Supporting Information

Waterborne Polyurethane: An easily available material for moist-electric generator with unique stretchability and water resistant

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Experimental section

Materials

Isophorone diisocyanate (IPDI), poly-(tetramethylene ether glycol) (PTMEG 2000, average Mn of ~2000), di-n-butyltin dilaurate (DBTDL), dimethylolpropionic acid (DMPA), butanediol (BDO), and Polyvinylpyrrolidone (PVP10, average Mn of ~58,000) were purchased from Macklin. Triethylamine (TEA), acetone, NaCl, $AgNO_3$, and ethylene glycol were purchased from National Medicine. Deionized (DI) water is produced by a water purification mechanism. The seawater was taken from Maidao, Qingdao City, Shandong province, China, and filtered.

Synthesis of WPU

Synthesis with reference to previously reported methods is demonstrated.[1] First, pre-dried PTMEG (23 g), IPDI (9.4 g) , and DBTDL (0.27 mL) were added to a three-port flask with a condenser tube on one side and an N_2 tube on the other, and then reacted for 1.5 h at 65 °C at 400 rpm. The temperature was adjusted to 80 °C, and the reaction continued for 1h. Secondly, DMPA (1.8 g) and BDO (0.7 g) were added to the three-port flask for chain extension reaction for 3.5 h, and a very small amount of acetone was added to adjust the viscosity during the reaction. Thirdly, the reaction temperature was reduced to 45 °C and neutralized with TEA (2 ml) for 15 min. Finally, the WPU emulsion was prepared by adding deionized water (DI) (60 mL) dispersion system, stirring at room temperature and 1000rpm for 1h.

Synthesis of AgNWs

AgNWs are synthesized with reference to previously reported methods.[2] The first is the synthesis

of silver chloride. Due to the photosensitivity of AgCl, the synthesis is performed in the dark. Mixture of silver nitrate aqueous solution (5 mL, 0.5 M) and sodium chloride aqueous solution (5 mL, 1 M), stirred at 800rpm for 1min. Upon NaCl addition, silver chloride flocculates immediately. The precipitate is separated from the supernatant, washed once with ultrapure water, and then dried in a vacuum to obtain silver chloride. 3.4 g PVP was dissolved in 200 mL ethylene glycol and stirred in 500 mL three-port flask at 330 rpm and heated to 160 °C. Once the solution reached a stable temperature, an excess of newly prepared AgCl (0.25 g) was added immediately, after 5 min, 1.1 g $AgNO_3$ was added at one time. The reaction mixture was left under stirring at 160 °C for 30 min. Finally, the reaction was stopped, cooled at room temperature, washed 3 times with DI and redistributed in deionized water at 2.17 wt%.

Preparation of MEG.

The aqueous AgNWs dispersion (2.17 wt%) was uniformly mixed with aqueous WPU solution (10 wt%), then the mixture was then slowly poured into a glass tray (10 cm×10 cm) and dried at room temperature. After drying, the flexible and stretchable WPU&AgNWs film could be manually peeled off from glass tray and cut into a number of 1.5 cm×0.5 cm MEFGs for use. We changed the mass of WPU to modulate the thickness of WPU&AgNWs film for studying its effect on energy output.

Characterization

The morphology of the surface and cross-section of the WPU&AgNWs film were investigated by using a field-emission scanning electron microscope (FE-SEM, JSM-7800F, Japan). Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was measured by using a FTIR spectrometer (IS10, Thermo, USA). The zeta potential of the WPU solution was measured by a Laser particle sizer (NanoBrook, 90Plus PALS, USA).

Electrical measurements

The electric signals of MEFGs (the actual test size of a single device is 5 mm × 5 mm) were collected in real-time through a Keithley 2450 under moisture. The voltage output test was set current into 0nA and the current output test was set voltage into 0mV. To avoid any interference from the static electricity, all the samples were short circuited before testing.

Washing and stretching tests

Place the device in a 20-ml silk-flask with 10ml deionized water and rotor, washing with 300 rpm for 20 minutes at a time, then remove and dry in a 60 ℃-blast oven for 30 min. The self-made stretch-recovery device as shown in Figure 5a was used to carry out the stretch-recovery cycle of different strains on MEG with an initial clamping distance of 5 mm and a stretch rate of 10 mm/min.

