Enhancement of $\beta$-Phase Crystal Content of Poly(vinylidene fluoride) Nanofiber Web by Graphene and Electrospinning Parameters

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Abstract Electrospun poly(vinylidene fluoride) (PVDF) nanofiber web has been widely utilized as a functional material in various flexible sensors and generators due to its high piezoelectricity, ease processability, and low cost. Among all the crystalline phases of PVDF, $\beta$-phase is a key property for PVDF nanofiber web, because the content of $\beta$-phase is directly proportional to piezoelectric performance of PVDF nanofiber web. Herein, the impact of graphene content (GC), tip-to-collector distance (TCD), and rotational speed of collector (RSC), as well as their interactions on the $\beta$-phase formation of PVDF nanofiber web is systematically investigated via design of experimental method. The fraction of each crystalline phase of PVDF nanofiber web is calculated by FTIR spectra, and the crystallinity is determined by XRD patterns. The influences of GC, TCD, and RSC on both $\beta$-phase fraction and crystallinity of PVDF nanofiber are analyzed using Minitab program. The results show that GC, TCD, and RSC all have significant effect on the $\beta$-phase content of PVDF nanofiber web, and GC is the most significant one. In addition, an optimal electrospinning condition (GC = 1 wt%, TCD = 4 cm, and RSC = 2000 r-min$^{-1}$) to fabricate high $\beta$-phase crystallinity of PVDF nanofiber web is drawn, under which the crystallinity can reach 41.7%. The contributions in this study could provide guidance for future research on fabricating high performance PVDF nanofiber web based sensors or generators.

Keywords Graphene; Electrospinning; Poly(vinylidene fluoride); Design of experiment; $\beta$ Crystal phase

INTRODUCTION

Electroactive poly(vinylidene fluoride) (PVDF) has aroused great attention in view of its high piezoelectric coefficient, flexibility, and excellent processability, and hence been widely used in various electronic devices such as sensors, generators, and non-volatile memories.$^{[1-8]}$ PVDF has several stable crystalline forms including $\alpha$, $\beta$, and $\gamma$ phases, which can be directly determined by preparation conditions.$^{[9-11]}$ Since $\beta$-phase shows the highest electrical dipole moment among three phases,$^{[12,13]}$ the content of $\beta$-phase plays a decisive role in PVDF nanofiber web based high-performance sensors and generators.$^{[14-16]}$ It is, therefore, of great importance to enhance the $\beta$-phase content of PVDF for the abovementioned applications.

Electrospinning is a straightforward, scalable, and cost-effective versatile technique to fabricate high $\beta$-phase content of piezoelectric PVDF material, which is PVDF nanofiber web.$^{[17-20]}$ However, there are a huge number of parameters that influence the $\beta$-phase formation during PVDF electrospinning such as additive, tip-to-collector distance (TCD), rotational speed of collector (RSC), PVDF concentration, solvent mixture, applied voltage, injection flow rate, needle tip gage, and so forth. Among them, doping additives, for instance silver nanoparticle,$^{[14]}$ nanoclay,$^{[21]}$ and graphene oxide,$^{[3,22]}$ into PVDF electrospinning solution is one of the most effective methods for improving the $\beta$-phase content, for they can serve as nucleation agents to promote the $\beta$-phase formation. Compared with these additives, graphene is a two-dimensional sheet with huge $\pi$-boned carbon atoms packed in a honeycomb crystal lattice, presenting extraordinary electrical and mechanical properties such as super electrical conductivity, excellent flexibility, large specific surface, and high mechanical strength.$^{[23,24]}$ It has also been reported that adding graphene into PVDF electrospinning solution could improve the $\beta$-phase content.$^{[19,25]}$ However, it is not always beneficial with the increase of graphene content. Some research revealed that the high content of graphene could have negative effect on the $\beta$-phase formation.$^{[7,26,27]}$ Therefore, it is necessary to investigate the relationship between the $\beta$-phase formation and the graphene content as well as its underlying mechanism. In addition, another efficient avenue to facilitate the $\beta$-phase formation is to increase the electric field to promote the dipolar polarization of PVDF nanofiber web.$^{[15]}$ There are two feasible methods for elevating the electric field during electrospinning. One is to increase applied voltage at a fixed TCD and the other one is to reduce TCD. It is rather difficult to elevate the applied voltage too high because every...
The electrospinning of each sample was conducted at an applied voltage of 18 kV and an injection flow rate of 40 mL/h. The electrospinning machine has its own maximum applied voltage to protect electronics; the latter is more effective and practical than the former. Besides, the β-phase is conventionally obtained from the α-phase through mechanical stretching. It was hypothesized that the drawn ratio of PVDF nanofiber could improve at a high RSC during collecting to promote the phase transformation from the α-phase to the β-phase, further increasing the β-phase content of PVDF nanofiber.

