# Solution-Processed Flexible Polymer Solar Cells with Silver Nanowire **Electrodes**

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Supporting Information

ABSTRACT: The conventional anode for organic photovoltaics (OPVs), indium tin oxide (ITO), is expensive and brittle, and thus is not suitable for use in roll-to-roll manufacturing of OPVs. In this study, fully solution-processed polymer bulk heterojunction (BHJ) solar cells with anodes made from silver nanowires (Ag NWs) have been successfully fabricated with a configuration of Ag NWs/poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/polymer: phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM)/Ca/Al. Efficiencies of 2.8 and 2.5% are obtained for devices with Ag NW network on glass and on poly(ethylene terephthalate) (PET), respectively. The efficiency of the devices is limited by the low work function of the Ag NWs/PEDOT:PSS film and the non-ideal ohmic contact between the Ag NW anode and the active layer. Compared with devices based on the ITO anode, the open-circuit voltage  $(V_{oc})$  of solar cells based on the Ag NW anode is lower by  $\sim$ 0.3 V. More importantly, highly flexible BHJ solar cells have been firstly



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fabricated on Ag NWs/PET anode with recoverable efficiency of 2.5% under large deformation up to 120°. This study indicates that, with improved engineering of the nanowires/polymer interface, Ag NW electrodes can serve as a low-cost, flexible alternative to ITO, and thereby improve the economic viability and mechanical stability of OPVs.

KEYWORDS: solution processing, transparent electrode, silver nanowires, flexible solar cell, organic photovoltaics

# ■ INTRODUCTION

Polymer-based bulk heterojunction (BHJ) solar cells are a promising low-cost alternative to existing silicon photovoltaics because of the low cost of the constituent materials and the potential for high-throughput roll-to-roll manufacturing.<sup>1</sup> Rapid progress in the development of new materials and device optimization has brought commercialization of organic photovoltaics (OPVs) closer to reality, with recent reports citing efficiencies greater than 7%.<sup>2-6</sup> However, a critical roadblock to the commercialization of OPVs is the transparent conductive electrode (e.g., the anode). The conventional anode of choice for organic solar cells has been indium tin oxide (ITO) due to its excellent transparency and conductivity. However, ITO has several longstanding disadvantages. First, the cost of ITO thin films is very high, primarily because ITO thin films must be vapor-deposited at rates orders of magnitude slower than solution-based coating processes. Second, indium is a relatively scarce element. Third, the brittleness of ITO renders it susceptible to mechanical damage, making it unsuitable for use with mobile, flexible electronic systems."

The research community has proposed several new transparent electrodes as viable replacements for ITO for OPV applications, including single-wall carbon nanotubes (SWNTs), multiwallcarbon nanotubes (MWNTs), and graphene.<sup>8-16</sup> However, the high sheet resistance of MWNTs or graphene-based electrodes

(typically several hundred  $\Omega/\Box$  at 80% optical transmittance in the visible range) results in solar cells fabricated with these electrodes having a relative low efficiency.<sup>12,16</sup> Conductive transparent SWNTs films have met with much more success: for example, Blackburn et al. achieved an efficiency greater than 3% with poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) cells on SWNTs electrodes with poly-(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) as the hole transport layer,<sup>17</sup> and 2.65% without the hole transport layer,<sup>18</sup> a noticeable improvement over previous literature results.<sup>13</sup> However, these SWNTs electrodes are fabricated via multiple steps, which could potentially lead to a high manufacturing cost. Metal nanogrids based on copper and silver have been developed as transparent electrodes with low sheet resistance,  $^{19-21}$  but the fabrication of these nanogrids requires costly lithography steps that cannot be easily scaled in a costeffective manner. More recently, a high-performance transparent electrode (90% at 50  $\Omega/\Box$ ) based on electrospun copper nanofiber networks was developed.<sup>22</sup> Organic solar cells using these copper nanowire networks as transparent electrodes have reached power efficiencies of 3.0%, comparable to control

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Scheme 1. a) Energy-level diagram showing the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and work functions of each of the component materials. b) The device structure of the solution-processed BHJ polymer solar cell with the Ag NW anode



devices made with ITO electrodes. Unfortunately, electrospinning is an inherently low-throughput process that has not yet witnessed much commercial success despite being first patented in the 1930's.<sup>23</sup>

