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Supporting Information

High-Performance Thermoelectric Fibers from Metal-Backboned Polymers for Body-Temperature Wearable Power Devices

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High-performance thermoelectric fibers from metal-backboned polymers for body-temperature wearable power devices

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Abstract: Metal-backboned polymers (MBPs), with a unique backbone consisting of bonded metal atoms, are promising for optic, electric, magnetic, and thermoelectric fields. However, the application of MBP remains relatively understudied. Here, we develop a shear-induced orientation method to construct a flexible nickel-backboned polymer/carbon nanotube (NBP/CNT) thermoelectric composite fiber. It demonstrated a power factor of 719.48 $\mu W \cdot m^{-1} \cdot K^{-2}$, which is *ca.* 3.5 times as high as the bare CNT fiber. Remarkably, with the regulation of carrier mobility and carrier concentration of NBP, the composite fiber further showed simultaneous increases in electrical conductivity and Seebeck coefficient in comparison to the bare CNT fiber. The NBP/CNT fiber can be integrated into fabrics to harvest thermal energy of human body to generate an output voltage of 3.09 mV at a temperature difference of 8 K. This research opens a new avenue for the development of MBPs in power supply.

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1. General Information

Materials. Nickel(II) acetate tetrahydrate and dimethyl sulfoxide were of reagent grade and purchased from Aldrich. These chemicals can be used directly.

Instruments and methods. SEM images and EDS elemental analysis were obtained by field-emission scanning electron microscopy (Zeiss Sigma, operated at 3.0 kV) at a work distance of 8.0 mm. The samples were covered with a thin golden coating before characterization by SEM.

Raman spectra of the bare CNT and NBP/CNT were investigated by polarized Raman spectroscopy (InVia Qontor/NTEGRA Spectra II) with a laser wavelength of 532 nm.

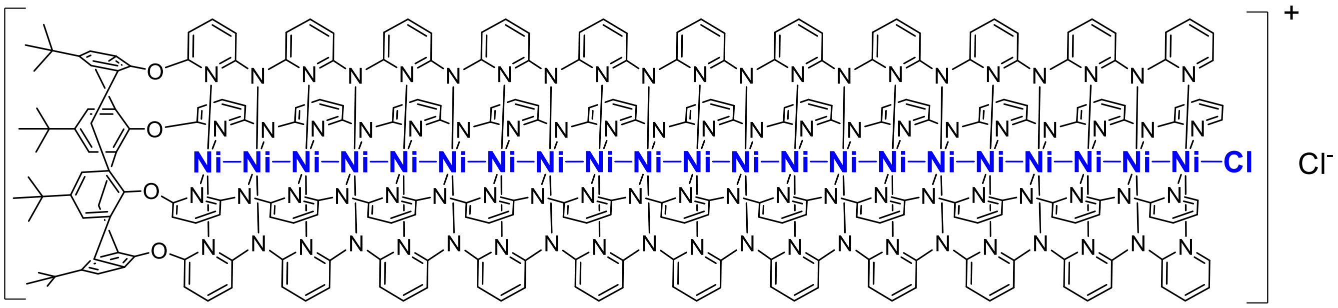
The resistances of fibers were measured by a Kelvin four-wire method.

The Seebeck coefficients of fibers were measured by a home-built equipment composed of two Peltier patches that were placed at both ends of the fiber to generate the temperature difference, an infrared thermal camera (Fotric 226) that was fixed vertically above the fiber to record the temperature difference ($\triangle T$), and a Keithley 2182A source meter that was used to measure the voltage difference ($\triangle V$) generated at both ends of the fiber[1]. The Seebeck coefficient was calculated by $S = -\triangle V/\triangle T$.

Carrier mobilities and carrier concentrations of fibers were tested by the Ecopia Hall effect tester (HMS-7000).

Fermi levels were tested by ultraviolet photoelectron spectroscopy (PHI 5000 Versaprobe III).

2. Fabrication Procedures



Scheme S1. Molecular structure of NBP.

Synthesis of NBP. The NBP was synthesized through direct metalation of the corresponding ligand by nickel(II) acetate according to the procedure reported in our previous work[2]. Poly(aminopyridine) ligand[2] (928 mg, 0.2 mmol) and nickel(II) acetate tetrahydrate (1.28 g, 5.0 mmol) were dissolved in dimethyl sulfoxide (300 mL) and transferred into a 500 mL flask. The resulting mixture was subjected to three cycles of argon degassing, followed by heating under reflux at 210 °C for 12 hours. After cooling to room temperature, the resulting deep-black solution was transferred into 1.0 L saturated brine. The resulting precipitate was obtained by vacuum filtration and then dissolved in dichloromethane. After filtration to remove insoluble material, the solvent was removed under reduced pressure to obtain a black solid product (10 mg, 6.5% yield).

