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The use of Polyvinylidene Fluoride (PVDF) based piezoelectric nanofibers for sensing and actuation has been reported widely in the past. However, in most cases, PVDF piezoelectric nanofiber mats have been used for sensing applications. This work fundamentally characterizes a single electrospun PVDF nanofiber and demonstrates its application as a sensing element for nanoelectromechanical sensors (NEMS). PVDF nanofiber mats were spun by far field electrospinning (FFES) process and complete material characterization was conducted by means of scanning electron microscope (SEM) imaging, Raman Spectroscopy and FTIR spectroscopy. An optimized recipe was developed for spinning a single suspended nanofiber on a specially designed MEMS substrate which allows the nano-mechanical and electrical characterization of a single PVDF nanofiber. Electrical characterization is conducted using a single suspended nanofiber to determine the piezoelectric coefficient (d_{33}) of the nanofiber to be -58.77 pm/V. Also the mechanical characterization conducted using a nanoindenter revealed a Young's Modulus and hardness of 2.2 GPa and 0.1 GPa respectively. Finally, an application that utilizes the single PVDF nanofiber as a sensing element to form a NEMS flow sensor is demonstrated. The single nanofiber flow sensor is tested in presence of various oscillatory flow conditions.
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Self-powered and zero-powered sensors have been the center of attention for last two decades. As technology progresses, the requirement of ultra-low power sensors is growing exponentially. To cope up with the growing demand, piezoelectric sensors in the form of thin and bulk films have been widely investigated for sensing applications in recent years.[1–4] Among all the piezoelectric materials, polyvinylidene fluoride (PVDF) which is a synthetic polymer has a special status because of its biocompatibility, flexibility, and low cost. For the past two decades, electrospun nanofibers and in specific PVDF nanofibers has been extensively studied.[5–11] Applications of PVDF nanofibers for sensing,[12–14] nano-generators for energy harvesting,[15,16] and passive biomimetic sensing[17] are emerging research topics. PVDF nanofibers are usually fabricated by means of an electrospinning process where the nanofibers are mechanically stretched and electrically poled in situ. Electrospinning can

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be of different types depending on the distance between the needle tip and the collector. Usually, a conventional far field electrospinning (FFES) process, requires the needle tip and the collecting electrode to have a distance greater than 10 mm. Alternatively, a near field electrospinning process (NFES), allows needle-collector gap as low as 1mm. In most of the applications of electrospun PVDF nanofibers in past, randomly spun nanofiber mats were used[12,14] where the response was lowered due to random orientation of fibers which cancel out each other.[18] Chang et al. have demonstrated PVDF nano-generators with high conversion efficiency[16] and Pu et al. have used direct write method to fabricate PVDF nanofibers for actuation.[18] However, fundamental nano-mechanical characterization of a single nanofiber in order to explore its potential as a sensing element has not been conducted before. This work fundamentally analyses the piezoelectricity in a single PVDF nanofiber through material, electrical and nano-mechanical characterizations. In addition, the development of a NEMS flow sensor that utilizes a single electrospun PVDF nanofiber as a sensing element is demonstrated. PVDF nanofibers were electrospun by FFES process using an electrospinning setup and characterized by means of scanning electron microscope (SEM), Raman Spectroscopy and Fourier Transform Infra-red (FTIR) spectroscopy.

Polyvinylidene fluoride (PVDF) is a polymer compound with semi-crystalline structure which is represented by $(CH_2–CF_2)_n$. Due to its structural characteristics, PVDF usually appears in different possible crystal phases which are α, β, γ and δ. Among all of the possible phases, α is the most abundant and forms naturally when PVDF is cooled down from solidified melt. Though α is natural and abundant, it is the β-phase which gives PVDF its piezoelectric properties by the virtue of its ferroelectric crystalline structure. In this work, FFES process has been used along with a rotating mandrel collector to align the spun PVDF nanofibers. In order to utilize single piezoelectric nanofiber as a sensing element, or as nano-generator, it is highly desirable that the piezoelectric coefficient of the PVDF nanofiber is maximized. The piezoelectric coefficient of the PVDF nanofiber depends on various electrospinning parameters such as electrospinning voltage, gap between the needle and collecting electrode, feed rate and size of the needle. Electric field applied during the electrospinning predominantly controls the piezoelectric performance. Therefore it is essential to know the piezoelectric ratio or the fraction of β-phase in the electrospun nanofibers. Thus, before depositing the single PVDF nanofiber for nano-mechanical characterization, a thorough optimization was carried out to maximize the fraction of β-phase (F (β)). In order to achieve that, an extensive electrospinning experiment was carried out where the nanofibers were electrospun at different voltages and FTIR and Raman spectroscopy was performed to detect the presence of piezoelectric β-phase. A PerkinElmer FTIR spectrometer is used for the analysis and signal averaging is done on twenty scans. The PVDF mat samples are placed face down on the attenuated total reflectance set and scanned from 650 to 1600 cm^{-1} with a resolution of 4 cm^{-1}. The spectral plots are used to determine the fraction of β-phase in the nanofibers using the following formula derived from Beer-Lambert law:

