

Article

Enhancement Research on Piezoelectric Performance of Electrospun PVDF Fiber Membranes with Inorganic Reinforced Materials

Chong Li ^{1,*}, Haoyu Wang ^{2,*}, Xiao Yan ³, Hanxige Chen ⁴, Yudong Fu ²  and Qinhua Meng ²

¹ Center for Engineering Training, Harbin Engineering University, Harbin 150001, China

² College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China; fuyudong@hrbeu.edu.cn (Y.F.); qinhua97@foxmail.com (Q.M.)

³ Shandong Institute of Space Electronic Technology, Yantai 264670, China; 13351987373@163.com

⁴ Heilongjiang Zhongmin Measurement and Control Instrument Engineering Co., Ltd., Harbin 150001, China; m18360823175@163.com

* Correspondence: lichong@hrbeu.edu.cn (C.L.); haoyuwang@hrbeu.edu.cn (H.W.)

Abstract: The electrospun PVDF fiber membranes with the characteristics of light weight, strong signal and measurability, have been widely applied in the fields of environment, energy sensors and biomedical treatment. Due to the weakness of the piezoelectric and service properties, the conventional PVDF fiber membranes cannot meet the operating requirements. Based on the obtained optimal technological parameter of electrospun pure PVDF fiber membranes (P-PVDF) in the previous experiment (unpublished), three inorganic reinforced substances (AgNO₃, FeCl₃·6H₂O, nanographene) were respectively used to dope and modify PVDF to prepare composite fiber membranes with the better piezoelectric performance. The morphology and crystal structure of the hybrid fiber membranes were observed and detected by scanning electron microscopy and X-ray diffraction, respectively. The results showed that the dopant could effectively promote the formation of β-phase, which can enhance the piezoelectric performance. The mechanical properties test and piezoelectric performance test exhibited that the static flexural strength, the elastic modulus, and the piezoelectric performance were improved with the addition of dopant. In addition, the influence on the addition of dopant and the doping modification mechanism were discussed. Finally, the conclusions showed that the minimum average diameter was obtained with the 0.3 wt% addition of AgNO₃; the piezoelectric performance reached the strongest with the 0.8 wt% addition of FeCl₃·6H₂O; the mechanical properties were best with the 1.0 wt% addition of nanographene.

Keywords: electrospinning; nanomaterials; PVDF; piezoelectric performance; surface engineering



Citation: Li, C.; Wang, H.; Yan, X.; Chen, H.; Fu, Y.; Meng, Q. Enhancement Research on Piezoelectric Performance of Electrospun PVDF Fiber Membranes with Inorganic Reinforced Materials. *Coatings* **2021**, *11*, 1495. <https://doi.org/10.3390/coatings11121495>

Academic Editor: Günter Motz

Received: 30 October 2021

Accepted: 3 December 2021

Published: 5 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the aggravation of the energy crisis and environmental problems, scientists have diverted their attention to safer and cleaner energy resources. The most important one is the conversion of mechanical energy to electrical energy. As one of the materials that are able to convert energy, piezoelectric materials have attracted many interests and have been used widely in various applications such as sensors, actuators, nanoelectronics, and energy harvesting [1–4]. Among them, PVDF and its co-polymer are becoming the focus of research regarding its low cost, high flexibility, quick response, and piezoelectric. These outstanding properties can be adopted as energy harvesters [5,6] and sensors [7–11].

It is known that PVDF has five different crystallite polymorphs (α , β , γ , δ , and ϵ) which can be transformed to each other under particular conditions [12]. The β -phase in these is the critical electroactive component of PVDF to exhibit the ferroelectric properties and piezoelectric properties [13]. However, what can be obtained by the traditional preparation process of PVDF membranes is the nonpolar α -phase [12]. The β -phase of obtained PVDF membranes should always be induced by some post-processing treatments,

such as mechanical stretching, annealing, and high voltage poling [13–16]. Compared with the complex traditional preparation process of PVDF piezoelectric membranes, the electrospinning process, including the ejection of the PVDF solution, volatilization of the solvent, stretching of the electrospinning streams, and high voltage polarization, could be completed in one step and the β -phase content of the prepared PVDF membranes were improved with the function of high voltage and stretching, which exhibit the better piezoelectric properties [17]. During the previous study, the pure PVDF membranes were fabricated with the optimized electrospinning technological parameters (the ratio of solvent, the concentration of PVDF solution, the voltage of electrospinning, the injection speed PVDF solution, and the rotate speed of collector). However, the pure PVDF fiber membrane cannot meet the operating requirements because of the weakness of the piezoelectric and service properties. Meanwhile, the inorganic dopant materials into PVDF is a simple and effective approach to enhance the piezoelectric properties of PVDF [18–20]. Therefore, it is quite crucial to prepare the inorganic-PVDF fiber membranes with better piezoelectric properties.

In this study, to further improve the performance of PVDF fiber membranes, three inorganic substances (AgNO_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, nanographene) were applied to dope and modify PVDF to prepare organic-inorganic composite fiber membranes based on the previous study. The morphology and crystal structure of the composite fiber membranes were observed, and the mechanical properties and piezoelectric performance of that were measured. Moreover, the research provides the possibility of wider application of PVDF composite fiber membranes.

2. Experimental Details

2.1. Materials

Poly (vinylidene fluoride) (PVDF) was supplied by Sigma-Aldrich Corp (Saint Louis, MO, USA). Acetone ($\text{C}_3\text{H}_6\text{O}$), nitric acid (HNO_3) and N, N-dimethyl-formamide (DMF) were obtained from Tianjin Tianda Chemical Reagent Factory (Tianjin, China). Ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$) was produced by Chinasun Specialty Products Co., Ltd. (Changshu, China). Citric acid ($\text{C}_6\text{H}_8\text{O}_7$), Ethylene Diamine Tetraacetic Acid (EDTA), carbamide ($\text{CO}(\text{NH}_2)_2$), argentum nitricum (AgNO_3), and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Lanthanum chloride ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) was provided by Jining Zhongkai New Materials Co., LTD (Jining, China). Nanographene was manufactured by Knano Graphene Technology Co., Ltd. (Xiamen, China).

2.2. Preparation of Modified Nanographene

It is well known that the nanographene is easily aggregated to unevenly dispersed in the matrix, because of its small particle size and large specific surface area. Thus, the rare earth modification solution is synthesized to modify the surface of nanographene. A certain quality of rare earth ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) was dissolved in the 100 mL ethanol solution. Then, according to a certain mass percent, the NH_4Cl , $\text{CO}(\text{NH}_2)_2$, EDTA, and $\text{C}_6\text{H}_8\text{O}_7$ were added into it to obtain mixed solution, as shown in Table 1. After the prepared modification solution was adequately stirred by a magnetic stirrer for 20 min and heated at 80 °C for 2 h, the PH value of that was adjusted to 4–6 by HNO_3 . Letting it stand for a period of time, the clear rare earth modification solution was obtained.

Table 1. Composition of the rare earth modification solution.

Name	Molecular Formula	Mass Percent
Ethyl alcohol	$\text{C}_2\text{H}_6\text{O}$	90%–99%
Citric acid	$\text{C}_6\text{H}_8\text{O}_7$	0.5%–1%
Urea	$\text{CO}(\text{NH}_2)_2$	0.5%–1%
Ethylene diamine tetraacetic acid	EDTA	0.5%
Ammonium chloride	NH_4Cl	0.1%–1%
Lanthanum chloride	$\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$	0.5%

After 10 mg nanographene adequately dispersed in modification solution by ultrasonication for 5 h, the modified nanographene dispersion was obtained. With filter units, the modified nanographene was collected and then washed several times with ethyl alcohol and hot deionized water. Finally, the modified nanographene was obtained after drying at 80 °C for 48 h in a drying oven.

2.3. Electrospinning of Nanocomposites

Four kinds of nanocomposites, including P-PVDF fibers, PVDF/AgNO₃ fibers (PVDF-Ag), PVDF/FeCl₃·6H₂O fibers (PVDF-Fe) and PVDF/Nanographene fibers (PVDF-G), will be prepared in this experiment. Initially, the powders of reinforced materials (AgNO₃, FeCl₃·6H₂O and modified nanographene) were dried for 24 h at 50 °C, 50 °C and 80 °C, respectively. Meanwhile, 15% of PVDF powders were dissolved and stirred in a mixed solvent of DMF and acetone (3:2 by weight) under magnetic stirring for 2 h. Then, the solution of PVDF was heated for 3 h under the 60 °C in a water bath to guarantee adequately dissolved and homogeneous. Afterwards, the powders of AgNO₃ (0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7 wt%) and FeCl₃·6H₂O (0.4 wt%, 0.8 wt%, 1.2 wt%, 1.6 wt%) were added into the solution of PVDF and stirred at 60 °C for 20 min to obtain PVDF/AgNO₃ and PVDF/FeCl₃·6H₂O solution. The electrical conductivity of PVDF/AgNO₃ and PVDF/FeCl₃·6H₂O solution was accordingly measured in Figure 1. Compared with that, the PVDF/modified nanographene solution was prepared differently. The dried modified nanographene (0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%) should be firstly dispersed in the DMF by ultrasonication for 2 h and then used to prepare the PVDF/modified nanographene solution. Finally, the four kinds of electrospinning solution were kept for 12 h in the syringe to exclude bubbles.

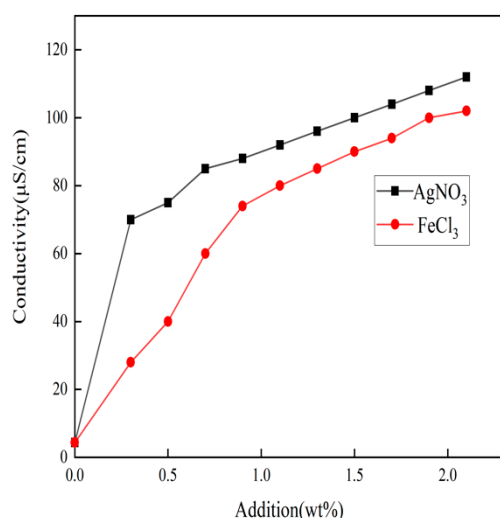


Figure 1. Electrical conductivity of PVDF/AgNO₃ and PVDF/FeCl₃·6H₂O solution.

The electrospinning device is shown in Figure 2. The prepared solution (P-PVDF, PVDF/AgNO₃, PVDF/FeCl₃·6H₂O and PVDF/nano-graphene) was respectively put into a 20 mL syringe connected to the conduit in the device. With the obtained optimal process parameters of P-PVDF, the syringe was placed in the groove with a high-voltage power supply of 22.5 kv. The roller twisted with aluminum foil was used as the collector of the electrospun fibrous membrane at the speed of 600 r/min. Electrospinning was done with an ejection rate of 1 mL/h from the syringe and 12 cm work distance between the spinneret and the collector. Finally, the prepared fibers were taken away from the roller and kept in plastic packaging bags for the coming test.

