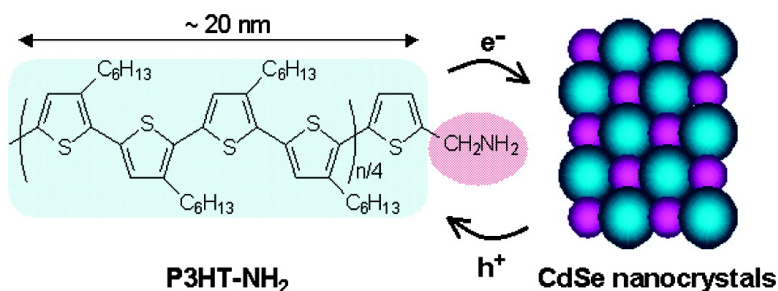Communication

Employing End-Functional Polythiophene To Control the Morphology of Nanocrystal–Polymer Composites in Hybrid Solar Cells

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Employing End-Functional Polythiophene To Control the Morphology of Nanocrystal−Polymer Composites in Hybrid Solar Cells

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π-Conjugated polymers are being developed as alternatives to traditional inorganic semiconductors for low-cost electronic or optical devices because of the ease of their solution processing and their mechanical flexibility. Such efforts are well exemplified by the intense R&D work in organic and organic−inorganic hybrid solar cells.[1−4] In these types of devices, the active layer is a solution-processed mixture of an electron donor phase (a π-conjugated polymer such as regioregular poly(3-hexylthiophene) (P3HT)[5]) and an electron acceptor phase (e.g., CdSe nanocrystals[4,6] or a fullerene derivative[1,3]). Since the blending morphology of the mixture can dramatically affect device performance,[7] a number of methods have been pursued to obtain a favorable three-dimensional interpenetrating network in organic photocells, using for example soluble "double cable" materials[8] or covalent or hydrogen-bonded molecular dyads or tryads.[9,10] However, much development is still needed to prepare intimate nanocomposites of conjugated polymers and semiconductor nanocrystals in hybrid solar cells. Although organic surfactants can facilitate the dispersion of nanocrystals in polymers, their presence severely reduces the device efficiency by impeding the transfer of charges between nanocrystal and polymer, as well as the transport of electrons between adjacent nanocrystals.[11] While surfactants can be stripped from the nanocrystals during film processing to afford direct contact between the nanocrystals and the polymer, it is difficult to control the morphology and dispersion of nanocrystals within the polymer when using this process.[4a,11,12] To address this challenge, we have synthesized an end-functional polythiophene that can effectively disperse CdSe nanocrystals to afford intimate nanocomposites with favorable morphology. Using this functional polythiophene, we have significantly improved the performance of P3HT/CdSe hybrid solar cells.

The end-functional P3HT (**4**) was prepared as shown in Scheme 1. P3HT with a Br chain end (**1**) was synthesized through a modified McCullough route according to published procedures.[13,14] Stille coupling reaction of polymer **1** with an organotin compound bearing a cyano group (**2**) afforded polymer **3**, which was transformed into **4** after reduction with LiAlH₄. The success of the synthesis was confirmed by NMR analysis and MALDI-ToF mass spectral characterization.

The composites of polymer **4** and CdSe nanocrystals were prepared using a procedure similar to that published.[12] CdSe nanorods about 7 nm in diameter and 30 nm in length (as estimated from TEM imaging) were synthesized by the injection of CdO and Se solution into a mixture of trioctylphosphine, trioctylphosphine oxide (TOPO), and tetradecylphosphonic acid (TDPA).[15] The TOPO and TDPA ligands on the surface of the nanorods were then replaced by refluxing the particles in pyridine. After precipitation in hexane and recovery by centrifugation, the particles were redispersed in a mixture of chloroform/pyridine (90:10, v/v) and were mixed with a solution of polymer **4** in the same solvent mixture to afford a

**Scheme 1.** Synthesis of P3HT with Amino End-Functionality
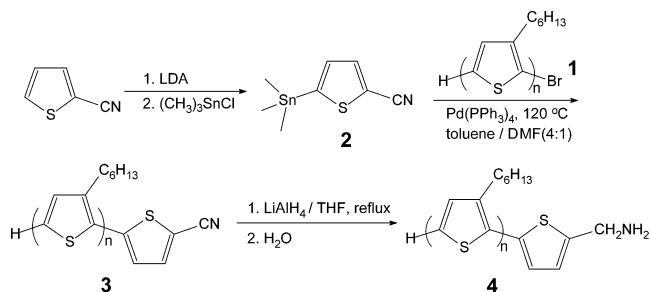
co-solution. Nanocomposite films were then obtained by spin-coating this co-solution of **4** and the nanorods.

