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n-Type thermoelectric behavior in oxyethylene surfactant/carbon nanotubes

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EXPERIMENTAL SECTION

Materials

Single-walled CNTs (Product ID EC1.5, purity > 90%, diameter: 1.5 ± 0.8 nm, metal/semiconductor ratio = 1:2) were obtained from Meijo Nano Carbon Co. Ltd., Aichi, Japan. Tetraethylene glycol monododecyl ether ($C_{12}EO_4$) was purchased from FUJIFILM

Wako Pure Chemical, Japan. Tetraethylene glycol (EO_4), hexaethylene glycol monododecyl ether, and octaethylene glycol monododecyl ether were obtained from Tokyo Chemical Industry Co., Ltd., Japan. All materials were used as received without further purification. Ultrapure water (specific resistance = 18.2 MΩ cm at 298 K) was used in all experiments.

Fabrication of the surfactant/CNT films in an aqueous medium

In all experiments, films fabricated using buckypapers, obtained by filtering the NT dispersions, were used as samples. Here, we describe the preparation of the $C_{12}EO_4$/CNT film as a representative example (Figure S2). The CNTs (60 mg) were added to an aqueous solution of 4.3 mM $C_{12}EO_4$ (30 mL) in a 100 mL tall-form glass beaker and dispersed using an ultrasonic homogenizer (Ultrasonic Cleaner, TAITEC; Branson Sonifier 250D, Central Scientific, Tokyo, Japan) for 15 min in an ice bath. The suspension was then filtered through a polytetrafluoroethylene (PTFE) membrane filter (pore size: 1.0 μm) in a single step without splitting. The deposited film was washed four times with water (1 L) to remove the excess surfactant and dried naturally for 3 h. The stripped film was then dried in a vacuum oven (333 K, < 0.1 MPa) overnight to obtain a dry-doped CNT film with a thickness of 20 ± 4.0 μm. This sample was cut into 4 mm × 16 mm specimens for the TE measurements. The EO_4/CNT film was prepared similarly. Other surfactant/CNT films were prepared using the appropriate reagents. For comparison, a CNT film without surfactants (i.e., pure CNT) was also prepared.

Characterization

The surfactant/CNT films were stored in a typical drying chamber under an ambient atmosphere, and their thermoelectric properties and structures were evaluated. The thickness of the fabricated films was measured five times at different spots using a thickness meter (LGK-0110, Mitutoyo Corporation, Japan), and the average value was calculated. The in-plane thermoelectric properties of the thermoelectric conversion films were measured using a commercial ZEM-3 M8 instrument (ULVAC-RIKO Inc., Japan) under purging with He gas. All samples were pretreated by heating at 370 K inside the instrument, and measurements were performed at least three times at 345 K.

The CNT films were observed by field-emission scanning electron microscopy (SEM; S-4800 Type2, Hitachi, Japan) at an accelerating voltage of 25 kV. For the SEM observations, each film sample was fixed to the sample holder using carbon tape and observed without any coating process (e.g., vapor deposition). Average bundle diameters and their standard deviations were calculated by counting the diameter of 200 CNT bundles in the enlarged SEM images. Thermogravimetric analysis (TGA) was performed using a TG-DTA8122 instrument (Rigaku, Japan). Experiments were conducted between 373 and 623 K at a heating rate of 10 K min^{-1} with 2–3 mg of each sample and an air flow of 150 mL min^{-1}. A Pt crucible was used in the TGA test, and the inlet gas was N_2/O_2 (8:2). Raman spectra were obtained over the wavenumber range of 1500–1640 cm^{-1} using an NRS-7100 laser Raman spectrometer (JASCO, Japan) with a 532 nm green-line laser at room temperature. N_2 and H_2O adsorption isotherms were measured at 77 K using a BELSORP-max instrument (MicrotracBEL, Japan) to calculate the Brunauer–Emmett–Teller surface areas of the specimens. Before each sorption measurement, all samples were activated by heating at 378 K under reduced pressure ($< 10^{-2}$ Pa) for 12 h.

