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# Superior Charge Density of Triboelectric Nanogenerator via Trap Engineering

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Triboelectric nanogenerator (TENG) offers a novel approach for converting high-entropy mechanical energy into electrical energy, yet achieving high charge density remains critical. Optimizations using dielectrics with high specific capacitance have mitigated air breakdown, but charge loss within dielectrics persists as a limiting factor. Here, based on poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) with high specific capacitance, (P(VDF-TrFE-CFE)) composites' trap density and energy are engineered using high-polarity interfaces from barium titanate (BTO) nanoparticles and dense chain segment stacking induced by electrostatic interaction with polyetherimide (PEI) to enhance charge retention capability. With modified high interfacial traps, an ultrahigh charge density of 9.23 mC m<sup>-2</sup> is achieved in external charge excitation (ECE) TENG using 0.2 vol% PEI/P(VDF-TrFE-CFE) film, marking the highest charge density reported for single-unit TENGs. This work provides novel material strategies for high-performance TENGs, paving the way for their large-scale practical applications.

## 1. Introduction

The artificial intelligence (AI) boom has led to shocking electricity consumption, thereby heightening the urgency for greater research in energy harvesting technologies.<sup>[1–3]</sup> Triboelectric nanogenerator (TENG), relying on triboelectrification and electrostatic induction, emerges as a promising technology for renewable energy, as it efficiently harvests mechanical energy from the

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environment.<sup>[4-6]</sup> With its notable advantages such as remarkable conversion efficiency for low-frequency vibrations, high voltage output, affordability, and flexible structure, TENGs find applications across diverse fields,<sup>[7]</sup> including micro-nano energy harvesting,[8,9] selfpowered sensing,<sup>[10,11]</sup> blue energy,<sup>[12,13]</sup> battery recycling,<sup>[14,15]</sup> etc. Meanwhile, the wide application of TENGs, along with advancements in miniaturization, integration, and biodegradable, stretchable and flexible materials<sup>[16,17]</sup> in the new era of the Internet of Things (IoTs) still face challenges due to their lower energy density. Thus, it is of great significance to develop TENGs with higher charge density, as the output energy is directly proportional to the square of charge density.<sup>[18]</sup>

Various strategies have been proposed to boost TENG's charge density, such as molecular structure design,<sup>[19–21]</sup> dielectric material filling,<sup>[22]</sup> environment

control,<sup>[23,24]</sup> charge excitation or injection technology.<sup>[25–27]</sup> However, the inevitable air breakdown persists in TENGs. We have introduced a novel triboelectric polymer, P(VDF-TrFE-CFE) with high dielectric permittivity, which successfully limited air breakdown benefiting from its high specific capacitance and resulted in a high-record charge density of 8.6 mC m<sup>-2</sup> in external charge excitation (ECE) TENGs.<sup>[28]</sup> However, the optimization of

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dielectric permittivity in polymers has reached a bottleneck. Although inorganic ceramics exhibit higher dielectric permittivity than polymers, this advantage is offset by significantly enhanced charge/energy loss. The higher dielectric permittivity tends to cause significantly increased charge/energy loss due to enhanced interaction between the electric field and charges, negatively impacting TENGs' output.<sup>[29]</sup> As the charge density increases further, this impact becomes more severe. Therefore, it's crucial to enhance TENGs' output to minimize charge loss within dielectrics while limiting air breakdown.

There have been a number of innovative approaches to suppressing charge loss within dielectrics including the use of a charge-trapping layer, charge-blocking layer, multilayer as an intermediate laver, and electrode surface modification.<sup>[30-34]</sup> Despite these methods effectively suppressing charge loss within dielectrics, the layer structure significantly increases the cost of large-scale production. Recently, by introducing self-assembled molecules (N, N-Dimethyl-3-aminopropyl) trimethoxysilane, KH556) with large energy gaps on polyethylene terephthalate (PET) fabric to prepare single layer structure and construct deep traps, charge retention was improved while decreasing dissipation rates.<sup>[35]</sup> Traps are localized states that can confine charges within potential wells and prevent charges from moving freely. Thus, rational trap design is an efficient method to suppress charge loss within dielectrics and improve the output performance of TENGs. However, the charge density was only improved to 0.0776 mC m<sup>-2</sup>, far lower than the requirement for practical applications. Therefore, there is an urgent need for suppressing charge loss within dielectrics by trap modification methods that are highly applicable, easy to scale up at low cost, and capable of achieving excellent output performance.

In this work, we report new strategies to optimize P(VDF-TrFE-CFE)'s charge retention capability through trap engineering. Traps are successfully introduced into P(VDF-TrFE-CFE) polymer using high-polarity interfaces from BTO nanoparticles and dense chain segment stacking induced by electrostatic interaction with PEI, respectively. Trap properties are systematically explored, revealing enhanced trap density and energy, which contribute to a high charge retention capability. Consequently, by simultaneous limiting air breakdown and charge loss, the ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) film achieves an ultrahigh charge density of 9.23 mC m<sup>-2</sup>, average power density of  $0.92 \text{ W} \text{ m}^{-2} \text{ Hz}^{-1}$  and energy density of 919 mJ m<sup>-2</sup> cycle<sup>-1</sup> under a load of 1 M $\Omega$ , marking the highest performance among singleunit TENGs. Moreover, ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) film shows exceptional humidity resistance, achieving a notable charge density of  $6.36 \text{ mC} \text{ m}^{-2}$  at 85% humidity, surpassing the previous best performance by 1.93 times under similar conditions. This work provides new material strategies for optimizing TENGs' performance and will accelerate the development of TENGs toward large-scale practical applications.

