In-situ Electric Field Facilitated Piezo- and Pyro-electric Nanogenerators

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A thesis submitted for the partial fulfillment of the degree of Doctor of Philosophy





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Dedicated to my beloved family, friends, and my teachers

Declaration

The work presented in this thesis has been carried out by me under the guidance of Dr. Dipankar Mandal, at the Institute of Nano Science and Technology, Mohali, India. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgment of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's thesis work, I certify that the above statements made by the candidate are true to the best of my knowledge.

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Abstract

Nanogenerators are one of the prominent means to harvest energy from mechanical vibrations, motions, and temperature fluctuations to convert it into electrical energy. Thus, the piezo- and pyroelectric devices are preferably endorsed and extensively explored to deliver clean, accessible, and sustainable energy alternatives for wearable electronics. However, to achieve these piezo- and pyroelectric properties in a flexible material, the electroactive phase nucleation within the crystalline region of semicrystalline polyvinylidene fluoride (PVDF) is the primary concern. The post-poling process is the next essential requisite for the unidirectional molecular dipole orientation within the polymer. Noteworthy to mention that during this process, a very high electric field strength of order $\sim 10^2$ MV/m is typically required, which causes dielectric fatigue and electrical breakdown. Hence, this high electric field treatment limits the traditional electroforming and poling processing and hinders the desired output of the device. This thesis presents an in-situ approach to nucleate the electroactive phases in polyvinylidene fluoride (PVDF) under a lower electric field (~ 0.1 MV/m), than the typically required field for the ex-situ process. The acquired electroactive PVDF has been utilized to fabricate piezo- and pyroelectric devices and demonstrated as self-powered sensors, including pressure mapping, breathing, and proximity sensor for practical applications. In this context, the δ -phase comprising PVDF nanoparticles have been fabricated during the in-situ process through an electrospray technique under electric field strength of ~ 0.1 MV/m, i.e., 10^3 times lower than the typical value required for δ -phase transformation. The kink propagation model, governed by the rotation of every secondary polymer chain unit along the main -c-c- chain axis, validates the δ -phase transformation in the electrospray process. The piezoelectric properties of δ -PVDF nanoparticles have been investigated through piezo response force microscopy, and the piezoelectric coefficient of ~ -11 pm/V was achieved. The δ -PVDF nanoparticle comprised piezoelectric nanogenerator (PNG) has shown a very prompt response as a self-powered pressure sensor with higher pressure sensitivity of ~80 mV/kPa, for realistic pressure mapping sensor applications. The electrode deposition over δ -PVDF nanoparticles was an utmost concern during the device preparation. To address this issue, we have adapted the in-situ vapor phase polymerization technique to deposit the electrodes over δ -PVDF nanoparticles and achieved an all-organic piezoelectric nanogenerator. This resulting all-organic stretchable, breathable, and flexible nanogenerator displayed an excellent electrical output with higher mechanical sensitivity due to the superior electrode compatibility between active materials and organic electrodes compared to metal electrodes. The obtained all-organic nanogenerator also exhibits excellent air permeability, enabling the advantage of wearable devices. Further, a machine learning algorithm was proposed to recognize different finger gestures efficiently to predict the source point with the highest possible accuracy of ~ 94%. Since the δ -PVDF nanoparticles are also expected to be pyroelectric in nature, a simultaneous temperature-dependent and pyroelectric study was also performed with an in-situ fabricated all-organic nanogenerator, and a prominent pyroelectric current and voltage response was recorded under different temperature stimuli. In PVDF, β-phase is another electroactive phase, which is successfully achieved in this study during the electrospinning process in the presence of external fillers for in-situ preparation of PVDF nanofibers. To improvise the pyroelectric response of PVDF nanofibers-based nanogenerators, we have introduced the MXene in PVDF nanofibers. The pyroelectric study for this composite system was performed under IR light. The PVDF-MXene nanofiber-based pyroelectric nanogenerator has shown remarkable improvement in

pyroelectric response, with an enhanced pyroelectric coefficient of ~ 130 nC $K^{-1} m^{-2}$ for the composite as compared to the pristine counterpart. This is due to the confinement effect of MXene in nanofibers and hydrogen bonding between the functional groups present in MXene and -CH₂-, -CF₂- groups in PVDF. In subsequent studies, we have demonstrated that the fabricated pyroelectric nanogenerator could also be utilized as an excellent pyroelectric breathing sensor, proximity sensor, and IR data transmission receiver. Further, supervised machine learning algorithms are proposed to distinguish different types of breathing signals with ~ 98 % accuracy for real-life applications. Finally, to study the in-situ electrical poling feasibility in PVDF film-based systems, we have performed a comparative study with the post-poling process. To validate this possibility, we have prepared solution casted PVDF films under corona discharge to induce the electroactive phase in PVDF under a lower electric field (~ 1.5 MV/m), which is ~ 60 times lower than the field required in the traditionally adopted post-poling process. The effective poling at this electric field strength also depends on the poling duration that facilitates the presence of oxygen and additional carbon species, as observed in XPS study. Consequently, the UPS study confirms the effective changes in surface potential and the associated density of states (DOS). The optimum poling duration is observed between 30-50 min to identify the prominent changes in the surface potential of PVDF film. Thus, we affirmed that insitu poling and solution casting approach could be one of the potential approaches to achieve electroactive PVDF film for piezo- and pyroelectric-based device fabrication. The resulting film was further used to demonstrate thermal energy harvesting abilities.

List of Publications

- V. Gupta, A. Kumar, B. Mondal, A. Babu, S. Ranpariya, D. K. Sinha, and D. Mandal. Machine Learning Aided All-Organic Air Permeable Piezoelectric Nanogenerator. ACS Sustain. Chem. Eng. 11, 6173, (2023).
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- P. Malik, V. Gupta, H. K. Mishra, A. Kumar, and D. Mandal. Low Voltage Local Ferroelectric Switching with Long Term Retention in δ-PVDF Thin Film. J. Appl. Poly. Sci. 140, 53714 (2023).
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- B. Mondal, R. Sarkar, D. Saini, V. Gupta, T. K. Kundu, and D. Mandal. All-Electrospun, Water-resistant, Breathable and Stable Metal Halide Perovskite Engineered Electroactive Polymer Textiles for Flexible Piezoelectric Nanogenerator. *Adv. Mater. Tech.* 2300614 (2023).
- B. Mondal, H. K. Mishra, D. Sengupta, A. Kumar, A. Babu, D. Saini, V. Gupta, and D. Mandal. Lead-Free Perovskite Cs₃Bi₂I₉-Derived Electroactive PVDF Composite-Based Piezoelectric Nanogenerators for Physiological Signal Monitoring and Piezo-Phototronic-Aided Strain Modulated Photodetectors. *Langmuir* 38, 12151 (2022).
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- M. Sharma, D. Sengupta, A. Babu, S. Choudhury, V. Gupta, D. Mandal, and J. J. Panda. Anti-amyloidogenic Potency of Acoustic Stimulus Activated Piezoelectric Polydopamine-PVDF Nanospheres, A Futuristic Approach Towards Alzheimer's Therapy (*Manuscript under communication*).

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- 6. Varun Gupta and Dipankar Mandal. Advanced Energy Materials & Devices (AEMD) 2022, CSIR-Central Glass & Ceramic Research Institute (CGCRI), Kolkata, India; Delta (δ)-PVDF Under Ultra Low Electric Field for Self-powered Piezoelectric Nanogenerator (Oral Presentation).

- 7. Varun Gupta and Dipankar Mandal. Institute of Nano Science and Technology (INST)- Indian Institute of Science Education and Research (IISER) Bilateral Meet 2022, INST and IISER Mohali, Mohali, Punjab, India; Revisiting Delta (δ)-PVDF Nanostructures formation for Self-powered Sensors and Mechanical Energy Harvesters (Poster Presentation).
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- 9. Varun Gupta and Dipankar Mandal. Department of Atomic Energy- Solid State Physics Symposium (DAE-SSPS) 2021, Bhabha Atomic Research Center (BARC), Department of Atomic Energy (DAE), Govt. of India, Mumbai, India; Morphology and Molecular Orientation of Nanofibers in Electrospinning and it's Piezoelectric Nanogenerator (Paper Presentation).
- Varun Gupta and Dipankar Mandal. *Materials of the Millennium: Emerging Trends and Future Prospects (MMETFP) 2021*, Department of Chemistry & Physics, School of Technology, PDPU, Gujarat, India; Self-Powered Pyroelectric Nanogenerator (Poster Presentation).
- Varun Gupta and Dipankar Mandal. Institute of Nano Science and Technology (INST)-Nanoday 2021, Institute of Nano Science and Technology, Mohali, Punjab, India; Revisiting Delta (δ)-PVDF Nanostructures Under Low Electric Field and Nanoprecipitation Technique with Self-powered Mechanical Energy Harvesters (Poster Presentation).

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List of Abbreviations

Abbreviations	Descriptions
PVDF	Polyvinylidene fluoride
P(VDF-HFP)	Poly(vinylidenefluoride-co-hexafluoropropylene)
P(VDF-TrFE)	Poly(vinylidenefluoride-co-trifluoroethylene)
PZT	Lead zirconate titanate
PNG	Piezoelectric nanogenerator
PDMS	Polydimethylsiloxane
EDOT	3,4-ethylenedioxythiophene
PEDOT	Poly(3,4-ethylenedioxythiophene)
DMF	N, N-dimethylformamide
DMAc	Dimethylacetamide
VPP	Vapour phase polymerization
AFM	Atomic force microscopy
PFM	Piezoresponse force microscopy
KPFM	Kelvin probe force microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
UPS	Ultra-violet photoelectron spectroscopy
ATR	Attenuated total reflectance
FTIR	Fourier transform infrared spectroscopy
FESEM	Field emission scanning electron microscopy
DSC	Differential scanning calorimetry
FEM	Finite elemental method
ML	Machine Learning
IoT	Internet of Things
FFT	Fast Fourier transform
TTTT	Trans-trans-trans
TTTG	Trans-trans-gauche
TGTG'	Trans-gauche-trans-gauche

List of Symbols

Symbol	Description
$\mathbf{P}_{\mathbf{i}}$	Polarization vector
d_{ijk}	Piezoelectric moduli
σ_{jk}	Stress tensor
d_{ij}	Converse charge coefficient
3	Strain/Permittivity
E	Electric field
S	Strain
Σ	Stress
D	Volumetric charge density
р	Pyroelectric coefficient
U	Internal energy density
Ps	Spontaneous polarization
Ec	Critical electric field
g	Gibbs free energy
Q	Charge
ΔT	Temparature difference
Δt	Time interval
А	Mechano acoustic sensitivity
\mathbf{P}_0	Reference sound pressure
L_p	Sound pressure level (SPL)
L	Crystallite size
В	Full width at half maxima (FWHM)
λ	X-ray wavelength of Cu-K $_{\alpha}$
θ	Bragg's angle
k	Shape factor
ΣA_{cr}	Total area of crystalline phase
$\Sigma A_{\rm m}$	Total area of amorphous phase

Xc	Fraction of crystallinity
Н	Hamiltonian of system
V _{OC}	Open circuit voltage
I _{SC}	Short circuit current
μ	Transition dipole moment
d ₃₃	Piezoelectric coefficient
τ	Response time
F _{EA}	Fraction of electroactive phase

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[Vita]

Chapter 1

Introduction

This chapter provides an overview on piezo- and pyro-electric materials, its properties, processing technique, requirement of electric field during poling and the applications as nanogenerator followed by a brief description of each chapter.
1.1 Basics of piezo- and pyro-electric properties

1.1.1 Piezoelectricity

The piezoelectric effect was discovered in 1880 by the physicists Pierre Curie and Paul-Jean Curie. It is the emergence of electric charges on the surfaces of certain crystals when they are subjected to mechanical stress [1-3]. The piezoelectric crystals are non-centrosymmetric in nature and displays a piezoelectric effect, whenever external stimuli are imparted. Therefore, these crystals generate the voltage across the terminals in response to applied mechanical stress. Conversely, when an electric field is applied, a deformation or contraction takes place in the material. This property of piezoelectric materials is used in actuator [4,5]. During the converse piezoelectric effect, the deformation in crystal structure is the order of nanometers in comparison to the original dimension in Lead zirconate titanate, but nevertheless it is useful in applications such as the production and detection of sound, frequency generation, for controlling nanoscale optical systems, and as a piezo stage in atomic force microscope. Many other materials exhibit the piezoelectric effect, including quartz analogue crystals like Berlinite (AlPO₄) and gallium orthophosphate (GaPO₄), ceramics structures like Barium titanate (BaTiO₃), Lithium niobate (LiNbO₃), Strontium titanium oxide (SrTiO₃), Lead zirconate titanate (PbZrTiO₃), Potassium niobate (KNbO₃), Lithium tantalate (LiTaO₃). Among the polymers, poly(vinylidene fluoride) (PVDF) and its copolymers are manifested superior piezoelectric properties due to involvement of highly polar bonds between fluorine and hydrogen atom. Besides this, odd nylons are also possess piezoelectricity due to their polar arrangement of hydrogen-bonded sheets arrangements. It has been also found that few biological materials, such as poly-L-lactic acid, chitin, hair, wood fiber, collagen and silk also exhibit piezoelectricity to some extent. In a non-centrosymmetric piezoelectric crystal, the polarization is defined as the separation between positive and

negative charge centers, resulting one end of the crystal as positive and the opposite side as negative. The application of mechanical stress eventually causes the change in polarization P. The polarization vector P_i is related to the stress tensor σ_{jk} and piezoelectric moduli d_{ijk} by the linear equation-

$$P_i = d_{ijk}\sigma_{jk} \tag{1.1}$$

In particular, there are total 32 crystal classes, out of them 21 crystal classes are noncentrosymmetric and 20 of those exhibits direct piezoelectricity. The Piezoelectric crystal classes are 1, 2, m, 23, 222, mm2, 3, 32, 3m, 4, 4, 422, 43m, 4 mm, 42m, 6, 6, 622, 6 mm, 62m. In the case of the converse piezoelectric effect, strain S is related to electric field *E*. The matrix form of the converse coefficient d_{ij} (electrostriction coefficients) is the transpose of the direct effect matrix.

$$S_j = d_{ij}E_i \tag{1.2}$$

The electrical response of piezo materials is a function of applied stress (σ) and the mechanical strain (S), experienced by the material. Piezoelectricity is the combined effect of the electrical behavior of the material D = ε *E and Hooke's Law S = s* σ , where D is volumetric charge density, ε is permittivity and *E* is electric field strength, *S* is strain, s is compliance and σ is stress. These may be combined into coupled equations.

$$D_i = d_{ij} \sigma_j + \varepsilon_{ii}^T E_i \tag{1.3}$$

$$S_j = s_{ij}^E \sigma_j + d_{ij} E_i \tag{1.4}$$

Where the superscripts, *E* indicates a zero, or constant electric field, σ indicates a zero, or constant, stress field and t stands for transposition of a matrix. The coupling of these two equations gives the piezoelectric strain coefficient d and the material compliance s and the permittivity ε [1-5].

1.1.2 Pyroelectricity

The pyroelectric effect was reported in early 1707, by Johann Georg Schmidt. The Pyroelectricity is defined as the temperature dependence of the spontaneous polarization in the anisotropic solids. When a pyroelectric material is provided a temporal thermal fluctuation under constant stress and electric field, a change in polarization occurs due to the application of applied thermal fluctuation [6-8]. This change in polarization causes a pyroelectric current in the circuit in a certain direction and when this external stimulus is removed, there is a current flow in the opposite direction. This current is related to the pyroelectric coefficient of the material [9,10]. If P is the polarization vector and T is the thermal input, then the pyroelectric coefficient (p) of the material is defined as-

$$p = \left(\frac{\partial P}{\partial T}\right)_{\sigma, E} \tag{1.5}$$

The other contributions in pyroelectric effect can also arise, as demonstrated in Figure 1.1. The primary pyroelectric effect is caused when the temperature charge causes electric displacement.



Figure 1.1 Schematic represents to show the relation between electrical, mechanical and thermal stimuli for a ferroelectric material and the primary and secondary pyroelectric coefficient (Adopted from Ref. [6]).

However, the secondary pyroelectric coefficient comes into effect when thermal expansion causes the strain that changes the electric displacement through piezoelectric behavior. Therefore, these two contributions come together in most of the pyroelectric materials, when measured experimentally. There are 10 pyroelectric crystal classes 1, 2 m, 2 mm, 3, 3 m, 4, 4 mm, 6 and 6 m. A certain asymmetry is present in the pyroelectric crystal structures, which hinders the polarization reversal that prevents a pyroelectric crystal from being ferroelectric. In case of polymers, PVDF and its copolymers have low pyroelectric coefficients. However, the lower dielectric constant and low thermal conductivity leads to quite effective role for large-area IR detectors for practical applications [6-11].

1.1.3 Piezoelectric polymers

Piezoelectric polymers are being widely used in various applications such as electromechanical transducers, sensors and vibration control actuators. These polymers have advantage over the ceramic based materials in terms of flexibility, durability and for e-skin electronics applications. Synthetic polymers such as and poly(methyl methacrylate), polypropylene, polystyrene semi-crystalline polyamides and amorphous polymers such as PVDF, polymethyl methacrylate (PMMA), vinyl acetate exhibits the piezoelectric properties. There are also biopiezoelectric polymers such as amino acids, wood cellulose, bones, collagen, genetic materials such as deoxyribonucleic acid (DNA), ribonucleic acid RNA [12-14] The piezoelectric properties observed in bio-piezo-materials are relatively weaker and usually unstable in comparison to synthetic polymers. In that respect, PVDF and its copolymers have shown better and strong piezoresponse [15-20]. There polymers can be semicrystalline in nature. In such piezoelectric polymers, the molecular dipoles and piezoelectric contribution appears from the crystalline lamella depending on the chain conformations, regardless of the amorphous region and morphology. It was reported earlier by Davis and Broadhurst, as (i) the presence of permanent molecular dipoles,

(ii) the ability to orient or align dipoles, (iii) the ability to sustain this dipole moment (μ) and (iv) the ability to undergo large strains when mechanically stressed. More often, to obtain the electroactive phase, stretching of the polymer can be performed in uniaxial and biaxial direction, to achieve better piezoelectric property. The requirement for it to be piezoelectric and stable, is that molecular dipoles must be uniformly distributed throughout the piezoelectric material and it should eliminate the localized electric field generated near to crystallites during dipolar reorientation. In case of the semicrystalline polymers, the crystal orientation and the ferroelectric polarization present till the Curie temperature only.

1.1.4. Poly(vinylidene fluoride)

PVDF is a semi-crystalline polymer (Figure 1.2) with amorphous and crystalline region. The electroactive properties of this polymer is governed by the crystalline lamella part. It considered as one of the potential ferroelectric polymer due to its nonlinear susceptibility and electroactive nature that gives rise to the piezo-, pyro-, and ferroelectric properties, which makes it applicable for achieving the mechanical, thermal, and electrical stimuli-based sensors and energy harvesters.



Amorphous region

Figure 1.2 Semicrystalline polymer nucleus and enlarged view of crystalline and amorphous region (Adopted from Ref. [15]).



Figure 1.3 Schematic represents the different polymorphs and their respective unit cell structure (Adopted from Ref. [51]).

PVDF exhibits five different polymorphs known as α , β , γ , δ , and ε phases [15-18]. The α and ε -phase polymorphs of PVDF are non-electroactive in nature, however, the β -, γ -, and δ -phases are polar and electroactive in nature. The different crystal forms of PVDF involve different chain conformations, each of which possesses a component of a net dipole moment perpendicular to the chain. The polymer chains of PVDF in unit cell lies in two different ways (Figure 1.3). Either they are additive and the crystal possesses a net dipole or it packs with dipoles in opposite directions, so there is no net dipole moment in the crystal.

The polar conformations are piezoelectric in nature, while the antipolar ones are not piezoelectric in nature. In normal processing, the polymerization under a standard path usually generates α -phase of PVDF. However, one needs to follow certain processing techniques to achieve the different electroactive phases in PVDF. These processing techniques requires the higher electric field, stretching, poling and higher temperature and pressure sometimes. The further achieved phases can be characterized by XRD and FTIR techniques to identify those electroactive phases to utilize them further for piezo- and pyroelectric applications [19-24].

1.1.5 Ferroelectric dipoles and their switching in electric field

In ferroelectric materials, the domain switching takes place when the work done due to the release of the electric field and the stress field overcomes the energy threshold i.e., the switching barrier, for flipping the dipoles in a certain direction (Figure 1.4). If the work done by the applied stress field and electric field exceeds the energy threshold, the switching of the polarization direction of the ferroelectric domain can take place without requiring any other external stimuli. In case of piezoelectric materials, the dipoles within the materials need to be aligned in a certain direction by the exposure of the electric field, for maximum piezoelectric response upon the application of external stress. Similarly, in the case of pyroelectric materials, the yproelectric response upon thermal fluctuations. Prof. Sun and Archutha (2001) put forward the concept of internal energy intensity, and also only considered the state before switching [25, 26, 52]. The principle for switching follows,

$$U \ge U^{c} \tag{1.6}$$

$$U = \frac{1}{2} D_3 E_3$$
 (1.7)

$$U = \frac{1}{2} (\sigma_{33} \epsilon_{33} + D_1 E_1)$$
 (1.8)

Where, U is the internal energy intensity. This principle agrees with the experimental results quite well in the aspect of predicting the influence of the applied stress field upon the coercive field. Based on the criterion of domain switch driven by Gibbs free energy put forward by Wei (1998), Zhang Zhen (2003) proposed the principle of switching two times, i.e., all 180° switching, as a matter of fact, is composed of two instances of 90° switching.



Figure 1.4 Polarization switching in ferroelectrics crystals induced by electric field and 90° domain switching in ferroelectrics induced by stress field (Adopted from Ref. [52])

($\Delta g \geq W^{\mathrm{f}}_{90}$;	$W_{90}^{f} = P_{s} E_{c};$	First 90° domain switch	(1 0)
$\left(\right)$	$\Delta g \geq W^{ m f}_{180}$;	$W_{180}^{f} = 2P_{s} E_{c}$;	Second 90° domain switch	(1.9)

Where, g is Gibbs free energy, w is work done, Ps is spontaneous polarization and E_c is critical electric field. Zhang Zhen et al. compared various principles for domain switching phenomenon with experimental results and observed that the criterion of switching in two steps precisely matches with the reported experiments.

1.1.6 Requirement of poling

During the application of high electric field in poling process, the positive and negative charge centers inside the dielectric material separates and consequently turn into dipoles. The polar molecules within the dielectric material can be treated as molecular dipoles. On the application of the applied electric field, the polar molecules shear off. Therefore, results in polar axis turned towards the direction of the electric field. This phenomenon is called the polarization of dielectrics. In some crystals, while considering the ideal situation, due to the asymmetric nature and the unit cell structure, the electric moment along a certain lattice orientation is non-zero, leading to the condition of the crystal surface having overall polarity, is known spontaneous polarization of the particular crystal. The spontaneous polarization of the ferroelectric material is closely related to its crystal structure. The specific regions where the spontaneous polarization orientation is coincident is known as the electric domains. Each electric domain has its own polarization orientation. A crystal can have a single domain, or can have multiple electric domains of different and even opposite poling orientations depending on its physical structure and processing pathways. Therefore, the particular structure of the electric domain of ferroelectrics is corelated to various parameters. Due to the application of applied electric or stress field, in terms of external stimuli, the orientation of the domain structure can change [27, 28, 52]. This process is known as switching of the electric domain, i.e., the electric domain flips from one orientation direction to another direction. However, when there is no external applied electric field, the average polarization strength of each crystal grain is mutually balanced out, resulting to the different electric moment orientations of different electric domains. Thus, the polarization intensity of ferroelectric ceramics appears as zero macroscopically. That is the primary reason for why polarization treatment under electric field is necessary for ferroelectric crystals before their practical applications. After being polarized by highvoltage electric field, the molecular dipoles turn towards the electric field (Figure 1.5) and orients themselves in a single direction, which makes the ferroelectric materials acquire macroscopic polarization intensity [27-30]. The ferroelectric properties of a crystal occurs in a particular temperature window. This temperature plays a crucial role in change in ferroelectric behavior. As the temperature exceeds a certain value, the ferroelectric crystal becomes a paraelectric crystal and doesn't show the spontaneous polarization behavior anymore. This transformation between ferroelectrics and paraelectric is known as ferroelectric-paraelectric phase transition. This particular temperature at which the ferroelectric to paraelectric phase change occurs is called Curie transition temperature.



Figure 1.5 Schematic representation of dipole alignment in semi-crystalline ferroelectric polymer under electrical field.

In case of semicrystalline polymers like PVDF, we require poling not only to align the dipoles in in these polymers, but poling is also an essential technique to obtain the unidirectional dipolar orientation and electroactive phases [27, 29, 52]

Depending on the requirements, there are different kinds of techniques for poling of process –

- (i) Contact poling
- (ii) Corona poling
- (iii) Electrospinning
- (iv) Electrospraying

1.1.7 Contact poling

In electrical poling process the electric field is most commonly applied through contact poling or corona poling. In contact poling an electric field is applied across the polymer by placing film between the both electrodes. The first electrode is over substrate for the sample while the other electrode evaporated on the sample to make it a parallel plate like structure. In order to allow polymer chains to align and reorganize, the polymer is held at high temperature near glass transition temperature and thereafter high electric field is applied. At a certain electric field and temperature, the dipoles within the polymer begins to align in the direction of electric field.