Chemical stability testing of the surfactant/CNT films

For the oxygen-resistance test, the samples (4 mm × 16 mm) were placed on glass petri dishes at 303 K and 65% relative humidity, and their TE properties were periodically evaluated. All samples were pretreated by heating at 370 K inside the ZEM-3 M8 instrument, and the measurements were performed at least three times at 345 K.

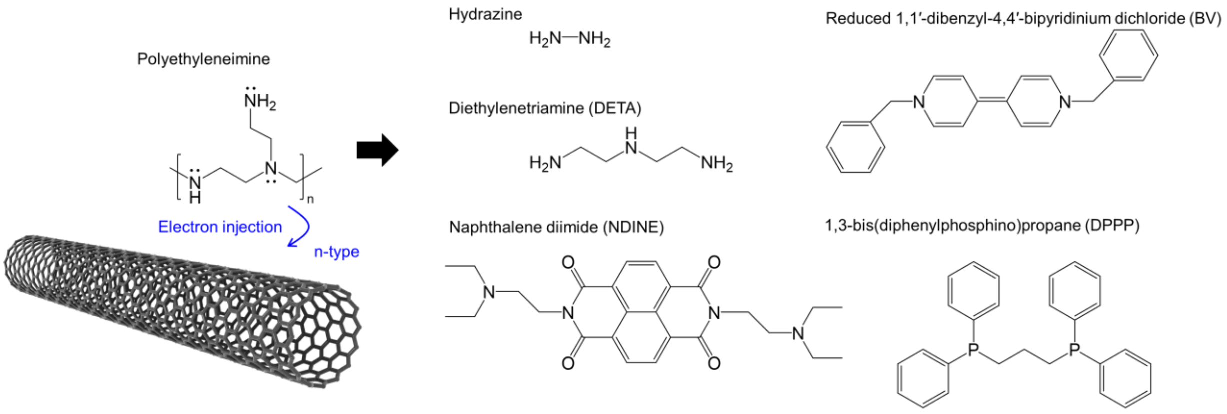

Figure S1. Chemical structures of the molecular dopants used to prepare n-doped CNTs.