## 2. Results and Discussion

### 2.1. Charge Decay Phenomenon and Optimization Strategies

The basic structure of an ECE-TENG is shown in **Figure 1a**. It is composed of an excitation TENG, a main TENG, and a charge excitation circuit (CEC) consisting of two diodes and an exter-

nal capacitor, and the detailed working mechanism is given in Figure S1 (Supporting Information) and Supplementary Note 1. For an ECE-TENG, the voltage across the external capacitor gradually stabilizes as charges accumulate, maintaining a high level during the contact and separation process at the equilibrium state (Figure S2, Supporting Information). The electric field across the air layer and dielectric of the main TENG was obtained (Detailed calculation shown in Supplementary Note 2). As shown in Figure 1b, both the air layer and dielectric sustain an instantaneous high electric field. On one hand, air breakdown would occur since the electric field across the air layer exceeds the air breakdown threshold, resulting in the deposition of reverse charges on the top electrode and dielectric's surface, thereby limiting the output of ECE-TENG. Both theories and experiments have shown that dielectrics, possessing high specific capacitance, can effectively mitigate air breakdown (Supplementary Note 3).<sup>[28]</sup> On the other hand, charge loss within dielectrics, including polarization loss from dipoles and conduction loss from weakly bound charges, tends to occur under an electric field, leading to transferred charges during separation are lower than those during contact (Detailed in Figure S3, Supporting Information and Supplementary Note 4). Moreover, larger electrical conductivity (Figure S4, Supporting Information) and a few reverse charges (Supplementary Note 5) of P(VDF-TrFE-CFE) film suggest high charge loss within P(VDF-TrFE-CFE), which results in the accumulation-decay balance to be reached prematurely, making it difficult to achieve the theoretical charge density.

Therefore, two strategies are proposed to limit P(VDF-TrFE-CFE)'s charge loss through modifying traps. As shown in Figure 1c, owing to P(VDF-TrFE-CFE)'s high specific capacitance, air breakdown is limited, and a charge density of  $8.31 \text{ mC m}^{-2}$  is obtained in ECE-TENG. By introducing high-polarity interfaces into P(VDF-TrFE-CFE) polymer using BTO nanoparticles, trap density and energy for both deep and shallow traps can be improved, which results in improved charge retention capability. Consequently, the charge density is increased to 8.85 mC m<sup>-2</sup> due to the simultaneous limitation of air breakdown and charge loss. In addition, interfacial traps are also modified by designing dense chain segment stacking using the electrostatic interaction between P(VDF-TrFE-CFE) and polyetherimide (PEI), and charge density is successfully improved to a high record of 9.23 mC m<sup>-2</sup> due to the simultaneous suppression of air breakdown and charge loss.

To compare with previous works, the development of charge density for single-unit TENGs is shown in Figure 1d.<sup>[20–22,24,28,36–41]</sup> Some methods, such as surface modification, soft contact, structure optimization, ultrathin dielectrics, improving charge retention, multilayer, and vacuum have been employed to enhance the triboelectric effect. Charge excitation technology also overcomes the limitation of the triboelectric effect. In our previous work, charge density has been improved to 8.6 mC m<sup>-2</sup> by mitigating air breakdown through high-specific capacitance's P(VDF-TrFE-CFE). In this work, charge loss is further limited by trap engineering, achieving a high-record charge density of 9.23 mC m<sup>-2</sup> in ECE-TENG using PEI/P(VDF-TrFE-CFE). It's worth noting that the charge density discussed in this work represents the transferred charge density during separation, providing an accurate measure of energy utilized for work. This is distinct from the average charge density, which



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**Figure 1.** Charge decay phenomenon and strategies for high output performance of ECE-TENG. a) Schematic diagram of ECE-TENG. b) The electric field across the air layer and dielectric during the contact-separation process for an ECE-TENG with P(VDF-TrFE-CFE) polymer. Schematic diagram of air breakdown and charge loss in dielectric for a main TENG within ECE-TENG. c) Results achieved by two strategies of trap engineering: introducing high-polarity interfaces by doping BTO nanoparticles into P(VDF-TrFE-CFE) polymer and engineering the chain segment stacking behavior via electrostatic interaction with polyetherimide (PEI) interchain. d) The comparison of output performance with previously reported works.

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incorporates testing errors, as outlined in Figure S7 (Supporting Information) and Supplementary Note 6.

