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1 **A Review of Material Design for High Performance Triboelectric Nanogenerators:**
2 **Performance Improvement Based on Charge Generation and Charge Loss**

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9
10 **Abstract:**

11 As a type of innovative device, triboelectric nanogenerators (TENGs) are capable
12 to convert mechanical energy into electrical energy through the triboelectric effect.
13 Based on the working mechanism, the output performance of TENGs heavily relies on
14 the triboelectric materials used. The modification of triboelectric materials is the most
15 efficient way to improve the TENGs' output performance. Herein, this review focuses
16 on the recent progress in triboelectric material design for high performance TENGs.
17 Firstly, the basic theory of TENGs is introduced. Second, the relationship between the
18 triboelectric materials and the TENGs' output performance is summarized in detail
19 based on a theoretical model of triboelectric charge dynamic equilibrium. Furthermore,
20 the relevant strategies are analyzed in detail. Finally, the challenges and shortcomings
21 of the triboelectric materials for high performance TENGs are pointed out. This review
22 provides the research basis for the research status and future development of
23 triboelectric materials.

24



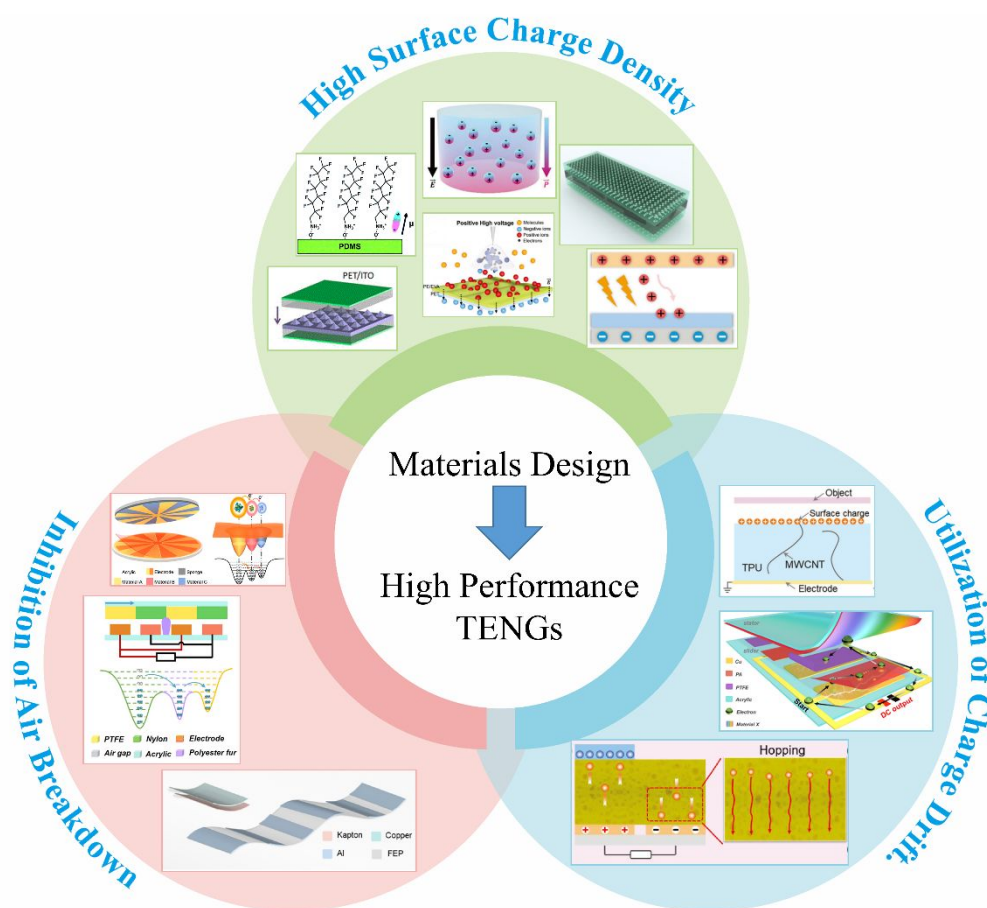
1 1 Introduction

2 Since the 21st century, the increasing demand for energy in human society has led
3 to the extensive use of fossil fuels such as coal, oil, and natural gas, resulting in
4 increasingly serious carbon emissions and environmental issues.^{1, 2} In recent years,
5 renewable energy, including solar energy, biological energy, ocean energy, thermal
6 energy, wind energy, and chemical energy, has gradually increased its share in society
7 due to its advantages of low carbon emissions and minimal environmental pollution.³⁻⁵
8 Various energy harvesting devices have been designed to collect different types of
9 renewable energy, such as electromagnetic generators (EMGs), solar cells,^{6, 7}
10 thermoelectric generators,^{8, 9} piezoelectric nanogenerators (PENGs),¹⁰⁻¹² triboelectric
11 nanogenerators (TENGs)¹³⁻¹⁶ and so on. Based on the coupling effect of
12 triboelectrification and electrostatic induction, TENGs were first invented by Wang's
13 group in 2012 and have attracted more attention among these devices for collecting
14 energy due to its simple design, high voltage output, low cost, wide materials selection,
15 and high energy conversion efficiency at low frequencies.¹⁷⁻²¹ Their seminal work laid
16 the foundation for further exploration of TENGs. Since its invention, TENGs have
17 developed rapidly with contributions from researchers all over the world and have
18 become an idea for energy harvesting technology to be applied in various applications
19 such as micro/nano power sources, self-powered sensing, blue energy harvesting, and
20 high-voltage power sources.²²⁻³³ Despite significant progress, the practical application
21 of TENGs is seriously hindered by its low output power and energy conversion
22 efficiencies.

23 Over the years, the improved output performance of TENGs has been significantly
24 propelled by advancements in mechanical structure design and power management.³⁴⁻



1 ³⁸ However, the TENG's output performance greatly depends on the dynamic
 2 equilibrium of triboelectric charge generation and charge loss; thus, it is not sufficient
 3 to further improve the TENGs' output by simply increasing triboelectric charge
 4 generation.³⁹ Triboelectric materials play a crucial role in determining the output
 5 performance of TENGs, as it directly influences triboelectric charge generation and
 6 charge loss.⁴⁰ Therefore, it is pivotal to study the working mechanisms of triboelectric
 7 materials in charge generation and charge loss to further improve the energy harvesting
 8 efficiency and expand the application range of TENGs.



9 **Figure 1.** Schematic overview of the strategies to improve the output performance of TENGs. Reprinted
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7 Here, various material design strategies that improve the output performance of
8 TENGs will be introduced accordingly, as shown in **Figure 1**. First, the basic working
9 modes of TENGs and the basic theory of TENGs are briefly introduced. Second, the
10 theoretical model of triboelectric charge dynamic equilibrium is described, and the
11 relationship between the triboelectric materials and the TENGs' output performance is
12 summarized. Then, the relevant material-design strategies for improving the output
13 performance of TENGs are described in detail, including surface engineering,
14 inhibition of air breakdown, and utilization of charge drift. Finally, the current
15 challenges in augmenting the output performance of TENGs have been discussed, and
16 a brief perspective on future opportunities has also been provided.

17 **2 Basic Working Principle of TENGs**

18 **2.1 Basic Working Modes of TENGs**

19 TENGs typically generate transferred charge through the physical contacts
20 between two different types of materials.⁵²⁻⁵⁴ Such transfer charge between two
21 materials can be attributed to the interaction of their electron clouds.^{55, 56} TENGs have
22 four basic working modes: vertical contact-separation (CS) mode, lateral-sliding (LS)
23 mode, single-electrode (SE) mode, and freestanding triboelectric-layer (FT) mode.^{40, 57-}



1 ⁵⁹ The working principle of the vertical CS-mode TENGs is shown in **Figure 2a**. When
2 two different types of triboelectric materials come into contact, opposite triboelectric
3 charges generate on the surface of the dielectric material due to contact electrification
4 (**Figure 2a(i)**). When the two materials are separated by external mechanical force,
5 the triboelectric charges generated by contact electrification also separate and create an
6 induced potential difference on the electrodes of the corresponding material, thereby
7 causing a current pulse in the external circuit (**Figure 2a(ii)**). When the two materials
8 are subjected to separation and contact under an external force, the potential difference
9 between the electrodes disappears, the electrons flow back to the original electrode, and
10 a reverse current pulse occurs in the external circuit (**Figure 2a(iv)**). By repeating this
11 contact-separation process, TENGs can continuously generate alternating current
12 output in the external circuit.

13 The other three working modes are shown in **Figure 2b-d**. In the case of SE mode
14 (**Figure 2b**), when the triboelectric material approaches or leaves the electrode, charges
15 will transfer from the electrode to the tribo-layer with high electron withdrawing ability.
16 As a result, an induction current is created in the electrode to balance the electrical
17 potential. This mode has only one electrode and allows the triboelectric materials to
18 move freely, which simplifies the device structure and makes integration with other
19 electronic devices or systems easier.⁶⁰⁻⁶³ **Figure 2c** shows a schematic diagram of the
20 LS mode TENGs. The LS mode TENGs are based on the contact sliding between two
21 tribo-layers. When the two tribo-layers slide against each other under external force,
22 the charges on the tribo-layers also separate and create a potential difference between
23 the two electrodes. When the external circuit is connected, due to the existence of a
24 potential difference, electrons will flow from one electrode to the other, forming an



1 electric current. Therefore, the LS mode TENGs is able to collect many forms of
 2 mechanical energy, such as human movement and mechanical vibration, and convert it
 3 into electrical energy for driving small electronic devices.⁶⁴ The schematic diagram of
 4 FT mode TENGs is shown in **Figure 2d**. The reciprocating slide of the independent
 5 tribo-layer on two stationary tribo-layers will cause a potential difference between two
 6 bottom electrodes, which drives electrons to flow back and forth between the two
 7 electrodes through an external circuit load. In this mode, the triboelectric charge can
 8 remain on the surface of the tribo-layer for a longer period, which enables stable output
 9 and high energy conversion efficiency.^{65, 66}

10 2.2 Basic Theory of TENGs

11 The theoretical source of TENGs comes from Maxwell's displacement current. In
 12 general, Maxwell's displacement current can be defined as follows:

$$13 \quad J_D = \frac{\partial \mathbf{D}}{\partial t} = \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} \quad (1)$$

14 where \mathbf{D} is the displacement field, \mathbf{E} is the electric field, \mathbf{P} is the electric field, and ε_0 is
 15 vacuum permittivity. However, in the case of TENGs, triboelectric charges generated
 16 by the physical contact between two different materials also contribute to the
 17 displacement current.⁶⁷ Therefore, to account for the influence made by triboelectric
 18 charges, Wang et al. added an additional polarization density term \mathbf{P}_S in \mathbf{D} and extended
 19 Maxwell's equations.^{68, 69} The specific Maxwell's displacement current in TENGs is as
 20 follows:

$$21 \quad J_D = \frac{\partial \mathbf{D}}{\partial t} = \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \frac{\partial \mathbf{P}_S}{\partial t} \quad (2)$$

22 The first two terms on the right side of Eq. 2 are induced currents generated by changing
 23 electric fields, which is the theoretical basis of electromagnetic wave existence.^{70, 71} The



1 final term is the current caused by the polarization field generated by the electrostatic
2 charge on the surface, which is the theoretical source of TENGs.²⁰

3 To predict the output behavior of TENGs, researchers have proposed several
4 theoretical models.⁷²⁻⁷⁵ Here, as the CS mode is the most commonly designed, taking
5 the CS mode as an example, the basic output parameter of TENGs can be deduced by
6 a planar plane capacitance model (**Figure 2e**).⁷³ As shown in **Figure 2e**, the vertical CS
7 mode normally consists of two electrodes and two tribo-layers. The two tribo-layers
8 have thickness of d_1 and d_2 and dielectric constants of ε_1 and ε_2 , respectively. The
9 distance between two tribo-layers is defined as $x(t)$ and changed by the external
10 mechanical force. When the two tribo-layers are contacted by an external force, the
11 inner surface of the two tribo-layers will produce the same amount of positive and
12 negative charge, respectively. During the separation of the two tribo-layers, an air gap
13 is formed between the two tribo-layers, and the induced potential (V) between the two
14 electrodes is generated. The transferred charge between metal 1 and metal 2 is Q . By
15 using Gauss's theorem, the induced potential (V) between the two electrodes can be
16 given by:⁷³

$$17 \quad \begin{aligned} V(t) &= E_1 d_1 + E_2 d_2 + E_{\text{air}} x \\ &= -\frac{Q}{S\varepsilon_0} \left[\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2} + x(t) \right] + \frac{\sigma}{\varepsilon_0} x(t) \end{aligned} \quad (3)$$

18 where ε_0 is vacuum permittivity, E_1 , E_2 , and E_{air} are the electric field intensity inside
19 dielectric 1, dielectric 2, and the air gap, respectively. From Eq. 3, at an open-circuit
20 condition, there is no charge transfer, so $Q = 0$. Therefore, the open-circuit voltage (V_{OC})
21 is given by:⁷³