Figure 1.6 Schematic of corona poling system and its basic components.

After that the film is cooled first then only electric field is removed to keep the dipoles aligned in particular direction. As a result of poling, the d_{33} value of obtained films significantly improves and therefore the piezoelectric response also enhances in comparison to unpoled samples.

1.1.8 Corona poling

Corona poling setup consist of a chamber with multiple corona needles just above the sample holder (Figure 1.6). When a high voltage V is applied over the corona needles, then the chamber for corona becomes ionized due to generation of high electric field and the corona formation takes place. The generated corona is directed towards the lower electrode (ground). In between the corona needle and the sample holder there is grid is also placed. That ensures the formation of equipotential surface over the sample. A constant grid voltage up to a certain limit is also applied, through the grid to control the ions generated in corona process, so that the grid itself doesn't generate the corona by striking the high momentum of corona ions. It ensures that ions and charges are evenly distributed over after corona starts.

1.1.9 Electrospinning



Figure 1.7 Schematic of basic electrospinning system and its basic components.

Electrospinning process was re-discovered by Doshi and Reneker in 1995, which can be used to fabricate the nanostructures including different types of nanofibers, nanoribbons, honeycombs and nanoparticles could be easily obtained at nanoscale diameters. In the electrospinning (Figure 1.7) setup the basic components include syringe pump, high electrical voltage, metal tip, a collector (ground) and the polymer solution of optimized concentration to fabricate the different morphologies including nanofibers, nanoparticles etc. To perform the electrospinning or electrospraying process, the polymer is loaded inside a syringe and mounted on the syringe pump with a particular flow rate and a high voltage is applied to the tip of the metallic needle and between the collector. When the droplets come out of tip of the syringe. It stays in drop shape until experiences the force applied by electric field. When the applied voltage is above a certain value, the electrostatic forces overcome the surface tension in the polymer drop causing it to stretch to form a cone (referred as Taylor cone) and eventually the cone breaks and jet accelerates toward the collector resulting the formation of nanofibers, nanoparticles etc [31,32]. The formation of a particular morphology also depends on the multiple parameters such as

applied voltage, viscosity of fluid, humidity of chamber, temperature and distance between tip and collector.

1.1.9.1 Taylor cone formation

In the electrospinning process a high voltage (typically 5–30 kV in EFES) between the tip and the collector is applied. During the flow of the polymer solution from syringe under electric field, there appears a situation when the round droplet on the needle starts slowly deforming under the influence of coulombic force acting on the charges of the polymer solution. Therefore, in that condition the droplet tries to stay in shape due to the surface tension force but the coulombic force acting over the drop tries to polarize and deform the solution droplet in the direction of electric field. At this point, the droplet takes a shape of cone shape due to more electrostatic repulsion over the droplet and the cone begins to form a convex side with a rounded tip. This resulting cone shape is referred as the Taylor cone, with angle of ~ 98.6°. This resulting cone shape is referred as the Taylor cone. After overcoming the threshold value of applied voltage, the tip of cone breaks and forms the jet in direction of the electric field to form the nanostructures.



Figure 1.8 Schematic representation of Taylor cone, straight jet and whipping jet of fibers during electrospinning formation.



Figure 1.9 Demonstration of electrical and viscous forces on droplet in electrospinning system under presence of electrical field (Adopted from Ref. [38]).

This fiber formation mechanism can be divided into 3 different steps to explain the proper pathway as represented in Figure 1.8. At over turn point of the jet, the coulombic forces and viscous force are mentioned to show the effective force direction. The entire electrospinning process and the electrically driven bending instabilities due presence of such effective force in electrospun fluid and can each be viewed as particular examples of Earnshaw theorem in electrostatics. This theorem leads to the conclusion that it is impossible to create a stable structure in which the elements of the structure interact only by Coulomb's law. Charges on or embedded in a polymer fluid move the fluid in quite complicated ways to reduce their Coulomb interaction energy. Next, charged jet breakups into smaller charged droplets via Coulomb repulsion forces. The jet rapidly thins and solidifies due to the strong, electrically driven elongational forces and the extremely fast solvent evaporation.

To demonstrate the type of force and effect of charge on the polymer solution, a model was proposed Kalayci et al., in which they have shown that on a particular instant after the formation of conical frustum, when there is a positive charge is present during the electrospinning process there are two simultaneous forces acting on the particles, one comes as electrostatic force (F_q) while other comes as viscous drag force (F_d) and considering no other factors. As we know that drag force is a kind of frictional force, which always acts in the opposite direction of flow to resist the motion. Therefore, in this case, if charge is positive then the forces on would be in the same direction as electric field and as a result both forces F_q and F_d comes in opposite direction as shown in schematic (Figure 1.9). In second case, when we consider the negative charge in between the stream jet, then also the force would be in opposite direction. Therefore, one the basis of this model, consider all the factors same, there would not be a significant change in the outcome if electric strength is having similar polarity, then even with the different charges of polymer solution, the result would be almost similar. This observation was also verified by them experimentally. However, the change in polarity of the electric field give different results and it is discussed in section 1.1.9.4 during the same experiment.

1.1.9.2 Far field electrospinning (FFES)

Far field is known as region of electromagnetic field at a distance from scattering object. The amplitudes of the electric field strength in far-field components fall off as 1/r. In case of far field electrospinning, usually the requirement of applied electrical voltage is from ~ 6 kV – 30 kV, with larger distance (10 - 20 cm) between the drum and the collector, also depending on the concertation, humidity and temperature required for the fiber formation. In this process, the electric field lines are spread as conical shape towards the collector. This electric field presence causes the formation of nanofibers as the jet burst out form the Taylor cone. However, the disadvantage of this procedure is the non-uniform distribution electric field strength over this long

distance, due to which the precise patterning of the nanofibers over small substrate is quite challenging.

1.1.9.3 Near field electrospinning (NFES)

Near field is known as region of electromagnetic field at closer distance from scattering object. The amplitudes of the electric field strength in near-field amplitudes fall off as $1/r^2$ or $1/r^3$, which is very rapid in comparison to the FFES. Due to above mentioned limitations of FFES process, the near field electrospinning process is preferred to perform better patterning, alignment and less sample requirement for targeted deposition of nanofibers [40]. In this case, the distance between the sample and collector is reduced (not further than 5 cm), resulting precise patterning of the fibers on substrates with lesser electrical voltage requirement than FEES.

1.1.9.4 Effect of applied polarity in electrospinning

There have been numerous articles on electrospinning procedure in which the Positive polarity High Voltage has been utilized to fabricated the nanofibers. However, very few groups have experimentally studied the effect of the negative polarity in the electrospinning procedure. These two polarities cause different type of fiber formation dynamics in presence of different charge carriers. In case of positive electrospinning procedure, the charged species are positive ions due to presence of positive polarity high voltage. In the work reported by V. E. Kalayci et al. [38], the authors have presented in their detailed study that in case of negative polarity the mobility of charge carriers are electrons and therefore causing the diffusion of the fibers from center is much faster than that of the positive charge carriers (ions) during the electrospinning procedure. Since, the mass of an electron is $\sim 10^4$ times lesser than that of a proton. Therefore, the negative charge carriers disperse to the liquid more rapidly and uniformly than the positive ions. The mobility of these charge particles is

also responsible for proper fiber formation from the liquid droplets. Hence, resulting negative polarity in electrospinning process yields the fibers with smaller diameter than that of that of positive polarity while applying the same magnitude of potential. However, few other groups have also reported that the presence of the functional groups within the polymer solution also plays a crucial role during the change in polarity of the applied voltage (Figure 1.9). If the polymer group is negatively charged, then during positive electrospinning process, the negative charged group partially neutralizes the applied positive electrostatic charges. However, when the negative electrospinning is performed with a negatively charged polymer group, the increase in negative charges cause the electrostatic stress during the jet flow and stretches the jet into much thinner fibers than during positive polarity for the same polymer [31-40].

1.1.10 Nanogenerators

The nanogenerators are the energy harvesters, which can convert the waste mechanical and thermal energy (in terms vibrations, deformations, external stress and thermal fluctuations) into the electrical energy with the help of the nanomaterials. The first nanogenerator term was introduced by Prof. Z. L. Wang's group, from Georgia Institute of Technology, USA, in 2006, by converting the mechanical deformations into electric energy using piezoelectric Zinc oxide (ZnO) nano-wires (NWs) as piezoelectric nanogenerator [45]. These nanogenerators have shown excellent capability for practical purposes by driving the low-powered electronic devices such as Bluetooth devices, pacemakers, self-charging cells, electrochromic devices, pressure sensors, wireless sensors by the converted electrical energy. Thereafter, Prof Z. L. Wang's group also introduced the pyroelectric nanogenerators in 2012 [46]. On the basis of energy harvesting mechanism, there are mainly four types of

nanogenerators. In the context of this thesis, we would discuss about piezoelectric and pyroelectric nanogenerators only. [45-47]

1.1.11 Piezoelectric nanogenerator

The piezoelectric nanogenerators (PNG) are the type of energy harvesters that can be used to convert the mechanical vibrations and stress into electrical energy, through nanoscale piezoelectric materials. The first piezoelectric nanogenerator was introduced in 2006 by using ZnO nanostructures. Thereafter many other groups have also reported different types of ZnO-based nanogenerators. During the subsequent years, piezoelectric nanogenerators are explored extensively due to the capability of harvesting energy from different available resources in terms of waste energy, motions, and biomechanical movements. Another advantage of these piezoelectric devices can be recognized in terms of flexibility, light weight, long life cycle, high power density, robustness and lesser maintenance concern. Due to these qualities, the piezoelectric nanogenerators can also be used as self-powered devices. That suggests it would no longer require the external energy sources, to use these devices as sensors. The output performance of these PNGs depends on the physical properties of piezoelectric nanomaterials. In the beginning, the low output performance of ZnO based PNGs, gave the researcher to look for another alternative material like lead zirconate titanate [Pb[Zr(x)Ti(1-X)O₃], PZT. In comparison, PZT has the higher piezoelectric charge coefficient as well as high dielectric constant and superior properties than ZnO (Figure 1.10). Thereafter, most of the PNGs were explored on the PZT. However, the hazardous nature and toxicity of lead caused a demanding situation to look for another alternative lead-free piezoelectric ceramic for PNGs. Piezoelectric perovskite ceramics are usually prepared by solid-state or sintering process, resulting in a polycrystalline material consisting irregular smaller grains [4143]. In this context, another perovskite material barium titanate (BaTiO₃) is extensively explored and still a remarkable lead-free material for PNGs based applications. In parallel, other materials including SrTiO₃, Potassium niobate (KNbO₃), Zinc Stannate (ZnSnO₃), Bismuth ferrite (BiFeO₃), LiNbO₃, LiTaO₃ are also explored for the piezoelectric nanogenerator to improve the output response upto 100 V with current in ~ μ A. However, the brittle nature of these perovskite materials limited the application of such nanogenerators and not useful for flexible or wearable self-powered applications. To overcome the toxicity, hazardous nature, flexibility, durability and biocompatibility concern, the research paradigm shifted to the polymer and polymer composite-based for piezoelectric nanogenerator. Thereafter Prof. Z. L. Wang and many other groups have reported the work of nanogenerators based on polymers and their hybrids. Further, Prof. Kim's group reported the PVDF copolymer nanogenerator (NG) in 2014, with output of 1.1 V.



Figure 1.10 The development of piezoelectric nanogenerators from 2006 to 2020 in terms of output voltage and current (Adopted from Ref. [53])

Further PVDF Hybrid NG was reported from Chenguo Hu and Yi Xi group in same year with output voltage of 192 V. In 2017, Hao Xue group reported on pure PVDF based thick film and reported 42 V output with 2.5 µA current. PVDF polymer is still being explored mostly. Apart from piezoelectric devices, people have also used this polymer to make pyroelectric, ferroelectric and triboelectric devices. There are techniques such as mechanical stretching, solvent casting, application of high pressure, heat control spin coating, addition of fillers, blending with PMMA, electrospinning, poling processes have been developed to obtain different electroactive phases in polymer-based systems. There have been many papers in which NG response of PVDF polymer, co-polymers and also with composites of PVDF have been reported [44-49].

1.11.111.1 Polymer based piezoelectric nanogenerators

Polymers with low dielectric constant, low density, results in a high voltage sensitivity which could be beneficial for a sensor fabrication, and low acoustic and mechanical impedance is effective for healthcare and underwater applications. In piezoelectric polymers, the piezoelectric strain constant (d_{31}) is smaller with higher piezoelectric stress constants (g_{31}) indicating that they are much more suitable for sensors than ceramics. Polymers also offers great the advantage of processing flexibility because they are lightweight, tough, easily manufactured into large areas, and can be altered into complex shapes.

PVDF and its co-polymer-based NG are widely explored so far with electroactive β phase of PVDF, due to its lower dielectric advantage, apart from other polymer properties. Recently the δ -phase of PVDF has also received lot of attention due to its electroactive properties equivalent to β -phase for nanogenerator application. However, the nanogenerators based on pristine PVDF and co-polymers have lower voltage and current response in comparison to their composite materials. To improve this performance, there are different approach to nucleate the electroactive phase and improve the combined physical properties of PVDF and its co-polymers. It is the synergistic effect of fillers in PVDF-based composites not only enhances the performance of piezoelectric devices (Table 1.1) but adds up more electrical physical and optical properties. At present, the incorporated fillers include metal salts, halide perovskites, lead-free piezoelectric ceramics, metal oxides, carbon-based fillers, hydrated ionic salts, ferroelectric and other materials. Here, in Table 1.1, PVDF composite based nanogenerators are listed with their methodology and output performance [61-78].

S. No.	Materials	Methodology	Voltage (V)	Current (µA)	Power density (µW/cm ²)	References
1.	P(VDF-TrFE)	Spin coating	7	0.56	_	61
2.	P(VDF-TrFE)	Electrospinning	50	0.7	8.75	62
3.	PVDF	Electrospinning	10	6.2	0.81	63
4.	PZT/PVDF	hot pressing	2.51	0.07843	_	64
5.	PZN-PZT/P(VDF-TrFE)	Electrospinning	3.4	0.24	_	65
6.	PMN-PT/P(VDF-TrFE)	Spin coating	8.5	3	6.1	66
7.	NKNS-LT-BZ/PVDF	Solution casting	18	2.6	_	67
8.	BCT-BZT/P(VDF-TrFE)	Electrospinning	13.01	0.9	1.44	68
9.	ZnO/PVDF	Solution casting	11	9.8	0.448	69
10.	BaTiO ₃ /PVDF	Sol- evaporation	35	0.6	_	70
11.	MAPbI ₃ /PVDF	Spin coating	17.8	2.1	_	71
12.	Chitin/PVDF	Solution casting	49	1.9	31.02	72
13.	Sugar/PVDF	Electrospinning	100	6	3.3	73
14.	Graphene/PVDF	Electrospinning	7.9	4.5	_	74
15.	CsPbI ₃ //PVDF	Solvent-casting	20	6	_	75
16.	Pt/PVDF	Electrospinning	30	6000	22	76
17.	Ag-BaTiO ₃ /PVDF	Solvent	14	0.96	0.986	77
		evaporation				
18.	VB ₂ /PVDF	Spin coating	61.5	12.2	465	78

 Table 1.1 PVDF composite based piezoelectric nanogenerators and their performance.

The addition of nanofillers like metal nanoparticles or hydrated salt, improvise the electroactive phase and overall dipolar orientation in thin films and thick films, in semicrystalline polymers [79]. In the reported literature, PVDF composite with metal salt (MgCl₂·6H₂O) improved the electroactive phase and nanogenerators have shown the response of ~ 4V under 4.45 kPa of input pressure. PVDF/Ag/BCZT composite film was prepared to improve electroactive phase as well dielectric properties of the composite. The performance of piezoelectric nanogenerator was obtained as output voltage of ~ 3.5 V with maximum output power density of ~ 4.5 mW/m². Further, this addition also provides plasmonic characteristics in composite material with piezoelectric output response for nanogenerator application. The addition of conductive filler like carbon nanotube (CNT), graphene, Multi-walled carbon nanotubes (MWCNT), Polyaniline (PANI), in polymer improves the induced charge transfer in the composite and the electroactive phase content in PVDF and therefore increases the piezoelectric output response. PVDF/graphene nanofibers based nanogenerators resulted with performance of an open circuit voltage of 7.9 V and a short circuit current of 4.5 µA under 0.3 MPa pressure at 1 Hz frequency. However, in case of neat PVDF nanofiber, the obtained open circuit voltage was 3.8 V, with the short circuit current of 2 µA. PVDF/rGO nanofibers were prepared by electrospinning process. The electroactive β phase of PVDF was also improved by addition of ~ 2 wt%. The short-circuit current of 700 nA with open-circuit voltage of 16 V was obtained. Therefore, we have also tried to explore carbon based 2D material with PVDF (Chapter 4). Further the addition ferroelectric filler such as Barium titanate (BaTiO₃), PZT in piezoelectric polymer enhances the piezoelectric response in multiple folds in composite along with the enhancement in dielectric response and therefore, also gives rise in pyroelectric and ferroelectric behavior. The nanogenerators made up of ferroelectric fillers can also be used as hybrid nanogenerators. The ferroelectric filler in piezoelectric polymer enhances the piezoelectric response in multiple folds in composite along with the enhancement in

dielectric response and therefore, also gives rise in pyroelectric and ferroelectric behavior. PVDF/CNT/KNN-based electrospun nanocomposite was prepared with incorporation of 0.1% CNTs in the PVDF/KNN composite, resulted improved electric phase content as well as piezoelectric properties in enhanced performance of the nanogenerator with open circuit voltage of 23 V, with the short circuit current of 9 μ A and a power density of ~ 52 μ W cm⁻² was obtained. The addition of non-ferroelectric fillers helps electroactive phase nucleation as well as brings the photo responsive properties in the composite system for photo-piezotronic like applications [57,58]. PVDF/ZnO-Li composite piezoelectric nanogenerator was fabricated and the open circuit voltage of ~ 3.43 V with output power density of 0.45 W/cm³ to light up an ultraviolet (UV) light-emitting diode (LED) [61-79].

1.1.12 Pyroelectric nanogenerator

The waste energy is mostly abundant kind of energy present in our surroundings. In terms of waste energy, heat energy is one of a kind which is being huge source of energy. This heat energy could arrive from different resources including different kind of exhaust, heaters, living bodies heat radiation, other radiative energy sources and bodies, IR radiation etc. If one can harvest this type of waste heat energy from various kind of devices such as different types of nanogenerator including pyroelectric and thermoelectric nanogenerators, then we can fulfil the reequipments of low powered energy devices and sensor very much efficiently. Since our primary focus is to utilize the waste heat energy through pyroelectric effect. As discussed, (section 1.1.2), the pyroelectric effect has the two components. In most of the ferroelectric and pyroelectric materials, the primary component governs the pyroelectric effect, in which the charges are induced by anisotropic thermal expansion. In materials such as ZnO, CdS, and some other non- centrosymmetric wurtzite materials the secondary pyroelectric effects dominate [45-50].



Figure 1.11 (a) Schematic of the ZnO pyroelectric nanogenerator. (b) PZT film based nanogenerators (Adopted from Ref [46,47]).

The pyroelectric nanogenerators can harvest the energy through smaller thermal fluctuations and convert it to electrical energy, which could be further utilized to operate the different types of low powered micro/nanoscale electronics devices and sensors including prospective thermal imaging, physiological monitoring, modulating interfacial heat transfer, IR sensor and proximity sensors etc. As we discussed in earlier section about the basics of pyroelectric effect. The pyroelectric effect arises in the materials, which has a non-centrosymmetric crystal structure with the temperature modulated spontaneous polarization. BTO, lithium niobate (LNB), lead zirconate titanate (PZT), KNbO₃ and PVDF are few of them. In this regard, the first pyroelectric nanogenerator term was introduced in 2012 by Prof. Z. L. Wang in which ZnO nanowires with ITO and Ag electrode based pyroelectric device (Figure 1.11 (a)) was used to harvest the electrical energy from small thermal fluctuations. During this work, the observed pyroelectric current and voltage coefficients were determined much higher for nanogenerators than that of bulk form. The explanation behind this enhanced response could be due to preferred orientation of the ZnO nanowire array.



Figure 1.12 (a) The cyclic change in temperature of the PENG. (b) the corresponding rate of change of temperature curve. (c) Measured output voltage and (d) current of the PENG under the change in temperature (Adopted from Ref. [46]).

Further the same group also presented an active temperature sensor based on a PZT nanogenerator with output of open-circuit voltage and short-circuit current density was reported up to 22 V and 171 nA/cm², respectively with a 45 K temperature of charge. This nanogenerator was also able to drive LCD (Figure 1.11 (b) and Figure 1.12 (a-d)) for more than a minute with pyroelectric coefficient of ~ -80 nC/cm² K. Further a lead-free KNbO₃ nanowire/PDMS polymer based pyroelectric nanogenerator have also been fabricated with pyroelectric coefficient of $\sim 8 \mu$ C/m² K. The significant decrease in pyroelectric coefficient was observed due to the presence of PDMS polymer [46-50].

1.1.13 Application of piezo- and pyro-electric nanogenerators

The nanogenerator based on piezoelectric and pyroelectric effect can be used for versatile applications in difference areas including healthcare for biosensors, e-skin electronics, security, smart textile, touchpad, robotics, low-powered electronics and IoT smart gadgets and others (Figure 1.13) for energy harvesting and sensing applications [70-80].



Figure 1.13 Different applications of piezoelectric and pyroelectric nanogenerators (Adopted from Ref. [54]).

In this context, we would like to discuss here about a few of them and also included in the thesis chapters, as real-life applications. These nanogenerators can be used as pressure mapping sensor (Chapter 2), thermal mapping sensor, glass impact sensor, breathing sensor, IR sensor (chapter 4), heartbeat monitoring, wearable electronics (chapter 3), proximity sensor (chapter 4), acoustic sensor, tactile sensor (chapter 1). Piezoelectric energy harvester can be used as piezoelectric pressure sensors for monitoring different type of pressure signals including the body weight, pressing, touching etc. Piezoelectric pressure sensors work as dynamic pressure sensor with higher (> 100 kPa) and lower pressure regime (< 10 kPa). Unlike other sensors, piezoelectric pressure sensor doesn't require any kind of voltage or current bias to detect the signals. Piezoelectric materials used for pressure sensors include BaTiO₃, PZT, PMMA, PVDF, and P(VDF-TrFE) etc. The pyroelectric nanogenerators could be

useful to detect the temperature of different bodies with the relative difference between the actual and relative temperature difference. This temperature could be mapped in a systematic pattern to covey the thermal mapping of the object. It would also be beneficial for healthcare sector for monitoring body temperatures through eskin based devices. The response time this sensor also depends on the type of material used for fabrication including the electrode preparation. Piezoelectric and pyroelectric energy harvesters both can be used for breathing sensor application. In case of piezoelectric breathing sensor, the smaller movement to the device over mask is detected. This requires a physical contact with the device. However, in case of pyroelectric breathing sensor, the change in temperature of inhaling and exhale air is detected without physical contact. Therefore, the triboelectric contributions and artifacts doesn't affect the pyroelectric breathing sensor. The piezoelectric energy harvesters could also be useful for monitoring the heartbeat of living body with very precise accuracy. Therefore, it could advantage in healthcare sector and early-stage cardiovascular disease detection [75-80]. As a self-powered sensor, it doesn't require any back up battery back unlike other device. The e-skin based piezoelectric and pyroelectric devices could also be useful to detect the oxygen and hemoglobin level inside the body. To calculate the Saturation of Peripheral Oxygen (SpO₂), the incident light intensities are corelated with the Beer-Lambert law because Hyperbaric oxygen (HbO_2) and Hemoglobin have different absorption rates at different wavelengths. The SpO₂ of healthy people ranges from 95 to 99%. To detect different kind of body movement and gestures of different joints can also be monitored through piezoelectric sensors [71-80]. This kind of sensor application would not only be useful for alarm and security purposes but also helpful for the healthcare sector for having the preliminary data of person movement (walking, running) problems. Also, the particular gesture detection is helpful to operate smart keyboards and switches.

1.2 Overview of the thesis

As we have discussed about the importance, advantage and associated problems with high field poling process in case ferroelectric polymers. Therefore, the primary focus of this research work was to resolve the electroactive phase processing limitations under high electric field strength and to explore the advantage of in-situ poling pathways in ferroelectric polymers, through which the nucleation of electroactive phases in PVDF can be controlled under a lower electric field (~ 0.1 MV/m), than the typically required field strength for the ex-situ process. The research work includes the different chapters addressing the in-situ phase nucleation phenomenon, studies of their physical properties at nanoscale, valuable optimization insights and their applications as piezo- and pyroelectric nanogenerators followed by different types of self-powered sensors. The mentioned sections below provide the insights and overview of each chapter.

Chapter 1

This Chapter includes the basics and fundamental introduction of the primary components of this thesis work. The chapter provides an overview on piezo- and pyro-electric materials, its processing and requirement of electric field and applications as nanogenerator followed by the overview of each chapter.

