

Simultaneously Improved Dielectric Constant and Breakdown Strength of PVDF-based Composites with Polypyrrole Nanowire Encapsulated Molybdenum Disulfide Nanosheets

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 Electronic Supplementary Information

Abstract High-performance dielectric polymer composites have received increasing attention due to their important applications in the field of energy storage. The rational structural design of hybrid fillers can lead to a balance between high dielectric constant and insulation in composites. In this work, novel hybrid fillers were fabricated by *in situ* synthesizing one-dimensional polypyrrole nanowires (PPynws) on the two-dimensional molybdenum disulfide (MoS_2), which integrated the good ion polarization ability of PPynws and the high insulation and adjustable band gap of MoS_2 . Compared with the binary poly(vinylidene fluoride) (PVDF)/ MoS_2 composites, the PVDF/ MoS_2 -PPynws composites exhibited remarkably improved dielectric constant and breakdown strength, while the dielectric loss was still maintained at a low level. An optimal ternary composite with 1 wt% MoS_2 -PPynws showed a high dielectric constant (15@1kHz), suppressed dielectric loss (0.027@1kHz), and high breakdown strength (422.1 MV/m). PPynws inducing strong interfacial polarization and the highly insulated MoS_2 nanosheets extending the breakdown path mainly contributed to the synchronously enhanced dielectric constant and breakdown strength. This intriguing synthesis method of PVDF/ MoS_2 -PPynws nanocomposite will open up new opportunities for fabricating nanostructured polymer composites to produce high dielectric materials.

Keywords Hybrid fillers; Molybdenum disulfide; Polypyrrole nanowires; Dielectric composites; Breakdown strength

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INTRODUCTION

Dielectric polymer capacitors have drawn extensive attention because of their lightweight, easy processing, low loss, and high breakdown strength, which can be applied in energy harvesting devices, digital memory devices, and pulsed power systems.^[1–3] However, most of the polymers possess a comparatively low dielectric constant, leading to a low capability of energy storage. For example, the commercial biaxially oriented polypropylene (BOPP) film capacitors with a low constant of 2.2 only can generate a discharged energy density (U_e) of $<2.5 \text{ J/cm}^3$, which obviously cannot meet the requirement for energy storage in practice.^[4] Therefore, it is urgent to develop new methods to increase the dielectric constant and meanwhile to preserve other desirable properties (e.g., high breakdown strength, low dielectric loss, flexibility, and easy processing).

Nowadays, aiming to achieve polymer composites with high dielectric constant, a large number of researches have

been focused on inorganic fillers with high dielectric constant into polymer matrix.^[5–9] Typical organic fillers involve ceramic dielectric fillers with large dielectric constant, such as barium titanate (BaTiO_3),^[10] strontium titanate (SrTiO_3),^[11] and calcium titanate (CaTiO_3).^[12] However, ceramic filled dielectric polymer composites are usually involved with a high loading of fillers and the mechanical properties and breakdown strength would be deteriorated owing to the introduction of a great amount of interface. On the other hand, the dielectric enhancement can be realized in the conductive fillers^[13] incorporated polymer composites, and the dielectric property of these composites obey the percolation theory. Thus, the high dielectric constant based on the percolation paths is always accompanied by the risk of sharply increased current leakage due to the continuous contact or close distance between conductive fillers. Apart from conductive and ceramic fillers, semiconductive fillers such as zinc oxide (ZnO)^[14] and silicon carbide (SiC)^[15] have unique nonlinear electrical behavior, which makes them great potential for high-voltage application. For example, in the previous work of poly(vinylidene fluoride) (PVDF)/ ZnO composites, high dielectric constant as well as the high working electric field can be realized.^[16] Recently, two-dimensional inorganic semi-

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conductors, particularly layered transition metal dichalcogenides, such as molybdenum disulfide (MoS_2), have been applied in polymer dielectric composites due to their feature about electric field tunable dielectric constant.^[17] Many researchers have corroborated that MoS_2 has a positive effect on enhancing the dielectric constant of polymers.^[18–20] However, there is still the main challenge for MoS_2 enhanced dielectric polymers that MoS_2 tends to agglomerate and stack in the polymer matrix, resulting in low capacitance, low capacity of charge polarization, poor interface compatibility, and relatively high dielectric loss. Therefore, it is urgent to seek an efficient way to fabricate the layer-structured MoS_2 with interface compatibility to the polymer matrix and also to preserve the excellent electric performance.

It is well recognized that interfacial engineering is an advantageous method to tune the interface structure and resultant interfacial polarization in polymer-based dielectric composites. A great number of modification methods for dielectric fillers have been demonstrated in the past several years.^[21–24] Among these methods, conductive polymer decorating fillers has been regarded to be an effective way to tune the electric conductivity as well as interfacial compatibility and polarization. For example, Maity *et al.* prepared polyaniline (PANI)@ MoS_2 hybrid fillers, in which the PANI behaved like an interfacial linker to optimize the interfacial adhesion between MoS_2 and polymer matrix, leading to an improved dielectric constant.^[18] Recently, conductive polymer polypyrrole has received widespread attention because of its easy preparation, good environmental stability, and tunable conductivity. PPy has been introduced into poly(vinylidene fluoride) trifluoro chloroethylene (PVDF-CTFE)^[25] and cellulose^[26] for dielectric enhancement. Based on its electric conductivity feature, PPy as a modifier to decorate fillers is also an effective way to tailor the dielectric property of hybrids. Chen *et al.* fabricated PPy decorated multiwalled carbon nanotubes (PPy@MWCNT) nanofillers via FeCl_3 oxidative polymerization of monomer pyrrole and introduced them into PVDF to prepare composite materials. The dielectric constant of the composites was increased to 83.^[27] Zhang *et al.* synthesized core-shell PPy encapsulated sepiolite (Sep) nanofibers, and the dielectric constant of the PVDF/PPy@Sep composites increased from 12 of neat PVDF to 40.^[28] The functions for the conductive layer coating on the inorganic fillers are generally ascribed to the enhanced interfacial charge accumulation, hierarchical interfacial polarization, and resultant micro capacitor effect in the composites.

In our previous study,^[29] the PPy nanoparticles have been

successfully introduced on the MoS_2 nanosheets, PPy- MoS_2 -PPy sandwiched hybrids endowed the PVDF matrix with enhanced dielectric constant as well as dielectric loss. As it is well known that PPy possesses a variety of morphologies, such as nanoparticles, nanowire or mixture, to exhibit different conductivities. Compared with the PPy nanoparticles, the PPy nanowires present a higher specific capacitance,^[30] exhibiting a greater potential for further enhancing the dielectric performance of the composites. In this work, the PPy nanowires (PPynws) were *in situ* synthesized on the MoS_2 nanosheets and the hybrids were incorporated into the PVDF matrix to fabricate the PVDF/ MoS_2 -PPynws composites. The morphology of the hybrids, crystalline structure, and dielectric behaviors of the polymer composites were systematically investigated in detail. The results showed that an enhanced dielectric constant of 21@1 kHz (at the frequency of 1 kHz) and a high breakdown strength of 422.1 MV/m were achieved for polymer composites at a low loading of hybrids. In a view of the PPynws interface inducing crystallization and polarization, the underlying mechanism for the dielectric enhancement was illuminated.