Solution-processed networks of silver nanowires (Ag NWs) have a sheet resistance and transmittance comparable to those of ITO (10-20  $\Omega/\Box$  at 80% transmittance), together with a relatively high work function of 4.5 eV (Scheme 1a).<sup>24-26</sup> Therefore, films of Ag NWs have been touted as one of the most promising alternatives to ITO for high-throughput roll-to-roll manufacturing of low-cost transparent conducting films for OPV applications. For example, solution-processed Ag NW transparent electrodes have recently been used as the cathode for a BHJ solar cell,<sup>27</sup> and as the anode for an inverted cell.<sup>28</sup> Ag NW films have also been demonstrated as the anode for a vacuumdeposited bilayer solar cell.<sup>24</sup> However, due to the relatively rough surface of the Ag NW network, it remains a significant challenge to replace ITO with a Ag NW electrode as the bottom anode underneath the solution-processed BHJ devices; for example, the Ag NWs that make up the film can easily penetrate the thin layer ( $\sim$ 100 nm) of solution-processed polymer/ PCBM blend atop the Ag NW electrode, resulting in a shortcircuited device. To address the challenge, Yu et al. transferred smooth Ag NW film from a glass substrate to a transparent crosslinked polymer overcoat;<sup>29</sup> and Gaynor et al. embedded Ag NWs into the conducting polymer PEDOT:PSS by lamination. Here, we fabricated highly conductive Ag NW films by spraying an aqueous solution of Ag NWs onto a substrate (glass or plastics) with an air brush. These highly transparent yet remarkably conductive Ag NW films successfully served as the anode for solution-processed, flexible BHJ organic solar cells with a typical configuration of Ag NWs/PEDOT:PSS/polymer:PCBM/Ca/Al (Scheme 1b). We were able to obtain cell efficiencies as high as 2.5% with a new low band gap polymer in our investigation (vide infra). To further probe the effects of the Ag NW electrode on the performance of OPVs and the underlying performance-limiting principles, we have investigated three different polymers, each having different energy levels and processing parameters in the

device fabrication, in OPV devices with Ag NW films as the anode. All these OPV devices exhibited satisfactory performance with little optimization, indicating that Ag NWs are a promising alternative to ITO as the anode for OPVs.

## RESULTS AND DISCUSSION

**Properties of Silver Nanowire Films.** Figure 1a presents a scanning electron microscopy (SEM) image of a flattened Ag NW film on a glass substrate fabricated by spraying a solution of nanowires, followed by pressing. A high-magnification image in the inset shows the Ag NWs appear to be squashed. The NWs used for the electrode were about 60 nm in diameter and 20  $\mu$ m in length. This Ag NW film appears to have a lower density compared with films of a similar conductivity (~36  $\Omega/\Box$ ) in a previous report.<sup>26</sup> This is likely due to the fact that the NWs used here are longer (from 10 to over 20  $\mu$ m) than those used previously (from 4 to 20  $\mu$ m). As the number density of NWs required for percolation is inversely proportional to  $L^2$ , where *L* is the length of a NW, the longer NWs used here can achieve the same conductivity as the shorter NWs at a number density 4 times smaller than that necessary for the shorter NWs.<sup>31</sup>

As shown in Figure 1b, a uniform film of PEDOT:PSS can be spin-coated onto the Ag NWs without washing away the NWs (Figure 1b). The PEDOT:PSS coating decreases the sheet resistance of the NW film from 36 to 23  $\Omega/\Box$ , which is very close to that of the commercial ITO (~15  $\Omega/\Box$ ) with similar transmittance in the visible region. It has previously been noted that the resistance at NW junctions is larger than that of individual Ag NWs.<sup>24,26</sup> The PEDOT:PSS coating likely decreases the overall conductivity of the film. Additionally, this PEDOT:PSS coating reduces the surface roughness of the Ag NWs from 100–120 nm in height (twice large as the diameter of Ag NWs due to their overlap) to ~80 nm, because the nanowires are partially embedded into the PEDOT:PSS coating (Figure 1c,d). This reduced roughness decreases the possibility of an electrical short<sup>13</sup> caused by protruding Ag NWs.

High optical transmittance over a large wavelength range from 400 to 2000 nm is an important property for the transparent electrode in solar cells and photodetectors, because one must minimize any optical loss due to the transparent electrode. Figure 2a compares the optical transmittance of Ag NW films on glass and on poly(ethylene terephthalate) (PET) substrates, with that of an ITO-coated reference substrate. Both of the Ag NW films (either on glass or PET) exhibit excellent transparency  $(\sim 80\%)$  from 400 to 2000 nm. For example, the optical transmittance of the Ag NW film (33.2  $\Omega/\Box$ ) on glass decreases slightly from 83.9% at 500 nm, to 74.0% at 2000 nm. The Ag NW film on PET exhibits a slightly lower transmittance compared with the Ag NW film on glass, but this is compensated for by its slightly lower sheet resistance (30.8  $\Omega/\Box$ ), indicating the transmittance to sheet resistance ratio is similar for Ag NWs on either substrate. On the other hand, the optical transmittance of the ITO-coated substrate peaks (96.2%) around 550 nm, but decreases to 42.1% at 2000 nm. Thus, while ITO substrates might be slightly advantageous for applications targeting the visible region, Ag NW electrodes outperform ITO for applications requiring optical transparency extending into longer wavelength (e.g., solar cells and photodetectors).