Chapter 2

In this chapter, we have demonstrated the formation δ -phase comprising PVDF nanoparticles, fabricated through an electrospray technique by applying a 0.1 MV/m electric field, which is 10³ times lower than the typical value, required for δ -phase transformation. The diffraction patterns clearly indicate the δ -phase formation that

limits the infrared vibrational spectroscopic technique due to identical molecular chain conformations to that of non-polar α -phase. The piezo- and ferroelectric response of δ -PVDF nanoparticles have been demonstrated through a scanning probe microscopic technique based on piezoresponse force microscopy. The localized piezoelectric response, indicated by d₃₃ coefficient, is found to be ~ -11 pm/V. To utilize the distinct electromechanical response of δ -PVDF nanoparticles, the piezoelectric nanogenerator (PNG) has been fabricated. Due to the stress confinement effect in the spherical shape of δ -PVDF nanoparticles, the PNG exhibits synergistic effect than that of the film-based counterpart. The maximum power, i.e., 930 μ W/m² determined by the PNG under ~4.5 N of periodic force impact, indicates the potential to use it as a self-powered sensor. As a proof of concept, a self-powered pressure sensor mapping has been demonstrated to represent its realistic technological applicability.

Chapter 3

In this chapter, we addressed the electrode preparation approach for the morphologies like nanospheres, nanorods and nanoparticles. All-organic piezoelectric mechanical energy harvesters display an excellent electrical output with higher sensitivity due to the superior electrode compatibility between active materials and organic electrodes in comparison to that of metal electrodes. Herein, a stretchable, breathable, and flexible all-organic piezoelectric nanogenerator, made up of PVDF nanofibers and δ -PVDF nanoparticles, fabricated through the electrospinning process in a single step, has been demonstrated for prospective machine learning applications. The δ -phase PVDF nanoparticles serve as efficient active piezoelectric and ferroelectric components with a piezoelectric coefficient of ~13 pm/V. In terms of electrical response, a maximum power density of ~1600 μ W/m² was obtained. The fabricated device also exhibits excellent stretchability and air permeability, enabling the properties of robust wearable devices with a water vapor transmission rate of ~250 g m⁻² day⁻¹. Here, we have shown that a machine learning algorithm proposed for the different finger motion responses can predict with 94.6% accuracy. Thus, it could recognize different finger gestures efficiently with the highest possible accuracy and predict the possible source point. This feature could be advantageous for prospective health care and security purposes apart from the device and sensor applications.

Chapter 4

This work shown the advantage of in-situ electrospinning process in alteration of PVDF dipoles in presence of an external filler and further to improvise the pyroelectric response in the composite nanofibers for an excellent breathing sensor. The MXene nanosheet coupled PVDF nanofibers with d_{33} value of ~-26 pm/V, are able to capture the smaller thermal fluctuation as pyroelectric behavior with increase in pyroelectric current of ~ 632 pA and pyroelectric coefficient of ~130 nC/Km². To demonstrate this significant enhancement in pyroelectric response, polarized IR and scanning probe microscopy (SPM) based technique is utilized to study the confinement effect of 2D MXene $(Ti_3C_2T_x)$ nanosheets within these nanofibers. In subsequent study, different types of self-powered pyroelectric sensor of MXene-PVDF have been demonstrated for thermal energy harvesting. The fabricated flexible, hydrophobic pyroelectric sensor could be utilized as an excellent pyroelectric breathing sensor, proximity sensor and ASCII-code IR data receiver for practical applications. Further, the supervised machine learning algorithms are proposed to distinguish different type of breathing signals with ~98 % accuracy for health-care monitoring purposes.

Chapter 5

In this work we have demonstrated the in-situ electrical poling process in PVDF filmbased system to perform a comparative study with the post poling process. During this study, we have found that the prepared solution casted PVDF films under corona discharge to induce the electroactive phase in PVDF, can be achieved under lower electric field (~1.5 MV/m), which is ~ 60 times lower than the field required in traditional post poling process. In subsequent study, we have noticed that the effective in-situ poling is also dependent on the poling duration that drives the presence of oxygen and additional carbon species during corona discharge. Consequently, the UPS study confirms the effective changes in surface potential and the associated density of states (DOS). Thus, we affirmed that in-situ solution phase poling method could be one of the potential approaches to achieve electroactive PVDF film for piezo- and pyroelectric based device fabrication. The resulting film was further used to demonstrate the thermal energy harvesting application as pyroelectric nanogenerator.

Chapter 6

This chapter includes the brief summary of each chapter of this thesis and finally provides the vision about future perspective of this work.

1.3 Material characterizations

In this thesis, the material characterizations are performed with the following instruments.

High-resolution surface morphology and selected area electron diffraction (SAED) was performed on high-resolution transmission electron microscopy (HRTEM) (JEM-

2100, JEOL, Japan). The surface morphology was obtained using field emission scanning electron microscopy (FESEM) (JSMIT-300, JEOL, Japan). X-ray diffraction pattern was obtained using X-ray diffractometer (D-8 Advances, Bruker, Germany) using Cu-K_{α} (λ = 1.5418 Å) source. Fourier transform infrared spectra was recorded using an IR spectrophotometer (Nicolet iS20, Thermo Fisher Scientific, USA) in ATR mode with a resolution of 4 cm⁻¹ and 64 scans. The surface topography was measured through atomic force microscopy (AFM) (Multimode-8, Bruker, Germany and CoreAFM, Nanosurf, Switzerland) using etched crystal silicon probe (spring constant 3 N/m) in non-contact mode. Piezoresponse Force Microscopy (PFM) was performed contact mode using the conductive Pt-Ir coated probe on ITO coated glass substrate. The thermal profile was obtained using differential scanning calorimeter (DSC) (STA-8000, PerkinElmer, USA) in liquid N2 environment. Dielectric measurements were performed using Impedance Analyzer (E4990A, Keysight Technology, USA) in parallel plate capacitor geometry with frequency range of 20 HZ - 10 MHz. To perform the surface sensitive analysis, X-ray photoelectron Spectrometer (XPS) (Kalpha, Thermo Fisher Scientific, USA) was used with a monochromatic X-ray source of Al-K α (1486.7 eV) in ultrahigh vacuum (~ 10⁻⁹ mbar). To estimate the workfunction and DOS, the ultraviolet photoelectron spectroscopy was performed in the same system, using He-I UV source (21.22 eV). Further, the electrical characterization of the fabricated devices and sensor was obtained in terms of open circuit voltage and short circuit current using DSO (X1102G, Keysight, USA) and source meter (B2902A, Keysight, USA), respectively. For all other measurements, the detailed discussion in mentioned in their respective chapters.

1.4 References

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Chapter 2

δ-Phase Comprising PVDF Nanostructures Under Lower Electric Field

In this chapter, we have demonstrated the formation δ -phase comprising PVDF nanoparticles, fabricated through an electrospray technique by applying a 0.1 MV/m electric field, which is 10³ times lower than the typical value, required for δ -phase transformation. The piezoelectric properties δ -PVDF nanoparticles have been demonstrated through a scanning probe microscopic technique based on piezoresponse force microscopy (PFM). To utilize the distinct electromechanical response of δ -PVDF nanoparticles, the piezoelectric nanogenerator (PNG) has been fabricated and also demonstrated its realistic application as pressure sensor.

2.1 Introduction

The flexible piezoelectric nanogenerators have gained much interest due to their selfpowered nature and applications as sensors and energy harvesters [1-5]. To keep the desirable flexibility and mechano-sensitivity, piezoelectric polymers are treated as the best alternative in comparison to the inorganic counterpart [6–8]. In particular, PVDF is one of such piezoelectric semi-crystalline polymer that has been widely investigated and considered to have at least five distinct crystalline phases [9]. These phases have different chain conformations designated as all trans (TTTT) planar zigzag β -phase (form I), T₃GT₃G' γ -phase (form III), ϵ -phase (form V), TGTG' (transgauche-trans-gauche) α -phase (form II), and δ -phase (form IV) [10,11]. Despite the same chain conformations of α and δ -phase, the α -phase is non-polar and paraelectric in nature due to its centrosymmetric ($P2_1/c$) unit cell [12–16]. The macromolecular chain of PVDF (chemical formula, -(-CH₂-CF₂-)_n-) consists of repeated units of - CH_2 - CF_2 - as a monomer. The electronegative F and electropositive H atoms are the basis of molecular dipoles (i.e., -CH2- and -CF2- dipoles) perpendicular to the molecular c-axis. The dipole moments inside the unit cell of the α -phase are aligned in the anti-parallel direction, resulting a non-polar state of PVDF [9]. In contrast, the δ phase exhibits a non-centrosymmetric (P2₁cn) unit cell [17], giving rise to piezoelectric, pyroelectric, and ferroelectric properties. In the case of the δ -phase, every second chain along the c-axis is rotated about 180°; as a result, the dipole moments in the unit cell of the δ -phase are aligned parallel to each other and perpendicular to the molecular axis, giving rise to a polar state of PVDF [18]. Also, the X-ray diffraction (XRD) studies have shown that the δ -phase has a similar interplanar d-spacing as of α -phase but with significant changes in their relative intensities for the specific set of (h k l) values. In a δ -phase unit cell, with an n glide perpendicular to c-axis, (h k 0) reflections are absent for h + k = 2n + 1.



Figure 2. 1 Different reported techniques to obtain the δ -phase in PVDF. (Respective references are mentioned in Table 2.1)

Theoretically, the most accepted mechanism to achieve δ -phase is to rotate each of the second polymer chains about its c-axis of the α -phase unit cell. Experimentally, in 1978, the pioneer group, Davis et al. had shown that δ -phase could be achieved from α -phase by applying a strong electrical field of ~170 MV/m. In subsequent years, many other groups have also demonstrated the formation of δ -phase by applying a higher electric field, with an electric field of more than 100 MV/m.

In addition, there have also been reported very few different techniques, such as electroforming, solid-state processing and quenching to achieve the δ -phase in PVDF as demonstrated in Figure 2.1, and Table 2.1. The δ -phase possesses ferroelectric properties like the β -phase and also reported as a prominent alternative for memory-based applications [19]. Therefore, it is also speculated that δ -phase should have immense potential to be utilized as a piezoelectric nanogenerator (PNG).

Noteworthy that so far, PVDF comprising PNG is explored based on electroactive β/γ -phases, but the δ -phase-based PNG has not been explored yet due to limitations in multistep processing in the presence of much higher electric field strength (~170 MV/m). PNGs and sensors based on free-standing films and electrospun fiber geometries have been extensively explored. In parallel, different types of structures of PVDF, such as rods, tubes, particles, and flakes, have also gained interest due to their technological importance [20–22]. Therefore, one must explore the possibility and overcome the relative challenges of fabricating the devices based on these structures.

Sample Type (Processing Technique)	Temperature (°C)	Electric Field (MV/m)	Reference
Biaxially oriented thick film, t ~ 12 μm (Electro-forming)	25	170	32
Thin film, t ~ 400 nm (Electro-forming)	25	250	14,19
Drawn film, t ~ - a μm (Corona poling)	25	200	17
Thick film, t ~ 20 μm (Constant current corona charging)	_a	220	43
Stretched film, t ~ _a μm (DC Poling)	24	150	31
Thin film, t ~ 400 nm (Corona poling)	25	500	44
Drawn thick film, t ~ 100 μm (DC poling)	80	100	45
Drawn thick film, t ~ 100 μm (Poling)	130	100	46
Biaxially drawn thick film, t ~ 10 μm (High electric field induction)	_a	300	34
Nanoparticles, (Diameter: 60 - 250 nm) (Electrospray)	25	0.1	This work

Table 2.1 Electric field strength and other details	s for achieving δ -phase in PVDF.
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a: Data not available

In this development, tactile sensing devices and pressure mapping elements with highspatial resolution, high sensitivity, and prompt responses are becoming one of the most powerful tools for healthcare monitoring, security systems, and humanoid robot applications [23–29].

In this work, we are reporting the formation of the piezoelectric δ -phase comprising PVDF (henceforth, abbreviated as δ -PVDF) nanoparticles and fabricated the PNG to demonstrate it as a self-powered pressure mapping sensor. The δ -phase comprising PVDF nanoparticles are achieved by a single-step process at the lowest possible electric field reported to date. The application of the lower electric field gives an advantage over the dielectric fatigue and electrical breakdown of the polymer samples in comparison to higher electrical poling fields. In this process, we have used the electrospray technique [30] to achieve the δ -PVDF nanoparticles. The procedure obtains the PVDF nanoparticles is explained in the experimental section.

2.2 Experimental Section

2.2.1 PVDF nanostructure formation

PVDF pallets (Aldrich, USA, Mw: 180,000 by GPC) were dissolved in N, Ndimethylformamide (DMF, Merck, India) solvent and stirred at 60 °C for 24 hours to obtain the final 12 wt% PVDF solution for electrospray. The prepared PVDF solution was loaded into a 10 ml syringe and mounted to an electrospray system (Figure 2.2). The electrospray process was performed at the optimum voltage of 12 kV to achieve the δ -PVDF nanoparticles.



Figure 2.2 Schematic of electrospray setup, where a high voltage is applied between the metallic tip and collector.

The distance between the metallic tip and collector was kept at ~ 12 cm, followed by the sample flow rate of 0.4 mL/hr. The distance affects the size and the morphology of the polymer nanostructures. The final sample was collected on an aluminium foil wrapped over the plate collector. During this experimental procedure, the relative humidity in the chamber was ~50%, at room temperature (25°C).

2.2.2 Device fabrication and performance test

To prepare the piezoelectric nanogenerator of these nanoparticles, we have placed a conducting fabric (polyester woven fabric with Nickle and Copper coating, Juyoung International Inc.) on the plate collector to deposit the δ -PVDF nanoparticles. We have also given a controlled feeding rate of (0.4 mL/h) to control particle deposition on the conducting fabric. As time progress, the particle density over the substrate increases with time as evident from the AFM topography images. Piezoelectric Nanogenerator was made with δ -PVDF nanoparticles layers of thickness ~50 µm with an active area of 7.1 cm × 4.4 cm.



Figure. 2.3 The schematic shows the packaging of the fabricated pressure sensor arrays for mapping the external pressure.

The top and bottom electrodes were prepared by using the conducting fabric with an active contact with the electrosprayed layer. Then both the electrodes were connected with copper wire to make the proper connection for electrical measurements (with the final device thickness of ~200 μ m) (Figure 2.3). Further, the PNG was coated with polydimethylsiloxane (PDMS) to protect it from external damage and heat.

2.2.3 Acoustic data measurement

The acoustic data was generated using i-ball Tarang Lion speaker (40 W), when PNG is placed on the speaker's surface and the output response was recorded in DSO. The pressure mapping voltage distribution data was recorded using Keysight DSO X1102G. The mechano acoustic sensitivity (S) of PNG has been calculated by using the following formula -

$$S = \frac{V}{P_0 \cdot 10^{L_P/20}}$$
(2.1)

 P_0 is the reference sound pressure of 2 x 10^{-5} Pa, P denotes sound pressure, V is the acoustic output voltage of PNG, and L_p is the sound pressure level (SPL) in decibels.

2.2.4 Fabrication of pressure sensor array

To fabricate the pressure sensors for array design, the δ -PVDF nanoparticles were collected directly on bottom electrode (Cu tape) surface as shown in the schematic in Figure 2.3. The bottom electrode was cut into the required smaller area (1 cm x 1 cm). Then a spacer was placed on the edges of the bottom electrode followed by upper electrode of similar area. Then both electrodes were attached to the external wires to complete the fabrication of a single pressure sensor. Later, pressure sensors were arranged in the form of 4 x 4 sensor matrix as in Figure 2.4(a). The digital image of a single pressure sensor is shown in Figure 2.4(b), along with the 4 x 4 sensor matrix with alphabet A, P and L shape 3D-printed blocks kept over the arrays Figure 2.4(c).



Figure. 2.4 (a) The real image of the pressure sensor matrix. (b) The enlarged view of a single $(1 \text{ cm} \times 1 \text{ cm})$ pressure sensor (scale bar ~0.5 cm) and thickness of the sensor shown at vernier calipers in mm. (c) The digital image of 4 x 4 pressure sensor matrix where A, P and L shape 3D-printed blocks are placed on the surface of pressure sensors arrays.

2.3 Results and discussion

2.3.1 Diffraction pattern and IR spectroscopy

The selected area electron diffraction (SAED) pattern (Figure 2.5(a)) obtained in the transmission electron microscope (TEM) confirms the diffraction pattern of δ -PVDF nanoparticles (the inset of Figure 2.5(a)) with similar interplanar spacing (d) values as obtained in X-ray diffraction (XRD). The d-spacing of 4.41 A° corresponding to the peak for (110) shows the brightest ring in electron diffraction. The (110) plane is consistent with the highest intensity peak in XRD. The reflections of plane (020) have not observed in SAED, since the (110) and (020) are very closely originated and cannot be distinguished in bright rings as diffraction angles are close for these two planes. The next diffraction ring is observed for the plane (111). Since (021) and (111) planes are closely spaced and have lesser intense rings due to structure factors dependency of these reflections, only (111) was observed.



Figure. 2.5 (a) SAED pattern of the δ -phase in PVDF nanoparticles. Inset shows TEM imaging of PVDF nanoparticles (scale bar 200 nm). (b) X-ray diffraction pattern of PVDF nanoparticles in different phases. Experimental observation of the δ -phase at 30°C (marked as δ) and its conversion to the α -phase at 170°C after temperature treatment (marked as α). (c) Morphology of δ -PVDF nanoparticles as uniform distribution in SEM (scale bar ~ 5 µm).

The diffraction rings for planes (041), (211), and (310) were also observed in SAED, which belongs to δ -phase PVDF [17] with much smaller d-spacing for higher 2 θ values above 40°. The XRD pattern of PVDF nanoparticles in Figure 2.5(b) (upper panel, marked as δ) resembles precisely with the δ -phase represented XRD patterns, having similar d-spacing [17] and interplanar reflections of (020), (110), (021), and (111) at 20 peak positions of 18.3°, 19.9°, 26.7°, and 28.1°, respectively, as reported earlier by pioneer groups [31,32] with lattice parameters of $a = 4.96 \text{ A}^{\circ}$, $b = 9.64 \text{ A}^{\circ}$, and c = 4.62A°. It confirms the presence of the δ -phase in these PVDF nanoparticles fabricated through the electrospray system. Furthermore, we have demonstrated the reverse phase transformation of PVDF from the δ -phase to the α -phase in nanoparticles. In this case, higher temperature treatment (170°C) was given to the δ -PVDF nanoparticles. The XRD pattern of the PVDF nanoparticles after heat treatment at 170°C (Figure 2.5(b)) lower panel, marked as α) shows the α -phase PVDF characteristic diffraction peaks, appeared at (20) 17.6°, 18.3°, 19.9°, 25.6°, 26.7°, and 28.1° attribute to lattice planes of (100), (020), (110), (120), (021), and (111), respectively [16,33]. This phase change from δ to α -phase has occurred due to the temperature treatment above the melt crystallization of PVDF that destroys dipolar alignments of the δ -phase (ferroelectric) and converts it to the non-polar α -phase (paraelectric). The comparative study of both phases (Figure 2.5(b)) shows that the only significant change has observed as a decrease in the peak intensities of reflections (100) and (120) at 2 θ positions 17.6° and 25.6° in the δ -phase compared to the α -phase PVDF with the same d-spacing and lattice parameters. So, it can be concluded that there is no disordering, contraction, or change in the lattice shape and size. Then the only possible changes in both phases could be due to symmetry change in the unit cell lattice [31]. This conclusion is consistent with the basic unit cell structure of α and δ -phase. This reconfirms the δ -phase formation in the electrospray system.

Further, the crystallite size in the δ -phase nanoparticle was calculated by Debye Scherrer formula-

$$L = \frac{k\lambda}{B\cos\theta}$$
(2.2)

where, L is crystallite size, λ is X-ray wavelength (~1.5418 Å) of Cu-K α , θ is Bragg's angle, B is line broadening (FWHM) and k is shape factor (~0.89). The crystallite size of δ -phase and α -phase was found to be ~6 nm and ~13 nm, respectively.

The percentage crystallinity of δ -phase and α -phase from XRD, was determined by the following equation-

$$\chi_{\rm C} = \frac{\sum A_{\rm cr}}{\sum A_{\rm cr} + \sum A_{\rm am}} 100\%$$
 (2.3)

Where, ΣA_{cr} is the total area of crystalline phase and ΣA_{am} is the total area of amorphous phase in deconvoluted XRD peaks. The crystallinity of δ -phase and α -phase was found to be ~ 47 % and 52 % respectively.

The crystallite size of the δ -phase and α -phase crystalline lamella was calculated to be ~6 and ~13 nm, respectively. Also, the degree of crystallinity (χ_c) of the δ -phase and α -phase, from XRD patterns, was found to be 47% and 52%, respectively. Fourier transform infrared (FTIR) spectroscopy of the nanoparticles (Figure 2.6) shows the IR absorption bands of δ -PVDF. The vibrational bands at 1182 and 1209 cm⁻¹ are one of the conclusive ways to identify the δ -phase through FTIR as reported by Tashiro et al. [34]. Additionally, the FTIR spectra (Figure 2.6) also confirms the phase change, occurring from the initial δ phase to the α -phase due to heat treatment at 170 °C. Scanning electron microscopy (SEM) of the δ -PVDF nanoparticles is illustrated in Figure 2.5(c), which shows the formation of nanoparticles, ranges between ~60 and 250 nm. The 2D and 3D atomic force microscopy (AFM) topography image (Figure 2.7) displays the spherical particles with a diameter range between ~90 and 260 nm.



Figure. 2.6 FT-IR spectra of PVDF nanoparticles with δ and α -phase. The upper panel (marked as δ) is for as prepared δ -PVDF nanoparticles and the lower panel (marked as α) is for α -PVDF, when the phase transformation is attained by thermal treatment at 170°C.



Figure. 2.7 AFM topography image (5 μ m × 5 μ m) of nanoparticles as (a) 2D image (scale bar ~2 μ m). (b) 3D view of the same image for proper height visualization of the nanoparticles (height scale bar ~440 nm).

2.3.2 PFM and impedance spectroscopy

To study the piezoelectric and ferroelectric properties of δ -PVDF nanoparticles, piezoresponse force microscopy (PFM) was performed. The DC bias voltage of +35 V to -35 V was applied to obtain the corresponding phase and amplitude response of δ -PVDF nanoparticles. The hysteresis plot (phase response) in Figure 2.8(a) shows that the dipoles of the δ -PVDF nanoparticles are reorienting themselves under the application of the external bias voltage. As the positive bias voltage is applied, the dipoles inside the crystalline lamella of δ -PVDF nanoparticles are aligned in the opposite direction of the applied electric field as a negative phase response. The maximum reorientation takes place until the bias voltage reaches to +35 V with maximum dipole switching with a phase of $\sim 130^{\circ}$ and, therefore, saturation takes place. The similar nature was observed for the negative bias voltage -35 V. The coercive voltage (V_c) was found to be \pm 2.5 V. This final hysteresis plot verifies the ferroelectric nature of the δ -PVDF nanoparticles. The butterfly loop (amplitude response) shown in Figure 2.8(b) is evidence of piezoelectric response. As the bias voltage crosses the coercive voltage, the crystal lattice expansion takes place, and it attains the maximum deformation of 0.27 nm at +35 V bias. As the applied DC voltage decreases, it starts contracting itself until it reaches the minimal amplitude position and follows the similar response for negative bias voltage. The final butterfly loop confirms the piezoelectric response of ferroelectric δ -PVDF nanoparticles. The magnitude of the d_{33} value was calculated from the slope of the butterfly loop [35–37]. The obtained d_{33} value for δ -PVDF nanoparticles is ~ -11 pm/V.



Figure. 2.8 (a) Phase and (b) Amplitude response of δ -PVDF nanoparticles in PFM, after applying a DC bias of ±35 V. Temperature-dependent study of δ -PVDF nanoparticles as (c) Heat flow in DSC at 1°C/min followed by (i) first heating and (ii) second heating cycle. (The inset shows the estimated crystallinity from DSC and XRD). (d) Dielectric constant (ϵ ') and loss tangent (tan δ) of δ -PVDF nanoparticles with a variable temperature range of 30 °C–155 °C at certain frequencies, viz., 1, 10, and 50 kHz.

