Novel Core-Shell Structured Ironbark-Like TiO_2 as Fillers for Excellent Discharged Energy Density of Nanocomposites

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Abstract

The perpendicular orientation of nanowires to electric fields would greatly improve the breakdown strengths (E_b) of polymer-based nanocomposites, however, the relatively small polarization at small filler fraction, and thus the unsatisfactory discharged energy density (U_d), greatly restrict their further application. In this study, x vol.% TO@TO/PVDF nanocomposites with superior energy storage performances have been fabricated, where the ironbark-like TiO_2 fillers (TO@TO) with core-shell structures lead to greatly enhanced polarization and E_b simultaneously. The former is due to the coupling effects of the increased interfacial polarization, the latter is due to the enhanced path tortuosity of electric tree growing at small TO@TO fraction. Strikingly, an excellent U_d of 13.1 J/cm^3 was achieved in the 1.5 vol % TO@TO/PVDF nanocomposite at 383 MV/m, which is greatly increased by 220% compared with that of pure PVDF (5.98 J/cm^3). The primary results might provide a strategy to design and fabricate nanocomposites with satisfactory energy storage performances as well as the flexible and easy-processing ability at small filler fraction.

Introduction

Polymer dielectrics have become one of the best candidates for dielectric capacitors because of the instant response ability, high power density, and flexibility and easy processing [1-3]. The stored and released energy densities of dielectric capacitors are dependent on the polarization and depolarization of dielectrics, and thus the polarization and breakdown strength (E_b) are two determined effects on the energy storage performances of dielectrics [4, 5]. Owing to the small dielectric constant/polarization, the discharged energy density (U_d) of polymer dielectrics is significantly restricted [6]. To increase U_d , polymer-based nanocomposites are proposed because of the inherent ability of integrating superior polarizations of the ceramic and excellent E_b of the polymer matrix [7]. For example, paraelectric TiO_2 particles are filled into the ferroelectric PVDF matrix, in which a decreased remanent polarization (P_r) and an enhanced maximum polarization are simultaneously obtained [8]. However, the greatly enhanced polarization usually obtained at high fractions of the ceramic filler, generating filler aggregations, gaps, and other structural defects as a result of the poor incompatibility. The defects above could greatly reduce the E_b of polymer-based nanocomposites, resulting in an unsatisfactory U_d . Additionally, the high ceramic fraction also greatly reduces the flexibility and easy processing of polymer matrix, restricting the application of nanocomposite-based capacitors in the modern flexible electronic devices [9, 10].

It has been reported that the orientation of nanowires or nanosheets has great effects on the E_b of nanocomposites. For example, the perpendicular orientation of nanowires to electric fields is contributed to decreasing local electric fields and enhancing E_b of nanocomposites; While the parallel distribution of nanowires leads to a more concentrated electric field, and thus reduces the E_b of nanocomposites [5, 9]. For example, Pan *et al.* introducing low fraction NaNbO_3 nanowires into PVDF matrix greatly enhances the E_b of PVDF-based nanocomposites, which is mainly induced by the ordered traps and the enhanced

path tortuosity of electric tree growing [1]. Moreover, because of the smaller specific surface area and surface energy of nanowires and nanosheets than that of nanoparticles, the significantly decreased nanowire agglomeration and other defects are also contributed to enhancing E_b of nanowire-filled nanocomposites [7]. Although low nanowire fraction would increase the E_b of nanocomposites to some extent, the remaining small dielectric constant/polarization are also restricted their practical applications due to the unsatisfactory U_d [8, 11]. For example, the small U_d (6.4 J/cm³) of the 2.5 vol % Ba_{0.6}Sr_{0.4}TiO₃ nanowire-filled nanocomposite is mainly caused by the unsatisfactory polarization [12]. By the way, high nanowire fraction would increase the dielectric constant/polarization of nanocomposites, however, a greatly reduced E_b might be induced by the formation of connected networks and the growth of breakdown phase. Therefore, how to simultaneously increase the dielectric constant/polarization and E_b is imperative for improving the U_d of nanocomposites.

