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# Significantly enhanced energy storage density for poly(vinylidene fluoride) composites by induced PDA-coated $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ nanofibers

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## EXPERIMENTAL AND METHODS

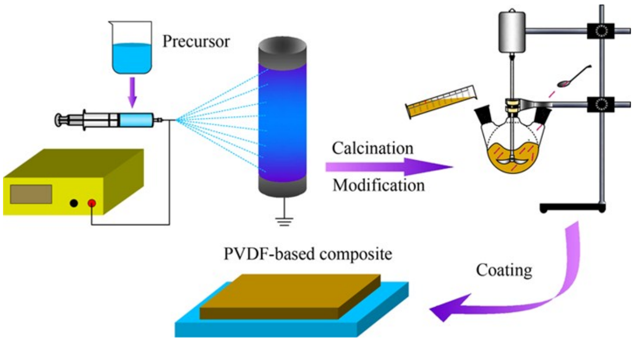

**Fig. S1** The preparation process of nanocomposite.

### Preparation of BT nanofibers

The typical procedures for the preparation of BT NFs were carried out as follows. First, 3.8 ml of ethanol, 9.1 ml of acetic acid were added into a 25.0 ml beaker to form a solution. Then, 2.17 g of $Ba(OH)_2$•$8H_2O$ and 2.48 g of $Ti(OCH_2CH_2CH_2CH_3)_4$ were added into the above solution in sequence interval half an hour, respectively. After all the reaction elements were fully mixed, 0.80 g of PVP was dissolved into the solution and stirring for more than 24 hours. Later, the precursor was electrospun into the positive and negative voltage was12.0 kV and the injection rate was 0.20 ml/min. Next, the textile was heated to 800 °C for 2 hours with a heating rate of 2 °C per min to obtain BT NFs.

**Preparation of CCTO nanofibers**

The typical procedures for the preparation of CCTO NFs were carried out as follows. Firstly, 2.6 mmol of $(CH_3COO)_2Cu$•$H_2O$, 0.9 mmol $Ca(NO)_2$•$4H_2O$ and 1.2 ml $C_{16}H_{36}O_4Ti$ were mixed with 0.4 ml acetic acid and 20.0 ml ethanol in a glove box to form a solution in sequence interval half an hour, respectively. After 30 min stirring, PVP was added to the solution, followed by stirring for 6 h to get a viscous green liquid, which was a precursor solution for electrospinning. Then, the precursor solution was subsequently electrospun with a feeding rate of 0.25 ml/min through a needle (its diameter was 2.3 mm) at 22.5 kV. The distance between the needle tip and collector (a piece of flat aluminium foil) was 18.0 cm. The obtained fibers on the collector were dried at 60°C for 120 min. In order to obtain pure phase nanofibers, the pristine NFs were further calcined at 400 °C for 1 h, then re-calcined at 950 °C for 1 h in oven at a heating rate of 2 °C/min, followed by cooling to room temperature, to obtain CCTO fibers.

## Preparation of $TiO_2$ nanofibers

The typical procedures for the preparation of $TiO_2$ fibers were carried out as follows. First, 27.0 ml of ethanol and 3.00 g of PVP were added into a 50.0 ml beaker to form a solution (A) by stirring for 6 h. Then, 3.0 ml of tetrabutyl titanate, 7.0 ml of ethanol and 6.0 ml of acetic acid were added into a 25.0 ml beaker to form a solution (B) by stirring for 1 h. Later, the solution (A) and the solution (B) were fully mixed, this was a precursor solution for electro spinning. Then, the precursor solution was subsequently electrospun using standard electrospinning equipment fabricated. The obtained fibers on the collector were dried at crystallizing it by sintering at 500 °C for 4 h, followed by cooling to room temperature to obtain $TiO_2$ fibers.

