

Article

Tuning Fillers via Multidimensional Synergistic Optimization for High-Temperature Capacitive Energy Storage

Linfei Lu ^{1,2,3}, Yipeng Tan ^{1,2}, Hang Gao ^{1,2}, Chiung Kuei Fu ⁴, Lingmin Yao ^{1,2,*} and Qinglin Deng ^{1,2,*} 

¹ School of Physics and Materials Science, Guangzhou University, Guangzhou 510006, China; yx393871@gmail.com (L.L.); a1693433393@outlook.com (Y.T.); a52878746@163.com (H.G.)

² Research Center for Advanced Information Materials, Huangpu Research & Graduate School of Guangzhou University, Guangzhou 510555, China

³ Joint Institute of Guangzhou University & Institute of Corrosion Science and Technology, Guangzhou University, Guangzhou 510275, China

⁴ Guangzhou Shengli New Materials Co., Ltd., Guangzhou 510665, China; j.k.fu.khh@gmail.com

* Correspondence: authors: lingminyao@gzhu.edu.cn (L.Y.); qldeng@gzhu.edu.cn (Q.D.)

Abstract: High-temperature performance is crucial for dielectric capacitors, especially in military and aerospace applications, as they offer superior charge–discharge rates and power density compared to supercapacitors and batteries. However, the stability of polymers based on commercial dielectric capacitors under extreme environmental conditions (i.e., ≥ 100 °C) presents significant challenges. Herein, with polyimide (PI) as the matrix, a middle layer is produced that is rich in zero-dimensional nanoparticles, BaTiO₃ (0DBTO@PI), to enhance dielectric polarization. The upper and lower layers integrate two-dimensional laminated Al₂O₃ (2DAO@PI) as thermal conductive and insulating layers to improve heat dissipation and electrical insulation. The composites combine polarization enhancement and thermal management to synergistically improve high-temperature capacitive energy storage. As a result, the designed composite capacitors maintain good performance at temperatures > 150 °C. Even at 200 °C, it retains 2.36 J cm^{-3} (a 203% increase over pure PI), demonstrating unprecedented stability under extreme temperatures. Layer-specific functionalization provides a new and significant paradigm for designing high-temperature polymer-based energy storage films.

Keywords: composite capacitors; dielectric composite; high-temperature properties; energy density; multidimensional synergetic effects



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1. Introduction

Polymer-based capacitors are essential energy storage devices due to their ultrahigh-power density, high voltage tolerance, and flexibility, making them pivotal in applications such as power grids, electronic control circuits, and advanced electromagnetic weaponry [1–3]. However, under harsh conditions, particularly high temperatures, the performance of polymer-based capacitors significantly deteriorates. Generally, ambient temperatures in automotive inverters can typically hit 140 °C, and in underground oil and gas exploration, they can soar to 200 °C. This poses an extremely tough challenge for the stable operation of capacitors. Most current capacitors use biaxially oriented polypropylene (BOPP). However, BOPP has inherent limitations, as its performance plummets once the operating temperature exceeds 105 °C, making it unsuitable for proper function in these high-temperature scenarios [4–7]. Therefore, an additional cooling system is required to ensure the normal functioning of BOPP. Therefore, intensive efforts have been devoted

to improving the performance of polymer-based capacitors at elevated temperatures by loading ceramic fillers, such as Al_2O_3 , BN, and HfO_2 [8–11]. Fan et al. [12] used solution casting to incorporate a small amount of Al_2O_3 into a polyetherimide (PEI) matrix. The composite film with 5 wt% Al_2O_3 nanoparticles showed the best energy storage performance. At 150 °C and 500 MV m^{−1}, it had a discharge energy density of 3.70 J cm^{−3} and a charge–discharge efficiency of 90.1%. Similarly, Sun et al. [13] incorporated 5 vol% SiO_2 nanoparticles into PEI via the solution casting method, and the resulting composite film achieved a discharge energy density of 6.30 J cm^{−3} and a charge–discharge efficiency of 90.5% under conditions of 150 °C and 620 MV m^{−1}. Up until now, most of the research has focused on exploring the performance conducted within 150 °C, with a few studies at 200 °C. However, polymer-based dielectric capacitors often face much higher operating temperatures in applications like military or aerospace exploration. The storage performance of existing polymer-based dielectric capacitors can significantly drop at high temperatures, and their operational stability can also decrease. Thus, there is an urgent need to develop polymer-based capacitors with high energy storage density and excellent thermal stability [14–17].

In high-temperature-resistant capacitive performance research, polymers like polyimide (PI), PEI, polyethylene naphthalate (PEN), and polyetheretherketone (PEEK) are commonly chosen. Their rigid components, like aromatic and heterocyclic rings, give them a high glass transition temperature, excellent heat resistance, and outstanding mechanical properties. However, these polymers still experience a significant decrease in energy storage efficiency at high temperatures and high electric field conditions [18,19]. Many researchers posit that the inherent low thermal conductivity of polymer films results in excessive Joule heat generation under harsh conditions. This, in turn, significantly increases dielectric losses and can ultimately trigger thermal runaway and premature electrical breakdown. Against this backdrop, enhancing the heat dissipation and insulating properties of polymer-based dielectric materials is critical for ensuring their stability at elevated temperatures. On the one hand, incorporating high thermal conductivity fillers with a bandgap (such as BN and Al_2O_3) into the polymer matrix is indeed a viable method. Liu et al. [20] show that when BN nanosheets (BNNs) are added to PEI at 10 vol%, the discharge energy density of the composite material can reach 4.58 J cm^{−3} at 150 °C and 500 MV m^{−1}.

Introducing inorganic particles with high thermal conductivity and a wide bandgap can increase the polymer matrix's thermal conductivity and reduce the leakage current, thereby enhancing the composite film's energy storage performance at high temperatures. However, this is often limited by the low dielectric constant of the fillers themselves, resulting in a relatively low energy storage density at high temperatures. Some studies have attempted to incorporate high dielectric constant ceramic fillers with surface modification into the polymer matrix, such as TiO_2 (TO), doped BaTiO_3 (BTO), and NaNbO_3 (NN). Although the energy storage density of these composites has seen some improvement, it often comes at the cost of sacrificing energy storage efficiency, which is a phenomenon that is particularly pronounced at high temperatures. Therefore, their energy storage performance is often far from ideal under high-temperature conditions. Hu et al. [21] prepared BaTiO_3 nanofibers (BTNFs) by electrospinning and incorporated 1 vol% BTNFs into PI; the composite film achieved a discharge energy density of 1.74 J cm^{−3} at 200 °C, with a charge–discharge efficiency of less than 30%.

It has been demonstrated that a sandwich structure can be designed to enhance the high-temperature stability of composite materials by simultaneously integrating high thermal conductivity fillers and high dielectric constant fillers into the polymer. The microstructural control of fillers, including their dimensions and orientation, has a significant impact on the high-temperature energy storage characteristics of the polymer matrix. It

is worth mentioning that the microstructural control of fillers, including their dimensions and orientation, has a significant impact on the high-temperature energy storage characteristics of polymer composites. Xu et al. [22] constructed PI-based nanocomposite dielectric materials using a ternary structure strategy. The composite films comprised BNNS/PI as the breakdown-resistant layer and BaTiO₃/PI as the central polarization layer. At the optimal BaTiO₃ volume ratio of 10% (denoted as N-10T-N), the N-10T-N composite film achieved a maximum discharge energy density of 11.6 J cm⁻³ and an efficiency of 87% at room temperature. At 150 °C, the discharge energy density of N-10T-N was 5.1 J cm⁻³, which is 3.17 times that of the original Kapton film. Similarly, Chen et al. [23] proposed a sandwich structure with hydroxyl-modified h-BNNSs added to the outer layers and core-shell structure SrTiO₃@Al₂O₃ nanoparticles (STO@AO NPs) in the middle layer, which simultaneously increased the dielectric constant and breakdown strength. The composite material exhibited an ultrahigh discharged energy density of 4.14 J cm⁻³ at 150 °C, with an efficiency above 90%, demonstrating excellent temperature stability.

