Supporting Information for

Significantly improved dielectric performances of sandwich-structured polymer composites induced by alternating positive-*k* and negative-*k* layers

Zhicheng Shi,*[a] Jing Wang,[a] Fan Mao,[a] Chaoqiang Yang,[a] Chao Zhang[a] and Runhua Fan[b]

Prof. Z. Shi, J. Wang, F. Mao, C. Yang, C. Zhang

[a]Institute of Materials Science and Engineering, Ocean University of China

Qingdao 266100, China

E-mail: zcshi@ouc.edu.cn

Prof. R. Fan

[b]Institute of Marine Materials Science and Engineering, Shanghai Maritime University

Shanghai 201306, China

Key words: Dielectric property; Polymer composite; Energy storage; Negative permittivity; Electronic device

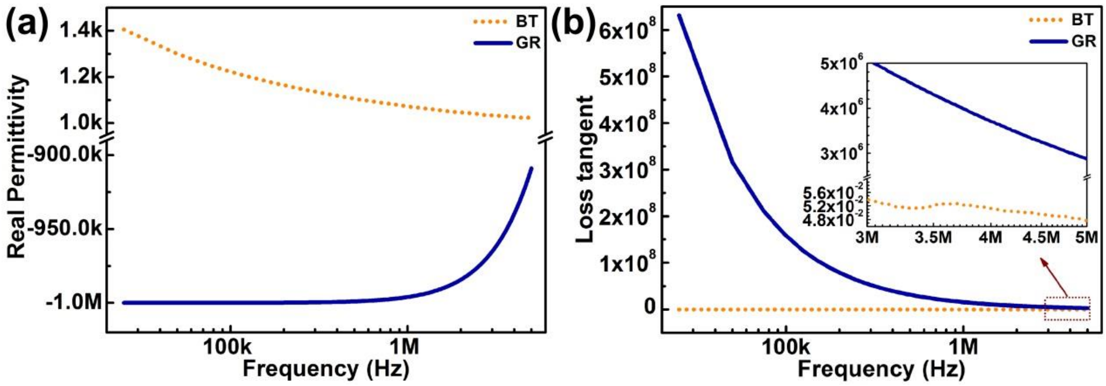

Figure S1. Experimentally obtained dielectric spectra of pure $BaTiO_3$ (BT) and calculated dielectric spectra of pure graphite (GR) using Drude model.

