

Supporting Information

Improved Energy Storage Property of Polypropylene-based Composite Dielectrics by Introducing Surface-Charged BaTiO₃@chitisan Ultrafine Constructions

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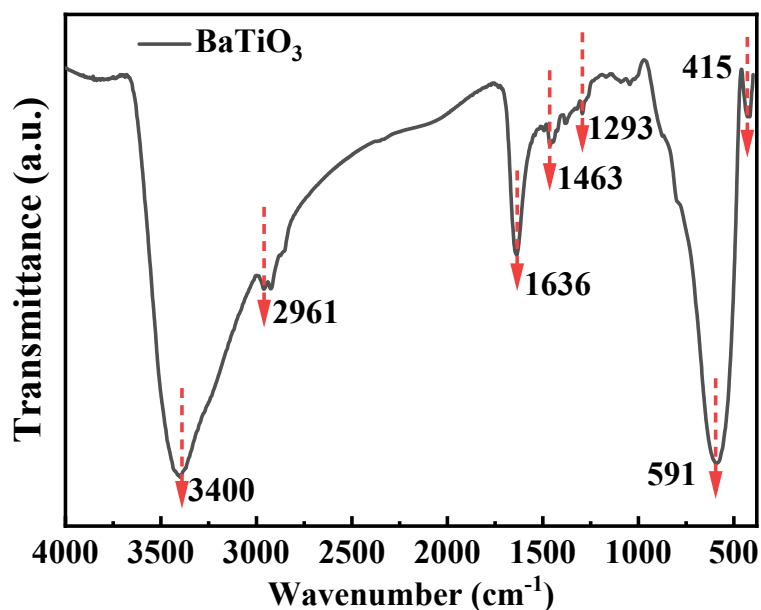


Fig. S1 FT-IR spectra of BaTiO₃.

As shown in Fig. S1, the bands at 591 and 415 cm⁻¹ in the BaTiO₃ spectrum correspond to the characteristic vibrations of Ti-O and Ba-O, respectively, indicating the formation of a perovskite structure. The C=O band at 1636 cm⁻¹ and the C-N band at 1293 cm⁻¹ observed from the BaTiO₃ spectrum are the characteristic bands for PVP. The band at 1463 cm⁻¹ can be identified as the bending vibration of the C-H bond. The appearance of a band at 3400 cm⁻¹ can be assigned to the stretching vibration of the O-H bond, and the band at 2961 cm⁻¹ is assigned to the stretching vibration of the C-H bond. These characteristic peaks also indicate the existence of organic functional groups on the surface of ultrafine BaTiO₃ during the fabrication process.

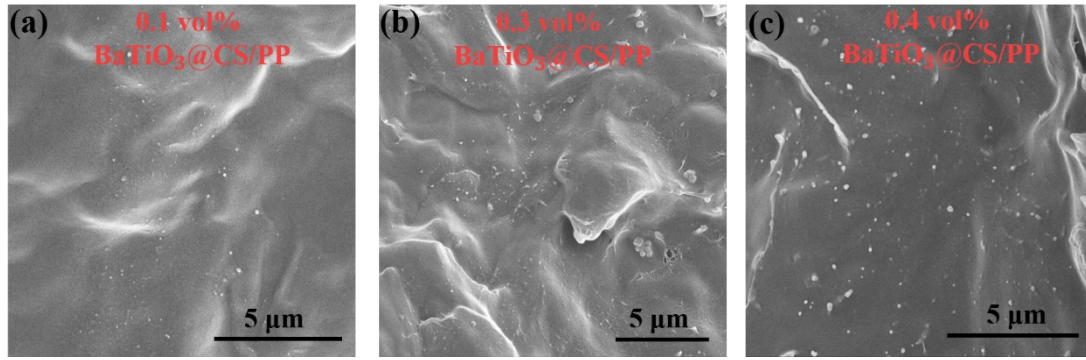


Fig. S2 Cross-section SEM images of the BaTiO₃@CS/PP composites filled with (a) 0.1vol%; (b) 0.3vol%; and (c) 0.4vol% of BaTiO₃@CS nanoparticles.

