Mechanical and Thermal Energy Harvesters for Selfpowered Wearable Electronics

HARI KRISHNA MISHRA

A thesis submitted for the partial fulfillment of

the degree of

Doctor of Philosophy (Science)





Institute of Nano Science and Technology (INST)

Knowledge City, Sector-81, Mohali-140306, India

&

Indian Institute of Science Education and Research (IISER)

Knowledge City, Sector-81, Mohali-140306, India

August 2023

Dedicated to my beloved family and respected

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. 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 acknowledgement 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.

Hari Krishna Mishra

(Ph.D. Student)

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

Date

Dr. Dipankar Mandal

(Thesis Supervisor)

Associate Professor (Scientist-E)

Institute of Nano Science and Technology, Mohali, India

Acknowledgments

First of all, I would like to express my heartfelt thanks to all the individuals who helped me throughout my PhD tenure. This doctoral dissertation thesis is possible with the support of several people in different areas of my research work throughout the last few years.

First and foremost, I would like to express my deepest gratitude to my principal advisor, **Dr. Dipankar Mandal**, for his guidance, continuous encouragement, support, meticulous care and constructive feedback. His immense knowledge, plentiful experience and enthusiasm for research have encouraged me at all times to approach academic research from a translation point of view. I consider it a great opportunity to pursue my doctoral program under his guidance and to learn from him. I would also want to thank for his unwavering support, patience, belief and understanding during the ups and downs of the research process. I thank him again to be a good mentor and kind person that helped me to keep up in many stages of my Doctoral journey.

I would like to extend my gratitude to my Doctoral committee members **Dr. Kiran Shankar Hazra** and **Dr. Ramendra Sundar Dey** for critically reviewing my research progress and giving me insightful suggestions and motivation.

I would like to express thanks to my research collaborators Prof. Debabrata Patra, Dr. Chandan Bera, and Dr. Tridib Kumar Sinha for their continuous support, help and suggestions. I consider it as a great opportunity to learn from their expertise.

I would also like to express my sincere thanks to Dr. Sujoy Kumar Ghosh, Dr. Kuntal Maity and Dr. Krittish Roy for their invaluable suggestion and feedback on my research and for always being so supportive of my work.

I would like to extend my sincere thanks to my senior colleagues Dr. Palwinder Singh, Dr. K. Justice Babu, Dr. Arti, Dr. Nandan Ghorai, Dr. Rohit Varshney, Dr. Mujeeb Alam and Dr. Rakesh Mishra, who inspired me in many aspects of my PhD journey. Their inspiring and right attitude of academic excellence and intellectual curiosity motivated me to strive for advanced standards and to push beyond my limits.

I would like to thank all of my fellow lab mates: Varun Gupta, Pinki Malik, Zinnia Mallick, Anand Babu, Ajay Kumar, Dalip Saini, Bidya Mondal, Sudip Naskar, Utsa Sarkar, Dr. Dipanjan Sengupta and Dr. Ujjal Das for their constant love, support, encouragement, and discussions. I will always feel glad to remember the late-night work in the laboratory and all the fun that we had among them throughout my PhD journey.

Furthermore, I would like to express my deepest gratitude to all my INST friends and batchmates for their support and love throughout my PhD journey.

Completing a PhD thesis can be a daunting task, but with the support of good roommates (Mr. Himadri Shekhar Roy and Ms. Silky Bedi), it was made easier. I would like to express my deepest gratitude to my best roommates, who have been my companions and friends during this journey. I am extremely grateful to both of you for the delicious food you cooked for me at any time. Their presence in my life has been a source of joy and inspiration. I am grateful for the countless times you cheered me up, made me laugh, and provided a home away from home. I am grateful for their love, patience, and understanding, and I will always cherish the memories we have shared.

Last but not least, I would like to thank my spiritual pillar of strength-my parents: Shri Pramod Kumar Mishra and Smt. Kanti Mishra. Their love, guidance, and sacrifices have been the foundation of my success, and I am forever grateful for everything you have done for me. Your guidance and mentorship have been invaluable, and I will always treasure the lessons that I have learned from you. I am eternally grateful for their selflessness, their boundless love, and their enduring belief in me. Without them, this achievement would not have been possible. Their presence in my life has been an irreplaceable source of strength and inspiration.