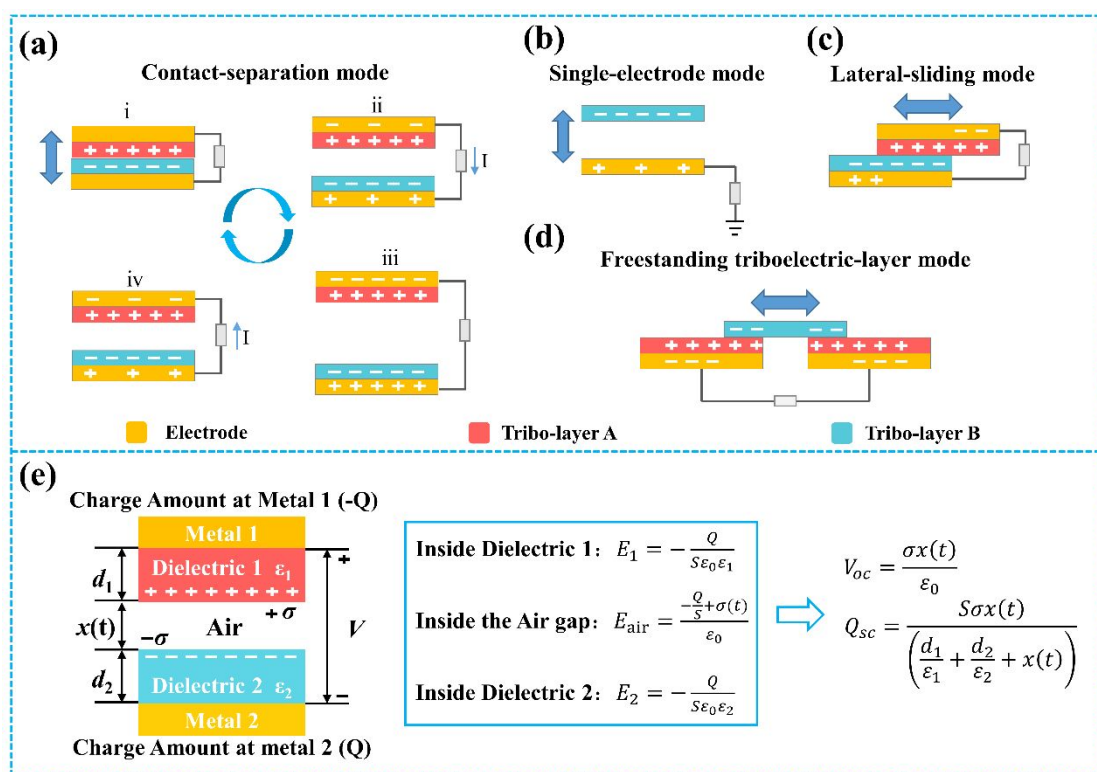
$$22 \quad V_{\text{OC}} = \frac{\sigma x(t)}{\varepsilon_0} \quad (4)$$

23 In the short-circuit condition, $V = 0$. Therefore, the transferred charges (Q_{SC}) and short
24 circuit current (I_{SC}) are:⁷³



$$Q_{sc} = \frac{S\sigma x(t)}{\left(\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2} + x(t)\right)} \tag{5}$$

$$I_{sc} = \frac{dQ_{sc}}{dt} = \frac{S\sigma\left(\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2}\right)v(t)}{\left(\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2} + x(t)\right)^2} \tag{6}$$



3
4 **Figure 2.** Four basic working modes of TENGs: (a) Vertical CS mode. (b). SE mode (c) LS mode. (d)
5 FT mode. (e) Schematic diagram showing the working principle of the vertical CS mode.

6 **3 The Relationship between the TENG’s output performance and Triboelectric**
7 **Materials**

8 In the actual testing process, the TENGs achieve a maximum output performance
9 only when triboelectric charge generation and charge loss reach a dynamic equilibrium.
10 In order to further improve the output of TENGs, a theoretical model about the dynamic
11 equilibrium was proposed by Zhang et al., as shown in **Figure 3a**.³⁹ In this model,



1 triboelectric charge generated on the surface of the triboelectric materials can be moved
2 or stored within the materials to accumulate the charge and then improve the output
3 performance of TENGs. Additionally, the triboelectric charges can diffuse into the
4 atmosphere or transfer to the bottom electrode, which then influences the output
5 performance. Therefore, the key factor limiting the maximum TENGs' output
6 performance is not only the triboelectric charge generation but also the triboelectric
7 charge loss.

8 Charge generation is closely related to the electron withdrawing/donating abilities
9 of triboelectric materials. Among these, the electron withdrawing/donating abilities of
10 triboelectric materials mainly depends on their chemical structure. Many studies have
11 proposed different physical properties to explain the connection between the electron
12 withdrawing/donating ability and chemical structure.⁷⁶⁻⁸⁰ However, only a limited
13 number of polymers adhere to these correlations. In 2019, Zou et al. built a standardized
14 quantified triboelectric series by summarizing the measurement results of over 50
15 triboelectric materials.⁸¹ The triboelectric series can help researchers choose the best
16 material pairs for high performance more carefully. Furthermore, the contribution of
17 functional groups on triboelectric materials to the contact electrification effect is also
18 recognized and proposed.⁸² In summary, there are various ways to modify the
19 triboelectric properties of triboelectric materials: surface morphological modification,
20 chemical modification, nanocomposite, and charge injection (**Figure 3b(i)**).

21 Charge loss can be divided into two subprocesses: air breakdown and charge
22 drift.^{40, 83} Furthermore, air breakdown that occurs between the surface of triboelectric
23 materials and the atmosphere has also been identified as another factor restricting the
24 output performance of TENGs.⁸⁴⁻⁸⁶ For air breakdown, it is important to select the

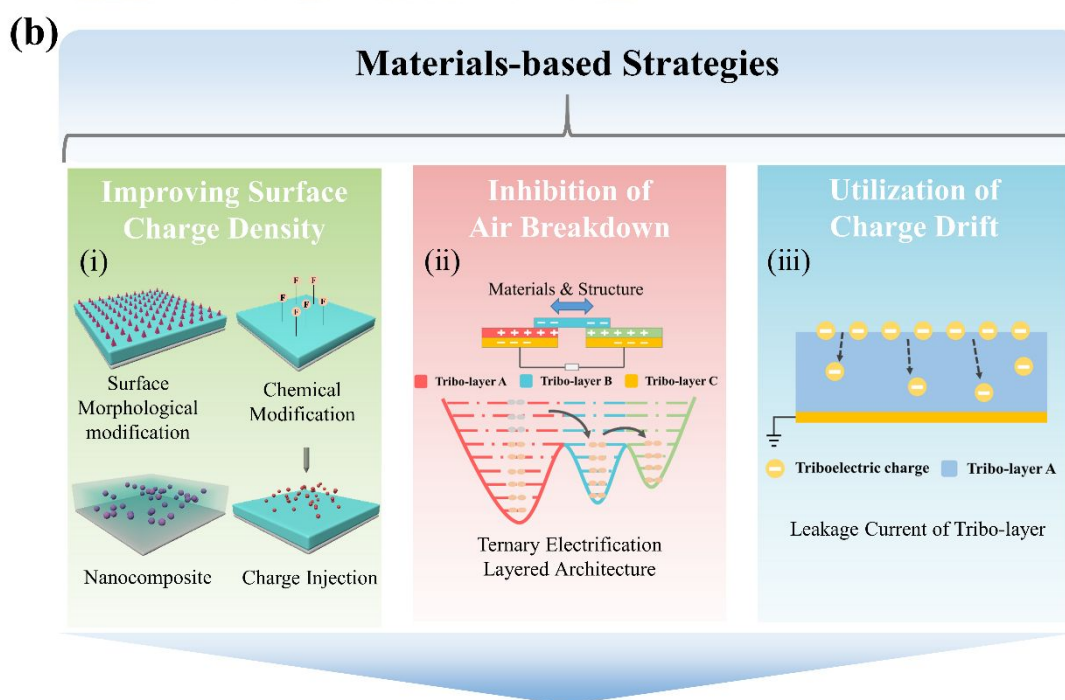
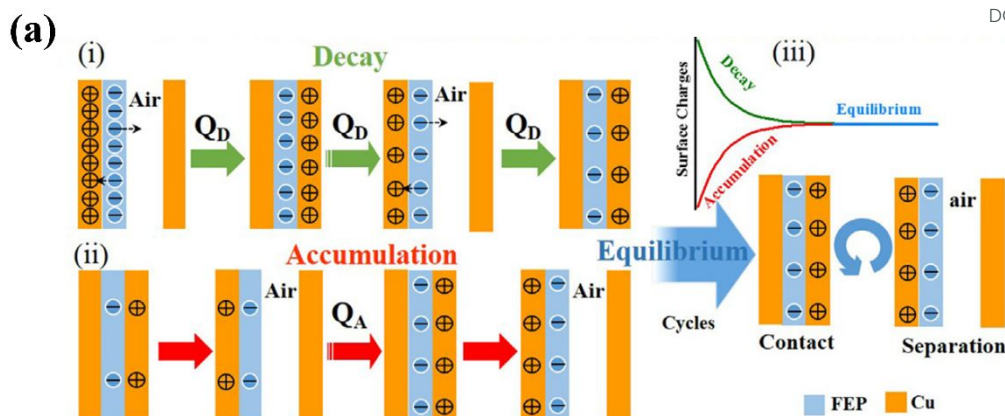


1 appropriate material and structure design to reduce the voltage and limit the air
2 breakdown, thus improving the output performance of TENGs, as shown in **Figure**
3 **3b(ii)**. In addition to air breakdown, triboelectric charge drift is also a major mode of
4 triboelectric charge loss. **Figure 3b(iii)** presents the strategy for the utilization of
5 charge drift. During the working process of TENGs, the triboelectric charges generated
6 on the surface of materials can transfer to the bottom electrode and achieve the
7 utilization of the transferred charges, thus enhancing the TENGs' output performance.⁴⁶

8 ⁸⁷

9 In summary, the process of contact electrification can be divided into three steps:
10 triboelectric charge generation, charge storage, and charge loss. All these steps are
11 mainly related to the triboelectric materials. TENGs can retain a high output
12 performance by improving the surface charge density, inhibition of air breakdown, and
13 utilization of charge drift through triboelectric material design.





High Performance TENGs

1

2 **Figure 3.** (a) Theory model of triboelectric charge in dynamic equilibrium. Reprinted with permission

3 from Ref. 39. Copyright 2020, Elsevier. (b) Various materials-related strategies to improve the

4 performance of TENGs.

5 **4 Material Design for Improving Surface Charge Density**6 **4.1 Surface Morphological Modification**

7 Surface morphological modification is the most commonly used method to

8 improve the output of TENGs, which primarily involves building micro/nanostructures



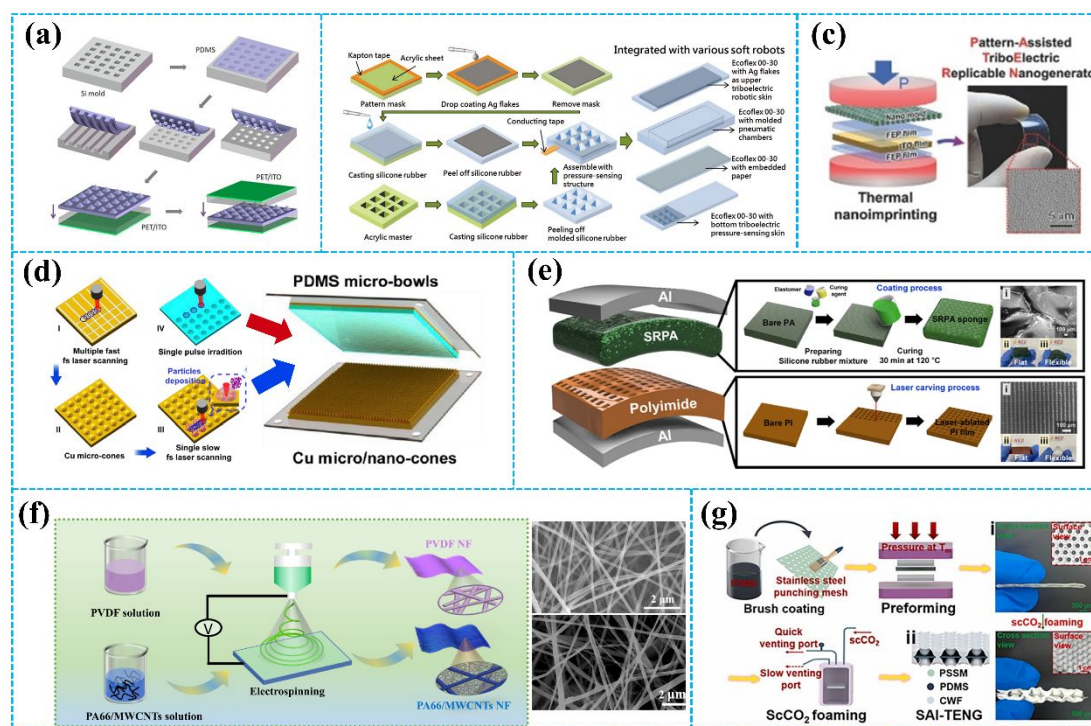
1 on the tribo-layer surface. The micro/nanostructures can efficiently improve the output
2 by increasing the contact area.

3 Owing to its simple and low-cost production process, the template method has
4 been widely used to construct micro/nanostructures on the tribo-layer surface. **Figure**
5 **4a** shows TENGs with three types of regular and uniform polymer patterned arrays (line,
6 cube, and pyramid) prepared by the template method,¹⁸ which improve the output
7 performance of the TENG by increasing the triboelectric effect and the capacitance
8 change. Similarly, in **Figure 4b**, Lai et al. proposed a stretchable and compliant
9 triboelectric robotic skin with triangular micro-prisms structure tribo-layer.⁸⁸ The tribo-
10 layer with triangular micro-prisms surfaces simultaneously possesses excellent
11 stretchability and excellent sensitivity in low-pressure regimes. Additionally, Choi et
12 al. printed regular nano-PATTERN on FEP films by using thermal nanoimprinting
13 (**Figure 4c**).⁸⁹ The test results show that the nano-PATTERN FEP film confers higher
14 electrical output performance compared with the flat-PATTERN FEP film.

15 In addition, researchers also constructed micro/nanostructures on the surface of
16 the tribo-layer by laser ablation. Compared with the template method, laser ablation
17 yields more accuracy and a shorter working period for creating the pattern on the
18 surface. As shown in **Figure 4d**, Huang et al. fabricated different micro/nano structures
19 on the Cu and PDMS films by laser ablation technology.⁹⁰ Laser scanning ablation
20 technology is used to create micro/nano dual-scale structures in stripes and cones on Cu
21 film surfaces. Additionally, micro-bowl structures in various sizes are fabricated on
22 polydimethylsiloxane (PDMS) surfaces through single pulse irradiation. This unique
23 surface topography effectively increases the contact area and achieves a 21-fold
24 increase in power density compared to the TENG without micro/nano-structures. In



1 **Figure 4e**, Cho et al. proposed a film-sponge-coupled TENG (FS-TENG) by using
 2 direct ultraviolet laser ablation.⁹¹ Various surface structures can be created on the
 3 surface of PI film in one minute by ultraviolet laser ablation. Next, a sponge made from
 4 non-woven polyamide and silicone rubber is designed to have full contact with the
 5 micro-/nano-scale structures on the surface of the PI film. The FS-TENG demonstrates
 6 an open-circuit voltage of 48.19 V and a short-circuit current of 1.243 μA , reflecting a
 7 threefold improvement in electrical performance compared to the FS-TENG with a
 8 pristine PI film.



