# Langmuir

## Semiconducting Conjugated Polymer–Inorganic Tetrapod Nanocomposites

Jaehan Jung, Xinchang Pang, Chaowei Feng, and Zhiqun Lin\*

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

**ABSTRACT:** Cadmium telluride (CdTe) tetrapods were synthesized via multiple injections of the Te precursor by utilizing bifunctional ligands. Subsequently, tetrapod-shaped semiconducting inorganic–organic nanocomposites (i.e., P3HT–CdTe tetrapod nanocomposites) were produced by directly grafting conjugated polymer ethynyl-terminated poly-(3-hexylthiophene) (i.e., P3HT– $\equiv$ ) onto azide-functionalized CdTe tetrapods (i.e., CdTe–N<sub>3</sub>) via a catalyst-free click chemistry. The intimate contact between P3HT and CdTe tetrapod rendered the effective dispersion of CdTe tetrapods in nanocomposites and facilitated their efficient electronic interaction. The success of coupling reaction was confirmed by



Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The grafting density of P3HT chains on the CdTe tetrapods was estimated by thermogravimetric analysis. The photophysical properties of P3HT–CdTe tetrapod nanocomposites were studied using UV–vis and photoluminescence spectroscopies. These intimate semiconducting conjugated polymer–tetrapod nanocomposites may offer a maximized interface between conjugated polymers and tetrapods for efficient charge separation and enhanced charge transport regardless of their orientation for potential application in hybrid solar cells with improved power conversion efficiency.

### **1. INTRODUCTION**

Recent research has witnessed rapid advances in synthesis of inorganic semiconductor nanocrystals (NCs) with various shapes and types. They possess size-dependent optical and electronic properties that open up opportunities for use in solar cells,<sup>1–7</sup> LEDs,<sup>8</sup> tunable lasers,<sup>9</sup> biosensors,<sup>10,11</sup> and bioimag-ing.<sup>12</sup> Compared to conjugated polymers used as the hole transporting component because of low electron mobility, semiconductor NCs have high electron mobility and are utilized as good electron acceptors. In comparison to quantum dots (QDs) in which hopping transport occurs and quantum rods (QRs) where the alignment of QRs perpendicular to the substrate may be necessary to realize the full potential of high electron mobility in QDs and QRs, tetrapods enable more effective charge transport due to their intrinsically threedimensional structures. CdTe is an appealing inorganic semiconductor for inorganic solar cells due to its optimum band gap energy ( $E_g = 1.45 \text{ eV}$ ) and high absorption coefficient ( $\alpha = 10^4 \text{ cm}^{-1}$ ),<sup>3</sup> thereby improving the light harvesting efficiency by extending into the near-infrared (NIR) range. Clearly, the replacement of CdSe with CdTe renders the absorption of higher amount of solar radiation as CdSe only absorbs the UV and visible photons (i.e., higher band gap). Additionally, CdTe possesses a much higher electron mobility than CdSe.

Conjugated polymers (CPs) have garnered increasing attention as they offer potential applications in biosensors, thin film transistors, light-emitting diodes, and solar cells.<sup>3-5,13-15</sup> In the latter context, the use of CPs may pave

a promising way to achieve easily manufactured, low-cost solar cells by capitalizing on the advantageous attributes of CPs, such as lightweight, flexibility, roll-to-roll production, low cost, and large area.<sup>13,16,17</sup> Among various types of CPs developed, poly(3-hexylthiophene) (P3HT) represents one of the most extensively studied organic semiconductors due to its solution-processability, tailorable electrochemical properties, high hole mobility, and well-matched energy level with CdSe or CdTe NCs.<sup>18</sup>

Hybrid solar cells composed of CPs and semiconductor NCs have been considered as a promising alternative to inorganic solar cells due to the complementary advantages of CPs and NCs as noted above.<sup>19–23</sup> As the hole mobility in CPs far exceeds the electron mobility, the incorporation of NCs favors the transport of electrons in hybrid solar cells. It is worth noting that most of CP/NC composites are prepared by simple physical mixing of these two constituents based on ligand exchange by utilizing a cosolvent or binary solvent mixture.<sup>19,24,25</sup> However, this approach has several issues such as the existence of insulating surface ligand and microscopic phase separation, thus limiting the performance of the resulting photovoltaic devices due to the decreased light collection through scattering and the reduced interfacial area and charge transfer between CPs and NCs as well as the electron transport between adjacent NCs in physically mixed composites.<sup>26,27</sup> In

```
Received:
March 12, 2013

Revised:
April 16, 2013

Published:
April 19, 2013
```