In addition to high optical transparency on par with ITO electrodes, Ag NW electrodes offer excellent mechanical flexibility



Figure 1. SEM images of Ag NW network (a) before and (b) after PEDOT:PSS coating; AFM images  $(10 \times 10 \,\mu\text{m}; \text{inset } 2 \times 2 \,\mu\text{m})$  of the Ag NW network (b) before and (c) after PEDOT:PSS coating.



Figure 2. (a) Transmission spectra (excluding the substrates) for ITO reference, Ag NW films on glass and on PET. Photographs of highly transparent Ag NW films transferred onto (b) glass and (c) PET.

while maintaining high conductivity, a significant advantage over traditional ITO electrode that will crack under a large degree of bending.<sup>16</sup> Figure 3 shows the electrical conductivity of Ag NW films on PET with or without PEDOT:PSS coating while bending the substrate. For concave bending angles (curvature radii) up to  $120^{\circ}$  (5.7 mm), a slight decrease in the resistance of the Ag NWs/PET film with increased bending angle was observed. In contrast, the resistance of the Ag NWs/PET film slightly increases with decreased bending angle from  $120^{\circ}$  to  $-120^{\circ}$ . This change in resistance with bending angle may be due to the change in pressure at the nanowire junctions, or a change in the number of nanowire junctions in given area. More importantly, the original conductivity of the Ag NW film can be fully recovered once the strain is released

from the Ag NWs/PET film, even after bending to 120° (5.7 mm in curvature radii) over one hundred times. Similar results were observed for the Ag NWs/PET film coated with PEDOT:PSS. The mechanical flexibility and recoverable conductivity of these Ag NW electrodes not only makes them compatible with low-cost, roll-to-roll manufacturing, but also helps them find promising applications in emerging technologies (such as foldable displays or flexible solar cells) in which the electrode must withstand mechanical deformation without a loss in the conductivity.

**Performance of BHJ Solar Cells Based on Silver Nanowires.** To comprehensively investigate the application of these Ag NW electrodes as the anode in solution-processed BHJ polymer solar cells, we selected a set of three representative polymers. The

first one is the well-studied and commercially available P3HT, widely used as a donor polymer in BHJ OPVs.<sup>32</sup> The other polymers (PBnDT-FTAZ<sup>5</sup> and PBnDT-DTffBT<sup>4</sup>) were recently synthesized following the weak donor-strong acceptor strategy,<sup>33,34</sup> by alternating benzo[1,2-b:4,5-b']dithiophene (BnDT) and either fluorinated 2-alkyl-benzo[d][1,2,3]triazoles (FTAZ) or 4,7-di(thiophen-2-yl)benzothiadiazole (DTffBT) (Scheme 2). This set of polymers represent a wide range of key material properties and processing conditions: (a) energy levels and band gaps: the HOMO energy level is varied from -5.2 eV in P3HT<sup>35</sup> to -5.36 eV in PBnDT-FTAZ<sup>5</sup> and -5.54eV in PBnDT-DTffBT,<sup>4</sup> and the optical band gap is varied from 1.9 eV in P3HT to 2.0 eV in PBnDT-FTAZ and 1.7 eV in PBnDT-DTffBT; (b) processing conditions: P3HT-based BHJ cells were processed in chlorobenzene (CB) followed by thermal annealing at 150 °C to reach maximum performance.<sup>36</sup> Devices based on the two amorphous donor polymers PBnDT-FTAZ and PBnDT-DTffBT were fabricated in 1,2,4-trichlorobenzene (TCB) and 1,2-dichlorobenzene (DCB), respectively, followed by a solvent annealing process. By comparing the properties of devices based on these three different polymers (in reference to the characteristics of devices based on ITO substrates), we aim to gain insights into the effect of the Ag NW electrode as the anode on the performance of solutionprocessed BHJ solar cells.