Quantum Materials and Devices Unit Institute of Nano Science and Technology Knowledge City, Sector-81, Mohali-140306, India (Hari Krishna Mishra)

Date

Abstract

The flexible, wearable, portable and wireless electronics have triggered the demand of sustainable and renewable energy sources. It has been found that mechanical and thermal energy sources are most ubiquitous and abundant in our surroundings which would be possible to harvest for building up self-powered wearable electronics. To fabricate mechanical and thermal energy harvesters, ferroelectric materials have centered crucial attention due to their inherent piezo- and pyro-electric properties. In particular, nanoscale energy harvesters, namely nanogenerators have shown the potential to harvest tiny mechanical motion or thermal fluctuation that has broadened their applicability as self-powered sensors and expanded the spectrum of applications in the healthcare sector. Therefore, the present thesis is primarily focused on the development of mechanical and thermal energy harvesters for self-powered electronics. Then some of their real-time applications in the healthcare sector have been also demonstrated. In this context, we report an approach to nucleate the electroactive phase in poly(vinylidene fluoride), (PVDF) by incorporating silver carbonate (Ag₂CO₃) nanomaterial that shows the ability to harvest mechanical energy. We found that the inter-fragment, non-covalent, intermolecular interactions between PVDF and Ag₂CO₃ are responsible for a stable electroactive phase in the PVDF/Ag₂CO₃ composite. We have demonstrated that a flexible piezoelectric nanogenerator (FPNG) comprising of PVDF/Ag₂CO₃ nanocomposite has an excellent electrical output response (i.e., 15 V and 6 µA, under the imparting force of 7 N) mechano-sensitivity (Sm ~ 45 mV/kPa), and acoustic signal detection (S_{acou} ~13 V/Pa). Furthermore, it has also shown the ability to recognize human gestures.

Furthermore, we have introduced a nanoprecipitation technique to machinate PVDF nanoparticles (NPs) with a predominant piezoelectric delta (δ) phase (which is the least studied

phase till date) using the bi-solvent phase separation technique. It is noteworthy that the δ -phase of PVDF possesses excellent piezoelectric properties which are comparable to β -phase, nevertheless, it has been rarely explored because of its ultra-high electric field (~MV/m) based processing conditions adopted so far. In this context, solvent-based phase separation approach is the most convenient and thus expected to be an industrially viable approach to scale up piezoelectric δ -PVDF nanoparticles which have enormous technological and commercial merits. As a proof of concept, a flexible piezoelectric nanogenerator (FPNG) was fabricated comprising of δ -PVDF nanoparticles. The FPNG shows the ability to track the physiological signal such as arterial pulse detection which indicates the potential utility of δ -PVDF nanoparticles (NPs) based self-powered sensors and actuators.

In continuation with earlier work, we have realized that aqueous processable piezoelectric ink would be the viable approach for large-area printable device fabrication. In this connection, we have employed polydopamine (PDA) and polyethylenimine (PEI) i.e., PDA-PEI to coat the surface of PVDF NPs, which ensures the well-aqueous dispersion. Then, we fabricated a flexible piezoelectric nanogenerator (FPNG) which shows a promising electrical output as a mechanical energy harvester. It also promises physiological signal detection abilities due to superior mechanoacoustic behavior. Furthermore, FPNG has shown excellent photo-detection and piezophototronic properties under light illumination and mechanical stimuli. Thus, it is expected that the PDA-PEI coated δ -phase comprising PVDF NPs can be utilized as a piezoelectric ink for flexible optoelectronic devices.

