

Electronic Supplementary Information

Enhancement of Breakdown Strength and Energy Density in BaTiO₃/Ferroelectric Polymer Nanocomposites *via* Processing- Induced Matrix Crystallinity and Uniformity

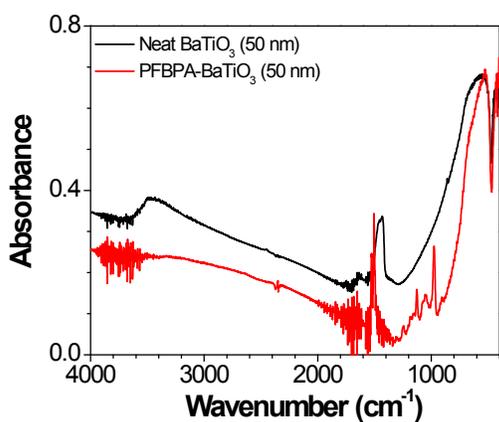
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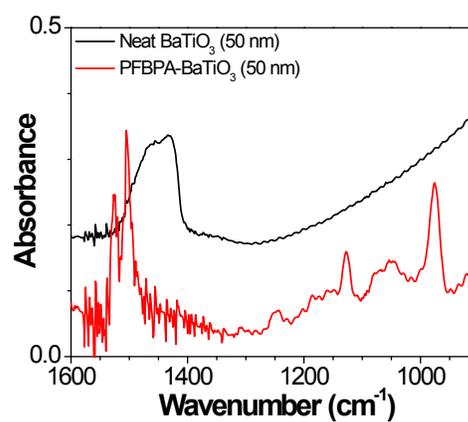
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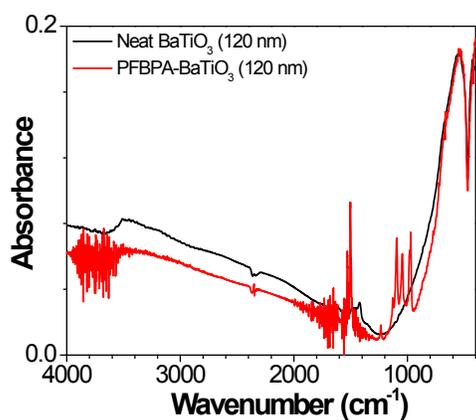
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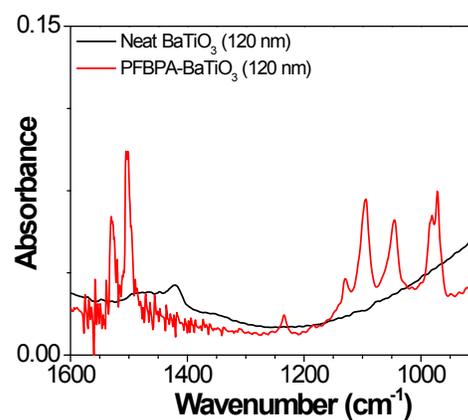
(a)



(b)



(c)



(d)

Fig S1 FT-IR absorption spectra of unmodified (in black) and PFBPA-modified BT (in red) ((a) and (b): 50 nm BT, (c) and (d): 120 nm BT). All spectra were normalized using Ti-O absorption peak at ~ 540 cm⁻¹.

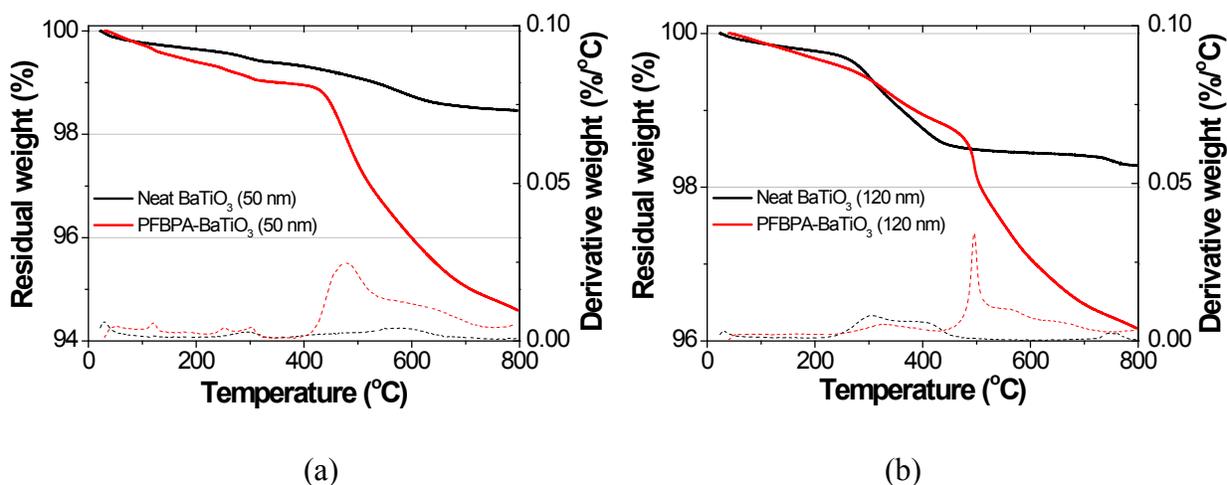


Fig. S2 Thermogravimetric analysis of unmodified (in black) and PFBPA-modified BT particles (in red) ((a) 50nm BT; (b) 120 nm BT). Residual weight is shown in solid lines and the derivative of residual weight is shown in dashed lines.