Herein, we utilize the synergistic effects of multi-dimensional fillers and control their orientation to enhance the high-temperature (200 °C) dielectric performance capacitor. By introducing an appropriate amount of 2DAI₂O₃ with a laminated structure in the outer layer and dopamine-modified 0DBaTiO₃ in the middle layer, the prepared sandwich structure (2DAI₂O₃-0DBaTiO₃-2DAI₂O₃)/PI composite thin film exhibits high polarization performance and thermal stability at high temperatures. Furthermore, the addition of 2DAI₂O₃ with a high bandgap (9.3 eV, 35 W (m K)⁻¹) in the outer layer increases the depth of molecular charge traps in the composite material, thereby significantly reducing current loss. The incorporation of BaTiO₃ (where the dielectric constant is approximately 3500) with a high dielectric constant in the middle layer significantly enhances the dielectric constant and polarization performance of the composite material. By integrating 2D and 0D materials into the PI matrix through a well-designed layered structure based on multidimensional synergy, the designed composite capacitors significantly enhance energy storage efficiency and density at 200 °C (2.36 J cm⁻³). Their performance surpasses that of current high-temperature dielectric composites, offering a new approach for high-temperature polymer-based capacitors.

2. Materials and Methods

2.1. Materials

We used aluminum oxide (Al₂O₃, 99.99%, α -phase, the thickness is 300 nm, Aladdin, Shanghai, China), barium titanate (BaTiO₃, 99.99%, 4 nm, Aladdin, Shanghai, China), polyimide (PI, Matrimid 5218, DuPont, Wilmington, NC, USA), N, N-dimethylformamide (DMF, AR, Aladdin), ethanol (AR, Aladdin, Shanghai, China), dopamine hydrochloride (98%, Aladdin), Shanghai, China, and deionized water.

2.2. Modification of BaTiO₃

To improve the dispersibility and compatibility of BaTiO₃ particles (0DBTO) in a PI matrix, the surface modification of 0DBTO with dopamine hydrochloride was employed. Firstly, a 50 mL solution of BaTiO₃ with a concentration of 3 g L⁻¹ was prepared. To this solution, 1.5 g of Tris was added and stirred at a temperature of 40 °C for 1 h to ensure complete dissolution and homogenization. Following this, dopamine hydrochloride (25 mg mL⁻¹) was introduced into the 0DBTO solution dropwise, resulting in a noticeable change in the solution color to a grayish-brown hue. The solution was then stirred for an additional 2 h at 40 °C to facilitate the modification process. Subsequently, the modified 0DBTO solution was subjected to centrifugal washing using ethanol at a speed of 7000 rpm for three consecutive washes to remove any unreacted dopamine. The residue was then

dried in an oven at a temperature of 60 °C for a period of 12 h to yield the final product: dopamine-modified 0DBTO powder (referred to as 0DBTO@PDA).

2.3. Preparation of Nanocomposite Films with (2DAI₂O₃-0DBaTiO₃-2DAI₂O₃)/PI

Figure 1 shows the preparation route of (2DAI₂O₃-0DBaTiO₃-2DAI₂O₃)/PI sandwich structure composite films (referred to as the ABA/PI composite film). ABA/PI composite films were fabricated using the sol-gel method combined with the tape casting technique. First, 1.5 g of PI and an appropriate amount of DMF were weighed, and the corresponding nanofillers were weighed according to the volume fraction of nanofillers in the PI matrix. The PI, DMF, and nanofillers were placed in a sample bottle and magnetically stirred at room temperature for 12 h to ensure the complete dissolution of PI and the inorganic fillers, forming a uniform coating solution. During the experiment, the volume ratio of 2DAO to PI was kept constant at 5 vol%, and after mixing and stirring, a castable 2DAO/PI solution was obtained. Meanwhile, the volume ratio of 0DBTO to PI was varied (2 vol%, 4 vol%, 6 vol%, 8 vol%) to obtain castable 0DBTO/PI solutions. Then, ITO conductive glass was placed on a coater, preheated to 50 °C, and the 2DAO/PI was cast onto the ITO and evenly spread with a blade to form the first layer, followed by a 5 min wait for the initial setting. Subsequently, the second and third layers were prepared in the same way, with the second layer being 0DBTO/PI and the third layer being 2DAO/PI. Finally, the prepared three-layer composite film was dried in an oven at 60 °C for 12 h to remove excess DMF; then, the temperature was raised to 200 °C and maintained for 10 min. The composite film was quickly immersed in 0 °C deionized water for quenching to obtain the densified ABA/PI composite film. This effectively eliminated pinhole formation during ABA/PI composite film preparation, laying a solid foundation for subsequent testing. Based on the different contents of incorporated 0DBTO, the prepared composite films were designated as ABA/PI-2, ABA/PI-4, ABA/PI-6, and ABA/PI-8.

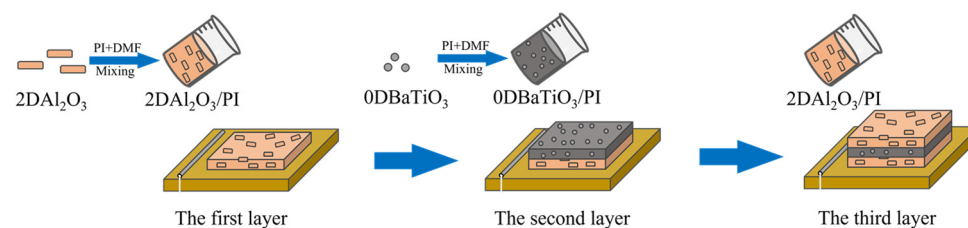


Figure 1. Preparation route of (2DAI₂O₃-0DBaTiO₃-2DAI₂O₃)/PI composite films.

The film thickness is controlled by adjusting the blade during coating, with each layer being approximately 5 µm thick, resulting in an average total thickness of 15 µm.

2.4. Characterizations

The structure of the prepared BaTiO₃ particles and dopamine-modified BaTiO₃ particles was characterized by X-ray diffraction (XRD, PW3040/60, PANalytical, Almelo, The Netherlands) with a scan range of 10–80°. Dopamine-modified BaTiO₃ particles were measured by X-ray photoelectron spectroscopy (XPS, Thermo Kalpha, Thermo Fisher Scientific, Waltham, MA, USA). Dopamine-modified BaTiO₃ particles were characterized by field emission transmission electron microscopy (FE-TEM, Titan G260-300, FEI Company, Hillsboro, OR, USA). Information on the microscopic morphology of the thickness of the prepared sandwich composite films was analyzed by field emission scanning electron microscopy (FE-SEM, JSM-7001F, JEOL, Tokyo, Japan). Fourier transform infrared (FTIR, Vertex 70, Bruker, Billerica, MA, USA) spectroscopy was employed to probe the functional groups in the sandwich composite films.

