Supporting Information for

Achieving Remarkable Energy Storage Enhancement in Polymer Dielectrics via Constructing an Ultrathin Coulomb Blockade Layer of Gold Nanoparticles

Shuimiao Xia[a], Zhicheng Shi[a,*], Kai Sun[b,*], Peng Yin[a], Davoud Dastan[d], Yao Liu[c], Hongzhi Cui[a], Runhua Fan[b,c]

[a] *School of Materials Science and Engineering, Ocean University of China, Qingdao 266100, China*

[b] *College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, P. R. China*

[c] *Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, China*

[d] *Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georagi-30332, USA*

*Corresponding author.

E-mail: zcshi@ouc.edu.cn (Z. Shi); kais@shmtu.edu.cn (K. Sun)

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Materials

poly (vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)) (15 % HFP), commercial biaxially oriented polypropylene (BOPP) film and poly (methyl methacrylate) (PMMA) are purchased from PolyK Technologies, 1-methyl-2-pyrrolidone (NMP) and N, N-dimethylformamide (DMF) are acquired from Sinopharm Chemical Reagent Co., Ltd, nickel foam (350 g m^{-2}, Hefei Kejing Material Technology Co., Ltd.) and acetone (≥ 99.7 %, Sinopharm Chemical Reagent Co., Ltd.).

Preparation of pure polymer films

At first, P(VDF-HFP) and PMMA powders were dispersed respectively into NMP and DMF solvent by rapid magnetic stirring at 75 °C for 5 h and moderate stirring at room temperature overnight to obtain the P(VDF-HFP) and PMMA casting solutions. Subsequently, the solutions were casted on the glass plates and dried in an oven at 100 °C for 4 h and 200 °C for 5 min. After that, the films were immediately quenched in ice water and stripped from the glass plate. Finally, the films were dried at 50 °C for 4 h in the oven.

Characterization and measurements

The morphologies of gold nanoparticles were characterized by transmission electron microscopy (TEM, JEM-2100PLUS). The crystal structure of the films was analyzed using an X-ray diffraction (XRD, Bruker D8 Advance, Germany). Fourier transform infrared spectroscopy (FTIR) was performed by a Nicolet iS5 instrument from 3200 cm^{-1} to 400 cm^{-1}. For the dielectric property measurements, gold electrodes were sputtered on the films. The dielectric permittivity and dielectric loss were tested using an Agilent E4980A Precision LCR analyzer in the frequency range of 100 Hz to 1 MHz. The permittivity was calculated by $\varepsilon_r = tC_p/A\varepsilon_0$, where t is the thickness of the sample, C_p is the parallel capacitance, A is the area of the electrode, and ε_0 is the absolute permittivity of free space (8.85×10^{-12} F m^{-1}). The breakdown strength was obtained using a machinery consisting of a Treck 610 C amplifier with a voltage ramping rate of 500 V/s at room temperature (PolyK Technologies, USA). The energy-storage performances were acquired by the *P*-*E* loops which were collected at 100 Hz using a ferroelectric test system based on a modified Sawyer-Tower circuit (PolyK Technologies, USA). The leakage current densities of the films under varied electric fields were collected by a source meter (2450, Keithley Instruments). Young's modulus was measured through the Discovery DMA 850. The fast charge-discharge performances were tested by using the capacitor charge-discharge test system with a load resistor (RL) of 10 kΩ (PolyK Technologies, PA, USA).

