Achieving Superior Capacitive Energy Storage in Polymer Nanocomposites via a Hierarchical Interfacial Engineering of Gradient-Dielectric Ba(Zr,Ti)O_3@BaTiO$_{3}$ Core-Shell Nanofibers

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Abstract

Harnessing dielectric polymers for next-generation pulsed-power capacitors mandates simultaneously ultrahigh energy density and efficiency, yet the antagonism between large polarization/dielectric constant and high breakdown strength remains a fundamental bottleneck. Here, we implement a hierarchical interfacial engineering approach that reconciles this conflict by constructing gradient-dielectric Ba(Zr,Ti)O_3@BaTiO$_{3}$ (BZT@BT) core–shell nanofibers via coaxial electrospinning and a mussel-inspired poly(catechol/polyamine) (PCPA) interlayer. The lattice-matched BZT core and BT shell suppress interfacial defects during co-calcination, while the progressive dielectric constant gradient mitigates severe field distortion in the polymer matrix. The PCPA interlayer facilitates to significantly strengthened bonding between the inorganic fibers and P(VDF-HFP) and the exceptional filler dispersion. The optimized nanocomposite containing only 2 wt.% BZT@BT@PCPA filler delivers a record-high discharged Ue of 33.8 J cm^{-3} with an η of 82.5 %. Phase-field simulations reveal that the introduction of gradient permittivity and PCPA interfacial modifier synergistically homogenizes the electric field and enhances the breakdown strength. This work demonstrates the profound effectiveness of synergistic lattice-matched core-shell filler design and tailored interfacial molecular engineering in overcoming the performance bottlenecks of polymer nanocomposites for high-power energy storage applications.

Full Text

Preamble

Achieving

Superior

Nanocomposites

Capacitive

Energy

Hierarchical

Storage

Interfacial

Polymer

Engineering

Gradient-Dielectric Ba(Zr,Ti)O_3@BaTiO$_{3}$ Core–Shell Nanofibers Wuwei Feng,1,,† *Wei Wang,1,* Weiping Gong,2,† Yu Huang,3 Jianwen Chen,3,† Yuqin Liu,1 Jingang Liu,1 Yuxin Wu,1 Yang Kang,1 Lingling Wu 1

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nanofibers

coaxial

electrospinning

mussel-inspired

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Keywords

Polyvinylidene fluoride hexafluoropropylene (P(VDF-HFP)); Dielectric energy

storage; Poly(catechol/polyamine); Coaxial electrostatic spinning; Interfacial engineering; Ba(Zr,Ti)O_3@BaTiO$_{3}$ Core–shell nanofibers

1. Introduction

Relative to electrochemical batteries, dielectric capacitors demonstrate considerably higher power density and charging/discharging rates, making them highly suitable for applications in advanced electronic power systems, hybrid vehicles, and smart grids [1, 2].

However, the relatively low energy density of dielectric capacitors restricts their further development [3-5]. The development of more compact and lightweight dielectric capacitors with higher energy storage density and efficiency has become a current research hotspot.

Compared with ceramic capacitors [6], polymer capacitors are distinguished by their lightweight nature, low cost, ease of processing, and high breakdown electric field (Eb) [7-9].

Generally, the discharge energy density, $= \int$, where Pm and P r are the maximum

and residual polarization [10]. Therefore, a high Pm and Eb, coupled with a low Pr, are conducive to enhancing the energy storage performance. The polar-

ization is positively correlated with the dielectric constant. Polymer dielectrics, despite their advantages, suffer from a low dielectric constant [11]. Although ceramic dielectrics can address this issue, their high rigidity and low Eb limit their application [12, 13]. To enhance the dielectric constant and energy storage density of polymer dielectrics, high-dielectric-constant inorganic

ceramics are introduced as fillers into organic polymer matrices [14-17]. However, incorporating ceramic fillers into polymers often increases the dielectric constant at the expense of the Eb [18]. This is primarily because filler aggregation and localized electric fields can compromise the Eb and stability of the composites. To address this, many strategies have been employed to modify the surface of high-dielectric-constant ceramic fillers, improving dispersion and interfacial compatibility in composites, with surface functionalization being the most common method [19-23].