3. Results and Discussion

Figure 2a–c show the XRD and XPS spectra of BTO and BTO@PDA. The XRD patterns show that the characteristic peaks of BTO and BTO@PDA correspond to the standard card PDF 01-080-0601, indicating that the modification process does not alter the crystal structure of BTO [24]. Figure 2b presents the XPS survey spectrum of BTO@PDA, where C 1s and N 1s peaks are observed at 284.8 eV and 400.8 eV, respectively, indicating the presence of carbon and nitrogen in the sample. Figure 2c shows the high-resolution N 1s spectrum of BTO@PDA, with an O 1s peak at 530.2 eV. This peak is attributed to the oxygen from dopamine, confirming its successful incorporation into the BTO surface. These results collectively confirm that dopamine successfully coated the surface of BTO, thereby affecting its chemical composition and structure.

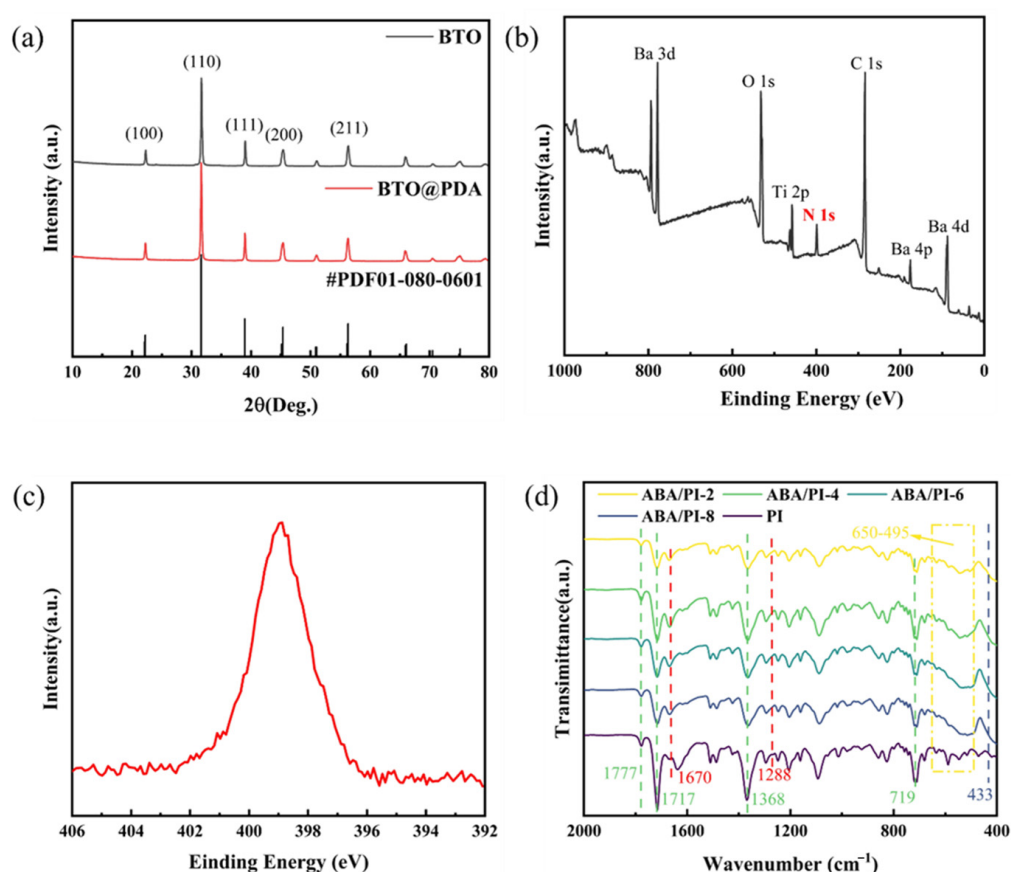


Figure 2. (a) XRD pattern of BTO and BTO@PDA. The XPS spectra of BTO@PDA include (b) the survey spectrum and (c) the regular N 1s spectrum; (d) FTIR spectra of ABA/PI composites and pure PI film.

To characterize the morphology of 0DBTO and 0DBTO@PDA, TEM was used to capture images at different magnifications. As shown in Figure S1, the BTO particles before and after surface modification were approximately 100 nm in diameter, with circular or square shapes. As depicted in Figure S1, it can be clearly observed that the 0DBTO@PDA particles were uniformly coated with an amorphous PDA layer, which is about 5 nm in thickness, and the BTO nanoparticles used in this study had a diameter of approximately 50–100 nm. Additionally, the presence of the (110) crystal plane was also observed in the modified 0DBTO@PDA (Figure S1e,f). Meanwhile, as shown in Figure S2, 2DAO exhibited an irregular flake-like structure with a smooth and uniform surface, and the thickness of 2DAO was approximately 300 nm.

Figure 2d compares the FTIR spectra of ABA/PI composite films with those of pure PI films. Both show characteristic imide ring absorption peaks at 1777 cm^{-1} , 1717 cm^{-1} , 1368 cm^{-1} , and 719 cm^{-1} , corresponding to the asymmetric and symmetric stretching, C-N stretching, and bending vibration of the C = O bond in the imide ring. These findings confirm that the PI matrix structure remains unchanged after incorporating alumina and barium titanate, as well as during the film preparation process. In the ABA/PI composite film, barium titanate (Ti-O) exhibits characteristic absorption between 495 and 650 cm^{-1} , with a prominent aluminum peak near 433 cm^{-1} . The $\alpha\text{-Al}_2\text{O}_3$ absorption at 564 cm^{-1} overlaps with the Ti-O peak. These results validate the fact that the composite film meets expectations.

Figure 3 presents the SEM images and Energy-Dispersive X-ray Spectroscopy (EDS, Thermo Fisher Scientific, Waltham, MA, USA) elemental analysis results of the cross-section of the ABA/PI composite film. It can be clearly observed that the cross-section of the composite film has a smooth fracture and no pinholes. This also confirms the rationality of the ABA/PI composite film's fabrication. The 2DAO/PI layer and the 0DBTO@PDA/PI layer are distinctly defined with tight interlayer adhesion and no gaps, with a thickness of approximately $15\text{ }\mu\text{m}$. The Al element is distributed in the outer layer of the composite film, while the Ba element is located in the middle layer. The aluminum oxide flakes in the 2DAO/PI layer and the barium titanate in the 0DBTO@PDA/PI layer are clearly visible. It is particularly noteworthy that barium titanate modified by dopamine is uniformly dispersed within the PI matrix without any aggregation.

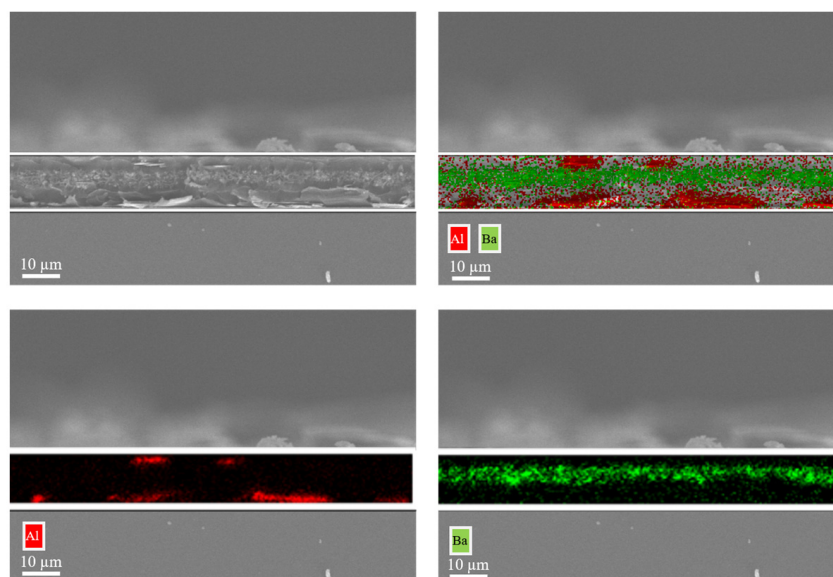


Figure 3. SEM image and EDS elemental distribution maps of the ABA/PI composite film.