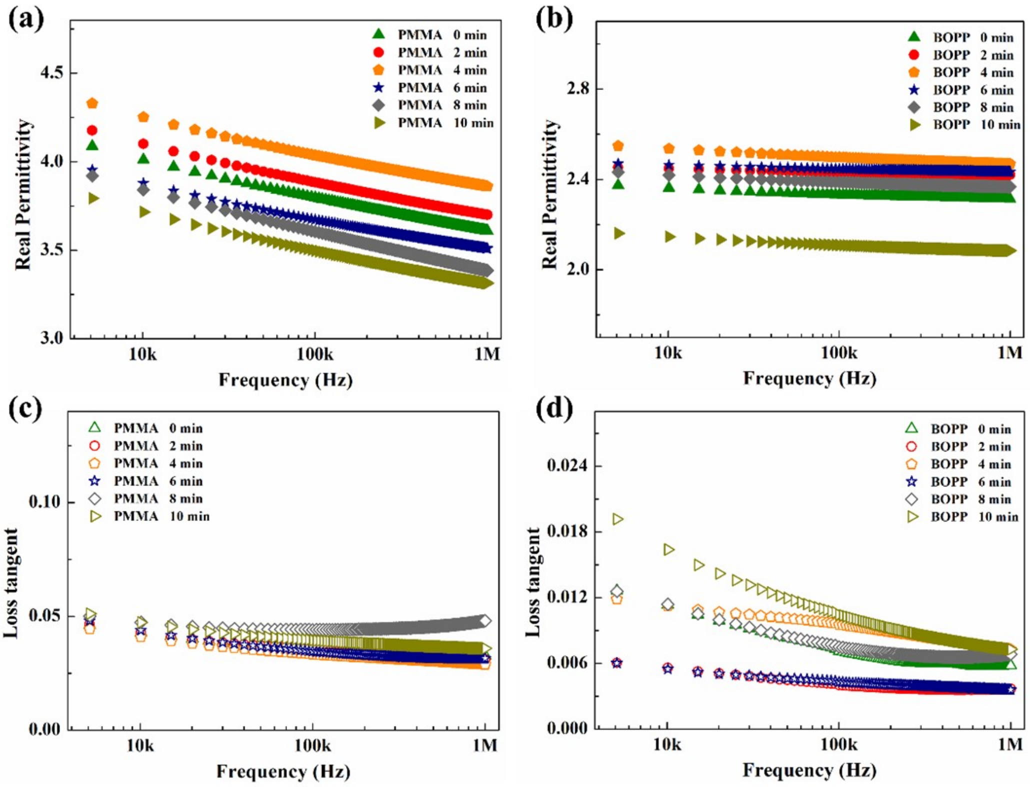

Fig. S1 (a, b) Dielectric permittivity and (c, d) loss tangent of PMMA-Au-PMMA and BOPP-Au-BOPP films.

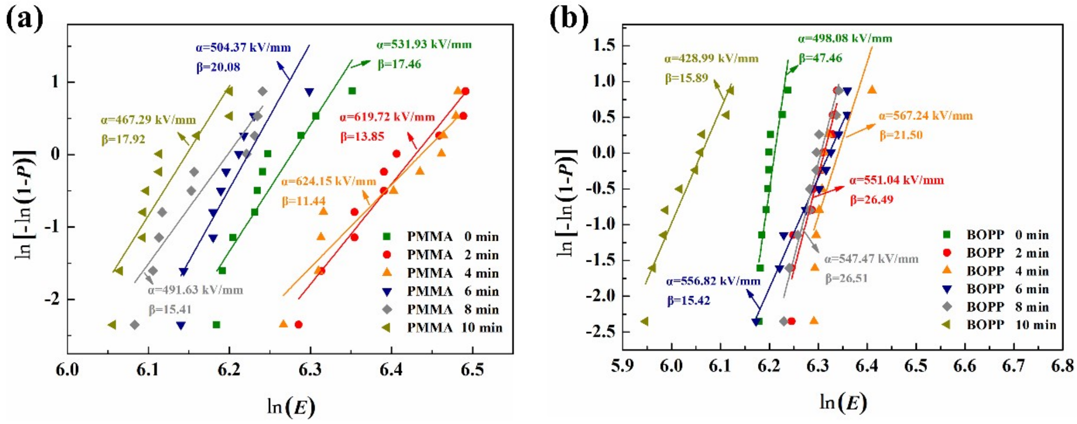

Fig. S2 Two-parameter Weibull distribution plots of (a) PMMA-Au-PMMA and (b) BOPP-Au-BOPP films.

