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**Highly oriented electrospun P(VDF-TrFE) fibers *via* mechanical stretching for
wearable motion sensing**

*Shaoyang Ma, Tao Ye, Ting Zhang, Zhe Wang, Kaiwei Li, Ming Chen, Jing Zhang, Zhixun Wang, Seeram Ramakrishna, and Lei Wei**

S. Ma, Dr. T. Zhang, Z. Wang, Dr. K. Li, Dr. M. Chen, J. Zhang, Z. Wang, Prof. L. Wei
School of Electrical and Electronic Engineering, Nanyang Technological University,
Singapore 639798, Singapore

E-mail: wei.lei@ntu.edu.sg

T. Ye, Prof. S. Ramakrishna

Department of Mechanical Engineering and Centre of Nanofibers and Nanotechnology
(NUSCNN), National University of Singapore, Singapore 117576, Singapore

Abstract

The advances in functional fabrics enable the realization of wearable devices in the form factor of fibers that can be seamlessly adapted in our daily lives. For mechanical-related sensing and power generation, piezoelectric materials are particularly favorable because they can convert mechanical shape changes into electric outputs. Electrospinning is a widely applied technique to produce extended length of fiber-shaped piezoelectric devices. However, this versatile process normally results in randomly distributed fibers with poor electrical properties and limited response to mechanical stimuli. Here, we demonstrate a stretching-induced alignment method to achieve highly oriented electrospun P(VDF-TrFE) fibers on a large scale. These globally aligned electrospun P(VDF-TrFE) fibers exhibit an enhanced piezoelectric property and high mechanical endurance. Using this simple stretching method, a high average output voltage of 80% aligned electrospun P(VDF-TrFE) fibers is 84.96 mV, about 266% of their original randomly distributed counterpart. Furthermore, when woven into outfit, the aligned electrospun P(VDF-TrFE) fiber bundle can work both individually and combinedly to monitor body gestures including angles of elbow bending and directions of swing arm, which may lead to the further development of motion-tracking technology.

Keywords

Fiber based sensor, stretching-induced alignment, P(VDF-TrFE), electrospinning, motion sensing

Introduction

Fibers are one of the most fundamental material forms, made by nature or humans. The integration of materials with disparate electrical or mechanical properties into a single fiber with diverse functionalities presents new opportunities for extending fiber applications in numerous fields, especially the realization of fiber-based wearable electronics.^[1-6] Among all the applicable functional materials, piezoelectric materials, which can convert mechanical shape changes into electric outputs, are particularly favorable to fabricate wearable devices for mechanical-related sensing and power generation.^[7-9] According to material molecular compositions, piezoelectric materials are generally divided into ceramics and polymers. Indeed, even though inorganic piezoelectric materials offer high piezoelectric property, they are mechanically hard and brittle, which have difficulties to be directly applied to wearable devices. Besides, many piezoelectric ceramics contain heavy metal elements such as lead, that are harmful to human and environment.^[10-12] On the other hand, piezoelectric polymers, represented by polyvinylidene fluoride (PVDF) and its copolymer poly[(vinylidene fluoride-co-trifluoroethylene)] (P(VDF-TrFE)), are more preferable for wearable devices as they are lightweight, stretchable, environment-friendly and chemically stable.^[13,14]

To construct piezoelectric polymer fibers, electrospinning, as a representative template-free method,^[15,16] is a versatile technique to produce extended length of fiber-shaped nanostructures with a number of advantages such as large surface area, tunable surface morphologies and enhanced mechanical performance.^[17-20] With electrospinning, when the droplet of polymer solution is charged by high applied voltage, the liquid droplet is pulled into a thin fiber and then collected by the grounded electrode. However, this liquid-to-solid transferring process normally results in randomly distributed fibers with poor electrical properties and limited response to mechanical stimuli. Therefore, to improve the performance of electrospun fibers, several methods have been demonstrated to obtain aligned electrospun fibers,^[21-25] Two most frequently adopted methods are: (1) using a high-speed rotating collector

with a very sharp edge,^[26-28] and (2) using two separated parallel electrodes.^[29,30] A very high rotating speed (>3000 rpm) is necessary for the rotating collector method, which brings high requirements to the fabrication facilities and increases electricity consumption. Also, the necessary role of sharp edge further restricts the amount of highly aligned electrospun fibers that can be collected. The parallel electrode method, on the other hand, can only fabricate aligned electrospun fibers in a very limited length, typically on millimetre scale.

