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Full Length Article

High dielectric constant and energy density induced by the tunable TiO_2 interfacial buffer layer in PVDF nanocomposite contained with core–shell structured $TiO_2@BaTiO_3$ nanoparticles

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ABSTRACT

To realize application in high-capacity capacitors and portable electric devices, large energy density is eagerly desired for polymer-based nanocomposite. The core–shell structured nanofillers with inorganic buffer layer are recently supposed to be promising in improving the dielectric property of polymer nanocomposite. In this work, core–shell structured TO@BT nanoparticles with crystalline TiO_2 buffer layer coated on $BaTiO_3$ nanoparticle were fabricated via solution method and heat treatment. The thickness of the TO buffer layer can be tailored by modulating the additive amount of the titanate coupling agent in preparation process, and the apparent dielectric properties of nanocomposite are much related to the thickness of the TO layer. The relatively thin TO layer prefer to generate high polarization to increase dielectric constant while the relatively thick TO layer would rather to homogenize field to maintain breakdown strength. Simulation of electric field distribution in the interfacial region reveals the improving effect of the TO buffer layer on the dielectric properties of nanocomposite which accords with the experimental results well. The optimized nanoparticle TO@BT-2 with a mean thickness of 3–5 nm buffer layer of TO is effective in increasing both the ε and E_b in the PVDF composite film. The maximal discharged energy density of 8.78 J/cm^3 with high energy efficiency above 0.6 is obtained in TO@BT-2/PVDF nanocomposite with 2.5 vol% loading close to the breakdown strength of 380 kV/mm. The present study demonstrates the approach to optimize the structure of core–shell nanoparticles by modulating buffer layer and provides a new way to further enlarge energy density in polymer nanocomposite.

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 commonly used electron components both in small-scale devices and large-scale equipment. Compared with other energy storage devices, the dielectric capacitor possesses the advantages of all solid state, high operating voltage, low loss, and ultrafast charging-discharging rate, which made it the key role in the most advanced fields nowadays of portable electronic products, hybrid electric vehicles, smart grid and pulsed power sources [1]. As the core element in dielectric capacitor, the high performance dielectric materials currently have been eagerly pursued. Compared with the traditional ceramic dielectrics, the polymer-based dielectrics with excellent flexibility, easy processability and lower cost are the better choice for many of the potential applications [2–5]. However, the energy density of dielectric capacitors is about ten times lower than their electrochemical counterparts, which limits their practical application. High energy density is greatly desired for polymer-based dielectrics to reduce the size and weight of the dielectric capacitors, especially significant for the pulsed power system and electric vehicles [6,7].

The energy density (U_e) of dielectrics is expressed as $U_e = \int E dD$, where E and D are the applied electric field and electric displacement, and for dielectric materials, there is relationship of $D = \varepsilon E$, where ε is dielectric constant. Thus, the energy density is determined by both dielectric constant and breakdown strength (E_b). With the intrinsic high E_b, polymer is superior for high energy density candidate. However, the energy density of the polymer dielectrics, such as the representative commercial polymer dielectrics,

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biaxially oriented polypropylenes (BOPP), is only 2–3 J/cm^3 which are much limited by their low ε (usually 2–3) [8,9]. To increase the ε of polymer dielectrics, a practicable strategy is to introduce ceramic nanofillers with high ε into the polymer matrixes to fabricate nanocomposites [10–14]. In principle, large energy density could be achieved in the ceramic-polymer composites attribute to the combination of high dielectric constant of the fillers and high breakdown strength of the matrixes. But in fact, the increased ε induced by high loading ceramic nanofillers is always at the cost of decreased E_b due to the poor compatibility and the large contrast in permittivity between the inorganic fillers and organic matrixes. During the past decade, many efforts have been made to compensate the reduced E_b, the surface modification by organics on nanofillers is the most commonly adopted [15–26]. It has been widely recognized that the interfacial polarization is the primary source of the electric displacement in polymer-based nanocomposite [27], so the organic interfacial layer was not perfect because of the paradox between the ε and E_b. Although the coated layer of organic molecules is effective in enhancing the compatibility of fillers and suppressing the dielectric loss and breakdown in nanocomposite, it simultaneously weakens the interfacial polarization to decrease ε.

