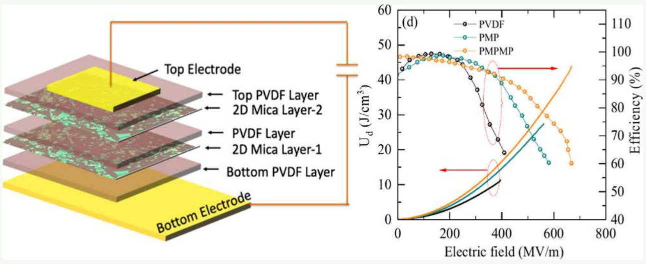
ACS APPLIED ELECTRONIC MATERIALS

pubs.acs.org/acsaelm Article

Enhanced Energy Density in a Heterostructure Capacitor of Multilayered PVDF and 2D Mica Nanocomposites

Sumit Bera, Rukshan M. Thantirige, Jiaen Wu, Emily C. Davidson, Sujit Anil Kadam, Anirudha V. Sumant, Brian T. Shook, Rahul Rao, Ryan Selhorst, Maninderjeet Singh, Alamgir Karim, Dharmaraj Raghavan, and Nihar R. Pradhan*

Cite This: *ACS Appl. Electron. Mater.* 2024, 6, 6582−6590 Read Online



ABSTRACT: The demand for energy storage devices with high energy density, power density, and higher efficiencies has motivated researchers to explore novel materials and designs beyond current limitations. Polymer-based dielectric capacitors are flexible, lightweight, self-healable, and compatible with a variety of nanofillers. Despite a plethora of studies on polymer nanocomposites with 2D nanofillers, the role of multilayered 2D nanofillers in polymer nanocomposites in the context of energy storage properties has yet to be determined. In this work, mechanically exfoliated 2D mica nanofillers were incorporated with poly(vinylidene fluoride) (PVDF) polymer to fabricate PVDF-mica-PVDF (PMP) multilayered heterostructure capacitors. A single exfoliated layer of mica with an average thickness of the flakes of 20 nm interfaced within layers of PVDF to form PMP and using two layers of mica to form PVDF/mica/PVDF/mica/PVDF (PMPMP) heterostructure capacitors. Average enhancements of 100% and 170% were measured for the dielectric constants of PMP ($\varepsilon_{av} \sim 22.9$) and PMPMP ($\varepsilon_{av} \sim 30.8$), respectively compared to that of the pristine PVDF ($\varepsilon_{av} \sim 11.4$) films measured using the same setup. The highest discharged energy density of PMP and PMPMP nanocomposite films reached 27.5 J/cm^3 ($E = 670$ MV/m) and 44 J/cm^3 ($E = 570$ MV/m), compared to 11.2 J/cm^3 ($E = 396$ MV/m) for the pristine PVDF capacitor. This work develops a detailed understanding of the use of multilayered 2D nanofillers to develop high-capacitance and high energy density polymeric dielectric capacitors and opens avenues for developing orientation-controlled 2D nanofiller-based capacitors for use in industrial applications.

KEYWORDS: *PVDF, Multilayer, Nanocomposite heterostructure, Dielectric, Breakdown strength*

INTRODUCTION

Polymer nanocomposite-based dielectric materials with high energy and high-power density with ultrafast charging−discharging are of great importance for use in energy storage devices and hybrid electric vehicles, electrical weapon systems, medical devices, modern electronics, etc.[1] Dielectric capacitors with higher capacitance, low equivalent series resistance (ESR), and smaller sizes are essential components for unmanned spacecraft and satellites due to reduced space usage and light weight, which are key factors for space electronics. Polymer-based capacitors are suitable for aerospace decoupling and filtering applications that require low ESR, improved capacitance retention at a high frequency, high energy density, and specific energy to reduce size and weight and long-term reliability. Polymer-based nanocomposite materials have been reported recently with improved dielectric constants, breakdown strengths, and storage energy densities where the nanomaterials were used as fillers within the polymer matrix to enhance the desired properties. For example the poly(vinylidene fluoride) (PVDF) polymer with 2D mica fillers shows enhanced dielectric constant, breakdown strength, and energy density.[2] Among the various polymer nanofiller composite materials systems, 2D nanomaterial-based polymer nanocomposites are at the forefront of this exploration compared to the 0D and 1D nanofillers due to their large surface area to volume ratio of the fillers,[1,3−5] which enables the larger polymer−2D surface interface areas to accumulate and trap charges more efficiently and increase the polarization.[1−3,6−11] Thus, a polymer−2D nanocomposite can significantly enhance the dielectric constant compared to the 0D and 1D nanofiller composites with similar vol % of the fillers.[12] In addition to improving the polarization, the integration of insulating 2D materials such as h-BN and mica hinders the flow of electric current within the polymer matrix.

Received: June 8, 2024
Revised: August 15, 2024
Accepted: August 16, 2024
Published: August 22, 2024

https://doi.org/10.1021/acsaelm.4c01037
ACS Appl. Electron. Mater. 2024, 6, 6582−6590

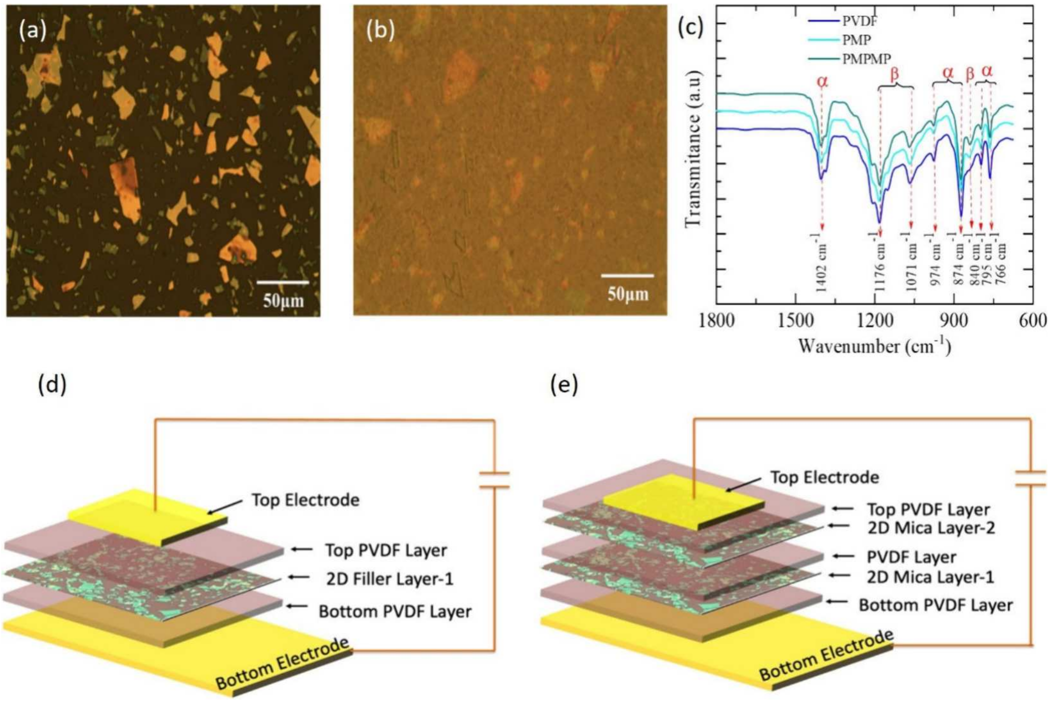


Figure 1. (a) Optical image of exfoliated mica on a Si/SiO$_2$ substrate. (b) PVDF coated on the transferred mica filler onto the ITO substrate. (c) Transmittance spectra of the polymer and polymer nanocomposite films obtained through FTIR spectroscopy. (d, e) Schematic diagram of the PVDF-2D mica-PVDF (PMP) and PVDF-2D mica-PVDF-2D mica-PVDF (PMPMP) capacitor devices, respectively.