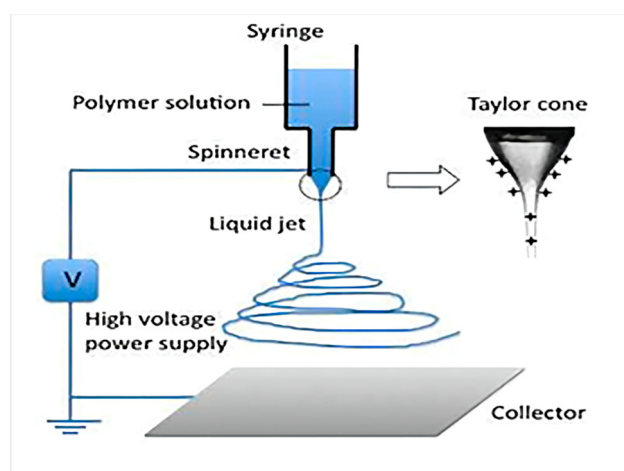


Figure 2. Electrospinning device map.

2.4. Material Characterizations

The morphology of fibers was investigated by scanning electron microscopy (SEM) (SEM, JSM-6480, Tokyo, Japan). The average diameter of fibers from the 100 randomly drawn fibers in one photo of SEM was measured by Image-J (Fiji image-J, National Institute of Health, Bethesda, Rockville, MD, USA). The crystalline phases of the samples were determined with the scan area of 10° – 40° and the scan speed of $2^{\circ}/\text{min}$ by X-ray diffraction (XRD) (Rigaku 5th miniflex, Tokyo, Japan) equipped with the Cu-K α tube operating at 40 kv and 40 mA. The mechanical properties of the fibers were tested by a universal testing machine (UTM, WOW-50, Jinan Liangong Testing Technology Co., Ltd., Jinan, China). According to the test standard of electrospun fibers (ASTMD 638), the samples were cut with the size of 20 mm $\times$ 30 mm and loaded in a constant deformation mode at a speed of 20 mm/min by the clamping length of 20 mm fiber. The viscosity was calculated by type and rotation speed of the rotor in the rotational viscometer (NDJ79, Shanghai INESA Scientific Instrument CO., LTD, Shanghai, China). With the dried and revised probe kept for 3 min in the solution, the conductivity of the solution was obtained by the conductivity tester (DDS-11A, Shanghai Changji Geological Instrument Co., Ltd., Shanghai, China).

2.5. Piezoelectric Properties Test

The structure of the piezoelectric signal generator with the size of 25 mm $\times$ 35 mm is shown in Figure 3. Aluminum foils were covered on both sides of fiber membrane samples with conducting adhesive as the electrode of the membrane. The tape of copper foils covered on the aluminum foils was used as a conductor and staggered electrode to the delivery charge. To protect the electrode from damage and short circuit, the insulated rubber tape was used to pack the electrode patches in the outermost layer. Finally, the piezoelectric signal generator was completed to conduct a piezoelectric performance test.

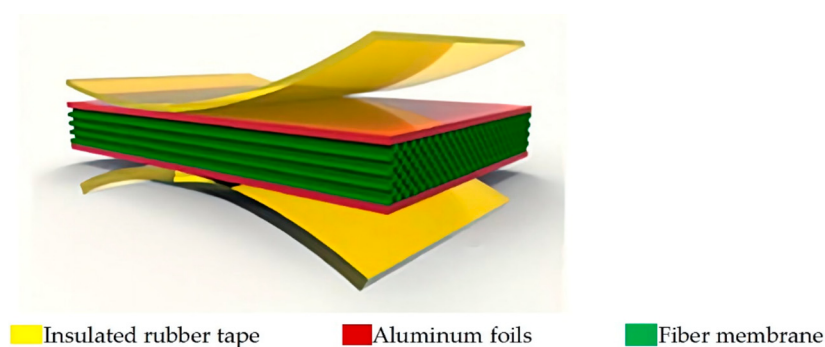


Figure 3. Piezoelectric signal generator.

As shown in Figure 4, the piezoelectric test device was composed of power plant, charge-amplifier and oscilloscope. The vibrostand as the power plant was used with a certain frequency (500 Hz) and amplitude (5 mm), as shown in Figure 5. Because of the weak electrical signal of the piezoelectric fiber membrane, the charge amplifier driven by the voltage of 5 V was used to amplify the resulting signal and restrain the influence of other interference signals. A chunk with a weight of 1 g was pressed on the piezoelectric signal generator to keep the vibration smooth. The piezoelectric signal generator fixed on the vibrostand was connected in turn to wire, charge amplifier and oscilloscope. When the piezoelectric properties test begins, the electrical signal can be harvested in the oscilloscope, and the piezoelectric test is completed.

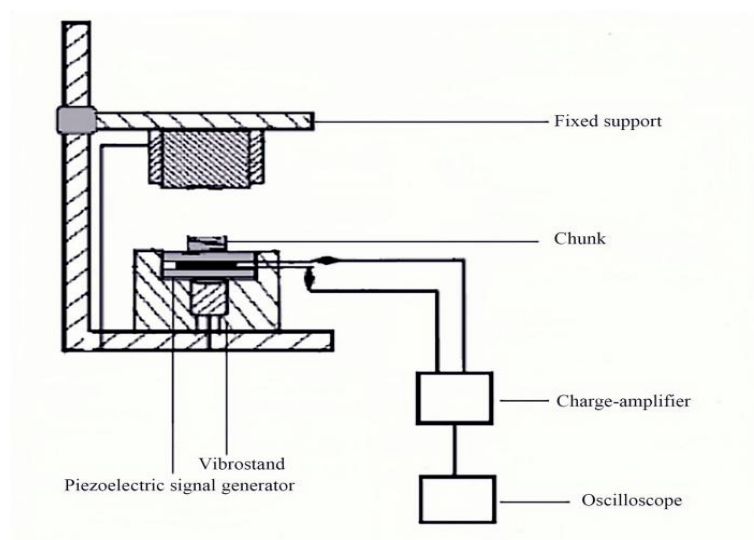


Figure 4. Piezoelectric test device.

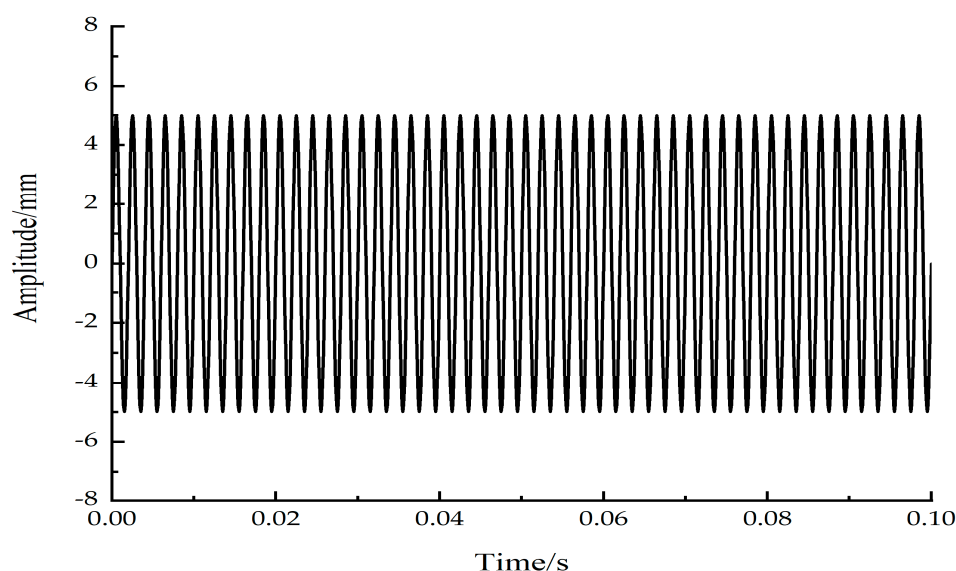


Figure 5. Waveform of the mechanical vibrations.

3. Result and Discussion

From the previous research (unpublished), the optimized technological parameters of pure PVDF (P-PVDF) fiber membrane were settled as mentioned in the Section 2.3. As shown in Figure 6a,b, the SEM images of P-PVDF fiber membranes exhibit that the continuous and fine P-PVDF fibers without any defect and beads were obtained with a

certain orientation. The tensile strength, modulus of elasticity and average diameter were presented in Table 2, revealing that the prepared fibers were uniform and fine with good mechanical properties. The voltage peak exhibiting piezoelectric performance reached 270 mV in Figure 6a. It was confirmed that the β -phase of P-PVDF fibers corresponding to the peak of 20.6° (110) formed with the decrease of the peak at 18.4° (020) corresponding to α -phase of PVDF (Figure 7b), resulting in that piezoelectric property could be enhanced with the function of high voltage and stretching during the electrospinning process. All the diffraction peaks are duly indexed from the JCPDS card no. 85-1436. All the results laid the groundwork for the following enhancement research of piezoelectric performance.

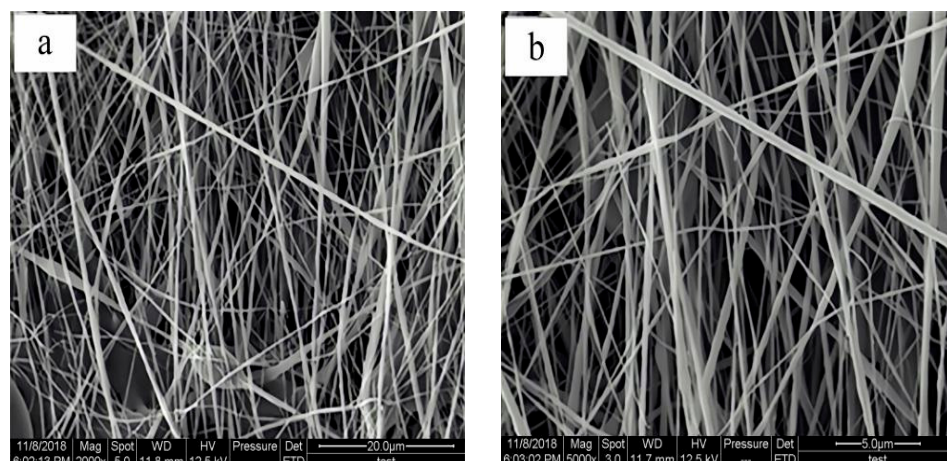


Figure 6. SEM image of the pure PVDF fiber membrane: (a) 2000 magnification; (b) 5000 magnification.

Table 2. Tensile strength, modulus of elasticity, average diameter, and diameter range of P-PVDF.

