



# Enhanced dielectric and energy storage density induced by surface-modified BaTiO<sub>3</sub> nanofibers in poly(vinylidene fluoride) nanocomposites

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## Abstract

A high energy-storage density ceramic–polymer nanocomposite is fabricated by incorporating high aspect ratio functionalized BaTiO<sub>3</sub> nanofibers (BT NF) prepared via electrospinning into a polyvinylidene-fluoride (PVDF) matrix. The functionalized BT NF by 3-aminopropyltriethoxysilane (APS) not only exhibited excellent compatibility with poly(vinylidene fluoride) (PVDF), but significantly enhanced the dielectric properties of the nanocomposites. The dielectric constant of the nanocomposite reached up to 24 with a dielectric loss of 0.018 at 1 kHz with a BT NF-APS concentration of 7.5 vol%. The maximal energy-storage density in the nanocomposite with 2.5 vol% BT NF-APS is about 5.6 J/cm<sup>3</sup> at 3300 kV/cm, which is over 220% higher than that of the PVDF at the same electric field. The enhanced energy-storage density could be attributed to the combined effects of the APS surface modification, large aspect ratio and ferroelectric polarization behavior of the BT NF.

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**Keywords:** BT NF; Energy-storage density; PVDF; APS modification

## 1. Introduction

In recent years, much attention has been paid to developing high energy-storage density polymer capacitors due to their potential applications in fields such as backup power sources for electronic components, pulsed power sources and power sources for electronic cars [1–3]. Polymer capacitors have some advantages such as fast charge/discharge (< 1 μs), high working voltage, simplified processing and low cost [4–9]. According to the definition of the energy-storage density of dielectric materials  $U = \int E dD$  (where  $E$  is the applied electric field and  $D$  is the electric displacement), obtaining a high energy-storage density in polymer dielectric materials requires a large electric displacement (dielectric constant) and high breakdown strength. However it is very difficult to optimize them synchronously [10–12]. At present, most polymers, including PVDF, BOPP, are flexible and easy to process and

show excellent electric breakdown properties, but are limited by their low dielectric constants. Whereas ferroelectric ceramics, such as Pb(Zr,Ti)O<sub>3</sub>, Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> and BaTiO<sub>3</sub>, have a high permittivity, but are brittle and have a low breakdown strength. Methods of enhancing the dielectric constant of polymers have received wide attention in recent years [13–16].

To enhance the dielectric constants of the polymers, one route focuses on dispersing conductive fillers such as carbon black, carbon nanotubes, graphene, and nickel particles into the polymer matrix to achieve percolative composites [17–22], which have high dielectric constant in company with a large increase of dielectric loss and low breakdown strength [23]. So the percolative composites are not suitable as effective materials for high energy-storage density capacitors. Another strategy is introducing ceramic particles with high dielectric constant, such as Pb(Zr,Ti)O<sub>3</sub>, Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> and BaTiO<sub>3</sub>, into the polymer matrix [24–26]. However, to achieve high dielectric constants for nanocomposites, a high volume fraction of ceramic filler is normally required, which simultaneously decreases the flexibility of the nanocomposite. Moreover,

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breakdown strength drops off precipitously with the high proportion of ceramic fillers due to an increased defect density, agglomeration of fillers, as well as percolation with the low dielectric strength ceramic fillers [27]. That leads to very minor enhancement of energy-storage density as compared with the pure polymer matrix. Therefore, for ceramic–polymer composites, it is important to determine an optimal volume fraction and packing organization/inclusion morphology.

One-dimensional nanostructured (1D) materials have attracted considerable interest in the recent years by virtue of their potential applications due to their remarkable dielectric, electric, and chemical properties. An 1D dielectric material often shows a high dipole moment due to its special size and structure. Compared with general dielectric materials, 1D dielectric materials have a large value of dielectric constant and a large aspect ratio. Such unique features render 1D dielectric materials more effective in enhancing the dielectric constants of composites at low concentration than particles. Recently, a micromechanical model and experimental efforts by Andrews et al. [28] and Song et al. [29], respectively, have shown that composites filled with high aspect ratio inclusions exhibit greater dielectric constants than the composites filled with nanoparticles at the same volume fraction. Moreover, phase-field modeling and experimental results all indicate that the orientation of large aspect ratios ceramic fillers perpendicular to the direction of external electric field is favorable for mitigating local field concentration in the nanocomposite and leads to higher breakdown strength. The use of high dielectric constant fillers with large aspect ratios is therefore a potential method to obtain desirable dielectric properties (large dielectric constant and high breakdown strength) necessary for a large energy-storage density in dielectrics.