The remarkable adhesive capabilities of mussel-like organisms have inspired the widespread application of polydopamine (PDA) to enhance the compatibility between

inorganic fillers and organic matrix. Wang et al. enhanced the Eb and energy storage density and efficiency of the composite film by leveraging interfacial coupling, which was induced through strong hydrogen bonding between PDA chain segments and macromolecular chains [24]. Ajay Kumar et al. effectively enhanced the dielectric constant and Eb of nanocomposite films concurrently by coating barium titanate (BT) nanoparticles with a PDA layer. The PDA coating promoted the uniform dispersion of BT@PDA nanoparticles within the polymer matrix, thereby increasing the content of the electroactive phase and improving the energy storage properties of the composite [25]. However, the high cost of dopamine restricts its widespread industrial application. The oxidative polymerization of dopamine, which results in the formation of adhesive coatings on surfaces, is critically dependent on the co-presence of catechol and amino groups. Inspired by this mechanism, low-cost catechol and polyamine monomers can be copolymerized, named poly(catechol/polyamine) (PCPA), and subsequently deposited onto substrate surfaces, yielding coatings that exhibit excellent adhesion properties analogous to those of PDA [26]. The catechol groups in PCPA are well-known for their strong adhesive properties and antioxidant capabilities, while the polyamine components exhibit excellent cross-linking ability and chemical stability. These characteristics have enabled extensive applications of PCPA in rubber materials, enhancing the mechanical properties, antioxidant capacity, and weather resistance of rubber.

Consequently, the service life of rubber in harsh environments, such as high temperatures or exposure to ultraviolet radiation, is significantly prolonged [26-28]. To date, PCPA has not yet been employed as a surface modifier in the field of dielectric energy storage.

The large dielectric constant difference at the interface between inorganic fillers and organic matrices causes electric field distortion [29-31], which can be miti-

gated by designing core-shell structured fillers [32]. Bi et al. encapsulated BaTiO3 particles with a highly insulating SiO_2 layer, reducing leakage current and dielectric loss by reducing the interfacial structural defects and limiting charge carrier mobility [33]. The incorporation of Al2O3 and TiO_2 layers between ceramic fibers and a polymer matrix can effectively improve electric field strength, potential distribution, and current density, thereby increasing energy storage density and efficiency of the composites [34,35]. However, commonly used shell materials, such as SiO_2 and Al_2O_3, possess low dielectric constants, thereby potentially diminishing the

overall dielectric constant of the composites. Moreover, the separate preparation of core and shell layers, along with significant differences in their calcination properties and lattice constants, increases process complexity and leads to interfacial defects and electric field distortion between core and shell layers.

Thereby, as shown in Fig. 1 [Figure 1: see original paper], we propose an effective method to enhance the energy storage properties of polymer-based composites through the preparation of core–shell structured fillers via a coaxial electrostatic spinning process and subsequent surface functionalization of the fillers. The barium zirconate titanate (BZT) core layer and the BT shell layer, prepared via coaxial electrostatic spinning, form a high-quality core–shell interface and a progressive dielectric gradient due to their similar calcination properties and lattice characteristics. After PCPA modification, the core–shell structured fibers possess good compatibility, dispersion and significantly enhanced bonding with the P(VDF-HFP) matrix.

Consequently, both of the polarization (dielectric constant) and breakdown strength of the composites

significantly

enhanced,

optimized

2wt.%

BZT@BT@PCPA/P(VDF-HFP) composite film achieved a state-of-the-art energy storage density of 33.8 J/cm3 and a high efficiency of 82.5% at the electric field of 587 kV/mm, surpassing those of previously reported energy storage materials. We thus believe that our results yield a significant advance in polymer composites dielectric energy storage and provide a practical route toward compact, reliable and efficient energy-storage capacitors.

composites via hierarchical interfacial engineering.

2. Results and Discussion

2.1. BZT@BT@PCPA/P(VDF-HFP) composite film quality

peaks at 2θ = 21.98°, 31.36°, and 55.86° correspond to the (100), (110), and (211) crystal planes of the perovskite structure, respectively, which are consistent with the PDF#31-0174 for BaTiO3. By optimizing the electrospinning rate and the magnitude of the applied electric field, fibers with diameters of approximately 300 nm were successfully fabricated. Fig. 2c [Figure 2: see original paper] displays the SEM image of BZT@BT fibers after ultrasonic dispersion in alcohol. This treatment results in a reduction in fiber length compared to the untreated BT fibers, as shown in Fig. 2b. Fig. 2d-f show the surface morphology of the composite films with BT, BT@PCPA, and BZT@BT@PCPA as fillers. As depicted in Fig. 2d, a slight agglomeration of the fillers is observed, with fibers partially exposed and not fully encapsulated within the P(VDF-HFP) matrix. In contrast, Fig. 1e-f reveal that fibers modified by PCPA exhibit no significant agglomeration and are well encapsulated within the P(VDF-HFP) matrix. These observations suggest that PCPA enhances the dispersion of the filler within the polymer matrix and improves the compatibility between the filler and the matrix. The uniform dispersion of the filler within the P(VDF-HFP) matrix and the homogeneity of the composite

film are further corroborated by the EDS mapping images presented in Supplementary Fig.

