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Highly Sensitive Flexible Pressure Sensor based on PVDF-TrFE-$BaTiO_3$ Piezoelectric Nanofibers

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Abstract—With the rapid advancement of wearable electronics, there is continuing demand to explore flexible sensors with high sensitivity to detect even the subtlest of mechanical stimuli enabling accurate and real-time monitoring for various applications. Among piezoelectric organic materials, Poly(vinylidene fluoride-co-trifluoroethylene) **(**PVDF-TrFE) stands out as a good candidate for the fabrication of flexible and wearable devices with stability and biocompatibility. This study presents the development and characterization of PVDF-TrFE-$BaTiO_3$ composite nanofibers fabricated by electrospinning, demonstrating that the addition of piezoelectric inorganic material $BaTiO_3$ enhances the crystallinity, amount of the β-phase, and the piezoelectric response. A conformal PVDF-TrFE-$BaTiO_3$ nanofiber-based piezoelectric sensor was further developed and tested under low pressure/vibration for potential wearable applications. The sensor exhibits an enhanced pressure sensitivity of 0.21 V/kPa at a pressure range from 6.4 kPa to 16 kPa at a fixed frequency of 7 Hz, and a frequency sensitivity of 1.72 V/Hz within a frequency range from 2 Hz to 5 Hz at a fixed pressure of 6.4 kPa. This means that the PVDF-$BaTiO_3$-based flexible sensor is particularly sensitive to low-regime mechanical movement holding great potential application in human motion monitoring and wearable devices such as heartbeat, pulse and respiration monitoring for sports performance tracking and healthcare.

Index Terms— Poly(vinylidene fluoride-co-trifluoroethylene) **(**PVDF-TrFE), Barium Titanet ($BaTiO_3$), electrospinning nanofibers, low-regime movement sensing

I. INTRODUCTION

The increasing development of wearable electronics has provided a strong motivation to further explore flexible sensors with high sensitivity. Flexible piezoelectric sensors have garnered significant attention due to their ability to convert mechanical strain into electrical energy, potentially powering autonomous systems sustainably. They offer a solution to the limitations posed by the bulky and rigid nature of traditional batteries, allowing for seamless integration and improved adaptability.

In particular, it is important for flexible biosensor with high-sensitivity to monitor low-regime mechanical force from human body movements such as the heart signal (10-250 Hz), relaxation of the human finger (less than 100 kPa) and body movement (100-370 kPa).[1] Poly(vinylidene fluoride) (PVDF) and its copolymers have attracted lots of attention because of its flexibility, biocompatibility and comparable piezoelectric coefficients compared to other organic piezoelectric materials.[2] Electrospinning offers the capability to apply high electrical field and stretching forces during processing, resulting in the self-poling of piezoelectric PVDF nanofibers (NFs) with a high β-phase ratio, thus rendering it a subject of extensive research.[3] In addition, their cost-effectiveness and ease of processing further enhance their appeal for large-scale production in various industries. In recent work, $BaTiO_3$ (BTO) as an inorganic piezoelectric material, with a piezoelectric coefficient of around 85.6 pC/N and the properties of low-cost and environmentally friendly, [4] was used as nanofillers to further improve the ratio of the ferroelectric β-phase of PVDF-based piezoelectric materials with a well-aligned polarization direction and piezoelectric coefficient. $BaTiO_3$, [5] $BaTiO_3$ mixed MXene [6] and PMMA coated $BaTiO_3$ nanowires [7] were used as nanofillers in electrospun PVDF-TrFE exhibiting improved piezoelectric performance under different mechanical stimuli.

Herein, we developed a piezoelectric sensor based on electrospun PVDF-TrFE-$BaTiO_3$ nanofibers with the ability to monitor low frequency and pressure force with high sensitivity for tiny mechanical force detection compared to the previous relative work.[5-8] The fabricated PVDF-TrFE with 2wt% $BaTiO_3$ NFs based sensor (PVDF-TrFE-BTO2) exhibited a sensitivity of 0.21 V/kPa at the pressure range from 6.4 kPa to 16 kPa at a fixed frequency of 7 Hz, which produced a maximum output voltage of 7.0 V at the pressure of 16 kPa. It also showed an ability to monitor different low-regime frequencies exhibiting a sensitivity of 1.72 V/Hz at the frequency range from 2 Hz to 5 Hz at a fixed pressure of 6.4 kPa. This signifies that the PVDF-TrFE-BTO-based flexible sensor exhibits exceptional

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sensitivity, especially in detecting subtle mechanical forces, thus presenting great potential for application in critical realms such as breathing monitoring, pulse, and heartbeat for wearable seismocardiography (SCG) and sports monitoring.