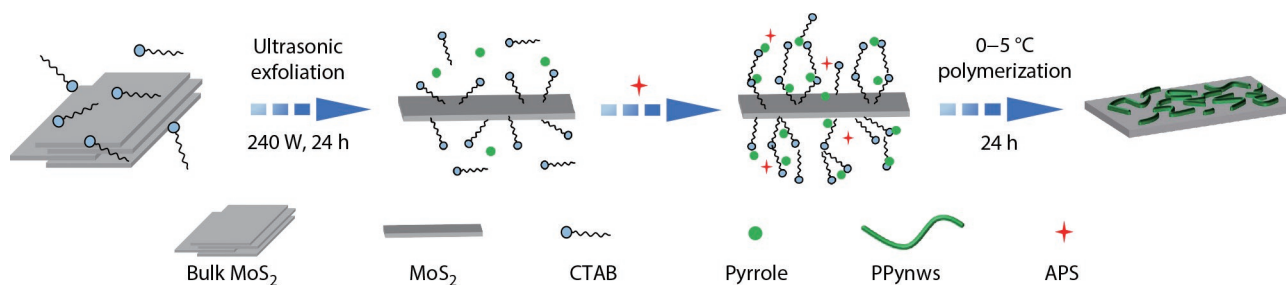
EXPERIMENTAL

Materials

The raw materials and reagents used in this work are all commercially available. PVDF (particles, Kynar720) was purchased from Arkema (France), and it has a weight-average molecular weight of 1.05×10^5 g/mol and a density of 1.78 g/cm³. Bulk MoS_2 was obtained from Aladdin Reagents (Shanghai) Co., Ltd. The average diameter of bulk MoS_2 is 2 μm , and the purity is about 99.5%. Pyrrole monomer with the purity above 98%, Cetyltrimethyl ammonium bromide (CTAB), ammonium persulfate, and dimethylformamide (DMF) were provided by Kelong Chemical Reagent Co., Ltd. (Chengdu, China), and all these reagents have analytical purity.

Preparation of MoS_2 -PPynws Hybrid Filler

The preparation of MoS_2 nanosheets is based on the method of ultrasonic liquid-phase exfoliation in the literature.^[31] The preparation mechanism and process of hybrid fillers are shown in Scheme 1. Firstly, 1 g of bulk MoS_2 was added into 200 mL of deionized water dissolved with 1.1 g of CTAB in a baker. The mixture in the baker was ultrasonicated for 12 h in ice water to exfoliate the bulk MoS_2 . Then the colloid was centrifuged at 2000 r/min for 20 min. The exfoliated MoS_2 nanosheets dispersion was obtained from two-thirds of the supernatant.



Scheme 1 CTAB-assisted liquid phase exfoliating of MoS_2 and preparation of MoS_2 -PPynws hybrid fillers by interface adsorption soft template method.

The concentration of the supernatant was determined by calibration.

In an ice-water bath, a certain amount of pyrrole monomer was added to a beaker containing a dispersion of MoS₂ nano-sheets and mixed evenly by stirring and ultrasonic. Then, ammonium persulfate aqueous solution (3.65 g in 40 mL of water) was added to the mixed solution of MoS₂ and pyrrole monomer slowly drop by drop under the condition of -5°C and stirred steadily for 24 h. The products were collected by vacuum extraction through the filter membrane, washed repeatedly with deionized water and anhydrous ethanol for three times, and then dried in a 60°C vacuum oven for 2 days.

Fabrication of PVDF/MoS₂-PPynws Composite Film

The nanocomposite films were prepared by solution casting method as shown in Figs. 1(a)–1(c). Firstly, PVDF powders were dissolved in DMF and stirred overnight to obtain a homogeneous solution with a concentration of 250 mg/mL. The obtained MoS₂-PPynws hybrids were homogeneously dispersed in DMF by tip-type sonication with the power of 250 W for 1 h and stirring for 2 h in the water bath with 1500 r/min, and then the two solutions were mixed in a certain proportion by ultrasound. The composite films containing different MoS₂-PPynws weight contents (e.g., 0 wt%, 1 wt%, 2 wt%, 5 wt%) were fabricated by casting the above suspensions onto a cleaned glass plate and named PVDF/XMoS₂-PPynws ($X=0,1,2,5$). The DMF solvent is removed completely at 70°C for 6 h. Finally, the dried films were annealed at 180°C for 4 h in the vacuum oven, and then immediately put into ice water for quenching treatment to reduce their crystallinity. The quenched films were dried at 70°C overnight.^[32,33] For the comparative experiment, the PVDF/MoS₂ composite films were fabricated by the same method. The thickness of the sample film prepared by solution casting and subsequent annealing was about 10–20 μm .

Characterization

Scanning electron microscopy (SEM)

The morphologies of the MoS₂-PPynws hybrid and the composite film were observed by scanning electron microscope (SEM) of Fei Inspect (FEI, the Netherlands). The MoS₂-PPynws hybrids fillers were firstly dispersed on the silicon plate, and then a layer of gold was sputtered on the surface of the sample for SEM observation. To investigate the dispersion of MoS₂-PPynws hybrids in the PVDF matrix, the composite films were put into the liquid nitrogen for 1 h and then fractured cryogenically. Energy dispersive spectrometer (EDS) measurements were also carried out during the SEM characterization process.

Transmission electron microscopy (TEM)

High-resolution transmission electron microscope (HR-TEM) characterization was conducted on a (JEOL, 2010F) instrument

with an accelerated voltage of 200 kV. To investigate the microstructure of the hybrid fillers, the fillers were dispersed in DMF to prepare a stable suspension, and then the suspended droplets were dried on a carbon-coated copper grid and were directly observed in the TEM instrument.

Atomic force microscopy (AFM)

The thickness and particle size of the exfoliated MoS₂ nano-sheets were characterized by an atomic force microscope model MULTIMODE8 (Bruker, German) in tapping mode. The exfoliated MoS₂ nanosheets dispersion was coated on a small silicon wafer by spin coating and then dried for 24 h to prepare a characterization sample.

Fourier transform infrared spectrometer (FTIR)

At room temperature, a Fourier transform infrared spectrometer analyzer (FTIR) of Avatar 360 (Thermo Nicolet, USA) was used to characterize the structure of the MoS₂-PPynws hybrid filler and the composite film. All samples were tested in a transmission mode and the test range was $4000\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .

