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Assembly of Poly(3-hexylthiophene)/CdSe Hybrid Nanowires by Cocrystallization

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S *Supporting Information*

Efficient polymer-based photovoltaic devices require well-segregated interpenetrating nanoscale domains of p- and n-type materials to enhance charge separation and reduce recombination, as well as highly crystalline materials to minimize losses during charge transport.[1] Current approaches to device processing usually rely on thermal[2−4] or solvent[5−7] treatment to promote crystallinity, but since extended annealing can lead to coarsening and eventually macrophase separation,[8] a delicate balance between molecular-scale crystallinity and nanoscale morphology is required.[9] Several recent reports have focused on "precrystallization" approaches in which conjugated polymers are crystallized from solution to form photoactive building blocks that are blended with fullerenes[10−12] or semiconductor nanoparticles[13,14] to yield device layers. These methods afford highly crystalline domains of conjugated polymers with appropriate nanoscale sizes, without the need for delicate annealing treatments. While the efficiencies obtained in this manner[10−13] have not reached the optimized values obtained by judicious annealing of blends prepared without precrystallization,[15] further improvements in nanoscale organization of p- and n-type materials into well-defined hybrid building blocks is anticipated to make such assembly routes advantageous for device fabrication.

Here we describe a new approach to simultaneously organize crystalline n- and p-type materials into hybrid inorganic/organic nanowires. As illustrated in Figure 1a, we begin with conjugated polymer ligands coordinated to the surfaces of semiconductor inorganic nanorods. By dispersing these nanorods along with freely dissolved conjugated polymer chains in a good solvent, subsequent addition of a nonsolvent drives assembly of hybrid nanowires through cocrystallization of ligands and dissolved polymers. We demonstrate the concept using regioregular poly(3-hexylthiophene) (rrP3HT; 20 kDa) mixed with CdSe nanorods bearing rrP3HT ligands (8 kDa), as developed previously by one of our groups.[16] While the association between CdSe nanoparticles and P3HT has been tuned by adsorption of end-functionalized polymers,[17] nonspecific physical interactions,[14] and exclusion of particles from crystalline P3HT lamellae,[18] our approach provides hybrid building blocks with a well-defined interface between crystalline polymer and nanocrystalline rod and can be applied generally to the co-organization of crystalline semiconductor nanostructures.

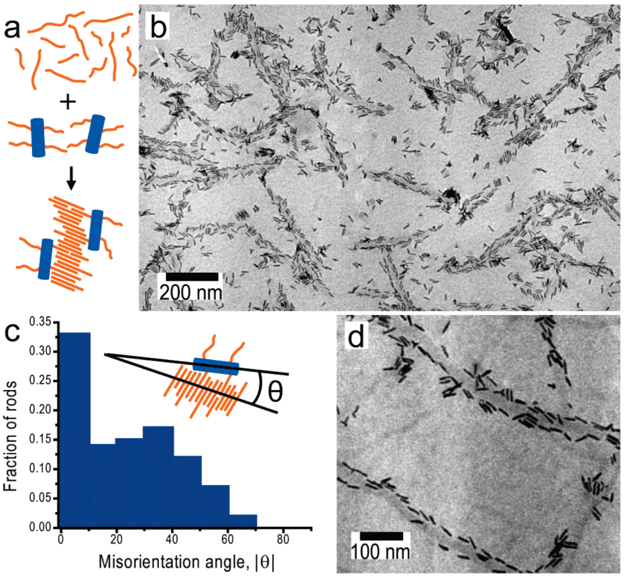

Figure 1. (a) Schematic of cocrystallization of free and grafted P3HT to yield hybrid nanowires. (b, d) TEM images of composite nanowires reveal preferential flanking of nanorods along the sides of P3HT fibrils. (c) Histogram of nanorod misorientation angle, $|\theta|$, indicates preferential orientation nearly parallel to the fiber axis.

Solution crystallization of P3HT to form nanowires[19] was induced by adding a poor solvent, CH_2Cl_2, to a solution of P3HT in $CHCl_3$ to yield a final polymer concentration of 0.75 or 1.1 mg/mL. A distinct solution color change from orange to purple, and the emergence of vibronic bands at 515, 550, and 600 nm in the UV−vis absorption spectrum (Supporting Information), indicated formation of aggregates and $\pi-\pi$ stacking. When crystallization was carried out in the absence of nanorods, transmission electron microscopy (TEM) revealed crystalline P3HT nanowires of ∼20−30 nm width and several micrometers in length (Supporting Information). When nanowire growth was conducted under otherwise identical conditions but in the presence of 0.15 or 0.21 mg/mL of P3HT-grafted CdSe nanorods (4 × 20 nm), similar changes to the UV−vis spectrum were observed (Supporting Information), and the resulting fibrils were found to incorporate P3HT-grafted CdSe nanorods, as shown by the representative TEM images in Figure 1. The graft density of P3HT ligands on the nanorods, estimated thermogravimetrically, is substantially below the density of chains within a crystalline fibril (see Supporting Information), providing a viable mechanism for interpenetration of grafted chains into the P3HT

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fibrils. As the photoluminescence of P3HT and CdSe is quenched by their close proximity, the fluorescence observed from the fibril-containing suspensions (Supporting Information) can be attributed to unassociated dissolved P3HT chains.

