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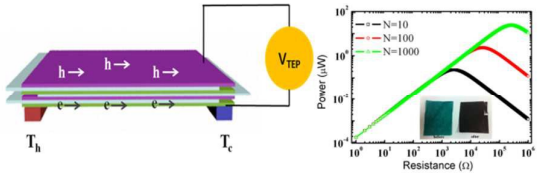
## Table of contents entry (TOCE)

Thermoelectric modules were fabricated made of p-type and n-type SWCNT composite papers, demonstrating as efficient thermoelectric materials.



Journal Name

ARTICLE

# Evaluation of power generated by thermoelectric modules comprising p-type and n-type single walled carbon nanotube composite paper

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We report on the p-type and n-type thermoelectric (TE) materials made of single-walled carbon nanotube (SWCNT) networks incorporated into the cellulose fiber structure of a common packaging paper. This leads the paper to possess both the mechanical flexibility of cellulose fibers as a supporting matrix and the high electrical conductivity originating from SWCNTs. Thermoelectric power of up to ±50 μV/K was successfully obtained as well, depending on their electronic type. Further, to demonstrate its thermoelectric voltage ($V_{TEP}$) and generating power, a couple of thermoelectric modules composed of both p-type and n-type composite layers were assembled in series. The produced $V_{TEP}$ shows a quasi-linearity with respect to the number of p-n couples and the temperature difference ΔT. Our testing module enables the provision of $V_{TEP}$ and power generation as large as ≈ 16.8 mV and ≈ 75.5 nW upon inducing a 50 K temperature difference. The feasibility of commercial TE modules consisting of 10, 100 and 1000 p-n SWCNT couples was numerically calculated, taking into account our experimental results.

## 1. Introduction

With the excessive consumption of the traditional energy, new eco-efficient, renewable and sustainable energy technologies have recently gained much attention.[1] Thermoelectric (TE) generators have been considered as a candidate for energy-harvesting technologies, converting heat into electricity. They offer a number of advantages: they are compact, have no moving parts, work silently and have low maintenance costs.[2, 3] Low band gap inorganic semiconductors such as $Bi_2Te_3$, $Sb_2Te_3$ and PbTe have been widely employed as TE materials [4, 5] even though they are well known to be toxic, brittle, and expensive for mass production. These disadvantages limit significantly their practical applications in future technologies.

Carbon nanotube (CNT) networks, due to their extraordinary electrical and mechanical properties, are considered for a variety of applications ranging from transparent conductive layers, sensors, conductive fillers for batteries to tissue engineering. To this end, several factors which affect their performance have been investigated on flexible, rigid and porous substrates.[6] Furthermore, it has been shown that single walled carbon nanotube (SWCNT) fibers made of SWCNT polyelectrolyte dispersions exhibit ultrahigh electrical conductivity after chemical doping.[7, 8] Also, high performance of multifunctional CNT fibers produced with a simple high throughput wet spinning method has been reported.[9] More recently, CNT/polymer composites were suggested to replace semiconductor-based TE materials.[2, 10-14] They can offer better mechanical flexibility, light weight as well as low fabrication costs. In particular, SWCNT/polycarbonate composites with a quite high positive Seebeck coefficient (≈ 65 μV/K) demonstrated strong capability to convert heat into electricity.[15] However, embedded SWCNTs lose some of their excellent intrinsic electrical conductivity, which is required for efficient TE performance, mainly owing to the insulating properties of polymers. But CNTs forming entangled mats or membranes (bucky papers) still have the potential to demonstrate a sufficient electrical conductivity and a moderate Seebeck coefficient (≈ 40 μV/K) that can be exploited in future TE generators.[16]

In this paper, we utilize the electrically percolating SWCNT networks to interpenetrate the cellulose fibers of a common paper (instead of bucky papers) to reduce the necessary amount of nanotubes.[17] The prepared composite papers serve as the p-type and n-type TE layers in the assembled TE modules. The following sections give details of the preparation

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of SWCNT composites, their TE characterization, the assembly of TE modules composed of up to five p-n couples, and performance evaluations of the prepared TE devices. The power generated by the up-scaled TE generators was analyzed for an increasing number of junctions up to 1000 p-n units, and as a function of the applied load resistance.

