Supplementary Information

Ultrahigh electric displacement and energy density in gradient layer-structured $BaTiO_3$/PVDF nanocomposites with interfacial barrier effect

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Experimental

Fabrication of the Nanocomposites: For the fabrication of single layer BT/PVDF nanocomposites, BT nanoparticles with an average size of 100 nm (sinocera Co., China) were dispersed into *N,N*-dimethylformamide (DMF) by ultrasonication for 1h. Then, PVDF powders (Alfa Aesar) were dissolved in the former solution and stirred for 12h to form a homogeneous solution. The mixture was cast on glass plate, and BT/PVDF films can be obtained after drying at 80 ^{o}C overnight. The GLN BT/PVDF films were also prepared layer by layer by the aforementioned solution casting method. The thickness of the films can be controlled by scrapers. Flexible freestanding films were peeled from glass substrates after thermal treatment at 200 ^{o}C for 10 min followed by quenching in ice water immediately. A further drying treatment is needed to evaporate residual water in the films at 80 ^{o}C.

Dielectric and Energy Storage Characterization: For electric measurement, gold electrodes with diameters of 2 mm were sputtered on both sides of composite films by the auto fine coater (JFC-1600, JEOL, LTD.). Permittivity and dielectric loss were measured with a precision impedance analyzer (4990A, Agilent Technologies, Inc.) at room temperature with a frequency range from 10^3 to 10^7 Hz. DC conductivity of the films was measured under an applied electric field of 10 MV m^{-1} by a high resistance meter (HP4339A, Hewlett Packard,

Ltd.). The D-E loops and electric breakdown strengths of the film samples were measured at 10 Hz by Precision Materials Analyzer (Radiant Technologies, Inc) with a limited current of 0.19 mA.

Finite element simulation of dielectric breakdown: The simulation system is designed as a rectangle lattice with a total size of 10×15 μm^2, which is discretized into a two-dimensional array of 500×500 grid points. BT nanoparticles represented by small circles are introduced into the PVDF matrix randomly. The number of small circles in each layer are decided by the BT contents. Equation is derived by the dielectric breakdown model (DBM):

$$p(i,k \to i'k') = \frac{(\phi_{i',k'})^{\eta}}{\sum (\phi_{i',k'})^{\eta}}$$

where ϕ is the electric potential for all points of the lattice, i, k and i', k' represents the discrete lattice coordinates, η is the fractal dimension.[1-3] The parameters in Equation 4 (A, B, C, and ϕ_0) of PVDF phase and BT phase are adjusted to make sure breakdown occurs about 60 times after 100 repeated simulation experiments in all the GLN when the value of applied electric field is endowed with their breakdown strength respectively.

