Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information to

Hierarchical Interfaces Induce High-Dielectric –Permittivity in Nanocomposites Containing $TiO_2@BaTiO_3$ Nanofibers: Phase-Field Simulation and in-situ Observation of Electrical Breakdown by TEM

Xin Zhang, Weiwei Chen, Jianjun Wang, Yang Shen*, Yuanhua Lin, and Ce-Wen Nan*

School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing Tsinghua University Beijing, China, 100084

E-mail: shyang_mse@tsinghua.edu.cn; cwnan@tsinghua.edu.cn

Supplementary Figures

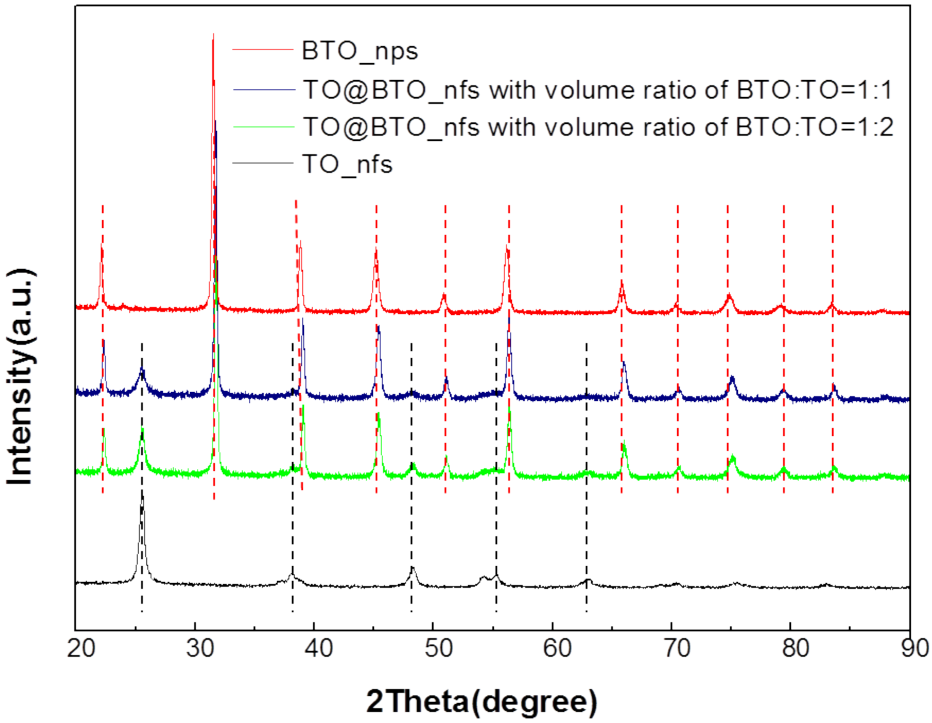

Figure S1. XRD patterns of TO_nfs, BTO_nps and TO@BTO_nfs calcined at 500^{o}C

Pure TO_nfs and TO@BTO_nfs with volume ratios of 1:1 and 1:2 have been synthesised through electrospinning method. As can be seen from the XRD patterns, the BTO_nps to be embedded into to TO_nfs were synthesized via a hydrothermal method in advance and presented fine cubic phase, since the latter thermal treatment temperature (500^{o}C) had little effect on the crystal structure of BTO_nps, in the TO@BTO_nfs the embedded BTO_nps still maintained the premier cubic phase, and the corresponding peaks have been marked with red dashed lines. For both TO_nfs and TO@BTO_nfs during the thermal treatment, PVP were removed and tetrabutyl titanate were transferred into anatase TiO_2 of tetragonal phase, the characteristic peaks were remarked with dark dashed lines. Both $BaTiO_3$ of cubic phase and anatase TiO_2 of tetragonal phase could be observed in TO@BTO_nfs, and the strength of XRD peaks changed continuously and obviously with the variation of the volume ratios of $BaTiO_3/TO_2$ in TO@BTO_nfs. When the volume ratios of $BaTiO_3/TO_2$ in the TO@BTO_nfs increased from 1:1 to 1:2, the peaks of anatase TiO_2 became much stronger and more notably compared to the $BaTiO_3$ of cubic phase.