Figure 4 shows how the dielectric constant and loss of ABA/PI vary with frequency and temperature. From Figure 4a, at room temperature, all materials clearly show stable frequency stability from 10^3 to 10^6 Hz , with the dielectric constant rising as the BTO content increases. At 10^3 Hz , the dielectric constants are 4.37 for ABA/PI-2, 4.71 for ABA/PI-4, 5.30 for ABA/PI-6, and 5.91 for ABA/PI-8. This increase is mainly because BTO, with a much higher dielectric constant than PI and a high specific surface area, enhances interfacial polarization and the composite film's polarization ability. Additionally, the interface between 2DAO and PI also contributes to the higher dielectric constant. The introduction of 2DAO with a wide bandgap provided deeper trap levels that captured free electrons, thereby reducing the leakage current and conductivity losses and keeping the ABA/PI composite film's loss factor low (<0.02).

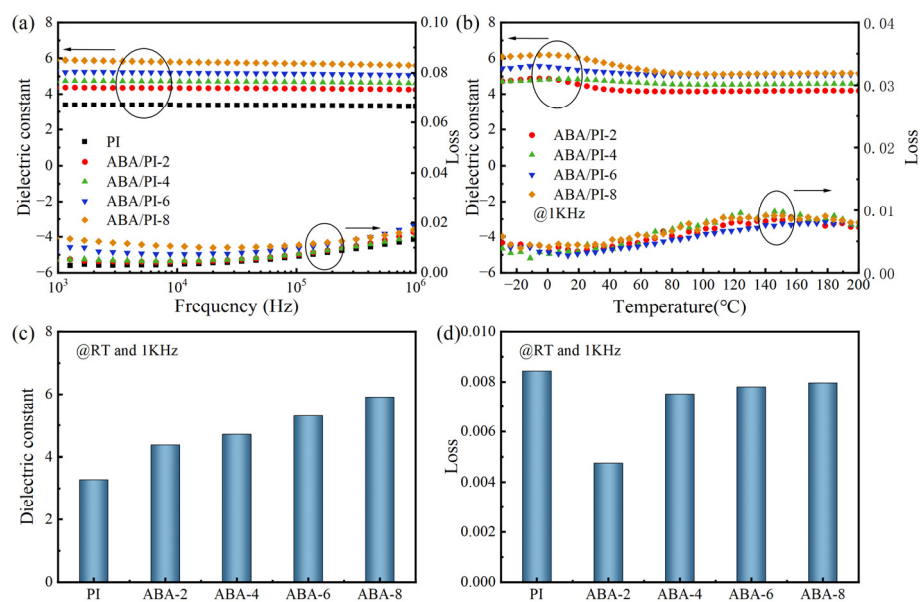


Figure 4. (a) Dielectric constant and loss of ABA/PI as a function of frequency. (b) Dielectric constant and loss of ABA/PI as a function of temperature at 1 KHz. (c,d) Comparison of dielectric constant and loss of ABA/PI at 1 KHz and room temperature.

As shown in Figure 4b, the ABA/PI composite film's dielectric properties were stable from 25 to 200 °C. The dielectric constant of ABA/PI showed a consistent upward trend in Figure 4a. Meanwhile, the dielectric loss of the composite material remained consistently low (<0.02) with rising temperatures, which is crucial for developing high-temperature energy storage films. Comparing Figure 4c,d, it is clear that as the BTO content increases, both the dielectric constant and loss of the ABA/PI composite film increase. All the dielectric constants exceed those of pure PI (3.2), while the losses remain lower than those of pure PI (0.00844). ABA/PI-8 shows the most significant increase in the dielectric constant but also has a higher dielectric loss. This is attributed to the addition of excessive BTO causing local agglomeration, increasing the leakage current and affecting the composite thin film's performance. To further confirm its high-temperature polarization, we conducted additional tests on the frequency dependence of the dielectric constant at 200 °C (Figure S3). The results indicate stable dielectric constant and loss at 200 °C, ensuring the reliable operation of the nanocomposite material in high-temperature environments.

Figure 5a presents the Weibull distribution of the ABA/PI composite film. The Weibull distribution, as shown in the equation, is utilized to analyze the breakdown field strength (E_b) and shape parameter (β) of the composite film:

$$P(E) = 1 - e^{-\left(\frac{E}{E_b}\right)^\beta}$$

where $P(E)$ represents the cumulative failure probability, E is the applied electric field strength, E_b is the breakdown strength at a cumulative breakdown probability of 63.2%, and β represents the shape parameter [25–27]. As illustrated in Figure 5a, the breakdown performance of ABA/PI at 25 °C first rises and then declines. At the optimal ratio, namely using the ABA/PI-6 composite film, the breakdown strength peaks at 482 MV m⁻¹, which is roughly 1.1 times higher than that of pure PI (449 MV m⁻¹). Additionally, β remains at 16.8, indicating high data reliability. On the one hand, BTO has been modified with dopamine to improve its dispersibility and compatibility in the PI matrix, effectively preventing the electrical breakdown of the composite film caused by filler aggregation. On the other hand, the two-dimensional flake-like structure of 2DAO can effectively act as an electron barrier

to suppress electron tree growth. Its wide bandgap allows the composite film to generate more electron traps for capturing electrons; after being compounded with PI, its outer layer can serve as an insulating protective layer for the composite film. This phenomenon indicates that an excessive addition of BTO cannot enhance the breakdown of the composite film, and there is a threshold.

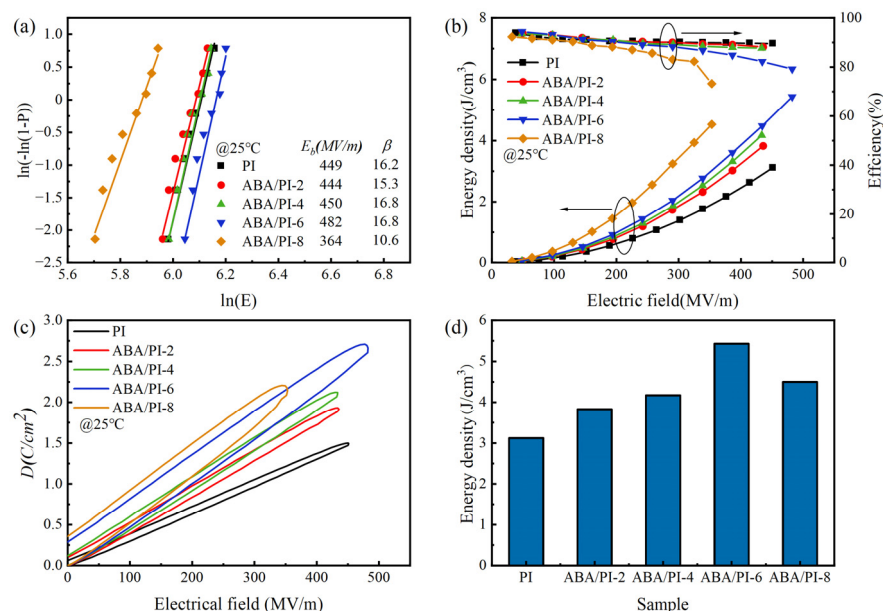


Figure 5. (a) The Weibull distribution of ABA/PI films at 25 °C. (b) The D-E curves of the ABA/PI films under different external electric fields applied at 25 °C. (c) The discharged energy density and charged–discharged efficiency of ABA/PI at 25 °C. (d) A comparison of the energy density of ABA/PI films at 25 °C.