We have also considered the 2D chalcogenide material due to the emerging piezo- pyro and ferro- electric properties. In this context, monoelemental chalcogenide i.e., tellurium (Te) (group-VI A element) is selected for our study due to its superior heat transfer rate that exhibits

unprecedented pyroelectric response from 2D Te nanosheets. It promises an excellent pyroelectric coefficient (p ~ 3000 μ C m⁻² K⁻¹) and figure of merits (FOMs) (F_i ~ 2.4 nC m/J and Fv ~ 54 m^2/C). The unprecedented pyroelectric coefficient is found to be more than 8 folds higher than well-known pyroelectric ceramics e.g., lead zirconate titanate ($p \sim 347 \ \mu C \ m^{-2} \ K^{-1}$). Thus, it is concluded that 2D Te is the potential candidate for thermal energy harvesting to use as a self-powered electronic device. The piezoelectric functionality of 2D Te is also studied by scanning probe microscopy-based techniques that are validated by theoretically as well. Finally, we have prepared a flexible piezo,- and pyro,- electric nanogenerator comprising PVDF/Te polymer nanocomposite. The fabricated piezo- and pyro-electric nanogenerator (HyNG) has shown an excellent mechano-sensitivity (Sm ~ 148 mV/kPa) that enables it to harvest very minute mechanical deflections and also able to sense human gestures from very tiny movements, e.g., eye blinking, elbow bending, kneed bending and finger bending. In conclusion, selfpowered flexible piezo,- and pyro,- electric nanogenerators have great potential to power smallscale devices and wearable electronics where the need of external power sources could be possibly avoided.

Quantum Materials and Devices Unit Institute of Nano Science and Technology Knowledge City, Sector-81, Mohali-140306, India (Hari Krishna Mishra)

List of Figures

Figure	Title	Page No.
1.1	Demonstration of various types of renewable energy sources.	4
1.2	Schematic diagram of wearable and portable self-powered devices and	6
	their applications.	
1.3	Magnitude of power and its corresponding applications. Macroscale	7
	energy is for powering a city and even a country; nanoscale energy is to	
	power tiny small electronics. Both applications are measured by	
	different characteristics.	
1.4	Schematic view of nanogenerators, classified into three major areas,	9
	namely, self-powered sensor/system, blue energy and micro/nano	
	energy systems with their representative applications.	
1.5	Schematic representation of (a) direct piezoelectric effect and (b)	11
	indirect piezoelectric effect.	
1.6	Piezoelectric nanogenerator based on ZnO NW array (a) mechanical	15
	deflection given by atomic force microscopy enabled conducting tip,	
	(b) schematic demonstration of nanogenerator design, (c) zig-zag	
	electrode and four types of nanowires, (d) generation of piezoelectric	
	potential when NW I and II realizes the mechanical deflection and (e)	
	when NWs touch the surface of adjacent teeth.	
1.7	Schematic demonstration of rapid development of piezoelectric	16
	nanogenerators in last few-years.	
1.8	Schematic representation of PVDF polymer (a) polymeric chain and (b)	18
	corresponding unit cells of polymorphs.	
1.9	(a) Schematic illustration to achieve electroactive phase from non-	19
	polar α -phase in PVDF and (b) current state-of-art of piezoelectric	
	nanogenerator-based research publications. (c) schematic of materials,	
	structures and applications of flexible piezoelectric nanogenerators	
	(PNGs).	

- (a) Schematic view of piezo-catalysis mechanism of PVDF/MoS₂ film
 (b) corresponding degradation of organic dyes (Acridine Orange (AO), Ethidium Bromide (ET), Eosin 23Y (EO) and Rhodamine B (RHO)) with time under ultrasonic bath mechanical vibration, (c) principal diagram of dye degradation with zinc oxide nanorods (ZnO) and (d) UV-visible absorbance spectra for dye degradation with time under mechanical vibration (e) probable mechanism of organic dye degradation and ROS generation in the presence of piezoelectric material BaTiO₃/PDMS, (f) UV-vis absorbance spectra for Rhodamine B dye degradation and (g) digital image representing the color of dye changes from pink to complete transparent after 120 min due to piezo-catalysis.
- 1.11 Schematic diagram showing the coupling among piezoelectric, 25 semiconducting and photoexciting material with their diverse spectrum of applications.
- **1.12** Representation of experimental set used to measure the performance of photodetector based on ZnO micro/nanowire. The I-V characteristics of photodetector (b) under dark and various light illumination with excitation intensity of 2.2×10^{-5} Wcm⁻². (c) with various compressive strains 28 under dark condition (d) with light illumination under variable strains from ~ -0.36 % to 0.36 % (e) variation in photocurrent with variable strains and (f) responsivity under different strains and illumination intensities.
- 1.13 Schematic demonstration of ultraflexible piezoelectric energy harvesting devices integrated on 1-μm thin parylene substrate. (a) Ultraflexible ferroelectric polymer transducer (UFPTs) are used for various parameters of physiological signal monitoring for healthcare when attached to the human skin. (b) attachment of UFPTs device when attached to human body for pulse wave measurement (c) demonstration of an arterial pulse detection with important features of signal (P1 and P2) of heart rate (54 min⁻¹ for 32-year-old women). (d)