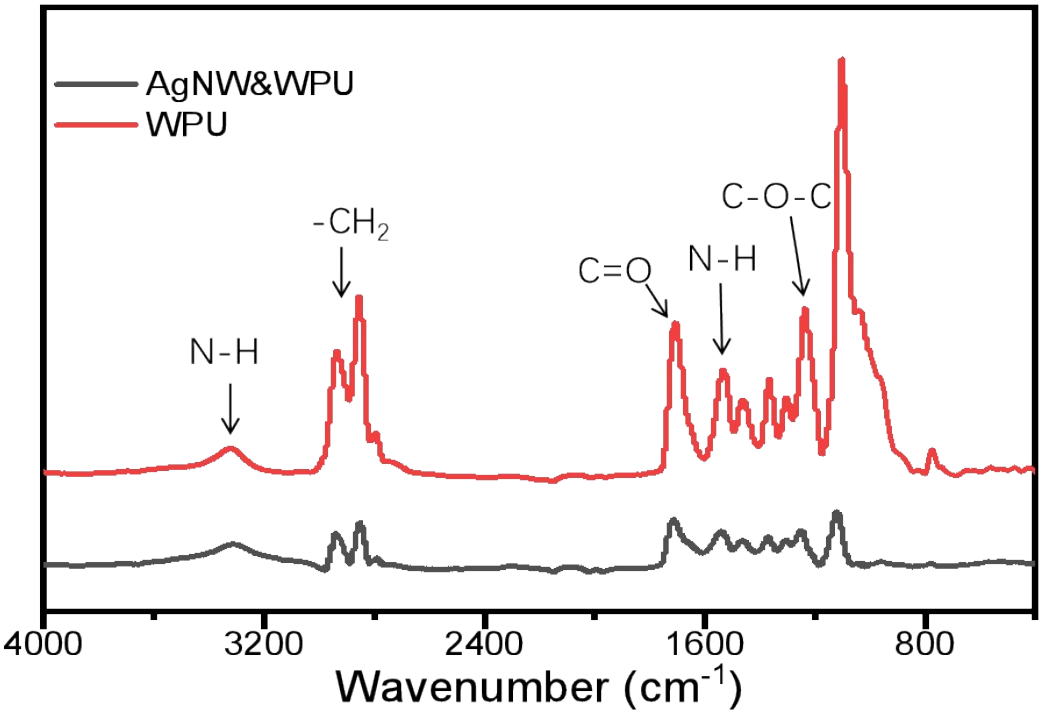

Fig. S1 FTIR spectra of WPU and WPU+AgNWs surfaces of MEG.

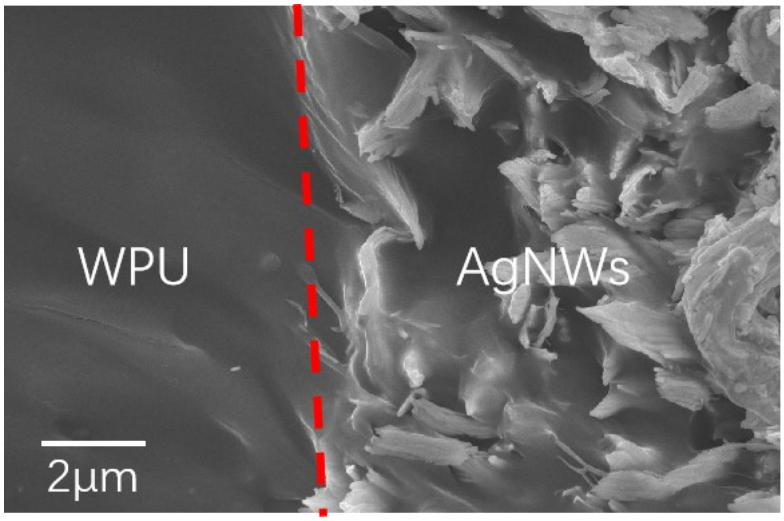

Fig. S2 The SEM cross-section image of the enlarged interface between WPU and silver nanowires.

