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High-performance organic thermoelectric modules based on flexible films of a novel n-type single-walled carbon nanotube

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Organic thermoelectric materials are emerging green energy materials, where n-type candidates are of special interest due to the strong demand for thermoelectric modules with flexibility, light weight, large-area fabrication and ease of processing into versatile shapes. Here, an exciting novel strategy to prepare an n-type single-walled carbon nanotube (SWCNT) is proposed by diethylenetriamine (DETA) doping (electron donation) and subsequent CaH₂ treatment of the pristine SWCNT (p-type). The Seebeck coefficient and the electrical conductivity for the obtained DETA-CaH₂-SWCNT are $-41.0 \pm 1.5 \mu\text{V K}^{-1}$ and $165 \pm 10 \text{ S cm}^{-1}$, respectively. A possible mechanism is discussed for the p- to n-type conversion. Then, a multilayered alternating stacked structure is employed to construct thermoelectric modules which realize the conduction layers electrically in series and thermally in parallel. Importantly, the module containing 14 couples displays large open circuit voltages of 62 mV and 125 mV at temperature gradients (ΔT) of 55 K and 110 K, respectively, and a maximum output power of 649 nW at $\Delta T = 55 \text{ K}$. The strategy proposed here opens a new way to fabricate organic n-type materials and flexible thermoelectric modules. These promising results show great potential in fabrication and applications of flexible and wearable power-conversion devices for next-generation power generators and waste-heat-recovery systems.

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1. Introduction

Organic thermoelectric materials are emerging green energy materials which have witnessed rapid progress in recent years.¹ They have obvious advantages over conventional inorganic materials, such as Bi₂Te₃, PbTe and Sb₂Te₃, including low toxicity, earth-abundance of raw materials, low thermal conductivity, *etc.* For example, conducting polymers and their composites have received special attention in thermoelectric applications to harvest low-grade waste heat to generate electricity,² where typical conducting polymers including poly(3,4-ethylenedioxythiophene) (PEDOT),³ polyaniline (PANI)⁴ and polypyrrole (PPy)⁵ have already been successfully employed. Moreover, in sharp contrast with the inorganic ones, the devices or modules made of organic thermoelectric materials possess mechanical flexibility and endurance, convenient processing into various shapes, light weight, large-area fabrication, *etc.*, which greatly facilitate their applications in wearable electronics and various complex environments.⁶ The thermoelectric

performance of materials can be evaluated by a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S , σ , T and κ stand for the Seebeck coefficient or thermopower, the electrical conductivity, the absolute temperature and the thermal conductivity, respectively. Due to the intrinsic property of low thermal conductivities for polymer materials ($0.1\text{--}0.5 \text{ W m}^{-1} \text{ K}^{-1}$),⁷ the power factor ($S^2\sigma$) is always adopted to replace ZT . As for the thermoelectric modules, the output thermoelectric voltage and the maximum power output have generally been employed for thermoelectric performance judgment.

Thermoelectric devices or modules rely on alternate connection of p- and n-type units in series, and further optimizing the utilization of temperature gradients by rational design of device structures. To date, most of the reported organic thermoelectric materials are p-type. Studies of organic n-type materials with decent electrical conductivity and Seebeck coefficient are very limited. Thus, high-performance n-type organic thermoelectric materials are strongly desired. Pristine semiconducting carbon nanotubes (CNTs) display characteristic p-type behavior due to oxygen doping in the atmosphere during synthesis and the presence of $-\text{OH}$ or $-\text{COOH}$ groups in the surface defects.⁸ Fortunately, by doping with electron donors and/or reducing by reducing agents to increase the electron concentration, the p-type behavior of the pristine CNTs can be dramatically changed to n-type characteristics.^{6,9–12} A few CNT surface functionalization techniques have been developed

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including using hydrazine,⁹ branched polyethyleneimine (PEI),^{6,10,11} sodium borohydride (NaBH_4),¹¹ and phosphine derivatives.¹² However, most have obvious disadvantages, which seriously hinder their thermoelectric application. For example, hydrazine is toxic, and difficult to handle or store. Due to its intrinsic electrical insulating properties, the large molecules of PEI inevitably result in a reduction of the electrical conductivity. Therefore, it still remains a great challenge to develop new strategies for n-type organic thermoelectric materials, especially with high electrical conductivity. On the other hand, device or module design of flexible films is also vital to maximally utilize the temperature gradients.

In this work, we report high performance thermoelectric modules consisting of flexible films of a novel n-type single-walled CNT (SWCNT). The pristine SWCNT was used as the p-type constituent. The n-type SWCNT was achieved by diethylenetriamine (DETA) doping and subsequent calcium hydride (CaH_2) treatment. A possible conversion mechanism of the conducting property from p-type to n-type is discussed. Flexible films of n- and p-type SWCNTs were obtained, whose morphology and structure were characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectra. Their thermoelectric performance was measured as well. Moreover, the multilayered alternating stacked modules made of three component films including the pristine SWCNT (p-type), DETA- CaH_2 -SWCNT (n-type) and polyimide (insulator) were designed to meet the requirement of conducting electrically in series and thermally in parallel. Finally, with the modules composed of up to 14 couples, the generated thermoelectric voltages and the output thermoelectric power were measured.

