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Poly-(3)hexylthiophene nanowire networks for versatile fabrication of bulk heterojunctions with increased active volume

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Spontaneous demixing of poly-(3)hexylthiophene (P3HT) and polystyrene (PS) generates a dense array of crystalline P3HT nanowires embedded in a PS matrix. The PS phase is subsequently removed, to form a network of P3HT nanowires with a greatly enhanced surface area-to-volume ratio relative to a planar P3HT film. Photovoltaic devices fabricated from these networks backfilled with either organic ([6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM)) or inorganic (cadmium selenide (CdSe) nanocrystals) material have dramatically increased short-circuit current and power conversion efficiencies relative to planar-bilayer-prepared devices, with increases of $\sim 8 \times$ and $\sim 3 \times$ for PCBM and CdSe nanocrystals, respectively, suggesting that these devices have increased P3HT active volume. This two-step backfill technique can produce nanostructured all-organic and hybrid organic/inorganic bulk heterojunction structures that cannot be formed with traditional one-step casting methods. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4802928]

I. INTRODUCTION

Organic bulk heterojunctions (BHJs) are a promising platform for solar energy conversion due to the low cost of the precursor materials, their high active volume fractions (i.e., film volumes within an exciton diffusion length of a donor-acceptor interface), and their potential for highthroughput production (i.e., roll-to-roll processing). The highest reported external quantum efficiencies (EQE) for such devices are over 8%.^{1–3} Attaining higher efficiencies will likely require new materials systems that absorb in the infrared (IR) portion of the solar spectrum. In particular, the use of inorganic IR sensitizing materials in conjunction with organic materials holds promise for enhancing the efficiency of low-cost photovoltaic (PV) devices.⁴⁻⁶ The current paradigm of depositing both the donor and the acceptor phases of a BHJ simultaneously from a common solvent limits the use of many such IR sensitizing materials. Such one-step methods of BHJ fabrication require each phase to meet a demanding set of electronic and miscibility criteria to attain good electrical characteristics as well as optimal nanoscale morphology.

Inorganic nanocrystals (NCs) have desirable optical and electronic properties and could serve as an optical sensitizing agent within a BHJ;^{7–9} however, limited NC solubility in

complementary organic materials can prevent the formation of an efficient BHJ morphology. Conventional techniques,¹⁰ such as spin casting NCs simultaneously with organic semiconducting materials, typically lead to NC aggregation, which limits device performance.^{11,12}

One strategy to avoid the aggregation of NCs (or any other complementary phase) when utilized in a composite material is to structure one phase of the composite first and then backfill the second phase.¹³ For PV devices, it is particularly desirable for the donor phase (where the majority of optical absorption occurs) to have a nanowire morphology which results in a high volume fraction of material within an exciton diffusion length¹⁴ of a donor–acceptor interface (i.e., active volume).

Considerable research has been dedicated to the development of low-dimensional structures composed of organic semiconductors,^{15–17} with organic PV performance being found to depend on both phase morphology and crystallinity.^{18–21} Poly-(3)hexylthiophene (P3HT) in particular has been found to spontaneously form nanowires in a variety of donor/acceptor blends. Annealing blends of P3HT and [6,6]-phenyl-C₆₁butyric acid methyl ester (PCBM) creates a network of highly crystalline P3HT nanowires within a PCBM rich phase,^{18,19,22–24} resulting in enhanced PV device performance. Distinguishing the beneficial influences of P3HT crystallization and P3HT nanowire morphology on PV device performance is difficult. Increased P3HT crystallinity provides enhanced hole

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mobility, while the evolution of an interpenetrating donor/ acceptor morphology facilitates exciton separation and charge carrier transport. Annealing of spin-cast P3HT/PCBM blends leads to P3HT nanowire crystallization, but PCBM diffusion within amorphous P3HT remains an active process even after crystallization of P3HT is complete. The continued improvement in PV device performance observed upon continued annealing, when P3HT crystallization has concluded, suggests that evolution of donor/acceptor morphology alone is important and can be utilized to improve the efficiency of PV devices.^{22,25,26}

The ability to control P3HT crystallization and morphology independently of the acceptor phase is difficult using traditional one-step casting methods.^{18,19,21,27} When using nonfullerene acceptor materials (such as NCs or planar conjugated molecules)^{8,9,28} the miscibility of donor and acceptor phases is expected to change dramatically compared to fullerene-based systems,²⁹ and may not lead to favorable blend morphologies. It will be advantageous to develop techniques in which the donor-acceptor morphology is decoupled from the choice of acceptor material. Also, although solution-phase methods for generating P3HT nanowires can yield efficient BHJ structures, their reliance on relatively large volumes of dilute P3HT nanowire solutions is undesirable from a production standpoint. The need for careful filtration of unwanted byproducts further limits the utility of solution-phase nanowire production.