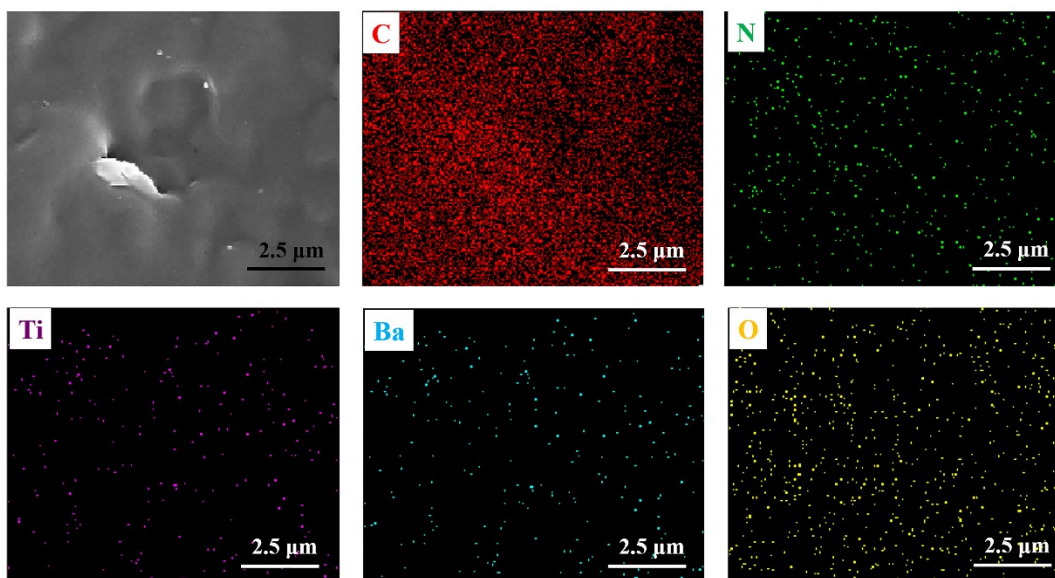


Fig. S3 The SEM image and the EDS chemical elements distribution of BaTiO₃@CS/PP composite filled with 0.2 vol% BaTiO₃@CS.

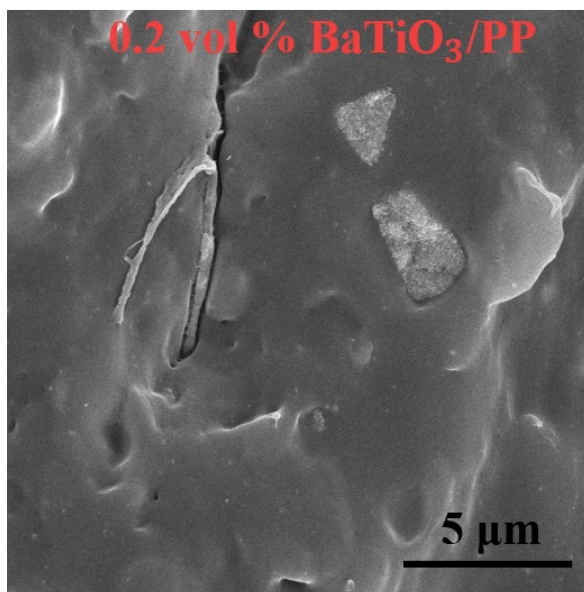


Fig. S4 Cross-section SEM image of the BaTiO₃/PP composite filled with 0.2 vol% BaTiO₃.