this context, the ability to chemically tether CPs onto the NC surface (i.e., forming intimate CP-NC nanocomposites) can provide an elegant means of achieving a uniform dispersion of NCs, and, more importantly, promoting the electronic interaction between these two semiconductors. For example, recently P3HT-CdSe quantum dot (QD) and P3HT-CdSe quantum rod (QR) nanocomposites have been successfully synthesized by directly grafting P3HT chains onto CdSe QDs<sup>4,6</sup> and CdSe QRs, 27,28 respectively, by coupling reactions with no need for ligand-exchange chemistry (e.g., Heck coupling of vinyl-terminated P3HT onto end-functionalized CdSe QRs). The CdSe NCs were well dispersed in intimate P3HT-CdSe NC (both CdSe QD and CdSe QR) nanocomposites.<sup>4,6,27</sup> The charge transfer from P3HT to CdSe in P3HT-CdSe NC nanocomposites was found to be much faster than that of P3HT/CdSe NC composites prepared by physical blending.

Herein, we report a robust strategy to place P3HT onto the surface of CdTe tetrapods in the absence of ligand exchange. CdTe tetrapods carry great advantages over CdSe QDs (or QRs) for use in solar cells due to the largely reduced recombination of electrons and holes, while retaining their large interfacial area.<sup>29,30</sup> This can be attributed to their threedimensional structure (four arms symmetrically emanating from the central core), which enables continuous charge transport pathway in the thin film regardless of their orientation.<sup>31</sup> The catalyst-free click reaction was employed to yield P3HT-CdTe tetrapod nanocomposites. First, CdTe tetrapods were synthesized by utilizing a bifunctional ligand (i.e., 4-bromobenzylphosphonic acid (BBPA) with phosphonic acid and aryl bromide at each end). The aryl bromide groups of BBPA were then transformed into azide groups, forming N<sub>3</sub>functionalized CdTe tetrapods. Finally, ethynyl-terminated P3HT synthesized by a quasi-living Grignard metathesis (GRIM) method was grafted onto N<sub>3</sub>-functioanlized CdTe tetrapods through a catalyst-free alkyne-azide cycloaddition, yielding intimate P3HT-CdTe tetrapod nanocomposites without introducing any metallic impurities, which could be detrimental to the photovoltaic device performance. The success of click reaction was confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). The number of P3HT chains tethered on the CdTe tetrapod surface was estimated by thermogravimetric analysis (TGA). The absorption and photoluminescence measurements suggested the intimate contact between P3HT and CdTe tetrapods. A nearly complete quench of P3HT emission in P3HT-CdTe tetrapods nanocomposites was indicative of the efficient charge transfer from electron-donating P3HT onto electron-accepting CdTe tetrapods.

#### 2. EXPERIMENTAL SECTION

All chemicals, including 4-bromobenzyl bromide, triethyl phosphite, cadmium oxide, tri-*n*-octylphophine (TOP, 90%), tellurium powder, sodium azide, 2,5-dibromo-3-hexylthiophene, Ni(dppp)Cl<sub>2</sub>, tert-butylmagnesium chloride (2 mol/L in diethyl ether), and ethynylmagnesium bromide (0.5 mol/L in THF) from Sigma-Aldrich, octadecylphosphonic acid (ODPA, 97%) from Alfa Aesar, and tri-*n*-octylphosphine oxide (TOPO, 90%) from Strem Chemicals were used as received. THF (Fisher, 99%) was refluxed over sodium wire and distilled from sodium naphthalenide solution.

**Synthesis of Bromobenzylphosphonic Acid (BBPA).** 4-Bromobenzyl bromide and triethyl phosphite at 1:2 molar ratio were heated under Ar at 150 °C for 5 h, yielding diethylphosphonate ester. The excess triethyl phosphite and byproducts were removed by rotary evaporator at 100 °C for several hours. Diethylphosphonate ester was hydrolyzed with concentrated aqueous HCl by heating at 100  $^{\circ}$ C overnight, yielding bromobenzylphosphonic acid (BBPA). After cooling to room temperature, BBPA was filtered out, redissolved in acetonitrile, and finally recrystallized in ethyl acetate.