26

21

29

the blood pressure measurement of human arteria in the neck by the pulse wave velocity (PWV).

31

- **1.14** Schematic representation of the different additive manufacturing techniques and procedures (a) Spray-coating, Screen Printing and Doctor blade. (b) layout of the all-printed touch screen sensors, (c) digital photograph of touch screen. (d) touch pad response upon finger pressing and release, (e) piezoelectric sensor under cycling pressing and releasing events, and (f) sensor matrix on touch event in one of the sensors and corresponding signals for each sensor.
- 1.15 Experimental measurement of PyNG based on KNbO₃ NW (a) 33 schematic demonstration of PyNG, TEM image and corresponding SAED pattern and HRTEM images of the NW, (b) the electrical response of PyNG under periodic turn on and off cycle of temperature fluctuation, (c) schematic view of PyNG mechanism for electrical output generation based on electric dipoles orientations under heating and cooling cycle.
- 2.1 Schematic demonstration of preparation of PVDF/Ag₂CO₃
 52 nanocomposite (PNC) film and FPNG
- 2.2 ATR-FTIR spectra of PNC film, (b) variation of electro-active fraction (F(γ)
 55 %) with Ag₂CO₃ content and damping factor variation, (c) variation of -CH₂-region of stretching in and (d) the intensity variation of 837 (for γ-phase) and 764 (for α-phase) in PNC films.
- 2.3 PXRD pattern of (a) as prepared Ag₂CO₃ nano/micro rods, (b) PNC
 57 films and symbol (*) marked for the peaks of Ag₂CO₃.
- 2.4 The interaction mechanism of electro-active γ-phase formation in PNC
 58 film (a) Ag₂CO₃ decompose to form Ag NPs and oxygen molecules in air forms Ag-O-O with Ag NPs (b) α-phase reorient through C-C bond rotation to form less strained γ-conformation (c, d) oxygen removal and effective charge nucleation stabiles the γ-conformation.
- **2.5** The optimized structure of γ -PVDF/Ag₂CO₃ in DMF showing Ag...F **59** and O...H distances.

vi

- 2.6 (a) SEM surface morphology of PNC0.50 film and inset shows the enlarged region of Ag_2CO_3 distribution within PVDF matrix, (b) as synthesized Ag₂CO₃ nanorod like surface morphology, (c, d) flexibility of as prepared PNC film in bending and rolling condition. AFM topography of PNC film and inset shows the variation of spherulites size of (e) PNC0 and (f) PNC0.50 film. The spherulite size is estimated by considering maximum length from one edge to other edge of the spherulite.
- 2.7 (a) UV-visible absorption spectra of PNC films and (b) corresponding 63 energy band gap (Tauc plot) and the marked region highlighted in inset is due to Ag₂CO₃ filler. (c) UV-visible transmission spectra to demonstrate the transparency in PNC film and (d) corresponding digital photographs of PNC film (scale bar 0.5 mm).
- 2.8 (a, b) Variation of dielectric constant and tangent loss of PNC film at 65 room temperature. (c) dependance of dielectric constant and loss tangent 1 kHz frequency with Ag_2CO_3 concentration, (d) the relaxation time of PNC films corresponding to the frequency of lowest dielectric loss.
- 2.9 Performance of FPNG (a) schematic representation of fabricated 67 FPNG, (b, c) the electrical output response, open circuit voltage (V_{OC}) and short circuit current (I_{SC}) under continuous hand imparting of force. Working mechanism of FPNG (d) no stress, (e) under stress and (f) when stress is removed.
- 2.10 FEM simulation-based theoretical model of FPNG (i-iii) the stress distribution into the FPNG upon the application of three different stress 30, 60 and 100 kPa and it can be observed by a scale (0.3 to 1 MPa range) and (iv-vi) corresponding to different stress the piezo-potential generation through the FPNG and value can be evaluated by a scale (ranges from 5 to 35 V).
- 2.11 Variation of electrical output of FPNG with the of external load resistance (a) voltage and current, (b) electrical output power density and inset shows an equivalent circuit, (c) capacitor charging of FPNG

