface dipole of the active layer and the PVPy-F coated active layer. The atomic force microscopy (AFM) topography images were taken using a Bruker (NanoScope V) operated in the tapping mode. The thickness of films was measured by an Alpha-Step IQ surface profiler (KLA-Tencor Co.). The J–V measurements under the 1.0 sun (100 mW/cm^2) condition from a 150 W Xe lamp with AM 1.5 G filter were performed using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm the 1.0 sun condition.

2.2. Fabrication of PSCs

For fabrication of PSC with a structure of ITO/PEDOT/active layer (P3HT:$PC_{61}BM$)/with or without buffer layer/Al, a thickness of 40 nm of PEDOT:PSS (Baytron P, diluted with 2-propanol 1:2 v/v) was spin-coated on pre-cleaned indium tin oxide (ITO) glass substrate. After being baked at 150°C for 10 min under the air, the active layer was prepared by the same condition for iPSCs. The typical thickness of the active layer was 200 nm. Before cathode deposition, a buffer layer was prepared by spin coating with the polymer solution in methanol. The typical thickness of a buffer layer was less than 5 nm. The Al layer was deposited with a thickness of 100 nm through a shadow mask with a device area of 0.09 cm^2 at 2×10^{-6} Torr.

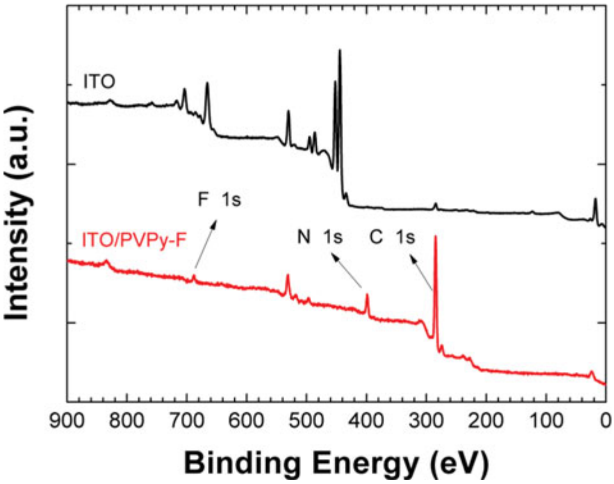

Figure 1. XPS spectra of ITO and ITO/PVPy-F.

After the cathode deposition, the device was thermally annealed at 150°C for 20 min in the glove box (N_2 atmosphere).

2.3. Synthesis of poly(4-vinyl N-heptadecafluorooctyl pyridinium iodide) (PVPy-F)

A mixture of 0.200 g (1.87 mmol) of poly(4-vinylpyridine) and 1.056 g (1.87 mmol) of hetadecafluorooctyl iodide in *N,N*-dimethylformamide (DMF)/nitromethane (CH_3NO_2) mixed solvent was stirred for 24 h at 80°C. After cooled down to the room temperature, the precipitate was filtered and washed by a portion of 20 mL of diethyl ether. Then the precipitate was dried under the vacuum at room temperature. The yield of titled polymer was 72.1%. Glass transition temperature appeared at 142°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.5–8.1 (br, 2H), 6.5–6.2 (br, 2H), 1.7–1.3 (br, 3H). Anal. Calcd. for C15H9F17IN: C, 27.58; H, 1.39; F, 49.45; I, 19.43; N, 2.14. Found: C, 26.55; H, 1.11; N, 2.99.

3. Results and discussion

PVPy-F was successfully prepared by the reaction between poly(4-vinylpyridine) and hetadecafluorooctyl iodide (Scheme 1). The titled polymer was characterized by elemental analysis and X-ray photoelectron spectroscopy (XPS). As shown in Figure 1, the peaks at 687, 398 eV and 284 eV are attributed to the binding energy of F 1s, N 1s, and C 1s, respectively, which are not observed in the ITO surface. PVPy-F was also characterized by FTIR spectroscopy and showed distinctive C-F stretch at 1200 cm^{-1} of the FT-IR spectrum. In addition, stretching vibration in 2900–3050 cm^{-1} region due to presence of aromatic and aliphatic (methylene and methane) hydrogens. C=C and C=N stretching vibration showed in the 1550–1650 cm^{-1} region.

We fabricated PSCs (shown in Figure 2 (a)) to investigate the effect of thin layer of PVPy-F (Scheme 1 and Figure 2 (b)) as an interlayer at the interface between the active layer and the Al cathode on the photovoltaic properties. As shown in Figure 2 (c), it is possible to modify the work function of Al by the thin layer of PVPy-F. Insertion of PVPy-F would readily lead to the formation of a dipole layer, which reduces the work function Al. This was experimentally confirmed by Kelvin probe microscopy (KPM) measurements. The contact potential difference

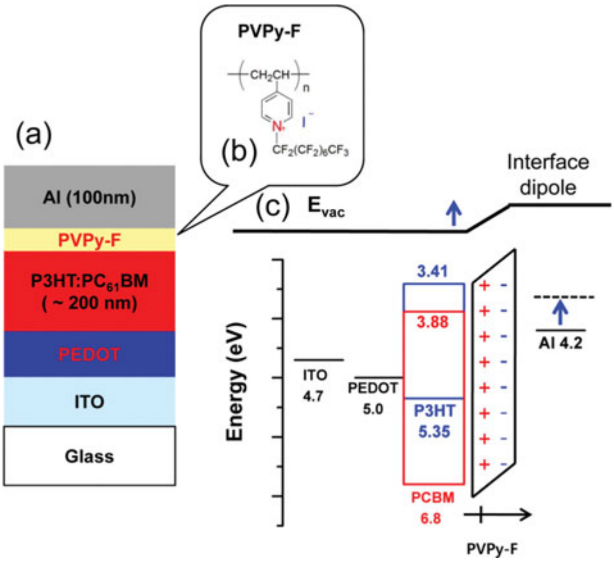

Figure 2. (a) The device structure in this research, (b) the chemical structure of PVPy-F, and (c) the energy level diagrams of materials and the schematic representation of the formation of interface dipole.

between reference probe (Kelvin probe) and the PVPy-F coated active layer was −180 mV, which are ca. 228 mV more negative than that of the active layer without interlayer. Thus, we confirm the negative dipole points away from the surface of PVPy-F by the formation of interface dipole at the surface of the active layer (as illustrated in Figure 2 (c)).