Preparation of CNT sheets. CNT sheets were prepared by floating catalytic chemical vapor deposition. The reaction was performed using ethanol as a carbon source and thiophene and ferrocene as a composite catalyst at 1200 °C. Argon (200 sccm) was used as carrier gas and hydrogen (1600 sccm) served as reducing gas. The CNT sheet was contracted through a water bath and collected on a roller[3].

Preparation of NBP/CNT fibers. The solution of NBPs was obtained during 1 hour of stirring. The bare CNT sheet was first immersed in ethanol for 1 hour to wash off the remaining catalyst particles on the surface. After drying at room temperature, the CNT/NBP sheet with an oriented structure was obtained by stretching in dichloromethane. The oriented structure can be strengthened by the shrinkage due to the evaporation of dichloromethane. At last, the above composite sheet was twisted into the composite fiber.

Preparation of the thermoelectric fabric. NBP/CNT fibers were integrated onto the cotton fabric, and the fibers were connected in series using silver-plated nylon thread. Silver glue was used to ensure ohm-level contact between NBP/CNT fibers and silver-plated nylon threads. The distances between neighboring NBP/ CNT fibers were 1.0 cm. The obtained fabric consists of nine fibers with a length of 10 cm and a width of 5 cm. The experiments concerned with the wrist of human conformed to the regulations of Animal and Human Experimentation Committee of Fudan University. A healthy subject from Fudan University had provided written informed consent before participating in the study.

3. Results and discussion

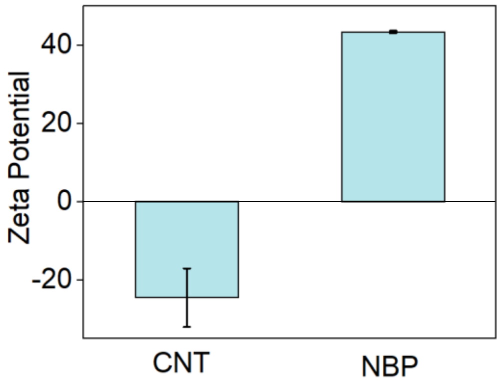


Figure S1. Zeta potentials of the bare CNT and NBP in ethanol solutions.

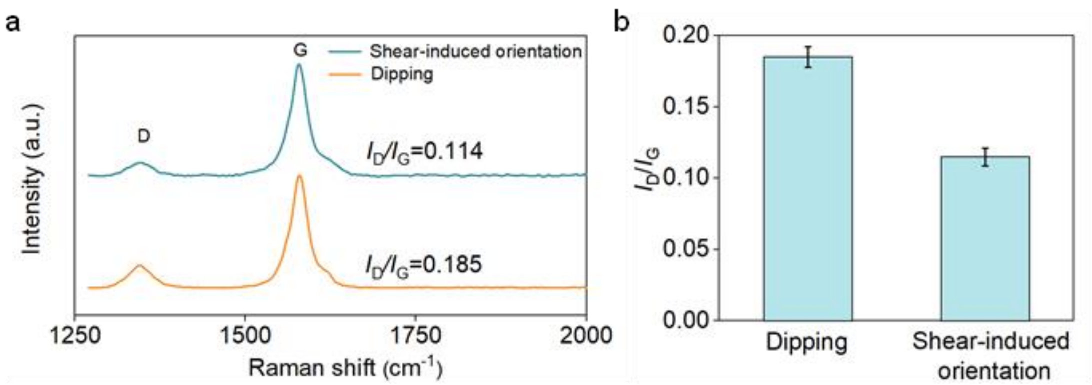


Figure S2. a, b) Raman spectra and calculated I_D/I_G of the NBP/CNT fiber produced by shear-induced orientation and dipping (without shear force) strategies, respectively.

