Efficient recyclable organic solar cells on cellulose nanocrystal substrates with a conducting polymer top electrode deposited by film-transfer lamination

Yinhua Zhou a, Talha M. Khan a, Jen-Chieh Liu b, Canek Fuentes-Hernandez a, Jae Won Shim a, Ehsan Najafabadi a, Jeffrey P. Youngblood b, Robert J. Moon b, c, Bernard Kippelen a, *

a Center for Organic Photonics and Electronics (COPE), School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States
b School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States
c U.S. Forest Service, Forest Products Laboratory, Madison, WI 53726, United States

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Abstract
We report on efficient solar cells on recyclable cellulose nanocrystal (CNC) substrates with a new device structure wherein polyethylenimine-modified Ag is used as the bottom electron-collecting electrode and high-conductivity poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, PH1000) is used as the semitransparent top hole-collecting electrode. The PEDOT:PSS top electrode is deposited by a film-transfer lamination technique. This dry process avoids swelling damage to the CNC substrate, which is observed when PEDOT:PSS is directly spin-coated from an aqueous solution. Solar cells on recyclable CNC substrates exhibit a maximum power conversion efficiency of 4.0% with a large fill factor of 0.64 ± 0.02 when illuminated through the top semitransparent PEDOT:PSS electrode. The performance of solar cells on CNC substrates is comparable to that of reference solar cells on polyethersulfone substrates.

1. Introduction
Organic solar cells represent a cost-effective and an environmentally friendly technology for the generation of renewable energy [1–7]. Over the last decade, the power conversion efficiency (PCE) of organic solar cells has been significantly improved up to values of about 10% [8,9]. Due to the ease of fabrication, organic solar cells have been demonstrated on various kinds of substrates, such as glass, plastic, metal foil and paper substrates. From a life-cycle perspective, substrate materials that can be synthesized from renewable feedstocks at a low-cost are particularly attractive for the realization of a sustainable solar cell technology [10–12]. Paper is considered a promising substrate for organic solar cells, because it is inexpensive, low-weight, flexible and recyclable [13–16]. However, the device performance of solar cells fabricated on paper has been low because of the high surface roughness and porosity of the substrates.

Recently, we demonstrated that polymer solar cells fabricated on cellulose nanocrystal (CNC) substrates, with the structure: CNC/Ag (20 nm)/polyethylenimine ethoxylated (PEIE)/active layer/MoO3/Ag, are easily recyclable [10]. The active layer in these solar cells was comprised of blends of poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] phenyl-C61-butyric acid methyl ester (PBDTTT-C:PC60BM). Solar cells on CNC substrates yielded a PCE of 2.7%; an unprecedented level of performance for a polymer solar cell fabricated on recyclable substrates derived from renewable feedstocks [10]. However, the efficiency of solar cells with a similar structure, but fabricated on glass/indium–tin oxide (ITO) substrates...
have yielded PCE values of around 6% [1,17]. The lower PCE values displayed by solar cells on CNC substrates were attributed to the low transmittance of the semitransparent Ag (20 nm) bottom electrode. We suggested that the PCE of solar cells fabricated on CNC substrates could reach values comparable to those obtained with devices fabricated on plastic substrates if electrodes with higher transmittance were employed [10].

The conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been widely used as a transparent electrode for organic solar cells and organic light-emitting diodes because of its high transmittance values across the visible spectrum and high-conductivity (over 1000 S/cm) [18–25]. However, we have found that direct coating of PEDOT:PSS, which is processed from an aqueous solution, damages the CNC substrates. CNC films can readily be redispersed at room temperature in water, thus leading to easily recyclable solar cell devices [10]. The damage of cellulose substrates by the aqueous processing of PEDOT:PSS leads to poor performance of solar cells [11]. Thus, it is important to find a dry deposition method for PEDOT:PSS electrodes on cellulose substrates to produce efficient recyclable solar cells. Recently, Wang et al. [26] and Gupta et al. [27] reported a deposition process in which a high-conductivity PEDOT:PSS film is first deposited onto a poly(dimethylsiloxane) (PDMS) stamp and then transferred by lamination onto the photoactive layer.