This results in an enhancement of breakdown strength (E_b) and the overall discharge energy density (U_d) of the polymer nanocomposite.[11,13−15] Besides, the higher thermal conductivity, increased stability, and high mechanical strength, 2D materials enable the system to have lower dielectric loss and contribute to the improved mechanical characteristics of nanocomposites.[16−18] However, the dielectric properties of 2D-nanocomposite capacitors also depend on the dielectric properties of the polymer. PVDF exhibits a high dielectric constant of $\varepsilon \sim 10$ at frequency between 100 and 1000 Hz[19] and a very low dielectric loss of 0.02−0.05 at 1 kHz.[20] It is worth noting that the high dielectric constant of PVDF depends on the suitable conformation adopted by the polymer chain, such as the highly polar β polymorphs and intermediate polar γ polymorphs. However, under most common processing conditions, the nonpolar α polymorph is preferred. Thus, adjusting the polymorph of PVDF is critical to guarantee its high dielectric constant.

Among the various 2D filler materials, h-BN, mica, and MXene are promising in improving the dielectric properties of the capacitors. The PVDF-h-BN nanocomposite shows an enhanced dielectric constant.[21] Two-dimensional crystal h-BN is a dielectric material with a static dielectric constant of 4.[22] The band gap of h-BN is ~6 eV for single to few atomic layers.[23] Mica is one of the largely available layered materials with band gap ranges from 2 to 6 eV from monolayer to bulk and is promising for dielectric energy storage.[24] On the other hand, MXene is one of the 2D layered materials known for high dielectric enhancement.[17,25] Similarly, the energy density of a 15 mm thick film of P(VDF-TrFE-CFE)/h-BN nanocomposite decorated with barium titanate (BaTiO$_3$) nanoparticles increased from 7 J/cm^3 at the electric field of 35 MV/m to 16 J/cm^3 at the electric field of 550 MV/m due to the enhanced dielectric constant as well as breakdown voltage.[26] The P(VDF-TrFE-CFE)/h-BN sample also shows a high power density (1080 MW/L) compared with the state-of-the-art BOPP polymer (100 MW/L). The composite also shows high stability, and no loss of energy (or change in energy) was observed until 50,000 cycles at an applied field of 200 MV/m. MXene is another commonly used 2D nanofiller. Tu et al. found that the dielectric constant of the P(VDF-TrFE-CFE)-Ti$_3$C$_2$T$_x$ nanocomposite increased from 50 to 10^5 with 15 wt % of MXene loading. However, dielectric loss was significantly high (loss ~1 at 15 wt % filler) since Ti$_3$C$_2$T$_x$ is metallic.[25] Further efforts are needed to decrease the dielectric loss when using this system for energy storage. Mica stands out as an economical, easily exfoliable, thermally stable, and high dielectric constant material, making it a promising nanofiller to integrate into the polymer to develop composite materials for energy-efficient dielectric capacitors. It shows an indirect band gap of approximately 5 eV, which decreases with reducing the thickness up to the monolayer limit.[3] Despite its excellent characteristics, its utilization as a nanofiller has not been well understood. Fu et al. reported that PVDF/mica nanosheets with 5 vol % of mica exhibit limited discharged energy densities up to 7.9 J/cm^3 at 450 MV/m.[1,27] In another report, Khalifa et al. reported an enhancement of dielectric constant up to 30% for PVDF-mica nanocomposites; however, they have not explored the energy storage performance of these nanocomposites.[28] Several studies demonstrated that multilayered films of 2D-polymer nanocomposites exhibit superior dielectric properties and energy storage performance compared to pure polymer films or monolayer 2D-polymer nanocomposites.[29−35] These different nanocomposites were obtained through the direct blending of the 2D material with the polymer, where the fillers are randomly distributed throughout the polymer matrix.

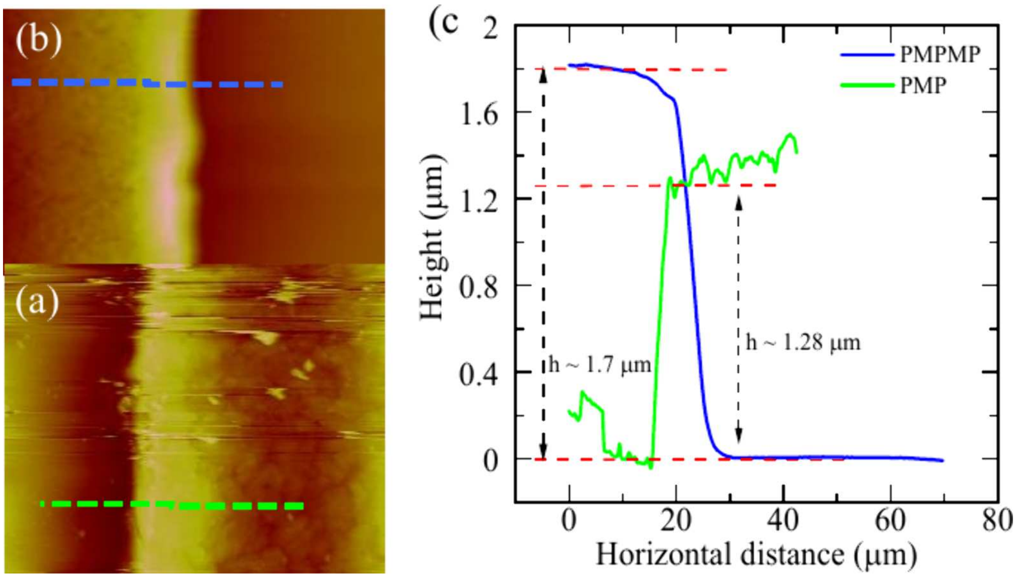


Figure 2. AFM topography images showing film thickness cross sections of (a) PMP and (b) PMPMP films. (c) Height profiles measuring the thickness of respective nanocomposite films and corresponding to the dashed lines in (a) and (b).

However, recently in a study by our group, the 2D mica was incorporated into PVDF in a stratified configuration using an alternative method of mechanical exfoliation involving poly(methyl methacrylate) (PMMA), and the PVDF/PMMA-mica/PVDF sandwiched capacitor showed an ultrahigh energy density of 75 J/cm^3 and high breakdown field of 1270 V/m only with a 1 vol % of exfoliated mica.[17] Notably, our previous work focused on the transfer of mica nanosheets using a PMMA thin film, resulting in PVDF-PMMA, PMMA-2D mica, and 2D mica-PVDF interfaces in the film.[12] However, the effect of the presence of stratified 2D nanofillers in a homopolymer matrix needs further elucidation to decouple the effect of multiple interfaces from the nanofillers. In this work, we directly incorporate 2D mica nanosheets into a homopolymer matrix (PVDF) through a simple mechanical exfoliation technique and form single interfaces between mica and the PVDF within the multilayer nanocomposite films. The advantage of adding 2D nanofillers inside the polymer using the mechanical exfoliation method is that a very low vol % of the 2D fillers can cover the maximum area of the capacitor, resulting in a huge improvement in the dielectric properties of the nanocomposite. We observe that the presence of stratified 2D mica nanofillers in the PVDF matrix shows significantly enhanced dielectric permittivity, with the enhancement of ~100% for a single exfoliated layer 2D mica nanosheet capacitor (PVDF/2D mica/PVDF, or PMP) and ~170% for bilayer 2D mica nanosheet capacitors (PVDF/2D-mica/PVDF/2Dmica/PVDF, or PMPMP) at room temperature. Furthermore, the 2D mica nanosheet-based PVDF nanocomposites show enhanced dielectric strength and capacitive energy density in the order of bilayer > single layer > pristine PVDF. We believe that this work enhances the understanding of the role of 2D nanofiller stratification in polymer nanocomposites and will help in the future development of high-energy-density polymeric nanocomposite capacitors.