Figure 5c shows the D-E curves of the composite film and pure PI film. Owing to the composite film's higher dielectric constant, its maximum polarization exceeds that of PI. Specifically, the ABA/PI-6 composite film exhibits the highest breakdown electric field at 25 °C, achieving a maximum polarization of $2.66 \mu\text{C cm}^{-2}$, which is 1.57 times higher than the pure PI film's $1.69 \mu\text{C cm}^{-2}$. Figure 5b illustrates the energy storage density and efficiency derived from the D-E curves for the composite and pure PI films. Figure 5b illustrates the energy storage density and efficiency derived from the D-E curves for the composite and pure PI films. As the content of 0DBTO@PDA increases, the energy storage density of the composite film first rises and then falls, remaining higher than that of the pure PI film. At the optimal formulation, the ABA/PI-6 composite film shows the highest energy storage density of 5.43 J cm^{-3} (Figure 5d), which is 1.74 times the 3.12 J cm^{-3} of the pure PI film. However, its energy storage efficiency (79.12%) is lower than that of the pure PI film (89.58%). This may be due to the dielectric mismatch between BaTiO₃ and the PI matrix, raising the composite film's leakage current density and lowering the storage efficiency. However, ABA/PI-2 and ABA/PI-4 composite films can maintain an energy storage efficiency comparable to PI, with energy storage performance improved to 3.83 J cm^{-3} at 88.21% and 4.17 J cm^{-3} at 87.70%, respectively. This improvement in high efficiency may be due to the addition of highly insulating 2DAO, which can reduce the leakage current density and the voltage-sharing protective effect of the 2DAO/PI layer and allow the lower 0DBTO@PDA content to be less affected by the dielectric mismatch.

To verify that the nanocomposite material maintains high performance at high temperatures, further D-E hysteresis loop tests were performed on the ABA/PI composite films in the temperature range of 50 to 200 °C. (Figure S4); the results are shown in Figure 6. As the temperature rises, both the ABA/PI composite and pure PI film show a gradual de-

crease in their maximum energy storage density and efficiency, which is consistent with the gradual reduction in the breakdown field strength. However, the ABA/PI composite film consistently outperforms pure PI in energy storage density. Notably, when the temperature exceeds 100 °C, the energy storage performance of the ABA/PI-4 composite surpasses that of the ABA/PI-6 composite. For instance, at 100 °C, the maximum energy storage density of the ABA/PI-4 composite film is 3.48 J cm^{-3} with an efficiency of 80.06%, while the ABA/PI-6 composite film drops to 3.18 J cm^{-3} with an efficiency of 67.50%; at 200 °C, the ABA/PI-4 composite film's maximum energy storage density is 2.36 J cm^{-3} with an efficiency of 60.27%, while the ABA/PI-6 composite film further decreases to 0.82 J cm^{-3} with an efficiency of 30.88%. This may be due to the increase in the internal electrical conductivity of the composite film as the temperature rises, leading to a decrease in the threshold of ODBTO in the PI matrix. It is noteworthy that although the energy storage efficiency of the ABA/PI-4 composite film is lower than that of pure PI films at 50 °C, 100 °C, and 150 °C, its efficiency curve at 200 °C is above the PI efficiency curve at high electric fields. This is because the inherent low thermal conductivity of PI cannot dissipate the heat generated by high electric fields into the environment, leading to local heat accumulation, increased local electrical conductivity, increased leakage current density, and a decrease in the energy storage performance to 1.16 J cm^{-3} with a 68.55% efficiency at 320 MV m^{-1} . In contrast, the ABA/PI-4 composite film, with the addition of the charge barrier of 2DAO and its thermal conductivity, is much higher than that of the pure PI film, which effectively alleviates the problem of local thermal runaway, preventing the composite film from failing due to electrothermal issues. Furthermore, as the temperature rises, the stability of the energy storage performance of the composite film becomes crucial. As shown in Figure S5, ABA/PI-4 has the best E_b and β at 200 °C.

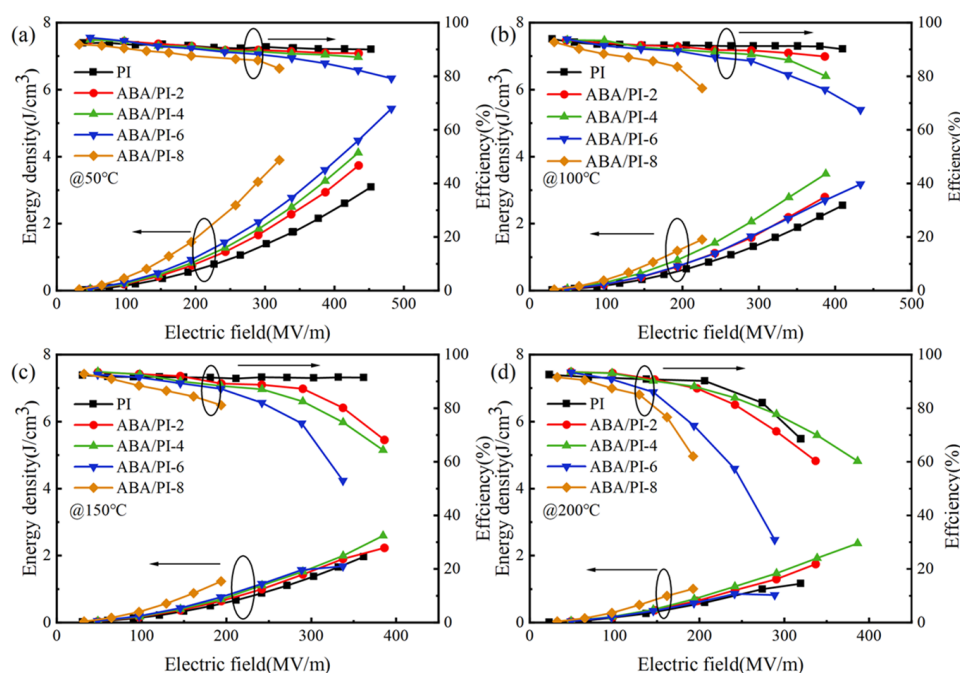


Figure 6. Energy storage performance of ABA/PI composites at (a) 50 °C, (b) 100 °C, (c) 150 °C, and (d) 200 °C.