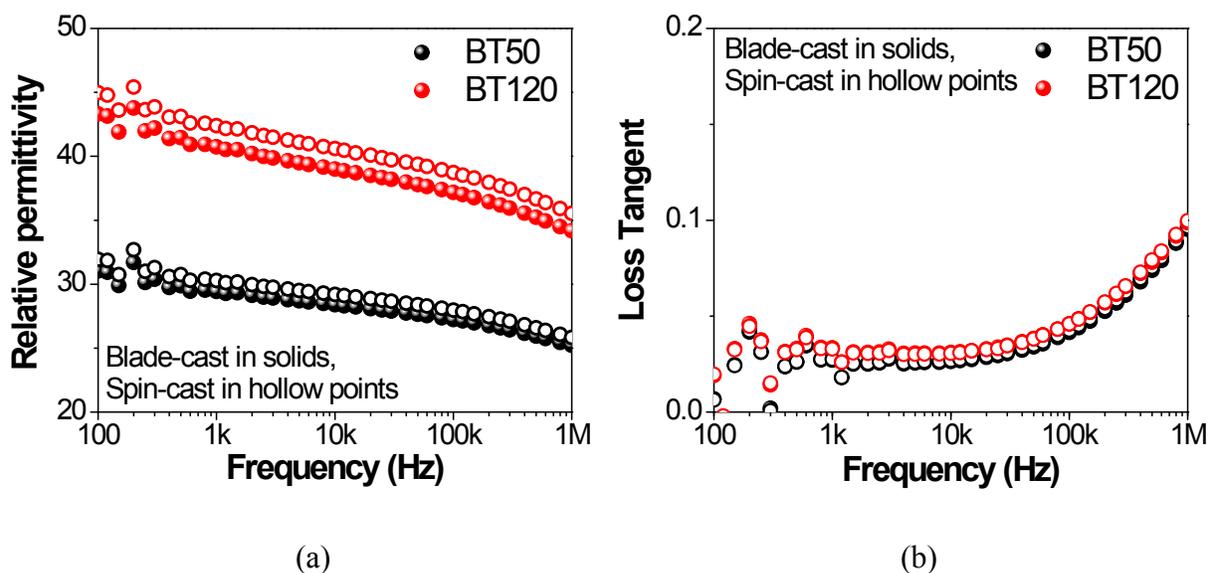


Fig. S3 Frequency dependent (a) permittivity and (b) loss tangent of PFBPA-BT/P(VDF-co-HFP) nanocomposite films. Data of blade-cast and spin-cast films are shown in solid circles and hollow circles, respectively.