9
 10 **Figure 4.** (a) The fabrication process of the flexible TENG. Reprinted with permission from Ref. 18.
 11 Copyright 2012, American Chemical Society. (b) The process of fabrication of the tribo-layer with
 12 triangular micro-prisms structure. Reprinted with permission from Ref. 88. Copyright 2018, Wiley. (c)
 13 One-step fabrication process of the nano-PATTERN using a thermal nanoimprint process. Reprinted with
 14 permission from Ref. 89. Copyright 2015, Wiley. (d) Preparing micro/nano structures by femtosecond
 15 laser direct writing. Reprinted with permission from Ref. 90. Copyright 2019, Elsevier. (e) Fabrication



1 procedure of a TENG with a coupled structure using a direct UV laser-ablated film and soft composite
2 of the sponge layer. Reprinted with permission from Ref. 91. Copyright 2021, American Chemical
3 Society. (f) Schematic preparation process of TENG incorporating electrospun PVDF and
4 PA66/MWCNTs nanowires. Reprinted with permission from Ref. 92. Copyright 2021, Elsevier. (g) The
5 fabrication process of TENG by scCO₂ foaming. Reprinted with permission from Ref. 93. Copyright
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7 The methods mentioned above are generally used to make regular
8 micro/nanostructures, while methods such as the electrostatic spinning process and so
9 on are used to build irregular micro/nanostructures on the surface of the tribo-layer. Sun
10 et al. reported a fabricating nanofiber-based TENG (NF-TENG) (**Figure 4f**).⁹² The NF-
11 TENG consisted of the electrospun PA66/MWCNTs nanofibers film serving as the
12 tribo-positive layer and the electrospun PVDF nanofibers film serving as the tribo-
13 negative layer, respectively. Electrospun fibers offer the benefits of uniformity, high
14 porosity, and a large surface area, which improves the output performance of TENGs.
15 Xie et al. used the dynamic supercritical carbon dioxide (scCO₂) foaming technique to
16 fabricate TPU foams with micro-sized pores, as shown in **Figure 4g**.⁹³ The biomimetic
17 wrinkles that are induced by the scCO₂ flow field facilitate contact electrification and
18 greatly enhance the triboelectric output performance.

19 The detailed output performance comparison of TENGs before and after the
20 surface morphology modification is shown in **Table 1**. In summary, surface
21 morphological modification can efficiently enhance the output performance of TENGs.
22 The modified TENG can collect energy from various mechanical movements more
23 efficiently, making it suitable for a wider range of application scenarios. However, the
24 method provides only minimal performance improvement and a limited impact on the



1 electron withdrawing/donating ability of triboelectric materials. Therefore, in the
2 following review, we will introduce several strategies to improve the electron
3 withdrawing/donating abilities of triboelectric materials.

4 **Table 1.** The summary of TENG with surface morphological modification.

| Surface Modification Method | Process | Special Structure | Before Modification | | After Modification | | Ref. |
|-----------------------------|--------------------------------------|---|---------------------|-------------------------|--------------------|-------------------------|------|
| | | | V_{OC} | I_{SC} | V_{OC} | I_{SC} | |
| Surface patterning | Template method | Pyramid | 3.4 V | 0.16 μ A (0.33 Hz) | 10 V | 0.7 μ A (0.33 Hz) | 18 |
| | | Nanopillar | 295 V | 10.4 μ A (5 Hz) | 568 V | 25.6 μ A (5 Hz) | 94 |
| | Thermal nanoimprint | Nano-PATTERN | 1.24 V | 0.102 mA/m ² | 3.19 V | 0.722 mA/m ² | 89 |
| Laser ablation | Laser direct writing | PDMS micro-bowls Cu micro/nano-cones | 5.34 V | 0.51 μ A (1.5 Hz) | 22.04 V | 2.6 μ A (1.5 Hz) | 90 |
| | Direct ultraviolet laser ablation | Square pattern | 16.82 V | 0.52 μ A (5 Hz) | 48.19 V | 1.243 μ A (5 Hz) | 91 |
| Other methods | Electrospinning | Nanofiber | — | — | 142 V | 15.5 μ A (5 Hz) | 92 |
| | Supercritical carbon dioxide foaming | Porous polymer | — | — | 78 V | 0.5 μ A (4 Hz) | 93 |

5 4.2 Chemical Modification

6 Chemical modification refers to introducing chemical functional groups on the
7 surface of triboelectric material by chemical reaction, which aims to change the



1 electronic structure of the material and thereby increase the transferred charge during
2 friction.

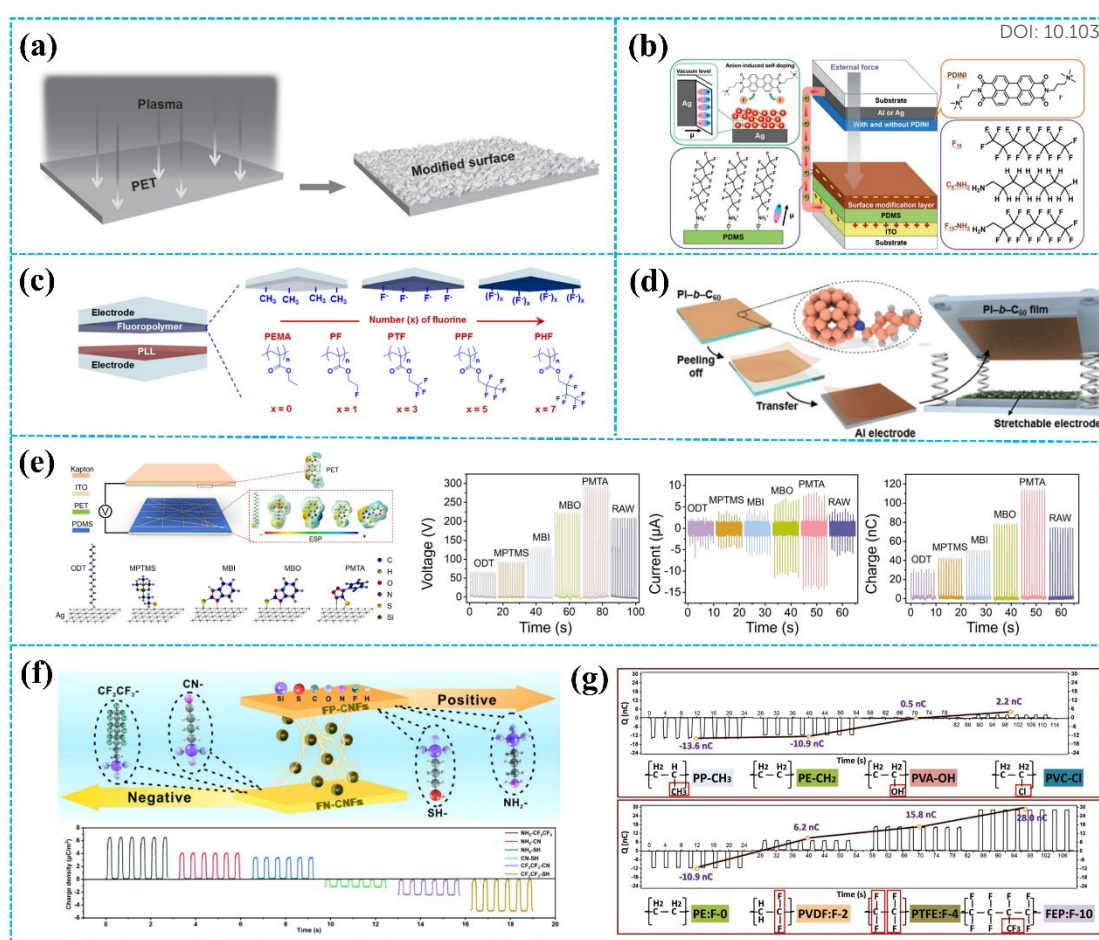
3 Importing appropriate chemical functional groups is the key to improving the
4 output performance of TENGs. Fluorine has garnered significant attention from
5 researchers due to its strong electron-absorbing ability. In **Figure 5a**, Le et al. reported
6 chemical modification of PET film via inductive-coupled plasma etching.⁹⁵ The
7 modification uses a gas mixture of carbon tetrafluoride (CF₄) and oxygen (O₂) as the
8 plasma source. The plasma etching not only occurred surface fluorination, but also
9 developed micro/nanostructures on the surface of PET film. Therefore, the TENG based
10 on modified PET film achieved a maximum V_{oc} of ≈ 220 V, an I_{sc} of ≈ 45 μ A, and an
11 induced charge of ≈ 130 nC, which are much higher than the unmodified PET film.
12 Except for plasma etching, electrostatic self-assembly was also used to introduce the
13 chemical functional groups. Based on electrostatic self-assembly, Yang et al. import
14 the molecule 1*H*,1*H*-perfluoro-octylamine (F₁₅-NH₂) as the chemical functional group
15 onto the surface of the PDMS layer (**Figure 5b**).⁴¹ Perfluoroalkyl chains have a
16 tendency to accumulate at the air interface due to their highly electronegative, which
17 improves the charge transfer efficiency between the electrode and tribo-layer. The V_{oc} ,
18 I_{sc} , and power density of the TENG based on treated PDMS film are 1392 V, 158.4 μ A,
19 and 57.1 W m⁻², respectively. The reports mentioned above have shown that surface
20 fluorination is an efficient method to increase the output performance of TENGs.
21 Moreover, the output performance of TENGs is also affected by the molecular
22 structures of fluorinated polymers and the number of fluorine units. Kim et al.
23 synthesized a TENG based on fluorinated polymers with different kinds of fluorine



1 units (**Figure 5c**).⁹⁶ The results show that the dielectric constant and the triboelectric
2 performance of the fluorinated polymers increase with increasing fluorine units.

3 In addition to the fluorinated group, the researchers also introduced different kinds
4 of chemical functional groups on the tribo-layer surface. As shown in **Figure 5d**, Lee
5 et al. fabricated a C₆₀-containing block polyimide (PI-b-C₆₀) by the cycloaddition
6 reaction of azide-containing PI with C₆₀.⁹⁷ C₆₀ is recognized as an effective electron
7 acceptor molecule. Therefore, the PI-b-C₆₀ film shows highly electronegative ability.
8 The TENG based on PI-b-C₆₀ achieved a superior charge density of over 300 $\mu\text{C m}^{-2}$.
9 Interestingly, based on its excellent triboelectric properties, the TENG based on PI-b-
10 C₆₀ also performs well in non-contact applications. Furthermore, Shin et al. introduced
11 a series of halogens on the surface of PET film.⁹⁸ The PET surface was functionalized
12 with halogen (Br, F, and Cl)-substituted phenyl or aminated molecules, resulting in a
13 diverse range of triboelectric properties. Importantly, testing results show that the
14 transferred charge density was arranged in the order of electron affinity. In 2019, Lee
15 et al. prepared sulfur backbone-based inorganic polymers.⁹⁹ Based on the high electron
16 affinity of sulfur, the open-circuit voltage output of the TENG can reach 1366 V and
17 light 630 LEDs under a minimal external force of ~ 30 N. Moreover, Yao et al.
18 introduced nitro groups and methyl groups on cellulose nanofibrils (CNF) to change
19 the tribopolarities of CNF.¹⁰⁰ Specifically, due to the nitro group has excellent electron-
20 absorbing ability and the methyl group has excellent electron-releasing ability, the
21 methyl-CNF and nitro-CNF have tribopositivity and tribonegativity, respectively. The
22 TENG, based on the methyl-CNF as the positive tribo-layer and the nitro-CNF as the
23 negative tribo-layer, demonstrated an average voltage output of 8 V and a current output
24 of 9 μA .





1
2 **Figure 5.** (a) Surface fluorination of PET film by inductive-coupled plasma etching. Reprinted with
3 permission from Ref. 95. Copyright 2015, Wiley. (b) Using an electrostatically self-assembled molecule
4 1H,1H-perfluoro-octylamine (F15-NH₂) as the surface modification for the PDMS dielectric layer.
5 Reprinted with permission from Ref. 41. Copyright 2021, Royal Society of Chemistry. (c) TENGs based
6 on fluorinated polymers with different kinds of fluorine units. Reprinted with permission from Ref. 96.
7 Copyright 2018, Elsevier. (d) Introduction of C₆₀ to PI film. Reprinted with permission from Ref. 97.
8 Copyright 2021, Royal Society of Chemistry. (e) Decorating different chemical functional groups (CFGs)
9 through the SAM treatment. Reprinted with permission from Ref. 101. Copyright 2023, Elsevier. (f)
10 Contact electrification performance of CNFs with chemically tailored molecular surface modification.
11 Reprinted with permission from Ref. 102. Copyright 2021, Elsevier. (g) Comparison of different
12 Functional Groups to contact electrification of polymers. Reprinted with permission from Ref. 82.
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1 To deeply explore the effect of chemical modification on the surface charge
2 density, in **Figure 5e**, Lei et al. decorated different chemical functional groups
3 (including octadecanethiol (ODT), 3-mercaptopropyl trimethoxysilane (MPTMS), 2-
4 mercaptobenzimidazole (MBI), 2-mercaptopbenzoxazole (MBO), and 1-phenyl-5-
5 mercaptotetrazole (PMTA)) on AgNW-based transparent conductive films by self-
6 assembled monolayer.¹⁰¹ According to the HOMO/LUMO theory, the low-lying
7 LUMO of the acceptor will dominate the electron transport. The electron absorbing
8 ability follows the sequence PMTA > MBO > MBI > MPTMS > ODT. Therefore,
9 TENG based on the PMTA-modified PDMS layer achieved the best output
10 performance, with the maximum V_{OC} , I_{SC} , and Q_{SC} reaching 290 V, 22.6 μ A, and 114
11 nC, respectively. As shown in **Figure 5f**, Liu et al. introduced different functionalities
12 (electron-withdrawing and electron-donating groups) on the cellulose nanofibrils
13 (CNFs).¹⁰² The charge density of CNFs is weakened by the introduction of electron-
14 withdrawing groups and enhanced by the introduction of electron-donating groups. The
15 strength of the electron-donating ability of each functional group is given by: $-NH_2 > -$
16 $SH > -CN > -CF_2CF_3$. Similarly, Li et al. ranked the electron-withdrawing ability of
17 halogen groups (in **Figure 5g**).⁸² It follows the order: $CH_3 < H < OH < Cl < F$. This
18 makes a great contribution to further elucidating the relationship between functional
19 groups and the triboelectric effect.