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right) A_\alpha + A_\beta}$$

where, A_α and A_β are the intensities of absorbance at 764 cm^{-1} and 840 cm^{-1} respectively. $K_\alpha = 6.1\times10^4$ cm^2mol^{-1} and $K_\beta = 7.7\times10^4$ cm^2mol^{-1} denote the absorption coefficients at those respective wave numbers.[19] In previous reports, this particular approach has been used to determine the fraction of β-phase in thin film PVDF samples containing only α and β-phases.[19–21]

The normalized FTIR spectral data are plotted (Fig. 1(a)) and Beer-Lambert law is used to determine the F (β) for various cases of electrospinning voltages (10 kV, 12 kV, 15 kV, and 18 kV). To confirm the presence of piezoelectric property, the crystal structure of the electrospun PVDF nanofibers are also studied using Renishaw in via Raman microscope (with 633 nm laser excitation). For the experiment, the instrument was calibrated using an inbuilt silicon reference. For data acquisition, the microscope is set to a high confocal mode with fifty percent laser power at 100X magnification for Raman shifts range of 500 cm^{-1} – 3000 cm^{-1}. Five accumulations were used for averaging the Raman data. As can be seen from the spectral analysis results (Fig. 1(a)), the presence of absorption peaks at 840 cm^{-1} (CH_2 rocking, skeletal C-C stretching, and CF_2 stretching) and 1279 cm^{-1} (Trans band) confirm the presence of β-phase and hence piezoelectric property of the

