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Electronic Supplementary Information for

A very small amount (0.1 wt%) of $Co(OH)_2$ nanoplates enhances triboelectric performance of polymers

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Experimental Section

General: SEM images of materials were obtained using JSM-7100F and JSM-7800F instruments at the Chiral Material Core Facility Center of Sungkyunkwan University. TEM images were obtained using a JSM2100F equipment. IR absorption spectra were obtained using a Bruker VERTEX70 spectrometer. PXRD patterns were obtained using a Rigaku MAX-2200 equipment. KPFM images with an area of 5 μm × 5 μm were obtained through atomic force microscopy (AFM) with a scanning speed of 0.3 Hz and set point of 13 nm using a XE-100 Park Systems. The sampling for AFM studies was conducted under air at room temperature. AC voltage of 2 V with a frequency of 17 kHz was applied at the AFM tip (NSC36, Cr/Au-coated silicon tips, tip radius < 35 nm, force constant 1 N m^{-1} , and resonance frequency of 90 kHz).

Synthetic procedures of $Co(OH)_2$ nanoplates

For the preparation of $Co(OH)_2$ nanoplates, tetramethylammonium bromide (0.52 g, 3.4 mmol) and degassed water (200 mL) were added to a 250 mL Schlenk flask under argon. The solution was bubbled with argon gas for 5 min through a needle connected to an argon gas container. After 2 M NaOH solution (1.6 mL, 3.2 mmol) was added to the solution, $CoCl_2$ hexahydrate (0.95 g, 4.0 mmol) in degassed and distilled water (1.5 mL) was added. The reaction mixture was stirred at 60 ^{o}C for 1 h. After cooling with an ice bath, the solids ($Co(OH)_2$ nanoplates) were separated by centrifugation, washed with a mixture of ethanol (40 mL) and water (10 mL) two times and ethanol (50 mL) once, and dried under vacuum.

Fabrication of PVP, PVP-Co, PU, and PU-Co films

For the preparation of PVP and PVP-Co films, PVP mother solution was prepared as follows. PVP (10 g, Mw: 1,300,000 Aldrich Co., Cat# 437190) was dissolved in ethanol (40 g) through stirring for 4 h at 50 ^{o}C in a 70 mL vial. To check the weight of PVP per volume in PVP solution in a empirical way, four sets of the PVP solutions (4 mL) were taken and transferred to 20 mL vials and the ethanol was completely evaporated at 80 ^{o}C under vacuum. The average weight of the remained PVP in four vials was analyzed to be 0.748 g. For the preparation of a PVP film, PVP solution (4 mL) described above was loaded onto a doctor blade (Kipae E&T Co., KP-3000 V). The target coating thickness of materials was set to 30 μm. Using a doctor blade, the PVP solution was loaded on the PVC mat (Hyundai Co., 20 cm × 20 cm). After drying the PVP solution on the PVC mat for several days under air, the PVP film with a thickness of 21 μm was detached from the PVC mat and cut to pieces with specific areas. For the preparation of PVP-Co films, $Co(OH)_2$ nanoplates (0.19, 0.37, 0.75, 1.87, 3.76, 7.56, 23.1, 39.4, 56.3, and 83.1 mg for 0.025, 0.05, 0.1, 0.25, 0.5, 1, 3, 5, 7, and 10 wt% $Co(OH)_2$ in PVP-Co films) were well dispersed in ethanol (1 mL). After PVP solution (4 mL) described above was added, the mixture was stirred to get the well dispersed $Co(OH)_2$ suspensions in PVP solution. The solutions were loaded onto a doctor blade (Kipae E&T Co., KP-3000 V). The target coating thickness of materials was set to 30 μm. The materials were spread on the PVC mat using a doctor blade. After drying the loaded PVP-$Co(OH)_2$ on the PVC mat for several days under air, the PVP-Co films with a thickness of 22 μm were detached from the PVC mat and cut to pieces with specific areas.