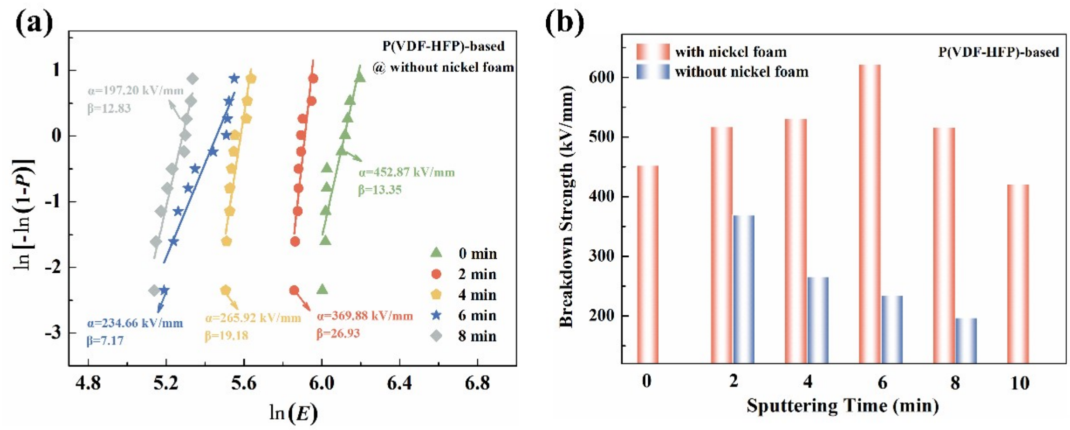

Fig. S3 Two-parameter Weibull distribution plots of (a) P(VDF-HFP)-based composite films without nickel foam and (b) the variation of breakdown strength of the P(VDF-HFP)-based composite films with different gold sputtering time.

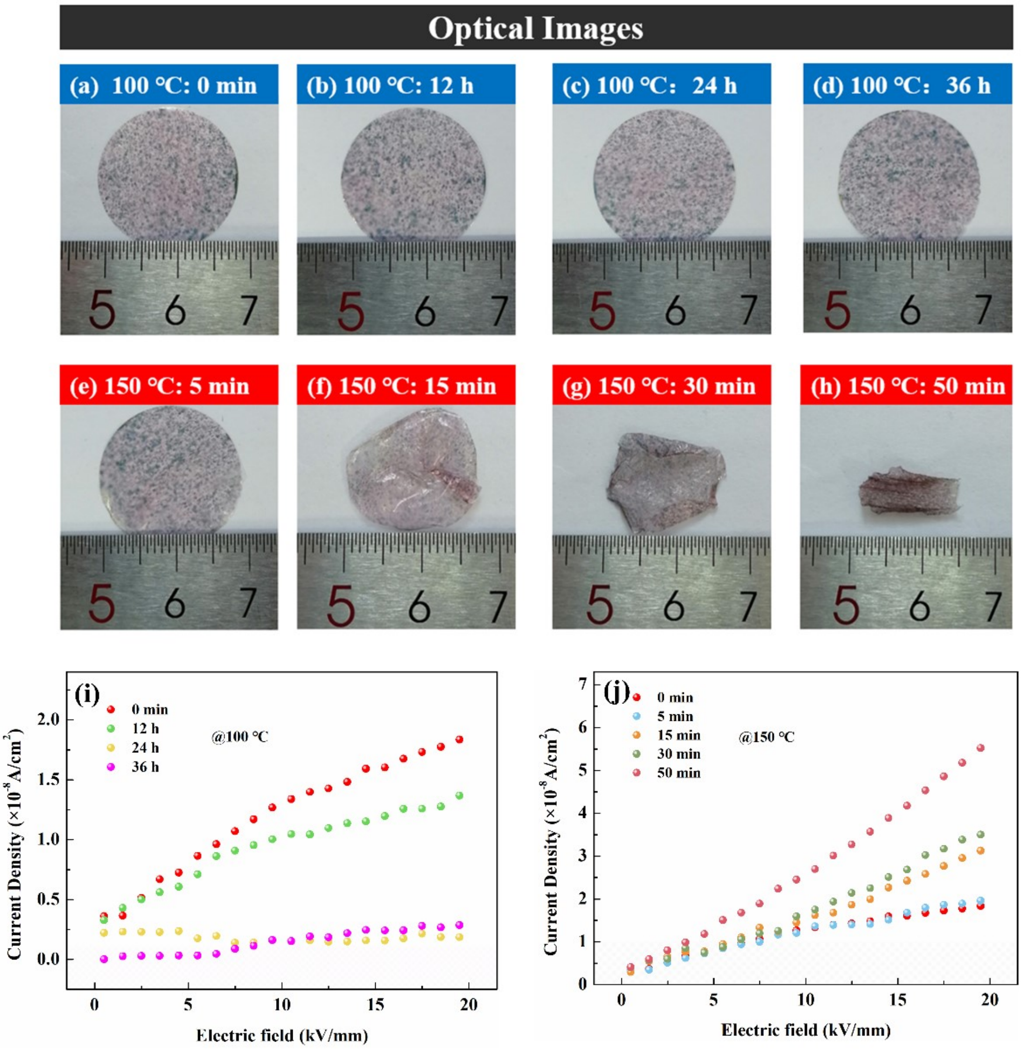

Fig. S4 (a-h) The optical images of P(VDF-HFP) film with 6 min gold sputtering baked at 100 °C and 150 °C. The current densities of P(VDF-HFP) film with 6 min gold sputtering at (i) 100 °C and (j) 150 °C.