■ EXPERIMENTAL PROCEDURE

Fabrication of Devices. A 10 wt % PVDF solution was prepared by dissolving PVDF powder (M_w ~ 534,000) in DMF, with continuous magnetic stirring for 4 h at 60 °C. Indium tin oxide (ITO) substrates were precleaned with acetone, IPA, and DI water using an ultrasonicator. A bottom layer of PVDF polymer was then spin-coated onto the cleaned ITO substrates, which were subsequently placed on a hot plate at 80 °C for 10 min and stored in desiccators. Meanwhile, 2D mica flakes of various sizes and thicknesses (Figure 1a) were exfoliated onto clean Si/SiO$_2$ substrates using the mechanical Scotch tape method. A PVDF layer was coated onto the mica-exfoliated Si/SiO$_2$ substrate followed by a postannealing of 80 °C for 10 min (Figure 1b). The etching of the 2D mica flakes along with the PVDF polymer from the Si/SiO$_2$ substrate was accomplished using a 30 wt % KOH solution. Later the film was transferred to DI water to remove the KOH residues. Finally, a 2D-polymer nanocomposite film composed of a PVDF-mica-PVDF monolayer heterostructure (PMP) was obtained by transferring the PVDF-coated mica film on top of the PVDF-coated ITO substrate. To fabricate the PVDF-mica-PVDF-mica-PVDF bilayer heterostructure (PMPMP), another mica-PVDF layer was transferred on top of PMP. After successive transfers of the polymer/2D layers onto the PVDF-coated ITO slides, we vacuum dried the devices for a few hours or overnight to remove any excess trapped water and/or gaps between the layers and formed a smooth sandwich layered structure. All 2D nanocomposite films were annealed at 180 °C for 45 min before conducting the characterizations and measurements. The detailed steps of the fabrication process of the heterostructure multilayer capacitor are provided in the Supporting Information, Figure S1. Figure 1(d,e) shows the schematic diagram of device fabrication for the PVDF-2D mica-PVDF (PMP) and PVDF-2D mica-PVDF-2D mica-PVDF (PMPMP) capacitor devices.

Measurement Procedures. The distribution of the 2D flakes was observed through an optical microscope with 20× and 50× objectives coupled with the Signatone Probe Station before and after transfer from the Si/SiO$_2$ substrates. We observed a 100% transfer of exfoliated flakes from the SiO$_2$ substrate onto the PVDF-coated ITO substrates. The thickness of the polymer and 2D-polymer nanocomposite was measured by a Veeco Dimension 3100 atomic force microscope (AFM) in contact mode. The thickness of the mica flakes was determined using tapping mode AFM after exfoliation on a Si/SiO$_2$ wafer. The presence of α and β polymorphs of PVDF was identified using FTIR measurements, which were carried out on a Nicolet iN10 MX infrared microscope with a Ge ATR crystal. A gold-coated glass slide was used to enhance the signal of the sample when measuring the FTIR spectrum of PVDF films (the gold has a high IR reflectance).

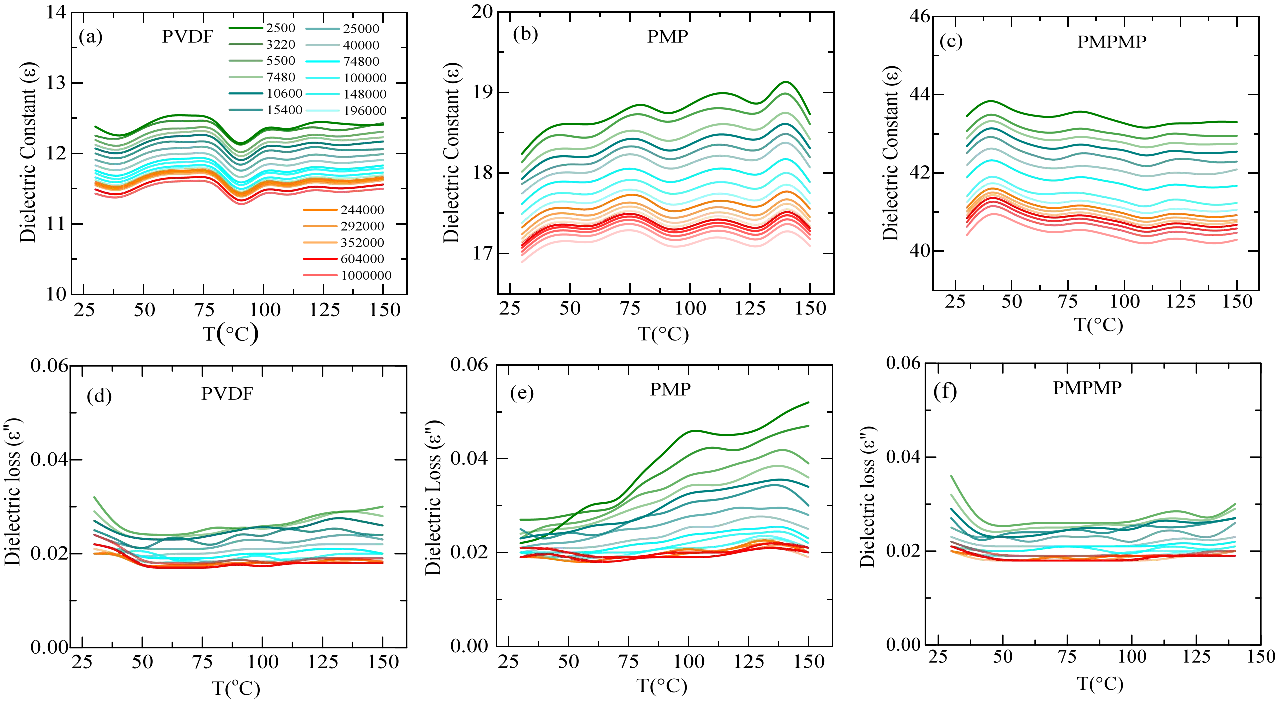


Figure 3. Temperature-dependent dielectric constant of PVDF (a), PMP (b), and PMPMP (c). Dielectric loss of PVDF (d), PMP (e), and PMPMP (f) capacitor films at varying frequencies from 1 kHz to 1 MHz.