For the preparation of PU and PU-Co films, PU mother solution was prepared as follows. PU (1 g, Aldrich Co., Cat.# 81367, Selectophore^{TM}) was dissolved in THF (9 g) through stirring for 4 h at 50 ^{o}C in a 30 mL vial. To check the weight of PU per volume of PU solution in a empirical way, four sets of the PU solutions (4 mL) were taken and transferred to 20 mL vials and the THF was completely evaporated at 80 ^{o}C under vacuum. The average weight of the remained PU in four vials was analyzed to be 0.472 g. For the preparation of a PU film, PU solution (4 mL) described above was loaded on a doctor blade (Kipae E&T Co., KP-3000 V). The target coating thickness of materials was set to 30 μm. Using a doctor blade, the PU solution was loaded on the polyethylene (PE) film. After drying the PU solution on the PE film for several days under air, the PU film with a thickness of 18 μm was detached from the PE film and cut to pieces with specific areas. For the preparation of PU-Co films, $Co(OH)_2$ nanoplates (0.12, 0.24, 0.48, 1.18, 2.73, 4.77, 14.6, 24.8, 35.5, and 52.4 mg for 0.025, 0.05, 0.1, 0.25, 0.5, 1, 3, 5, 7, and 10 wt% $Co(OH)_2$ in PU-Co films) were well dispersed in THF (1 mL). After PU solution (4 mL) was added, the mixture was stirred to get the well dispersed $Co(OH)_2$ suspensions in PU solution. The solutions were loaded on a doctor blade (Kipae E&T Co., KP-3000 V). The target coating thickness of materials was set to 30 μm. The materials were spread on the PE film using a doctor blade. After drying the loaded PU-$Co(OH)_2$ on the PE film for several days under air, the PU-Co films with a thickness of 20 μm were detached from the PE films and cut to pieces with specific areas.

Studies of triboelectric performance

As tribopositive materials, PVP, PVP-Co, PU, PU-Co films with thicknesses of 18~22 μm and an area of 2 cm × 2 cm were attached to the Au electrode (2 cm × 2 cm, 35 μm) of the printed circuit board (PCB, 3 cm × 3 cm, a PR-4 glassy epoxy film) using a carbon tape (2 cm × 2 cm). The tribopositve part was fixed using a tape on the bottom and the Au electrode was connected to the negative electrode of the measurement device. As a tribonegative material, a perfluoroalkoxy alkanes (PFA, Alphafion) film with a thickness of 25 μm and an area of 2 cm × 2 cm was attached on the Cu electrode (3M^{TM} Coductive Copper Foil Tape 3313, 2 cm × 2 cm) on the polycarbonate support (2 cm × 2 cm) using a carbon tape (2 cm × 2 cm). The Cu electrode of the electronegative part was connected to probes (P6139B voltage probe for the measurement of PVP and PUV-Co films, TMDP0200 Differential Probe. Tektronix for the measurement of PU and PU-Co films). The probe was connected to the ocilloscope (DPO 3052, Tektronix) to measure potentials. The output currents were obtained through conversion using a low noise current amplifier (DLPCA-200, FEMTO). For the studies of triboelectric performance, two tribopositve materials and the tribonegative material were contacted using a pushing tester (JIPT-120, JUNIL TECH Co.). The pushing forces with 0.5, 1, 1.5, 2, and 2.5 kgf and the pushing frequencies with 0.23, 0.30, 0.42, 0.73, and 2.76 Hz were scanned. The effect of relative humidity was studied at RH 30, 50, and 80%. The stability tests of triboelectric performance were conducted for 30,000 cycles.

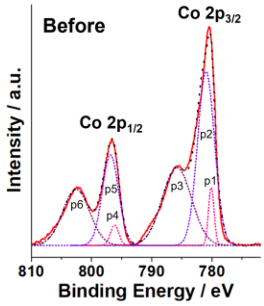
The resistance-dependent currents and power densities were obtained at the resistances of 10 kΩ, 30 kΩ, 60 kΩ, 100 kΩ, 300 kΩ, 600 kΩ, 1 MΩ, 3 MΩ, 6 MΩ, 10 MΩ, 30 MΩ, 60 MΩ, and 100 MΩ using a low noise current amplifier (DLPCA-200, FEMTO). For the measurement of the maximum power density, a working area and film thicknesses of the PVP-Co0.1 and PU-Co0.1 films were 1 cm × 1 cm and 20 ~ 22 μm, respectively. The pushing force and frequency were 1 kgf and 3 Hz, respectively. The measurement was conducted at RH 30%. The perfluoroalkoxyalkane (PFA) film with a working area of 1 cm × 1 cm and a thickness of 25 μm was used as a counting tribonegative material.