Based on the improved E_b of nanowire-filled nanocomposites, designing special structured nanofillers containing the advantages of nanowires might help to increase the polarization and E_b simultaneously. For example, Li *et al.* reported that the interfacial polarization caused by accumulated charges at the ceramic/polymer interfaces, which is proportional to the interfacial areas, could be beneficial in the corresponding polarization increase [13]. Along this line, the increased polarization mainly related to the interfacial polarization might be achieved via increasing the interfacial polarizations/areas, which could be realized through the strategy for interfacial design, such as adsorption, star-like polymer, core-shell structure and so on [14]. For example, Hu *et al.* reported a BaTiO₃@TiO₂ core-shell structure by coating the TiO₂ shell onto BaTiO₃ nanoparticles, where more charges would be accumulated at the interfacial region to increase the interfacial polarizations of nanocomposites, resulting in an excellent energy storage performance [15]. Therefore, interfacial design, for example, introducing a rough structure onto nanowires, might be an access path to further increase the polarization and E_b of nanocomposites simultaneously, where a satisfactory energy storage performance might be expected.

Taking all the above into consideration, in this study, the ironbark-like TiO₂ fillers (TO@TO, Fig. 1) with core-shell structure were prepared by decorating plicate TiO₂ (p-TO) onto TiO₂ nanowires (TO NWs). The experimental and simulation results show that the ironbark-like TO@TO nanofillers are not only able to increase the E_b and polarization of nanocomposites by utilizing the dielectric anisotropy of the TO NWs [9], but also able to greatly increase the interfacial polarization due to the coated p-TO, leading to a simultaneously enhanced polarization and E_b at small TO@TO fractions. The primary results prove that the x vol.% TO@TO/PVDF nanocomposite films, where x represents the volume fraction of TO@TO, deliver excellent U_d because of simultaneously enhanced polarization and E_b . For example, the 1.5 vol.% TO@TO/PVDF nanocomposite film delivers an excellent performance with U_d of 13.1 J/cm³ and the efficiency (η) of 64% under 383 MV/m. The U_d of the 1.5 vol.% TO@TO/PVDF nanocomposite film is greatly increased by 220% and 368% compared with that of the pure PVDF (5.98 J/cm³ at 337 MV/m) and the commercial BOPP (3.56 J/cm³ at 600 MV/m), respectively [16].

Experimental

Materials

HCl (36–38%), deionized water and ethanol (AR 99.7%) were provided by Sinopharm Chemical Reagent Corporation, Poly (vinylidene fluoride) (PVDF) was produced by 3F Corporation, Shanghai, China. N, N-dimethylformamide (DMF, AR 99.5%), NaOH (electronic grade, 99.9%), titanium dioxide powder (99.8%, 5–10 nm, anatase), isopropyl alcohol (IPA, 99.8%), diethylenetriamine (DETA, 99%), and titanium (IV) isopropoxide (TIP, 95%) were offered by Aladdin Industrial Corporation, China. All chemicals were used as bought.

Preparation of TO NWs

According to previous reports [17, 18], TO NWs were prepared via hydrothermal. First, 1.15 g of TO powders were dissolved into 56 ml NaOH aqueous solution (10 M). After 0.5 h sonicated and magnetic stir, the as-obtained mixture was move to the autoclave (80 mL) for hydrothermal reaction (200 °C, 24 h). After washing, the as-prepared sodium titanate nanowires were soaked in HCL solution (0.2 M) for 4 h to obtain $\text{H}_2\text{Ti}_3\text{O}_7$ NWs, which were then collected and heat treated at 400 °C for 3 h to obtain TO NWs.

Preparation of ironbark-like TO@TO

The ironbark-like TO@TO was synthesized according to the previous literature [11]. First, the TO NWs (0.08 g) were dissolved into 40 mL isopropanol with 0.5 h magnetic stirring, and then 0.06 mL DETA is added. Subsequently, the mixed solution of TIP (4 mL) and isopropanol (20 ml) was dropwise added. Finally, the dispersion was transferred into the autoclave (100 ml) for hydrothermal reaction (200 °C, 24 h) to obtain the TO@TO.

Preparation of x vol.% TO@TO/PVDF nanocomposite films.

