

## Highly Efficient Solar Cells Based on Poly(3-butylthiophene) Nanowires

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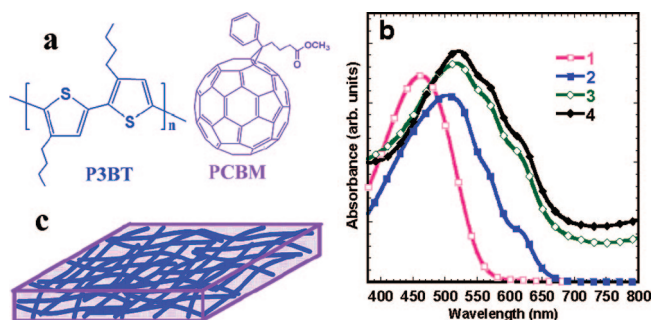
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Photovoltaic cells based on polymer semiconductors are of great interest as a low cost approach to solar energy conversion.<sup>1</sup> Although numerous polymers have to date been explored as the donor in polymer/fullerene bulk heterojunction solar cells,<sup>2–5</sup> regioregular poly(3-hexylthiophene) (P3HT) has emerged from extensive studies as the most promising donor polymer semiconductor in such devices.<sup>3–5</sup> The power conversion efficiency of photovoltaic devices based on P3HT blends with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (C<sub>61</sub>-PCBM) has reached 3–5%.<sup>3–5</sup> The recent progress in raising the performance of polymer/fullerene blend solar cells has come from various annealing protocols,<sup>3–5</sup> which are thought to result in improved two-phase nanoscale morphology, induced by phase separation of the blend, with increased crystallinity, charge carrier mobilities, and absorption coefficient.<sup>1,3–6</sup> Finding a means to achieve a bicontinuous nanoscale morphology that facilitates high crystallinity and carrier mobilities, maximum absorption, and high power conversion efficiency (PCE) in polymer/fullerene bulk heterojunction solar cells remains a fundamental challenge.

Surprisingly, the performance of polymer/fullerene bulk heterojunction solar cells based on regioregular poly(3-butylthiophene) (P3BT) has to date been poor (ca. 0.2–0.3% PCE), even in most recent studies utilizing annealing protocols similar to those used in P3HT devices.<sup>5</sup> The more than an order of magnitude difference in the photovoltaic properties of regioregular P3HT and P3BT has been attributed to various factors, including poor solubility,<sup>6</sup> poor crystallinity,<sup>6</sup> smaller conjugation length,<sup>5a</sup> and lower carrier mobility.<sup>7</sup> Our prior comparative study of the field effect mobility of spin-coated thin films of regioregular poly(3-alkylthiophene)s indeed found a large variation with alkyl chain length; the mobility of holes in P3BT was 9 times less than in P3HT and was explained by the poor self-assembly of crystalline aggregates in the P3BT films.<sup>7</sup>

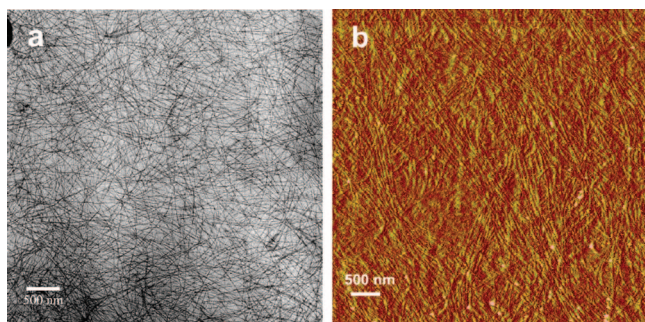
In this Communication, we describe highly efficient polymer/fullerene (both C<sub>61</sub>-PCBM and C<sub>71</sub>-PCBM were employed) solar cells in which a 3-D network of preassembled polymer-semiconductor nanowires serves as the donor component in a sea of fullerene acceptors (Figure 1). In this approach, an electrically bicontinuous nanoscale morphology is realized without going through the difficult path of blend phase-separation phenomena. Photovoltaic cells with 3.0% power conversion efficiency (at 100 mW/cm<sup>2</sup>, AM1.5, 10 mm<sup>2</sup> device area, in air) were achieved by using poly(3-butylthiophene) nanowires (P3BT-nw) as the donor and C<sub>71</sub>-PCBM as the acceptor. P3HT/C<sub>71</sub>-PCBM blend photovoltaic cells, prepared by the conventional annealing-induced phase separation and similarly tested, gave a 3.0% PCE. Thus, we demonstrate that poly(3-butylthiophene) can exhibit photovoltaic properties that are comparable to the much studied poly(3-hexylthiophene).