Wide-angle X-ray diffraction (WAXD)

The crystal textures of MoS₂ and MoS₂-PPynws were characterized using a wide-angle X-ray diffraction (X'pert PRO diffractometer, Panalytical, the Netherlands) with Ni-filtered Cu K α radiation in the angle range of 5° to 50° .

Dielectric property measurement

The dielectric property measurements were conducted on a broad frequency dielectric spectrometer (Concept 80, Novo control, Germany) at 220 V in the frequency range of $10^2\text{--}10^7$ Hz. Before measurement, 4 mm round gold electrodes were sprayed onto the composite film to erase the contact resistivity.

The dielectric breakdown strength of the sample was measured using a breakdown voltage tester (BDJC-50 KV, Bei-guang Jingyi Instrument, PR China). The voltage was increased with a rate of 1.5 kV/s using an alternating current, and the highest voltage measured was 30 kV.

RESULTS AND DISCUSSION

Characterization of MoS₂-PPynws Hybrid Fillers

The growth of PPy nanowire was derived from the CTAB soft template method^[34] as shown in Scheme 1. Here, the bulk MoS₂ was exfoliated into few layers MoS₂ nanosheets by sonication in CTAB aqueous solution, and the CTAB tended to adsorb on the MoS₂, which is beneficial to the dispersion of MoS₂ due to its amphiphilic features. In this case, the hydrophobic pyrrole monomers are predominately located at the core of the CTAB micelles and polymerized into PPy with the initiation of

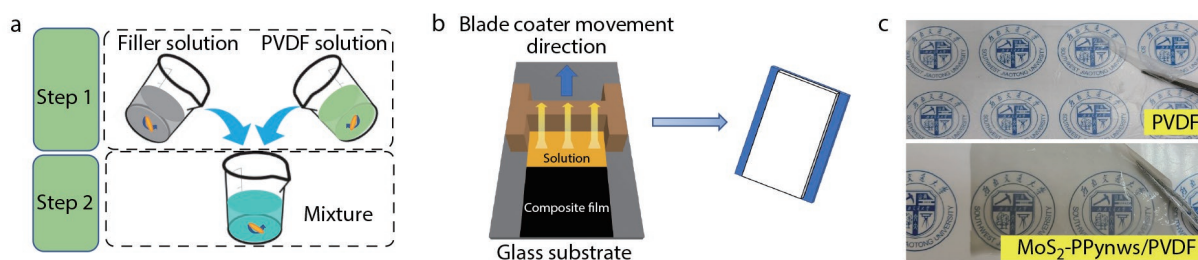


Fig. 1 Schematic diagram of the preparation process of the composite film.

ammonium peroxydisulfate ((NH_4) $_2\text{S}_2\text{O}_8$, APS). The bulk MoS_2 and exfoliated MoS_2 nanosheets were observed as shown in Figs. 2(a) and 2(b), respectively. It can be seen that the bulk MoS_2 has an aggregates-like morphology with a thickness of several micrometers. It suggests that bulk MoS_2 exhibits multiple layers which are stacked along the Z-axis direction. The reduced size and thickness can be found in Fig. 2(b), which can be identified in the exfoliated MoS_2 with the aid of CTAB. To evaluate the exfoliation of bulk MoS_2 , the AFM was applied to observe the lateral size and thickness as shown in Figs. 2(c) and 2(d). AFM images show the 2-dimensional (2D) sheet-like morphology with lateral size in the range of 1–2 μm . The corresponding height profile reveals that the height of MoS_2 nanosheets is about 4 nm, which is higher than that of monolayer MoS_2 (0.8–1 nm). It suggests that the MoS_2 was exfoliated with few layers. FTIR spectra for the bulk MoS_2 and exfoliated MoS_2 nanosheets are presented in Fig. 2(e). Firstly, the

vibration band of $\text{Mo}-\text{S}$ bonding at $\sim 460\text{ cm}^{-1}$ can be found in the spectra of MoS_2 and exfoliated MoS_2 . Compared with the bulk MoS_2 , there are some new characteristic bands in the spectrum of the exfoliated MoS_2 nanosheets. The adsorption bands located at $2900\text{--}2850\text{ cm}^{-1}$ are assigned to the CH_2 antisymmetric and symmetric stretching vibration of CTAB.^[35] Besides, the band at 1447 cm^{-1} is attributed to ammonium salt. It suggests that the CTAB was adsorbed on the MoS_2 nanosheets.

Based on the exfoliated MoS_2 nanosheets, the PPy was *in situ* polymerized on MoS_2 nanosheets. The morphology of MoS_2 -PPynws hybrids was characterized by SEM and TEM. The typical SEM images varying with different feed ratios of Py monomer are shown in Fig. 3. SEM images show that Py monomer polymerizes on the surface of MoS_2 to form randomly coiled nanowires with a diameter of about 50–100 nm, which are wound around the MoS_2 nanosheets. At a low feed