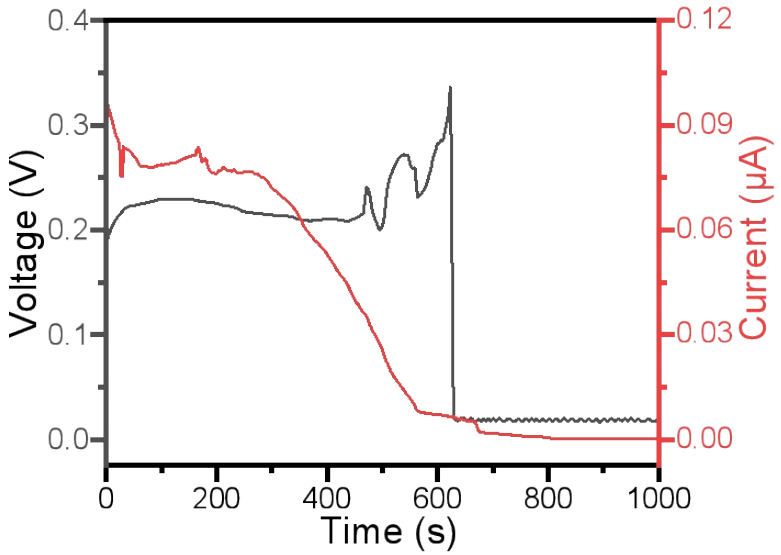

Fig. S3 Changes in voltage and current during the drying of a single device.

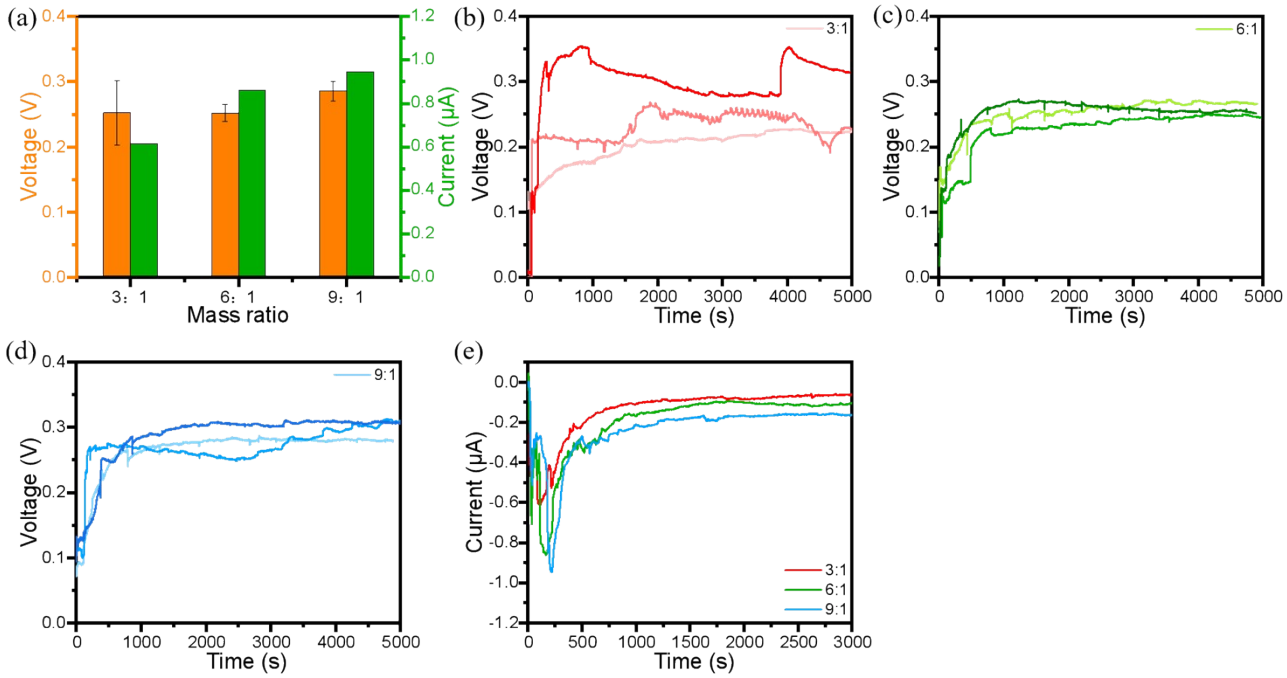

Fig. S4 (a) Electric performance as a function of varying mass ratios of WPU/AgNWs within the MEG. The MEFG voltage output (b-d) and current output (e) graphs of WPU and AgNWs with different mass ratios (3:1, 6:1, 9:1) were obtained.