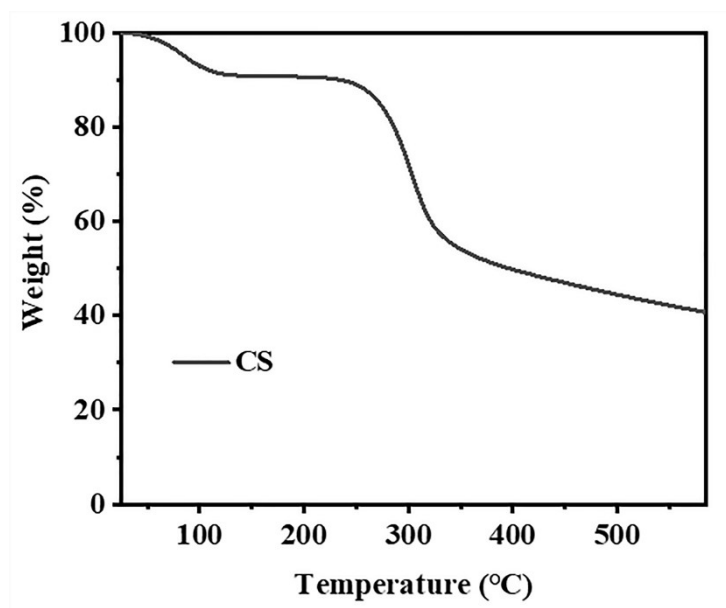


Fig. S5 The TGA result of CS within the testing temperature range of 25 to 600 °C.