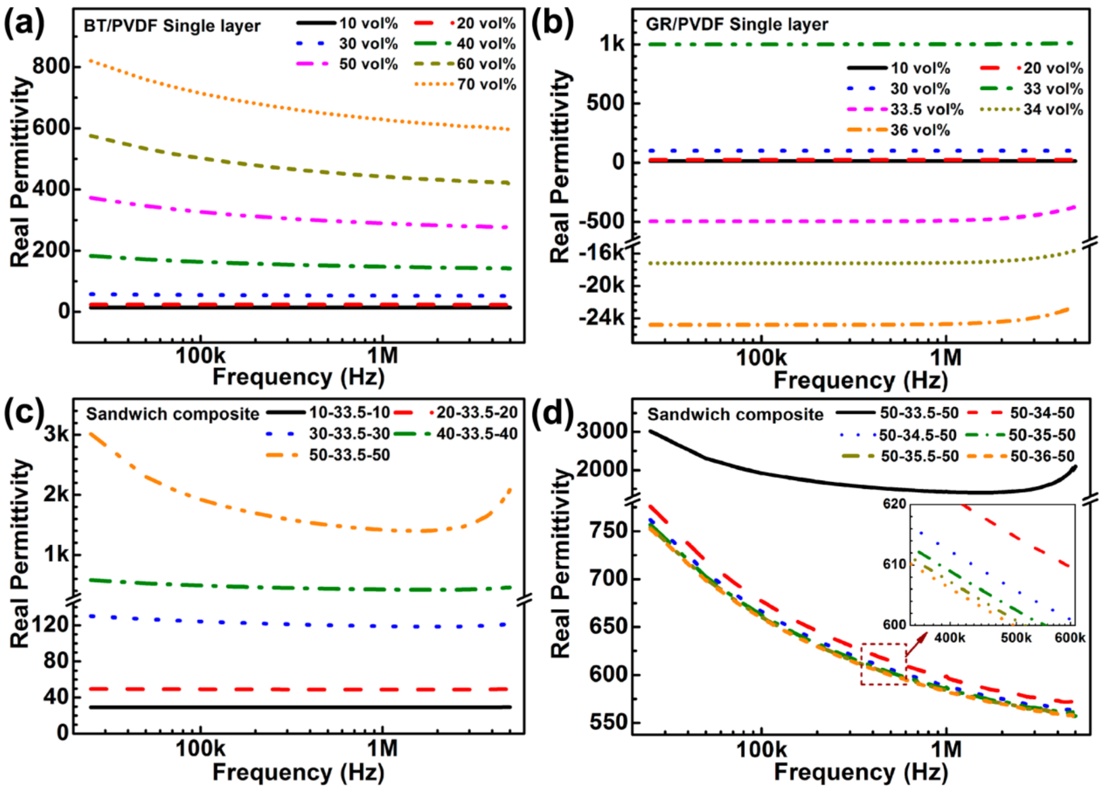

Figure S2. Calculated dielectric spectra of single layer (a, b) and sandwich-structured (c, d) composites using Effective Medium Theory (EMT).

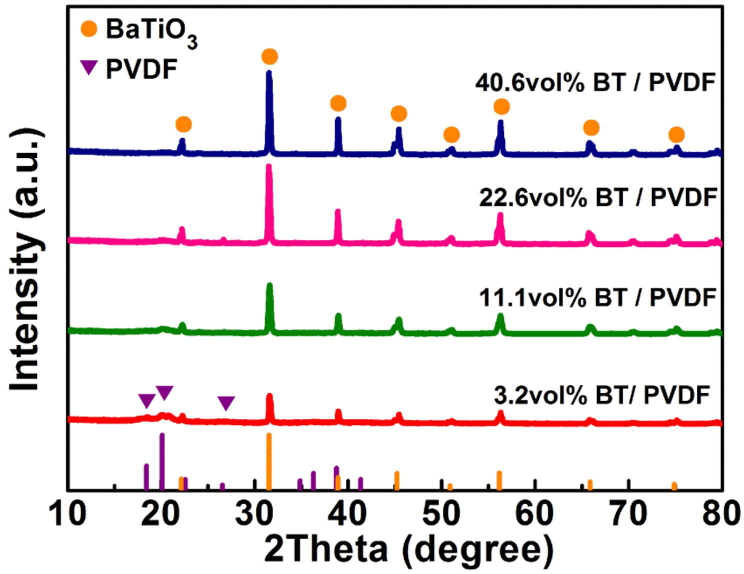

Figure S3. XRD patterns of single-layer $BaTiO_3$/PVDF composites.