#### 2.2. The Modification of Traps via High-Polarity Interfaces

High-polarity interfaces have been shown to enhance dielectric properties, leading to improved charge storage capability.<sup>[42]</sup> Therefore, introducing high-polarity interfaces into P(VDF-TrFE-CFE) can potentially introduce traps, minimizing air breakdown and charge loss simultaneously. To introduce high-polarity interfaces into P(VDF-TrFE-CFE) polymer, BTO nanoparticles are selected to be doped into P(VDF-TrFE-CFE) polymer. BTO exhibits excellent dielectric permittivity (≥1000) and is environmentally friendly. BTO nanoparticles have a cubic crystal structure (Figure 2a) and a size range of  $72 \pm 15$  nm, which facilitate more high-polarity interfaces and higher dielectric permittivity for P(VDF-TrFE-CFE) composites owing to the large specific surface of nanoparticles.<sup>[42,43]</sup> The X-ray diffraction (XRD) peaks of BTO/P(VDF-TrFE-CFE) composites, as illustrated in Figure 2b, become more pronounced with increasing BTO content, suggesting successful doping of BTO nanoparticles into the P(VDF-TrFE-CFE) film.

The trap energy (shallow or deep traps) and trap density determine a dielectric's ability to capture and retain charge. When electrons or holes are injected into the dielectric surface, they are initially trapped by shallow traps, while some continue to migrate to deeper traps.<sup>[44]</sup> The higher trap density and the deeper traps make charges difficult to dissipate, contributing to a more stable charge retention. The hole trap properties of BTO/P(VDF-TrFE-CFE) films were characterized by the isothermal surface potential decay (ISPD) method and a detailed calculation process is provided in Supplementary Note 7. As shown in Figure 2c,d and Figure S8 (Supporting Information), with the introduction of high-polarity interfaces, trap density and energy are successfully modulated to varying extents. Specially, in comparison to P(VDF-TrFE-CFE) film, the trap energy and density of 0.2 vol% BTO/P(VDF-TrFE-CFE) film are enhanced for both deep and shallow traps. The higher trap density facilitates the capture of more weakly bound charges, and the deeper trap can impede the deintercalation of these captured charges, indicating that 0.2 vol% BTO/P(VDF-TrFE-CFE) film has the potential for high charge retention capability. Despite the increase in trap energy is observed in composites with higher BTO content, the significant reduction in trap density compared to the 0.2 vol% BTO/P(VDF-TrFE-CFE) film may lead to variations in the charge retention capability of BTO/P(VDF-TrFE-CFE) composites.

To explore the effect of traps on charge retention capability, the relevant electrical properties were characterized. As seen in Figure 2e, 0.2 vol% BTO/P(VDF-TrFE-CFE) film with enhanced traps exhibits the highest breakdown strength of  $\approx$ 495 V µm<sup>-1</sup> (Detailed analysis shown in Supplementary Note 8 and Figure S9, Supporting Information). As the BTO content increases, 7 vol% BTO/P(VDF-TrFE-CFE) film exhibits more pronounced agglomeration compared to the 0.2 vol% BTO/P(VDF-TrFE-CFE) film, resulting in the decreased breakdown strength and thus reduced charge retention capability at high voltage. According to the electromechanical model, the breakdown strength of dielectric polymers is proportional to their mechanical strength.<sup>[45]</sup> As

shown in Figure 2f, a significant improvement in Young's modulus for the 0.2 vol% BTO/P(VDF-TrFE-CFE) film (219 MPa) is achieved compared to that of P(VDF-TrFE-CFE) (140 MPa) due to the enhancement effects of BTO nanoparticles and favorable interfacial interaction between polymer and BTO nanoparticles.<sup>[46]</sup> Subsequently, the Young's modulus of the 0.5 vol% BTO/P(VDF-TrFE-CFE) film decreases likely due to stress concentration resulting from the agglomeration of BTO nanoparticles. Following this, a progressive improvement is observed in Young's modulus of BTO/P(VDF-TrFE-CFE) films owing to the increase in the high Young's modulus of BTO. Moreover, 0.2 vol% BTO/P(VDF-TrFE-CFE) film with favorable interfacial interaction shows the lowest leakage current compared to other BTO/P(VDF-TrFE-CFE) films (Figure 2g, the test parameters shown in Figure S10, Supporting Information). These characteristics indicate that the enhanced traps introduced by high-polarity interfaces successfully capture weakly bound charges and thus improve BTO/P(VDF-TrFE-CFE) films' charge retention capability. The temporal changes in surface potential (Figure S11, Supporting Information) further confirm that BTO/P(VDF-TrFE-CFE) films with enhanced traps exhibit a slower surface potential decay, suggesting a reduced charge dissipation rate.

In addition, the specific capacitances of BTO/P(VDF-TrFE-CFE) films are successfully improved caused of the doped BTO nanoparticles with high dielectric permittivity (Figure 2h; Figure S12, Supporting Information), indicating the suppressed air breakdown in BTO/P(VDF-TrFE-CFE) films. Moreover, the self-polarization effect within the BTO/P(VDF-TrFE-CFE) composites is also advantageous for achieving improved output performance (Figure S13, Supporting Information and Supplementary Note 9).<sup>[22]</sup> As shown in Figure 2i, the charge density of ECE-TENG is improved to 8.85 mC m<sup>-2</sup> for ECE-TENG with 0.2 vol% BTO/P(VDF-TrFE-CFE) film, suggesting the attainment of a higher equilibrium between charge accumulation and decay (The complete dynamic charge density curves and current density curves shown in Figures S14 and S15, Supporting Information).

