Systematic Conversion of Single Walled Carbon Nanotubes into n-type Thermoelectric Materials by Molecular Dopants

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Thermoelectrics is a challenging issue for modern and future energy conversion and recovery technology. Carbon nanotubes are promising active thermoelectric materials owing to their narrow bandgap energy and high charge carrier mobility, and they can be integrated into flexible thermoelectrics that can recover any waste heat. We here report air-stable n-type single walled carbon nanotubes with a variety of weak electron donors in the range of HOMO level between ca.

\[ \text{ca.} \quad -4.4 \quad \text{eV} \quad \text{and} \quad \text{ca.} \quad -5.6 \quad \text{eV} \], in which partial uphill electron injection from the dopant to the conduction band of single walled carbon nanotubes is dominant. We display flexible films of the doped single walled carbon nanotubes possessing significantly large thermoelectric effect, which is applicable to flexible ambient thermoelectric modules.

P-type and n-type doping based on charge transfer interaction represents important functionalization technique of carbon-based electronic materials for future flexible electronics1-3. Pristine single walled carbon nanotubes (SWNTs) exhibit p-type majority charge carriers because of oxygen impurity4, and their controlled n-type doping has been exploited. Alkali-metal doping has been studied in early promising cases to alter their majority carriers, although it is unstable in ambient conditions5. Chemical vapor deposition synthesis with hetero-atom sources is available to introduce nitrogen and phosphine atoms into the side walls of SWNTs6,7. SWNTs have recently been converted into air-stable n-type form after noncovalent functionalization with organic nitrogen-containing electron-donors such as, polyethyleneimine (PEI)8 and reduced benzyl viologen (BV)9,10. These pioneering studies motivated us to exploit rational control of dominant charge carriers in SWNTs and improved n-type performance as well as understanding of charge carrier alteration in the SWNTs with organic dopants. In this report, we report efficient tuning of n-type SWNTs with phosphine-containing aromatic dopants through thermoelectric charge carrier determination. For the practical thermoelectric power conversion materials in a temperature range lower than 400 K, flexibility is crucial to cover and adhere closely to the heat sources that emit low thermal radiation. While pristine SWNTs and conjugated polymers such as PEDOT are the promising p-type flexible thermoelectric materials11,12, flexible and stable n-type ones are still challenging13. We herein demonstrated unprecedented advantages of SWNT films with phosphate-based molecular dopants for flexible n-type thermoelectric materials. We elucidated, after investigation for 33 organic compounds as dopants, that ionization potential of dopants plays a dominant role in the negative (n-type) thermoelectric performance of the doped SWNT films.

Results
Seebeck effect measurements would provide unambiguous discrimination of majority carriers, where positive and negative Seebeck coefficients (\( \alpha \)) are indicative of p-type and n-type majority carriers, respectively. Self-standing
flexible films made from long SWNTs were used for the measurements of thermoelectric properties and conductivity (Figure S1). A Seebeck coefficient of pristine SWNT films (+49 µV/K) was drastically converted into negative values after treating SWNTs in suspended solutions with a wide range of electron donors (Figure 1a). All the dopants modulated the Seebeck coefficients ranging from +90 µV/K to −80 µV/K. Among them, eighteen dopants listed in Figure 2 successfully switched the majority carriers of SWNT materials from p- to n-type. This methodology is not limited to previously-known dopants such as PEI, but a series of electron donors can be effective for altering p-type SWNTs into n-type materials. Interestingly, we found that most phosphate derivatives promoted SWNTs into n-type form, as well as several amine-, and imine-containing molecules (PEI, PVP, Tetronic1107, Id, and PVPy). SWNT films combined with bidentate phosphate ligands, 1,3-bis(diphenylphosphino)propane (dppp), showed enhanced conductivity (σ) up to 100 S/cm with a large negative Seebeck coefficient (α ~ −52 µV/K), while undoped SWNT films showed σ ~ 36 S/cm and α ~ +49 µV/K, respectively. The Seebeck coefficient of triphenylphosphine (tpp)-doped SWNT films (~72 µV/K) was roughly twice as large as that of a PEI-doped film (α ~ −34 µV/K). These characteristics are advantageous for constructing thermoelectric devices, indicating that phosphate dopants therefore have potential for constructing a wide range of thermoelectric SWNT-based materials. Synthetic rigid oligo-phosphine ligands such as bis([diphenylphosphinomethyl]phenylphosphino)methane (dppmpm) also served as efficient n-type dopants.

Power factors (σα) are a useful measure of thermoelectric properties. To find unprecedented, flexible n-type thermoelectric materials, we evaluated the power factors of pristine and doped SWNT films after conductivity measurements. In particular, films doped with tpp and dppp showed enhanced power factors reaching 25 µW/mK² (Figure 1b). This value was 2.5 times larger than that of films doped with PEI. These results clearly indicated that the enhanced Seebeck coefficients contributed to larger power factors. So far, there were several attempts to enhance the power factors of SWNT-based materials by increasing their conductivity. In contrast, the present results emphasized the importance of the Seebeck coefficients of SWNT materials.

