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Electronic Supplementary Information for

Triboelectric Energy Harvesting by Conjugated Microporous Polymer Nanoparticles in Polyurethane Films

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Experimental

General: SEM images were obtained by JSM6700F. N₂ adsorption-desorption isotherm curves were obtained at 77K by Micromeritics ASAP2020. Surface areas were calculated based on the Brunauer-Emmett-Teller (BET) theory. The pore size distribution diagrams were obtained by the analysis of adsorption curves based on the density functional theory (DFT) method. IR absorption spectra were obtained by Bruker VERTEX70. Solid state ¹³C NMR spectra were obtained in the CP/TOSS mode by a 500 MHz Bruker ADVANCE II NMR spectrommeter. PXRD patterns were obtained by Rigaku MAX-2200. TGA curves were obtained by Seiko Exstar 7300. Water contact angles were measured by a Theta Optical tensiometer (KSV Instruments, Ltd.) and electrooptics that comprised a CCTV camera connected to a computer (software Attension Theta).

Synthetic procedures of CMP-X

For the preparation of CMP-H, (PPh₃)₂PdCl₂ (28 mg, 40 µmol), CuI (7.6 mg, 40 µmol), distilled triethylamine (40 mL), and distilled DMF (20 mL) were added to a flame-dried 100 mL Schlenk flask under argon. After 1,3,5-triethynylbenzene (60 mg, 0.40 mmol) and 1,4-diiodobenzene (0.20 g, 0.60 mmol) were added, the reaction mixture was stirred at 80°C under argon for 24 h. After being cooled to room temperature, CMP-H powders were isolated by centrifugation, washed with methylene chloride (40 mL) two times, methanol (40 mL) two times, and acetone (40 mL) two times, and dried under vacuum.

In the case of CMP-NH₂, the synthetic procedures were the same as those of CMP-H except for using 1amino-2,5-diiodobenzene (0.21 g, 0.60 mmol) instead of 1,4-diiodobenzene (0.20 g, 0.60 mmol). In the case of CMP-OMe, the synthetic procedures were the same as those of CMP-H except for using 1,4-diiodo-2,5dimethoxybenzene (0.27 g, 0.60 mmol) instead of 1,4-diiodobenzene (0.20 g, 0.60 mmol). In the case of CMP-F, the synthetic procedures were the same as those of CMP-H except for using 1,2,4,5-tetrafluoro-3,6diiodobenzene (0.24 g, 0.60 mmol) instead of 1,4-diiodobenzene (0.20 g, 0.60 mmol).

Synthetic procedures of CMP-X@PU films

For the preparation of polyurethane (PU) matrix, poly(ethylene glycol) (PEG, Mw: 950~1050, Aldrich Co., 2.34 g) was dissolved in tetrahydrofuran (THF, 5 mL) in a 10 mL vial through sonication for 15 min. The solution was added to a flame-dried 50 mL Schlenk flask under argon. After 1,6-diisocyanatohexane (1.0 mL, 6.2 mmol) was added, the reaction mixture was stirred at 60°C under argon for 12 h. Then, after pentane-1,5-diol (0.35 mL, 3.3 mmol) and glycerol (40 μ L, 0.55 mmol) were added, the reaction mixture was stirred at 60°C under argon for 4 h. After being cooled, THF was added to the reaction mixture until the total PU solution volume became 10 mL.

For the fabrication of a PU (only) film, PU solution (1.75 mL) was added to a circular Teflon mold with a diameter of 3.75 cm and the solvent was slowly evaporated at room temperature. The weight of the resultant PU film was 0.61 g. The PU film was cut to an area of 2 cm \times 2 cm.

For the fabrication of CMP-H@PU films, PU solution (1.75 mL) and CMP-H (1.5 mg for 0.25% CMP-H@PU, 3.1 mg for 0.50% CMP-H@PU, 6.2 mg for 1.0% CMP-H@PU, 16 mg for 2.5% CMP-H@PU, and 32 mg for 5.0% CMP-H@PU) were mixed and sonicated for 2 h. The mixture was added to a circular Teflon mode with a diameter of 3.75 cm and the solvent was slowly evaporated at room temperature. The CMP-H@PU films were cut to an area of 2 cm \times 2 cm.

For the fabrication of CMP-NH₂@PU, CMP-OMe@PU, and CMP-F@PU films, the same synthetic procedures as those of the 5.0% CMP-H@PU were applied except using CMP-NH₂, CMP-OMe, and CMP-F powders instead of CMP-H.

Measurement of triboelectric output performance

PU and CMP-X@PU films (2 cm \times 2 cm) were placed on the printed circuit board (PCB) support (Au/Cu electrode: area of 2 cm \times 2 cm and thickness of 35 µm, FR-4 glass epoxy substrate: thickness of 1.0 mm). The PU and CMP-X@PU films were attached onto the PCB supports through heat-treatment at 100°C for 12 h in an oven. Perfluoroalkoxy alkanes (PFA, Alphaflon, thickness of 25 µm) were used as counter contact materials. An Al tape was attached onto the acrylate polymer substrate (thickness of 5 mm, area of 1 cm \times 1 cm). After a carbon tape was attached onto the Al tape, the PFA film was placed on the carbon tape.