inset

shows

macroscopic

photograph

BZT@BT@PCPA/P(VDF-HFP) composite film. The film exhibits excellent flexibility in its pristine state and demonstrates a high capacity for accommodating deformation. Fig. 2g-i show the cross-section morphology of the composite films with BT, BT@PCPA, and BZT@BT@PCPA as fillers. In the BT/P(VDF-HFP) composite, voids and defects can be observed.

However,

PCPA-modified

BT@PCPA/P(VDF-HFP)

BZT@BT@PCPA/P(VDF-HFP) composites, no voids or defects are detected, indicating that PCPA effectively enhances the interfacial compatibility between the fiber fillers and the

polymer matrix. In addition, BT fibers are randomly oriented in the BT/P(VDF-HFP) composite. In contrast, in BT@PCPA/P(VDF-HFP) and BZT@BT@PCPA/P(VDF-HFP) composites, the fibers tend to be uniformly

oriented parallel to the upper and lower surfaces of the composite film. This phenomenon is likely attributed to the stronger interfacial bonding and improved interfacial compatibility between the PCPA-modified fibers and the P(VDF-HFP) matrix. During hot pressing, the fibers align with the polymer chains in the plane.

BZT@BT

fibers.

Surface

BT@PCPA/P(VDF-HFP),

Cross-section

images

images

BT/P(VDF-HFP),

BZT@BT@PCPA/P(VDF-HFP)

composites.

2wt.%BT/P(VDF-HFP),

2wt.%BT@PCPA/P(VDF-HFP), and (i) 2wt.% BZT@BT@PCPA/P(VDF-HFP) composites.

2.2 Enhanced mechanical and energy storage performance of composite films We first optimized the content of BT fibers in BT/P(VDF-HFP) composites. As shown in Supplementary Fig. S2, the 2wt.% BT/P(VDF-HFP) composite yields the best dielectric

and energy-storage performance. Subsequent material design was based on incorporating 2wt.% fillers into the P(VDF-HFP) matrix. Fig. 3a [Figure 3: see original paper] shows a comparison of the dielectric constant and loss for different samples. Incorporation of 2wt.% BT fibers into the P(VDF-HFP) matrix resulted in an enhanced dielectric constant. Furthermore, modification of the interface with PCPA further enhanced the dielectric constant of the composites. The 2wt.% BZT@BT@PCPA/P(VDF-HFP) composite exhibited highest permittivity while maintaining relative low dielectric loss. Fig. 3b shows the Weibull distribution plots for different samples. A shape parameter (β) value exceeding 14 indicates a higher degree of reliability in the experimental data [36,37]. As shown in Fig. 3c, the incorporation of 2wt.% BT fibers into P(VDF-HFP) matrix enhances the Eb of the composite. This improvement can be attributed to the increased tortuosity of the electrical breakdown paths within the composite matrix, which effectively impedes and repels the movement of charge carriers [18,36]. Furthermore, the surface modification of the BT fibers through the introduction of PCPA effectively reduces the presence of defects and pores within the composites. Surface functionalization with PCPA endows BT

fibers with robust interfacial bonding to the P(VDF-HFP) matrix, markedly improving filler dispersion, which also suppresses local electric-field concentration and yields a more uniform field distribution throughout the composite [38,39]. As a result, the Eb of the composite is significantly enhanced. More interestingly, the incorporation of BZT with higher permittivity did not compromise the Eb of the composites due to the formation of coaxial core-shell structured BZT/BT fibers in which the BT layer creates a dielectric gradient between BZT and P(VDF-HFP) and thus alleviate

electric

field

distortion

interface

[32,40].

Consequently,

2wt.%

BZT@BT@PCPA/P(VDF-HFP) composite exhibited highest polarization, Eb, and energy storage performance, as shown in Fig. 3c-f. Specifically, compared with pure P(VDF-HFP), the dielectric constant increased from 7.3 to 12, the Pmax increased from 6.3 μC/cm2 to 13.4 μC/cm2, the Eb increased from 409 kV/mm to 587 kV/mm, the Wrec increased from 10.1 J/cm3 to 33.8 J/cm3, the efficiency near Eb increased from 74.3% to 82.6%. Especially the efficiency always exceeds 90% at the electric field below 300 kV/mm, as shown in Fig. 3e.