Herein, the effects of graphene content (GC), TCD, and RSC as well as their interactions on the β-phase formation of PVDF nanofiber web were systematically investigated through design of experiment (DOE). The results showed that GC, TCD, and RSC all have significant impact on the β-phase content of PVDF nanofiber web, and GC is the most significant one (P < 0.05). In addition, an optimal electrospinning condition (GC = 1 wt%, TCD = 4 cm, and RSC = 2000 r·min⁻¹) to prepare high β-crystallinity of PVDF nanofiber web was drawn, and the crystallinity can reach 41.7%. More importantly, the underlying mechanism of GC, TCD, and RSC on the β-phase formation was also fully discussed.

**EXPERIMENTAL**

**Materials**

PVDF pellets (Mw ≈ 2.75 × 10⁶) were supplied by Sigma-Aldrich (UK). Graphene nanoplatelets with the average thickness of 5–7 atomic layers and the sheet size of about 25 μm were purchased from Sigma-Aldrich (UK) as well. Silver nitrate (Mw ≈ 169), N,N-dimethylformamide (DMF), and acetone were purchased from Fisher Scientific (UK).

**Electrospinning Process**

GC and two electrospinning parameters, i.e., TCD and RSC, were selected as research objects for DOE and two levels (low and high levels) were set in each parameter as shown in Table 1. The center level of each parameter was set to repeat four times to calculate the variation within the experiment.

| Parameter                  | Levels          |
|----------------------------|-----------------|
| Graphene content (GC)      | 0 wt%, 0.5 wt%, 1 wt% |
| Tip-to-collector distance (TCD) | 4 cm, 10 cm, 16 cm |
| Rotational speed of collector (RSC) | 5 r·min⁻¹, 1000 r·min⁻¹, 2000 r·min⁻¹ |

The protocols of electrospinning process are as follows. PVDF solution (12 wt%) was prepared by dissolving PVDF in a binary solvent system of DMF/acetone (6/4, V/V). Then a small amount (1 wt%) of silver nitrate was added into PVDF solution by stirring for 4 h to form silver nanoparticles, which acted as the phase stabilizer. The required amount of graphene (Table 1) was added and stirring was continued for 6 h at 60 °C. Next, the prepared solution was placed into an ultrasonic bath for 30 min to make the homogeneous dispersions just before electrospinning. The prepared solution was filled into a 10 mL syringe with a needle of 23 gage. Lastly, the PVDF nanofiber web was fabricated according to the conditions of TCD and RSC presented in Table 1 with an applied voltage of 18 kV and an injection flow rate of 0.6 mL/h. The electrospinning of each sample was conducted for 6 h to obtain the uniform thickness of ~100 μm of PVDF nanofiber web. Table 2 lists the sample specifications for PVDF nanofiber webs obtained with different conditions. Twelve samples (S01–S12), which were all treated samples, were prepared for DOE analysis, S09–S12 were repeated samples for the variation calculation within the experiment, and an untreated extra sample (S13), in which silver nanoparticles and graphene were not added, was prepared as a reference sample.

### Table 2 Sample codes and corresponding specifications.

| Sample code | Specifications |
|-------------|----------------|
| S01         | GC (wt%) | TCD (cm) | RSC (r·min⁻¹) |
| S02         | 0       | 16       | 5             |
| S03         | 0       | 4        | 5             |
| S04         | 0       | 4        | 2000          |
| S05         | 1       | 16       | 5             |
| S06         | 1       | 16       | 2000          |
| S07         | 1       | 4        | 5             |
| S08         | 1       | 4        | 2000          |
| S09         | 0.5     | 10       | 1000          |
| S10         | 0.5     | 10       | 1000          |
| S11         | 0.5     | 10       | 1000          |
| S12         | 0.5     | 10       | 1000          |
| S13         | 0       | 10       | 5             |