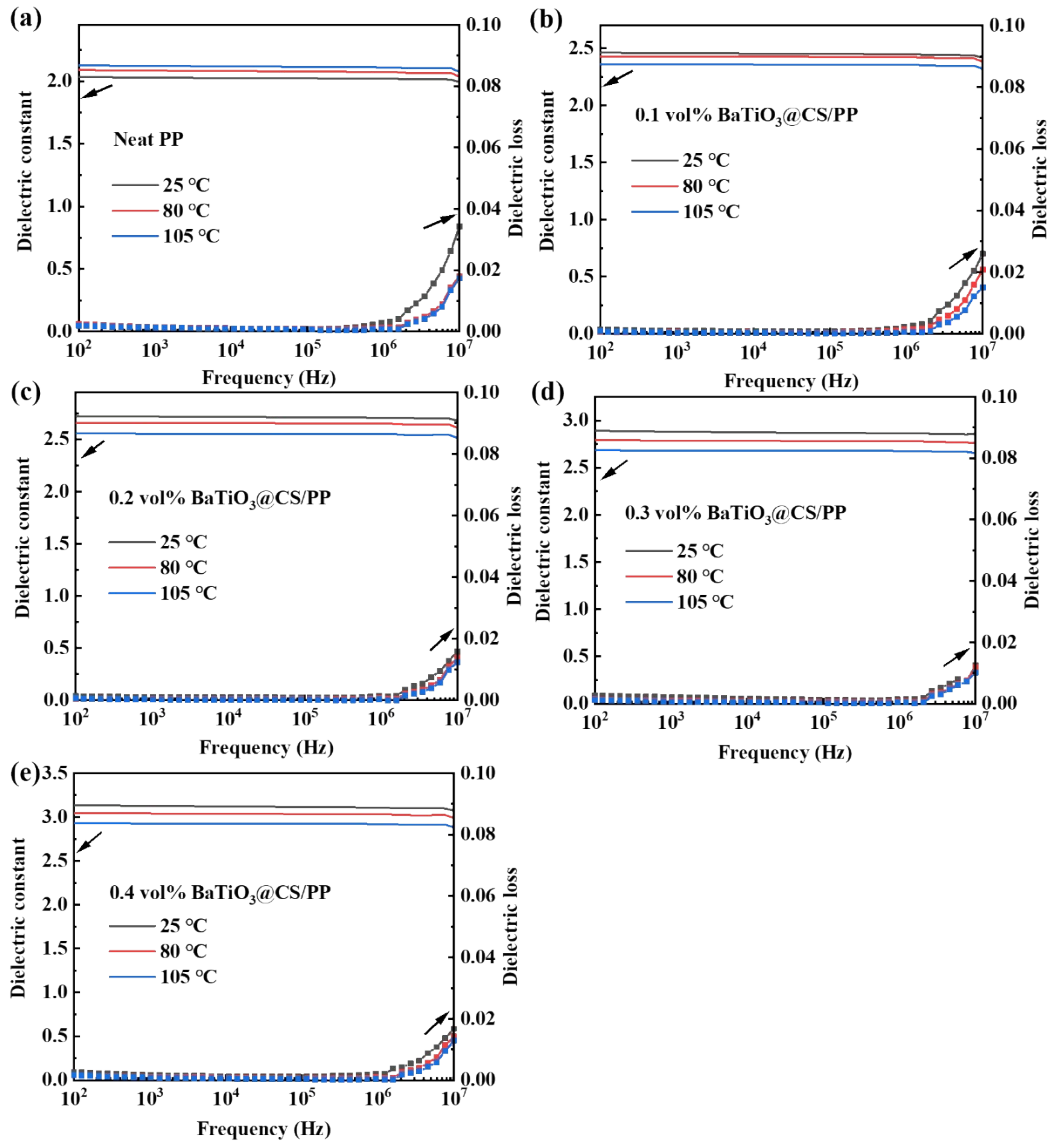


Fig. S6 Frequency-dependent dielectric properties of PP and BaTiO₃@CS/PP composites at different temperatures.

Supplementary method 1-Weibull statistical distribution

The calculation formula is as follows: $P(E) = 1 - \exp\left(-\left(\frac{E}{E_b}\right)^\beta\right)$, where $P(E)$ is the cumulative failure probability, E is the applied electric field, E_b is the characteristic breakdown strength at the cumulative failure probability of 62.8%, and β is the shape parameter for evaluating the dispersion of experimentally tested data. The β value is related to the reliability of the experimental data. The higher β value indicates the better structural stability of a dielectric material.

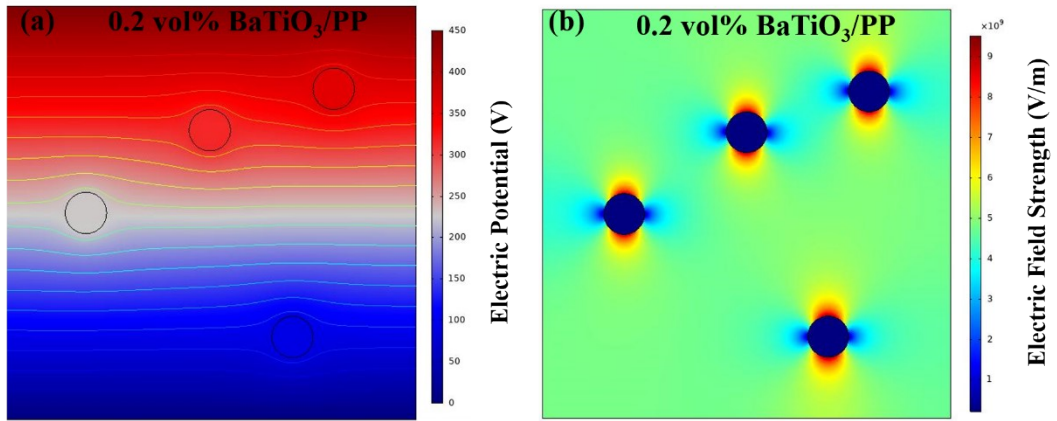


Fig. S7 (a) Electric potential distribution; and (b) electric field distribution of 0.2 vol% BaTiO₃/PP composite by the finite element simulation.