Demonstration studies of triboelectric devices as power suppliers

For the charging test of a capacitor, an Al electrolytic capacitor (2.2 μF, Panasonic co., ECA1HM2R2) and a full wave bridge rectifier (Rectron Semiconductor co., W04M) were connected to the TENG consisting of PVP-Co0.1 and PU-Co0.1 films with an working area of 1 cm × 1 cm and film thicknesses of 20~22 μm and a PFA film with an working area of 1 cm × 1 cm and a thickness of 25 μm. The charged voltages of the capacitor were measured for 200 s using an oscilloscope (Tektronix co., DPO3020) with a voltage probe (Tektronix co., P5100A) at 40 MΩ input impedance. The pushing force of 1 kgf and a pushing frequency of 3 Hz were applied with a pushing tester (Z-Tech, ZPS-100) at RH 30%. For the irradiation test of a LED, 100 green LEDs (Photron co., PV525-5A5D-NNISLA-Z) and a full wave bridge rectifier (Rectron Semiconductor co., W04M) were connected to the TENG consisting of PVP-Co0.1 and PU-Co0.1 films with an working area of 1 cm × 1 cm and film thicknesses of 20~22 μm and a PFA film with an working area of 1 cm × 1 cm and a thickness of 25 μm. The pushing force of 1 kgf and a pushing frequency of 3 Hz were applied with a pushing tester (Z-Tech, ZPS-100) at RH 30%. The photographs were obtained in a dark room.

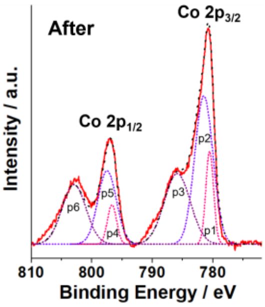
For the operating test of a calculator, after its built-in battery was removed, the commercial calculator (Canon co., AS-120II) was connected to a 100 μF Al electrolytic capacitor (Samyoung Electrinics co., SHL series), a full wave bridge rectifier (Rectron Semiconductor co., W04M), and the TENG of PVP-Co0.1 and PU-Co0.1 films with an working area of 3 cm × 3 cm and film thicknesses of 20~22 μm and a PFA film with an working area of 3 cm × 3 cm and a thickness of 25 μm. The pushing force of 2 kgf and a pushing frequency of 3 Hz were applied with a pushing tester (Z-Tech, ZPS-100) at RH 30%. The charged and discharged voltages of the capacitor were measured for 200 s using an electrometer (Keithley 6514) with an input impedance at 200 GΩ.

Fig. S1 XPS Co 2p orbital spectra of $Co(OH)_2$ on carbon tapes before and after pushing tests: a pushing force of 2 kgf, a pushing frequency of 0.75 Hz for 12 h, RH 30%, perfluoroalkoxyalkane (PFA) as a counting tribonegative material with a thickness of 25 μm.



	Peak	p1	p2	p3	p4	p5	p6
Before	position (eV)	780.149	781.020	785.858	796.206	796.897	802.588
	FWHM	1.090	3.312	5.724	1.615	3.192	5.224
	Area (%)	3.702	33.906	26.207	1.925	16.998	17.262
	r^2	0.99					