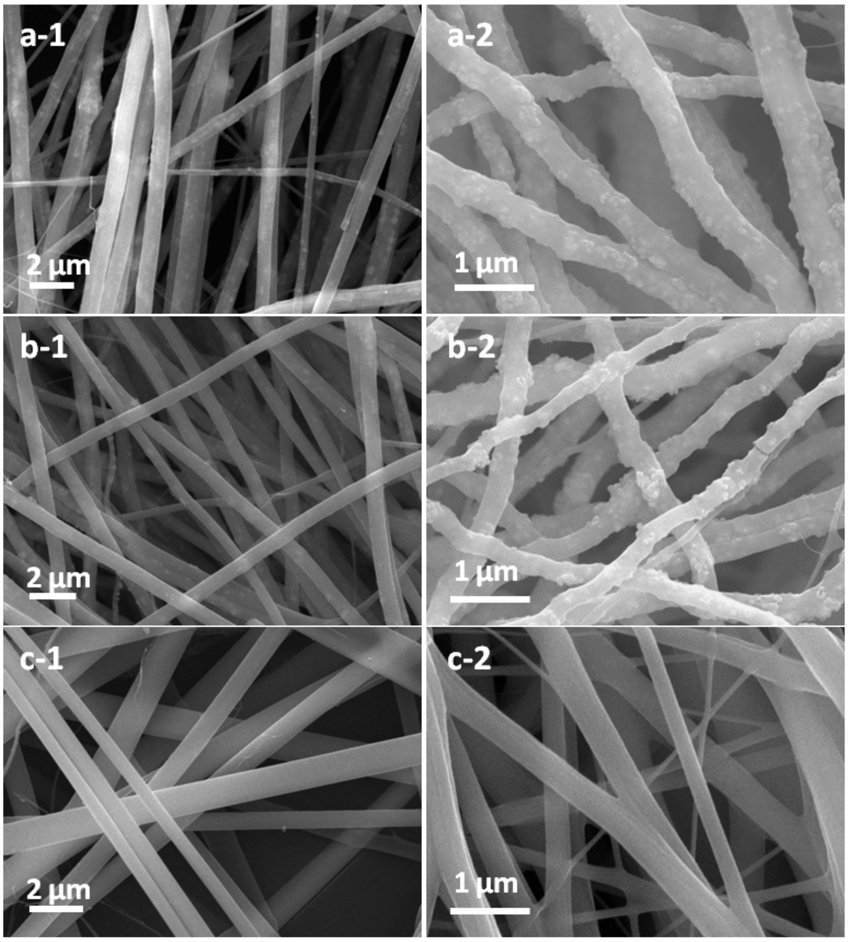

Figure S2.SEM images of electrospun nanofibers before(x-1) and after(x-2) calcinations: a) TO@BTO_nfs with volume ratio of BTO:TO = 1:1; b) TO@BTO_nfs with volume ratio of BTO:TO = 1:2; c) pure TO_nfs.

All the fibers including TO_nfs and TO@BTO_nfs were prepared by electrospinning, Figure S2 present the morphology of the fibers before and after calcinations. Before the calcinations, the diameter of fibers were much larger due to the existence of organic components. However, after the thermal treatment organic components were decomposed, and the diameters of fibers were diminished and still in good shape of nanofibers.

