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High discharged energy density of nanocomposites filled with double-layered core-shell nanoparticles by reducing space charge polarization

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ABSTRACT

Polymer-based nanocomposite capacitors for energy storage with high discharged energy density and charge-discharge efficiency are of great importance to modern electronic devices and electrical systems. Herein, the energy storage properties are improved by applying double-layered core-shell nanoparticles as fillers. The dopamine was adopted as the outermost layer to improve the dispersibility and compatibility between the fillers and matrix. The high resistance of SiO_2 works as a barrier to limit the movement of space charge over the $BaTiO_3$ (BT) surface when a high electric field is applied, leading to an enhancement of breakdown strength as well as a decreased space charge polarization, so that an enhancement of discharged energy density and charge-discharge efficiency are achieved. The SiO_2@BT/P(VDF-CTFE) also shows weaker frequency dependence, indicating the reduction of space charge polarization. A possible mechanism of reduced space charge polarization was proposed to explain the effects of SiO_2. This work demonstrates that constructing a core-shell structure with high resistance is an effective way to improve the energy properties of nanocomposite capacitors.

1. Introduction

With the rapid development of modern electronic devices and electrical systems, compact, reliable, and efficient energy storage devices are receiving tremendous attention and research interest [1]. In some specific fields, such as high-frequency inverters, medical defibrillators, pulsed power systems, hybrid electric vehicles, power factor corrections, and so on, an ultrahigh power density is required [2–5]. Among these existing energy storage devices, dielectric capacitors not only present a giant power density (MW/cm^3) but also deliver the highest operating voltage ($\sim 10^3$ V) and long cycle life time [6,7]. However, the most successful commercial dielectric capacitor (Biaxially-oriented Polypropylene, BOPP) at present only delivers a low discharged energy density of only ~ 2 J/cm^3 [8,9], which severely limits the application of dielectric capacitor due to its large volume.

It is known that the charge and discharge process of dielectric capacitors occur based on the polarization and depolarization of dielectric medium [10]. Generally, the stored energy density during polarization is determined by the following equation [11]:

$$U = \int_{D_{max}}^{0} E\mathrm{d}D \tag{1}$$

where U is the stored energy density, E and D are applied electric field and electric displacement, respectively. Nevertheless, not all stored energy can be released during depolarization, a part of energy transfers into Joule heat or some other kind of unusable energy. Therefore, the discharged energy density (U_e) is also affected by ferroelectric loss, which should be determined by the following equation:

$$U_e = \int_{D_{max}}^{P_r} E\mathrm{d}D \tag{2}$$

Namely, the discharged energy density is strongly associated with the applied electric field, maximum electric displacement, and remanent polarization. The maximum applied electric field before the failure of dielectric materials is termed as breakdown strength (E_b). Normally, polymer presents ultrahigh breakdown strength and low dielectric permittivity, while inorganic material, especially ferroelectric ceramic, is characterized by high electric displacement and low breakdown strength. Combining the merits of polymer and inorganic material, high breakdown strength and dielectric permittivity (electric

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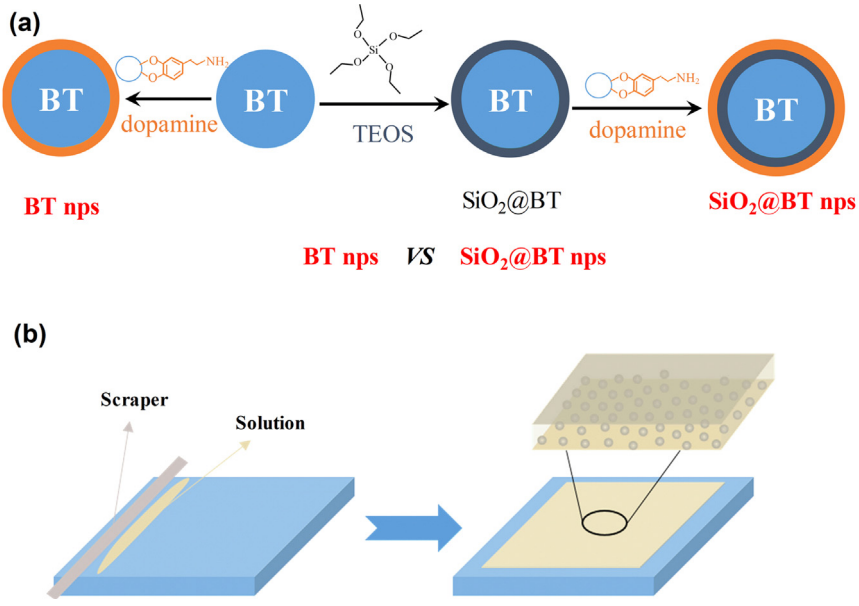

Fig. 1. The schematic diagrams of (a) synthesizing core-shell nps and (b) films making using solution tape-casting method.

displacement) can be obtained simultaneously in polymer-based nanocomposites. On this account, tremendous efforts have been devoted to designing the polymer-based nanocomposites filled with inorganic particles [12–18]. It also should be noted that some current work based on piezoelectric ceramics has achieved great progress [5,19].