2. Experimental section

2.1 Materials

Commercialized single-walled carbon nanotubes (SWCNTs) with a diameter <3 nm and a purity >85.0 wt% were bought from Shenzhen Nanotech Port Co. Ltd, China, and prepared by chemical vapor deposition. Diethylenetriamine (DETA, C.P. pure grade with a purity of $>97.0\%$) was purchased from Aladdin Company. All of the other reagents, including poly(vinylidene fluoride) (PVP), calcium hydride (CaH_2), anhydrous ethanol (A.R.) and distilled water, were used as received without further purification.

2.2 Preparation of n- or p-type films

A typical procedure for the preparation of the n-type film is described in the following. First, 15 mg of SWCNT was added into 30 mL of mixed ethanol aqueous solution (ethanol/water v/v, 1 : 4) containing 0.15 wt% PVP. Then, the mixture was magnetically stirred for 2 min, and then ultrasonically treated for 60 min with a bath type sonicator. Later, 1 g of DETA was titrated into the above system. After another pen-type ultrasonication treatment for 30 min, the solution was stirred for 5 h for DETA doping. After that, the mixture was vacuum-filtered, and washed with anhydrous ethanol several times. A solution

containing CaH_2 (0.2 g) in 10 mL anhydrous ethanol was employed in the washing process as the reducing agent. Finally, the DETA-SWCNT films were vacuum-filtered and dried under vacuum at 80°C for 40 min, providing a round n-type SWCNT bucky paper ~ 13 μm in thickness. For the p-type SWCNT film, 15 mg of SWCNT was dispersed in 30 mL ethanol under a bath-type ultrasonic treatment for 60 min. The mixture was vacuum-filtered, and subsequently dried under vacuum at 80°C for 40 min.

2.3 Fabrication of thermoelectric modules

The thermoelectric modules were made of films of the pristine SWCNT and the DETA- CaH_2 -SWCNT as p-type and n-type components, respectively. The p- and n-type SWCNT films were cut into a rectangular shape with dimensions of 40×10 mm^2 . The multilayered alternating stacked structure shown in Fig. 5a clearly shows the fabrication strategy. The p- and n-type SWCNT films were electrically connected in series by aluminum foils with a silver adhesive (3 M Company). Insulating layers of polyimide with a thickness of 40 μm were inserted between the p-type and the n-type films to avoid electrical contact. Thermal conduction in parallel was realized along the film plane from the hot end to the cold end along the multilayered films. Copper (Cu) wires were embedded into the multilayered films to detect the temperature gradient (ΔT) between the hot end and cool end of the module. Finally, the modules were achieved by pressing them and laminating with two insulating polyimide films. Ohmic contact was established, as confirmed by I - V curves.

2.4 Characterizations

The morphology of the SWCNTs was directly observed using a HITACHI S-4800 scanning electron microscope with an acceleration voltage of 15 kV. Fourier transform infrared (FTIR) spectra were collected using a spectrophotometer (Perkin-Elmer System 2000 FTIR) with 32 scans in the wavenumber range of 4000 – 400 cm^{-1} .

2.5 Measurements of thermoelectric performance

The films used for thermoelectric measurements of the p-type and n-type SWCNTs were rectangular in shape with dimensions of $40 \text{ mm} \times 10 \text{ mm} \times 13 \mu\text{m}$. The electrical conductivities and the Seebeck coefficients at room temperature were measured by a commercial instrument, Film Thermoelectric Parameter Test System (Namicro-F3), made by JiaYiTong Company. During the measurements, a quasi-steady-state mode was adopted. At least five samples were measured, and the average values were used. In the measurements of the module thermoelectric performances, a temperature gradient between 4 K and 110 K was applied across the surface on the top of the modules made up of 2 to 14 couples. The output open circuit voltages were measured directly without any load resistance. In the case where various load resistances were applied, then the output currents and voltages generated at a temperature difference of 55 K were monitored. Thus, the generated output powers were calculated.

3. Results and discussion

3.1 Preparation of n-type SWCNTs

Fig. 1a shows a schematic illustration of the preparation process of the n-type SWCNTs, *i.e.* DETA doping and subsequent CaH_2 treatment. The details are described in the Experimental section. In brief, the pristine SWCNT (p-type) was first de-bundled and uniformly dispersed in an ethanol-water mixed solution aided by polyvinyl pyrrolidone (PVP). Then, DETA was added and this adsorbed onto the surfaces of the SWCNTs. After vacuum filtration, the CaH_2 was titrated into the filtrated product of the DETA modified SWCNT (DETA-SWCNT). Finally, the n-type SWCNT (DETA- CaH_2 -SWCNT) film was obtained, whose thickness was about 13 μm , after vacuum drying. Fig. 1b reveals that the surface of the film is essentially flat and uniform in thickness. The diameter and thickness of the n-type SWCNT film can be conveniently adjusted by changing the filter paper and the amount of the raw materials including the SWCNTs and the modifying agents. As shown in Fig. 1b, the diameter is approximately 7.0 cm. Importantly, the as-prepared n-type SWCNT film displays high flexibility, as shown in Fig. 1c, and can endure a high degree of bending without distinct breakage or damage. The high flexibility enables possible applications in wearable electronics or complex conditions.