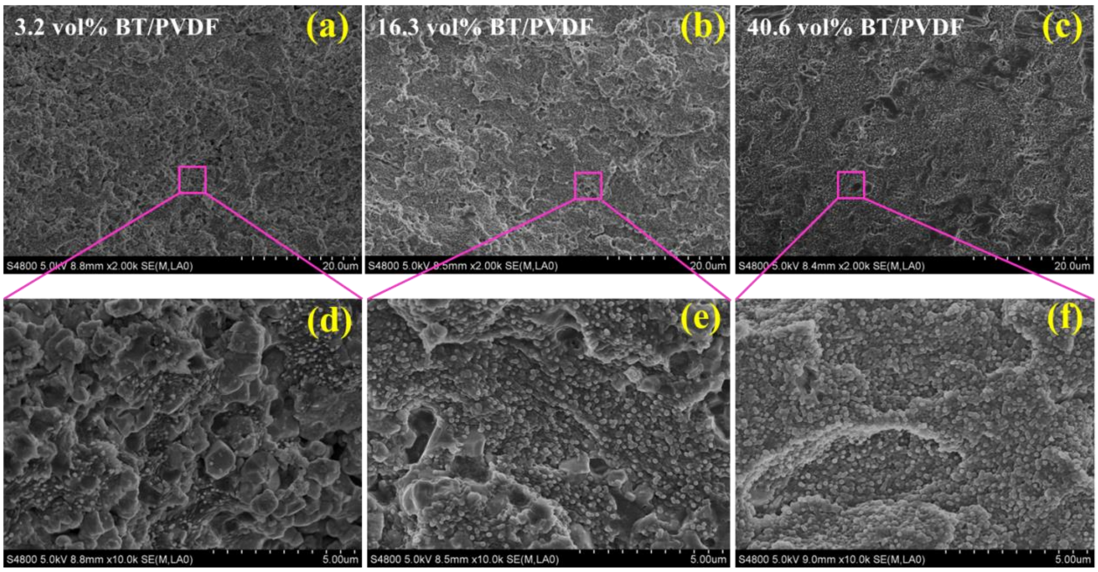

Figure S4. Cross-section SEM morphologies of $BaTiO_3$/PVDF composites with different $BaTiO_3$ volume fractions.

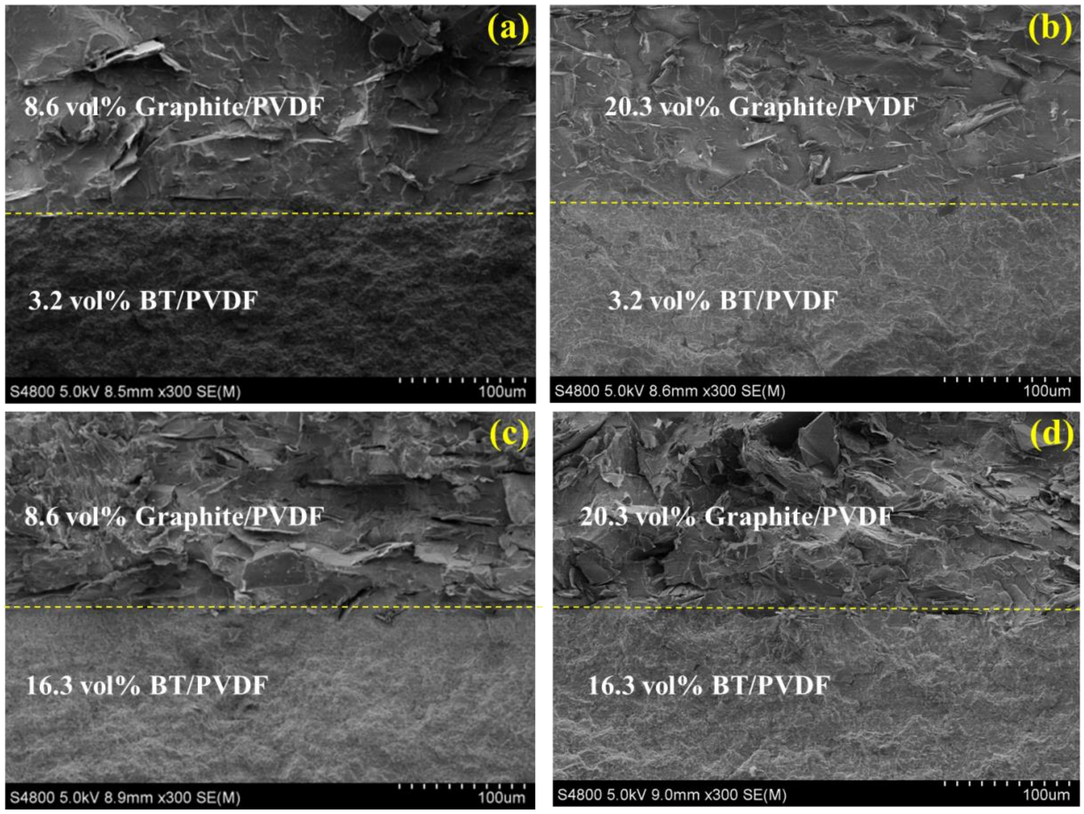

Figure S5. Cross-section SEM morphologies of the joint regions between Graphite/PVDF and BT/PVDF layers.

