

## Supporting Information

### **Effect of the Coverage Level of Carboxylic Acids as Modifier for BT Nanoparticles on the Performance of Barium Titanate/Poly(vinylidene fluoride) Nanocomposites for Energy Storage Applications**

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- **DSC Curves.**
  
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■ DSC Curves:

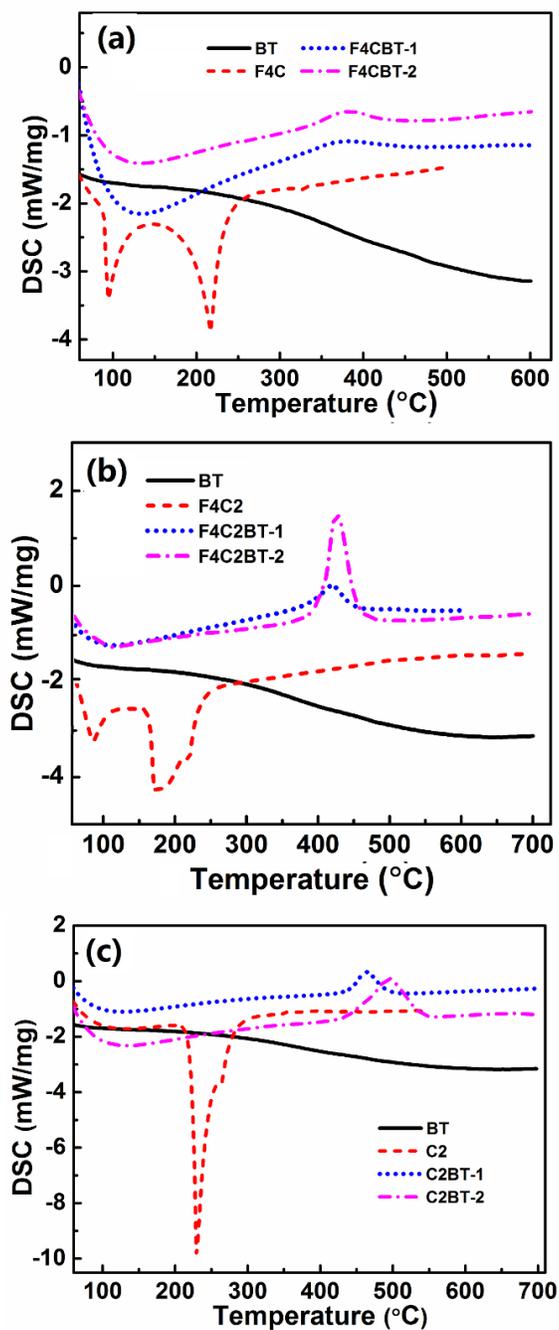


Figure S1. DSC curves of the modifiers, BT, and mBT nanoparticles with different surface coverage level, the modifiers are: (a) F4C, (b) F4C2, (c) C2.

## ■ BET (Brunauer-Emmett-Teller) Adsorption Isotherms Method

The surface areas (S) of BT nanoparticles were characterized by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. The BET method is the most widely used procedure for the determination of the surface area of solid materials and involves the use of BET equation:

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left[ \frac{P}{P_0} \right] \quad (S1)$$

$W$  is the weight of gas adsorbed at a relative pressure  $P/P_0$ ,  $W_m$  is the weight of adsorbate constituting a monolayer of surface coverage,  $C$  is the BET constant and related to the energy of adsorption in the first adsorbed layer and consequently its value is an magnitude of the adsorbent/adsorbate interactions. The BET equation requires a linear plot of  $\frac{1}{W((P_0/P)-1)}$  versus  $\frac{P}{P_0}$ , which for most solids using nitrogen as adsorbate, and is restricted to a limited region in the  $P/P_0$  range of 0.05 to 0.35.