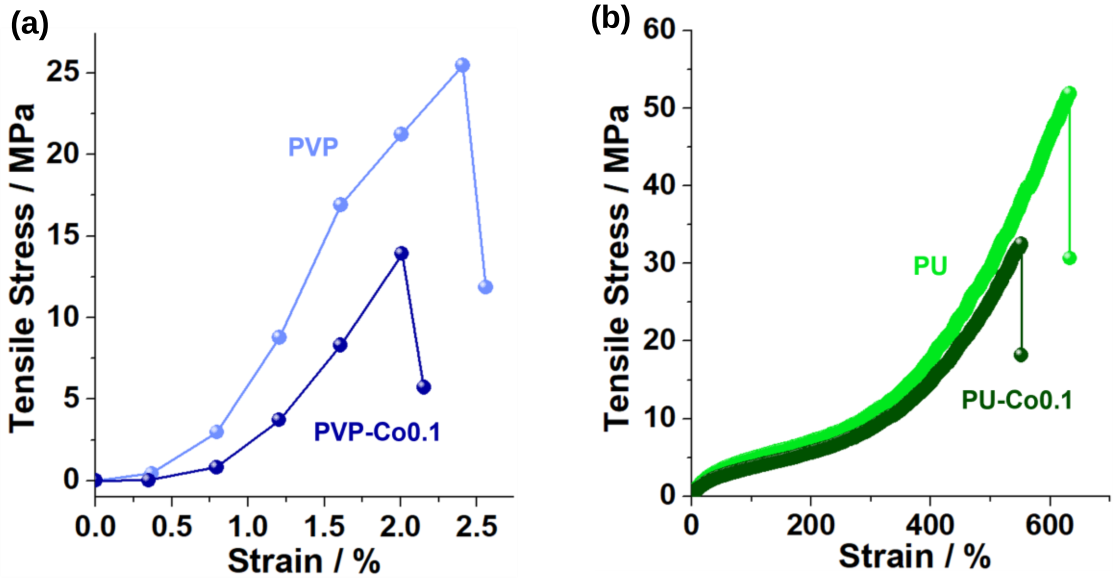
$Co^{2+} : Co^{3+} = 1 : 0.11$



	Peak	p1	p2	p3	p4	p5	p6
After	position (eV)	780.539	781.503	785.899	796.676	797.492	802.961
	FWHM	1.504	3.546	5.050	1.781	3.577	4.661
	Area (%)	8.54037	32.184	21.875	4.273	16.092	17.036
	r^2	0.99					

$Co^{2+} : Co^{3+} = 1 : 0.26$

Fig. S2 Tensile tests of (a) PVP and PVP-Co0.1 films with thicknesses of 21 and 22 μm, respectively, and (b) PU and PU-Co0.1 films with thicknesses of 18 and 20 μm, respectively, and (c) corresponding parameters.



(c)

Materials	Max. Strain (%)	MAX. Strength (Mpa)	Young’s Modulus (Gpa)
PVP	2.56	25.5	1.43
PVP-Co0.1	2.00	13.9	1.08
PU	630	51.9	0.015
PU-Co0.1	550	32.5	0.009

Fig. S3 Side view SEM images of (a) PVP, (b) PVP-Co0.1, (c) PU, and (d) PU-Co0.1 films.

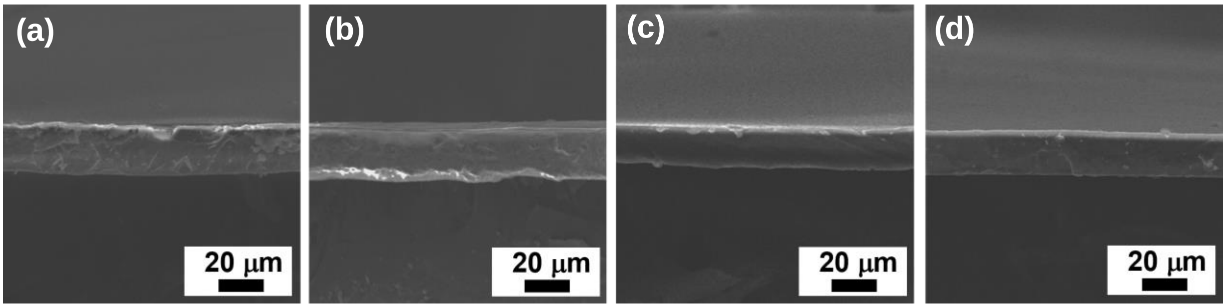


Fig. S4 Output currents of triboelectric devices fabricated with (a, c, e) PVP-Co0.1 films and (b, d, f) PU-Co0.1 films depending on pushing forces, frequencies, and relative humidity (RH). Standard conditions: a working area of 2 cm × 2 cm, film thickness of 22 μm (PVP-Co0.1) and 20 μm (PU-Co0.1), pushing force of 2 kgf, a pushing frequency of 0.75 Hz, RH 30%, PFA as a counting tribonegative material with a thickness of 25 μm.