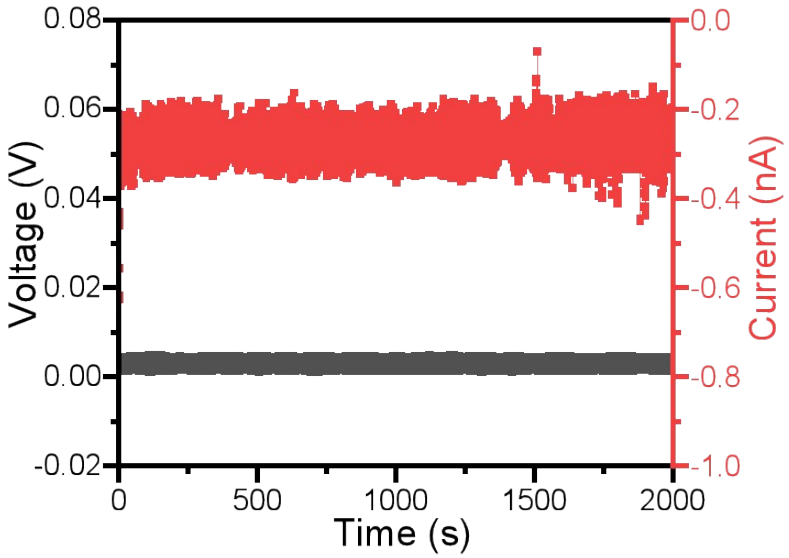

Fig. S5 The voltage output and current output of the MEG at 0% relative humidity and 20 ± 3 ℃.

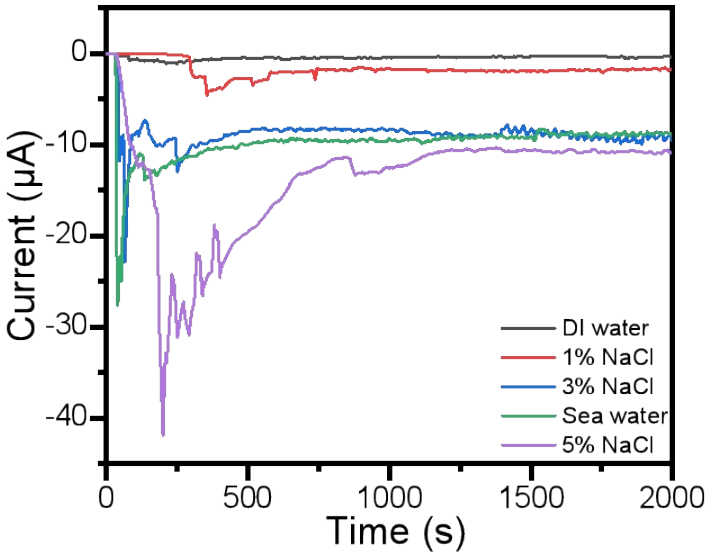

Fig. S6 Effect of humidification with different NaCl concentrations on short-circuit current of devices.

