



# Improved interaction between semiconducting polymer and carbon nanotubes in thermoelectric composites through covalent grafting



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## ABSTRACT

We developed an unconventional route to produce uniform and intimately interfaced nanocomposite films for their potential application in thermoelectric (TE) devices. Here, amino-terminated poly(3-hexylthiophene-2,5-diyl) (P3HT) was chemically adhered onto the surface of a functionalized double-walled carbon nanotube (DWCNT), via an amidation reaction, to form P3HT-grafted DWCNT (P3HT-g-DWCNT). As the P3HT chains are intimately and permanently tethered on the DWCNT surface, a well-defined P3HT/DWCNT interface prevents the DWCNT from aggregating by promoting the solubility of P3HT-g-DWCNT nanocomposites in organic solvent. Such characteristic changes in DWCNT by polymer grafting can improve the thermoelectric properties of DWCNT films. The covalently grafted P3HT-g-DWCNT film exhibits a significantly enhanced Seebeck coefficient of  $116.6 \mu\text{V K}^{-1}$ , as compared to a physically mixed P3HT/DWCNT composite ( $69.2 \mu\text{V K}^{-1}$ ), in conjunction with a high power output in TE modules. This facile approach would open a new way to synthesize intimately connected nanocomposites made up of conductive polymers and carbon materials for high performance thermoelectrics.

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## 1. Introduction

Remarkable progress of high-performance thermoelectric (TE) materials has been achieved in the past several decades. TE materials directly convert temperature difference into an electric voltage for power generation, and can also be used for refrigeration [1,2]. The fundamental challenge in developing TE materials showing superior performance lies in delicately adjusting the interrelated TE parameters, such as the Seebeck coefficient  $S$ , electrical conductivity  $\sigma$ , and thermal conductivity  $\kappa$  [3]. In recent years, intensive research efforts have been devoted to improve the efficiency of TE materials through different approaches, including reducing the lattice thermal conductivity by suppressing phonon scattering [4,5] and enhancing the TE power factor ( $S^2\sigma$ ) by quantum confinement [6–9], energy filtering [10,11], and tuning the electronic band structure (i.e. the density of states) of the material [12]. A high TE power factor has also been achieved through the formation of nanocomposites with conducting polymers [13–16]. In particular, nanocomposites based on conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), or poly(3-

hexylthiophene) (P3HT) and low-dimensional carbon materials (e.g. carbon nanotube (CNT), and graphene) have received considerable attention as hybrid polymer-carbon nanocomposites due to the various advantages from the combined high  $S$  and low  $\kappa$  values of the conducting polymer, with the high  $\sigma$  of the carbon material. In 2009, Meng et al. reported that multi-walled carbon nanotube (MWCNT) sheet/PANI nanocomposites prepared by a two-step method showed simultaneously enhanced electrical conductivities and Seebeck coefficients [17]. These enhancements were attributed to the size-dependent energy-filtering effect at the nano-interfaces between the PANI coating layer and the CNT. In 2011, Yu et al. [18] reported a notable increase in the electrical conductivity of CNT/polymer composites, without a decrease in the Seebeck coefficient, by the addition of CNT. In 2014, Yao et al. [19] demonstrated SWCNT/PANI hybrid films with power factor of  $176 \mu\text{W m}^{-1} \text{K}^{-2}$ , by forming highly ordered PANI interface layer on the single-walled carbon nanotube surface. In 2015, Cho et al. [20] prepared PANI/graphene/PANI/DWNT nanocomposites by using layer by layer deposition and this ordered molecular structure enabled the maximum power factor to reach  $1825 \mu\text{W m}^{-1} \text{K}^{-2}$ .

Although such nanocomposites have been demonstrated to be an effective approach to improve the performance of a material by synergistically combining the advantages of each component, some critical issues regarding the nanocomposite formation for TE

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materials still need to be resolved. In conventional methods, where the carbon materials are physically mixed with conjugated polymers to produce hybrid CNT-conjugated polymer nanocomposites, the agglomeration of CNT is likely to take place in CNT/conducting polymer composite films. Even materials with a low loading of CNT lead to unexpected interfaces between the two components, which prevent the development of advantageous features from the combination of CNT with conjugated polymers. Moreover, it remains challenging to form a good interfacial connection between carbon materials and conducting polymers, because the intimate interfacial contact between these two constituents could facilitate carrier transport without the scattering of carriers (electrons or holes) at the interface.

In this study, P3HT was covalently grafted on to the surface of double-walled carbon nanotube (DWCNT), by the amidation reaction between the acyl moieties on the surface of the DWCNT, and the amine groups in the amino-terminated P3HT. Such surface modification increases the dispersibility of DWCNT in organic solvents, thus leading to much smaller bundle sizes by avoiding the formation of big agglomerates, as compared to directly mixed P3HT/DWCNT composites. Furthermore, the well-dispersed combination at the nanometer level can maximize the integration effect, and the TE performance, by fully taking advantage of the benefits from each component, such as the high Seebeck coefficient and low thermal conductivity. The increased figure of merit ( $ZT$ ) with high power output of the TE modules is not only affected by the enhanced dispersity of the material, but also by the intimate interactions between the DWCNT and P3HT.

## 2. Experimental

### 2.1. Materials

The pristine DWCNT was purchased from XinNano Materials ([www.xinnanomaterials.com](http://www.xinnanomaterials.com)). DWCNT was adopted due to its relatively low price and high electrical conductivity. The pristine DWCNTs are in the form of powder with 3 nm of outer diameter and over 10  $\mu\text{m}$  of length. 2,5-Dibromo-3-hexylthiophene, *t*-BuMgCl,  $\text{Ni}(\text{dppp})\text{Cl}_2$  and other solvents were purchased from Aldrich and used without any further purification.