II. EXPERIMENTAL METHODS

A. Preparation of Electrospun PVDF-TrFE/$BaTiO_3$ nanofibers (NFs) Film and Sensors fabrication

A 15 wt% PVDF-TrFE solution was prepared by dissolving PVDF-TrFE powder (75/25, Piezotech, France) in a DMF and acetone (Sigma-Aldrich, UK) mixed solvent (1:1 ratio) for 10 h under stirring at 300 rpm and 25°C until the solution is homogeneous and completely transparent. PVDF-TrFE and $BaTiO_3$ (BTO) (Tetragonal, Sigma-Aldrich, UK) composite solutions were prepared by mixing BTO with the resulting PVDF-TrFE solution at 1wt% and 2wt%. The nanocomposite solutions were then stirred at 300 rpm at 25°C for 4 h to disperse the BTO in the PVDF-TrFE solution uniformly.

Electrospinning of the nanofibers (NFs) was conducted using an electrospinning machine. Fig.1 shows the schematic of the electrospinning machine setup. The prepared solutions were filled into a 10 mL syringe and connected to a spinneret with a 21 G-gauge needle (needle length: 38mm). After that, the electrospinning of the solution was executed at a high voltage of 17 kV and a flow rate of 0.5 mL/h with a 15 cm distance between the needle and drum collector. The electrospun NFs were collected by a drum collector covered by an aluminium foil, with a 2 kV voltage rotating at 1500 rpm. All three polymer solutions (PVDF-TrFE, PVDF-TrFE/1wt%BTO and PVDF-TrFE/2wt%BTO) were electrospun using the same fabrication parameters at room temperature and humidity. The fabrication process of piezoelectric fibers is depicted in Fig.1. To develop the piezoelectric pressure sensors, the NFs film was sandwiched between two Al electrodes and encapsulated with a polyimide tape.

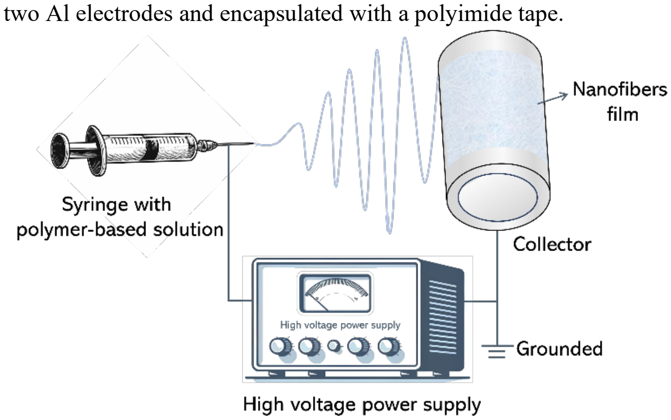

Fig. 1. Schematic of electrospinning setup.

B. Characterization and Performance Tests

The morphologies of NFs were investigated by Field emission scanning electron microscopy (SEM) using a FEIHelios Nanolab 600 at 5 kV. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance in Bragg–Brentano geometry with a Lynx-eye detector and Cu Kα radiation. Perkin Elmer Frontier Fourier transform infrared spectrometer (FTIR) system equipped with a Quest Specac attachment was used to determine the chain conformations and crystalline phases. Performance test under different vibration frequencies was supplied by a bespoke assembled set up consisting of a frequency generator and magnetic shaker (Brüel & Kjær, LDS V406). The vibration from the magnetic shaker was used to induce bending in the device by utilizing a resonant mass-spring system, formed by a spring steel cantilever with a tip mass (30 g), on which the device was attached. Tektronix TDS2012C oscilloscope was used to monitor the corresponding voltage output. Short-circuit current was measured using Low-Noise Current Preamplifier SR570 connected with Tektronix TDS2012C oscilloscope. Performance tests under different pressures and frequencies were supplied by an oscillating using an electrodynamic shaker system (TIRA, TV 50018, Germany). The output voltage was recorded by a digital storage oscilloscope (DSOX3014T). A nominal contact area of 2.5 × 2.5 cm^2 was fixed during the measurements.