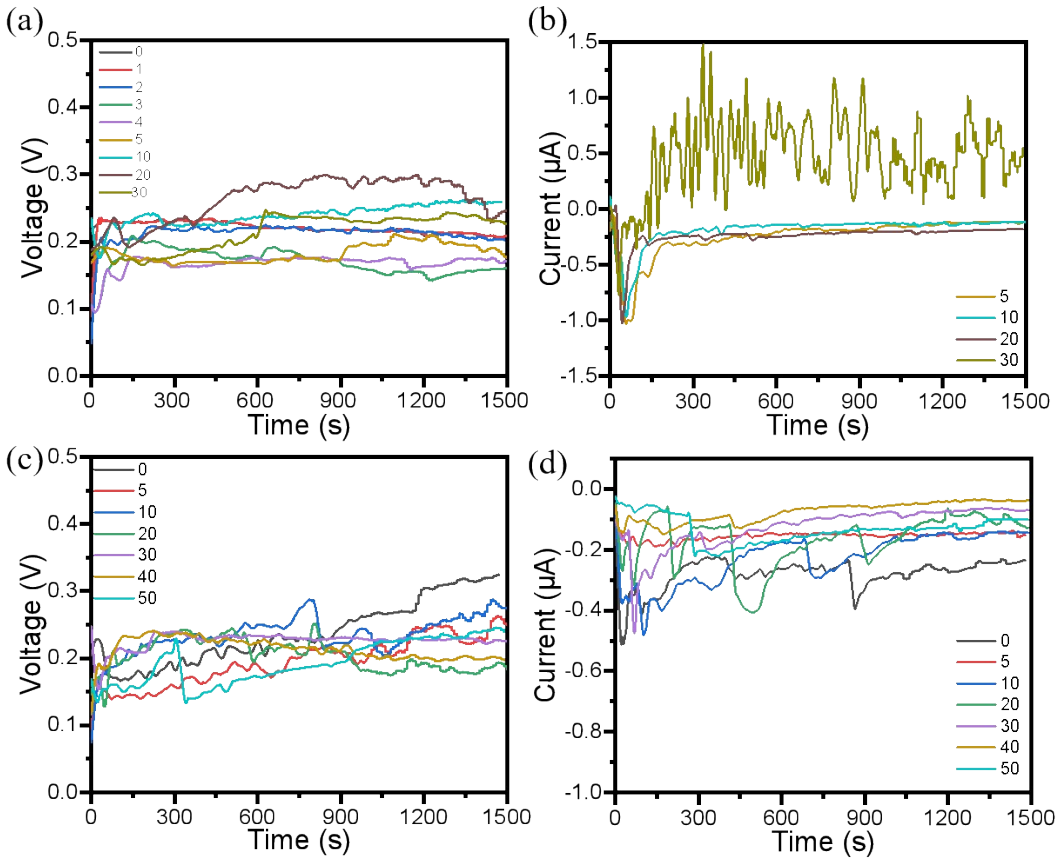

Fig. S7 Raw data of electrical properties of MEG after washing. (a) and (b) are the output voltage and current of a device with a thickness of 65 μm (w/w 3:1), respectively. (c) and (d) are the output voltage and current of a device with a thickness of 160μm (w/w 3:1), respectively. (w/w 9:1).

Table S1 Comparison of our MEFG with other MEG devices

Material	Open circuit Voltage (mV)	Short circuit Current density ($\mu A/cm^2$)	Test environment	Duration	Flexible	Stretchable	Reference
rGO/GO framework	450	0.9	85%	>500s		NO	[3]
PSSA	800	100	80%ΔRH	>1500s		NO	[4]
TEMPO-CNFs	110	25×10^{-3}	99%RH	>166 hours	YES	NO	[5]
GO/PAAS	600	12	80±5%RH	>120 hours		NO	[6]
Cationic SilkNFs/Negative SilkNFs Bilayer	120	/	99%RH	<40 minutes		NO	[7]
P(MEDSAHco-AA)	400	±1	100%RH	>2000s		NO	[8]
PVA-PA-Glycerol hydrogel	800	240	85%RH	>20 hours	YES	NO	[9]
Sodium alginate, SiO_2 and rGO composite	500	/	100%RH	>12000s	YES	NO	[10]
G.s. hybrid with carbon nitride polymer	350	2.8	90%RH	>20 hours	NO	NO	[11]
Coating multi-walled carbon nanotubes (MWCNTs) on a stretchable electrospun fiber mat composed of polysulfone (PSF) and polyurethane (PU)	419	/	10 μL water	>600s	YES	60%	[12]
MXene-cellulose nanocrystals (CNCs)-tamarind gum (TG)-polyacrylamide (PAM) hydrogel	164	/	90%RH	/	YES	2000%	[13]
Acrylamide (PAM), 2-acrylamide-2-methyl propane sulfonic acid (AMPS), and inorganic salt (LiCl).	810	480	80%RH	>3 hours	YES	506%	[14]
WPU	300	/	100%RH	>80hours	YES	100%（600%）	This work