## ■ Degree of Crystallinity

Crystallization studies were conducted by means of DSC (NETZSCH STA449C). The samples were analyzed between 50 and 200 °C at a heating or cooling rate of 10 °C/min. The DSC curves of the nanocomposites are shown in the Figure S2. The degree of crystallinity is defined as the ratio between the melting enthalpy of the material under study and the melting enthalpy of totally crystalline, which was calculated by equation (2):

$$X_c^m = \frac{\Delta H_m}{\Delta H_{100}} \quad (\text{S2})$$

where  $X_c^m$  is the degree of crystallinity,  $\Delta H_m$  is the melting enthalpy of the sample and  $\Delta H_{100}$  is the melting enthalpy for a 100% crystalline sample.<sup>1</sup> The melting enthalpy value for 100% crystalline PVDF is 102.7 J/g.<sup>2</sup> The results are shown in Table S1.

The results show that the introduction of the modifier will reduce the degree of crystallinity of the PVDF in the nanocomposites, but when the coverage level of the modifier increasing, the degree of crystallinity of the PVDF is also increase, which can be interpreted as the addition of modifier interrupts the crystallization and increases the fraction of free volume of amorphous region. However, when the coverage level of the modifier is increased, it is converted from a small amount of impurities to functional groups which can limit the movement of the polymer chains.

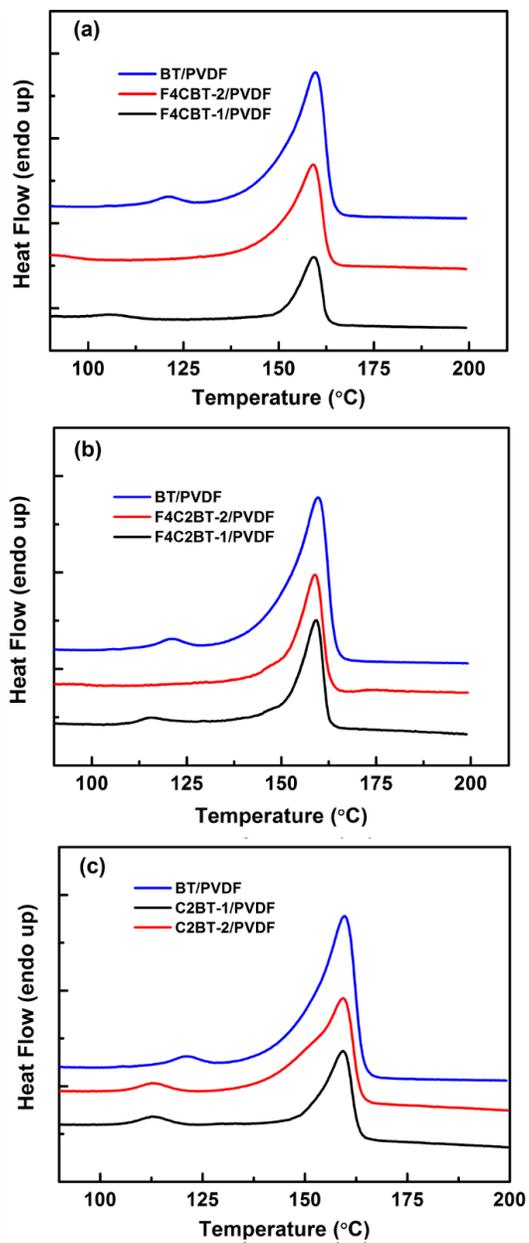


Figure S2. DSC heating curves of BT/PVDF and mBT/PVDF nanocomposites.

Table S1. Data from Differential Scanning Calorimetry (DSC) of the Nanocomposites

filler	$T_m$ (°C)	$\Delta H_m$ (J/g)	$X_c^m$ (%)
BT	159.6	22.7	22.0
F4CBT-1	159.1	9.8	9.4
F4CBT-2	159.1	15.1	14.6
F4C2BT-1	159.1	10.5	10.1
F4C2BT-2	158.7	11.7	11.3
C2BT-1	159.1	11.2	10.8
C2BT-2	159.1	15.5	15.0

■ **The Increase Rate of Breakdown Strength:**

$$\Delta E_b / E_b = \frac{E_{b\text{modified}} - E_{b\text{unmodified}}}{E_{b\text{unmodified}}} \quad (\text{S3})$$

$\Delta E_b/E_b$  is the rate of increase of the breakdown strength,  $E_{b\text{-modified}}$  and  $E_{b\text{-unmodified}}$  are the breakdown strengths of the nanocomposites filled with modified nanofillers and unmodified nanofillers.