Most work about energy storage materials is mainly focused on the fabrication of homogeneous ceramic–polymer nanocomposites consisting of ferroelectric ceramic nanoparticles as fillers and a high energy-storage density ceramic–polymer nanocomposite is up to now still a challenging task. We have prepared high energy-storage density nanocomposites incorporating high aspect ratio functionalized BaTiO<sub>3</sub> nanofibers (BT NF) prepared via electrospinning into a polyvinylidene-fluoride (PVDF) matrix. The dielectric properties and energy-storage properties of the composites have been investigated as a function of the functionalized BT NF content. Enhanced dielectric constants and energy-storage density of the composites were obtained at a low volume fraction of functionalized BT NF.

## 2. Experimental

The BT NF were synthesized by electrospinning. Barium acetate (99.0%, Alfa Aesar), titanium(IV) n-butoxide (99.0%, Alfa Aesar) and acetylacetone at a molar ratio of 1:1:1 were dissolved in acetic acid and stirred for 1 h. The solution was mixed with a solution consisting of poly(vinyl pyrrolidone) (PVP, MW = 1,300,000) dissolved in ethanol. The mixture was stirred at room temperature for 1 h to get a lucid and viscous barium titanate precursor sol. The precursor sol was loaded into a plastic

syringe and electrospun with an applied electric field of 1.5 kV cm<sup>-1</sup>. The composite nanofibers were collected on the copper plate during the electrospinning processes. The BT NF were finally obtained by calcination at 900 °C for 3 h in air to remove PVP completely.

Functionalization of BT NF by 3-aminopropyltriethoxysilane (APS): 2 g of BT NF were dispersed into 120 mL of ethanol and then 0.3wt % APS was added and the mixture was heated at 80 °C for 2 h under moderate stirring. The obtained powders were then washed with water four times through centrifugation, and subsequently dried at 80 °C for 12 h to obtain the APS-modified BT NF (BT NF-APS).

For the fabrication of the BT NF-APS/PVDF composites, first, the BT NF-APS were dispersed into N, N-dimethylformamide (DMF) under 30 min sonication and stirred at room temperature for 4 h. At the same time, PVDF was dissolved in DMF under vigorous stirring at 50 °C for 10 h. The suspension of DMF and BT NF-APS were then mixed with the PVDF/DMF solution at 50 °C under stirring for 5 h. The resulting mixture was cast onto an indium tin oxide (ITO) glass and dried at 60 °C for 10 h. Finally, the resulting composite films were heated at 200 °C for 10 min and quenched in ice-water bath immediately, and subsequently dried at 40 °C for 24 h. The nanocomposite films are about 10 μm in thickness. Top Au electrodes were deposited on the films using a shadow mask for electrical measurements. The schematic diagrams of the fabrication of BT NF-APS/PVDF nanocomposites are shown in Fig. 1.

## 3. Characterization

Fourier-transform infrared spectroscopy (FTIR) was conducted with a Bruker Tensor 27 spectrometer. X-ray diffraction (XRD) (D8 Advanced, Bruker, Germany) was employed to investigate the crystal structure of the composites using Cu/K alpha radiation. The morphology of the samples was characterized by field emission scanning electron microscopy (XL30-FEG, Philips, Netherlands). Thermogravimetric analysis (TGA) was conducted using a NETZSCH STA449C instrument at the heating rate of 10 °C/min in flowing air (20 mL min<sup>-1</sup>). Dielectric properties of

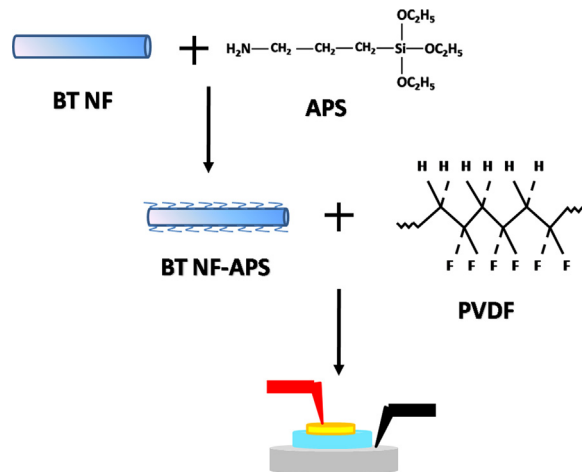


Fig. 1. Schematic diagrams of the fabrication of BT NF-APS/PVDF nanocomposites.

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