It has been figured out that the favorable construction of the interface in nanocomposite, including a moderate buffer layer to ease the dielectric contract between the fillers and matrix [28]. Recently, the contributions on the "interfacial engineering" develop the strategy to fabricate inorganic buffer layer at the external surface of the nanofillers, and the compounds with moderate permittivity fall in between ceramic fillers and polymer matrix have been the appropriate choice, such as SiO_2, Al_2O_3, TiO_2 [29,30]. For example, BTO nanoparticles with SiO_2 coating layer reduced the energy loss of the PVDF nanocomposites under high electric field via reducing the interfacial polarization and space charge polarization, and a low loading core–shell structured BTO@SiO_2 nanofibers reduced the energy loss in PVDF nanocomposites to obtain an energy density of 6.28 J/cm^3 at 3.3 MV/cm [31,32]. In another case, an insulating Al_2O_3 shell layer with moderate dielectric constant was created on the surfaces of BT nanofibers, and realized improved energy density in nanocomposite [33,34]. In the nanocomposites contained with core–shell fillers, the inorganic buffer layers with moderate permittivity confine the mobility of charge carriers to reduce leakage current and loss, and moreover, increased interfacial polarization can also be induced by the hierarchical interfaces [35–38].

The nanofillers coated with moderate buffer layer are promising in highly enhancing the energy density in flexible polymer-based nanocomposites. However, to fabricate more efficient nanofillers, the action of the intrinsic properties of the buffer layer on the dielectric performances of the nanocomposite is needed to be further studied. In this work, to investigate the effect of the thickness of the buffer layer on the dielectric properties in nanocomposite, a series of core–shell structured TiO_2@$BaTiO_3$ (TO@BT) nanoparticles (NPs) with crystalline TO layers coated onto BT nanoparticles were prepared. The thickness of the TO buffer layer is tunable that can be tailored by modulating the additive amount of titanate coupling agent in the preparation process. The dielectric properties of the PVDF-based nanocomposites contained TO@BT NPs with different thickness of TO layers were comparatively investigated. Both the simulated and experimental results demonstrate that the buffer layer increased the dielectric constant through inducing interfacial polarization. The relative thin layer was more effective in improving dielectric displacement while the relative thick one was beneficial for maintaining breakdown strength. The optimized TO@BT nanoparticles coated with a uniform TO buffer layer in 3–5 nm thickness highly enhanced the energy density and energy efficiency of the nanocomposite. The preparation and modulation on buffer layer in core–shell nanoparticles reported here provides an effective strategy to design and fabricate dielectric nanocomposites for high energy density application.

2. Experimental

2.1. Materials

Barium titanate ($BaTiO_3$, 99.5%) particles with an average size of 100 nm were purchased from Aladdin (China). Titanate coupling agent (Product NO. TC-2) was purchased from Taicang Chemical Co., Ltd (Anhui, China). Poly(vinylidene fluoride) (PVDF) was supplied by 3F (Shanghai, China). Hydrogen peroxide (H_2O_2, 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. Synthesis of core-shell nanoparticles

The core–shell structured TO@BT nanoparticles were prepared via a surface coating approach in solution and following heat treatment. The syntheses procedures are schematically exhibited in Fig. 1. First, 3 g of hydroxylated BT nanoparticles were added into 80 ml of isopropyl alcohol in a three-necked round-bottomed flask followed by an ultra-sonication and stirred for 30 min at room temperature. The liquid mixture was equally divided into 3 parts and the titanate coupling agent TC-2 was dropwise added with the target amount (0.1, 0.2, 0.3 ml), and then the suspensions were stirred for 1 h, and refluxed at 70 °C for 2 h. The precipitates of BT NPs coated with TC-2 organic molecule (BT-TC-2) were then centrifuged and washed with deionized water and ethanol for several times to remove the solvent and unreacted reagents (see Fig. S1 in Supplementary Information). At last, the cleaned powders were dried at 70 °C for 12 h and calcined at 800 °C for 3 h under ambient atmosphere to obtain crystallographic TO@BT nanoparticles.

2.3. Fabrication of nanocomposite films

For the fabrication of the TO@BT/PVDF nanocomposite films, the hydroxylated TO@BT nanoparticles and PVDF powder were proportionally dispersed in DMF by 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 10 μm (See Figs. S2 and S3 in Supplementary Information).

2.4. Characterization

The morphologies of the pristine BT, BT treated by TC-2, and TO@BT nanoparticles were observed by scanning electron microscopy (SEM, S-4700, Hitachi, Japan) and transmission electron microscope (TEM, H-800, Hitachi, Japan), respectively. The crystallographic TO layers coated on the BT nanoparticles and corresponding element analysis were performed on field emission transmission electron microscopy (FE-TEM, Tecnai G2 F20, FEI, USA). X-ray powder diffraction (XRD) instrument (X'Pert Powder PW3040/60, PANalytical, Holland) was used to identify the crystallinity of the TO layer. The appearances and the inside morphologies of the TO@BT/PVDF nanocomposite films were observed by SEM (JEM-7500F, JEOL Ltd., Japan). For electric measurement, copper electrodes of 60 nm in thickness were sputtered on both sides