Name	Value	Standard Deviation
Tensile strength/MPa	13	0.35
Modulus of elasticity/MPa	3665	70.71
Diameter range/ μm	0.1–0.7	
Average diameter/ μm	0.342	
Piezoelectric signal/V	0.27	

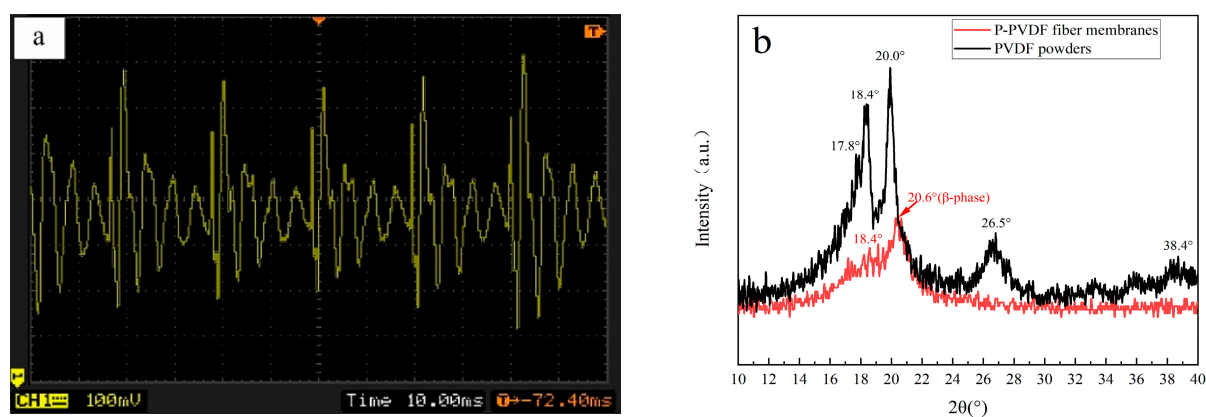


Figure 7. Piezoelectric signal image and XRD of the pure PVDF fiber membrane: (a) Piezoelectric signal image of the pure PVDF fiber membrane; (b) XRD of the pure PVDF fiber membrane.

3.1. PVDF/AgNO₃ Fiber Membrane Studies

Figure 8a–d shows the SEM images of PVDF-Ag fiber membranes at different addition of AgNO₃ (0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7 wt%), and the corresponding fibers diameter distribution is shown in Figure 9a–d and Table 3. All the fibers are randomly arranged with a smaller average diameter (0.201 μm –0.312 μm), compared with the P-PVDF fibers (0.342 μm). With the addition of 0.3 wt%, the fine and continuous fibers exhibiting the best morphology are obtained without any beads and defects, corresponding to the minimum average diameter (0.201 μm) and the uniform fibers diameter distribution. Although the fibers with the addition of 0.1 wt% and 0.5 wt% are continuous, the uniformity of fibers decreases with the broader average diameter. When the addition is up to 0.7 wt%, the beads are apparent with the cluttered morphology in Figure 8d, and the average diameter reach to maximum in Figure 9d. Meanwhile, along with the conductivity of PVDF/AgNO₃ solution, the charged droplet is directly dripped from the spinneret to result in the hard electrospinning process.

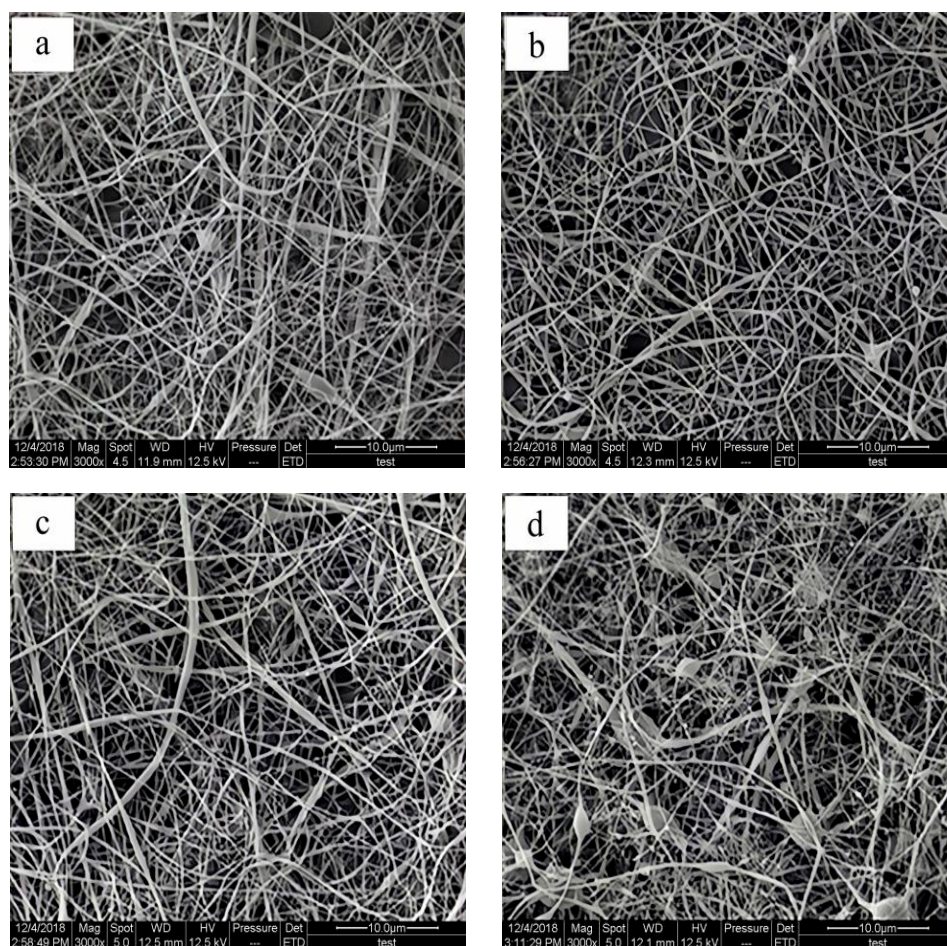


Figure 8. SEM images at different addition of AgNO₃: (a) the addition of 0.1 wt%; (b) the addition of 0.3 wt%; (c) the addition of 0.5 wt%; (d) the addition of 0.7 wt%.

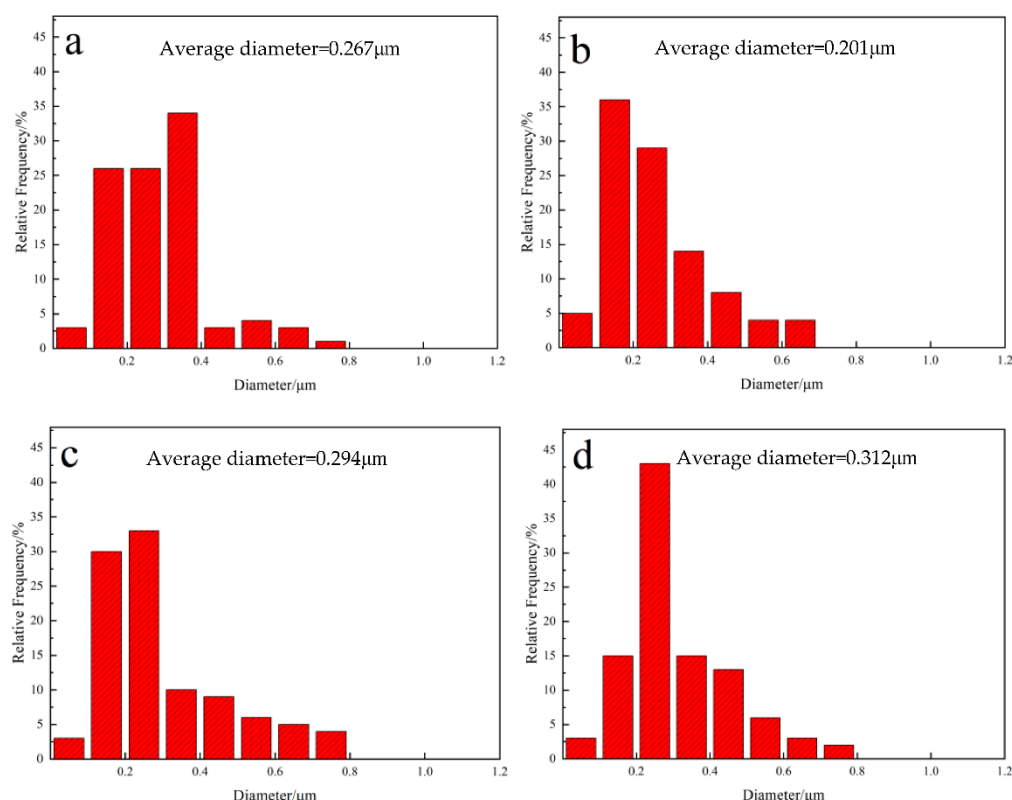


Figure 9. The fiber diameter distribution at different addition of AgNO_3 : (a) the addition of 0.1 wt%; (b) the addition of 0.3 wt%; (c) the addition of 0.5 wt%; (d) the addition of 0.7 wt%.

Table 3. The average diameter of the fiber membrane at different loading of AgNO_3 .

Addition/wt%	0.1	0.3	0.5	0.7	P-PVDF
Diameter distribution/ μm	0–0.8	0–0.7	0–0.8	0–0.8	0.1–0.7
Average diameter/ μm	0.267	0.201	0.294	0.312	0.342

The arrangement of fibers is attributed to the whipping of jet flow, which was a kind of nonaxisymmetric unstable motion affected by surface charge density. Owing to the increasing Ag^+ concentration of the polymer solution with the addition of AgNO_3 , the instability of jet flow was dominated to restrain the mechanical stretching of the roller and further to generate the little steam from the jet flow. That was in favor of generating random superfine fibers to weaken the oriented characteristic of fibers. In addition, more charge accumulation during the depositional process can produce greater electrostatic repulsion, also resulting in the weak-oriented characteristic of fibers. With the addition of Ag^+ increasing to 0.3 wt%, the conductivity of Ag^+ polymer solution (Figure 1) increased, and the jet can be sufficiently stretched by the enhanced electrostatic field force to generate the finest fibers. Meanwhile, the fibers became well defined, also ascribed to the corresponding thermal conduction increased in the presence of Ag^+ , and contributed to the improved solvent evaporation during the fly in the electrostatic field. With the addition continuing to 0.5 wt%, the rise speed of conductivity slowed down, and the speed of evaporation may be faster, and the fibers were insufficiently stretched, resulting in that the diameter of fibers increased. When the addition exceeds 0.7 wt%, the produced beads are attributed to the influence of jet flow motion, caused by the effect of the two competitions. One is that the increased surface tension of solution by the excessive inorganic salt enhances the resistance of the jet flow to make the electrospinning solution divert to liquid droplet. On the other hand, the electrostatic repulsion as the power of jet flow motion was enlarged by

the increasing addition of inorganic salt to prevent the solution from clumping together into droplets. Under the two competitions, the motion of jet flow happens. When the addition increases to 0.7 wt%, the surface tension is greater than electrostatic repulsion and the drop directly sputters rather than forming jet flow. So, with the addition of AgNO_3 increased, the jet flow motion was enhanced and then weakened due to the greater surface tension, the same as the change of fiber morphology.