Differential scanning calorimetry (DSC) was performed at the ramping rate of 1°C/min under N₂ environment [Figure 2.8(c)]. The first heating cycle [Figure 2.8(c-i)] from 120 °C to 200 °C indicates the melting of different phases of PVDF. In this cycle, two peaks arise due to the presence of two different phases of PVDF [38], which could be predicated as δ and α -phase melting at 165 °C and 170 °C, respectively. In the cooling cycle, the sample crystallization takes place. Finally, the second heating cycle (Figure 2.8(c-ii)) indicates only a single melting peak at 169 °C that belongs to a single phase of PVDF. It can be interpreted as the presence of the α -phase only, since this observation is consistent with XRD (Figure 2.5(b)) and FTIR

(Figure 2.6) results obtained from the δ -phase to α -phase transformation when high temperature ~170 °C is employed. The degree of crystallinity (χ_c) was calculated from a DSC thermogram, and it is consistent with estimated crystallinity from XRD (Figure 2.8(c), inset). The subtle difference in the crystallinity value arises as compared to XRD due to the melting enthalpy provided to the polymer chain during the DSC process, which results in the reorientation of the molecular chain and changes the overall crystalline region in the polymer chain. The dielectric constant and loss tangent measurements of δ -PVDF nanoparticles were performed at different frequencies (viz., 1, 10, and 50 kHz) within the temperature range of 30°C - 155°C as shown in Figure 2.8(d). At room temperature (30 °C) and 1 kHz frequency, the dielectric constant (ϵ ') for δ -PVDF nanoparticles was measured ~ 7.5 with the loss tangent (tan δ) ~ 0.25. At a constant frequency, the dielectric constant and loss tangent gradually increase with the temperature. At lower temperatures, the molecular dipoles do not possess the flexibility to reorient themselves in the polymer chain. However, as the temperature increases, the possibility of the molecular reorientation due to the relaxation process in the polymer chain results in overall increase in the dielectric constant. In this scenario, the dielectric response is governed by the anomalous behavior of the glass transition of the polymer but a further increase in the temperature results in intense thermal vibrations that leads to suppression of the degree of reorientation, resulting a reduction in the dielectric constant of the polymer [38,39]. This particular behavior at the higher temperature region could be explained as the ferroelectric to paraelectric like phase transition in δ -PVDF. Further, to validate the experimental results in theoretical aspects, the kink propagation model is adopted to validate the δ -phase formation in the electrospray system.

2.3.3 Kink propagation model

The piezoelectric δ -PVDF nanoparticles were obtained at a significantly lower electric field (0.1 MV/m) in comparison to earlier reported work. The reason for the formation of δ -phase nanoparticles, is majorly governed by Taylor cone [47] formation in the electrospray process, in the presence of the applied external electric field [48-50]. It also demonstrates that at lower electric fields, this phase transformation is significantly dependent on the temperature and the kink propagation velocity. To explain the kink rotation mechanism of TGTG' chain unit by 180°, the motion of the chain has been defined by the following model.



Figure. 2.9 Kink propagation model for δ -phase conversion in the electrospray system demonstrated by double Sine-Gordon solution. The ordinate shows the x/c, i.e. the distance (x) traveled by kink along the c-axis of unit cell and abscissa shows the kink rotation angle at any time given t, in presence of electric field generated through electrospray system (Figure 2.2). The beginning of the kink (right red dot) shows initial orientation of the polymer chain at Taylor cone and at the final stage of the kink (left red dot) shows the 180° rotated PVDF polymer chain.

The rotational kinetic energy of the molecular chain is defined as

$$T = \frac{1}{2} I \sum_{i} \left(\frac{\partial \theta_{i}}{\partial t}\right)^{2}$$
(2.4)

where, *I* is moment of inertia of monomer unit about center of mass axis of the chain, θ_i is the rotation angle of *i*th monomer unit from the a-axis of the crystal, at a given time *t*.

The potential energy of the molecular chain is defined as -

$$U = \sum_{i} \left[A_1 \left(1 - \cos \theta_i \right) + A_2 \left(1 - \cos 2\theta_i \right) + \frac{1}{2} k \left(\theta_i - \theta_{i+1} \right)^2 \right]$$
(2.5)

where, A_1 and A_2 are constants associated with dipole moment of TGTG' unit and k is torsional constant. The first two terms (in Eq. 2.5) denote the combined inter-chain interaction potential with external electric field and last term appears as potential energy due to the torsional rigidity of the molecular chain.

The Hamiltonian for this modelled system can be written as-

$$H = \frac{1}{2} I \sum_{i} \left(\frac{\partial \theta_{i}}{\partial t} \right)^{2} + \sum_{i} \left[A_{1} \left(1 - \cos \theta_{i} \right) + A_{2} \left(1 - \cos 2\theta_{i} \right) + \frac{1}{2} k \left(\theta_{i} - \theta_{i+1} \right)^{2} \right]$$
(2.6)

Taking the Brownian motion of adjacent chains and anharmonic phonon forces into consideration for energy transfer, the modelled system can be approximated to Langevin equation [44]. The approximation to minimize the thermal contribution force term into the continuum limit, results a generalized double Sine - Gordon equation:

$$I \frac{\partial^2 \theta}{\partial t^2} = -A_1 \sin \theta - 2 A_2 \sin 2\theta + kc^2 \frac{\partial^2 \theta}{\partial x^2} - \lambda I \frac{\partial \theta}{\partial t}$$
(2.7)

where, λ is the damping constant and c is the periodicity along chain axis. The possible solution to the above equation can be written as

$$\theta(x,t) = 2 \arctan exp\left(\frac{2(x+vt)}{d}\right)$$
 (2.8)

where, *d* is the width of the kink. The above equation represents the motion of the soliton wave of electric polarization. For $\theta = 0$ to $\theta = \pi$ at any time *t*, θ (*x*, *t*) gives the probable propagation direction of kink that could travel from unpoled state to the poled state under the influence of applied electric field with kink velocity *v*. Eventually, resulting as a chain segment rotation by 180°; i.e. the possible favorable pathway to achieve of the δ -phase in PVDF chain by rotating its alternate second chain around c-axis.

Now, following the continuum approximation as mentioned elsewhere, the propagation speed of kink along c-axis is given by

$$v = v_0 \left[1 + \left(\frac{E_0}{E} \right)^2 \right]^{-\frac{1}{2}}$$
(2.9)

where, V_o is the max kink velocity at larger electric field E_o [49]. As discussed by DveyAharon et al. that at larger electric fields, the kink velocity doesn't depend on temperature. But at lower electric fields, the temperature plays a significant role to achieve the sufficient kink velocity for rotation. In our case, E_o has been approximated to the limit to achieve a stable Taylor cone formation, i.e. ~0.1 MV/m, for δ -phase in electrospray system. We have predicted an approximated pathway, for δ -phase conversion in electrospray process (Figure 3) by simulating the kink propagation model for a lamella size of ~12 nm [51]. Also, it is notable that, in Taylor cone formation, the polymer is initially present in gaseous state, associated with molecular chains having higher entropy and free energy. Eventually, leading the kink propagation at very much faster rate as compare to thin films, in presence of electric field of same strength. This is also might be the further reason for even lesser field requirement to achieve the δ -phase in electrospray process. This theoretical model significantly predicts the phase conversion into δ -phase at lesser electric field that observed experimentally.

2.3.4 Performance of δ-PVDF based nanogenerator

The δ -PVDF nanoparticles comprised PNG was prepared by depositing the nanoparticles over the electrode for a long period of time to fabricate the PNG and to demonstrate the application as a potential mechanical energy harvester. The mechanical energy harvesting mechanism of the PNG was explored by finite element method (FEM) based theoretical simulation. It is observed that the δ -PVDF based PNG generates higher stress (3.8MPa) (Figure 2.10(a-i)) in comparison to that of the planar PVDF film device (Figure 2.10(a-ii)) due to the stress confinement effect at the interfacial area between nanoparticles (Figure 2.10(a-iii)) under application of mechanical impact, e.g., 100 kPa of the pressure amplitude is employed here and, therefore, results in enhanced piezo-potential (Figure 2.10(b)) in the δ -PVDF based PNG (1.36 V) in comparison to the planar PVDF film (0.64 V). To demonstrate the energy harvesting performance of the PNG, the open circuit output voltage (V_{OC}) and short-circuit current (I_{SC}) of PNG is recorded by repetitive finger imparting motion with the applied force amplitude of ~4.5 N. The peak-to-peak response generated (Figure 2.10(c)) as $V_{OC} \sim 2.6$ V and $I_{SC} \sim 1$ µA. The imparting response was also recorded with a linear motor (Figure 2.11(a)) for the device in terms of V_{OC} and I_{SC} (Figure 2.11(b,c)). The slight variation in small magnitude current peaks is caused due to higher impedance mismatch between the piezoelectric device and the instrument (electrometer).



Figure. 2.10 (a) FEM based theoretical simulation of piezoelectric response in the PNG made with δ -PVDF nanoparticles. (i) Stress distribution of nanoparticles-based δ -PVDF PNG under 100 kPa pressure. (ii) Stress-distribution of the planar δ -phase PNG showing no variation of stress throughout the film. (iii) Stress confinement between the interfacial area of nanoparticles. (b) Piezo-potential distribution of the δ -PVDF PNG and planar PVDF film under the pressure of 100 kPa. Piezoelectric response of fabricated PNG as (c) open circuit output voltage (V_{oc}) and short-circuit current (I_{sc}). (d) Power density and output voltage as a function of the external load resistance (R_l). (e) Capacitor charging response with different capacitors, corresponding circuit diagram is shown in the inset. (f) Acoustic response of PNG at various frequencies with an acoustic sensitivity of ~2.75 V/Pa.

The piezoelectric output voltage response was also measured at different frequencies (Figure 2.11(d)) and also with several external load resistances (Figure 2.10(d)). As the load resistance, R_i was gradually increased (from 100 k Ω to 100 M Ω), the magnitude of voltage across the resistor also increases. The maximum voltage of 1.2 V was attained at 100 M Ω resistance.

The power density of δ -PVDF was calculated by the following equation-

$$P = \frac{V^2}{R_L \times A}$$

Where, R_L and A are the external load resistance and effective area of the δ -PVDF PNG and V is the voltage response obtained against the external load resistance [3].

The output power density curve shows (Figure 2.10(d)) the maximum power density obtained is ~930 μ W/m² at ~10 MΩ. It attains the maxima at the point, where the external resistance resonates with internal impedance of the device. The practical application of the PNG has been demonstrated through charging external capacitors (C) of several capacitances such as 1, 2.2, and 10 μ F within 70 s (Figure 2.10(e)). Capacitors were connected via the parallel connection through a full wave bridge rectifier circuit (the inset of Figure 2.10(e)). Interestingly, the PNG was able to charge the 1 μ F capacitor up to the maximum charging voltage of ~1.3 V within 60 s. Furthermore, the PNG has also found to be sensitive under the sound waves exposure, thus serving as an excellent acoustic sensor. The acoustic response (Figure 2.10(f)) of the PNG has been measured (with 40W RMS) and calculated [40] at ~80 dB of the sound pressure level (SPL) with tunable sound frequencies (40–140 Hz) indicating an acoustic sensitivity of ~2.75 V/Pa.

2.3.5 Pressure sensor pixel mapping

Furthermore, to demonstrate the practical application of the PNG as a pressure sensor [6,29,41], the pressure sensors were fabricated as shown in Figure 2.3. Then devices of size $(1 \times 1 \text{ cm}^2)$ are arranged as a 4×4 sensor array, as shown in Figure 2.12(a). Also, Figure 2.4(a) shows the digital photograph of the designed sensor array with an enlarged view of a single sensor (Figure 2.4(b)). The spatial pressure distribution over the matrix was recorded in terms of the corresponding open circuit voltage obtained from the sensor arrays, when the 3D printed alphabet blocks of shapes A, P, and L were dropped from a height of 10 cm, over the array of the sensor matrix (Figure 2.12(b) and Figure 2.4(c)). As the alphabet block A drops over the 4×4 matrix of the sensor array, it generates an instantaneous voltage response against each sensor in contact with the block.



Figure. 2.11 (a) Digital photograph of the data acquisition system interfaced with electrometer and linear motor integrated with a force gauge. (b) Open circuit output voltage (V_{OC}) and (c) short-circuit current (I_{SC}) response of PNG imparted by a linear motor integrated with a force gauge under with 5 Hz of frequency and 3.2 N of impact force. (d) Output voltage response of the PNG at different frequencies of at 1, 3 and 5 Hz under fixed impact force of 3.2 N.



Figure. 2.12 Schematics of a 4×4 pixel pressure sensor matrix, where alphabets A, P, and L shape 3D-printed blocks were kept over the each sensor matrix. (b) Spatially mapped pressure distribution over each pixel as the corresponding output voltage of the respective alphabetical blocks.

There was no voltage response was obtained for the sensors, which are not in physical contact with the block. As a result, for alphabet block A, we obtained the voltage distribution for each sensor except sensors 1, 5, 7, 9, 13, and 15. The voltage response of individual sensors was counted as a single pixel of the matrix. The spatially mapped pressure response of block A shows each pixel with different contrasts and signifies that the pressure at each point was different, and the pixels with zero pressure response have no voltage output. The resultant pressure mapping response as pixels clearly indicates the presence of block A over the matrix. Similarly, the response for alphabets P and L blocks was also recorded.

2.3.6 Device stability and pressure sensitivity

The durability and repeatability of the pressure sensor is shown in terms of the constant current output ~ 0.9 μ A for ~2200 cycle measurements (Figure 2.13(a,b)). The response time (Figure 2.13(c)) of the pixel pressure sensor was found to be ~7 ms.



Figure. 2.13 (a) The durability and repeatability of the pressure sensor recorded the short circuit current response of the pressure sensor on (a) Day 1 (b) Day 7 for ~2200 cycles. (c) Single enlarged peak of voltage vs time, to show the response time ($\tau \sim 7$ ms) of fabricated pressure sensor. (d) Pressure sensitivity of the pressure sensor for higher and lower pressure region (inset plot shows the sensitivity of low-pressure range).

The pressure sensitivity of the sensor was measured for higher as well as the lower pressure region. The sensitivity curve (Figure 2.13(d)) shows the sensitivity of the pressure sensor for the low-pressure range is ~80 mV/kPa and for higher pressure range is ~23 mV/kPa. This decrease in the pressure sensitivity occurs due to the effective strain limits in the high-pressure region in piezoelectric materials [42]. The resolution of the pressure sensor data of the fabricated sensor is ~50 Pa with a sensing range of ~75 Pa – 40 kPa. This self-powered pressure sensor can be utilized in human

health monitoring, weight distribution mapping, and for security purposes, etc. This kind of various applicability of the δ -PVDF comprised PNG also suggests that single step, in situ poled δ -PVDF nanoparticles prepared under the electrospray process do not require further electrical poling like other typical piezoelectric based sensors, actuators, and energy harvesters.

2.4 Conclusions

In summary, we conclude that the δ -phase comprising PVDF nanoparticles are possible to accomplish through the electrospray process under 0.1MV/m of the electric field. The ferro- and piezo-electric response of δ -PVDF nanoparticle is evident from phase and amplitude responses in PFM under the sweeping voltages, respectively. The piezoelectric coefficient (d_{33}) was obtained ~ -11 pm/V, which is competitive to that of the β -phase. The thermal study indicates that the δ -phase has relatively lower melting temperature than the α -phase. In addition, the ferroelectric to paraelectric like phase transition is also observed that determines the wider device operating temperature range, i.e., up to 165 °C. The δ-phase transformation in the electrospray process can be predicated by the kink propagation model. The δ -PVDF nanoparticle comprised PNG has shown a very prompt response with an output voltage of ~ 2.6 V and ~ 1 µA of open circuit current, along with the power density of 930 μ W/m² under ~4.5 N of the force amplitude. Aside from that ~2.75 V/Pa of the acoustic sensitivity is also pave the way to harvest the mechanical energy from environmental noises as well. The PNG can also be utilized as a self-powdered pressure sensor with a pressure sensitivity of ~23 mV/kPa for higher pressure regions and $\sim 80 \text{ mV/kPa}$ for lower pressure regions with a resolution of $\sim 50 \text{ Pa}$ for the realistic pressure mapping sensor applications.

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Chapter 3

All Organic Single Step In-situ Nanogenerator Fabrication Through Electrospinning

In this chapter, we addressed the electrode preparation approach for the morphologies like nanospheres, nanorods and nanoparticles. All-organic piezoelectric mechanical energy harvesters display an excellent electrical output with higher sensitivity due to the superior electrode compatibility between active materials and organic electrodes. Herein, a stretchable, breathable, and flexible all-organic piezoelectric nanogenerator, made up of PVDF nanofibers and δ -PVDF nanoparticles, fabricated through the electrospinning process in a single step, has been demonstrated for prospective machine learning applications.

3.1 Introduction

PVDF is considered as one of the potential material due to their nonlinear susceptibility and electroactive nature that gives rise to the piezo-, pyro- and ferroelectric properties to this semicrystalline polymer, that makes it applicable for achieving the mechanical, thermal and electrical stimuli-based sensors and energy harvesters [1-3]. PVDF exhibits in five different polymorphs known as α , β , γ , δ and ϵ phase. The α and ϵ -phase polymorphs of PVDF are non-electroactive in nature. While the β , γ , δ -phases are polar and electroactive in nature [2,3]. In these polymorphs, δ phase has been least explored electroactive phase due to its processing limitation due the requirement of a higher electric field [4,5]. However, recently, we have successfully reported the formation of δ -phase at lowest possible electric field via single-step electrospinning process [6] as well as its formation via phase separation technique [7]. The δ -phase PVDF has shown excellent piezoelectric and ferroelectric response in the reported studies so far [6-9]. It is noteworthy to mention that the ferroelectric and piezoelectric properties of δ -phase, are as comparable as β -Phase PDVF. The coercive field value of δ -phase is found to be ~115 MV/ m, which is comparable to the coercive field of β -phase ~ 90 MV/m [8]. Further, δ -PVDF has higher thermal operating range than that of β -phase PVDF copolymers. The copolymer P(VDF-TrFE) could provide the device operating temperature range up to ~140 °C only, while δ -phase PVDF could work till 165 °C having another advantage over β -phase PVDF [6]. Due to such potential advantages of δ -phase PVDF, it should be studied extensively. The fabricated δ -PVDF nanoparticles could be further extensively utilized under external stimuli such as pressure, temperature and in memory-based devices that includes applications sensors, actuators, and energy harvesters [10,11]. To utilize these nanoparticles in such application, one has to successfully deposit the electrodes on active materials. So far, there have been reported various approaches to deposit the metal electrodes on PVDF based films and fibers structures. Those approaches include top-bottom techniques [12-14] and inplane metallic electrode deposition techniques [15]. However, electrode deposition on morphologies like nanorods, nanospheres and nanoparticles of PVDF, in dried state are still a major concern [16,17]. To fabricate the devices and sensors, based on the δ -PVDF nanoparticles are also quite challenging task, due to this major drawback of electrode deposition/fabrication on the active material, as it is not possible to easily hold these nanoparticles, in proper stacked layers like nanofiber or film and then deposit the electrodes over it (Table 3.1). Further, the hydrophobic nature of PVDF nanoparticles and its incompatibility with metal electrode along with presence of air gaps between the active material and electrode material, enhances major concern for the device fabrication. In some of the earlier work, people have also tried to deposit the organic the electrodes on PVDF by using the ozone treatment/ surface functionalization to overcome the hydrophobic incompatibility between the electrode material and PVDF [18,19]. However, such surface treatment functionalization causes defluorination of active layer, affects the surface roughness, physical and electrical properties between the active later and electrode material. Therefore, such approach needs a better alternative solution. The poor adhesion and brittle nature of metal electrodes further limits the application of devices and sensors fabricated with metal electrodes in terms of flexibility and durability [20]. So, it is required to look for alternate metal free electrode devices, which would be biocompatible, organic and flexible in nature, to be utilized as wearable and flexible devices and sensors. In this context, conducting polymers are one of excellent way out to address major part of this problem [21].

Conducting polymers such as polyacetylene (PA), polypurrole (PPy), polyanailine (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and its complex with

poly(styrene sulfonate) (PEDOT:PSS) are widely used due to their versatile properties and stimuli dependent conductivity and other electrochemical properties for device and sensor fabrication [21,22]. They could be an excellent candidate such metal free, flexible, conductive organic electrode choice. However, since these conducting polymers are not easily soluble in organic solvents, so it difficult to utilize them directly in electrospinning process to prepare the electrodes [23-25]. In such cases, oxidative in-situ vapor phase polymerization (VPP) is one of effective process to coat and obtained the conductivity in insulating polymers, with the polymerization of monomer unit of conducting polymers [26]. The polymerization process significantly depends on the monomer to oxidant ratio, VPP reaction temperature and time of exposure. As per reported literatures, the obtained VPP coated insulting fibers demonstrate similar mechanical and conductive properties as that of conducting polymers. PEDOT as organic electrodes from VPP is quite established techniques due to its effectiveness (easy large area PEDOT coating with very much less amount of EDOT (monomer), degree of conductivity and stability) as electrodes [27-30]. This process is extremely useful to prepare the electrodes in electrospun samples and to fabricate the flexible devices and sensors in desirable size and shape [21,25]. It could be further useful to fabricate all organic metal free electrode-based wearable, breathable and stretchable devices and sensors that could overcome the limitation and durability with metal electrodes [20]. PEDOT is one of such conducting polymers with its high conductivity, flexibly and biocompatibility. It is widely accepted as flexible electrode material due to its facial synthesis processing during VPP [31-33]. To obtain the PEDOT coating in VPP process, the oxidant treated sample are used as substrate in the closed environment and exposed to the monomer vapors of EDOT. The vapor phase polymerization process in presence oxidant, converts the EDOT into the PEDOT during this process and resulting the conductivity in sample due the presence PEDOT [33,34].

Here, in this work, to address electrode preparation approach for the morphologies like nanospheres, nanorods and nanoparticles, we have demonstrated the *in-situ* device fabrication approach. This work has demonstrated electrode fabrication on electrospun PVDF nanoparticles, without the separate need of surface treatment/functionalization with a much cheaper and more effective approach to obtain a flexible energy harvesting device in single step. This fabrication technique would not only provide metal free, flexible and compatible organic electrode but also it would provide the air-permeable, breathable and stretchable devices and sensors for next generation wearable devices. The δ -PVDF nanoparticles were successfully collected in between the oxidant coated PVDF nanofibers, during electrospinning. Then successful EDOT to PEDOT conversion using vapor phase polymerization technique was performed, to achieve the conducting electrode layer for the final device structure. The fabricated device has further shown an excellent response, in terms of mechanical energy harvester and successfully able to the obtain different types of physiological response. We also included thorough study of the piezoelectric and ferroelectric responses δ -PVDF nanoparticles. Further, we have demonstrated the machine learning technique to distinguish between the different type of physiological signals and to process it for further understanding for health-care monitoring purposes.

3.2 Experimental Section

3.2.1 Materials

PVDF pellets (Aldrich, USA, Mw: 180,000 by GPC), N, N- dimethylformamide (DMF), Acetone and Dimethylacetamide (DMAc, Merck, India), FeCl₃ (Aldrich, USA), EDOT (TCI).

3.2.2 δ-PVDF nanoparticles preparation

PVDF pallets (Mw: 180,000 by GPC, Aldrich, USA) were dissolved in N, N-Dimethylformamide. (DMF) solution and then stirred at 90 °C for 4 hours, to obtain the final 12 wt % PVDF/DMF solution for electrospinning. The prepared PVDF solution was loaded into a 5ml syringe and electrospinning was performed with flow rate, maintained between 0.3 - 0.5 mL/hr, with voltage of 10-12 kV at 40% relative humidity. The δ -PVDF nanoparticles were collected on a drum collector.

3.2.3 Fabrication of oxidant treated nanofibers

A solution of PVDF (Mw: 180,000 by GPC, Aldrich, USA) and Dimethylacetamide (DMAc, Merck, India) of was prepared at 60 °C. In the prepared solution, 8 ml of acetone was added to the solution to obtain the final PVDF solution. After stirring for 24 hours, 2 wt % of FeCl₃ was added in 12 wt % of PVDF/DMAc solution and further kept it for overnight stirring. Finally, the electrospinning was performed at 12 kV, with tip to collector distance of 12 cm and flow rate of 0.5 mL/hr. The PVDF/FeCl₃ nanofibers layer was obtained on the drum collector, with 2000 rpm, at 50% of relative humidity.

3.2.4 Fiber and particle layer stacking for device

Initially, the FeCl₃ oxidant coated PVDF nanofiber mat of thickness ~ 200 μ m, was obtained at the drum collector. Then PVDF/DMF nanoparticles was deposited, of thickness around ~ 500 μ m, on the earlier obtained PVDF/FeCl3/DMAc nanofiber mat on the drum collector. Later, the final layer of FeCl₃ oxidant coated PVDF nanofiber of thickness ~ 200 μ m was deposited on nanoparticles layer to obtain the final stacked structure as δ -PVDF nanoparticles between the PVDF/FeCl₃/DMAc nanofiber mats. This higher active layer thickness approximation was helpful to avoid

any short-circuits between the upper and bottom layer of nanofibers after PEDOT coating.

3.2.5 EDOT to PEDOT conversion and device fabrication

The finally obtained stacked layer (in section 3.2.4) was held on the top of the container, with EDOT drops in a glass petridish at the bottom. This setup was kept inside vacuum over for 24 h at 60 °C. During this vapor phase deposition process, EDOT vapors reacts with the oxidant present in the PVDF nanofibers and converts to PEDOT, followed by polymerization of EDOT monomers into NF mat matrix template. As a result, the conducting PEDOT fiber layer were obtained on the both sides of δ -PVDF nanoparticles. Thereafter, the device was pressed between roller to reduce the possible air gaps. Finally, the electrical wires were attached to the both electrodes to obtain an all organic flexible nanogenerator.

3.2.6 Sample preparation for AFM and PFM Study

To analyze the surface topography of the nanoparticle and nanofiber samples in atomic force microscopy (AFM), the samples were directly deposited on the glass substrate. Further, the AFM was performed in tapping mode with probe oscillation frequency of 372 kHz. To study the ferroelectric and piezoelectric properties of the δ -PVDF nanoparticles, Piezo response force microscopy (PFM) was performed. The sample was collected on the ITO coated conducting glass substrate. An AC modulated voltage was applied between the conductive probe (Pt/Ir) and substrate in contact mode. The lock-in drive frequency of 12 kHz with drive amplitude of 6V was employed along with an external DC bias of \pm 18 V, to get the proper amplitude and phase response of PVDF nanoparticles in PFM spectroscopy mode.

