



## Exploring different doping mechanisms in thermoelectric polymer/carbon nanotube composites



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### ABSTRACT

This work compares various methods to prepare polymer/carbon nanotube (CNT) composites for thermoelectric applications, focusing on the different doping mechanisms. We first look at the general trends observed in the Seebeck coefficient and power factor for a large number of composites as a function of electrical conductivity. Then we discuss two methods of nitrogen doping the carbon nanotubes in these composites, namely either during synthesis, or afterwards by ammonolysis. Finally, we discuss doping of the carbon nanotubes through charge transfer from the polymer counterpart, including photo-induced switching of the majority carrier type. As a general remark, we note that processability is negatively influenced by some doping procedures. Best results were achieved for unfunctionalized single-walled carbon nanotubes with a high content of semiconducting CNT species. © 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Both conjugated polymers and carbon nanotubes (CNTs) are promising materials for low temperature thermoelectric applications such as waste heat harvesting. Polymers have very low thermal conductivity  $\kappa$  and high Seebeck coefficient  $S$ , whereas CNTs show excellent electrical conductivity  $\sigma$ , and high Seebeck coefficient in the case of precisely doped pure semiconducting CNTs [1]. In both cases a precise control of the Fermi level is necessary to find the optimal trade-off between  $S$  and  $\sigma$  and to maximize the thermoelectric power factor  $S^2\sigma$ .  $S^2\sigma$  is a measure of the effectiveness of a thermoelectric material, as opposed to its efficiency, which can be gauged by the dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$ , where  $T$  is the average temperature. The weak point of conjugated polymers and CNTs are the relatively low  $\sigma$  and the very large  $\kappa$  respectively. Still, a precise control of the doping level of conjugated polymers allowed to significantly reduce the performance gap that exists between inorganic and organic materials [2]. However, as experimental methods catch up, allowing for increasingly precise measurements of  $\kappa$  and  $\sigma$  in

the same direction or even on the same sample, it has been demonstrated that the thermal conductivity strongly depends on the electrical conductivity, even in conjugated polymers [3,4].

A promising alternative that could allow surpassing neat conjugated polymers or CNTs in terms of performance are polymer/CNT composites, because they have several inherent advantages. In these composites, polymers serve a dual purpose. They can improve thermoelectric performance as well as facilitate processing. By increasing the scattering of phonons at inter-tube interfaces, they can decrease the high thermal conductivity of CNTs by several orders of magnitude [5,6]. Charge transfer between the polymer and CNTs also allows for doping the CNTs [7]. It is even possible to indirectly dope the CNTs, by doping the surrounding polymer which acts as a bridge for molecular dopants that otherwise would not directly dope CNTs [8]. On the other hand, polymer-wrapping has been demonstrated as a simple and highly effective way to selectively disperse only semiconducting CNTs, or even only CNTs of a single, well-defined chirality [9–12]. These polymer-wrapped CNTs are well dispersed in solution, greatly facilitating solution processing and minimizing bundling. Furthermore, the final dried composites exhibit better mechanical properties than neat CNT films, particularly if using shorter CNTs. This is of particular advantage if working with flexible substrates, or unencapsulated samples. Importantly, neat CNTs may constitute

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a respiratory hazard, whereas CNT composites are inert, with no danger of CNTs leaking into the air, an important aspect when considering possible applications.

Conjugated polymers are typically doped by carefully controlling the concentration of a small molecular dopant [13] or counterion [14]. For multicomponent systems like CNT composites, naturally a wider range of options exists, such as the encapsulation of dopants within tubes [15], the preparation of composites with self-doped polyelectrolytes [16] or even complex concoctions of multiple polymer and small molecule dopants [17].

For an optimal thermoelectric module both p- and n-type thermoelectric materials are needed. CNTs in air are normally p-doped by atmospheric oxygen. Because of this, and due to the inherent instability of many n-type dopants towards oxidation in air, research into air-stable n-doping is of particular importance [18,19].

In this work we first survey the performance of composites of CNTs with conjugated polymers in general. We do not observe a maximum in power factor as a function of conductivity, thus further improvement in performance is anticipated by an additional increase in conductivity, which encourages exploring different doping mechanisms for polymer/CNT composites. We discuss and present new results concerning first, methods for directly doping the CNTs before blending; and secondly, two alternatives for tuning the doping in the CNT through the polymer counterpart.

## 2. Materials and methods

### 2.1. Materials

SG65i CoMoCAT<sup>®</sup> SWCNTs (SouthWest NanoTechnologies) containing  $\approx 40\%$  (6,5) tubes were bought from Sigma-Aldrich.

Nitrogen doped multi-walled CNTs (n-MWCNTs) were synthesized from a saturated solution of acetonitrile/ferrocene feedstock by chemical vapour deposition (CVD) using a continuous process [20]. n-MWCNTs contain approximately 7 wt% nitrogen, as determined by scanning transmission electron microscopy/electron energy loss spectroscopy. The n-MWCNTs typically contained residual iron from the catalyst used in their formation.