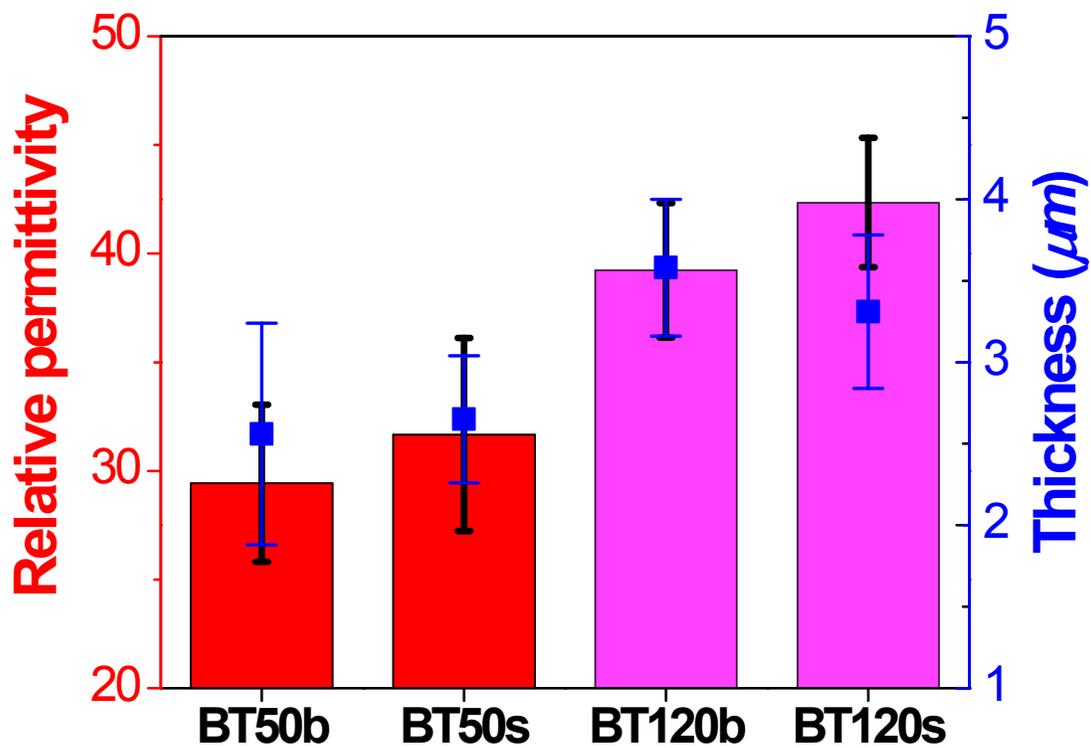


Fig. S4 Relative permittivities and thicknesses of nanocomposite films containing either 50 nm or 120 nm BT nanoparticles with a volume loading of 50%, fabricated by either blade or spin casting. The error bars represent the standard deviations (1σ) of relative permittivity and thickness.

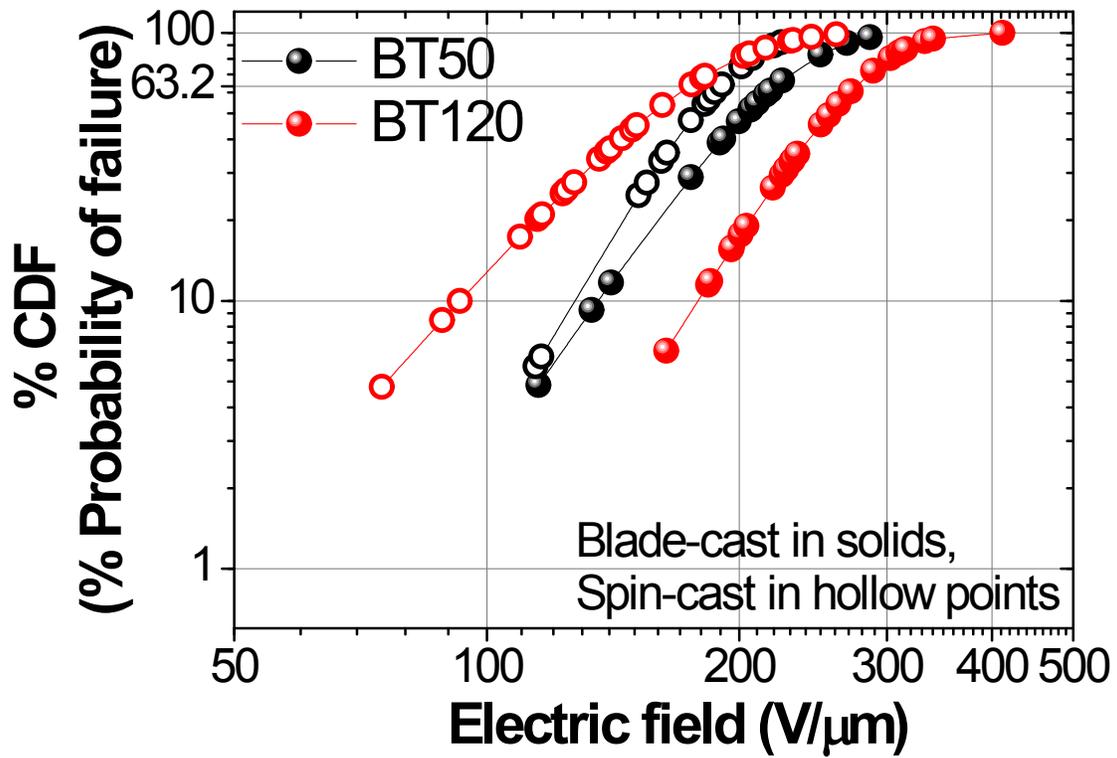


Fig. S5 The % cumulative distribution functions (% CDF) of nanocomposite films containing either 50 nm or 120 nm BT nanoparticles with a volume loading of 50%, fabricated by either blade or spin casting, as a function of electric field.

We have performed SEM/EDX analysis of nanocomposite films using a Zeiss SEM. The top surface SEM image and the elemental map (Ba, Ti, P, and F) of the nanocomposite over a 12 μm (height) x 9 μm (width) area are included in the Fig. S6 below. Note that the bright positions in the map indicate the presence of the particular elements. The nanoparticles (average diameter of ~ 50 nm, close to the pixel resolution in the EDX maps) appear to be well distributed in the nanocomposite. The distribution of the Ba and Ti intensities are perfectly correlated, as expected, based on difference maps and 2D correlations. The P EDX peak is overlapped with that of the peak of the Au conductive coating, which introduces some potential coincidences. Nonetheless, the processing of the P map AND Ba map, where AND is the logical AND operator for the images, shows a high degree of correlation between the two elements, which strongly associates the positions of P with those of Ba, and therefore Ti as well. We have included the map of P AND Ba in the ESI as well. Additionally, the positions of the F in the film was not well correlated with those of Ba and Ti, which is expected due to the presence of F in the p[VDF-co-HFP].