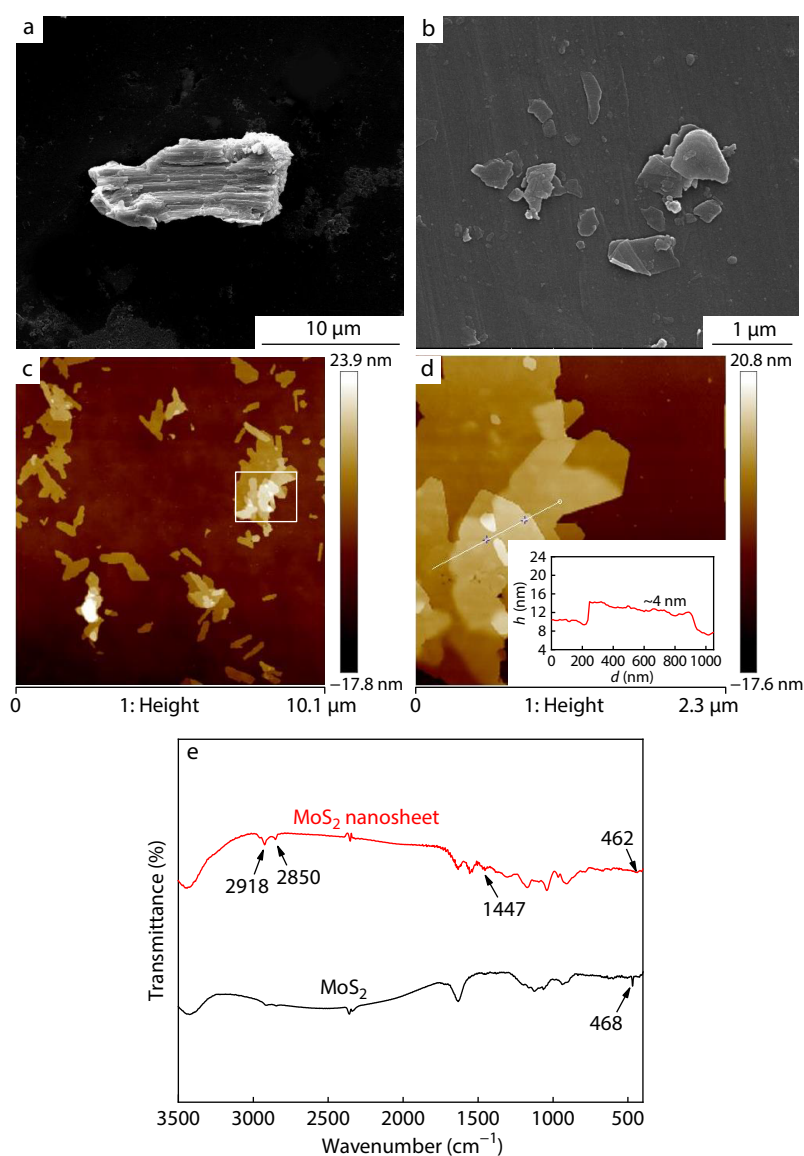


Fig. 2 (a, b) SEM images of bulk MoS_2 and exfoliated MoS_2 nanosheets, respectively; (c, d) AFM images of exfoliated MoS_2 nanosheets with height profiles; (e) The FTIR spectra of bulk MoS_2 and MoS_2 nanosheet.

ratio (MoS_2/Py), PPy_nws are directly grown on the surface of MoS_2 as shown in Fig. 3(a), and form a hybrid filler with a three-dimensional interconnection structure. By increasing the content of Py, the PPy_nws grow longer and exhibit a higher entanglement density, however weak significant linkage between MoS_2 and PPy_nws can be found as shown in Fig. 3(b). When the feed ratio continues to increase, no PPy_nws can be found, and the MoS_2 is covered by a layer of uncertain particles as shown in Fig. 3(c). Based on these results, the feed ratio of 1:1 (*W/W*) was chosen for the fabrication of MoS_2 -PPy_nws hybrids in large-scale production because, at a highly increased feed ratio, the PPy is more prone to be self-polymerized.

For a clearer characterization of MoS_2 -PPy_nws hybrids, EDS was used for qualitative analysis of the related elements of the hybrids, and the results were shown in Figs. 4(a) and 4(b). In the selected point area as shown in Fig. 4(a), the appearance of S elements confirms the existence of MoS_2 . The high

weight percentage of C and O elements indicates the PPy nanowires cover the MoS_2 nanosheets, which is well-matched with an observation from SEM images. In order to obtain more intuitive visual structure information for the hybrids, TEM images are obtained and shown in Figs. 4(c) and 4(d). It can be clearly seen that one-dimensional PPy nanowires are stacked and wound on the surface of the MoS_2 nanosheet. Fig. 4(d) is an enlarged image of the nanowire from the edge view, showing a helical nanowire with a length of 400–500 nm and a diameter of 40–50 nm.

To further analyze the structural information of the hybrids, MoS_2 -PPy_nws and PPy_nws were characterized by FTIR and WAXD, and the corresponding spectra are shown in Fig. 5. In the FTIR spectrum of MoS_2 -PPy_nws (Fig. 5a), the characteristic absorption bands at 1542, 1173, 1042 and 902 cm^{-1} are assigned to the in-ring stretching vibration of C=C bond in pyrrole ring, stretching vibration of polypyrrole ring, stretching vibration of C—H and N—H bond and out-of-plane

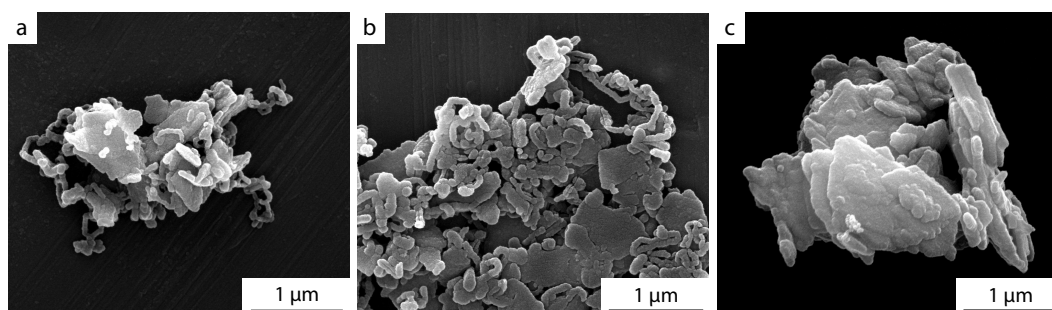


Fig. 3 SEM images of MoS_2 -PPy_nws hybrids varying with feed ratio between MoS_2 and Py monomer. The feed ratios (wt%) are (a) 1:1; (b) 1:2; (c) 1:4.

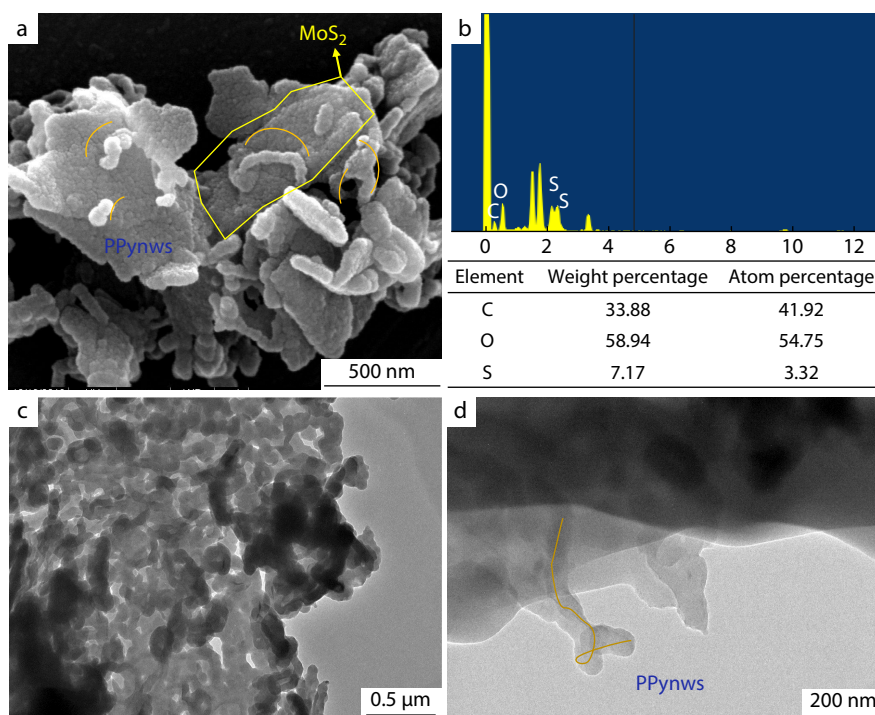


Fig. 4 (a) SEM image of MoS_2 -PPy_nws; (b) EDS images and corresponding data of MoS_2 -PPy_nws; (c) TEM image of MoS_2 -PPy_nws and (d) a partially enlarged TEM image of PPy_nws.