We then obtained an almost five-fold enhanced thermoelectric figure of merit, ZT (σαT/k), for the tpp-doped one in comparison with that of the PEI-doped one (see Table 1). Thermal conductivity (k) of some samples was also studied for elucidating ZT values. The SWNT films in this study showed small thermal conductivity presumably due to their highly porous entangled structures. The films were made simply by filtration of flocculated SWNT dispersions, and were

![Graph](image-url)
consequently flexible and light with their low density (~0.5 g cm\(^{-3}\)). These flexible n-type materials with higher ZT can be the counter parts with any flexible p-type thermoelectric materials\(^{11,12,18–20}\).

In addition to tpp-doped SWNTs, TCNQ-doped SWNTs film in this work (ZT ~ 0.073) also serve as an active component for fully-flexible thermoelectric modules\(^{24}\) as demonstrated in Figure 3. A fully-bendable thermoelectric module was made from tpp-, and TCNQ-doped SWNTs as n-type and p-type materials (Figure 3a). Three p-type/n-type cells were electrically connected in series by

| Table 1 | Thermoelectric figure of merit (ZT) of pristine, PEI-doped, and phosphine-doped SWNT films at 310 K |
|---------|-----------------------------------------------|
| dopant  | \(k/W \cdot m^{-1} \cdot K^{-1}\) | ZT | Carrier type |
| pristine | 0.098 | 0.028 | p |
| PEI   | 0.205 | 0.016 | n |
| dppp | 0.174 | 0.047 | n |
| tpp | 0.103 | 0.078 | n |

Figure 2 | Chemical structures of eighteen n-type molecular dopants used in this study. See Scheme S1 for those of p-type molecular dopants.
flexible copper tapes on a thin polyimide film. The module was laminated between fluorinated polymer films (DAI-ELTM G-901, Daikin) by hot-press under vacuum. This module generated roughly 6 mV of thermo-voltage and 110 nW of the corresponding power output at a temperature gradient of 20 °C (Figure 3b), which agreed well to the values predicted by combining Seebeck coefficients of both p-type, and n-type materials. Considering practical thermoelectric modules consist of hundreds of p-n couples, they would generate more than several microwatts of power which can drive small devices, or be capable of cooling. Also, this module can work on the round glass surface (Figure 3c).

Discussion

We herein point out an apparent tendency of highest occupied molecular orbital (HOMO) of dopants to determine the n-type nature of SWNT materials (Figure 4a), which is a convenient parameter for evaluating tendency of electron-transfer interaction in solid state. Dopants with HOMO energy above roughly 2.56 eV under the vacuum level, successfully altered the sense of majority carriers from holes in pristine SWNTs to electrons. This tendency is helpful for designing n-type SWNT materials. Several dopants with HOMO-level around −5.6 eV exhibited exceptional behavior. The relative electrochemical potential of CNTs depends on the diameter of CNTs.25,26 Regarding previously reported results, the present CNTs of diameter in the range of 2–5 nm is possible to have distribution of oxidation potential in a range of about 0.1 V, which should be considered for detailed analysis. As another exception, tetrathiafulvalene with 3.9 eV of HOMO level couldn’t form a stable n-type SWNT composite, probably because such a strong electron donor is not stable in air and in the preparation solvents (DMSO) after the electron injection to the conduction band of SWNTs. HOMO could be one of the evaluating parameter although exact mechanism should be further investigated.

Upon n-type doping, the work function27,28 was raised from ~4.75 eV of pristine one to ~4.60 eV of n-type doped materials (Figure 4c), indicating Fermi level shift by charge transfer doping to conduction band of SWNTs. The present SWNTs showed ~ 0.15 eV of band gap energy (Figure S3)29–31, which agrees with the shift of work function after the n-type doping. Other n-type doping with PEI, polyvinylpyrrolidone (PVP), and indole (Id) also led to similar energy shift. These observations explain that molecular
dopants first fill the hole states in the valence band of SWNTs under light doping conditions (Figure 4d, middle panel) and then pour the electrons into the conduction band in the higher doping regime (Figure 4d, right panel)\textsuperscript{34}. We assume that these partial uphill electron transfers were driven by thermal distribution of electrons over energy levels of SWNTs and the dopants. Even a small number of electrons promoted in the conduction band of SWNTs dramatically altered the sense of majority carriers. Opposite work function shift was observed for p-type doping with phenylboronic acid and tetracyanoquinodimethane (TCNQ) (Figure 4c). This shift to deeper levels could correspond to electron deficiency in the valence band of p-type doped SWNTs. The phosphine-doped films also showed relatively high

