Supplementary Information

Non-Intuitive Concomitant Enhancement of Dielectric Permittivity, Breakdown Strength and Energy Density in Percolative Polymer Nanocomposites by Trace Ag Nanodots

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Characterization Details

Fourier transform infrared spectra (FT-IR) was obtained on a spectometer (Vertex 70, Bruker, Germany). Nuclear magnetic resonance (NMR) measurement was carried out by a spectrometer (JNM-ECA600, JEOL, Japan). Electrostatic force microscopy (EFM) was carried out by a scanning probe microscopy (Asylum MPF 3D, Oxford instrument, UK). Thermogravimetric analysis (TGA) were performed on a thermal analyzer (TGA/DSC 1, Mettler Toledo, Switzerland) from 30 to 600 °C in air flow with heating rate 10 °C min⁻¹.



Fig. S1 (a) Fourier transform infrared spectra (FT-IR) of pure P(VDF-HFP), 0.1% *in situ* composite, and 0.1% *ex situ* composite. (b) ¹⁹F Nuclear magnetic resonance (NMR) of pure P(VDF-HFP), 0.05%, 0.1% and 0.5% *in situ* composite. The reagents and products of *in situ* synthesis do not modify, decompose or react with the polymer matrix in the reaction.



Fig. S2 Electrospinning fibrous mat upon different processing method. (a) Photo image, (b) XRD results.

Reduction of AgNO₃ could be observed from the color and confirmed by X-ray diffraction (XRD) results. Fig. S2(a) shows the color change due to different processing of the fibrous mat containing 2.72 wt.% AgNO₃ (precursor of 0.3 vol.% *in situ* composite). Color is an indicator of size and agglomeration of nanoparticles.¹⁻³ (left) The fibrous mat was treated as spun. The color of the fibrous mat was white. (middle) *In situ* treatment: in a vacuum drier with DMF vapor of 0.04 g L⁻¹, kept in 100 °C for 60 min. The color changed to yellow or brown. (right) Heated only: in the vacuum drier without DMF vapor, only kept in 100 °C for 60 min. The color changed to beige. If we continue to put "heat only" fibrous mat in the vacuum drier with same condition of "*in situ* treatment", the color would change to yellow or

brown. This phenomenon suggests "heat only" may not finish the reaction completely. Moreover, light exposure is enable to decompose the AgNO₃, according to our observation. However, AgNO₃ could not be completely and homogeneously decomposed due to the different amount of light is absorbed on different depth of the fibrous mat.



Fig. S3 (a) Transmission electron microscopy (TEM) image and (b) histogram of nanodots' diameter of 0.1% *in situ* electrospinning fiber. Most nanodots keeps the size from \sim 5–15 nm.



Fig. S4 Scanning electron microscopy (SEM) images of nanocomposite membranes' sections. (a) 0.2% *in situ* composite. (b) 0.2% non *in situ* composite (*i.e.* without *in situ* treatment in preparing process. Big particles are Ag, and are reduced from AgNO₃ in hot press procedure.). (c) 0.05% *in situ* composite. (d) pure P(VDF-HFP) matrix. Nanodots by *in situ* synthesis would homogeneously disperse in matrix with no agglomeration.



Fig. S5 (a) Weibull distribution and (b) the Ag content dependence of characteristic breakdown strength $E_{\rm b}$.



Fig. S6 Electrostatic force microscopy (EFM) of 0.05% *in situ* composite in (a) height (morphology) and phase shift under different tip bias: (b) 0 V, (c) +3 V, (d) -3 V. Ag nanodots would trap charges in the matrix, so the forces to the tip are opposite and opposed phase images are obtained when tip bias changed from +3 V to -3 V. Scale bar: 1 μ m.



Fig. S7 Electric displacement–electric field (*D*–*E*) hysteresis loops.



Fig. S8 Conductivity of composites upon temperature 30–200 °C: (a) pure P(VDF-HFP), (b)

0.05% ex situ composite, (c) 0.05% in situ composite.



Figure S9. Thermogravimetric analysis (TGA) of pure P(VDF-HFP), 0.05% and 0.1% *in situ* composite, 0.05% and 0.1% *ex situ* composite.

The polymer degrades to fragments including dimers, monomers and oligomers of vinylidene fluoride from backbone and the side chain above 400 °C. The *in situ* composites have more active backbones by the interaction with Ag and exhibit a shifted temperature of decomposition ~ 400 °C, compared to ~ 420 °C of pure polymer and *ex situ* composites.



Fig. S10 4 models used in calculation: F-c, F-t, H-c, H-t.

The calculation models were constructed from the nanocomposites in the experiment. 4 models were considered: Ag at the site above the center of four F atoms, named "F-c"; Ag at the site above the middle of two F atoms, "F-t"; Ag at the site above the center of four H atoms, "H-c"; Ag at the site above the middle of two H atoms, "H-t". After full relaxation of all atoms, the polymer chain kept its shape and did not have twist or distortion along the chain direction, and Ag stayed with a slight movement in perpendicular direction (*b* axis).



Fig. S11 Charge density difference of before and after silver atom doping in threedimentional view (3D). Yellow and cyan isosurface depicts electron accumulation and depletion in space, respectively. Isosurface: ± 0.0001 e Å⁻³.



Fig. S12 Two-dimensional (2D) sections of charge density difference of model F-c. Section view are foucus on the charge transfer of the backbone, the nearest dipole, and the next nearest dipole. Red and blue area depects the increase and decrease of chagre density, respectively. Color bar unit: $e Å^{-3}$.



Fig. S13 2D sections of charge density difference of model F-t. Color bar unit: $e Å^{-3}$.



Fig. S14 2D sections of charge density difference of model H-c. Color bar unit: e $Å^{-3}$.



Fig. S15 2D sections of charge density difference of model H-t. Color bar unit: e $Å^{-3}$.



Fig. S16 Differences of Bader charge after Ag doping. Color bar unit: e.



Fig. S17 Changes of Born effective charge after Ag doping. Mobilities of polymer chain segments and dipoles are enhanced.



Fig. S18 Band structure and density of state (DOS). No insulator-conductor transition is observed.

References

- 1. A. Chhatre, P. Solasa, S. Sakle, R. Thaokar and A. Mehra, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2012, **404**, 83-92.
- 2. M. Quinten, Applied Physics B: Lasers and Optics, 2001, 73, 317-326.
- 3. S. Elzey and V. H. Grassian, Journal of Nanoparticle Research, 2009, 12, 1945-1958.