Synthesis of BBPA-Capped CdTe Nanocrystals (NCs). BBPAcapped CdTe NCs were synthesized by modifying the reported method for CdTe NCs.  $^{32}$  In all experiments, the molar ratio of cadmium to phosphonic acid ligands (i.e., ODPA and BBPA) was set to 1:1.8 while the BBPA/ODPA ratio was changed. A mixture of CdO (0.5 mmol), ODPA, BBPA, and TOPO (2 g) was degassed in a threeneck flask for 1 h at 120 °C before increasing the temperature under Ar to above 300 °C, at which the solution turned clear and colorless. Subsequently, 0.2 M tellurium/trioctylphosphine (Te TOP) solution was prepared in the glovebox. The temperature was decreased to 300 °C, and 0.5 mL of Te TOP solution was rapidly injected to initiate the nucleation and growth. In addition to the single injection method as noted above, 0.1 mL of 0.2 M Te TOP solution was injected 10 times at the interval of 1 min (i.e., multiple injection method) to prepare CdTe tetrapod with longer arms. CdTe NCs were allowed to grow at 300 °C for 10 min. The heating mantle was then removed to stop reaction. After the solution was cooled to 60 °C, 2 mL of THF was added. The resulting BBPA-capped CdTe NCs were precipitated twice with methanol and dissolved in THF.

Synthesis of Ethynyl-Terminated P3HT. Ethynyl-terminated P3HT (i.e., P3HT $-\equiv$ ) was synthesized by a quasi-living Grignard metathesis (GRIM) method.<sup>33,34</sup> Briefly, 2,5-dibromo-3-hexylthiophene (0.815g, 2.5 mmol) was dissolved in THF (5 mL) in a threeneck flask and stirred under Ar. tert-Butylmagnesium chloride (1.25 mL, 2.5 mmol) was added. The mixture was stirred for 2 h at room temperature. Subsequently, it was diluted to 25 mL with THF, followed by the addition of Ni(dppp)Cl<sub>2</sub> (11.2 mg, 0.020 mmol). The resulting solution was stirred for 30 min at room temperature, producing intermediate P3HT; it was then reacted with ethynylmagnesium bromide (2 mL, 1 mmol) in THF for 30 min. The product, P3HT-≡, was obtained by precipitating the reaction mixture in methanol, filtering in an extraction thimble, and washing by Soxhlet extraction with methanol, hexane, and chloroform sequentially. It was recovered after chloroform evaporated. The regioregularity of P3HT was greater than 97%, as determined by <sup>1</sup>H NMR. The numberaverage molecular weight and polydispersity index (PDI) of P3HT were 50 kDa and 2.2, respectively, as measured by gel permeation chromatography (GPC). Yield: 41.2%.

Synthesis of P3HT–CdTe Tetrapod Nanocomposites by Click Reaction. Sodium azide  $(NaN_3)$  was added to BBPA-capped CdTe tetrapods THF solution. The mixture was then sealed and stirred at room temperature for 3 days. Excess amount of NaN<sub>3</sub> was removed by centrifugation. The resulting azide–benzylphosphonic acid-capped CdTe tetrapods (CdTe-N<sub>3</sub>) were then precipitated in methanol. Subsequently, 50 mg of P3HT– $\equiv$  and 50 mg of CdTe–N<sub>3</sub> tetrapod were mixed in 10 mL of THF and kept at 65 °C under Ar for 2 days. The final product (i.e., P3HT–CdTe nanocomposites) was cooled to room temperature and diluted 10 times with THF. The resulting solution was precipitated in methanol twice to remove free P3HT which was not coupled with CdTe tetrapods.

**Characterization.** The morphology of CdTe NCs and P3HT– CdTe tetrapod nanocomposites was imaged by a low-resolution and high-resolution transmission electron microscope (JEOL 100cx and Tecnai F30). The <sup>1</sup>H NMR spectra were taken using a Varian VXR-400 spectrometer. The grafting density of P3HT chains on the CdTe tetrapod surface was determined by thermogravimetry analysis (TGA; TA Instruments TGA Q50) in a nitrogen atmosphere. The temperature was increased to 800 °C at the rate of 5 °C/min. The absorption and emission spectra were recorded with a UV–vis spectrometer (UV-2600, Shimadzu) and a spectrofluorophotometer (RF-5301PC, Shimadzu), respectively. All samples were excited at  $\lambda_{ex}$ = 445 nm, and the emission was collected at  $\lambda_{em}$  > 500 nm.