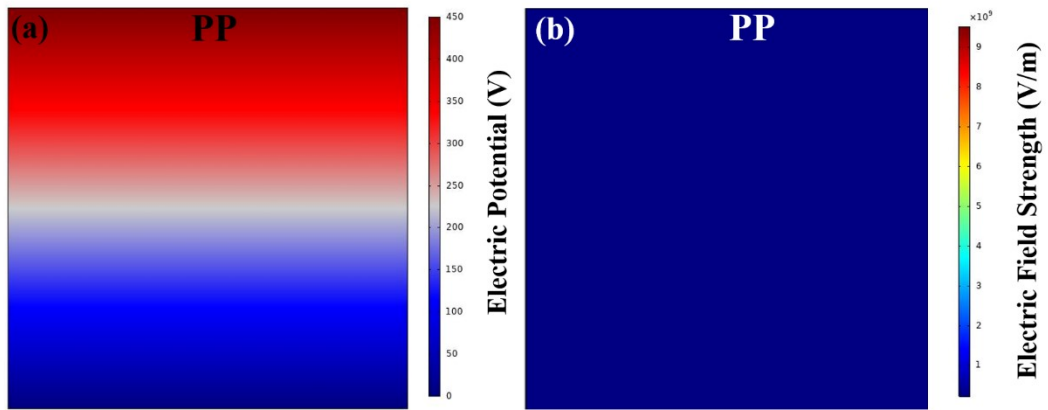


Fig. S8 (a) Electric potential distribution; and (b) electric field distribution of PP by finite element simulation.

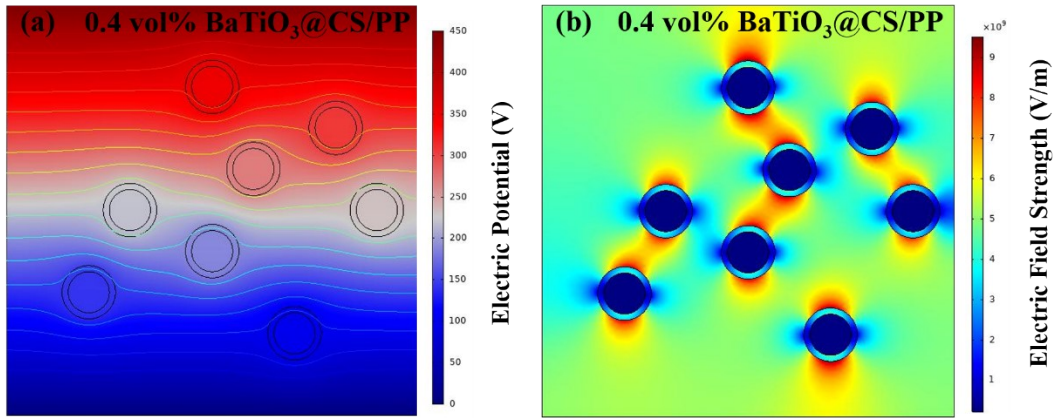


Fig. S9 (a) Electric potential distribution; and (b) electric field distribution of 0.4 vol% BaTiO₃@CS/PP composite by finite element simulation.