The results of piezoelectric properties are shown in Figure 10 and Table 4. Compared to the piezoelectric properties of the pure PVDF fiber membrane, the piezoelectric property of the PVDF/ AgNO_3 fiber membrane was significantly enhanced. The voltage peak of PVDF/ AgNO_3 fiber membranes reached 2 V with the addition of 0.3 wt%, thus attributed to the fact that the positive Ag^+ was attracted by the electronegativity $-\text{CF}_2-$ dipoles of PVDF and repelled by the $-\text{CH}_2-$ dipoles of PVDF [21]. The interaction of attraction and repulsion and enhanced interfacial polarization takes place to promote all trans confirmations and the generation of β -phase in PVDF, as shown in Figure 11. Meanwhile, with the addition of AgNO_3 increasing, the conductivity of polymer solution increased and corresponding the stretching in the electric field enhanced, as well as the more generated the β -phase.

However, with the addition of AgNO_3 increased, the voltage began to descend. The voltage was even down to 1.6 V with the addition of 0.7 wt%. It is due to that the aggregation of the Ag^+ would result in current leakage during the working process of piezoelectric signal generator. Moreover, with the addition beyond 0.3 wt%, the Ag^+ and NO_3^- were mutually and intensively attracted to each other, restricting the ions moving to the surface of jet flow in time. The inhomogeneous ions on the surface of jet flow led to weakened stretching and unstable jet flow. Therefore, the excess addition of Ag^+ and NO_3^- was not applied to the stronger piezoelectric property.

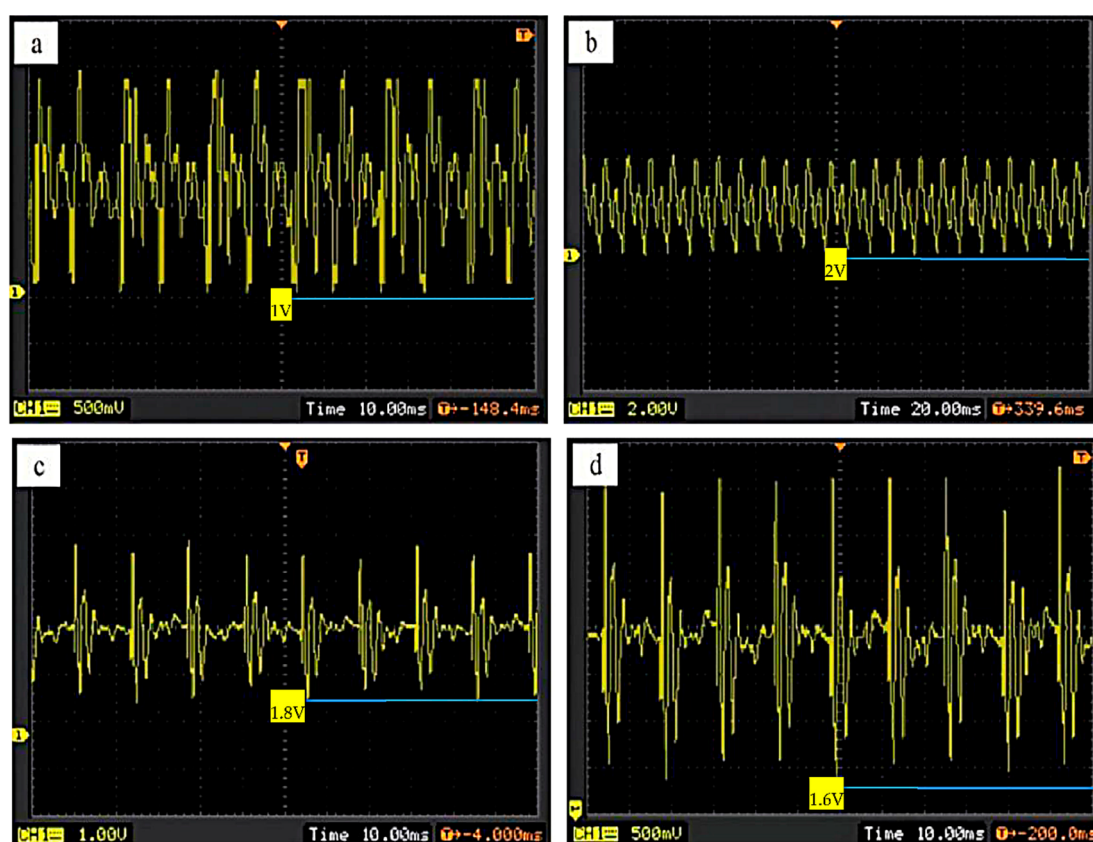


Figure 10. Piezoelectric signal of the fibers membrane at different addition of AgNO_3 : (a) the addition of 0.1 wt%; (b) the addition of 0.3 wt%; (c) the addition of 0.5 wt%; (d) the addition of 0.7 wt%.

Table 4. Piezoelectric signal of the fiber membrane at different loading of AgNO₃.

Addition/wt%	0.1	0.3	0.5	0.7	P-PVDF
Piezoelectric signal/V	1.0	2.0	1.8	1.6	0.27

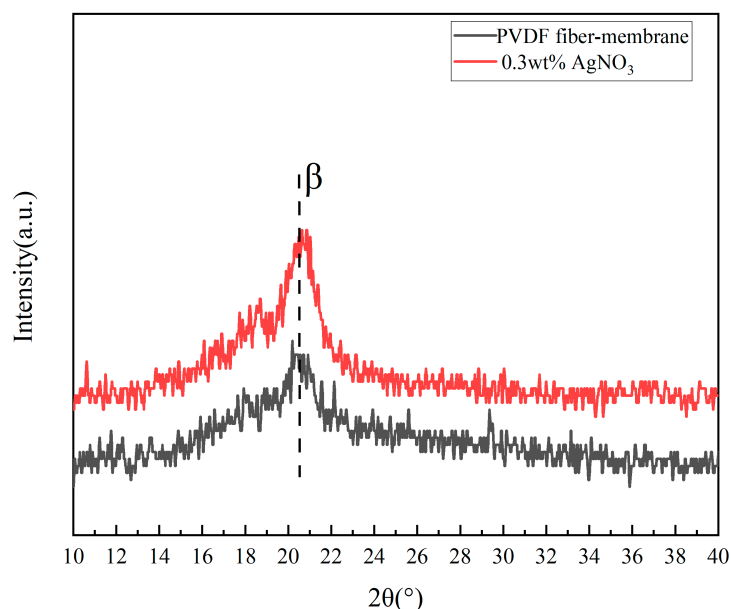
**Figure 11.** XRD patterns of the P-PVDF fibers membrane and PVDF/AgNO₃ fiber membrane at the addition of 0.3 wt% AgNO₃.

Table 5 shows the mechanical property of the fiber membrane at different loading of AgNO₃. The tensile strength and modulus of elasticity were improved by the addition of AgNO₃. The tensile strength and modulus of elasticity enlarged firstly and then dropped with the addition of AgNO₃ increased. When the load was at 0.3 wt%, the tensile strength and modulus of elasticity reached the maximum. Compared to the P-PVDF, the improved mechanical property of PVDF-Ag was contributed to the decreasing diameter of the fiber. The finer diameter affected by the stronger stretching has a higher molecular orientation, and more fiber was obtained in the same amount of spinning. Due to the fiber nearby mutually transferring energy, the tensile strength and modulus of elasticity of the fiber membrane were significantly improved.

Table 5. Mechanical properties of the fiber membrane at different loading of AgNO₃.

Addition/wt%	Tensile Strength/MPa	Standard Deviation	Modulus of Elasticity/Mpa	Standard Deviation
0.1	20	0.11	3652	72.89
0.3	22	0.16	4047	148.24
0.5	21	0.33	3920	96.21
0.7	20	0.19	3785	77.20
P-PVDF	13	0.35	3665	70.71

3.2. PVDF/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Fiber Membrane Studies

The morphology of PVDF/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ fiber membrane, the average diameter and the distribution of fibers are shown in Figures 12a–d and 13a–d and Table 6, respectively. All the diameter of the fiber is fined and distributed uniformly. With the addition of 0.4 wt% and 0.8 wt%, the gap between fibers is obviously seen along with a few beads in the dense accumulation of fibers. Owing to the lower conductivity, the fibers are deposited in a certain orientation with a loading of 0.4 wt%. However, with the concentration of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ increased, the arrangement of fibers is absolutely random. Beyond the addition of 0.8 wt%, the diameter significantly increases from $0.254 \mu\text{m}$ to $0.399 \mu\text{m}$. Particularly, when the addition is up to 1.6 wt%, the exhibiting adhered structure severely affects the continuity and uniformity of fibers.

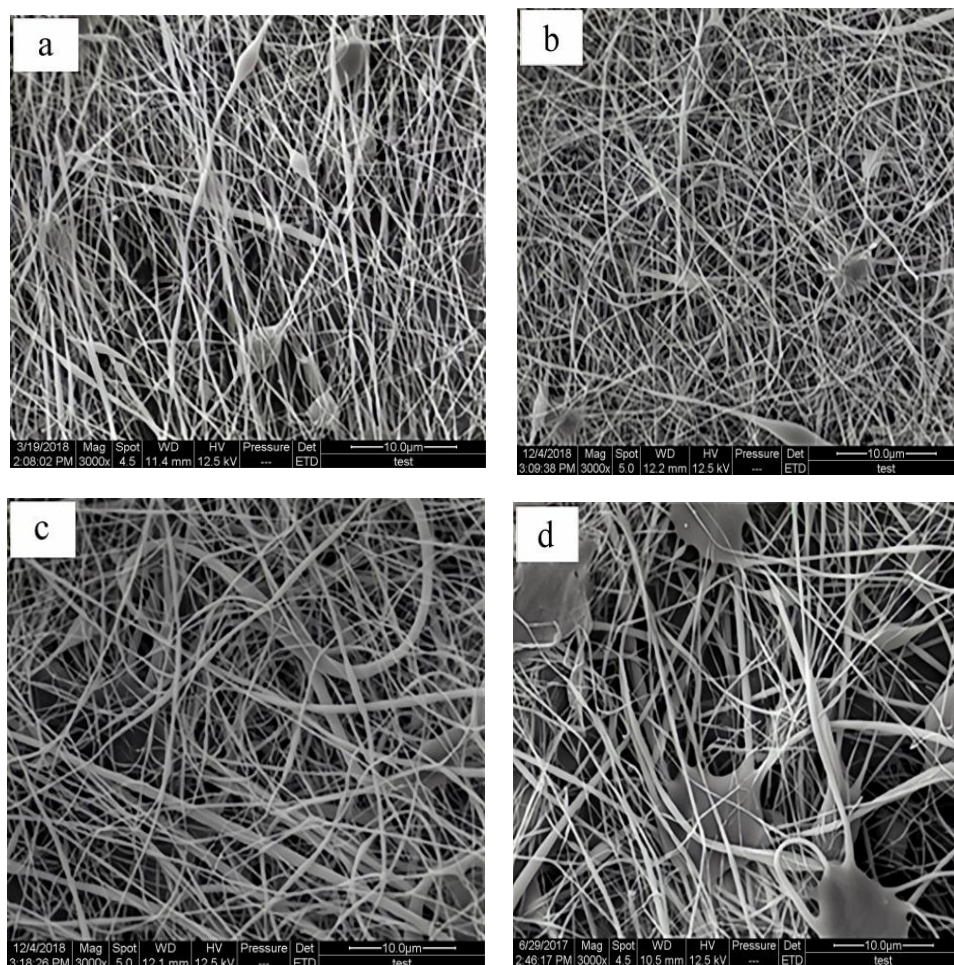


Figure 12. SEM images at different addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: (a) the addition of 0.4 wt%; (b) the addition of 0.8 wt%; (c) the addition of 1.2 wt%; (d) the addition of 1.6 wt%.

