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Supporting Information

On the Enhancement of Contact Electrification of Piezo-Assisted Triboelectric Nanogenerators via Control of Piezoelectric Polarization

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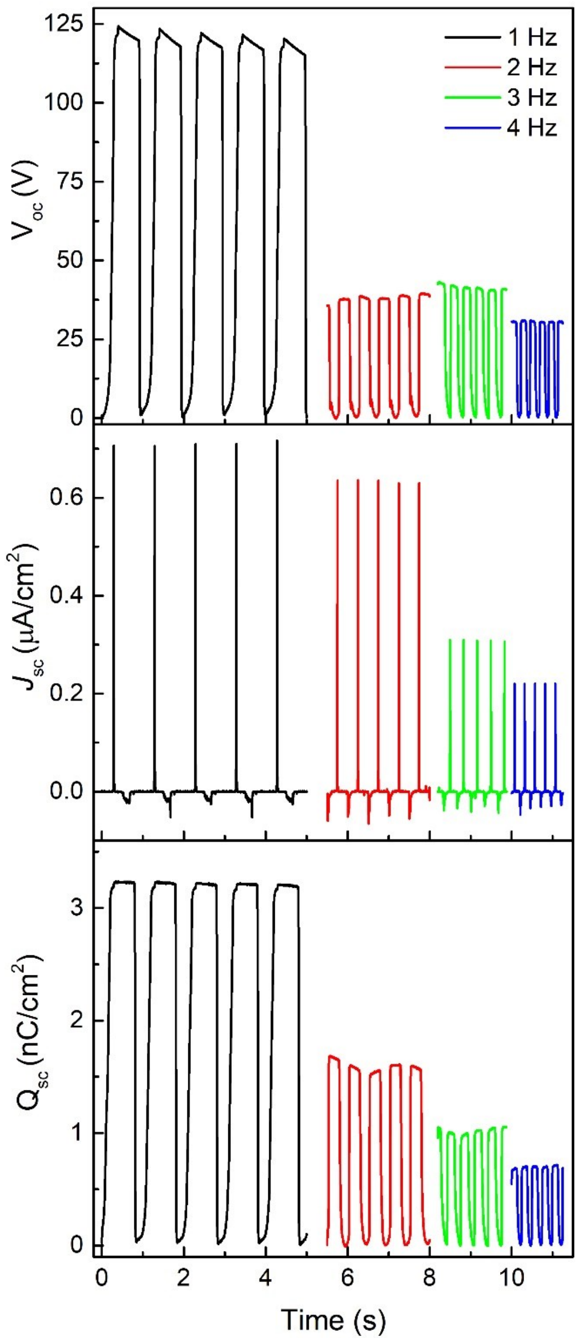
Figure S1 V_{oc}, J_{sc}, and Q_{sc} of the TENG PVA with silicone rubber under different frequencies ranging from 1 Hz to 4 Hz.



The electrical outputs of the TENG PVA with silicone rubber were tested under different frequencies ranging from 1 Hz to 4 Hz to mimic the frequency of human motion. The frequency of 1 Hz yielded the highest electrical output, hence this frequency was chosen to be used in the electrical output measurements of the P-TENGs.

Figure S2 V_{oc}, J_{sc}, and Q_{sc} of the TENGs: non-polarized P(VDF-TrFE) with silicone rubber, PTFE with silicone rubber, PMMA with silicone rubber and PVA with silicone rubber.