In this paper, we demonstrate a simple dynamical mechanical stretching process that enables the formation of large-scale highly oriented electrospun P(VDF-TrFE) fibers obtained under low rotation speed. As a result, these globally parallel fibers exhibit enhanced mechanical and piezoelectric properties. Furthermore, the resulting fibers are twisted into fiber bundles and then woven into daily outfit for body motion sensing.

Results and discussion

Fabrication of Electrospun P(VDF-TrFE) Fibers

Figure 1a illustrate the schematic diagram of a far-field electrospinning process. During the electrospinning process, a high static voltage is applied between the metal needle and the collector to generate a strong electric force that draws charged droplets of P(VDF-TrFE) solution into thin fibers. Different from a conventional electrospinning setup in which a flat collector, we use a low speed rotating drum wrapped with aluminum foil as the collector. P(VDF-TrFE) solution (see Experimental Section) is prepared and transferred into a syringe, and then loaded in electrospinning setup (ET-2535, Ucalery). The electrospinning process is conducted with an applied voltage of 20 kV, feed rate of 2 mL/h. The distance between needle tip and the collector is 10 cm, and the rotating speed of collecting drum is fixed at 300 rpm. Dehumidifier is used to accelerate the solvent evaporation. The as-spun P(VDF-TrFE) thin film consist of fibers with the average diameter of 1.1 μm is shown in Figure 1b which is very flexible and can be wrapped on different curved surfaces.

Dynamical Mechanical Stretching

Since the drum is rotating while collecting, the as-spun fibers fallen on the surface of the collector possess similar initial orientations along the rotating direction. Meanwhile, the as-spun P(VDF-TrFE) fibers still contain residual solvent, thus they are easy to deform under applied external force. The electrospun P(VDF-TrFE) thin film is then peeled off the aluminum foil and mounted in the clamps of a linear travel stage driven by a controller for the following mechanical stretching process, as shown in Figure S1. The drawing velocity is precisely controlled at 2 mm/s. As a result, the initial orientations can be globally unified, which leads to the realignment of a large amount of electrospun P(VDF-TrFE) into highly oriented fiber bundles. As shown in Figure 1c, this mechanical stretching process is so simple and feasible that could be completed without the assistance of any equipment. The proportion of parallelly aligned electrospun P(VDF-TrFE) fibers increases with the extension of the sample, eventually reaching a globally aligned state for the entire sample, as SEM images shown in Figure 1d. To verify that P(VDF-TrFE) in the fibers is indeed in the ferroelectric phase, X-ray diffraction (XRD) patterns of the electrospun P(VDF-TrFE) fibers before and after the stretching process are shown in Figure 1e, and fitting of the patterns can reveal the quantification of each phase (shown in Figure S2)^[31]. Both samples exhibit identical peaks at $2\theta = 17.14^\circ$ corresponding to (200)/(110) peak of the α -phase, $2\theta = 19.98^\circ$ corresponding to (200)/(110) peak of the β -phase, and $2\theta = 18.73^\circ$ corresponding to amorphous phase, respectively. These results show that the electrospun P(VDF-TrFE) fibers consist of both paraelectric and ferroelectric crystal forms as well as a small amount of amorphous phase, but the ferroelectric β -phase is a majority (>60%), thus confirming the piezoelectric property of this electrospun P(VDF-TrFE) fiber.

To better observe the stretching-induced alignment process, a small amount of organic dyes (RH590) are doped into the P(VDF-TrFE) solution and then fabricated into electrospun P(VDF-TrFE) fibers. The organic dyes emit red light when illuminated by light source with

wavelength of 532 nm due to its fluorescence effect. Figure 2 is the fluorescence optical microscope images of electrospun P(VDF-TrFE) fiber films at different stages of mechanical stretching (see Experimental Section). As revealed in Figure 2a, the distribution of as-spun P(VDF-TrFE) fibers is extremely random that it is very difficult to indicate the major orientation of these fibers. However, with the mechanical stretching process proceeding, the P(VDF-TrFE) fibers begin to show different levels of unified orientation towards the direction of stretching, as shown in Figure 2b and 2c. When the mechanical stretching process is completed, majority of the electrospun P(VDF-TrFE) fibers are aligning in a highly paralleled way, as illustrated in Figure 2d.