The equilibrium state of an ECE-TENG is influenced by both charge accumulation and decay processes. Factors such as the performance of the excitation TENG, the capacitance, and the performance of the main TENG play crucial roles in the charge accumulation process. Since the excitation TENG is controlled to be constant in the experiment, its influence can be considered negligible. Although the increase in specific capacitance of BTO/P(VDF-TrFE-CFE) benefits the main TENG's capacitance, the contact efficiency of the main TENG, affected by the surface condition of films, impacts the actual capacitance of the main TENG. As the BTO content increases, the surface becomes rougher, yet still within the low level (<100 nm) and consistent with scanning electron microscopy (SEM) results (Figures S16 and \$17, Supporting Information). As a result, the actual capacitances of 0.2 vol%, 1 vol% and 3 vol% BTO/P(VDF-TrFE-CFE) films in contact with 1 cm<sup>2</sup> copper (Cu) are higher than those of P(VDF-TrFE-CFE), 0.5 vol% and 7 vol% BTO/P(VDF-TrFE-CFE) films (Figure S18, Supporting Information). Moreover, the similar intrinsic output (Figure S19, Supporting Information) and similar actual capacitance for main TENGs with 0.2 vol% and 1 vol% BTO/P(VDF-TrFE-CFE) films indicate that the superior charge density of ECE-TENG with 0.2 vol% BTO/P(VDF-

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Figure 2. The trap modification via high-polarity interfaces and output performance of ECE-TENGs. a) i) the 3D crystal structure of BTO nanoparticles, ii) the SEM image of BTO nanoparticles, and iii) the distribution of BTO's size. b) XRD patterns, c) trap density, d) trap energy, e) breakdown strength and shape parameter ( $\beta$ ), f) Young's modulus, g) leakage currents, h) specific capacitances, i) charge density of BTO/P(VDF-TrFE-CFE) composites with different BTO contents. j) Average power of ECE-TENG with 0.2 vol% BTO/P(VDF-TrFE-CFE) composite at different external load resistance. k) Charge density of ECE-TENG with 0.2 vol% BTO/ P(VDF-TrFE-CFE) composite at different humidity environment.

External load resistance (ohm)

10<sup>6</sup>

107

20%

40%

Relative humidity

60%

80%

10<sup>5</sup>

ED

3

0

0.5

BTO content (vol%)

1 3

0.2

7

10<sup>4</sup>

TrFE-CFE) film is more likely attributed to reduced charge loss, demonstrating the effectiveness of enhanced traps in suppressing charge loss and fully illustrating the significant potential of optimizing charge loss in P(VDF-TrFE-CFE) for achieving superior output performance while concurrently suppressing air breakdown.

Furthermore, the effect of frequency on charge density for ECE-TENG was measured (Figure S20, Supporting Information). ECE-TENGs show similar charge density at 1 and 2 Hz, but a decrease with increasing frequency thereafter, possibly due to insufficient contact at higher frequencies. Moreover, the peak current density, voltage, and average power of the ECE-TENG were tested at different resistances from 10 k $\Omega$  to 10 M $\Omega$ , and the maximum peak power density reaches 0.85 W  $m^{-2}~Hz^{-1}$  with a load of 1  $M\Omega$ (Figure 2j; Figure S21, Supporting Information). To evaluate the performance of ECE-TENG with BTO/P(VDF-TrFE-CFE) composite at practical application, we measured the charge density of ECE-TENG at different humidity. As shown in the charge densityhumidity change curve (Figure 2k), the charge density of the ECE-TENG increases with the decrease in relative humidity under the atmosphere environment. This can be attributed to the formation of a water layer on the triboelectric surface which leads to the charge leakage from the triboelectric surface to air.[47] Remarkably, even when the relative humidity of the atmosphere reaches up to 80%, the ECE-TENG with 0.2 vol% BTO/P(VDF-TrFE-CFE) still maintains an ultrahigh charge density of  $\approx 6.58$  mC m<sup>-2</sup>. Then, working stability was tested under a random atmosphere, employing a Zener diode of 350 V to prevent the device from damaging during prolonged operation. As seen in Figure S22 (Supporting Information), although the Zener diode exhibits a negative impact on output performance, the charge density of the ECE-TENG with 0.2 vol% BTO/P(VDF-TrFE-CFE) remains ≈6.16 mC m $^{-2}$  even after 50 000 cycles, retaining 90% of the maximum output (6.87 mC m<sup>-2</sup>). These results demonstrate the outstanding performance of ECE-TENG with 0.2 vol% BTO/P(VDF-TrFE-CFE) film, highlighting the effectiveness of optimizing the output performance of ECE-TENG through trap modification using a small number of BTO nanoparticles' high-polarity interfaces.