The 2wt.% BZT@BT@PCPA/P(VDF-HFP) composite exhibited superior fatigue endurance.

As illustrated in Fig. 3g, after 105 cycles of testing under an electric field of 2000 kV/cm, the Wrec and efficiency exhibited no decline, and the efficiency remained above 90%. The

leakage current of BZT@BT@PCPA/P(VDF-HFP) composite was reduced compared with pure P(VDF-HFP), and maintained at 1x105 A/cm2 at high temperature of 100 oC, indicating good high-temperature stability, as shown in Fig. 4a [Figure 4: see original paper] and Supplementary Fig. S3. Inorganic BZT@BT fillers and the P(VDF-HFP) organic matrix achieve high-quality interfacial bonding and uniformity through PCPA modification, thereby enhancing the mechanical properties of the composite. As shown in Fig. 4b, BZT@BT@PCPA/P(VDF-HFP) composite exhibited enhanced Young modulus, yield strength, and much longer uniform plastic deformation range, compared with pure P(VDF-HFP). Finally, the present composite exhibits state-of-the-art capacitive energy-storage performance among recently reported polymer-based dielectrics, as demonstrated in Fig. 3h.

(c) P-E curves at the electric field near BDS, (d,e) electric field dependent

maximum

polarization, energy storage density and efficiency, (f) energy storage density, efficiency and BDS for pure P(VDF-HFP) and P(VDF-HFP)-based composites with 2wt.% BT, 2wt.% BT@PCPA, and 2wt.% BZT@BT@PCPA as fillers, respectively. (g) fatigue endurance for 2wt.% BZT@BT@PCPA/P(VDF-HFP) composite. (h) Comparison of energy storage performance of recently reported polymer-based dielectrics [34, 41-54]

of temperature, the inset shows a comparison of leakage current between pure P(VDF-HFP) and BZT@BT@PCPA/P(VDF-HFP) composite at 20 oC; (b) Mechanical properties of

uniaxial stretched pure P(VDF-HFP) and BZT@BT@PCPA/P(VDF-HFP) composite.

2.3. Hierarchical interface engineering

To confirm the formation and structural integrity of the PCPA layer, the surface chemistry and architecture of pristine BT and BT@PCPA fibers were investigated by X-ray photoelectron spectroscopy (XPS). A new peak of N1s at approximately 400 eV was observed in BT@PCPA (Fig. 5b [Figure 5: see original paper]), which was absent in pure BT (Fig. 5a). The C1s spectrum of BT@PCPA (Fig. 5c) exhibited four distinct carbon species (C-C, C-N, C-O-C, and O-C=O), while the N1s spectrum (Fig. 5d) revealed two nitrogen species (C-NH_2 and C=N).

These findings correspond to the chemical structure of PCPA (Fig. 5e), thereby indicating the successful copolymerization of catechols and polyamines and the effective deposition of PCPA onto the surface of BT fibers. Fig. 5e-f illustrates the synthesis process and possible structure of PCPA. Catechol is oxidized to generate a quinone structure, which subsequently undergoes Michael addition or Schiff base reaction with tetraethylene pentamine to form a crosslinked network [55, 56]. The adhesive properties of polydopamine are attributed to the simultaneous presence of phenolic hydroxyl groups and amine groups [57]. Analogous to polydopamine, the PCPA synthesized in this study is rich in catecholic hydroxyl and primary amine moieties, endowing it with interfacial reactivity comparable to that of polydopamine.

When PCPA is deposited on the surface of BT fibers, the catechol hydroxyl groups might form a hydrogen-bonding network with the hydroxyl groups on the surface of BT, thereby enhancing the interfacial affinity [58]. The amino groups bind to the surface of BT through electrostatic interactions or van der Waals forces, further reducing interfacial defects. The N-H groups at the terminal positions of PCPA are also capable of forming hydrogen bonds with the fluorine atoms in P(VDF-HFP), thereby reducing the interfacial energy [59,60].