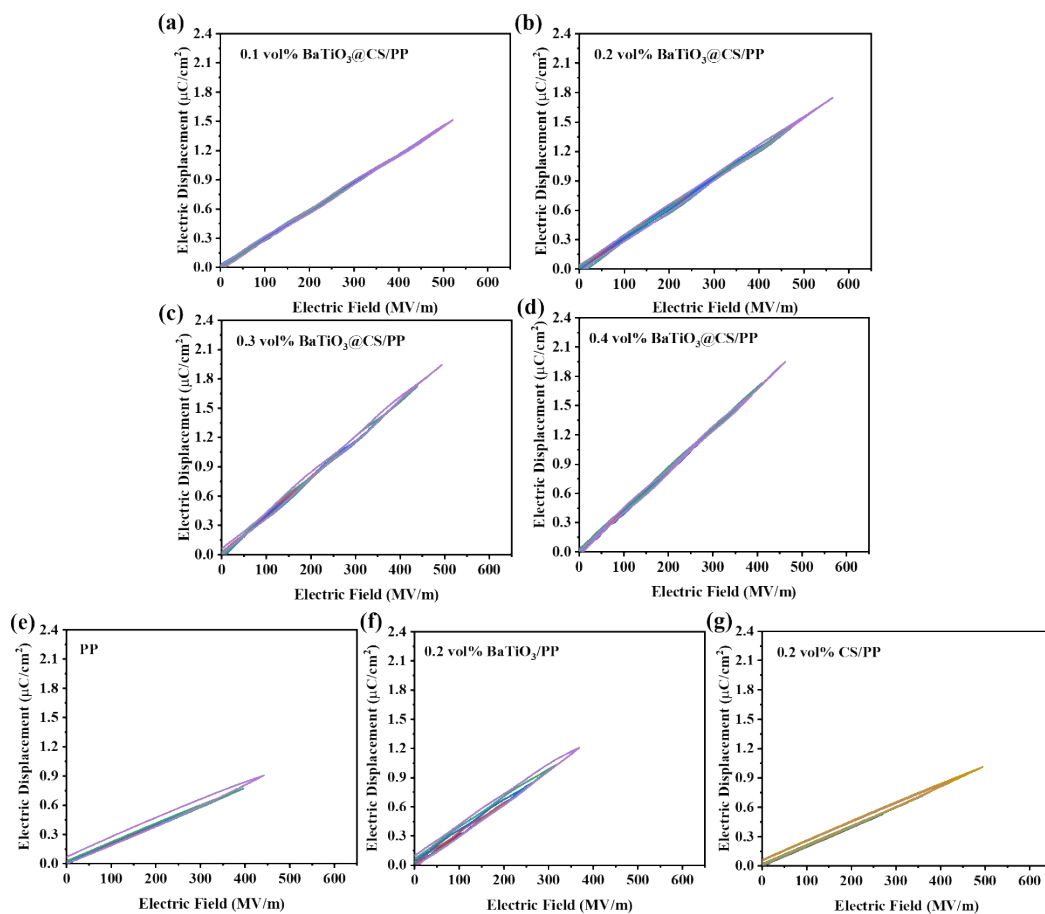


Fig. S10 The D - E loops of (a) 0.1 vol% BaTiO₃@CS/PP composite; (b) 0.2 vol% BaTiO₃@CS/PP composite; (c) 0.3 vol% BaTiO₃@CS/PP composite (d) 0.4 vol% BaTiO₃@CS/PP composite; (e) neat PP; (f) 0.2 vol% BaTiO₃/PP composite and (g) 0.2 vol% CS/PP composite.

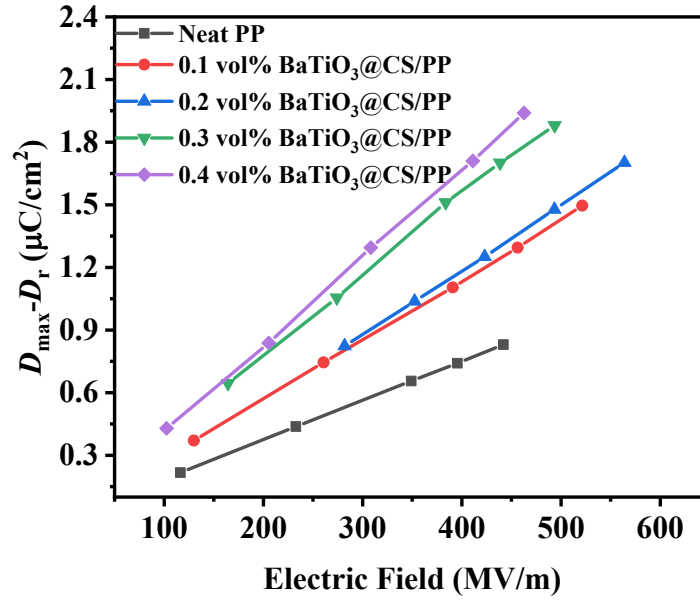


Fig. S11 $D_{max}-D_r$ dependence of BaTiO₃@CS/PP composites with the different loading contents of BaTiO₃@CS nanoparticles at varied electric fields.

