Supplementary information

A Triboelectric Generator Based on Self-poled Nylon-11 Nanowires Fabricated by Gas-flow Assisted Template Wetting

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S1. Crystal structure of Nylon-11

The crystal structure of Nylon-11 has been extensively studied due to their extensive degree of polymorphism.^{1–6} Nylon-11 displays several crystal structures depends on the processing condition as summarised below.

phase	Unit cell	Processing condition
α	triclinic	Solution casting using m-cresol
α'	triclinic	Melt & slow cooling / annealing of δ'
β	monoclinic	Precipitation from TEG solution
γ	monoclinic	Solution casting from TFA
γ	pseudo-hexagonal	Solvent treatment of α
γ'	pseudo-hexagonal	Solvent treatment of δ'
δ	pseudo-hexagonal	High temperature of α'
δ΄	(smectic) pseudo-hexagonal	Melt quenching

Table S1. Various crystal structures of Nylon-11

At room temperature, Nylon-11 have been demonstrated at least four crystalline forms (the triclinic α and α ', the monoclinic β , and the pseudo-hexagonal γ phase) and one smectic-like pseudo-hexagonal phase.⁷

In terms of electrical property, although all Nylon-11 has a polar crystal structure due to its molecular configuration, the electric polarisation can be maximised from a specific type of crystalline phase. In the case of the most stable and well-organized α -phase, Nylon-11 does not display remnant polarisation due to the strong hydrogen bond, which is originated from the highly-packed crystal structure. In contrast, the highest electric polarisation could be observed from the meta-stable pseudo-hexagonal phase (γ , γ' , δ , δ').^{8–10} Disordered, short-range hydrogen bond and breakage of gauche bonding originated from rapid crystallisation are likely to enable dipole reversal.¹⁰ Despite disordered configuration in the perpendicular direction to the chain and randomly oriented hydrogen bonds, pseudo-hexagonal phase shows more ordered crystalline structure along the chain direction, which was referred to be a smectic-like phase, with aligned amide groups.¹¹

S2. Cross-sectional SEM image



Figure S2. Cross-section SEM image of a nanowire-filled AAO template. White threads indicate the Nylon-11 nanowires, which are stretched during the template breaking process.

S3. Surface area of the nanowires in the template

The effective surface area of the nanowires was calculated by an image analyser using a SEM image of the bare AAO template.



Figure S3. The SEM image (a) was transformed into the black and white image (b). The number of black pixels (pores) were counted and divided by the total number of pixels (whole surface area of the template). As a result, the average effective area was calculated to be ~ 48.25 %.

S4. Theoretical calculation of the GANT method

Using COMSOL Multiphysics simulation, the simulation is demonstrated based on these three different effects: the turbulent flow of the assisted gas, heat transfer in all components, and the vaporisation of the solvent in the Nylon solution. For the turbulent flow, we assumed that the gas flow rate and pressure field are independent of the property of gas, such as moisture content level and temperature. Heat transfer in the model is considered to have two different aspects: conduction and convection. The heat transfer between the template wall and the solution is governed by conduction. In the gas flow, the heat transfer is originated from the convection and the effect of turbulent flow. The cooling effect during the solvent evaporation needs to be considered as well based on the heat of vaporisation H_{vap} . To calculate the amount of vaporised solvent to the air, the material transport equation is used with the turbulent flow as a diffusion coefficient.



Figure S4. The symmetry geometry used in the simulation.

The geometry was built based on the experimental conditions. (Figure S4) The inner diameter and thickness of the nanopore is 200 nm (measured from SEM images) and 100 nm, respectively. The height of the nanopore is assumed 5 μ m filled with 70 °C formic acid with H_{vap} of 23.1 kJ/mol. The assisted gas is air with an initial temperature of 20 °C and enters to the right side of the geometry. The inlet velocity of the turbulent flow was set by the gas flow rate.

S5. DSC thermogram



Figure S5. DSC thermogram of template-freed δ' -phase nanowire during the first heating with glass transition temperature Tg and melting temperature Tm.