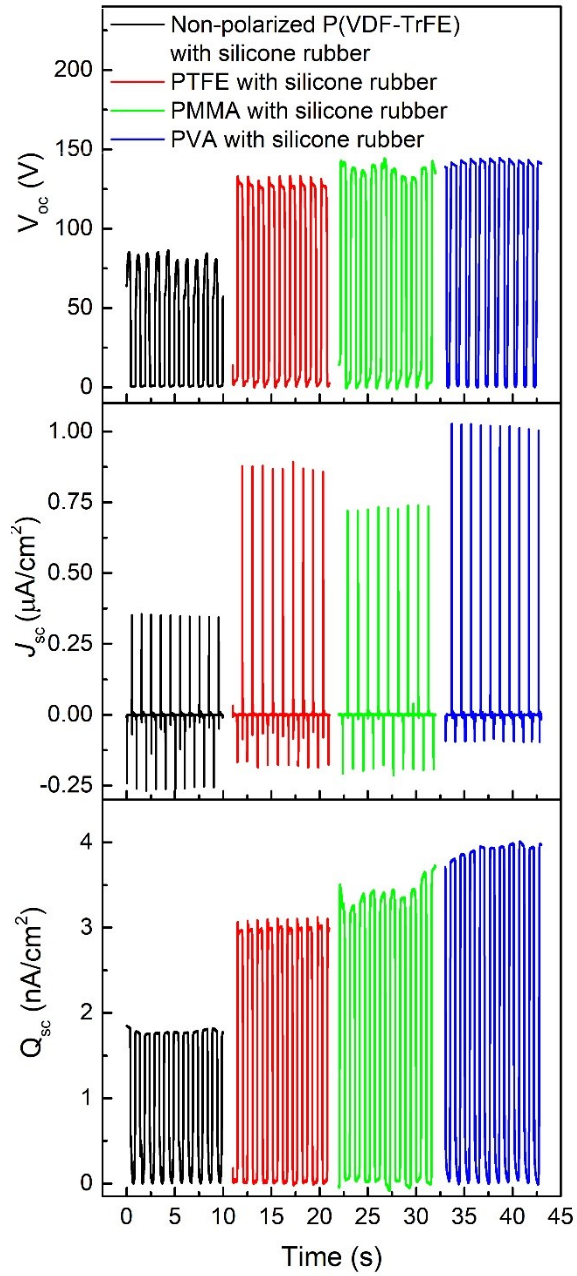


Figure S2 shows the electrical outputs of four TENGs made up of different triboelectric pairings. Silicone rubber was used as the control tribonegative material due to its extreme electronegativity, and it is paired against non-polarized P(VDF-TrFE), polytetrafluoroethylene (PTFE), poly(methyl methacrylate) (PMMA) and PVA. It is observed that among the four TENGs, the pairing of PVA with silicone rubber exhibits the highest electrical outputs, with V_{oc} of 140 V, J_{sc} of 1.1 μA/cm^2 and Q_{sc} of 4 nA/cm^2. The results suggest PVA and silicone rubber are ranked the furthest apart in the triboelectric series. Hence, they were respectively chosen as the tribopositive and tribonegative materials for this study.

Figure S3 Wide range XRD pattern of P(VDF-TrFE).

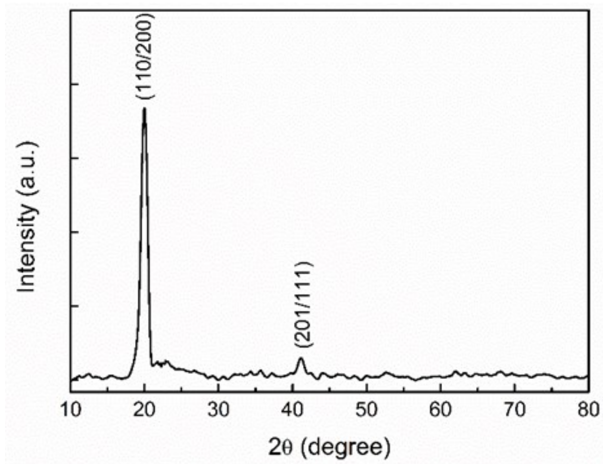


Figure S3 shows two β crystalline phase peaks at 2θ = 19.90° and 41°. The first peak is assigned to the (110/200) reflections and the latter is assigned as (201/111) reflections.

Figure S4 Scanning electron microscopy (SEM) images of the surface morphology of (a) P(VDF-TrFE) annealed at 120 °C; (b) as-cast PVA and (c) silicone rubber.