3.3 Results and discussion

3.3.1 Crystallographic phase identification and morphology

The XRD spectra of fabricated PVDF nanoparticles in Figure 3.1(a) (upper panel) shows the presence of δ -phase, with the peaks at 18.3°, 19.9°, 26.7°, and 28.1° having reflections of (020), (110), (021), and (111), respectively. It confirms the δ -PVDF [6-8] formation in PVDF, via electrospinning technique. Further, the XRD spectra of PVDF with the oxidant $FeCl_3$ in nanofibers is presented in Figure 3.1(a) (lower panel), shows the presence of electroactive β -phase of PVDF, having the peak at 20.8° with (200/110) plane reflection. The single peak around 28.5° is due to the oxidant in the PVDF nanofiber. The morphology confirmation of the fabricated δ -PVDF nanoparticle is shown Figure 3.1(b), with the uniform particle distribution (scale bar ~10 um). The inset shows the FFT of the overall nature of nanoparticle distribution throughout the sample. Further, the proper bead free fiber formation of the PVDF with the oxidant-coated $FeCl_3$ (Figure 3.2(a)) can be concluded by Figure 3.1(c) (at scale bar ~ 5 um). The elemental analysis ((Figure 3.2(b)) shows the presence of oxidant (FeCl₃) within the fibers uniformly. The inset FFT of Figure 3.1(c) shows the overall fiber distribution in terms of its random nature and uniformity present in the sample. This result is consistent with the results obtained from AFM topography of these oxidant nanofibers (Figure 3.3(a)) with the roughness of 60-80 nm on the fiber surface. Further, to demonstrate the thermal stability of the electrospun nanofibers, Differential scanning calorimetry (DSC) was performed at ramping rate of 1°C/min (Figure 3.3(b)), shows as two heating cycles. In first heating cycle, one can observe the melting of β -phase of PVDF occurs as

temperature reaches ~ 160°C. Further, in the second cycle of heating, the melting peak was observed at bit higher temperature than the earlier heating cycle. It indicates that the first cycle of heating up to 210°C, PVDF converted to to α -phase, i.e., thermodynamically most stable phase of PVDF.

So, in second heating cycle, there is only indication of presence of α -phase at higher temperature ~168°C. i.e. These nanofibers can easily hold the electroactive properties of the PVDF till ~ 160°C (β -phase) and could contribute in the piezoelectric and ferroelectric properties as well.



Figure 3.1. (a) The X-ray diffraction pattern of δ -PVDF nanoparticles (upper panel) and β -phase (lower panel) PVDF nanofibers. SEM image of (b) the δ -PVDF nanoparticles (scale bar ~10 µm) (c) nanofibers (scale bar ~5 µm), and also the FFT analysis of the nanoparticles and nanofibers distribution shown in the inset, respectively.



Figure 3.2 (a) TEM Image of PVDF/FeCl₃ oxidant coated nanofiber. (b) Elemental mapping of the oxidant coated PVDF nanofibers.

The ferroelectric and piezoelectric properties of these oxidant-coated nanofibers are demonstrated by PFM, in terms of hysteresis and butterfly loop (Figure 3.8(ac)). We have followed the single-step approach to address the essential problem of electrode formation for the nanoparticles. In this methodology, the δ -PVDF nanoparticles are collected over the oxidant treated nanofiber during the electrospinning process itself, as a second layer over Thereafter, another layer of oxidant treated nanofibers were again deposited over the thicker layer of nanoparticles, to make sure that the particles layer is much thicker between the fiber layers. In this procedure, we have fabricated the primary device like sandwich structure through electrospinning technique, as δ -PVDF nanoparticles layers are embedded within the nanofibers. To achieve the all-organic flexible electrodes through vapor phase polymerization (VPP), the experimental steps were followed as shown in schematics (Figure 3.5(a)).



Figure 3.3. (a) AFM image loop of Oxidant coated PVDF nanofiber. (b) DSC thermogram of the PVDF nanofibers in different cycles, showing the thermal stability of different phases.

Initially, the nanofibers of oxidant coated PVDF was prepared in electrospinning and then δ -PVDF particles was deposited on the fiber layer, followed by next oxidant coated fiber layer. This sandwich structure (primary structure) was obtained directly from electrospinning. After achieving the primary device structure, the electrode formation was performed in the next stage of experiment, to achieve the final top-bottom electrode device for nanoparticles. Therefore, the primary sandwich structure as, oxidant treated PVDF Nanofiber/PVDF Nanoparticle/PVDF nanofiber was exposed for the vapor phase polymerization process. The polymerization process was followed as shown in schematics in Figure 3.5(a). The primary structure mat was exposed to EDOT vapors in a closed vacuum chamber, at 60 °C for 12 h. The monomer vapors of EDOT react to the oxidant present in the PVDF nanofibers and PEDOT polymerization (Figure 3.4) takes place over the nanofibers as a template [31-33]. While the PEDOT coated nanofibers few other peaks present at positions 984 cm⁻¹ and 1502 cm⁻¹ as a signature of PEDOT coating over the PVDF nanofibers.



Figure 3.4. EDOT to PEDOT conversion pathway through Vapor phase polymerization (VPP) process.

These peaks appear due to the vibration of C-S-C and C=C bonds from the thiophene ring [35,20] in PEDOT (Figure 3.4). This all-organic conducting electrode were obtained, over the PVDF nanoparticles in a single-step electrospinning process followed by VPP as shown in schematics. As a result, achieving a conducting PEDOT coating over the PVDF nanofibers. i.e. the fibers layers were converted to conducting electrodes for the PVDF nanoparticles, embedded in between the fibers. So, finally we have achieved PEDOT coated all organic device with fibers as electrodes via a single-step in-situ electrospinning process for device fabrication. To analyze the morphology of the prepared primary sandwich device structure, FESEM was performed as shown in Figure 3.5(b). It is clear from the cross-sectional view that the PVDF nanoparticles are uniformly embedded between the oxidant treated PVDF nanofibers. Further, to conclude the proper EDOT to PEDOT conversion of the nanofibers, the FTIR spectra of PVDF nanofibers are shown in Figure 3.5(c), before and after the PEDOT coating via VPP technique. The FTIR spectra of only oxidant treated PVDF nanofibers shows the predominant β -phase characteristic peaks with absorbance at wavenumbers 1275 cm⁻¹ and 840 cm⁻¹. The FTIR results confirm the presence of only β -phase in the only oxidant treated PVDF nanofibers having only characteristic bands of PVDF and consistent with the XRD results.



Figure 3.5. (a) Schematic representation of all the experimental steps to fabricate all organic piezoelectric nanogenerator through vapor phase polymerization (VPP) process. (b) SEM showing the stacked layers of PVDF Nanofibers/ PVDF Nanoparticles/ PVDF Nanofibers (Scale bar ~ 10 μ m). (c) FTIR spectra of PVDF Nanofibers without and with PEDOT coating. Inset shows the color of fibers, before PEDOT coating (white) and after PEDOT coating (black).

3.3.2 X-ray photoelectron spectroscopy study

To study the changes in chemical composition and chemical environment of oxidant treated nanofibers of PVDF, X-ray photoelectron spectroscopy (XPS) was performed before and after the PEDOT coating. In case of oxidant treated PVDF nanofibers, before coating PEDOT, one can notice that, for C 1s, the two peaks obtained at 286.6 eV and 291 eV represented -CH₂- and -CF₂-, respectively (Figure 3.6 (a)). These two peaks obtained in case of C 1s, has similar intensity (1:1), due to the equal contribution from both the groups in polymer chain, resembles with the characteristics of PVDF [36]. The XPS peaks for the oxidant (FeCl₃) present before the coating in the PVDF nanofibers was also observed with the presence of Fe (~710 eV) and Cl (~198 eV) visible in the survey scan (Figure 3.6 (b)). This indicates the proper oxidant treatment was done to PVDF nanofibers. Further, after the PEDOT polymerization reaction (Figure 3.4), it is expected to find the presence of $-CH_2$ - group with much higher intensity that the $-CF_2$ - group, which is also evident from the obtained XPS spectra for C 1s after coating in Figure 3.7(a).



Figure 3.6. (a) XPS spectra of C 1s of Oxidant coated PVDF nanofibers. (b) XPS Survey spectra of Oxidant coated PVDF nanofibers.



Figure 3.7 High resolution XPS spectra of the PEDOT coated PVDF nanofibers indicating the presence of (a) Carbon (b) Oxygen (c) Fluorine and (d) Sulphur elements. (e) UPS spectra of uncoated and PEDOT coated nanofibers. (f) I-V plot of PEDOT coated nanofibers.

The -CH₂- group contribution significantly enhances w.r.t the uncoated sample. There was not significant changes F 1s spectra suggest Figure 3.7(b) that presence of F is only from PVDF and not have been altered after the PEDOT polymerization. However, one can notice the presence of Oxygen and Sulphur in the XPS spectra as well, which is due the polymerization with monomer vapors with the help of oxidant and indication of presence of thiophene group after polymerization in PEDOT [37,38]. As a result of this thiophene group, one can see the XPS signatures of O 1s (Figure 3.7(c)) and S 1s (Figure 3.7(d)), which was not there before PEDOT coating. Therefore, this XPS result also indicates the successful PEDOT coating of PVDF nanofibers from vapor phase polymerization of EDOT vapors. Further, we have performed the ultraviolet photoelectron spectroscopy (UPS) of uncoated and PEDOT coated fibers (Figure 3.7(e)) to observe the modulation in the molecular orbitals near the fermi level. It can be observed that the PEDOT coated nanofibers have higher density of states (DOS) present near the Fermi energy level, with highest occupied molecular orbitals (HOMO) having band edge ~ 3.89 eV, in comparison to than that of uncoated samples ~ 4.63 eV. This demonstrates the shift in the DOS of the PEDOT coated nanofibers towards the Fermi edge. To measure the conductivity of the coated PEDOT nanofibers, I-V measurement was performed with applied bias voltage of +/-6V. The conductive value of the nanofibers layer was obtained ~ 220 S/cm. The linear conducting behavior (Figure 3.7(f)), with current in ~mA order, indicates a good conductive nature of VPP coated PEDOT nanofibers and thus it could be further utilized as a electrode for flexible device preparation.

3.3.3 PFM and Impedance Spectroscopy

To study the piezoelectric and ferroelectric properties of the active material i.e., δ -PVDF nanoparticles, piezo response force microscopy (PFM) was employed [39]. An AC modulating voltage was applied between the conductive probe and ITO-coated

substrate, to induce the mechanical oscillation normal to the surface in contact mode. The lock-in drive frequency of 12 kHz with drive amplitude of 6V was employed along with an external DC bias of \pm 36V to get the proper PFM spectroscopic of δ -PVDF nanoparticles. Under the application of the external positive bias, the hysteresis loop (Figure 3.10(a)) shows the switching of the molecular dipoles of δ -PVDF nanoparticles in opposite direction, attaining the phase value of ~ -120° and after that, it reaches to the max saturation. As the negative bias was applied, the molecular dipoles start to orient themselves and achieves the max phase value ~ 56°. This obtained hysteresis response supports the ferroelectric nature of δ -PVDF nanoparticles. Further, the amplitude loop (Figure 3.10(b)) was also obtained for the δ -PVDF nanoparticles under the same external bias, with the maximum deformation value of ~ 0.3 nm for positive bias and ~0.4 nm, for the negative bias.



Figure 3.8 PFM (a) phase image (scale ~ 4 μ m) (b) Hysteresis loop and (c) Butterfly loop of Oxidant coated PVDF nanofiber.

This obtained deformation indicates the converse piezoelectric effect in the δ -PVDF nanoparticle under application of external electric field stimuli. Therefore, one can conclude that the obtained hysteresis (phase) and butterfly (amplitude) response indicates the ferroelectric and piezoelectric nature of δ -PVDF nanoparticles [6,7]. The piezoelectric coefficient (d₃₃) of δ -phase PVDF electrospun nanoparticles was estimated by correlation of change in amplitude for each applied excitation voltage, followed by the relation-

$$d_{33} = \frac{\Delta z}{V} \tag{3.1}$$

where, Δz is the change in vertical amplitude and V is the applied excitation voltage.⁴⁰ The piezoelectric coefficient (d₃₃) was obtained ~ 13 pm/V for the δ -PVDF nanoparticles.



Figure 3.9 Dielectric constant and loss of δ -PVDF nanoparticles, with PEDOT electrodes at room temperature.



Figure 3.10 PFM spectroscopic response of δ -PVDF nanoparticles, in terms of (a) phase (hysteresis) and (b) amplitude (butterfly) response under external bias. Impedance spectroscopy response of δ -PVDF nanoparticles, in terms of (c) dielectric constant (d) dielectric loss tangent with PEDOT electrodes.

Further, the impedance spectroscopy of δ -PVDF nanoparticles with EDOT electrodes was also performed. The dielectric constant (ϵ ') value of ~ 13 and dielectric loss tangent of ~ 0.3 was obtained (Figure 3.9) at room temperature, at 1 kHz. To study the phase transition behavior, the temperature dependent spectroscopy at different frequencies were also recorded. The dielectric constant at a particular frequency, of δ -PVDF (Figure 3.10(c)) increases, as the temperature rises. This process occurs due molecular chain relaxation in polymers at higher temperature [41,42]. At temperature ~ 164 °C, the ferroelectric to paraelectric like phase transition can be observed and consistent with the observations in DSC in this temperature regime. It can be noticed that dielectric constant (Figure 3.10(c)) decreases as result of increase in frequency, at higher temperature. Since the higher frequency disrupts the surface charge polarization and results in decrease in the dielectric constant value. This frequency variation also causing the increase in dielectric loss of the PVDF nanoparticles (Figure 3.10(d)) with temperature. This temperature dependent study also helped us to conclude the effectiveness of PEDOT in-situ electrode over the nanoparticles at higher temperatures and attaining the similar transition response as it is expected. The room temperature dielectric permittivity and dielectric loss data is also measured (Figure 3.9). Here, it can be noticed that the obtained dielectric constant value is bit higher than usually obtained for neat PVDF polymer with metal electrode for dielectric measurement. This slight increase in the dielectric constant of the active material is observed due to increase in interfacial polarization between the active material and electrode, along with the intrinsic polarization of the active material, that contributes in overall effective increase in dielectric constant value [43].

3.3.4 Piezoelectric energy harvesting

After the PEDOT coating of PVDF Nanofibers, the devices were processed under roller to reduce the possible airgaps and to minimize the chances of triboelectricity. Finally, we achieved the δ -PVDF nanoparticles based flexible piezoelectric nanogenerator (PNG), to harvest the energy from mechanical vibrations and motions

[44-49,52]. The working mechanism of the fabricated PNG is demonstrated (Figure 3.12) in the related section (3.3.5).

In that aspect, we have studied the piezoelectric responses of this fabricated δ -Phase device, in terms of experimental and theoretical piezoelectric device performance.

To experimental obtain the piezoelectric energy harvesting data from δ -PVDF nanogenerator, the periodic hand imparting was performed on the device as per schematic (Figure 3.11(a)) and the output response was recorded in terms of open circuit voltage (Figure 3.11(b)) and short circuit current (Figure 3.11(c)).



Figure 3.11 (a) Schematic represents the all-organic δ -PVDF with PEDOT coated nanogenerator for mechanical energy harvester application. (b) Open circuit voltage (V_{oc}), (c) Short circuit current (I_{sc}) response of the piezoelectric nanogenerator, (d) Power density plot, output voltage and output current response of δ -PVDF PNG, as a function of external load resistance.





Figure 3.12 Schematic representing the working mechanism of PNG device with (i) initial (ii) stressed and (iii) relaxed states.

The peak-to-peak output voltage was obtained ~ 4 V, with current value of ~ 1.8 μ A. The working mechanism of δ -PVDF based PVDF PNG is shown (Figure 3.12) in stepwise manner. The fabricated PENG is having active material as δ -PVDF nanoparticles in between the PEDOT coated PVDF nanofiber layers as shown in schematic in Figure 3.12. In initial condition (Figure 3.12 (i)), when there is no mechanical stress (σ) in applied, the device stays equilibrium state with no external output, due to the superimposition of equivalent charge centers of all dipoles. Thereafter, as the external stress is being applied on the device, there occurs a change in polarization (i.e., $\frac{\partial \mu}{\partial \sigma}$) due to shifting of charge centers ((Figure 3.12(ii)) and net

resultant piezo-potential can be observed between the upper and bottom layers of the

electrodes. Due to this piezo potential, external free charges on the electrode flows to counterbalance the piezo-potential difference. As a result, output single can be seen in the circuit in terms of short circuit current/ open circuit voltage. Further, when the applied stress is removed from the device, the charge centers would shift back to initial position ((Figure 3.12(iii)), and would try to attain the earlier equilibrium position. It results the change in piezo potential between the electrode surface and hence a short circuit current/ open circuit voltage could be seen in the reverse direction to counterbalance the potential difference and the device goes back to relaxed state and attains the initial position. Therefore, a continuous external stress/ imparting force can provide a continuous piezoelectric output signal, which is shown as open circuit voltage and short circuit current as electrical output (Figure 3.11 (b, c)).

3.3.6 FEM simulation of δ-PVDF piezoelectric nanogenerator

The FEM based theoretical simulation was performed to demonstrate the stress distribution and piezo-potential generated within the fabricated nanogenerator, with δ -PVDF nanoparticles and PEDOT nanofibers as electrodes. The 3D view of δ -PVDF based device is shown (Figure 3.13 (a)) for proper visualization of device structure before the simulation. For convenience, the two-dimensional (2D) simulation of the device is shown as a cross-sectional view (Figure 3.11(b)), with stress distribution all over the device under an applied stress of ~ 200 MPa ((Figure 3.11(c)), and the corresponding piezo-potential is shown (Figure 3.11(d)) with maximum piezo-potential of change ~ 3.5V, slightly higher than the experimental voltage (2V) obtained for this device, which is certainly expected, due to theoretical constraints and assumptions taken into account for simulation with respect to the experiments condition.



Figure 3.13 FEM simulation of the δ -PVDF based device (a) 3D view (b) 2D cross-sectional view (c) stress distribution (d) piezo-potential distribution of the device under external applied load.

As the external stress is applied over the device, this response is mainly concentrated at the interfacial area of the nanoparticles. This stress confinement over nanoparticles develops a higher effective polarization (than films) under the applied mechanical stimulus, causing the charges induced over the electrodes and, therefore, creating a piezo-potential difference between the opposite surfaces that result as an open circuit voltage between the electrodes. This kind of layered structures provide the advantage to fabricated the devices with maximum contact to the electrode surface, which is beneficial to achieve maximum vertical polarization from the device, with normal directional applied stress. Also, making a device with nanoparticles with such structure are greater advantage to stack the particle between electrodes and to apply the stress to maximize the stress confinement effect within the stacked layer of particles.

These theoretical results are in well consistency with the experimentally observed output (2V) [50]. Further, to compare the experimental device output of the PNG, we have also listed out PVDF-based energy harvester for the performance comparison, with respect to the electrode fabricated in each nanogenerator (Table 3.1). Further, if we compare in terms of piezoelectric device, this device is very effective in terms of avoiding the triboelectric contribution. Since, in this case, electrodes are not placed manually, wearing gloves while tapping the device, fixing the device properly while taking data and keeping the grounding level of the device and instrument at the same level. therefore, lesser chance of triboelectric contribution between the active material and electrode. Hence, it is very much suitable to capture the real response from finger motion rather than the tribo/frictional contribution from the motion, which makes this device having piezoelectric origin [51]. So, the δ -PVDF based piezoelectric nanogenerator performance can be called more effective with PEDOT electrodes. The voltage and current values are also fair enough in comparison to listed literature for a piezoelectric nanogenerator (PNG). It is noteworthy to mention here that the obtained voltage and current outputs are much improved than our earlier reported work based on metal electrode for δ -PVDF nanoparticles. This might be due to the proper synergistic effect of organic active material with organic the electrode as well as the intrinsic piezoelectric contribution from the electrode [18].

S.N.	Active material (type)	Electrode type	Current	Voltage	References
			(µA)	(V)	
1.	PVDF- KxNaxNbO ₃ (film)	Top-bottom Cu			
		electrodes,	0.08	4	73
		placed manually			
2.	PVDF (nanofibers)	Two in-plane			
		copper foils,	0.005	0.04	74
		placed manually			
3.	PVDF-TrFE-Ag-BCZT (film)	Top-bottom Al			
		foil electrodes,	1.8	3.5	75
		placed manually			
4.	(BaTi(1-x)ZrxO ₃)/	Al electrodes, by			
	PVDF	thermal	1.35	11.9	76
	(film)	evaporation			
		Two in-plane			
5.	PVDF (nanofiber)	copper foils,	0.03	0.076	77
		collected on ES			
6.	PVDF-TrFE (film)	Au electrodes,			
		by thermal	0.058	7	78
		evaporation			
		Top-bottom			
	PVDF- MgCr ₂ O ₄	polyester fabric			
7.	(nanofiber)	(Ni/Cu) collected	0.020	1.05	79
		on ES			
8.	PVDF– polycarbazole (nanofiber)	Top-bottom Cu			
		tapes, placed	2	2	80
		manually			
9.	PVDF- BaTiO ₃ (nanofiber)	Top-bottom Cu			
		tapes collected	0.32	3.4	81
		on ES			
10.	δ-PVDF (nanoparticles)	In-situ PEDOT	1.8	4	
		Top-bottom			This work
		electrode			
		formation			

Table 3.1 Performance comparison of PVDF-based energy harvesters and their electrode fabrication techniques.

Further, the power density output of the device was also recorded with external load resisters of 50 k Ω -100 M Ω (Figure 3.11(d)). The maximum voltage of ~ 2V was obtained at 100 M Ω . The maximum current of ~0.9 μ A was found at 50 k Ω and the maximum power density of ~1600 μ W/m² was obtained at 1M Ω , when the impedance of the external load was matching with the internal resistance of the device [44,45]. Further, to show the stability of the fabricated δ -PVDF PNG, we have performed the device stability test for 14,000 cycles under constant imparting with a linear force imparting system and have observed a similar current amplitude, without any significant changes in the current (Figure 3.14). It indicates the PEDOT electrodes are effectively stable and compatible with electrospun PVDF nanoparticles. Further, to show the practical application of the piezoelectric nanogenerator, capacitors of different capacitance were charged (Figure 3.15(a)). The capacitor of 1, 2.2 and 4 μ F capacitance was able to charge maximum value up to 0.18, 0.15 and 0.10 V, respectively.



Figure 3.14 Device stability performance test of all organic δ -PVDF nanogenerator.



Figure 3.15 (a) Charging response of 1, 2.2 and 4 μ F capacitors from δ -PVDF PNG under the external applied force. (b) Hand bending response signal of δ -PVDF PNG at different bending angles of 0, 30, 60 and 90 degrees for gesture monitoring (inset shows the average voltage response during bending).

It is notable that the 1 μ F capacitor was charged up to 0.18 V in 7s only, with the longer discharge time, demonstrates the feasibility to be used for practical application. Also, to demonstrate the different type of hand gesture responses, the device data was taken for different bending angle of the device with hand. One can notice that the bending response (Figure 3.15(b)) achieved against each angle (i.e.; 0, 30, 60 and 90 degrees) is different and the corresponding achieved voltage is also different and highest for the 90° bending angle as it causes the maximum deformation in the device at that point, resulting in maximum voltage output.

3.3.7 Physiological motion monitoring and machine learning

As different types of physiological data could be recorded through the fabricated device. Therefore, this large data could be utilized to develop a machine learning model as shown in schematic chart flow (Figure 3.16(a)), to recognized the proper response and its origin, which could be helpful for healthcare and security purposes. Once the sensor data is obtained, it could be further preprocessed and separated in the training and test data. Further, this training data can be run over different machine

learning algorithms to obtain the maximum precision with respect to the test data [43-55]. Once the model is successfully trained then we can expose this model with new dataset and see the predicted results as shown in above schematics (Figure 3.16(a)).



Figure 3.16 (a) Flow chart of sensor data processing through Machine learning. (b) Various finger motion response recorded by the PNG for little, ring, middle, thumb and index finger. (c) Confusion matrix output obtained from the developed machine learning algorithm to recognize the different type of finger motions.