20 The detailed output performance comparison of TENGs before and after chemical
21 modification is shown in **Table 2**. Among the results, 1-phenyl-5-mercaptopetrazole is
22 the most effective chemical to improve the output performance of TENGs. However,
23 it's important to note that the choice of chemicals and their application methods should
24 be tailored to the specific type of TENG and the materials used. Additionally, the



1 environmental impact and long-term stability of the chemicals should also be
 2 considered when enhancing TENGs' output performance.

3 **Table 2.** The summary of TENG with chemical modification.

| Chemical Modification Process | Functional Group | Before Modification | | | After Modification | | | Ref. |
|--|------------------------------|---------------------|----------------------------------|------------------|--------------------|-----------------------------------|-------------------|------|
| | | V_{OC} | I_{SC} | Q_{SC} | V_{OC} | I_{SC} | Q_{SC} | |
| Inductive-coupled plasma etching | CF_n | 86.1 V | 19.4 μA (1.66 Hz) | 46.9 nC | 217.2 V | 46.3 μA (1.66 Hz) | 124.4 nC | 95 |
| Electrostatically self-assembled | C_8-NH_2 | 182 V | 19.6 μA (14 Hz) | 10.8 nC | 186 V | 20.2 μA (14 Hz) | 11.4 nC | 41 |
| | F_{18} | | | | 287 V | 21.2 μA (14 Hz) | 14.6 nC | |
| | $F_{15}-NH_2$ | | | | 540 V | 44.8 μA (14 Hz) | 47.9 nC | |
| Cycloaddition reaction | C_{60} | 158.8 V | 32.1 mA/m ² (3 Hz) | 32.7 $\mu C/m^2$ | 505.1 V | 117.9 mA/m ² (3 Hz) | 107.2 $\mu C/m^2$ | 97 |
| Self-assembled monolayer | 1-phenyl-5-mercaptotetrazole | 90 V | 5 μA (1 Hz) | 35 nC | 290 V | 22.6 μA (1 Hz) | 114 nC | 101 |
| Chemically tailored molecular surface modification | NH_2- | 50.3 V | — | 8.77 $\mu C/m^2$ | 76 V | — | 13.2 $\mu C/m^2$ | 102 |
| | $SH-$ | | | | 65 V | — | 10.75 $\mu C/m^2$ | |
| | $CN-$ | | | | 42.2 V | — | 7.9 $\mu C/m^2$ | |
| | CH_3CH_2- | | | | 33.1 V | — | 6.5 $\mu C/m^2$ | |

4 To sum up, the output performance of TENGs is greatly enhanced by the
 5 introduction of suitable chemical functional groups. Furthermore, some chemical
 6 functional groups not only increase the surface charge density but also improve the



1 moisture resistance and temperature resistance of triboelectric materials, making the
2 TENG maintain high output performance in harsh environments.^{100, 103-105} Additionally,
3 chemical modification also broadens the range of available materials for high
4 performance TENGs.^{95, 106}

5 4.3 Nanocomposite

6 4.3.1 Simple Blending

7 The dielectric constant of the triboelectric material also plays an important factor
8 in the output performance of TENGs. Doping nanomaterials into the polymer is an
9 effective method to improve the dielectric constant of the triboelectric material, thereby
10 improving the TENG's output performance.¹⁰⁷⁻¹¹⁰

11 By adding a small amount of 2D conductive nanomaterials (such as graphene and
12 MXene) to the polymer matrix, the dielectric constant of the composite material will be
13 significantly improved due to the conductive two-dimensional planar structure of the
14 materials and the insulating polymer together constituting many microcapacitors,
15 improving the ability of the composite material to store charge.¹¹¹⁻¹¹³ As shown in
16 **Figure 6a**, Bhatta et al. doped MXene nanosheets into the PVDF matrix.¹¹⁴ The
17 dielectric constant of the PVDF composite film increased as the MXene concentration
18 increased. For the MXene concentration of 25 wt%, the dielectric constant of the PVDF
19 composite film is 44.1, which is much higher than pristine PVDF (13.35). Therefore,
20 the demonstrated TENG based on the PVDF composite film can reach maximum V_{OC} ,
21 I_{SC} , and transferred charge of 724 V, 163.6 μ A, and 182 nC, respectively.

22 Except for conductive nanomaterials, high-dielectric materials are also appropriate
23 for doping selection. Wang et al. fabricated lead-free $ZnSnO_3$ nanocubes @

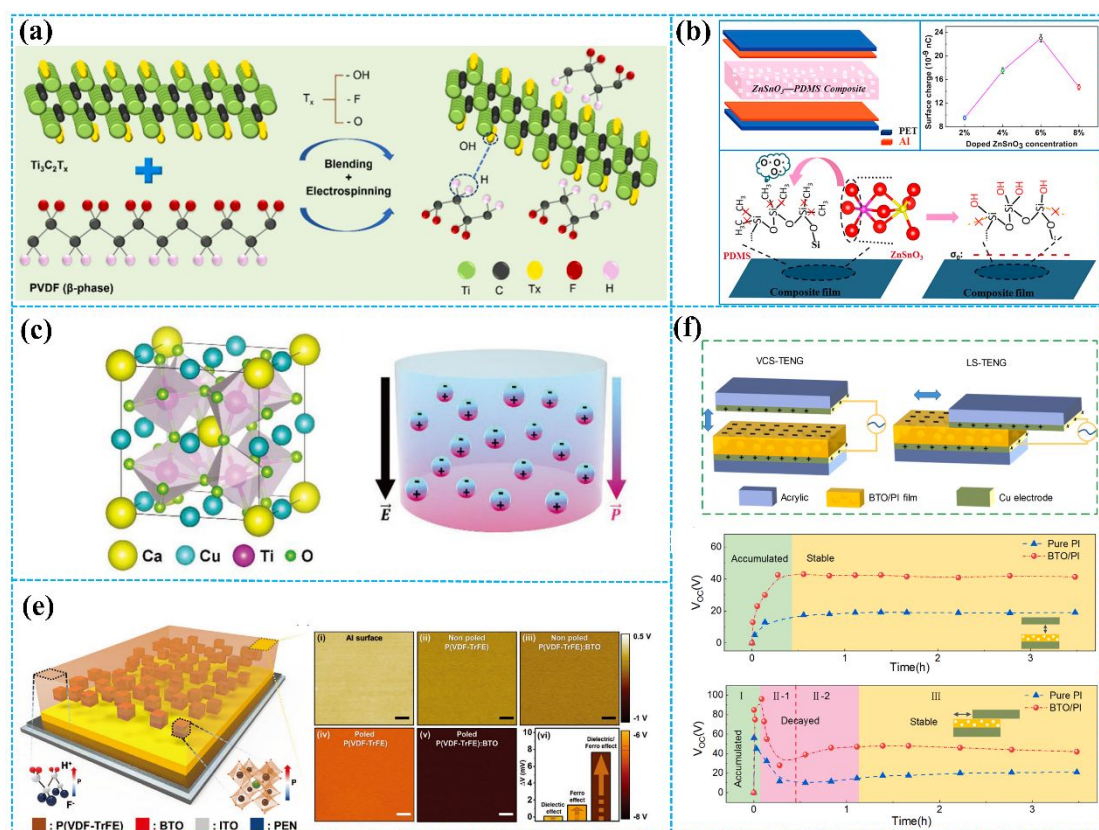


1 polydimethylsiloxane (PDMS)-based TENG by dispersing ZnSnO₃ nanocubes into
2 PDMS (in **Figure 6b**).¹¹⁵ The TENG based on a composite PDMS film with a doped
3 ZnSnO₃ concentration of 6 wt% achieved the best output performance, with a greater
4 output current that was up to 6.2 times greater than the pure PDMS film-based TENG.
5 In **Figure 6c**, Kim et al. added high permittivity CaCu₃Ti₄O₁₂ (CCTO) particles into
6 butylated melamine formaldehyde (BMF).⁴² CCTO particles with a high permittivity
7 of 7500 can induce strong internal polarization within the dielectric material when
8 subjected to an electric field generated by triboelectric charges. Under identical electric
9 field conditions, the BMF-CCTO 1 wt% composite exhibited three times the internal
10 polarization of pure BMF. A rotation-type freestanding mode TENG based on BMF-
11 CCTO 1 wt% composite film generated high RMS voltage and current density with 268
12 V and 25.8 mA m⁻², respectively.

13 In recent years, ferroelectric materials have attracted much attention because of
14 their high dielectric constant and ferroelectric effect. Suo et al. prepared a novel hybrid
15 piezo/triboelectric nanogenerator based on BaTiO₃ (BTO)/PDMS composite film.¹¹⁶
16 The PDMS composite film with a BTO concentration of 20 wt% showed the best
17 performance due to its ferroelectric polarization strength and dielectric constant. This
18 work confirmed that piezoelectric and triboelectric effects can coexist in a single
19 material component and interact to improve electric output performance. In **Figure 6d**,
20 Sueng et al. reported a nanocomposite material system that consists of a high-dielectric
21 ceramic material, barium titanate (BTO), and a ferroelectric copolymer matrix,
22 Poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)).¹¹⁷ The surface charge
23 potential dramatically increased due to the electrically induced ferroelectric
24 polarization inside the P(VDF-TrFE) with dielectric BTO NPs. Under the combined



1 action of triboelectric and ferroelectric effects, the TENG based on BTO/PVDF-TiFE
 2 composite films achieved a boosted power-generating performance that improved by
 3 about 150 times compared with typical triboelectric material-based devices. Li et al.
 4 selected BaTiO₃ nanoparticles (BTO NPs) as the doping material, which was dispersed
 5 into the PI matrix, as displayed in **Figure 6e**.¹¹⁸ Interestingly, the ideal doping mass
 6 concentration of BTO NPs for maximizing electrical performance depends on the
 7 operating mode of TENGs. For LS-TENG, 5 wt% BTO NPs show the best performance,
 8 doubling the steady-state open-circuit voltage compared to the pure PI film. Similarly,
 9 18 wt% BTO NPs display the best results for CS-TENG with steady-state open-circuit
 10 voltage doubled compared with the pure PI film.



11 **Figure 6.** (a) Fabrication process PVDF/MXene composite film and property of PVDF with different
 12 MXene concentration. Reprinted with permission from Ref. 114. Copyright 2021, Elsevier. (b) Structure
 13 of ZnSnO₃-PDMS based TENG and schematic illustration of the charges in the molecular structure.
 14



1 Reprinted with permission from Ref. 115. Copyright 2015, Elsevier. (c) Chemical structure of CCTO
2 and the dielectric constant of BMF–CCTO composite film under electric field. Reprinted with permission
3 from Ref. 42. Copyright 2020, Wiley. (d) Schematic description of a ferroelectric composite-based
4 TENG and KPFM study of the ferroelectric composite film. Reprinted with permission from Ref. 117.
5 Copyright 2017, Wiley. (e) The output performance of the BTO/PI nanocomposite film based VCS-
6 TENG and LS-TENG. Reprinted with permission from Ref. 118. Copyright 2022, Elsevier.

7 4.3.2 *Multilayer Structure of composite film*

8 It is a common strategy to prepare polymer-based composite films by
9 incorporating high-dielectric nanomaterials for high performance tribo-layers.¹¹⁹⁻¹²¹
10 However, it is a challenge to uniformly disperse high-dielectric nanomaterials in
11 polymers.¹²² A valid way to achieve high dielectric constant and output performance is
12 by fabricating high-dielectric nanomaterials/polymer composites with multilayer
13 structures. Firstly, interfacial polarization can form at the interfaces between different
14 layers, resulting in charge accumulation at the multilayer interfaces and enhancing the
15 dielectric constant. Secondly, polymer film on the high dielectric constant layer surface
16 can effectively inhibit breakdown and charge leakage. Last but not least, the multilayer
17 structure prevents high dielectric material agglomeration and minimizes defect
18 formation.