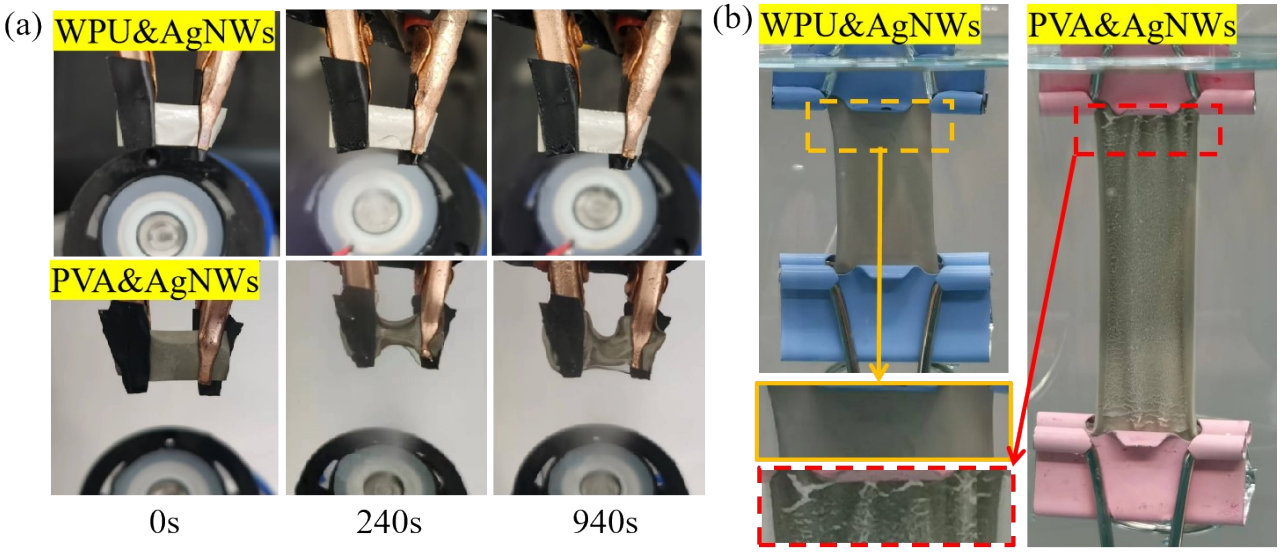

Fig. S8 Comparison of water tolerant stability of PVA&AgNWs and WPU&AgNWs films. (a) Under the moisture. (b) In water with 20g weight.

We can see in Fig. S5(a), PVA film is easy to deform while WPU film can keep good shape during humidification test. And Fig. S5(b) shows that when we put two kinds of films with 20g weight in a beaker, and then slowly pour water into the beaker, we find that PVA&AgNWs films rapidly deform after being submerged, and we can see the film surface has some cracks through the local magnification picture, which is the poor combination of AgNWs and PVA and poor water resistance of PVA caused. On the contrary, we can see that WPU&AgNWs film does not change in the water.