A typical device consists of Ag NWs/PEDOT:PSS (40 nm) as the anode, polymer:PCBM as the active layer, and Ca (30 nm)/ Al (70 nm) as the cathode. The cross-section SEM images (Figure 4a-c) clearly show the flattened Ag NWs were covered



**Figure 3.** Sheet resistance of the pure Ag NW and PEDOT:PSS coated Ag NW films on PET substrates under different bending conditions. Inset shows the experimental setup of the two-probe electrical measurement. Direct contact of alligator clips to copper tape electrodes on Ag NW films was used in order to ensure good electrical contact during bending.

by the polymer/PCBM active layer. The PEDOT:PSS layer was difficult to observe in the cross-section images, since it is relatively thin compared to the Ag NW film. We found it was necessary to use thick active layers ( $\sim$ 300 nm) to prevent the Ag NWs from penetrating the device and causing a short circuit. Fortunately, unlike other high-performance polymers with an optimized thickness around  $\sim 100$  nm,<sup>37</sup> the polymers used in this study perform well with thicker films. For example the PBnDT-FTAZ and PBnDT-DTffBT polymers exhibit an optimized thickness over 200 nm.<sup>4,5</sup> For comparison, reference devices with identical polymer:PCBM blends were fabricated on the conventional ITO anode with identical processing parameters in order to control for factors such as active layer thickness. As shown in Figure 4d, the thickness ( $\sim$ 300 nm) of the ITO reference device based on PBnDT-DTffBT is nearly identical to that of the device fabricated with the Ag NW electrode (Figure 4c). Therefore, any observed difference in the performance of the otherwise identical solar cells can be safely ascribed to the difference in the properties of Ag NW and ITO electrodes.

Representative current-voltage curves of devices under both illumination and dark are shown in Figure 5, with key photovoltaic characteristics and processing conditions summarized in Table 1. The series resistance  $(R_s)$  and shunt resistance  $(R_{sh})$ were calculated from the slope of the dark current curves. In general, all devices fabricated with Ag NW electrodes demonstrate lower performance than their counterparts based on ITO electrodes, with a slightly smaller short circuit current  $(I_{sc})$  and significantly lower fill factor (FF) and open circuit voltage  $(V_{oc})$ . We ascribe the reduced  $J_{sc}$  and FF to the decreased  $R_{sh}$  and increased R<sub>s</sub> in devices based on Ag NW electrodes. In general, both a high  $R_{\rm sh}$  and a low  $R_{\rm s}$  are desirable for any solar cell. Compared with the reference devices with conventional ITO anodes, there is a noticeable decrease in the  $R_{\rm sh}$  of all devices based on Ag NW electrodes, but still large enough for use in OPVs. This decreased R<sub>sh</sub> is attributed to the poor ohmic contact between Ag NW films and the polymer/PCBM active layer. On the other hand, the  $R_s$  of the Ag NW-based devices is significantly greater than that of the ITO-based device, which is likely the main reason for a 10% decrease in  $J_{sc}$  for the device based on Ag NW electrodes when compared with the reference device based on ITO electrodes. Although the conductivity of Ag NW electrodes is comparable with that of ITO, these Ag NW networks are not as continuous and smooth as the sputtered ITO thin film, thereby resulting in more conduction taking place through the polymer in the device based on Ag NWs. This fact could explain the increased  $R_s$  in the Ag NW-based devices. Taken together, the larger  $R_s$  and lower  $R_{sh}$ , lead to a 20% decrease in the FF for the Ag NW-based solar cells.







Figure 4. Cross-sectional SEM images of Ag NW-based devices made with (a) P3HT, (b) PBnDT-FTAZ, and (c) PBnDT-DTffBT; (d) ITO-based reference device based on PBnDT-DTffBT.

The primary reasons for the lower efficiency of all the devices based on Ag NWs is the significantly smaller  $V_{\rm oc}$  compared with that of the ITO-based device. It is generally accepted that the Voc of polymer/fullerene BHJ solar cells is primarily determined by the difference between the HOMO energy level of the polymer and the LUMO of the acceptor.<sup>38-40</sup> In our study, the V<sub>oc</sub> of devices based on ITO electrodes traces the different HOMO energy levels of the polymers that were used (Table 1). However, we observed a consistent decrease of  $\sim 0.3$  V for the Ag NW-based devices compared with their ITO-based counterparts, regardless of the HOMO energy level of the donor polymer. One plausible reason could be the change in the microstructure and intermolecular interaction in the polymer active layer when switching from ITO electrodes to Ag NW electrodes, which could affect the  $V_{\rm oc}$ .<sup>41</sup> However, the absorbance and incident photon to current efficiency (IPCE) of the Ag NW-based devices exhibit nearly identical absorption edge and IPCE curve shape compared with those of ITO reference devices of each polymer (Figure 5b, d, and f), indicating that the microstructure and intermolecular interaction in the polymer active layer was not strongly affected by the Ag NW electrode. Therefore, we are inclined to the alternative explanation that the observed difference in the  $V_{oc}$  between ITO-based devices and Ag NW-based devices could be due to the difference in the work function of these electrode materials (ITO, Ag NWs, and PEDOT:PSS), because a non-ohmic contact between the anode and the active layer (e.g., polymer) could diminish the  $V_{\rm oc}$  of polymer solar cells.<sup>38,42,43</sup> To explore this hypothesis further, we performed ultraviolet photoelectron spectroscopy (UPS) to measure the work function ( $\phi_{\rm m}$ ) of the Ag NW

