Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

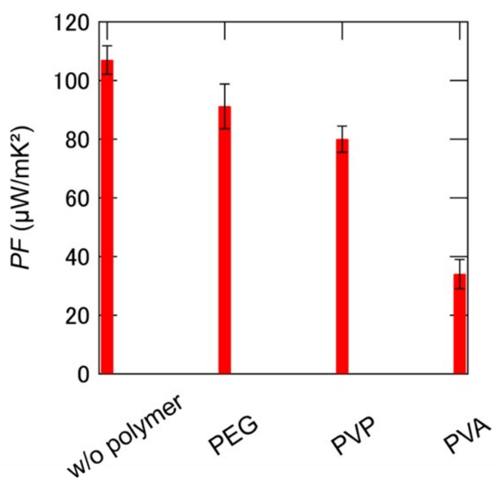
Supplementary Information

From materials to device design of a thermoelectric fabric for wearable energy harvesters

Mitsuhiro Ito, Takuya Koizumi, Hirotaka Kojima, Takeshi Sato, and Masakazu Nakamura

Thermoelectric properties of CNT/polymer threads with different binding polymers

Three kinds of water-soluble polymers — polyethylene glycols (PEG, MW: 35000), polyvinyl pyrrolidone (PVP, MW: 40000), and polyvinylalcohol (PVA, MW: 67000) — were added to CNT dispersion (0.01 wt%) for reinforcement of the CNT threads. Figure. S1 shows the power factor of the CNT/polymer threads. The decrease in power factor is mainly due to the decrease in electrical conductivity, and the Seebeck coefficient was mostly independent of the polymer type. As mentioned in the main text, electrical conductivity decreases with PEG concentration increase, which is because the larger volume of insulating polymer inhibits carrier transport between CNTs. If the densities of these polymers are different, the electrical conductivity of the composites with the same weight ratio may also be due to the difference of volume ratio. However, there is no clear dependence of conductivity on their densities (PEG: 1.13, PVP: 1.69, and PVA: 1.19～1.31 g/cm^3). The residual amount of polymers in the final state of the CNT threads may also depend on the material because most part of the polymers were confirmed to be dissolved in methanol during the wet spinning process. Therefore, the decrease in power factor would reflect the real amount of the polymer in the thread.



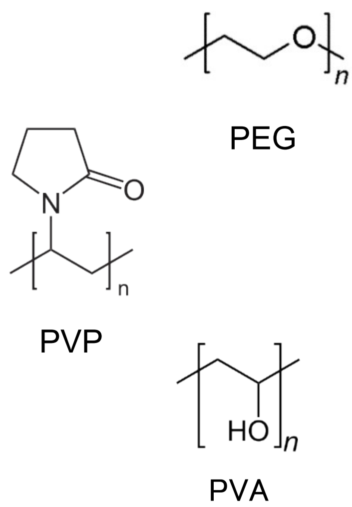


Fig. S1 Power factors of CNT/polymer composites.

n-type doping of CNT/PEG thread

There are several air-stable n-type dopants for CNTs so far reported (Y. Nonoguchi et al., Adv. Func. Matter., 2016, **26**, 3021; C. Cho et al., Nano. Energy, 2016, **28**, 426). They were, however, not appropriate for the stripe-doping method used in this work because their dopant solutions infiltrated to the neighboring sections easily and all sections eventually become n-type. On the contrary, we found that one of the typical ionic liquids (ILs), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), works as an n-type doping agent for CNTs. Because the IL has higher viscosity [over 100 mPa·s at room temperature (P. N. Tshibangu et al., Int. J. Electrochem. Sci., 2011, **6**, 2201)] than other dopant solutions, we used it as a doping agent in the striped-doping method shown in Fig. 5(a). Fig. S2 shows the core level spectra of undoped and doped CNT/PEG threads with energy dispersive X-ray spectroscopy. The peaks of N, F, and P in [BMIM]PF_6 are observed in the doped CNT/PEG thread. Table S1 shows the atomic ratio of N, F, and P in a doped thread using the pristine [BMIM]PF_6 as a reference of the stoichiometric ratio (N:F:P =2:6:1). The decrease of the ratio of F and P to ca. 80% of the stoichiometric composition indicates that the amount of the cation remaining on the thread is larger than that of the anion. From this result, it is assumed that part of F^- in ionization equilibrium ($PF_6^- \rightleftarrows PF_5 + F^-$) may exchange electrons with CNTs as:

$$CNT + F^- \rightarrow [CNT]^- + 1/2F_2, \qquad \text{(S1)}$$

and then PF_5 and F_2 escape into the gas phase. Because the final vaporization is nonequilibrium, the n-type doping would proceed even if the probabilities of the first and second steps are small.