## 2. Experimental

The SWCNTs used in this study were synthesized by the chemical vapor deposition method and purchased from Thomas Swan & Co. Ltd, Crockhall, Consett, UK (product reference: PR0920), in the form of a 'wet cake' (containing ≈ 5.36 wt.% of SWCNT powder) which improved SWCNT dispersibility in water-based solutions. According to our investigations based on the absorption spectrum, the purchased sample was a heterogeneous mixture of metallic and semiconducting SWCNTs. We estimated the content of semiconducting SWCNTs to be about 60 % in a thin self-supporting film using our experimentally determined relationship between the Seebeck coefficient and the ratio of precisely adjusted pure semiconducting SWCNT to pure metallic SWCNT networks.[18] The diameter of SWCNTs was in the range of 1 - 2 nm, and the nominal length was in the range of > 1 µm.

To prepare the SWCNT embedded paper samples, the nanotubes (≈ 100 mg) were dispersed in a 0.5 wt.% solution (100 ml) of sodium dodecylbenzenesulfonate (SDBS, purchased from Aldrich), using a probe sonicator for 20 min. A thin (17 µm), flexible and commercially available colored giftwrap paper was used as SWCNT support due to its outstanding tear resistance and its absorptivity. The well dispersed SWCNT solution was introduced dropwise onto the paper until it was saturated with liquid. It was observed that the SWCNT solution was easily absorbed by the fiber structure of the paper, due to capillary forces. After being completely dried in an oven at 80°C, the paper was then immersed into deionized water for 20 min to remove SDBS. This entire process was carried out six times until the paper was sufficiently soaked with nanotubes, identified by its change in color from green to black and its improved electrical conductivity. The untreated paper was an electrical insulator. Pristine as-prepared SWCNTs are commonly p-doped through ambient oxygen. Incorporated into cellulose fibers of paper, they serve as a p-type TE material. A chemical post-treatment of the composite paper with polyethyleneimine (PEI) changes the doping of SWCNTs from p-type to n-type, producing an n-type TE material. To this end, the prepared SWCNT composite papers were immersed in a water solution (0.6 wt.%) of PEI (capped with amine groups at the end of polymer chain, average molecular weight of 600, purchased from Aldrich) for 15 min and then dried in air for 30 min. Both p-type and n-type SWCNT composite papers were completely black, electrically conductive and flexible, with an unchanged thickness of 17 µm. The papers were cut into strips (10 × 30 mm), combined into p-n couples and assembled into TE modules. The electrical contact at the ends of the strips was achieved by mechanical compressing of the ends of the sample strips. Compact TE modules were arranged as an alternating assembly of p-n SWCNT composite papers, with polyethylene terephthalate (PET) acting as an insulating layer between them.

The measurement of the electrical resistance of the prepared samples was performed using the standard four probe method at room temperature, applying the electrical current (Keithley 238) and measuring the voltage (34401A multimeter, Hewlett-Packard). The measured resistance was converted into electrical conductivity by multiplying it by the geometric factor of the sample. To determine the Seebeck coefficient, the thermoelectric voltage ($V_{TEP}$) induced along the paper sample by temperature difference ($\Delta T = T_h - T_c$, where $T_h$ and $T_c$ were the temperatures of the hot and cold side, respectively) was measured simultaneously. The detailed method for the Seebeck coefficient measurement along with the performance determination of the fabricated TE modules has been described elsewhere.[15]

## 3. Results and discussion

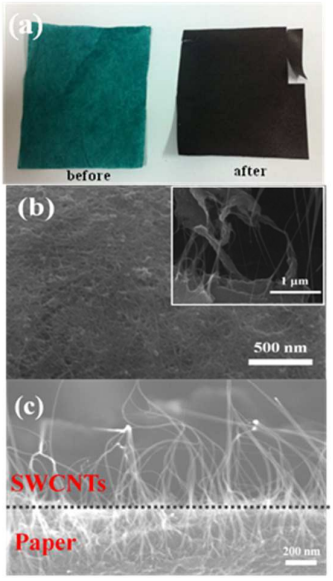


**Fig. 1** (a) Optical images of a commercial packaging paper before (left) and after (right) absorption of the SWCNT dispersion. Representative FESEM images of (b) the paper surface covered with a dense copacted SWCNT network (Inset: cellulose fibers and stretched nanotube bundles bridging the paper pore), (c) the cross-sectional image of the SWCNT/paper composite, respectively.