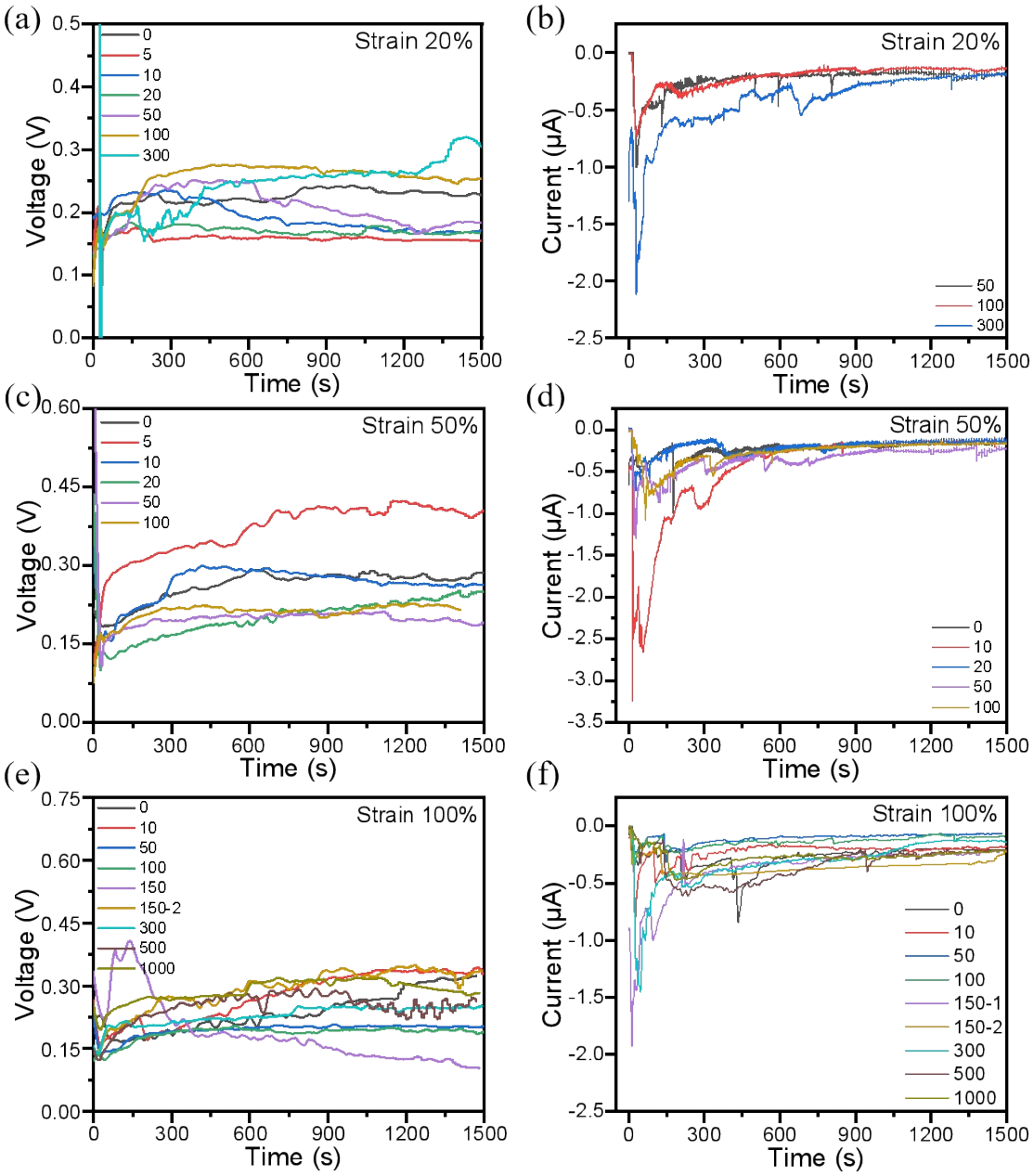

Fig. S9 The electrical output of MEG with different thickness and stretching cycles for strain of 20% to 100%. (a, b) 65μm, 20% strain, (c, d) 65μm, 50% strain, (e, f) 160μm, 100% strain. These are the raw data graphs for Fig. 5(d-f) in the paper.

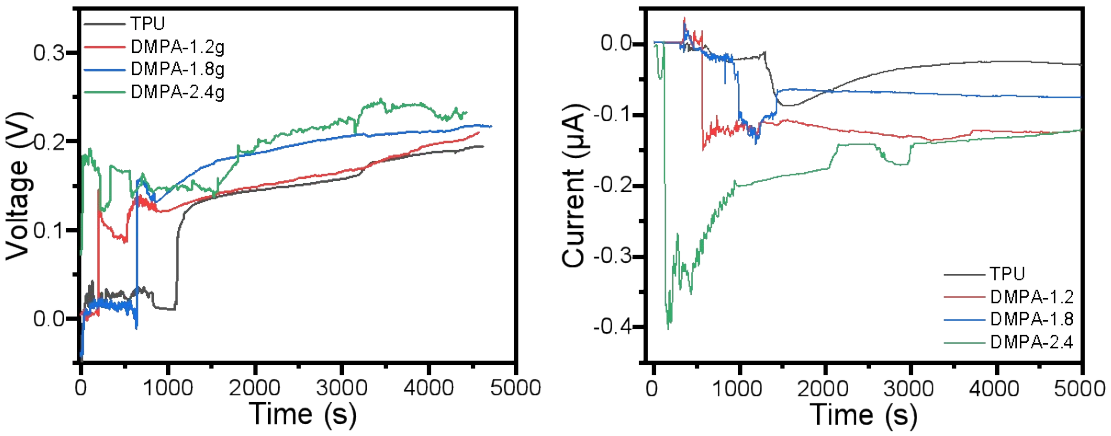

Fig. S10 (a) Voltage and (b) current output based on the MEG with different amounts of DMPA. TPU film and WPU film are used as power generation layer, and copper foil and test copper clip are used as electrodes respectively.

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