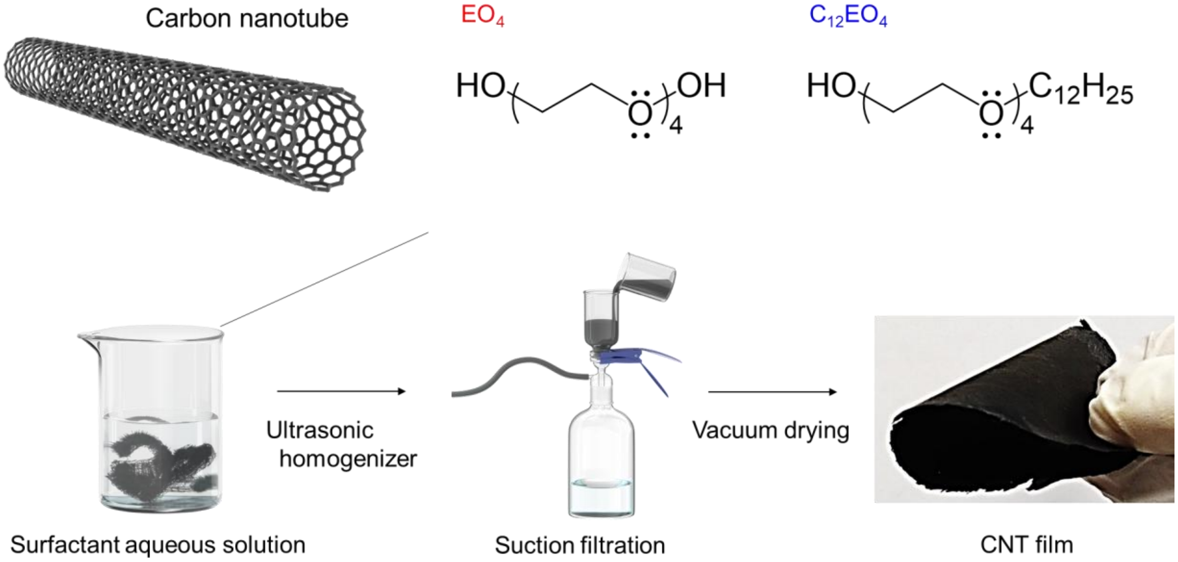

Figure S2. Schematic of the preparation process of the surfactant/CNT films. The CNTs were dispersed in 4.3 mM EO_4 or $C_{12}EO_4$ solution in an ice bath using an ultrasonic homogenizer for 15 min. The dispersion was then filtered through a PTFE membrane filter to deposit the film. The deposited film was washed four times with water (1 L) to remove the excess surfactant and then dried. Finally, the films were dried in a vacuum oven (333 K, < 0.1 MPa). The inset shows a photograph of a CNT film prepared using the $C_{12}EO_4$ aqueous solution. The resulting films were examined in air without impregnation by dopant solutions or other solutions containing organic solvents to prevent unexpected doping; moreover, sealing processes, such as lamination, were not performed.

N_2 adsorption isotherms were obtained at 77 K to investigate the surface properties of the CNTs. The N_2 adsorption isotherms of pure CNTs showed the behavioral characteristics of mesoporous materials over a wide range of relative pressures (Figure S3)[1]. By contrast, the amount of adsorbed N_2 generally decreased in the presence of EO_4 ($0 < P/P_0 < 0.4$). Furthermore, the decrease in the amount of adsorbed N_2 was more pronounced for $C_{12}EO_4$ than for EO_4. This finding suggests that the adsorbed surfactant eliminates mutual forces between the CNT surface and adsorbed N_2. The apparent BET N_2 surface areas calculated for pure CNT, EO_4/CNT, and $C_{12}EO_4$/CNT were 445.0, 195.0, and 67.0 $m^2 g^{-1}$, respectively. In the $C_{12}EO_4$/CNT, the specific surface area occupied by bare NTs is ~56% smaller than that of pure CNTs, and most of the CNT surface is an interface accessible to molecular O_2. By contrast, the specific surface area of the $C_{12}EO_4$/CNT film occupied by bare NTs is approximately 85% smaller than that of pure CNTs. These results indicate that $C_{12}EO_4$ functions effectively as a wrapping agent to seal the NT surface[2].

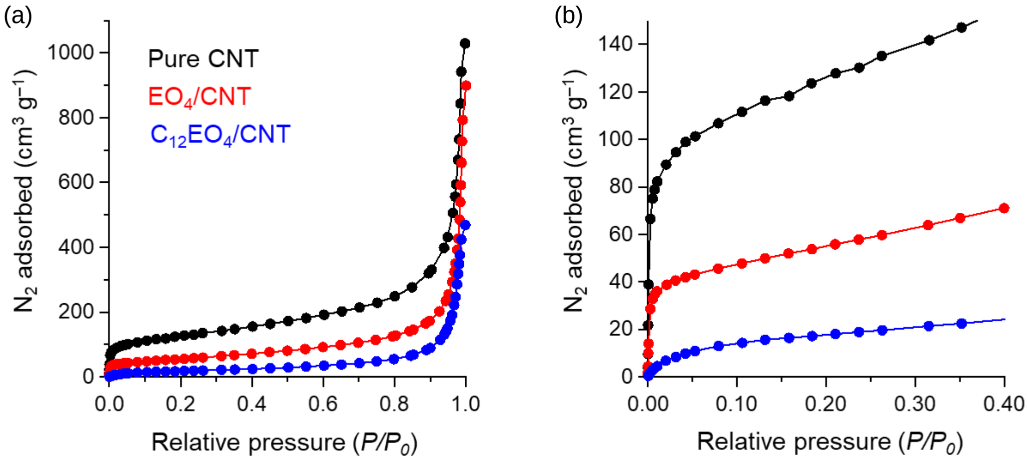

Figure S3. N_2 adsorption isotherms at 77 K over (a) wide and (b) narrow ranges of relative pressures.