Table S2. The Increase Rate of the Breakdown Strength of Nanocomposites PDA-BT/PVDF with TG = 14.4%.<sup>3</sup>

volume fraction (%)	$E_b$ (BT/PVDF)	$E_b$ (PDA-BT/PVDF)	$\Delta E_b/E_b$
2	175	229	0.31
3.8	163	212	0.30
5	149	191	0.28
7	136	188	0.38

Table S3. The Increase Rate of the Breakdown Strength of Nanocomposites PDA-BFT/PVDF with 5nm modifier layer.<sup>4</sup>

volume fraction (%)	$E_b$ (BFT/PVDF)	$E_b$ (PDA-BFT/PVDF)	$\Delta E_b/E_b$
1	170	200	0.18
3	110	130	0.18
5	70	80	0.14
7	50	70	0.40

Table S4. The Increase Rate of the Breakdown Strength of Nanocomposites

F4CBT/PVDF with TG = 0.8%.<sup>5</sup>

volume fraction (%)	$E_b$ (BT/PVDF)	$E_b$ (F4CBT/PVDF)	$\Delta E_b/E_b$
10	280	400	0.43
20	260	370	0.42
30	220	320	0.45
40	160	290	0.81
50	120	165	0.38

Table S5. The Increase Rate of the Breakdown Strength of Nanocomposites CA-

BT/PVDF with different TG values.

	TG (%)	$E_b$	$\Delta E_b/E_b$
PVDF/BT	0	188	0.00
PVDF/F4CBT -1	0.6	328	0.74
PVDF/F4CBT -2	0.76	277	0.47
PVDF/C2BT-1	1.05	334	0.78
PVDF/C2BT-2	3	260	0.38
PVDF/F4C2BT-1	0.92	235	0.25
PVDF/F4C2BT-2	2.34	305	0.62

### ■ Current Density of the Nanocomposites:

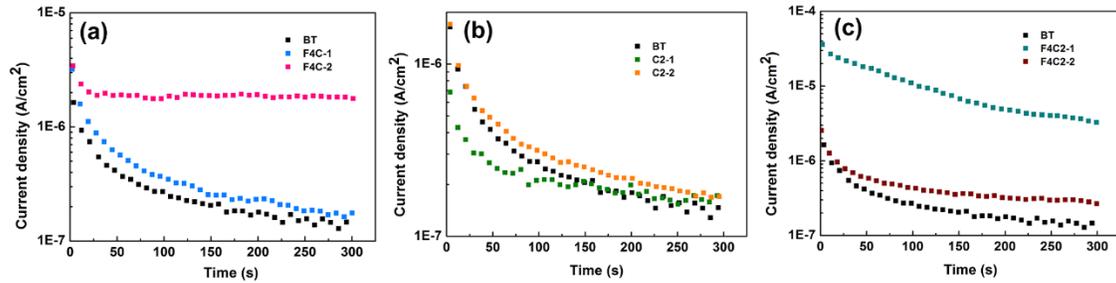


Figure S3. Current density of nanocomposites filled with BT and mBT nanoparticles under a DC bias of 50 MV/m at room temperatures, the modifiers are (a) F4C, (b) C2, and (c) F4C2.

In Figure S3, by compared the current density of mBT/PVDF with different coverage level of modifiers on surface of BT nanoparticles, it is found that the trend of leakage current and breakdown strength with the increase of modifier content is opposite for same modifier. At the same time, Figure 3 shows that the introduction of electron-rich functional groups (Fluoro-functional groups, -F) in the modifier molecule will lead to increase of the leakage current in nanocomposite.