**Figure 1.** Low-magnification TEM images of CdTe NCs at different molar ratio of BBPA to ODPA: (a) BBPA:ODPA = 1:7, (b) BBPA:ODPA = 1:5, (c) BBPA:ODPA = 1:4 by single injection of Te TOP solution, and (d) BBPA:ODPA = 1:4 by multiple injections of Te TOP solution.

#### 3. RESULTS AND DISCUSSION

CdTe NCs functionalized with bifunctional ligands were synthesized in the absence of ligand-exchange procedure. 4-Bromobenzylphosphonic acid (BBPA) was employed as bifunctional ligands as phosphonic acids are the most widely used ligands and they are powerful additive to control the branching and anisotropic growth.<sup>32</sup> The effect of molar ratio of BBPA to octadecylphosphonic acid (ODPA) on the shape of the resulting CdTe NCs was studied. As shown in Figure 1a, BBPA-functionalized CdTe QDs were produced at the BBPA/ ODPA ratio of 1:7. As the ratio increased to 1:5, the anisotropic NCs including rods, dipods, and tripods were obtained (Figure 1b). More regular CdTe tetrapods were yielded at the BBPA/ ODPA ratio of 1:4 (Figure 1c), which was due to the influence of small molecules (i.e., ligands) that triggered the twinning as well as anisotropic growth.<sup>32</sup> Clearly, the higher the BBPA/ ODPA ratio, the more branched and elongated CdTe NCs were observed (Figure 1a-c). In order to extend the length of each arm, the multiple injection method (i.e., 10 times in the present study) was used by simple replenishing Te (i.e., Te TOP solution) to the reaction solution at a certain time interval.<sup>35,36</sup> Figure 1d shows the TEM micrograph of CdTe tetrapods with the increased size and aspect ratio as compared to those obtained from the single injection method (Figure 1c).

The BBPA-functionalized CdTe tetrapods prepared by the multiple injection method (Figure 1d) were then utilized to synthesize P3HT-CdTe tetrapod nanocomposites as these tetrapods have advantageous size and shape for use in hybrid solar cells as compared to other structures in Figure 1a-c. Given the typical thickness of hybrid solar cells ranging from 70 to 200 nm, the intrinsic three-dimensional structures of CdTe tetrapods are beneficial for efficient charge transport to the electrode in comparison to the corresponding QDs where electron hopping between particles would be required. The high-resolution TEM images revealed that CdTe tetrapods were  $85 \pm 10$  nm in size with a diameter of  $5 \pm 0.3$  nm for each arm. The HRTEM image clearly showed the tetrapod morphology of CdTe NCs (Figure 2b). Interestingly, planar defects were observed in some arms of CdTe tetrapods (the inset in Figure 2b), which may be due to the effect of short ligand (i.e., BBPA).<sup>32</sup> The formation of tetrapods can be rationalized according to the multiple-twin model.<sup>32</sup> In the multiple-twin model the arms grow from an octahedrally twinned wurtzite core; thus, the number of arms depends on the types of twins in the core, which yield a distribution of the number of arms. The coexistence of rods, dipods, tripods, and tetrapods in Figures 1 and 2 suggested that tetrapods were grown from twinned wurtzite core. After CdO was decomposed



Figure 2. TEM images of (a) BBPA-functionalized CdTe tetrapods; (b) close-up of individual BBPA-functionalized CdTe tetrapod, the close-up of arm marked with a dashed circle is shown as the inset; and (c, d) P3HT-CdTe tetrapod nanocomposites.

Scheme 1. Grafting Ethynyl-Terminated P3HT (i.e., P3HT $=\equiv$ ) onto Azide-Functionalized CdTe (i.e., CdTe $=N_3$ ) Tetrapods by Catalyst-Free Click Chemistry, Yielding P3HT=CdTe Tetrapod Nanocomposites



by phosphonic acid, a Cd–phosphonic acid complex (i.e., Cd– BBPA and Cd–ODPA) was formed as Cd<sup>2+</sup> readily reacted with phosphonates. The Cd–BBPA complex was much more mobile than the bulkier Cd–ODPA. As a result, the probability of yielding planar defects (i.e., twins) was increased in the presence of BBPA; this led to the formation of twinned core and was responsible for the emergence of rods, dipods, tripods, and tetrapods.