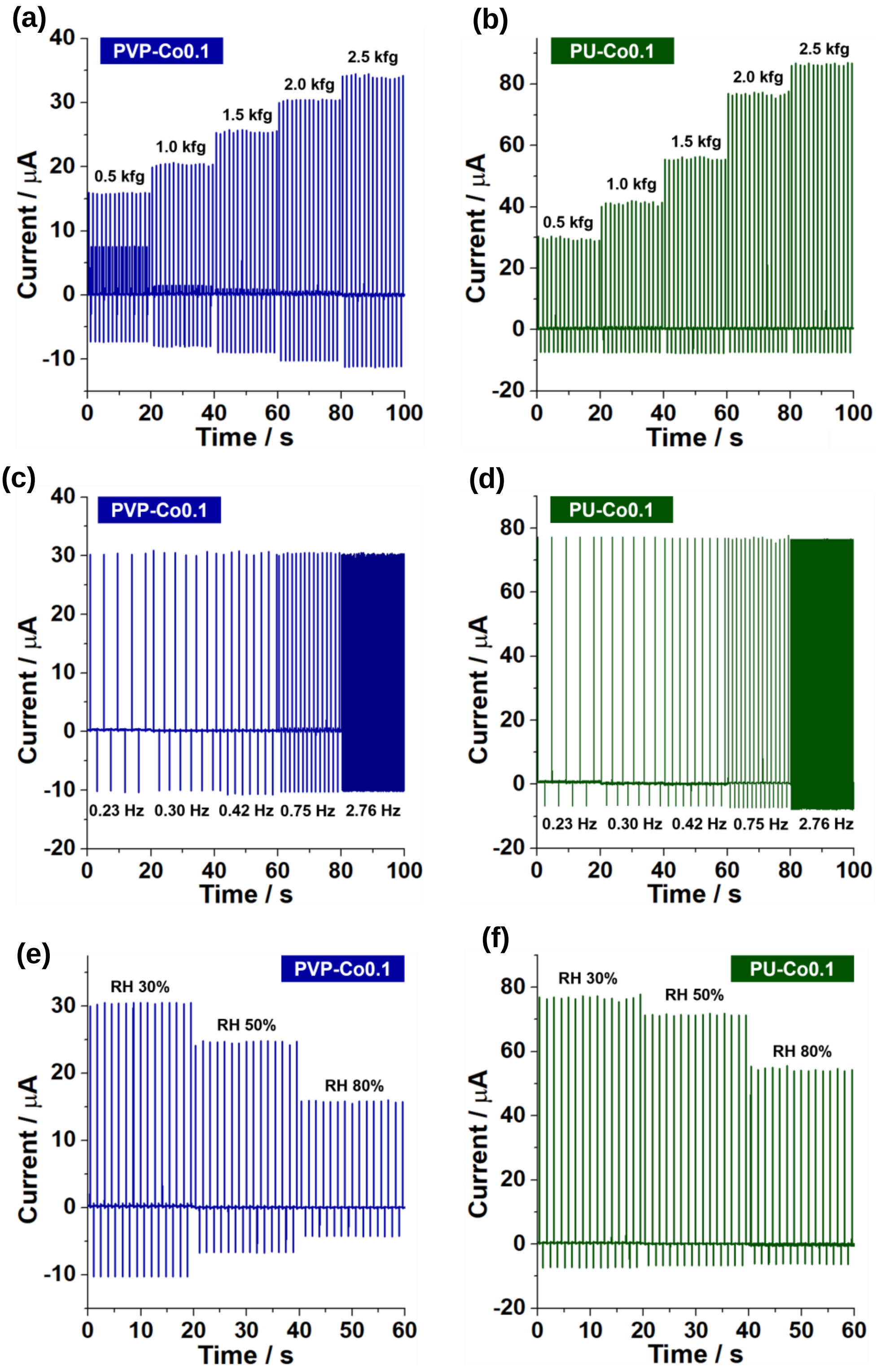


Fig. S5 Output voltages of triboelectric devices fabricated with PVP-Co0.1 and PU-Co0.1 films depending on temperature. Standard conditions: a working area of 2 cm × 2 cm, film thickness of 22 μm (PVP-Co0.1) and 20 μm (PU-Co0.1), pushing force of 2 kgf, a pushing frequency of 0.75 Hz, RH 30%, PFA as a counting tribonegative material with a thickness of 25 μm.