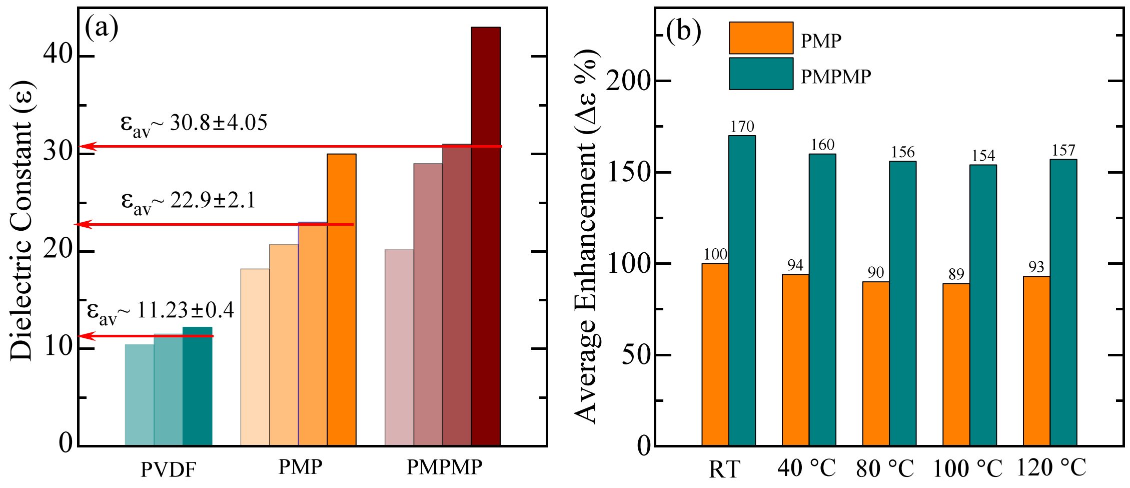


Figure 4. (a) Histogram data of the dielectric constant for pristine PVDF, PMP, and PMPMP capacitors showing average values of dielectric constant increases with the mica filler contents. (b) The % enhancement of the dielectric constant of PMP and PMPMP compared to the pristine PVDF.

The temperature-dependent dielectric properties of 2D-nanocomposite films were measured by a HIOKI LCR tester (3522) at frequencies from 1 kHz to 1 MHz. The polarization and breakdown strength measurements were performed using a Radiant ferroelectric precession instrument with a high-voltage power source (Poly K, 10 kV).

■ RESULTS AND DISCUSSION

The FTIR spectra of PVDF and nanocomposite films were measured at room temperature, as shown in Figure 1(c). The thickness of the PMP and PMPMP nanocomposite films, measured using AFM in tapping mode, was 1.2 and 1.7 μm, respectively, as illustrated in Figure 2(a−c). The absorbance intensities at 840, 1072 1170, and 1401 cm^{-1} imply the presence of a polar β phase. Similarly, absorbances at 762, 840, and 872 cm^{-1} corroborate the existence of a nonpolar α phase. Numerous studies have documented the coexistence of nonpolar and polar phases in PVDF with different proportions.[12,26,28,36−38]

Figure 3 shows the temperature-dependent dielectric constant (ε) and dielectric loss of PVDF, PMP, and PMPMP nanocomposite films measured at a frequency range between 100 kHz and 1 MHz. These data were extracted from the frequency-dependent capacitance measurements presented in Supporting Information, Figure S2. Figures 3(a−c) clearly indicate that the incorporation of 2D mica into PVDF significantly enhances the dielectric constant across the temperature range studied, suggesting that 2D mica effectively improves the dielectric properties of PVDF. Conversely, Figures 3(d−f) show that the dielectric loss factor remains

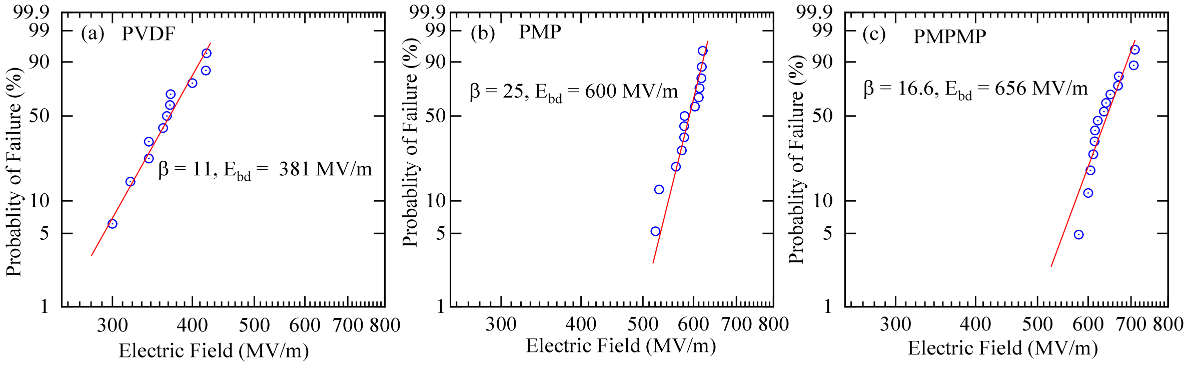


Figure 5. Probability of failure distribution and Weibull fits of the (a) PVDF, (b) PMP, and (c) PMPMP capacitors measured at room temperature. The β value and E_{bd} extracted from the fitting are displayed in the figure for each type of capacitor.

largely unchanged with the addition of 2D mica. This indicates that while the dielectric constant is improved, the dielectric loss does not increase significantly, maintaining the material's efficiency. We measured several capacitors, and the average dielectric constants measured from the 3 pristine PVDF capacitors and 4 capacitors for PMP and PMPMP capacitors are shown in Figure 4.

The average dielectric constant is calculated by using the following eq 1:

$$\varepsilon_{av} = \sum \varepsilon_i / 4 \tag{1}$$

where i = 1−4, was calculated as 11.4 ± 0.4, 22.9 ± 2.1, and 30.8 ± 4.05 for PVDF, PMP, and PMPMP nanocomposites, respectively, as shown in the histogram in Figure 4a. The error calculation is shown in the Supporting Information Table S1. The higher error values in PMP and PMPMP samples are due to the nonuniform distribution of 2D mica flakes on the substrate, which play a crucial role in the large deviation of the dielectric constant from the average value. The mechanical exfoliation provides a nonuniform distribution of fillers, which can be improved with large-area chemical vapor deposition (CVD) growth of 2D fillers. Furthermore, we have analyzed the average enhancement of the dielectric constant ($\Delta\varepsilon$) using eq 2 at 2.5 kHz frequency as compared to pristine PVDF.

$$\Delta\varepsilon\ (\%) = \frac{\varepsilon_{Composite} - \varepsilon_{PVDF}}{\varepsilon_{PVDF}} \times 100 \tag{2}$$

We observed that the PMP nanocomposite film shows an average dielectric constant enhancement of 100% at room temperature and 93% at 140 °C, while it is 170% and 157% for PMPMP nanocomposites at the same temperatures, as shown in Figure 4b. The enhancement of the dielectric constant in the nanocomposites can be attributed to the presence of insulating mica flakes within the polymer and the interfacial polarization effect. The enhancement in dielectric properties is expected to manifest as an increase in the number of interfaces within a multilayer nanocomposite film.[11,13,15,39] A multilayer nanocomposite interface between the fillers and polymer, such as the interface between ITO-PVDF, PVDF-mica, and PVDF with top Ag-metal contact, plays a substantial role in holding the charge carriers. Charges can accumulate at these interfaces, creating additional polarization and contributing to an increase in the dielectric constant. Khalifa et al. reported that 1 wt % mica in PVDF increases its dielectric constant from 11.5 to 29.5 at a frequency of 10 kHz.[28] The enhancement of the dielectric constant due to the multilayer interfacial effect has also been observed in other polymer nanocomposites such as P(VDF-HFP)/$BaTiO_3$, PVDF-TiO_2, BNNS-P(VDF-HFP)/MoS_2/BNNS-P(VDF-HFP), PVDF-0.55 $Bi_{0.5}Na_{0.5}TiO_3$, and PVDF-0.45($Sr_{0.7}Bi_{0.2}$) TiO_3.[11,29,40] In our multilayer capacitor, where two layers of mica flakes are interfaced in stratified geometry between the PVDF polymer films in a sequential manner, the PMPMP capacitor (Figure 1e) has higher polarization than the PMP (one layer mica interfaced) capacitor. Figure 3(c) displays the higher dielectric constant of the PMPMP capacitor compared to the single mica interfaced capacitor. The dielectric constant is consistently higher for PMPMP capacitors in the whole temperature range measured. In our PMPMP capacitor device, we increased the density of the fillers by introducing two layers of mica between the polymer film, which resulted in the enhanced dielectric constant. The difference between randomly dispersed fillers and our stratified technique is the low volume percentage (~1 vol %) of filler content required to observe the enhanced dielectric constant.[2,12]