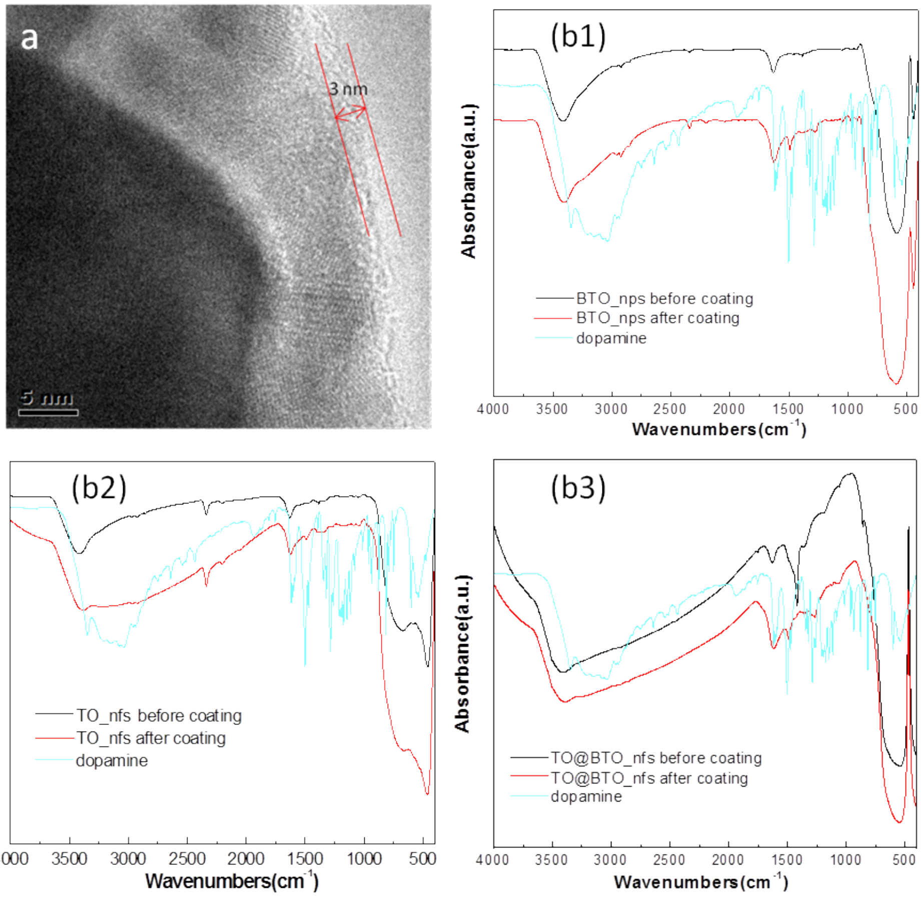

Figure S3.The FT-IR of inorganic fillers before and after dopamine coating processing: b1) BTO_nps; b2) TO_nfs; b3) TO@BTO_nfs. a) HRTEM image of TO@BTO_nfs after coated with dopamine.

Nanoparticles or nanofibers with large specific surface area are easy to aggregate in liquid media, surface modification is one of effective solutions to maintain the stability. Coating a thin layer of dopamine on the surface of inorganic fillers can improve the dispersity and homogeneity of the nanocomposites as well as enhance the dielectric properties. So, all the inorganic fillers to be filled into PVDF matrix including BTO_nps, TO_nfs and TO@BTO_nfs received surface modification processing. After which, thin amorphous layers with thickness of 3 nm were coated on the surface of inorganic nanofibers and nanoparticles(Figure S3a), which can be attributed to the adsorption of dopamine molecular, this can be further evidenced by Fourier Transform Infrared Spectroscopy(FT-IR) tests. For samples after surface modification with dopamine, new absorbance signal appeared at $1488cm^{-1}$, $1267cm^{-1}$, which respectively correspond to aromatic C–C stretching vibrations and aromatic amine C–N stretching vibrations and belong to dopamine, while no such signals were observed when it comes to unmodified samples.