PCPA is rich in catechol and amine groups that could also form more stronger chelate/coordination bonds with Ti/Zr atoms on the BZT@BT surface, while

its amine terminals undergo nucleophilic substitution with the -CF_2-segments of P(VDF-HFP) [59-61]. Therefore, the PCPA layer functions as a molecular brush, establishing robust covalent and non-covalent interactions at the filler-P(VDF-HFP) interface and thereby ensuring strong interfacial adhesion. This not only minimizes interfacial voids, suppresses

interfacial debonding, and reduces the interfacial defect density between the filler and the polymer matrix, but also facilitates the uniform dispersion of the filler within the matrix. The reduction in interfacial porosity and defects, in conjunction with the cross-linked structure of PCPA, results in a more uniform distribution of mechanical stress [59,60]. This effect inhibits the propagation of interfacial cracks, mitigates local electric field concentration, and delays the electro-mechanical breakdown process. As shown in Fig. 4b, the yield strength, Young

modulus,

uniform

plastic

deformation

range

BZT@BT@PCPA/P(VDF-HFP) composite are all significantly enhanced compared to pure

P(VDF-HFP). In addition, the hydroxyl and amino groups in PCPA might serve as deep-level traps (1.2 eV below the conduction band of P(VDF-HFP)), capable of capturing migrating electrons or holes, thereby suppressing leakage current [58]. Trap-assisted charge localization may also reduce the accumulation of space charges from the high-field electrode, preventing electric field distortion [59,62].

(c) C1s and (d) N1s spectra of BT@PCPA fiber. (e) Schematic of the structure of PCPA. (f) Schematic of the interface formed by surface-functionalized BT with P(VDF-HFP). (g) FTIR spectra of BT and BT@PCPA fibers. (h) TEM image of BT@PCPA fiber.

To further corroborate the efficacy of the PCPA surface modification, BT, and BT@PCPA fibers were subjected to Fourier-transform infrared (FTIR) spectroscopy and high-resolution transmission electron microscopy (HR-TEM) analyses. As shown in Fig. 5g, compared with the pristine BT fiber, the BT@PCPA fiber exhibited new characteristic peaks

at 3350 cm^{-1} (N-H and O-H), 2910 cm^{-1} (C=N), 1650, 1580, and 1520 cm^{-1} (aromatic ring), 1580 and 1530 cm^{-1} (N-H), 1360 and 1300 cm^{-1} (C-O and O-H), and 1260 cm^{-1} (C-O) in the infrared spectrum [63]. These peaks are consistent with the chemical structure of PCPA, thereby confirming the successful modification of the fibers by PCPA. Fig. 5h and Supplementary Fig. S4b

present the TEM image of the BT@PCPA and BZT@BT@PCPA fibers, revealing a distinct resin layer on the surface of the fibers. The thickness of the PCPA layer is approximately 6–10 nm. This finding offers unequivocal evidence that PCPA has been deposited on the fiber surface, thereby validating the efficacy of the surface modification.

Supplementary Fig. S5 shows the DSC curves of pure P(VDF-HFP) and P(VDF-HFP)-based composites with BT, BT@PCPA, and BZT@BT@PCPA as fillers. The derived melting temperature (Tm), crystallization temperature (Tc), melting enthalpy (ΔHm) and crystallinity (χc) are given in Supplementary Tab. S1. The Tm of the BT/P(VDF-HFP) composite (132.4°C) is distinctly lower than that of pure P(VDF-HFP) (135.7°C), while the

significantly

elevated.

contrast,

PCPA-modified

BT@PCPA/P(VDF-HFP) composite (135.8°C) remains nearly unchanged. This observation can be attributed to the fact that the incorporation of inorganic fillers introduces defects within the composite structure, thereby compromising its thermal stability and resulting in lower melting temperatures. Conversely, the PCPA modification of the filler enhances the interfacial bonding with the P(VDF-HFP) matrix, reducing the formation of interfacial defects and consequently yielding composites with melting and crystallization temperatures

comparable to those of the pristine polymer. BZT@BT@PCPA/P(VDF-HFP) composite even exhibited slightly increased Tm of 136.2°C. The interfacial modification with PCPA strengthens the interfacial interactions between the inorganic filler and the P(VDF-HFP) matrix. This increased interaction restricts the mobility of the polymer chain segments on the surface of the inorganic filler, thereby necessitating higher energy for their movement.

Consequently, the Tm of the modified composites can be further elevated compared to that of the unmodified composites. Furthermore, the incorporation of BT and BZT@BT fibers into the P(VDF-HFP) matrix, in conjunction with interfacial modification by PCPA, results in an increase in the crystallinity of the P(VDF-HFP) matrix and the proportion of the

P(VDF-HFP) crystalline phase. This is evidenced by the data in Supplementary Tab. S1, where the χc increases from 13.3% for pure P(VDF-HFP) to 22.1% for the BZT@BT@PCPA/P(VDF-HFP) composite. This enhancement in crystallinity is expected to lead to an increase in the dielectric constant and polarization of the composites.