First, various fractions of TO@TO were dispersed in DMF with 1 h sonicating and 2 h vigorously stirring to form a homogeneous mixture. After that, 0.5 g PVDF was added to the above mixture and stirred for another 12 h. The x vol.% TO@TO/PVDF nanocomposite films were fabricated through solution casting as previously reported [4], whose thicknesses were carefully controlled to nearly 12 μm as evidenced by the following SEM.

Characterization

The morphology and phase structure of TO NWs, ironbark-like TO@TO, and cross-section images of x vol.% TO@TO/PVDF nanocomposites were conducted by SEM (SU-70, Hitachi) and XRD (D8 Advance, Bruker), respectively. Prior to the electrical measurements, Au electrodes (2 mm) were sprayed via a sputter coater (Cressington Scientific Instruments, UK). Additionally, the dielectric properties of nanocomposites from 500 to 10^6 Hz were performed on the impedance analyzer (Agilent 4294A). The P – E (100 Hz) and I – V loops were recorded on a ferroelectric test system (Radiant Technologies, USA).

Results And Discussion

The XRD patterns and SEM images of TO NWs, ironbark-like TO@TO and the 1.5 vol.% TO@TO/PVDF nanocomposite are shown in Fig. 2. It could be clearly observed from Fig. 2a that the diffraction peaks of TO NWs could be clearly indexed according to the standard PCPDF (No. #35-0088). Moreover, Fig. 2b show that most TO NWs are monodisperse with high aspect ratios and smooth surfaces. Meanwhile, the characteristic peaks of TO for ironbark-like TO@TO become vaguely (Fig. 2a), due to the insufficient crystallization of the outside p-TO shells with the metastable monoclinic $\text{TiO}_2(\text{B})$ [19], which is in good agreement with previous reports because of the low temperature treatment ($< 300\text{ }^\circ\text{C}$) [20, 21]. Although the average diameter of TO@TO increase from 218 nm to 480 nm after p-TO shells coated onto the TO NWs (Fig. S1), the core-shell ironbark-like TO@TO nanofillers are still monodisperse and show a successive and rough surface with an average shell-layer of 131 nm (Fig. 2c), which could greatly enhance the corresponding surface areas [11], and thus an enhanced interfacial polarization is highly expected. Additionally, the continuous interfaces rather than random adsorption interfaces (inset in Fig. 2c) suggest the 'two-phase' distortion is small at the interfaces between TO NWs and p-TO shell, which might greatly decrease the defect formation at the interfaces [22], and thus a low leakage current and high E_b might be anticipated. Although the crystallization of annealed TO@TO ($450\text{ }^\circ\text{C}$ treatment, Fig. S2) is greatly improved due to the phase transition from metastable monoclinic $\text{TiO}_2(\text{B})$ to anatase TO [21], the collapsed p-TO shell (Fig. S2) might significantly decrease the surface area of ironbark-like TO@TO, therefore, the unannealed ironbark-like TO@TO nanofillers are used in the following study. Furthermore, expect for the FTO diffraction peaks, the diffraction peaks of the 1.5 vol.% TO@TO/PVDF nanocomposite (Fig. 2a) at $2\theta = 17.9^\circ$, 18.5° and 20.1° could be indexed to the non-polar α and γ phases of PVDF respectively, in which the ferroelectric phase (β phase) is not clearly observed [23]. By the way, the relatively high content of non-phases in the nanocomposites might lead to lower energy loss and higher discharged energy density [24]. Meanwhile, no diffraction peaks of TO in the XRD pattern of the 1.5 vol.% TO@TO/PVDF nanocomposite are mainly caused by small ironbark-like TO@TO fraction, which is helpful to maintain the flexibility and easy processing of polymer matrix. Additionally, the freeze-fractured cross-sectional images of pure PVDF and x vol.% TO@TO/PVDF nanocomposite ($x=0.5, 1, 1.5$ and 2) are characterized to observe its microscopic homogeneity. As shown in Fig. 2d and Fig. S3, the ironbark-like TO@TO nanofillers are uniformly distributed across the polymers, and the fracture of TO@TO (Fig. 2d and Fig. S3) suggests its superior adhesion ability with polymers. Moreover, almost no pores, cracks, and defects between the PVDF matrix and the TO@TO filler could be observed, which is beneficial in decreasing leakage currents and enhancing E_b of nanocomposites.