19 Ravichandran et al. developed a multilayer flexible composite structure by
20 employing an insulator-metal-insulator architecture in place of a single insulator
21 material (in **Figure 7a**).¹²³ The multilayer composite structure consists of an
22 intermediate gold (Au) metal inclusion sandwiched in between a charge generation and
23 retention layer, parylene-C (PaC), and polytetrafluoroethylene (PTFE). The metal

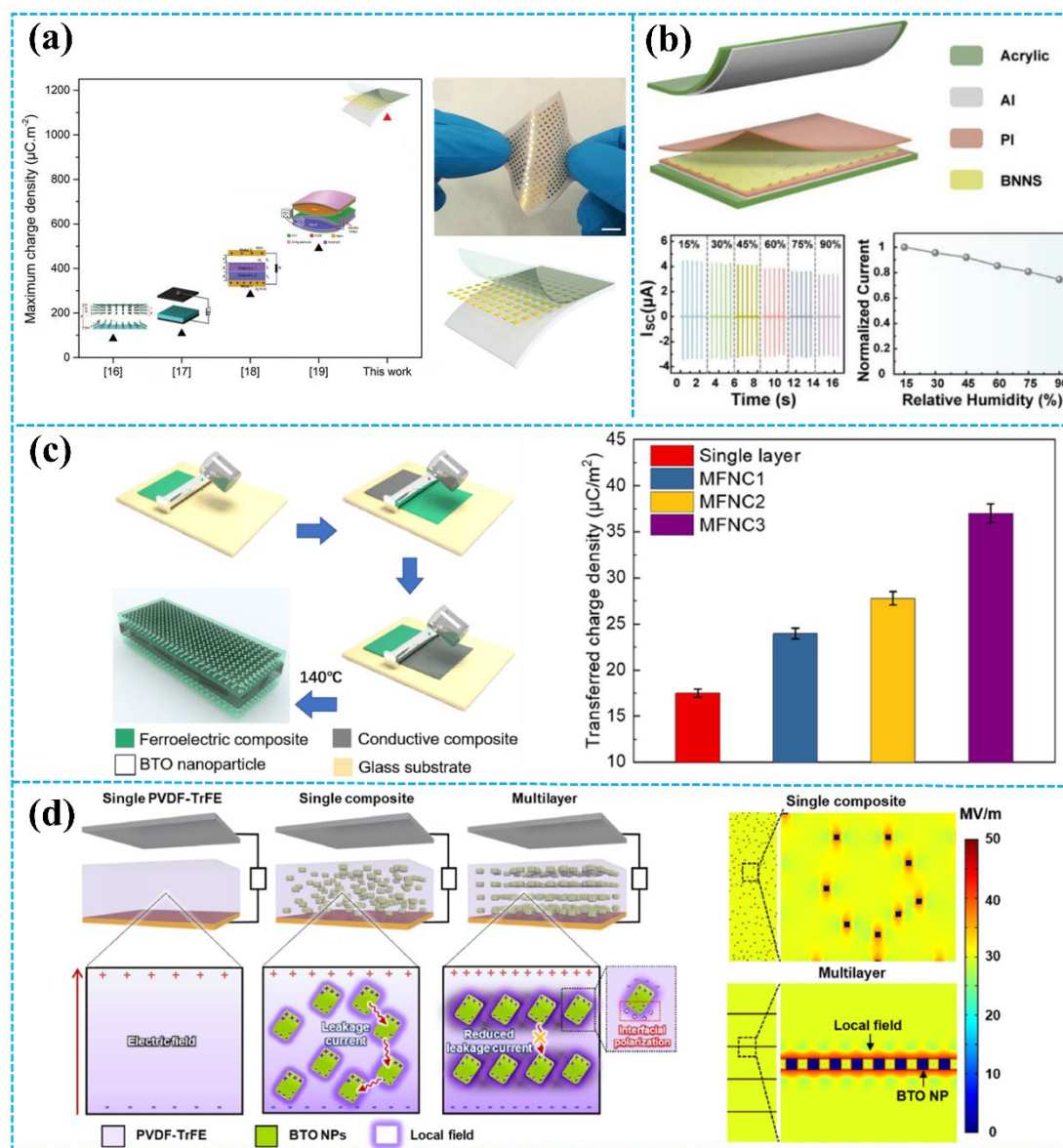


1 inclusion acts as a charge storage site and its storage is several orders of magnitude
2 greater than that of the bare insulator, enabling it to accumulate the triboelectric charge
3 generated at each cycle. Based on the unique structural design, the output performance
4 of the TENG made a great process, resulting in a maximum charge density of 1076.56
5 $\mu\text{C m}^{-2}$ and a maximum output power density of 4.8 W m^{-2} . In **Figure 7b**, Pang et al.
6 fabricated a TENG based on a sandwich-structured polyimide (PI)/boron nitride
7 nanosheet (BNNS)/PI nanocomposite film (PBP).¹²⁴ The introduction of the BNNS
8 interlayer significantly enhances the triboelectric performance of the PI nanocomposite
9 film. Aluminum (Al) and PBP multilayers were used as the positive and negative
10 contacting triboelectric layers. The short-circuit current of the TENG based on the PBP
11 multilayer was 4.5 μA , which was 5 times that of the TENG without the BNNS
12 interlayer. In addition, at an external load resistance of 10 $\text{M}\Omega$, the TENG based on
13 PBP multilayer achieved a maximum power density of 21.4 $\mu\text{W}/\text{cm}^2$.

14 Similarly, to increase the TENG's output power, Chai et al. prepared multilayered
15 ferroelectric nanocomposites (MFNCs) as negative tribo-layer, as shown in **Figure 7c**.⁴⁹
16 A conductive interlayer (multiwalled carbon nanotube (MWCNT) filled P(VDF-TrFE))
17 sandwiched in two ferroelectric nanocomposites ($\text{BaTiO}_3/\text{P(VDF-TrFE)}$). The output
18 performance of the TENG achieved great improvement, resulting in maximum
19 transferred charge density and power density of 105.70 $\mu\text{C}/\text{m}^2$ and 7.21 W/m^2
20 respectively, at 2 Hz, due to the enhanced polarization of ferroelectric materials by
21 introducing a conductive interlayer. Moreover, the conductive interlayer can also trap
22 triboelectric surface charges. Additionally, Cao et al. prepared X-Y-X sandwich
23 structured copper calcium titanate/polyimide (CCTO/PI) nanocomposites for TENG by
24 using a layer-by-layer casting method.¹²⁵ In X-Y-X sandwich-structure, polyimide (PI)



1 with a high dielectric constant copper calcium titanate (CCTO), and pure PI film were
 2 used as the outer layer and charge storage layer, respectively. By introducing a charge-
 3 storage layer of PI, the output performance was also improved. The V_{OC} , I_{SC} , and Q_{SC}
 4 of the TENG based on the X-Y-X sandwich-structure were 96.6 V, 5.6 μA , and 30.8
 5 nC, respectively.



6
 7 **Figure 7.** (a) Design, structure, and working mechanism of the insulator-metal-insulator TENG.
 8 Reprinted with permission from Ref. 123. Copyright 2020, Wiley. (b) A sandwich-shaped
 9 nanocomposite film based TENG and the output performance of the TENG. Reprinted with permission



1 from Ref. 124. Copyright 2022, American Chemical Society. (c) The fabrication process and output
2 performance of of MFNCs. Reprinted with permission from Ref. 49. Copyright 2022, Elsevier. (d)
3 Schematic of the three different types composite film and the FEM simulations of electric field
4 distribution in the single and multilayered PVDF-TrFE/BTO composite films. Reprinted with permission
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6 Ferroelectric composites have been found to improve the performance of TENGs,
7 but their output performance is hindered by randomly dispersed particles. Therefore,
8 Park et al. introduced a high-performance TENG based on ferroelectric multilayer
9 nanocomposites with alternating poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-
10 TrFE) and BaTiO₃ (BTO) nanoparticles (NP) layers, as shown in **Figure 7d**.¹²⁶ From
11 the COMSOL Multiphysics result, it is clear that the multilayer structure featuring BTO
12 NPs on the coplanar layer facilitates more efficient connectivity of interfacial charges
13 at closer distances compared to composites with randomly dispersed BTO NPs, which
14 leads to a significantly enhanced local field while boosting the ferroelectric polarization
15 of the polymer. Moreover, with characteristics that induce stress concentration, the
16 dielectric constant of multilayers consisting of alternating soft/hard layers surpasses
17 that of single PVDF-TrFE/BTO nanocomposites (15.9) and pure PVDF-TrFE films
18 (13.9). Consequently, the multilayered TENG showed 2.3 and 1.5 times higher current
19 densities than pure PVDF-TrFE and PVDF-TrFE/BTO nanocomposites without a
20 multilayer structure, respectively.

21 The detailed output performance comparison between TENGs based on pristine
22 polymer and TENGs based on composite film is shown in **Table 3**. Among the results,
23 the TENG based on ferroelectric materials/polymer composite films shows the best
24 output performance by coupling the triboelectric effect and the piezoelectric effect.



1 Additionally, the TENG based on the multilayer structure has better output performance
2 compare with the TENG based on single blending (single layer). All in all, the surface
3 charge density of the triboelectric materials is effectively enhanced by doping
4 nanomaterials into the polymer. By designing a multilayer composite membrane
5 structure, the dielectric properties of the single-layer composite film are efficiently
6 improved. Furthermore, the coupling of the triboelectric effect and piezoelectric effect
7 is achieved by doping ferroelectric nanoparticles, thereby efficiently increasing the
8 surface charge density and hence boosting TENGs' output performance.
9



1 **Table 3.** The summary of TENG with nanocomposite film.

| Nanocomposite | Composite Film | Inclusions | Pristine Polymer | | | | Composite Film | | | | Ref. |
|-----------------|---|--------------------|------------------|--|---------------------------|-----------------------|----------------|---|----------------------------|----------------------------|------|
| | | | V_{oc} | I_{sc} | Q_{sc} | Output Power | V_{oc} | I_{sc} | Q_{sc} | Output Power | |
| Simple blending | Ag/Chitosan | Ag nanowires | 17.1 V | 0.9 μ A (3 Hz) | 7.2 nC | — | 47.9 V | 4.1 μ A (3 Hz) | 17.5 nC | 137.6 mW/m ² | 127 |
| | MWCNTs/Chitosan | MWCNTs | 14.4 V | 0.3 μ A (2 Hz) | 5.8 nC | — | 85.8 V | 8.7 μ A (2 Hz) | 29 nC | 180 mW/m ² | 128 |
| | LM/PDMS | Liquid metal (LM) | 52 V | 3.9 μ A (3 Hz) | 30 nC | 36 mW/m ² | 210 V | 10.3 μ A (3 Hz) | 119 nC | 1020 mW/m ² | 129 |
| | Mxene/PVDF | Mxene | 470 V | 89.4 μ A (8 Hz) | 101 nC | — | 724 V | 163.6 μ A (8 Hz) | 182 nC | 11.213 W/m ² | 114 |
| | MoS ₂ /Nylon MoS ₂ /PVDF | MoS ₂ | 120 V | 130 μ A/m ² (0.8 Hz) | 42 μ C/m ² | 6 mW/m ² | 270 V | 645 μ A/cm ² (0.8 Hz) | 20.2 nC/cm ² | 50 mW/m ² | 130 |
| | BNNs/PDMS | BNNs | 935 V | 63.9 mA/m ² (5 Hz) | 86 μ C/m ² | 33.6 W/m ² | 1870 V | 230 mA/m ² (5 Hz) | 234 μ C/m ² | 100 W/m ² | 131 |
| | MOFs/PDMS | Zr-based MOFs | 52.8 V | 4.1 μ A (1 Hz) | 7.5 nC | — | 130 V | 7.1 μ A (1 Hz) | 18.1 nC | — | 132 |
| | ZnSnO ₃ /PDMS | ZnSnO ₃ | 224 V | 3.2 μ A (2 Hz) | 3.8 nC | — | 330 V | 16 μ A (2 Hz) | 40.5 nC | 3 mW | 115 |



| Nanocomposite | Composite Film | Inclusions | Pristine Polymer | | | | Composite Film | | | | Ref. |
|----------------------|--|-------------------------------|------------------|--------------------------------------|-----------------------------|----------------------------|----------------|---------------------------------------|-----------------------------|-----------------------|------|
| | | | V_{oc} | I_{sc} | Q_{sc} | Output Power | V_{oc} | I_{sc} | Q_{sc} | Output Power | |
| | BaTiO ₃ /P(VDF-TrFE) | BaTiO ₃ | 93 V | 40 μ A (0.5 Hz) | — | — | 331V | 300 μ A (0.5 Hz) | — | 6.4 mW | 117 |
| Multilayer structure | PI-MoS ₂ :PI-PI (sandwich structure) | MoS ₂ :PI layer | 30 V | — | 50 nC | 0.21 W/m ² | 400 V | — | 200 nC | 25.7 W/m ² | 107 |
| | IZO-PDMS (bilayer structure) | IZO layer | 35 V | 20 μ A/cm ² (1 Hz) | 28 μ C/m ² | 0.75 mW/cm ² | 140 V | 180 μ A/cm ² (1 Hz) | 108 μ C/m ² | 25 mW/cm ² | 133 |
| | PI-BNNs-PI (sandwich structure) | BNNs layer | 9.3 V | 0.9 μ A (2 Hz) | 2.8 nC | 14.3 mW/m ² | 65.9 V | 4.5 mA (2 Hz) | 17.2 nC | 214 mW/m ² | 124 |
| | BTO/P(VDF-TrFE)- MWCNTs/P(VDF- TrFE)-BTO/P(VDF- TrFE) (sandwich structure) | MWCNTs/P(VDF- -TrFE) layer | 70 V | 4.6 μ A | 33.4 μ C/m ² | 0.11 W/m ² | 131.2 V | 10.4 μ A | 65.4 μ C/m ² | 7.21 W/m ² | 49 |

1 MWCNTs: multi-walled carbon nanotubes; BNNs: boron nitride nanosheets; IZO: indium zinc oxide.



1 4.4 Charge Injection

2 The output performance of TENGs is strongly influenced by their surface charge
3 density. Injecting charge into the surface of the tribo-layer is the most direct and
4 effective way to increase the surface charge density.

5 Wang et al. utilized an air-ionization gun to bring the negative charges onto the
6 surface of FEP film (in **Figure 8a**).¹³⁴ The air-ionization gun could generate positive
7 and negative charges by ionizing air inside the gun. To monitor the negative charges on
8 the FEP surface, researchers used a coulomb meter to measure the charge flow from the
9 ground to the bottom electrode. The result shows that each ion injection event transfers
10 charges with a charge density of approximately 40 $\mu\text{C}/\text{m}^2$ from the ground to the bottom
11 electrode, introducing charges of the same density onto the FEP surface. After the 17
12 consecutive instances of charge injection, the negative static charge density on the FEP
13 surface finally reached $\sim 630 \mu\text{C}/\text{m}^2$. In this study, the maximum surface charge density
14 for the CS-mode TENGs can be determined by comparing the threshold voltage for the
15 air breakdown with the actual voltage drop (V_{gap}) across the air gap. The V_{gap} has the
16 following relationship with the gap distance (x):¹³⁴

$$17 \quad V_{\text{gap}} = \frac{d\sigma_0 s}{\epsilon_0(d+x\epsilon_r)} \quad (7)$$

18 where d is the thickness of the FEP film, ϵ_r is the relative permittivity of the FEP layer,
19 σ_0 is the surface charge density, and ϵ_0 is the vacuum permittivity. The air breakdown
20 voltage (V_{AB}) curve can be described according to the empirical formula of Paschen law:

21 135-137

$$22 \quad V_{\text{AB}} = \frac{A(Px)}{\ln(Px) + B} \quad (8)$$

23 where P is the atmospheric pressure, x is the gap distance, and A and B are the constants



1 determined by humidity, temperature, etc. in the environment. During the contact-
2 separation process, to obtain the maximum surface charge density, the V_{gap} must be
3 smaller than the V_{AB} . Therefore, in the whole contact-separation process, the
4 relationship between V_{gap} and V_{AB} should be satisfied for: ¹³⁴

$$5 \quad \frac{A(Px)}{\ln(Px)+B} > \frac{d\sigma_0s}{\varepsilon_0(d+x\varepsilon_r)} \quad (9)$$

6 According to Eq. 8, the maximum surface charge density (σ_{max}) for the CS-mode
7 TENGs is:

$$8 \quad \sigma_{\text{max}} = \left\{ \frac{AP\varepsilon_0(d+x\varepsilon_r)}{d(\ln(Px)+B)} \right\} \min \quad (10)$$

9 From this equation, it is proposed that thinner dielectric films are the preferred
10 choice for achieving a higher surface charge density. Liu et al. introduced the surface
11 charges to the surface of different polymer films using an air-ionization gun, to
12 investigate the surface charge decay trend of the TENGs in a high-humidity
13 environment. ¹³⁸ It was discovered that increasing the hydrophobicity of dielectric
14 materials can lead to higher surface charges, particularly in high humidity conditions.
15 The TENG based on PTFE film retained 90% of its initial output performance after
16 5000 cycles under 90% relative humidity.