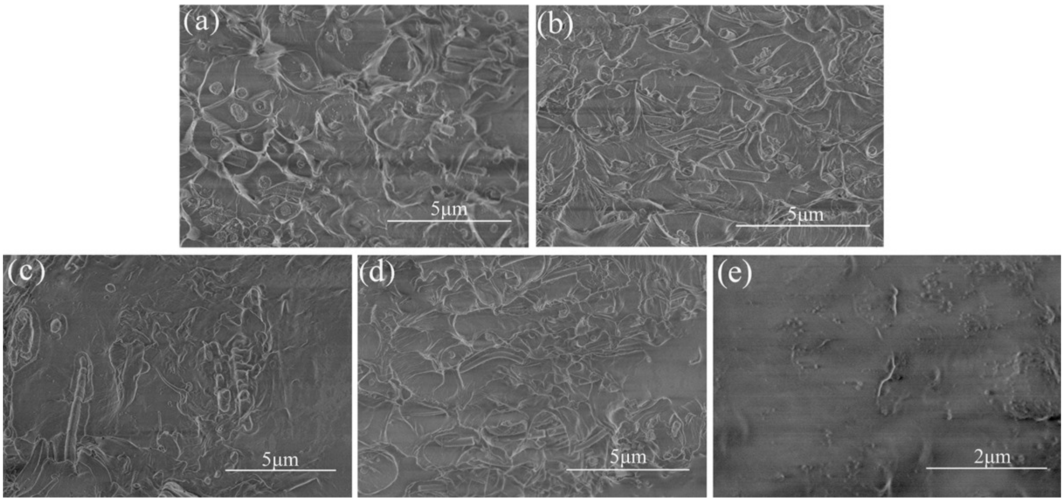

**Fig. S2** The SEM images of five composites with the same filling of 5 vol.%. (a)BZT-BCT NFs/PVDF, (b)BT NFs/PVDF, (c)CCTO NFs/PVDF, (d)$TiO_2$ NFs/PVDF, (e)BT NPs/PVDF.

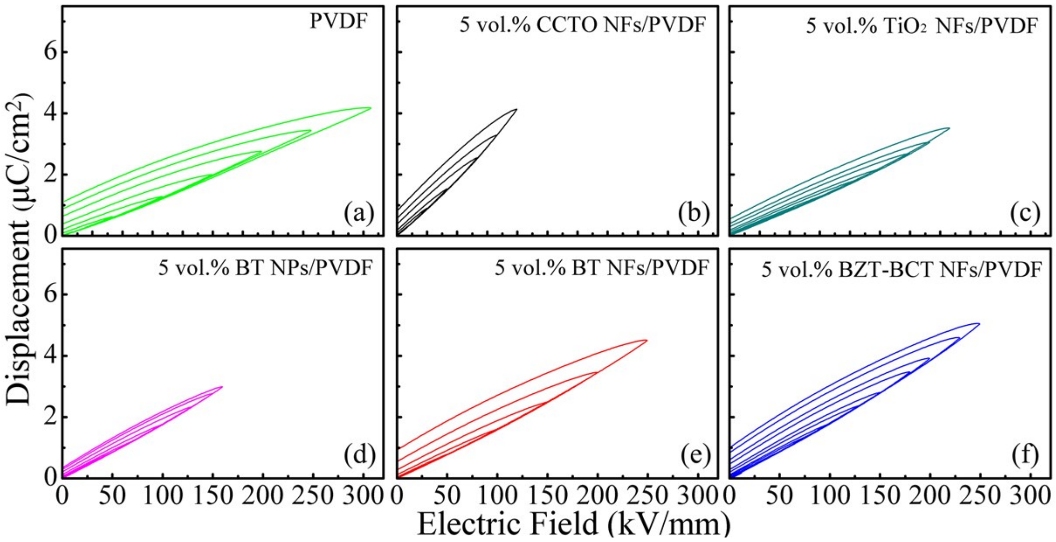

**Fig. S3** Hysteresis loops of the PVDF-based composites with 5 vol.% fillers. (a)PVDF, (b)CCTO NFs/PVDF, (c)$TiO_2$/PVDF, (d)BT NPs/PVDF, (e)BT NFs/PVDF, (f)BZT-BCT NFs/PVDF.

From shown in Fig. S3, the electric displacement of PVDF was 4.2 μC/cm$^2$ at 310 kV/mm.

**Characteristic of breakdown strength for composites**

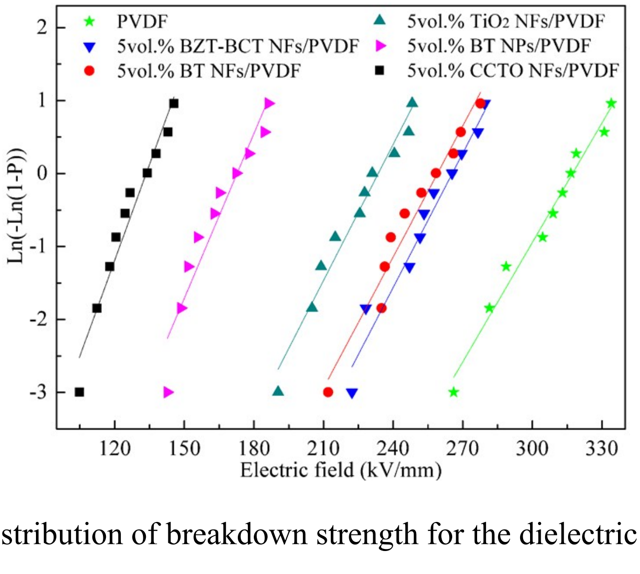

**Fig. S4** Weibull distribution of breakdown strength for the dielectric materials. 5 vol.% CCTO NFs/PVDF, 5 vol.% $TiO_2$ NFs/PVDF, 5 vol.% BT NPs/PVDF, 5 vol.% BT NFs/PVDF, 5 vol.% BZT-BCT NFs/PVDF composite and PVDF.