The dielectric performances of x vol.% TO@TO/PVDF nanocomposites as a function of frequency are presented in Fig. 3a and Fig. 3b. As shown in Fig. 3a, the dielectric constants of pure PVDF and x vol.% TO@TO/PVDF nanocomposite films gradually decrease with the frequency increase, which is mainly induced by Maxwell–Wagner–Sillars effects [25].

More importantly, as TO@TO fraction increases, the dielectric constants of the pure PVDF film and x vol.% TO@TO/PVDF nanocomposite films increase from 10 to 20 at 1 kHz due to the high dielectric constant of TO [8, 26]. Additionally, the dielectric constant of the 1.5 vol.% TO@TO/PVDF nanocomposite film (16 at 1 kHz, Fig. 3a) is much higher than that of the 1.5 vol.% TO/PVDF nanocomposite film (13 at 1 kHz, Fig. S4a). The enhanced dielectric constant at the same fraction could be induced by high interfacial polarizations of 1.5 vol.% TO@TO/PVDF nanocomposites as expected. Moreover, although the dielectric loss of the 1.5 vol.% TO/PVDF and x vol.% TO@TO/PVDF nanocomposites increases slightly with the dielectric constant increase, all films show a small dielectric loss, especially at low frequencies (Fig. 3b and Fig. S4b). For example, the dielectric losses of all films are smaller than 0.05 at 1 kHz (Fig. 3b and Fig. S4b). In one word, the x vol.% TO@TO/PVDF nanocomposites exhibit a greatly enhanced dielectric constant and a slightly increased dielectric loss in comparison with the pure PVDF film, which might be highly beneficial in facilitating their energy storage performances.

In the view of energy storage, E_b is another key factor for dielectrics [1]. The representative E_b values of the pure PVDF and x vol.% TO@TO/PVDF nanocomposite films are investigated via the Weibull distribution (Fig. 3c), where high Weibull modulus (β) means a high reliability [27]. The relatively high β value (> 15) of the x vol.% TO@TO/PVDF nanocomposites (Fig. 3c) suggests the high reliability of the corresponding E_b of nanocomposites. Additionally, as shown in Fig. 3c and Fig. S4c, the E_b values of the 1.5 vol.% TO/PVDF and x vol.% TO@TO/PVDF ($x = 0.5 - 1.5$) nanocomposites are significantly higher than that of the pure PVDF (335 MV/m). The increased E_b could be mainly attributed to the perpendicular orientation of ironbark-like TO@TO and TO NWs to the external electric field, which helps to enhance the path tortuosity of the electrical tree growth during breakdown [18]. Moreover, the outside p-TO shell with metastable phase might show smaller dielectric constant than that of TO with anatase phase due to the insufficient crystallization, which could further alleviate the distortion of electric field in the TO@TO/PVDF nanocomposites, and therefore the 1.5 vol.% TO@TO/PVDF could possess a higher E_b (388 MV/m, Fig. 3c) than that of 1.5 vol.% TO@PVDF (364 MV/m, Fig. S4c). By the way, with further increase the TO@TO fraction ($x = 2$), the structural imperfections, such as pores and cracks are inevitably formed [28], leading to a decreased E_b of 334 MV/m for the 2 vol.% TO@TO/PVDF nanocomposite (Fig. 3c).

To further clarify the effects of ironbark-like TO@TO on electrical conductions of nanocomposites, the leakage currents of the PVDF and x vol.% TO@TO/PVDF nanocomposites are recorded. Fig. 3d shows the leakage currents of the PVDF and x vol.% TO@TO/PVDF nanocomposites lie within the range of 10^{-9} to 10^{-6} A/cm², indicating the prepared films have excellent quality. Moreover, the leakage current densities of x vol.% TO@TO/PVDF nanocomposites exhibit a first decrease and then increase tendency with TO@TO fraction increase as a result of the paradox between TO@TO orientation and structural imperfection formation, which agrees with the E_b result above. Furthermore, compared with the 1.5 vol.% TO/PVDF nanocomposite (Fig. S4d), the small leakage current density of the 1.5 vol.% TO@TO/PVDF nanocomposite indicates that the p-TO outside TO@TO might act as effective barriers to resist space-charge migrations, and thus to reduce leakage currents [3]. Considering all the above, the greatly enhanced U_d might be realized in the x vol.% TO@TO/PVDF nanocomposites.

