



## Research paper

Simple, low-cost, water-processable *n*-type thermoelectric composite films from multiwall carbon nanotubes in polyvinylpyrrolidone

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## ABSTRACT

A significant challenge facing the advancement of organic thermoelectric devices is developing low-cost, solution-processable, air-stable, high performance *n*-type materials. In this work, we fabricate multiwall carbon nanotube (MWCNT)/polyvinylpyrrolidone (PVP) composite films by simply dispersing MWCNTs and PVP in water and spraying the resulting ink onto a substrate. We report a switch in the Seebeck coefficient of the MWCNTs from *p*-type to *n*-type behavior, even when the concentration of MWCNTs is as high as 90 wt.% in PVP. Additionally, we observe a great enhancement of the thermoelectric properties of the material when low quantities of polyethyleneimine (PEI) are added, reaching an *n*-type power factor of  $1.98 \mu\text{W m}^{-1} \text{K}^{-2}$  for a composite film containing 30 wt.% MWCNTs in PVP and 0.05 PEI/MWCNT wt. ratio. Furthermore, the material shows good air and thermal stability. We believe that the low-cost of the components, the air-stability and the simplicity of the water-processable system make PVP/MWCNTs a potential *n*-type organic material for future thermoelectric applications.

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## 1. Introduction

Ubiquitous potential for waste heat energy scavenging has motivated increasing interest in new thermoelectric (TE) power generation materials. The TE material performance is evaluated by the dimensionless figure of merit,  $ZT$ , defined as  $ZT = S^2\sigma T/\kappa$ , where  $S$ ,  $\sigma$ ,  $T$  and  $\kappa$  denote the Seebeck coefficient, electrical conductivity, average absolute temperature and thermal conductivity, respectively. The power factor (PF),  $S^2\sigma$ , is also commonly used as a performance parameter since it is directly related to the usable power that can be achieved. Hence, in order to achieve high TE performance, high  $S$ , high  $\sigma$  and low  $\kappa$  are desirable. However, these parameters are heavily interrelated and optimization is challenging [1].

New organic TE materials have garnered great interest due to their flexibility, low thermal conductivity and relative abundance, which make them relatively inexpensive [2–5]. Despite this interest, these materials are still less efficient than their inorganic counterparts. Although *p*-type organic materials have experienced a considerable advancement in the last few years [6,7],

development of *n*-type organic TE materials has lagged. This has been in part due to their air-instability and the difficulty of the doping process, which can render them non-amenable for solution-processing and, thus, mass scale production and large area applications are not viable [4,5].

Among all approaches considered for high performance *n*-type organic materials, the most successful has been combining inorganic and organic materials [5,8–10]. Unfortunately, these materials are not solution-processable, therefore limiting their application. Recent studies have also investigated doped small molecules and conductive polymers as a promising approach to obtain solution-processable *n*-type organic materials [4,11,12]. However, from a processing point of view, much simpler systems are required in order to keep the production costs low.

A simpler, cost-effective and promising approach to *n*-type organic solution-processable TE materials is the utilization of doped carbon nanotubes (CNTs) in various ways. Nonoguchi et al. [13] recently demonstrated the high *n*-type thermoelectric performance ( $ZT \sim 0.1$ ) of SWCNTs doped with a series of ordinary salts which also displayed great air stability. Additionally, different authors have investigated the thermoelectric properties of single-wall CNTs (SWCNTs) treated with different doping molecules or polymers. While SWCNTs usually exhibit *p*-type behavior due to air induced oxygen doping [14], it has been reported that polymers or

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molecules with electron donor groups such as poly(vinylpyrrolidone) (PVP) [15,16], poly(ethyleneimine) (PEI) [15,17–20] and triphenylphosphine (tpp) [16] can decorate the walls of the SWCNTs, and are able to change the majority charge carriers from holes to electrons, causing the Seebeck coefficient to change sign from positive to negative. Following this strategy, PFs as high as  $8 \mu\text{W m}^{-1} \text{K}^{-2}$  for PEI decorated SWCNTs [15],  $9 \mu\text{W m}^{-1} \text{K}^{-2}$  for PVP decorated SWCNTs [16] and  $25 \mu\text{W m}^{-1} \text{K}^{-2}$  for tpp decorated SWCNTs [16] were obtained. Nevertheless, the amount of decorating polymer or molecule used in these studies was small compared to the SWCNTs and therefore relatively high thermal conductivities are expected [21]. Furthermore, since the SWCNT surfaces are exposed to air due to poor surface coverage, reversion to *p*-type material may occur [19]. In order to solve these issues, SWCNT/polymer composites, with sufficient polymer matrix for SWCNT coverage, have great potential. The advantages of these composites are that while they largely conserve the electrical properties of SWCNTs and the thermal properties of the polymer, the Seebeck coefficient can be tuned to moderate *n*-type values and, moreover, they are flexible and air stable since the SWCNTs are embedded in the polymer matrix. For instance, poly(vinylalcohol) (PVA)/SWCNT/PEI composites [19] reached a  $S$  of  $-57 \mu\text{V K}^{-1}$  rendering a PF of  $0.04 \mu\text{W m}^{-1} \text{K}^{-2}$ . Poly(vinylidene fluoride) (PVDF)/SWCNT/doublewall CNT (DWCNT) films were *n*-type doped by spraying with a PEI solution [20] obtaining a  $S$  of  $-32 \mu\text{V K}^{-1}$  and a PF of  $1.47 \mu\text{W m}^{-1} \text{K}^{-2}$ . PEI functionalized SWCNT composites with polyvinyl acetate matrix and dodecylbenzenesulfonate as the dispersion agent [18] exhibited a Seebeck coefficient as large as  $-100 \mu\text{V K}^{-1}$  and a PF of  $8.4 \mu\text{W m}^{-1} \text{K}^{-2}$ . More recently, SWCNT/DWCNT/PVDF composite films were used to combine piezoelectric and thermoelectric technologies that showed synergistic effects resulting in increased device performance [22].