61

vii

70

69

under continuous imparting force with three different capacitors (1, 2.2 and 10) μ F and inset shows the bridge rectifier circuit (d) the mechanosensitivity of FPNG by using free fall of force.

- 2.12 The human gesture sensing performance of FPNG (a) electrical output voltage when mounted below the sole, (b) the enlarged region of a single peak of different oscillation and inset shows during pressing and releasing motion (c) the STFT model of gesture sensing to examine the signals at different oscillations, (d) acoustic sensing response of FPNG at different SPL and saturated at 90 dB of SPL, (e, f) electrical output signal for flexibility of FPNG when attached to the index finger and its bending movement at different angles.
- 2.13 Schematic illustration of ROS generation under continuous ultrasound 76 frequency (b) UV-visible absorbance spectra of MO dye degradation treated with ultrasound frequency at different times (0 to 100 min) and (c) the percentage of dye degradation due to piezo-catalysis at different time.
- 3.1 Schematic representation of δ–PVDF nanoparticles preparation by
 91 nanoprecipitation method (a) the solvent and non-solvent interface is marked with rectangular region, where arrows are indicating the accumulated nanoparticles precipitated at the bottom of the tube (b) photograph of mechanism at 0, 10, 20, 40 and 60 m of solvent and non-solvent interfaces.
- 3.2 Schematic view of hydrophobic interaction of water molecules with –
 92 CF2– dipoles of PVDF polymer.
- 3.3 (a) TEM image of spherical δ–PVDF nanoparticles with the histogram
 93 (inset) for particles diameter distribution (b) SAED pattern of δ–PVDF nanoparticles.
- **3.4** XRD pattern of (a) δ -PVDF NPs in upper panel and (b) PVDF α -phase **95** film prepared by heating of δ -PVDF NPs at high temperature 170 °C in lower panel. The region between $2\theta \sim 24^\circ$ to 30° has been magnified

6-fold to provide a clearer representation and facilitate the differentiation of characteristic features of both the δ - and α -phases in the XRD pattern within this range.

- 3.5 The ATR-FTIR spectra of (a) δ- and α-phase of PVDF and enlarge 97 view of spectra in the region (b) 758 cm⁻¹ to 767 cm⁻¹ and (c) 860 cm⁻¹ to 890 cm⁻¹, (d) Raman spectra and (e) thermal DSC thermogram of PVDF both δ- and α-phase.
- 3.6 SPM based AFM analysis of δ -PVDF NPs (a) schematic view of 100 measurement setup for the local piezo- and ferro-electricity, (b) 3D surface topography (3 × 3 μm^2). Piezo-response force microscopy (PFM) spectroscopic (c) phase (ferroelectric hysteresis loop) and (d) amplitude (piezoelectric hysteresis loop) under the application of ± 10 V DC bias voltage.
- 3.7 PFM writing a bit image $(3.6 \times 3.6 \ \mu m^2)$ over to δ -PVDF NPs from 102-103 right panel (a) the amplitude images and corresponding change in amplitude ($\Delta Z \approx 330 \ \mu V$) with line profile of marked triangular area in (a, i), (b) phase image and corresponding change in phase ($\Delta \varphi \approx 180^\circ$) along with the dipole switching in (b, i, ii). PFM erasing a bit illustrated in the right panel (c) amplitude and corresponding change in amplitude ($\Delta Z \approx 0 \ \mu V$) in (c, i), (d) phase image and corresponding change in phase ($\Delta \varphi \approx 0^\circ$) along with the dipole switching in (d, i, ii).
- **3.8** Electrical output performance of FPNG as (a) open circuit voltage **105** (V_{OC}) and inset shows the schematic view of FPNG preparation, (b) short circuit current (I_{SC}), the repeatability and stability response of FPNG as short circuit current over 3000 cycles on (c) day 1 and (d) day 30.
- 3.9 2D FEM based theoretical simulation model for piezo-potential
 107 generation upon the application of 100 kPa stress (a-d) with varying concentration of δ–PVDF nanoparticles in the PDMS matrix, (e) planer
 PVDF film-based geometry.