It would be advantageous to generate nanowire P3HT films directly on a substrate prior to application of the acceptor phase. Previous work has shown that it is possible to deposit a mat of P3HT nanowires on a variety of substrates utilizing rigid templates^{30–33} and electrospinning,^{34,35} as well as by growing P3HT nanowires in a marginal solvent and casting these fibers on a substrate.^{36–38} Using such techniques it is possible to backfill a high active volume P3HT morphology with a complementary acceptor material, in some cases yielding photovoltaic devices with power conversion efficiencies of over 3%.^{36,37} More recently, it has been shown that various organic nanowires (including P3HT) can be decorated with NCs while still in solution prior to casting on to a substrate.^{39–41}

Qiu and coworkers demonstrated that it is possible to generate P3HT nanowires on a substrate by annealing planar films of P3HT and poly(methylmethacrylate) (PMMA), followed by the removal of the PMMA using acetic acid.⁴² This technique employs a low initial P3HT concentration (<5 wt. %) and also relies on an oxidizing selective solvent (acetic acid) that is expected to degrade the performance of most organic semiconducting polymers.

We report a versatile two-step method for generating P3HT nanowires directly on a substrate, producing an improved nanoscale BHJ morphology. By using a nonoxidizing selective solvent to remove PS from a P3HT/PS blend, we generate a dense mat of highly crystalline P3HT nanowires that are 20–40 nm in diameter and hundreds of nm long. Others have used blends of P3HT and polystyrene (PS) to create similar structures,²⁷ but to our knowledge it has not been demonstrated that the PS phase can be removed from a P3HT blend with a selective orthogonal solvent to expose

nanowires of P3HT. Our nanowire mat can subsequently be backfilled with various complementary materials, such as PCBM or cadmium selenide (CdSe) NCs using an orthogonal solvent. This process enables scalable, on-chip fabrication of P3HT nanowire networks suitable for fabrication of BHJ devices composed of complementary materials that would not otherwise form a BHJ morphology using traditional one-step casting methods when the acceptors do not have suitable solubility/miscibility characteristics to promote nanowire growth while avoiding acceptor phase aggregation (as with NCs).

II. EXPERIMENTAL METHODS

A solution of polystyrene (used as received from Polymer Standard Services) and poly-(3)hexylthiophene (used as received from Luminescent Technologies) was dissolved in dichlorobenzene (DCB) under an inert atmosphere (nitrogen filled glove box). The P3HT content was held constant at 15 mg/ml while the PS:P3HT ratio was varied from 1 to 4. Unless otherwise stated, the molecular weight (MW) of PS was 10.4 kg/mol. After stirring for ~8 h at room temperature, the solution was spin-cast (1000 rpm for 60 s) on poly(3,4-ethylene dioxythiophene) (PEDOT):poly(styrene sulphonate) coated substrates. Silicon wafers with native oxide were used as substrates for morphology studies. Glass substrates with patterned indium tin oxide (ITO, 5–15 Ω per square) films were used for device measurements.

Immediately after spin-casting, films were subjected to solvent annealing with a DCB-rich atmosphere at room temperature for 1 h. The films were then baked at 135 °C for 30 min. After baking, films were submerged in a 1:2 solution of tetrahydrafuran:ethanol (THF/EtOH) for 30 min to remove the PS phase. Films were rinsed in pure ethanol prior to drying at room temperature (see the supplementary material⁵⁹ for more details). Finally, films were baked at 70 °C for 30 min to remove any remaining solvents. For device fabrication, these films were backfilled with an electron accepting material.