#### 2.3. The Modification of Traps via Designing Chain Stacking

Air breakdown can be effectively suppressed by introducing a very small number of high-polarity interfaces (BTO nanoparticles and P(VDF-TrFE-CFE) polymer). However, the effectiveness of this approach in reducing charge loss is limited by the agglomeration of BTO nanoparticles. The electrostatic interaction between different components in dielectrics can promote interchain interaction, leading to dense chain packing and suppressing charge migration.<sup>[48,49]</sup> Therefore, the polyetherimide (PEI), containing positively charged imide groups, was introduced into P(VDF-TrFE-CFE) for reducing charge loss and enhancing the charge retention capability of composite.

Density functional theory (DFT) calculation results of the distribution of electrostatic potential in P(VDF-TrFE-CFE) and PEI (Figure 3a) show that P(VDF-TrFE-CFE) has a strongly negative charged fluorine group (highlighted in red), whereas PEI has positively charged amide groups (highlight in blue), suggesting possible electrostatic interaction between them. Then, PEI/P(VDF- TrFE-CFE) films were prepared to examine the packing of P(VDF-TrFE-CFE) chains. As shown in Figures S23 and S24 (Supporting Information). PEI/P(VDF-TrFE-CFE) films exhibit structural integrity and low roughness. Moreover, no chemical bonds are formed between PEI and P(VDF-TrFE-CFE) (Figure 3b). Taking advantage of the addition of PEI, the interchain spacing (Figure 3c; Figure S25, Supporting Information) in PEI/P(VDF-TrFE-CFE) composites is decreased from 4.9004 Å for P(VDF-TrFE-CFE) to 4.8671 Å for 5 vol% PEI/P(VDF-TrFE-CFE), which indicates the denser chain packing in PEI/P(VDF-TrFE-CFE) films due to the electrostatic crosslinking of PEI. As a result, Young's modulus of 0.2 vol% PEI/P(VDF-TrFE-CFE) films is significantly improved to 566.9 MPa compared with pure P(VDF-TrFE-CFE) for 139.5 MPa, emphasizing the strengthening effect of electrostatic crosslinking by rigid PEI (Figure 3d). After that, due to the incompatibility characteristics of PEI and P(VDF-TrFE-CFE), Young's modulus decreased. Summarily, the formation of electrostatic crosslinking networks effectively densifies the polymer chain packing and strengthens the polymers, implying improved charge retention capability.

As shown in Figure 3e, although the specific capacitance of PEI/P(VDF-TrFE-CFE) decreases from  $5.5 \times 10^{-5}$  to  $4.3 \times 10^{-5}$ F  $m^{-2}$  as the content of PEI increases from 0 to 5 vol% owing to the low dielectric permittivity of PEI (3.3 at 1 kHz), the 0.2 vol% PEI/P(VDF-TrFE-CFE) film exhibits the lowest loss and leakage current among PEI/P(VDF-TrFE-CFE) films (Figure 3f,g; Figure S26, Supporting Information). To explain this suppressed loss and leakage current of 0.2 vol% PEI/P(VDF-TrFE-CFE) film, electron affinities were determined through DFT calculation for the molecular orbital energy level of PEI and P(VDF-TrFE-CFE) (Figure S27, Supporting Information). As shown in Figure 3h, PEI possessing higher electron affinity ( $\Phi_{PEI}$ , 3.17 eV) than that of P(VDF-TrFE-CFE) ( $\Phi_{CFE}$ , 1.52 eV) can capture the injected and weakly bound electrons via strong electrostatic attraction. This results in a large trap energy level ( $\Phi_{\text{trap}}$ , 1.65 eV) making it difficult for captured electrons to escape from the trap sites. To demonstrate this, trap parameters were measured. As shown in Figure 3i, incorporating PEI into P(VDF-TrFE-CFE) simultaneously amplifies trap energy and density for both deep and shallow traps, indicating that the effective suppression of loss and leakage current is caused by enhanced traps. As demonstrated in Figure S28 (Supporting Information), this enhanced trap state leads to a slower charge dissipation process. In addition, the ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) achieves the highest charge density of 9.04 mC  $m^{-2}$  (Figure 3j) despite its higher air breakdown (The dynamic accumulation curves are shown in Figures S29 and S30, Supporting Information), fully demonstrating that the 0.2 vol% PEI/P(VDF-TrFE-CFE) film exhibits improved charge retention capability due to enhanced traps facilitated by PEI.

#### 2.4. The Optimal Equilibrium State of ECE-TENG

To further explore and achieve the optimal equilibrium state of ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE), annealing treatment was applied to suppress air breakdown and charge loss in 0.2 vol% PEI/P(VDF-TrFE-CFE) films. The 0.2 vol% PEI/P(VDF-TrFE-CFE) films are simplified as pristine (without



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**Figure 3.** The trap modification via designing chain stacking. a) Schematic chemical structures and electrostatic potential distribution of P(VDF-TrFE-CFE) and PEI polymers. b) FTIR, c) spacing, d) Young's modulus, e) specific capacitances, f) Tanδ, g) leakage current of PEI/P(VDF-TrFE-CFE) composites with different PEI contents. h) Schematic illustration of trap energy level introduced by PEI. i) Trap parameters of P(VDF-TrFE-CFE) and 0.2 vol% PEI/P(VDF-TrFE-CFE) composite. j) Charge density of ECE-TENGs with PEI/P(VDF-TrFE-CFE) composites.