As shown in Figure 7a, the D-E curves of ABA-4 become wider in shape, and the residual polarization gradually increases. As shown in Figure 7b, the energy storage performance of the ABA/PI-4 composite film decreases from 3.32 J cm^{-3} with 88.03% at 25 °C to 2.36 J cm^{-3} with 66.27% at 200 °C, maintaining a retention rate of over 70%, which is a relatively good level. Both ABA/PI-6 and ABA/PI-4 composite films have

a higher energy storage performance than PI films at ambient and high temperatures, respectively. Therefore, based on the concept of multidimensional synergy, by combining the high polarization of 0DBTO@PDA particles with the wide bandgap and high thermal conductivity of 2DAO, the dielectric and energy storage performance of polymer-based composite dielectric films can be comprehensively improved from 25 to 200 °C.

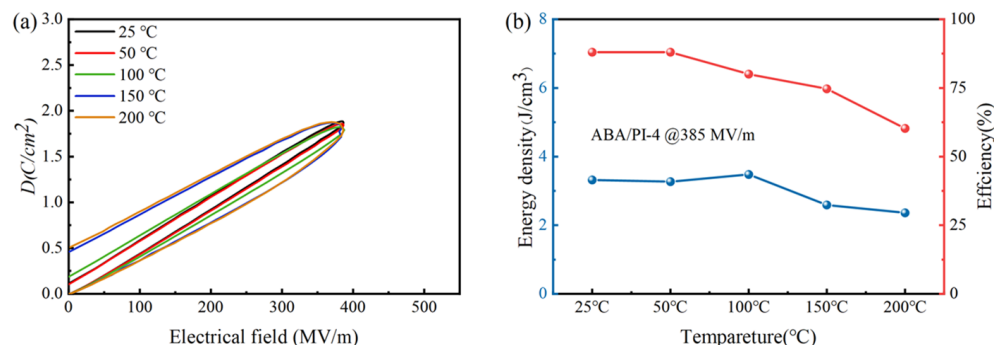


Figure 7. At 385 MV m^{−1}, the ABA/PI-4 composite film exhibits (a) D-E curves and (b) energy storage performance across a temperature range of 25–200 °C.

As shown in Figure 8, the energy storage performance of the ABA/PI-4 composite film remains near 1.5 J cm^{−3}, with an energy storage efficiency of approximately 77%. This indicates that even after 10,000 cycles at 200 °C, the composite film demonstrates excellent cyclic stability and reliability.

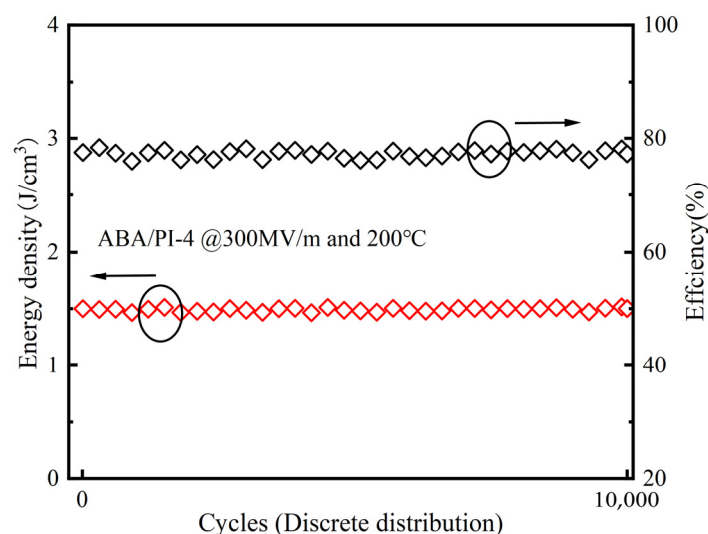


Figure 8. Energy storage performance of ABA/PI-4 at 10,000 cycles of charging and discharging at 200 °C and 300 MV m^{−1}.

As shown in Figure 9, based on the established dielectric breakdown model, the evolution of the breakdown current path over time in the ABA/PI composite film has been simulated through finite element simulation [28,29]. In this simulation, we defined material properties such as conductivity and relative permittivity. Breakdown was observed from 0 to 10 s, with calculations performed every 0.1 s. The white paths in the figure represent the current paths, with the upper and lower rectangular particles representing 2DAO and the central circular particle representing a BTO particle. It can be clearly seen that the flake-like alumina located in the upper and lower layers can hinder the growth of the current and extend the current path, indicating that the introduction of an appropriate amount of 2DAO improves dielectric breakdown, providing a basis for achieving high capacitive energy storage. Furthermore, the difference in the dielectric constant between

the 2DAO/PI and 0DBTO@PDA/PI layers leads to the redistribution of the electric field. If the three-layer composite film is considered as three independent layers, it can be regarded as a series of three capacitors. The 2DAO/PI layer serves as an insulating layer with a high dielectric to withstand voltage, while the 0DBTO@PDA/PI layer plays the role of a polarization layer with a high dielectric constant, thereby enhancing the energy storage and breakdown performance of the composite material at 200 °C. This also offers a certain theoretical foundation for this thesis.

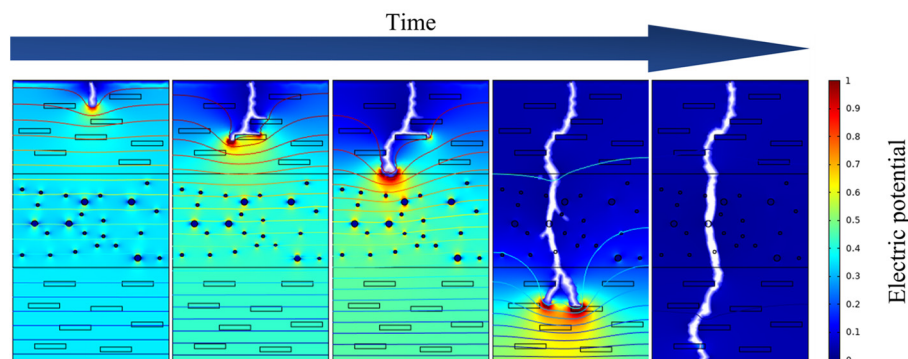


Figure 9. Simulation of breakdown current evolution of ABA/PI composites.

Figure 10 compares this work with other achievements in the industry under high-temperature conditions [2,21,25,30–34]. The ABA/PI composite film we prepared achieved a higher energy storage density at a lower electric field strength, which also provides a new perspective for the industry.

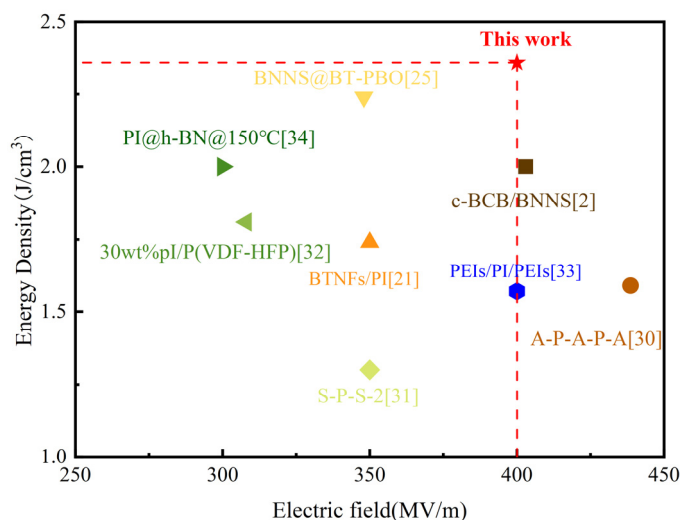


Figure 10. Comparison of other energy storage systems at 200 °C.

