

Supporting Information

Construction of 3D-BaTiO₃ Network Leading to Significantly Enhanced Dielectric Permittivity and Energy Storage Density of Polymer Composites

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1. Experimental

1.1 Materials: Barium titanate powders (100 nm) were provided by Shandong Guoci Functional Materials Co., Ltd, China. Untreated lignocelluloses dispersion was purchased from Tianjin Haojia Nanocellulose Co., Ltd, China. Epoxy resin Epon828 was obtained from Hexion Specialty Chemicals. Curing agent Methyltetrahydrophthalic anhydride (MeTHPA) and catalytic agent 2-ethyl-4-methylimidazole (2E4MZ) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. All the materials were used as received.

1.2 Preparation: The aerogels composites of BT and lignocelluloses were prepared by mixing BT with different weights in lignocelluloses dispersion and milling for 24 hours, then vacuum freeze-drying for 48 hours. The 3D-connected BT was fabricated by sintering the aerogels at 1000 °C for 15 hours. The epoxy solution was prepared by

mixing 40 g Epon828, 32 g MeTHPA and 0.4 g 2E4MZ together under stirring. Then, the prepared porous BT was placed in a mould and the epoxy solution was injected. After curing at 100 °C for 1 hour and 180 °C for 2 hours, the 3D BT/epoxy composites (Composite-1) were cut into thin pieces and polished for properties testing. For comparison, the 100nm BT powders were treated at 1000 °C for 15 hours and used to prepare the epoxy composites by simple mixing (Composite-3). The untreated BT/epoxy composites (Composite-2) were fabricated with the purchased 100 nm BT. The slurry containing BT, Epon828, MeTHPA, and 2E4MZ were prepared through a ball-milling process. Then, the slurry was coated on copper foil with bar coating method. Finally, it was cured at 100 °C for 1 hour and 180 °C for 2 hours and painted with silver paste for electrical testing.

1.3 Characterization: Scanning electron microscope (SEM) was conducted by using FEI Nova NanoSEM 450 at 10 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku-Dmax 2500 diffractometer with Cu K α radiation. The measurement of permittivity and loss tangent was performed with an Agilent 4294A impedance analyzer in the frequency range from 1 kHz to 10 MHz at room temperature. Breakdown strength analysis was studied using a dielectric strength tester (CS9912BX, Allwin Instrument Science and Technology co. Ltd, China). The energy storage property was acquired using Radiant Precision Multiferroic and Precision 10 kV HVI-SC Precision Materials Analyzer. The area of all the samples for energy storage property testing is 0.295 cm² (**6.0mm in diameter**). For each formulation, five samples were tested to ensure repeatability.

1.4 Theoretical models^{1,2} for predicting effective permittivity

$$\text{Parallel model: } \epsilon_{\text{eff}} = f \epsilon_f + (1 - f) \epsilon_m \quad \text{eq.S1}$$

$$\text{Series model: } \epsilon_{\text{eff}} = \frac{\epsilon_f \epsilon_m}{f \epsilon_m + (1 - f) \epsilon_f} \quad \text{eq.S2}$$

$$\text{Logarithmic model: } \epsilon_{eff} = e^{f \ln \epsilon_f + (1-f) \ln \epsilon_m} \quad \text{eq.S3}$$

$$\text{Jayasundere-Smith model: } \epsilon_{eff} = \frac{\epsilon_m(1-f) + \epsilon_f f \frac{3\epsilon_m}{\epsilon_f + \epsilon_m} \left[1 + \frac{3f(\epsilon_f - \epsilon_m)}{\epsilon_f + \epsilon_m} \right]}{1-f + f \frac{3\epsilon_m}{\epsilon_f + \epsilon_m} \left[1 + \frac{3f(\epsilon_f - \epsilon_m)}{\epsilon_f + \epsilon_m} \right]} \quad \text{eq.S4}$$

$$\text{Maxwell-Garnett model: } \epsilon_{eff} = \epsilon_m \frac{(2f+1)\epsilon_f + 2(1-f)\epsilon_m}{(1-f)\epsilon_f + (2+f)\epsilon_m} \quad \text{eq.S5}$$

Where ϵ_m and ϵ_f are the permittivities of polymer matrices and fillers, respectively, f is the volume fraction of fillers and ϵ_{eff} is the effective permittivity of the composites.