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**Figure 4.** The optimal equilibrium state of ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE). a) Trap density, b) trap energy of pristine, pristine-115 and pristine-220 composites. c) Charge density and charge loss of ECE-TENG, the roughness of pristine, pristine-115, and pristine-220 composites. d) Tanδ, e) Leakage current, f) Specific capacitances of pristine, pristine-115 and pristine-220 composites.

annealing treatment), pristine-115 (annealing at 115 °C for 4 h) and pristine-220 (annealing at 220 °C for 4 h), respectively. As shown in **Figures 4**a and **S31** (Supporting Information), compared to the pristine film, trap densities of pristine-115 and pristine-220 are significantly improved for both deep and shallow traps. For example, the deep trap density of pristine-220 is

up to  $3.23 \times 10^{24} \text{ eV}^{-1} \text{ m}^{-3}$ , higher than its shallow trap density ( $2.98 \times 10^{24} \text{ eV}^{-1} \text{ m}^{-3}$ ). In addition, only a slight change is observed in trap energy (Figure 4b), suggesting suppressed charge loss in pristine-115 and pristine-220 compared to the pristine film. This is further supported by the slower charge dissipation process (Figure S32, Supporting Information). To quantitatively

characterize the charge loss, the difference in charge density between the contact and separation processes at equilibrium state was obtained. As shown in Figure 4c, pristine-220 exhibits the lowest charge loss (0.1 mC m<sup>-2</sup>) compared to pristine (2.28 mC m<sup>-2</sup>) and prisitine-115 (1.53 mC m<sup>-2</sup>). Moreover, the dielectric loss in AC voltage and leakage current in DC voltage exhibit the same trend with charge loss in practical measurement of ECE-TENG with three composites (Figure 4d,e and the tan $\delta$  measurement method shown in Figure \$33, Supporting Information), further demonstrating the effective regulation of charge loss by traps.

Although the charge loss in pristine-115 is not the smallest, the maximum charge density (9.23 mC m<sup>-2</sup>) is achieved in ECE-TENG with pristine-115. This may be attributed to the annealing process, which enhances the contact efficiency or specific capacitance of pristine-115. To confirm this hypothesis, the roughness was tested to explore the effect of contact efficiency. Figure 4c shows pristine-115 exhibits the lowest roughness ( $R_{\rm a}$ : 41.945 nm) compared to the pristine film ( $R_a$ : 66.021 nm) and pristine-220 (R<sub>a</sub>: 53.585 nm), indicating that there is higher contact efficiency between Cu electrode and pristine-115. Notably, the pristine-115 exhibits the highest specific capacitance compared to others (Figure 4f), likely due to its high crystallinity and smaller crystalline size,<sup>[28,50]</sup> indicating the lowest degree of air breakdown in ECE-TENG. Summarily, by further suppressing charge loss through trap modification, the optimization of specific capacitance and roughness enables ECE-TENG with pristine-115 to achieve an optimal equilibrium state. This suggests that minimal air breakdown and charge loss in dielectrics are prerequisites for achieving a high equilibrium state, provided the excitation TENG supplies sufficient energy. This guideline is also validated in ECE-TENGs with PEI film as a dielectric layer (Figure S34 and Supplementary Note 10).

#### 2.5. Application Demonstrations of the ECE-TENG

To demonstrate the practical applicability of this remarkable ECE-TENG, we conducted comprehensive tests to evaluate its performance of ECE-TENG using 0.2 vol% PEI/P(VDF-TrFE-CFE) film. As shown in Figure 5a-c, the ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) achieves an average power output of  $0.92 \text{ W} \text{ m}^{-2} \text{ Hz}^{-1}$  and  $919 \text{ mJ} \text{ m}^{-2} \text{ cycle}^{-1}$  at a 1 M $\Omega$  load, surpassing the performance of all existing CS-TENGs.<sup>[28,51-57]</sup> Additionally, the ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) exhibits good moisture resistance (Figure \$35, Supporting Information). For instance, at 85% relative humidity, it achieves a charge density of up to 6.36 mC  $m^{-2}$ , which is 1.93 times higher than the previous best performance under similar humid conditions (Figure 5b; Table S1, Supporting Information).<sup>[22,28,58-62]</sup> Moreover, the stability of ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) film was evaluated through the measurement for 320 000 cycles (Figure 5e). Even after extensive testing, the charge density remains at  $\approx 6.18$  mC m<sup>-2</sup>, demonstrating the outstanding stability of the device at such a high charge density. Notably, this result was obtained using a Zener diode (390 V) which has an adverse effect on the output (Figure \$36, Supporting Information).