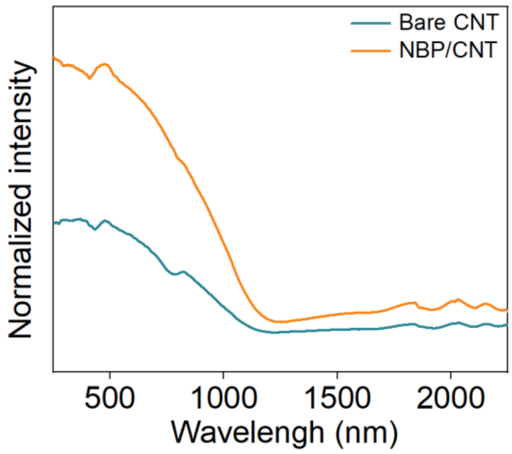


Figure S3. UV-vis spectra of the bare CNT and NBP/CNT fibers.

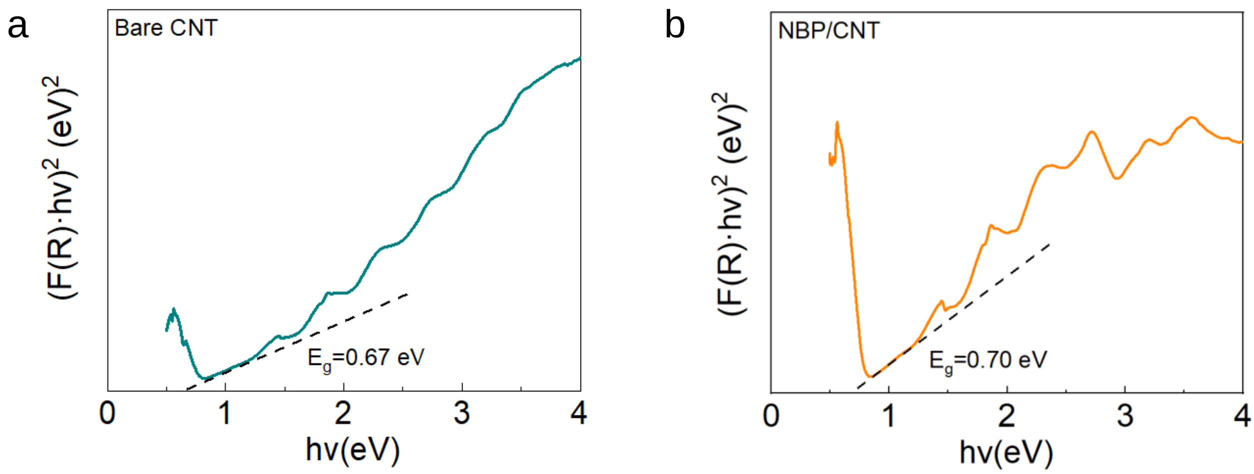


Figure S4. Band gaps of the bare CNT and NBP/CNT fibers calculated from the measured spectra in **Figure S3**.

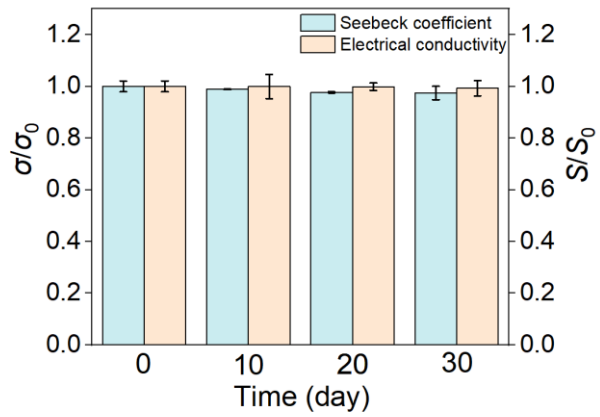


Figure S5. Long-term stability test for the evolution of Seebeck coefficient and resistance of thermoelectric fabrics under room temperature and humidity conditions (25 ^oC/40% relatively humidity).

Table S1. Electrical conductivities (σ), Seebeck coefficients (S) and power factors (PF) of bare CNT fibers.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	σ ($S\cdot cm^{-1}$)	S ($\mu V\cdot K^{-1}$)	PF ($\mu W\cdot m^{-1}\cdot K^{-2}$)
1	60.70	5.00	58.70	609.07	54.23	179.12
2	60.60	5.00	56.76	652.49	56.05	204.99
3	62.30	5.00	58.25	602.63	55.57	186.09
Average	61.20	5.00	57.90	605.85	55.28	190.07

Table S2. Electrical conductivities (σ), Seebeck coefficients (S) and power factors (PF) of NBP/CNT fibers at a concentration of 0.1 $mg\cdot mL^{-1}$.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	σ ($S\cdot cm^{-1}$)	S ($\mu V\cdot K^{-1}$)	PF ($\mu W\cdot m^{-1}\cdot K^{-2}$)
1	63.50	5.00	46.44	930.19	57.69	309.58
2	65.40	5.00	46.76	890.85	59.99	320.60
3	66.70	5.00	48.32	818.00	57.70	272.33
Average	65.20	5.00	47.17	879.68	58.46	300.84

