Phase-Separation-Induced PVDF/Graphene Coating on Fabrics toward Flexible Piezoelectric Sensors

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ABSTRACT: Clothing-integrated piezoelectric sensors possess great potential for future wearable electronics. In this paper, we reported a phase-separation approach to fabricate flexible piezoelectric sensors based on poly(vinylidene fluoride) (PVDF)/graphene composite coating on commercially available fabrics (PVDF/graphene@F). The structural units of −CH− and −CF− of PVDF chains were arranged directionally due to the structural induction of graphene and water during phase separation, which is the key for electroactive phase enrichment. In optimized case, integrating into fabric substrates endows the phase-out PVDF/graphene composite coating 4 times higher voltage output than its film counterpart. Piezoelectric sensor based on PVDF/graphene@F exhibits a sensitivity of 34 V N−1, which is higher than many reports. It also shows low detecting threshold (0.6 mN), which can be applied to distinguish the voices or monitor the motion of body. This simple and effective approach toward PVDF/graphene@F with excellent flexibility provides a promising route toward the development of wearable piezoelectric sensors.

KEYWORDS: PVDF, graphene, piezoelectric materials, fabric, sensors

INTRODUCTION

In situ, real-time biomedical monitoring and human motion sensing require wearable electronic devices that can transform mechanical to electrical signals.1,2 Compared with traditional resistance-based testing system sensors,3 piezoelectric sensors (PZSs) show more precise response to outside strength because of the nature of piezoelectricity. Furthermore, piezoelectric materials generate voltage signals themselves without outside energy source.4 In this regard, clothing-integrated piezoelectric sensors for body monitoring have become a current thrust of research in the field of piezoelectric materials.5 Flexible piezoelectric polymers, especially poly(vinylidene fluoride) (PVDF), have been extensively used to fabricate flexible motion sensors due to the nature of lightweight, high processability, and the piezoelectric property.6−8

Graphene is a kind of two-dimensional material with unique properties. Due to its superior mechanical strength, high specific area, and unique electrons structure,8,9 it has been combined with PVDF to prepare flexible piezoelectric device with excellent mechanical strength and enhanced piezoelectric efficiency.10−12 PVDF/graphene composites have been widely studied in past decades, and different types of graphene, such as graphene oxide (GO) and reduced GO (rGO), will bring different enhanced results. GO can boost the β-PVDF content for the interaction between negative sheets and fluorine group (−CF−) in PVDF.13,14 Recently, Liu et al. utilized electrospinning to fabricate PVDF/GO core−shell fibers.15 They increased the piezoelectric constant (d33) of PVDF to 93.75 pm V−1 (the highest d33 of pure electrospinning nanofiber was 58.5 pm V−1),16 which testified the superiority of GO enhancement. In comparison, pristine graphene (or rGO) could provide higher mechanical property enhancement while inducing the formation of β-PVDF.17−20 Karan et al. designed highly durable piezoelectric nanogenerator by integrating...
PVDF with rGO/Al2O3, which provided higher voltage output of 36 V and 10 weeks’ usage without damping. It is indicated that graphene provides PVDF with higher endurance owing to its mechanical strength. In summary, pristine graphene can be the most promising nanofiller for both mechanical and electrical enhancement of PVDF-based piezoelectric sensors.

However, it remains challenging to fabricate PVDF/graphene composite with high flexibility, low energy cost, and time-saving merits. Soft PVDF/graphene films can be fabricated through solution-casting method. But, the solidifying process of film shows low efficiency to volatilize out the high-boiling-point organic solvent (N-methyl-2-pyrrolidone, for example). Electrospinning method shows great hope for the batch preparation of flexible PVDF/graphene fibers. And, the piezoelectric performance of electrospinning nanofibers can satisfy the demands of flexibility. Nevertheless, the strength of fabric based on PVDF fibers is hardly satisfying compared with other existing fabric-like polyester, and electrospinning method relies on expensive equipment. In comparison, to achieve remarkable flexibility of PVDF/graphene composite, existing fabrics can be optimum substrates for PVDF/graphene coating, which are safe for the body, flexible in motion, and sewable for integration with electronics. But, few reports have focused on the combination of the existing fabrics and PVDF.

Here, we report a fast phase-separation method to fabricate flexible piezoelectric device based on PVDF/graphene composite on fabrics (PVDF/graphene@F). Due to interactions between PVDF and graphene, as well as water, the electroactive phase (β/g phase) crystallinity in PVDF can be increased to 87%. Compared with traditional methods, our approach using the existing fabric as substrates would provide both scalability and better reliability in practical applications. Motion sensors based on PVDF/graphene@F are demonstrated when integrated into day-to-day garments.