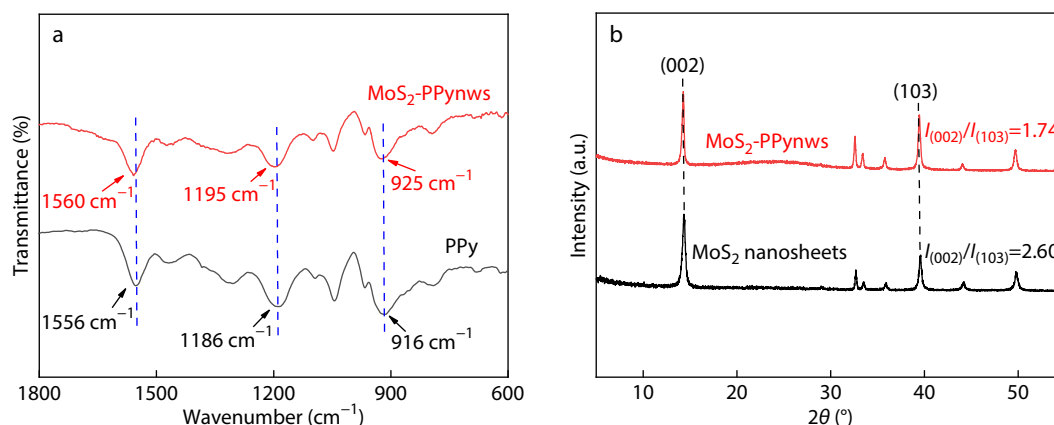


Fig. 5 (a) FTIR spectra of MoS₂-PPynws and PPy; (b) WAXD patterns of MoS₂-PPynws and MoS₂ nanosheets.

stretching vibration of C—H bond in pyrrole ring, respectively. These bands confirm the existence of PPy in the hybrids. Seen from WAXD spectra in Fig. 5(b), there are several distinct diffraction peaks at 14.4°, 32.7°, 39.7°, and 49.8° corresponding to the plane of (002), (100), (103), and (105), respectively, which relate to the hexagonal structure of MoS₂ nanosheets.^[36] The spectrum of MoS₂-PPynws hybrids has the same diffraction peaks as those of MoS₂ nanosheets. A wide peak at 15°–30° is attributed to the amorphous PPynws. It should be noted that the relative ratios of diffraction peak intensity for the (002) plane and (103) plane can be applied to evaluate the effects of PPy nanowire on the thinning of MoS₂. Here, the ratios of $I_{(002)}/I_{(103)}$ are calculated and the ratio of hybrid is 1.74, much lower than that of MoS₂, indicating that the growth of PPy nanowires can realize the thinning of MoS₂ and prevent the restacking of exfoliated MoS₂. It should be noted that the interaction between PPy nanowires and MoS₂ is originated from the soft template effect of CTAB reported by this study.^[37] In detail, in the process of exfoliation, many S atom vacancy defects can be formed on the surface of MoS₂, which can provide loading sites for the subsequent PPy loading process. Then, the CTAB will form a soft template at these sites to provide a template for the polymerization of the pyrrole monomer to form PPy, which is loaded on the surface of the MoS₂.

Microstructure of PVDF/MoS₂-PPynw Composites

The dispersion state of hybrids in the PVDF matrix is vital in determining the dielectric performance of the composites. Here, the images of the cross-section were taken via SEM measurement, as shown in Figs. 6(b)–6(d). Firstly, it can be found that the thickness of the composite film is about 15 μm with few defects or voids, and the direction indicated by the yellow arrow in the figure is the direction of the film plane as shown in Fig. 6(b). Besides, some MoS₂ nanosheets can be observed in the cross-section image and there are no obvious MoS₂ aggregates. In the enlarged image as shown in Fig. 6(c), individual MoS₂ nanosheets can be clearly observed with a lateral size of about 1 μm, which is matched with that of exfoliated MoS₂ nanosheets observed above. Fig. 6(d) shows the exposed MoS₂ in the matrix, on which PPynws with a diameter of 10–30 nm are found to be randomly penetrating the PVDF matrix. EDS elemental mapping was carried out to confirm the homogeneity of the composite system, and the representative images are

presented in Fig. 6(e). The key elements S for MoS₂ and O for PPy are observed to be distributed evenly throughout the samples, indicating the presence of both MoS₂ and PPy. It should be noted that the O elements representing PPy exhibit a lamellae-like aggregation statement as shown by the arrow, indicating that the PPy nanowires were epitaxially grown on the MoS₂ nanosheet. Owing to the encapsulating of PPy on the MoS₂ nanosheet, the resolution of S elements representing MoS₂ is lowered down. Compared with the bulk MoS₂ aggregates in PVDF (Fig. S1 in the electronic supplementary information, ESI), the dispersion and interfacial adhesion of PVDF/MoS₂-PPynw are greatly improved due to helical PPy nanowires enhancing bonding or entanglement with polymer matrix.

In addition, the exfoliated MoS₂ nanosheets are parallel aligned along the film plane direction, and the hybrid orientation is mainly induced by the shear force induced by blade coating processing. It also should be noted that the parallel distribution of MoS₂ nanosheets is beneficial for preventing the electric tree from propagation under high voltage.^[19]

It is well known that PVDF possesses five different crystalline phases, such as α, β, γ, δ and ε. Among these types, the β phase PVDF exhibits the highest electroactive properties owing to its higher dipole moment. Here, FTIR and WAXD experiments were carried out to determine the effect of MoS₂-PPynws hybrids on the PVDF crystalline phase. The FTIR spectra of neat PVDF and PVDF/MoS₂-PPynws composites are shown in Fig. 7(a). In the infrared spectrum of neat PVDF, the characteristic absorption bands at 762 and 839 cm⁻¹ correspond to the bending vibration of CH in α-PVDF and the variable-angle vibration of CH₂ in β-PVDF and the anti-symmetric stretching vibration of C—F, respectively. However, after introducing MoS₂-PPynws, the absorption peak intensity of the α phase decreases with the increase of hybrid loading. Fig. 7(b) shows the WAXD patterns of PVDF and PVDF/MoS₂-PPynws, where the diffraction peak at 20° is ascribed to the α-PVDF (110) crystal plane, and the peak at 20.7° is ascribed to the diffraction of (110) and (200) crystal plane of β-PVDF. It can be observed that neat PVDF and PVDF/MoS₂-PPynws composite have obvious broad peaks at 20.7°, and the peak at 20.7° gradually strengthens with the increase of filler content, indicating the increased β-PVDF crystal content. This is also consistent with the results of decreased content of α-PVDF as