The morphology of the donor phase was investigated using a Hitachi 4700 scanning electron microscope (SEM) operated at 10 kV. For improved imaging resolution, SEM samples were coated with 1.8 nm Au-Pd. Surface contact measurements conducted using 8 μ l drops of deionized water served as an indication of the effective surface area factor (cm² of wetted P3HT per areal cm²).

Wide angle x-ray scattering (WAXS) measurements were performed at the Stanford Synchrotron Radiation Lightsource (beamline 11-3) to investigate molecular packing within the P3HT nanowires as well as the PS matrix. WAXS data were collected in a helium atmosphere with an incident angle of 0.10° (chosen just below the critical angle for total internal reflection in order to reduce any background scattering from the substrate and provide a large diffracting volume), a sample-to-detector distance of 400.25 mm, and a photon energy of 12.7 keV.

Photovoltaic devices were fabricated by spin-coating an acceptor material onto P3HT nanowire mats that had been

formed on ITO. The acceptor phase solution was made by dissolving 15 mg/ml of either PCBM (used as received from Luminescent Technologies) or pyridine-capped CdSe NCs (Ref. 43) (\sim 3.5 nm diameter, see the supplementary material for details of NC synthesis) in an orthogonal solvent consisting of 1:2 DCB:diphenylether (DPE). These solutions were spun onto either planar P3HT films or P3HT nanowire mats at 800 rpm for 60 s and subsequently baked at 75 °C for 30 min; these former films will be called planar-bilayer-prepared (or, for short, planar-prepared) films. Cathode electrodes were formed using thermal evaporation of 0.5 nm LiF, followed by 50 nm aluminum. PV device performance was characterized under an AM 1.5 solar spectrum generated by a Newport Instruments 91160 light source (300 W Xe Arc lamp). The current-voltage (I-V) response was recored on a Keithley 2400 sourcemeter. Additional WAXS measurements were performed at the Brookhaven National Laboratory (BNL) NSLS (beamline X9A) on samples after PCBM solutions were spun onto planar P3HT films to form planar-bilayer-prepared films.

III. RESULTS

After removing PS (10.4 kg/mol) from the initial P3HT/ PS blend, the films contain an abundance of P3HT nanowires that are 20–40 nm in diameter and hundreds of nm long. The SEM image in Fig. 1 reveals the morphology that results from a typical blend of P3HT and PS initially containing 50 wt. % P3HT after removal of the PS phase. The influence of the P3HT:PS ratio on the P3HT nanowire network morphology was explored by fixing the P3HT concentration at 15 mg/ml and varying the concentration of PS (MW of 10.4 kg/mol) from 15 to 60 mg/ml.

As seen in Figs. 2(a) and 2(b) [and also in lower magnification in Figs. 3(a) and 3(b)], an initial P3HT content of 40 wt .% or less (10.4 kg/mol PS) results in a mat of P3HT nanowires covering the majority of the substrate with raised micron-scale circular mesas of planar P3HT. This structure is inverted for blends of P3HT and PS initially containing 50 wt.% or more P3HT; when P3HT is the majority constituent



FIG. 2. SEM images of P3HT nanowires generated from blended films initially containing (a) 30 wt. % P3HT, (b) 40 wt. % P3HT, (c) 50 wt. % P3HT, and (d) 75 wt. % P3HT. The remaining balance of all films is 10.4 k MW PS. The scale bars are 1 μ m wide in parts (a)-(c) and 500 nm wide in part (d).

[Figs. 2(c) and 2(d), and also in Figs. 3(c) and 3(d)] there are small pockets of P3HT nanowires surrounded by a planar P3HT film that covers large portions of the substrate. AFM traces show that the thickness of the planar film regions approximately equals the thickness of the original blended film, suggesting that the planar regions in these films are the original blended film surface. (See the supplementary material for additional details of the AFM analysis.)

As the P3HT weight fraction is reduced the areal fraction of the chip covered by the nanowire mat steadily increases, as seen in Fig. 3(e). The SEM images of these films were analyzed by image processing (pixel counting), with nanowire pockets and planar P3HT mesas approximated as ellipsoids to determine the areal fraction of the film covered with P3HT nanowires. Figure 3(e) shows an approximately linear decrease in exposed P3HT nanowire coverage as the P3HT weight fraction in the initial polymer blend is



Fig. 1. SEM image of P3HT nanowires generated from a blended film initially containing 33 wt. % P3HT and 77 wt. % 6.4 k MW PS. The scale bar is 200 nm wide.