As seen in Figure 1, within the hybrid nanowires, CdSe nanorods predominantly flank the P3HT fibrils and have their long axes oriented preferentially parallel to the fibril axis. A histogram of the average misorientation angle between rod and fibril axes $|\theta|$, where $-90° < \theta < 90°$, was collected from 100 rods in five TEM images, as shown in Figure 1c. Nearly 40% of the nanorods are oriented within 10° of parallel to the nanowire axis, while ~85% are oriented <40° from parallel. The orientations are not consistent with a single Gaussian distribution about 0° (99.9% confidence), instead suggesting a secondary preferred orientation near 35°. We speculate that this may reflect a competition between the preferred packing of nanorods along the fibril edge and insertion of ligands into the fibril; however, we note that the orientation distribution may not be fully representative of that in suspension, since rods may be able to reorient to some degree during TEM sample preparation. Nonetheless, the images support our model for hybrid nanowire formation through ligand insertion into the crystal, as this should disfavor nanorod localization on the top or bottom surfaces of the fibril, or orientation at 90° relative to the nanowire axis. (Since the fibers are only ~5 nm thick, as determined by scanning force microscopy, they lie almost exclusively with the P3HT chain axes and long fiber directions in the plane of the TEM grid.) Although the nanorods might be expected to serve as branching or cross-linking points between multiple hybrid fibrils, this was not observed, likely due to the relatively low concentrations used during crystallization.

The hybrid nanowires were typically ≤500 nm long, considerably shorter than fibrils formed in the absence of nanorods (Supporting Information). This may reflect the nanorods acting to slow crystal growth by "capping" the growing fibrils and also possibly serving as heterogeneous nucleation sites, both of which would shorten the average fibril length. The nanowires grow into stable structures over a 1−2 day period and remain suspended with no significant structural changes for at least many months. By analyzing a series of six representative TEM images, we estimate that for a 1:1 solvent mixture ~ 60% of nanorods were associated with fibrils, while over 90% of fibrils were coated with nanorods.

Control experiments verified that successful formation of these hybrid nanowires require cocrystallization and nanorod functionalization. For example, adding P3HT-grafted CdSe nanorods to a suspension of preformed fibrils gave only bare P3HT fibrils (of micrometer lengths) with unassociated nanorods (Figure 2b). In another example, use of CdSe nanorods functionalized with the native alkane-based ligands during the solvent-driven fibril formation process showed a similar lack of fibril−nanorod association (Figure 2c). These results establish that the desired association occurs during fibril formation, rather than postcrystallization or during TEM sample preparation, and is enabled by the polymer ligand coverage on the nanorods.

Numerous parameters are anticipated to influence the efficiency of hybrid nanowire formation, including P3HT molecular weight (both in solution and as ligands), nanorod size and ligand density, temperature, solvent quality, and the concentrations of both polymer and nanoparticles. Detailed studies are underway. We note that removal of the low molecular weight fraction of P3HT by Soxhlet extraction precluded the formation of the hybrid nanowires and that optimal hybrid nanowire formation was found after aging the stock solution of P3HT in $CHCl_3$ for 10−12 days. We speculate that lower molecular weight P3HT, present in the nonextracted polymer and also generated upon aging in solution,[20] compatibilizes the growing fibrils with the P3HT ligands.

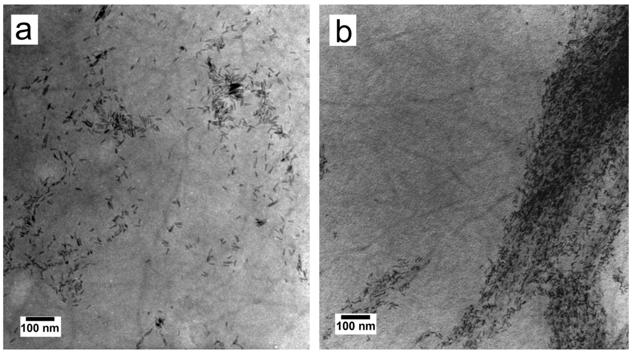

Figure 2. Control experiments conducted by (a) adding P3HT-grafted CdSe nanorods after formation of P3HT fibrils and (b) forming P3HT fibrils in the presence of CdSe nanorods with alkane ligands (the native ligands resulting from nanorod synthesis). Both approaches give aggregation of nanorods and no association with fibrils.

In summary, we present a new method to preorganize electron donor and acceptor materials into hybrid nanowire structures, enabled by crystallization of rrP3HT in solution in the presence of CdSe nanorods functionalized with the same polymer. These well-organized nanocomposite fibers are potentially attractive building blocks for optoelectronic devices and active layers in photovoltaics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, UV−vis and photoluminescence spectra, and TEM micrographs of stable nanowires aged in solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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