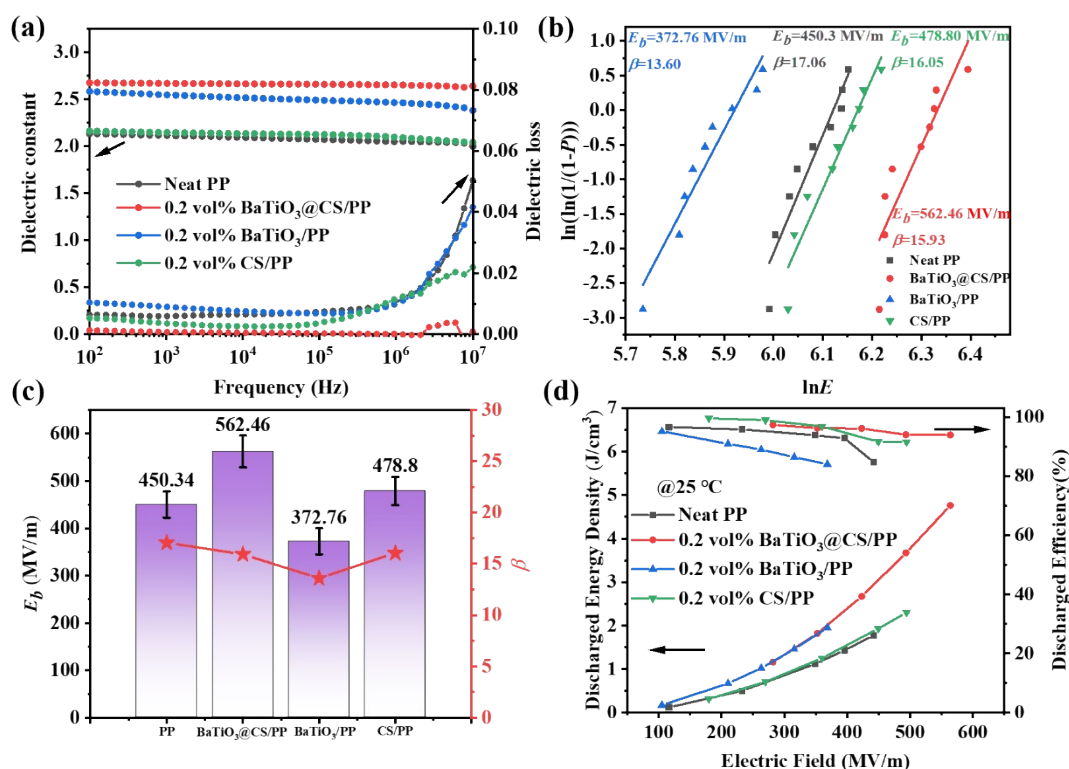


Fig. S12 (a) Frequency dependency of dielectric constant and dielectric loss, measured at 25 °C; (b) Weibull statistic breakdown strength; (c) deduced characteristic breakdown strength; and (d) Discharged energy density and charge-discharge efficiency of PP; 0.2 vol% BaTiO₃/PP composite; 0.2 vol% CS/PP composite and 0.2 vol% BaTiO₃@CS/PP composite at varied electric fields.

To further verify the obtained excellent energy storage performance is originated to the well-designed electrically-charged BaTiO₃@CS ultrafine nanoparticles, the comparisons of dielectric and energy storage performances among PP, BaTiO₃/PP, CS/PP, and BaTiO₃@CS/PP composites (filler fraction of these composites is constant as 0.2 vol%) are made and shown in Fig. S12.

To evaluate the influence of the BaTiO₃@CS nanoparticles on the dielectric property of the composites, both dielectric constant and dielectric loss as a function of

frequency were studied by using broadband dielectric spectroscopy (Fig. S12 a). The ϵ_r values of BaTiO₃/PP and CS/PP composites are 2.58 and 2.16 at 100 Hz, respectively, which are slightly higher than that of neat PP. However, the BaTiO₃@CS/PP composite dielectric exhibits the highest ϵ_r value of 2.67 and the lowest $\tan \delta$.