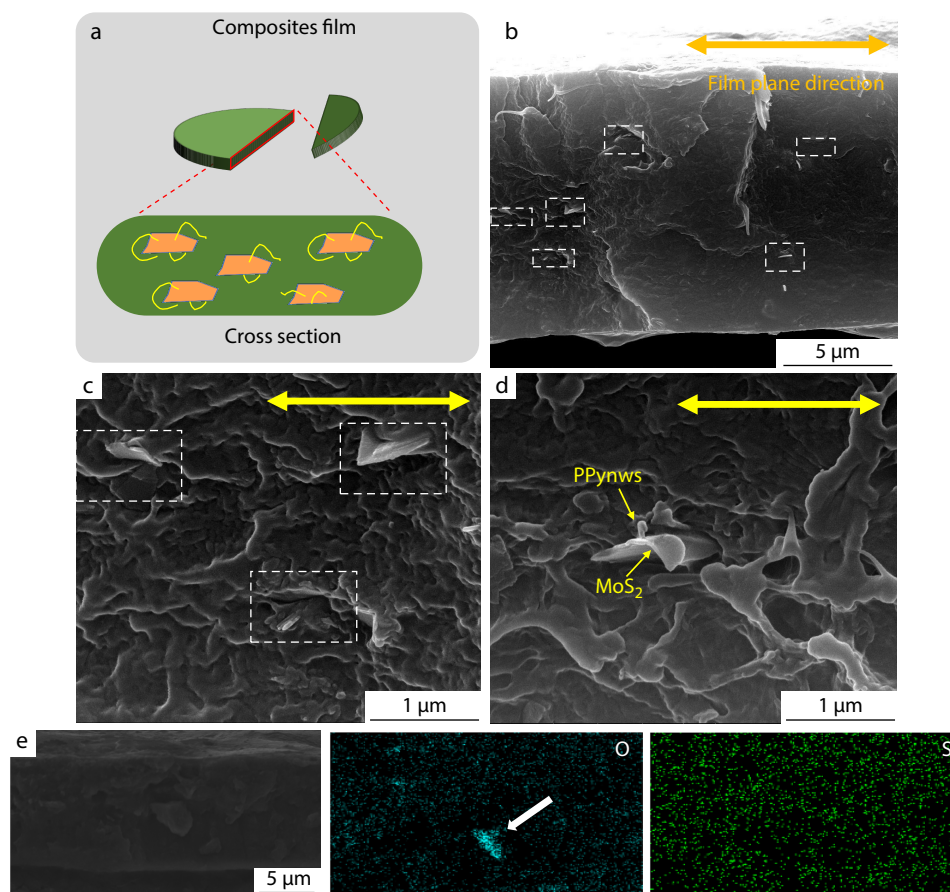


Fig. 6 (a) Schematic diagram of filler distribution inside the matrix; (b, c, d) SEM images of PVDF/5MoS₂-PPynws composite film cross-sections at the same position and different magnifications; (e) elemental mapping of PVDF/5MoS₂-PPynws composite film.

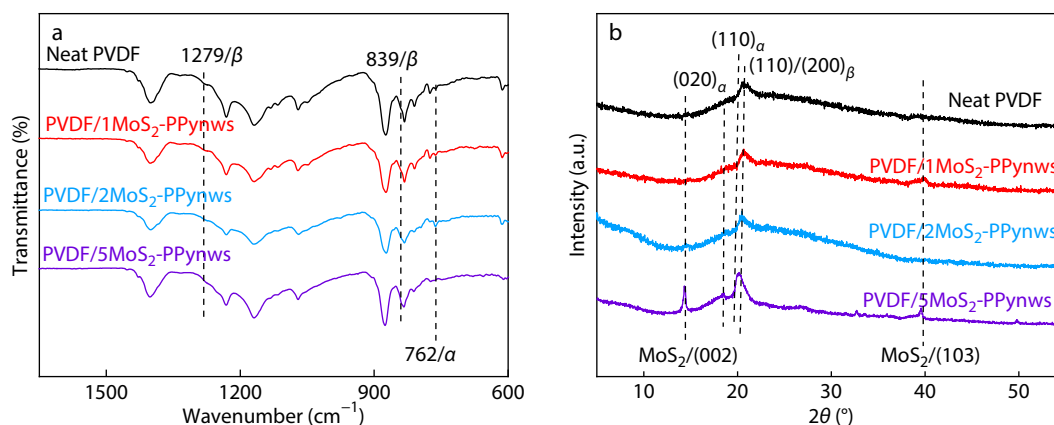


Fig. 7 (a) ATR-FTIR spectra and (b) WAXD profiles of neat PVDF film and PVDF/MoS₂-PPynws composite films.

shown in the FTIR spectroscopy. On the other hand, with increasing the loading of MoS₂-PPynws, the strengthening of diffraction peak intensity indicates the increased crystallinity of composites. This can be attributed to the sufficient nucleation ability of MoS₂-PPynws on PVDF crystallization. Besides, Fig. S2 (in ESI) shows the FTIR spectra of the PVDF/MoS₂ composite. One can see that without the introduction of PPy_nws, the crystalline form of PVDF is dominated by non-polar α-phase, and the characteristic bands of 766, 796, and 976 cm⁻¹

can be observed. The above results indicate that the introduction of hybrid fillers can benefit the formation of PVDF polar crystals. The mechanism for the formation of β phases in the MoS₂ based composites is not clear. It is expected that the electrostatic interaction between the surface of the negatively charged MoS₂ nanosheet and the CH₂ dipole in the PVDF chain and the introduction of PPy_nws with a high aspect ratio may promote the formation of β-PVDF in the "TTTT" conformation.^[38–40] The formation of the polar phase can ob-

viously enhance the dipole polarization.