3.2 Thermoelectric performance of p- and n-type SWCNTs

The thermoelectric performances of the p-type (pristine) SWCNT and the n-type SWCNTs (DETA-SWCNT and DETA- CaH_2 -SWCNT) are shown in Fig. 2. First, the thermopower or the Seebeck coefficients were measured to check whether the

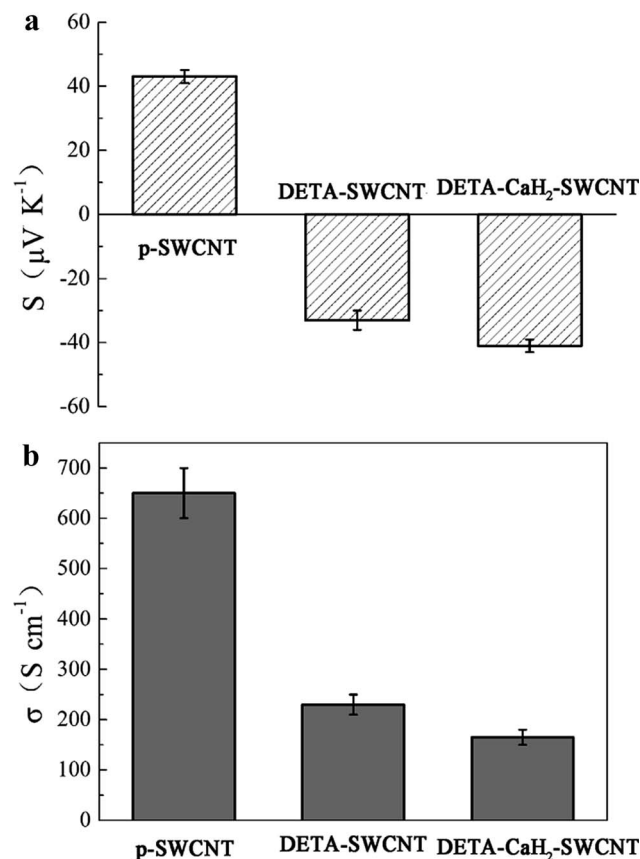


Fig. 2 Thermoelectric performances including (a) Seebeck coefficient and (b) electrical conductivity for the p-type SWCNT (pristine) and the n-type SWCNTs (DETA-SWCNT and DETA- CaH_2 -SWCNT).

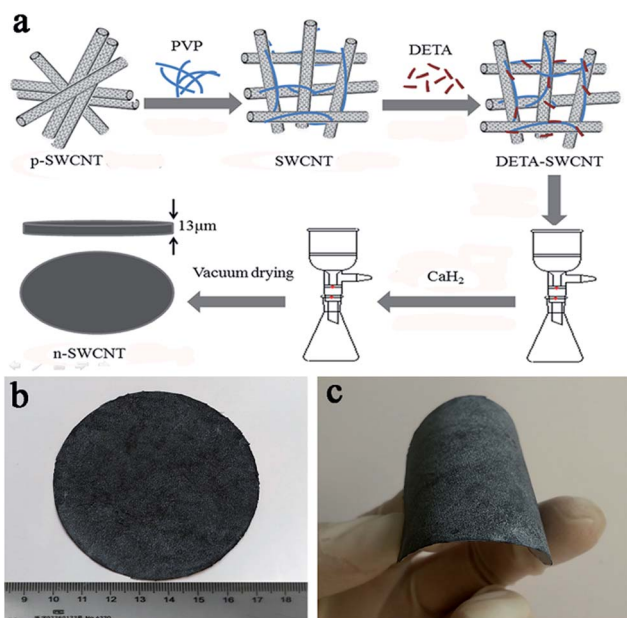


Fig. 1 (a) Schematic illustration of the preparation of the n-type SWCNT by DETA doping and subsequent CaH_2 treatment. (b) Optical image of the n-type (DETA- CaH_2 -SWCNT) film. (c) Optical image showing the flexibility of the n-type (DETA- CaH_2 -SWCNT) film.

transition from p-type to n-type had been successfully completed for the pristine SWCNT, since thermoelectric materials of p- and n-types possess positive and negative Seebeck coefficients, respectively. The pristine SWCNT displays a positive thermopower of $43.0 \pm 1.5 \mu\text{V K}^{-1}$. In sharp contrast, the DETA doped SWCNT (DETA-SWCNT) reveals a negative Seebeck coefficient ($-33.0 \pm 2.5 \mu\text{V K}^{-1}$), and subsequent CaH_2 treatment leads to better n-type characteristics with an enlarged Seebeck coefficient of $-41.0 \pm 1.5 \mu\text{V K}^{-1}$. Therefore, we conclude that the p-type conducting behaviour of the pristine SWCNT can be effectively and conveniently converted into that of an n-type SWCNT by DETA doping, and a subsequent CaH_2 treatment results in enhanced-type characteristics. The electrical conductivity for the pristine SWCNT is high, around $650 \pm 50 \text{ S cm}^{-1}$. The two n-type SWCNTs, *i.e.* DETA-SWCNT and DETA- CaH_2 -SWCNT, present decreased electrical conductivities of 230 ± 15 and $165 \pm 10 \text{ S cm}^{-1}$, respectively. Obviously, these are much higher than those of the n-type SWCNTs modified by PEI doping (39 S cm^{-1}) as well as PEI doping and subsequent NaBH_4 reduction (52 S cm^{-1}).^{11b} Taking into account that most n-type organic thermoelectric materials have low or moderate electrical conductivities, the Seebeck coefficients and the electrical conductivities reported herein are among the highest performances for n-type organic thermoelectric materials so