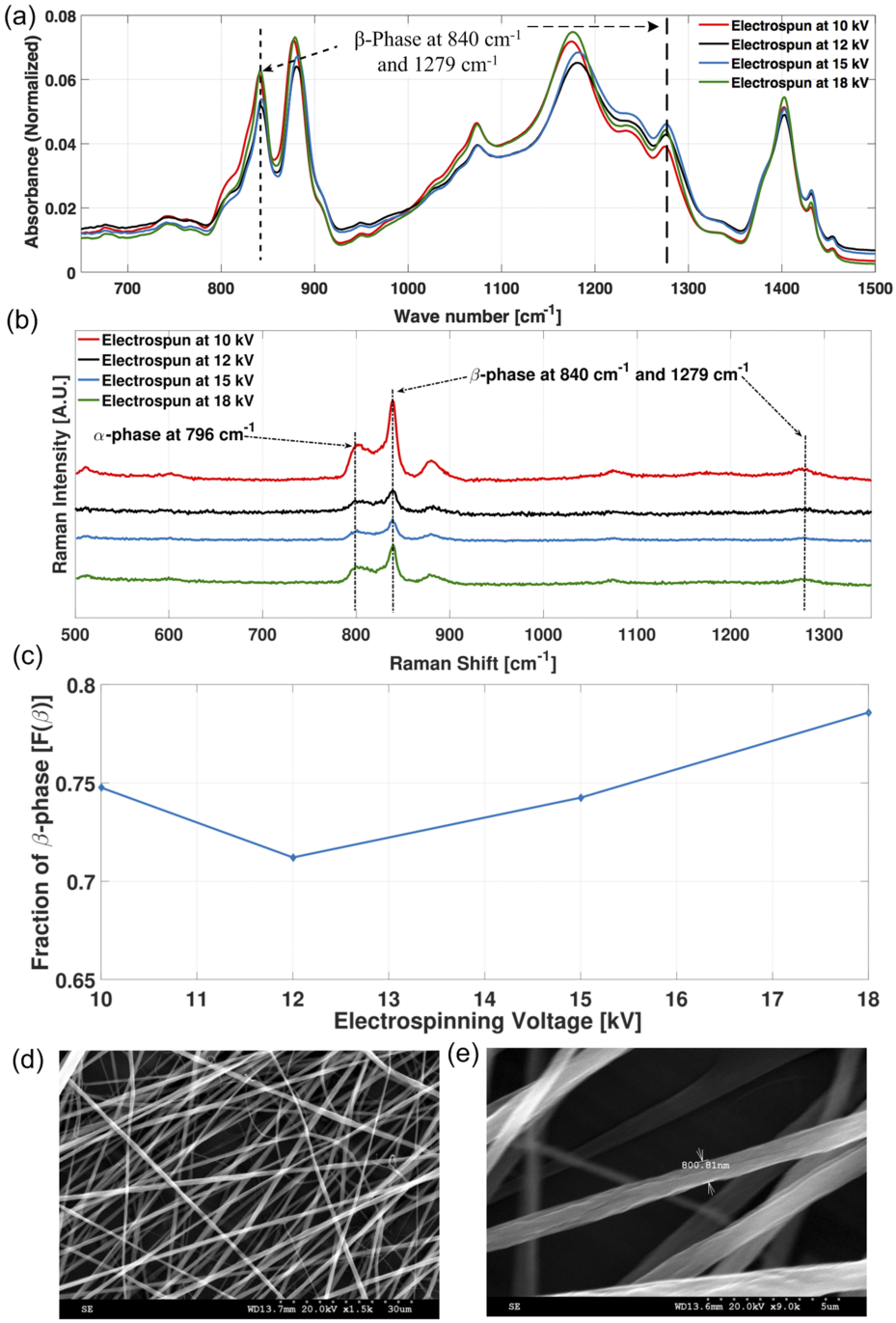

FIG. 1. (a) Analysis of the normalized FTIR spectrum of the nanofibers electrospun at various voltages (b) Analysis of the Raman spectrum of the nanofibers electrospun at various voltages (c) Plot showing the dependence of F(β) on electrospinning voltage (d, e) SEM images of electrospun PVDF nanofiber on aluminium foil substrate (scale bar (d): 30μm, scale bar (e): 5μm).

electrospun PVDF nanofiber. As it can be seen in the Raman spectroscopic plot (Fig. 1(b)), in addition to the usual β-phase peaks at 840 and 1279 cm^{-1}, the peak at 796 cm^{-1} corresponding to α-phase is also observed which is otherwise invisible in the FTIR spectroscopic plot.

The normalized FTIR plot shows gradual evolution of the β-phase (at 840 cm^{-1}) with change in electrospinning voltage. From the plot, it can be confirmed that the normalized intensity for the absorption peak at 840 cm^{-1} is maximum for the case of nanofiber mat electrospun at 18 kV.

The data for F (β) derived from the FTIR spectral analysis are plotted (Fig. 1(c)) and the trend of the plot shows that the fraction of β-phase generally increases with increasing electrospinning voltage (with 10 kV being the point of exception which shows more F(β) than 12 kV and 15kV). It is observed that the relative intensity of the β-phase increased from 12 kV up to 18 kV. The nanofiber mat spun at 18 kV shows highest fraction of β-phase which is in agreement with the plot (Fig. 1(a)).

It is a well-studied fact that the possible mechanism behind β-phase formation in electrospun PVDF nanofibers is the intense stretching of the polymer jet generated due to the electric field which emulates mechanical stretching.[21] Increasing the applied electric field increases the mechanical stretching of the polymer jet which leads to the increase in percentage of β-phase. Also, the strong electric field used during electrospinning plays the role of poling the nanofibers in-situ. Hence, it can be argued that the increase in electrospinning voltage increases the fraction of β-phase in the electrospun nanofibers.[14] It is important to note that, it is observed that for a particular needle to collector distance, there is a threshold voltage below which electrospinning does not start. We observed that the electrospun fiber generation occurred at a threshold voltage of 6 kV for a needle to collector distance of 15 cm. After the optimization of electrospinning voltage, the nanofibers are electrospun using the optimized recipe and further characterizations are carried out by means of SEM imaging and spectral analysis. Highly aligned and uniform nanofibers of an average diameter of 800 nm are achieved and the process was highly repeatable. The as-spun nanofibers on an aluminum foil and a close-up view of a single nanofiber viewed under SEM are shown in Fig. 1(d) and (e) respectively.

For further characterization and experimental testing of the single PVDF nanofiber, MEMS substrate with a trench was fabricated which allows the nanofiber to be suspended over a cavity. Fig. 2(a) shows the process flow steps for fabrication of the NEMS substrate. The fabrication process commences with the deposition of a 1 μm thick SiO_2 insulating layer by plasma enhanced chemical vapor deposition (PECVD) on a 500 μm thick silicon wafer. After patterning the SiO_2, a 300 nm thick gold layer was sputtered followed by lift-off. This was followed by defining gold contact electrodes, the substrate was patterned and dipped in HF for defining a window opening in SiO_2 layer. This step was followed by deep reactive ion etching (DRIE, Bosch Process) using SiO_2 as a mask layer to form a 300 μm deep cavity.