Fig. 1a displays two photographs of the paper used for our experiment, taken before and after introduction of SWCNTs. The composite paper was completely black, electrically conductive, tear-proof and flexible, with a thickness of 17 µm. Observations of the surface and cross-section of the SWCNT/paper composite *via* a field emission scanning electron microscope (FESEM) revealed long, numerous and uniform



 

SWCNT bundles homogenously dispersed on the paper surface as well as interpenetrating the porous paper structure, as presented in Fig. 1b and 1c. Furthermore, stretched nanotube bundles bridging the paper pore were visible besides some cellulose fibers (inset of Fig. 1b). As a result, the formation of percolated conducting paths on the surface, partially penetrating the volume of the supporting matrix has been achieved. The paper soaked with SWCNTs provides a composite material, where mechanical flexibility of cellulose fibers is combined with high electrical conductivity of SWCNTs. While pristine SWCNTs incorporated between cellulose fibers of paper deliver a p-type TE material due to commonly p-type doping of SWCNTs under ambient conditions, a chemical post-treatment of the composite paper with PEI changes the doping of SWCNTs from p-type to n-type, producing an n-type TE material. PEI as an amine-rich polymer is often applied as an effective n-type dopant for SWCNTs.[19] The composite papers were characterized as possible materials for TE power generation.

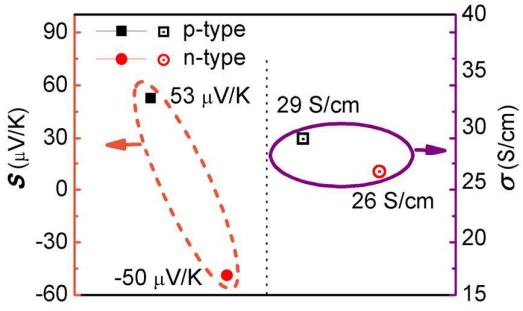


**Fig. 2** The Seebeck coefficient (S) and electrical conductivity ($\sigma$) of the p-type and n-type SWCNT composite papers.

The electrical conductivity and the Seebeck coefficient of both p-type and n-type SWCNT composite papers are shown in Fig. 2. The electrical conductivity of the p-type and n-type SWCNT papers was found to be almost equal and independent of the available majority charge carriers at ≈ 29 S/cm and ≈ 26 S/cm, respectively. This result demonstrates that the doping with PEI did not greatly affect the charge mobility and the electrical conductivity of SWCNTs in the composite paper. The value of electrical conductivity is comparable or even higher that measured for pure self-supporting CNT films (bucky papers).[20-23] Similarly, the absolute values of the Seebeck coefficient were almost identical for the p-type and n-type SWCNT papers with + 53 μV/K and -50 μV/K, respectively. The Seebeck coefficient of the p-type paper was slightly higher than that of SWNCT bucky paper (+40 μV/K), indicating that the cellulose fibers of the paper filtered the low energy carriers through increasing the phonon scattering in the composite.[24] The Seebeck coefficient of the n-type SWCNT papers (-50 μV/K) indicates clearly that the majority of charge carriers in p-type SWCNT networks were completely converted from holes to electrons by the efficient adsorption of PEI molecules on the surface of the SWCNTs.[25] Accordingly to the TE properties of the p-type and n-type composite papers, the power factor $P=S^2\sigma$, commonly used as a measure of TE efficiency, was also compared (≈ 8.15 μW/mK$^2$ for p-type and ≈ 6.5 μW/mK$^2$ for the n-type papers, respectively).