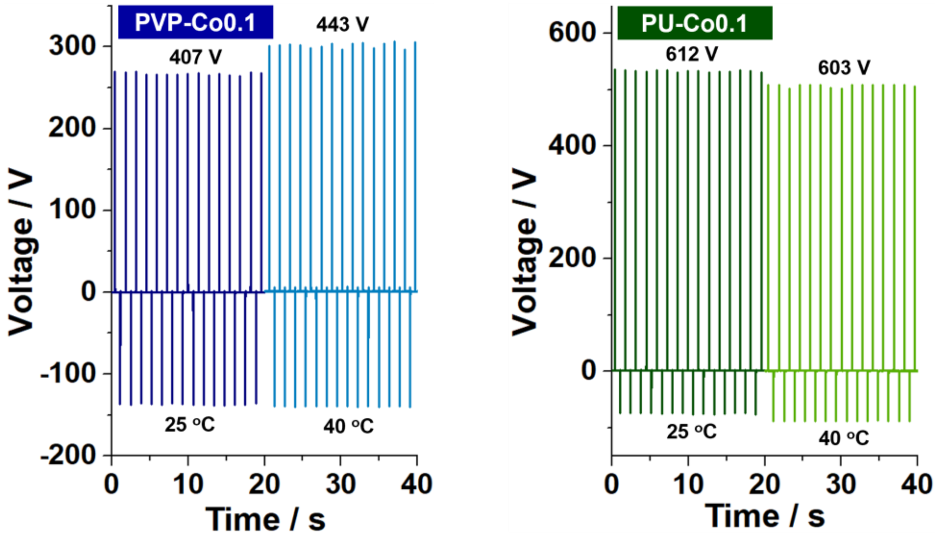


Table S1 Triboelectric performance of polymer-based systems in the literature.[S1]

Entry	Tribo-positive materials	Tribo-negative materials	V_{pp} (V)	P_{max} (mW/cm^2)	Year	Ref.
1	PPy	PTFE	28	0.55	2016	S2
2	Silk fibroin	PET	268	0.194	2016	S3
3	Porous chitosan	Porous PI	56	0.45	2018	S4
4	PLA nanofiber	Gelatin	500	0.5	2018	S5
5	Silk fibroin	Mxene-PVA	~225	0.109	2019	S6
6	TPU	PDMS	400	0.27	2020	S7
7	FAS/PVDF-HFP/SiO_2/EVOH	PTFE	144.9	0.214	2020	S8
8	SPS/P2VP/APEO	FOTS-SAM/PDMS	~70	0.077	2020	S9
9	Cellulose aerogel	PTFE	65	0.0127	2020	S10
10	Graphene-PDMS	PTFE-PDMS	128	0.041	2020	S11
11	CMP	PFA	411	0.80	2021	S12
12	Waste PP	Mylar	200	0.007116	2021	S13
13	PMMA	PVDF	120	0.00018	2021	S14
14	PI	PVDF-TrFE/PEDOT:PSS	15.6	0.00128	2022	S15
15	COF@PVDF	PVDF	420	0.2858	2022	S16
16	PVA/Tp-TFAB	PVC	177.8	0.000824	2023	S17
17	PANI/EC-CPCF	FEP	130	0.065	2023	S18
18	PU-Co0.1	PFA	612	1.22		This work

PPy: poly(pyrrole), PTFE: poly(tetrafluoroethylene), PET: poly(ethylene terephthalate), PI: polyimide, PLA: poly(lactic acid), PVA: poly(vinyl alcohol), TPU: thermoplastic polyurethane, PDMS: polydimethylsiloxane, FAS: perfluorodecyltriethoxysilane, PVDF: poly(vinylidene fluoride), 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, PFA: perfluoroalkoxyalkane, PP: polypropylene, PMMA: poly(methyl metacrylate), PI: polyimide, PVDF-TrFE: poly(vinylidene fluoride-co-trifluoroethylene), PEDOT: poly(3,4-ethylenedioxythiophene), PSS: poly(styrenesulfonate), COF: covalent organic framework, TFAB: 1,3,5-tris(2,3,5,6-tetrafluoroaniline)benzene, Tp: triformylphloroglucinol, PANI: polyaniline, EC: ethylcellulose, CPCF: conductive polymer composite film, FEP: fluorinated ethylene propylene, PU: polyurethane.