Polarization plays an important role in the energy storage as shown in Eq. (2). In nanocomposites, polarization can be divided into four categories according to frequency range: electronic polarization, ionic polarization, dipole polarization, and space charge polarization (or interfacial polarization) [20,21]. Among them, space charge polarization is related to the macroscopic movement of charge carriers which are easily captured by defects, impurity, phase boundary, and so on. In nanocomposite, space charge polarization has significant effects on total polarization due to the interface where contains layers with different dielectric permittivity and resistance. However, these space charges need to move long distance, so the relaxation of these space charges occurs from seconds to hours. This feature determines that space charge polarization is not suitable for high voltage power and radio frequency applications [22,23].

Core-shell structured nanoparticles (nps) have been applied as fillers in nanocomposite capacitors due to their high compatibility, good dispersing ability, improved dielectric permittivity, high breakdown strength, and decreased dielectric loss [24–28]. But in fact, effects may vary for different core-shell nps. Zhang et al. prepared ZnO@Zn core-shell structure, the dielectric permittivity of Zn@ZnO/PVDF composites is obviously increased at relatively low content due to the duplex interfacial polarization induced by metal-semiconductor and semiconductor-insulator interface [29]. Rahimabady et al. coated a thin layer of TiO_2 on $BaTiO_3$ nanoparticles, it is confirmed that TiO_2 can simultaneously improve the dielectric constant and breakdown strength of the core-shell nanocomposite. The Maxwell-Wagner interfacial polarization originated from the interactive interfaces significantly improved the electric displacement. The TiO_2 interlayer also worked as an intermediate layer to reduce the local electric field resulting from the gradient of dielectric permittivity in core/shell $BaTiO_3$@TiO_2, which eventually gave a rise to the breakdown strength [30,31]. The striking work by Zhang et al. which obtained an ultrahigh discharged energy density, demonstrated the hierarchical interfaces inside the BTO@TO_nfs can induce a quite high interfacial polarization [3,32,33]. Using the same idea, a SiO_2 layer was coated on the surface of $BaTiO_3$ to obtain the filler with core-shell structure and incorporated it with a polymer to form a nanocomposite. Compared with the pure BT-filled nanocomposites, the nanocomposites filled with SiO_2@BT exhibit much lower energy loss, consequently, a higher discharged energy density with higher breakdown strength was achieved. These results demonstrate that SiO_2 layer is able to reduce energy loss by decreasing the interfacial polarization and space charge polarization, as a result, the discharged energy density increases tremendously [34–38]. Al_2O_3 was also proven to be a valid shell which can minimize the interfacial polarization [39]. This complexity of interface should be noted, the interface can improve the interfacial polarization in some situations, while reducing the interfacial polarization in another condition. Therefore, it is of great significance to figure out the real effects of the interface on space charge polarization.

In this work, core-shell structured SiO_2@BT nanoparticles (SiO_2@BT nps) and corresponding SiO_2@BT/P(VDF-CTFE) nanocomposite films were prepared, BT/P(VDF-CTFE) nanocomposite films were also obtained as contrast. To avoid the influence of fillers/matrix interface, dopamine was coated to encapsulate SiO_2@BT nps and BT nps. The breakdown strength and energy storage properties were evaluated. More importantly, different polarization can exist in nanocomposites at different frequency, interfacial polarization and space charge polarization need long time to relax [22]. Hence the frequency-dependent properties were also carefully tested to verify the reduced space charge polarization in SiO_2@BT/P(VDF-CTFE).

2. Experiment

2.1. Synthesis of SiO_2@BT core-shell nanoparticles

By a facile sol-gel method, a layer SiO_2 was coated on the surface of BT nps as presented in Fig. 1(a). First, 1 g commercially available BT nps (Aladdin Inc, 99.9%) with average particle sizes of ~ 100 nm were added to 80 mL absolute ethanol, followed by ultrasonication for 5 min with 40% power. Ethanol was added to make the total volume reach 500 mL, after that, 14 g ammonium hydroxide (Sinopharm Chemical Reagent Co. Ltd, 25–28%) and 1 g tetraethyl orthosilicate (TEOS, Aladdin Inc, 99.99%) were slowly added into the solution. The solution was magnetically stirred for 12 h at room temperature. The SiO_2 @BT nps were obtained after washing with deionized water until the pH reached ~ 7. At last, the dried SiO_2@BT nps were calcined at 800 °C for 2 h to remove the remaining crystal water.