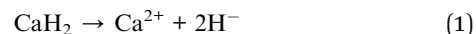
far.^{6,9–12} However, note that they are among the excellent organic n-type materials.^{6,9–12} The power factors for the DETA-SWCNT and DETA-CaH₂-SWCNT are 25.1 ± 3.7 and $27.7 \pm 2.3 \mu\text{W}^{-1} \text{K}^{-2}$, respectively. Considering that the DETA-CaH₂-SWCNT exhibits a similar thermopower to the p-type SWCNT and a higher power factor than the DETA-SWCNT, it was chosen as the n-type component in the following module design and fabrication.

3.3 Mechanism of p- to n-type conversion

In order to explain the conversion of p-type to n-type conducting SWCNTs, Fig. 3 presents a possible mechanism based on previous investigations.^{12,13} The p- to n-type transition is directly defined by the switching of the majority carrier type, where electrons and holes correspond to n-type and p-type conducting behaviors, respectively. Holes are the dominant carriers in the pristine SWCNT, thus exhibiting p-type behavior. After doping, due to the charge transfer interaction between dopants and SWCNT, the Fermi level clearly shifts upwards towards the conduction band of the SWCNTs, which has been demonstrated by theoretical calculations¹³ and experimental data.¹² Therefore, the Fermi level moves much closer to the conduction band, resulting in the conversion into n-type conducting SWCNTs and a reduction of electrical conductivity.

In the present investigation, a novel conversion method of p- to n-type SWCNTs is proposed using DETA doping and subsequent CaH₂ treatment. DETA is a small organic molecule with amine groups in its molecular structure, which contain lone pairs of electrons to donate to the SWCNT (*i.e.* doping). The surface functionalization of the SWCNT by DETA doping makes the CNT surface electron-rich, thus realizing the conducting conversion from p-type to n-type behavior. Compared with insulating PEI macromolecules, DETA is superior in that it does not considerably sacrifice the electrical conductivity. In addition, the reduction/doping mechanism of CaH₂ is described in the following. First, CaH₂ is unstable and easy to be initially ionized into Ca²⁺ and H[−], as shown in eqn (1). Then, 2H[−] combine to afford H₂ (eqn (2)), which reduces the surface defects and donates electrons to the SWCNTs. Note that the reaction is exothermic, which accelerates as the reaction proceeds. Therefore, the conducting conversion from p-type to

n-type SWCNTs can be realized by electron donation by DETA and subsequent reduction/doping by CaH₂.



3.4 Morphological and structural characterizations

Fig. 4 shows the surface SEM images for (a) the p-type and (b) n-type SWCNTs. The pristine p-type SWCNT bundles (a) are relatively straight, whereas the DETA-CaH₂-SWCNT (b) becomes curled to a greater extent. Moreover, due to the surface coating by the organic molecules of DETA, the diameters of the p-type SWCNTs are less than those of the DETA-CaH₂-SWCNTs (n-type). These observations are in good agreement with previous research on n-type SWCNT treated with the organic polymer (PEI).¹¹ Furthermore, the SWCNT doping by DETA is demonstrated by FTIR spectra (Fig. 4c). Compared with the spectrum of the pristine SWCNT, a series of novel absorption bands resulting from DETA occur in the spectrum of the DETA-SWCNT. The strong band at 1574 cm^{−1} and the weak sharp band at 817 cm^{−1} result from the in-plane and out-of-plane bending modes of N–H vibrations, respectively.¹⁴ The strong band at 1481 cm^{−1} and the band at 1315 cm^{−1} with medium intensity can be ascribed to the primary and the secondary C–N stretching vibrations, respectively.¹⁵ As for the broad band with a maximum absorption around 3361 cm^{−1}, it corresponds to the stretching mode of –OH groups for the pristine SWCNT or a mixed band contributed by the –OH stretching and N–H stretching modes for the DETA-SWCNT.

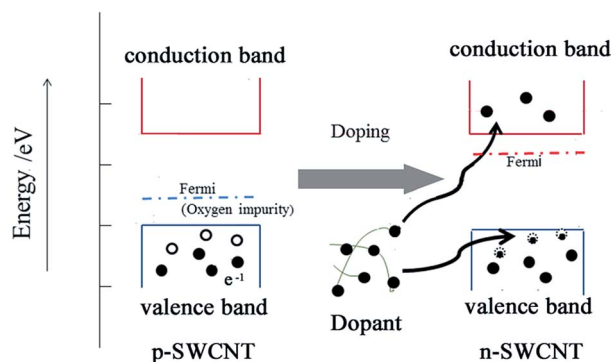


Fig. 3 A possible mechanism for the conversion from p-type to n-type SWCNT.