**Characterizations**

The formation of crystalline phases in PVDF nanofiber web was determined by Fourier transform infrared (FTIR, Perkin Elmer Spectrum 1000) spectroscopy in the range between 400 and 1600 cm⁻¹ with a resolution of 4 cm⁻¹ using attenuated total reflection mode. The band at 841 cm⁻¹ reflecting a common characteristic of electroactive phases (β+γ phases) was used to calculate the fraction of the electroactive (FEA) phase within PVDF nanofiber using Eq. (1). Furthermore, the fractions of β-phase (Fβ), γ-phase (Fγ), and α-phase (Fα) were calculated using Eqs. (2), (3), and (4), respectively:

\[ F_{\text{EA}} = \frac{A_{641}}{K_{641}A_{764} + A_{841}} \times 100\% \quad (1) \]

\[ F_{\beta} = F_{\text{EA}} \times \frac{\Delta H_{764}}{\Delta H_{764} + \Delta H_{641}} \times 100\% \quad (2) \]

\[ F_{\gamma} = F_{\text{EA}} \times \frac{\Delta H_{641}}{\Delta H_{764} + \Delta H_{641}} \times 100\% \quad (3) \]

\[ F_{\alpha} = 1 - F_{\text{EA}} \quad (4) \]

where A₆₄₁ and A₇₆₄ are the absorbance intensities at 841 and 764 cm⁻¹, respectively, and K₆₄₁ (7.7 × 10⁴ cm²·mol⁻¹) and K₇₆₄ (6.1 × 10⁴ cm²·mol⁻¹) are the absorption coefficients at the respective wavenumber. ΔH₆₄₁ is the height difference (absorbance differences) between the band around 1275 cm⁻¹ and the nearest valley around 1260 cm⁻¹, while ΔH₇₆₄ is that between the band around 1234 cm⁻¹ and the nearest valley around 1225 cm⁻¹.

The crystalline structure of PVDF nanofiber web was analyzed by X-ray diffraction (XRD, Bruker, D8 Advance) in the 2θ range of 10° to 40° with a CuKa (λ = 1.54 Å) radiation source under an operating 40 kV voltage and 40 mA current. The
area corresponding to each crystalline peak was obtained through the curve deconvolution of each XRD pattern using PeakFit program. Based on the data, the total crystallinity ($C_t$), the $\beta$-phase crystallinity ($C_\beta$), the $\gamma$-phase crystallinity ($C_\gamma$), and the $\alpha$-phase crystallinity ($C_\alpha$) were calculated using the following Eqs. (5)–(8):\(^\text{[29,30]}\)

$$C_t = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{amr}} \times 100\% \quad (5)$$

$$C_\beta = C_t \times \frac{\sum A_\beta}{\sum A_\alpha + \sum A_\beta + \sum A_\gamma} \% \quad (6)$$

$$C_\gamma = C_t \times \frac{\sum A_\gamma}{\sum A_\alpha + \sum A_\beta + \sum A_\gamma} \% \quad (7)$$

$$C_\alpha = C_t \times \frac{\sum A_\alpha}{\sum A_\alpha + \sum A_\beta + \sum A_\gamma} \% \quad (8)$$

where $\sum A_{cr}$ and $\sum A_{amr}$ are the summation of the integral area of the crystalline peaks and the amorphous halo from PVDF, respectively. $\sum A_\alpha$, $\sum A_\beta$, and $\sum A_\gamma$ indicate the total integral area from $\alpha$, $\beta$, and $\gamma$-crystalline phases peaks, respectively.

The morphology of PVDF nanofiber web was observed by a field emission scanning electron microscope (FE-SEM, Hitachi S4800) operated at an acceleration voltage of 1.5 kV.

**Statistical Analysis**

The effects of GC, TCD, and RSC as well as their interactions on the $\beta$-phase fraction, the total crystallinity, and the $\beta$-phase crystallinity of PVDF nanofiber web were all analyzed by Minitab program, in which a two-level factorial design analysis with three factors was used. The statistical distributions of the fiber diameters were calculated using ImageJ software.

**Piezoelectric Response Testing**

The piezoelectric pressure sensor was fabricated by attaching Ni-Cu plated polyester tapes as electrodes on both sides of the PVDF nanofiber web. The open-circuit output voltage of pressure sensor was measured using a Biopac system (MP160 and HL101000), a piezo film lab amplifier with voltage mode (Measurement Specialties), and an electromechanical universal testing system (Instron, 3400).