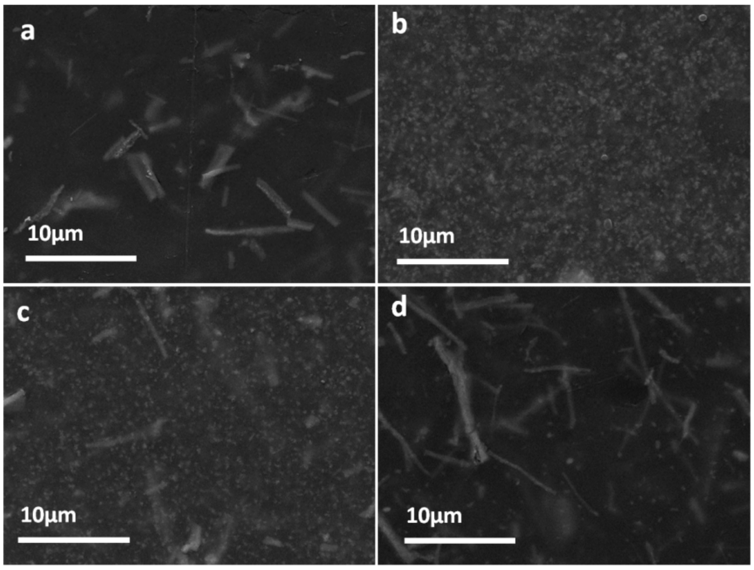

Figure S4.Surface SEM images of PVDF based nanocomposites with volume faction of fillers equals to 4.1%: a)TO_nfs/PVDF; b) BTO_nps/PVDF; c) BTO_nps/TO_nfs/PVDF; d) TO@BTO_nfs/PVDF.

By adding different inorganic fillers including TO_nfs, BTO_nps, BTO_nps/TO_nfs, TO@BTO_nfs into PVDF matrix, four pre-designed composites structure could be achieved, all composites were casted into thin films with thickness of 15-20 um, microscopic morphologies of films surfaces were studied by scanning electron microscope (SEM). As can be seen from the , owning to the previously surface modification processing, all nanofibers and nanoparticles were favorably dispersed in the PVDF matrix, which gave rise to homogeneous and uniform films with smooth and flawless surfaces (Figure S4). In the nanocomposites films a, c and d, majority of the nanofibers introduced lied parallelly in the films because of mutual effect of gravity and shear forces. This introduced in-plane-oriented directions of nanofibers provided reference for the latter further microscopic study of interfacial effects.

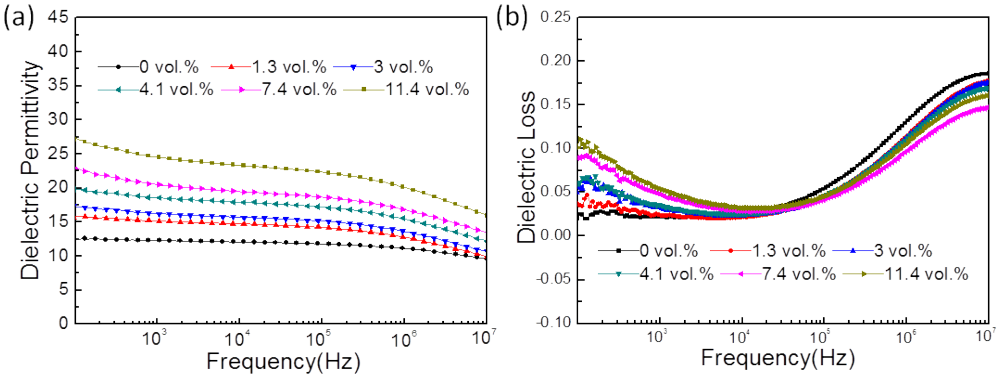

Figure S5.The dependence of dielectric permittivity (a) and dielectric loss (b) on frequency for TO_nfs/PVDF nanocomposites with different of volume fraction of TO_nfs.