FIG. 3. Areal fraction of P3HT films with nanowire morphology in (e), along with SEM images of P3HT nanowires generated from blended films initially containing (a) 30, (b) 40, (c) 50, and (d) 75 wt. % P3HT. The scale bars are $5 \,\mu$ m wide.

increased. This suggests that films cast from solutions initially containing relatively low P3HT content (<30 wt. %) exhibit the greatest areal fraction of P3HT nanowires upon PS removal.

Surface contact angle measurements were performed to test this apparent monotonic correlation between initial P3HT fraction and nanowire coverage (Table I). We assume that the intrinsic interfacial energy of P3HT does not depend on P3HT morphology. On the macroscopic scale (such as the area contacted by a water droplet), we assume that there is a surface roughness factor *S* that describes the larger interfacial surface area of a nonplanar morphology and the correspondingly larger effective interfacial energy, as given by

$$\gamma^{NW} = S\gamma^{P},\tag{1}$$

where γ is the effective interfacial energy and the superscripts *P* and *NW* denote the planar and nanowire morphologies, respectively. Using Young's equation $[\gamma_{gl} \cos(\theta) = \gamma_{sg} - \gamma_{sl}]$ to describe the contact angle θ at the circumference of a liquid droplet in contact with a solid substrate, Eq. (1) becomes

$$S[\gamma_{sg}^{P} - \gamma_{sl}^{P}] - \gamma_{gl}\cos(\theta^{NW}) = \gamma_{sg}^{P} - \gamma_{sl}^{P} - \gamma_{gl}\cos(\theta^{P}), \quad (2)$$

where γ_{sg} , γ_{sl} , and γ_{gl} denote the solid–gas, solid–liquid, and gas–liquid interfacial energy, respectively.

Substituting Young's relationship into Eq. (2) leads to

$$S = 1 + \frac{\gamma_{gl}[\cos(\theta^{NW}) - \cos(\theta^{P})]}{\gamma_{sg}^{P}\cos(\theta^{P})},$$
(3)

which upon making the assumption $\gamma_{gl} \approx \gamma_{sg}$ reduces to the Wenzel relationship⁴⁴ for liquid droplets in contact with a rough surface

$$\cos(\theta^{NW}) = S\cos(\theta^{P}). \tag{4}$$

Using this equation and the measured values of θ^{NW} (Table I), we arrive at the estimates of the surface roughness *S* shown in Fig. 4. These data suggest that the nanowire morphology produces a maximum effective surface area that is

TABLE I. Average surface contact angles made by water droplets in contact with P3HT films after removal of PS from blends containing different initial P3HT content.

Initial P3HT content (wt. %)	Average contact angle (°)
20	101.2 ± 4.8
30	106.4 ± 1.8
40	109.4 ± 4.6
50	119.7 ± 2.2
60	117.5 ± 4.2
70	114.6 ± 3.0
80	111.8 ± 1.5
100	102.0 ± 2.7



FIG. 4. Effective surface roughness (S) and wetting fraction (f) as calculated from surface-contact angle measurements presented in Table I.

approximately twice that of the planar (100 wt. % P3HT) film.

Cassie and others have explored the influence of incomplete wetting by a liquid droplet in contact with a hydrophobic porous substrate due to trapped air.^{45,46} Assuming an idealized substrate described by a repeating array of parallel cylinders, it can be shown that

$$\cos(\theta^{NW}) = f[\cos(\theta^{P}) + 1] - 1, \tag{5}$$

where f is the fraction of the liquid-substrate interface in contact with the solid material and 1 - f (the areal porosity) is the fraction of the droplet in contact with trapped air. Applying Eq. (5) to the surface contact data reveals that P3HT nanowire films (Fig. 4) have up to 40% areal porosity (i.e., $f \sim 0.6$). The reasons for the differences in results in Figs. 3(e) and 4 (for S) are discussed below.