Dielectric Properties of PVDF/MoS₂-PPynw Composites

The frequency-dependent dielectric properties of the PVDF/MoS₂-PPynw composites were measured by broadband dielectric spectroscopy at room temperature. The dependence of the dielectric constant and dielectric loss ($\tan\delta$) on frequency are shown in Fig. 8. Firstly, the dielectric constant of neat PVDF at a frequency of 1000 Hz (marked as @10³ Hz) is 9.82, which is basically the same as reported in the literature.^[41] With the addition of the MoS₂-PPynw hybrids, a continuous increase in the dielectric constant is observed which can be attributed to the interfacial polarization.^[42] When the loading of MoS₂-PPynw hybrids increases to 5 wt%, a sharp increase of constant at low frequency can be found and the frequency dependence on constant is more significant. Such a dramatic increase in dielectric constant can be explained by the micro capacitor model, in which the composites are considered to contain a network of several local capacitors formed by a thin layer of the polymer between two adjacent conducting particles. In this case, the thickness between adjacent MoS₂-PPynw hybrid decreases when the loading increases, resulting in a higher number of micro capacitors in the polymer composites and a high dielectric constant. On the other hand, $\tan\delta$ also exhibits a gradual but slight increase with increasing the loading of hybrids. Also, the dielectric loss increases with increasing fre-

quency due to the gradual generation of relaxation resulting from the fact that the dipole cannot rapidly shift with the inverting rate of an alternating electric field.^[43] For comparison, the dielectric properties of the PVDF/MoS₂ were also been measured as shown in Fig. S3 (in ESI). The corresponding constant and loss @10³ Hz for both PVDF/MoS₂ composites and PVDF/MoS₂-PPynw composites are summarized in Figs. 8(c) and 8(d). It can be found that the dielectric constants of polymer composites with hybrids are significantly higher than those of the PVDF/MoS₂ composites. When the loading of hybrids reaches up to 5 wt%, the constant is as high as 20.5@1kHz, which is almost double of PVDF composites containing 5 wt% MoS₂. Moreover, all the dielectric loss exhibit an increasing trend with increasing the loading of fillers. However, the increasing trend is slow and slight, the highest dielectric loss is 0.045 for PVDF containing 5 wt% MoS₂-PPynws hybrid, which is still at a low level and acceptable for the high-charge-storage application. As shown in Fig. S4 (in ESI), the higher loss for the composites containing MoS₂-PPynws could be ascribed to the conduction loss due to the higher conductivity of PPynws.^[29]

Dielectric breakdown strength is also one of the important parameters to evaluate the dielectric properties of composite films. Usually, the two-parameter Weibull distribution is used to analyze the breakdown characteristics of the dielectrics as follows:

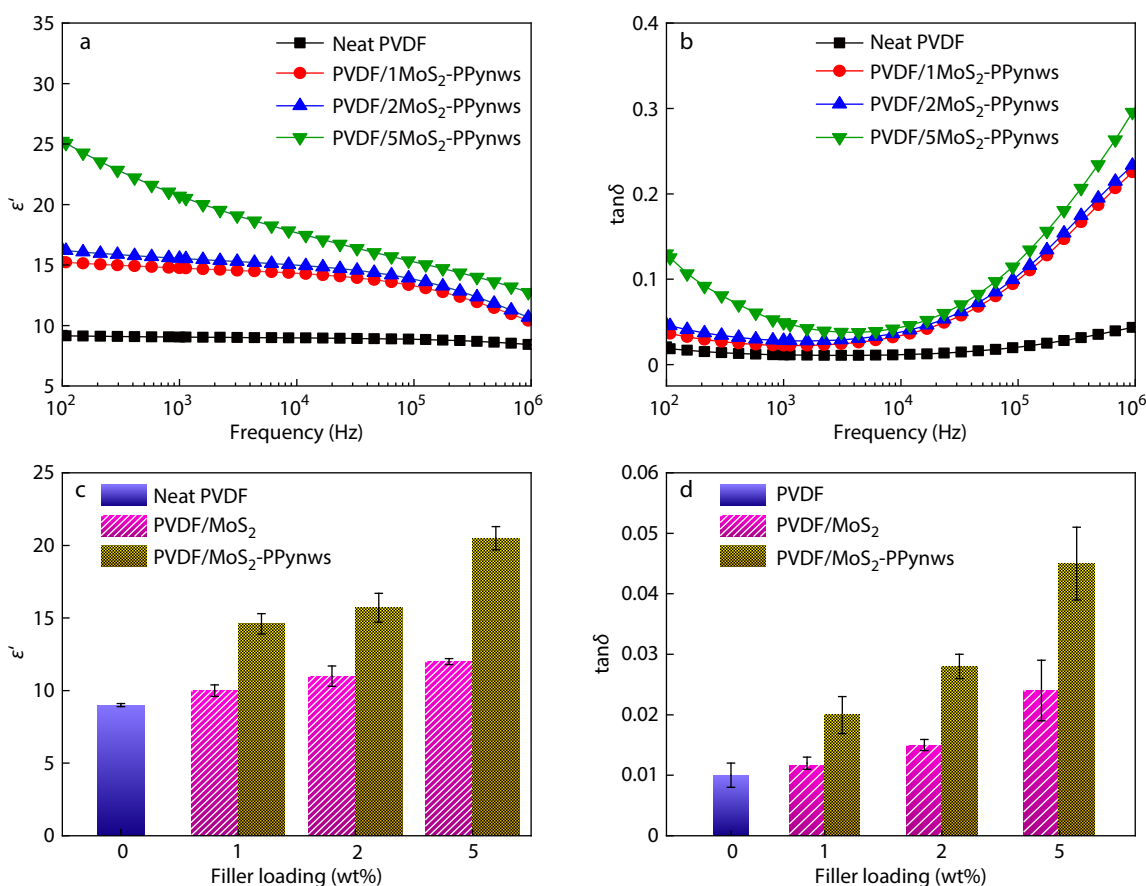


Fig. 8 Frequency dependence of (a) permittivity and (b) dielectric loss of the composites with different loadings of MoS₂-PPy; (c, d) Comparison for (a) dielectric constant and (b) dielectric loss with PVDF/MoS₂ composites@10³ Hz.

$$P = 1 - \exp \left[- \left(\frac{E}{E_b} \right)^\beta \right] \quad (1)$$

where P represents the cumulative failure probability, and β is a parameter connected with the degree of dispersion of the test value, which reflects the reliability of the experimental E_b .^[29] The relationship between the cumulative failure probability P and breakdown field E was plotted for each specimen in Fig. 9. The breakdown strength (E_b) of polymer composites is higher than that of neat polymer, although the E_b gradually decreases with increasing the loading of MoS₂-PPynws. When introducing 1 wt% MoS₂-PPynws hybrid to the PVDF matrix, the E_b of the composite exhibits a highest value of 422.1 MV/m. With further increasing the loading of hybrids, the difference of electrical properties between PPy nws with good conductivity and insulating PVDF matrix further causes a great amount of electric field distortion at the interface and finally triggers electrical tree breakdown. However, when the filler content is 5 wt%, the composite still has a high breakdown strength (345.5 MV/m), which is mainly due to the barrier effect of layer MoS₂ nano-sheets vertical to the electric field, resulting in suppression of electrical tree. Some studies have shown that the introduction of a small amount of two-dimensional filler improves the breakdown strength of the material.^[44,45] Compared with the breakdown strength of PVDF/MoS₂ composites (Fig. S5 in ESI), the

PPynws exhibit an enhancement effect on E_b and the composite films can be applied to withstand a higher voltage.