**RESULTS AND DISCUSSION**

**FTIR Analysis of PVDF Nanofiber Web**

The formation of three crystalline phases, $\alpha$, $\beta$, and $\gamma$-phases, was analyzed by FTIR spectra with the prepared PVDF nanofiber webs. Fig. 1(a) compares the FTIR spectra of the treated PVDF nanofiber webs (S01–S12) and the untreated reference PVDF nanofiber web (S13) in the wavenumber region from 400 cm$^{-1}$ to 1600 cm$^{-1}$. The two characteristic bands at 489 and 764 cm$^{-1}$ correspond to the nonpolar $\alpha$-phase, and two vibrational bands at 1234 and 1275 cm$^{-1}$ are attributed to $\gamma$-phase and $\beta$-phase, respectively.\(^\text{[25,30]}\) Observably, the treated samples have no obvious band at 489 ($\alpha$-phase), 764 ($\alpha$-phase), or 1234 ($\gamma$-phase) cm$^{-1}$, indicating they are mainly composed of $\beta$-phase. By contrast, the untreated sample, S13, consists of a relatively large amount of $\alpha$-phase, which can be proved by the two clear bands at 489 and 764 cm$^{-1}$.

Figs. 1(b)–1(e) show the calculated fraction of each phase. As shown in Fig. 1(b), S13 possesses the lowest content of $F_{\alpha}$ (85.4%), while S08 exhibits the highest content of $F_{\beta}$ (98.3%). Moreover, $F_{\gamma}$ of all treated samples are significantly higher than that of S13 ($P < 0.01$). There is no remarkable difference between the silver doped samples (S01–S04) and the silver/graphene doped samples (S05–S08), illustrating that the graphene cannot significantly change the $F_{\alpha}$ of PVDF nanofiber web. Similarly, in Fig. 1(c), S13 reveals the lowest content of $F_{\beta}$, 83.1%, which is notably lower than those of the treated sample ($P < 0.01$). Moreover, the four repeated samples (S09–S12) show higher $F_{\gamma}$ among treated samples whereas the silver/graphene doped samples (S05–S08) exhibit lower $F_{\beta}$ by comparing with the silver doped sample (S01–S04). This means adding graphene of 0.5 wt% into PVDF nanofiber web elevates $F_{\beta}$, but graphene more than 0.5 wt% in turn reduces $F_{\gamma}$, even worse than that of the only silver doped samples. In addition, the effect of TCD on $F_{\gamma}$ can be determined by comparing S01 with S03, S02 with S04, S05 with S07, and S06 with S08. However, there is no significant difference between each-two samples, implying the impact of TCD on $F_{\beta}$ is not significant. Similarly, the impact of RSC on $F_{\gamma}$ can also be evaluated by comparing neighboring samples, i.e., S01 with S02, S03 with S04, S05 with S06, and S07 with S08. The results show that $F_{\gamma}$ increases with the increase of RSC, which means RSC has influence on $F_{\beta}$ of PVDF nanofiber web. As shown in Fig. 1(d), S13 exhibits the highest $F_{\beta}$ (14.6%), which is almost three times higher than those of the treated samples ($P < 0.01$), and S08 exhibits the lowest $F_{\beta}$ (1.7%). This result can be ascribed to the additives i.e., silver nanoparticles and graphene, which serve as the nucleation agents to promote the $\beta$-phase formation. However, there is no notable difference between the silver doped samples and the silver/graphene doped samples, which means graphene dose not influence $F_{\beta}$. In Fig. 1(e), the four repeated samples (S09–S12) and the reference sample S13 show lower $F_{\gamma}$, even than other samples, but it is not significant ($P > 0.05$).

Overall, although electrospinning process promotes the $\beta$-phase formation, doping with some additives, i.e., graphene and/or silver nanoparticles, can further increase $F_{\beta}$ and reduce $F_{\gamma}$. However, adding too much graphene into PVDF nanofiber web can reduce $F_{\beta}$. In addition, TCD has no significant influence on $F_{\beta}$ whereas the higher RSC presents the higher $F_{\gamma}$.