UV-vis absorption spectra taken before and after PS removal of blended films reveal that very little P3HT is lost in the PS removal process when the initial P3HT blend contains 50 wt. % P3HT or greater (from the <3% decrease in film absorption at 560 nm). For blended films initially containing 40 wt. % P3HT or less there is a decrease in P3HT absorption at 560 nm of over 10%, indicating that some P3HT is lost when the PS is removed. (See the supplementary material for typical P3HT UV-vis absorption profiles.) Thickness measurements using AFM confirm that the P3HT nanowire mats generated from blended films containing <40 wt. % P3HT are extremely thin (<40 nm) and may contain only one or two monolayers of P3HT nanowires, while those containing ≥ 50 wt. % P3HT are relatively thick (\sim 60 nm).

The influence of the PS molecular weight on P3HT nanowire morphology was investigated by varying the PS MW from 6.4 to 96k kg/mol, while keeping the P3HT:PS ratio constant (33 wt. % P3HT). The final P3HT morphology is relatively insensitive to PS MW and is characterized by nanowires covering approximately ~80–90% of the substrate surface. However, for PS MW of 19 k g/mol or higher,



FIG. 5. (Color) WAXS data from (a) pristine planar P3HT, (b) a blended P3HT/PS film containing 50 wt. % P3HT, and (c) a P3HT nanowire film generated by removal of PS from an initial P3HT/PS film containing 50 wt. % P3HT.

two 30 min immersions in fresh PS selective solvent (1:2 THF/EtOH) were needed to fully remove the PS phase, resulting in a P3HT nanowire morphology equivalent to those discussed above. (See the supplementary material for additional details.)

The WAXS data presented in Fig. 5(c) demonstrate that P3HT nanowire films produced by selective removal of PS from a P3HT/PS blend exhibit a degree of crystallinity similar to that of the pristine P3HT film [Fig. 5(a)]. Diffraction peaks from the first, second, and third order (h00) reflections appear along the q_z axis at values of 0.38, 0.8, and 1.2 Å⁻¹, respectively, in all samples. This indicates that the lamellar side-chain stacking between adjacent thiophene molecules is normal to the substrate 47-49 and that the π -conjugated plane of the thiophene repeat unit has an edge-on orientation to the substrate. A weak signal from the (010) reflection at a $q_{xy} \sim 1.6 \text{ Å}^{-1}$ suggests that the π -stacking of thiophene molecules is partially crystalline. The diffuse reflection signal at $q \sim 1.8 \text{ Å}^{-1}$ is attributed to scattering from the underlying PEDOT and is seen in control samples of pure PS as well as bare PEDOT on ITO (see the supplementary material).

A line trace of q_z (Fig. S6) reveals a slight shift of the (100) peak to lower q_z values for the P3HT/PS blend film relative to pristine P3HT and suggests a very slight (~1%) expansion of the *d*-spacing along the a-axis of the P3HT crystal when the PS phase is present. When the PS phase is removed, the position of the (100) reflection shifts to higher q_z values, consistent with a ~3% decrease in lamellar stacking distance relative to pristine P3HT. The fact that this

expansion/contraction is small and not accompanied by significant broadening of the (100) peak suggests that the P3HT crystal structure is only slightly perturbed by the presence of the PS phase or by its subsequent removal. It is therefore likely that only a very small fraction of the PS is intercalated into the P3HT crystallites that compose the resulting nanowires. The WAXS image of this P3HT/PS film after PS removal presented in Fig. 5(c) shows that the crystallinity is virtually unaffected by the PS removal, indicating that the THF/EtOH selective solvent is orthogonal. Overall, the crystallinity of the pristine P3HT film and the P3HT/PS film after PS removal is very good, and that of the P3HT/PS blend film is slightly better.

The *J*–*V* curves of four photovoltaic devices fabricated by backfilling P3HT nanowire network films with organic and inorganic acceptor materials are shown in Fig. 6. As seen in Fig. 6(a), a planar-prepared P3HT/PCBM device (50 wt. % P3HT) has a short-circuit current density (J_{sc}) of 0.8 mA/cm², an open circuit voltage (V_{oc}) of ~0.43 V, and a fill factor (FF) of 0.37, yielding a power conversion efficiency (PCE) of 0.13%. For a nanowire P3HT/PCBM device fabricated from an initial P3HT/PS blend containing 50 wt. % P3HT, the J_{sc} increases to 7.75 mA/cm², with $V_{oc} = 0.62$ V and FF = 0.25, yielding a PCE of 1.22%. This represents an increase in efficiency of 840% compared to similarly processed planar-prepared devices.