Here, we have recorded the response of motion of different fingers in a human hand. One can easily notice that each finger motion has different kind of output pattern (Figure 3.16(b)), if we compare the normalized responses. The motion of each fingers joint is different from other finger joint in terms of the bending freedom/movement of each finger, in the cases of opening and closing of each finger. The bottom side peaks are higher, as the bending strain caused of top surface is lesser than the bottom surface. Further, to overcome the statistical errors for each response, we have recorded these signals several times for generating the larger dataset. Thereafter, we have taken this gesture recognition behavior data to the next step for practical application and have developed a machine learning (ML) algorithm to recognize the different type of finger motions successfully with our developed ML model [53-58]. The machine learning algorithm was implemented by using python 3 and MATLAB 2021a. The input dataset was created by acquiring the data with the sensor, which is trained by pattern recognition algorithm. The data used in the different steps of implementation of the algorithm such as training, testing and validation are 70 %, 15 %, and 15 %, respectively of the total dataset. Python 3 is primarily use to visualize and pre-processing the data, while MATLAB is used for creating the algorithm. We can observe the confusion matrix (Figure 3.16(c)), plotted between the predicted and true finger response, for the developed machine learning model [59-65]. It is able to recognize and predict the finger motion responses precisely with 94.6 % accuracy. This indicates a good machine leaning model for pattern recognition as well as gesture monitoring purpose for health-care and security purpose as prospective applications in real time [54, 56]. Apart from these, we have also shown that our fabricated flexible, all-organic device is also air permeable for wearable electronics applications [66-72] by performing the air permeability test with water vapors, from our lab made setup. In our test, we have obtained the water vapor transmission rate (WVTR) of ~ 250 g m⁻² day⁻¹, which indicates better air permeability, breathability and appropriate for wearable device and sensor applications.

3.4 Conclusions

Here, in this work, we have successfully demonstrated the *in-situ* device fabrication approach to address electrode preparation approach for the morphologies like nanospheres, nanorods and nanoparticles. The δ -PVDF nanoparticles have shown good piezo and ferroelectric response. The successful EDOT to PEDOT conversion using vapor phase polymerization technique was performed, to achieve the conducting electrode layer for the final device structure. The fabricated device has further shown an excellent response, in terms of mechanical energy harvester with peak-to-peak open circuit voltage of ~ 4V and short circuit current of ~ 1.8 μ A and successfully able to the record the different types of gestures and finger bending responses. This fabrication technique provides metal free, flexible and compatible organic electrode along with the air-permeable, breathable and stretchable devices with (WVTR) of ~ 250 g m⁻² day⁻¹. Further, we have demonstrated the machine learning technique to distinguish between the different type of finger motion recognition with 94.6% accuracy that could be beneficial for prospective applications in health care monitoring and security purpose.

3.5 References

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Chapter 4

MXene-PVDF Pyroelectric Nanogenerator for Breathing Sensor and Machine Learning Applications

In this chapter, we shown the advantage of in-situ electrospinning process in alteration of PVDF dipoles in presence of MXene and further to improvise the pyroelectric response in the composite nanofibers for an excellent breathing sensor. To demonstrate this significant enhancement in pyroelectric behaviour, polarized IR and scanning probe microscopy-based technique is utilized to study the dipolar orientation of MXene ($Ti_3C_2T_x$) nanosheets within these nanofibers along with the other physical properties. Further, the fabricated pyroelectric nanogenerator is utilized successfully as breathing sensor, proximity sensor and IR data receiver, along with machine learning applications.

4.1 Introduction

The first discovery of two-dimensional (2D) graphene with excellent electrical, mechanical, energy storage and thermal properties has led to a new frontier of the existence of 2D materials [1-4]. Therefore, 2D materials are receiving significant attention due to their high electrical and thermal conductivity [5], low electrical resistivity [6], and higher thermal stability [7], including other mechanical properties. [8] In experimental practice the 2D materials are usually obtained by exfoliating layered 3D materials or bulk material, by overcoming the weak Vander Waals interaction between the layers. [9] In this sequence, several other 2D materials including metal dichalcogenides [10], layered hydroxides [11] and boron nitrides [12] etc. have also been reported by the exfoliation process from 3D/ bulk material. The first 2D transition metal carbides (MXenes) was synthesized by Naguib et al. by exfoliating their MAX phases; *i.e.* Ti₃AlC₂, Ti₂AlC as 3D precursors [13]. MXenes are basically obtained by selective etching of specific atomic 'A' layers (Group 13 and 14 elements) from their corresponding three-dimensional MAX phases in presence of few selective etchants [14]. The chemical formula of the MAX phase is $M_{n+1}AX_n$ where, 'M' implies the early transition metal (Sc, Ti, V, Zr, Hf, Cr etc.), 'A' represents Group IIIA or IVA elements, and 'X' can be either carbon (C) or nitrogen (N) element. Depending on the value of 'n', these phases are divided into 3 categories, known as M₂AX, M₃AX₂ and M₄AX₃ type with hexagonal crystal structure (space group P6₃/mmc) [15]. A typical MAX phase consists of metallic layers "A" and ceramic layers $M_{n+1}X_n$. These metallic (A) layers are chemically more active than $M_{n+1}X_n$ layers. 2D MXenes are made by removing metallic (A) layers from MAX phases by etching. The surfaces of MXene prepared in HF, are usually terminated by -F, =O and/ or -OH groups due to the high surface energy. The etching results in layers of 2D MXenes [13].

Further, the delamination process is followed to obtain the thin layer or nanosheets of 2D MXene [13,14]. The MXene exhibits exciting properties like higher light transmission, tunable electronic structure, higher flexibility, higher young modulus (~14 GPa), EMI shielding effectiveness (58,929 dB cm²/g) and better in-plane tensile strength (~436 MPa) and compressive strength [16–18]. Conductivity of these 2D MXene layers could be up to ~15000 S/cm for even 200 nm thickness layers. Due to such higher electrical conductivity, MXenes are also used as electrode material for electrochemical energy storage [19]. As per recent literatures, MXenes also exhibit strong light-matter interaction at mid-IR and Terahertz frequencies with high carrier mobility [20–22]. Therefore, these exciting electronic, thermal, and mechanical properties of MXenes under the mid-IR range could be effectively utilized for pyroelectric devices under variable thermal stimuli.

To harvest the ambient thermal energy, photothermal energy, heat and smaller temperature fluctuation, pyroelectric nanogenerators are one of the most efficient tools. The first pyroelectric nanogenerator was proposed in 2012, by Prof. Z. L. wang's group, with pyroelectric current density of 171 nA/cm³ and voltage of 22 V, in PZT films [23]. The pyroelectric effect is governed by change in spontaneous polarization in particular class of materials due to thermal fluctuation [24]. In this aspect, PVDF is one of the excellent pyroelectric materials with its nonlinear susceptibility, flexibility, mechano-sensitivity, and electroactive nature [25,26]. PVDF is a semi-crystalline polymer that has been widely explored due to its remarkable ferroelectric, pyroelectric and piezoelectric properties [27,28]. These electroactive properties are governed by the crystalline region of PVDF. Depending on the polymeric chain conformations, there are 5 different phases of PVDF known as α -

phase TGTG · (trans-gauche-trans-gauche), β -phase (TTTT), γ -phase (T3GT3G·), δ phase and ε-phase [29–31]. PVDF-MXene based coupling effect of pyroelectricity and thermoelectric is haven't been explored much. In this context, pyroelectric device of PVDF-MXene have been explored with 1D nanofibers, in the presence of IR light exposure. The practical applications of such self-powered devices and sensors could be further explored in health care sector and the security sector in terms of pyroelectric breathing sensor, proximity sensor etc [32-34]. In today's modern IoTbased lifestyle, the data obtained from such sensors and applications could be accumulated in larger amount that manual processing of such data and obtaining a concrete conclusion could be extensively tedious work. Also, the kind of patterns obtained from such sensors are often have very similar nature and complex enough to be distinguished by a normal human eye observation. Therefore, to resolve such issues one needs to take help from artificial intelligence. Machine learning is one of such strong tools to recognize and extract the smaller features and patterns and categorize in an effective manner. Therefore, also can be helpful to draw very effective conclusion from its remarkable visualization technique and to study the data in an effective manner [35-37]. For the same reason, here in this work, we have also tried to utilized supervised machine learning to identify the breathing patterns from a pyroelectric sensor, and could be beneficial for human health-care to identify the symptoms and preliminary problems related to breathing at earlier stage. Therefore, such machine learning applications with the pyroelectric sensor could provide us the edge in security applications, IoT based health monitoring, surveillance and as effective data transmission tool as strong prospective application [47].

In this work, we are reporting the excellent composite properties of PVDF-MXene nanofibers fabricated through a negative electrospinning process and reported for the first time to date. The negative electrospinning process not only alters the surface properties, including surface energy and surface potential of the composite nanofibers but also provides an excellent hydrophobic and enhanced pyroelectric response of in composite nanofiber due to thermometric and pyroelectric coupling for the device and sensor application with higher pyroelectric coefficient and ~10 times enhanced pyroelectric current. The dipolar orientation within the fibers have also been studied here by polarized FTIR and PFM. Further, the fabricated pyroelectric device has been used as a breathing sensor, a proximity sensor and ASCII-code data transmission along with machine learning applications.

4.2 Experimental Section

4.2.1 Materials

PVDF pellets (Aldrich, USA, Mw: 250,000 by GPC), N, N- dimethylformamide (DMF), Acetone (Merck, India), Max Phase Ti₃AlC₂ (Aldrich, USA), Hydrofluoric acid ((Merck, India) Dimethyl sulfoxide (DMSO, Merck, India).

4.2.2 MAX phase to MXene

To convert the MAX phase into MXene, 0.25 gm of Ti_3AlC_2 was added in 10 ml HF (10 wt%) followed by stirring for the etching process. Thereafter, it was kept for stirring at room temperature for 24 h. Further, the solution was centrifuged and washed in multiple steps at 5000 rpm. Then DMSO was used to exfoliate the MXene nanosheets and washed with DI water multiple times and later MXene powder was collected after drying the sediment. We have used the higher rpm centrifugation while washing and then the sonication process to decrease the size of these flakes.

4.2.3 Nanofiber fabrication

A solution of PVDF (Mw: 250,000 by GPC, Aldrich, USA) and N, N - dimethylformamide (DMF, Merck, India) of 12 wt% was prepared at 60 °C. In the prepared solution, 8 ml of acetone was added to the solution to obtain the final PVDF solution. To prepare the PVDF-MXene composite solution, the different (0.5, 0.75 and 1.25) wt % of etched and washed MXene was added in the PVDF-DMF solution and thereafter kept it for overnight stirring. To fabricate the fibers, the final solution was loaded in 10 ml syringe and electrospinning was performed with optimum tip-to-collector distance of 12 cm, at -20 kV with a flow rate of 0.4 mL/h. The composite nanofibers were obtained on the drum collector, with 2500 rpm, at 52 % of relative humidity.

4.3 Results and discussion

4.3.1 Crystallographic phase identification and morphology

The X-Ray diffraction (XRD) pattern of Ti₃AlC₂ (Figure 4.1(a)) confirms the presence of 312 Max phase with the reflection planes of (002), (004), (101), (103), (104) and (105) at 20 value of 9.57°, 19.2°, 34.05°, 36.79°, 39.05° and 41.86° respectively. In the inset, the field emission scanning electron microscopy (FESEM) image of the Ti₃AlC₂ MAX phase shows the initial morphology of the sample before etching. After etching the MAX phase Ti₃AlC₂ with HF, the Al layers are removed from the MAX phase and therefore stacked layers of Ti₃C₂T_x nanosheets are observed, as it can be seen in Figure 4.1(b). Further, to delaminate these stacked layers, the sample was treated with DMSO and thin layers of MXene nanosheets are obtained and can be observed in TEM images as nanosheets (Figure 4.1(c)), with the proper inter-atomic layers arrangement in HRTEM with interplanar d-spacing of ~0.256 nm (inset). The XRD spectra of the heat-treated MXene was also obtained for these flakes. The thickness of the obtained MXene nanosheets (Figure 4.1(d)) were observed in atomic force microscopy (AFM) between ~2 and 4 nm at marked point 1 and point 2, respectively. After successfully obtaining the 2D MXene nanosheets, the composite nanofibers of PVDF-MXene were fabricated in electrospinning as shown in Figure 4.1(e), with nanofiber diameter ranging from ~100 - 190 nm with on an average diameter of ~120 nm. In transmission electron microscopy (TEM), fiber diameter of the range of ~40 -60 nm was observed in Figure 4.3. The FFT analysis of PVDF-MXene composite nanofiber confirms the aligned distribution of nanofibers along with the degree of orientation plot, which shows that the majority of the fibers are orientated at -65° with vertical axis (inset Figure 4.1 (e) and 4.2).



Figure. 4.1 (a) The X-ray diffraction pattern of Ti_3AlC_2MAX phase. Inset shows the FESEM image of the MAX phase Ti_3AlC_2 (scale bar ~1 um). (b) FESEM image of HF etched $Ti_3C_2T_x$ sheets with multiple stacked layers (scale bar ~200 nm). (c) Delaminated layers of 2D MXene nanosheets (scale bar ~50 nm). The inset shows the HR-TEM image with inter-planar spacing of 2D MXene nanosheets (scale bar ~2 nm). (d) AFM image of 2D MXene flakes with different thickness marked as point 1 and 2 with ~2 nm and 4 nm, respectively (scale bar ~500 nm). (e) FESEM image of fabricated PVDF-MXene nanofibers. (Scale bar ~1 um). The inset shows the TEM image of single nanofiber (scale bar ~50 nm). X-Ray diffraction pattern of PVDF-MXene nanofiber.

The FESEM of the PVDF-MXene nanofibers shows successful incorporation of MXene in PVDF Matrix (Figure 4.3 (b,c)). Further, to identify the electroactive phases present in PVDF-MXene composite material, the XRD spectra of composite nanofiber was recorded and the reflection planes of (110 / 200) for the electroactive β -phase is observed.



Figure. 4.2 Histogram of aligned PVDF-MXene fibers. The inset shows the FESEM of aligned fiber and the colormap shows the radial distribution plot.



Figure. 4.3 TEM images of PVDF-MXene aligned composite fibers at scales (a) 2 μ m (b) 50 nm (c) 20 nm.



4.3.2 Piezoresponse force microscopy (PFM) topography and spectroscopy

Figure. 4.4 PFM response of neat PVDF nanofibers. (a) Phase (b) Amplitude image, of neat nanofiber in lateral (LFM) and vertical (VFM) mode, respectively (scale bar ~ 0.5 μ m). (c) V-PFM hysteresis and butterfly loop of PVDF nanofibers.

Further to analyze the nanoscale properties of PVDF-MXene nanofibers, scanning probe microscopy was performed. The PFM phase and amplitude response, in terms of topography and spectroscopy was recorded for neat PVDF (Figure 4.4) and PFM topography phase response shows that the dipoles are uniformly distributed from 180° to 180° in case of L-PFM (Figure 4.4(a)) with smaller amplitude change (Figure 4.4(b)). A similar in response in case of V-PFM (Figure 4.4(a)) with better amplitude change for V-PFM in Figure 4.4(b)). However, in case of PVDF-MXene nanofibers the response are enhanced as it can be seen in Figure 4.5. It shows the lateral and vertical piezoresponse force microscopy (PFM) phase image response of PVDF-MXene composite Nanofibers. From the phase contrast, it can be observed that in case of lateral PFM response (L-PFM), the degree of molecular dipole orientation within the nanofibers, could be varying from ~-180° to 180°. While, the Vertical phase response (V-PFM) image demonstrates that the molecular dipoles within the

nanofibers are predominantly aligned in vertical direction with ~-180° orientation to the electric field than that of orientation observed in L-PFM. The amplitude images of L-PFM and V-PFM (Figure 4.4(b)) also verify that deformation in PVDF-MXene nanofibers is random for L-PFM and unidirectional in case of V-PFM. Thus, one would expect the proper spectroscopy response for V-PFM of these Nanofibers. In consistency with our observation in images, while performing the PFM spectroscopy measurement, proper hysteresis (phase) and butterfly (amplitude) loop opening was also observed for PVDF-MXene Fibers. While, there was negligible L-PFM spectroscopy response was observed for PVDF-MXene fibers. In particular, for vertical piezoresponse (Figure 4.5(c)), as the positive external DC bias was applied to the AFM probe, the dipoles within the fibers starts aligning itself in the negative phase direction and crosses over the critical positive coercive voltage (V_c+) to attain a saturation phase value of ~-80°, at maximum applied positive bias.



Figure 4.5 PFM response of PVDF-MXene nanofibers. (a) Phase and (b) Amplitude image of composite nanofiber in lateral (LFM) and vertical (VFM) mode, respectively. (c) V-PFM hysteresis and butterfly response of the composite nanofiber.

Further, follows the similar switching behavior as the negative external bias with a highest phase saturation value of $\sim 100^{\circ}$ after overcoming the negative coercive voltage (V_c -). The obtained hysteresis loop confirms the presence of the ferroelectric nature in the composite fiber PVDF-MXene fiber. The evidence of converse piezoelectric effect was obtained in terms of butterfly loop. As the external positive bias was applied with AC tip voltage, the loop opening was observed as the bias value crosses the positive coercive field (V_c+) and reaches to the maximum deformation of \sim 150 pm and the contraction takes place, as the bias is decrease and attains it minimum amplitude value. A similar response was obtained for the applied negative bias with max deformation of ~ 210 pm. This expansion and contraction in the loop shows the proper piezoelectric nature of the PVDF-MXene composite nanofiber and hence the butterfly loop is achieved. This behavior is expected due to the inherent piezoelectric behavior of the PVDF and not contributed from the MXene as it does show any piezoelectric or ferroelectric properties by itself. Further, it is important to mention that the lateral spectroscopy response has shown no prominent changes. Since, the dipoles within the nanofiber are mostly aligned in the vertical direction as it can be also seen from the phase images. The maximum d_{33} value of the PVDF-MXene nanofiber was calculated \sim -26 pm/V, with the help of obtained butterfly loop [38-40].

4.3.3 FTIR and X-ray photoelectron spectroscopy study

Further, the FTIR spectroscopy of PVDF-MXene composite and PVDF nanofiber was performed to verify the presence of electroactive phases present in nanofibers. Firstly, in terms of electroactive phase identification, it can be observed that PVDF nanofibers (Figure 4.6(a), lower panel) are predominantly consisting of the β -phase (1275 and 840 cm⁻¹) with a slight amount of electroactive γ -phase and non-electroactive α -phase.



Figure 4.6 (a) Polarized FTIR spectroscopy of PVDF-MXene (upper panel) and PVDF (lower panel) nanofibers in perpendicular and parallel modes. (b) XPS profile of PVDF-MXene (upper panel) and PVDF nanofiber (lower panel) representing (b) C 1s (c) F 1s region.

The addition of MXene in PVDF results further in increase of β -phase (1275 cm⁻¹) band intensity with and decrease in γ -phase of the PVDF-MXene nanofiber (Figure 4.6(a), upper panel). Secondly, to further analyze and quantify the molecular dipolar orientation within the nanofibers, the FTIR spectroscopy in parallel and perpendicular IR modes were recorded. During this measurement, fiber stretch axis in electrospinning is considered as z-axis and considered parallel to IR beam for polarized FTIR measurement. To identify such changes under change in IR polarization, one need to first identify the different vibrational transition dipole moments μ of PVDF, that exists within the unit cell, defined as B₂($\vec{\mu} \parallel \vec{a}$), A₁($\vec{\mu} \parallel \vec{b}$) and B₁($\vec{\mu} \parallel \vec{c}$) as defined in literature. These transition dipoles can be correlated with different vibration mode and peak intensity observed at position 1275 cm⁻¹ and 840 cm⁻¹ for A₁, 1075 and 1400 cm⁻¹ for B₁, and 1182 and 884 cm⁻¹ for B₂, respectively [27,41]. In case parallel mode measurements (Figure 4.6(a), upper panel) for PVDF-MXene nanofibers, the intensity of B₁($\vec{\mu} \parallel \vec{c}$) and B₂($\vec{\mu} \parallel \vec{a}$) vibration bands increase

significantly, corresponding to peak position 1075 & 1400 cm⁻¹ and 1182 & 884 cm⁻¹, respectively. While in case of perpendicular mode IR measurements, the intensity of A₁ ($\ddot{\mu} \parallel \ddot{b}$) vibrational bands increase corresponding to peak position 1275 cm⁻¹ & 840 cm⁻¹. This observation indicates that the -CH₂ and -CF₂ dipoles are oriented perpendicular to fiber chain axis, in case of PVDF-MXene fibers.

On the other hand, in case of neat PVDF fibers the changes in perpendicular and parallel IR modes are very similar (Figure 4.6(a), lower panel). It indicates that dipolar orientation within the neat PVDF nanofibers is much random and non-coherent with respect to PVDF-MXene nanofibers. Therefore, it can be concluded that the dipoles within PVDF-MXene fibers are in a perpendicular direction to the chain axis, which is prominently consistent with the observation in PFM, with major dipoles aligned in vertical direction to the chain axis as demonstrated from PFM phase image.



Figure 4.7 XPS spectra of C 1s (a) Max phase (b) MXene. Ti 2p spectra of (c) Max phase (d) MXene. UPS spectra of (e) Max phase (f) MXene.

Further to verify the chemical entities present in the Max phase and MXene, the X-ray photoelectron spectroscopy (XPS) was performed. The differences in bulk phase and 2D MXene can be clearly identified by the XPS spectra (Figure 4.7). The Max phase shows the presence Ti, Al, C in the XPS spectra. After etching the MAX phase and delamination, by converting into MXene, one can see the prominent changes in C 1s spectra (Figure 4.7(a,b)) and Ti spectra (Figure 4.7(c,d)) with only two peaks, without any presence of Al. This also supports the successful etching to convert into $Ti_3C_2T_x$ nanosheets, with some amount of F element seen in the XPS. This might be due to the HF, which was used for etching; as a result, fluorine group is also visible there. After obtaining the successful MXene, we have incorporated in the PVDF solution to make the PVDF-MXene based nanofibers. From the XPS spectra (Figure 4.6(b) and 4.6(c)), the changes in PVDF nanofibers are observed in the XPS, for neat PVDF and after addition of MXene. In XPS, for C 1s, it can be seen (Figure 4.6(b)) that the -CH₂ and -CF₂ are present in the neat PVDF in with a peak intensity of 1:1 (lower panel, Figure 4.6(b)), as in PVDF molecular chain, both groups have similar contribution in terms of the chemical environment. Further, in XPS spectra of PVDF-MXene, the prominent changes can be seen in C 1s spectra, with presence other C peak in -CH₂ region and slight shifting in the whole C 1s spectra. This shifting is due to the interfacial interaction between the PVDF and the MXene, i.e. $Ti_3C_2T_x$. For the F 1s present in the PVDF, a single F peak is observed. While in PVDF-MXene fiber for F 1s, a similar shifting is observed in the spectra as of C 1s (upper panel, Figure 4.6(c)), due to the PVDF-MXene interaction. The slight changes in F spectra is due to the MXene functional group (-F) appeared due to HF treatment, with smaller peak appeared around \sim 684 eV, in composite fiber.



Figure 4.8 Chemical interaction schematic between the (a) $Ti_3C_2T_x$ nanosheets and (b) PVDF molecular chain within the (c) PVDF-MXene nanofiber, through (d) H-bonding formation between functional groups of $Ti_3C_2T_x$ nanosheets and $-CH_2$ group from PVDF.

The XPS results conclude the successful incorporation of MXene in PVDF. The possible interaction model is demonstrated in Figure 4.8 (a-d), which represents the possible hydrogen bonding between the functional group ($T_x =$ -F, -OH, -O) of MXene nanosheets and -CH₂ from PVDF molecular chain. Further, to analyze the changes in the density of states (DOS) and Fermi energy levels, the UPS spectra of PVDF and MXene-PVDF sample was also performed (Figure 4.7 (e,f) and Figure 4.10 (a)). It can be observed PVDF-MXene, containing of conducting MXene, has higher DOS closer to the Fermi edge than that of neat PVDF fibers, with highest occupied molecular orbitals (HOMO) with a band edge of ~ -3.47 eV. while, in case of neat PVDF fibers, the DOS are much below from the Fermi level with a HOMO band edge of ~ -4.67 eV. These changes in UPS spectra of the composite nanofibers further confirms the presence and effect of addition of MXene in the PVDF-MXene, we have further preformed the hydrophobicity test on PVDF and PVDF-MXene nanofibers

(Figure 4.10(b)). It has been observed that the incorporation of MXene in PVDF nanofibers increases the hydrophobicity of PVDF-MXene fibers. It can due the presence of increment of amount of -F group in the matrix, which is responsible for the hydrophobic nature. This result indicates that this composite fiber could be used as water-repellent fiber with efficient device applications.

4.3.4 Temperature-dependent impedance spectroscopy

Further, the impedance spectroscopy of the neat PVDF nanofiber (Figure 4.9) and the PVDF-MXene composite was performed for a variable temperature range of 30 °C to 160 °C at different frequencies, viz. 1 kHz, 10 kHz, 50 kHz, 100 kHz and 1 MHz. For the PVDF-MXene composite nanofibers (Figure 4.10(c)), the dielectric constant ~17 and loss of ~0.2 observed at room temperature. The addition of MXene has mediated the increase in dielectric constant value of the composite nanofiber in comparison to neat PVDF. Further, it can be noticed that dielectric constant and dielectric loss value increases with temperature up to a certain temperate at a particular frequency. This increase can be explained by the effect of the molecular relaxation process under the effect of the temperate as the polymer chain would have more thermal enthalpy to govern the relaxation process.



Figure 4.9 Dielectric (a) constant and (b) loss tangent of PVDF neat fibers.



Figure 4.10 (a) UPS spectroscopy study of PVDF and PVDF-MXene. (b) Water hydrophobicity test (c) Dielectric constant and loss of PVDF and PVDF-composite nanofibers at different frequencies with increasing temperature.