III. RESULTS AND DISCUSSION

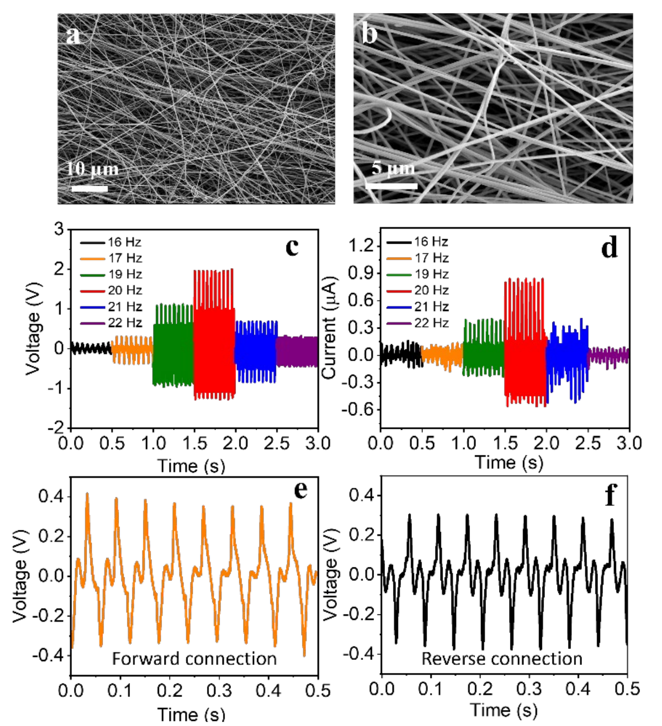

Fig. 2. (a-b) SEM images of pure electrospun PVDF-TrFE. (c-d) Typical output voltage and current of PVDF-TrFE sensor at different vibration frequencies. The typical output signal from PVDF-TrFE sensor at 17 Hz vibration under forward connection (e) and reverse connection (f).

The surface morphology of the PVDF-TrFE electrospun nanofibers was checked by using SEM as shown in Fig.2a-b exhibiting an average NFs diameter of 240 nm. Fig. 2c-d shows the response from the fabricated PVDF-TrFE NFs-based sensor tested at frequencies ranging from 16 to 22 Hz. The averaged voltage values obtained were 0.14 V, 0.38 V, 0.98 V, 1.5 V, 0.76 V and 0.98 V at shaking frequencies of 16 Hz, 17 Hz, 19 Hz, 20 Hz, 21 Hz and 22 Hz, respectively, corresponding to average current values of 0.13 μA, 0.15 μA, 0.31 μA, 0.67 μA, 0.44 μA and 0.12 μA shown in Fig. 2d, respectively. It shows the average output voltage and current of 1.5 V and 0.67 μA at the resonant vibration frequency of 20 Hz, where the highest displacements and strains were observed. Before the resonant vibration frequency of 20 Hz, the output performance gradually increases as the frequency increases, while the output performance gradually decreases when the frequency away from resonance causing strain amplitude decrease. To further verify the performance signal from the piezoelectric sensor rather than the system, a switching polarity test was carried out by reversing the electrode connection. The generated output voltages from the device in forward and reverse connection at a vibration frequency of 17 Hz are shown in Fig. 2e-f. An opposite signal is detected when the PVDF-TrFE NFs-based sensor is in a reversed connection confirming that the output signals recorded from the device are generated because of piezoelectricity rather than environmental noise.

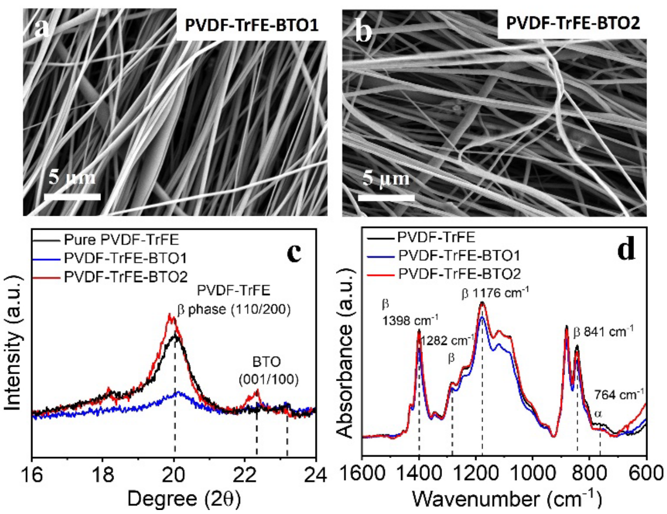

Fig. 3. SEM images of (a) PVDF-TrFE-BTO1 and PVDF-TrFE-BTO2 electrospun nanofibers. (c) XRD results of PVDF-TrFE and PVDF-TrFE/BTO samples with crystalline β-phase (110/200) and the tetragonal BTO nanoparticles (001/100). (d) FTIR spectra of PVDF-TrFE and PVDF-TrFE/BTO samples.