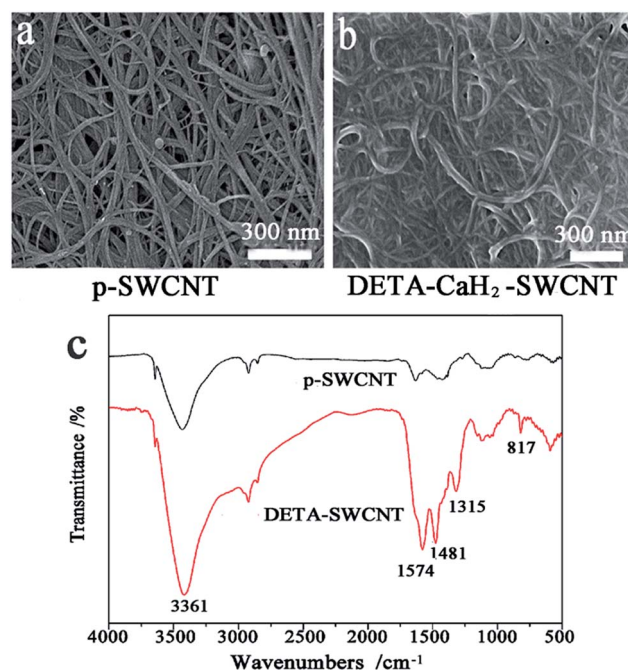


Fig. 4 (a and b) SEM images and (c) FTIR spectra of the p-type and the n-type SWCNTs.

3.5 Design of thermoelectric modules

In order to generate a sufficient power output, p-type and n-type thermoelectric units are always assembled into modules. In this study, the pristine SWCNT films and the DETA-CaH₂-SWCNT films are used as the p-type and n-type units, respectively. An optimized design principle is required: the p-type and the n-type conduction layers need to be electrically in series and thermally in parallel. Here, a multi-layered alternating stacked structure was used, as shown in Fig. 5a. The p-type (pristine SWCNT) films and the n-type (DETA-CaH₂-SWCNT) films were cut into rectangular shapes with dimensions of 40 mm in length, 10 mm in width and $\sim 13\ \mu\text{m}$ in thickness. The alternating p- and n-type films were electrically connected in series, where excellent electrical conductivity was guaranteed by aluminium foils. Additionally, the insulating films of polyimide were inserted between the p-type and the n-type films in order to block the electrical conduction among adjacent SWCNT films, and simultaneously ensure thermal conductivity in parallel. As clearly shown in Fig. 5a, the heat transfers from the left side (hot end) to the right side (cold end). In other words, the heat transfers along the film planes from the left to the right in the

parallel SWCNT films, while the electricity moves along the SWCNT films alternately connected in series.

Fig. 5b displays a principle illustration of a film thermoelectric module. The module was heated from the left side on the top surface. Copper (Cu) wires were embedded into the multi-layered films to detect the temperature difference (ΔT) between the hot end and cool end of the module. On the other hand, the output thermoelectric voltage was measured to evaluate the properties of the module. Fig. 5c shows a photograph of the thermoelectric module made in the present investigation. The multilayered films containing p-type, n-type and insulator layers were pressed and laminated inside two polyimide films. Eight wires were drawn to ensure the effective working of the module. Note that the module is flexible and distinctly bendable.

3.6 Output voltage and power of a thermoelectric module

In order to evaluate the thermoelectric performance of a module, open circuit voltage as a function of temperature gradient (ΔT), load circuit voltage and output power as a function of applied load resistance were measured. Fig. 6 displays the thermoelectric performance of a module consisting of 2 to 14 couples without any external resistance loading. With the increase of ΔT , the open circuit voltages increase essentially linearly for all thermoelectric couples. In addition, with the increase of the number of thermoelectric couples, the voltage enhances at the same ΔT . These results are in very good coincidence with previous reports.^{9–12} Importantly, when the ΔT values are 55 K and 110 K, the generated voltages for the module made of 14 thermoelectric couples can reach 62 mV and 125 mV, respectively, which are comparable to the highest performance of organic thermoelectric modules available to date.