An optimized recipe has been used for spinning a single nanofiber on the MEMS substrate and both ends of the nanofiber is secured firmly on the gold electrode by conductive epoxy. Fig. 2(b) shows the SEM image of a single PVDF nanofiber suspended across the cavity. In order to characterize the mechanical properties of the single nanofiber, a nano-indention test is performed using the Hysitron Triboscan TI-950. The experiment has been performed in the scanning probe microscope (SPM)

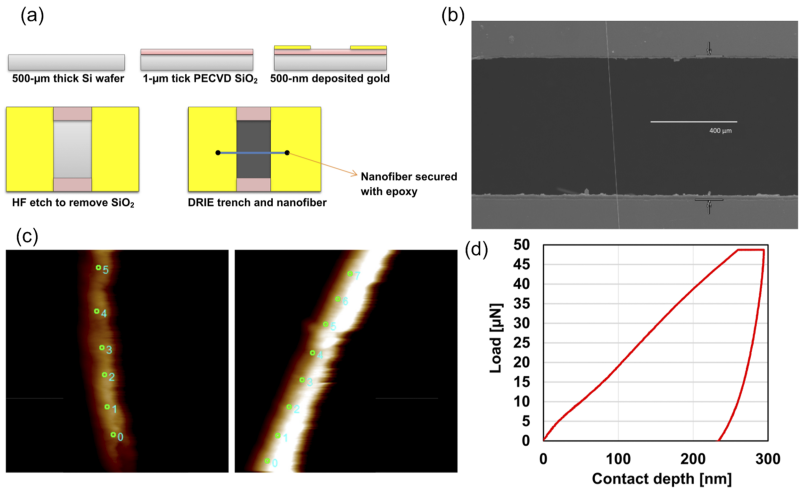

FIG. 2. (a) Individual steps involved in the fabrication process flow for the MEMS substrate. (b) SEM Image of the fabricated MEMS substrate along with the spun PVDF nanofiber. (c) SPM images of the electrospun single nanofiber (d) Load vs contact depth for nanoindenter test.

mode. For this experiment, a load of 50μN is used in loading-holding-unloading mode (5s-2s-5s) in piezo automation mode (Fig. 2(d)). The calibration for the cube corner tip is done using a standard fused quartz sample for 100 nm - 400 nm contact depths. The nanoindentor test was repeated eight times (at eight different zones on a single nanofiber, Fig. 2(c)). From the nano-indention experiments, the maximum and minimum deviation for the Young's modulus is found to be 2.54 GPa and 1.89 GPa respectively. Maximum and minimum deviation for the hardness is found to be 0.13609 GPa and 0.05593 GPa respectively. The median values of the Young's modulus and hardness of the nanofiber are calculated as 2.2 GPa and 0.1 GPa respectively with standard deviations of 0.23584 and 0.03023 respectively.

Furthermore, in electrical characterization of the single suspended nanofiber is conducted in order to determine the piezoelectric coefficient of the single PVDF nanofiber. In this experiment, an electric field is applied between the two electrodes of the MEMS substrate and the maximum deflection is measured at the center of the nanofiber by means of a confocal microscope (Nikon A1R + Multiphoton) for each field point (Figure 3(a)). The electric field is varied from 0.1 V/μm to 1 V/μm in step-wise increments of 0.1 V/μm. Fig. 3(b) shows that the maximum displacement induced in the nanofiber increased almost linearly with the increase in the electric field and resulted in a piezoelectric d_{33} coefficient value of -58.77 pm/V. The derived d_{33} -coefficient along with the hardness and Young's modulus is used to mathematically model the behavior of the nanofiber. The whole system has been model in COMSOL™ Multiphysics to simulate and study the properties of the PVDF nanofiber. Results of the FEM simulation matched well with the experimental results within an error of ±10% (Fig. 3(b)).