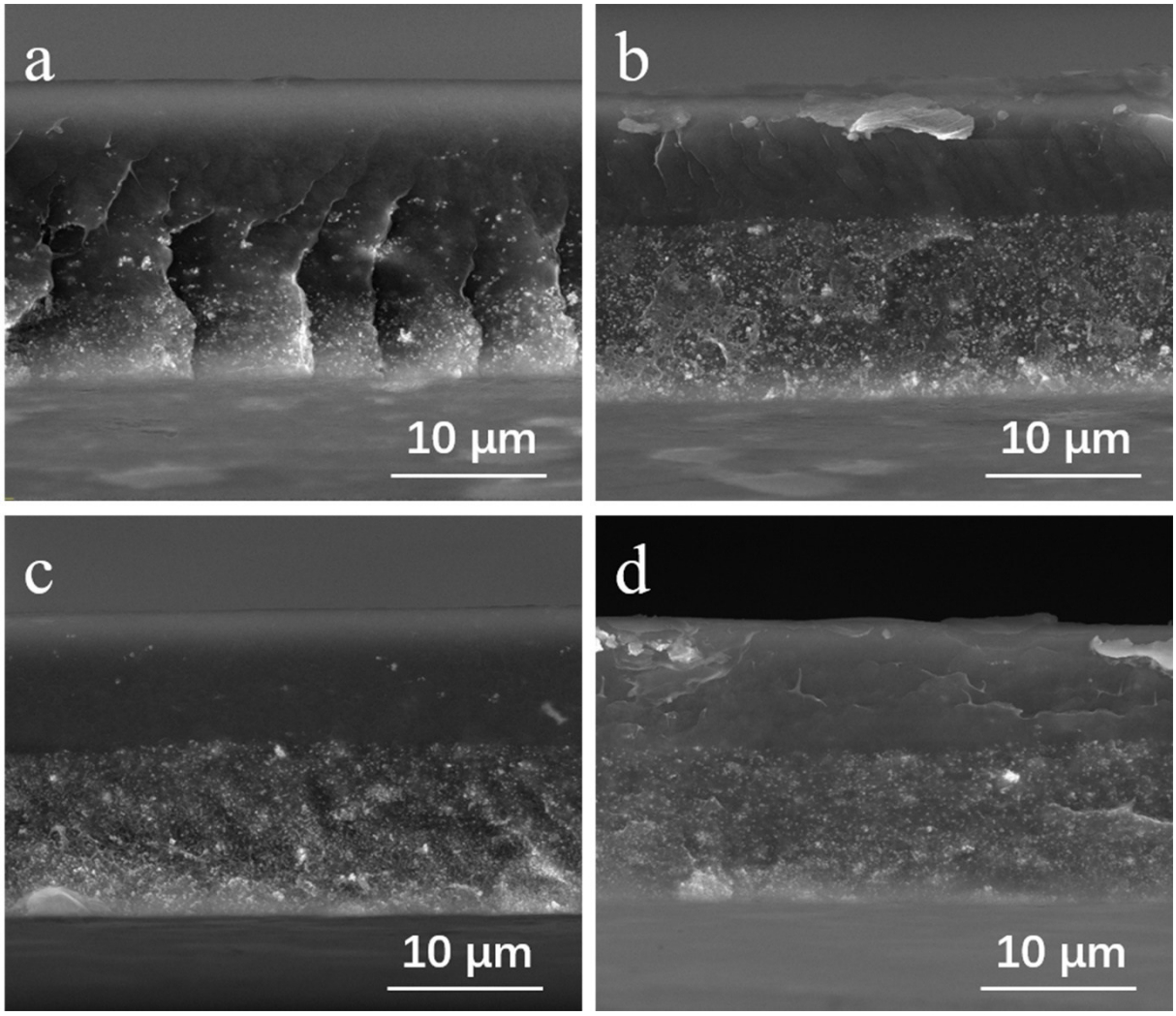

Fig. S1. Cross-section SEM image of GLNs a) "20-5-1", b) "20-15-1", c) "25-20-1", and d) "30-20-1".

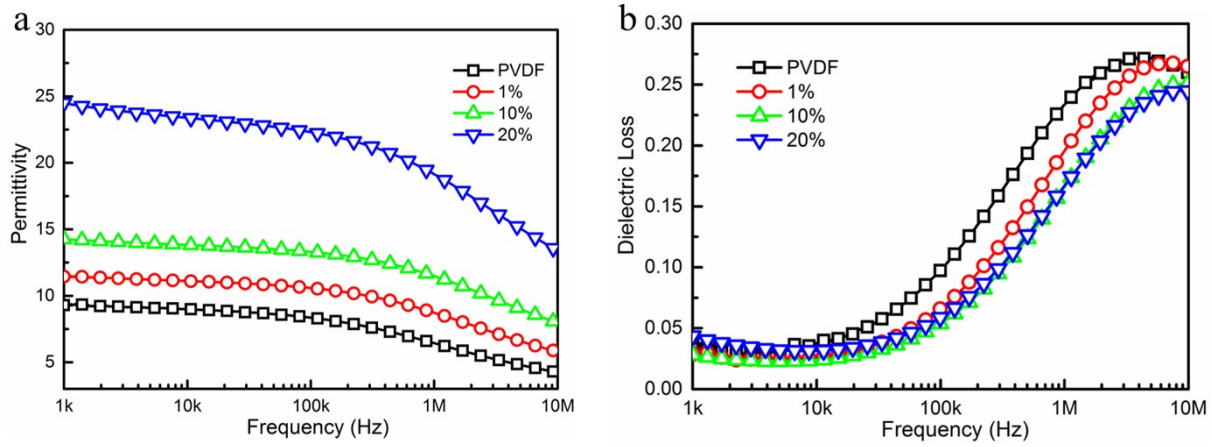

Fig. S2. The dependences of a) permittivity and b) dielectric loss on frequency for pure PVDF, and single layer BT/PVDF nanocomposites with BT contents of 1 vol%, 10 vol%, and 20 vol% respectively.

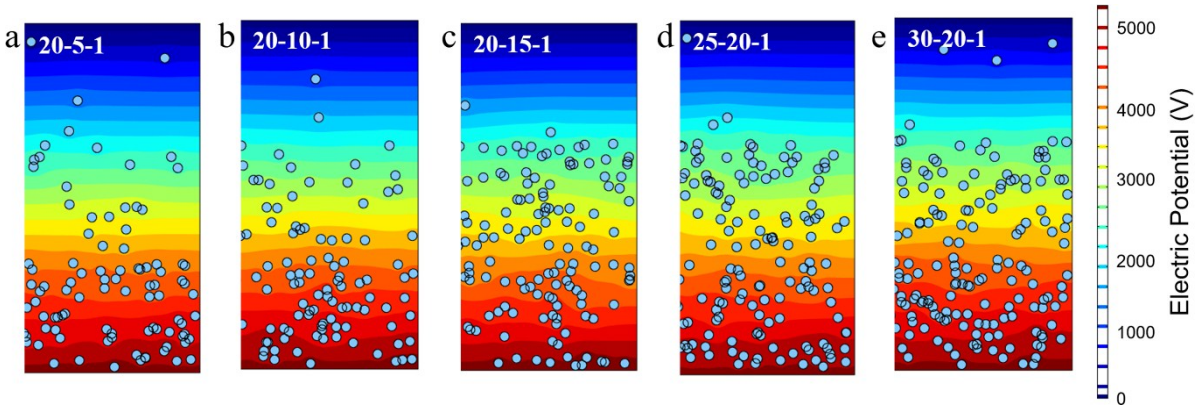

Fig. S3. The electric potential distribution in GLN a) "20-5-1", b) "20-10-1", c) "20-15-1", d) "25-20-1" e) 30-20-1 at 360 MV m^{-1}, simulated by finite element methods. (The color of the particles was artificially given to the uniform light blue for conveniently distinguish the shape and distribution of ceramic fillers.)