The n-type doping effect by "painting" [BMIM]PF_6 on CNTs was reproducible and the doped state was stable enough in air, as shown in Fig. S2, even without any passivation coating.

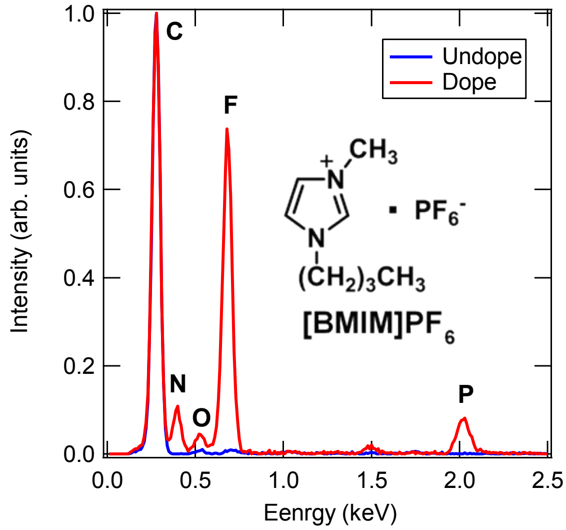


Fig. S2 EDS spectra of undoped and doped CNT/PEG threads.

Table S1 Element ratio of ionic liquid and doped yarn

Element	Atomic ratio		
	Ionic liquid (reference)	Doped thread	Ratio
N	2	2	–
F	6	4.62	0.77
P	1	0.79	0.79

Stability of the stripe doping during operation

The stability of thermopower in the CNT/PEG thread with stripe doping was tested in air. A π-type structure was fixed on a glass substrate at three points, with both edges of a 10-mm long thread and the p/n boundary position at the center of the thread, by silver paste. By applying the temperature difference between the edges and the p/n boundary [ΔT=1 (K)], the short-circuit current was continuously recorded for 12 hours as shown in Fig. S4. Although diffusion of the dopant from the n-type section to the p-type one was concerned about, it was not recognized in this experiment because the output current was stable for about 12 hours.

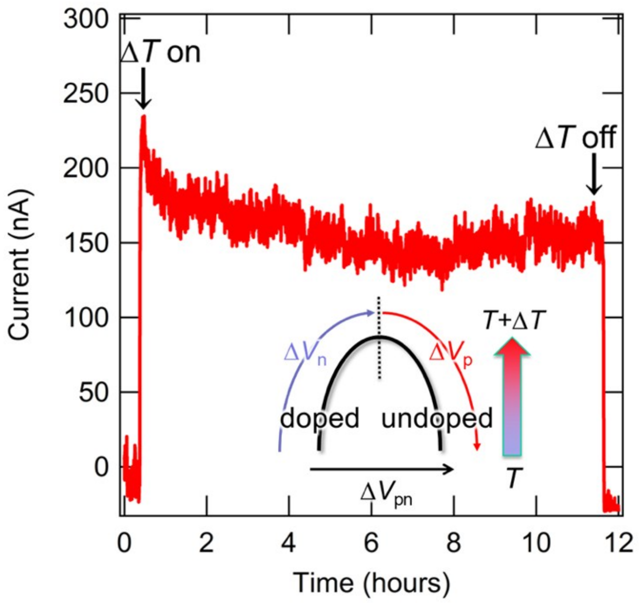


Fig. S3 Stability of output current of a CNT/PEG thread with stripe doping.