Table S3. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.2 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	56.50	5.00	41.33	1319.93	63.73	536.09
2	51.50	5.00	46.17	1160.39	64.69	485.60
3	43.50	5.00	48.47	1246.51	64.92	525.35
Average	50.50	5.00	45.32	1242.28	64.45	515.68

Table S4. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.3 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	42.80	5.00	48.65	1257.54	67.57	574.15
2	52.20	5.00	46.57	1125.25	67.18	507.84
3	46.60	5.00	46.76	1250.25	68.67	589.56
Average	47.20	5.00	47.33	1211.01	67.81	557.18

Table S5. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.4 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	46.10	5.00	48.70	1165.12	71.79	600.48
2	55.60	5.00	42.31	1279.88	72.68	676.08
3	50.40	5.00	47.65	1113.20	74.85	623.67
Average	50.70	5.00	46.22	1186.07	73.11	633.41

Table S6. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.5 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	49.50	5.00	43.99	1309.89	76.66	781.55
2	50.30	5.00	45.47	1224.93	75.72	702.32
3	41.90	5.00	51.29	1155.71	76.40	674.59
Average	47.23	5.00	46.92	1236.85	76.26	719.48

Table S7. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.6 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	51.90	5.00	46.44	1138.10	73.72	618.51
2	46.30	5.00	46.80	1256.20	76.18	729.02
3	48.40	5.00	44.51	1328.53	76.20	771.40
Average	48.87	5.00	45.92	1240.94	75.37	706.31

Table S8. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.7 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	45.40	5.00	50.70	1091.59	75.21	617.46
2	41.20	5.00	50.73	1201.44	77.86	728.34
3	47.00	5.00	49.72	1096.40	75.28	621.34
Average	44.53	5.00	50.38	1129.81	76.12	655.71

Table S9. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.8 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	39.30	5.00	54.84	1077.81	77.15	641.53
2	40.20	5.00	50.96	1220.24	75.19	689.87
3	39.70	5.00	51.81	1195.40	76.15	693.19
Average	39.73	5.00	52.54	1164.48	76.16	674.86

Table S10. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 0.9 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	43.20	5.00	47.91	1284.68	74.55	713.99
2	42.20	5.00	48.91	1261.89	77.43	756.56
3	43.10	5.00	50.76	1147.12	73.71	623.25
Average	42.83	5.00	49.19	1231.23	75.23	697.93

Table S11. Electrical conductivities (*σ*), Seebeck coefficients (*S*) and power factors (*PF*) of NBP/CNT fibers at a concentration of 1.0 mg·mL^{-1}.

Sample	Resistance (Ω)	Length (cm)	Diameter (μm)	*σ* (S·cm^{-1})	*S* (μV·K^{-1})	*PF* (μW·m^{-1}·K^{-2})
1	45.10	5.00	49.09	1172.11	75.44	667.07
2	45.00	5.00	50.97	1089.65	77.95	662.10
3	45.90	5.00	48.72	1169.24	75.80	671.80
Average	45.33	5.00	49.59	1143.67	76.40	666.99

Reference

[1] Y. Zheng, Q. Zhang, W. Jin, Y. Jing, X. Chen, X. Han, Q. Bao, Y. Liu, X. Wang, S. Wang, Y. Qiu, C.-a. Di, K. Zhang, Journal of Materials Chemistry A 2020, 8, 2984–2994.

[2] K. Zeng, Y. Yang, J. Xu, N. Wang, W. Tang, J. Xu, Y. Zhang, Y. Wu, Y. Xu, G. Wang, P. Chen, B. Wang, X. Sun, G. Jin, H. Peng, Angew. Chem. Int. Ed. 2023, 62, e202216060.

[3] Q. Zhang, N. Wei, P. Laiho, E. I. Kauppinen, Top. Curr. Chem. 2017, 375, 90.

Author Contributions

N. W. and K. Z. conceived and designed the experiments. H. P. directed the project. N. W., Y. Z., H. J. and Y. Y. performed the experiments on the syntheses, characterizations, and property studies. N. W. and Y. Z. analyzed the data. N. W. drew the figures. All authors reviewed and critiqued the results, and made key revisions to the manuscript.