Supporting Information for

Dielectric behaviors and high energy storage density of nanocomposite with core-shell $BaTiO_3$@TiO_2 in poly(vinylidene fluoride-hexafluoropropylene)

Mojtaba Rahimabady[a,b], Meysam Sharifzadeh Mirshekarloo[a], Kui Yao[a, *)] and Li Lu[b]
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[a]*Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Research Link, 117602 (Singapore)*

[*]*E-mail: (k-yao@imre.a-star.edu.sg)*

[b]*Department of Mechanical Engineering, National University of Singapore, 21 Lower Kent Ridge Road, 119260 (Singapore)*

As shown in Figure S1, XRD pattern of the core-shell nanoparticle powder was consistent with the TEM results of the $BaTiO_3$ and TiO_2 structures. It should be noted that as the result of the small thickness of the TiO_2 shells, the intensity of the XRD peaks at (210), (111), (211), (102), (112), (122), (321), and (421) that related to TiO_2 (Brookite) structure are very low.

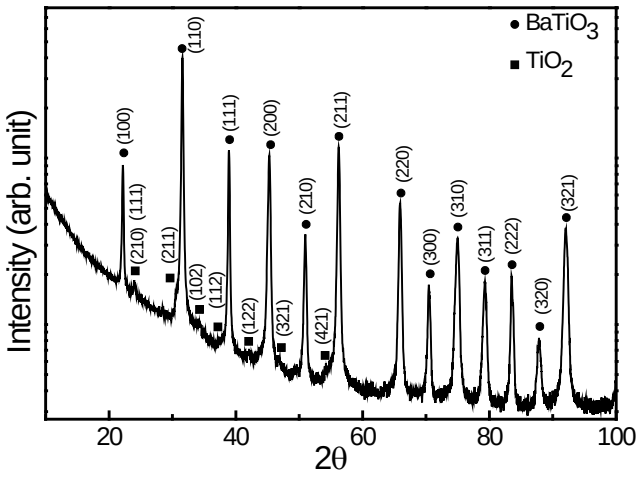


Figure S1. XRD pattern of BT@TiO_2 powder

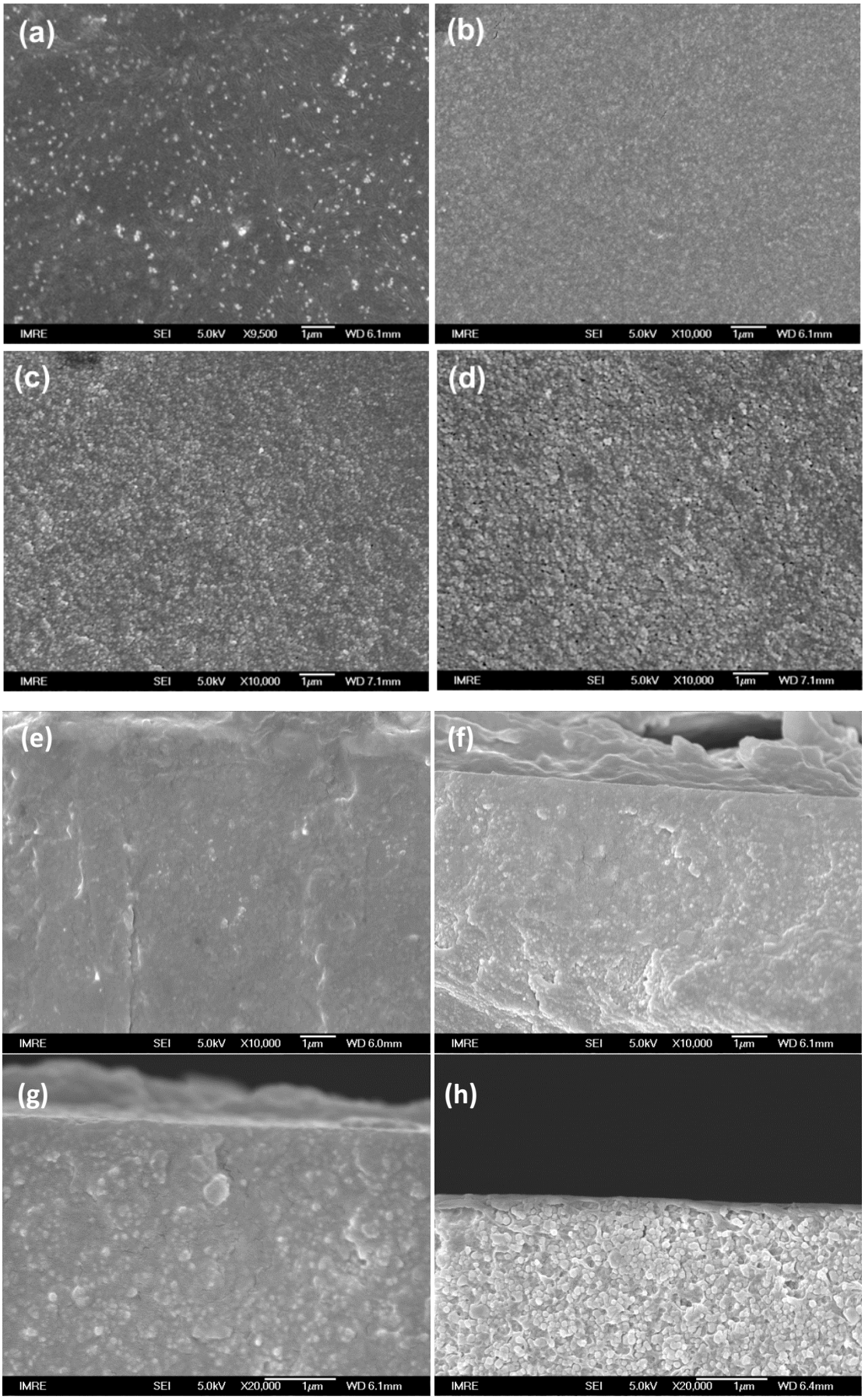


Figure S2. FESEM images of the surfaces of P(VDF-HFP)/BT@TiO_2 nanocomposite samples, (a)10 Vol %, (b) 30 Vol %, (c) 40 Vol %, (d) 50 Vol % BT@TiO_2 core-shell nanoparticle; and freeze-fractured cross-section images with (e) 10 Vol %, (f) 30 Vol %, (g) 40 Vol %, (h) 50 Vol % BT@TiO_2 core-shell nanoparticle.

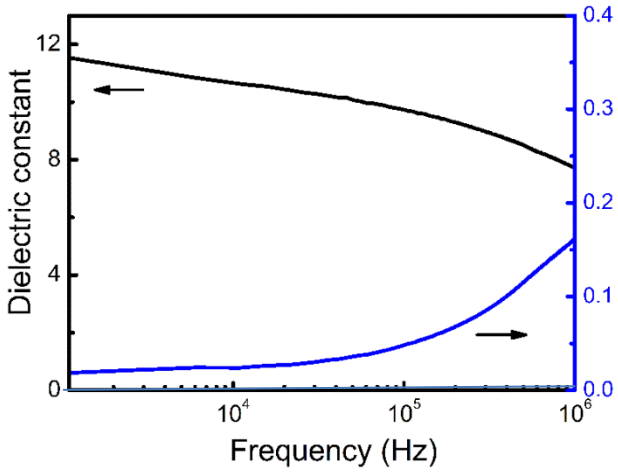
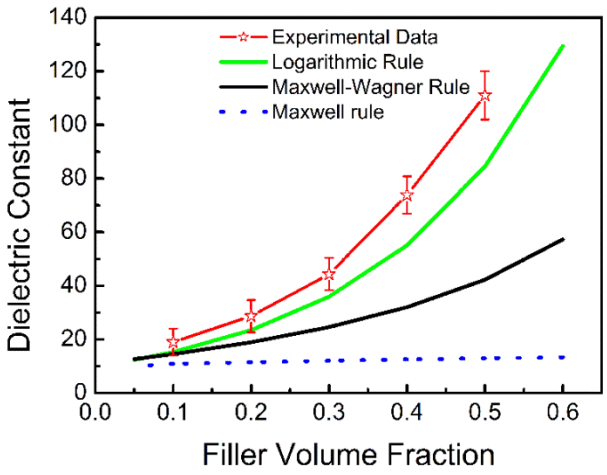


Figure S3. Frequency dependent dielectric constant and loss of the pure P(VDF-HFP)



FigureS4. Comparison between the calculated dielectric constant according to Maxwell, Maxwell-Wagner and Logarithmic rules with experimental data on P(VDF-HFP)/BT@TiO_2 nanocomposite.