**EXPERIMENTAL SECTION**

**Materials.** Sodium persulfate (Na2S2O8, ≥99 wt %, Sinopharm), sulfuric acid (H2SO4, 95–98 wt %, Sinopharm), poly(vinylidene fluoride) powder (PVDF, molecular weight: 900 000, Sigma), and N-methyl pyrrolidone (NMP, AR, Sigma) were purchased and used as received without further purification. Deionized water obtained through a Milli-Q system was used throughout all experiments. Graphite powders (325 mesh) were purchased from Qingdao Xinge graphite Co., Ltd. (Qingdao, China).

**Fabrication of PVDF/Graphene/NMP.** Graphene was fabricated as we reported before and the detailed process can be found in the Supporting Information. The corresponding graphene characterization can be found in Figure S1. To obtain the graphene/PVDF/NMP dispersions, prepared graphene powder, PVDF powder (5 g), and NMP (100 mL) are mixed and ultrasonicated (50 °C, 200 W) for 5 h to get the final homogeneous dispersion. The solution will be cooled to room temperature for next usage.

**Fabrication of PVDF/Graphene@F and PVDF/Graphene Membrane.** First, fabric was immersed in the PVDF/graphene/NMP solution (coating process). After dipping completely, the fabric coated with PVDF/graphene/NMP went through a tank of water to conduct phase-separation process. After that, the wet PVDF/graphene@F was dried in the air (60 °C). The dried PVDF/graphene@F was collected for the next usage.

The membrane was fabricated through the same process. First, PVDF/NMP or PVDF/graphene/NMP (about 2 mL) was cast onto surface dish. Then, water was poured in the dish slowly to conduct the phase-separation process. After 1–2 min, the wet membrane was dried in 60 °C air for further test.

**Fabrication of the PVDF/Graphene@F-Based Sensors.** First, aluminum foils were cut into squares. Two pieces of foils were then put on the two sides of the fabric and sealed with tapes. Such sensors can be sewed into pants or marks for further testing.

**Characterization.** Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-4700S equipped with an EDSINCA X-Max at 30 kV. Fourier transform infrared spectroscopy (FT-IR) was recorded by a Bruker Vertex 70v FT-IR spectrometer. Raman spectra excited by Ar+ laser (λ = 532 nm) were collected by Thermo Fisher DXR. Differential scanning calorimetry (DSC, TAQ200) was conducted at 100–200 °C temperature range (10 °C min−1) under N2 atmosphere. X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Bruker D8 ADVANCE) with a monochromatic source of Cu Kα radiation (λ = 0.15405 nm) at 1.6 kW (40 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) was recorded on a PHI Quantera II system (Ulvac PHI, INC, Japan). Transmission electron microscope (TEM) was carried out on a Hitachi H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating voltage of 300 kV.
RESULT AND DISCUSSION

Figure 1a shows the facile fabrication process of PVDF/graphene@F including three steps: continuous impregnation, phase separation, and drying. When using polyester as the fabric, the polyester was immersed in the PVDF/graphene/NMP solution for continuous impregnation. The impregnation time in this solution was 9–10 s, which allowed sufficient coating. For the continuity of fabrication, the stability of PVDF/graphene/NMP solution should be considered. After 3 weeks’ settling down, no clear delamination or sediment in the solution was observed, as shown in Figure 1b, indicating good dispersibility of graphene. Actually, graphene is very stable in NMP solution, as reported before. The dipped polyester fabric was further immersed in water to separate out the solid PVDF/graphene composite from the liquid NMP system (a typical phase-separation process). Long immersion time (>1 min) in water was necessary to ensure the removal of NMP and sufficient polarization of the PVDF molecules. After air-drying, polyester coated with PVDF/graphene (PVDF/graphene@P) was acquired (the average mass uptake of PVDF/graphene was about 0.5 g m\(^{-2}\)). The polyester becomes darker, as shown in Figure 1c, with the addition of graphene. Noticeably, after coating, the polyester was stiffer than the original state. The fabric with one coating still exhibits good flexibility but becomes rigid after fifth coating, as shown in Figure S2. The more coatings, the more rigid the crystal PVDF fabric, which leads to greater rigidity. Fortunately, PVDF/graphene@P with one coat retains the flexibility and can be folded as an uncoated fabric substrate. The folded PVDF/graphene@P generates a strong electrostatic attraction with butyronitrile gloves, which prevents it from falling (Figure S3), and indicates a strong piezoelectricity. Moreover, the mechanical property of PVDF/graphene@P and polyester was tested. The maximum load of PVDF/graphene@P is about 1.55 MPa, close to the 1.51 MPa of raw polyester fabric (Figure S4), which means that a short immersion time in NMP does not cause significant degradation of the polyester’s strength. Moreover, this approach can also be applied to various fabrics: as shown in Figure S5, various types of fabric (nylon, tissue, cotton, bamboo fibers, and flax) can also be uniformly coated with PVDF/graphene after similar treatment. This approach was convenient and time-saving for the mass-production of soft piezoelectric fabrics (productivity exceeding 36 m\(^2\) h\(^{-1}\)). Besides, the water-triggered phase-separation process greatly improves the elimination efficiency of the high-boiling-point solvent (such as NMP) and decreases the pollution of the organic solvent steam.