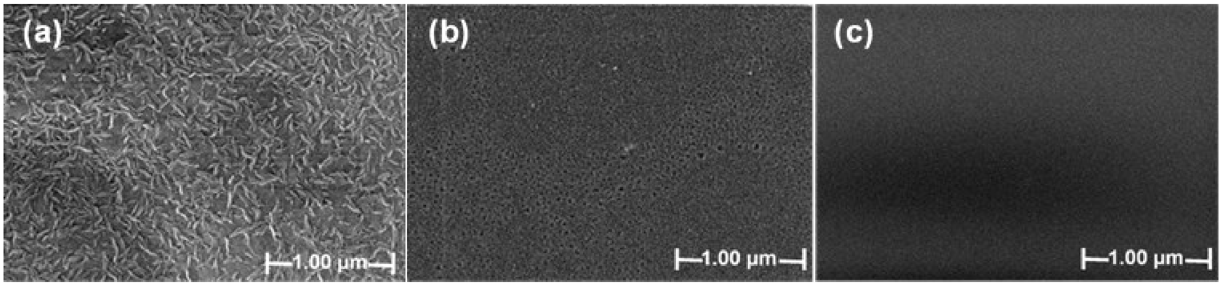


Figure S4 (a) shows the surface morphology of the P(VDF-TrFE) annealed at 120 °C using SEM at 30k magnification. Rod-like crystals are observed suggests that small crystallites undergo a transition into a paraelectric phase. Crystals grew by incorporating surrounding non-crystalline molecules and thus contributed to an increase in the crystalline structure. Figure S4 (b) and (c) show the surface morphology of PVA and silicone rubber, respectively. The average pore size of around 30 nm was measured from SEM micrograph for PVA; whereas relatively smooth surface was observed in silicone rubber.

Figure S5 Effect of piezoelectric polarization strength on the electrical outputs of P-TENGs comprising of (a) PVA with forward-polarized P(VDF-TrFE) (b) reverse-polarized P(VDF-TrFE) with silicone rubber