2. Results

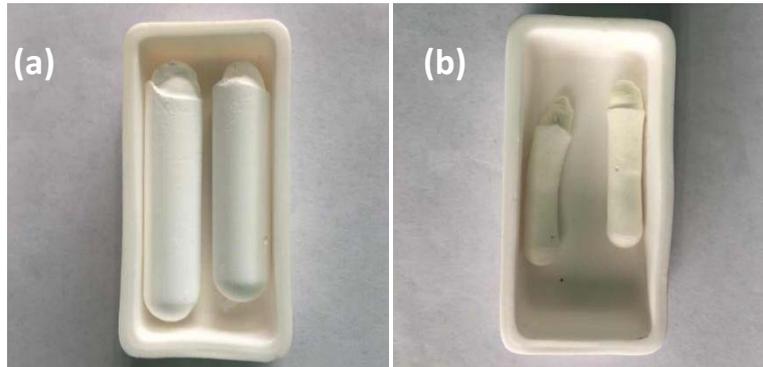


Fig.S1 Photo images of the milled BT-lignocelluloses slurry continuously treated with (a) freeze-drying, and (b) 1000 °C sintering for 15 hours.

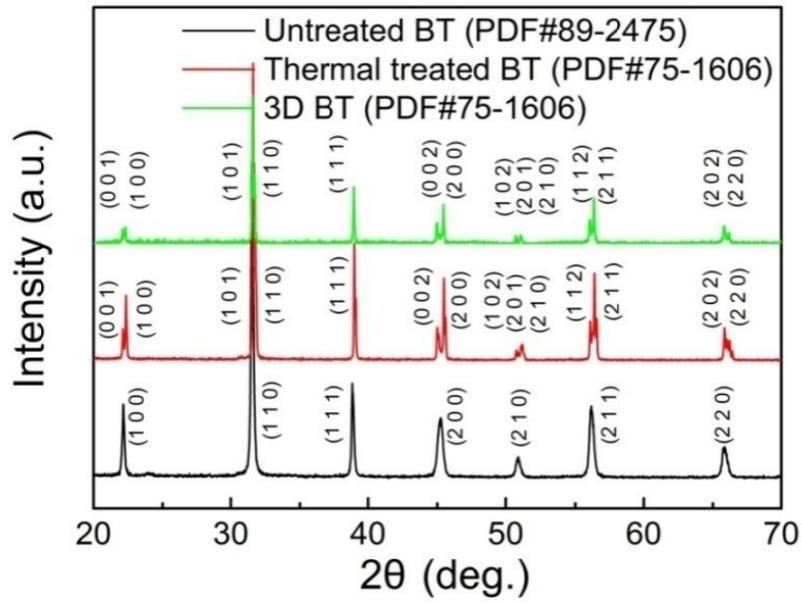


Fig.S2 XRD patterns of untreated BT, Thermally treated BT and 3D-BT.