Nitrogen doped single-walled CNTs (N-doped SWCNTs) were synthesized by ammonolysis treatments of CVD SWCNTs (Elicarb<sup>®</sup>, supplied by Thomas Swan & Co). The as-received SWCNTs were initially purified using steam, in order to remove the amorphous carbon and graphitic nanoparticles resulting from the synthesis. A 6 M hydrochloric acid solution was then employed to remove the catalytic metal nanoparticles exposed after the steam treatment [21]. Afterwards, the purified SWCNTs were functionalized with carboxyl and hydroxyl groups by treating them in nitric acid [22]. These functionalized SWCNTs (f-SWCNTs) were then placed into a sintered Al<sub>2</sub>O<sub>3</sub> boat in the centre of a silica furnace tube. The sample was then annealed at 500 °C and 700 °C in the presence of pure NH<sub>3</sub> gas (Carburos Metálicos 99.99%), flowing at 300 mL min<sup>-1</sup> [23]. The NH<sub>3</sub> treatments lead to nitrogen-doped SWCNTs with N contents of 5.9 wt% (500 °C) and 3.1 wt% (700 °C), as determined by chemical analysis.

Poly(3-hexylthiophene-2,5-diyl) (P3HT,  $M_w \approx 82$  kg mol<sup>-1</sup>,  $M_w/M_n \approx 2.4$ , regioregularity >90%, Rieke Metals), branched polyethylenimine (PEI,  $M_w \approx 800$  g mol<sup>-1</sup>,  $M_w/M_n \approx 1.33$ ), Sodium dodecylbenzenesulfonate (SDBS, technical grade), ortho-dichlorobenzene (oDCB 99% ReagentPlus) and chloroform (>99.9% CHROMASOLV) were obtained from Sigma-Aldrich. Materials were used as received.

### 2.2. Solution preparation

CNTs were dispersed in oDCB at a concentration of 0.5 g L<sup>-1</sup> and sonicated in ice water for 60 min (Bransonic CPX2800H). P3HT was

dissolved in chloroform and an appropriate amount was added in three steps to the CNT dispersion, each time followed by additional sonication for 30 min. For the PEI composites, dispersions of 1 g L<sup>-1</sup> of SWCNTs in deionized water that contained 4 g L<sup>-1</sup> of SDBS were sonicated for 60 min. An amount of PEI equal to the amount of SWCNTs by weight was added in three steps, followed each time by 30 min sonication.

### 2.3. Sample preparation

The prepared solution was drop-cast onto PET substrates and left to evaporate. Some samples were irradiated for 60 s with 50 mW cm<sup>-2</sup> of UV-light directly after deposition in a Jelight UVO-Cleaner 42.

### 2.4. Physical characterization

Sample thickness was measured using a KLA Tencor P16+ profilometer. Typically, samples were  $\approx 1$   $\mu$ m thick.

Scanning electron microscopy (SEM) images of samples drop cast on PET substrates were acquired using a Quanta FEI 200 ESEM FEG microscope, operating between 15.0 and 20 kV.

### 2.5. Electrical characterization

The average Seebeck coefficient between 310 K and 350 K was measured using a custom built setup, employing the differential method at quasi steady state in ambient atmosphere. The Seebeck voltage was measured using a Keithley 2400 sourcemeter, and the temperature at the same contacts was measured using a pair of fine wire K-type thermocouples (0.075 mm diameter). For each composition, several 2 by 1 cm<sup>2</sup> samples, contacted with silver paste were measured.

The electrical conductivity measurements were performed on 1 by 1 cm<sup>2</sup> samples from the same batch with an Ecopia HMS-5000 Hall measurement system, using the van der Pauw method [24].

## 3. Results and discussion

### 3.1. General trends in polymer/CNT thermoelectrics

Fig. 1 shows a summary of the Seebeck coefficients and power factors of CNTs and CNT-composites plotted as a function of their electrical conductivity. The presented data is a summary of the SWCNT/P3HT and SWCNT/PEI composites prepared for this work, data from Avery and co-workers [1] as well as data from our group [7,8]. This plot allows us to have a general picture of the thermoelectric behaviour of composites as it includes data from different types of nanotubes (single- and multi-walled, p-type and n-type, and purely semiconducting tubes) and polymers (polyethylenimine, polythiophenes, polyfluorenes). Here,  $\sigma$  is used as a proxy for the charge density, which is harder to determine experimentally [13].

Generally speaking,  $S$  decreases with  $\sigma$  for all data sets, while the power factor increases. Interestingly, no maximum is observed for the power factor, which suggests that the limit for the best CNT/polymer composites has yet to be reached. It is also apparent, that different classes of materials follow the aforementioned trend to a varying degree. MWCNTs and their composites, plotted in red, generally perform worst, owing to the generally low Seebeck coefficient associated to the metallic character of MWCNTs. At very low conductivity values, the plotted data points with high Seebeck coefficient correspond to high polymer content composites containing only a few weight percent of non-percolating CNTs. The performance is, thus, close to that of the pure polymers. SWCNTs plotted in blue represent a step up in performance with a

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