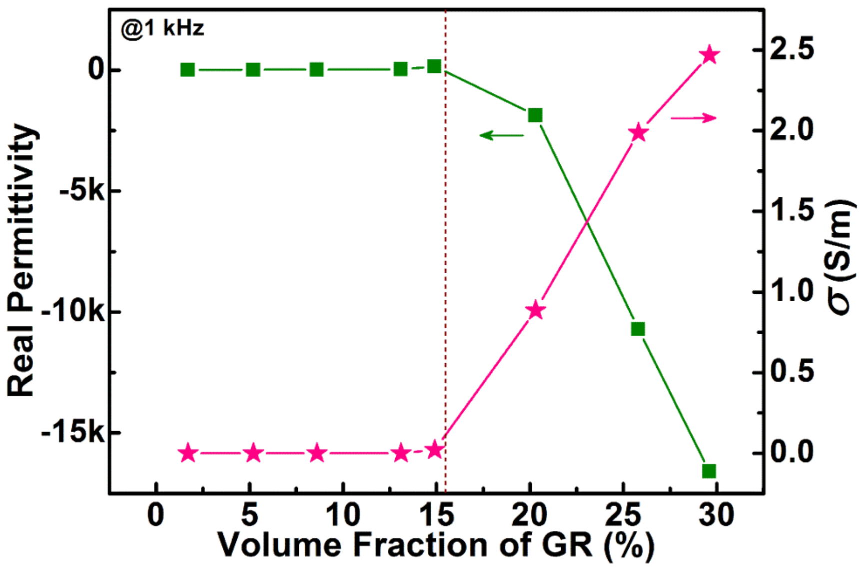

Figure S6. Variations of dielectric constant and conductivity with volume fraction of GR for GR/PVDF composites.

As shown in **Figure S6**, the permittivity of GR/PVDF composite maintains positive when the graphite content below 14.9 vol%. But the GR/PVDF permittivity changes from positive to negative value when the graphite content beyond 15 vol%. Meanwhile, the conductivity of GR/PVDF composite increases dramatically, indicating a percolation phenomenon. Generally, the dielectric performance of composite with GR content near the percolation is not stable. Therefore, GR/PVDF composites with graphite contents of 8.6 vol% and 20.3 vol% were selected as positive-*k* and negative-*k* layers, respectively.