In addition, the incorporation of inorganic filler into the polymer matrix may result in the creation of an interfacial phase, thereby inducing interfacial po-

larization and subsequently influencing the dielectric constant of the composite. The introduction of PCPA enhances the interfacial bonding between the fillers and the polymer matrix, thereby reducing the presence of the air phase with a low dielectric constant at the interface [64, 65].

The amine and hydroxyl groups within PCPA facilitate the orientational polarization of polymer dipole moments at the interface upon the application of an external electric field.

Based on the mean field theory, Maxwell-Garnett equation [66] is expressed as follows.

$$1 + 2\,2 - 2(1 - \ 2\ )(\ 2 - \ 1\ )\ \ 1 + 2\,2 + (1 - \ 2\ )(\ 2 - \ 1\ )\ 2$$

In this equation, 1 and 2 are the dielectric constants of the filler and matrix, respectively, and ϕ is the volume fraction. For the calculations, the densities of $BaTiO_3$ and P(VDF-HFP) are 6080 kg/m^3 and 1170 kg/m^3, respectively, and their corresponding dielectric constants are 1700 and 7.4, respectively. The experimentally determined permittivity of the composite markedly exceeds the calculated value, corroborating the pronounced contribution of interfacial polarization at the filler–matrix interface. As shown in

BT/P(VDF-HFP), thereby indicating the positive contribution of PCPA to the polarization enhancement. The incorporation of BT fibers into the P(VDF-HFP) matrix was also observed to result in a slight increase in dielectric loss. This phenomenon can be attributed to the fact that the presence of BT within the polymer matrix acts as an impurity, thereby inducing an increase in relaxation loss. Consequently, the overall dielectric loss of the composites is elevated. Nevertheless, the PCPA-modified composites incorporating BT and BZT@BT fibers as fillers do not exhibit a degradation in dielectric loss. This is because PCPA serves as an insulating layer that effectively inhibits the migration and accumulation of space charge.

Besides the PCPA interface engineering, the design of coaxial core–shell structure of BZT@BT fibers (Supplementary Fig. S6) is also unique for the performance improvement.

Conventionally, the separate preparation of core and shell layers, along with significant differences in their calcination properties and lattice constants, increases process complexity and leads to interfacial defects and electric field distortion between core and shell layers, pronounced polarization losses, and consequently diminished performance. In our case, the permittivity of $Ba(Ti,Zr)O_3$ is 1000–2000 higher than that of $BaTiO_3$. The lattice constant of $Ba(Ti,Zr)O_3$ is slightly larger than that of $BaTiO_3$ due to the substitution of Zr for Ti, which causes lattice expansion. However, the overall lattice parameters and calcination properties of $Ba(Ti,Zr)O_3$ are still quite similar to those of $BaTiO_3$, as shown in Fig. 2a. The core and shell layers of the BZT@BT fibers are anticipated to exhibit high crystallinity and coherent lattice matching, as evidenced in Supplementary Fig. S4c,d. Therefore, The BZT core layer and the BT shell layer,

prepared via coaxial electrostatic spinning, form a defect-minimized core–shell interface and a progressive dielectric gradient; this simultaneously elevates the overall permittivity of the fillers while preserving the permittivity disparity at the filler/P(VDF-HFP) interface.

The synergistic introduction of high-permittivity BZT@BT fibers and PCPA-mediated interfacial engineering establishes a defect-minimized interface that exhibits exceptional compatibility and a well-defined dielectric gradient. As a result, the polarization is substantially increased, and the Eb of the composites is further elevated, thereby achieving state-of-the-art capacitive energy storage performance.

2.4. Real-time evolution of the electric potential and electric field distribution

To further elucidate the underlying mechanism governing the breakdown strength, the real-time distribution evolving of the electric potential and electric field in the pristine BT/P(VDF-HFP),

BT@PCPA/P(VDF-HFP),

BZT@BT@PCPA/P(VDF-HFP)

composites were simulated via COMSOL Multiphysics and MATLAB, as shown in Fig. 6 [Figure 6: see original paper].