Given the remarkable output performance of this ECE-TENG, an AC-DC transformation is essential for powering daily appli-

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ances (Figure 5f). A simple bridge rectifier was used, achieving the average charging speeds of  $\approx$ 4.6, 4.7, and 4.3 µC s<sup>-1</sup> when charging capacities of 100, 470, and 1 µF, respectively (Figure S37, Supporting Information). To maximize the use of ECE-TENG's energy, the power management circuit (PMC) becomes indispensable. The PMC used in this work is shown in Figure S38 (Supporting Information).<sup>[63]</sup> As shown in Figure 5g, the charging speed of ECE-TENG with PMC is improved  $\approx$ 5 times compared to that of ECE-TENG without PMC. For example, the charging speed increases from  $\approx$ 4.6 to 22 µC s<sup>-1</sup> when charging a capacitance of 100 µF, strongly demonstrating the effectiveness of PMC.

Subsequently, ECE-TENG was used to power practical applications. As shown in Figure 5h, 100 LEDs were effortlessly lighted and operated reliably, powered solely by an ECE-TENG with a mere 1 cm<sup>2</sup> effective area (Supplementary Video S1, Supporting Information). Furthermore, an ECE-TENG with an effective area of only 1 cm<sup>2</sup> can continuously stably supply power to 4 hygrothermographs in parallel, as evidenced in Figure 5i and Supplementary Video S2 (Supporting Information). These applications fully demonstrate the exceptional performance and practicability of the ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE).

## 3. Conclusion

In summary, we propose two strategies to optimize P(VDF-TrFE-CFE)'s charge retention capability through modifying traps. High-polarity interfaces are introduced into P(VDF-TrFE-CFE) polymer via the incorporation of BTO nanoparticles with high dielectric permittivity. By effectively enhancing trap density, trap energy, and specific capacitance, charge retention capability is improved and air breakdown is suppressed, resulting in an increased charge density of 8.85 mC m<sup>-2</sup> for ECE-TENG with 0.2 vol% BTO/P(VDF-TrFE-CFE) film. In addition, by designing dense segment stacking behavior of P(VDF-TrFE-CFE) through electrostatic interaction with PEI, charge retention capability is enhanced due to the introduction of high interfacial traps. This effective suppression of charge loss leads to an increase in charge density, despite increased air breakdown in ECE-TENG with PEI/P(VDF-TrFE-CFE) composites. Traps are further enhanced through annealing treatment, and the optimal equilibrium state of ECE-TENG with pristine-115 is achieved by simultaneously suppressing charge loss and air breakdown. As a result, the ECE-TENG with 0.2 vol% PEI/P(VDF-TrFE-CFE) film achieves a highrecord charge density of 9.23 mC m<sup>-2</sup>, average power density of 0.92 W m<sup>-2</sup> Hz<sup>-1</sup> and energy density of 919 mJ m<sup>-2</sup> cycle<sup>-1</sup> under a load of 1 M $\Omega$ . Moreover, a record-breaking humidity resistance of 6.36 mC m<sup>-2</sup> at 85% humidity is achieved, which is 1.93 times higher than the previous best performance under similar humidity conditions.

This study provides valuable guidance for optimizing TENGs' performance with respect to triboelectric materials (The optimal equilibrium state of TENGs requires minimal air breakdown and charge loss in dielectrics, necessitating dielectrics with high specific capacitance and high electrical insulation.), and offers novel and effective material strategies for enhancing charge retention capability by modifying traps. Given the availability of numerous materials with high dielectric permittivity and high electron affinity, these approaches are highly applicable. Additionally,

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**Figure 5.** Application demonstrations: output, stability, and powering capabilities. a) Output performance of ECE-TENG with 0.2 vol% PEI/ P(VDF-TrFE-CFE) composite at different external load resistance. b) V-Q curve of the ECE-TENG under a load of 1 M $\Omega$ . c) Comparison of the energy density for different works before power management. d) The charge density comparison in reported TENGs under a high humidity environment. e) Working stability of ECE-TENG with 0.2 vol% PEI/ P(VDF-TrFE-CFE) composite. f) The powered system's structure of composed of ECE-TENGs. g) Charging curves of 100, 470  $\mu$ F, and 1  $\mu$ F capacitors by ECE-TENG with PMC. h) Real-time voltage curve of LEDs and photo of powering 100 LEDs by 1 cm<sup>2</sup> ECE-TENG. i) Real-time voltage of the hygrothermographs and photo of powering 4 hygrothermographs by 1 cm<sup>2</sup> ECE-TENG.

considering the ready accessibility of raw materials and the simplicity of film preparation, this composite strategy can effectively tackle the challenge of scalable fabrication for high-performance, large-area triboelectric films in TENGs.

## 4. Experimental Section

*Materials*: Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE), 64.6/26.2/9.2 mol%) and PEI pellets were obtained from the Arkema, Shanghai Macklin Biochemical Technology Co., Ltd., respectively. Barium titanate (BTO) nanoparticle was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. N, N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. and Shanghai Aladdin Biochemical Technology Co., Ltd., respectively. All the chemicals were used without further purification.