Figure 4 | Factors governing the n-type doping. (a) Relationship between Seebeck coefficients of SWNT films, and HOMO levels of dopants, at 310 K. All the SWNTs were subjected to 5 wt% molecular dopant solutions. (b) Relationship between conductivity (○), Seebeck coefficient (□), and doping level of tpp-doped SWNT materials. Doping levels were fixed by dopant concentration of the solutions in the preparation step. (c) Photoelectron spectra of doped and undoped SWNT materials. Onset points correspond to work function of the materials. tpp: triphenylphosphine, PVP: polyvinylpyrrolidone, PhB(OH)\textsubscript{2}: phenylboronic acid, and TCNQ: tetracyanoquinodimethane. (d) A plausible n-type doping mechanism; left panel: the pristine SWNTs are p-doped with oxygen and/or defects which are possible to inject holes into the valence band and trap thermally activated electrons on the conduction band of SWNTs, middle panel: the electron injection from the dopants compensates the holes in SWNTs and decrease the p-type thermoelectric power and conductivity, right panel: further electron transfer induces n-type charge carriers in SWNTs and increase both conductivity and n-type thermoelectric power. These uphill electron transfers undergo with thermal activation.
air-stability (Figure S4), as indicated in the supporting information. The present air-stable n-type doped SWNTs seems to be especially suitable for the thermoelectric materials regarding the thermally activated electron injection mechanism.

In conclusion, we developed an easy and reliable way to produce n-type SWNT films. Among them, we exploited the highest ther-moelectric performance of flexible n-type SWNT films. Especially, these air-stability (Figure S4), as indicated in the supporting information. The present air-stable n-type doped SWNTs seems to be especially suitable for the thermoelectric materials regarding the thermally activated electron injection mechanism.

Methods
All the dopants except for BV, dpmp and dpmpm were used as received. As-purchased benzyl viologen chloride was neutralized with NaBH₄ in water/toluene biphasic solution before use. SWNTs were synthesized by “supergrowth” chemical vapour deposition with C₂H₄ and iron nanoparticles as a carbon source and catalysts, respectively. 10 mL of 5 wt% dopant-containing DMSO solution was poured into 5 mg of SWNTs, and the mixture was homogenized at 20,000 rpm for 10 minutes (Ultra Turrax T25, IKA). Doping levels were fixed by dopant concentration of the solution, this preparation step. For low-solvability dopants, dopant concentration was fixed at 1 wt%, or other solvents as acetone were used. SWNT buckypapers were prepared by filtration of SWNT dispersions on a 64 mm² round PTFE membrane. Finally the film was dried under vacuum at 80°C, providing round SWNT films roughly 80 µm in thickness.

DC electrical conductivity was measured using the 4-point probe method (Loresta GP Model MCP-T610, Mitsubishi Chemical). Thermoelectric voltage was recorded using a Seebeck coefficient measurement system (K205B100-3R, MMR technology) with a Joule–Thomson effect temperature controller. The roughly 100 µm-thick buckypapers were transferred to, and stuck on a sample stage of the measurement system by conducting silver pastes. Work function was determined using photoelectron spectroscopy in air (AC-3, Riken Keiki). The hot-wire method was used to measure thermal conductivity (TCi thermal conductivity analyzer, C-TCERM). For thermal conductivity measurements, thicker films (~500 µm) were prepared for reliability of the data. Thermo-voltage was measured by the DC Voltage/Current Source (6124A, Agilent). HOMO calculations were performed with the density functional theory (DFT) method at the B3LYP/6-31G* level using the Gaussian 03 program package. We here excluded polymers because structural ambiguity of polymers makes it difficult to estimate their correct HOMO potentials. HOMO level of a specific monomer unit of PEI was estimated to be 5.1 eV, that is still reasonable for n-type doping of SWNTs.

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Acknowledgments
This research was supported in part by Grant-in-Aid for Research Activity start-up (No. 23810021, to Y.N.) and for Scientific Research on Innovative Areas (Coordination Programming, No. 24108728, to T.K.) from MEXT from JSPS, and NAIST Green Photonics Research Project from MEXT.

Author contributions
Y.N., K.O. and K.A. measured the electronic properties. K.O. and R.K. did the computational calculation. Y.N., K.H., and T.T. synthesized materials. T.N. and C.A. measured the work function. All the authors analyzed the data. Y.N. and T.K. planned the work, evaluated the mechanism, and wrote the manuscript.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports
Competing financial interests: The authors declare no competing financial interests.
How to cite this article: Nonoguchi, Y. et al. Systematic Conversion of Single Walled Carbon Nanotubes into n-type Thermoelectric Materials by Molecular Dopants. Sci. Rep. 3, 3344; DOI:10.1038/srep03344 (2013).

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