electrodes, the PEDOT:PSS and the ITO. The  $\varphi_{\rm m}$  was calculated according to eq  $1^{44}$ 

$$\varphi_{\rm m} = E_{\rm min} + h\nu - E_{\rm max} \tag{1}$$

where  $E_{\min}$ , the low photoelectron kinetic energy, defines the lowest energy electrons able to overcome the work function of the surface;  $E_{\text{max}}$  the high kinetic energy onset of the photocurrent, is a manifestation of the electron population around the Fermi level of the metal; and hv is a known energy provided to the electrons (21.2 eV in our experiment). As summarized in Table 2, due to the high work function of PEDOT:PSS, the  $\varphi_{\rm m}$ of the ITO anode coated with PEDOT:PSS is 0.17 eV higher than that of the bare ITO anode. This thin PEDOT:PSS layer on top of ITO enhances the ohmic contact between the anode and the polymer, thereby improving the  $V_{oc}$  of BHJ devices. It proved difficult to determine the  $\varphi_{\rm m}$  of the pure Ag NW film due to charges build-up on the insulating substrate, likely due to the low density of the Ag NWs. Thus the  $\varphi_{\rm m}$  of a highdensity Ag NW film was measured instead (~4.04 eV) to estimate the  $\varphi_m$  of the pure Ag NW film. As we demonstrated earlier (Figure 1d), an  $\sim$ 40 nm thin PEDOT:PSS layer cannot fully cover these Ag NW networks; therefore, the  $\varphi_{\rm m}$  of Ag NW electrode after coating PEDOT:PSS is only slightly increased to 4.19 eV, 0.39 eV lower than that of ITO coated with PEDOT:PSS electrode. The lower  $\varphi_m$  of the Ag NW electrode (even after coated with PEDOT:PSS), combined with its greater roughness, would very likely make the contact between the anode (Ag NWs) and the polymer less ohmic than that between the smooth films of ITO and the same polymer.



Figure 5. Characteristic J-V curves of the BHJ solar cell devices based on (a) P3HT, (c) PBnDT-FTAZ, and (e) PBnDT-DTffBT under one Sun condition (100 mW/cm<sup>2</sup>); IPCE and absorption of the BHJ solar cell devices based on (b) P3HT, (d) PBnDT-FTAZ, and (f) PBnDT-DTffBT.

Table 1. Fabrication Parameters and Photovoltaic Performances of Devices<sup>a</sup>

polymer	polymer: PCBM	solvent	$conc \; (mg/mL)$	$J_{\rm sc}  ({\rm mA/cm}^2)$	$V_{\rm oc}\left({\rm V} ight)$	FF (%)	$\eta$ (%)	$R_{\rm s}\left(\Omega\right)$	$R_{\mathrm{sh}}\left(\Omega\right)$
P3HT (Ag NWs/glass)	1:1	СВ	10	8.12	0.31	43	1.1	285	$3.3  imes 10^4$
P3HT (Reference)	1:1	СВ	10	9.22	0.58	57	3.1	29.3	$2.0\times10^5$
PBnDT-FTAZ (Ag NWs/glass)	1:2	TCB	15	8.84	0.45	49	1.9	125	$5.0\times10^4$
PBnDT-FTAZ (Reference)	1:2	TCB	15	10.3	0.79	67	5.5	32.3	$2.5\times10^5$
PBnDT-DTffBT (Ag NWs/glass)	1:1	DCB	10	9.64	0.59	48	2.8	196	$2.0\times10^5$
PBnDT-DTffBT (Reference)	1:1	DCB	10	11.2	0.91	58	5.8	29.6	$1.0\times10^{6}$
<sup>4</sup> All polymer/PCBM solutions were spun cast at 400 rpm for 30 s to obtain similar film thicknesses.									