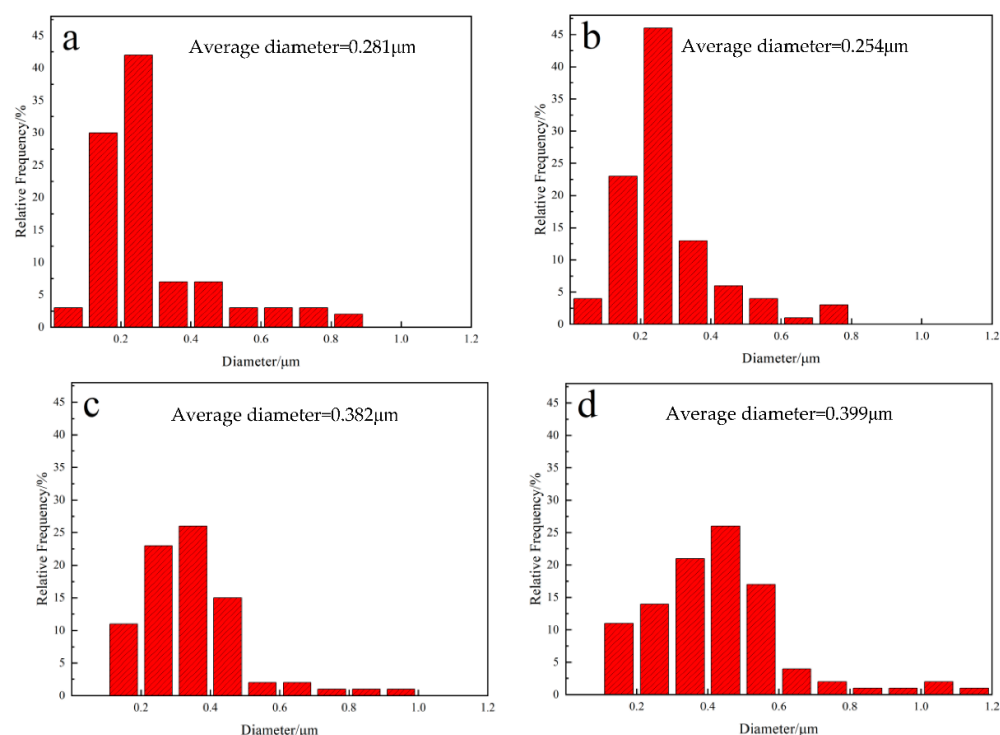


Figure 13. The fiber diameter distribution at different addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: (a) the addition of 0.4 wt%; (b) the addition of 0.8 wt%; (c) the addition of 1.2 wt%; (d) the addition of 1.6 wt%.

Table 6. The average diameter of the fiber membrane at different loading of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Addition/wt%	0.4	0.8	1.2	1.6	P-PVDF
Diameter distribution/ μm	0.1–0.9	0.1–0.8	0.1–1.2	0.1–1.2	0.1–0.7
Average diameter/ μm	0.281	0.254	0.382	0.399	0.342

With the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ below the loading of 0.8 wt%, the charge in the surface of the jet flow increased with the increasing addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Owing to that, the fine morphology of membrane representing uniform and small diameter fibers is obtained under sufficient stretching. However, when the addition continues to increase, the diameter of fibers is sharply broader. A similar phenomenon was not observed in the PVDF-Ag study. By testing the viscosity of the electrospinning solution with the different addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the curve of viscosity is obtained in Figure 14. It was observed that the viscosity of solution decreased by the increasing addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Especially, above the loading of 0.8 wt%, the viscosity decreasing rate of the solution increased, and the corresponding rate of conductivity slowed down. Therefore, with the flux and surface tension of the jet flow increased, the jet flow is not sufficiently stretched under the poor stretching in the electric field. In addition, the shorter duration of jet flow in the electric field with the flux increasing also broadens the fibers. Thus, the adhered structure is observed with the broadest fibers with the addition of 1.6 wt%.

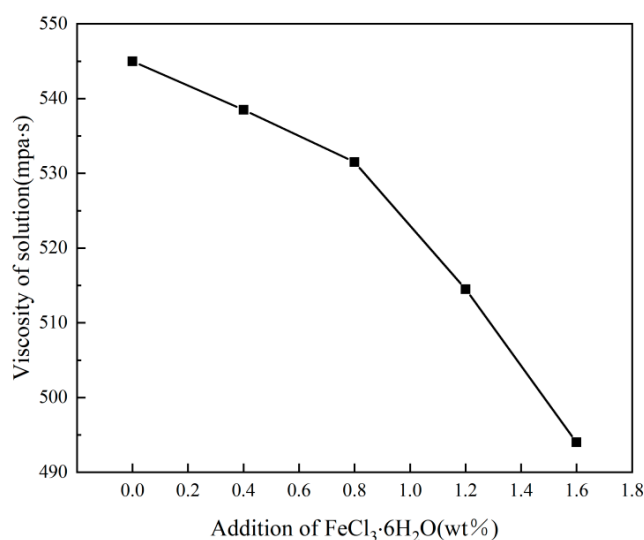


Figure 14. The viscosity of electrospinning solution at different loading of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

From Figure 15 and Table 7, the piezoelectric property of PVDF-Fe fiber membrane is significantly improved. With the addition of 0.8 wt%, the peak voltage is 4.8 V and 140% higher than that of the PVDF-Ag with the addition of 0.3 wt%. However, the peak voltage obviously begins to weaken with the addition increasing. The voltage is respectively down to 2.2 V and 500 mV, corresponding to the addition of 1.2 wt% and 1.6 wt%. Meanwhile, with the excess addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the broader diameter and the decreasing performance state that the β -phase formation is restrained by the weak stretching of jet flow.

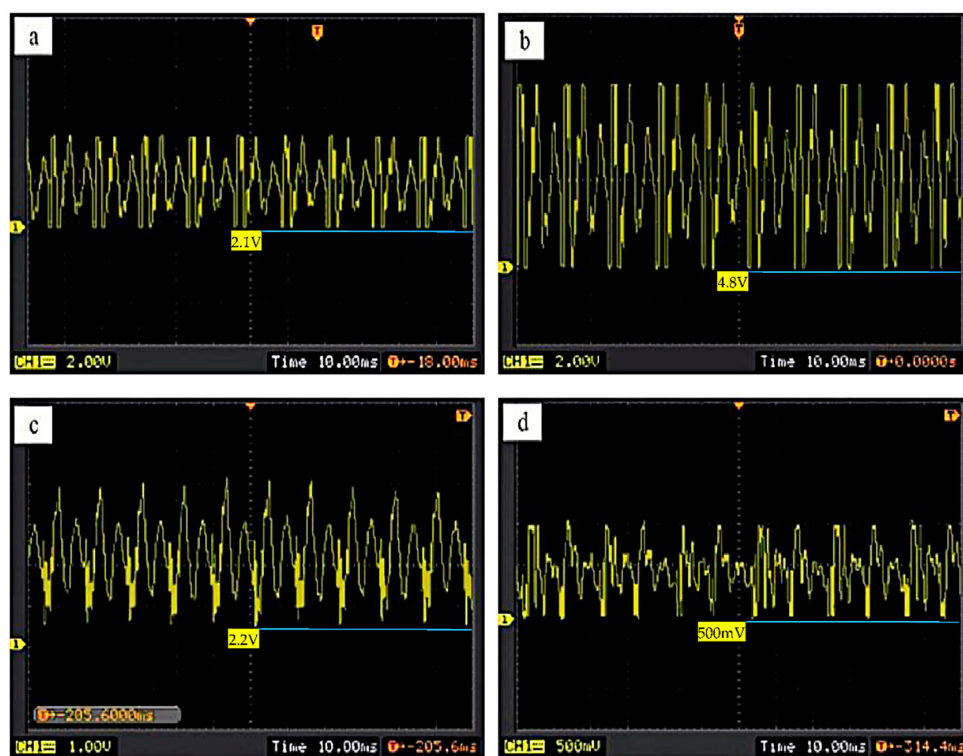


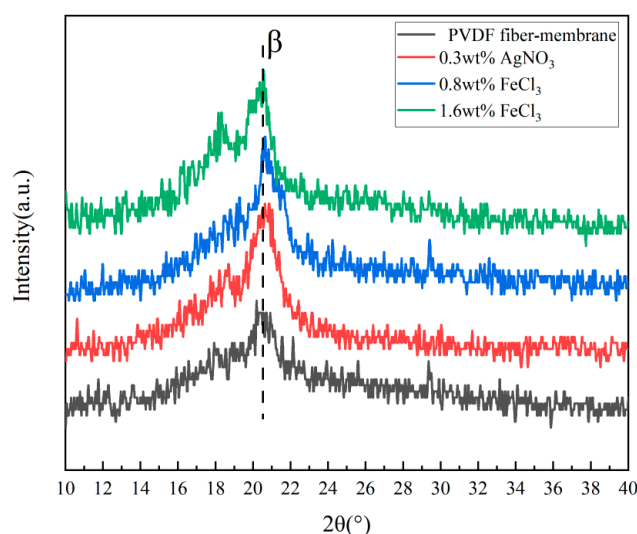
Figure 15. Piezoelectric signal of the fiber membrane at different addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: (a) the addition of 0.4 wt%; (b) the addition of 0.8 wt%; (c) the addition of 1.2 wt%; (d) the addition of 1.6 wt%.

Table 7. Piezoelectric signal of the fiber membrane at different loading of AgNO_3 .