### 2.2. Synthesis of amino-terminated P3HT

Amino-terminated P3HT (P3HT-NH<sub>2</sub>) was polymerized through the Grignard metathesis reaction. Following the typical reaction, 2,5-dibromo-3-hexylthiophene (1.68 g, 5.2 mmol) and anhydrous THF (10 mL) were mixed in a dry Schlenk flask under the protection of N<sub>2</sub>. The reaction mixture was cooled to 0 °C by using an ice/water bath, and then *t*-BuMgCl (1 M solution in THF, 5.9 mL, 5.2 mmol) was added into the flask. After the reaction was allowed to take place at room temperature for 3.5 h,  $\text{Ni}(\text{dppp})\text{Cl}_2$  (70 mg, dissolved in 40 mL of anhydrous THF) was added into the flask. After the polymerization reaction was allowed to take place for 6 h, 3-(bis(trimethylsilyl)amino)phenylmagnesium chloride (1.0 M solution in THF, 6 mL) was added into the reaction mixture, and stirred for 10 min. The reaction was terminated by adding a HCl solution (12 mL of a 5 N aqueous solution). Finally, the polymer was precipitated in a methanol/DI water mixture (7/3, 1000 mL). In this process, the alcoholysis reaction of the bis(trimethylsilyl)amino groups led to the formation of amine groups. The precipitate was obtained by centrifugation and drying in a vacuum oven. The polymer was further purified by a Soxhlet extraction with chloroform. The solution was concentrated and precipitated in methanol again.

### 2.3. Synthesis of P3HT-g-DWCNT

To graft P3HT onto the surface of the DWCNT, they were first oxidized using nitric acid to produce carboxyl groups. In a typical reaction, pristine DWCNT (150 mg) were first dispersed in a diluted HNO<sub>3</sub> solution (150 mL) by sonication for 2 h, followed by refluxing at 120 °C for 48 h. The reaction mixture was then additionally sonicated for 1 h, and refluxed for 48 h. To obtain the oxidized DWCNT the solution was filtered under vacuum, and purified by redispersing in a 1 M HCl solution (30 mL), washing with deionized water, and drying in a vacuum oven at 60 °C overnight. For an acylation reaction of the oxidized DWCNT, the oxidized DWCNT (30 mg) were dispersed in DMF (10 mL) under sonication for 3 h. Then, SOCl<sub>2</sub> (30 mL) was added into the reaction mixture, followed by refluxing for 24 h. The acyl chloride activated DWCNT (DWCNT-COCl) were obtained by centrifuging, and washed by cycles of dispersing the DWCNT-COCl in anhydrous THF and centrifuging. For the amidation reaction on the surface of the DWCNT, the DWCNT-COCl suspension in anhydrous THF (30 mL) was added into a P3HT-NH<sub>2</sub> in anhydrous THF (P3HT-NH<sub>2</sub> 200 mg, THF 50 mL). To the reaction mixture, triethylamine (3 mL) was slowly added at 0 °C and the reaction was allowed to carry out at room temperature for 9 h, and at 50 °C for 48 h. Finally, the P3HT-g-DWCNT was obtained by centrifuging, and purified by removing any ungrafted P3HT by repeated centrifugation.

### 2.4. Preparation of the P3HT-g-DWCNT and P3HT/DWCNT film

The suspension was prepared by dispersing P3HT-g-DWCNT (30 mg) in chloroform (30 mL, 10 mg mL<sup>-1</sup>), with the aid of a sonication bath, for 3 h. Afterwards, the nanocomposite film was retained with a PMMA membrane by using the vacuum filtration method. The P3HT-g-DWCNT composite film on the PMMA membrane was dried in an oven at 60 °C overnight, and detached spontaneously from the supporting substrate. The thickness of resulting P3HT-g-DWCNT film was measured to be 30  $\mu\text{m}$  with a variation of 5  $\mu\text{m}$  and weight fraction of DWCNT in P3HT-g-DWCNT film was 89 wt%. For the physically mixed suspension, the P3HT (3.3 mg) and DWCNT (26.7 mg) was dispersed simultaneously in chloroform (30 mL), followed with bath sonication for 3 h. The film with thickness of approximately 40  $\mu\text{m}$  was fabricated using identical process of vacuum filtration method.

### 2.5. Characterization

The surface morphology was characterized by scanning electron microscopy (SEM) (SigmaHD, Carl Zeiss). FT-IR spectra were recorded on an Excalibur 3100 spectrometer (Varian, Inc.) with a resolution of 2 cm<sup>-1</sup> using KBr pellets. Raman images were obtained by Raman spectroscopy (excitation at 514 nm using a high-resolution dispersive Raman microscope, LabRAM HR UV/vis/NIR, Horiba). Thermalgravimetric analyses (TGA) were performed with a Q50 TGA (TA instruments) at a scanning rate of 5 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. Transmission electron microscopy (TEM) observations were performed on a JEM-2100 (JEOL) operated at 200 kV. The TEM samples were prepared by dropping the suspension of pristine DWCNT, or P3HT-g-MWNT, in chloroform on 400 mesh Cu grids with a supporting carbon film.

### 2.6. Experimental setup for Seebeck coefficient measurements

The Seebeck coefficients of the free-standing P3HT-g-DWCNT were measured using a custom system. A dot-shaped Au electrode was deposited by thermal evaporation on top of the samples, through a shadow mask, in order to minimize the contact

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