S6. Polymer crystallisation mechanism in the nano-pores



Figure S6. Schematic of the polymer crystallisation process in the nano-dimensional pore of the GANT infiltration method.

S7. The degree of crystallinity

Using the average data of the four distinct DSC peaks of Nylon-11, the crystallinity was calculated by means of the equation

Crystallinity (%) =
$$\frac{\Delta H_m}{\Delta H_m^0} \times 100$$
 (%)

where ΔH_m and ΔH_m^0 are the equilibrium heat of fusion enthalpies of the semi-crystalline Nylon-11 samples and the perfect crystalline Nylon-11 ($\Delta H_m^0 \sim 189 \text{ J/g}$)¹², respectively. ΔH_m is achieved from the area under the DSC melting peak. The results of the calculations are given in table below.

Table S7. Enthalpy of fusion and degree of crystallinity of various morphologies of Nylon-11

	Film	Stretched film	Nanowire
ΔH_m (J/g)	54	76	74
Crystallinity (%)	29	40	39

Typically, the degree of crystallinity of melt-quenched films is usually around 30 % since the rate of crystallisation is very fast compared to other polymers.^{10,12} The crystallinity of δ' -phase nanowires is similar to the crystallinity of stretched film due to the self-stretching effect.

S8. FT-IR measurement condition



Figure S8. Schematic of the FT-IR samples: (a) stretched film and (b) template-freed nanowires mat. The IR spectra direction (red arrow) for the FT-IR measurement with the draw direction of the polymer materials (grey arrow).

S9. Theoretical calculation of TENG device



To confirm the working mechanism of the self-poled nanowire based TENG, we carried out a theoretical analysis based on Gauss theorem.^{13,14} In the dielectric-to-dielectric contact mode TENGs, the electric potential difference (ΔV) between two electrodes can be given by

$$\Delta V = E_1 t_1 + E_2 t_2 + E_{air} d$$

$$= \left[-\frac{Q}{S\varepsilon_0 \varepsilon_{r_1}} t_1 \right] - \left[\frac{Q}{S\varepsilon_0 \varepsilon_{r_2}} t_2 \right] + \left[\frac{S\sigma - Q}{S\varepsilon_0} d \right]$$

$$= -\frac{Q}{S\varepsilon_0} \left(\frac{t_1}{\varepsilon_{r_1}} + \frac{t_2}{\varepsilon_{r_2}} + d \right) + \frac{\sigma d}{\varepsilon_0}$$
(1)

where *E* is electric field strength, t_1 and t_2 are the thickness of the two surfaces, *d* is the distance between two different layers, *Q* is the value of transferred charges, *S* is the area of the electrode, σ is the triboelectric charge density, ε_0 is the vacuum permittivity, and ε_{r1} and ε_{r2} are the relative permittivity (dielectric constant) of dielectric materials, respectively. In the conductor-to-dielectric structure, t_1/ε_{r1} can be ignored because the metal layer acts as triboelectric layer and electrode.

Under open-circuit conditions, the value of transferred charges (Q) become zero since no charge is transferred between the two top and bottom electrodes. Thus, if we assume electric potential of the bottom electrode to be zero, the equation for the open-circuit voltage (V_{oc}) can be calculated by

$$V_{oc} = \frac{\sigma d}{\varepsilon_0} \tag{2}$$

Using experimentally determined V_{oc} of each TENGs, we can obtain a theoretical triboelectric charge density (σ).

$$\sigma = \frac{V_{oc}\varepsilon_0}{d} \tag{3}$$

When d is maximum (0.5 mm) and σ of aluminium, the melt-quenched Nylon film, and the nanowire-filled template are 0.78, 1.06, and 1.95 μ C m⁻², respectively.