The P3HT-CdTe tetrapod nanocomposites were subsequently synthesized via click reaction between ethynyl-terminated P3HT (i.e., P3HT- $\equiv$ ) and azide-functionalized

CdTe (i.e., CdTe–N<sub>3</sub>) tetrapods after converting aryl bromine groups in BBPA-functionalized CdTe tetrapods into azide groups as illustrated in Scheme 1. On the basis of the disappearance of ethynyl peak at 3.5 ppm (Figure 4b) after the click reaction between CdTe–N<sub>3</sub> and P3HT– $\equiv$ , it is clear that the amount of azide functional groups on the CdTe tetrapod surface was enough to render the complete coupling with ethynyl groups on P3HT– $\equiv$ . We note that aryl halides have been converted to azides by the reaction with sodium azide using copper catalyst.<sup>37</sup> It is plausible that the Cd in the system catalyzed the reaction in the present study. The azide groups converted from aryl bromine groups by reacting with sodium azide was sufficient for the complete grafting of P3HT = =.

Figure 2c,d shows the TEM images of P3HT-CdTe tetrapod nanocomposites, where CdTe tetrapods were well dispersed in the nanocomposites. The success of grafting P3HT- $\equiv$  chains onto CdTe-N<sub>3</sub> tetrapods was confirmed by the Fourier transform infrared (FTIR) spectroscopy measurements as shown in Figure 3. Strong absorptions of P3HT at



Figure 3. FTIR spectra of BBPA-functionalized CdTe tetrapods (black), azide-functionalized CdTe tetrapods (i.e., CdTe $-N_3$  tetrapods; red), and P3HT-CdTe tetrapod nanocomposites (blue).

2954, 2915, and 2850 cm<sup>-1</sup> were assigned to the asymmetric C–H stretching vibrations in  $-CH_{32}$ ,  $-CH_{22}$ , and the symmetric C-H stretching vibration in  $-CH_2$ , respectively,<sup>38</sup> from the alkyl side chains in P3HT and ligands. Notably, the characteristic  $-N_3$  vibration appeared at 2040 cm<sup>-1</sup> after the aryl bromine groups of BBPA-functionalized CdTe tetrapods were converted into azide groups, forming CdTe-N<sub>3</sub> tetrapods. This peak then disappeared after the CdTe-N3 tetrapods coupled with P3HT-≡, suggesting the successful grafting of P3HT chains onto the CdTe tetrapods (i.e., producing P3HT-CdTe tetrapod nanocomposites; Figure 3) via 1,3-dipolar cycloaddition between ethynyl group in P3HT-≡ and azide group in CdTe-N<sub>3</sub> tetrapods. It is worth noting that such coupling reaction was conducted in the absence of catalysts, thus circumventing the introduction of any metallic impurities, which may influence the performance of the P3HT-CdTetetrapod-based photovoltaic devices. The <sup>1</sup>H NMR data shown in Figure 4 also strongly supported the occurrence of grafting P3HT- $\equiv$  onto CdTe-N<sub>3</sub> tetrapods. A proton signal at 3.5 ppm from the ethynyl group on the P3HT chain (Figure 4a) disappeared in P3HT-CdTe tetrapod nanocomposites (Figure 4b) after the P3HT- $\equiv$  chain was coupled with the CdTe-N<sub>3</sub> tetrapod. The appearance of the peak between 3.5 and 4 ppm in Figure 4b was from the proton of -CH<sub>2</sub> in CdTe-N<sub>3</sub> tetrapods (i.e., in CdTe-BPA-N<sub>3</sub>) after grafting of P3HT- $\equiv$ onto CdTe-N<sub>3</sub> tetrapods.