To judge the uniformity of coating, the morphology of the PVDF/graphene-coated polyester fabric (PVDF/graphene@P) was observed through FE-SEM in Figure 2. Figure 2a,b indicates that the interwoven structure of PVDF/graphene@P is well retained during coating processes. Figure 2a shows polyester fibers with an average diameter of 13 μm and the insert image shows a smooth surface; in contrast, the average diameter increases to about 16 μm with a much rougher surface after PVDF/graphene coating (Figure 2b shows the diameter; for statistic results, see Figure S6). The increased diameter indicates that the average coating thickness is approximately 1.5 μm because PVDF/graphene tends to form shell covering the whole polyester fiber. And, the rougher surface was induced by the contraction of PVDF during water-triggered phase-separation process. The folding state of PVDF/graphene@P is also observed in SEM, and there is no obvious crack on the surface of the folding place (Figure S7),
which would ensure the integrity of PVDF/graphene@P during practice applications. X-ray energy-dispersive spectroscopy (EDS) mapping (Figure 2c) reveals the presence of well-spread F element (blue) along with the C element (red), which indicates uniform coating of PVDF.

To observe coated PVDF more carefully, focused ion beam (FIB) was applied to obtain a little cross section of PVDF/graphene@P, which can be observed in TEM. Figure 2d presents the microstructure of a PVDF/graphene composite. Between Pt coating (protecting the structure from destruction of FIB) and polyester substrates, graphene dominates the black area and is surrounded by transparent PVDF. More details of the interfaces in PVDF/graphene are shown in a higher-resolution image (Figure 2e). In the PVDF layer, the crystal area is clear with a lattice spacing of 0.256 nm (Figure 2f), corresponding to the typical lattice spacing along c-axis in the orthorhombic β-PVDF crystal. Among three main phases (α, β, γ) of PVDF, polar β/γ-PVDF are highly desirable electroactive phases and α-PVDF is a non-electroactive phase. And, we observed that the majority of PVDF areas in the TEM images are crystal β-PVDF, which illustrates strong piezoelectric properties. It should be pointed out that the presence of significant crystal particles of β-PVDF has not been reported yet by previous work, to the best our best knowledge, which emphasizes the importance of phase-separation strategy. Selected area electron diffraction (SAED) patterns of the crystal area in PVDF also shows the diffraction spots corresponding to the crystallographic plane of β (100) (Figure S8). And, the lattice fringe of graphene (d = 0.248 nm) can be seen in Figure 2g, which proves the high quality of graphene (see discussion on graphene in the Supporting Information).

The above results demonstrate a uniform PVDF/graphene coating layer with significant presence of the piezoelectric
PVDF phase. How the crystal piezoelectric PVDF is formed should be investigated further. FT-IR, XRD, and DSC measurements are commonly used to assess the phase composition. However, it is not suitable to test PVDF/graphene@P directly with these analyses because the strong signals of textile substrates like polyester will blur that of PVDF/graphene. Therefore, PVDF and PVDF/graphene membranes were prepared through similar phase-separation process (Figure S9) and used for FT-IR, XRD, and DSC measurement.

