



Cathode modification of polymer solar cells by electrostatically self-assembled zwitterionic non-conjugated polyelectrolyte



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ARTICLE INFO

Article history:

Received 27 May 2015

Received in revised form 21 August 2015

Accepted 24 August 2015

Available online 3 September 2015

Keyword:

Polymer solar cell

Cathode buffer layer

Electron collection layer

Zwitterion

ABSTRACT

A non-conjugated zwitterionic polyelectrolyte (PVPy-ZW) based on poly(4-vinylpyridine) is applied to polymer solar cells (PSCs) as a cathode buffer layer either inverted or conventional type polymer solar cells. The Kelvin probe microscopy measurement support the formation of favorable interface dipole at the cathode interface, indicating the reduction of a Schottky barrier for an electron collection from the active layer to the cathode. Inverted type PSC with the PVPy-ZW as a cathode buffer layer demonstrate the power conversion efficiency (PCE) of 3.55% (open circuit voltage (V_{oc})=0.62 V, short circuit current (J_{sc})=9.49 mA/cm², fill factor (FF)=60.4%), which is better than the device without interlayer (PCE=2.95%, V_{oc} =0.60 V, J_{sc} =8.11 mA/cm², FF=60.6%). This is due to that the reduction of a Schottky barrier at the cathode interface. Conventional type PSC with PVPy-ZW (3.45%) at the cathode interface also exhibit better the PCE compared to that of the device without interlayer (2.88%). Most increase in the PCE of the devices with interlayer is resulted from enhancement of the J_{sc} .

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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]. PSC is comprised of conjugated organic materials, transparent inorganic electrode, and metal cathode. 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. Non-conjugated polar polymers such as poly(4-vinylpyrrolidone), poly(4-vinylalcohol), poly(sodium 4-styrenesulfonate), and polyviologen [14–19] have been applied to PSCs as a cathode buffer layer to improve the efficiency. The efficiency of the device is improved relative to that of the devices lacking these materials by introducing the ultra thin film of these materials between the active layer and the cathode. By the formation of interface dipole at the cathode interface, the J_{sc} of the devices is mainly enhanced by the reduction of a Schottky barrier at the interface. In addition, the

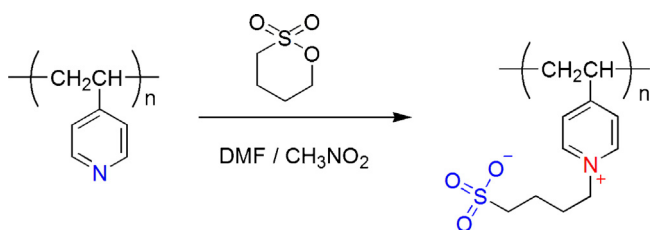
fill factor (FF) and the open circuit voltage (V_{oc}) could be improved by interfacial layer.

By comparing with the polyelectrolytes with counterions such as sodium, bromide, and tetraphenylborate, which can migrate under the biased condition and lead to redistribution of the internal electric field [20]. Recently, conjugated and non-conjugated zwitterionic (ZW) materials have been developed as a cathode buffer layer for polymer light-emitting diodes (PLEDs) and attracted interest as a new kind of electron injection materials due to their unique chemical structure, in which both the positive and the negative ions are combined. As the ions are not mobile, the device response time is improved significantly. Furthermore, the solubility of the materials in polar solvents is good enough for multilayer-device fabrication as a result of the presence of the charged groups [21,22].

In this research, we synthesize a non-conjugated ZW polymer based on poly(4-vinylpyridine) to take advantage of the property of ZW materials for electron transporting layer, which is simply prepared by the reaction between poly(4-vinylpyridine) and butanesultone (PVPy-ZW) (Scheme 1). We introduce PVPy-ZW as a cathode buffer layer in inverted type PSCs (iPSCs) by electrostatically self-assembly process on the ITO (or the ZnO) surface and the zwitterionic ionic component in the polymer backbone, the interface dipole at the cathode will be generated. This lowers the electron injection barrier at the cathode interface. Thus, the

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Scheme 1. Synthesis of poly(4-vinylpyridinebutanesultone) (PVPy-ZW).

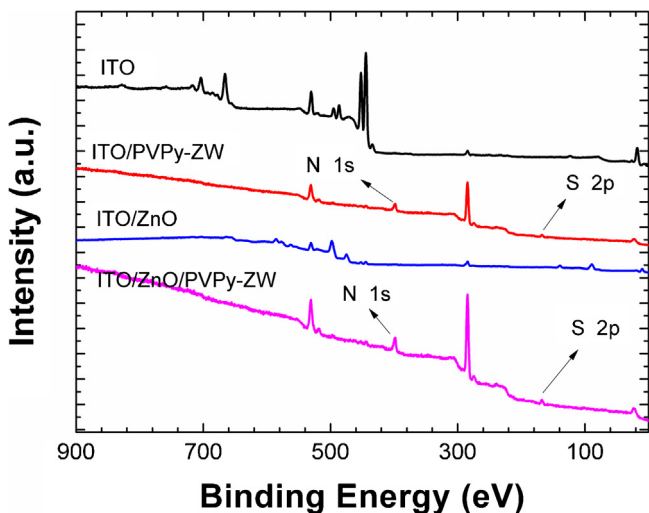


Fig. 1. XPS spectra of PVPy-ZW on the surface of ITO and ITO/ZnO.