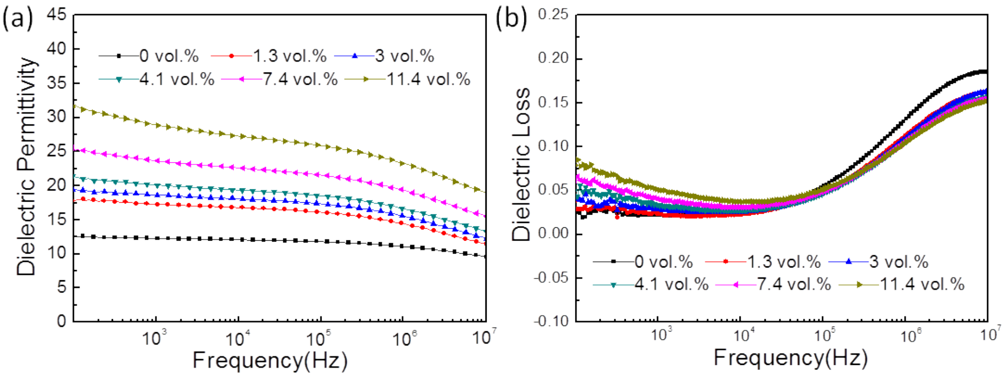

Figure S6.The dependence of dielectric permittivity (a) and dielectric loss (b) on frequency for BTO_nps/PVDF nanocomposites with different of volume fraction of BTO_nps.

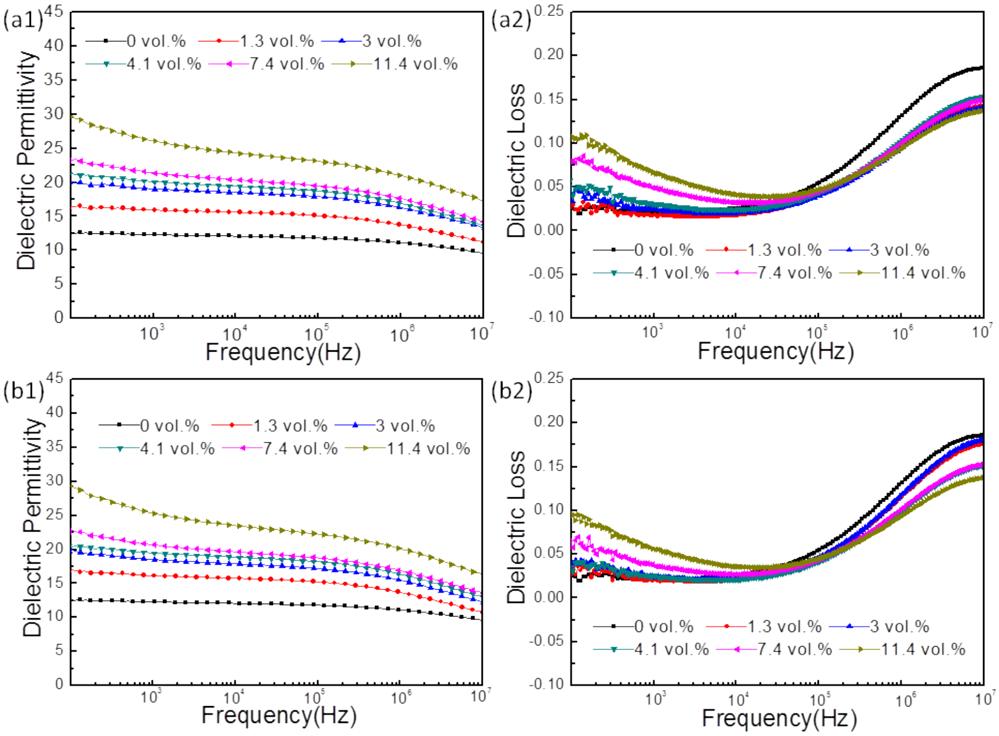

Figure S7.The dependence of dielectric permittivity (a1, b1) and dielectric loss (a2, b2) on frequency for BTO_nps/TO_nfs/PVDF nanocomposites with different of volume fraction of fillers(a) the volume ratio of BTO/TO = 1:1, a2) the volume ratio of BTO/TO = 1:2)