To optimize the maximum output power, the generated current and voltage from the thermoelectric modules were measured as a function of applied load resistance at a temperature difference of 55 K. The thermoelectric performance for

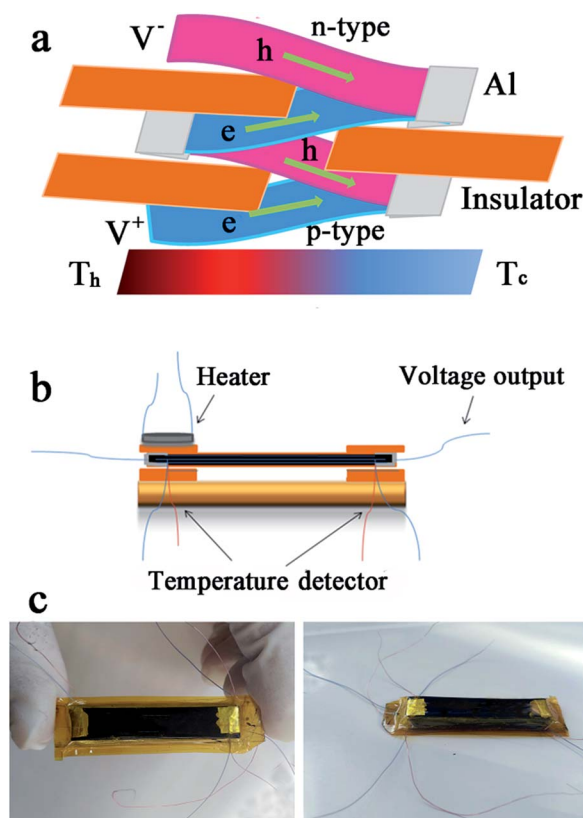


Fig. 5 (a) Schematic of the multilayered alternating stacked structure for a module consisting of 2 p-type and 2 n-type films, inserted with insulating polyimide films. T_h and T_c represent the heating and cooling ends, respectively, while Al foils are used as the electrical connectors. (b) Principle illustration of a working thermoelectric module. (c) Photographs of thermoelectric modules made of pristine SWCNT (p-type unit) and DETA-CaH₂-SWCNT (n-type unit), which were laminated with polyimide films.

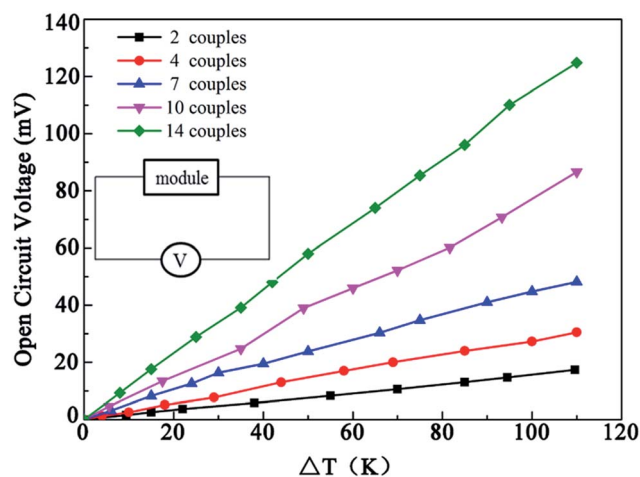


Fig. 6 Thermoelectric output voltage as a function of temperature gradient (ΔT) for thermoelectric modules consisting of 2 to 14 couples of p- and n-type SWCNT films.

a module is presented in Fig. 7. As shown in Fig. 7a, with the increase of the load resistance, the load circuit voltage obviously increases, while the current decreases remarkably. On the other hand, at each ΔT , both the voltages and the current increase with increasing numbers of the thermoelectric couples. In addition, the dependence of the output power with varying load resistance is studied as well. Fig. 7b clearly shows that with the increase in the number of thermoelectric couples, the output power increases dramatically. However, the impact of the load resistance on the output power is important. For example, the output powers of modules consisting of 14 couples increase abruptly first, when the circuit resistance is less than $\sim 1500 \Omega$. Then, the output thermoelectric powers decrease dramatically with the applied load resistance. Thus, the output powers exhibit a maximum at a resistance of around 1500Ω . As distinctly shown in Fig. 7b, the maximum output thermoelectric power for the module containing 14 couples is 649 nW at a temperature gradient of 55 K . Considering that the performance for thermoelectric modules strongly depends on various parameters (such as temperature difference, the number of couples and even the shape and dimensions of the thermoelectric units), it is somewhat difficult to precisely compare the

thermoelectric performance for modules and devices. For example, Yu *et al.* reported that modules consisting of n-type (PEI- NaBH_4 -CNT) films could produce $\sim 6 \text{ mV}$ and $\sim 25 \text{ nW}$ under an $\sim 22 \text{ K}$ temperature gradient.¹¹ The devices made by Kawai *et al.* containing organic phosphine-doped SWCNT as the n-type unit displayed a maximum output voltage of 6 mV and $\sim 110 \text{ nW}$ of power at a temperature difference of 20 K .¹² At a temperature gradient of 50 K , the devices consisting of PEI treated SWCNT (n-type) exhibited a maximum output voltage and power of $\sim 16.8 \text{ mV}$ and $\sim 75.5 \text{ nW}$, respectively.^{10b} Despite the difficulties in an exact performance comparison, it is reasonable to believe that the module thermoelectric performance in the present study is among the highest performance in flexible organic thermoelectric modules reported to date.^{9–12}