To further investigate the polarization phase of electrospun PVDF-TrFE NFs and improve the piezoelectric responsivity, PVDF-TrFE-BTO composites NFs were electrospun through PVDF-TrFE/BTO slurry with different BTO concentrations. Fig. 3a and b shows the SEM images of electrospun PVDF-TrFE NFs with 1wt% BTO (PVDF-TrFE-BTO1) and 2wt% BTO (PVDF-TrFE-BTO2), respectively. It exhibits the uniform distribution of nanofibers, which is not affected after the addition of BTO nanoparticles. The diameter of PVDF-TrFE-BTO1 is 0.24 μm, while the diameter of PVDF-TrFE-BTO2 shows a bit increase to 0.29 μm due to the increased amount of BTO addition. As shown in the XRD patterns in Fig. 3c, it was found that a dominant peak around 2θ = 20° for all three samples, corresponds to the reflection of the crystalline β-phase (110/200) of PVDF-TrFE. With the increasing amount of $BaTiO_3$, it was observed that the PVDF-TrFE/BTO NFs diffraction pattern exhibits more obvious typical peak splitting at 22.2°, corresponding to the (hkl) Miller index (001) and (100).[8] The full width at half maximum (FWHM) was calculated to determine the β-phase crystalline quality of the different samples, where the smaller value of FWHM corresponds to the higher β-phase crystallinity according to Scherrer's equation as the following equation, [9]

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} cos\theta} \quad (1)$$

in which D_{hkl} is the average crystallite size along the $(110)/(200)_\beta$ crystal plane of PVDF-TrFE, K is the shape factor which varies with the crystallite shape (0.89 was chosen in this case), λ is the wavelength of the incident X-rays, β_{hkl} is FWHM of the $(110)/(200)_\beta$ reflection, θ is the diffraction angle. Here, the FWHM values for pristine PVDF-TrFE, PVDF-TrFE-BTO1 and PVDF-TrFE-BTO2 are 1.52, 1.19 and 1.15, respectively, indicating that the existence of β-phase with higher crystallinity in PVDF-TrFE-BTO2 NFs. [10] In addition, we also determined the amount of β-phase of the three types of electrospun NF via FTIR. As shown in Fig. 3d, there is no obvious α-phase characteristic peak on 764 cm^{-1} due to the instinct high β-phase powder of PVDF-TrFE (75/25). The content of polar phases (F(β)) can be calculated by using the below formula derived using the Lambert-Beer Law,

$$F(\beta) = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (2)$$

where A_α and A_β are the absolute absorbance intensities of the peaks at 764 cm^{-1} and 841 cm^{-1}, respectively. [11] It was found that the amount of β-phase was higher for PVDF-TrFE-BTO2 (90.13%) than of pure PVDF-TrFE (84.82%) and PVDF-TrFE-BTO1 (89.70%). Thus, PVDF-TrFE-BTO2 exhibit β-phase with higher crystallinity and higher proportions, which will improve dipole alignment and polarization in the PVDF-TrFE/BTO matrix leading to an increase in the performance of piezoelectric sensor.

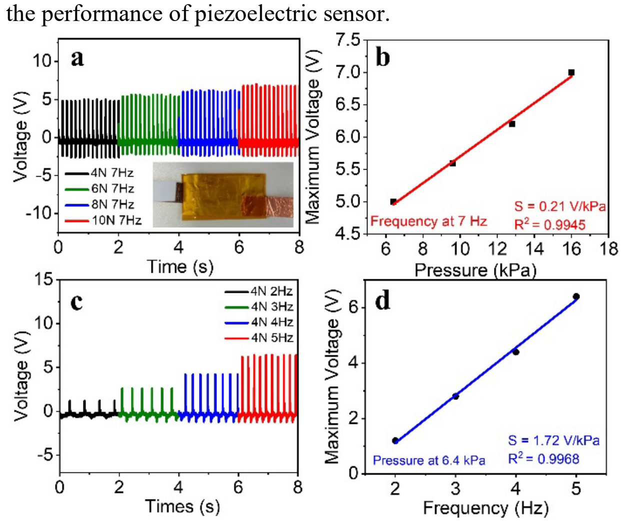

Fig. 4. (a) Typical output voltage signal and (b) pressure sensitivity of PVDF-TrFE-BTO2 under different pressures at a constant frequency of 7 Hz. (c) Typical output voltage signal and (d) frequency sensitivity of PVDF-TrFE-BTO2 under different frequencies at a constant pressure of 4 N.