Thermal analysis measurements were used to indirectly investigate the stability of the thermoelectric films and the amount of surfactant in each film (Figure S4). The prepared CNT films exhibited a weight loss of < 1% upon heating to temperatures of up to 423 K, and no significant thermal degradation was observed. As the NTs used in this experiment can become defective at temperatures of > 623 K,[3] the apparent weight loss corresponding to the $C_{12}EO_4$ content of the films at this temperature was tabulated (pure $C_{12}EO_4$ burns completely at 523 K). Compared with the pure CNT film, the surfactant-laden films exhibited a greater degree of weight loss.

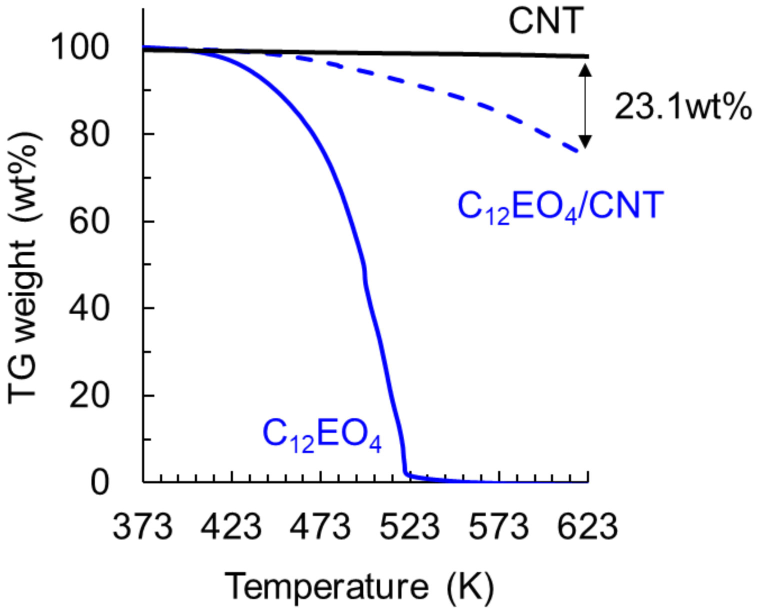

Figure S4. TGA curves of the surfactant-free CNT, $C_{12}EO_4$/CNT, and $C_{12}EO_4$ films under a N_2/O_2 (8:2) flow of 150 mL min^{-1} at a heating rate of 10 K min^{-1}.

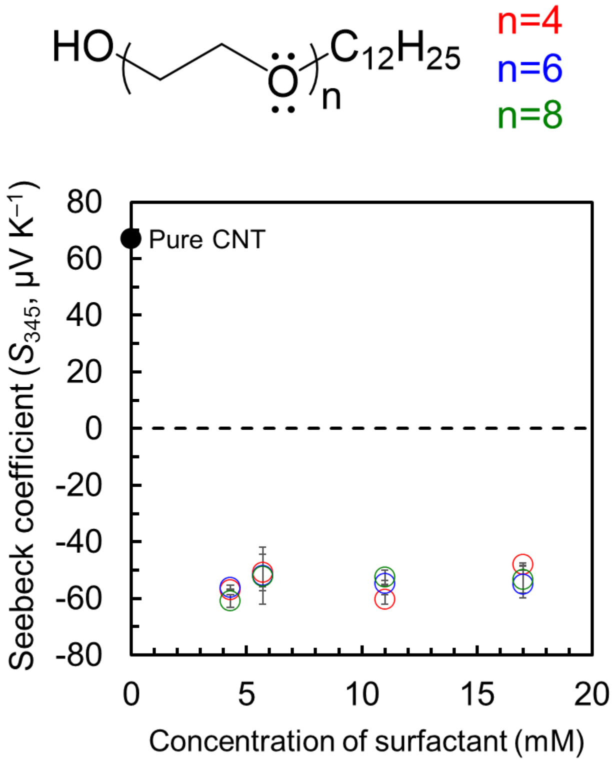

Figure S5. Seebeck coefficients (*S*) of CNTs doped with various concentrations of the oxyethylene surfactant. All measurements were performed at 345 K in He.