To determine the coverage of P3HT chains on the CdTe tetrapod surface, thermogravimetric analysis (TGA) was performed (Figure 5). BBPA-functionalized CdTe tetrapods showed a significant mass loss from 300 to 450 °C due to the degradation of surface capping ligands (i.e., BBPA and ODPA), which was about 26% of BBPA-functionalized CdTe tetrapods (Figure 5a). TGA curve of ethynyl-terminated P3HT homopolymer (i.e., P3HT $-\equiv$ ) (molecular weight = 50 kDa) also revealed the onset of degradation in the temperature range

Article



**Figure 4.** <sup>1</sup>H NMR spectra of (a) ethynyl-terminated P3HT(i.e., P3HT $-\equiv$ ) and (b) P3HT-CdTe tetrapod nanocomposites. The peak between 3.5 and 4 ppm in (b) was assigned to the proton of  $-CH_2$  from CdTe $-BPA-N_3$  tetrapods after grafting of CdTe $-BPA-N_3$  tetrapods (i.e., CdTe $-N_3$  tetrapods) onto P3HT $-\equiv$ .

400–450 °C, leaving behind a char-like yield of 28% (Figure Sb). The mass reduction in P3HT–CdTe tetrapod nanocomposites (i.e., the sum of grafted P3HT and ligands) in this temperature range was roughly 60% (Figure 5c). Taken together, the weight ratio of P3HT to CdTe tetrapods was about 3.82:1. Based on the TEM images in Figure 2, the molecular weight of CdTe tetrapods was estimated to be  $1.11 \times 10^7$  g/mol. Thus, the molar ratio of P3HT chains to CdTe tetrapods was estimated to be approximately 800:1.

The photophysical properties of P3HT-CdTe tetrapod nanocomposites were explored by UV-vis absorbance and photoluminescence (PL) studies. The absorption spectra of ethynyl-terminated P3HT (i.e., P3HT-≡), BBPA-functionalized CdTe tetrapods, and P3HT-CdTe tetrapod nanocomposites in THF are shown in Figure 6a. The absorption maxima for P3HT and CdTe tetrapods were at 445 and 657 nm, respectively. Clearly, the absorption spectrum of nanocomposites was simply a sum of their constituents (i.e., two maxima in nanocomposites at 445 and 657 nm can be ascribed to P3HT and CdTe tetrapod, respectively), suggesting the successful coupling of end-functionalized P3HT and CdTe tetrapods. Figure 6b shows the PL spectra of P3HT- $\equiv$  and P3HT-CdTe tetrapod nanocomposites in THF. Obviously, the nearly complete quenching of the emission of nanocomposites relative to the pristine P3HT homopolymer indicated the efficient charge transfer from electron-donating P3HT onto electron-accepting CdTe tetrapods. This observation further confirmed the intimate chemical contact between P3HT and CdTe tetrapods.

#### 4. CONCLUSIONS

In summary, CdTe tetrapods were synthesized by multiple injections of the Te precursor. A simple strategy for semiconducting P3HT–CdTe tetrapod nanocomposites was then explored by anchoring ethynyl-terminated P3HT onto azide-functionalized CdTe tetrapods via a catalyst-free click chemistry. The direct contact between P3HT and CdTe tetrapod enabled the good dispersion of CdTe tetrapods in nanocomposites. The success of click reaction was confirmed by FTIR and <sup>1</sup>H NMR measurements. The molar ratio of P3HT chains to CdTe tetrapods was approximately 800:1. The absorption spectrum of P3HT–CdTe tetrapod nanocomposites was the sum of the absorption spectra of P3HT and CdTe tetrapods. The nearly complete quenching in the emission of nanocomposites was indicative of efficient charge transfer at the P3HT/CdTe tetrapod interface. These intimate semiconduct-

Figure 5. Thermogravimetry analysis (TGA) of (a) BBPA-functionalized CdTe tetrapods, (b) ethylnyl-terminated P3HT homopolymer, and (c) P3HT-CdTe tetrapod nanocomposites prepared by click reaction.



**Figure 6.** (a) Absorption spectra of ethynyl-terminated P3HT (black square), BBPA-functionalized CdTe tetrapods (red circle), and P3HT–CdTe tetrapod nanocomposites (blue triangle) prepared by click chemistry. (b) Emission spectra of ethynyl-terminated P3HT (black square) and P3HT–CdTe tetrapod nanocomposites (red circle).

ing organic-inorganic nanocomposites may serve as promising materials, by improving optical absorption and electron transport owing to the incorporation of intriguing three-dimensional structures of CdTe tetrapods, for a wide range of applications, including hybrid solar cells, LEDs, FETs, and sensors.

#### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: zhiqun.lin@mse.gatech.edu (Z.L.).

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We gratefully acknowledge support from Georgia Institute of Technology.