- 3.10 2D FEM based theoretical simulation model for piezo-potential 108 generation (a) δ–PVDF nanoparticles comprising system, (b) planer PVDF film-based geometry. The stress confinement under the application of 100 kPa of pressure (c) δ–PVDF nanoparticles and enlarged image of rectangular marked region shows the distribution on nanoparticles (d) stress distribution in the planer PVDF film.
- 3.11 Performance of FPNG with external load resistance (a) voltage and 111 current variation (b) electrical power density under the load resistance ranging from $10^5 \Omega$ to $10^8 \Omega$ and inset shows 5 blue LED lightening by FPNG, (c) capacitor charging and discharging of FPNG with an equivalent circuit diagram in the inset and (d) mechano-sensitivity of FPNG by using free fall force of different weights from a constant height of 10 cm.
- 3.12 Schematic illustration of human running during exercise on treadmill
 113 machine and then device was placed in the shoe to record the electrical output response (b) corresponding output voltage signal.
- 3.13 Physiological signal monitoring as (a) arterial pulse detection and inset
 114 shows enlarged view of a single peak with the typical nature of blood pressure wave (d) 2D-STFT processed spectrogram of an arterial pulse signal.
- 4.1 Schematic demonstration of fabrication method of δ-PVDF
 130 nanoparticles via phase separation technique at ternary phase system
 i.e., PVDF-DMF-water.
- 4.2 The surface morphology of PVDF nanoparticles when different w/v % 130 of PVDF/DMF are considered, in particular FE-SEM images of (a) 1 w/v %, (b) 2 w/v % and (c) 4 w/v % of PVDF/DMF cases.
- 4.3 TEM image of PVDF NPs coated with PDA-PEI, i.e., PVDF@f Ink at
 (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min of reaction time and the symbol (#) represent the unmarked nanoparticles surface to visualize the coating layer (e) The plot illustrates the variation of PDA-PEI coating (layer thickness) with reaction time.

- 4.4 (a) PXRD pattern (b) SAED pattern of as fabricated δ-PVDF133 nanoparticles.
- 4.5 Schematic demonstration for surface coating of δ -PVDF with PDA-PEI. 134
- 4.6 Digital image of water contact angle (WCA) measurement of a deionized water droplet on (a) PVDF@f Ink layer, (b) bare PVDF NPs
 (c) Digital photographs of word "INST" written by using piezoelectric ink on different substrates (i) Glass, (ii) PET sheet and (iii) Glossy paper.
- **4.7** Zeta (ζ) potential distribution with respect to time (days). **136**
- 4.8 Rheological properties of piezoelectric ink (PVDF@f Ink) and control137 solution (PDA:PEI) (a) shear stress and (b) viscosity vs strain.
- 4.9 The high-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) N 1s and (d)F 1s for functionalized PVDF nanoparticles with PDA-PEI i.e.,PVDF@f Ink.
- **4.10** AFM topography of (a) Control (PDA-PEI), (b) δ -PVDF nanoparticles **140** functionalized sample with PDA-PEI i.e., PVDF@f Ink and the marked region shows the presence of δ -PVDF nanoparticles into the PDA:PEI matrix. Piezoresponse force microscopy (PFM) response of piezoelectric ink (PVDF@f Ink) (c) Phase hysteresis loop and (d) Amplitude response upon the application of DC bias voltage of \pm 7 V.
- 4.11 Kelvin probe force microscopy (KPFM) response of both control and piezoelectric ink i.e., PVDF@f Ink samples, firstly the surface topography of (a, c) control sample before and after poling respectively, (b, d) piezoelectric ink before and after poling. Schematic representation of electronic energy band diagram based on the work function measured by KPFM and corresponding shift in Fermi level (E_F) of control (e and g) and PVDF@f Ink (f and h) in unpoled and poled cases, respectively.
- **4.12** Ultraviolet photoelectron spectroscopy (UPS) is performed to measure **144** the (a) work function under poled (P) and unpoled (UP) conditions, (b)
 - xi

comparison plot of work function obtained from both KPFM and UPS study and (c) energy band diagram and shifting of Fermi level (E_F) based on UPS results under poled and unpoled conditions.