Output characteristics measurement of the prototype thermoelectric fabric

The output characteristics of the prototype thermoelectric fabric were measured by a lab-made instrument [Fig. S5(a)]. Measurements were made at several temperature differences, $\Delta T = T_{high} - T_{low} = 5, 10, 15, 20, 25$ (K). The low-side temperature (T_{low}) was fixed at 300 K and the high-side (T_{high}) was controlled with a heater and a thermocouple built in a copper block. Thin *Kapton* sheets, the thermal resistance of which is sufficiently lower than the sample, were inserted between the copper blocks and the sample to prevent electrical leakage. Since the sample to be measured is a soft fabric, the gap between two copper blocks was maintained to be the natural thickness of the fabric and no contact pressure was applied. As shown in Fig. S4(b), the open circuit voltage was proportional to the temperature difference up to 25 K.

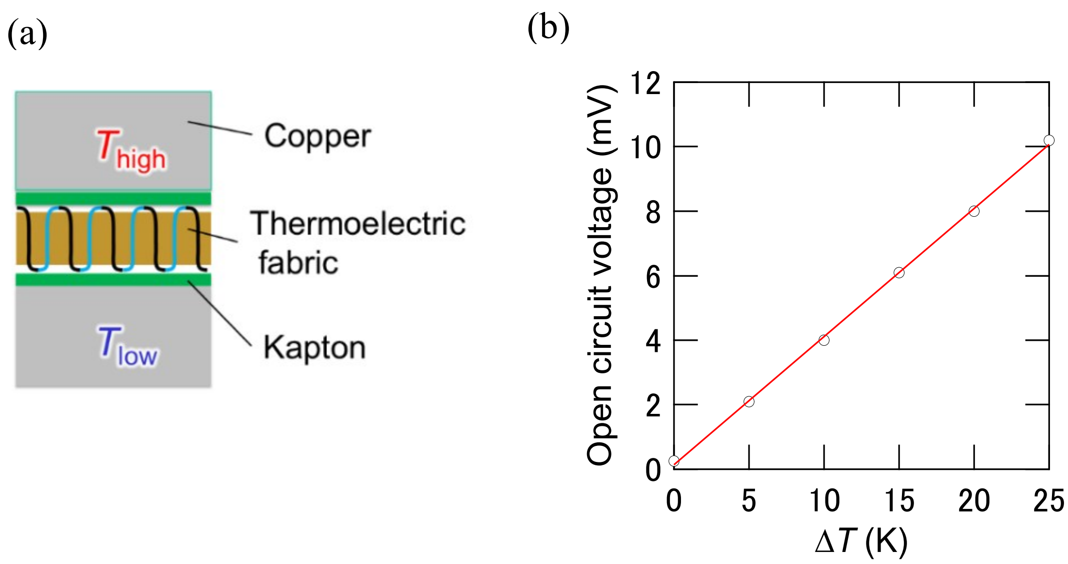
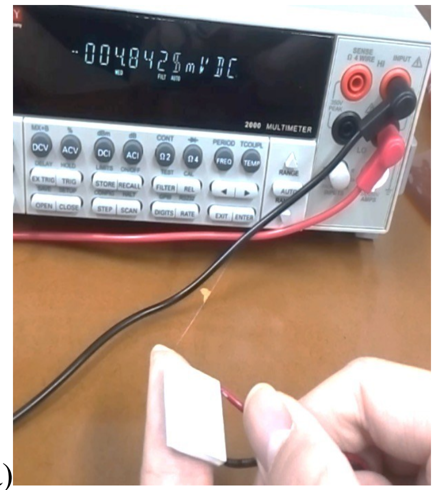


Fig. S4 Output characteristics measurement of a prototype device: (a) schematic illustration showing the method to apply the temperature difference and (b) open circuit voltage against temperature difference.

