



# Surface modified BaTiO<sub>3</sub> nanoparticles by titanate coupling agent induce significantly enhanced breakdown strength and larger energy density in PVDF nanocomposite

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## ABSTRACT

Dielectric capacitors are promising in micro-electronics, portable equipment and hybrid electric vehicles due to their specific features of flexibility, ultrahigh operating voltage and fast charging-discharging rate. The dielectric properties of polymer-based nanocomposite are much related to the interface binding between fillers and matrix. In this work, a surface modification approach employed newfound titanate coupling agent was developed to improve the compatibility between BT nanoparticles and PVDF matrix. After treated by the modifier TC-2, a coating layer contained with active organic groups was formed on the surface of BT nanoparticles. Benefited from the improved dispersibility and compatibility of modified BT nanoparticles in PVDF matrix, the breakdown strength of the nanocomposites was much enhanced. The monodisperse mBT-2 nanoparticles treated with appropriate amount of modifier dramatically enlarged the breakdown strength from 397 kV/mm for neat PVDF to 517 kV/mm for 4 vol% mBT-2 loading nanocomposite. Compared with BT/PVDF, the improvements on the energy storage performance in mBT-2/PVDF are significant. The maximum discharged energy density of 11.27 J/cm<sup>3</sup> for 4 vol% loading mBT-2/PVDF is nearly double of that for 4 vol% loading BT/PVDF, and the energy efficiency for mBT-2/PVDF is also increased. The modification method originally represented here has great potential in developing high energy density nanocomposites for advanced applications.

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## 1. Introduction

As one of the important energy storage devices, dielectric capacitor plays a crucial role in the fields of modern compact electronic components and power systems. High energy density capacitors are promising in micro-electronics, portable equipment and hybrid electric vehicles [1]. Although dielectric polymers are becoming the regnant materials for capacitor attributed to their specific features of flexibility, ultrahigh operating voltage and fast charging-discharging rate, the relatively low energy density much limits their application [2–4]. As expressed by the formula  $U_e = \int E dD$  and  $D = \epsilon E$ , where the  $U_e$ ,  $D$ ,  $\epsilon$ ,  $E$  represents the electric energy density, electric displacement, dielectric permittivity and electric field, respectively. Thus, the energy density of a capacitor generally depends on the dielectric permittivity and the withstand

voltage (breakdown strength,  $E_b$ ) of its core dielectrics, and the low energy density of polymer is precisely due to their low dielectric permittivity (commonly 2–3). The ferroelectric polymer such as poly (vinylidene fluoride) (PVDF) and its co-polymers have been widely investigated due to their relatively high  $\epsilon$  of about 10, which are the promising matrixes for the new generation of energy storage dielectrics [5].

To further increase the dielectric permittivity to achieve larger energy density, the polymer-based nanocomposites contained with high- $\epsilon$  nanofillers have been received extensive research [6–8]. The introducing of high- $\epsilon$  ceramic nanofillers (such as BaTiO<sub>3</sub>, TiO<sub>2</sub>, Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> and so on) into polymers was effective in achieving increased  $\epsilon$  in nanocomposites, but it's hard to obtain higher  $U_e$  because they dramatically reduced the  $E_b$  of polymer matrix. It's found that the weakening of  $E_b$  is mainly attributed to the poor compatibility between the inorganic fillers and the organic matrixes. Both the aggregation of the fillers and the defects existing at the interfaces between ceramic nanofillers and polymer matrix facilitate charges passing and thus result in the  $E_b$  deterioration.

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It's necessary to improve the compatibility between fillers and matrix to maintain the breakdown strength of the polymer nanocomposites, and several approaches were developed during the past decade, including grafting functionalized polymer chains onto the surface of nanofillers [9–12], *in situ* polymerization of monomer on nanofillers [13–16], introducing hydroxyl onto the surface of nanofillers [17–19], and modifying nanofillers with coupling surfactant [20–24]. In these methods, the surface modification is facile and the most commonly adopted. The modifier contained functional groups was coated onto the surface of nanofiller and form a bonding shell layer. The active shell layer on one hand changes the surface energy of the nanofillers to reduce the aggregation and on the other hand enhances the combination between fillers and matrix by molecular bonding, which is beneficial for eliminating the negative effect on the breakdown strength by nanofillers [25]. For instance, Kim et al. modified BaTiO<sub>3</sub> (BT) nanoparticles with a pentafluorobenzyl phosphonic acid to improve their compatibility with P(VDF-HFP) matrix, and achieved  $E_b$  of above 200 kV/mm even in 50 vol% loading composite [26]. Song et al. fabricated PVDF nanocomposites contained with functionalized BT nanofillers coating with polydopamine, the  $E_b$  of which was much increased compared with the uncoated ones [27]. In the work of Yu et al. the BT nanoparticles treated with polyvinylpyrrolidone (PVP) present lower current density and higher breakdown strength in PVDF composite films [28]. Zhang et al. enhanced the dielectric tunability and breakdown strength of Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub>/PVDF nanocomposite via interface modification by a silane coupling agent (KH550), and found 4 wt% as the optimal content of modifier [29]. Consequently, with the quadratic dependence on  $E_b$ , the  $U_e$  is largely increased in the nanocomposites with enhanced breakdown strength [30,31].

