Research Article

Synthesis of High-Quality Carboxyl End-Functionalized Poly(3-hexylthiophene)/CdSe Nanocomposites

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Carboxyl end-functionalized poly(3-hexylthiophene) (P3HT-COOH) was grafted chemically with CdSe nanocrystals (NCs) by a phosphine-free method. The particle quality of P3HT-COOH/CdSe nanocomposites was better than that of P3HT/CdSe nanocomposites, which were synthesized using the same method. Nanocrystals with controllable particle size exhibited a wurtzite crystalline structure and showed excellent nanocrystal dispersion in the P3HT-COOH matrix. Photoluminescence (PL) characterization performed on nanocomposites suggested the efficient charge transfer at the P3HT-COOH/CdSe interface. This approach based on the phosphine-free method is not only environmentally friendly but also highly efficient.

1. Introduction

P3HT has been extensively utilized as conjugated polymers (CPs) for CP/CdSe nanocomposites due to its well-matched energy level with CdSe [1–5]. However, P3HT/CdSe was widely prepared by physically mixing P3HT and CdSe. Phase separation of P3HT and CdSe is inevitable, thereby limiting the direct electronic interaction between them [6–8]. Grafting P3HT with CdSe by a chemical method is an effect strategy to eliminate phase separation and to promote the electronic interaction between P3HT and CdSe [6, 8]. Previously, the ligand exchange process was used to graft CPs to NCs because the derivatization of the composite has a broad range of functional groups [9, 10]. In spite of the fact that the original ligands can be replaced by the desired ligands, NCs still tend to aggregate when mixed with CPs, which leads to phase separation [11–14].

A strategy to decrease or eliminate macrophase separation is to use end-functionalized P3HT as ligands [2, 8, 15–17]. End-functionalized P3HT equipped with alcohol, ethynyl, carboxylic acid, pyridines, thiols, amine, and phosphate groups has been developed [14, 17–19]. The research shows that it also generates chemically defined interfaces that improve elec-

tronic communication between the CPs and NCs. Polythiophene with carboxylic acid functional groups has been used to prepare many nanocomposites because it increases the interactions at the interface with the NCs [20–22]. Photoinduced electron transfer from CPs to NCs was also improved by replacing the P3HT with P3HT-COOH [23].

Many works on the synthesis of CP/NC nanocomposites have been reported [9, 19, 24–31]. But some key chemicals, such as tri-*n*-octylphosphine oxide (TOPO) and trioctylphosphine (TOP), used in traditional routes are extremely toxic, expensive, explosive, and pyrophoric [7, 11, 12, 28, 31]. So phosphine-free synthesis schemes have extended to green and low-cost cadmium carboxylate precursors, fatty acid ligands, and noncoordination solvents (ODE, heat transfer fluids, and paraffin liquid) [32–34]. P3HT/CdSe has been successfully synthesized in ODE without using TOP and TOPO [4]. The result shows that it is a uniform dispersion of NCs without any indication of phase separation. However, this method is not desirable because dimethylcadmium is used, which is a pyrophoric and explosive reagent. CdSe NCs obtained from the phosphine-free solvent systems are generally imperfect. The size of CdSe NCs is not easily controlled [9, 32, 35], and their surface is not suitable for epitaxial

growth [36, 37]. An environmentally friendly, effective, and ligand exchange-free method should be developed to achieve chemically grafted CPs on the QD surface.

In this paper, two kinds of P3HT-COOH/CdSe nanocomposites were prepared by an in situ synthesis method without using organophosphine as a ligand. The p-type/n-type hybrid nanocomposites have high quality and show fluorescence quenching, indicating an effective charge transfer at the interface between P3HT-COOH and CdSe.

2. Experiment

2.1. General Procedures and Chemicals. All reactions were carried out under nitrogen gas flow using a standard Schlenk line. The glassware was predried before use at 120°C. All chemicals, including 1-octadecene (ODE), trichlorobenzene, selenium powder, ethynylmagnesium bromide (1 mol/L in THF), and P3HT (number average molecular weight was 30,000 g/mol), were purchased from J&K (China). Cadmium stearate was purchased from Aladdin (China). THF (Aladdin, 99%) was refluxed over sodium wire.