4. Conclusions

Herein, we utilized the sol–gel method combined with tape casting to incorporate 0DBTO@PDA and 2DAO into a PI matrix, creating ABA/PI tri-layer composite films with a distinctive structure. The central layer was rich in 0DBTO@PDA, serving as the polarization layer, while the outer layers were combined with 2DAO, functioning as thermally conductive and insulating layers. We comprehensively characterized and tested the composite films' morphology, dielectric properties, breakdown strength, and energy storage performance to thoroughly investigate the optimization mechanism of their energy storage performance. Our findings reveal that by employing multidimensional synergistic concepts and a multilayer structural design, the synergistic enhancement of the dielectric constant, breakdown strength, and high-temperature tolerance can be achieved. The

inclusion of 0DBTO@PDA boosts the polarization capability, while the addition of 2DAO ensures the composite film's stable operation under high-temperature and high-voltage conditions. At 10^3 Hz, the dielectric constant of the ABA/PI composite films was enhanced compared to pure PI (3.38), with values of 4.37 for ABA/PI-2, 4.71 for ABA/PI-4, 5.30 for ABA/PI-6, and 5.91 for ABA/PI-8. At 25 °C, the ABA/PI-6 composite film demonstrated the highest energy storage density of 5.43 J cm^{-3} , which is 1.74 times higher than that of the pure PI film. At 200 °C, the ABA/PI-4 composite film achieved the maximum energy storage density of 2.36 J cm^{-3} , representing a 203% increase compared to pure PI. This work introduces innovative ideas for the development of high-temperature dielectric materials.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings15050555/s1>. Figure S1: (a–c) TEM images of BTO at different magnifications. (d–f) TEM images of 0DBTO@PDA powder at different magnifications. Figure S2: SEM images of 2DAO. (d–f) TEM images of 0DBTO@PDA powder at different magnifications. Figure S3: Temperature dependence of (a) ABA/PI-2, (b) ABA/PI-4, (c) ABA/PI-6, and (d) ABA/PI-8 from 25 to 200 °C. Figure S4: Summarizing the D-E of composites and PI at 50 °C, 100 °C, 150 °C, and 200 °C. Figure S5: Summarizing the E_b and β of composites and PI at 25 °C, 50 °C, 100 °C, 150 °C, and 200 °C.

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References

1. Yoon, S.; Shin, D.-J.; Ko, Y.-H.; Cho, K.-H.; Koh, J.-H. Flexible Energy Harvester Based on Poly(vinylidene fluoride) Composite Films. *J. Nanosci. Nanotechnol.* **2019**, *19*, 1289–1294. [CrossRef] [PubMed]
2. Li, Q.; Chen, L.; Gadinski, M.R.; Zhang, S.; Zhang, G.; Li, H.U.; Jagodkine, E.; Haque, A.; Chen, L.-Q.; Jackson, T.N.; et al. Flexible High-temperature Dielectric Materials from Polymer Nanocomposites. *Nature* **2016**, *536*, 112. [CrossRef] [PubMed]
3. Wang, Y.; Chen, J.; Li, Y.; Niu, Y.; Wang, Q.; Wang, H. Multilayered Hierarchical Polymer Composites for High Energydensity Capacitors. *J. Mater. Chem. A* **2019**, *7*, 2965–2980. [CrossRef]
4. Zhang, G.; Zhang, X.; Lu, J.; Zhu, B.; Ma, T.; Dai, Y. Structural Dielectric and Mechanical Changes in BOPP Films under Different Thermal Aging Conditions. *J. Mater. Res. Technol.* **2025**, *36*, 998–1004. [CrossRef]
5. Zha, J.-W.; Xiao, M.; Wan, B.; Wang, X.; Dang, Z.-M.; Chen, G. Polymer Dielectrics for High-Temperature Energy Storage: Constructing Carrier Traps. *Prog. Mater. Sci.* **2023**, *140*, 101208. [CrossRef]
6. Wang, F.; Cai, J.; Yang, C.; Luo, H.; Li, X.; Hou, H.; Zou, G.; Zhang, D. Improved Capacitive Energy Storage Nanocomposites at High Temperature Utilizing Ultralow Loading of Bimetallic MOF. *Small* **2023**, *19*, 2300510. [CrossRef]
7. Zhu, L.; Zhang, Y.; Xu, W.; Zhu, X.; Niu, S.; Zhang, Y.; Jiang, Z. Crosslinked Polyetherimide Nanocomposites with Superior Energy Storage Achieved via Trace Al_2O_3 Nanoparticles. *Compos. Sci. Technol.* **2022**, *223*, 109421. [CrossRef]
8. Zhang, Z.; Wang, D.H.; Litt, M.H.; Tan, L.; Zhu, L. High-Temperature and High-Energy-Density Dipolar Glass Polymers Based on Sulfonylated Poly(2,6-dimethyl-1,4-phenylene oxide). *Angew. Chem.* **2018**, *130*, 1544–1547. [CrossRef]