**XRD Analysis of PVDF Nanofiber Web**

The crystalline structures of PVDF nanofibers were identified from XRD patterns as well. On the basis of the results of FTIR analysis, two typical samples, the untreated reference sample S13 and the treated representative sample S08, were compared and discussed for XRD analysis. Figs. 2(a) and 2(b) present the XRD patterns of S13 and S08, respectively. The characteristic peaks at 18.3° and 19.2° are $\alpha$-characteristic diffractions, the two peaks at 20.6° and 36.5° reflect to $\gamma$-characteristic diffractions, and the peak at 20.2° refers to $\beta$-characteristic diffraction.\(^\text{[9,10]}\) It can be found that S13 (Fig. 2a) has a clear peak at 18.3°, which can be attributed to the $\alpha$-phase diffraction, while the peak does not appear for sample S08 (Fig. 2b). This result is in agreement with the FTIR analysis. On the other hand, S08 has two distinct peaks at 26.7° and 38.2°, which are attributed to graphene and silver nanoparticle, respectively. It should be noted that the peak at 26.7° is the graphite-characteristic
diffraction rather than graphene peak. This is because the graphene size used in this experiment is about 25 \( \mu \)m with the average thickness of 5–7 atomic layers. As expected, the thin and flexible graphene sheets could be folded in each PVDF nanofiber with the diameter of several hundred nanometers during electrospinning.\[9,15\]

Figs. 2(c) and 2(d) display the curve deconvolution of S13 and S08, respectively, ranging from 15° to 25°. The crystallinity of PVDF nanofiber web including \( C_t \), \( C_\beta \), \( C_\gamma \), and \( C_\alpha \) was calculated from the curve deconvolution of XRD patterns. Table 3 lists the calculated crystallinity of each phase of the PVDF nanofiber webs prepared. S13 shows the lowest \( C_t \) (29.4%), and the treated samples exhibit significantly higher than that of S13. Remarkably, S08 shows the highest \( C_t \), which can reach 45.5%. Although \( F_\beta \) of S08 is lower than those of other treated samples, its \( C_\beta \) is the highest (41.7%) among treated samples in view of its high \( C_t \). The four samples (S05–S08) with graphene of 1 wt% exhibit the higher \( C_\beta \) than that of the four repeated samples (S09–S12) with a graphene of 0.5 wt%, illustrating that \( C_\beta \) of PVDF nanofiber web increases with the rise of graphene content. In addition, the influence of TCD on \( C_\beta \) is determined by comparing S01 with S03, S02 with S04, S05 with S07, and S06 with S08, showing the lower TCD with the higher \( C_\beta \). Similarly, the impact of RSC on \( C_\beta \) is evaluated as well by comparing neighboring samples, i.e., S01 with S02, S03 with S04, S05 with S06, and

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**Fig. 1**  (a) FTIR spectra of the treated PVDF nanofiber webs (S01–S12) and the untreated reference PVDF nanofiber web (S13) in the wavenumber region from 400 cm\(^{-1}\) to 1600 cm\(^{-1}\), and the calculated fractions of (b) the electroactive \((\beta+\gamma)\)-phases, (c) \( \beta \)-phase, (d) \( \alpha \)-phase, and (e) \( \gamma \)-phase.
Fig. 2  XRD patterns of (a) the untreated reference PVDF nanofiber web (S13) and (b) the typical treated PVDF nanofiber web (S08) ranging from 10° to 45°, and curve deconvolution of (c) the untreated reference sample (S13) and (d) the typical treated sample (S08) ranging from 15° to 25°.

Table 3  Calculated crystallinity of each phase of PVDF nanofiber.

| Sample code | Crystallinity (%) | $C_t$ | $C_d$ | $C_f$ | $C_a$ |
|-------------|-------------------|-------|-------|-------|-------|
| S01         |                   | 36.9  | 34.0  | 1.7   | 1.2   |
| S02         |                   | 37.6  | 34.6  | 1.5   | 1.5   |
| S03         |                   | 39.3  | 36.4  | 2.0   | 0.9   |
| S04         |                   | 40.5  | 37.2  | 1.9   | 1.4   |
| S05         |                   | 40.0  | 37.0  | 2.1   | 0.9   |
| S06         |                   | 40.7  | 38.3  | 1.8   | 0.6   |
| S07         |                   | 43.0  | 39.9  | 2.0   | 1.1   |
| S08         |                   | 45.5  | 41.7  | 2.7   | 1.0   |
| S09         |                   | 38.3  | 35.7  | 1.3   | 1.3   |
| S10         |                   | 38.3  | 36.0  | 1.0   | 1.3   |
| S11         |                   | 38.2  | 35.8  | 1.2   | 1.2   |
| S12         |                   | 38.8  | 35.1  | 1.2   | 2.5   |
| S13         |                   | 29.4  | 24.1  | 0.9   | 4.3   |