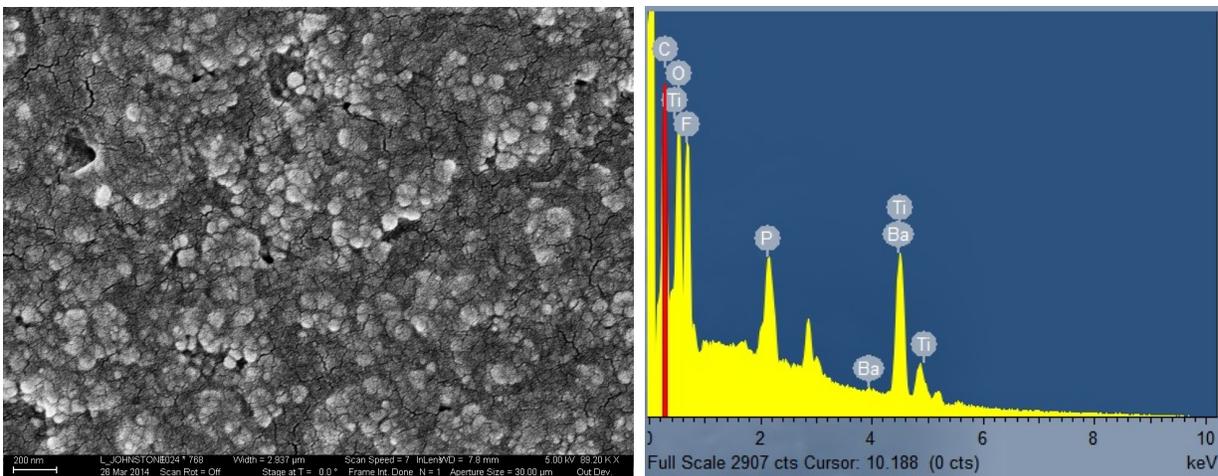


Fig. S6 (left) Top-surface SEM image of BT/P(VDF-co-HFP) nanocomposite film containing 50 nm BT particles with a volume loading of 50% prepared by blade casting and (right) its energy dispersive spectroscopy (EDS) data showing the presence of phosphorous, fluorine, Ba, and Ti.