17 In addition to the air-ionization gun, a corona discharge treatment (CDT) can also
18 be used to deposit charges onto the surface of tribo-layer. As shown in **Figure 8b**, Park
19 et al. reported an Ag nanowires (NWs)-embedded laminating structure (AeLS) for ionic
20 charge injection by CDT. ⁴³ Based on their unique laminated structure, Ag nanowires
21 dissipate positive charges, allowing negative ions to accumulate on the outermost
22 surface. The testing results show that the AeLS with CDT exhibited higher durability
23 and resistance to moisture and water molecules. The output current, charge, and power

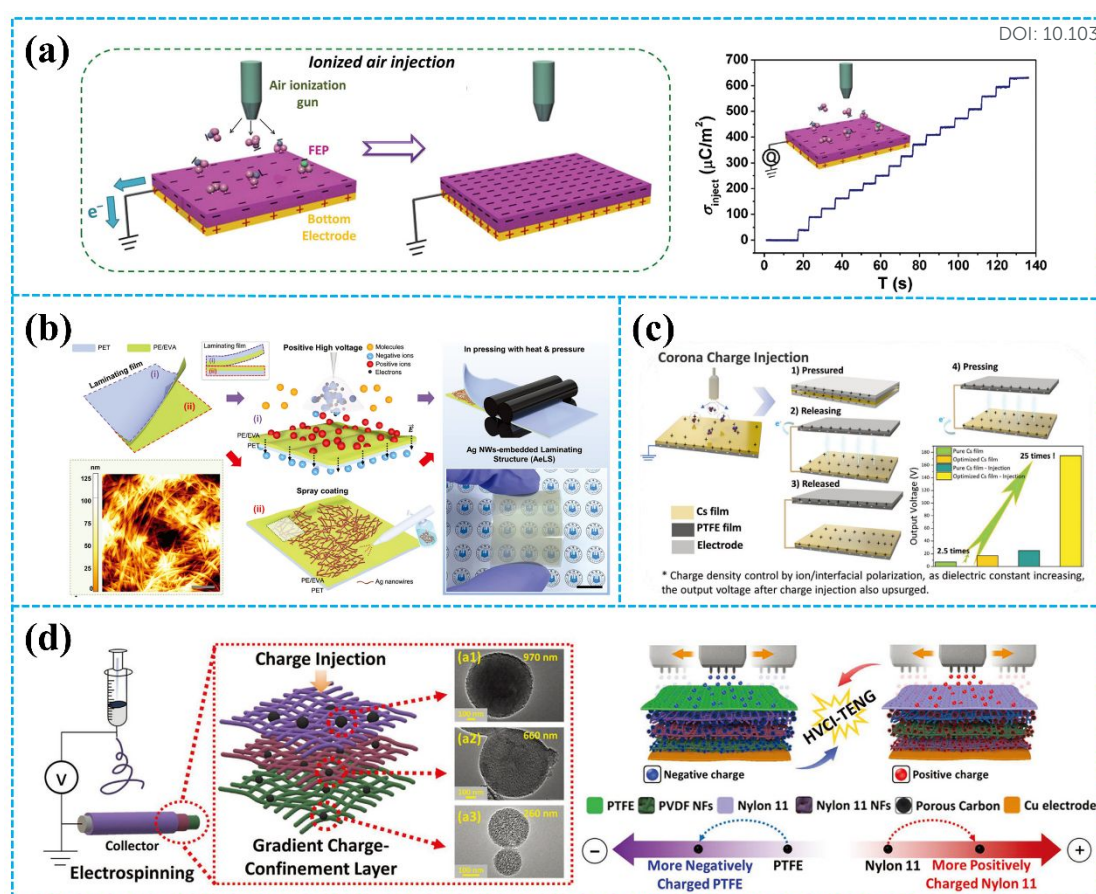


1 density of the TENG based on AeLS were $\approx 146 \mu\text{A}$, $\approx 300 \text{ nC}$, and $\approx 1.6 \text{ W m}^{-2}$,
2 respectively. In addition to introducing charges onto the surface of tribo-layer, the
3 corona discharge treatment can also optimize the polarization of triboelectric materials.
4 Sun et al. enhanced the interfacial polarization of the chitosan blends by corona charge
5 injection to enhance the output performance (in **Figure 8c**).¹³⁹ During the corona charge
6 injection, the ion in the chitosan blends will move in the direction of the electric field,
7 which leads to enhanced polarization and then increases the dielectric constant of the
8 chitosan blends. Therefore, after corona charge injection, with the increasing dielectric
9 constant and surface charge density, the TENG based on the treated chitosan blends
10 exhibited an output voltage 25 times (200 V) higher than that of the TENG based on
11 the initial film.

12 In another study, Cha et al. proposed the improvement of the output performance
13 of TENGs through introducing charge to the gradient charge-confinement layer based
14 on electrospinning fibers by high-voltage charge injection (HVCI), as displayed in
15 **Figure 8d**.¹⁴⁰ Each successive nanofibrous layer in the gradient charge-confinement
16 layer included a larger number of mesoporous carbon spheres (mCSs) in increasing size.
17 The gradient distribution of mCSs facilitated the movement of injected charge from the
18 surface to the inner layers of the nanofibrous structure. When an external field of 7 kV
19 was applied upon charge injection, the surface charge density on the gradient-charge
20 confinement layer increased approximately 7.5 times compared to the case without
21 mCSs. Consequently, the output voltage of the TENG was 600 V after charge injection,
22 which represented an increase of ≈ 40 times compared to the output before charge
23 injection.

24





1
2 **Figure 8.** (a) Injecting negative ions onto the FEP surface from an air-ionization gun and the output
3 performance of the treated FEP film. Reprinted with permission from Ref. 134. Copyright 2014, Wiley.
4 (b) Fabrication process of AeLS with i-CDT. Reprinted with permission from Ref. 43. Copyright 2023,
5 Wiley. (c) Schematic diagram of corona charge injection and structure/working principle of the TENG.
6 Reprinted with permission from Ref. 139. Copyright 2022, Wiley. (d) Schematic of the fabrication
7 process of the TENG and injected the negative and positive charges to PTFE and Nylon-11. Reprinted
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9 However, the traditional charge injection process is more complex compared to
10 the simple contact electrification process, and may require additional equipment
11 support, such as an air-ionization gun, a high-voltage source for corona charge injection,
12 and so on. Therefore, developing a new simple charge injection method is urgent.

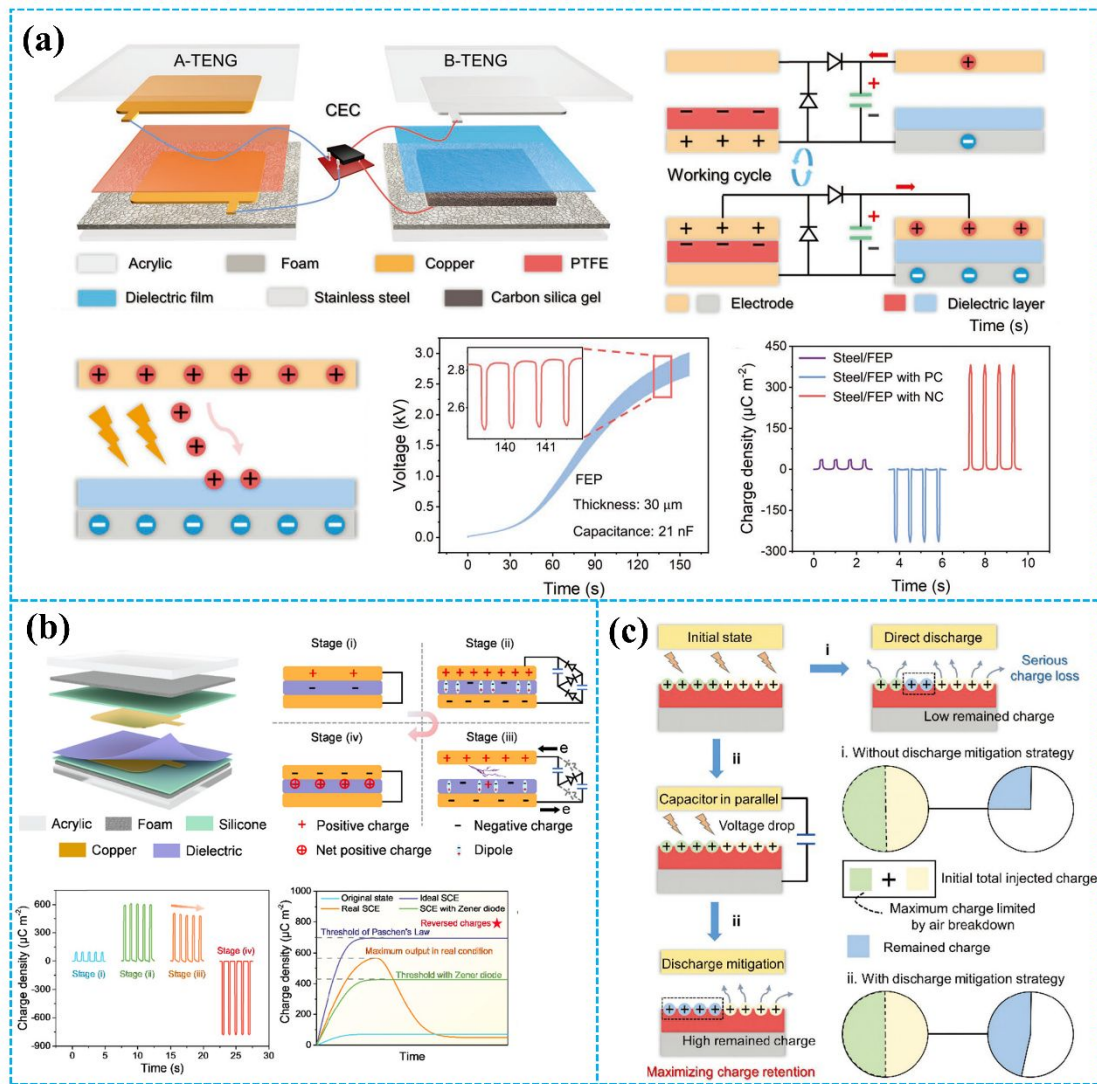


1 In recent years, Wu et al. reported a simple and effective surface charge injection
2 technology through a half wave charge excitation circuit (CEC) (**Figure 9a**).⁵⁰ In
3 previous work, it has been confirmed that the CEC can be used to improve the surface
4 charge density of TENGs. In this research, the half wave charge excitation circuit was
5 used to provide a stable, high excitation voltage to achieve air breakdown and thus
6 charge injection. A smaller capacitance in the CEC is beneficial for achieving a higher
7 excitation voltage to improve charge injection efficiency. Interestingly, the injected
8 charge polarity on the surface of dielectric polymers can be controlled by adjusting the
9 connection mode of the CEC. After parameter optimization, the TENG based on PI film
10 reached an ultrahigh output charge density of 880 $\mu\text{C}/\text{m}^2$ through this technology.
11 Moreover, they also established a charge transfer model to quantify the surface charge
12 density. This study enhances the understanding of the output charge density of TENGs,
13 which is essential for enhancing TENG performance.

14 Additionally, Guo et al. designed a high performance TENG based on a charge
15 reversion process generated by the electrostatic breakdown effect (**Figure 9b**).³⁷ This
16 report used the high voltage generated by the voltage-multiplier circuit (VMC) to cause
17 an electrostatic breakdown effect. The charge-reversion process could be divided into
18 four stages. In the initial stage, the tribo-layer (PTFE film) carries a small amount of
19 negative charge. In the second stage, the TENG starts charging the capacitors in the
20 VMC, and the gap voltage of the TENG also starts to increase. In the third stage, with
21 the increasing gap voltage of the TENG, the electric field between the upper electrode
22 and the dielectric film of the TENG eventually reaches the threshold for air breakdown
23 to occur, which leads to positive charge being transferred to the surface of the dielectric
24 film. Therefore, in the fourth stage, when the VMC is removed, the surface charges of



1 the dielectric film are reversed to a positive polarity. Based on the charge reversion
 2 process, the surface charge density of the PTFE-based TENG increased from $97 \mu\text{C m}^{-2}$
 3 to $780 \mu\text{C m}^{-2}$, which surpassed Paschen's Law theoretical limit.



4
 5 **Figure 9.** (a) Structure and principle of charge injection enabled by air breakdown achieved by a half
 6 wave charge excitation circuit. Reprinted with permission from Ref. 50. Copyright 2022, Wiley. (b)
 7 Theory analysis for the charge reversion process. Reprinted with permission from Ref. 37. Copyright
 8 2023, Royal Society of Chemistry. (c) Discharge mitigation strategy to decrease the dissipation of the
 9 injected surface charge. Reprinted with permission from Ref. 141. Copyright 2023, Wiley.