S07 with S08, presenting the higher RSC with the larger $C_f$. S08 shows the highest $C_f$ (~2.7%) whereas S13 exhibits the lowest $C_f$ (~0.9%). In contrast, S13 shows the highest $C_d$ (~4.3%), which is consistent with the result from the FTIR analysis, implying doping additives could reduce $C_d$.

Overall, S08 exhibits the highest $C_d$ while S13 shows the lowest $C_d$, which is in agreement with the result of FTIR analysis. Nevertheless, there are also some results obtained from XRD analysis which are different with those of the FTIR analysis. One conflicting result is that $C_d$ increases with the GC raise continuously, while the maximum $F_B$ is reached at the GC of 0.5 wt%. Another one is that both TCD and RSC have effect on $C_d$, whereas RSC only has impact on $F_B$. These results clearly imply that $F_B$ is different from $C_d$.

**Design of Experiment Analysis via Minitab**

Minitab program was employed to evaluate the effect of GC, TCD, and RSC on $F_B$, $C_d$, and $C_f$ of the PVDF nanofiber web. Meanwhile, their interaction was also analyzed.

Fig. 3(a) displays the effect of GC, TCD, and RSC on $F_B$ of PVDF nanofiber web. It presents that only GC has significant influence on $F_B$ since GC goes beyond the dash line (the standardized effect of 3.182), while others do not. This means that the other two parameters (TCD and RSC) do not significantly affect $F_B$. On the other hand, in Fig. 3(b), all three parameters have significant impact on $C_d$ and the most contributive parameter is GC as well. It is noteworthy that the interaction between GC and TCD is a significant parameter for $C_d$. Similarly, in Fig. 3(c), GC, TCD, and RSC all have significant influence on $C_f$ and the most contribution to $C_f$ is also from GC, but there is no interaction among them. According to Fig. 3(d), the main effect plot for $C_f$, the relationship between each parameter and $C_f$ could be determined. GC and RSC have positive relationship with $C_f$, but TCD has a negative one. Based on such relationship, the optimal electrospinning conditions to prepare PVDF nanofiber with the maximum $C_f$ can be drawn. The maximum $C_f$ (41.7%) was obtained when
Garlic, β-Carotene, and Zink (GC, TCD, RSC) in β-Phase Formation

From statistical analysis, it shows that GC is the most significant parameter to Fp, Cβ, and Cβ of PVDF nanofiber web. Incorporation of graphene in electrospinning solution notably increased Cβ and Cβ of PVDF nanofiber. This is because graphene serves as the nucleation agent to assist the β-phase formation due to the specific interaction of the surface charge of graphene with the CH2 dipoles of β-phase.\textsuperscript{[14]} To be specific, graphene has a huge amount of free electron from n-bonded carbon atoms packed in a honeycomb crystal lattice, showing electro-negative (upper inset of Fig. 4). Therefore, the graphene surface can attract the electro-positive CH2 dipoles to be oriented in one side of the PVDF chain, inducing the β-phase formation. This electrostatic interaction mechanism has been proven by several reported studies. Lou et al.\textsuperscript{[9]} added silver nanowires that exhibited electro-negative into PVDF nanofiber to increase the β-phase content. Mi et al.\textsuperscript{[10]} reported that hydrogen bonds between PVDF/poly(methyl methacrylate) interface could facilitate the β-phase formation by aligning the dipoles. Zhu et al.\textsuperscript{[11]} obtained enhanced β-phase content of PVDF nanofiber web by doping graphene oxide. Furthermore, graphene can effectively confine and direct the arrangement of PVDF chains to promote crystalline formation, which is defined as a "molecule movement restriction" effect due to ultra-strong mechanical property.\textsuperscript{[7,18]} In addition, adding graphene into PVDF can enhance its electrical property, i.e., permittivity.\textsuperscript{[7]} Consequently, the PVDF nanofibers are more efficiently polarized by electric filed during electrospinning to promote β-phase formation.\textsuperscript{[21]}