FT-IR spectra can be applied to detect the structure information in PVDF chains. From the black curve in Figure 3a (raw PVDF), the vibration bands at 766, 795, and 976 cm⁻¹ can be observed, which correspond to the −CF₂− bending vibration and −CH₃− rocking or out-of-plane vibration of α-PVDF.25 In the red curve (representing the PVDF membrane fabricated by phase-separation method in water), vibration bands at 840, 1234, and 1279 cm⁻¹ are enhanced intensively. These peaks can be attributed to the −CH₃− wagging vibration and −CF₂− symmetric stretching of β/γ-PVDF, respectively.26,29 This indicates the enriched β/γ-PVDF phases through the phase-separation process. By contrast, the FT-IR spectrum of PVDF/graphene (blue curve) shows a significant decrease in α-PVDF signals at 766, 795, and 976 cm⁻¹ wavenumbers. It indicates that interaction of graphene sheets with PVDF chains induces amorphous macromolecular chains into the crystal electroactive PVDF instead of α-phase. These FT-IR results showed that phase separation and graphene sheets were very effective to form an electroactive phase. Through Raman investigation, we found that, compared to the G band at 1600 cm⁻¹, this G band splits into two distinct peaks at 1580 and 1605 cm⁻¹ in PVDF/graphene. The G band splitting of PVDF/graphene hybrid may indicate an interaction between PVDF and graphene surface, as shown in Figure S10.30 Additionally, DSC is a thermoanalytical technique that is complementary to other identification techniques.39 As shown in Figure 3b, the raw PVDF powder (the black curve) shows the melting temperature of 148−177 °C.29 After phase separation, PVDF (red curve) and PVDF/graphene (blue curve) membranes show higher melting temperature (about 172 °C). However, higher melting temperature of γ-PVDF at 179 °C cannot be recognized, which means the β-PVDF is dominant. DSC is also used to calculate the crystallinity (χₜ) of PVDF through eq 1.31

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χₜ = \frac{ΔH_f}{ΔH_{100}}
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where ΔH_f represents the melting enthalpy of the composite and ΔH_{100} (taken as 104.6 J g⁻¹) the melting enthalpy for a 100% crystalline sample of pure PVDF.32 According to the calculation result, χₜ of PVDF/graphene films reaches about 89%, which is much higher than that of pure processed PVDF film (70%). The above results illustrate that water-induced phase separation and graphene sheets help the crystallization of the electroactive phase.

XRD characterization could determine the phases of PVDF clearly.29 Figure 3c gives the XRD patterns of the raw PVDF powder (black curve), phase-separated PVDF (red curve), and PVDF/graphene membranes (blue curve). The obvious peaks at 2θ = 17.6, 18.3, 19.8, and 26.5° in raw PVDF (black curve) corresponded to the (100), (020), (110), and (021) planes of α-PVDF, respectively.29,33 But, the peaks disappeared after phase separation (red curve) and new peaks are observed at 2θ = 20.2 and 18.5°, which can be attributed to the (200) or (110) plane of β-PVDF and (110) plane of γ-PVDF, respectively.24,34 After adding graphene to PVDF, these characteristic peaks of β-γ-PVDF are significantly enhanced. To explore the role of graphene, different graphene weight contents of PVDF/graphene composite, like 0, 0.1, 0.3, 0.5, 1, 2, and 3 wt %, were examined with the XRD test. The relative electroactive phase content (Cβγψ) and their contribution to crystallinity (χβγψ) can be calculated by deconvolution method, as given in Figure S11 (Supporting Information). We define the value Cβγψ to explore the relative content of electroactive phases and χβγψ to depict the absolute content of crystal β/γ-phase in whole PVDF. As we can see in Figure 3d, when the graphene content is 0 wt %, the phase-separated PVDF already has 77% Cβγψ and 60% χβγψ. The enrichment of χβγψ is contributed by a strong interaction between water and PVDF chains, as reported before.36 With addition of 0.1, 0.3, and 0.5 wt % graphene, Cβγψ increases from 77 to 83, 90, and 97% and χβγψ increases from 60 to 68, 80, and 87%, respectively, indicating that graphene can induce more crystal-polarized PVDF during phase separation. But, decrease in Cβγψ and χβγψ with higher content of graphene (more than 1 wt %) indicated that more graphene obstructs the formation of electroactive phase. We assume that too much graphene would obstruct the continuous diffusion of NMP in PVDF during phase separation. This leads to less interaction between water and PVDF, which inhibited the bulk formation of β/γ-PVDF. According to Density Function Theory calculations (see the Supporting Information) of the interaction between graphene, water, and PVDF, as shown in Table S1, the action between water and PVDF chains (25.5 kJ mol⁻¹) is much stronger than that between graphene and PVDF (19.2 kJ mol⁻¹). Once the water was blocked, the weaker interaction between graphene and PVDF would be insufficient to help form a large content of electroactive phase.