To quantify the alignment level of electrospun P(VDF-TrFE) fibers, we use aligned fiber proportion. To be more specific, as long as the orientation of a fiber falls in the range from -5° to $+5^\circ$ to a certain direction, this fiber is regarded as along this certain direction, as indicated in Figure S3. Based on this, we can define the aligned fiber proportion as the ratio of the fiber population with a certain direction to the total fiber population. Next, the aligned fiber proportion is calculated at different stages of mechanical stretching process of the electrospun P(VDF-TrFE) fiber by counting both the aligned fiber number and the total number, and the result is shown in Figure 3a. The distribution of as-electrospun P(VDF-TrFE) fibers is random that we can hardly find a certain direction of the fibers. If the electrospun P(VDF-TrFE) fibers are completely random, the theoretical value of the aligned fiber proportion in any direction should be $\sim 5\%$ (10° out of 180° totally). But the average aligned fiber proportion along the drum rotating direction is $\sim 10.3\%$ which is slightly higher due to the fact that drum is rotating while collecting. After being stretched along the rotating direction, the aligned fiber proportion has substantially increased to $\sim 38.4\%$ at stage 2 (stretched to 150% of its original length) and $\sim 78.6\%$ at stage 3 (stretched to 200% of its original length). Finally, a highly aligned fiber proportion of $\sim 91.4\%$ is achieved globally when stretched to 400 % of its original length.

Mechanical and Electrical Characterization

To investigate the effect of mechanical stretching process on mechanical property of electrospun P(VDF-TrFE) fibers, the strain and stress curves are measured as plotted in Figure 3b. With the increasing of aligned fiber proportion, the electrospun P(VDF-TrFE) fibers can withstand larger external stress under the same strain, which means the shape change of better aligned electrospun P(VDF-TrFE) fibers is smaller than its random distributed counterpart under the same applied tension. This advantageous mechanical property makes highly aligned P(VDF-TrFE) fibers more suitable for wearable motion sensors.

Then, the electrical property is characterized by applying external periodical positive and negative forces (shown in Figure S4), and then measuring the corresponding output voltage. Figure 3c is the output voltage curve of electrospun P(VDF-TrFE) fibers with different aligned fiber proportions. These curves indicate that the electrical respond increases with the increase of aligned fiber proportion. However, when the electrospun P(VDF-TrFE) fibers become highly paralleled (aligned fiber proportion > 80%), the output would drop. As summarized in Figure 3d about the average output regarding the aligned fiber proportion, the highest output of 84.92 mV is achieved by P(VDF-TrFE) fibers with ~80% aligned proportion, about 266% of their randomly distributed counterpart (31.92 mV). This is because, for randomly distributed fibers, the increase in fiber alignment proportion is mainly attributed to the stretch of originally coiled fibers from the electrospinning process (Figure 2a), while further alignment of relatively well-oriented fibers (aligned fiber proportion > 80%) will cause the shape deformation which consumes the overall shape capacity for piezoelectric response generation. The increased resistance brought by longer device length result in lower output values, but the increasing in efficient functioning device length can achieve higher sensitivity on the motion sensing.

Applications in Wearable Motion Sensing

To use the resulting 80% aligned P(VDF-TrFE) fibers as wearable sensors, they are further twisted into bundles and yarns. Figure 4a illustrates the details of these P(VDF-TrFE) fiber bundles and the way they are woven into fabrics acting as motion sensors. From the SEM image in Figure 4a, the P(VDF-TrFE) fibers within each bundle are highly parallel to each other and following the twisting direction, which provide the enhanced performance in both mechanical and electrical aspects due to their highly oriented nature and efficient signal conduction.^[20]

To demonstrate the motion sensing function, we firstly use a single P(VDF-TrFE) fiber bundle to monitor the bending angle of the elbow. Figure 4b shows the three different bending angles of the elbow, 45°, 90°, and 135°, which are three representative gestures, respectively. At each angle, the elbow repeats to bend and extend periodically. The corresponding voltage signals are plotted in Figure 4c and 4d, and the average output is 10.6 mV, 20.3 mV, and 42.5 mV, respectively. The reason that the responding output is not increasing linearly with the elbow bending angle is that, with the increasing of the bending angle, the functioning length of the P(VDF-TrFE) fiber bundle also increases, leading to a higher enhanced output voltage under 135° bending angle. These results prove that the change of gesture can be reconstructed using a single wearable P(VDF-TrFE) fiber bundle. The detection limit of this single P(VDF-TrFE) fiber bundle based gesture sensor is less than few degrees, mainly due to the way that fiber bundle is integrated into the outfit.