Here, MoS₂-PPynws play a positive role in simultaneously enhancing the dielectric constant and breakdown strength. Possible microscopic mechanisms about the role of MoS₂-PPynws hybrid in enhancing the dielectric constant and breakdown strength of composite are described in Fig. 10. The underlying mechanism can be illuminated via the micro capacitor model. Firstly, the introduction of hybrid fillers increases the dielectric constant of the composite material mainly due to the introduction of PPy nws, which can generate more polar phase of PVDF and enhance the interface polarization due to the large aspect ratio of coiled PPy nanowires. At the same time, with the random dispersion of MoS₂-PPynws in the PVDF matrix, the Maxwell-Sillars-Wagner interfacial polarization across the MoS₂-PPynws and PVDF interface indicates that any pair of adjacent MoS₂-PPynws layer can be used as a micro capacitor. Therefore, millions of nano-micro capacitor networks are formed inside the composite material, which can store a large amount of electric charge, so that the composite material has a superior dielectric constant. From SEM images as shown in Fig. 6 that the morphology of PPy nws loaded on the surface of MoS₂ is helical and coiled, therefore it is not easy for PPy nws to overlap internally to

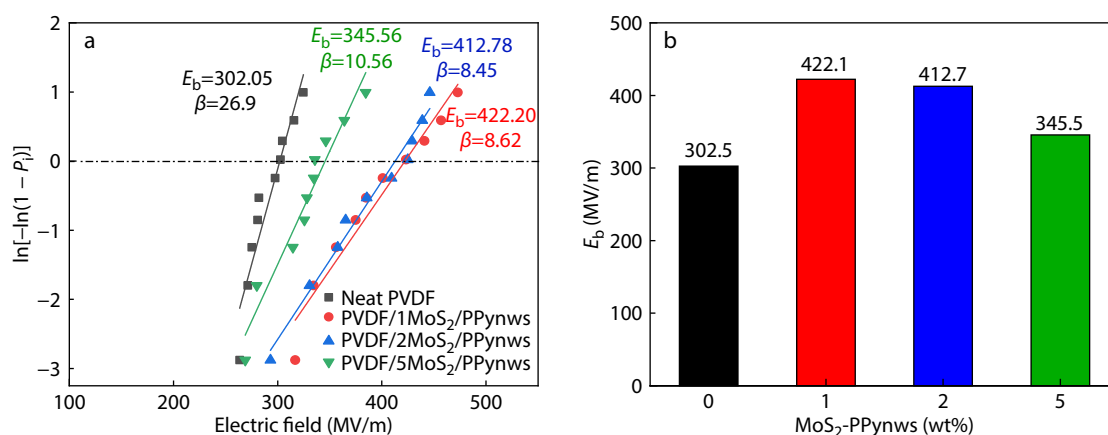


Fig. 9 (a) Weibull-distribution plots of breakdown strength and (b) the corresponding characteristic breakdown strength (at the failure probability of 63.2%) for different contents of MoS₂-PPynws.

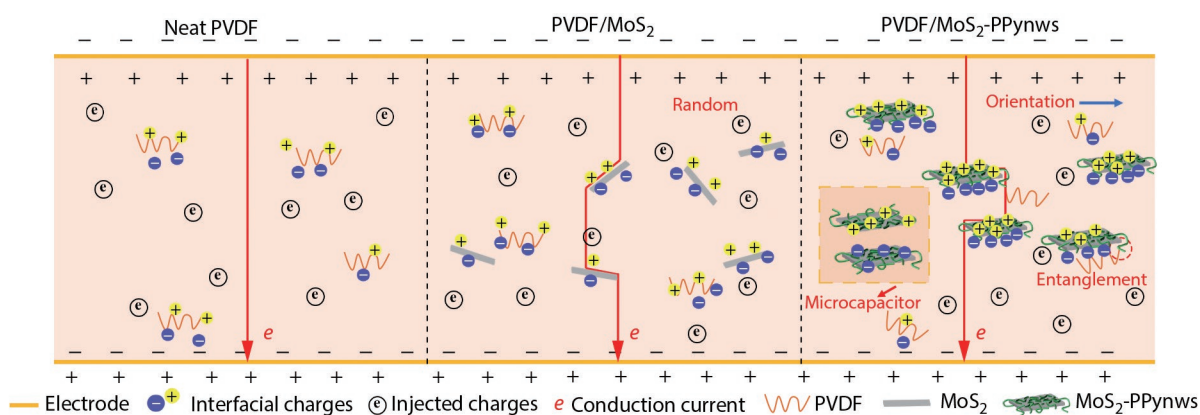


Fig. 10 Possible microscopic mechanisms about the role of MoS₂-PPynws in improving the dielectric constant and breakdown strength of composites.

form a conductive network. Thus, the barrier effect of insulating MoS₂ plays a key role, the current leakage is greatly suppressed and the loss of the composite material is still maintained at a low level. In terms of breakdown strength, compared with zero-dimensional (0D) PPy nanoparticles,^[29] 1D PPy nanowires have more advantages in improving the breakdown strength of composite materials. Coiled PPy nanowires exhibit stronger interaction with PVDF molecular chains due to the electrostatic interaction and the entanglement with the molecular chains of PVDF, which make it easier for the hybrid fillers to align in the matrix during solution casting. Finally, an insulating barrier can hinder or prolong the growth of the breakdown electrical tree, thereby improving the breakdown strength of the composites. In addition, for the first time, the addition of PPy nanowires improves the dispersion of MoS₂ in PVDF and reduces the generation of internal defects, which is also a factor in improving the breakdown strength.

CONCLUSIONS

In summary, the MoS₂-PPy nanowires hybrid fillers have been successfully prepared by *in situ* polymerization of PPy nanowires on the exfoliated MoS₂ nanosheets. The introduction of the MoS₂-PPy nanowires hybrids not only improves the compatibility between the filler and the matrix, but also improves the dielectric properties of the composite material. Compared with neat PVDF, PVDF/MoS₂-PPy nanowires composites possess a higher dielectric constant (15@1 kHz) and breakdown strength (422.1 kV/m). The reason for the high dielectric properties is attributed to the introduction of PPy nanowires, which form a lot of tiny interfaces inside the matrix, making the carriers and free charges inside the matrix accumulate at the interface to produce high interface polarization. And the introduction of MoS₂ nanosheets can create an insulating barrier perpendicular to the electric field, thereby prolonging and hindering the growth of the breakdown tree, so that the breakdown strength of the composite material is improved. The research results provide a new way for utilizing MoS₂ to develop high-performance polymer-based dielectric nanocomposites.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

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