It could be found from the typical P - E curves (Fig. 4a and Fig. S5) that the polarizations of x vol.% TO@TO/PVDF nanocomposites enhance with TO@TO fraction increase at the same electric field, which are agreement with the dielectric constant variations. By the way, the high polarization of the 1.5 vol.% TO@TO/PVDF nanocomposite (Fig. S5) compared with that of the 1.5 vol.% TO/PVDF nanocomposite (Fig. S6) at the same electric field is also mainly caused by the strong interfacial polarization as expected. More importantly, the variation of polarization difference ($P_m - P_r$) and E_b , both of which are the two key effects on U_d , are extracted from P - E curves and shown in Fig. 4b. First of all, the $P_m - P_r$ values of x vol.% TO@TO/PVDF nanocomposites (Fig. 4b) increase from $4.5 \mu\text{C}/\text{cm}^2$ ($x = 0$) to $8.0 \mu\text{C}/\text{cm}^2$ ($x = 1.5$ and 2), suggesting the TO@TO have great contribution to polarization increase. Subsequently, in accordance with the Weibull distribution, the E_b of x vol.% TO@TO/PVDF nanocomposites (Fig. 4b) increase first from 335 MV/m ($x = 0$) to 383 MV/m ($x = 1.5$), and then decrease to 334 MV/m ($x = 2$) with TO@TO fraction increase. Therefore, the 1.5 vol.% TO@TO/PVDF nanocomposite exhibits both highest $P_m - P_r$ ($8.0 \mu\text{C}/\text{cm}^2$) and E_b (383 MV/m), where a superior U_d might be achieved in this case.

For the sake of understanding the mechanism of interfacial polarization, the related distribution of space charge density in the pure PVDF, TO/PVDF and TO@TO/PVDF nanocomposites are simulated, respectively. The 2-dimensional simulation results are presented in Fig. 5, in which the color scale bars indicate the magnitude of the logarithmic of the absolute values of the space charge density. As shown in Fig. 5a, the space charge density ($-13.32 \text{ C}/\text{m}^3$) is hardly observable in the pure PVDF due to the nature of homogeneous PVDF [29]. In contrast, owing to the introduction of nanofillers into PVDF matrix, the distributions of space charge density in TO/PVDF ($-7.53 \text{ C}/\text{m}^3$) and TO@TO/PVDF ($-5.90 \text{ C}/\text{m}^3$) nanocomposites are much more different from the pure PVDF, as shown in Fig. 5b and Fig. 5c. Additionally, compared with the TO/PVDF, the stronger space charge density in TO@TO/PVDF is mainly attributed to the following two reasons: (i) the enhanced specific surface area after p-TO shell coated onto the TO core, which could provide much more interface between nanofillers and matrix, and therefore a stronger space charge density might be obtained [15]; (ii) owing to the insufficient crystallization of p-TO shell with a metastable phase, some defects could be existed in the TO@TO surface. These defects could serve as traps for space charges under electric field, which could further enhance the space charge density in the TO@TO/PVDF [29]. The enhanced space charge density could further induce the improved interfacial polarization [11], which is further evidenced by the enhanced dielectric constant and polarization discussed previously [4]. Therefore, the interface effects (interface area and surface defects) of TO@TO core-shell structures could greatly enhance the dielectric constant and polarization of TO@TO/PVDF nanocomposites.