TCD is the second significant parameter for Cβ and Cβ. Changing TCD has two-sided effect. Although reducing TCD could increase the electric field, promoting the dipolar polarization of PVDF nanofiber web to enhance the β-phase content, it may hinder the crystal development because of the shortened formation time. However, according to the result from DOE analysis, it shows that the lower TCD is more beneficial than the higher TCD for improving Cβ and Cβ of the PVDF nanofiber. Fig. 4 illustrates the PVDF electrospinning process with the optimal condition (TCD = 4 cm and RSC = 2000 r·min\textsuperscript{-1}) drawn from the DOE analysis. The route of PVDF nanofiber formation by electrospinning can be divided into two zones, liquid flow zone and transition zone.\textsuperscript{[21]} The PVDF solution jet coming out from the Taylor cone firstly goes through the liquid flow zone. In this zone, the directions of electric field and the PVDF chains are parallel (Fig. 4), and

Fig. 3 Pareto chart of the standardized effects (GC, TCD, RSC) on (a) the β-phase fraction, (b) the total crystallinity, and (c) the β-phase crystallinity of PVDF nanofiber web; (d) The main effect plot for β-phase crystallinity. A, B, and C represent GC, TCD, and RSC, respectively.

GC = 1 wt%, TCD = 4 cm, and RSC = 2000 r·min\textsuperscript{-1}.

Role of GC, TCD, and RSC in β-Phase Formation

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GC = 1 wt%, TCD = 4 cm, and RSC = 2000 r·min\textsuperscript{-1}.

Role of GC, TCD, and RSC in β-Phase Formation

From statistical analysis, it shows that GC is the most significant parameter to Fp, Cβ, and Cβ of PVDF nanofiber web. Incorporation of graphene in electrospinning solution notably increased Cβ and Cβ of PVDF nanofiber. This is because graphene serves as the nucleation agent to assist the β-phase formation due to the specific interaction of the surface charge of graphene with the CH2 dipoles of β-phase.\textsuperscript{[14]} To be specific, graphene has a huge amount of free electron from n-bonded carbon atoms packed in a honeycomb crystal lattice, showing electro-negative (upper inset of Fig. 4). Therefore, the graphene surface can attract the electro-positive CH2 dipoles to be oriented in one side of the PVDF chain, inducing the β-phase formation. This electrostatic interaction mechanism has been proven by several reported studies. Lou et al.\textsuperscript{[9]} added silver nanowires that exhibited electro-negative into PVDF nanofiber to increase the β-phase content. Mi et al.\textsuperscript{[10]} reported that hydrogen bonds between PVDF/poly(methyl methacrylate) interface could facilitate the β-phase formation by aligning the dipoles. Zhu et al.\textsuperscript{[11]} obtained enhanced β-phase content of PVDF nanofiber web by doping graphene oxide. Furthermore, graphene can effectively confine and direct the arrangement of PVDF chains to promote crystalline formation, which is defined as a "molecule movement restriction" effect due to ultra-strong mechanical property.\textsuperscript{[7,18]} In addition, adding graphene into PVDF can enhance its electrical property, i.e., permittivity.\textsuperscript{[7]} Consequently, the PVDF nanofibers are more efficiently polarized by electric filed during electrospinning to promote β-phase formation.\textsuperscript{[21]}