#### REFERENCES

(1) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Hybrid nanorod-polymer solar cells. *Science* **2002**, *295*, 2425–2427.

(2) Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. Air-stable allinorganic nanocrystal solar cells processed from solution. *Science* **2005**, *310*, 462–465.

(3) Kang, Y. M.; Park, N. G.; Kim, D. W. Hybrid solar cells with vertically aligned CdTe nanorods and a conjugated polymer. *Appl. Phys. Lett.* **2005**, *86*, 113101-1–113101-3.

(4) Xu, J.; Wang, J.; Mitchell, M.; Mukherjee, P.; Jeffries-EL, M.; Petrich, J. W.; Lin, Z. Q. Organic-inorganic nanocomposites via directly grafting conjugated polymers onto quantum dots. *J. Am. Chem. Soc.* **2007**, *129*, 12828–12833.

(5) Lin, Z. Q. Organic-inorganic nanohybrids via direct tailoring semiconductor nanocrystals with conjugated polymers. *Chem.—Eur. J.* **2008**, *14*, 6294–6301.

(6) Goodman, M. D.; Xu, J.; Wang, J.; Lin, Z. Q. Semiconductor conjugated polymer-quantum dot nanocomposites at the air/water interface and their photovoltaic performance. *Chem. Mater.* **2009**, *21*, 934–938.

(7) Xu, J.; Xia, J.; Lin, Z. Q. Evaporation-induced self-assembly of nanoparticles from a sphere-on-flat geometry. *Angew. Chem., Int. Ed.* **2007**, *46*, 1860–1863.

(8) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer. *Nature* **1994**, 370, 354–357.

(9) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H. J.; Bawendi, M. G. Optical gain and stimulated emission in nanocrystal quantum dots. *Science* **2000**, *290*, 314–317.

(10) Chan, W. C. W.; Nie, S. Quantum dot bioconjugates for ultrasensitive nonisotopic detection. *Science* **1998**, *281*, 2016–2018.

(11) Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. Quantum dot bioconjugates for imaging, labelling and sensing. *Nat. Mater.* **2005**, *4*, 435–446.

(12) Alivisatos, A. P. The use of nanocrystals in biological detection. *Nat. Biotechnol.* **2004**, *22*, 47–52.

(13) Coakley, K. M.; McGehee, M. D. Conjugated polymer photovoltaic cells. *Chem. Mater.* **2004**, *16*, 4533–4542.

(14) He, M.; Qiu, F.; Lin, Z. Conjugated rod-coil and rod-rod block copolymers for photovoltaic applications. *J. Mater. Chem.* **2011**, *21*, 170239–17048.

(15) He, M.; Han, W.; Ge, J.; Yu, W.; Yang, Y. L.; Qiu, F.; Lin, Z. Annealing effects on the photovoltaic performance of all-conjugated poly(3-alkylthiophene) diblock copolymer-based bulk heterojunction solar cells. *Nanoscale* **2011**, *3*, 3159–3163.

(16) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.-S.; Ree, M. A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene:fullerene solar cells. *Nat. Mater.* **2006**, *5*, 197–203.

8091

(17) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated optoelectronic devices based on conjugated polymers. *Science* **1998**, 280, 1741–1744.

(18) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated, high-mobility polymer field-effect transistors driving polymer light-emitting diodes. *Synth. Met.* **1999**, *102*, 857–860.

(19) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Hybrid nanorod-polymer solar cells. *Science* **2002**, 295, 2425–2427.

(20) Zhou, Y.; Riehle, F. S.; Yuan, Y.; Schleiermacher, H.-F.; Niggemann, M.; Urban, G. A.; Kruger, M. Improved efficiency of hybrid solar cells based on non-ligand-exchanged CdSe quantum dots and poly(3-hexylthiophene). *Appl. Phys. Lett.* **2010**, *96*, 013304-1–013304-3.

(21) Dayal, S.; Kopidakis, N.; Olson, D. C.; Ginley, D. S.; Rumbles, G. Photovoltaic devices with a low band gap polymer and CdSe nanostructures exceeding 3% efficiency. *Nano Lett.* **2009**, *10*, 239–242.

(22) Sun, B.; Snaith, H. J.; Dhoot, A. S.; Westenhoff, S.; Greenham, N. C. Vertically segregated hybrid blends for photovoltaic devices with improved efficiency. *J. Appl. Phys.* **2005**, *97*, 014914-1–014914-6.

