

Supporting Information

PVDF Nanocomposites with Aligned Boron Nitride Nanosheets and Dispersed BaTiO₃@PEG Nanoparticles by Superspreading Strategy towards High Energy Density

Dajun Hou,^{abc} Jingjing Zhou,^d Wen Chen,^{abc} Jing Zhou^{*abc} and Pengchao Zhang^{*abc}

^a Hubei Longzhong Laboratory, Wuhan University of Technology Xiangyang Demonstration Zone, Xiangyang 441000, China.

^b State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China.

^c Sanya Science and Education Innovation Park, Wuhan University of Technology, Sanya 572024, China.

^d Key Laboratory of Functional Materials and Devices for Informatics of Anhui Education Institutes, Fuyang Normal University, Fuyang 236037, China

* Corresponding author.

E-mail address: pczhang@whut.edu.cn (P. Zhang); zhoujing@whut.edu.cn (J. Zhou)

Experiments

Materials

Barium titanate (BT) nanoparticles (average diameter ~100 nm) were procured from Shandong Guoci Functional Materials Co., Ltd.. Boron nitride nanosheets (BNNS) with a flake diameter range of 1 - 5 μm were obtained from Jiangsu Xianfeng Nano Material Technology Co., Ltd.. PVDF powder, tris(hydroxymethyl)aminomethane, hydrochloric acid dopamine, and methoxy polyethylene glycol amine were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.. N,N-Dimethylformamide (DMF) was acquired from the National Pharmaceutical Chemical Reagent.

Methods

- Synthesis of BT@PEG:** (i) Dissolve 100 mg of dopamine hydrochloride and 240 mg of tris(hydroxymethyl)aminomethane (Tris) in 200 mL of deionized water to prepare a solution with a pH of 8.5. (ii) Add 4 g of BT powder to the solution and stir vigorously at room temperature for 48 hours. (iii) Centrifuge the resulting suspension at 5000 rpm to collect the precipitate, then wash it three times with deionized water via centrifugation. The obtained precipitate is polydopamine-modified BT (BTP). (iv) Subsequently, disperse the BTP precipitate in 200 mL of deionized water, then mix with 0.5 g of mPEG-NH₂ powder, and continuously stir the suspension at 60 °C for 12 hours. (v) Afterward, centrifuge the suspension at 5000 rpm to collect the precipitate, followed by three washes with deionized water via centrifugation. (vi) Collect the precipitate and dry it in a vacuum oven at 60 °C for 12 hours. The resulting powder is mPEG-NH₂-modified barium titanate (BT@PEG) nanoparticles.
- Pre-treatment of BNNS:** The pre-treatment process of BNNS is as follows: Prepare a mixed solution by dispersing boron nitride powder at a concentration of 1 mg/mL in DMF. Subsequently, subject the mixture to ultrasonication in an ice-water bath for 30 minutes to achieve a uniformly dispersed BNNS/DMF suspension.
- Fabrication of PVDF-based composites:** (i) A specific amount of BT@PEG powder and a designed volume of BNNS/DMF dispersion (1 mg/mL) are added to 10 mL of DMF to form a suspension, which is then subjected to 15 minutes of ultrasonic treatment. (ii) Subsequently, under continuous stirring, 1 g of PVDF powder is added to the suspension from the previous step. (iii) The suspension is stirred continuously at 40 °C for 12 hours to ensure complete dissolution of PVDF, and then degassed in a vacuum oven for 30 minutes to prepare the casting solution. (iv) The mixed casting solution of PVDF, BT@PEG, and BNNS from step (iii) is used to fabricate PVDF/BNNS/BT@PEG composite films via the superspreading strategy developed by our group.^{1, 2} The wet composite films are pre-dried at room temperature for 24 hours, then laid flat on clean glass plates and heat-treated at 200 °C for 10 minutes on a hot

plate, followed by rapid quenching in ice water for annealing. After that, the films are dried in a vacuum oven at 60 °C for 12 hours, then vacuum hot-pressed at 150 °C and 15 MPa for 15 minutes. Finally, the films are ultrasonically delaminated in a water bath, sandwiched between dry filter papers, and dried again in a vacuum oven at 60 °C for 12 hours to obtain the PVDF/BNNS/BT@PEG composite films. The PVDF/BNNS composite film is fabricated in the way reported in the reference [13] of the manuscript. The loading of BNNS in the PVDF/BNNS composite film is the optimized 3.6 wt% in reference [13].