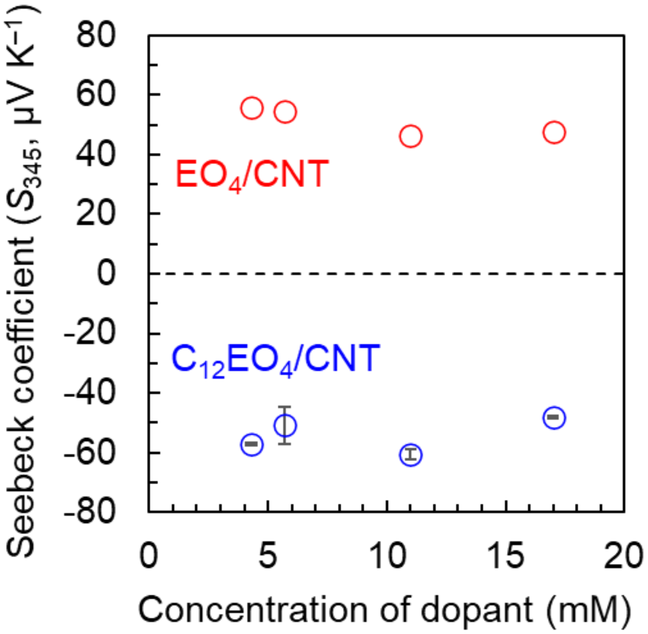

Figure S6. Seebeck coefficients (*S*) of the CNTs doped using various concentrations of EO_4 and $C_{12}EO_4$. All measurements were performed at 345 K in He.

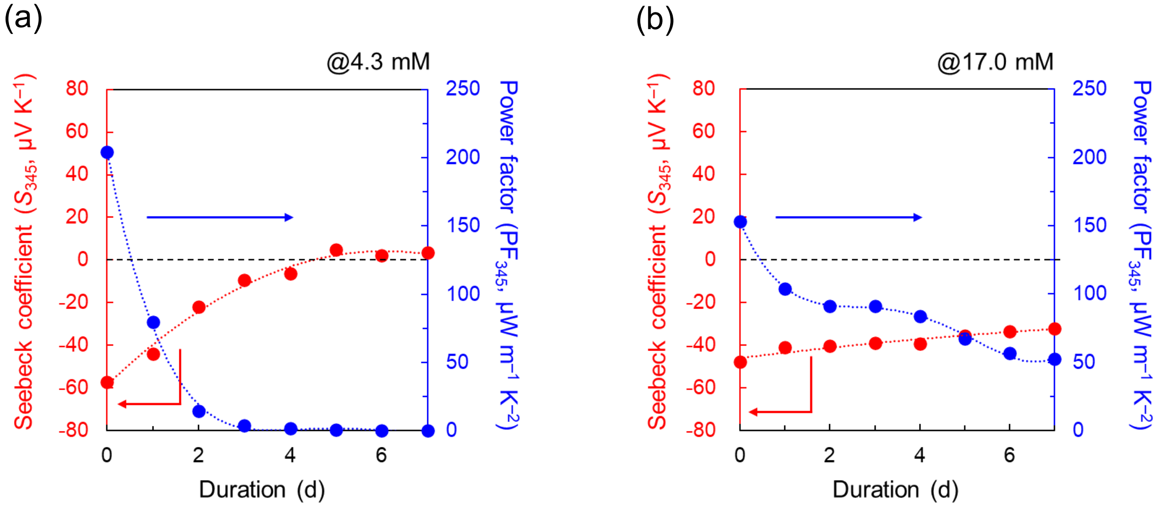

Figure S7. Variation in Seebeck coefficients and thermoelectric power factors of (a) 4.3 mM and (b) 17.0 mM $C_{12}EO_4$/CNT with duration of submergence in air at 303 K. Measurements were performed at 345 K in He.