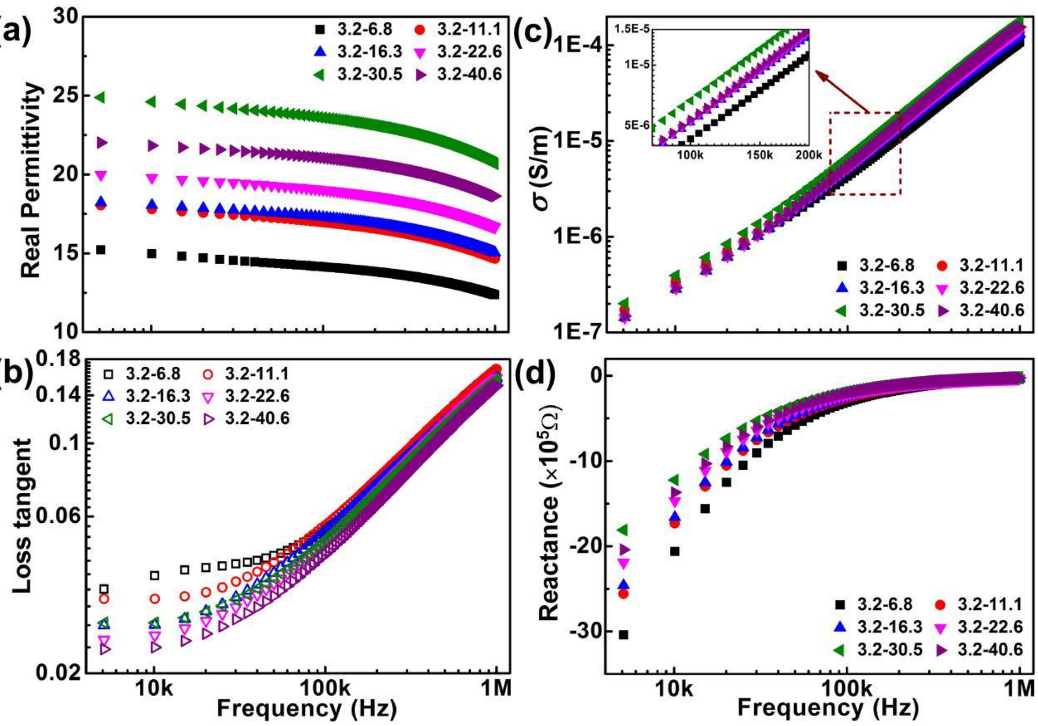

Figure S7. Frequency dependences of permittivity (a), loss tangent (b), conductivity (c) and reactance for bilayer $BaTiO_3$/PVDF composites.

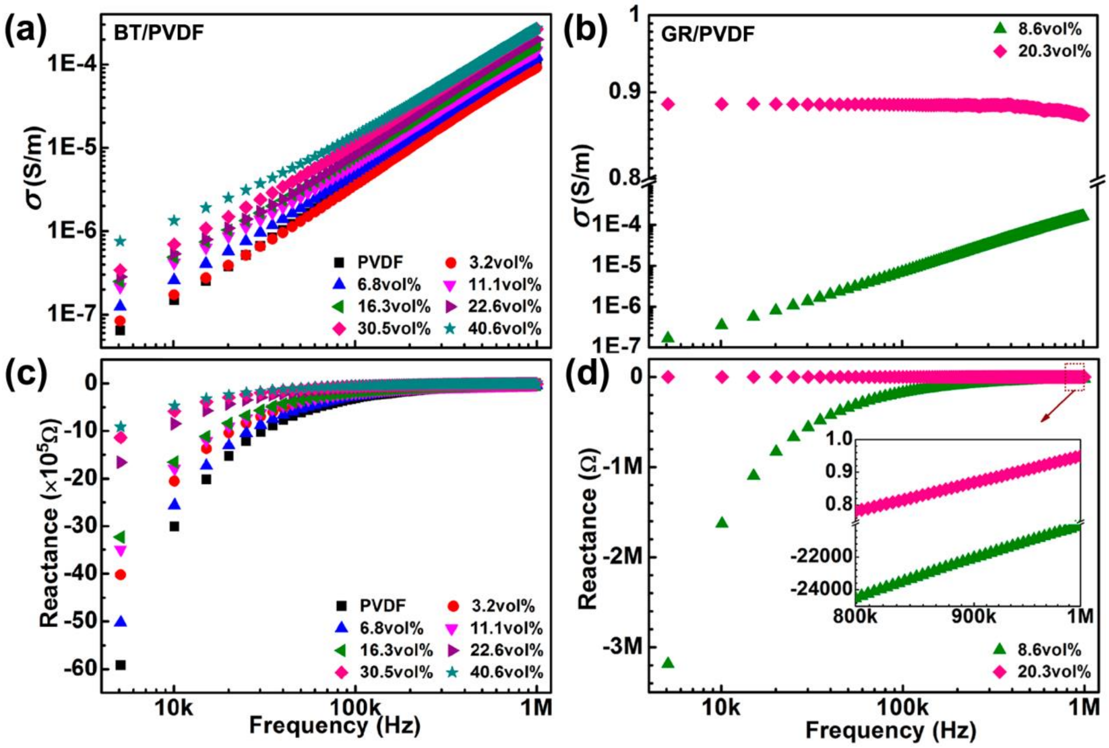

Figure S8. Frequency dependences of conductivity and reactance for single layer BT/PVDF (a, c) and GR/PVDF composites (b, d).