**Figure 1.** (a) Chemical structures of P3BT and C<sub>61</sub>-PCBM. (b) UV-vis absorption spectra: (1) P3BT solution in ODCB; (2) P3BT-nw suspension in ODCB; (3) P3BT:C<sub>61</sub>-PCBM blend on ITO/PEDOT substrate; and (4) P3BT-nw/C<sub>61</sub>-PCBM nanocomposite on ITO/PEDOT substrate. (c) Schematic illustration of nanowire network of P3BT/PCBM composites.

P3BT nanowires were prepared as dispersions by solution-phase self-assembly similar to reported methods for other poly(3-alkylthiophene)s.<sup>8</sup> A heated solution (6 mg/mL) of P3BT in 1,2-dichlorobenzene (ODCB) was slowly cooled from 90–100 °C to room temperature in a dark environment, allowing P3BT nanowire self-assembly. The resulting P3BT-nw suspension is quite stable; the nanowires do not dissolve in the solvent by dilution and they do not settle or precipitate in over one month. The P3BT-nw/PCBM nanocomposites were prepared by mixing the nanowire suspension with fullerene solution, whereas the P3BT:PCBM blends were made by mixing the hot P3BT solution with PCBM solution before spin-coating (Supporting Information). Figure 1b shows the absorption spectrum of P3BT solution in ODCB along with the absorption spectrum of P3BT-nw suspension. In addition to the absorption maximum ( $\lambda_{\text{max}}$ ) of the nanowire suspension ( $\lambda_{\text{max}} = 502$  nm) which is red-shifted from the solution ( $\lambda_{\text{max}} = 463$  nm), two additional lower-energy shoulder peaks appear at 565 and 615 nm and are characteristic of the crystalline P3BT.<sup>7,8a</sup> The optical absorption spectra of spin coated thin films of P3BT-nw/C<sub>61</sub>-PCBM (1/1 wt ratio) nanocomposite (70 nm) and P3BT:C<sub>61</sub>-PCBM (1:1 wt ratio) blend (80 nm) on ITO/PEDOT substrates are also shown in Figure 1b. The absorption features,  $\lambda_{\text{max}}$  and shoulder peaks, are identical in the P3BT-nw/PCBM nanocomposite and P3BT:PCBM blend films as well as similar to the P3BT-nw suspension. We note that the absolute absorption in the 700–800 nm seen in the thin film spectra (Figure 1b) is due to the ITO/PEDOT substrate.

The morphology of P3BT-nw/C<sub>61</sub>-PCBM nanocomposite films was investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). P3BT nanowires with 8–10 nm width and up to 5–10  $\mu\text{m}$  length were observed in the TEM and AFM images (Figure 2). These nanowires form



**Figure 2.** TEM (a) and AFM (b) images of P3BT-nw/C<sub>61</sub>-PCBM (1/1 wt ratio) nanocomposites.

**Table 1.** Charge Carrier Mobility and Photovoltaic Properties of P3BT-nw, P3BT, and P3HT as Active Donor Materials.<sup>a</sup>

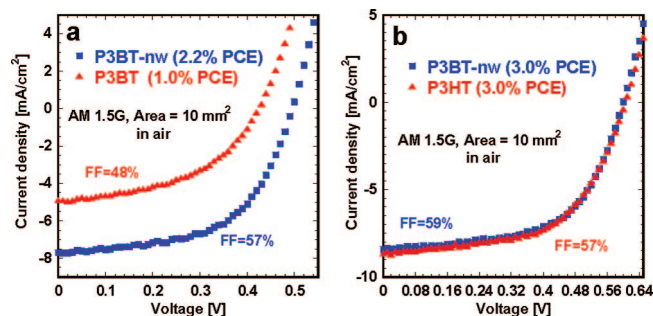
active layer	thickness [nm]	$\mu_h$ [cm <sup>2</sup> /Vs]	$V_{oc}$ [V]	$I_{sc}$ [mA/cm <sup>2</sup> ]	FF	PCE (%)
P3BT-nw/C <sub>61</sub> -PCBM	70	$8.0 \times 10^{-3}$	0.50	7.68	0.57	2.2
P3BT/C <sub>61</sub> -PCBM	80	$3.8 \times 10^{-5}$	0.42	4.90	0.48	1.0
P3BT-nw/C <sub>71</sub> -PCBM	90	$1.9 \times 10^{-3}$	0.60	8.43	0.59	3.0
P3HT/C <sub>71</sub> -PCBM	120	$5.0 \times 10^{-4}$	0.61	8.67	0.57	3.0