9. Li, X.; Liu, B.; Wang, J.; Li, S.; Zhen, X.; Zhi, J.; Zou, J.; Li, B.; Shen, Z.; Zhang, X.; et al. High-Temperature Capacitive Energy Storage in Polymer Nanocomposites through Nanoconfinement. *Nat. Commun.* **2024**, *15*, 6655. [\[CrossRef\]](#)
10. Meng, Z.; Zhang, T.; Zhang, C.; Shang, Y.; Lei, Q.; Chi, Q. Advances in Polymer Dielectrics with High Energy Storage Performance by Designing Electric Charge Trap Structures. *Adv. Mater.* **2024**, *36*, 2310272. [\[CrossRef\]](#)
11. Liu, B.; Yang, M.; Zhou, W.-Y.; Cai, H.-W.; Zhong, S.-L.; Zheng, M.-S.; Dang, Z.-M. High Energy Density and Discharge Efficiency Polypropylene Nanocomposites for Potential High-Power Capacitor. *Energy Storage Mater.* **2020**, *27*, 443–452. [\[CrossRef\]](#)
12. Fan, M.; Hu, P.; Dan, Z.; Jiang, J.; Sun, B.; Shen, Y. Significantly Increased Energy Density and Discharge Efficiency at High Temperature in Polyetherimide Nanocomposites by a Small Amount of Al₂O₃ Nanoparticles. *J. Mater. Chem. A* **2020**, *8*, 24536–24542. [\[CrossRef\]](#)
13. Sun, B.; Hu, P.; Ji, X.; Fan, M.; Zhou, L.; Guo, M.; He, S.; Shen, Y. Excellent Stability in Polyetherimide/SiO₂ Nanocomposites with Ultrahigh Energy Density and Discharge Efficiency at High Temperature. *Small* **2022**, *18*, 2202421. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Zhou, Y.; Yuan, C.; Wang, S.; Zhu, Y.; Cheng, S.; Yang, X.; Yang, Y.; Hu, J.; He, J.; Li, Q. Interface-Modulated Nanocomposites Based on Polypropylene for High-Temperature Energy Storage. *Energy Storage Mater.* **2020**, *28*, 255–263. [\[CrossRef\]](#)
15. Ai, D.; Li, H.; Zhou, Y.; Ren, L.; Han, Z.; Yao, B.; Zhou, W.; Zhao, L.; Xu, J.; Wang, Q. Tuning Nanofillers in In Situ Prepared Polyimide Nanocomposites for High-Temperature Capacitive Energy Storage. *Adv. Energy Mater.* **2020**, *10*, 1903881. [\[CrossRef\]](#)
16. Wang, P.; Yao, L.; Pan, Z.; Shi, S.; Yu, J.; Zhou, Y.; Liu, Y.; Liu, J.; Chi, Q.; Zhai, J.; et al. Ultrahigh Energy Storage Performance of Layered Polymer Nanocomposites over a Broad Temperature Range. *Adv. Mater.* **2021**, *33*, 2103338. [\[CrossRef\]](#)
17. Wang, P.; Guo, Y.; Zhou, D.; Li, D.; Pang, L.; Liu, W.; Su, J.; Shi, Z.; Sun, S. High-Temperature Flexible Nanocomposites with Ultra-High Energy Storage Density by Nanostructured MgO Fillers. *Adv. Funct. Mater.* **2022**, *32*, 2204155. [\[CrossRef\]](#)
18. Zhang, K.; Ma, Z.; Fu, Q.; Deng, H. Multi-Layered Boron Nitride/Polyimide High-Temperature Capacitor Dielectric Film. *Mater. Today Energy* **2022**, *29*, 101093. [\[CrossRef\]](#)
19. Li, H.; Zhou, Y.; Liu, Y.; Li, L.; Liu, Y.; Wang, Q. Dielectric Polymers for High-Temperature Capacitive Energy Storage. *Chem. Soc. Rev.* **2021**, *50*, 6369–6400. [\[CrossRef\]](#)
20. Liu, X.-J.; Zheng, M.-S.; Chen, G.; Dang, Z.-M.; Zha, J.-W. High-Temperature Polyimide Dielectric Materials for Energy Storage: Theory, Design, Preparation and Properties. *Energy Environ. Sci.* **2022**, *15*, 56–81. [\[CrossRef\]](#)
21. Hu, P.; Sun, W.; Fan, M.; Qian, J.; Jiang, J.; Dan, Z.; Lin, Y.; Nan, C.-W.; Li, M.; Shen, Y. Large Energy Density at High-Temperature and Excellent Thermal Stability in Polyimide Nanocomposite Contained with Small Loading of BaTiO₃ Nanofibers. *Appl. Surf. Sci.* **2018**, *458*, 743–750. [\[CrossRef\]](#)
22. Xu, A.; Zhou, J.; Tan, H.; Zhong, H.; Deng, L.; Luo, H.; Chen, S. Constructing Polyimide-Based Nanocomposite Dielectrics with Superior High-Temperature Energy Storage Performance via Using Ternary Structure Strategy. *Compos. Part A Appl. Sci. Manuf.* **2024**, *186*, 108405. [\[CrossRef\]](#)
23. Chen, H.; Pan, Z.; Cheng, Y.; Ding, X.; Liu, J.; Chi, Q.; Yang, M.; Yu, J.; Dang, Z.-M. Ultrahigh Charge–Discharge Efficiency and High Energy Density of a High-Temperature Stable Sandwich-Structured Polymer. *J. Mater. Chem. A* **2022**, *10*, 1579–1587. [\[CrossRef\]](#)
24. Chen, S.; Skordos, A.; Thakur, V.K. Functional Nanocomposites for Energy Storage: Chemistry and New Horizons. *Mater. Today Chem.* **2020**, *17*, 100304. [\[CrossRef\]](#)
25. Wang, X.; Yuan, Y.; Zhang, Y.; Qian, J.; Zuo, P.; Liu, X.; Zhuang, Q. Covalently Modified and Hierarchically Structured Corn-like BNNS@BT/Benzoxazole Composites with Enhanced Dielectric Properties over an Ultra-Wide Temperature Range. *Compos. Part A Appl. Sci. Manuf.* **2022**, *160*, 107027. [\[CrossRef\]](#)
26. Zhu, Y.; Shen, Z.; Li, Y.; Chai, B.; Chen, J.; Jiang, P.; Huang, X. High Conduction Band Inorganic Layers for Distinct Enhancement of Electrical Energy Storage in Polymer Nanocomposites. *Nano-Micro Lett.* **2022**, *14*, 151. [\[CrossRef\]](#)
27. Ren, L.; Yang, L.; Zhang, S.; Li, H.; Zhou, Y.; Ai, D.; Xie, Z.; Zhao, X.; Peng, Z.; Liao, R.; et al. Largely Enhanced Dielectric Properties of Polymer Composites with HfO₂ Nanoparticles for High-Temperature Film Capacitors. *Compos. Sci. Technol.* **2021**, *201*, 108528. [\[CrossRef\]](#)
28. Cao, Q.; Zhu, W.; Chen, W.; Chen, X.; Yang, R.; Yang, S.; Zhang, H.; Gui, X.; Chen, J. Nonsolid TiO_x Nanoparticles/PVDF Nanocomposite for Improved Energy Storage Performance. *ACS Appl. Mater. Interfaces* **2022**, *14*, 8226–8234. [\[CrossRef\]](#)
29. Cheng, Y.; Pan, Z.; Chen, H.; Ding, X.; Li, Z.; Fan, X.; Liu, J.; Li, P.; Yu, J.; Zhai, J. Novel Inorganic Fillers of 1D Hydroxyapatite Nanowires Induced Superior Energy Storage Performances of P(VDF-HFP)-Based Composite Films. *J. Mater. Chem. A* **2022**, *10*, 21650–21658. [\[CrossRef\]](#)
30. Dong, J.; Hu, R.; Xu, X.; Chen, J.; Niu, Y.; Wang, F.; Hao, J.; Wu, K.; Wang, Q.; Wang, H. A Facile In Situ Surface-Functionalization Approach to Scalable Laminated High-Temperature Polymer Dielectrics with Ultrahigh Capacitive Performance. *Adv. Funct. Mater.* **2021**, *31*, 2102644. [\[CrossRef\]](#)
31. Dong, J.; Hu, R.; Niu, Y.; Li, L.; Li, S.; Sun, L.; Liu, Y.; Deng, X.; Li, L.; Xu, X.; et al. Scalable In-Situ Surface-Coated Polymer Dielectrics with Significantly Enhanced High-Temperature Breakdown Strength. *Mater. Today Energy* **2022**, *30*, 101158. [\[CrossRef\]](#)

32. Feng, Q.-K.; Liu, D.-F.; Zhang, Y.-X.; Pei, J.-Y.; Zhong, S.-L.; Hu, H.-Y.; Wang, X.-J.; Dang, Z.-M. Significantly Improved High-Temperature Charge-Discharge Efficiency of All-Organic Polyimide Composites by Suppressing Space Charges. *Nano Energy* **2022**, *99*, 107410. [[CrossRef](#)]
33. Azizi, A.; Gadinski, M.R.; Li, Q.; AlSaud, M.A.; Wang, J.; Wang, Y.; Wang, B.; Liu, F.; Chen, L.; Alem, N.; et al. High-Performance Polymers Sandwiched with Chemical Vapor Deposited Hexagonal Boron Nitrides as Scalable High-Temperature Dielectric Materials. *Adv. Mater.* **2017**, *29*, 1701864. [[CrossRef](#)] [[PubMed](#)]
34. Niu, Y.; Dong, J.; He, Y.; Xu, X.; Li, S.; Wu, K.; Wang, Q.; Wang, H. Significantly Enhancing the Discharge Efficiency of Sandwich-Structured Polymer Dielectrics at Elevated Temperature by Building Carrier Blocking Interface. *Nano Energy* **2022**, *97*, 107215. [[CrossRef](#)]

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