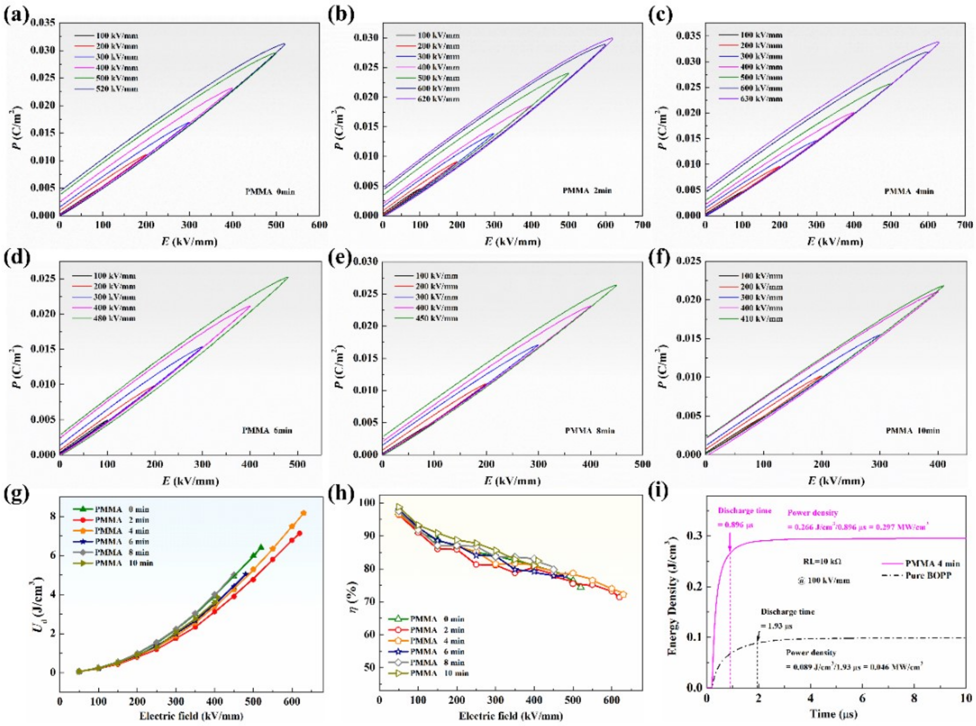

Fig. S5 (a-f) *P*-*E* loops. (g) The discharged energy density U_d and (h) efficiency η of PMMA-Au-PMMA films. (i) Discharge energy density as a function of time of pure BOPP and PMMA film with 4 min gold sputtering.