In order to evaluate the flow sensing ability of the single nanofiber, a vibrating sphere stimulus has been used to generate an oscillatory pressure around the nanofiber (Fig. 4(a)). As the sphere vibrates a dipolar air flow field is generated, whose velocity depends on the frequency and amplitude of the vibration of the sphere. A sinusoidal dipole stimulus of amplitude of 250 mV_{RMS} is used for the experiment. The experiment is repeated for three different frequencies of 5 Hz, 15 Hz and 35 Hz. The response of the nanofiber is fed into a low noise amplifier (SRS560) with an amplification factor of 100x, digitized and acquired for the three different cases (5, 15 and 35 Hz) by means of a National Instruments DAQ-card. The acquired data is processed by applying a digital notch filter to filter out the spurious noise signals and intrinsic natural vibration modes of the nanofiber. When the nanofiber is placed within the dipolar flow field, the drag force induced on the nanofiber due to the air flow vibration causes the nanofiber to vibrate at the same frequency. As the PVDF nanofiber vibrates, it generates charges due to the stress generated on the fiber. It is observed that, the voltage generated by the single nanofiber in response to the dipole flow field followed the sinusoidal signal output with the same frequency as that of the flow stimulus. In addition, it is also noted that the amplitude of the output voltage from the nanofiber sensor increases with increase in dipole stimulus frequency (as evident from the amplitude of 5 Hz response which is 300 mV peak-to-peak in comparison to 35 Hz which is roughly 800 mV peak-to-peak). This is due to the increase in the air flow velocity generated at higher frequencies of vibrations. The observed results (Fig. 4(b, c, and d)) demonstrate good response of the nanofiber towards dipole stimulus. The intrinsic embedded noise in the acquired signals due to the nanofibers' natural resonant modes is filtered out.

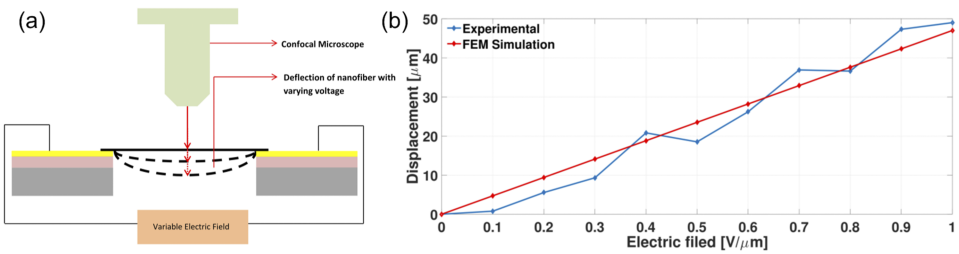

FIG. 3. (a) Schematic showing the experimental set up for determining piezoelectric d_{33} coefficient of the single PVDF nanofiber (b) Electrical characterization of piezoelectric coefficient showing the experimental and FEM simulation results for the single PVDF nanofiber in d_{33} -mode of actuation.

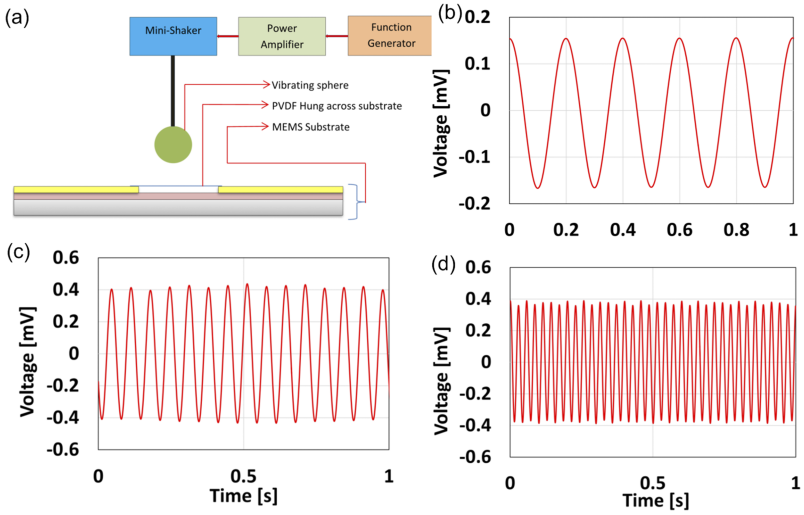

FIG. 4. (a) Schematic diagram of the experimental set-up used for testing dynamic response of the single nanofiber; Response of the single nanofiber at different oscillatory flow frequencies generated by the dipole (b) 5 Hz, (c) 15 Hz, and (d) 35 Hz.

In summary, in this work a single PVDF based nanofiber sensor has been fabricated and applied for detection of oscillatory flow. A systematic study is carried out to characterize the electrospun nanofibers by means of SEM imaging and spectroscopic analyses. Results from the characterization experiments are used to optimize the electrospinning process to get a single nanofiber with optimized piezoelectric coefficient. The single electrospun nanofiber is used for piezoelectric and nano-mechanical characterization. The behavior of the single nanofiber is studied with the help of FEM software tool COMSOL™ Multiphysics. In this paper, we have successfully demonstrated the use of a single PVDF nanofiber to sense dynamic flow generated by oscillatory dipole stimulus.

SUPPLEMENTARY MATERIAL

See supplementary material for experimental details of electrospinning PVDF nanofibers and flow characterization and testing.

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