The breakdown field (E_{bd}) of these polymer films was calculated using the Weibull probability distribution function given in eq 3:

$$P(E) = 1 - \exp^{-\left(\frac{E}{E_{BD}}\right)^{\beta}} \tag{3}$$

where P is the cumulative probability of failure, E is the electric field at dielectric failure, E_{BD} is the dielectric breakdown strength (the dielectric strength at 63.2% probability of failure), and β is a shape parameter that defines the uniformity of the sample. The fittings for PVDF, PMP, and PMPMP are shown in Figure 5 with equal scales to show the difference of fitting and breakdown strength between these parameters. The obtained breakdown fields of PVDF, PMP, and PMPMP capacitors are 381, 600, and 656 MV/m, respectively. The presence of an interface mitigates the formation of electrical trees and deviates their propagation from the direction of an applied electric field to the in-plane direction. Interfacial polarizations in a multilayer nanocomposite film reduce the local electric field, enabling reduction of dielectric breakdown strength as reported by Baer et al.[12] However, we observe a significant enhancement of the dielectric breakdown fields, 57% for the PMP capacitor compared to the pristine PVDF and 72% for the PMPMP. The breakdown field does not show a linear increase with the number of mica layers interfaced within the polymer matrix. The shape parameter β value also increased from the pristine PVDF sample (11) to PMP (25)

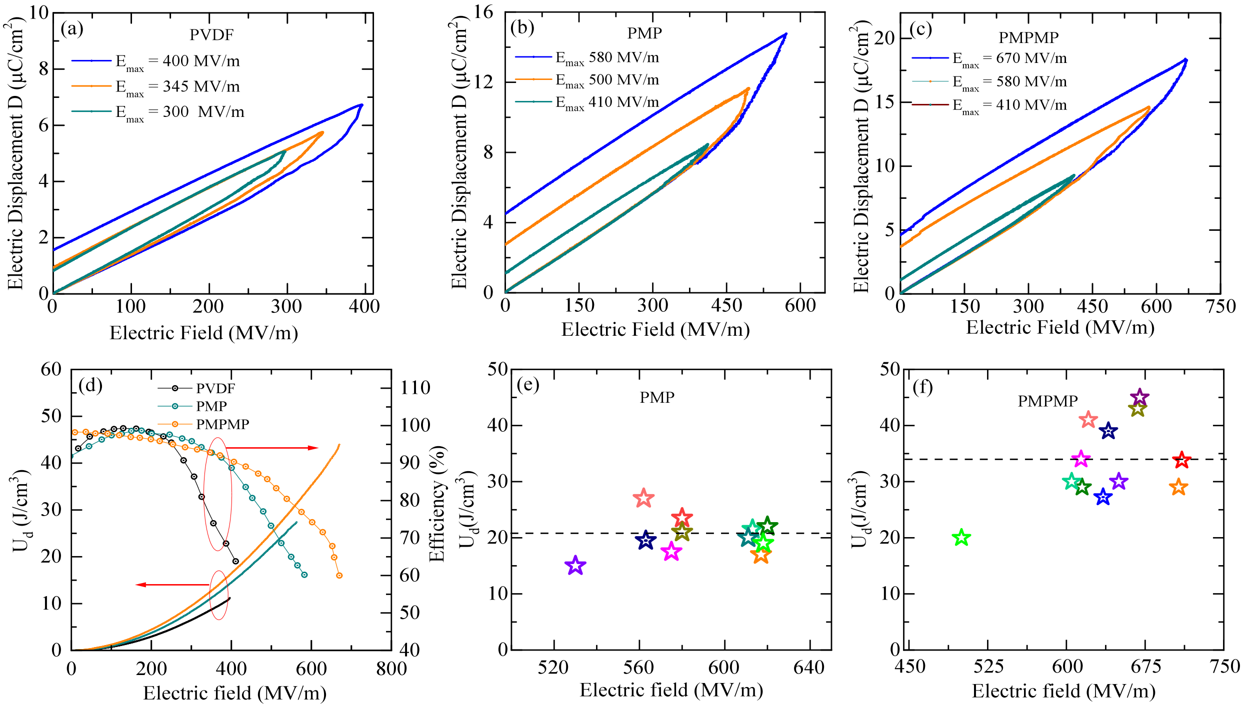


Figure 6. (a, b, and c) *D*−*E* loop measurements of PVDF, PMP, and PMPMP capacitors, respectively, as a function of applied electric field. The three loops are measured, gradually increasing the maximum limit of the applied electric field until its breakdown. (d) Variation of discharged energy density (left scale) and efficiency (right scale) as a function of electric field for the PVDF, PMP, and PMPMP capacitors. (e) Discharge energy densities as a function of electric field measured for PMP and (f) PMPMP capacitors. The dotted lines in (e) and (f) show the average values, indicating the higher energy density in PMPMP capacitors.

and PMPMP (16.6), suggesting the greater reliability of the experimental data in the polymer-based nanofiller composite.

The electric polarization of the polymer nanocomposite films was measured at room temperature. Figure 6(a−c) shows the electric displacement (D) as a function of applied field strength for PVDF, PMP, and PMPMP capacitor films. We gradually increased the applied electric field to obtain different $D-E$ loops without breaking them, as shown in each graph. The electric displacement for a pristine PVDF shows $D_{\max} \sim 6.7\ \mu C/cm^2$ (at $E = 395$ MV/m), and for the PMP capacitor $D_{\max} \sim 14.7\ \mu C/cm^2$ (at $E = 568$ MV/m), while the PMPMP capacitor shows the highest $D_{\max}$ of $\sim 18.3\ \mu C/cm^2$ (at $E = 670$ MV/m). The increase in electric displacement in the multilayer PVDF-mica nanocomposites is attributed to interfacial interactions between the polymer and mica. The integration of mica into the PVDF matrix creates numerous interfaces or boundaries within the nanocomposite. A previous study predicted the dielectric enhancement due to the interface polarization between mica and PVDF using density function theory simulation.[12] When an electric field is applied to the nanocomposite, these interfaces serve as sites for charge accumulation, resulting in the amplification of interfacial polarization. The enhancement of interfacial polarization by increasing the number of layers in multilayer dielectrics has been documented in previous studies.[11,13,31,41]

Figure 6(d) summarizes the variation of the maximum discharged energy density (U_d) and efficiency (η) of the nanocomposite capacitors as a function of applied field strength extracted from the $D-E$ loop measurements.