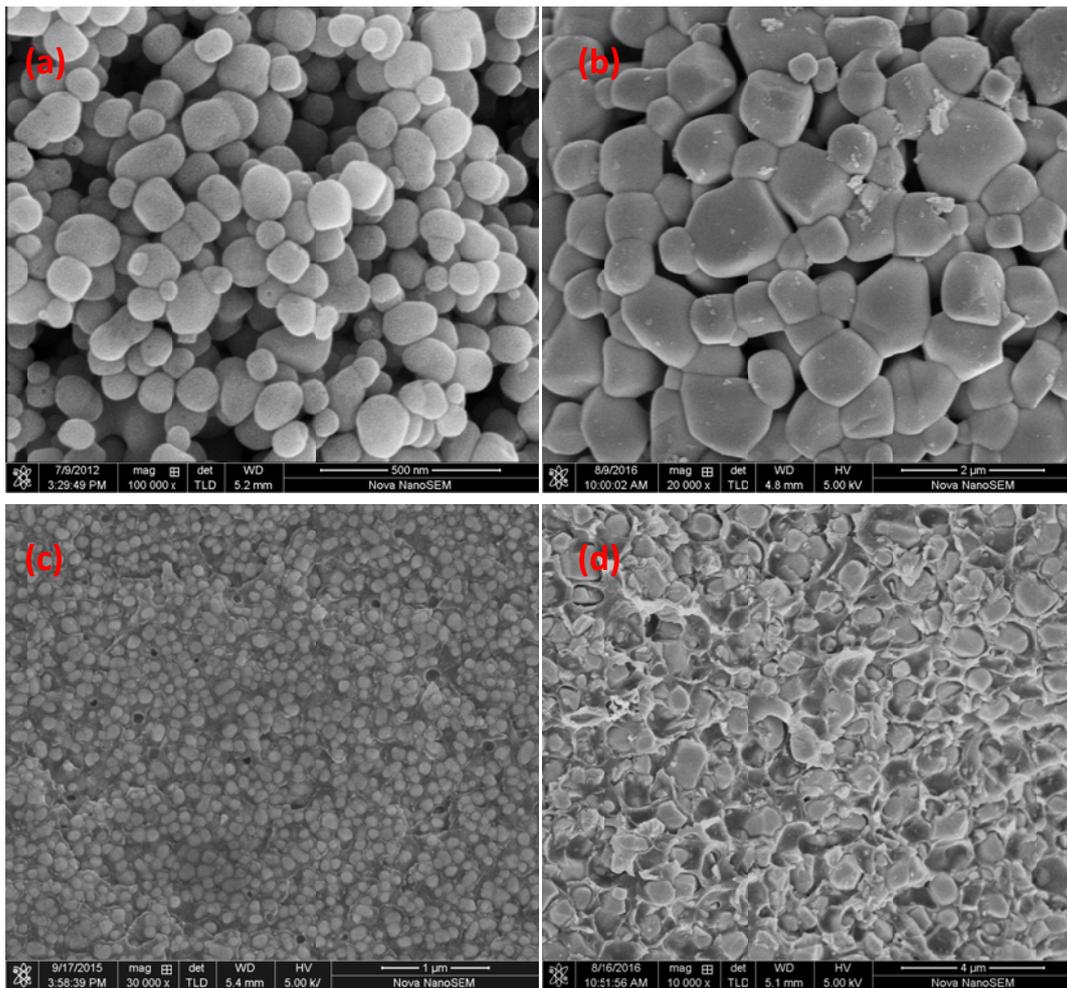


Fig.S3 SEM images of (a) untreated BT and (b) thermally treated BT. SEM images of (c) untreated BT/Epoxy composites and (d) thermally treated BT/Epoxy.

The sizes of untreated and thermally treated BT were 100 nm, and 500 nm~1000 nm respectively.

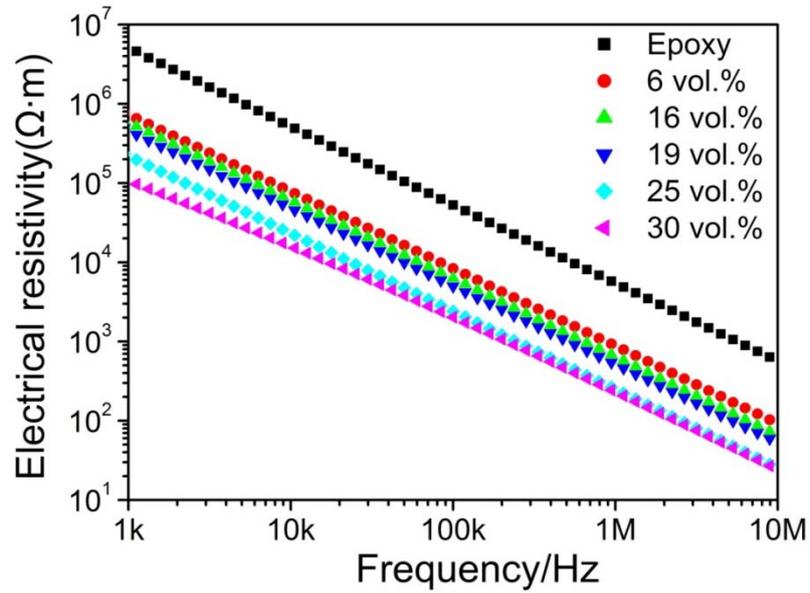


Fig.S4 Frequency dependence of electrical resistivity of epoxy resin and 3D-BT/Epoxy composites.