The Weibull statistical distribution of PP, BaTiO₃@CS/PP, BaTiO₃/PP and CS/PP composite dielectrics are shown in Figs. S12 b and c. The BaTiO₃@CS/PP composite shows the highest E_b , the E_b of the CS/PP composite is medium, the E_b of BaTiO₃/PP composite is lowest. In fact, since the ϵ_r values of BaTiO₃/PP, CS/PP and BaTiO₃@CS/PP composites are approximative, so the trend of recoverable energy storage density is similar to the trend of E_b . As shown in Fig. S12 d, the energy storage density of BaTiO₃@CS/PP composite is the optimal (4.76 J/cm³), that of the CS/PP composite (2.31 J/cm³) is the medium and that of the BaTiO₃/PP composite is the lowest (1.95 J/cm³). Based on the results of D - E loops, the charge-discharge efficiency (η) is calculated. The η decreases as electric field increases. Moreover, the BaTiO₃@CS/PP composite shows the highest η of 94%, the CS/PP composite also maintains a high level of 91.5%, the lowest η is achieved by the BaTiO₃/PP composite, with a η value of only 84% (Fig. S12 d). It is further confirmed that the obtained outstanding energy storage capability is mainly due to the synergistic effect of ultrafine BaTiO₃ and charged CS.

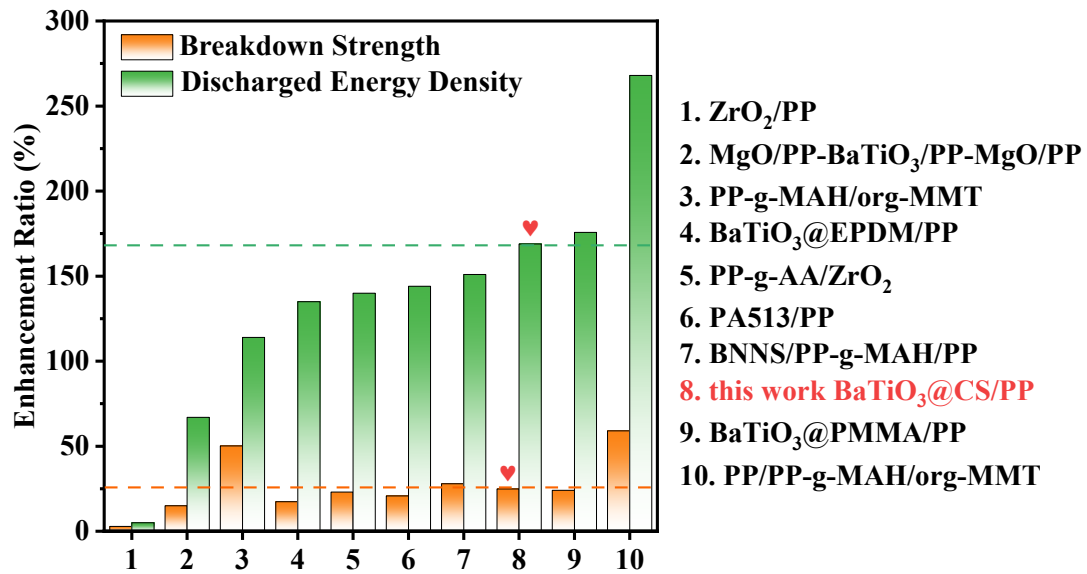


Fig. S13 The comparison of the enhancement ratios of breakdown strength and discharged energy density of PP-based composite dielectrics that reported in this work and previously published works of literature.

Since the energy storage performance such as E_b and U_e of a composite is related to the corresponding polymer matrix, the relative enhancements in E_b (defined as $(E_b/E_p-1) \times 100\%$) and U_e (defined as $(U_e/U_p-1) \times 100\%$) are calculated respectively. Where E_p and U_p were used to represent the breakdown strength and discharge energy density of the polymer matrix, respectively.