<sup>a</sup> At 100 mW/cm<sup>2</sup> (AM1.5) and 10 mm<sup>2</sup> device area.

an interconnected network surrounded by a continuous PCBM phase, forming a quasi-bicontinuous nanoscale morphology (illustrated in Figure 1c). In contrast, more globular domains with no obvious interconnectivity were seen in the AFM image of P3BT:C<sub>61</sub>-PCBM blends (Supporting Information). The blend morphology is neither characteristic of nucleation and growth demixing nor of spinodal decomposition.<sup>9</sup>

The charge transport properties of the P3BT-nw/fullerene nanocomposites, P3BT:C<sub>61</sub>-PCBM blends, and P3HT:fullerene blends were investigated by using the field-effect transistor (see Supporting Information). The average field-effect mobility of holes ( $\mu_h$ ) was  $8.0 \times 10^{-3}$  cm<sup>2</sup>/Vs in P3BT-nw/PCBM nanocomposite films but only  $3.8 \times 10^{-5}$  cm<sup>2</sup>/Vs in P3BT:PCBM blend films (Table 1). Clearly, the interpenetrating two-phase morphology enabled by the P3BT nanowires offers far superior hole transport than the phase-separated P3BT blend. A similar comparison of hole mobility among P3BT-nw/C<sub>71</sub>-PCBM nanocomposite and P3HT:C<sub>71</sub>-PCBM blend showed that the nanowire nanocomposite was far superior.

Photovoltaic cells with 10 mm<sup>2</sup> area were fabricated from P3BT-nw/C<sub>61</sub>-PCBM (1/1) nanocomposite and P3BT:C<sub>61</sub>-PCBM (1/1) blend films and tested in air under 100 mW/cm<sup>2</sup> AM1.5 illumination (see Supporting Information). The current density–voltage characteristics of these two devices are shown in Figure 3a and the photovoltaic parameters, short-circuit current density ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF), and power conversion efficiency (PCE), are given in Table 1. The photovoltaic cells based on the P3BT nanowires have a 2.2% PCE and indeed are far superior in all performance parameters compared to the conventional P3BT blend cells. The more than 2-fold enhancement in efficiency of P3BT nanowire-based solar cells comes from the substantially better charge transport enabled by the nanowire network since both absorbed the same amount of light (Figure 1b). We also fabricated and tested photovoltaic cells from P3BT-nw/C<sub>71</sub>-PCBM (1/0.75) nanocomposite and P3HT:C<sub>71</sub>-PCBM (1:1) blend. The results seen in Figure 3b and Table 1 show that the power conversion efficiency (3.0%) is identical and the other photovoltaic parameters are comparable for P3BT-nw and P3HT.



**Figure 3.** The current–voltage characteristics of solar cells with different active layers. (a) P3BT-nw/C<sub>61</sub>-PCBM nanocomposite (1/1) (70 nm) (■) and P3BT:C<sub>61</sub>-PCBM blend (1:1) (80 nm) (▲). (b) P3BT-nw/C<sub>71</sub>-PCBM composite (1/0.75) (90 nm) (■), P3HT:C<sub>71</sub>-PCBM (1:1) blend (120 nm) (▲). The films in panel a were dried in a vacuum oven at 60 °C overnight and films in panel b were annealed in a glovebox at 110 °C for 10 min.

In conclusion, we have combined TEM and AFM imaging, field-effect charge transport, and photovoltaic measurements to show that the fullerene/P3BT-nanowire nanocomposites exhibit an electrically bicontinuous morphology. Our results demonstrate the achievement of highly efficient solar cells from P3BT nanowires and that the photovoltaic properties of poly(3-butylthiophene) can be comparable to the much studied P3HT. This discovery expands the scope of promising materials and architectures for efficient bulk heterojunction solar cells.

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**Supporting Information Available:** Preparation of P3BT nanowires, solar cell and field-effect transistor device fabrication and testing, and AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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