Multiwall CNTs (MWCNTs) are a cheaper alternative to SWCNTs (around 50–100 times less expensive).<sup>1,2</sup> Recently, a solution processable P3HT/MWCNT composite with the ability to switch from *p*-type to *n*-type after UV irradiation was presented by Dörfling et al. [23]. The material has great advantages in terms of processability since to fabricate large area devices it is only necessary to cover the area with the starting solution followed by UV irradiation of the masked area. Our group's capabilities include pilot-scale production of aligned MWCNTs using a continuous chemical vapor deposition process [24–26]. Motivated by the promising potential of SWCNTs, we investigated the *n*-type thermoelectric response of MWCNTs with different polymers that contain oxygen or nitrogen groups such as PVA, polyacrylonitrile, PVP and gum arabic, and found the best results for PVP (see Fig. S6 of Supplementary material for details). Other studies have observed PVP to perform well as *n*-type dopant polymer for SWCNTs [15,16], but little has been done to investigate this in detail. Further, to the best of our knowledge, no reports investigating TE properties of MWCNTs in PVP have been published. In this work, we report for the first time the thermoelectric performance of *n*-type PVP/MWCNT composites through a wide range of MWCNT concentrations. A simple, low-cost, scalable and environmentally friendly water-solution aerosol spray process was used to make *n*-type PVP/MWCNT thin films. Furthermore, the effect of adding PEI was also investigated. These composite films showed a significant increase in the *n*-type Seebeck coefficient resulting in commensurately enhanced TE performance. Additionally, both the stability over time and the

effect of removing Fe catalytic impurities from the MWCNTs (stemming from the MWCNT synthesis [24,27]), using graphitized MWCNTs (GrMWCNTs), were studied showing good stability and an enhancement of the TE properties when Fe was removed from the MWCNTs in the PEI-containing composite films. Finally, the temperature dependence of the thermoelectric properties is also studied and an increase of the power factor with temperature is observed.

## 2. Experimental

To prepare the PVP/MWCNT dispersions, scale measured quantities of PVP powder (approx. Mw 40000, Scientific Polymer Products) and MWCNTs [24–26] were mixed together. The quantity of MWCNTs remained constant at 0.25 g while the quantity of PVP powder was varied in order to achieve the MWCNT concentration desired. Then, 100 g of deionized water (DI water) was added to the mix and bath sonicated (Branson Ultrasonic Cleaner Model B300) for 15 min. Mixtures were placed in an ice bath and horn sonicated (Fisher Scientific 550 Sonic dismembrator) at 20% power. For each 30 s of sonication, the horn was idled 10 s off and the total time on was 30 min. In order to improve the wettability of the dispersion on the polyethylene terephthalate (PET) substrate onto which PVP/MWCNT films were sprayed, 80 mL of methanol was added to the dispersion followed by an additional 15 min of bath sonication. A MWCNT dispersion was also prepared following the same method but without adding PVP powder. Since the dispersion in the absence of polymer was not stable, it was used immediately after preparation. When studying the effect of PEI (approx. Mw 60000, 50 wt.% water solution of branched PEI), the quantity of PEI/water solution necessary to achieve the desired PEI/MWCNT wt. ratio was added at the same time as MWCNT and PVP powder. Before spraying, PET substrates were lightly sanded with 240 grit sand paper and four gold contacts were sputter coated on them. Once the dispersions and the PET substrates were ready, the spraying process was performed keeping the substrate horizontal, and at an approximate temperature of 100 °C to facilitate solvent evaporation. In order to prepare the films containing GrMWCNTs the same procedure described above was followed adding GrMWCNTs instead of MWCNTs. Dried films were flexible and approximately 5 cm long and 1.5 cm wide (see Fig. S3 of Supplementary material) and had thicknesses between 1 and 2  $\mu\text{m}$  measured by SEM imaging (see Fig. S4 of Supplementary material).

Electrical conductivities of the samples were measured using a four-point probe resistance method, passing a current (Lambda LP-412A-FM power source) through the two outer contacts and measuring the voltage (Greenlee DM-40 voltmeter) difference between the inner ones. The resistance of the film was extracted from the slope of the current-voltage lines and a geometrical factor was applied to calculate the electrical conductivity. Seebeck coefficients were determined by the slope of the linear relationship between the thermal electromotive force and the temperature difference between the two ends of each film (see Supplementary material, Fig. S5). The average values and standard deviation presented were calculated from three different samples, except in the time study, where they were calculated from nine different samples.

For materials and methods sections see Supplementary material.

## 3. Results and discussion

Fig. 1a and b show the electrical conductivity and Seebeck coefficient of the PVP/MWCNT composite films measured at room temperature. When MWCNTs are introduced into the PVP matrix,

<sup>1</sup> Cheaptubes. Accessed 08/06/2016. Available from: <https://www.cheaptubes.com/>.

<sup>2</sup> US-nano. Accessed 08/06/2016. Available from: <http://www.us-nano.com/>.

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