PCE of iPSC based on PVPy-ZW treated ZnO is improved from 2.95% ($J_{sc}=8.11 \text{ mA/cm}^2$, open circuit voltage (V_{oc})=0.59 V, fill factor (FF)=60.6%) to 3.55% ($J_{sc}=9.49 \text{ mA/cm}^2$, $V_{oc}=0.62 \text{ V}$, FF=60.4%). Also, the thin layer of PVPy-ZW enhances the PCE in conventional type PSC (cPSC) from 2.88% ($J_{sc}=9.15 \text{ mA/cm}^2$, $V_{oc}=0.61 \text{ V}$, FF=51.6%) to 3.45% ($J_{sc}=11.5 \text{ mA/cm}^2$, $V_{oc}=0.62 \text{ V}$, FF=48.5%).

2. Experimental

Chemicals were purchased from Aldrich Chemical Co. and Alfa Aesar and were used as received unless otherwise described. Poly(4-vinylpyridine) (average $M_w \sim 60000$, Cat. No. 472344) was purchased from Aldrich. Regioregular poly(3-hexylthiophene) P3HT (Cat. No. 4002-EE) and 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 $K\alpha$ 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 effective WF of the buffer layer-coated ITO and ZnO and the direction of interface dipole of the buffer layer on the active layer. Schematic illustration of sample preparation showed in Fig. S1 (see Supplementary data). 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

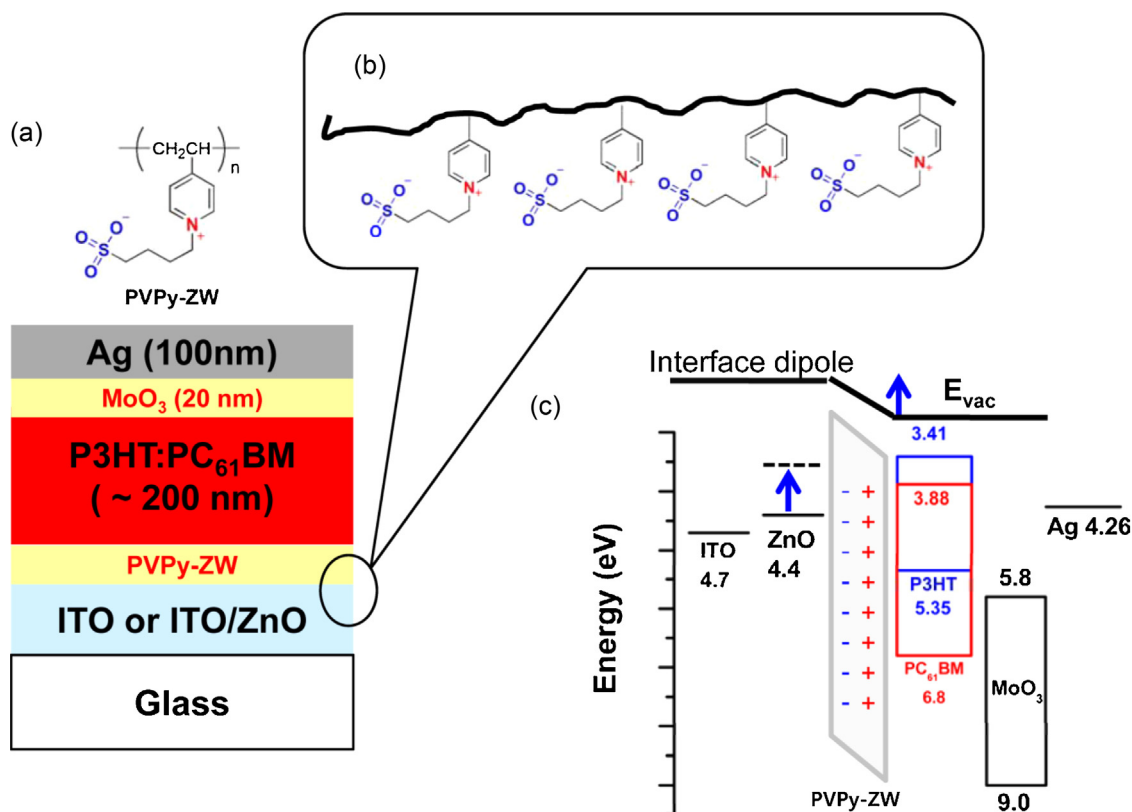


Fig. 2. (a) The chemical structure of PVPy-ZW and the device structure of iPSC, (b) schematic illustration of self-assembly of PVPy-ZW, and (c) the energy level diagrams of materials and the schematic representation of interface dipole.

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