Characterization

The microstructure of the nanofillers was characterized using a transmission electron microscope (TEM, JEM-2100F). Fourier-transform infrared spectroscopy (FTIR, Nexus) was employed to analyze the infrared spectra of the nanofillers and PVDF composite films. Differential scanning calorimetry (DSC, STA449F3) was utilized to measure the crystallization and melting behavior of the PVDF-based composite materials under a nitrogen atmosphere at a rate of 10 °C/min. The cross-sectional structure of the PVDF composite films was analyzed using a field-emission scanning electron microscope (FESEM, JEOL-7100F). The crystalline state of the PVDF-based composite materials was examined with an X-ray diffractometer (XRD, Rigaku, Miniflex 600/600-C) using a Cu K α radiation source over a scan range of 5° to 90° at a rate of 2°/min. Optical images of the sedimentation experiment of BT@PEG nanofillers in DMF were captured using a digital camera (Canon, DS126621). A shadow mask was used to cover the nanocomposite films, and circular copper electrodes with a sputtering diameter of 3 millimeters were applied. The films with electrodes were used to measure the dielectric properties and energy storage performance of the nanocomposite materials. A precision impedance analyzer (4990A, Agilent, USA) was used to measure the dielectric constant and loss of the PVDF-based composite materials at room temperature, ranging from 100 Hz to 10 MHz. The energy storage performance of the PVDF-based composite materials was obtained by measuring the polarization-electric field (P-E) curves of the thin films using a multi-ferroic ferroelectric test system (Premier II, Radiant Technologies, Inc., USA) equipped with a high-voltage amplifier (TREK MODEL 609B) in a monopolar mode at 10 Hz and room temperature. A breakdown tester (CS2674AX, Nanjing Changsheng Instrument Co., Ltd.) was used to measure the breakdown electric field values of the films by gradually increasing the direct current voltage on the PVDF-based composite films until electrical breakdown occurred. The obtained breakdown field values were utilized for Weibull failure probability analysis to calculate the statistical breakdown strength (E_b) of these PVDF-based composite films.

In the dielectric energy storage field, it is usual to randomly select 10 to 15 different regions of the same sample and put progressively increasing voltages on them. The electric field at these regions experience breakdown is then determined based on the thickness of the same sample. The electric breakdown field (E) values of these regions are recorded in ascending

order and then sorted in sequence from 1 to 10 or 15. The smallest E corresponds to the lowest point and the largest E corresponds to the highest point. Typically, $\ln E$ or E is employed as the abscissa, while $\ln(-\ln(1-P))$ serves as the ordinate to derive the corresponding data points. P is calculated according to the following formula: " $P_i = (i-0.3)/(n+0.4)$ ". Among them, i refers to the ordinal number of the electric breakdown strength of the tested sample in order from small to large, and n represents the total number of times of the tested breakdown sample. The i of the lowest E is 1, and the i of the highest E is 10, the n is 10 in this work. Subsequently, we employ Origin software to perform linear fitting on these data points to obtain the fitted line. Once the fitted line is generated, the electric field corresponding to an ordinate of 0 is taken as the theoretical breakdown strength (E_b) of the sample.

Supporting figures

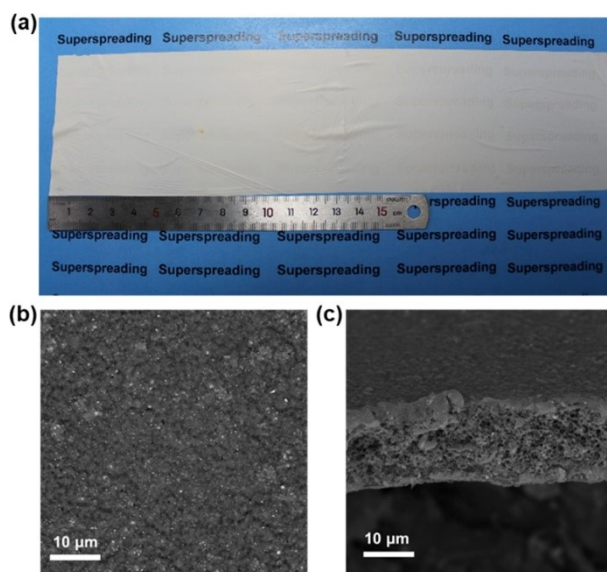


Figure S1. The porous PVDF/BNNS/BT@PEG nanocomposite film. (a) Digital image of the film. The surface (b) and cross-section (c) SEM images of the film.