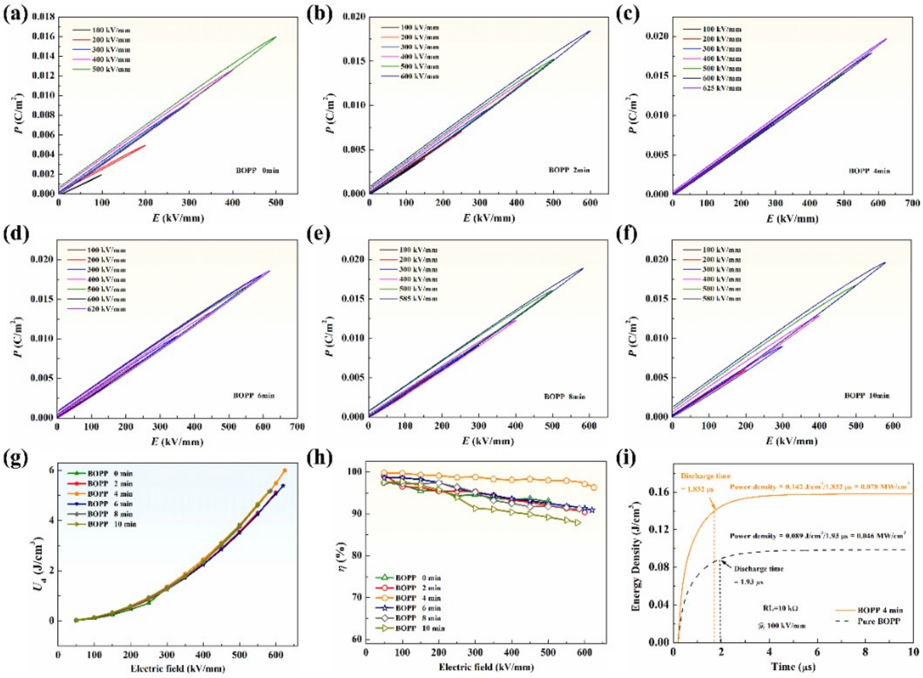

Fig. S6 (a-f) *P-E* loops. (g) The discharged energy density U_d and (h) efficiency η of BOPP-Au-BOPP films. (i) Discharge energy density as a function of time of pure BOPP and BOPP film with 4 min gold sputtering.

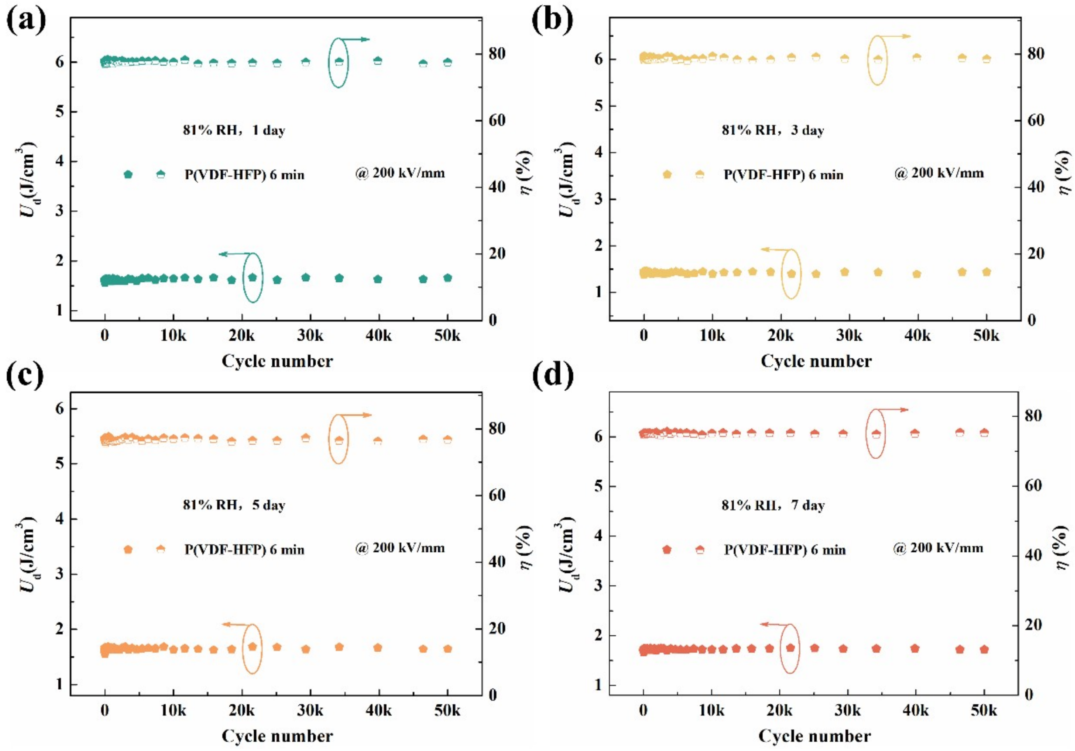

Fig. S7 The cycling stabilities of P(VDF-HFP) films with 6 min gold sputtering at 81% relative humidity (RH) for (a) 1 day, (b) 3 days, (c) 5 days, and (d) 7 days.

Table:

Table S1. Coulomb blockade barrier energy of gold particles with different sizes in polymer films.

r(nm)	p	C_1(F m^{-1})	C(F)	$e^2/2C$(meV)
1	5	1.2×10^{-11}	1.08×10^{-19}	740
2	5	1.2×10^{-11}	2.16×10^{-19}	370
3	5	1.2×10^{-11}	3.24×10^{-19}	250
4	5	1.2×10^{-11}	4.32×10^{-19}	185
5	5	1.2×10^{-11}	5.4×10^{-19}	148
6	5	1.2×10^{-11}	6.48×10^{-19}	123