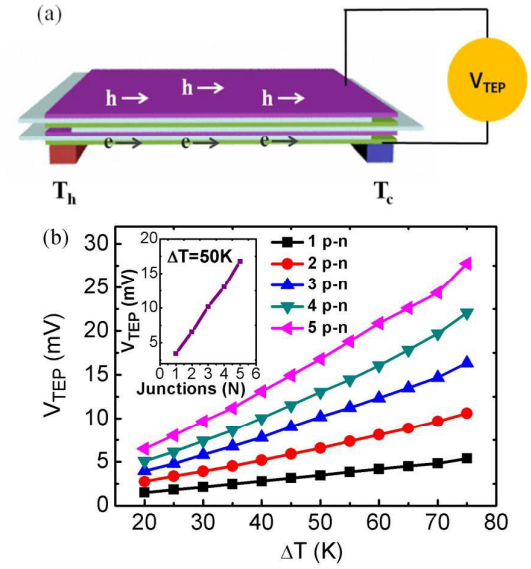


**Fig. 3** (a) Schematic of the TE module involving two couples composed of p- type (violet) and n-type (green) SWCNT composite papers and insulating films of PET (blue) exposed to the temperature gradient $\Delta T= T_h-T_c$, the flow of the charge carries is indicated by the arrows, (b) The measured $V_{TEP}$ as a function of ΔT for a series of TE modules with up to five p-n couples, the inset shows the linear dependence of $V_{TEP}$ on the number of p-n couples in the assembled modules when ΔT=50 K.

In order to generate a sufficient power output, p-type and n-type TE materials are usually combined into TE modules.[26-29] Here, the p-type and n-type composite papers were assembled in modules with alternative p-n couples electrically connected in series (compressed ends of paper strips) and thermally in parallel, as shown in Fig. 3a. The induced $V_{TEP}$ as a function of ΔT with respect to the number of p-n couples in the module was measured and displayed in Fig. 3b. It clearly demonstrates the Seebeck effect, *i.e.*, the measured $V_{TEP}$ increases almost linearly with the gradual change of ΔT. Moreover, the linear dependence of $V_{TEP}$ on the number of p-n couples in the module at ΔT = 50 K is visible in the inset of Fig. 3b. This property is meaningful for the fabrication of commercial TE modules consisting of hundreds of p-n couples.

For a module testing, a set of ΔT values was induced across it and $V_{TEP}$ and current were measured simultaneously to calculate the power generation. To optimize the maximum power generation, the voltage and current from TE modules composed of one, three and five p-n couples were measured at ΔT = 50 K as a function of different load resistance values ($R_L$). The generated power is illustrated in Fig. 4a. The achieved maximal power (when the load resistance matched the corresponding internal module resistance), was ≈ 14.7, ≈ 54.5

and ≈ 75.5 nW for one, three and five p-n couples, respectively. The maximal power output and the internal module resistance as a function of the number of p-n couples N are shown in the inset of Fig. 4a. It might be naturally accepted that both the $V_{TEP}$ and the maximal power output could be significantly improved by increasing N, while the internal module resistance was simply the sum of the unit resistances of N involved p-n couples. The development of $V_{TEP}$ produced by five p-n couples for several different load resistances upon application ΔT = 50 K is shown in Fig. 4b. At the load resistance related to the maximum power generation, the $V_{TEP}$ ≈ 7.8 mV compared to an open circuit $V_{TEP}$ ≈ 16.8 mV at the same ΔT. Above this resistance, the $V_{TEP}$ continuously increased with the load resistance approaching the open circuit voltage, whereas the power output dramatically decreased with an exponentially increasing load resistance. The power output versus ΔT at a load resistance of 850 Ω is shown in the inset of Fig. 4b and demonstrates a squared behavior of the generated power as a function of ΔT as a result of the relationship $V_{TEP}^2/R_L$. Thus, the maximum power ≈ 75.5 nW generated by TE module exposed to a ΔT = 50 K could be improved up to ≈ 180 nW by enhancing ΔT up to 70 K.

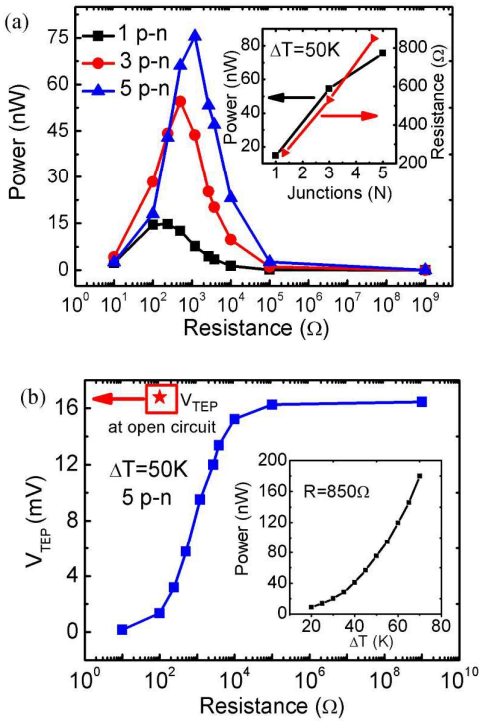


**Fig. 4** (a) The generated power as a function of load resistance for modules with one, three and five p-n couples at ΔT = 50 K, the inset shows the maximal power and the internal resistance of the TE device as a function of the junction number N in the module, (b) $V_{TEP}$ produced by five p-n couples at open circuit and under loading with resistance at ΔT = 50 K, the inset shows the power output as a function of ΔT for a load resistance of 850 Ω.

