Silver-adsorbed Ti<sub>0.87</sub>O<sub>2</sub> Nanosheets and UV Irradiation Synergistically Improve Energy Storage Performance of Polyvinylidene fluoride-based Nanocomposites Hexing Liu<sup>a</sup>, Yi Sun<sup>a</sup>, Cong Wang<sup>a</sup>, Jiayu Chen<sup>a</sup>, Zhong-Hui Shen<sup>b</sup>, Xin Zhang<sup>b</sup>, Bao-Wen Li<sup>a</sup>, <sup>b\*</sup>

<sup>a</sup> State Key Laboratory of Silicate Materials for Architectures, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China <sup>b</sup> School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China



**Figure S1.** (a) The low-resolution, (b) High-resolution TEM images, and (c) selectedarea electron diffraction pattern of TiNS nanosheets.



**Figure S2.** STEM image (a) and EDS elemental mapping images (b-d) of TiNSs@1Ag nanosheets.



**Figure S3.** STEM image (a) and EDS elemental mapping images (b-d) of TiNSs@3Ag nanosheets.



**Figure S4.** STEM image (a) and EDS elemental mapping images (b-d) of TiNSs@5Ag nanosheets.



**Figure S5.** EDS-elemental mapping analysis diagram and element content of (a) TiNSs@1Ag, (b) TiNSs@3Ag, and (c) TiNSs@5Ag nanosheets in Figure S2-S4.



**Figure S6.** The fitted XRD patterns of PVDF/TiNSs nanocomposites with (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.7 and (f) 1.0 wt. % of Ti<sub>0.87</sub>O<sub>2</sub> nanosheets. With the addition of only 0.1 wt.% of TiNSs, we observed the onset of diffraction peaks from the crystalline  $\beta$ -phase of PVDF. The content of  $\beta$ -PVDF was found to increase with the increasing content of TiNSs, and reached about 98% at 1.0 wt% of TiNSs, suggesting the "complete" phase transformation from  $\alpha$ - to  $\beta$ -phase PVDF. This phenomenon is in contrast to those observed in BNNS-P(VDF-CTFE) nanocomposites, in which the  $\alpha$ -phase PVDF only changed in the mean size of the crystalline domains as derived from several main diffraction peaks, while the content of  $\beta$ -phase PVDF remained nearly unchanged at a rather low fraction (< 2.0%) with the increasing addition of BNNS.

**Table S1.** Relative contents of  $\alpha$ - to  $\beta$ -phase and crystallinity for pure PVDF and PVDF/TiNSs nanocomposites, as estimated from the fitted XRD patterns in terms of the integral area of relevant diffraction peaks for each phase and amorphous hola of the PVDF matrix.

Sample	α (%)	β (%)	Crystallinity (%)
PVDF	45.1	0	45
0.1 wt.% TiNSs	27.2	8.8	36
0.3 wt.% TiNSs	11.6	19.2	31
0.5 wt.% TiNSs	0.2	19.6	20
0.7 wt.% TiNSs	1.3	24.7	26
1.0 wt.% TiNSs	0.7	23.0	24



**Figure S7.** Fourier transforms infrared (FTIR) spectra of pure PVDF and TiNSs /PVDF nanocomposites with different filler contents.



**Figure S8.** Thermogravimetric analysis (TGA) curves of pure PVDF and TiNSs /PVDF nanocomposites during a cooling cycle with a ramp of 10 °C min<sup>-1</sup>.



**Figure S9.** Frequency dependence of dielectric constant (solid) and dielectric loss (hollow) for TiNSs/PVDF nanocomposite films.



**Figure S10.** Frequency dependence of dielectric constant (solid) and dielectric loss (hollow) for 0.3 wt.% TiNSs@Ag/PVDF nanocomposite films.

The Coulomb-blockade effect of Ag nanoparticles can be described using a simplified energy level model, where N electrons are confined between two electrodes. The high charging energy of the Ag nanoparticles induces local electron repulsion, restricting the mobility of electrons in the interfacial TiNSs@Ag ( $\mu_{N+1}$ ). The electrostatic energy of the Ag nanoparticles increases by  $e^2/2C$ , which corresponds to the energy gap, where C represents the self-capacitance of the Ag nanoparticles. As a result, the (N + 1)th electron cannot tunnel through the Ag nanoparticles unless the charging energy exceeds the thermal energy ( $k_BT$ ), where T is the room temperature and  $k_B$  is the Boltzmann constant. However, if a bias voltage is applied to the left electrode ( $\mu_L$ ), raising its potential above that of  $\mu_{N+1}$ , the (N + 1)th electron can then undergo quantum mechanical tunneling through the Ag nanoparticles, as illustrated in Fig. S11(b).



**Figure S11.** Illustration of the Coulomb-blockade effect in Ag nanoparticles: (a) The energy gap induced by Ag nanoparticles between the energy states of  $\mu_{n+1}$  and  $\mu_{n}$ .(b) The (N + 1)th electron can tunnel quantum mechanically once the applied voltage V is sufficiently high to overcome the Coulomb repulsion, closing the energy gap.



**Figure S12.** (a) Weibull breakdown strength of the pure PVDF and TiNSs/PVDF nanocomposite films. (b) Variation of breakdown strength as a function of TiNSs content. (c) Variation of leakage current density with electric field. (d) Electric displacement-electric field loops obtained at 10 Hz. (e) The discharged energy density and (f) charge-discharge efficiency are plotted as a function of an electric field.



Figure S13. (a) Weibull breakdown strength of the TiNSs@Ag nanocomposite films. (b) Electric displacement-electric field loops obtained at 10 Hz. (c) The discharged energy density and (d) charge-discharge efficiency are plotted as a function of an electric field.



**Figure S14.** (a) UV-visible absorption spectra and (b) plots of the optical bandgap for pristine PVDF and PVDF-UV 15 min films.