We also observe different samples through TEM to deepen our understanding. For PVDF without graphene (phase separation), β-PVDF crystal particles show up only in the outermost layer (Figure S12a,b). Compared with the result in Figure 2e, the existence of graphene helps the formation of electroactive phases, as discussed above. However, PVDF/graphene sample with graphene content of 2 wt % shows less crystal area ratio. As shown in Figure S12c,d, graphene sheets encase PVDF, which impedes the diffusion of NMP. More importantly, when PVDF was cast onto Si from NMP solution (0.05 g mL⁻¹), no clear crystal area was observed (Figure S12e,f).

We build a structure model to help understand the process of phase separation in Figure 3e. Upon the introduction of water, PVDF and graphene in NMP simultaneously separate from the liquid phase to form a solid PVDF/graphene composite coating on the fibers. The electron injection groups (−CH₃−) in PVDF chains exhibiting electropositive property promote intense interaction with π-conjugation electrons of graphene.31,37 Simultaneously, at the interface of PVDF and water, electronnegative −CF₂− units of other chains tend to form hydrogen bonds with H₂O.36 Under the synergistic effect of water and graphene, the dissolved PVDF chains can be polarized into an electroactive phase instead of a non-electroactive phase. Actually, the coating thickness and the coating substrates also have influence on the crystallinity of the electroactive.

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With increase in the PVDF/graphene membranes' thickness (from 0.15 to 1.50 mm, measured by a thickness gauge), the crystallinity decreases, as shown in Figure S13a. Despite the inverse relationship between crystallinity and thickness (between 0.15 and 1.50 mm), this influence maybe not as apparent because of a much thinner coating on fabric in the micrometer range, which allows fast and complete phase-out after water introduction. On the other hand, the hydrophilic substrates will improve the crystallization of PVDF (see Figure S13b). But, the ester substrates have no obvious improvement or impairment to PVDF. In brief, the results from film are analogous to those of the PVDF/graphene layer coated on polyester fibers.

According to the above results and discussion, the phase-separation approach is convenient and effective to coat electroactive PVDF/graphene composite on fabrics. Here, we integrated PVDF/graphene@P with electrodes into piezoelectric sensors to evaluate piezoelectricity. At the same time, to give a constant testing environment, an electromagnetic punch was selected as the strength source for the piezoelectric test (Figures 4a and S14). The electromagnetic punch could impart constant strength at a given frequency and ensure the same testing conditions for different samples. A piezoelectric sensor (PS) device based on PVDF/graphene@P was manufactured to test piezoelectric property, as shown in Figure S15. PSs based on pure PVDF film and PVDF-coated polyester (PVDF@P) were also integrated with Al foils (Figure 4b; for details see the Supporting Information). As shown in Figure 4c, the pure-PVDF-film-based PS generated less than 10 V, whereas PVDF@P PS generated over 15 V. In contrast, PVDF/graphene@P generated the strongest voltage signal of about 20 V, which is 4 times higher than that for PVDF films and much higher than in many reports (less than 5 V).14,38,39 It is clear that porous structure can absorb more mechanical energy than film, a fact that has been testified in many reports.30,41 The textile fabric provided a natural porous structure that contributes to the intense voltage output enhancement. Furthermore, the graphene's addition is also confirmed to contribute to the increase in the piezoelectric performance compared with PVDF@P and PVDF/graphene@P. As a sensor, the higher voltage signals under the same strength causes lower signal-to-noise ratio, which is useful for wearable sensors. As shown in Figure 4d, we hit the front side of PS and will generate the voltage signals of hit and release. The voltages were found to reverse when we overturn the PS and hit its back side. The highest voltage of back side was almost the same as that of the front side, indicating indirect dipole reversibility due to the alignment of $-\text{CH}_2-$/$-\text{CF}_2$ dipoles of PVDF.21

To realize human motion monitoring, sensors with ultrasensitivity to force changes, high stability for practical application, and high flexibility for wearable devices are required. To test the sensitivity, we controlled the strength applied on the PS by adjusting the duty ratio of relay (Table S2). As shown in Figure 4e, with the increase in input strength from 0.05 to 0.45 N gradually, the voltage signals also show a linear growth from 3 to 18 V, indicating excellent signal correspondence. We fitted the relationship between input and output signals linearly, as shown in Figure S16, and the slope was 34 V N$^{-1}$. We can consider this value as the sensitivity of our PS based on our fabrication, which is much higher than that based on the electrospinning method (0.041 V N$^{-1}$).42 Table S3 lists the sensitivity comparison of other reports; the highest value of sensitivity of our PVDF/graphene@P illustrates the superiority of our method. The highest voltage of PVDF/graphene@P was over 60 V (Figure S17) when we