As a demonstration of the versatility of this fabrication method we also constructed PV devices consisting of P3HT nanowires backfilled with CdSe NCs [Fig. 6(b)]. This type



FIG. 6. (a) *J–V* curves of all-organic PV devices fabricated by backfilling with PCBM a planar P3HT film (dashed line) (cast from a solution of 15 mg/ml P3HT), and a nanowire P3HT film (solid line) (P3HT/PS solution containing 15 mg/ml (50 wt. %) P3HT). (b) *J–V* curves of hybrid PV devices fabricated by backfilling with CdSe NCs a planar P3HT film (dashed line) (15 mg/ml P3HT), and a nanowire P3HT film (solid line) (P3HT/PS solution containing 15 mg/ml (33 wt. %) P3HT). The films represented by dashed lines are called planar-bilayer-prepared in the text.

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of device is unique in its ability to combine both organic and inorganic materials in a PV device with well-defined BHJ morphology. The planar-prepared P3HT/CdSe NC device has $J_{sc} = 0.32 \text{ mA/cm}^2$, $V_{oc} = 0.80 \text{ V}$, and FF = 0.42, yielding a PCE of 0.11%. When a nanowire device (33 wt. % P3HT) is similarly backfilled with CdSe NCs, $J_{sc} = 3.0 \text{ mA/cm}^2$, $V_{oc} = 0.53 \text{ V}$, and FF = 0.26, yielding a PCE of 0.41%, which is a 270% increase over the equivalent planarprepared device.

The WAXS data presented in Fig. S7 (see the supplementary material) demonstrate that the crystallinity of P3HT is not substantially affected by treatment with PCBM in DCB/DPE.

IV. DISCUSSION

Spontaneous demixing of P3HT and PS generates a dense array of crystalline P3HT nanowires embedded in a PS matrix. The PS matrix is subsequently removed using a selective solvent, exposing a network of P3HT nanowires that has substantially greater surface area and active volume than a planar P3HT film. The WAXS measurements reveal that these P3HT nanowires are highly crystalline and that PS is absent from the interior of the P3HT nanowires.

Our results suggest that the formation of P3HT nanowires is driven by the crystallization of the P3HT phase and the corresponding exclusion of the PS phase from the P3HT crystallites. The P3HT phase appears to preferentially adhere to the substrate and upon crystallization forces the PS phase to migrate toward the exposed film surface. This phenomenon is fortuitous given that many PV devices are fabricated utilizing ITO as both the substrate and the anode (hole acceptor).

At low P3HT fractions, this method produces many small P3HT crystals that are surrounded by a continuous matrix of PS. Upon PS removal from these films some of the P3HT is left unsupported, leading to a loss of P3HT to the selective solvent. There must be sufficient P3HT in the initial blend so that during film drying the P3HT domains form a continuous and interconnected network of nanowires. This type of network appears to occur only for P3HT fractions >40 wt.%. The molecular weight of the PS sacrificial phase appears to have relatively little effect on the final film morphology.

The observed transition from "pockets" of nanowires in a "sea" of planar material to a sea of nanowires with mesas of planar material is clearly influenced by P3HT content. When the P3HT loading is high (>40%), we see that PS is excluded into approximately cylindrical regions resulting in pockets of P3HT nanowire. When P3HT loading is 40 wt. % or less we observe the formation of cylindrical regions of high P3HT concentration, which upon PS removal results in circular mesas of planar P3HT surrounded by a mat of P3HT nanowires.

The surface contact angle analysis in Fig. 4 suggests that the maximum film roughness of P3HT nanowire mats occurs with an initial P3HT content of \sim 50 wt. %, whereas the image processing technique [Fig. 3(e)] suggests maximum nanowire coverage at lower P3HT loading. The UV-vis absorption and AFM measurements suggest that the apparent decrease in *S* at lower P3HT content results from contact of the water droplet with exposed regions of the silicon substrate. This is reasonable given the likelihood of pinholes in the thin P3HT nanowire mats that result from low initial P3HT loading fractions. Because the native oxide present on the silicon wafer substrate is hydrophilic, the existence of pinholes will reduce the effective solid–liquid interfacial energy, decreasing the droplet contact angle, leading to an apparently low roughness factor. Photovoltaic device measurements show that these low weight fraction P3HT content P3HT/PS blends do not yield efficient device performance (see the supplementary material). In some cases (initial P3HT < 20 wt. %), PV performance is entirely absent as a result of pinholes in the P3HT leading to shunt pathways between the cathode and the anode.