S1 A. Chen, C. Zhang, G. Zhu and Z. L. Wang, *Adv. Sci.*, 2020, **7**, 2000186.

S2 J. Wang, Z. Wen, Y. Zi, P. Zhou, J. Lin, H. Guo, Y. Xu and Z. L. Wang, *Adv. Funct. Mater.*, 2016, **26**, 1070-1076.

S3 X. -S. Zhang, J. Brugger and B. Kim, *Nano Energy*, 2016, **20**, 37-47.

S4 Q. Zheng, L. Fang, H. Guo, K. Yang, Z. Cai, M. A. B. Meador and S. Gong, *Adv. Funct. Mater.*, 2018, **28**, 1706365.

S5 R. Pan, W. Xuan, J. Chen, S. Dong, H. Jin, X. Wang, H. Li and J. Luo, *Nano Energy*, 2018, **45**, 193-202.

S6 C. Jiang, C. Wu, X. Li, Y. Yao, L. Lan, F. Zhao, Z. Ye, Y. Ying and J. Ping, *Nano Energy*, 2019, **59**, 268-276.

S7 F. Chen, Y. Wu, Z. Ding, X. Xia, S. Li, H. Zheng, C. Diao, G. Yue and Y. Zi, *Nano Energy*, 2019, **56**, 241-251.

S8 S. Yan, K. Dong, J. Lu, W. Song and R. Xiao, *Nanoscale*, 2020, **12,** 4527-4536.

S9 C. Park, M. Koo, G. Song, S. M. Cho, H. S. Kang, T. H. Park, E. H. Kim and C. Park, *ACS Nano*, 2020, **14**, 755-766.

S10 L. Zhang, Y. Liao, Y. -C. Wang, S. Zhang, W. Yang, X. Pan and Z. L. Wang, *Adv. Funct. Mater.*, 2020, **30**, *2001763*.

S11 X. Zhao, D. Zhang, S. Xu, W. Qian, W. Han, Z. L. Wang and Y. Yang, *Nano Energy*, 2020, **75**, 104920.

S12 S. I. Park, D. -M. Lee, C. W. Kang, S. M. Lee, H. J. Kim, Y. -J. Ko, S. -W. Kim and S. U. Son, *J. Mater. Chem. A*, 2021, **9**, 12560-12565.

S13 H. Varghese and A. Chandran, *ACS Appl. Mater. Interfaces*, 2021, **13**, 51132-51140.

S14 H. Varghese and A. Chandran, *Sustainable Energy Fuels*, 2021, **5**, 5287-5294.

S15 M. H. Chung, H.-J. Kim, S. Yoo, H. Jeong and K. -H. Yoo, *RSC Adv.*, 2022, **12**, 2820-2829.

S16 C. Lin, L. Sun, X. Meng, X. Yuan, C. -X. Cui, H. Qiao, P. Chen, S. Cui, L. Zhai and L. Mi, *Angew. Chem. Int. Ed.*, 2022, **61**, e202211601.

S17 L. Shi, V. S. Kale, Z. Tian, X. Xu, Y. Lei, S. Kandambeth, Y. Wang, P. T. Parvatkar, O. Shekhah, M. Eddaoudi and H. N. Alshareef, *Adv. Funct. Mater.*, 2023, **33**, 2212891.

S18 P. Manchi, S. A. Graham, M. V. Paranjape and J. S. Yu, *ACS Appl. Polym. Mater.*, 2023, **5**, 8650-8659.

Table S2 Triboelectric performance of inorganic nanomaterials/polymer composite-based systems in the liaterature.