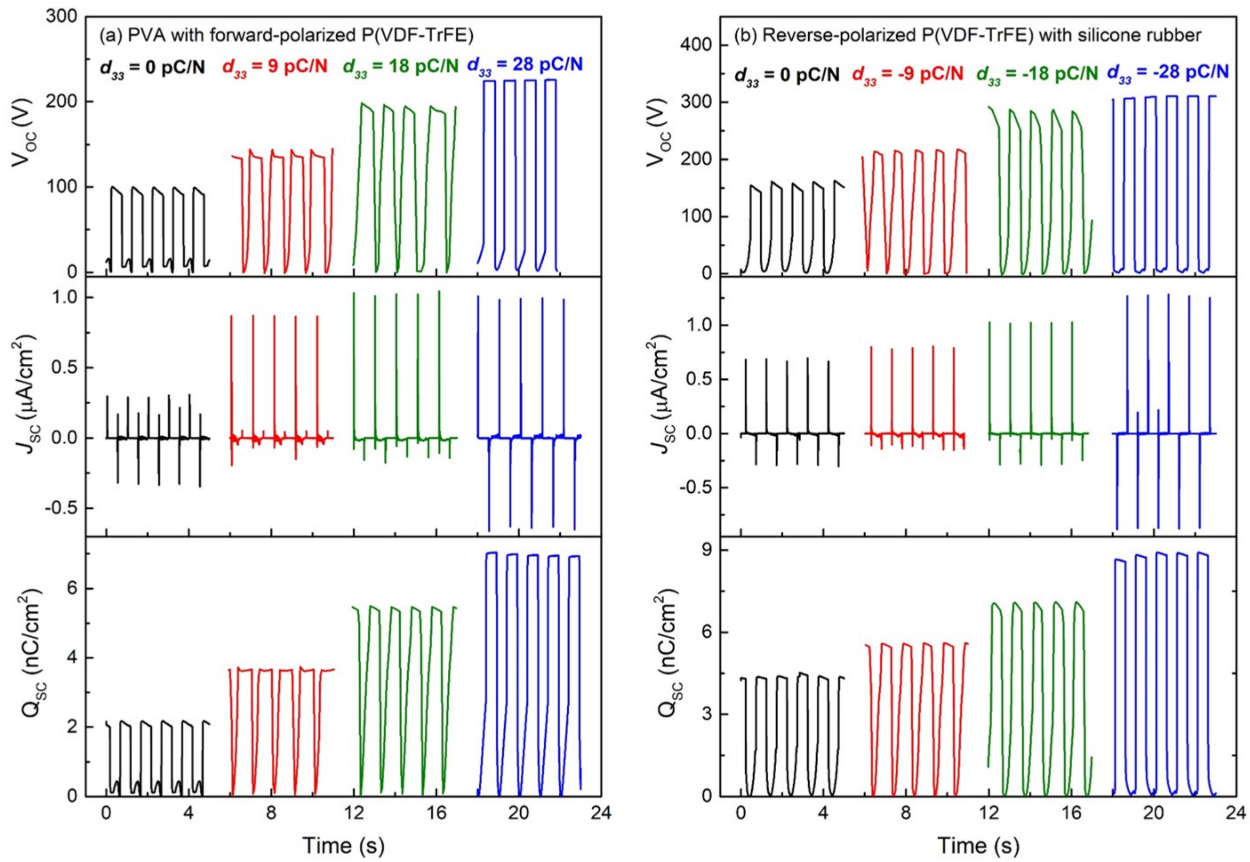


Figure S5 shows the effect of different d_{33} magnitudes on the electrical outputs of the two P-TENGs, i.e. PVA with forward-polarized P(VDF-TrFE) and reverse-polarized P(VDF-TrFE) with silicone rubber. In the P-TENG of PVA with forward-polarized P(VDF-TrFE), the d_{33} values are positive because the piezoelectric polarization is pointing towards the contact surface. All the characterized electrical outputs are increased when the magnitude of d_{33} increases from 0 pC/N to 28 pC/N, which is the maximum obtainable value. On the other hand, in the P-TENG of reverse-polarized P(VDF-TrFE), the d_{33} values are negative because the piezoelectric polarization is pointing away from the contact surface. A similar trend is also observed in this P-TENG, where the increase in the magnitude of d_{33} results in a larger electrical outputs. This indicates that a larger piezoelectric polarization will give a larger enhancement to the electrical output in the P-TENG. The increase in piezoelectric polarization strength will give rise to a larger intrinsic electric field, E_P, causing a larger shift in the electron energies of P(VDF-TrFE). Hence, the difference between the highest electron energies of the two materials, ΔE, will be larger, resulting in more enhanced electron transfer during contact electrification (CE). Thus, there will be more triboelectrically-induced charges when the piezoelectric polarization strength is larger, resulting in larger electrical outputs. Note that a constant force of 100 N with maximum separation distance of 10 mm was applied on this measurement.

Figure S6 Effect of separation distance, d, on the electrical output of the P-TENG consisting of reverse-polarized P(VDF-TrFE) with silicone rubber.

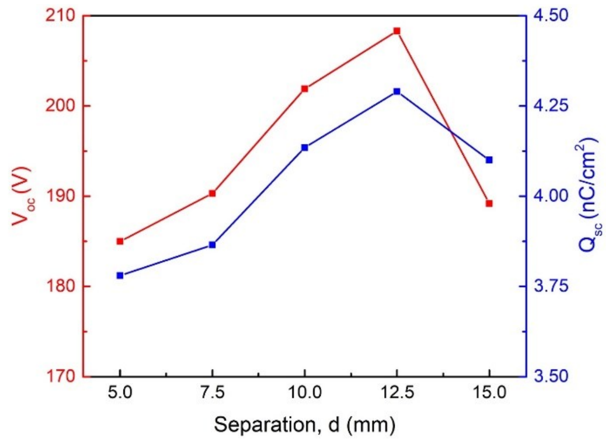


Figure S6 shows the effect of different separation distances, d, on the open-circuit voltage and short-circuit charge of the P-TENG consisting of reverse-polarized P(VDF-TrFE) with silicone rubber. A constant force of 25 N at 1 Hz was applied throughout the measurement of electrical outputs. It was noted that at 25 N, the optimum distance was 12.5 mm, where the highest open-circuit voltage and short-circuit charge were recorded. The decrease of electrical outputs after 12.5 mm is due to the weakening attractive forces between the oppositely charged contact surfaces, resulting in a smaller electric field. Note that a constant force of 25 N was applied to allow maximum separation distance of 15 mm due to the experimental set-up limitations.