Addition/wt%	0.4	0.8	1.2	1.6	P-PVDF
Piezoelectric signal/V	2.1	4.8	2.2	0.5	0.27

As analyzed, the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is a kind of covalent compound and dissolves in water as part of FeCl_3 molecule, other than AgNO_3 . Thus, with the same addition, the conductivity of AgNO_3 solution is higher than that of the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution. However, the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ has another promoting effect except that promoting the β -phase formation by the enhanced conductivity. The specific interactions near the Fe/PVDF interfaces can effectively induce the nucleation of the polar (ferroelectric) phase of PVDF, promoting the polarization of PVDF and the generation of β -phase [22]. The Cl^- nearby is attracted by the Fe^{3+} , which has a small ionic radius and strong polarizability, making its distribution distorted to generate electric dipole moment. Moreover, a strong electrostatic interaction between the water molecules of iron salts and the polar $-\text{CF}_2$ via the formation of hydrogen bonds may be the possible driving factor for the nucleation of polar β -phase in PVDF-Fe thin films. Owing to these, the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ molecules exhibit strong polarity. As known, the piezoelectric property of polar PVDF is attributed to the structure of all trans (TTTT) in the β -phase molecule generated by stretching in the electric field. With moderate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ added, the polarized electric dipole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ by the electric field is veered and arranged regularly to promote the formation of β -phase, drastically improving the piezoelectric properties.

Figure 16 depicts the XRD patterns of P-PVDF, PVDF- Ag (0.3 wt% AgNO_3) and PVDF-Fe (0.8 wt% and 1.6 wt% FeCl_3). The peak arising at 20.6° corresponds to the β -phase of PVDF, and the highest peak corresponds to the addition of 0.8 wt% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Accordingly, the piezoelectric property is best. The reason is that the spinnability of the electrospinning solution is restricted by conductivity which depends on the addition of inorganic salt. At the same conductivity, the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is more than it of AgNO_3 . Meanwhile, with the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ added, not only is the jet flow stretched adequately, but also the phase transformation is enhanced, exhibiting the piezoelectric properties further improved. However, with the excess addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the duration of jet flow in the electric field is short, resulting in the inadequate stretch and phase transformation, weakening the piezoelectric properties sharply. Therefore, the peak of PVDF-Fe (1.6 wt% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) is weak, as shown in Figure 16.

**Figure 16.** XRD patterns of the P-PVDF fiber membrane, PVDF/ AgNO_3 fiber membrane at the addition of 0.3 wt%, PVDF/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ fiber at the addition of 0.8 wt% and 1.6 wt%.

As shown in Table 8, the mechanical properties of fiber membrane are obviously changed with the different addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. With the loading of 0.8 wt%, the tensile strength and modulus of elasticity reach the max value (19 MPa and 4056 MPa). However, with the addition increased, the tensile strength and modulus of elasticity decreased rapidly. Corresponding to the loading of 1.6 wt%, the tensile strength and modulus of elasticity are only 9 MPa and 2602 MPa, which is even lower than that of P-PVDF because of the inhomogeneous and broader fiber diameter.

Table 8. Mechanical properties of the fiber membrane at different loading of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Addition/wt%	Tensile Strength/MPa	Standard Deviation	Modulus of Elasticity/MPa	Standard Deviation
0.4	18	0.20	3301	70.99
0.8	19	0.15	4056	74.50
1.2	12	0.11	2746	63.23
1.6	9	0.09	2602	58.29
P-PVDF	13	0.35	3665	70.71

3.3. PVDF/Nanographene Fiber Membrane Studies

The nanographene has lots of excellent performance indicators, but it is easily aggregated because of the van der Waals force between carbon atoms. For the sake of making nanographene disperse more uniformly in the solution, the La rare-earth modification is adopted to modify the surface of nanographene. Figure 17 shows the dispersion of nanographene in the distilled water before and after modification. The unmodified nanographene cannot disperse well in the distilled water, but the modified one does well. The reason is that the La polarized by the non-metallic element in the rare earth modifier can clean the surface of Nanographene and form the La-C bonds to make the nanographene stable.

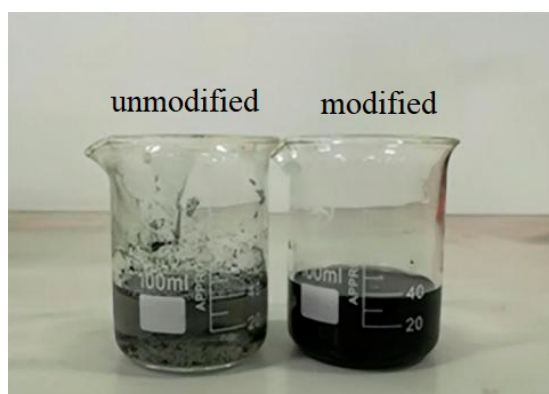


Figure 17. Dispersion image of nanographene in the distilled water before and after modification.

Figures 18a–d and 19a–d and Table 9 depict the SEM images of the modified PVDF-G, the average diameter, and fiber diameter distribution at different additions. It is observed that all the fibers of modified PVDF-G have uniform distribution, and the gap between fibers is obviously separated without beads. The average diameter of fibers decreases and then increases. The smoothly improved conductivity with the addition of modified nanographene contributed to the result. With the addition increasing to 1 wt%, the morphology has a great change, revealing the flattening structure and aggravated tangle of fibers. Accordingly, the average diameter reaches a minimum (0.296 μm). With the increase, the increasing conductivity accelerates the motion of graphene particles in the electric field; thus, the fibers are poorly stretched and deposited on the roller in a thicker size. Ultimately, the thicker fibers subjected to larger centrifugal force from the roller fiber form the flattening structure after the solvent evaporation. So, when the loading was up to

2 wt%, the flattening structure of fibers is obvious with the broadest diameter ($0.692\ \mu\text{m}$) as shown in Figures 18d and 19d. Compared to the PVDF-Ag and PVDF-Fe, there are no beads and adhesive organizations in the PVDF-G, illustrating that the nanographene is combined with the molecular chain of PVDF. In addition, on account of conductivity, whose improvement is limited, the fiber of PVDF-G is less poorly stretched than that of PVDF-Ag and PVDF-Fe, revealing that the average diameter of PVDF-G fibers is smaller compared to the fiber of PVDF-Ag and PVDF-Fe.

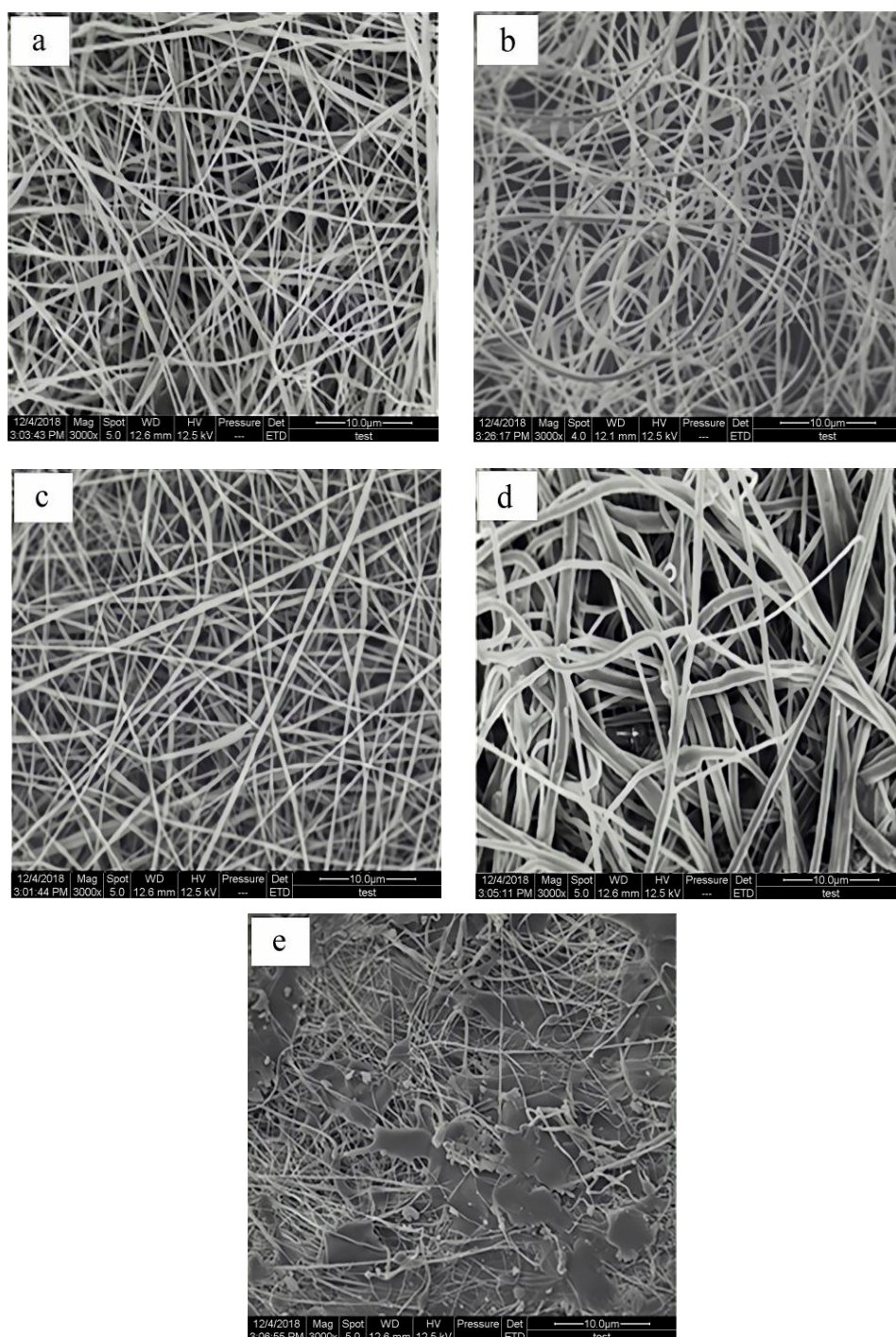


Figure 18. SEM images at different addition of nanographene: (a) the addition of 0.5 wt%; (b) the addition of 1.0 wt%; (c) the addition of 1.5 wt%; (d) the addition of 2.0 wt%; (e) 1 wt% unmodified nanographene.