But after a certain temperature, the thermal vibrations become much more predominant at higher frequencies and results in hindering the dielectric polarization process within the material [42,43]. Therefore, the dielectric constant decreases and increases the dielectric loss value. This particular behavior observed in dielectric nature is like ferroelectric to paraelectric transition in PVDF-MXene composite. Also, from the dielectric study spectra, one can observe that the dielectric transition in PVDF-MXene fibers occurs at a much higher temperature range than the neat PVDF fibers. It shows the higher operating range for the composite system suitable for pyroelectric applications for wide range of thermal fluctuations after incorporation of MXene.

4.3.5 Pyroelectric energy harvesting

Since, 2D materials, including MXene shows very prominent thermal conductivity and thermal properties, therefore we have tried to utilize the thermal properties of MXene based PVDF nanofibers in a pyroelectric nanogenerator. Therefore, a pyroelectric nanogenerator was fabricated as mentioned in the device fabrication section. The basic mechanism of pyroelectricity (Figure 4.11(a)) is based on the rate of change of temperate with time (thermal fluctuations) at a particular instant in a ferroelectric or pyroelectric material. In the initial condition, at dT/dt = 0, when no thermal fluctuations are provided, the spontaneous dipoles within the device remains at equilibrium, hence no current flow is there. As the external stimuli, in terms of thermal fluctuation is provide, i.e; dT/dt > 0, it causes the net effective polarization in a certain direction and decrease in the spontaneous polarization occurs. As a result, the no. of bound changes decreases at the electrode surface. To overcome this change, the redistribution of charge flow takes place in the device circuit and as a result we obtained the pyroelectric current in a particular direction. Similar, when the provided thermal fluctuation is in such a condition that dT/dt < 0, then the net effective polarization phenomenon takes place as result of increase in spontaneous polarization and as a pyroelectric current in reverse direction can be seen w.r.t the earlier condition. Through this simple mechanism, the pyroelectric current can be obtained through a pyroelectric device. A similar mechanism is represented in Figure 4.11(a), for a vivid understanding. As per the experimental procedure is concerned, the thermal fluctuations were provided to the device from the PHILIPS IR bulb (150 W) and responses including temperature profile (ΔT), rate of change of temperature (dT/dt), pyroelectric open circuit voltage (V_{OC}) and short circuit current (I_{SC}) was recorded [32,34,44].



Figure 4.11 (a) Mechanism of pyroelectric device as a result of rate of change of temperature with time. (b) Pyroelectric (i) temperature input response and (ii) rate of change of temperature with time. Pyroelectric open circuit voltage (V_{oc}) and short circuit current (I_{sc}) response of Neat PVDF (c) PVDF-MXene Nanofibers. (d) Response time (τ) plot for PVDF-MXene device (inset shows the response time for negative pyroelectric signal.

The pyroelectric response of neat PVDF nanogenerator was recorded in terms of ΔT (Figure 4.11(b-i)), with its derivation as dT/dt (K/s) (Figure 4.11(b-ii)), peak to peak V_{oc} of ~ 130 mV (Figure 4.11(b-iii)) and peak to peak I_{sc} of ~ 60 pA (Figure 4.11(b-iv)) at 0.1 Hz frequency. This pyroelectric response of the device was further increased when PVDF-MXene fiber-based device was exposed to the thermal fluctuations. The thermal fluctuation gradient was obtained with $\Delta T \sim 10$ K (Figure 4.11(c-i)), with its derivation as dT/dt (K/s) (Figure 4.11(c-ii)). The peak-to-peak pyroelectric V_{oc} response of PVDF-MXene device was found to be ~2.5 V (Figure

4.11(c-iii)) with I_{sc} of ~ 632 pA (Figure 4.11(c-iv)) at 0.1 Hz frequency. This obtained pyroelectric current is ~ 10 times higher than the device with neat PVDF. The effective increase in pyroelectric current and voltage in composite fiber system is governed by thermal properties of MXene and strong interaction with mid-IR region with smaller emissivity. These two basic properties of MXene are responsible the increment in pyroelectric response of this composite pyroelectric device. The pyroelectric coefficient of the PVDF-MXene device was found $\sim 130 \text{ nC/Km}^2$, which is much higher the device only made up of PVDF neat fibers (Table 4.1). Further, it is also observed that the response time (Figure 4.11(d)) for fabricated PVDF-MXene nanogenerator is very faster, with response time of 112 ms for a pyroelectric device for forward pyroelectric current and 116 ms for reverse direction (inset Figure 4.11(d)). The reason for enhancement in pyro response could be explained by the confinement phenomenon. As the thermal fluctuations are applied to the PVDF-MXene nanofibers, the effectively induced polarization due to pyroelectric effect is more prominent, unidirectional and perpendicular to the fiber axis, due to the unidirectional molecular dipolar orientation and 1D confinement in during the electrospinning process, within the fabricated PVDF-MXene nanofibers. It evident from the polarized FTIR and the PFM phase image of PVDF-MXene nanofibers. The confinement of MXene within the nanofibers restricts the random dipolar orientation in the device plane. However, the molecular orientation within the neat PVDF fibers are confined but not unidirectional, as it can be observed in polarized FTIR and PFM image that the dipoles are randomly aligned within the fiber. Therefore, the response pyroelectric response obtained from the neat PDVF is not as much higher as of PVDF-MXene fibers. Also, the higher IR sensitivity and low emissivity properties of MXene adds up further to obtain a better pyroelectric response in PVDF-MXene based pyroelectric device.

4.3.6 Pyroelectric breathing sensor, proximity sensor and IR data receiver

In terms of healthcare applications, it is realized that the PVDF-MXene sensor can be utilized as an excellent pyroelectric breathing sensor. The breathing response of a person could provide several critical information about the cardiac and pulmonary conditions. The symptoms could be recorded in terms of faster breathing, exhausted breathing, shortness of breath or hyperventilation, which be having different patterns of breathing. The different kind of breathing nature could also monitored in different terms including the air inhale and exhale process from nose, rise and fall motion of abdomen, from the thoracic cavity and with a plethysmograph [33,45]. Here to record the breathing sensor response from our pyroelectric sensor, we have followed the air inhale and exhale process from the temperature gradient obtained between the breathing process.

S.N.	Active Material	Pyroelectric Coefficient (nC m ⁻² K ⁻¹)	References
1.	PVDF-GO Nanofibers	27	48
2.	PVDF-MWCNT nanofibers	60	49
3.	PVDF nanofibers	62	50
4.	PVDF-CH ₃ NH ₃ PbI ₃ nanofibers	44	51
5.	PVDF-MXene nanofibers	130	This work

 Table 4.1 Comparison of pyroelectric coefficients for PVDF composite-based pyroelectric devices.

For such small-scale thermal fluctuations in the breathing process, the fabricated device is highly sensitive to record such pyroelectric response. This device was placed

on the inner layer of the mask to record such lower thermal fluctuations in terms of breathing. The response obtained for the breathing signal had the similar nature (Figure 4.12(a)) as that of a pyroelectric signal from device. It indicated that response is generated due to the exhaling and inhaling process during breathing, which is causing the change in temperature in the device. The normal breathing response was obtained with respect to the real-time. The breathing rate was obtained ~ 14 breaths/ per minute. This breathing rate is consistent with the expected normal breath rate for a human being, which could be from ~ 12-16 breaths/ per minute.

S. N.	Active Material	Response time	References
1.	ZnO/perovskite-heterostructured	53 µs	52
2.	Sb-ZnO nanobelts	12.7 s	53
3.	ZnO Nanowires	0.8 s	54
4.	PVDF- CH ₃ NH ₃ PbI ₃ nanofibers	1.14 s	51
5.	PVDF-MWCNT nanofibers	1.48 s	49
6.	PVDF-MXene nanofibers	112 ms	This work

Table 4.2 Comparison of response time (τ) for PVDF composite based pyroelectric devices.

These results demonstrated the ability of the PVDF-MXene pyroelectric device to quantify the breathing rate of a normal and exhausted breathing of a person and helpful in diagnosing preliminary early-stage cardiac and pulmonary problems. This measurement demonstrates the successful utilization of PVDF-MXene sensor for health care monitoring.

In the next application part of the PVDF-MXene sensor, we have successfully shown its response as a proximity sensor. To demonstrate the application as a proximity sensor, it was placed at different variable distances from the IR source and the proximity signal was recorded in terms of the voltage obtained (Figure 4.12(b)). It was noticed that the device could detect the various distances from the IR source with three different regions marked as S_1 , S_2 and S_3 . From the plot, it can be observed that if IR source is much closer to device (distance < 2m) then the response lies in region S_1 , showing the exponential nature. As the distance between device and the source is increased above 2 cm, the response of the device is more like a linear region from 2-6 cm (region S_2). Further, as the distance increased between source and sensor goes above 8 cm, then the device response has another linear region with steeper slope (region S_3) for the proximity sensor. This analysis shows that the depending on the distance between IR source and sensor the proximity response could lie either of these regions and the sensitivity could vary rapidly or slowly depending the region of interest.



Figure 4.12 (a) The normal breathing response of pyroelectric sesnor data. (b) Proximity sensor response plot of the PVDF-MXene pyroelectric device. (c) IR thermal fluctuation based remote ASCII-code transmission with PVDF-MXene pyroelectric sensor.

Thus, from the above observation, the sensitivity of this proximity sensor could be defined for 3 different regions. This remarkable proximity detection property of PVDF-MXene pyroelectric sensor is another successful demonstration of the utilization of this device for technological and security purpose application.

In the next application, we have used this device as remote ASCII-code transmission detector from PVDF-MXene sensor. For this purpose, the IR signal detection was performed with PVDF-MXene sensor in a particular pattern. To detect a specific word, firstly that particular word is broken down into alphabets (Figure 4.12(c)). Then IR response is recorded in term of ASCII code for that particular alphabet. The IR signal detection in device is recorded in terms of "ON" and "OFF". To co-relate the obtained response with binary system, here "ON" is represented as "1" and "OFF" represents as "0", in reference to the binary codes. In this manner, the response for each single alphabet was recorded and converted in binary number system. Each set of obtained binary combination represents a single ASCII code and could be decoded as a particular English alphabet. In later step, on combining these alphabets in the recorded/received sequence, one can easily find the whole meaningful word. Therefore, this coding and signal processing combination could be used as successful ASCII-code transmission in remote areas with PVDF-MXene sensor as a IR signal detector. This proposed methodology with pyroelectric sensor could also be useful for the places, where there is no medium present to transmit or communicate, i.e.; space. Thus, this pyroelectric IR sensor could be useful to transmit/communicate the messages including the remote locations.



Figure 4.13 (a) Schematics for ML algorithm. Confusion matrix obtain from (b) Random forest (c) logistic regression (d) Support vector machine and (e) K-nearest neighbor. Here, 0 represents the breathing response after exercise (exhaustive breathing), while 1 represents normal breathing response.
4.3.7 Machine learning prediction for pyroelectric breathing sensor

Further, to quantify our results in better manner and validate our pyroelectric sensor for advanced application purposes, we have performed the machine learning algorithm on our obtained pyroelectric sensor data (Figure 4.12(a)). For this, we have taken the breathing response as pyroelectric sensor data in two different cases. In one case, the normal breathing response is recorded before exercise and in another case, the breathing response is recorded after the exercise. In both cases, the breathing response recorded from the pyroelectric sensor would be different as it is expected, because of the different breathing rate. In case of normal breathing, the breath rate is obtained \sim 14 breaths/ min, while in case of breathing after exercise, the breath rate is quite higher \sim 30 breaths/ min. Also, the response of the breathing peaks would be different in case of after exercise than the normal condition. Based on these two factors, we have selected these pyroelectric sensor data for machine learning applications to distinguish a response between before and after exercise breathing single.

4.3.8 PVDF-MXene pyroelectric breathing sensor data processing

The proposed machine learning algorithm in this work could predict whether the provided pyroelectric sensor dataset is from normal or exhausted breathing, based on two input features: time and voltage. The sensor data was collected using the PVDF-MXene pyroelectric sensor by placing it under the breathing mask to capture breathing patterns and the recorded data was preprocessed further using min-max scaling to normalize the range of input features. The stepwise procedure is mentioned below.



Figure. 4.14 Area under the ROC Curve (AUC) for each of used algorithms (a) Random forest (b) logistic regression (c) Support vector machine and (d) K-nearest neighbor.

4.3.8.1 Data Collection

The data was collected using pyroelectric sensor that was designed to measure the time and voltage of breaths. The sensor was placed under the mark to capture the breathing patterns of individuals.

4.3.8.2 Data pre-processing

Once the data was collected, it was pre-processed to ensure that it was in a suitable format for machine learning analysis. In this case min-max scaling is applied. Minmax scaling involves rescaling the range of input features, so that they all have the same minimum and maximum values. This is done by subtracting the minimum value of each feature from each value in that feature and then dividing by the range of that feature (i.e., the difference between its maximum and minimum values). The result is that all features will have a range of values between 0 and 1.

4.3.8.3 Model Selection and Training

After the data was pre-processed, four different machine learning algorithms were selected and trained on the sensor dataset. These algorithms were Logistic Regression (LR), K-Nearest Neighbors (KNN), Support Vector Machine (SVM), and Random Forest (RF). Further, this training algorithm was optimized for each model to predict whether breathing data was normal or exhausted breathing type based on the input features of time and voltage.

To develop the machine learning (ML) algorithm, numerous datasets of sensor data was generated and then prepossessed to predict the breathing phenomenon. After preprocessing the datasets, it was separated into training and test data and thereafter the models were trained with 4 types of algorithms as mentioned in section 4.3.9. [36,37,45-47]

4.3.9 Machine Learning Algorithms

The following algorithms are used for pyroelectric sensor data processing

4.3.9.1 Logistic Regression

Logistic Regression is a statistical method used to analyze and model the relationship between a dependent variable and one or more independent variables. It is used for classification problems, where the dependent variable is categorical.

$$\sigma(z) = \frac{1}{1+e^{-z}}$$
 (4.1)

where, z is a linear combination of the input features x_i and their respective coefficients w_i then-

$$z = \sum_{i=1}^{n} w_i x_i + b \tag{4.2}$$

Here, $\sigma(z)$ is the sigmoid function, which transforms the output of the linear combination of input features into a probability between 0 and 1. The model predicts the class of an input based on whether the probability is above or below a certain threshold.

4.3.9.2 K-Nearest Neighbor

K-Nearest Neighbor is a non-parametric machine learning algorithm used for classification and regression problems. In the KNN algorithm, the input is classified based on the majority vote of its k-nearest neighbors in the training set.

For a given new data point x, KNN finds the k nearest training data points based on a distance metric, such as Euclidean distance:

$$(x_i x) = \sqrt{\sum_{j=1}^k (x_{ij} + x_j)^2}$$
(4.3)

where, p is the number of features and xij is the jth feature of the ith training data point. The class of the new data point is then determined by the majority class among its k-nearest neighbors.

4.3.9.3 Support Vector Machine

Support Vector Machine is a supervised learning algorithm used for classification and regression problems. It separates the data points in feature space by finding the best hyperplane that maximizes the margin between the two classes. The SVM model finds the hyperplane with the largest margin by solving the following optimization problem-

$$min_{w,b}\frac{1}{2} \|w\|^2$$
 subject to $y_i(w^t x_i + b) \ge 1$ for all $i = 1, ..., n$ (4.4)

Here, w is the weight vector, b is the bias term, and yi is the class label of the ith training data point.

4.3.9.4 Random Forest

Random Forest is an ensemble learning algorithm used for classification and regression problems. It combines multiple decision trees to improve the accuracy and robustness of the model. Each decision tree in the Random Forest is trained on a random subset of the training data and a random subset of the features. The class of a new data point is then predicted by taking the majority vote of the classes predicted by all the trees in the forest.

The Random Forest model can be represented as:

$$y = mode\{T_1(x), T_{12}(x), \dots, T_m(x)\}$$
(4.5)

where, \vec{y} is the predicted class, T_i is the ith decision tree, and m is the number of trees in the forest.

The performance of these ML modes was evaluated using four different metrics: recall, precision, F1 score, and accuracy. Based on the input features, these metrics were used to predict how well each model could classify between normal and exhausted breathing. Based on the performance metrics, it appears that the Random Forest (RF) (*Figure 4.13(b)*) and K-Nearest Neighbor's (KNN) (*Figure 4.13(e)*) models performed the best in predicting normal vs. exhausted breathing, with high scores for recall, precision, F1 score, and accuracy. The Logistic Regression (*Figure 4.13(c)*) and Support Vector Machine models (*Figure 4.13(d)*) also performed reasonably well, but had slightly lower scores overall. The KNN algorithm has a very high recall and precision score, which suggests that it is able to correctly identify and classify a large proportion of the positive instances in the dataset. Additionally, KNN has a very high F1 score, indicating that it is able to balance precision and recall well. However, KNN's accuracy score is slightly lower than that of Random Forest, meaning it has a slightly higher number of misclassifications than Random Forest. However, the Random Forest algorithm has the highest accuracy score, indicating the fewest overall errors in its predictions. Random Forest also has very high precision and recall scores, indicating that it is able to correctly classify both positive and negative instances with a high degree of accuracy. The F1 score of Random Forest is also better, indicating that it is able to balance precision and recall well. The Support Vector Machine (SVM) algorithm (*Figure 4.13(d)*) also performs relatively well, with a high precision score indicating that it correctly classifies a high proportion of the positive instances.

 Table 4.3 Comparison of LR, KNN, SVM and RF model recall, precision, F1 score and accuracy.

Model Name	Recall	Precision	F1 Score	Accuracy
Logistic Regression (LR)	75.39	75.21	75.30	75.40
K-Nearest Neighbor (KNN)	98.62	98.50	98.50	98.60
Support Vector Machine (SVM)	82.14	84.69	83.40	83.20
Random Forest (RF)	98.20	98.19	98.23	98.20

However, SVM's recall and F1 scores are somewhat lower than those of KNN and Random Forest, indicating that it may miss some positive instances in the dataset. Finally, the Logistic Regression algorithm (Figure 4.13(c)) appears to perform poorly across all four metrics, with relatively low scores for accuracy, precision, recall, and F1 (Table 4.3). This suggests that Logistic Regression may not be the best choice for this data classification. Figure 4.13(c) shows that of the 1803 records in the dataset considered exhaustive breathing cases, 1366 were correctly predicted and 437 were misclassified. This means that the number of correctly predicted rows (true positives, or TP) is 1366 and the number of misclassified rows (false negatives, or FN) is 437. On the other hand, 1366 rows were projected properly as false negatives (TN), while 545 were incorrectly labeled as positives (FP), out of a total of 1638 records labeled as normal breathing. It demonstrates how TP and TN were computed in a similar fashion for all possible outcomes in Figure 4.13(b-e).

Further, to evaluate the performance of the proposed models, AUC (Area under the ROC curve) for each model was also calculated. The ROC curve is a graphical representation of the trade-off between a binary classifier's true positive rate (TPR) and false positive rate (FPR). The AUC is area under ROC curve that provides the measure of the classifier's ability to distinguish between the positive and negative classes. In Figure 4.14(a-d), the AUC values provide an additional measure of the performance of each of the machine learning algorithms that has been tested. Here, AUC of 0.5 indicates random guessing, while an AUC of 1 indicates perfect classification. An AUC value between 0.5 and 1 indicates varying degrees of performance, with higher values indicating better performance. Based on the accuracy, precision, recall, and F1 values shown in Table 4.3, it can be concluded that the K-Nearest Neighbors (KNN) and Random Forest (RF) models had the highest AUC values, indicating better performance compared to the other models. This provides additional evidence that these models could be the best choice for predicting normal vs. exhausted breathing for the pyroelectric sensor dataset. Based on these results, it can be concluded that K-Nearest Neighbors and Random Forest models could be the most effective algorithms in identifying the breathing nature based on the input features.

4.4 Conclusions

In conclusion, we have successfully fabricated PVDF-MXene nanofiber based pyroelectric nanogenerator with enhanced pyroelectric response in pyroelectric current with I_{sc} of ~ 632 pA, with ~10 times increment and voltage of ~ 130 mV, followed by high pyroelectric coefficient of $\sim 130 \text{ nC/Km}^2$. The piezoresponse force microscopy (PFM) study has validated the unidirectional dipolar orientation, perpendicular the molecular chain axis within the composite nanofibers, with piezoelectric coefficient value of \sim -26 pm/V. The fabricated pyroelectric sensor could be utilized as an excellent pyroelectric breathing sensor with breathing rate of ~14 breaths/min, proximity sensor with 3 different sensitivity regions, which could be advantage for advanced position co-ordinate-based sensing applications and as ASCII-code IR data receiver for practical applications to send the messages in remote locations. Further, to utilize the enormous amount of device/sensor data successfully with an effective outcome, we have proposed machine learning algorithms to distinguish and recognize the different type of breathing signals with ~ 98 % accuracy with KNN and RF machine learning models, for health-care monitoring and earlystage disease detection purposes.

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Chapter 5

Solvent Phase Poling in Ferroelectric Polymer for Thermal Energy Harvesting

In this chapter, we have designed and demonstrated *in-situ* electrical poling process in PVDF film-based system to perform a comparative study with the post-poling process. It is observed that the *in-situ* prepared electroactive PVDF films under corona discharge, can be achieved under lower electric field ~1.5 MV/m, than the electric field required in traditional post poling process. Further, we have studies about different physical parameters along poling time, to explore the optimum poling duration for maximum electroactive phase and surface potential. The resulting film was further used to demonstrate the thermal energy harvesting application as pyroelectric nanogenerator.

5.1 Introduction

Ferroelectric polymer like PVDF and its copolymers are promising dielectric soft materials which has excellent mechanical properties, chemical stability, flexibility, and processability along with their piezoelectric, pyroelectric and ferroelectric properties. Due to these properties, PVDF is also renowned for its potential applications as mechanical and thermal energy harvesters, memory applications, wearable sensors for e-skin electronics and for membrane and ferroelectric porous materials [1-7]. PVDF is a semicrystalline polymer with crystalline and amorphous regions. It is notable that the piezo-, pyro and ferroelectric are contributed from the crystalline region of this polymer. There are five different polymorphs of PVDF known as α , β , γ , δ and ϵ -phase. In these, α and ϵ -phases are non-polar and not electroactive in nature. However, the β , γ , δ -phase of PVDF are polar and electroactive phase of PVDF, which governs the piezo, pyro and ferroelectric properties [8-12]. In order to achieve the polar phase and electroactive properties in PVDF different processing techniques are adopted, including electrospinning, mechanical stretching, high temperature annealing, spin coating, electroforming, LB method, and high electrical poling. These processing approaches have their own advantages and disadvantages. However, the processing techniques which involves the poling steps results with higher mechanical and thermal sensitivity for piezo- and pyroelectric properties [13-15]. Therefore, poling in ferroelectric polymers are one of the important requisites to obtain the enhanced polarization and ferroelectric properties in the material [16,17]. It has been also observed in literatures that under high DC field (~ 100 MV/m) application across the PVDF film at a certain temperature above the crystalline transition, one can obtain the well-oriented electroactive phase or better dipolar orientation in PVDF. However, the exposure of

such higher electric field strength during process poling can also cause the dielectric fatigue and breakdown of the samples [18, 19]. Therefore, it makes the process quite tedious and complex to achieve a proper electroactive film. To overcome this issue, we have proposed the in-situ poling and simultaneous film preparation of PVDF film under corona poling at a certain temperature. This simultaneous process would require lesser electric field as it would lesser free energy to reorient the dipoles in the direction of electric field due the solvent phase corona poling.

Therefore, in this work, we have demonstrated the in-situ poling approach by solvent casting of the PVDF solution under corona. To validate this possibility, we have casted PVDF solution under corona discharge to induce the electroactive phase in PVDF under lower electric field (~ 1.5 MV/m), which is ~ 60 times lower than the field required in traditionally adopted post poling process. Further, we have done performed the in-depth study of the change in surface potential and chemical behavior of the in-situ prepared PVDF films through KPFM and XPS study. Further to study the effect of oxygen radical and corona poling time, the UPS study is further performed to observe the changes in binding energy and density of the states of the poled films. The obtained poled films are further utilized to demonstrate the thermal energy harvesting application with the metal and PEDOT:PSS electrodes for a comparative study.

5.2 Experimental section

5.2.1 Materials

PVDF pellets (Aldrich, USA, Mw: 180,000 by GPC), N, N- dimethylformamide (DMF), Methylethylketone (DMAc, Merck, India).

5.2.2 In-situ PVDF film preparation

Initial stock solution 6 wt% of PVDF pallets (Mw: 180,000 by GPC, Aldrich, USA), dissolved in N, N- Dimethylformamide (DMF) was prepared by stirring it at 80 °C for 6 hours. After obtaining the homogeneous solution, MEK was added in the same volume amount and was further kept for stirring for next 4 hours at 60 °C. Thereafter, the solution was dropcasted on the glass slide (2×2 cm²) and kept inside the poling chamber at 80 °C, under corona for different time intervals. For comparison, one film was prepared in the same condition without any external filed exposure, as control sample.

5.2.3 In-situ electrical poling

After optimizing the parameters like electric field strength, solvent, and poling temperature with several sets of samples, in this work, the final electrical poling was performed inside corona poling with an electric field strength of 1.5 MV/m at 80 °C. The grid was held between the sample and the corona poling needles at 5 kV. The casted samples on conducting substrates were exposed under corona in the chamber for different time intervals.