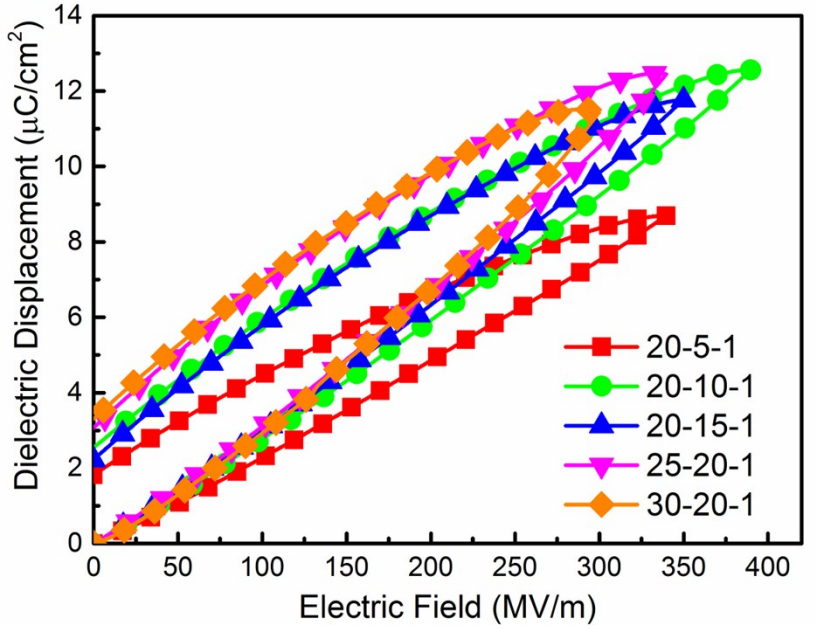

Fig. S4. D-E loops of GLNs with varied BT contents in middle layer and bottom layer near their breakdown strength respectively.

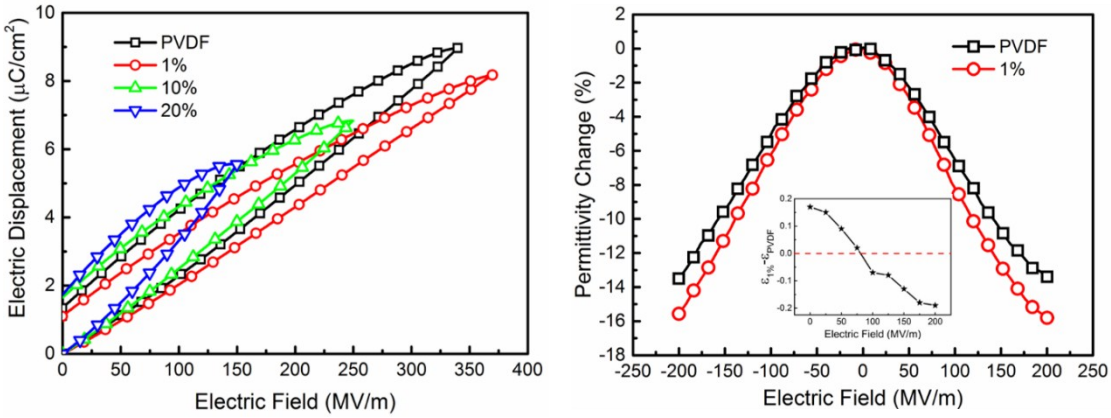

Fig. S5. a) D-E loops of pure PVDF, and single layer BT/PVDF nanocomposites with BT contents of 1 vol%, 10 vol%, and 20 vol% near their breakdown strength respectively. b) Electric field dependent permittivity change of pure PVDF and BT/PVDF nanocomposites with 1 vol% BT nanoparticles. (Inset. The difference of permittivity between 1 vol% BT/PVDF nanocomposites and PVDF. Test frequency: 1kHz.) The permittivity change (PC) is defined by the following equation: $PC=((\varepsilon(E)-\varepsilon(0)))/(\varepsilon(0)\times 100\%)$, where $\varepsilon(E)$ and $\varepsilon(0)$ refer to the permittivity with an applied DC bias field and without DC bias, respectively. An abnormal phenomenon can be observed that the electric displacement of 1% is lower than that of PVDF. The abnormal phenomena are caused by the influence of the ceramic fillers on PVDF grain size. The introduction of ceramic fillers can decrease the grain size of PVDF, which benefits for dipole switching under high frequency and weak electric field. Compared with 1%, the grain size in pure PVDF is larger, where the big dipoles can only show their full polarization under high applied electric field, which alleviate the decreasing speed of ε with increasing electric field.

References

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