The SEM image of nanowires persisting after treatment with that solvent system used for backfilling (Fig. S4, see the supplementary material) suggests that backfilling does not dissolve the P3HT nanowire network and does not lead to any significant plasticizing effects (which could allow the diffusion of, say the PCBM). Still, we note that it is known that there can be bilayer mixing in P3HT and PCBM layers formed by solution processing even without thermal annealing and even when supposedly orthogonal solvents are used;⁵⁰ consequently, it is possible that there is intermixing in our planar-prepared and backfilled P3HT nanowire films. The WAXS data presented in Fig. S7 (see the supplementary material) suggest that any such mixing does not significantly affect P3HT crystallinity.

It is known that annealing causes some intermixing between sequentially deposited P3HT and PCBM lavers.^{26,29,51-54} and the extent of this mixing can be very significant for >100 °C.^{26,53} Therefore in this study it could be expected that the sequentially deposited layers of P3HT and acceptor material (PCBM or CdSe NCs) do not form a discrete interface, but more likely form a mixed region near to the nominal donor-acceptor interface. The intermixing of P3HT and PCBM has been found to occur predominantly through intercalation of PCBM into regions of amorphous P3HT, but does not impact the structure or morphology of existing P3HT crystallites. However, in light of the high P3HT crystallinity and lower annealing temperature (75 °C) employed in this study, relatively little PCBM is expected to diffuse into the P3HT phase due to annealing,^{26,53} thus preserving the morphological distinction between planarprepared and nanowire blends.

In PV devices fabricated from P3HT nanowire films backfilled with PCBM J_{sc} increases by 870% relative to that of planar-prepared film devices (for which there may be some intermixing between the P3HT and the PCBM layers), yielding a 840% relative increase in PCE. Similar to PCBM backfilled devices, we observe a 840% increase in J_{sc} for hybrid P3HT/CdSe NC nanowire devices compared to a similar planar-prepared device. However, the FF (0.26) associated with an "S"-shaped J-V curve is relatively low, so the hybrid nanowire device exhibits a comparatively modest 270% increase in PCE compared to a similar planar-prepared device. The low FF observed for the nanowire hybrid NC device may be the result of an increase in the number of interfacial trap sites⁵⁵⁻⁵⁷ arising from both increased surface area as well as the presence of unbound pyridine in the NC solution.⁵⁸

Photovoltaic devices fabricated by backfilling the P3HT nanowires with an acceptor material are more efficient than the corresponding planar-prepared devices, likely as a result of higher active volume fraction of P3HT with the nanowire morphology (even with some interphase mixing in the planar-prepared devices); the P3HT crystallinity is expected to be high in both structures. Moreover, PV devices with the highest PCE correspond to the films possessing the largest S and smallest f, suggesting a direct correlation between surface area, film porosity, and active volume of the P3HT phase of a BHJ PV device, and that the reduced dimensionality of the nanowire morphology enables a larger fraction of photo-excited excitons to be extracted from the P3HT phase.

V. CONCLUSIONS

A method is described to fabricate large surface area networks of crystalline P3HT nanowires in which the PS phase is removed from blended P3HT/PS films. Photovoltaic devices fabricated by backfilling these P3HT nanowire structures with acceptor materials have enhanced PCE. Increases in PCE of 840% and 270% are observed in devices backfilled with PCBM and CdSe NCs, respectively, compared to planar-bilayer-prepared devices. The observed increase in PCE results from an increase in J_{sc} attributed to greater active volume within BHJ devices containing a P3HT nanowire morphology. PV devices fabricated from P3HT nanowire films backfilled with CdSe NCs demonstrate the unique capability of combining both organic and inorganic materials in a device with well-defined BHJ morphology. This two-step process enables scalable, on-chip fabrication of P3HT nanowire networks for large BHJ interfacial areas and holds promise for bringing together complementary materials in a BHJ geometry that cannot be cast simultaneously with the traditional one-step casting methods.

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