The energy storage density is calculated by integrating the loop using the following eq 4:

$$U_d = \int E\ dD \tag{4}$$

where E is the electric field and D is the electric displacement. The energy efficiency η was calculated from the following relation: η = discharged energy density/charged energy density = $U_{\text{charging}}/U_{\text{discharging}}$, where discharged and charged energies were calculated using the discharging and charging curves, respectively. We calculated the charging and discharging energies using the highest applied field of $D-E$ loops from the three $D-E$ loops shown in Figure 6(a−c). The maximum discharged energy densities are displayed in Figure 6(d). Energy densities for the pristine PVDF capacitor, where $U_d \sim 11.2$ J/cm^3 at $E = 395$ MV/m, for the PMP capacitor, $U_d \sim 27.4$ J/cm^3 at $E = 568$ MV/m, and for the PMPMP capacitor, $U_d \sim 44.5$ J/cm^3 at $E = 670$ MV/m. The slope of these curves increases from PVDF to PMPMP capacitors further clarified the increase in average dielectric constant from pristine PVDF to PMPMP capacitors as we measured directly using a dielectric spectrometer. We fabricated several PMP and PMPMP capacitors and measured their energy density by applying the electric field near the breakdown field strength. The distribution of the highest discharged energy density with the electric field of different capacitor devices from the PMP and PMPMP nanocomposite films is shown in Figure 6(e) and (f). These values are lower than the value recently reported in PMP capacitors using a single 2D mica interface layer.[12] We believe the lower values of energy density in PMP and PMPMP capacitors compared to the previously reported results of PVDF/mica/PVDF capacitors are due to the higher thickness of the film, which reduces the breakdown strength and limits the energy density. Our PMP capacitor is 1.2 μm compared to the 600 nm thick capacitor reported earlier. The energy density of the 600 nm PMP capacitor is higher (U_d = 75 J/cm^3 at 1200 MV/m) than the current measured value of 27.4 J/cm^3 at 568 MV/m. These values are higher compared to the pristine and polymer-based nanocomposites blends.[1,42−46] The charge−discharge efficiencies (η) of pristine PVDF, PMP, and PMPMP capacitors were approximately 63%, 88%, and 90%, respectively, at E = 395 MV/m, as depicted in Figure 6(d). Both PMP and PMPMP demonstrated higher efficiencies compared to pristine PVDF, with PMPMP showing a slightly higher efficiency than PMP. The gradual enhancement of the dielectric constant and polarization value in the nanocomposite films with increasing the number of interfacial layers clearly shows the higher discharge energy density and efficiency in PMP and PMPMP nanocomposite films than the pure PVDF film. The maximum discharge energy densities measured from several capacitors for PMP and PMPMP capacitors are displayed in Figure 6(e) and (f), providing evidence of how the number of interface layers of mica in the polymer matrix can improve the energy density of the polymer film.

The pristine PVDF shows the lowest discharged energy density of 10 J/cm^3 at an electric field of 400 MV/m, while those produced with the PMPMP nanocomposite show the highest discharged energy density of 44 J/cm^3 at an electric field of 570 MV/m. These discharge energy density values are higher than those of PVDF/mica,[1] PVDF/2D MXene,[45] h-BN/PVDF/h-BN film,[47] and TiO_2/polymer nanocomposites.[48] These results make the PMPMP nanocomposite a potential 2D nanofiller-based capacitor-based energy storage candidate.

CONCLUSION

In summary, mechanically exfoliated 2D mica flakes are incorporated in a stratified geometry into PVDF polymer to fabricate single interface mica layer PVDF-2D mica-PVDF (PMP) and two mica layer interfaced (bilayer) PVDF-2D mica-PVDF-2D mica-PVDF (PMPMP) nanocomposite films. The dielectric constants of the composite films exhibited a significant enhancement, 100% and 170% for the PMP and PMPMP thin films, respectively, over pristine PVDF. The enhancement of the dielectric constant is not a linear increment as a function of the number of 2D filler layers, which could be due to several possible reasons. The increase of thickness of the capacitor also decreases the effective dielectric constant as the effective electric field decreases to produce interface polarized charges. The filler concentration may vary on the respective layers of the PMPMP capacitors, which have the effect of a nonlinear increment of the dielectric constant and is due to the nonuniform distribution of fillers by the mechanical exfoliation technique. One would expect a higher dielectric constant in a multilayer structure by keeping the capacitor thickness constant and decreasing the individual layer thickness to accommodate the higher vol % of the fillers. A uniform, high-density 2D filler distribution in each layer would increase the dielectric constants. Our experimental observation clearly demonstrates that the engineering of the 2D nanofiller in stratified geometry between polymer layers is one of the major strategies in enhancing the dielectric constant as well as breakdown strength, which provides the increase in energy density. Having a number of 2D nanofillers in a stratified geometry sandwiched between the thin polymer films forms several microcapacitors and increases the polymer−2D interface area to build the polarized charges. The stratified 2D mica fillers also provide the barrier of charge percolation due to their insulating properties and reduce the electric treeing process, which provides the higher breakdown field strength. A large-area CVD-grown 2D filler that can cover the whole capacitor area could enhance the breakdown strength much more than the exfoliated flakes, as exfoliated fragmented flakes are not continuous, and the gap between them allows charge carriers to penetrate through with increasing applied field. Whether a CVD-grown large-area 2D filler can enhance the dielectric strength substantially could be a topic of interest. The edges of 2D fillers may play a substantial role in charge trapping and helping to increase the dielectric constant substantially compared to the large-area CVD fillers and needs to be explored experimentally.

The dielectric polarization of the films exhibits enhanced electric displacement (D) with an increase in the number of mica layers or mica−polymer interfaces from PMP to PMPMP capacitors. The stratified geometry makes the dielectric polarization much higher in higher interface samples of mica and PVDF. This is reflected in the calculation of discharged energy density, which drastically increased in PMP and was further enhanced in PMPMP films. The mica−PVDF interfacial interaction suppresses the charge migration by inhibiting the formation of electrical trees in the direction of the applied field, which increases the electric breakdown field strength in mica-incorporated capacitors compared with that of pure PVDF films. Thus, our reported method of integrating a 2D nanofiller with the polymer matrix and fabrication of a nanocomposite in multilayer films where 2D fillers are integrated in a stratified geometry can be extended to other 2D material−polymer combinations to develop high-density thin-film-based energy storage capacitor for myriads of applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.4c01037.

> Sample preparation, dielectric measurements as a function of frequency, and a table containing a calculation of standard deviation and error of dielectric constants (PDF)

AUTHOR INFORMATION

Corresponding Author

Nihar R. Pradhan − *Department of Chemistry, Physics and Atmospheric Science, Jackson State University, Jackson, Mississippi 39217, United States;* orcid.org/0000-0002-3912-4233; Email: nihar.r.pradhan@jsums.edu

Authors

Sumit Bera − *Department of Chemistry, Physics and Atmospheric Science, Jackson State University, Jackson, Mississippi 39217, United States*

Rukshan M. Thantirige − *Department of Chemistry, Physics and Atmospheric Science, Jackson State University, Jackson, Mississippi 39217, United States*

Jiaen Wu − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States*

Emily C. Davidson − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States;* orcid.org/0000-0001-5819-9233

Sujit Anil Kadam − *Department of Chemistry, Physics and Atmospheric Science, Jackson State University, Jackson, Mississippi 39217, United States;* orcid.org/0000-0002-7980-0291

Anirudha V. Sumant − *Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois 60439, United States;* orcid.org/0000-0002-6028-0038

Brian T. Shook − *Department of Chemistry, Physics and Atmospheric Science, Jackson State University, Jackson, Mississippi 39217, United States*

Rahul Rao − *Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States;* orcid.org/0000-0002-6415-0185

Ryan Selhorst − *Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States*

Maninderjeet Singh − *Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77004, United States;* orcid.org/0000-0001-8891-8454

Alamgir Karim − *Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77004, United States;* orcid.org/0000-0003-1302-9374

Dharmaraj Raghavan − *Department of Chemistry, Howard University, Washington, D.C. 20059, United States;* orcid.org/0000-0002-7634-0656

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsaelm.4c01037

Funding

This work was supported by the Princeton Alliance for Collaborative Research and Innovation (PACRI) Grant #PACRI-JSU-02. N.R.P. acknowledge by NSF HBCU-UP Excellence in Research NSF-DMR-1900692.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Use of the Center for Nanoscale Materials, a Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

■ REFERENCES

(1) Hu, J.; Zhang, S.; Tang, B. 2D filler-reinforced polymer nanocomposite dielectrics for high-k dielectric and energy storage applications. *Energy Storage Mater.* **2021**, *34*, 260−281.