In the model, we consider the same mass ratio (2wt.%) for the filler concentration in the matrix, and assume that unmodified nanofiber fillers adopt a random orientation and are susceptible to agglomeration. After PCPA functionalization, the interfacial compatibility

between the nanofibers and the P(VDF-HFP) matrix is significantly improved, so the fillers tend to align preferentially in a horizontal, parallel orientation under the shear imparted during solution casting and doctor-blading, in agreement with experimental observation. The applied electric field redistributes in the composites owing to the different dielectric constants of P(VDF-HFP), BT/BZT fibers, and PCPA layer. As shown in the second column of Fig. 6, as for the BT/P(VDF-HFP) composite, the local electric-field magnitude at the ends of the BT nanofibers is approximately one order of magnitude higher than that in the surrounding P(VDF-HFP) matrix. This is understandable that the high-permittivity BT phase acts as a "solute" that redistributes the potential, producing sharp field gradients at the interface [67]. The PCPA shell in BT@PCPA/P(VDF-HFP) lowers the effective permittivity contrast between BT and P(VDF-HFP), thus reducing the peak field around the BT fibers significantly. Once the local field surpasses the critical tree-inception threshold, a single conductive filament nucleates at the filler–matrix interface and propagates along the direction of maximum electric energy density. It is clear that the single filament propagation velocity

decreases

monotonically

along

series

BT@PCPA/P(VDF-HFP) → BZT@BT@PCPA/P(VDF-HFP).

BT/P(VDF-HFP) After

morphology

transitions from a single needle to a fractal tree, the shells suppress not only the velocity but also the branching instability. Progressing from simple BT incorporation to the BT@PCPA core–shell configuration and further to the BZT@BT@PCPA hierarchical core–shell architecture yields a pronounced enhancement in electrical-tree suppression and a markedly more uniform electric-field distribution. Notably, the field concentration around fibers and at

potential tree tips is drastically reduced. These results demonstrate that deliberate structural design—particularly the interfaces engineering—is essential for improving the breakdown strength and overall performance of composite dielectrics. The results in Fig. 6 therefore provides direct phase-field evidence that hierarchical core–shell architectures can be engineered to flatten the interfacial electric field, reduce the tree growth velocity, and delay the onset of catastrophic branching.

hierarchical

core–shell

architecture

could

progressively

smooths

dielectric-constant gradient, mitigates interfacial field enhancement, suppresses filler agglomeration to eliminate localized high-field regions, improves interfacial compatibility

and bonding to reduce defects and voids, and introduces deep traps that capture energetic electrons and holes to inhibit impact ionization and partial discharges. By employing BZT as the core, BT as the intermediate layer, and PCPA as the outermost shell to optimize the interface, this multilevel configuration is expected to yield a synergistic effect in charge trapping, electric-field homogenization, and mechanical-stress dissipation, offering a rational design pathway toward polymer nanocomposites with simultaneously enhanced dielectric constant and breakdown strength.

BT/P(VDF-HFP),

BT@PCPA/P(VDF-HFP),

BZT@BT@PCPA/P(VDF-HFP)

composite films by finite element method.

3. Conclusion

In summary, by constructing a defect-minimized, hierarchical BZT@BT@PCPA core–shell–shell structure, our approach achieves exceptional interfacial compatibility and a well-defined dielectric gradient. The PCPA layer establishes robust covalent/non-covalent bonds that effectively suppress interfacial defects, enhance filler dispersion, and act as deep charge traps to mitigate leakage current. Concurrently, the high-permittivity BZT@BT core–shell nanofibers, prepared via coaxial electrospinning, provide a progressive dielectric gradient that significantly elevates overall polarization while preserving the critical permittivity disparity at the filler/polymer interface. As a result, the optimized 2wt.%

BZT@BT@PCPA/P(VDF-HFP) nanocomposite simultaneously exhibits a state-of-the-art energy storage density of 33.8 J cm^{-3}, along with excellent efficiency and fatigue endurance.

This work offers a rational and synergistic strategy to break the traditional trade-off between high dielectric constant and high breakdown strength in polymer nanocomposites for next-generation polymer dielectrics, pushing the boundaries for advanced capacitive energy storage applications.

4.1. Sample preparation

Dimethylformamide (DMF), tetraethylenepentamine, glacial acetic acid, barium acetate, tetrabutyl titanate, polyvinylpyrrolidone (PVP), and glycol methyl ether were purchased from Aladdin biochemical Polytron Technologies Co. Ltd., China. P (VDF-HFP), catechol, and acetylacetone were purchased from Macklin. The purity of the reagents is analytical grade or above 99.0%.

Solution A was prepared by dissolving barium acetate in a 1:1 mixture of glacial acetic acid and ethylene glycol methyl ether. Solution B was obtained by mixing zirconium acetylacetonate with acetylacetone and tetrabutyl titanate. Solution C was formulated by mixing acetylacetonate with tetrabutyl titanate. Subsequently, Solution D was prepared by dropwise addition of Solution B into Solution A, while Solution E was prepared by dropwise addition of Solution C into Solution

A. Polyvinylpyrrolidone (PVP) was then added to

Solutions D and E to adjust their concentrations. The resulting mixtures were left undisturbed for a period exceeding twelve hours.