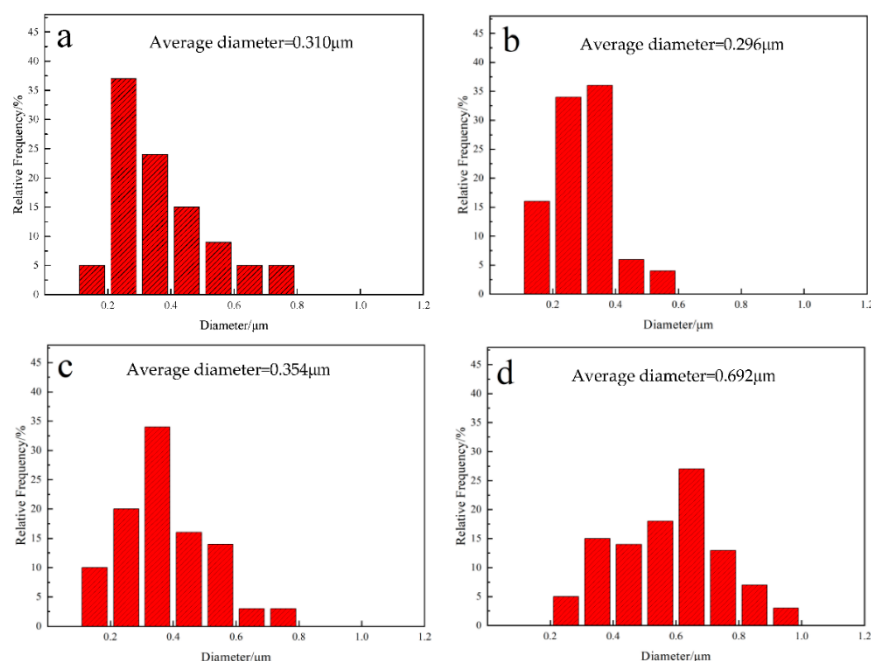


Figure 19. The fiber diameter distribution at different addition of nanographene: (a) the addition of 0.5 wt%; (b) the addition of 1.0 wt%; (c) the addition of 1.5 wt%; (d) the addition of 2.0 wt%.

Table 9. The average diameter of the fiber membrane at different loading of nanographene.

Addition/wt%	0.5	1.0	1.5	2.0	P-PVDF
Diameter distribution/ μm	0.1–0.8	0.1–0.6	0.1–0.8	0.2–1.0	0.1–0.7
Average diameter/ μm	0.310	0.296	0.354	0.692	0.342

Figure 18e shows that the fibers of unmodified PVDF-G distribute inhomogeneously without a uniform diameter of fibers. In the fibers is a mass of adhesive tissue and agglomerated unmodified nanographene absorbed on the surface of fibers. Owing to that, the fiber continuity was drastically affected to result in the large defect of fiber.

The piezoelectric signal of the fiber membrane at different loading of nanographene is shown in Figure 20a–d and Table 10. Compared to the P-PVDF, the piezoelectric property is greatly improved with the addition of modified nanographene. Corresponding to the change of diameter, the piezoelectric properties improve smoothly. With the loading increases, the peak voltage increases and then decreases. At the loading of 1.0 wt%, the peak voltage reaches the max value of 1.8 V, exhibiting the best piezoelectric property. That is illustrated by the XRD patterns of P-PVDF and PVDF-G at different loading of modified nanographene in Figure 21. It is observed that the peak of β -phase has the same variation tendency corresponding to the peak voltage. At the loading of 1.0 wt%, the strength of β -phase is strongest. The results indicate that the nanographene can promote the transformation from α -phase to β -phase. Except for promoting the stretching of jet flow by improving the conductivity of a solution, the added nanographene can also promote the formation of β -phase in other ways. One is the interface interactions. With the addition of nanographene, the partial electric field is strengthened and generates the induced charge. By the enhanced Coulombic force, the induced PVDF chains with the structure of all trans (the molecular structure of β -phase) are attracted to form crystal on the surface of nanographene. Under the interface interaction, the other phase of PVDF transforms to the β -phase. The other one is that the nanographene affects the orientation of $\text{CH}_2\text{-CF}_2$ electric dipole. The image (Figure 22) of the β -phase facilitated by nanographene illustrates that the $\text{CH}_2\text{-CF}_2$ electric dipole is oriented to F atom and closer to the nanographene particles.

By modifying nanographene, the functional group is generated on its surface. The H atoms in the functional group are tightly integrated with the F atom by the hydrogen bonding interaction. In addition, the combined action of the polar solvent (DMF) and the PVDF molecule chains affect the motion and arrangement of $\text{CH}_2\text{-CF}_2$ electric dipole. All these are of great benefit to the formation of β -phase and the improvement of the piezoelectric property. However, the addition of unmodified nanographene is easily aggregated and hinders the movement of PVDF molecule chains, resulting in that the peak voltage (200 mV) being lower than that of the P-PVDF fiber membrane with unmodified nanographene (Figure 20e).

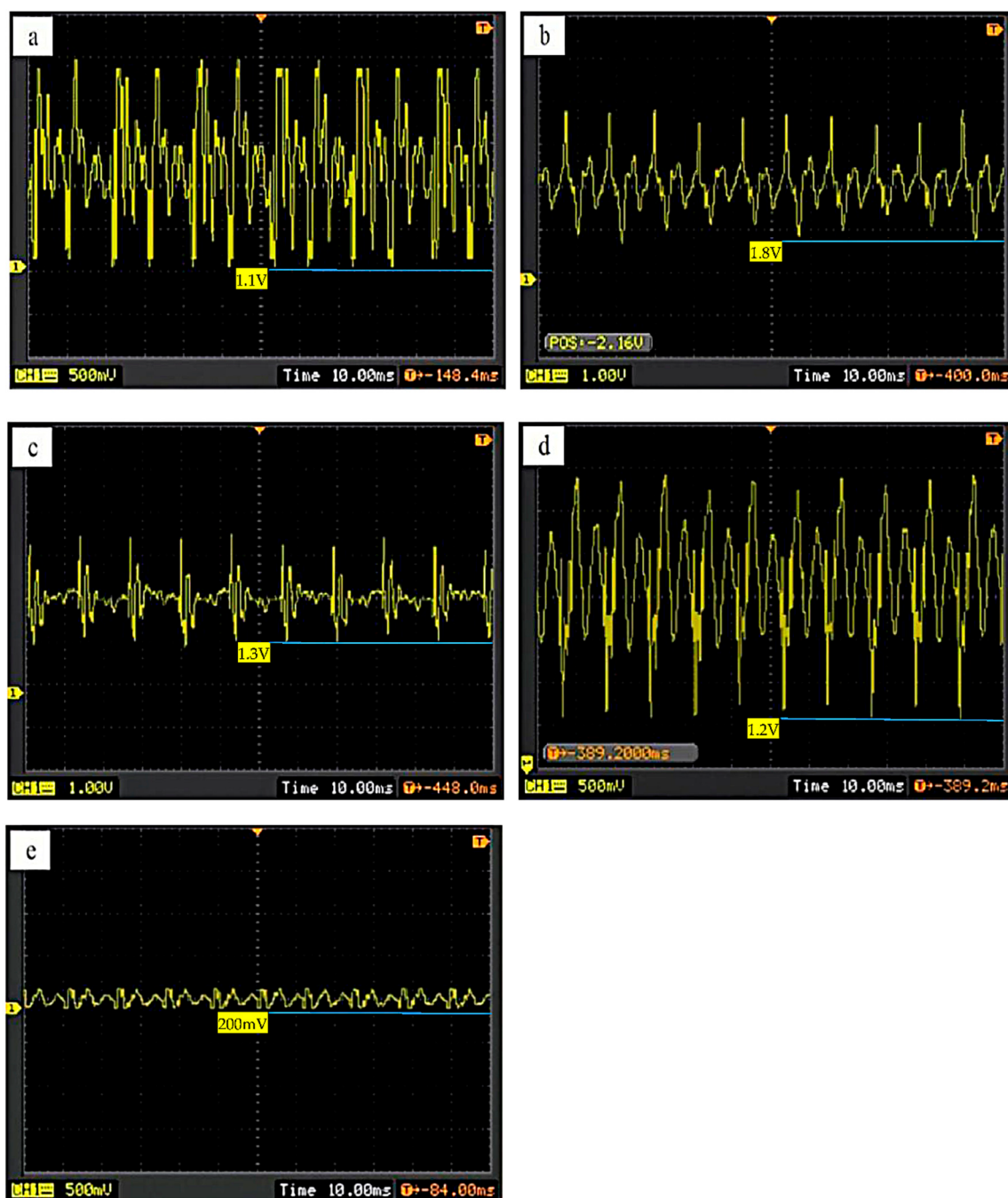


Figure 20. Piezoelectric signal of the fiber membrane at different addition of nanographene: (a) the addition of 0.5 wt%; (b) the addition of 1.0 wt%; (c) the addition of 1.5 wt%; (d) the addition of 2.0 wt%; (e) 1 wt% unmodified nanographene.

Table 10. Piezoelectric signal of the fiber membrane at different loading of nanographene.

Addition/wt%	0.4	0.8	1.2	1.6	1 wt% Unmodified	P-PVDF
Piezoelectric signal/V	1.1	1.8	1.3	1.2	0.2	0.27

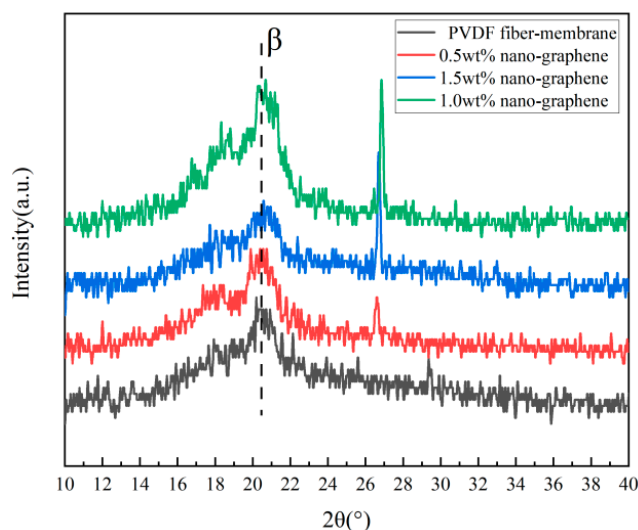
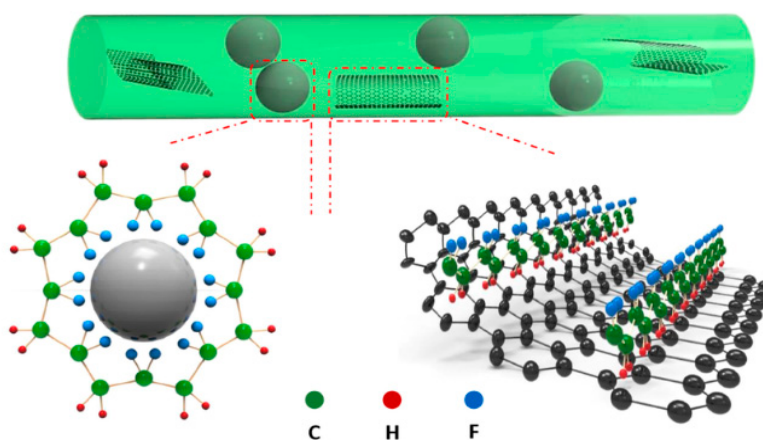
**Figure 21.** XRD patterns of the P-PVDF fiber membrane, PVDF/nanographene fiber membrane at the addition of 0.5 wt%, 1.5 wt%, and 2.0 wt%.**Figure 22.** Image of the β -phase facilitated by nanographene.