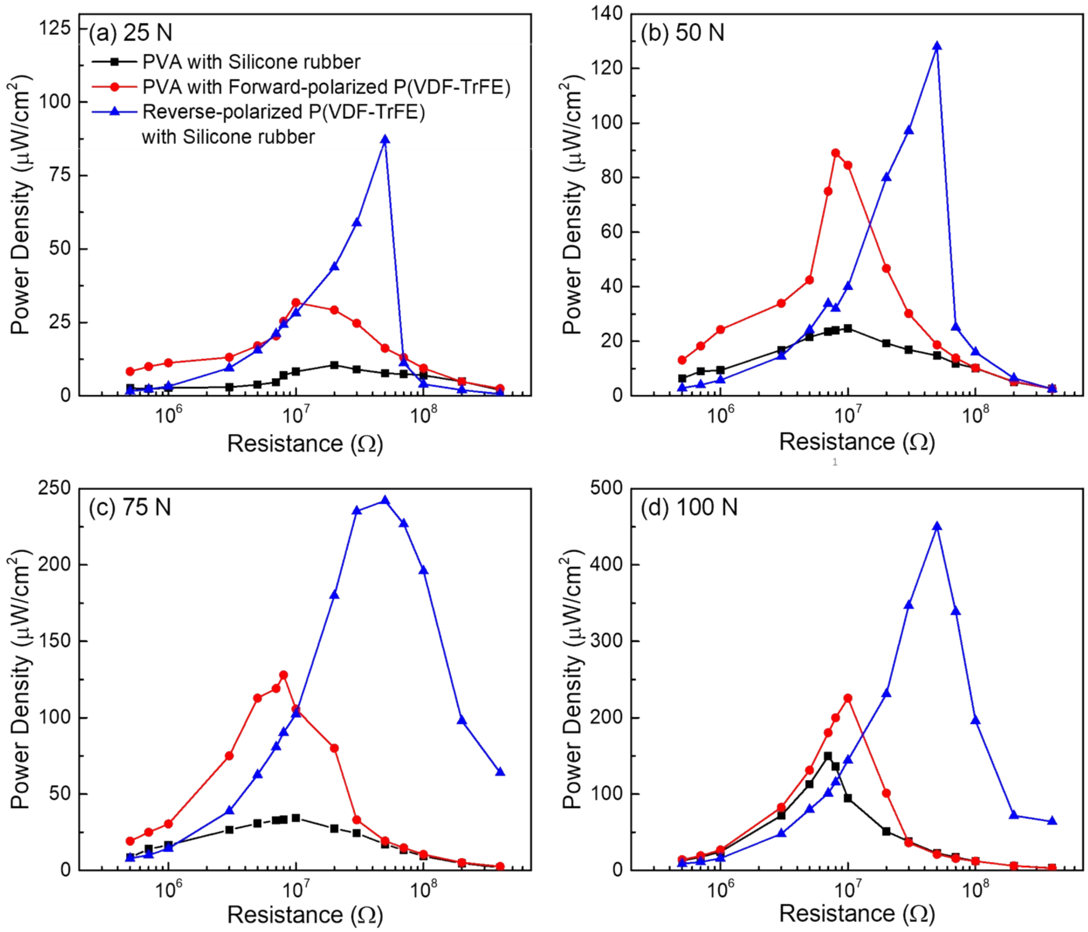
Table S1 **A** list of triboelectric pairings used in determining the effect of piezoelectric polarization of P(VDF-TrFE) on the electrical output of P-TENG.

No.	**Triboelectric pairing of P-TENGs**	
	Tribopositive	**Tribonegative**
(i)	PVA	Non-polarized P(VDF-TrFE)
(ii)	PVA	Forward-polarized P(VDF-TrFE)
(iii)	PVA	Reversed-polarized P(VDF-TrFE)
(iv)	Non-polarized P(VDF-TrFE)	Silicone rubber
(v)	Forward-polarized P(VDF-TrFE)	Silicone rubber
(vi)	Reversed-polarized P(VDF-TrFE)	Silicone rubber

Table S2 Parameters used in calculation of triboelectrically induced surface charge densities.

	Parameters
PVA	d = 150 µm, ε = 3.5 measured at 1kHz
P(VDF-TrFE)	d = 50 µm, ε = 10 measured at 1kHz
Silicone rubber	d = 30 µm, ε = 5 measured at 1kHz
Maximum height	H_{max} = 1 cm

Figure S7 Comparison of power densities of various NGs for externally connected load resistances at (a) 25 N, (b) 50 N, (c) 75 N and (d) 100 N.



The impedances of the NGs used in this study are as follows:

PVA with silicone rubber: 7 MΩ to 20 MΩ

PVA with forward-polarized P(VDF-TrFE): 8 MΩ to 10 MΩ

Reverse-polarized P(VDF-TrFE) with silicone rubber: 50 MΩ