Therefore the difference in the work function (0.39 eV) between Ag NWs/PEDOT:PSS and ITO/PEDOT:PSS can account for the observed roughly 0.3 V decrease of  $V_{\rm oc}$  in all the Ag NW-based devices. Although the performance of Ag NW-based devices is currently lower than the ITO-based reference devices, we still achieved a respectable power conversion efficiency of 2.8%, including a high  $J_{\rm sc}$  of 9.64 mA/cm<sup>2</sup>, a  $V_{\rm oc}$  of 0.59 V and a fill factor of 48% with the solution-processed BHJ solar cell based on the Ag NW anode and a novel polymer (PBnDT-DTffBT).

Photovoltaic Properties of Flexible BHJ Solar Cells. A significant advantage of the Ag NWs over ITO is their excellent resilience to mechanical deformation with minimal loss of their conductivity and transparency (Figure 3). To investigate the impact of flexion on the performance of solar cells based on these flexible electrodes, we fabricated BHJ solar cells made from each of these three polymer:PCBM blends as the active layer on Ag NWs/PET films. The photovoltaic data of the flexible BHJ solar cells were acquired with two probe electrical measurements performed by the direct contact of an alligator clip to the

Ca/Al cathode and to the copper tape covered Ag NW anode, respectively. The copper tape between the alligator clip and the Ag NW anode was used in order to ensure good electrical contact during the measurement (Figure 6a). This setup allowed us to monitor the change in photovoltaic properties of flexible solar cells as a function of the bending angle without detaching and repositioning the electrical contacts. Unfortunately, solar cells using P3HT/PCBM as an active layer always exhibited the characteristics of a short circuit, even when fabricated with thicker polymer layers. This is likely due to the fact that the annealing process for P3HT:PCBM cells takes place at 150 °C, a temperature much higher than the glass transition temperature ( $T_g$ ) of PET (75 °C), which would cause the PET substrate to deform. The deformation of the PET substrate would in turn

Table	2.	Work	Function	of Anode	Electrodes"
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substrates	E <sub>min</sub> (eV)	E <sub>max</sub> (eV)	$arphi_{ m m}$ (eV)
ITO	9.41	26.2	4.41
ITO (coating PEDOT)	9.58	26.2	4.58
Ag NWs	9.04	26.2	4.04
Ag NWs on glass (coated with PEDOT:PSS)	8.49	25.5	4.19
Ag NWs on PET (coated with PEDOT:PSS)	9.44	26.2	4.44

<sup>*a*</sup> Ultraviolet photoelectron spectrum are provided in support information.

increase the likelihood of Ag NWs penetrating the active layer. Devices made with the amorphous donor polymers PBnDT-FTAZ and PBnDT-DTffBT did not require annealing, so these devices were successfully fabricated (Figure 6 b,c).

The current-voltage characteristics of Ag NWs/PET-based flexible solar cells made with either PBnDT-FTAZ or PBnDT-DTffBT under different bending conditions are shown in Figure 7a and b, respectively. Representative performance parameters of solar cells are tabulated in Table 3. Compared with the devices fabricated on Ag NWs/glass substrates, there is a noticeable decrease in  $J_{sc}$  for both of the flexible solar cells, which perhaps resulted from the technical challenge of achieving a uniform coating of the active layer on top of Ag NWs/PET via spin coating, since these flexible PET substrates are prone to deformation. Interestingly, the Voc of PBnDT-FTAZ and PBnDT-DTffBT based flexible devices improves from 0.45 V to 0.67 V and from 0.59 V to 0.75 V, respectively. This large improvement of  $V_{\rm oc}$  (~0.2 V) is likely due to a higher work function of the PEDOT:PSS/Ag NWs/PET film (~0.25 eV higher) compared with the PEDOT:PSS/Ag NWs/Glass substrate (Table 2); however, the exact nature of the observed higher work function of the PEDOT:PSS/Ag NWs/PET film is not yet clear.

As shown in Figure 7 and Table 3, with increased bending angle, the current density drops for both of the flexible Ag NWs/ PET devices, which is likely due to the decreased angle of



Figure 6. (a) The experimental setup used for measuring the J-V curves of flexible devices. (b) Direct contact of alligator clips to copper tape on the Ag NW anode was used in order to ensure good electrical contact during the bending.



Figure 7. Characteristic J-V curves of flexible devices during bending.