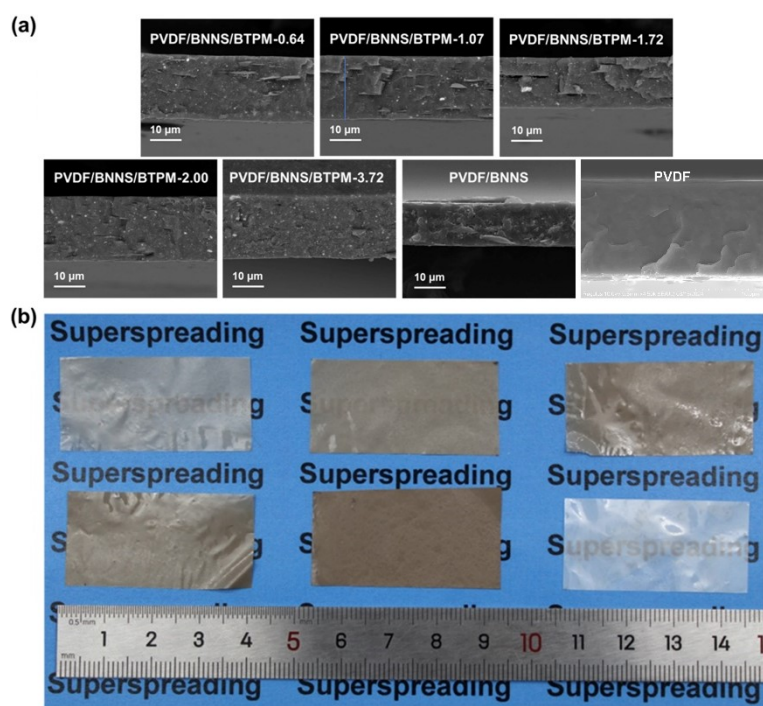


Figure S2. Cross-section SEM images (a) and optical photos (b) of the PVDF/BNNS/BT@PEG nanocomposites.

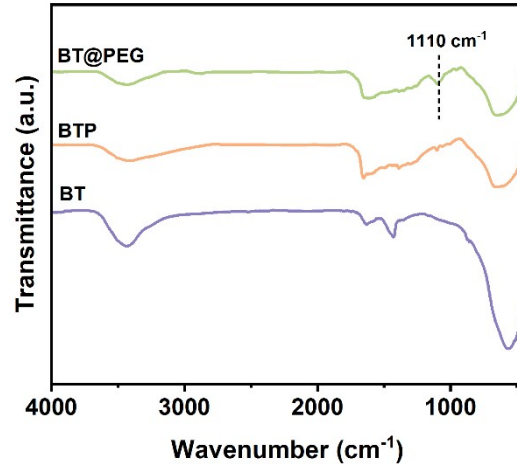


Figure S3. FTIR spectra of BT, BTP, and BT@PEG.

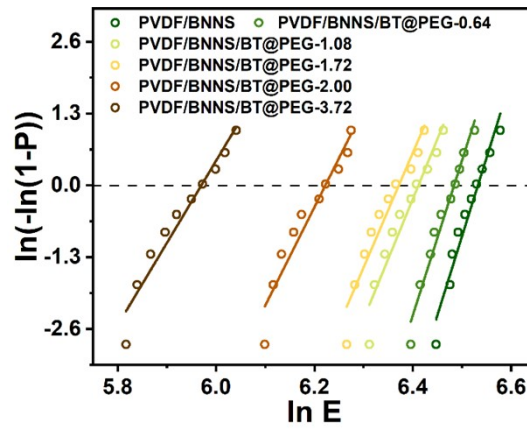


Figure S4. Weibull failure probability analysis of the PVDF/BNNS/BT@PEG nanocomposites with different volume fraction of BT@PEG nanofillers.