The human body always generates low frequency and intensity regime mechanical force. Herein, the PVDF-TrFE-BTO2 sensor was further tested under low pressure and frequency under fixed frequency and pressure, respectively. As shown in Fig. 4a, at a fixed frequency of 7 Hz, the output voltage shows a roughly linear increase as the increasing of pressure, which can produce a maximum positive voltage of 5.0 V, 5.6 V, 6.2 V and 7.0 V at the pressure applied of 6.4 kPa, 9.6 kPa, 12.8 kPa and 16 kPa, respectively. Fig. 4b shows the pressure sensitivity and linearity of the PVDF-TrFE-BTO2 sensor at fixed 7 Hz with

Table 1. Comparison of recent works of flexible nanofiber-based piezoelectric sensors with the present work.

Year	Device made of	Peak Output Performance	Sensitivity	Applied forces range
2019	$BaTiO_3$ /PVDF-TrFE [5]	12.5 nA Pressure ~7 kPa	/	Pressure range 0.77 ~7.0 kPa at 10 Hz
2020	$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ PVDF-TrFE [12]	~6 V Compressed force of 6 N, 10 Hz	1.5 V/N (0.15 V/kPa)	Compression range 1 N-10 N (10 kPa-100 kPa) at 10 Hz
2020	ZnO nanorods on PVDF [13]	~1.5 V Pressure of 451 kPa	3.12 mV/kPa	Pressure range 1.8-451 kPa
2021	PMMA@$BaTiO_3$/ PVDF-TrFE [7]	~15 V	/	Bending range 0.25-3 Hz, 4 mm displacement
2023	$BaTiO_3$/MXene/ PVDF-TrFE [6]	7.6 V Compressed under 400 kPa	/	Compression range 0.2–400 kPa
2023	PVDF-TrFE@ polymeric core [14]	126 V Bend frequency at 2 Hz, 1 cm deformation	/	Bending range 0.5 Hz-3 Hz, 1 cm deformation
This work	PVDF-TrFE - BTO2	7.0 V Compressed force of 10 N (16kPa), 7 Hz	0.21 V/kPa	Compression range 6.4-16 kPa at 7 Hz

different pressures are 0.21 V/kPa and 0.9945, respectively. In addition, the device was also tested at a low-regime frequency from 2 Hz to 6 Hz at the fixed pressure of 6.4 kPa. As shown in Fig. 4c-d, the maximum voltage of the PVDF-TrFE-BTO2 sensor is 1.2 V, 2.8 V, 4.4 V and 6.4 V at 2 Hz, 3 Hz, 4 Hz and 5 Hz, respectively, with the frequency sensitivity and linearity of 1.72 V/Hz and 0.9968, respectively. It can be explained that the piezoelectric response of the PVDF-$BaTiO_3$ nanofiber-based sensor is influenced by the variation in applied pressure and frequency. The device demonstrates linear output response characteristics under both low pressure and frequency regimes. The piezoelectric response of the PVDF-TrFE-BTO2 sensor improves at higher frequencies, enhancing its sensitivity to external vibrations. The high linear piezoelectric sensitivity of the device holds good potential for the detection of subtle physiological signals and minor external forces.

IV. CONCLUSION

Herein, have demonstrated that PVDF-TrFE/BTO2 NFs can be obtained by using electrospinning. With an increase in the BTO concentration, the PVDF-TrFE-BTO2 NFs show higher crystallinity and proportion of β phase. The piezoelectric sensor based on the PVDF-TrFE-BTO2 sensor exhibited good pressure and frequency sensitivity at low-regime mechanical force. The maximum average output voltage of the device can reach 7 V under the pressure of 16 kPa and 7 Hz with the pressure sensitivity of 0.21 V/kPa exhibiting considerable high sensitivity compared to the previous relative work as shown in Table 1. Hence, the developed flexible PVDF-$BaTiO_3$ nanofiber-based piezoelectric sensor holds great potential for application in human motion monitoring and physiological signal tracking such as heartbeat, pulse and respiration monitoring.

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