5.2.4 Device fabrication

To fabricate the piezoelectric and pyroelectric energy harvester of these films, the final film was chosen with highest electroactive phase content (i.e. film at 60 min) prepared in 3×1 cm² shape. The electrodes were prepared on film with silver paste. Then both side electrodes were connected to the copper wire. Another set of the device was also fabricated by doing plasma treatment on both side of the PVDF film and then making the electrodes with PEDOT:PSS. So, the two different devices were

obtained, one with Ag electrode and another with PEDOT electrode to perform the comparative study between both the electrodes.

5.3 Results and discussion

5.3.1 Morphology and IR spectroscopic study

The in-situ prepared samples under corona poling were further examined in FESEM for changes in morphologies. In case of controlled sample, the films were prepared without application of any electric field in same chamber at 80 °C. Now onwards we would be calling it as unpoled film. If we compare the unpoled and poled films obtained after 60 min time interval, we can observe that the unpoled film doesn't have any circular microstructures (Figure 5.1(a)) in the FESEM images, while the poled film can be spotted with multiple microstructures (Figure 5.1(b)) on the film after the corona exposure. These spots could have formed due to the exposure highly charged ions and oxygen containing radicals on the surface during corona process, and have resulted the microstructures on the surface of PVDF sample. In the subsequent study, during the AFM topography of these two films, we have observed in the case of unpoled film (Figure 5.1c), that fibrils like structures over PVDF spherulites are present there when there is no corona is exposed while the film formation. However, in case of poled films, the fibril structure diminishes and shows more flatten surface with smaller spherulite size (Figure 5.1(d)). This image could provide a quick overview of the morphology of poled and unpoled sample. The change in spherulite size can be explained by the change in electroactive phase of the film, as previous literatures have shown that different electroactive phases have different kind of spherulites in PVDF.



Figure 5.1 FESEM image of (a) unpoled (b) poled film (60 min) films. AFM amplitude error image to show the proper contrast between (c) unpoled and (d) poled image (inset shows the height image) (scale bar \sim 5 µm).

Further, we have also performed the FTIR and XRD measurements of the PVDF films obtained at different time intervals and observed that there are not much significant changes in XRD spectra of these films and showing the electroactive γ -phase in each case poled case. However, in FTIR study one can observe the changes in normalized intensity of the peaks ~ 762, 795 and 855 cm⁻¹ (Figure 5.2(a)). The changes in FTIR intensity are due to the to change in molecular orientation of dipoles within the PVDF crystal, while film formation during in-situ electric field exposure. One can observe that the increment in peak at ~ 762 cm⁻¹. However, we don't see the first peak in XRD at 17.6° peaks in poled films.



Figure 5.2 FTIR Spectra of PVDF poled samples at different time intervals at 0 (unpoled), 10, 20, 30, 45, 60 and 120 min. (a) for region 720 - 930 cm⁻¹ (b) for region 855 - 920 cm⁻¹.

Therefore, it can be concluded that the changes ~ 762 cm⁻¹ peak during poling confirms the rise of poled alpha (i.e. δ -phase) of PVDF. This observation is consistent with the other results as we obtained much better piezoelectric and pyroelectric response in comparison to the unpoled films. So, it rules out the possibility of increment of non-electroactive phase after poling. Further, we have observed the enlarged region of FTIR spectra (Figure 5.2(b)) from 855 – 920 cm⁻¹ and it can be seen that there is significant shifting in the peak ~ 880 cm⁻¹. The peak has shifted to lower wavenumbers for poled samples in comparison to the unpoled sample. The shifting in this vibration band could be due the change in orientation of dipole moment caused by the electrical poling. Therefore, shifting in FTIR bands also indicates the poling effect in the sample.

To demonstrate the effect of in-poling in further detail, we have performed a systematic study of the poled samples for different time intervals. Here for the AFM

study, we have represented the amplitude error images, instead of only height images (inset) to properly visualize the changes in the topography of poled samples with time. The AFM study, amplitude error image along with the inset height image (Figure 5.3(a-f)) shows the effect of corona exposure on PVDF spherulites. We can observe that (Figure 5.3(a)) at initial state the spherites and fibril structure were properly visible in sample. However, as time progressed for corona poling, firstly the fibril structures on the PVDF spherulite starts disappearing (Figure 5.3(a-c)) and we start seeing the surface more flatten on spherulite (Figure 5.3(d-e)) and the further exposure not only diminishes the fibrils but also destroys the PVDF spherulites (Figure 5.3(f)) for 120 min poling. Therefore, this time dependent topography study suggested few more important factors during poling process to be noticed apart from the electroactive phases signature in FTIR and XRD.



Figure 5.3 AFM amplitude error image to visualize the morphology changes in the film with poling exposure time during in-situ poling process (scale bar ~ 5 μ m).



Figure 5.4 KPFM images of the in-situ poled films to study the change in surface potential with time during in-situ poling process (scale bar $\sim 5\mu m$).

This topography study demonstrates the importance of poling time in a sample, if all other factor such as electric field strength, temperature and poling distance are take similar. After a time in destroys the spherulites of the PVDF film. Also, there can be noticed that as the electric field exposure is provided the size of spherulites are much smaller than the earlier time. It implies two important things into consideration. Firstly, the relation of spherulite size relation with electroactive phase. Also, the nucleation growth of spherulite is minimized as the poling time is increased as it can be observed (Figure 5.3(a-f)).

5.3.2 KPFM and XPS study

To understand this phenomenon in better way and to co-related it with the high voltage exposure, we have also performed the KPFM study of these films (Figure 5.4(a-f)). From the KPFM image, we can observe the surface potential trend in the corona poled films. As the poling time is increasing, the max potential difference on PVDF film is increasing up to a certain time interval (till 90 min). However, after 90 min, the further exposure of corona poling drastically decreases the potential difference from the initial value. Also, it can be noticed that as the poling time is

increasing, the negative potential is increasing significantly. It could be due the fact that the exposure of electric field is aligning the dipoles in such a way that the negatively charged group (possibly F) is oriented outside the surface on the PVDF film. Therefore, as the exposure time increases, the alignment reaches more in upward direction causing more negative potential due to fluorine. But after a certain exposure time there can be observed the drastic change in surface potential with very less potential difference. The reason behind this change could be due the fact that the highly charged corona causes a significant amount of defluorination in the PVDF molecular chain, causing the overall effective change in the surface potential for longer exposure. Therefore, it should be noticed that the poling time has its importance in terms of how long a sample should be kept for poling on a certain parameters. Therefore, apart from poling voltage and temperature, the poling exposure time is also important parameter for the ferroelectric polymers as it plays crucial role for obtaining electroactive properties as well as the surface potential change, which could be also useful for single triboelectric materials.



Figure 5.5 XPS Spectra of the in-situ poled films to demonstrate the changes in the chemical entities of Carbon 1s with time during in-situ poling process.



Figure 5.6 Possible pathways of corona poling originated radical interaction with fluorine and hydrogen, in PVDF molecular chain.

Further to study the changes in the chemical composition in the in-situ poled PVDF films, the XPS of each sample was performed. During the XPS study, we have observed two major changes in the poled films. In the first case, for poled samples, we have observed other peaks apart from C 1s and F 1s peak in XPS. There were extra peaks were observed for oxygen and some other carbon content in poled samples. The presence of other carbon species in C 1s can be seen significantly from Figure 5.5(b-f) at the binding energy of 284.6 eV. The origin of this peak can be explained by the bond breaking and new bond formation phenomenon over the PVDF molecular chain due to oxygen radicals. The possible chemical reaction due to corona expose and oxygen radical interaction, can be predicted as mentioned in Figure 5.6. Due the corona treatment there is a chance to replace atoms from either from the -CF₂- group or from the -CH₂- group (mentioned as route a and route b here) as it leads to the formation of the -C=O groups formation, due to which one can see the presence of other carbon species in C 1s XPS spectra. There radicals and ions are highly active, there they break the carbon-hydrogen bond easily and form a species with carbon as making double bonds. As reported by an earlier research group [20], where the

possible pathways of another bond formation due to active radical interaction occurs (Figure 5.6). Therefore, we see a new carbon peak around 284.6 eV, apart from the - CH₂- and -CF₂- groups, which are usually present in the PVDF sample. Another new peak was observed in XPS in the in-situ poled PVDF films was due to the oxygen. These oxygen peaks are arising due active oxygen radicals and ions, which are present in the corona poling setup during the corona discharge and due to high corona exposure, we find the presence of oxygen in poled samples. However, this presence of oxygen is not prominent in unpoled sample. Therefore, the possibility of the presence of oxygen species is caused by the corona discharge process in the poling setup, as it can be seen by the above possible radical reactions.



Figure 5.7 (a) Changes in oxygen content (b) Normalized UPS spectra to study the changes in binding energy (c) Measured Surface potential value (d) Relative Change in $E-E_f$ value extracted from UPS spectra, of the poled films at different time intervals.

Now, the presence of extra carbon and oxygen content in the poled samples are quantified (Figure 5.7(a)) in proper manner to understand the role of in-situ poling process and its effect on the chemical composition of the polymer chain. Here in, we have plotted the relative oxygen and carbon peak (~ 284.6 eV) area vs time. It can be seen that for C fitted curve that the content of ~ 284.6 eV peak increases with time up to first 25 minute (Figure 5.7(a)) and thereafter it starts decreasing and completely decreases after a certain time interval. However, in case of oxygen, we can find the trend is similar to carbon but the gaussian curve has more FWHM in comparison to carbon, and follows a similar behavior and decreases around 80 min and further exposure diminishes presence of both the species with longer time. In Figure 5.7(b), we have shown the surface potential measurement through a macroscopic process here apart from local KPFM (Figure 5.4). In case of macroscopic surface potential measurement, the negative gaussian tread can be observed. It is suggested up to a certain time interval, the surface potential of the sample starts getting more negative under corona exposure. The reason behind this could be due the orientation of negatively charged groups towards the top surface of the sample, as this nature is consistent with the observation noticed in KPFM study. However, after a time (~ 45 min), the negative behavior of surface potential starts diminishing and further reaches to less negative state, it could due the fact that after longer exposure, the defluorination process starts taking place. As a result, the negative potential starts vanishing and thereafter comes a point where the surface potential behavior is almost similar (in magnitude) to the unpoled sample and it would also diminish the response of pyroelectric nanogenerator.

5.3.3 UPS spectra of poled and unpoled samples

In further study, we have also performed the UPS spectra of these samples. In UPS spectra, we have presented here the selective sample for the comparative study to

present the trend of the of change in the binding energy after the in-situ poling treatment (Figure 5.7(c)). For each sample the binding energy $(E-E_f)$ difference varies with the poling time of the sample. It also indicates that the poling is affecting the distribution of density of states (DOS) on the surface, for different poling time of samples. After plotting (Figure 5.7(d)) the difference $(E-E_f)$ of the binding energy in all cases, it can be seen that the difference in energy value decrease up to a certain interval of ~ 25 min and there after it starts following the similar pattern as of the surface potential with attaining the negative gaussian and further reaches to max value of ~ 5.3 eV for 60 min poled sample and further comes down to the difference as unpoled sample. This behavior of the curve suggests a strong co-relation of the surface potential curve at macroscopic level. So, we can conclude that the behavior changes the DOS of states and the difference in binding energy is occurring due the same reason of orientation of fluorine towards the surface followed by the defluorination process. After thorough analysis of the effect of *in-situ* poling under corona discharge, the suitable poling exposure windows is estimated \sim 45-60 min at 80 °C, for obtaining the maximum response of the electroactive phase under proper poling. Therefore, the poled film (with higher electroactive phase response) and unpoled film sample were taken for further study for pyroelectric energy harvesting application.

5.3.4 Woking principle of pyroelectric nanogenerator



Figure 5.8 Schematic of the pyroelectric nanogenerator for effective polarization change under different thermal stimuli inputs (a) no temperature change (dT/dt = 0) (b) heating (dT/dt > 0) (c) cooling (dT/dt < 0).

To demonstrate the mechanism of the pyroelectric nanogenerator, the schematic (Figure 5.8) is shown, where the change in effective changes polarization vector can be observed under different thermal stimuli. At the initial condition ((Figure 5.8(a)), when there is no temperature change (dT/dt = 0), all the dipoles are aligned in one direction, with the lesser angle difference between the dipoles and polarization axis, with no effective current in the circuit at equilibrium condition. However, when thermal stimuli is provided in terms of infrared (IR) light (dT/dt >0), the temperature increases and the spontaneous dipoles within the pyroelectric material starts wiggling back and forth around the main polarization axis (Figure 5.8(b)), with the higher deflection angle between the main axis and dipoles. As we know that the thermal input would affect the molecular motions within the material, resulting the motion of molecular dipoles under thermal fluctuations. This phenomenon results in decrease in the overall spontaneous polarization and the reduction in induced surface charges on the electrode. Therefore, a current flow can be seen in the circuit to maintain the charge imbalance over the electrode. Now, when the thermal stimuli is removed/off (dT/dt > 0), the oscillation of the molecular dipoles reduces having a smaller angle with respect to main polarization axis ((Figure 5.8(c)), and an increase in over polarization vector can be seen [25]. Therefore, the increase in induced charges at the electrode causes a current in the reverse direction to balance across the electrode and finally to achieve the equilibrium state under no external stimuli.

5.3.5 Pyroelectric energy harvesting

To harvest the thermal energy, two different pyroelectric devices were made up with two different electrodes. In one case, the Ag electrode was used to fabricate the device while in another case, PEDOT:PSS electrode was utilized to fabricate all organic PVDF pyroelectric nanogenerators.



Figure 5.9 (a,c) Temperature change profiles (b,d) rate of change of temperature, of the Ag electrode and PEDOT:PSS electrode based pyroelectric nanogenerator response, respectively.

Further, to record the pyroelectric response the thermal fluctuations were given to the device from IR bulb at 0.1 Hz frequency and respective change in temperature of the device is recorded. In case of Ag electrodes, one can observed the change in temperature is maximum ~ 4 °C (Figure 5.9 (a)), with the rate of change of temperature ~ 1.5 K/s (Figure 5.9 (b)). However, in case of PEDOT:PSS electrode, the change in temperature (Figure 5.9 (c)) can be observed ~ 14 °C with the rate of change of ~ 4 K/s (Figure 5.9 (d)). These results implies that the PEDOT electrodes has higher absolute temperature and faster rate of change of the temperatures with respect to the Ag electrodes. The reason behind this phenomenon could be due to crucial factor that the metal electrodes have a much higher reflective surface, therefore it does not take all the IR heat in, and also due to higher thermal

conductivity, it cools down as soon as it is heated up. On the other hand, in the case of PEDOT, the maximum IR light passes in the non- refelective surface and gives better heating response and therefore, gives large increment in temperature of the device. Also, the compatibility of PEDOT electrodes with PVDF film is much better after depositing it successfully in comparison to the metal electrodes [20].

Due to this enhancement of the PEDOT electrodes over the Ag electrodes for temperature input, the pyroelectric open circuit voltage and short circuit current data were also recorded for the poled sample with Ag and PEDOT electrodes based pyroelectric device for proper comparative study. In first case (Figure 5.10 (a)), we have tried to record the pyroelectric response of unpoled sample with Ag electrode and the response current response has very noisy response (Figure 5.10 (a-i)), with small voltage of \sim 5 mV (Figure 5.10 (a-ii)). Since, this device was unpoled sample, therefore the dipole alignment within the sample in not proper and not much contribution from electroactive response of PVDF.



Figure 5.10 Open circuit Voltage (V_{OC}) and short circuit current (I_{SC}) of (a) PVDF unpoled-Ag (b) PVDF poled-Ag (c) PVDF poled PEDOT:PSS, electrode-based pyroelectric device response.

Therefore, there was no significant pyro response was obtained for unpoled samples. However, in case of the poled sample with Ag electrode, the pyroelectric response of device was much better and significant in comparison to unpoled sample. For the poled pyroelectric device, the open circuit voltage of ~ 856 mV (Figure 5.10 (b-i)) with short circuit current of ~ 1 nA (Figure 5.10 (b-i)) for poled PVDF film with Ag electrode. Later, when we recorded the pyroelectric response of poled sample with PEDOT electrodes then multifold current and voltage increment was obtained. The obtained pyroelectric voltage ~ 4 V (Figure 5.10 (c-i)) with current of ~ 3.1 nA (Figure 5.10 (c-ii)) for PEDOT coated electrode on the over the poled PVDF film. This response is consistent with the observation for faster and enhanced heating response of PEDOT, with respect to the metal electrodes (Figure 5.9) for the same IR light input parameters. This comparative study indicates that non-reflective all organic electrode are more compatible with PVDF for pyroelectric response than the metal electrode based devices, with higher pyroelectric coefficient and figure of merit. Therefore, these pyroelectric devices based on PEDOT could be extremely useful for very lower thermal fluctuation energy harvesting and sensing purposes [21-25].

5.4 Conclusions

The solution casted PVDF films was successfully obtained under corona poling process and the electroactive phase was obtained at ~ 60 times lower (~ 1.5 MV/m) electric field strength than the field required in traditional post poling process. We could conclude that the poling duration plays a crucial role to facilitates the electroactive phase this particular electric field strength and also alters the functional groups in main polymer chain with oxygen and additional carbon species, due to the corona exposure and radical formation. The UPS study confirms the effective changes

in surface potential and the associated density of states (DOS). The optimum poling duration is observed between ~ 30-50 min to identify the prominent changes in surface potential of PVDF film. The resulting film was further used to demonstrate the thermal energy harvesting with two different types of electrodes to perform the comparative study and found that the pyroelectric nanogenerator response with PEDOT:PSS electrodes works much better in comparison to the metal electrodes with higher pyroelectric current (~ 3 nA) and voltage (~ 4 V) response. The PEDOT electrode based nanogenerator is able to detect the thermal fluctuations effectively.
5.5 References

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Chapter 6

Summary and Future Perspective

This chapter includes the brief summary of potential findings of each chapter in thesis and further have shed light on future perspective of this work.

6.1 Summary

In this chapter, we present the essential findings of the research work performed in this thesis. The primary focus of this research work was to explore the advantage of *in-situ* poling pathways in ferroelectric polymers, through which the nucleation of electroactive phases in polyvinylidene fluoride (PVDF) can be controlled under a lower electric field than the typically required field strength for the *ex-situ* process. The research work includes the different chapters addressing the *in-situ* processing and electroactive phase nucleation phenomenon, the physical properties study at nanoscale, valuable optimization insights and their applications as piezoand pyro-electric nanogenerators followed by different kind of self-powered sensors. A part of thesis also provides valuable insights about machine learning advantages of self-powered sensor data for real life applications. This final chapter presents the summary of the overall findings, highlights and key outcomes of this research work.

Chapter 1

This Chapter includes the broad and basic introduction of piezoelectric and pyroelectric materials followed by the detailed discussion of requirement of electric field application on such materials. The chapter further includes the different methodology used for such polymers to achieve the electroactive phases in PVDF and its composite materials. The last part of this chapter presents the discussion about piezoelectric and pyroelectric nanogenerators and their applications in various fields as self-powered device and sensor.

Chapter 2

In summary of this work we conclude that the δ -phase comprising PVDF nanoparticles are possible to accomplish through the electrospray process under 0.1MV/m of the electric field. The ferro- and piezo-electric response of δ -PVDF nanoparticle is evident from phase and amplitude responses in PFM under the sweeping voltages, respectively. The piezoelectric coefficient (d_{33}) was obtained ~ -11 pm/V, which is competitive to that of the β -phase. The thermal study indicates that the δ -phase has relatively lower melting temperature than the α -phase. In addition, the ferroelectric to paraelectric like phase transition is also observed that determines the wider device operating temperature range, i.e., up to 165 °C. The δ -phase transformation in the electrospray process can be predicated by the kink propagation model. The δ -PVDF nanoparticle comprised PNG has shown a very prompt response with an output voltage of ~2.6 V and ~1 μ A of open circuit current, along with the power density of 930 μ W/m² under ~4.5 N of the force amplitude. Aside from that \sim 2.75 V/Pa of the acoustic sensitivity is also pave the way to harvest the mechanical energy from environmental noises as well. The PNG can also be utilized as a selfpowdered pressure sensor with a pressure sensitivity of ~23 mV/kPa for higher pressure regions and $\sim 80 \text{ mV/kPa}$ for lower pressure regions with a resolution of ~ 50 Pa for the realistic pressure mapping sensor applications.

Chapter 3

Here, in this work, we have successfully demonstrated the in-situ device fabrication approach to address electrode preparation approach for the morphologies like nanospheres, nanorods and nanoparticles. The δ -PVDF nanoparticles have shown good piezo and ferroelectric response. The successful EDOT to PEDOT conversion using the vapor phase polymerization technique was performed, to achieve the conducting electrode layer for the final device structure. The fabricated device has further shown an excellent response, in terms of mechanical energy harvester with peak-to-peak open circuit voltage of ~ 4V and short circuit current of ~ 1.8 μ A and successfully able to record the different types of gestures and finger bending responses. This fabrication technique provides metal-free, flexible and compatible organic electrodes along with air-permeable, breathable, and stretchable devices with water vapor transmission rate of ~ 250 gm⁻² day⁻¹. Further, we have demonstrated the machine learning technique to distinguish between the different type of finger motion recognition with 94.6% accuracy that could be beneficial for prospective applications in health-care monitoring and security purpose.

Chapter 4

In conclusion, we have successfully fabricated PVDF-MXene nanofiber based pyroelectric nanogenerator with enhanced pyroelectric response in pyroelectric current with Isc of ~ 632 pA, with ~10 times increment and voltage of ~ 130 mV, followed by high pyroelectric coefficient of ~ 130 nC/Km². The piezoresponse force microscopy (PFM) study has validated the unidirectional dipolar orientation, perpendicular the molecular chain axis within the composite nanofibers, with piezoelectric coefficient value of ~ -26 pm/V. The fabricated pyroelectric sensor could be utilized as an excellent pyroelectric breathing sensor with a breathing rate of ~ 14 breaths/min, a proximity sensor with 3 different sensitivity regions, which could be advantage for advanced position co-ordinate-based sensing applications and as ASCII-code IR data receiver for practical applications to send the messages in remote locations. Further, to utilize the enormous amount of device/sensor data successfully with an effective outcome, we have proposed machine learning algorithms to distinguish and recognize the different type of breathing signals with \sim 98 % accuracy with KNN and RF machine learning models, for health-care monitoring and early-stage disease detection purposes.

Chapter 5

To study the in-situ electrical poling feasibility in PVDF film-based system, we have performed a comparative study with the post poling process. To validate this possibility, we have prepared solution casted PVDF films under corona discharge to induce the electroactive phase in PVDF under lower electric field (~1.5 MV/m), which is ~ 60 times lower than the field required in traditionally adopted post poling process. The effective poling at this electric field strength is also dependent on the poling duration that facilitates the presence of oxygen and additional carbon species as observed in XPS study. Consequently, the UPS study confirms the effective changes in surface potential and the associated density of states (DOS). The optimum poling duration is observed between 30-50 min to identify the prominent changes in the surface potential of PVDF film. In comparative study we observed that the pyroelectric nanogenerator response with PEDOT:PSS electrodes works better in comparison to the metal electrodes with higher pyroelectric current (~ 3 nA) and voltage (~ 4 V) response. Thus, we affirmed that this in-situ poling and solution casting approach could be one of the potential approaches to achieve electroactive PVDF film for piezo- and pyroelectric based device fabrication.

Chapter 6

This chapter presents the summary and future perspective of this thesis work.

6.2 Future Perspective

Here we would like to discuss about the prospective aspects of this thesis, where the findings of the thesis could be beneficial in terms of scientific progress as well as for the futuristic applications. I would like to mention these points –

- a) The proposed in-situ δ -phase processing technique in lowest possible electric field till date (~ 0.1 MV/m), will open new alternate methodologies to fabricate other δ -phase nanostructures at lower field, which is much more beneficial and effective than the traditional approach. Also, in terms electroactive phase, it has given the opportunity to explore PVDF in different directions for ferroelectric applications, which was so far limited till β/γ phases only. Since, the recent literature suggest the δ -phase can exhibit the equivalent/better ferroelectric and piezoelectric behavior than that of β -phase. Further, regarding real-life application, these nanostructures can be potentially beneficial for bio-medical applications including Alzheimer's therapy.
- b) The vapor phase polymerization technique is extremely useful for fabricating *in-situ* electrodes on complex nanostructures, including nanofibers and nanoparticles. Also, the electrode preparation through this technique doesn't require the any surface modification. Therefore, it provides huge advantage for the fabrication of flexible all-organic nanogenerators as biocompatible wearable sensors.
- c) The demonstrated Machine Learning approach on the large-scale breathing sensor and gesture monitoring dataset, would be extremely beneficial to predict the origin of source of such signal output for early-stage healthcare

monitoring as preliminary observation. It would work as next-generation advanced tool for pattern recognition for security purposes from the obtained sensor data.

d) The *in-situ* corona poling process with solution phase poling at 1.5 MV/m provides advantage over the traditional phase nucleation approach in poling at ~ 60 times lower than typically required field strength. The time-dependent study in this work demonstrates the proper poling exposure time limit for maximum surface potential and proper dipolar orientation in PVDF films. The change is surface potential suggests that these poled films can also be utilized for uni-material triboelectric application. These fabricated electroactive films can also be helpful for memristor applications.

[Vita]



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-Varun Gupta