- 4.13 (a) UV-visible absorbance spectra under poled (P) and unpoled (UP) 145 condition and (b) Tauc's plot for band gap (Eg) of PVDF@f Ink.
- 4.14 (a) Schematic demonstration of (i) FPNG preparation (ii) encapsulation 146 with PDMS, (b) open circuit voltage (V_{OC}) and (c) short circuit current (I_{SC}) on continuous mechanical impart with different amplitude of pressure (3, 6 and 11 kPa).
- 4.15 Electrical output response of as prepared control FPNG (i.e., only 147 PDA-PEI) (a) open circuit voltage (V_{OC}) and (b) short circuit current (I_{SC}) under the application of 5 Hz frequency and imparting pressure amplitude, *e.g.*, 3, 6 and 11 kPa, respectively.
- **4.16** The piezoelectric output performance of control FPNG (i.e., only PDA-PEI) as (a) open circuit voltage (V_{OC}) and (b) short circuit current (I_{SC}) when the measurement is performed on day 0 and day 90.
- **4.17** The piezoelectric performance of as-fabricated f-PNG with PVDF@f **148** Ink as (a) open circuit voltage (V_{OC}) and (b) short circuit current (I_{SC}) when the measurement is performed on day 0 and day 90.
- **4.18** Performance of FPNG with variable external load resistance (a) V_{OC} **150** and power density, (b) capacitor charging with three different capacitors (1, 4.7 and 10) μ F. The stability and repeatability of FPNG is examined by short circuit current (I_{SC}) over 24000 cycles in (c) day 0 and (d) day 60.
- **4.19** Cyclic bending and unbending response of FPNG with three different **151** arc radii $(r_1, r_2 \text{ and } r_3)$.
- 4.20 The human physiological signal (acoustic sensitivity of FPNG) 152 recorded during pronunciation of alphabet (a) "N-A-N-O" and "H-E-L-L-O" independently and (b, c) corresponding STFT processed 2D spectrogram (i, ii).
- 4.21 Schematic demonstration of as prepared photodetector (PD), (b) 154
 - xii

switching response of photocurrent vs time under periodically turn on and off cycles at different light illumination intensities (c) rise and decay time of single cycle of photoresponse. Energy band diagram representing the working mechanism of photodetector (d) at equilibrium under dark and (e) under light illumination.

- 4.22 Current-voltage (I-V) characteristics of PD under (a) without strain, 156 with dark and light illumination and (b) corresponding schematic of energy band diagram.
- **4.23** Current-voltage (I-V) characteristics of PD under (a) under **157** compressive force, (c) tensile strain upon illumination of 0.64 mW/cm² light and corresponding insets shows the schematic illustration of PD under external mechanical stimuli. The corresponding energy band diagram represents the charge carrier transportation upon (c) compressive strain, (d) tensile strain ($\Delta \varepsilon > 0$) at constant illumination intensity of 0.64 mW/cm².
- 5.1 Geometric structure of α-Te (a) monolayer with side-view and topview, (b) and (c) side-view of P-3m1 space group, and C2 space group of trilayer. The unit cells of α-Te are highlighted in light green color. The phonon dispersion curve of α-Te (d) monolayer and (e) trilayer.
- 5.2 AFM surface topography of (a) bulk tellurium (scale bar is 2 μm) (b)
 171 corresponding height profile with three different colors marked line profiles (c) LPE exfoliated 2D tellurium nanosheets (scale bar is 2 μm) and (d) corresponding height profile of marked rings with different colors.
- 5.3 (a) TEM image of exfoliated Te nanosheets and corresponding inset in 173 top left side for average nanosheet size distribution and right bottom inset (scale bar 2 nm) shows the SAED pattern with the reflection planes. (b) The XRD pattern, (c) Raman spectra and (d) corresponding Raman active vibration modes of tellurium.
- 5.4 Piezoresponse force microscopy (PFM) spectroscopy of 2D tellurium174 nanosheets (a) ferroelectric phase reversal hysteresis and (b) amplitude

xiii

hysteresis under the applied DC bias voltage of ± 10 V.