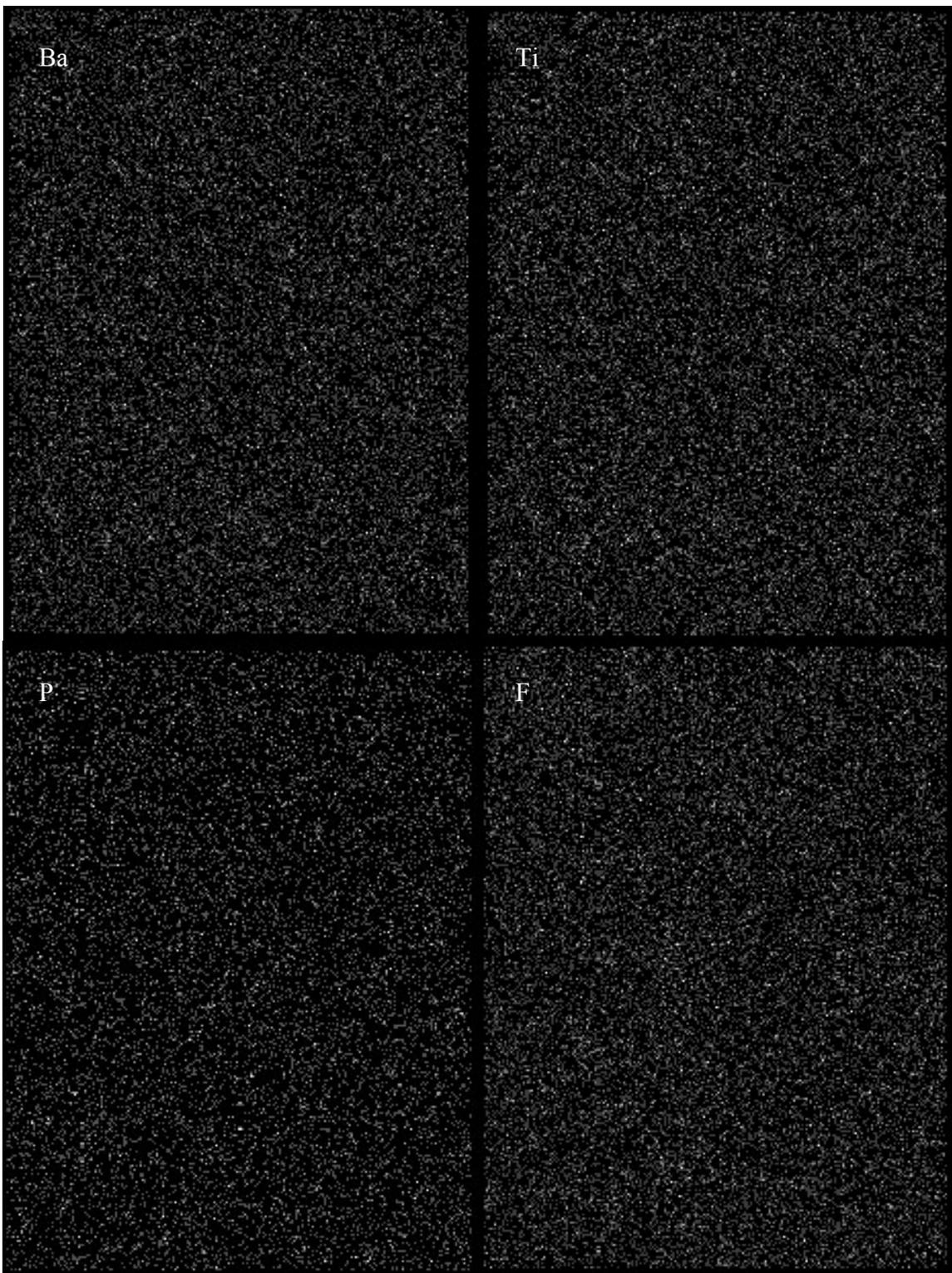


Fig. S7a The elemental maps (from top left to bottom right) of Ba, Ti, P, and F obtained from SEM/EDX analysis in Fig. S6, showing the homogeneous distribution of surface-modified BaTiO₃ nanoparticles in P(VDF-*co*-HFP) matrix. The dimensions of the EDX image are 12 μm in height and 9 μm in width.



Fig. S7b Image of the logical AND operation for the phosphorus and barium EDX maps.