Taking into account the fact that commercial TE modules consist of hundreds of p-n couples, we calculated the feasible power generated when N = 10, 100, and 1000 p-n couples as a function of load resistance keeping ΔT = 50 K. The results are presented in Fig. 5a. As expected, the increase in N dramatically improved the module power. Here, a module of N = 10 p-n units generated ≈ 232 nW for load resistance of 2.6 kΩ, while the maximum power of a module containing 1000 units was as high as ≈ 23 μW. However, the corresponding load resistance also increased up to ≈ 290 kΩ. We also investigated the power output with an increasing number N of p-n couples while taking into account three different load resistances ($R_L$ = 1.2, 10 and 100 kΩ), as illustrated in Fig. 5b. At first the generated power increased rapidly with increasing N, and then reached saturation even though the number of p-n couples continued to increase. The number of p-n couples required for maximal power was increased depending on the load resistance. For example, at a load resistance of 1.2 kΩ, the generated power reached saturation when the module comprised 16 p-n couples. This number increased to 550 when the load resistance was increased to 100 kΩ. Hence, depending on the applied load resistance, an appropriate TE module composed of a required number of p-n couples can be fabricated for an optimal use of the generated power.

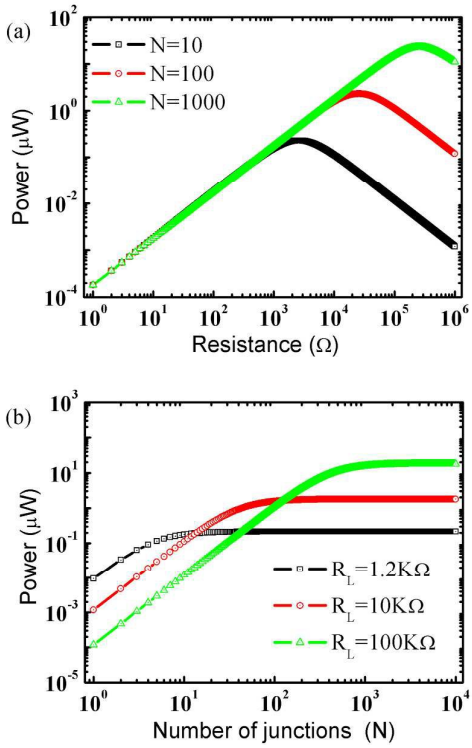


Fig. 5 (a) Theoretical power output calculated for modules with 10, 100 and 1000 p-n couples under different load resistances and exposed to ΔT = 50 K, (b) The numerically simulated results of generated power as a function of the number of p-n couples in a module when loaded with three different resistance values.

## 4. Conclusions

Both p-type and n-type SWCNT composite papers were prepared. The electrical conductivity and the Seebeck coefficient were determined in order to use the papers as TE materials. To this end, several TE modules were fabricated by combining p-type and n-type SWCNT composite papers into electrically conductive junctions. Their TE performances, including $V_{TEP}$ and generated power, were investigated as a function of the number of p-n couples, temperature difference ΔT and load resistance $R_L$. It was demonstrated that a TE module composed of five p-n couples produced $V_{TEP}$ as high as ≈ 16.8 mV when exposed to ΔT = 50 K and generated ≈ 75.5 nW of power when the load resistance $R_L$ ≈ 850 Ω. The power output could be improved by increasing the number of p-n couples and the applied temperature difference ΔT. The theoretical estimated power output could be as high as ≈ 23 μW for 1000 p-n couples. Our results open up new possibilities to fabricate flexible, low cost, organic TE devices involving the extraordinary electrical and thermal transport properties of SWCNT networks incorporated in the structure of cellulose fibers of common paper.

## Acknowledgements

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