With the increase of BT content, the interconnectivity of BT particles was enhanced, yielding the slight increase of σ_{ac} (**Figures S6a**). And the frequency dependence of σ_{ac} follows the power law $\sigma_{ac} \sim (2\pi f)^s$ with $0.6 \leq s \leq 1.0$ characterizing hopping conduction.[S1] Additionally, the reactance Z'', which represents the opposition of a circuit element to a change of electric current or voltage, of these BT/PVDF composites are negative and their frequency dispersions follow the equation $Z'' = -1/\omega C$, indicating their capacitive characteristics. Moreover, the conductivity and reactance spectra of the GR/PVDF composites containing 8.6 vol% graphite exhibit similar behaviors with BT/PVDF composite. In particular, a considerable enhancement of σ_{ac} is observed when the graphite content of GR/PVDF composites increases from 8.6 vol% to 20.3 vol% (**Figure S6b**), which should be attributed to the percolation behavior. [S2] And the σ_{ac} of the percolative GR/PVDF composite shows a slight decrease with increasing frequency owing to the skin effects. As is well known, σ_{ac} decreases with smaller skin depth. And the skin depth of lossy media can be expressed as $\delta = (2/\sigma\omega\mu)^{1/2}$, where δ is the skin depth, σ is the DC conductivity, ω is the angular frequency, and μ is permeability. Generally, σ is constant for a certain material and μ is 1 for nonmagnetic materials. Consequently, the skin depth decreases with higher frequency, leading to the decrease of ac conductivity σ_{ac}. In addition, the reactance of the GR/PVDF composite containing 20.3 vol% graphite is positive, indicating a lag of the current behind of the voltage, which gives rise to the inductive behavior. [S3]

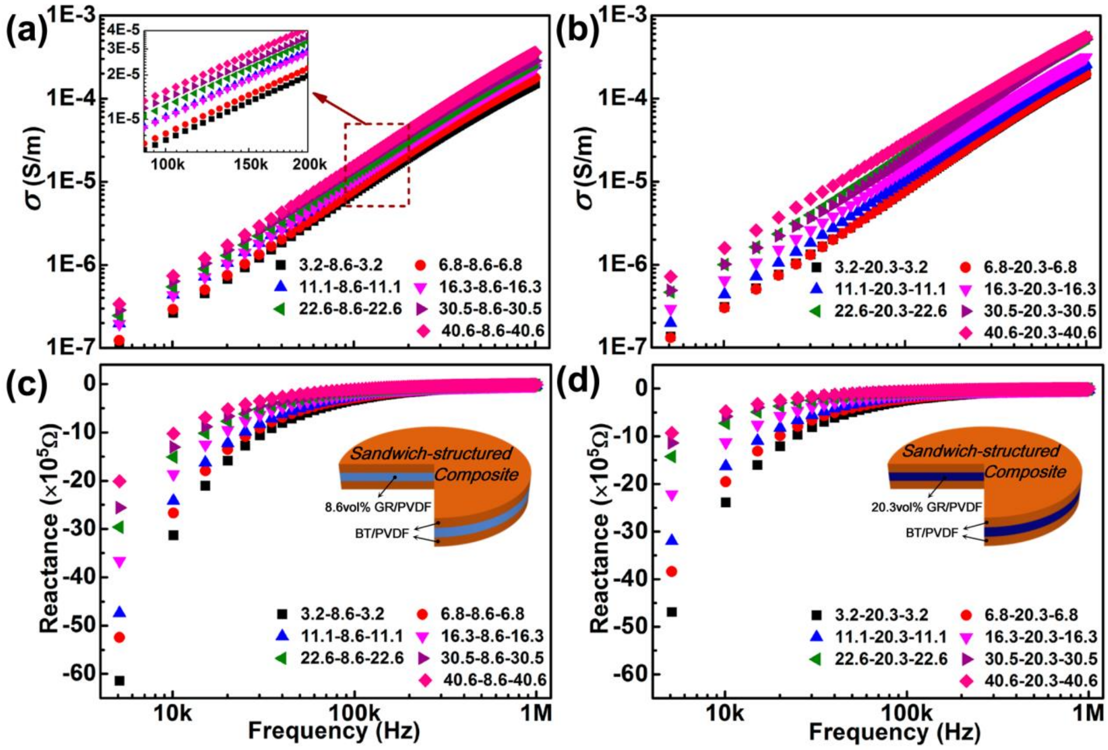

Figure S9. Frequency dependences of conductivity (a, b) and reactance (c, d) for sandwich-structured composites.

Additional References

[S1] J. C. Dyre, T. B. Schrøder, *Rev Mod Phys*. **2000**, *72*, 873.

[S2] C. Pecharromµn, J. S. Moya. *Adv. Mater.* **2000**, *12*, 294.

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