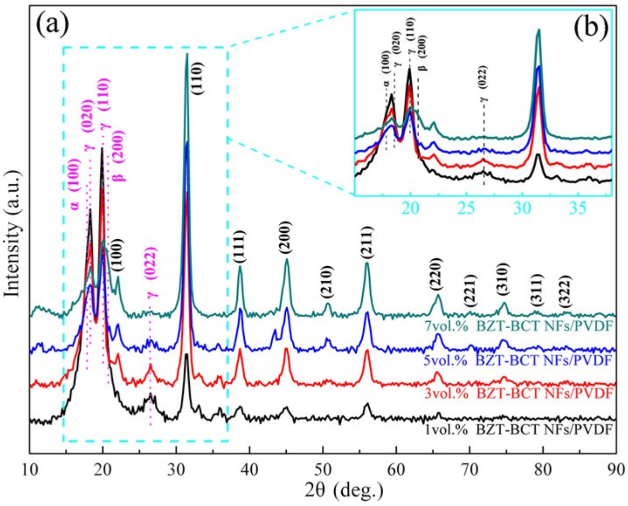

**Fig. S5** XRD patterns of the *x* vol.% BZT-BCT NFs / PVDF composite (*x* = 1, 3, 5 and 7). (a) 2θ=10-90 °, (b) 2θ=15-38 °.

## Characteristic of breakdown strength for the *x* vol.% BZT-BCT NFs/PVDF composite (*x*=0, 1, 3, 5 and 7)

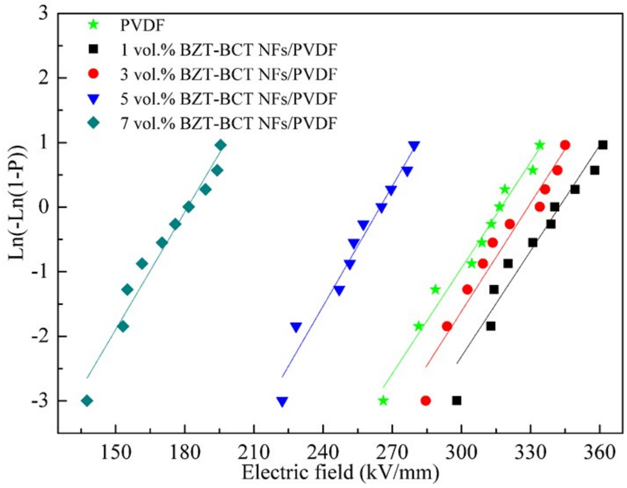

**Fig. S6** Weibull distribution of the breakdown strength for the *x* vol.% BZT-BCT NFs/PVDF composite (*x*=0, 1, 3, 5 and 7)

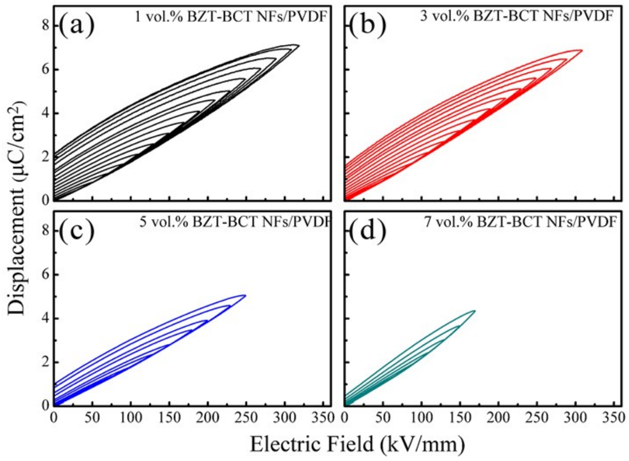

**Fig. S7** The *D*-*E* of the *x* vol.% BZT-BCT NFs/PVDF composite (*x* = 1, 3, 5 and 7). (a) *x*=1, (b) *x*=3, (c) *x*=5, (d) *x*=7.