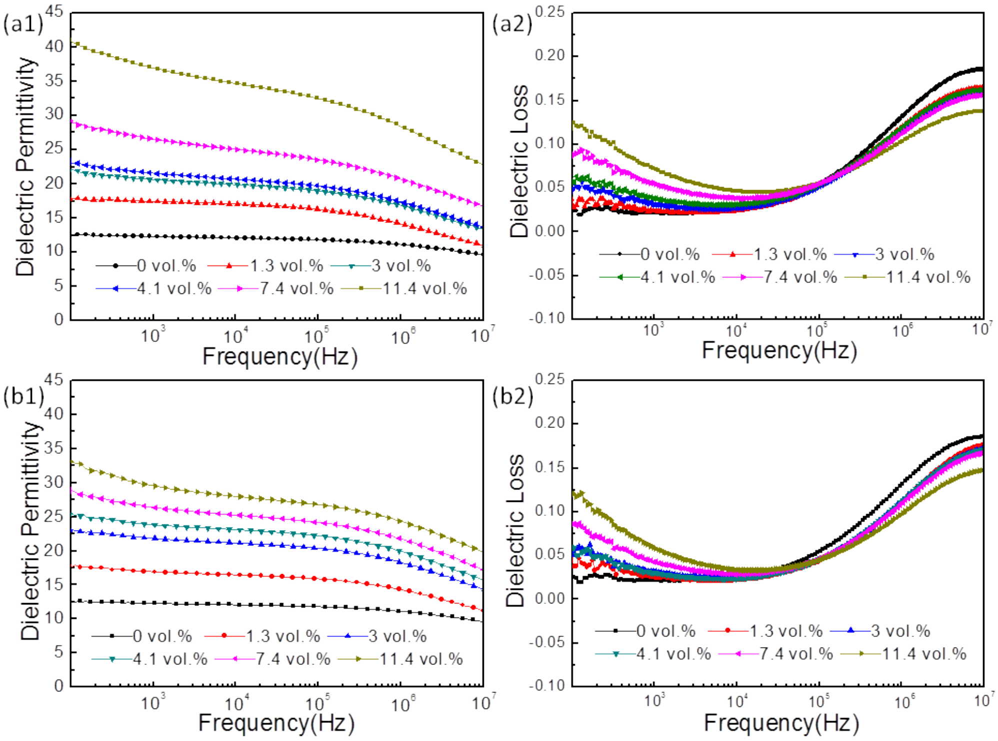

Figure S8.The dependence of dielectric permittivity (a1, b1) and dielectric loss (a2, b2) on frequency for TO@BTO_nfs/PVDF nanocomposites with different of volume fraction of fillers (a) the volume ratio of BTO/TO = 1:1, b) the volume ratio of BTO/TO = 1:2)