■ D-E Loops of the Nanocomposites:

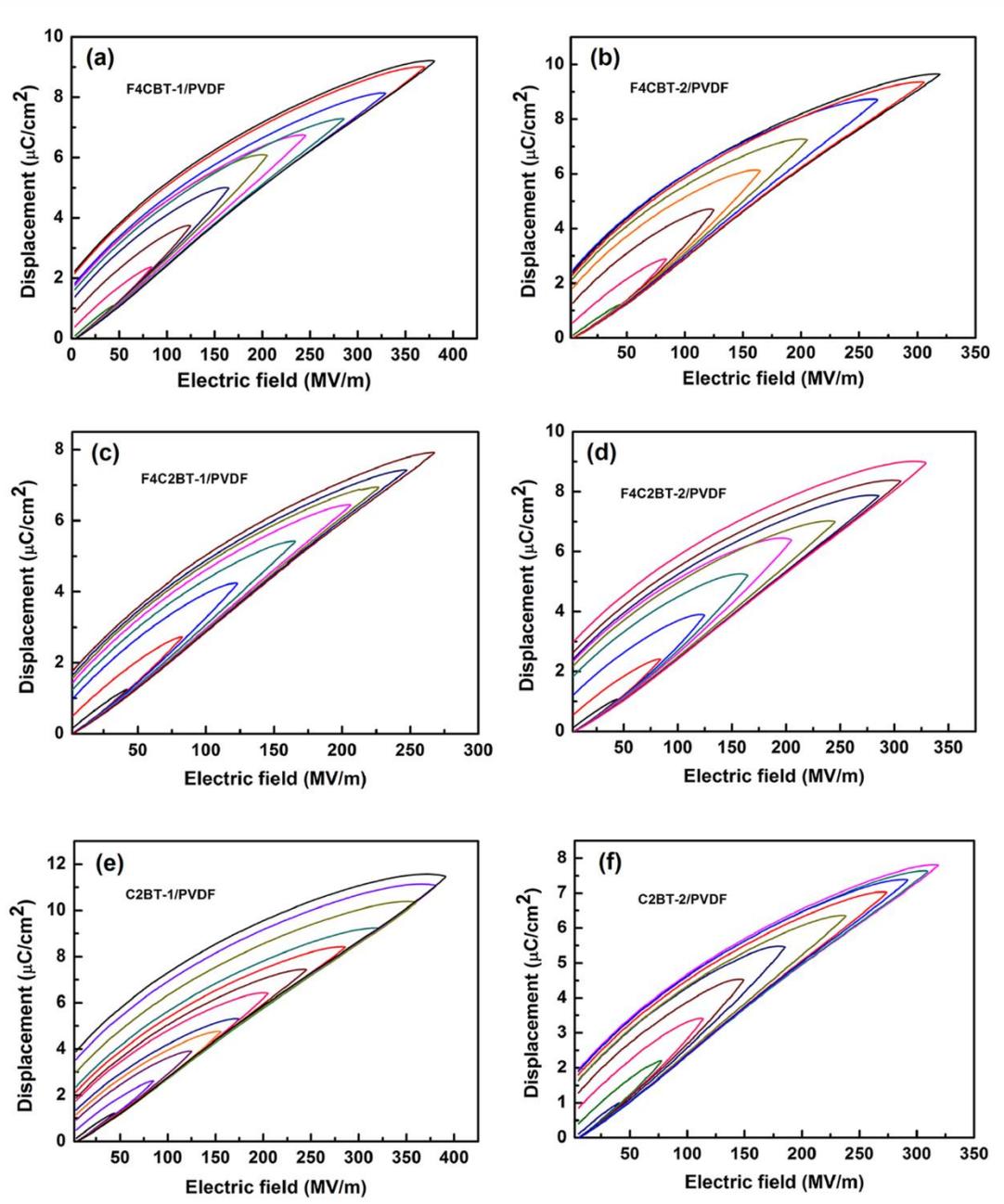


Figure S4. D-E loops of the nanocomposites filled with mBT nanoparticles with different surface coverage level under electric field.

■ **Influencing Factors of Energy Storage Density (Table 3 with Scientific Data):**

Table S6 Influencing Factors of Energy Storage Density (scientific data)

modifiers	F4C-1	F4C-2	F4C2-1	F4C2-2	C2-1	C2-2
TG%	0.60	0.76	1.05	3.00	0.92	2.34
polarization ( $\mu\text{C}/\text{cm}^2$ )	6.99	<b>8.73</b>	<b>7.90</b>	7.41	<b>7.35</b>	7.03
breakdown (MV/m)	<b>328</b>	277	235	<b>305</b>	<b>334</b>	260
dielectric loss	<b>0.038</b>	0.043	<b>0.035</b>	0.041	<b>0.038</b>	0.050

**References:**

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