4. Conclusions

We have developed a novel exciting strategy to prepare n-type single-walled carbon nanotubes (SWCNTs), and fabricated flexible modules with a multilayered stacked structure with excellent thermoelectric performance. By diethylenetriamine (DETA) doping and subsequent CaH_2 treatment, the pristine SWCNTs (p-type) can be effectively converted to possess n-type conducting behavior. The Seebeck coefficient and the electrical conductivity for the DETA- CaH_2 -SWCNT are $-41.0 \pm 1.5 \mu\text{V K}^{-1}$ and $165 \pm 10 \text{ S cm}^{-1}$, respectively. A possible mechanism is proposed to explain the conversion from p-type to n-type conduction. Then, a multilayered alternating stacked structure is employed to achieve high-performance thermoelectric modules, which can realize conduction electrically in series and thermally in parallel. Finally, the thermoelectric module containing 14 couples displays large open circuit voltages of 62 mV and 125 mV at 55 K and 110 K temperature gradients, respectively, and a maximum output power of 649 nW at a temperature difference of 55 K . These promising thermoelectric performances are among the best in organic thermoelectric modules so far. The strategy proposed here opens a new avenue to achieve organic n-type materials and flexible devices with excellent thermoelectric properties. These results will benefit the research of organic thermoelectric materials and speed up the applications of flexible and wearable power-conversion devices.

Acknowledgements

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Notes and references

- (a) O. Bubnova, Z. U. Khan, H. Wang, S. Braun, D. R. Evans, M. Fabretto, P. Hojati-Talemi, D. Dagnelund, J.-B. Arlin,

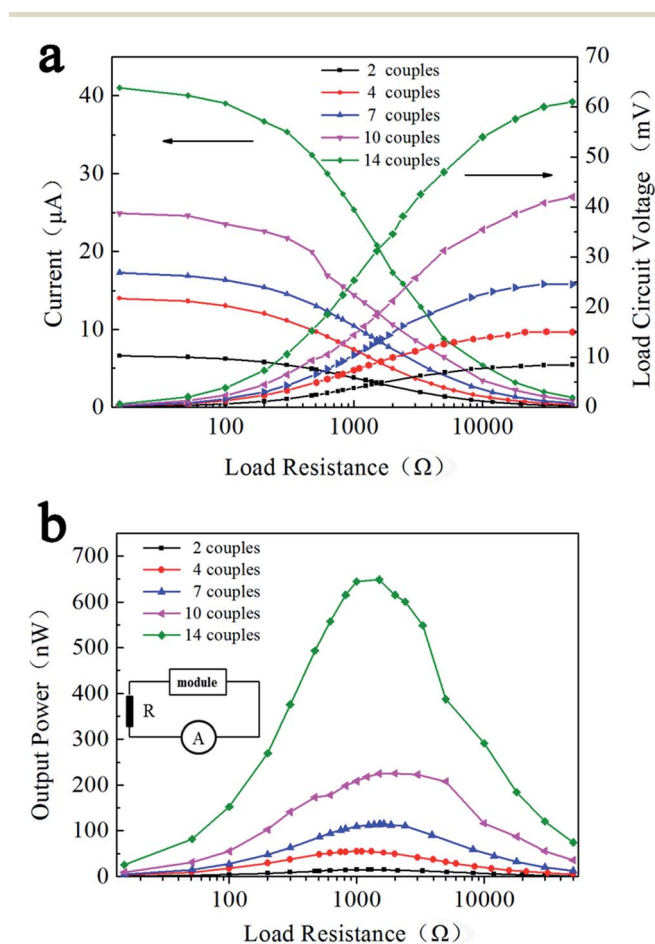


Fig. 7 Thermoelectric output (a) voltage and current, and (b) power as a function of applied load resistance for thermoelectric modules consisting of 2 to 14 couples of p- and n-type SWCNT films at a temperature gradient of 55 K .