(2) Bera, S.; Singh, M.; Thantirige, R.; Tiwary, S. K.; Shook, B. T.; Nieves, E.; Raghavan, D.; Karim, A.; Pradhan, N. R. 2D-Nanofiller-Based Polymer Nanocomposites for Capacitive Energy Storage Applications. *Small Sci.* **2023**, *3*, No. 2300016.

(3) Singh, M.; Apata, I. E.; Samant, S.; Wu, W.; Tawade, B. V.; Pradhan, N.; Raghavan, D.; Karim, A. Nanoscale Strategies to Enhance the Energy Storage Capacity of Polymeric Dielectric Capacitors: Review of Recent Advances. *Polym. Rev.* **2022**, *62*, 211−260.

(4) Dang, Z.-M.; Zheng, M.-S.; Zha, J.-W. 1D/2D Carbon Nanomaterial-Polymer Dielectric Composites with High Permittivity for Power Energy Storage Applications. *Small* **2016**, *12*, 1688−1701.

(5) Li, J.; Liu, X.; Feng, Y.; Chen, D.; Li, Y.; Yue, D.; Huang, B.; Yin, J. Constructing bidirectional-matched interface between polymer and 2D nanosheets for enhancing energy storage performance of the composites. *Energy Storage Mater.* **2023**, *54*, 605−614.

(6) Feng, Y.; Xue, J.-P.; Zhang, T.-D.; Chi, Q.-G.; Li, J.-L.; Chen, Q.-G.; Wang, J.-J.; Chen, L.-Q. Double-gradients design of polymer nanocomposites with high energy density. *Energy Storage Mater.* **2022**, *44*, 73−81.

(7) Wang, Q.; Zhu, L. Polymer nanocomposites for electrical energy storage. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 1421−1429.

(8) Liu, F.; Li, Q.; Cui, J.; Li, Z.; Yang, G.; Liu, Y.; Dong, L.; Xiong, C.; Wang, H.; Wang, Q. High-Energy-Density Dielectric Polymer Nanocomposites with Trilayered Architecture. *Adv. Funct. Mater.* **2017**, *27*, No. 1606292.

(9) Li, Q.; Liu, F.; Yang, T.; Gadinski, M. R.; Zhang, G.; Chen, L.-Q.; Wang, Q. Sandwich-structured polymer nanocomposites with high energy density and great charge-discharge efficiency at elevated temperatures. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 9995−10000.

(10) Huang, X.; Jiang, P. Core-Shell Structured High-k Polymer Nanocomposites for Energy Storage and Dielectric Applications. *Adv. Mater.* **2015**, *27*, 546−554.

(11) Jiang, J.; Shen, Z.; Qian, J.; Dan, Z.; Guo, M.; He, Y.; Lin, Y.; Nan, C.-W.; Chen, L.; Shen, Y. Synergy of micro-/mesoscopic interfaces in multilayered polymer nanocomposites induces ultrahigh energy density for capacitive energy storage. *Nano Energy* **2019**, *62*, 220−229.

(12) Singh, M.; Das, P.; Samanta, P. N.; Bera, S.; Thantirige, R.; Shook, B.; Nejat, R.; Behera, B.; Zhang, Q.; Dai, Q.; Pramanik, A.; Ray, P.; Raghavan, D.; Leszczynski, J.; Karim, A.; Pradhan, N. R. Ultrahigh Capacitive Energy Density in Stratified 2D Nanofiller-Based Polymer Dielectric Films. *ACS Nano* **2023**, *17*, 20262−20272.

(13) Peng, S.; Du, X.; Liang, Z.; Ma, M.; Guo, Y.; Xiong, L. Multilayer polymer nanocomposites based on interface engineering for high-performance capacitors. *J. Energy Storage* **2023**, *60*, No. 106636.

(14) Baer, E.; Zhu, L. 50th Anniversary Perspective: Dielectric Phenomena in Polymers and Multilayered Dielectric Films. *Macromolecules* **2017**, *50*, 2239−2256.

(15) Mackey, M.; Hiltner, A.; Baer, E.; Flandin, L.; Wolak, M. A.; Shirk, J. S. Enhanced breakdown strength of multilayered films fabricated by forced assembly microlayer coextrusion. *J. Phys. D: Appl. Phys.* **2009**, *42*, No. 175304.

(16) Shanmugam, V.; Mensah, R. A.; Babu, K.; Gawusu, S.; Chanda, A.; Tu, Y.; Neisiany, R. E.; Försth, M.; Sas, G.; Das, O. A Review of the Synthesis, Properties, and Applications of 2D Materials. *Particle Part. Syst. Charact.* **2022**, *39*, No. 2200031.

(17) Byun, K.-N.; Yamamoto, E.; Kobayashi, M.; Osada, M. Improved Energy Storage Performance of PVDF Nanocapacitors by Utilizing 2D Inorganic Barrier Layers. *Chem. Lett.* **2023**, *52*, 51−54.

(18) Pinto, G. M.; Cremonezzi, J. M. O.; Ribeiro, H.; Andrade, R. J. E.; Demarquette, N. R.; Fechine, G. J. M. From two-dimensional materials to polymer nanocomposites with emerging multifunctional applications: A critical review. *Polym. Compos.* **2023**, *44*, 1438−1470.

(19) Xia, W.; Zhang, Z. PVDF-based dielectric polymers and their applications in electronic materials. *IET Nanodielectrics* **2018**, *1*, 17−31.

(20) Padurariu, L.; Brunengo, E.; Canu, G.; Curecheriu, L. P.; Conzatti, L.; Buscaglia, M. T.; Stagnaro, P.; Mitoseriu, L.; Buscaglia, V. Role of Microstructures in the Dielectric Properties of PVDF-Based Nanocomposites Containing High-Permittivity Fillers for Energy Storage. *ACS Appl. Mater. Interfaces* **2023**, *15*, 13535−13544.

(21) Zhu, X.; Ng, L. W. T.; Hu, G.; Wu, T.-C.; Um, D.-S.; Macadam, N.; Hasan, T. Hexagonal Boron Nitride−Enhanced Optically Transparent Polymer Dielectric Inks for Printable Electronics. *Adv. Funct. Mater.* **2020**, *30*, No. 2002339.

(22) Laturia, A.; Van de Put, M. L.; Vandenberghe, W. G. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Mater. Appl.* **2018**, *2*, 6.

(23) Wickramaratne, D.; Weston, L.; Van de Walle, C. G. Monolayer to Bulk Properties of Hexagonal Boron Nitride. *J. Phys. Chem. C* **2018**, *122*, 25524−25529.

(24) Kim, S. S.; Khai, T. V.; Kulish, V.; Kim, Y.-H.; Na, H. G.; Katoch, A.; Osada, M.; Wu, P.; Kim, H. W. Tunable Bandgap Narrowing Induced by Controlled Molecular Thickness in 2D Mica Nanosheets. *Chem. Mater.* **2015**, *27*, 4222−4228.

(25) Tu, S.; Jiang, Q.; Zhang, X.; Alshareef, H. N. Large Dielectric Constant Enhancement in MXene Percolative Polymer Composites. *ACS Nano* **2018**, *12*, 3369−3377.