As shown in Figure 3, the J_{sc} of the device with PVPy-F was 10.8 mA/cm^2 with a PCE of 3.46% which is higher than that of the device without PVPy-F (J_{sc} = 9.15 mA/cm^2, PCE = 2.88%) whereas the V_{oc} (0.62 V) and the FF (51.7%) of the device with PVPy-F were almost identical to those of the device without PVPy-F (V_{oc} = 0.61 V, FF = 51.6%). The most increase in the PCE of PSC with interlayer was resulted from enhancement of the J_{sc}. This is due to the transition from a Schottky contact to an Ohmic contact at the cathode interface. The energy difference between the work function of the ITO/PEDOT and the work function of the Al

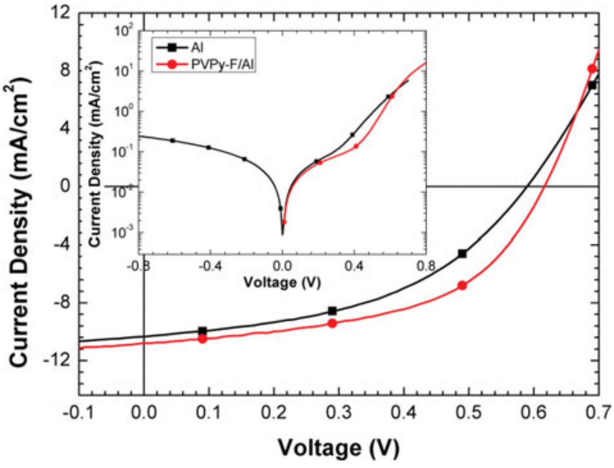

Figure 3. Current density–voltage curves of PSCs under AM 1.5 G simulated illumination with an intensity of 100 mW/cm^2 (filled square: ITO/ZnO; filled circle: ITO/PVPy-ZW; filled triangle: ITO/ZnO/PVPy-EtBr; inset: under the dark condition).

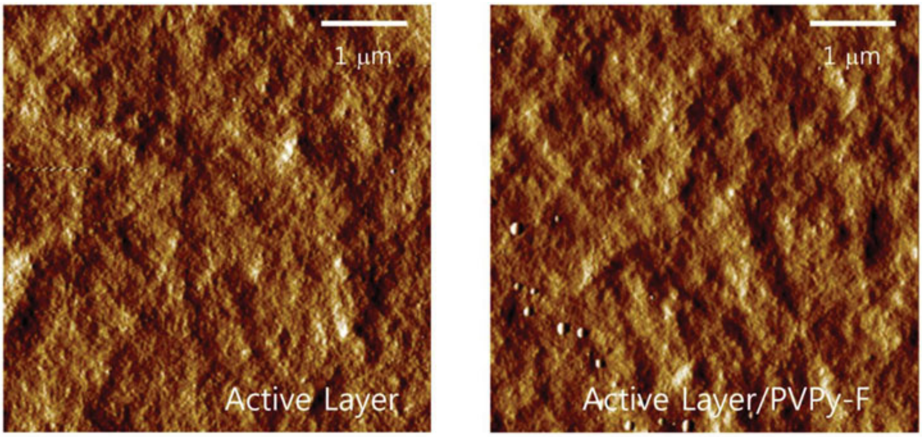

Figure 4. AFM images of the surface of ITO, PVPy-ZW treated ITO, ITO/ZnO, and PVPy-ZW treated ITO/ZnO.

is increased by the insertion of PVPy-F layer, indicating a larger internal electric field in the device with interlayer is induced than the device without interlayer. Thus, more efficient collection of electrons from the active layer to the cathode under the short-circuit condition is occurred.

The R_s of PSC with PVPy-F (6.62 Ωcm^2), which is smaller than that of the device without interlayer (8.16 Ωcm^2) whereas the R_{sh} of the device with PVPy-F (3.82 $k\Omega cm^2$) was slightly bigger than the device without interlayer (3.24 $k\Omega cm^2$). This data coincident with the performance of the devices. The surface roughness (Figure 4) of the active layer with PVPy-F (r.m.s. = 7.72 nm) was slightly larger than that of the device without interlayer (r.m.s. = 6.20 nm). Here, we found that the V_{oc} data of either iPSC or cPSC were not sensitive to the insertion of interlayer. Similar features were observed in the previous research.[15–19] From the results, ultrahydrophobic PVPy-F might be potential material as a cathode buffer layer in PSC.

4. Conclusion

A non-conjugated polyelectrolyte, PVPy-F, has been successfully demonstrated as a cathode buffer layer for solar cell. The increase in the PCE resulted from enhancement of the J_{sc}. The KPM study indicates that a Schottky barrier at the cathode interface is reduced by the formation of favorable interface dipole.

Acknowledgments

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