- Y. H. Geerts, S. Desbief, D. W. Breiby, J. W. Andreasen, R. Lazzaroni, W. M. Chen, M. Zozoulenko, M. Fahlman, P. J. Murphy, M. Berggren and X. Crispin, *Nat. Mater.*, 2014, **13**, 190; (b) S. Wen, J. Chen, J. Xi, D. Wang and Z. Shuai, *Chem. Mater.*, 2014, **26**, 2669; (c) A. M. Glaudell, J. E. Cochran, S. N. Patel and M. L. Chabinyc, *Adv. Energy Mater.*, 2015, **5**, 1401072; (d) D. Wang, W. Shi, J. Chen, J. Xi and Z. Shuai, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16505.
- 2 (a) C. Gao and G. Chen, *Compos. Sci. Technol.*, 2016, **124**, 52; (b) Q. Zhang, Y. Sun, W. Xu and D. Zhu, *Adv. Mater.*, 2014, **26**, 6829; (c) H. He, F. Qiu and Z. Lin, *Energy Environ. Sci.*, 2013, **6**, 1352; (d) N. Lu, L. Li and L. Liu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **91**, 195205.
- 3 (a) W. Shi, T. Zhao, J. Xi, D. Wang and Z. Shuai, *J. Am. Chem. Soc.*, 2015, **137**, 12929; (b) K. Xu, G. Chen and D. Qiu, *J. Mater. Chem. A*, 2013, **1**, 12395; (c) X. Hu, G. Chen, X. Wang and H. Wang, *J. Mater. Chem. A*, 2015, **3**, 20896; (d) K. Xu, G. Chen and D. Qiu, *Chem.-Asian J.*, 2015, **10**, 1225; (e) Z. Zhang, G. Chen, H. Wang and X. Li, *Chem.-Asian J.*, 2015, **10**, 149; (f) D. Kim, Y. Kim, K. Choi, J. C. Grunlan and C. Yu, *ACS Nano*, 2010, **4**, 513.
- 4 (a) Q. Wang, Q. Yao, J. Chang and L. Chen, *J. Mater. Chem.*, 2012, **22**, 17612; (b) Y. Zhao, G.-S. Tang, Z.-Z. Yu and J.-S. Qi, *Carbon*, 2012, **50**, 3064; (c) K. Xu, C. Gao, G. Chen and D. Qiu, *Org. Electron.*, 2016, **31**, 41.
- 5 (a) Z. Zhang, G. Chen, H. Wang and W. Zhai, *J. Mater. Chem. C*, 2015, **3**, 1649; (b) S. Han, W. Zhai, G. Chen and X. Wang, *RSC Adv.*, 2014, **4**, 29281; (c) L. Liang, C. Gao, G. Chen and C.-Y. Guo, *J. Mater. Chem. C*, 2016, **4**, 526; (d) L. Liang, G. Chen and C.-Y. Guo, *Compos. Sci. Technol.*, 2016, **129**, 130.
- 6 (a) J. Choi, J. Y. Lee, S.-S. Lee, C. R. Park and H. Kim, *Adv. Energy Mater.*, 2016, **6**, 1502181; (b) D. S. Montgomery, C. A. Hewitt, R. Barbalace, T. Jones and D. L. Carroll, *Carbon*, 2016, **96**, 778; (c) M. Piao, G. Kim, G. P. Kennedy, S. Roth and U. Dettlaff-Weglikowska, *Phys. Status Solidi B*, 2013, **12**, 2529.
- 7 T. M. Tritt and M. A. Subramanian, *MRS Bull.*, 2006, **31**, 188.
- 8 (a) P. G. Collins, K. Bradley, M. Ishigami and A. Zettl, *Science*, 2000, **287**, 1801; (b) K. Bradley, S.-H. Jhi, P. G. Collins, J. Hone, M. L. Cohen, S. G. Louie and A. Zettl, *Phys. Rev. Lett.*, 2000, **85**, 4361; (c) C. Wang, G. Zhou, H. Liu, J. Wu, Y. Qin, B.-L. Gu and W. Duan, *J. Phys. Chem. B*, 2006, **110**, 10266.
- 9 (a) T. M. Barnes, J. L. Blackburn, J. Van de Lagemaat, T. J. Coutts and M. J. Heben, *ACS Nano*, 2008, **2**, 1968; (b) M. Yu, W. Tian, C. S. Jaynathi and S. Wu, *Chem. Phys. Lett.*, 2011, **518**, 93.
- 10 (a) H. Bark, W. Lee and H. Lee, *Macromol. Res.*, 2015, **23**, 795; (b) M. Piao, M.-K. Joo, J. H. Choi, J. M. Shin, Y. S. Moon, G. T. Kim and U. Dettlaff-Weglikowska, *RSC Adv.*, 2015, **5**, 78099.
- 11 (a) C. Yu, A. Murali, K. Choi and Y. Ryu, *Energy Environ. Sci.*, 2012, **5**, 9481; (b) S. L. Kim, K. Choi, A. Tazebay and C. Yu, *ACS Nano*, 2014, **8**, 2377.
- 12 Y. Nonoguchi, K. Ohashi, R. Kanazawa, K. Ashiba, K. Hata, T. Nakagawa, C. Adachi, T. Tanase and T. Kawai, *Sci. Rep.*, 2013, **3**, 3344.
- 13 (a) V. Barone, J. E. Peralta, J. Uddin and G. E. Scuseria, *J. Chem. Phys.*, 2006, **124**, 024709; (b) S. Suzuki, F. Maeda, Y. Watanabe and T. Ogino, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **67**, 115418; (c) J. Zhao, J. Han and J.-P. Lu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 193401.
- 14 (a) G. D. Vukovic, A. D. Marinkovic, S. D. Skapin, M. D. Ristic, R. Aleksic, A. A. Peric-Grujic and P. S. Uskokovic, *Chem. Eng. J.*, 2011, **173**, 855; (b) Y. Huang, I. Lin, C. Chen, Y. C. Hsu, C. C. Chang and M. J. Lee, *Nanoscale Res. Lett.*, 2013, **8**, 267.
- 15 (a) E. V. Basiuk, V. A. Basiuk, J. G. Banuelos, J. M. Saniger-Blesa, V. A. Pokrovskiy, T. Y. Gromovoy, A. V. Mischanchuk and B. G. Mischanchuk, *J. Phys. Chem. B*, 2002, **106**, 1588; (b) A. Misra, P. K. Tyagi, M. K. Singh and D. S. Misra, *Diamond Relat. Mater.*, 2006, **15**, 385.