(23) Liao, H.-C.; Chen, S.-Y.; Liu, D.-M. In-situ growing CdS singlecrystal nanorods via P3HT polymer as a soft template for enhancing photovoltaic performance. *Macromolecules* **2009**, *42*, 6558–6563.

(24) Greenham, N. C.; Peng, X.; Alivisatos, A. P. Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity. *Phys. Rev. B* **1996**, *54*, 17628–17637.

(25) Ren, S.; Chang, L.-Y.; Lim, S.-K.; Zhao, J.; Smith, M.; Zhao, N.; Bulović, V.; Bawendi, M.; Gradečak, S. Inorganic–organic hybrid solar cell: Bridging quantum dots to conjugated polymer nanowires. *Nano Lett.* **2011**, *11*, 3998–4002.

(26) Zhao, L.; Lin, Z. Crafting semiconductor organic-inorganic nanocomposites via placing conjugated polymers in intimate contact with nanocrystals for hybrid solar cells. *Adv. Mater.* **2012**, *24*, 4353–4368.

(27) Zhao, L.; Pang, X.; Adhikary, R.; Petrich, J.; Jeffries-EL, M.; Lin, Z. Organic-inorganic nanocomposites by placing conjugated polymers in intimate contact with quantum rods. *Adv. Mater.* **2011**, *23*, 2844–2849.

(28) Zhao, L.; Pang, X.; Adhikary, R.; Petrich, J. W.; Lin, Z. Semiconductor anisotropic nanocomposites obtained by directly coupling conjugated polymers with quantum rods. *Angew. Chem.* **2011**, *123*, 4044–4048.

(29) Yi, Z.; Yunchao, L.; Haizheng, Z.; Jianhui, H.; Yuqin, D.; Chunhe, Y.; Yongfang, L. Hybrid nanocrystal/polymer solar cells based on tetrapod-shaped  $CdSe_{x}Te_{1-x}$  nanocrystals. *Nanotechnology* **2006**, *17*, 4041.

(30) Goodman, M. D.; Zhao, L.; DeRocher, K. A.; Wang, J.; Mallapragada, S. K.; Lin, Z. Self-assembly of CdTe tetrapods into network monolayers at air/water interface. *ACS Nano* **2010**, *4*, 2043– 2050.

(31) Milliron, D. J.; Gur, I.; Alivisatos, A. P. Hybrid organicnanocrystal solar cells. *MRS Bull.* **2005**, *30*, 41–44.

(32) Carbone, L.; Kudera, S.; Carlino, E.; Parak, W. J.; Giannini, C.; Cingolani, R.; Manna, L. Multiple wurtzite twinning in CdTe nanocrystals induced by methylphosphonic acid. *J. Am. Chem. Soc.* **2005**, *128*, 748–755.

(33) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. Regioregular, head-to-tail coupled poly(3-alkylthiophenes) made easy by the GRIM method: Investigation of the reaction and the origin of regioselectivity. *Macromolecules* **2001**, *34*, 4324–4333.

(34) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. A simple method to prepare head-to-tail coupled, regioregular poly(3-alkylthiophenes) using Grignard metathesis. *Adv. Mater.* **1999**, *11*, 250–253.

(35) Shieh, F.; Saunders, A. E.; Korgel, B. A. General shape control of colloidal CdS, CdSe, CdTe quantum rods, and quantum rod heterostructures. *J. Phys. Chem. B* **2005**, *109*, 8538–8542.

(36) Yu, W. W.; Wang, Y. A.; Peng, X. Formation and stability of size-, shape-, and structure-controlled CdTe nanocrystals: Ligand

effects on monomers and nanocrystals. *Chem. Mater.* **2003**, *15*, 4300–4308.

(37) Markiewicz, J. T.; Wiest, O.; Helquist, P. Synthesis of primary aryl amines through a copper-assisted aromatic substitution reaction with sodium azide. J. Org. Chem. **2010**, 75, 4887–4890.

(38) Khan, M. T.; Kaur, A.; Dhawan, S. K.; Chand, S. In-Situ growth of cadmium telluride nanocrystals in poly(3-hexylthiophene) matrix for photovoltaic application. *J. Appl. Phys.* **2011**, *110*, 044509-1–044509-7.