The morphology of our composite films was studied using transmission electron microscopy (TEM). Figure 1, right, shows two typical TEM images of CdSe/polymer **4** composite films. They suggest a high degree of homogeneity for the films as no aggregation of CdSe can be seen. In contrast, films prepared under the same processing conditions from a co-solution of the nanorods and polymer **1**, which is the precursor of polymer **4**, always exhibited significant phase segregation (Figure 1, left), suggesting poor dispersion of nanocrystals in the polymer. This significant morphology difference is also observed by TEM when the composite films are thicker.[16]

To investigate the impact of this morphology difference on the photovoltaic device performance, two sets of devices were fabricated in an identical manner, except for the choice of polymer (either polymer **4** or its precursor **1**) for the composite of the active layer. The detailed fabrication of these devices, which consisted in all cases of an indium tin oxide/PEDOT [poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate)]/polymer−CdSe/Al layered structure, was as described in the literature.[4b,12] Characterization of the devices was performed under illumination by a solar simulator.[16]

A plot of the AM 1.5 power conversion efficiency versus the volume ratio of CdSe nanorods in the active layer for each type of device is shown in Figure 2. The volume ratios were calculated on the basis of the bulk densities of both materials. When their volume ratios of nanorods in the active layer were the same, devices made using **4** exhibited significant increases in power efficiency when compared to devices made using polymer **1**. It is unlikely that the small end group difference between **4** and **1** can have a significant effect on their intrinsic hole mobilities. In addition, UV/vis analysis of the active layer films made using **4** and **1** showed essentially identical optical transmission spectra. Therefore, we surmise that the enhanced performance of devices made using **4** is due to the unique morphology this functional polymer confers to the active layer. The plots of Figure 2 also indicate that the efficiency enhancement obtained with **4** is especially substantial at lower concentrations of CdSe. This is consistent with our TEM observa-
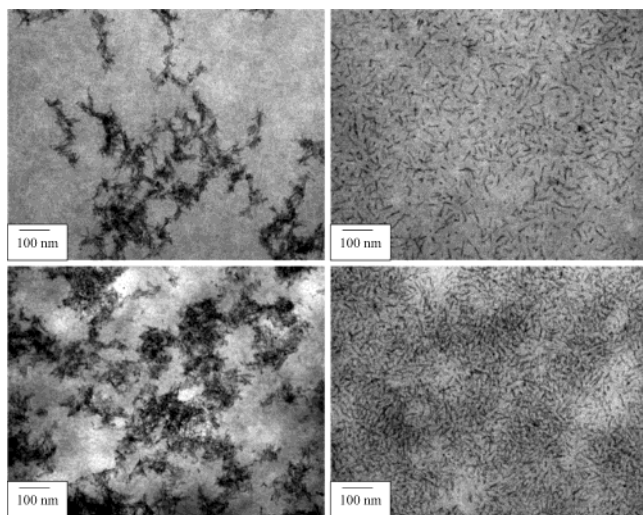
Figure 1. TEM images of four films consisting of CdSe (20 wt %)/polymer **1** (top left), CdSe (20 wt %)/polymer **4** (top right), CdSe (40 wt %)/polymer **1** (bottom left), and CdSe (40 wt %)/polymer **4** (bottom right), respectively.
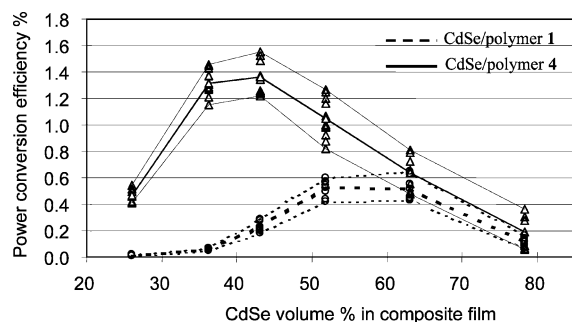
Figure 2. Plots of power conversion efficiency (AM 1.5) versus the volume ratio of CdSe in the active layer of the devices made using polymer **4** (solid lines) and polymer **1** (dashed lines). Note the very high reproducibility of our measurements in numerous duplicate devices with lowest, highest, and average performance shown for each type of polymer.

tion that the morphology contrast is more significant at relatively low ratios of CdSe.

The morphology and device performance improvement discussed above appear to be directly attributable to the amino end group present in **4**. We speculate that polymer **4** partially replaces the pyridine surfactant on the surface of the nanorods through coordination of its amino end group with the CdSe and thereby enhances the miscibility of the polymer with the nanocrystals. The improvement of device performance displayed in Figure 2 might be explained by the larger interfacial area for exciton charge separation due to the good dispersion of CdSe in polymer **4**. Figure 2 also reveals that the most favored ratio of CdSe in the film made using **4** is about 40 vol %, which is lower than that (~65 vol %) observed using **1**. This could also be due to the suppression of nanocrystal segregation by polymer **4** enabling the incorporation of a larger proportion of polymer while still retaining the continuous interpenetration network of nanorods and providing a better balance of percolation at lower rod density. Our results suggest that the use of end-functional P3HT could be an attractive route to obtain more

efficient as well as more "plastic" hybrid photocells. Further work is currently underway to optimize the end group functionality and nanocrystal shapes to bring out the full potential of this system.

In summary, we have shown that an end-functional P3HT enhances the performance of P3HT/CdSe solar cells by increasing the dispersion of CdSe nanocrystals without introducing insulating surfactants. Using end-functional conjugated polymers could provide a general tool to control morphology and optimize efficiency not only in polymer/nanoparticle photovoltaic devices, but also in other composite electronic devices, such as LEDs and photodetectors.[17,18]

Supporting Information Available: Full experimental details on synthesis, device preparation and testing, and TEM studies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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