Coaxial electrostatic spinning was employed, with Solution D serving as the core layer and Solution E as the shell layer, as depicted in Supplementary Fig. S7. The electrostatic spinning process was conducted under an applied electric field comprising a high voltage of 15 kV and a low voltage of -3 kV. The injection rate was maintained at 1.5 mL/h, and the distance between the needle and the grounding rollers was set at 12 cm. The obtained green specimens through electrostatic spinning were subsequently sintered at 700°C for 2 hours, yielding the BaZr0.2Ti0.8O3@BaTiO3 (BZT@BT) fiber.

A solution of PCPA was prepared by dissolving a specific proportion of catechol and tetraethylenepentamine in water. Subsequently, a predetermined amount of fiber was introduced into the solution, which was then continuously stirred for a duration of six hours to form a suspension. The suspension was subsequently subjected to centrifugation to isolate the precipitate. The precipitate was washed with pure water and ethanol three times until the supernatant became clear and transparent. The washed precipitate was then dried in an oven at 60°C for 12 hours to obtain the PCPA-modified fiber.

The P(VDF-HFP)-based composites were fabricated via a solution casting technique.

Initially, a specified quantity of BZT@BT fibers was dissolved in a DMF solution, which was then stirred for 48 hours. Subsequently, P(VDF-HFP) was introduced into the stirred solution, followed by continuous stirring for an additional 12 hours. The resultant sol was maintained at 40°C for 1 hour and then was poured onto a glass plate and spread evenly using a glass rod. The sol-coated film was then heated at 80°C to facilitate the complete evaporation of the solvent, thereby forming the composite film. The film was subsequently subjected to thermal treatment at 160°C for 15 minutes and rapidly quenched in cold water.

The composite film was then carefully detached from the glass plate, yielding a film with a thickness of 15–18 μm. Finally, the film was hot-pressed at 180°C for 15 minutes under a pressure of 200 MPa.

4.2. Characterization

The crystal structure of the fibers was analyzed using X-ray diffraction (XRD, Cu Kα radiation $\lambda = 1.5418$ Å, D8 Advance). The morphology of the fibers, as well as the surface

and cross-sectional morphology of the composite films, was examined by scanning electron microscopy (SEM, Hitachi-Su5000, Japan). The core-shell structure of the fibers was characterized by transmission electron microscopy (TEM, Talos F200X, FEI, USA). The binding bonds of the modifiers were identified through infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). The dielectric properties of the composites were evaluated using an LCR meter (HP 4294A, Agilent). The energy storage properties and ferroelectric P-E hysteresis loops were measured using a ferroelectric analyzer (Precision Premier II,

Radiant, USA).

4.3. Simulation

According to the thickness characterization of the composites, a 2D region with the similar thickness of 2 μm was designed for finite element simulations of breakdown evolution, in which the variables and analytic functions were set based on the following two equations [68].

where s is defined as the phase-field variable, the interpolation function f(s) = 4s3 − 3s4 valued between 0 and 1 [69], η is a number used for numerical calculation and much smaller than the value of f(s), and ϕ, t and xi with an overbar are the normalized electric potential, time, and horizontal or vertical component of the in-plane designed zone, respectively.

Subsequently, BT or BZT@BT fibers are homogeneously generated within the designated region, while the remaining volume is treated as pure P(VDF-HFP). The properties of BT, BZT@BT fibers, and P(VDF-HFP) —including particle size and dielectric constant—are set to values reported in the literature or measured experimentally in our work. After setting parameters, the Poisson equation was introduced to emulate the distribution of electric potential in the region and the convection—diffusion equation was used to study the breakdown evolution. Finally, the designed zone was separated into 2D 100 × 100 grids before performing a calculation.

4.4. Declaration of AI Use in This Study

Artificial-intelligence tools were employed to (i) survey the literature for prior work pertinent to the present study during study design, identification of scientific novelty, and interpretation of experimental data, and (ii) refine the English prose. All data reported herein were generated exclusively by graduate-student experiments; the only AI-generated content is part of the schematic model shown in Fig.

1. Every other section of the manuscript was conceived, analyzed, and written by the authors without algorithmic assistance.

In summary, AI was used judiciously and transparently; the submitted paper nonetheless

constitutes an authentic account of the authors' empirical findings, their independent analysis, and their scholarly composition.

Data availability All data supporting this study and its findings are available within the article and its Supplementary Information. The data corresponding to this study are available from the

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Note: Figure translations are in progress. See original paper for figures.