Further, multiple P(VDF-TrFE) fiber bundles can be used in a combined way to monitor the direction of arm swing. As demonstrated in Figure 4e, two P(VDF-TrFE) bundles are woven separately into the front side and back side of a sportswear's shoulder parts. When the demonstrator's arm is swing backward, the P(VDF-TrFE) bundle attached to the front side is stretched and the one on the back side is loose. So, a signal pulse generated by the front side bundle indicates the backward direction of swing. Similarly, the forward direction of swing is recorded by the back side bundle, as shown in Figure 4f. The average voltage outputs of backward and forward motion are 8.87 mV and 8.38 mV, respectively. The slight difference is

due to the motion-induced distinction between backward and forward swings. Therefore, together with the sensing of bending angle of the elbow, these wearable P(VDF-TrFE) fiber bundles can be woven into multi-dimensional fabrics to achieve gesture recognition, such as motion-tracking technology for virtual reality (VR).

Conclusions

In summary, we have developed a stretching-induced alignment method to fabricate highly oriented electrospun P(VDF-TrFE) fibers on a large scale. These globally aligned electrospun P(VDF-TrFE) fibers exhibit an enhanced piezoelectric property. The average output voltage of 80% aligned electrospun P(VDF-TrFE) fibers is 84.96 mV, about 266% of their original randomly distributed counterpart. Also, highly oriented electrospun P(VDF-TrFE) fibers possess better mechanical endurance. When woven into outfit, the aligned electrospun P(VDF-TrFE) of fiber bundle can work both individually and combinedly to monitor body gestures including angles of elbow bending and directions of swing arm, which may lead to the further development of motion-tracking technology.

Experimental Section

Materials: Unless specified, all materials are from Sigma-Aldrich. 15 wt% P(VDF-TrFE) (Piezotech, 70/30) solution is prepared by adding 1.5 g P(VDF-TrFE) in a mixed organic solvent (Dimethylacetamide(DMAC)/acetone = 3/7), magnetic stirred at 75 °C for an hour, and then cooled down to room temperature to obtain a homogenous clear solution.

Characterization: To better observe the stretching-induced alignment processing, organic dyes (Rhodamine 590 Chloride, Exciton) are doped into P(VDF-TrFE) solution, and fluorescence images of the electrospun P(VDF-TrFE) fibers are obtained by using Olympus fluorescence microscope with a 100 W mercury lamphouse and a U-MWGS3 mirror cube. Scanning electron microscope (SEM) images are obtained using a field emission SEM

(FESEM 6340F) at 5 kV, and X-ray diffraction (XRD) experiments are conducted by a Shimadzu XRD-6000 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The mechanical property of the electrospun P(VDF-TrFE) fibers is measured by a forcemeter (YISIDA, DS2-5N) while extending by the same linear travel stage at a constant speed of 1 mm/s. The aligned P(VDF-TrFE) fibers are twisted into fiber bundles manually and woven into a sweater and a sport suit. Both the bending response and the real-time motion monitoring signal are measured by a Keithley 6517B electrometer/high resistance meter and data is recorded by a customized software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) Schematic of the electrospinning process. (b) As-spun flexible P(VDF-TrFE) thin film and the corresponding SEM image (c) and (d) Images of electrospun P(VDF-TrFE) fibers during mechanical stretching process under axial stress (scale bar is 5 μm). (e) XRD patterns of electrospun P(VDF-TrFE) fibers before and after mechanical stretching process.

Figure 2. Fiber distribution at different stages of the mechanical stretching process (scale bar is 50 μm). The percentage value in each image indicates the aligned fiber proportion.

Figure 3. Characterization of electrospun P(VDF-TrFE) fibers with different aligned proportions. (a) Aligned proportions of different experimental groups. (b) Strain and stress curve of electrospun fiber at different aligned proportions. (c) Voltage output curves and (d) average output of 4 groups of aligned proportions.

Figure 4. Applications of highly oriented electrospun P(VDF-TrFE) fibers. (a) Twisted electrospun P(VDF-TrFE) fiber bundle woven into outfit. (b) Monitoring different bending angles of elbow movement (45°, 90° and 135°) using twisted P(VDF-TrFE) fiber bundle. (c) Corresponding voltage outputs and (d) their average values. (e) Two directions of the arm swing (forward and backward) and (f) their corresponding voltage outputs.