Preparation of BTO/P(VDF-TrFE-CFE) and PEI/P(VDF-TrFE-CFE) Composites: As for BTO/P(VDF-TrFE-CFE) films, a certain amount of BTO nanoparticles and DMF solvent were ultrasonicated to make BTO dispersed evenly. Then, P(VDF-TrFE-CFE) powders were dissolved in the above-mixed solution and a uniform dispersion solution was obtained after vigorous stirring for 10 h. The as-prepared solution was cast onto the aluminum foil (thickness  $\approx 20 \,\mu$ m) and moved into the oven to remove the residual solvent. As for PEI/P(VDF-TrFE-CFE) films, the PEI pellets were dissolved in NMP solvent and the rest of the steps are the same as above. The thickness of the composites is controlled to 8  $\mu$ m by scraper.<sup>[28]</sup>

Fabrication of the External Charge Excitation (ECE) TENG: The ECE-TENG consists of a main TENG and an external TENG, both constructed with similar components including acrylic sheets (45 × 45 × 3 mm), foam (2 mm thickness), a silicone layer (2 mm thickness), electrodes, and a dielectric layer. The silicone layer was applied to the foam's upper surface which has been attached to the acrylic sheet. Afterward, for a main TENG, the prepared BTO/P(VDF-TrFE-CFE) or PEI/P(VDF-TrFE-CFE) film with Al foil was affixed to the silicone layer. The corresponding opposing electrode is a circular electrode (1 cm<sup>2</sup>) sputtered onto Kapton film (thickness  $\approx 30 \,\mu$ m) which is also adhered to the silicone layer. For an external TENG, a 50  $\mu$ m FEP film was used as the dielectric layer and the opposing electrode is 10 cm<sup>2</sup> Cu. The main TENG and the excitation TENG were connected by a charge-excited circuit consisting of a half-wave rectifier and a capacitor. The maximum working voltage of rectifier diodes is 1 kV. The parameters of the capacitor are 10 nF and 2 kV.

*Characterization*: TENGs were controlled by a linear motor (TSMV120-1S) and working frequency and separation distance were set to 2 Hz and 1 cm, respectively. The ECE-TENG's current and transferred charges were measured by an electrometer (Keithley model 6514). The voltage was tested using both the electrometer (Keithley model 6514) and an electrostatic voltmeter (Trek, 347). The humidity environment was controlled by a humidifier (Yadu, SZ300-TG01).

The capacitance, dielectric permittivity, and  $tan\delta$  were obtained using a precision LCR meter (Tonghui, TH2838). The contact capacitance was assessed using a digital multimeter (Victor, 9808). Surface and crosssectional micromorphology of films were characterized through a Scanning Electron Microscope (SEM, FEI Nova Nano 450). Young's modulus of films tested by nano-indenter (Ti980 SLAB-SPM-0004). 3D morphology and roughness were measured using a 3D profile instrument (Keyence, VR6000, 100  $\mu$ m  $\times$  100  $\mu$ m). The X-ray diffraction (XRD) patterns were measured at ambient temperature using a diffractometer (Bruker, Xpert3) (40 kV, Cu K<sub>α</sub> radiation, step size 0.001°, 40 mA, scan rate 20 s per step). The d-spacing was calculated through XRD data according to Bragg's law. Fourier transform infrared spectroscopy (FTIR) was obtained by Bruker, VERTEX80v at air condition and room temperature. Conductivity, breakdown strength, and leakage currents were obtained by a multiferroic ferroelectric test system (Radiant Technologies, Inc. Premier II). For the hole trap properties and surface potential dissipation of the dielectrics, the dielectrics were corona-charged for two minutes and then the surface potential was measured using both the electrometer (Keithley model 6514) and an electrostatic voltmeter (Trek, 347).

Density Functional Theory (DFT) Calculation of Electrostatic Potential: All calculations based on density functional theory (DFT) were performed by utilizing the DMol3 package.<sup>[64]</sup> The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof form and Semicore Pseudopotential method (DSPP) with the double numerical basis sets plus the polarization functional (DNP) were used.<sup>[65,66]</sup> The double numerical basis sets plus the polarization functional (DNP) was adopted. A DFT-D correction with the Grimme scheme accounted for the dispersion interaction.<sup>[67]</sup> The SCF convergence for each electronic energy was set as  $1.0 \times 10^{-6}$  Ha and the geometry optimization convergence criteria were set up as follows:  $1.0 \times 10^{-6}$  Ha for energy, 0.001 Ha Å<sup>-1</sup> for force, and 0.001 Å for displacement, respectively.

DFT Calculation of Molecular Energy Level: The Vienna Ab Initio Package (VASP) was used to perform DFT calculations within GGA using the Perdew, Burke, and Enzerhof (PBE) formulation.<sup>[65,68]</sup> The projected augmented wave (PAW) potentials were adopted to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV.<sup>[69]</sup> Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method with a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was  $<10^{-5}$  eV. A geometry optimization was considered convergent when the force change was <0.05 eV Å<sup>-1</sup>. Grimme's DFT-D3 methodology was applied to describe the dispersion interactions.<sup>[70]</sup> The vacuum spacing perpendicular to the plane of the structure is 20 Å. The Brillouin zone integral utilized the surface structures of  $1 \times 1 \times 1$  monkhorst pack K-point sampling.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

# **Keywords**

high charge density, suppressing charge loss, triboelectric material, triboelectric nanogenerator, trap engineering

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