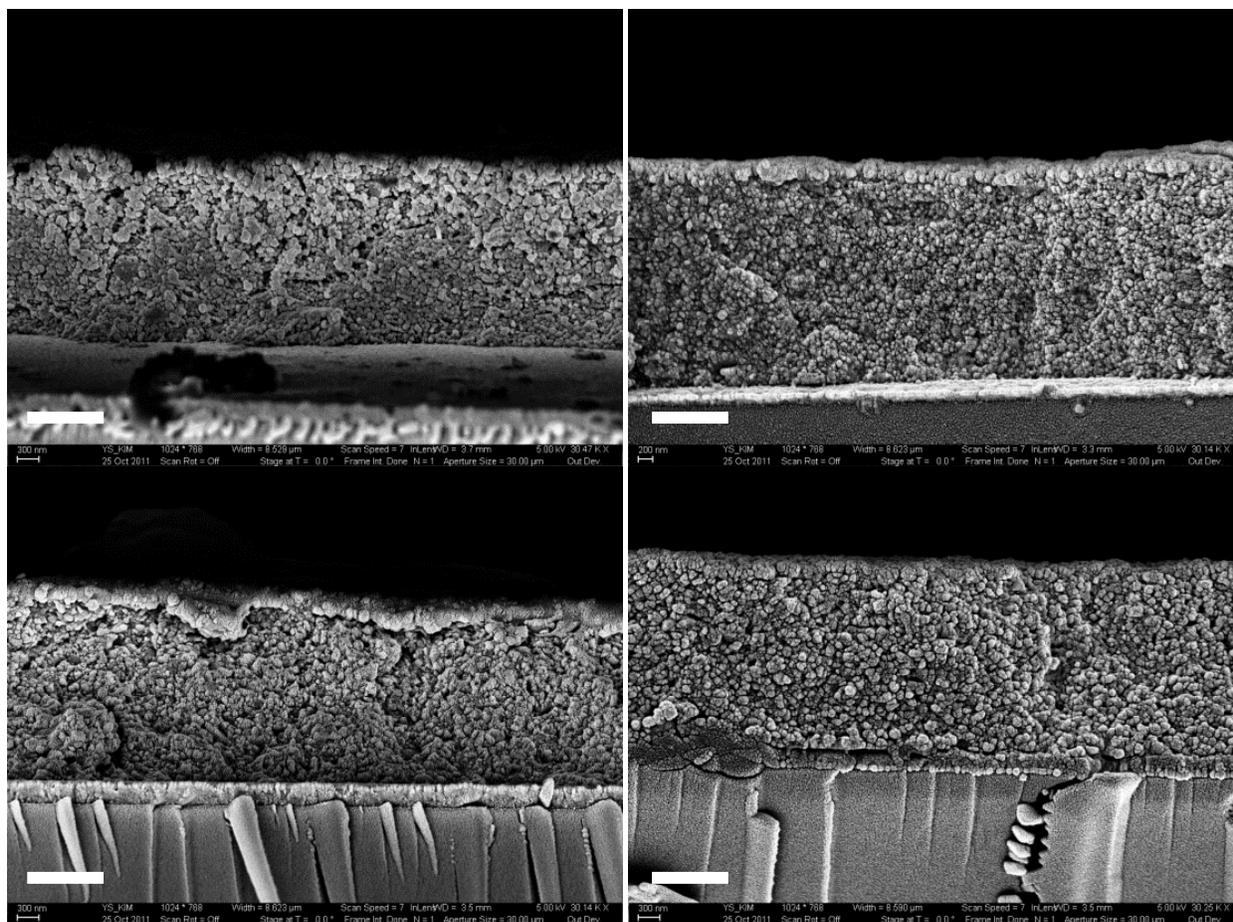


Fig. S8 Low-magnification cross-sectional SEM images of BT/P(VDF-*co*-HFP) nanocomposite films containing 50 and 120 nm BT nanoparticles with a volume loading of 50%, fabricated *via* spin or blade casting: BT50s (top left), BT50b (top right), BT120s (bottom left), and BT120b (bottom right). (scale bar 1 μ m).

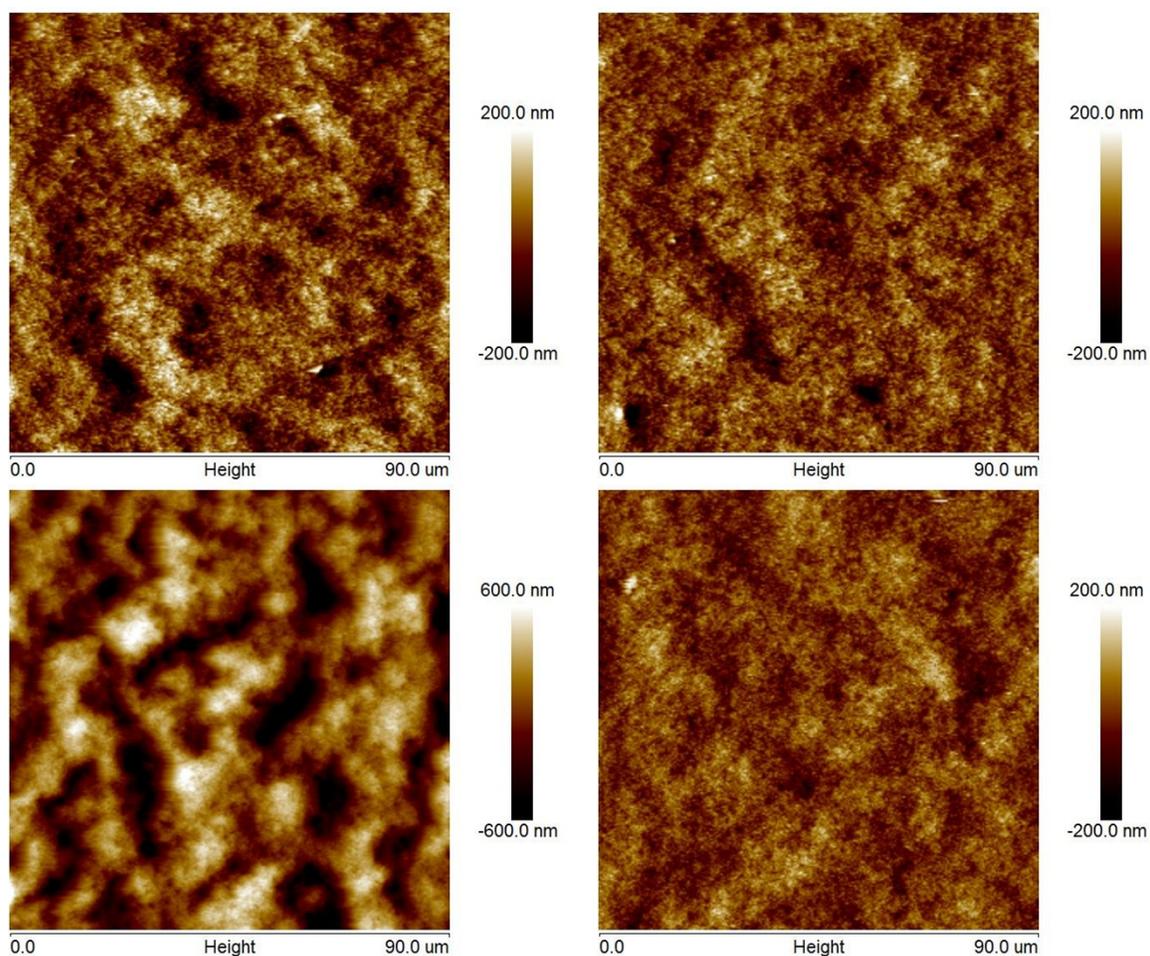


Fig. S9 AFM images of BT/P(VDF-*co*-HFP) nanocomposite films containing 50 nm and 120 nm BT nanoparticles with a volume loading of 50%, *via* spin or blade casting: BT50s (top left), BT50b (top right), BT120s (bottom left), and BT120b (bottom right).