Figure 4. Three-dimensional (3D) models schematically representing (a) electromagnetic punch and (b) PVDF film, PVDF@P, and PVDF/graphene@P. (c) Voltage output of PVDF film, PVDF@P, and PVDF/graphene@P. (d) The voltage signals of hitting the front (black signals) and back (red signals) side of PVDF/graphene@P. (e) The relationship between voltage output and different strength input (from 0.05 to 0.45 N). (f) More than 125 cycles of voltage output illustrating the durability of PVDF/graphene@P.
hit the PS with 2 N force, and only few reports could reach such a high voltage based on the PVDF composite piezoelectric devices.\textsuperscript{19} In fact, due to integration with daily cloth, repetitive motion may cause the deformation of such a piezoelectric-based device. To prove the stability of PVDF/graphene@P-based PS, we ran the electromagnetic punch successively; after 125 circles (Figure 4f), the PS generates stable voltage signals of about 20 V, which promises multiple usages in our daily life.\textsuperscript{43} All of these results prove the excellent piezoelectric properties of PVDF/graphene@P.

Interestingly, the testing threshold of PS is very low. We put melon seeds (0.6 mN), microcapacitor (1 mN), and scindapsus leaf (1.8 mN) on the piezoelectric sensors for testing (Figure 5a). According to the results, the threshold of our device is 0.6 mN, which corresponds to the force created by melon seeds. It is illustrated that even tiny disturbance outside could be detected if we integrated this PS with our daily garment. When we sewed the PS into the mask (Figure 5b), the air flow coming out from our mouth will cause the vibration of PS when we speak. As we can see in Figure 5c, the voices of “graphene” and “PVDF” bring out the different signals. When we say graphene, the mouth motion during speaking /gr/ pronunciation brings the first signal at 3 s and the air flow of /fi: n/ voice creates the second signal at 4 s. And, the signals of saying PVDF is different and the voltage will show up when we say the /pi:/ and /et/ voices. Also, the /vi/ and /di/ voices can generate some signal fluctuation. We believe that it can distinguish the voices by evaluating the air flow during speaking. Furthermore, we embedded PVDF/graphene@P PS in the pants to test the body shake while running (Figure 5d). Because of the intensive shake in the pants, there was intensive deformation of the PS devices. The fibers in fabric pull and strike each other, thus contributing to the harsh change in voltage signal. From the enlarged part of voltage signals in 3.4−3.7 s (Figure 5e), we can distinguish the landing moments of legs. Compared with the conventional piezoelectric ceramic,\textsuperscript{5,7} every pulse signal width is narrower because of the less electric quantity. Less electric quantity but higher voltage signals ensure the safe application and easy collection of signals. The easy fabrication process compared to other methods gives the promise for the wide usage in future. Compared with the solution casting method, this approach provides a much greater work efficiency and scale-up capability. Compared with the electrospinning method to prepare piezoelectric fibers, our approach is energy efficient and independent of special equipment.

\section*{CONCLUSIONS}

In summary, a convenient, continuous, and time-saving strategy for the fabrication of flexible piezoelectric fabric (PVDF/graphene@F) with high-voltage output was developed. The PVDF/graphene solid phase formed with enriched electroactive PVDF when the liquid NMP phase dissolved in water. The structural units of −CH$_2$− and −CF$_2$− in PVDF chains were arranged directionally due to the induction of graphene and water during phase separation, which contributed to the highest of 87% electroactive phase crystallinity. Such a PVDF/graphene@F-based sensor with 34 V N$^{-1}$ sensitivity and 0.6 mN testing threshold could be integrated into the apparel, which can be applied to monitor the speaking and body motions. This work is helpful, not only for the development of PVDF composites with high β-PVDF content but also for the development of promising wearable piezoelectric sensors.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b10552.

Fabrication details of graphene and PVDF/graphene@F; SEM images of bended fabrics; XPS, TEM, Raman characterization of graphene; XRD data analysis; piezoelectric voltage testing system; HR-TEM, SAED, and additional data (PDF)
Sensors with Fish-Scale-Like Graphene-Sensing Layers for Full-Range and Torsion.

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