Herein, we report on the demonstration of efficient recyclable solar cells fabricated on CNC substrates using a film-transfer lamination technique to produce a semitransparent PEDOT:PSS top hole-collecting electrode, while using a reflective Ag/polyethylenimine (PEI) bottom electron-collecting electrode (Fig. 1). Polymer solar cells fabricated on CNC substrates with a poly(3-hexylthiophene) (P3HT):indene-C60 bisadduct (ICBA) photoactive layer display a high fill factor (FF) of 0.64 ± 0.02 and a high average PCE of 3.8 ± 0.2%; a level of performance that is nearly identical to that of solar cells fabricated on polyethersulfone (PES) substrates.

2. Experimental section

2.1. Solar cells fabricated on CNC and PES (Ref. device) substrates with PH1000-L top electrodes

CNC substrates were prepared as described before [10]. CNC and PES (i-components Co., Ltd.) substrates were adhered onto polydimethylsiloxane (PDMS)-coated glass. Then, an 80 nm thick Ag film was deposited on half of the area of the CNC substrates through a shadow mask using a thermal evaporation system (SPECTROS, Kurt J. Lesker). Polyethylenimine (PEI, branched, #408727, Sigma–Aldrich) was spin-coated on Ag at 5000 rpm for 1 min in a N2-filled glove box from a 0.4 wt.% solution in 2-methoxyethanol (#284467, Sigma–Aldrich) and annealed at 100°C for 10 min. An effective thickness of 10 nm (PEI) was derived through measurement and modeling with spectroscopic ellipsometry (J.A. Woollam Co., M-2000) [1,28]. P3HT (4002-E, Rieke Metals Inc.):ICBA (Luminescence Technology Corp.) (1:1, weight ratio, total 40 mg/ml) was spin-coated at 800 rpm for 30 s in the N2-filled glove box from a chlorobenzene (#284513, Sigma–Aldrich) solution and annealed on a hot plate at 150°C for 15 min. The film thickness was about 200 nm as measured by spectroscopic ellipsometry.

![Fig. 1](image-url) (a) Device structure of solar cells on CNC substrates: CNC/Ag/PEI/P3HT:ICBA/PH1000–L where PH1000–L indicates the PEDOT:PSS PH1000 prepared by film-transfer lamination as the top electrode; (b) chemical structure of branched polyethylenimine used to lower the work function of Ag; (c) the fabrication procedure of recyclable solar cells on CNC substrates: (1) thermal deposition of Ag and spin coating of PEI and P3HT:ICBA on top of the CNC substrates; thermal annealing applied on PEI and P3HT:ICBA layers after each spin coating; (2) mild O2-plasma treatment (5 s) on PDMS followed by spin coating of PH1000; (3) PDMS with PH1000 was transferred onto mild plasma treated (1 s) P3HT:ICBA surface facedown with PH1000 contacting the active layer; (4) Peeling-off the PDMS and thermal annealing to cure PH1000–L to finish the device fabrication. Light was illuminated through the top PH1000–L electrode during the photovoltaic performance measurement.
To deposit PEDOT:PSS PH1000 (Heraeus Clevios) by film-transfer lamination, first, a piece of PDMS (1–2 mm thick) was attached to a glass substrate and exposed to O\textsubscript{2}-plasma (Plasmatic Systems Inc.) for 5 s to tune its surface hydrophilicity. PH1000 with 5 wt% DMSO (#472301, Sigma–Aldrich) was spin-coated onto the PDMS at 1000 rpm for 30 s and drying in air for 10 min without thermal annealing. The film thickness was 150 nm. Before transfer, samples of CNC (or PES)/Ag/PEI/P3HT:ICBA were exposed to O\textsubscript{2}-plasma for about 1 s (flash). Then, the PDMS with PH1000 was cut into 2 mm-wide finger-electrode shapes and transferred onto the P3HT:ICBA active layer face down with PH1000 contacting the photoactive layer. Then, the top PDMS was slowly peeled off and PH1000–L was left on the active layer to finish the PH1000–L lamination process. Ag paint (#16035, Ted Pella Inc.) was applied onto PH1000–L for electrical contact during the measurement. The cells were annealed in a N\textsubscript{2}-filled glove box at 110 °C for 5 min to dry the PH1000–L top electrode. The device areas ranged between 1 and 6 mm\textsuperscript{2}, as determined under an optical microscope (BX51, Olympus).