In Vo-Shi model, the effective dielectric constant of the composite, expressed by Equation (S1)

$$\varepsilon_c = \frac{h + 2l}{h - l} \qquad (S1)$$

where

$$h = \left[1 + 2\frac{(\varepsilon_M - \varepsilon_{int})(\varepsilon_{int} - \varepsilon_F)}{(2\varepsilon_M + \varepsilon_{int})(2\varepsilon_{int} + \varepsilon_F)}\frac{a^3}{b^3} - 2\frac{(\varepsilon_M - 1)(\varepsilon_M - \varepsilon_{int})}{(\varepsilon_M + 2)(2\varepsilon_M + \varepsilon_{int})}\frac{b^3}{c^3}\right.$$

$$\left. - 2\frac{(\varepsilon_M - 1)(\varepsilon_M + 2\varepsilon_{int})(\varepsilon_{int} - \varepsilon_F)}{(\varepsilon_M + 2)(2\varepsilon_M + \varepsilon_{int})(2\varepsilon_{int} + \varepsilon_F)}\frac{a^3}{c^3}\right]$$

$$l = \left[\frac{(\varepsilon_M - 1)}{(\varepsilon_M + 2)}j - \frac{(2\varepsilon_M + 1)m}{(\varepsilon_M + 2)(2\varepsilon_M + \varepsilon_{int})}\frac{b^3}{c^3}\right]$$

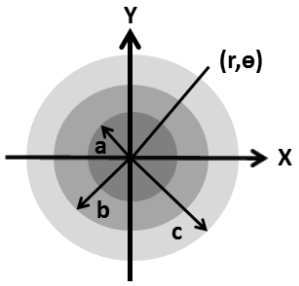
and

$$j = \left[1 + 2\frac{(\varepsilon_M - \varepsilon_{int})(\varepsilon_{int} - \varepsilon_F)}{2(\varepsilon_M + \varepsilon_{int})(2\varepsilon_{int} - \varepsilon_F)}\frac{a^3}{b^3}\right]$$

$$m = \left[(\varepsilon_M - \varepsilon_{int}) + \frac{(\varepsilon_M + 2\varepsilon_{int})(\varepsilon_{int} - \varepsilon_F)}{(2\varepsilon_{int} + \varepsilon_F)}\frac{a^3}{b^3}\right]$$

and

$\varepsilon_c, \varepsilon_M$, ε_{int}, and ε_F represent the dielectric constants of composite, matrix, interphase, and filler, respectively. a is the radius of the filler, $b - a$ is the thickness of the interphase region, and c is the radius of the equivalent composite (sphere with radius c and dielectric constant ε_c).



The interphase volume fraction between the filler and the matrix is

$$\emptyset_{int} = k\emptyset_F\emptyset_M$$

$$\frac{a^3}{b^3} = \frac{V_F}{V_{int} + V_F} = \frac{\emptyset_F}{\emptyset_{int} + \emptyset_F} = \frac{(1 + k\emptyset_F)}{1 + k}$$

$$\frac{a^3}{c^3} = \frac{V_F}{V_C} = \emptyset_F$$

$$\frac{b^3}{c^3} = \frac{V_F + V_{int}}{V_C} = \emptyset_F + k\emptyset_F \frac{(1 - \emptyset_F)}{(1 + k\emptyset_F)} = \emptyset_F \left[1 + k\frac{(1 - \emptyset_F)}{(1 + k\emptyset_F)}\right]$$

where $\emptyset_{int}, \emptyset_F, \emptyset_M$ are volume fractions of interphase, fillers, and polymer, respectively, and k is the interphase volume constant. This constant reflects the matrix-filler interaction strength. A large positive k indicates strong polymer-filler interaction. The interphase characteristics may be affected by filler size (surface area), and chemical structure of interphase region that is related to the bonding between polymer and filler.

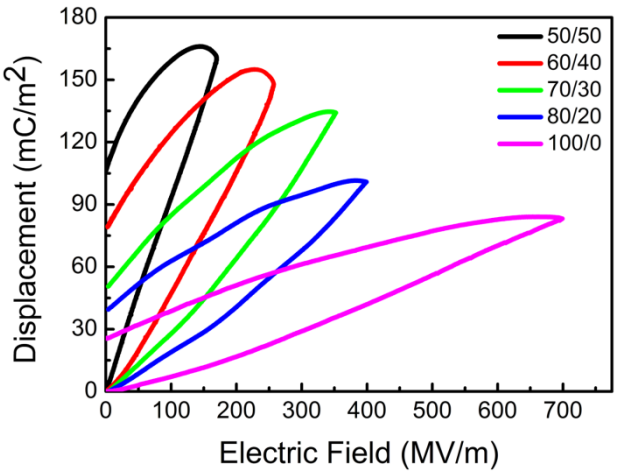


Figure S5. Displacement hysteresis loops of the P(VDF-HFP)/BT@TiO_2 nanocomposites with different volume fractions at breakdown field.