2.2. Synthesis of Ethynyl-Terminated P3HT. Ethynyl-terminated P3HT (i.e., P3HT-≡) was synthesized by the quasiliving Grignard metathesis (GRIM) method [38]. P3HT (0.09 g, 0.03 mmol) was dissolved in 20 mL THF, and Ni(dppp)Cl₂ (0.0225 g, 0.041 mmol) was added. The resulting mixture was first stirred for 10 min at room temperature, followed by a reaction with ethynylmagnesium bromide (0.03 mL, 0.03 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, hexanes, and chloroform sequentially.

2.3. Synthesis of P3HT-COOHs. P3HT-COOHs contain P3HT-Z-COOH, and P3HT-M-COOH is synthesized by click reaction [38] (Scheme 1). The 4-aminophenylacetic acid (i.e., Z) and sodium azide were mixed in water to substitute the amino group of 4-aminophenylacetic acid into azide (N₃), yielding N₃-functionalized-phenylacetic acid complexes (Z-N₃). The 4-(bromomethyl)benzoic acid (i.e., M) and sodium azide were mixed in DMF to substitute the bromide group of 4-(bromomethyl)benzoic acid into azide (N₃), yielding N₃-functionalized-methylbenzoic acid complexes (M-N₃).

Subsequently, the synthesized P3HT-≡ and Z-N₃ or M-N₃ were mixed in THF and kept at 60°C under Ar for 3 days, yielding P3HT-Z-COOH or P3HT-M-COOH complexes. The resulting solution was precipitated in methanol to remove the excess amount of Z-N₃ or M-N₃, which was not coupled with P3HT-≡.

2.4. Synthesis of the Se Precursor. Selenium powder 0.079 g (1.0 mmol) was added to a three-necked flask with 2 mL of oleylamine and 10 mL of ODE, and the mixture was then stirred under Ar at 220°C to produce an optically clear solution.

2.5. Synthesis of P3HT-COOH/CdSe Nanocomposites. P3HT-COOHs 0.009 g (0.500 mmol) and cadmium stearate 0.395 g (0.500 mmol) were mixed in ODE (13 mL) and trichloroben-

zene (1 mL) and kept at 220°C under Ar until the liquid color was bright orange. The product is P3HT-COO-Cd solution (P3HT-Z-COO-Cd or P3HT-M-COOH-Cd). Subsequently, 10 mL Se precursor solution was rapidly injected into the P3HT-COOH-Cd solution. The reaction solution color immediately changed to brown from bright orange indicating the formation of CdSe nanoparticles. Nanoparticles were allowed to grow at 220°C for 1 h. The resulting P3HT-COOH/CdSe nanocomposites were cooled down and precipitated with methanol and redissolved in chloroform.

3. Characterizations

The morphology of P3HT-COOH/CdSe nanocomposites was imaged by using transmission electron microscopes (Tecnai G2 F20 S-TWIN, FEI). The absorption and emission spectra were recorded with a UV-vis spectrometer (UV-2600, Shimadzu) and a spectrofluorophotometer (CaryEclipse, Varian), respectively. All samples were excited at $\lambda_{\text{ex}} = 445$ nm, and the emission was collected at $\lambda_{\text{em}} > 400$ nm. The Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a FT-IR spectrometer (FTIR-8400s, Shimadzu). The X-ray diffraction (XRD) (XD8-Advan- ceX, Bruker Corporation, Germany) measurement was carried out using a Cu-K α radiation source ($\lambda = 1.5418$ Å), and the 2θ range used was from 5° to 80°.

4. Results and Discussion

The synthesis routes of P3HT-COOH/CdSe nanocomposites are illustrated in Scheme 2. The P3HT-COOH (e.g., P3HT-M-COOH and P3HT-Z-COOH in Scheme 1) plays an important role in the synthesis of CdSe nanocrystals. The growth process of nanocrystals can be controlled via P3HT-COOH as a template. First of all, according to a recent report, the carboxyl of P3HT-COOH can react with Cd²⁺ to form P3HT-COO-Cd compounds linked by metal carboxylate linkage [39, 40]. The Se precursor was then injected and subjected to a subsequent nucleation-and-growth process.