1 The dissipation of the injected surface charge is still a limitation for charge
2 injection. To improve the stability of the surface charge introduced by excessive charge
3 self-injection, a step-by-step discharge mitigation strategy was proposed by Zhao et al.,
4 as shown in **Figure 9c**.¹⁴¹ They induced air ionization for charge injection onto the
5 surface of dielectric material by utilizing the directional high electric field generated by
6 the charge excitation strategy of the voltage-multiplying circuit. At the operating
7 frequency of 1.5 Hz, the injected charge on the dielectric film could be saturated in 22
8 seconds by using the charge excitation strategy. As shown in **Figure 9c-(i)**, when the
9 gap voltage of CS-TENG is higher than the air breakdown voltage, the discharge
10 phenomenon occurs between the dielectric material and the electrode, leading to charge
11 loss. Therefore, to reduce charge loss, a paralleling external capacitor was used to
12 decrease the gap voltage of CS-TENG and then retain the maximum charge on the
13 dielectric material surface, as displayed in **Figure 9c-(ii)**. Based on the step-by-step
14 discharge mitigation strategy, after charge injection, the TENG based on 7 μm thick PI
15 film obtained an ultrahigh charge density of $1480 \mu\text{C m}^{-2}$ under the condition of 5%
16 relative humidity.

17 To better demonstrate the current situation of charge injection, we compared the
18 output performance of the TENGs before and after charge injection in Table 4. As can
19 be seen from the output performance of TENGs in Table 4, these advanced methods of
20 charge injection significantly improve the output performance of TENGs compared to
21 TENGs without charge injection. According to the latest research, charge self-injection
22 strategy (charge injection technology through a half wave charge excitation circuit) is
23 the most effective way to improve the output performance of TENGs. Compared with
24 the traditional charge injection method, it can achieve a higher surface charge density.



1 With all that said, regardless of the used material, charge injection can increase the
 2 surface charge density of the triboelectric materials by directly increasing the number
 3 of charges. However, the injected charge is easily dissipated, which severely limits the
 4 application of charge injection in TENGs.

5 Table 4. The summary of TENG with charge injection.

| Charge Injection Method | Material | Before Injection | | | | After Injection | | | | Ref. |
|---|------------------|------------------|---------------------------------|-----------------------------|------------------------|-----------------|----------------------------------|-----------------------------|------------------------|------|
| | | V_{oc} | I_{sc} | Q_{sc} | Output Power | V_{oc} | I_{sc} | Q_{sc} | Output Power | |
| Ionized-air injection | FEP | 200 V | 18 mA/m ² | 50 μ C/m ² | — | 1000 V | 78 mA/m ² | 240 μ C/m ² | 315 W/m ² | 134 |
| High-voltage charge injection | Nylon 11 PTFE | 15.2 V | 1.84 μ A | — | — | 600 V | 12.8 μ A | — | 5.83 mW | 140 |
| Ion-injection | PTFE/PEO | 77 V | 1.6 mA/m ² (5 Hz) | 13.5 μ C/m ² | — | 900 V | 20 mA/m ² (5 Hz) | 149 μ C/m ² | 9 W/m ² | 142 |
| Tunneling electron injection | FEP | — | — | 120 μ C/m ² | 0.49 W/m ² | — | — | 252 μ C/m ² | 2.08 W/m ² | 143 |
| Prior-charge injection | PVDF | 584 V | 15.3 mA/m ² | 79 μ C/m ² | — | 1008 V | 32.1 mA/m ² | 121 μ C/m ² | — | 144 |
| Charge injection enabled by air breakdown | PI | — | — | 21 μ C/m ² | 0.09 W/m ² | — | 40 mA/m ² (1 Hz) | 880 μ C/m ² | 9.04 W/m ² | 50 |
| Charge reversion process | PTFE | — | 4 mA/m ² (1 Hz) | 97 μ C/m ² | 1.5 mW/m ² | — | 81.7 mA/m ² (1 Hz) | 720 μ C/m ² | 89.4 mW/m ² | 37 |
| Charge self-injection strategy | PI | — | 2.8 mA/m ² (3 Hz) | 23 μ C/m ² | 86.9 mW/m ² | 960 V | 350 mA/m ² (3 Hz) | 1480 μ C/m ² | 86 W/m ² | 141 |

6

7 5 Materials Design for Controlling Charge Loss



1 Except for charge generation, charge loss is also an essential factor that determines
2 the output performance of TENGs.^{137, 145} Charge loss can be divided into two parts: air
3 breakdown, and charge drift in the triboelectric materials.^{39, 83} In this section, we will
4 emphatically introduce two strategies to improve the output performance of TENGs:
5 inhibition of air breakdown and utilization of charge drift.

6 5.1 Inhibition of Air Breakdown

7 In the actual TENGs output test, air breakdown is widespread and greatly affects
8 the output performance of TENGs. Wang et al. utilized a dual dielectric layer to inhibit
9 air breakdown.¹³⁷ PVDF is chosen for the air breakdown suppression layer due to its
10 high relative permittivity, while PI is chosen for the dielectric charge leakage
11 suppression layer because of its low dielectric charge leakage. By suppressing air
12 breakdown and dielectric charge leakage simultaneously, the maximum peak power
13 density at 2 Hz is 61.3 W m^{-2} and the output charge density of the TENG is 2.2 mC
14 m^{-2} . To suppress air breakdown under high charge density conditions, Liu et al.
15 demonstrated a new triboelectric polymer, poly(vinylidene fluoride-trifluoroethylen-
16 chloroethylen) (P(VDF-TrFE-CFE)).¹⁴⁶ The high dielectric permittivity of
17 P(VDF-TrFE-CFE) can inhibit air breakdown. The increased upper limit of air
18 breakdown in TENGs leads to unprecedented levels of charge density and energy
19 density. The charge density and energy density of the TENG can reach 8.6 mC/m^2 and
20 0.808 J/m^2 per cycle, respectively. These studies effectively suppressed air breakdown
21 in the TENG, preventing triboelectric charge decay and boosting the TENG output.

22 Recent studies indicate that air breakdown is inevitable when the TENGs work in
23 the air and limits the maximum surface charge density of the TENG.^{147, 148} In addition
24 to the working environment, the working mode of TENGs also has an influence on air



1 breakdown.^{84, 149} Especially in freestanding triboelectric-layer (FT) mode, air
2 breakdown greatly limits the output performance of the TENG.

3 In a recent year, Deng et al. reported a ternary electrification layered architecture
4 TENG (TEL-TENG) system to inhibit air breakdown, as shown in **Figure 10a**.⁴⁴
5 Compared with previously reported binary electrification layered TENG (BEL-TENG),
6 the upper rotator of the TEL-TENG is constructed by using copper and fluorinated
7 ethylene propylene (FEP) as the two kinds of triboelectric materials and another
8 triboelectric material Kapton used for the stator of the TEL-TENG. Based on the unique
9 structure design, the output performance of the TEL-TENG has been greatly improved,
10 which leads to a 2.5-fold enhancement of the peak power compared to a BEL-TENG
11 consisting of copper and FEP. Moreover, as the simulation results illustrated in **Figure**
12 **10b**, a ternary electrification layered architecture can effectively reduce the electric field
13 and then inhibit air breakdown. Additionally, in 2021, Li et al. proposed a polyester fur-
14 reinforced rotary triboelectric nanogenerator (PFR-TENG), as displayed in **Figure 10c**.
15 ⁴⁵ This report also used the ternary electrification layered architecture, and polyester fur
16 was chosen as the third triboelectric material. The PFR-TENG electric output remains
17 at 100% after 100k cycles of continuous testing using partial soft-contact and non-
18 contact modes, effectively reducing abrasion on the dielectric layers' surface and
19 improving the stability of the TENG.

20 The ternary electrification layer (TEL) structure has proven to be helpful in
21 improving the output performance of TENG.^{44, 45} However, air breakdown could also
22 occur on the interface of tribo-layers, which limits the maximization of the output of
23 the TEL-TENGs. Therefore, to further improve the TENG's output, in 2023, An et al.
24 reported a new design of TEL-TENG with a shielding layer and shrouded-tribo-area

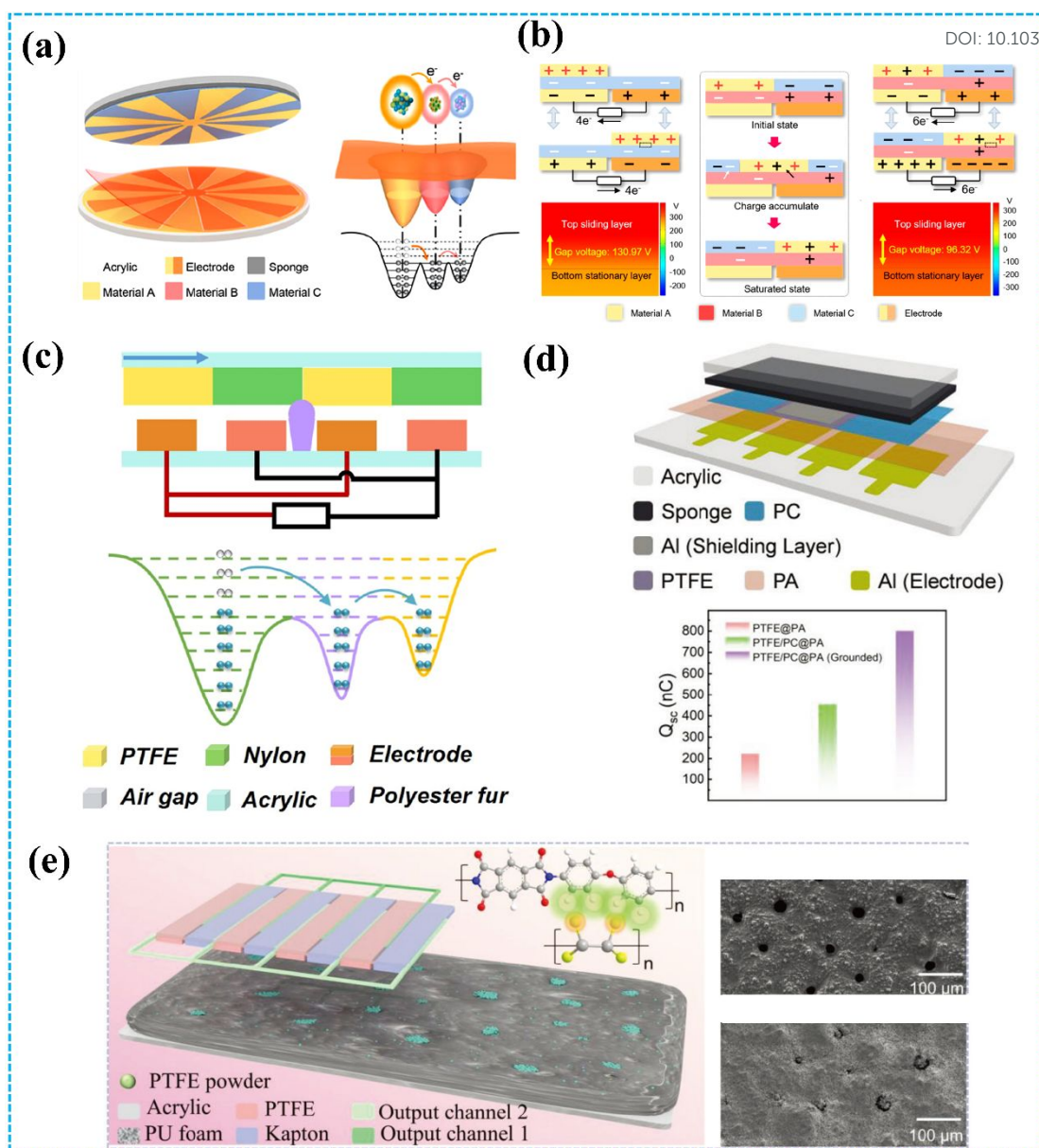


1 (SS-TEL-TENG) to prevent air breakdown (**Figure 10d**).¹⁵⁰ Air breakdown is
2 effectively suppressed based on the grounded conductive shielding layer and the
3 increased shrouded area. Through structure and material optimization, SS-TEL-TENG
4 demonstrates a 3.59-fold increase in output charge compared to traditional S-TENG
5 and a 1.76-fold increase compared to TEL-TENG. Additionally, the TEL structure can
6 also be used to improve the output performance of DC-TENG. As shown in **Figure**
7 **10e**, Shan et al. proposed a multiple unit ternary electrification strategy based on
8 triboelectrification and corona discharge.¹⁵¹ The triboelectric properties of PU film can
9 be controlled by adding PTFE powder, resulting in the realization of its
10 electropositivity/electronegativity during friction with PTFE/Kapton. The output
11 charge density of the optimized rotary TENG can reach 5.5 mC m^{-2} with an $82 \text{ }\mu\text{C}$
12 transfer charge per round, which exceeds all previous sliding DC-TENG records.

13 To illustrate the present development of inhibition of air breakdown in TENGs,
14 we summarized the output performance of TENGs using different methods to inhibit
15 air breakdown in **Table 5**. From **Table 5**, it is clear that high-dielectric polymers can
16 achieve high output performance by inhibiting air breakdown. Additionally, TENGs
17 based on FT working mode with a ternary electrification layered architecture have
18 realized high output performance by inhibiting air breakdown. Inhibition of air
19 breakdown has been achieved based on the triboelectric effect between three types of
20 triboelectric materials, providing a new thought to reduce charge loss through material
21 design.

22





1
2 **Figure 10.** (a) Structural design of the TENG system and the electron-cloud-potential-well model during
3 contact. (b) Schematics of operating principle of the TENG system. Reprinted with permission from Ref.
4 44. Copyright 2020, American Chemical Society. (c) The cross-section schematic of the TENG and the
5 electron cloud potential well model for surface charge transfer. Reprinted with permission from Ref. 45.
6 Copyright 2021, Elsevier. (d) Structural schematic and output performance of TENG. Reprinted with
7 permission from Ref. 150. Copyright 2023, Wiley. (e) Structure of ternary dielectric electrification
8 TENG and SEM images of PU with/without PTFE powder. Reprinted with permission from Ref. 151.
9 Copyright 2024, Wiley.