2.2. Characterization

Current density–voltage (J–V) characteristics were measured inside a N\textsubscript{2}-filled glove box using a source meter (2400, Keithley Instruments). A solar simulator (91160, Newport Oriel) equipped with a 300 W xenon lamp (6258, Newport) with an air mass (AM) 1.5 filter and providing an irradiance of 100 mW/cm\textsuperscript{2} was used as the light source. A Si photodiode (Hamamatsu S1133) calibrated by NREL was used to calibrate the intensity of the solar simulator. Optical images of the photoactive layers on CNC/Ag/PEI and PES/Ag/PEI were taken using an optical microscope (BX51, Olympus). The surface profile of CNC films and PES films was characterized using a stylus profiler (Dektak 6 M, Veeco).

3. Results and discussion

The new device structure is shown in Fig. 1(a). PH1000–L indicates a high-conductivity PEDOT:PSS PH1000 film prepared by film-transfer lamination process. A reflective 80 nm-thick Ag film modified by a thin layer of PEI is used as the bottom electrode. We have shown that the PEI or PEIE modification leads to significant improvement of the electron collection and enhancement of the PCE values of various types of solar cells, including single-junction and tandem solar cells [1,10,28–31], as has also been confirmed by other groups [32–34]. Fig. 1(c) illustrates the procedure whereby solar cells were fabricated on CNC substrates. This procedure is summarized and discussed as follows (fabrication details are shown in Section 2): an 80 nm-thick Ag film is first thermally evaporated on top of the CNC substrates. Then, a thin layer of PEI is spin-coated on Ag to reduce its work function to enable efficient electron collection in solar cells. Samples are then thermally annealed in a N\textsubscript{2}-filled glove box. A P3HT:ICBA photoactive layer is spin-coated onto the CNC/Ag/PEI substrates. Samples undergo a second annealing step in a N\textsubscript{2}-filled glove box. CNC films attached onto glass slides do not deform during the two thermal annealing steps performed during solar cell fabrication. Independently, the PH1000–L layer is fabricated as follows: PH1000 is spin-coated onto a plasma-treated PDMS substrate and left to dry in air for 10 min. To produce top PH1000–L electrodes, the PH1000 layer on PDMS is first cut into a stamp that has the shape of the desired top finger-electrodes. This pattern is then transferred on top of the active layer by contact lamination. The ease of patterning is another advantage of the film-transfer technique as compared to the spin-coating technique. The patterned PH1000/PDMS stamp is transferred on top of the photoactive layer (P3HT:ICBA) with the PH1000 side facing down onto the active layer. The transfer of PH1000 onto the photoactive layer is then completed by peeling-off the thick PDMS substrate. Prior to transfer of the PH1000 film, the surface of P3HT:ICBA is treated by a flash of an O\textsubscript{2}-plasma (about 1 s) to turn the surface hydrophilic and to assist the separation of the thick PDMS substrate from the PH1000 layer. To make the transfer reliable, we found that the PH1000 layer should not be left to dry in air for more than 20 min nor be thermally annealed. Otherwise, the transfer of the PEDOT:PSS layer and the delamination from the PDMS substrate is more difficult. The device performance was tested in the dark and under illumination inside a N\textsubscript{2}-filled glovebox. Note that top illumination through the PH1000–L layer is required in this device architecture.
Fig. 2(a) shows the current density–voltage (J–V) characteristics of a solar cell fabricated on a CNC substrate in the dark and under illumination. In the dark, the device shows low reverse saturation current and a large rectification ratio of $10^4$ at ± 1 V. This indicates an active layer with low density of defects and a large work function contrast between Ag/PEI and PH1000–L. This also indicates that the steps of thermal annealing and dry deposition of the PH1000–L layer do not damage the CNC substrate. Under 100 mW/cm$^2$ of AM 1.5G illumination, the devices show $V_{OC} = 0.80 \pm 0.01$ V, $J_{SC} = 7.3 \pm 0.4$ mA/cm$^2$, and $FF = 0.64 \pm 0.01$, yielding average PCE = 3.8 ± 0.2%, averaged over 7 devices (Table 1). This efficiency is significantly higher than that reported previously in solar cells on CNC substrates with a thin semitransparent Ag electrode (PCE of 2.7 ± 0.1%) [10]. This improvement represents a significant step towards the realization of a truly recyclable solar cell technology. This enhancement is attributed to the higher transmittance of the PH1000–L layer as compared to that of a 20 nm-thick Ag layer.