FT-IR spectroscopy in Figures 1(a) and 1(b) was used to identify and characterize the metal carboxylate linkage between Cd²⁺ and -COOH. In Figure 1(a), the absorption peaks at 1639 cm⁻¹ and 3433 cm⁻¹ assigned to the characteristic C=O stretching vibration and -O-H stretching vibration of P3HT-Z-COOH disappeared in the FT-IR spectrum of P3HT-Z-COOH/CdSe nanocomposites, and the absorption peaks at 1556 cm⁻¹ (carboxylate stretching) appeared, clearly indicating the success of chemical coupling (see Scheme 1) between CdSe and P3HT-Z-COOH. The same happens in Figure 1(b). Figure 1(c) compares the FT-IR spectra of P3HT-Z-COOH/CdSe nanocomposites and P3HT-M-COOH/CdSe nanocomposites. As shown in the FT-IR spectra, the -CH₂- characteristic vibration shifts from 1103 to 991 cm⁻¹ due to the different locations of -CH₂- in the two kinds of P3HT-COOHs.

The high boiling point solvent ODE was employed to dissolve P3HT-COO-Cd (P3HT-Z-COO-Cd and P3HT-M-COO-Cd) for the synthesis of high-quality P3HT-COOH/CdSe NC nanocomposites. The injection of Se-

SCHEME 1: Synthetic route to P3HT-COOHs by click reaction.

SCHEME 2: Synthetic route to carboxyl end-functionalized P3HT/CdSe nanocomposites by P3HT-M-COOH (left panel) and P3HT-Z-COOH (right panel).

oleylamine solution initiated the nucleation and growth of CdSe NCs having direct contact with P3HT-COOH (see Experiment). The presence of P3HT-COOH imposed steric hindrance during the growth of CdSe NCs, thereby preventing the agglomeration of CdSe NCs.

As a result, despite the absence of hazardous organometallic ligands (e.g., widely used tri-*n*-octylphosphine oxide (TOPO) and trioctylphosphine (TOP) for high-quality CdSe QD synthesis), uniform CdSe QDs tethered with P3HT chains were obtained. It is clear that transmission electron

FIGURE 1: (a) FTIR spectrum of P3HT-Z-COOH and P3HT-Z-COOH/CdSe. (b) FTIR spectrum of P3HT-M-COOH and P3HT-M-COOH/CdSe. (c) FTIR spectra of P3HT-Z-COOH/CdSe nanocomposites and P3HT-M-COOH/CdSe nanocomposites.

microscopy (TEM) measurements revealed a homogeneous dispersion of P3HT-COOH/CdSe QD nanocomposites as shown in Figure 2. The diameters of these spherical CdSe nanocrystals increase to about 6.7 nm (P3HT-Z-COOH/CdSe) and 7.9 nm (P3HT-M-COOH/CdSe), respectively. It must be pointed out that the diameters of these spherical CdSe nanocrystals can be controlled by changing reaction conditions. In the same reaction time, the size of P3HT-M-COOH/CdSe NCs increased more obviously than P3HT-Z-COOH/CdSe NCs, revealing that P3HT-M-COOH is more effective for nucleation and growth of nanocrystals as the polymer matrix. It was found in TEM images that there is a narrow size distribution of the nanoparticles, and the shapes of these nanocrystals are regular, the dispersion of CdSe nanoparticles in P3HT-COOH is greatly improved, and the majority of the nanoparticles are spherical with an average grain size of 6 to 8 nm.