Table 11 depicts the mechanical properties of the fiber membrane at different loading of nanographene. At the addition of 1.0 wt%, the mechanical properties are greatly improved, revealing that the tensile strength and modulus of elasticity reach to the maximum value of 31 MPa and 6538 MPa. It is illustrated that the nanographene disperses uniformly in the fibers and improves the interface combination between the PVDF and nano-reinforced phase. The tightly combined polymer chains of the nanoparticle matrix are in favor of stress transfer. Meanwhile, the C-C bonds in the nanographene can also improve the mechanical properties. However, with the addition increasing, the tensile strength and modulus of elasticity decrease. It is attributed to that the excess modified nanographene is easy to aggregate in the solution and form the defect in the membrane. And the stress concentration happened in the use process to weaken the mechanical properties. Compared with PVDF-G with modified nanographene, the tensile strength and modulus of elasticity with unmodified nanographene was only 6 MPa and 1480 MPa at the same loading, because

the aggregated unmodified nanographene makes the fiber continuity weaken and form the defect on the surface of fibers.

Table 11. Mechanical properties of the fiber membrane at different loading of nanographene.

Addition/wt%	Tensile Strength/MPa	Standard Deviation	Modulus of Elasticity/MPa	Standard Deviation
0.4	22	0.15	3781	68.11
0.8	31	0.22	6583	90.19
1.2	29	0.18	5128	64.49
1.6	17	0.15	4429	73.28
Unmodified 1.0 wt%	6	0.10	1480	108.81
P-PVDF	13	0.35	3665	70.71

4. Conclusions

In summary, we successfully fabricated the composite fiber membrane with three inorganic reinforced materials (AgNO_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and modified nanographene). The addition of three inorganic reinforced materials, their mechanism of action, the morphology, the mechanical and piezoelectric properties are studied. It has been found that all the addition of the inorganic reinforced materials has great benefit to morphology and the piezoelectric property improvement compared to the pure PVDF membrane. When the optimal addition of AgNO_3 is 0.3 wt%, the minimum average diameter, peak voltage, tensile strength and modulus of elasticity are respectively 0.201 μm , 2 V, 19.76 MPa and 4047 MPa. When the optimal addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is 0.8 wt%, the minimum average diameter, peak voltage, tensile strength and modulus of elasticity are respectively 0.254 μm , 4.8 V, 19 MPa and 5621 MPa, where the best piezoelectric properties were obtained. When the optimal addition of modified nanographene is 1.0 wt%, the minimum average diameter, peak voltage, tensile strength and modulus of elasticity are respectively 0.296 μm , 1.8 V, 31 MPa and 6583 MPa. With the addition of modified nano-graphene, the improvement of morphology and properties is obvious, especially the mechanical properties. In addition, we demonstrate that the electroactive β -phase of PVDF induced by inorganic reinforced materials plays a crucial role in enhancing the piezoelectricity of nanocomposites. All results indicate that the addition of inorganic reinforced materials is a promising candidate for the further piezoelectric nanocomposite membrane as nucleating agents.

Author Contributions: Conceptualization, C.L.; Methodology, C.L.; Software, H.W.; Validation, C.L. and Y.F.; Formal Analysis, C.L.; Investigation, C.L., H.W., X.Y. and Q.M.; Resources, C.L.; Data Curation, Q.M. and H.C.; Writing–Original Draft Preparation, C.L. and H.W.; Writing–Review & Editing, C.L. and H.W.; Visualization, H.W.; Supervision, C.L.; Project Administration, C.L.; Funding Acquisition, C.L. All authors have read and agreed to the published version of the manuscript.

Funding: The research was funded by high technology ship research project (grand No. SSBQ-2020-HN-06-02).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available as the data is a part of an ongoing study.

Acknowledgments: This work was supported by high technology ship research project (grand No. SSBQ-2020-HN-06-02).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Manish; Sukesha, S. Piezoelectric energy harvesting in wireless sensor networks. In Proceedings of the 2015 2nd International Conference on Recent Advances in Engineering & Computational Sciences (RAECS), Chandigarh, India, 21–22 December 2015; pp. 1–6.
- Nechibvute, A.; Chawanda, A.; Luhanga, P. Piezoelectric Energy Harvesting Devices: An Alternative Energy Source for Wireless Sensors. *Smart Mater. Res.* **2012**, *2012*, 853481. [\[CrossRef\]](#)
- Jung, M.; Kim, M.G.; Lee, J.-H. Micromachined ultrasonic transducer using piezoelectric PVDF film to measure the mechanical properties of bio cells. In Proceedings of the Sensors, Christchurch, New Zealand, 25–28 October 2009.
- Shi, L.; Jin, H.; Dong, S.; Huang, S.; Kuang, H.; Xu, H.; Chen, J.; Xuan, W.; Zhang, S.; Li, S.; et al. High-performance triboelectric nanogenerator based on electrospun PVDF-graphene nanosheet composite nanofibers for energy harvesting. *Nano Energy* **2021**, *80*, 105599. [\[CrossRef\]](#)
- Yang, Y.; Zhou, Y.; Zhang, H.; Liu, Y.; Lee, S.; Wang, Z.L. A Single-Electrode Based Triboelectric Nanogenerator as Self-Powered Tracking System. *Adv. Mater.* **2013**, *25*, 6594–6601. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yang, Y.; Guo, W.; Pradel, K.C.; Zhu, G.; Zhou, Y.; Zhang, Y.; Hu, Y.; Lin, L.; Wang, Z.L. Pyroelectric Nanogenerators for Harvesting Thermoelectric Energy. *Nano Lett.* **2012**, *12*, 2833–2838. [\[CrossRef\]](#)
- Tang, E.; Wang, L.; Han, Y. Space debris positioning based on two-dimensional PVDF piezoelectric film sensor. *Adv. Space Res.* **2019**, *63*, 2410–2421. [\[CrossRef\]](#)
- Li, Y.-J.; Wang, G.-C.; Cui, H.-Y.; Cao, S.-K.; Wang, X.-Y. Dynamic characteristics and optimization research on PVDF piezoelectric film force sensor for steel ball cold heading machine. *ISA Trans.* **2019**, *94*, 265–275. [\[CrossRef\]](#) [\[PubMed\]](#)
- Li, Q.; Xing, J.; Shang, D.; Wang, Y. A Flow Velocity Measurement Method Based on a PVDF Piezoelectric Sensor. *Sensors* **2019**, *19*, 1657. [\[CrossRef\]](#) [\[PubMed\]](#)
- Turdakyn, N.; Medeubaye, V.A.; Abay, I.; Adair, D.; Kalimuldina, G. Preparation of a piezoelectric PVDF sensor via electrospinning. *Mater. Today Proc.* **2021**. [\[CrossRef\]](#)
- Sun, C.; Zhang, J.; Zhang, Y.; Zhao, F.; Ye, Z.G. Design and fabrication of flexible strain sensor based on ZnO-decorated PVDF via atomic layer deposition. *Appl. Surface Sci.* **2021**, *562*, 150126. [\[CrossRef\]](#)
- Alluri, N.R.; Chandrasekhar, A.; Ji, H.J.; Kim, S.-J. Enhanced electroactive β -phase of the sonication-process-derived PVDF-activated carbon composite film for efficient energy conversion and a battery-free acceleration sensor. *J. Mater. Chem. C* **2017**, *5*, 4833–4844. [\[CrossRef\]](#)
- Mohammadi, B.; Yousefi, A.A.; Bellah, S.M. Effect of tensile strain rate and elongation on crystalline structure and piezoelectric properties of PVDF thin films. *Polym. Test.* **2007**, *26*, 42–50. [\[CrossRef\]](#)
- Hess, C.M.; Rudolph, A.R.; Reid, P.J. Imaging the Effects of Annealing on the Polymorphic Phases of Poly (vinylidene fluoride). *J. Phys. Chem. B* **2015**, *119*, 4127–4132. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lau, K.; Liu, Y.; Chen, H.; Withers, R. Effect of Annealing Temperature on the Morphology and Piezoresponse Characterisation of Poly(vinylidene fluoride-trifluoroethylene) Films via Scanning Probe Microscopy. *Adv. Condens. Matter Phys.* **2013**, *2013*, 435938. [\[CrossRef\]](#)
- Ahn, Y.; Lim, J.Y.; Hong, S.M.; Lee, J.; Ha, J.; Choi, H.J.; Seo, Y. Enhanced Piezoelectric Properties of Electrospun Poly (vinylidene fluoride)/Multiwalled Carbon Nanotube Composites Due to High β -Phase Formation in Poly (vinylidene fluoride). *J. Phys. Chem. C* **2012**, *117*, 11791–11799. [\[CrossRef\]](#)
- Baqeri, M.; Abolhasani, M.M.; Mozdianfard, M.R.; Guo, Q.; Oroumei, A.; Naebe, M. Influence of processing conditions on polymorphic behavior, crystallinity, and morphology of electrospun poly (Vinylidene fluoride) nanofibers. *J. Appl. Polym. Sci.* **2015**, *132*. [\[CrossRef\]](#)
- Yz, A.; Lw, A.; Jian, Z.A.; Qr, A.; Li, L.A.; Pc, A.; Hy, C.; Jian, G.; Xn, A. Bottom-up lithium growth guided by Ag concentration gradient in 3D PVDF framework towards stable lithium metal anode. *J. Energy Chem.* **2022**, *65*, 666–673. [\[CrossRef\]](#)
- Gao, X.; Liang, S.; Ferri, A.; Huang, W.; Rou Xe, L.D.; Devaux, X.; Li, X.G.; Yang, H.; Chshiev, M.; Desfeux, R. Enhancement of ferroelectric performance in PVDF: Fe₃O₄ nanocomposite based organic multiferroic tunnel junctions. *Appl. Phys. Lett.* **2020**, *116*, 152905. [\[CrossRef\]](#)
- Clausi, M.; Grasselli, S.; Malchiodi, A.; Bayer, I.S. Thermally conductive PVDF-graphene nanoplatelet (GnP) coatings. *Appl. Surf. Sci.* **2020**, *529*, 147070. [\[CrossRef\]](#)
- Pusty, M.; Sinha, L.; Shirage, P.M. A flexible self-poled piezoelectric nanogenerator based on a rGO-Ag/PVDF nanocomposite. *New J. Chem.* **2019**, *43*, 284–294. [\[CrossRef\]](#)
- Martins, P.; Costa, C.M.; Benelmekki, M.; Botelho, G.; Lanceros-Mendez, S. On the origin of the electroactive poly(vinylidene fluoride) β -phase nucleation by ferrite nanoparticles via surface electrostatic interactions. *CrystEngComm* **2012**, *14*, 2807–2811. [\[CrossRef\]](#)