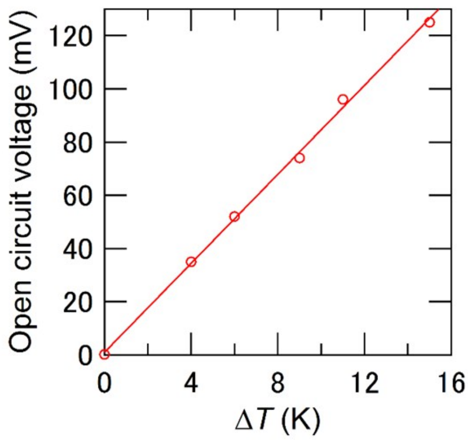
Operation of a conventional TEG in the same manner as in Fig. 6(b)

Operation of a conventional TEG module (*Thermal Electronics Corp.*, TEC1-03104, 31 couples) by finger touch and natural air cooling was tested as shown in Fig. S5(a) for comparison with the demonstration of thermoelectric fabric in the main text. The voltage generated by a finger touch in the same manner as in Fig. 5(b) was ca. 4.8 mV as seen in the photo.

Open circuit voltage of the conventional TEG used for this experiment against temperature difference is shown in Fig. S5(b). From the slope of this graph, the total Seebeck coefficient of the TEG was estimated to be 8.4 mV/K, indicating that the temperature difference caused by the finger touch is only around 0.6 K. This value is much smaller than that obtained with our thermoelectric fabric, 5 K, which implies that the typical thermal conductance of conventional TEGs is too large for wearable applications.



(a)



(b)

Fig. S5 Operation of a conventional TEG by a finger touch and natural air cooling.

Weight fraction of PEG in CNT/PEG composite threads

The weight fraction of PEG in the CNT/PEG composite threads was estimated by thermogravimetry analysis (TGA) using *STA7200 Thermal Analysis System* (*Hitachi High Technologies*). Figure S6 is one of the typical TGA results obtained for a CNT/PEG composite thread which was made with a CNT dispersion with a relatively high PEG concentration (0.15 wt% CNT, 5 wt% PEG, and 4 wt% SDBS dispersed in pure water). The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained after keeping the thread at 120°C for 30 min to remove the water included in the thread. By preliminary experiments, we concluded that the DTG peak at around 300°C is associated with the decomposition of PEG and that in the range of 600–800°C with CNT. The residue at the end of the temperature sweep is due to the oxidized metal catalysts included in the CNT material. From these TGA data, the thread is estimated to contain 27 wt% of PEG.

In the main part of this work, we used CNT/PEG composite threads made using the dispersion with 0.01 wt% PEG. Because such a small fraction (1/500 of the case measured in Fig. S6) was difficult to be measured by TGA, we presumed the weight fraction of PEG by assuming that the amount of PEG in the thread is proportional to the PEG concentration in the dispersion. A typical composite thread used in this work is thus presumed to contain 0.074 wt% of PEG.

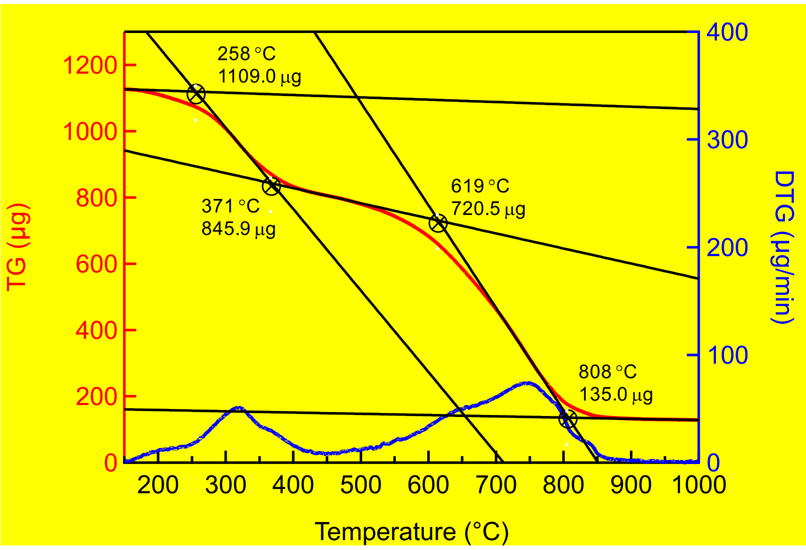


Fig. S6 Thermogravimetric (TG, red line) and differential thermogravimetric (DTG, blue line) curves for a CNT/PEG composite thread (PEG 5 wt% in the source dispersion) obtained at a heating rate of 20 °C/min under a 100 ml/min flow of dry air.