(26) Li, Y.; Zhou, Y.; Zhu, Y.; Cheng, S.; Yuan, C.; Hu, J.; He, J.; Li, Q. Polymer nanocomposites with high energy density and improved charge−discharge efficiency utilizing hierarchically-structured nanofillers. *J. Mater. Chem. A* **2020**, *8*, 6576−6585.

(27) Fu, Y.; Wang, Y.; Wang, S.; Gao, Z.; Xiong, C. Enhanced breakdown strength and energy storage of PVDF-based dielectric composites by incorporating exfoliated mica nanosheets. *Polym. Compos.* **2019**, *40*, 2088−2094.

(28) Khalifa, M.; Schoeffmann, E.; Lammer, H.; Mahendran, A. R.; Wuzella, G.; Anandhan, S. A study on electroactive PVDF/mica nanosheet composites with an enhanced γ-phase for capacitive and piezoelectric force sensing. *Soft Matter* **2021**, *17*, 10891−10902.

(29) Li, X.; He, S.; Jiang, Y.; Wang, J.; Yu, Y.; Liu, X.; Zhu, F.; Xie, Y.; Li, Y.; Ma, C.; Shen, Z.; Li, B.; Shen, Y.; Zhang, X.; Zhang, S.; Nan, C. W. Unraveling bilayer interfacial features and their effects in polar polymer nanocomposites. *Nat. Commun.* **2023**, *14*, 5707.

(30) Li, W.; Song, Z.; Zhong, J.; Qian, J.; Tan, Z.; Wu, X.; Chu, H.; Nie, W.; Ran, X. Multilayer-structured transparent MXene/PVDF film with excellent dielectric and energy storage performance. *J. Mater. Chem. C* **2019**, *7*, 10371−10378.

(31) Cheng, Y.; Pan, Z.; Bai, H.; Chen, H.; Yao, L.; Ding, X.; Shi, S.; Liu, J.; Xie, Z.; Xu, J.; Zhai, J. Two-Dimensional Fillers Induced Superior Electrostatic Energy Storage Performance in Trilayered Architecture Nanocomposites. *ACS Appl. Mater. Interfaces* **2022**, *14*, 8448−8457.

(32) Sun, C.; Deng, H.; Ji, W.; Zhou, H.; Zhao, G.; Du, R.; Fu, Q. The effect of multilayered film structure on the dielectric properties of composites films based on P(VDF-HFP)/Ni(OH)$_2$. *Nanocomposites* **2019**, *5*, 36−48.

(33) Guo, R.; Luo, H.; Yan, M.; Zhou, X.; Zhou, K.; Zhang, D. Significantly enhanced breakdown strength and energy density in sandwich-structured nanocomposites with low-level BaTiO$_3$ nanowires. *Nano Energy* **2021**, *79*, No. 105412.

(34) Prateek; Siddiqui, S.; Bhunia, R.; Singh, N.; Garg, A.; Gupta, R. K. Interface modulation in multi-layered BaTiO$_3$ nanofibers/PVDF using the PVP linker layer as an adhesive for high energy density capacitor applications. *Mater. Adv.* **2020**, *1*, 680−688.

(35) Bai, H.; Zhu, K.; Wang, Z.; Shen, B.; Zhai, J. 2D Fillers Highly Boost the Discharge Energy Density of Polymer-Based Nanocomposites with Trilayered Architecture. *Adv. Funct. Mater.* **2021**, *31*, No. 2102646.

(36) Anithakumari, P.; Mandal, B. P.; Abdelhamid, E.; Naik, R.; Tyagi, A. K. Enhancement of dielectric, ferroelectric and magnetodielectric properties in PVDF−BaFe$_{12}$O$_{19}$ composites: a step towards miniaturized electronic devices. *RSC Adv.* **2016**, *6*, 16073−16080.

(37) Kaur, S.; Kumar, A.; Sharma, A. L.; Singh, D. P. Influence of annealing on dielectric and polarization behavior of PVDF thick films. *J. Mater. Sci.: Mater. Electron.* **2017**, *28*, 8391−8396.

(38) Ekbote, G. S.; Khalifa, M.; Venkatesa Perumal, B.; Anandhan, S. A new multifunctional energy harvester based on mica nanosheet-dispersed PVDF nanofabrics featuring piezo-capacitive, piezoelectric and triboelectric effects. *RSC Appl. Polymers* **2023**, *1*, 266−280.

(39) Tseng, J.-K.; Tang, S.; Zhou, Z.; Mackey, M.; Carr, J. M.; Mu, R.; Flandin, L.; Schuele, D. E.; Baer, E.; Zhu, L. Interfacial polarization and layer thickness effect on electrical insulation in multilayered polysulfone/poly(vinylidene fluoride) films. *Polymer* **2014**, *55*, 8−14.

(40) Liu, Y.; Luo, H.; Xie, H.; Xiao, Z.; Wang, F.; Jiang, X.; Zhou, X.; Zhang, D. Microstructures Trilayer PVDF nanocomposites with significantly enhanced energy density and energy efficiency using 0.55 Bi$_{0.5}$Na$_{0.5}$TiO$_3$-0.45(Sr$_{0.7}$Bi$_{0.2}$)TiO$_3$ nanofibers. *Mater. Adv.* **2023**, *3*, No. 2023008.

(41) Zhu, J.; Luo, S.; Cao, B.; Shen, J.; Guo, S. Dielectric hysteresis behaviors of polyvinylidene fluoride-based multilayer dielectrics controlled by confined distribution of conductive particles. *RSC Adv.* **2015**, *5*, 65927−65931.

(42) Wang, H.-Q.; Wang, J.-W.; Wang, X.-Z.; Gao, X.-H.; Zhuang, G.-C.; Yang, J.-B.; Ren, H. Dielectric properties and energy storage performance of PVDF-based composites with MoS$_2$@MXene nanofiller. *Chem. Eng. J.* **2022**, *437*, No. 135431.

(43) Zhou, J.; Hou, D.; Cheng, S.; Zhang, J.; Chen, W.; Zhou, L.; Zhang, P. Recent advances in dispersion and alignment of fillers in PVDF-based composites for high-performance dielectric energy storage. *Mater. Today Energy* **2023**, *31*, No. 101208.

(44) Xie, Y.; Wang, J.; Yu, Y.; Jiang, W.; Zhang, Z. Enhancing breakdown strength and energy storage performance of PVDF-based nanocomposites by adding exfoliated boron nitride. *Appl. Surf. Sci.* **2018**, *440*, 1150−1158.

(45) Feng, Y.; Deng, Q.; Peng, C.; Hu, J.; Li, Y.; Wu, Q.; Xu, Z. An ultrahigh discharged energy density achieved in an inhomogeneous PVDF dielectric composite filled with 2D MXene nanosheets via interface engineering. *J. Mater. Chem. C* **2018**, *6*, 13283−13292.

(46) Shen, Z.-H.; Wang, J.-J.; Lin, Y.; Nan, C.-W.; Chen, L.-Q.; Shen, Y. High-Throughput Phase-Field Design of High-Energy-Density Polymer Nanocomposites. *Adv. Mater.* **2018**, *30* (2), No. 1704380.

(47) Meng, G.; She, J.; Wang, C.; Wang, W.; Pan, C.; Cheng, Y. Sandwich-Structured h-BN/PVDF/h-BN Film With High Dielectric Strength and Energy Storage Density. *Front. Chem.* **2022**, *10*, No. 910305.

(48) Zhu, Y.; Yao, H.; Jiang, P.; Wu, J.; Zhu, X.; Huang, X. Two-Dimensional High-k Nanosheets for Dielectric Polymer Nanocomposites with Ultrahigh Discharged Energy Density. *J. Phys. Chem. C* **2018**, *122* (32), 18282−18293.