Table S1. Comparison of the thermoelectric properties of n-type doped CNTs

Dopant	Chemical structure	Doping solvent	S (μV K^{-1})	σ (S cm^{-1})	PF (μV m^{-1} K^{-2})	Ref.
Polyethyleneimine + $NaBH_4$[a]	amine compound with metal ion addition	Water	−77	60	36	*Energy Environ. Sci.*, 2012, 5, 9481-9486.
1,3-bis(diphenylphosphino)propane[b]	phosphine compound	Dimethyl sulfoxide	−42	432	27	*Sci. Rep.*, 2013, 3, 3344.
polyethylenimine + diethylenetriamine + $NaBH_4$[a]	amine compound with metal ion addition	Water	−86	52	38	*ACS Nano*, 2014, 8, 2377–2386.
Cobaltocene[c]	metallocene	*N*-methyl pyrrolidone	−40	430	71	*Sci. Rep.*, 2015, 5, 7951.
KOH + 18-crown-6-ether[d]	oxygen compound-based metal complexes	*N*,*N*-dimethylformamide	−33	2,050	223	*Adv. Funct. Mater.*, 2016, 26, 3021.
Amino-substituted rylene dimide[e]	amine compound	Dimethyl sulfoxide	−56	432	135	*ACS Nano*, 2017, 11, 5746-5752.
Polyethyleneimine[f]	amine compound	Ethanol	−64	3,630	1,487	*Nat. Commun.*, 2017, 8, 14886.
Polyvinyl alcohol[g]	oxygen compound	Water	−40	~0.7	~0.11	*Mol. Syst. Des. Eng.,* 2017 2, 616–623.

Cetyltrimethylammonium bromide[e]	ammonium salt	*N*,*N*-dimethylformamide	−45	919	186	*J. Mater. Chem. A*, 2018, 6, 19030-19037.
Acridine analog[h]	amine compound	Dimethyl sulfoxide	−61	530	195	*ACS Appl. Mater. Interfaces*, 2019, 11, 29320-29329.
Imidazolium salt[i]	ammonium salt	Water	−53	660	180	*Chem. Phys. Lett*. 2020, 755, 137801.
Polyethyleneimine[j]	amine compound	Ethanol	−51	2,030	522	*ACS Appl. Energy Mater*. 2020, 3, 6929.
KOH + polyethylene glycol[h]	oxygen compound with metal ion addition	Ethanol	−32	1,708	174	*ACS Appl. Mater. Interfaces*, 2021, 13, 22, 26482–26489.
N-methyl pyrrolidone + ferrocene derivatives[k]	metal complex with amine compound attached	*N*-methyl pyrrolidone	−46	2,675	568	*Chem. Eng. J.*, 2021, 421, 129718.
Guanidine[i]	amine compound	*N*,*N*-dimethylformamide	−34	1,220	141	*Nat. Commun*., 2022, 13, 3517.
Sodium dodecylbenzenesulfonate + imidazolium compound[l]	benzenesulfonic acid derivative + amine compound	Dimethyl sulfoxide	−24	3,490	195	*Nano Energy,* 2022, 93, 106804.

$C_{12}EO_4$[i]	oxygen compound	Water	−62	548	214	This work

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[a]The SWCNT/MWCNT mixture used in these studies were obtained from Cheap Tubes, Inc. [b]The SWNTs used in this study were prepared by supergrowth chemical vapor deposition. [c]The SWNTs were prepared by high-pressure carbon monoxide method. The SWCNTs used in these studies were obtained from [d]Meijo Nano Carbon Co., Ltd., Japan (MEIJO eDIPS EC2.0), [e]Shenzhen Nanotech Port Co. Ltd., China, [h]Nanjing XFNANO Materials Tech Co., Ltd., China, [i]Meijo Nano Carbon Co., Ltd., Japan (MEIJO eDIPS EC1.5), [k]Jiangsu Xianfeng Nanomaterials Technology Co., Ltd., and [l]Shenzhen Nanotech Port Co. Ltd., China (NTP8022). [f]The SWCNTs used in this study were prepared by the floating catalyst chemical vapor deposition method. [g]The SWCNTs used in this study were synthesized by the direct-injection pyrolytic synthesis method. [j]The MWCNT used in these studies were obtained from Suzhou Xinyin nanotechnology company.

References

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