A COMSOL Multiphysics simulation demonstrated the triboelectric potential difference of three different structure TENGs with Teflon as the top part and: (a) aluminium, (b) Nylon film, and (c) nanowires in the template as the bottom parts. We assumed that the length of the dielectric and electrodes are infinite because they are significantly larger than the thickness of the dielectric layer. The nanowire-filled alumina template structure (c) was simplified in the simulation, considering the surface area of the nanowires (~ 50 %). Because of the charge density (σ) difference, the nanowire sample (c) shows the highest potential different between the top and bottom electrodes. In addition, the self-poled Nylon nanowire region exhibits relatively higher electric potential than the alumina template region. It indicates that further enhanced triboelectric performance of nanowires.



The ideal electric potential of self-poled Nylon-11 nanowire based TENGs can be calculated based on the experimental result of remnant polarisation.¹⁵

Under short-circuit conditions (V = 0), the transferred charges (Q_{sc}) are given by

$$Q_{sc} = \frac{S\sigma d\varepsilon_{r1}\varepsilon_{r2}}{t_1\varepsilon_{r2} + d\varepsilon_{r1}\varepsilon_{r2} + t_2\varepsilon_{r1}}$$
⁽⁴⁾

The value of Q_{sc} can therefore be varied as a function of d. When the generator is fully released (d = 0.5 mm), the maximum transferred charges per unit area was theoretically calculated to be 0.65, 0.94, and

1.75 μ C m⁻² for aluminium, melt-quenched Nylon film, and the nanowire-filled template, respectively. The transferred charges (Q_{sc}) are also calculated using the integration of short-circuit current (I_{sc}).



The dimensions in the table below were used for the calculation.

Table S9. Dimensions of the TENG devices

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Symbol	Meaning	Value	unit
d	max. separation distance	0.5	mm
t_l	thickness of PTFE	100	μm
t_2	thickness of Nylon film & AAO template	60	μm
S	surface area of the electrode	3.14	cm^2
$V_{OC,Al}$	V_{OC} of aluminium based TENG	40	V
$V_{OC, film}$	V_{OC} of melt-quenched film based TENG	60	V
$V_{OC,NW}$	V_{OC} of Nylon NW filled template based TENG	110	V
ε_0	vacuum permittivity	8.85E-12	F / m
$\mathcal{E}_{r.film}$	relative permittivity of Nylon-11 film ^{16,17}	3.7	
$\mathcal{E}_{r.AAO}$	relative permittivity of AAO template	9	
$\mathcal{E}_{r.NW}$	relative permittivity of oriented Nylon ^{16,17}	4.5	
$\mathcal{E}_{r.PTFE}$	relative permittivity of PTFE	2.1	
P_r	remnant polarization of Nylon-1115	55	mC / m ²

S10. Output performance as a function of different load resistances



Figure S10. The gradual increase and a decrease of voltage and current density across the various load resistors, respectively: a) nanowires filled template, b) melt-quenched film and c) aluminium based TENGs. The power density is calculated by the multiplication of current density squared and load resistance.

S11. Various input condition



Figure S11. TENG performance under various input condition. Short circuit current density of the nanowire device was measured under the application of a periodic impacting force a) at variable frequency between $2 \sim 20$ Hz with amplitude of 6 V and b) at different amplitude between $3 \sim 12$ V with frequency of 5 Hz. In our energy generator system, force amplitude of magnetic shaker can be controlled by applied voltage.



Figure S12. Device Reliability test. a) Fatigue testing: short circuit current density recorded over time in response to continuous impacting at a frequency of 5 Hz and amplitude of 6 V on the same Nylon-11 nanowire based TENG device for 30 h (~ 540,000 cycles impacting cycles in total). Data were recorded after 2 h (18 k cycles), 5 h (90 k cycles), 10 h (180 k cycles), 20 h (360 k cycles), and 30 h (540 k cycles). b) TENG device performance under various humidity condition. The maximum (orange) and minimum peak of short circuit density were collected at certain humidity. (right image)

S13. Template freed nanowire



Figure S13. a-c) SEM images of a template freed nanowire mat. The inset illustrates the random direction of the remnant polarisation. d) and e) show the output performance of the nanowire mat based TENG device.

S14. LEDs operation



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