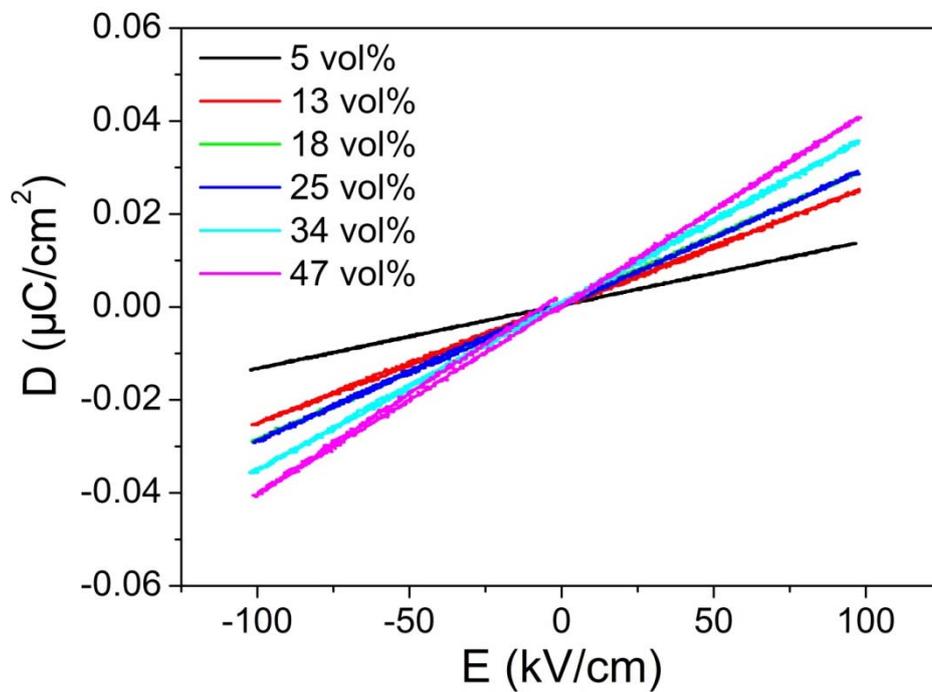


Fig.S5 D-E loops of Composite-3 under 100 kV/cm.

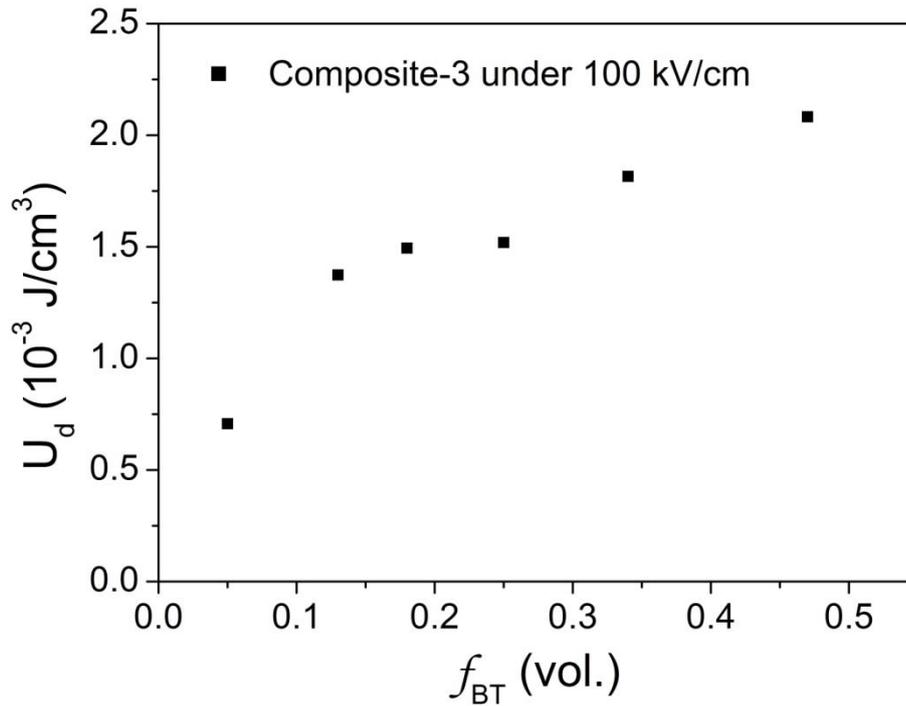


Fig.S6 Calculated discharged energy density of Composite-3 under 100 kV/cm.

Table S1: Detailed data of the properties of Composite-1 with 16 vol.% BT and the composites prepared by simply mixing method with 3 vol.% BTO@TO, C2 and 10 vol.% BTNW.

	$\epsilon_{eff}/\epsilon_m$	E_b/E_m	U_d/U_m	η
3D BT-16 vol.%	9.6	0.83	16.6	90.3%
BTO@TO-3 vol.% ³	1.43	1.17	1.80	78%
C2 ⁴	1.1	1.71	2	83%
BTNW-10 vol.% ⁵	2	0.66	1.82	57%

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