TCD is the second significant parameter for Cβ and Cβ. Changing TCD has two-sided effect. Although reducing TCD could increase the electric field, promoting the dipolar polarization of PVDF nanofiber web to enhance the β-phase content, it may hinder the crystal development because of the shortened formation time. However, according to the result from DOE analysis, it shows that the lower TCD is more beneficial than the higher TCD for improving Cβ and Cβ of the PVDF nanofiber. Fig. 4 illustrates the PVDF electrospinning process with the optimal condition (TCD = 4 cm and RSC = 2000 r·min\textsuperscript{-1}) drawn from the DOE analysis. The route of PVDF nanofiber formation by electrospinning can be divided into two zones, liquid flow zone and transition zone.\textsuperscript{[21]} The PVDF solution jet coming out from the Taylor cone firstly goes through the liquid flow zone. In this zone, the directions of electric field and the PVDF chains are parallel (Fig. 4), and
PVDF chains cannot be polarized. The jet then flows into transition zone. As the solution jet in flight, it gradually transforms from liquid phase to solid phase. Simultaneously, the jet is stretched and bended by electrostatic repulsion, forming a nanofiber with helical structure. Because of this shape deformation, the directions of electric field and PVDF chains become vertical, which polarizes the PVDF chains to promote β-phase formation. Compared to the traditional TCD of 10–16 cm for PVDF electrospinning, [6,14,32] the lowest TCD in this study is about 4 cm, which is almost the minimum spinning distance to fabricate PVDF nanofiber. The lowest TCD significantly multiplies the electric field, which is three times higher than that of TCD of 16 cm. As a result, the elevated electric field polarizes the PVDF nanofiber to facilitate the β-phase formation more efficiently. [21,22] The PVDF nanofiber contains high permittivity folded graphene. Consequently, the polarization effect can be magnified by doping with graphene due to the increased permittivity of PVDF nanofiber web. This makes the interaction between GC and TCD a significant parameter for $C_G$. Moreover, the electric force induced by the strong electric field stretches the PVDF nanofiber more intensively to promote the transformation from α-phase into β-phase formation shown in the bottom inset of Fig. 4. [23]

RSC has significant influence on $C_I$ and $C_P$ of the PVDF nanofiber web as well. This is because the PVDF nanofiber would be drawn again in the collecting process due to the high RSC, resulting in a further increased crystallinity. This could be observed by SEM images of S13 and S08. As shown in Fig. 5, the PVDF nanofibers of S13 fabricated at a low RSC of 5 r·min$^{-1}$ are entangled with each other whereas most individual PVDF nanofiber of S08 fabricated at a high RSC of 2000 r·min$^{-1}$ is oriented, indicating they were stretched when collected. In addition, the average nanofiber diameter of S13 is around 150 nm (Fig. 5a, inset), but that of S08 is below 100 nm (Fig. 5b, inset), also implying the PVDF nanofibers of S08 were drawn at the high RSC.

**Piezoelectric Performance Evaluation**

To investigate the effect of $C_G$ on their piezoelectric response, the piezoelectricity of two typical samples, S13 and S08, was measured. Instron was employed to apply periodic pressure (10 kPa) to the fabricated sensors and the open-circuit output voltage of the sensor was measured using Biopac system as shown in Fig. 6(a). To simplify the piezoelectric performance evaluation, the peak-to-peak output voltage ($V_{p-p}$) was measured and compared in this work. Figs. 6(b) and 6(c) compare the $V_{p-p}$ of S13 and S08. As expected, S08 exhibits a $V_{p-p}$ of 0.14 V whereas S13 presents a relatively low $V_{p-p}$ of 0.06 V, which means the piezoelectric response of S08 is more than two times of that of S13. The increased piezoelectric performance is mainly attributed to the higher $C_G$ of S08 (41.7%) in comparison with that of S13 (24.1%), strongly demo-
nstrating the impact of Cβ on the piezoelectric performance.

CONCLUSIONS

A series of PVDF nanofiber webs have been fabricated with different GC and diverse electrospinning parameters, i.e., TCD and RSC. Then their crystalline phases, α, β and γ-phases, have been thoroughly analyzed by FTIR spectra and XRD patterns. The effects of GC, TCD, and RSC as well as their interactions on the β-phase formation of PVDF nanofiber have been investigated by Minitab program. The results showed that GC, TCD, and RSC all have significant effect on Cβ of PVDF nanofiber web; especially, GC is the most significant one. An optimal electrospinning condition (GC = 1 wt%, TCD = 4 cm, and RSC=2000 r·min⁻¹) to prepare high Cβ (S08, 41.7 %) of PVDF nanofiber web has been drawn, and such optimal sample (S08) exhibited better piezoelectric response than that of graphene untreated reference sample (S13).

It should be noted that the large β-phase fraction from FTIR spectra does not mean the high β-phase crystallinity from XRD patterns; additionally, the effect of three parameters on the β-phase fraction is not the same as those on the β-phase crystallinity, indicating the crystalline fraction is a totally different factor from the crystallinity. Significantly, both GC and electrospinning parameters such as TCD and RSC were systematically analyzed via DOE, which can have positive impacts on developing high β-phase content of PVDF nanofiber webs for high-performance flexible sensors and generators.

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