Table S1 Coherence length for the polymer crystallites in BT/P(VDF-*co*-HFP) nanocomposite films calculated from low angle peaks after baseline correction using Scherrer equation.

	Coherence length (nm)	FWHM
BT50b	8.7	0.91 ± 0.02
BT50s	6.2	1.3 ± 0.05
BT120b	23	0.35 ± 0.03
BT120s	2.8	2.8 ± 0.17

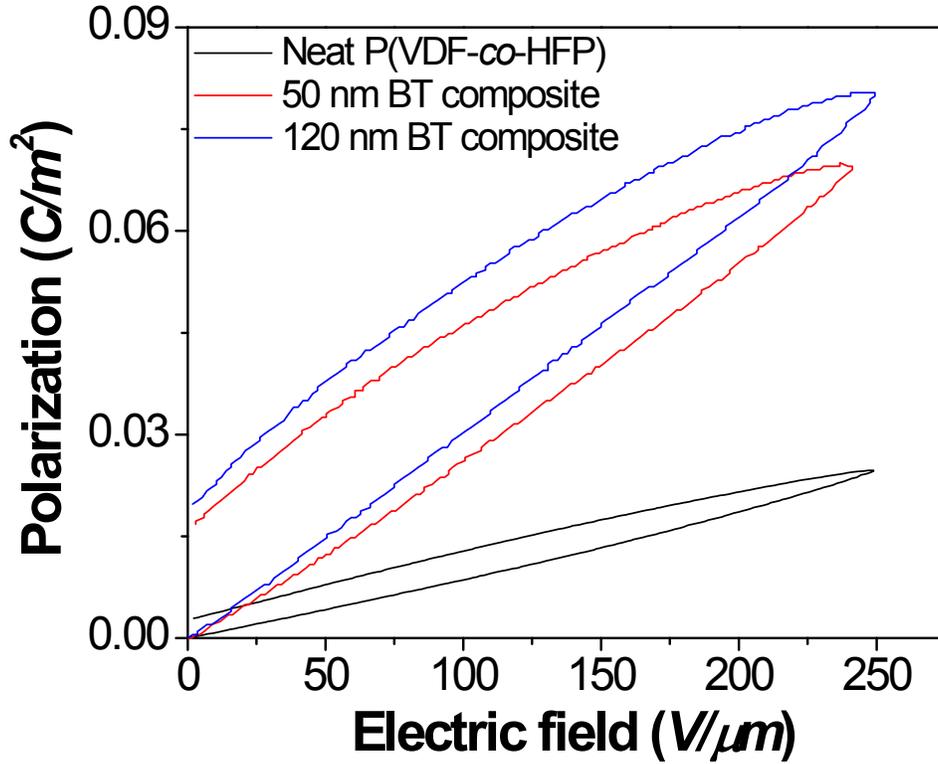


Fig. S10 P-E loops of blade-cast BT/P(VDF-co-HFP) nanocomposite films at ~ 250 V/ μm containing either 50 nm or 120 nm BT nanoparticles. Neat P(VDF-co-HFP) is also laid out to show the effect of BT incorporation on the hysteresis of P-E loops. Unlike neat polymer matrix, P-E loops of nanocomposites exhibit significantly increased remnant polarization, which is due to ferroelectric response of BT nanoparticles.¹