Entry	Composites	Nanomaterials	Triboelectric Polymer Materials	V_{p-p} (V)	P_{max} (mW/cm^2)	Year	Ref
1	$ZnSnO_3$/PDMS	$ZnSnO_3$	PDMS	400	0.75	2015	S1
2	ZnO NR/PDMS-PVDF	ZnO NR	PDMS-PVDF	40	0.007	2016	S2
3	$BaTiO_3$@PDMS	$BaTiO_3$	PDMS	60	0.009741	2016	S3
4	ZnO-PVDF/PTFE	ZnO	PVDF/PTFE	97	0.0245	2018	S4
5	PVDF-BTO	$BaTiO_3$	PVDF/PTFE	150	0.32	2019	S5
6	Y-ZnO MFs/PDMS	Y-ZnO MFs	PDMS	247	0.6	2021	S6
7	Chitosan/$BaTiO_3$ NRs	$BaTiO_3$ NRs	Chitosan	111.4	0.756	2021	S7
8	Porous PDMS/BTO CF	$BaTiO_3$	Porous PDMS	280	0.04	2021	S8
9	$BaTiO_3$/PVDF	$BaTiO_3$	PVDF	444	0.04	2022	S9
10	PVDF-MoS_2/CNT	MoS_2/CNT	PVDF	300	0.0134	2022	S10
11	ZnO@MOP	ZnO	MOP	534	1.19	2022	S11
12	MXene-PVDF	$Ti_3C_2T_x$	PVDF	24	0.00408	2023	S12
13	TM6S/PET	$Ti_3C_2T_x$	PET	390	0.666	2023	S13
14	Mxene/Leather	MXene	Leather	199.56	0.469	2023	S14
15	PU-Co0.1	$Co(OH)_2$	PU	612	1.22		This work

PDMS: polydimethylsiloxane, NR: nanorod, PVDF: poly(vinylidene fluoride), PTFE: poly(tetrafluoroethylene), BTO: $BaTiO_3$, CNT: carbon nanotube, MOP: microporous organic polymer, TM6S: $Ti_3C_2T_x$, PET: poly(ethylene terephthalate), PU: polyurethane

S1 G. Wang, Y. Xi, H. Xuan, R. Liu, X. Chen and L. Cheng, *Nano Energy*, 2015, **18**, 28-36.

S2 X. Yang and W. A. Daoud, *Adv. Funct. Mater.*, 2016, **26**, 8194-8201.

S3 B. Shi, Q. Zheng, W. Jiang, L. Yan, X. Wang, H. Liu, Y. Yao, Z. Li and Z. L. Wang, *Adv. Mater.*, 2016, **28**, 846-852.

S4 H. H. Singh and N. Khare, *Nano Energy*, 2018, **51**, 216-222.

S5 S. Sriphan, T. Charoonsuk, T. Maluangnont and N. Vittayakorn, *ACS Appl. Energy Mater.*, 2019, **2**, 3840-3850.

S6 H. Patnam, S. A. Graham and J. S. Yu, *ACS Sustainable Chem. Eng.*, 2021, **9**, 4600-4610.

S7 S. Pongampai, T. Charoonsuk, N. Pinpru, P. Pulohol, W. Vittayakorn, P. Pakawanit and N. Vittayakorn, *Composites Part B*, 2021, **208**, 108602.

S8 M. Sahu, V. Vivekananthan, S. Hajra, D. K. Khatua and S. -J. Kim, *Appl. Mater. Today*, 2021, **22**, 100900.

S9 J. -H. Zhang, Z. Zhou, J. Li, B. Shen, T. Zhu, X. Gao, R. Tao, X. Guo, X. Hu, Y. Shi and L. Pan, *ACS Mater. Lett.*, 2022, **4**, 847-852.

S10 C. Sun, G. Zu, Y. Wei, X. Song and X. Yang, *Langmuir*, 2022, **38**, 1479-1487.

S11 C. W. Kang, D. -M. Lee, J. Park, S. Bang, S. -W. Kim and S. U. Son, *Angew. Chem. Int. Ed.*, 2022, **61**, e202209659.

S12 M. M. Hasan, M. S. B. Sadeque, I. Albasar, H. Pecenek, F. K. Dokan, M. S. Onses and M. Ordu, *Small*, 2023, **19**, 2206107.

S13 S. Answer, M. U. Khan, B. Mohammad, M. Rezeq, W. Cantwell, D. Gan and L. Zheng, *Chem. Eng. J.*, 2023, **470**, 144281

S14 S. Zhang, Y. Xiao, H. Chen, Y. Zhang, H. Liu, C. Qu, H. Shao and Y. Xu, *ACS Appl. Mater. Interfaces*, 2023, **15**, 13802－13812