## Supporting Information

## Ultrahigh Energy Density of Poly(vinylidene fluoride) from Synergistically Improved Dielectric Constant and Withstand Voltage by Tuning Crystallization Behavior

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Figure S1. Cross section SEM image of PVDF films with different stretch ratio.



**Figure S2.** The surface  $(a_1, b_1)$  and cross-section  $(a_2, b_2)$  SEM image of R=1 and R=5 PVDF film, respectively.



**Figure S3.** (a) Load force–Displacement curve for PVDF films by uniaxially stretch. (b) The variation of true tensile stress with the increase of drawing ratio, calculated by load divided the cross-sectional area of stretched PVDF films. The increasing tensile stress during uniaxial stretching characterized by the universal mechanical testing machine provide a driving force for the structural changes (phase transformation, orientation enhancement and crystallinity reduction) of PVDF films.



 10
 15
 20
 25
 30

 2θ (°)

 Figure S4. Peak fitting results of 1D WAXD profiles for the PVDF films with different stretch ratio.



Figure S5. PFM graph morphology, amplitude and phase response of the uniaxially stretched

PVDF films with scanning area of 10×10um<sup>2</sup>.



Figure S6. The Electric displacement - Electric field (D-E) loops for PVDF polymer with

different stretched PVDF films.



Figure S7. The load-displacement curves for PVDF polymer with different stretched PVDF

films by nanoindentation test to characterize out-of-plane mechanical behaviors.



**Figure S8.** Schematic diagram of electrostatic compressive force produced by applying electric field for dielectric PVDF films.