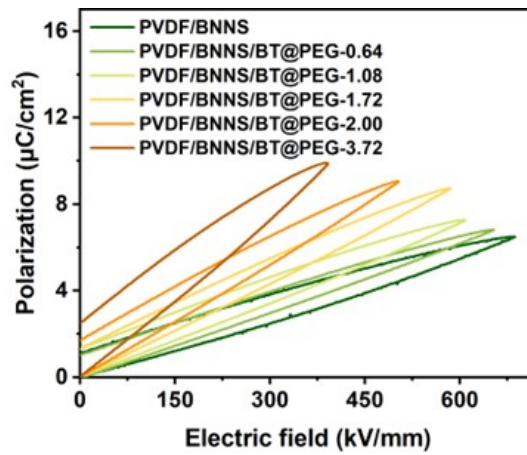


Figure S5. P-E curves of the PVDF/BNNS/BT@PEG nanocomposites with different volume fraction of BT@PEG nanofillers.

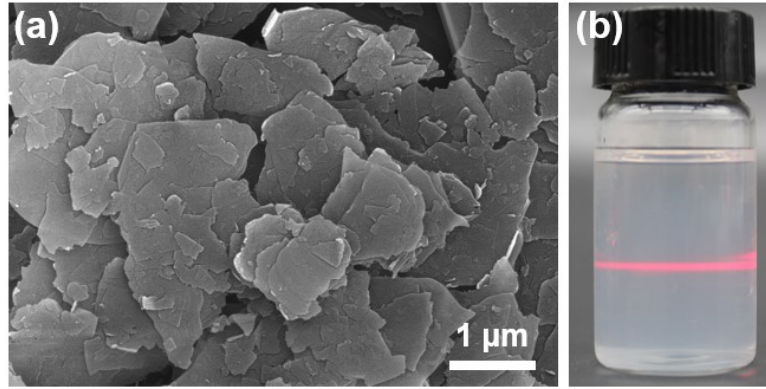


Figure S6. (a) Scanning electron microscopy image of the pre-treated boron nitride nanosheets (BNNS) used in this study; (b) Optical photograph of the dispersion liquid formed by boron nitride nanosheets in N,N-dimethylformamide (DMF) solvent.

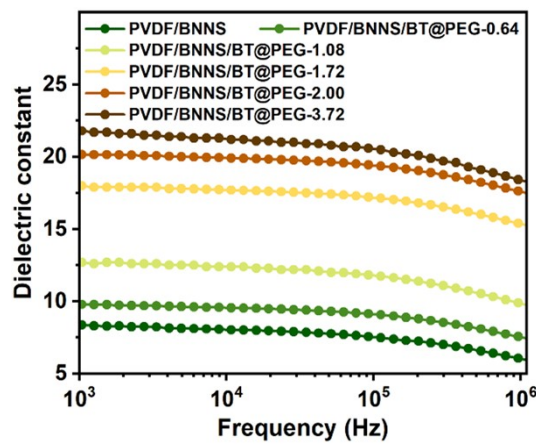


Figure S7. Dielectric constant from 10³ Hz to 10⁶ Hz of the PVDF/BNNS/BT@PEG nanocomposites with different loading of BT@PEG.

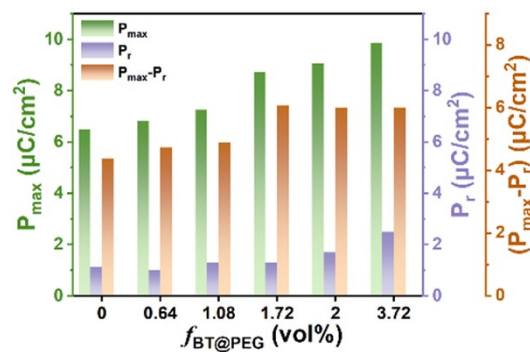


Figure S8 P_{max}, P_r and ΔP of the PVDF/BNNS/BT@PEG nanocomposites with different f_{BT@PEG}.

Reference

1. C. Zhao, P. Zhang, J. Zhou, S. Qi, Y. Yamauchi, R. Shi, R. Fang, Y. Ishida, S. Wang, A. P. Tomsia, M. Liu and L. Jiang, *Nature*, 2020, **580**, 210-215.
2. P. Zhang, F. Zhang, C. Zhao, S. Wang, M. Liu and L. Jiang, *Angew. Chem. Int. Ed.*, 2016, **55**, 3615-3619.