 Table 3. Photovoltaic Performances of Flexible Devices under Bending Condition

polymer	bending angle (deg)/curvature radii (mm)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	$V_{ m oc}$ (V)	FF (%)	$\eta$ (%)
PBnDT-FTAZ	0/-	5.11	0.67	40.77	1.4
	60/14	4.56	0.65	39.25	1.2
	90/9.5	3.84	0.63	40.11	1.0
	120/7.2	3.79	0.63	39.17	0.69
	recover	4.95	0.63	39.45	1.2
PBnDT-DTffBT	0/-	8.58	0.75	38.72	2.5
	60/14	7.33	0.71	40.37	2.1
	90/9.5	6.35	0.69	40.57	1.8
	120/7.2	4.68	0.69	36.05	1.2
	recover	8.52	0.75	35.58	2.3

incidence of the illumination. The  $V_{oc}$  also decreased slightly under bending, which can be explained by eq 2<sup>41,45</sup>

$$V_{\rm oc} \approx \frac{nkT}{q} \ln\left(\frac{J_{\rm sc}}{J_{\rm so}}\right) + \frac{\Delta E_{\rm DA}}{2q} \tag{2}$$

where *n* is the diode ideality factor,  $J_{so}$  is related to intermolecular interaction, and  $\Delta E_{\rm DA}$  is the energy difference between the LUMO level of the PCBM and the HOMO level of the donor polymer. Because *n*,  $J_{so}$ , and  $\Delta E_{DA}$  remain unchanged for devices based on the identical polymer/PCBM blend, a smaller  $J_{sc}$  for an increased bending angle would slightly diminish the  $V_{\rm oc}$  of the flexible device. There is no noticeable change on the FF under bending, implying that the  $R_{\rm s}$  and  $R_{\rm sh}$  of the devices barely change while varying the bending bn angle. This observation is consistent with the minimal change of the conductivity of these Ag NW electrodes as shown in Figure 3. More importantly, even after 10 convex bending-recovery cycles with significantly large deformation (e.g., a bending angle/curvature radii of 120°/7.2 mm), these flexible devices can still recover their original performance with only little performance degradation. For example, we achieved an efficiency of 2.3% for the PBnDT-DTffBT/PCBM based flexible devices even after these devices were bent to 120° (7.2 mm) and returned to 0°, 90% of the original value (2.5%)before bending. In sharp contrast, BHJ devices based on ITO/ PET only withstood bending to curvature radii of 15.9 mm with poor performance. Further, these devices failed completely (becoming an open circuit) after being bent to curvature radii of 9.5 mm because of the development of micro-cracks generated by the mechanical stress in ITO.<sup>16</sup> These results clearly exhibit the superiority of these Ag NWs over ITO in fabricating highly flexible solar cells with high efficiency.

# CONCLUSIONS

Fully solution-processed polymer BHJ solar cells with Ag NW anodes have been fabricated with three representative donor polymers (P3HT, PBnDT-FTAZ, and PBnDT-DTffBT). Comparison of these devices with reference devices based on ITO revealed several unique characteristics of Ag NW anodes when they are paired with different polymers. As Ag NW electrodes offer electrical and optical properties comparable to those of ITO, the short circuit current is not strongly affected by the type of anode that was used. In contrast, the open circuit voltage of Ag NW-based BHJ devices is consistently ~0.3 V lower than

that of corresponding ITO-based devices, which significantly reduces the observed efficiency of the Ag NW-based devices. This lower open circuit voltage is ascribed to the low work function of the Ag NWs/PEDOT:PSS film and the poor ohmic contact between the Ag NW anode and the active layer. Future work will focus on engineering the nanowire anode to improve the work function matching. However, even with this relatively low open circuit voltage, devices on glass substrates can still exhibit efficiencies as high as 2.8%. Further, we demonstrated for the first time that highly flexible BHJ solar cells can be fabricated on Ag NWs/PET anode with simple solution processing. The flexible devices retained an efficiency of 2.3%, even after 10 convex bending-recovery cycles with large deformation up to 120° (7.2 mm in curvature radii), whereas devices based on ITO/PET exhibited an open circuit after being bent to a radii of curvature of 9.5 mm. This study demonstrates that the Ag NW electrode meets the most important criteria of conductivity, transparency, flexibility, and solution-processability necessary to replace ITO in organic photovoltaics. Such nanowire electrodes will likely enable high-throughput roll-to-roll manufacturing of low-cost OPVs.

## METHODS

Reagents and Instrumentation. All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, Strem, Fluka) and used without further purification unless stated otherwise. Reagent grade solvents were dried when necessary and purified by distillation. Glass substrates coated with patterned indium-doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. with a 150 nm thick sputtered ITO pattern and a resistivity of 15  $\Omega/\Box$ . Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed with a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. The obtained molecular weight is relative to the polystyrene standard. UV-Visible absorption spectra were obtained by a Shimadzu UV-2401PC spectrophotometer. Work function of electrodes was investigated via ultraviolet photoelectron spectroscopy (UPS) using a Kratos Axis Ultra DLD Ultraviolet Photoelectron Spectrometer. AFM images were collected using an Asylum Atomic Force Microscope (Asylum MFP-3D, Asylum Research). The microscope was operated in AC mode at ambient conditions ( $T = 21 \degree$ C, RH = 45 %), using silicon cantilevers (BudgetSensors, Tap300Al) with resonance frequencies of approximately 300 kHz. Nanostructure features were characterized by scanning electron microscopy (SEM) using a FEI Helios 600 Nanolab Dual Beam System (accelerating voltage 20 kV, beam current 0.69 nA).