1 Table 5. The summary of TENG with inhibition of air breakdown.

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| Strategy | Triboelectric Material | Output Performance | | | | Ref. |
|--|--|--------------------|-----------------|------------------------------|---|------|
| | | V_{OC} | I_{SC} | Q_{SC} | Output Power | |
| Dual dielectric layer | PVDF/PI (with charge excitation technology) | — | — | 2.2 mC/m ² | 30.7 W m ⁻² Hz ⁻¹ | 137 |
| High dielectric layer | P(VDF-TrFE-CFE) (with charge excitation technology) | — | — | 8.6 mC/ m ² | 0.77 W m ⁻² Hz ⁻¹ | 146 |
| Ternary electrification layered architecture | Cu/FEP@Kapton (Kapton as the intermediate material) | 993.6 V | 21.7 μ A | — | 4.4 mW | 44 |
| | Nylon/PTFE@polyester fur (polyester fur as the intermediate material) | 10 KV | 15 μ A | 580 nC | 201.83 mW | 45 |
| | PC/PTFE@PA (PA as the intermediate material) | — | 25.8 μ A | 3.69 μ C | 25.4 mW | 150 |

2

3 5.2 Utilization of Charge Drift.

4 In previous studies, the leakage current of the tribo-layer has been a key factor
5 limiting the output performance of TENGs. However, in recent research progress,
6 researchers have started to use the leakage current of the tribo-layer to achieve charge
7 migration and then improve the output of the TENG.

8 In 2018, Lai et al. investigated the transport and storage process of triboelectric
9 charges in the tribo-layer by imbedding criss-crossed gold layers in the near-surface of
10 the tribo-layer.¹²¹ The main dynamic motion for triboelectric charges in the tribo-layer
11 is the drift process caused by the electric field, and the direction of this process is
12 vertically downward (from the surface to the inside of the material). The drift process



1 of triboelectric charges decreases the surface charge density of tribo-layer, which
2 contributes to the further accumulation of triboelectric charges on the surface. The
3 charge density of the TENG reaches $168 \mu\text{C m}^{-2}$, which is nearly 4 times the value of
4 the TENG based on pure polymer.

5 Fu et al. reported a high output performance and durability of TENG by changing
6 the dielectric surface effect into a volume effect through the leakage current of the
7 millimeter-thick porous polyurethane (PU) foam film (in **Figure 11a**).⁴⁶ The high
8 leakage property of the porous film allows it to transfer electrical charges from the
9 surface to the inside of the material, thus realizing high charge migration. Utilizing the
10 strong charge migration characteristics of the porous PU foam film, the average power
11 density of the TENG increased to $20.7 \text{ W m}^{-2} \text{ Hz}^{-1}$. Moreover, after 200,000 cycles,
12 the output performance of the rotary-mode TENG did not change significantly, which
13 showed high durability. This study offers a novel method to enhance TENGs' output
14 performance and broaden the selection of materials for high performance TENGs.
15 Similarly, as shown in **Figure 11b**, Sun et al. introduced multi-walled carbon nanotubes
16 (MWCNT) in polyurethane (TPU) to realize charge migration.⁴⁷ The charges generated
17 by contact electrification could be transferred from the surface of the TPU to the interior
18 due to the excellent electrical conductivity of the MWCNT. Moreover, with the
19 increasing content of MWCNTs, the electrical conductivity of MWCNT/TPU sharply
20 increased, which led to strong charge migration. Based on the above characteristics, the
21 short-circuit current of the TENG based on MWCNT/TPU composite film improved
22 100 times compared to the traditional dielectric TENG. Furthermore, even in high
23 humidity environments, this TENG could maintain a stable output. Similarly, Wu et al.
24 utilized the hysteretic and ordered charge drift behavior of dielectric polymers to



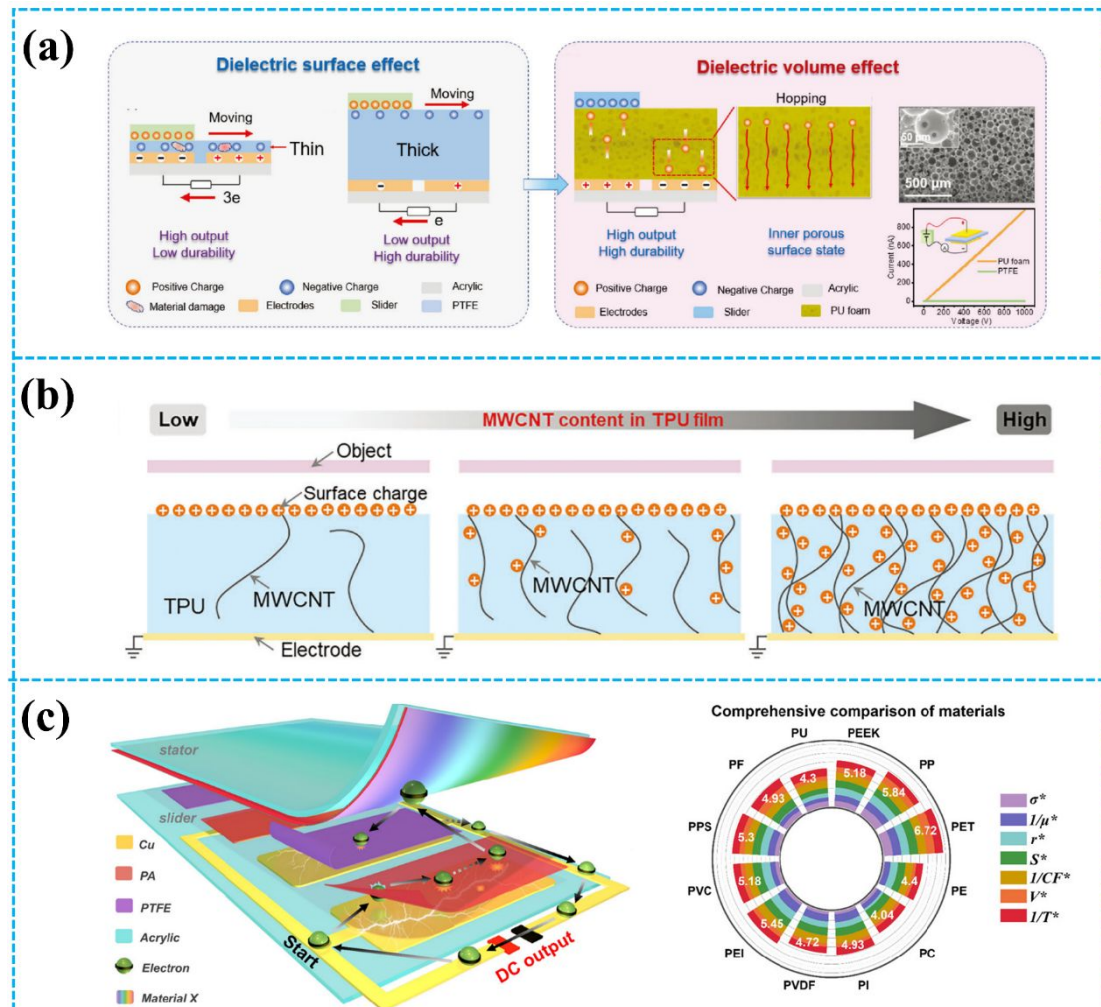
1 construct TENGs with a stable and continuous (SC) output ability (SC-TENG).⁸⁷ Under
2 the action of the triboelectric electric field, the charge generated by triboelectrification
3 migrates directionally from the surface to the inside of the polyurethane (PU) due to its
4 high leakage property. Additionally, using a 1 mm-thick PU film ensures both the
5 excellent wear resistance and high output performance of the TENG.

6 In addition, charge migration can be also used to achieve high-performance DC
7 output. By coupling the charge migration and the ternary dielectric triboelectrification
8 effect, Li et al. developed a DC-TENG with improved output performance, as shown in
9 **Figure 11c**.⁴⁸ After continuous friction, a lot of positive and negative charges
10 accumulated on the surface of PA and PTFE films. The leakage current occurred
11 between the electrode and PA film due to the high electric field, resulting in a DC output
12 in the external circuit. The testing results show that the charge density output has a
13 highly linear relationship with the leakage current of the positive tribo-layer. Moreover,
14 the electronegativity of the triboelectric material is also vital for the charge density
15 output. Therefore, they established the ternary dielectric evaluation rules for material
16 selection and improving performance. After parameter optimization, the DC-TENG
17 based on PA/PET/PTFE achieved an ultrahigh average power density of 6.15 W m^{-2}
18 Hz^{-1} . Similarly, Zhang et al. proposed a novel insulator-based quasi-tribovoltic
19 nanogenerator (I-Q-TVNG) with ultrahigh voltage and power by utilizing charge drift
20 in the dielectric material.¹⁵² This I-Q-TVNG exhibits an ultrahigh output voltage of
21 2324 V, and an average power of 11.8 mW. Additionally, it can also maintain a nearly
22 constant DC output with a crest factor of approximately 1.0204.

23 The detailed output performance of TENGs with utilization of charge drift is
24 shown in **Table 6**. Given the above, the triboelectric charges generated by



1 triboelectrification can migrate from the surface of the material to the inside of the
 2 material through the selection of triboelectric materials with high leakage current,
 3 achieving utilization of charge drift and thus further output performance improvement.



4
 5 **Figure 11.** (a) Dielectric volume effect-based TENG. Reprinted with permission from Ref. 46. Copyright
 6 2023, Wiley. (b) Schematic diagrams and charge dispersion of CN-TENGs with different MWCNT
 7 contents. Reprinted with permission from Ref. 47. Copyright 2024, Wiley. (c) Conceptual diagram of the
 8 TENG and comprehensive selection rules of intermediate triboelectric materials. Reprinted with
 9 permission from Ref. 48. Copyright 2023, Royal Society of Chemistry.



1 Table 6. The summary of TENG with utilization of charge drift.

| Strategy | Triboelectric Material | Output Performance | | | | Ref. |
|--|--|--------------------|----------------------------|------------------------------|---|------|
| | | V_{OC} | I_{SC} | Q_{SC} | Output Power | |
| Internal-space-charge zones | Au/PDMS | — | — | 168 $\mu\text{C}/\text{m}^2$ | 1 W/ m^2 | 145 |
| Dielectric volume effect | Polyurethane foam film | 9 kV | 100 μA | 2.8 μC | 40.9 W m^{-2} Hz^{-1} | 46 |
| Charge dispersion strategy | MWCNTs/TPU | 320 V | 400 μA | — | 20 mW | 47 |
| Charge migration | Polyurethane | — | 7.4 μA | 879 nC | 9.4 W m^{-2} Hz^{-1} (average) | 87 |
| Charge leakage effect and the ternary dielectric triboelectrification effect | PA/PTFE@PET (PET as the intermediate material) | 3000 V | — | 7.12 mC/m^2 | 6.15 W m^{-2} Hz^{-1} (average) | 48 |
| Charge extraction | Nitrocellulose /PU | 2324 V | 1.7 mA/m^2 | — | 11.8 mW (average) | 152 |

2

3 **6 Conclusion and Future Perspectives**

4 In conclusion, this work outlined the recent research in the development of
5 material design for improving TENG's output performance. Strategies discussed for
6 high surface charge density include surface morphological modification, chemical
7 modification, dielectric material doping, and charge injection. Furthermore, methods
8 for improving the TENG's output by inhibiting air breakdown and utilizing charge drift
9 have also been discussed. This paper is of great significance to the research of
10 triboelectric materials and also helpful to the practical research and innovation of
11 TENGs. This review can significantly contribute to the research on triboelectric
12 materials and advance practical studies of TENGs. The challenges and future
13 perspectives for improving the output performance of TENGs have been summarized
14 below.



1 6.1 Challenges

2 (1) The fundamental mechanisms of contact electrification still need further research.

3 Several hypotheses of contact electrification have been proposed, but a definitive
4 conclusion has not yet been established.

5 (2) The coupling mechanisms between the triboelectric effect and other effects such as
6 the piezoelectric effect, photovoltaic effect and magnetization effect need to be
7 further systematically and comprehensively understood.

8 (3) The study of the leakage current of triboelectric materials for high performance
9 TENGs is insufficient. Most of the past research proposed that the leakage current
10 of the material limited its output performance. However, a recent study shows that
11 proper leakage current is beneficial to the improvement of TENGs output
12 performance.

13 (4) The applications of TENGs in harsh environments. Triboelectric materials must be
14 endowed with functional characteristics while maintaining their triboelectric
15 properties to meet the diverse requirements of TENGs in different environments
16 and then advance the commercial development of TENGs.

17 6.2 Future Perspectives

18 Although progress has been achieved in enhancing the output performance of
19 TENGs, more work is required to effectively tackle the remaining challenges. The
20 strategies for improving the TENGs' output performance are prospected from the
21 following aspects: Triboelectric material is the most important part of TENGs, which
22 directly affects the output performance of TENGs. Additionally, the output
23 performance of TENGs is also affected by the environment, such as high humidity, high
24 temperature, etc. Therefore, the ideal triboelectric material should have a high charge



1 density, good mechanical stability, and environmental adaptability. New triboelectric
2 materials need to be developed to obtain high output performance in harsh
3 environments. In high humidity environments, on the one hand, the properties of the
4 triboelectric material can be changed by chemical modification so that it can maintain
5 high output performance under high humidity conditions. On the other hand, it would
6 also be a good choice to search for a material that can couple the triboelectric effect and
7 the moisture-generating effect. At present, the most obvious technology to improve the
8 TENG output performance is the power management system (PMS), which is one of
9 the key technologies to realize the application of TENG technology. Some power
10 management systems would provide a bias voltage to the friction material during
11 operation. This bias voltage polarizes the triboelectric material, then improving the
12 output performance of TENGs. Composite films (especially those filled with high-
13 dielectric nanoparticles) are also a promising research topic in this realm.

14 These important issues highlight great opportunities for researchers across
15 different sectors to enhance the output performance of TENGs. The continuous
16 technical innovation and theoretical research promote its application prospects in the
17 field of energy harvesting and self-powered sensing, which is crucial for the widespread
18 commercial applications of TENGs.

19 **Author Contributions**

20 X. Li: investigation, data curation, formal analysis, visualization, writing - original draft,
21 editing. Q. Yang and D. Ren: investigation, review, editing. Q. Li, H. Yang, X. Zhang:
22 review, editing. Y. Xi: resources, supervision, funding acquisition, writing - review &
23 editing.



1 **Conflicts of interest**

2 There are no conflicts to declare.

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Data availability is not applicable to this article as no new data were created or analyzed in this study.

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