Semiconducting Conjugated Polymer–Inorganic Tetrapod Nanocomposites

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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−≡) onto azide-functionalized CdTe tetrapods (i.e., CdTe−N₃) 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,1,2 LEDs,8 tunable lasers,9 biosensors,10,11 and bioimaging.12 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 three-dimensional structures. CdTe is an appealing inorganic semiconductor for inorganic solar cells due to its optimum band gap energy (Eₛ = 1.45 eV) and high absorption coefficient (α = 10⁶ cm⁻¹),13 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.14

Conjugated polymers (CPs) have garnered increasing attention as they offer potential applications in biosensors, thin film transistors, light-emitting diodes, and solar cells.3–5,13–15 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.5,16 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.17

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.19–23 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.9,24,25 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.26,27 In

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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 and CdSe QRs, 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.6,22 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 interfacial area.29,30 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.31 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 N3-functionalyzed CdTe tetrapods. Finally, ethynyl-terminated P3HT synthesized by a quasi-living Grignard metathesis (GRIM) method was grafted onto N3-functionalyzed 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 on the CdTe tetrapod surface was estimated by thermogravimetry (NMR). The number of P3HT chains tethered without introducing any metallic impurities, which could be detrimental to the photovoltaic device performance.

2. EXPERIMENTAL SECTION

All chemicals, including 4-bromobenzyl bromide, triethyl phosphate, cadmium oxide, tri-n-octylphosphine (TOP, 90%), tellurium powder, sodium azide, 2,5-dibromo-3-hexylphosphonic acid (OPDA), 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 phosphate at 1.2 molar ratio were heated under Ar at 150 °C for 5 h, yielding diethylphosphonate ester. The excess triethyl phosphate 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 °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).** BBPA-capped 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 TOP (2 g) was degassed in a three-neck 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/triethylphosphine (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–N3) was synthesized by a quasi-living Grignard metathesis (GRIM) method.5,34 Briefly, 2,5-dibromo-3-hexylphosphonic acid (0.815g, 2.5 mmol) was dissolved in THF (5 mL) in a three-neck 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)Cl2 (11.2 mg, 0.022 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 1H NMR. The number-average 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 (NaN3) 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 NaN3 was removed by centrifugation. The resulting azide–benzylphosphonic acid-capped CdTe tetrapods (CdTe-N3) were then precipitated in methanol. Subsequently, 50 mg of CdTeN3 were mixed in 10 mL of THF and kept at 65 °C under Ar for 2 days. The final product (i.e., P3HT–CdTe-N3 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 1H NMR spectra were taken using a Varian VXR-400 spectrometer. The grafting density of P3HT chains on the CdTe tetrapod surface was determined by thermogravimetric 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 spectrophotometer (RF-S301PC, Shimadzu), respectively. All samples were excited at λex = 445 nm, and the emission was collected at λem > 500 nm.
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. 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. 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. 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 ± 10 nm in size with a diameter of 5 ± 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). The formation of tetrapods can be rationalized according to the multiple-twin model. 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...
by phosphonic acid, a Cd–phosphonic acid complex (i.e., Cd–BBPA and Cd–ODPA) was formed as Cd²⁺ 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 twin nuclei 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−≡) and azide-functionalized CdTe (i.e., CdTe−N₃) 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–N₃ and P3HT–≡, 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–≡. We note that aryl halides have been converted to azides by the reaction with sodium azide using copper catalyst. It is plausible that the Cd in the system catalyzed the reaction in the present study. The azide groups

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−≡) onto Azide-Functionalized CdTe (i.e., CdTe−N₃) Tetrapods by Catalyst-Free Click Chemistry, Yielding P3HT–CdTe Tetrapod Nanocomposites
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−≡ chains onto CdTe−N3 tetrapods was confirmed by the Fourier transform infrared (FTIR) spectroscopy measurements as shown in Figure 3. Strong absorptions of P3HT at 2954, 2915, and 2850 cm⁻¹ were assigned to the asymmetric C–H stretching vibrations in –CH₂–CH₃ and the symmetric C–H stretching vibration in –CH₃, respectively, from the alkyl side chains in P3HT and ligands. Notably, the characteristic –N₃ vibration appeared at 2040 cm⁻¹ after the aryl bromine groups of BBPA-functionalized CdTe tetrapods were converted into azide groups, forming CdTe−N₃ 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−N₃ 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−CdTe tetrapod-based photovoltaic devices. The ¹H NMR data shown in Figure 4 also strongly supported the occurrence of grafting P3HT−≡ onto CdTe−N₃ 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−≡ chain was coupled with the CdTe−N₃ tetrapod. The appearance of the peak between 3.5 and 4 ppm in Figure 4b was from the proton of –CH₂ in CdTe−N₃ tetrapods (i.e., in CdTe−BPA−N₃) after grafting of P3HT−≡ onto CdTe−N₃ 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−≡) (molecular weight = 50 kDa) also revealed the onset of degradation in the temperature range 400–450 °C, leaving behind a char-like yield of 28% (Figure 5b). 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 × 10⁵ 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−≡ 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 ¹H 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-
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.

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Notes

The authors declare no competing financial interest.

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