Fabrication of Silver Nanowires Films. Ag NW films were fabricated by spraying an aqueous solution of Ag NWs onto a surface, followed by pressing. The wire solution (details in the Supporting Information) was diluted to 800 ppm of Ag with DI water. A microscope glass slide was cut into 1 inch squares and plasma cleaned in a Harrick plasma cleaner/sterilizer (model PDC) for 5 min. The squares were preheated on a heating pad covered by aluminum foil for 5 min at 130 °C. Temperature was controlled with a Staco Energy type 3-PN-1010 variable autotransformer. The spray rate was set to between .05 and .09 mL/s. Spraying was performed in a laboratory hood with an Aztek A470 airbrush with a 0.4 mm nozzle attached to a Sun Mines Electrics mini air compressor. The spray gun was moved back and forth across the slides from a height of several inches. It was important that the temperature of the heating pad did not drop below 100 °C during the spraying process. The conductivity of the slides was measured by a Signatone S-1160A-5 four-point probe every 2 min. Spraying continued until the average conductivities of all slides were below 50  $\Omega/\Box$ . The percent transmittance of each slide was measured at 550 nm using a Cary 6000i UV-vis-NIR spectrophotometer.

The same procedure was used with the polyethylene terephthalate (PET) film as the substrate. The material was cut into 1 inch by 3 inch strips and plasma cleaned for 5 min. The strips were then taped to a large glass slide for the spraying and conductivity measurements to ensure they were not blown away by the spray gun, and to obtain good contact with the four-point probe.

The glass slides were pressed between aluminum plates using a Model C Carver Laboratory Press. The slides were placed on an aluminum plate with the wires facing up, and then a clean microscope slide was carefully placed on the wires before setting the other plate on top. The slides were then pressed with 1000 psi of pressure at room temperature for 10 s. The same pressing procedure was used with the PET slides, but the clean microscope slides were fluorinated before pressing to reduce the amount of nanowire transfer from the polyethylene terephthalate to the glass. To fluorinate the microscope slides, they were plasma cleaned for 1 min, and then placed in a desiccator under a vacuum with 50  $\mu$ L of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (98%, Sigma-Aldrich, Product Code 667420) for at least 1 day before pressing.

Polymer Solar Cell Fabrication and Testing. Prior to use, the ITO substrates were ultrasonicated for 20 min in acetone followed by deionized water and then 2-propanol. The ITO substrates were dried under a stream of nitrogen and subjected to the treatment of UV-Ozone over 30 minutes. No further treatment was applied to Ag NW substrates before using. A filtered dispersion of PEDOT:PSS in water (Baytron PH500) was then spun cast onto clean ITO and Ag NW substrates at 4000 rpm for 60 seconds and then baked at 140 °C for 10 minutes to give a thin film with a thickness of 40 nm. Blends of polymer and PCBM were dissolved in corresponding solvents with heating at 120 °C for 6 h. All the solutions were spun cast at 400 rpm for 30 seconds onto the PEDOT:PSS layer. The substrates were then dried at room temperature in the glovebox under a nitrogen atmosphere for 12 h. The devices were finished for measurement after thermal deposition of a 30 nm film of calcium and a 70 nm aluminum film as the cathode at a pressure of  $\sim 2 \times 10^{-6}$  mbar. There are 8 devices per substrate, with an active area of 12 mm<sup>2</sup> per device. Device characterization was carried out under AM 1.5G irradiation with an intensity of  $100 \text{ mW/cm}^2$  (Oriel 91160, 300 W) calibrated by a NREL certified standard silicon cell. Current versus potential (I-V) curves were recorded with a Keithley 2400 digital source meter. EQE were detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp) and the calibration of the incident light was performed with a monocrystalline silicon diode. All fabrication and characterization steps after adding the PEDOT:PSS layer onto ITO and Ag NW substrates were performed in gloveboxes under a nitrogen atmosphere.

#### ASSOCIATED CONTENT

**Supporting Information.** Supplementary information including preparation of sliver nanowires solution, UV-vis absorption of Ag NWs/PET-based flexible solar cells, ultraviolet photoelectron spectrum of all electrodes, IPCE of Ag NWs/PET-based flexible solar cells. This material is available free of charge via the internet at http://pubs.acs.org.

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