We fabricated identical solar cells on PES substrates (Ref. device) to compare their performance with devices fabricated on CNC substrates. Fig. 2(b) shows the J–V characteristics of a Ref. device in the dark and under illumination. Again, the devices exhibit a large rectification ratio in the dark J–V characteristics and under illumination, display values of PCE = 4.0 ± 0.2%, averaged over 15 devices (Table 1). The results are comparable to those obtained in devices fabricated on CNC substrates; with differences found to be within the statistical variations from batch-to-batch (Table 1). The only clear difference between processing devices onto PES vs. CNC substrates was found on the device yield. For PES substrates, 15 out of 16 devices worked, whereas for CNC substrates only 7 out of 16 devices worked. This low yield is attributed to the rougher surface of the batch of CNC substrates. Fig. 3(a) displays a representative surface profile of a CNC film. The height variation of the CNC film is 200–300 nm. The thickness of the photoactive layer is 200 nm. The large height variation of the CNC film can cause the devices to short circuit thereby reducing device yield. Fig. 3(c) is an optical image of the photoactive surface of a CNC film. The inhomogeneities of the photoactive layer can be clearly observed. On the contrary, the surface of PES films is very smooth. The height variation is within 5 nm (Fig. 3b). The photoactive layer on PES/Ag/PEI also turns out to be very smooth (Fig. 3d). The Ref. devices on the PES substrates exhibit high yield. Although the surface of the CNC substrate is inhomogeneous, working devices perform similarly to those on PES substrates. Optimization of the processing conditions for the CNC films will be required to achieve higher device yield. It should be noted that although surface roughness affects the device yield, it does not affect the yield of the

Table 1 Photovoltaic performance of top-illuminated solar cells on CNC substrates (CNC/Ag/PEI/P3HT:ICBA/PH1000–L, averaged over 7 devices) and PES substrates (Ref. device, averaged over 15 devices) with PH1000–L as the top electrodes. Numbers in parentheses indicate the photovoltaic performance of the most efficient solar cell on a CNC substrate.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNC</td>
<td>0.80 ± 0.01</td>
<td>7.3 ± 0.5 (7.8)</td>
<td>0.64 ± 0.02 (0.64)</td>
<td>3.8 ± 0.2 (4.0)</td>
<td>7/15</td>
</tr>
<tr>
<td>PES (Ref. device)</td>
<td>0.80 ± 0.01</td>
<td>7.8 ± 0.4</td>
<td>0.63 ± 0.01</td>
<td>4.0 ± 0.2</td>
<td>15/16</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Surface profile of CNC and PES substrates (b) enlarged surface profile of PES substrates. Optical images of top surface of (c) CNC/Ag/PEI/P3HT:ICBA and (d) PES/Ag/PEI/P3HT:ICBA.
film-transfer laminate procedure itself. Once the surface of the active layer is treated by a short-time oxygen plasma and tuned hydrophilic, without further thermal annealing or too long air drying to remove the effect of plasma, the PEDOT:PSS layer is always easy to be laminated and transferred onto the active layer.

4. Summary

In this work we have demonstrated that solar cells fabricated on recyclable CNC substrates can reach a level of performance comparable to that of solar cells fabricated on PES substrates and to that of devices fabricated on ITO-coated glass. These solar cells use a polyethyleneamine-modified Ag electrode at the bottom and laminated PEDOT:PSS-PH1000 as the top electrode. The dry process used to laminate PEDOT:PSS avoids swelling-related damage to the CNC substrates and yields very low reverse saturation current and good diode rectification. Solar cells fabricated on recyclable CNC substrates exhibit PCE up to 4.0%. This is an unprecedented level of performance for solar cells fabricated on substrates derived from renewable feedstocks such as wood. While further optimization of the CNC substrate will be required to provide the same device yield as plastic substrates, these results represent a significant step towards the realization of a low-cost and truly recyclable solar cell technology.

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References

performance influenced by ultraviolet irradiation and air exposure,