**Table S1** Comparison of electric field strength (*E*) and discharged energy density ($U_e$) of this work and the related dielectric composites reported in previous literatures

| Samples | *E* (kV/mm) | $U_e$ (J/cm$^3$) | η | Ref. |
|---|---|---|---|---|
| 2.1 vol.% BCZT NFs/PVDF | 340 | 5.9 | 0.53 | 2017[13] |
| 2.1 vol.% BCZT@PATP NFs/PVDF | 380 | 8.2 | 0.64 | 2017[13] |
| 2.5 vol.% BST NF-APS/PVDF | 380 | 6.8 | 0.60 | 2014[15] |
| 5 vol.% BST NF-APS/PVDF | 340 | 6.0 | 0.48 | 2014[15] |
| 7 vol.% BST NF-APS/PVDF | 310 | 5.2 | 0.44 | 2014[15] |
| BT/PVDF | 183 | 4.2 | 0.59 | 2015[16] |
| F3C2BT/PVDF | 228 | 3.8 | 0.40 | 2015[16] |
| F4C2BT/PVDF | 242 | 4.5 | 0.44 | 2015[16] |
| F4CBT/PVDF | 272 | 6.5 | 0.56 | 2015[16] |
| C2BT/PVDF | 288 | 6.7 | 0.53 | 2015[16] |
| BST/P(VDF-HFP) | 200 | 2.2 | 0.55 | 2015[17] |
| PPFPA@BST/P(VDF-HFP) | 200 | 2.2 | 0.58 | 2015[17] |
| 2.5 vol.% BST NF/PVDF | 300 | 2.9 | 0.40 | 2015[18] |
| 2.5 vol.% F-BST NF/PVDF | 390 | 7.5 | 0.60 | 2015[18] |
| 7.5 vol.% F-BST NF/PVDF | 310 | 6.3 | 0.45 | 2015[18] |
| 3.6 vol. % BT@AO-DA NFs/PVDF | 420 | 10.6 | 0.66 | 2017[19] |
| 8 vol. % BT@AO-DA NFs/PVDF | 300 | 6.5 | 0.53 | 2017[19] |
| Epoxy | 100 | 0.1 | 0.42 | 2017[20] |
| 2.7 vol.% h-BN-RGO/epoxy | 100 | 0.2 | 0.77 | 2017[20] |

| | | | | |
|---|---|---|---|---|
| 18 vol.% h-BN-RGO/epoxy | 100 | 0.2 | 0.58 | 2017[20] |
| 26 vol.% h-BN-RGO/epoxy | 100 | 0.2 | 0.41 | 2017[20] |
| D-h-BT/PVDF | 260 | 4.2 | 0.49 | 2014[24] |
| D-BT/PVDF | 249 | 2.9 | 0.48 | 2014[24] |
| PVDF | 249 | 2.7 | 0.80 | 2014[24] |
| BOPP | 400 | 1.5 | 0.88 | 2017[26] |
| PMMA | 250 | 1.2 | 0.84 | 2017[26] |
| 12 wt% BNNS/PMMA | 400 | 3.5 | 0.85 | 2017[26] |
| 3.6 vol.% BT nfs/PVDF | 350 | 7.6 | 0.63 | 2016[28] |
| 3.6 vol.% BT@Al$_2$O$_3$ nfs/PVDF | 400 | 12.2 | 0.65 | 2016[28] |
| 10 vol. % sg$_8$CCTO/PC | 8 | 0.02 | 0.73 | 2015[53] |
| 10 vol. % TiO$_2$/P(VDF-CTFE) | 180 | 4.7 | - | 2009[54] |
| 0.4 vol.% MoS$_2$ flower/PVDF | 200 | 2.4 | 0.57 | 2016[55] |
| 0.4 vol.% MoS$_2$ cluster/PVDF | 200 | 1.9 | 0.63 | 2016[55] |
| 5 vol.% CCTO NFs/PVDF | 120 | 1.7 | 0.66 | this work |
| 5 vol.% TiO$_2$ NFs/PVDF | 220 | 2.9 | 0.71 | this work |
| 5 vol.% BT NPs/PVDF | 160 | 1.8 | 0.76 | this work |
| 5 vol.% BT NFs/PVDF | 250 | 4.6 | 0.63 | this work |
| 5 vol.% BZT-BCT NFs/PVDF | 250 | 5.6 | 0.64 | this work |
| 3 vol.% BZT-BCT NFs/PVDF | 310 | 7.9 | 0.58 | this work |

Table S3 shows the comparison of electric field strength (*E*) and discharged energy density ($U_e$) of this work and the related dielectric composites reported in previous literatures.