The photophysical properties of the resulting P3HT-COOH/CdSe nanocomposites were examined by UV-vis absorbance and photoluminescence (PL) studies. The absorp-

tion spectra of P3HT-COOH/CdSe nanocomposites are shown in Figure 3. As seen from Figure 3(a), the peak at 636 nm and 652 nm corresponds to P3HT-Z-COOH/CdSe and P3HT-M-COOH/CdSe absorption, respectively. The diameters of these spherical CdSe nanocrystals obtained by the calculation according to published equations [41] are consistent with the observation from TEM images. After the carboxyl functionalization, their optical properties both varied and the wavelength range of nanocomposites exhibited a red shift in comparison with the P3HT/CdSe nanocomposite [42]; it means that the size of the nanocomposites increased, indicating that carboxyl functionalization is sufficient for forming size-tunable P3HT-COOH/CdSe nanocomposites. In comparison with P3HT/CdSe nanocomposites [42], the size of P3HT-M-COOH/CdSe nanocomposites increased more obviously than that of P3HT-Z-COOH/CdSe NCs, which is in line with the TEM analysis.

The PL spectra of P3HT-Z-COOH/CdSe nanocomposites and P3HT-M-COOH/CdSe nanocomposites are shown in Figure 3(b). In contrast with P3HT-COOHs, nearly complete

FIGURE 2: TEM images of P3HT-Z-COOH/CdSe nanocomposites (a, b) and P3HT-M-COOH/CdSe nanocomposites (c, d).

FIGURE 3: UV-vis spectra (a) and photoluminescence spectra (b) of P3HT-COOH/CdSe nanocomposites.

quenching of nanocomposite fluorescence was seen, implying efficient charge transfer from P3HT-COOHs to CdSe NCs. This observation further confirmed intimate chemical contact between P3HT-COOHs and CdSe NCs. It must be mentioned that the PL intensity of P3HT-M-COOH/CdSe nanocomposites is relatively higher. In contrast, nearly complete quenching of P3HT-Z-COOH/CdSe nanocomposite

fluorescence was seen. One of the possible reasons for the different PL intensities could be attributed to different chemical structures of the two P3HT-COOHs. In P3HT-M-COOH, the carboxyl group is connected with phenyl. On the contrary, the carboxyl group is connected with methylene in P3HT-Z-COOH. Methylene has lower steric hindrance so that it can react with the CdSe NCs more easily. In

FIGURE 4: XRD patterns of P3HT-COOH/CdSe nanocomposites: (a) P3HT-Z-COOH/CdSe; (b) P3HT-M-COOH/CdSe.

comparison to the P3HT/CdSe nanocomposites [42], the significant PL quenching of nanocomposites after the carboxyl functionalization suggested the efficient charge transfer from P3HT-COOHs to CdSe NCs, which confirmed the intimate chemical contact between P3HT-COOH and CdSe QDs.

X-ray diffraction (XRD) analysis was performed to investigate the crystalline structure of P3HT-COOH/CdSe nanocomposites (Figure 4). In the XRD patterns of the carboxyl end-functionalized P3HT/CdSe nanoparticles, a series of characteristic peaks of (100), (002), (102), (110), (103), and (112) are observed, which are in accordance with the wurtzite phase of CdSe Qdots (JCPD No. 08-0456). Moreover, in TEM images, the lattice spacing of the spherical CdSe nanocrystals is 0.35 nm, corresponding to the (111) plane of cubic CdSe.

5. Conclusions

In summary, we demonstrated phosphine-free synthetic routes of P3HT-COOH/CdSe nanocomposites to achieve chemical tethering between the polymer matrix and the NC surface. P3HT-COOH can first react with Cd^{2+} to form P3HT-COOCd compounds linked by a metal carboxylate linkage. The precursor of Se was then injected and subjected to a subsequent nucleation-and-growth process. The scrutiny on the effects of P3HT-COOH/CdSe nanocomposites revealed that the carboxyl end-functionalized P3HTs were more effective in improving the characteristics of CdSe NCs than the pure P3HT and promoted CdSe NCs' effective charge transport and good dispersion of nanoparticles. In addition, the particle size of CdSe NCs was controllable. Therefore, this phosphine-free method provides a promising platform to craft a variety of functionalized polymer-nanocrystal nanocomposites.

Data Availability

The experimental data used to support the findings of this study are included within the article.

Conflicts of Interest

There are no conflicts to declare.

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