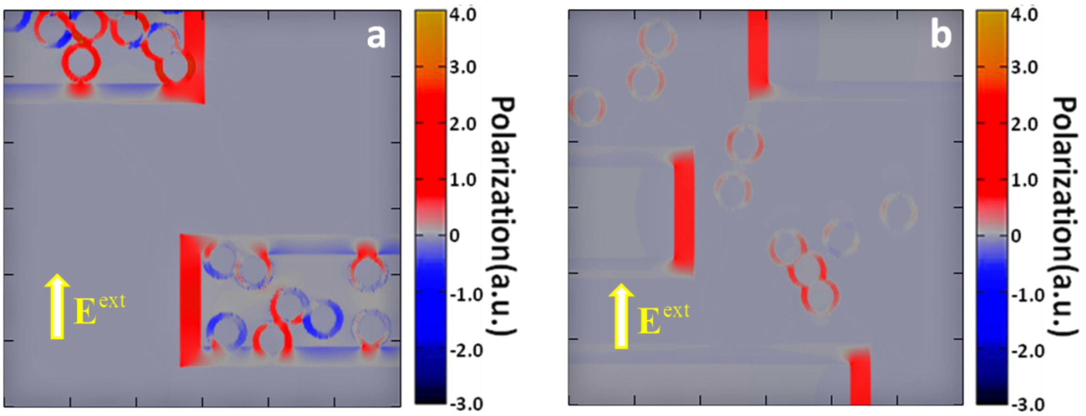

Figure S9. The distribution of interfacial polarization simulated for the (a)PVDF/TO@BTO_nfs nanocomposites and (b)PVDF/BTO_nps/TO_nfs nanocomposites with volume ratio of BTO:TO = 1:2.

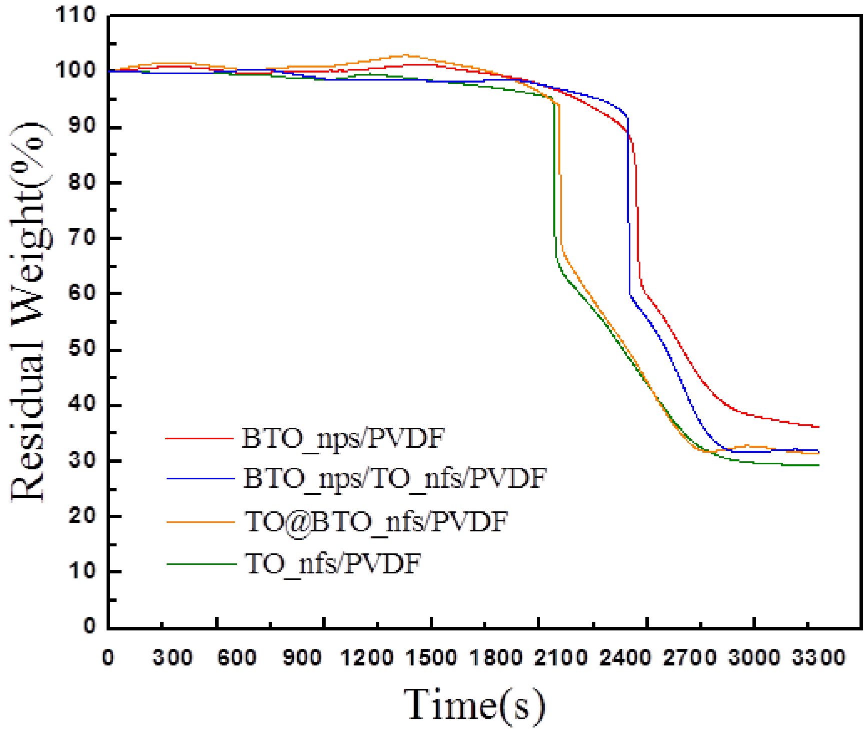

Figure S10. The TGA curves of PVDF based nanocomposites filled with different nano-inclusions at the volume fraction of 11.3%.

Table S1. The related figures of the mass and volume fraction of nano-inclusions in four composites

Composites	**Weight percentage of fillers (%)**	**Density of fillers (g/cm3)**	**Calculated volume fraction (%)**
TO_nfs/PVDF	27.65	3.92	11.42
BTO_nps/PVDF	36.25	6	11.34
BTO_nps/TO_nfs/PVDF	31.81	4.96	11.26
TO@BTO_nfs/PVDF	31.35	4.96	11.11

Thermo gravimetric analysis were carried out in the temperature range of 50^{o}C to 500^{o}C at a ramping rate of 10^{o}C/min, and soaked at 500^{o}C for 10 min for the full decomposition of polymer matrix. The mass fraction of nano-inclusions were obtained from the TGA curves (Figure S10) and then translated into volume fraction with the known density of fillers and PVDF matrix(the density of which is 1.35g/cm^{3}), as listed in Table S1.

Supplementary Videos