For the measurement of triboelectric output performance, a pushing tester (Z-Tech, ZPS-100) was used to apply uniform force (1 kgf = 9.8 N) in a regular contact-separation mode (3.5 Hz). To measure the output voltages, a voltage probe (Tektronix P5100A) with 40 M Ω input impedance and an oscilloscope (Tektronix DPO3052) were used. To measure the output currents, a low noise current amplifier (FEMTO, DLPCA-200) was used. To measure the changes of current densities depending on the loaded resistances, the resistances of

10 K Ω , 100 K Ω , 1 M Ω , 10 M Ω , 50 M Ω , 100 M Ω , 500 M Ω , and 1 G Ω were applied. The current changes were measured by a low noise current amplifier (FEMTO, DLPCA-200).

Measurement of KPFM

For the measurment of KPFM, Park Systems XE-100 (NSC36, Cr/Au-coated silicon tips, tip radius < 35 nm, force constant 1 N m⁻¹, and resonance frequency of 90 kHz) were used. KPFM images with an area of 5 μ m × 5 μ m were obtained under the following measurement conditions; scanning speed of 0.3 Hz, set point of 13 nm from a sample in atmospheric pressure at room temperature, applied AC voltage of 2 V, and a rock-in amplifier with a phase of - 90° and frequency of 17 kHz.

Fabrication of an Arch-type TENG

The arch-type TENG consists of top and bottom materials. For the fabrication of the top material, a PET film (thickness of 0.17 mm, area of 2 cm \times 4.5 cm) was used as a substrate. An aluminum tape (area of 2 cm \times 5 cm) was loaded on the PET substrate as an electrode. After a carbon tape was loaded on the Al layer, a PFA film (thickness of 25 µm, area of 2 cm \times 4.5 cm) was loaded on the carbon tape as a tribo-negative material. For the fabrication of the bottom material, a copper foil (thickness of 0.5 mm, area of 2 cm \times 4 cm) was loaded on another PET film. After 5.0% CMP-H@PU (area of 2 cm \times 2 cm) was loaded on the copper foil, the 5.0% CMP-H@PU/Cu/PET was heat-treated at 100 °C for 12 h in an oven. Both tribo-positive and negative materials were integrated by a polyimide tape.

Capacitor charging and LED operation tests

For the capacitor charging tests, an electrolytic Al capacitor (Samyoung Electronics, MHA series, 4.7 μ F, 450 V) was used. The charged voltages of the capacitor were measured for 100 s using an electrometer (Keithley 6514) with 200 G Ω input impedance. For the LED operation tests, 100 green LEDs (photron, PV525-5A5D-NNISLA-Z) were used. Triboelectric energy was generated by the arch-type TENG with the combination of the 5.0% CMP-H@PU film/Cu with the PFA film/Al. The 1 kgf (9.8 N) force was applied with a frequency of 3.5 Hz.

Fig. S1. Solid state ¹³C NMR spectrum of polyurethane prepared by the polymerization of 1,6diisocyanatohexane with a mixture of polyethylene glycol, pentane-1,5-diol, and glycerol.



Fig. S2. PXRD patterns of CMP-X powders.



Fig. S3. TGA curves of CMP-X powders and PU.







Fig. S5. Water contact angles of CMP-X materials.



Fig. S6. (a) Output voltages and (b) currents of triboelectric energy harvesters with 0.5% CMP-H@PU film depending on the relative humidity (RH).



Table S1. Maximum power densities of the recent polymer-related TENGs in the literature and the 5.0% CMP-H@PU-based triboelectric energy harvesters in this work (Also, refer to the recent review paper^{S1} of polymer-based TENGs).

Entry	Tribo-positive materials	Tribo-negative materials	Maximum power density	Ref.	Reported year
			(mW/cm^2)		
1	Silk fibroin film	PET	0.194	S2	2016
2	Micro/nanostructured PPy	PTFE	0.55	S3	2016
3	PLA nanofiber	Nanostructured gelatin	0.5	S4	2018
4	Porous chitosan aerogel	Porous PI arerogel	0.45	S5	2018
5	Silk fibroin nanofiber	Mxene-PVA	0.109	S6	2019
6	TPU	PDMS	0.27	S7	2020
7	Silicone with nylon	Silicone rubber	1.12	S8	2020
8	FAS/PVDF-HFP/SiO ₂ /EVOH	PTFE	0.214	S9	2020
9	SPS/P2VP/APEO	FOTS-SAM/PDMS	0.077	S10	2020
10	Cellulose aerogel	PTFE	0.0127	S11	2020
11	Graphene-PDMS	PTFE-PDMS	0.041	S12	2020
12	CMP-H@PU	PFA	0.80	This work	

PET: Poly(ethylene terephthalate), PPy: Poly(pyrrole), PTFE: Poly(tetrafluoroethylene), PLA: Poly(lactic acid), PI: Polyimide, PVA: Poly(vinyl alcohol), TPU: Thermoplastic polyurethane, PDMS: Polydimethylsiloxane, FAS: Perfluorodecyltriethoxysilane, PVDF-HFP: Poly(vinylidene fluoride-co-hexafluoropropylene), EVOH: Poly(ethylene-co-poly(vinyl alcohol)), SPS: Sulfonic acid-terminated poly(styrene), P2VP: Poly(2-vinylpyridine), APEO: Amine-terminated poly(ethylene oxide), FOTS: Perfluorooctyltrichlorosilane, SAM: Self-assembled monolayer, CMP: Conjugated microporous polymer, PU: Polyurethane, PFA: Perfluoroalkoxyalkane.

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