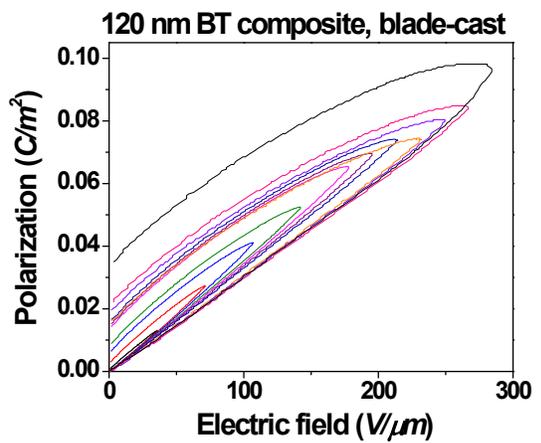
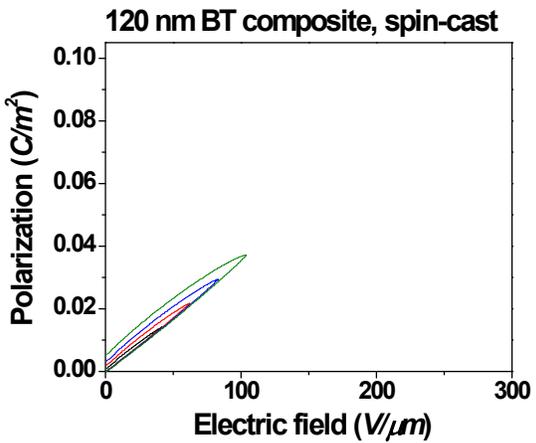
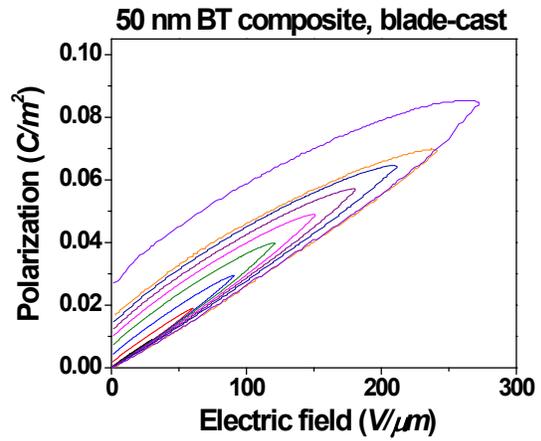
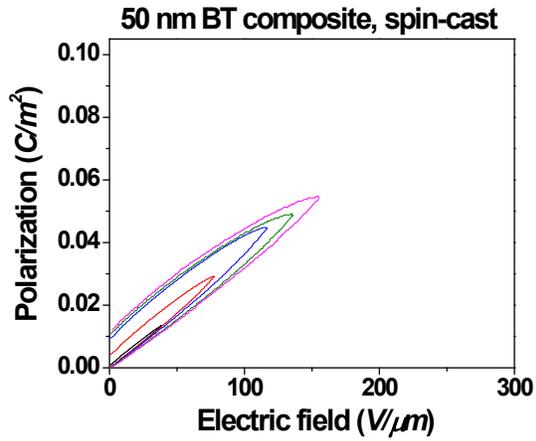


Fig. S11 Unipolar P-E loops of BT/P(VDF-co-HFP) nanocomposite films.

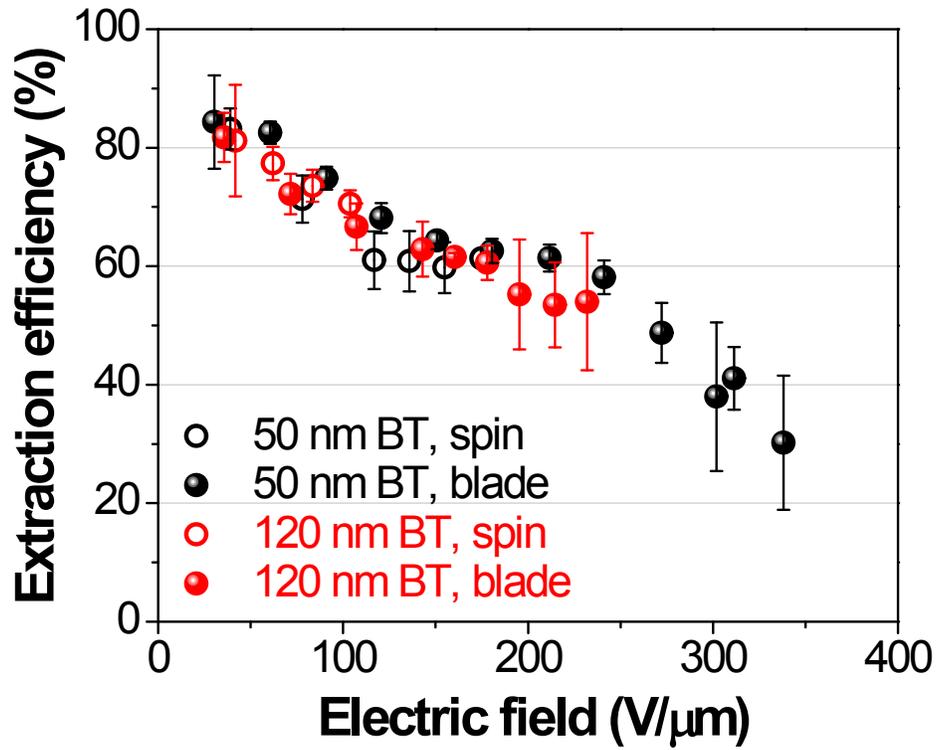


Fig. S12 Energy extraction efficiency of BT/P(VDF-co-HFP) nanocomposite films determined from polarization-electric field (P-E) method.

1. Choi, K. J. Enhancement of Ferroelectricity in Strained BaTiO₃ Thin Films. *Science* **2004**, *306*, 1005-1009.