Up to date, benefited from comprehensive approach, the breakdown strength in some of PVDF-based nanocomposite films is close to and even beyond the value of the neat polymer, and the surface modification on nanofillers has been an essential process in the strategy to achieve high energy density [32–38]. In the present work, a titanate coupling agent (TC-2) is adopted as the surface modifier to improve the compatibility of BT nanoparticles (NPs) in polymer nanocomposite. The modified BT (mBT) NPs coated with TC-2 molecules are obtained via facile solution method and are introduced in PVDF matrix. Benefited from the decrease of both interfacial polarization and defects, the breakdown strength of mBT/PVDF is much enhanced compared with that of neat PVDF and BT/PVDF nanocomposite. The effect of additive amount of TC-2 on the dispersity of mBT in matrix is investigated in detail. Insufficient or excessive amount of modifier of TC-2 leads to different levels of aggregation of nanofillers in matrix which is inefficient for improving breakdown strength. Uniform dispersion is observed in nanocomposite contained with nanoparticles treated with appropriate amount of TC-2 which breakdown strength was highly enhanced. Besides the breakdown strength, the stored energy density, discharged energy density and energy efficiency are all increased in mBT/PVDF, especially the maximal discharged energy density of 11.27 J/cm<sup>3</sup> is nearly double of that of BT/PVDF with the same content loading. The original surface modification process with TC-2 reported here are promising in fabricating high energy density polymer nanocomposites.

## 2. Experimental

### 2.1. Materials

Barium titanate (BaTiO<sub>3</sub>, 99.5%) particles with an average size of 100 nm were purchased from Aladdin (China). Titanate coupling agent (Product NO. TC-2, more information can be found in

Ref. [39]) was purchased from Taicang Chemical Co., Ltd (Anhui, China). Poly (vinylidene fluoride) (PVDF) was supplied by ARKEMA (Shenzhen, China). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) and solvents such as ethanol (A.R.), isopropyl alcohol (A.R.) and *N,N*-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co., Ltd (China).

### 2.2. Surface modification of BT nanoparticles

The BT nanoparticles were surface coated by TC-2 molecule via a solution method, which is schematically exhibited in Fig. 1. Firstly, the BT NPs were treated by H<sub>2</sub>O<sub>2</sub> for hydroxylation, and then the hydroxylated BT nanoparticles was added into isopropyl alcohol in beaker followed by an ultra-sonication and then stirred for 30 min at room temperature. Secondly, the TC-2 was dropwise added into the liquid mixture with stirring, after that the suspensions were continuously stirred at 70 °C for 4 h. Thirdly, the precipitates were centrifuged and washed with deionized water and ethanol for several times to remove the solvent and unreacted reagents. After drying at 70 °C for 24 h in oven, the modified BT nanoparticles were obtained.

### 2.3. Fabrication of nanocomposite films

The pristine BT or mBT nanoparticles and PVDF powder with fillers contents of 2, 4, 6, 8, 10 vol% were proportionally dispersed in DMF respectively. All the mixtures were processed according to the similar procedure that ultrasonication for 1 h, followed by stirring for 12 h, to form a stable suspension. The suspension was then cast onto glass plate with a laboratory casting equipment. The as-cast films were dried at 45 °C for 10 h for solvent volatilizing and were heated at 200 °C for 5 min and then immediately quenched in ice water. The final composite films were dried at 70 °C and peeled from the substrates, the thickness of which was about 15 μm.

### 2.4. Characterization

The morphologies of the mBT nanoparticles and corresponding element analysis were performed on field emission transmission electron microscopy (FETEM, Tecnai G2 F20, FEI, USA). Fourier-transform infrared spectroscopy (FT-IR) was measured with a spectrometer (Nexus 670, Nicolet, USA) over the range of 500–4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was characterized using an X-ray photoelectron spectrometer equipment (AXIS ULTRADLD, Kratos, USA) with Al K<sub>α</sub> radiation. Contact angles between pressed pellet of pristine BT or mBT NPs and DMF solution of PVDF were measured on the instrument (JC2000DF, Powereach, China) under ambient conditions by a sessile solution drop method. Reported data are averages of five measurements at different places on the sample. The cross-section morphologies of the BT/PVDF and mBT/PVDF nanocomposite films were observed by scanning electron microscope (SEM, JEM-7500F, JEOL Ltd., Japan). For electric measurement, copper electrodes of about 60 nm in thickness were sputtered on both sides of the nanocomposite films using a mask with 3 mm diameter eyelets. The dielectric permittivity and the loss of the nanocomposite films were measured by a precision impedance analyzer (HP 4294A, Agilent Technologies Inc., USA) at room temperature. Electric breakdown strength was tested by Dielectric Withstand Voltage Test (HT-50, Guilin Electrical Equipment Scientific Research Institute, China) at a ramping rate of 200 V/s and a limit current of 5 mA. The electric displacement-electric field (*D-E*) loops were measured at 10 Hz by a ferroelectric tester (Model TF Analyzer 1000, aixACCT, Germany) with a limited current of 1 mA.

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