According to the P - E curves, the U_d and η of x vol% TO@TO/PVDF nanocomposites are calculated and presented in Fig. 6a and Fig. 6b, respectively. As expected, the 1.5 vol% TO@TO/PVDF nanocomposite delivers the highest U_d of $13.1 \text{ J}/\text{cm}^3$ at 383 MV/m (Fig. 6a) because of the simultaneously enhanced $P_m - P_r$ and E_b . The U_d ($13.1 \text{ J}/\text{cm}^3$) of the 1.5 vol% TO@TO/PVDF nanocomposite at 383 MV/m seems better than that of previous works [15, 26, 29], which is increased by 220%, 200% and 368% compared

with that of the PVDF film (5.98 J/cm³ at 337 MV/m) and the 1.5 vol.% TO/PVDF nanocomposite (6.3 J/cm³ at 370 MV/m, Fig. S7), and the commercial BOPP (3.56 J/cm³ at 600 MV/m), respectively. Moreover, with the U_d increase, the η of all nanocomposites still maintain a high level (> 60%), for example, the 1.5 vol.% TO@TO/PVDF nanocomposite still presents a high η of 64%. The remaining high η is mainly ascribed to linear dielectrics, restricted charge transfers and leakage currents of TO@TO [3]. Furthermore, it is worth noting that the simultaneously enhanced P_m - P_r , E_b and U_d at such a small TO@TO fraction (1.5 vol.%) are also highly desirable for practical applications due to the maintained superior flexibility and easy-processing of polymer matrix.

To further illustrate the superior energy storage performances of TO@TO-filled nanocomposites, recently reported U_d of PVDF-based nanocomposites with low filling fraction and low E_b (< 400 MV/m) have been summarized in Fig. 7. As shown in Fig. 7, the excellent U_d (13.1 J/cm³ at 383 MV/m) of the 1.5 vol.% TO@TO/PVDF nanocomposite is much superior than that of other reports [2, 9, 12, 15, 26, 27-37]. The benefits of using TO@TO may originate from several aspects. First, the TO NWs could greatly improve the E_b of nanocomposites at low filler fraction; Second, because of the large surface areas of p-TO, the interfacial polarization could be improved with a small filler fraction; Meanwhile, the outside p-TO shell is also benefit to restrict the electric tree growth and increase the E_b ; Finally, TO as a paraelectric ceramic might greatly reduce the P_r of the PVDF. Therefore, the introduction of well-designed ironbark-like TO@TO into polymer matrices with small filler fraction might possess the potential applications of energy storages.

Conclusions

In summary, the x vol.% TO@TO/PVDF nanocomposites with superior energy storage performances have been fabricated, where core-shell structured ironbark-like TO@TO leads to an enhanced P_m - P_r and E_b simultaneously at small TO@TO fraction. The 1.5 vol.% TO@TO/PVDF nanocomposite delivers the highest U_d of 13.1 J/cm³ at 383 MV/m, which is greatly increased by 220% and 368% compared with that of the pure PVDF (5.98 J/cm³ at 337 MV/m) and the commercial BOPP (3.56 J/cm³ at 600 MV/m). The present results prove that the introduction of well-designed core-structured filler will pave a new way to obtain polymer-based nanocomposites with excellent energy storage performances at low filler fraction, which is highly desirable to the practical applications.

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

Synthetic diagram for ironbark-like TiO₂ and x vol.% TO@TO/PVDF nanocomposite films

Figure 2

a XRD patterns of TO NWs, ironbark-like TO@TO and 1.5 vol.% TO@TO/PVDF nanocomposite, SEM images of b TO NWs, c ironbark-like TO@TO and d the cross-section image of the 1.5 vol.% TO@TO/PVDF nanocomposite

Figure 3

a Dielectric constant, b dielectric loss, c E_b , and d leakage currents of the PVDF and x vol.% TO@TO /PVDF (x = 0.5, 1, 1.5 and 2) nanocomposite films.

Figure 4

a P-E curves b variation of Pm-Pr and Eb of pure PVDF and x vol.% TO@TO/PVDF nanocomposite films

Figure 5

The 2-dimensional simulation for logarithmic absolute values of the space charge density distributed at the a pure PVDF, b TO/PVDF and c TO@TO/PVDF nanocomposite films interfacial region, insert is the statistical result of space charge density.

Figure 6

a Ud, and b η of pure PVDF and x vol.% TO@TO/PVDF nanocomposite films

Figure 7

Contrastive analysis of energy storage performances for representative polymer-based nanocomposites

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