- 5.5 Schematic demonstration of fabrication of pyroelectric nanogenerator 175
 (a) flexible PET substrate (b) preparation of inter digital electrode (IDE) on PET substrate with Gold (c) 2D tellurium nanosheets transferred over the IDE and (d) two terminal wire connection established for electrical output measurement.
- 5.6 Pyroelectric measurement set up for the electrical output measurement 177 with periodic turn on and off temperature oscillation profile with the IR source and function generaor.
- 5.7 Pyroelectric thermal energy harvesting (a) acquired profile of 178 temperature oscillation and (b) corresponding rate of change in temperature at constant frequency of 0.1 Hz. The electrical output performance as (c) open circuit voltage and (d) short circuit current of pyroelectric nanogenerator comprising of Te nanosheets.
- 5.8 Pyroelectric electrical output performance of commercial PZT disc 179 sensor (a) acquired temperature oscillation profile, (b) first order derivative of heat transfer and corresponding (c) open circuit voltage and (d) short circuit current.
- 5.9 Pyroelectric electrical output performance of commercial PVDF sensor 180
 (a) acquired temperature oscillation profile, (b) first order derivative of heat transfer and corresponding (c) open circuit voltage and (d) short circuit current.
- 5.10 FEM based theoretical simulation of (a) temperature profile acquired 181 for simulation ($\Delta T \sim 6$ K) (b) enlarged view for heat rate transfer (c) bottom surface of device when temperature oscillation is applied. Further, thermal strain distribution in 2D tellurium nanosheets with the same temperature profile and (e) enlarged of thermal strain induced in nanosheets.
- 5.11 The variation of electrical output performance of (a) open circuit
 182 voltage and (b) short circuit current with respect to distance from IR source to pyroelectric device.

5.12 Schematic demonstration of pyroelectric mechanism of 2D tellurium 185 nanosheets based nanogenerator on dipole orientation from their alignment axis when (a) temperature is constant i.e., dT/dt = 0, (b) dT/dt > 0 and (c) dT/dt < 0. (d) the comparative illustration of pyroelectric coefficient, current and voltage figure of merits, marked red color rectangle represent the 2D tellurium nanosheet (this work). 6.1 Schematic illustration of tellurium nanoflakes preparation. 194 Schematic demonstration of PVTe nanocomposite film preparation. 6.2 195 6.3 (a) PXRD pattern, (b) SEM surface morphology, (c) SAED pattern and 197 (d) Raman spectra of as-synthesized tellurium NFs. 6.4 Electroactive phase nucleation in PVDF nanocomposite film as (a) 198 FTIR spectra and (b) XRD pattern, symbol (*) shows the respective peaks of Tellurium. 6.5 FE-SEM surface morphology of (a) neat PVDF and (b) PVTe50 200 nanocomposite film. 6.6 Frequency-dependent dielectric performance of PVTe nanocomposite 201 film (a) variation of the real part of dielectric constant and (b) dielectric loss at room temperature. 6.7 performance of HyNG 202 Piezoelectric output (a) schematic demonstration of HyNG fabrication and (b) open circuit voltage and (c) short circuit current under variable mechanical force from 3 to 12 N at 5 Hz of frequency. 6.8 Piezoelectric response of HyNG prepared by bare PVDF film (a) open 203 circuit voltage and (b) short circuit current under the 12 N of force and 5 Hz frequency. 6.9 Piezoelectric output performance of HyNG (a) variation of output 204 voltage and power density and (b) pressure sensing performance of 6.10 HyNG. 205 Pyroelectric output performance of HyNG (a) acquired temperature oscillation profile (b) corresponding first order derivative of temperature, (c) open circuit voltage with single enlarge peak in inset

xv

and (d) short circuit current with single enlarged peak in the inset.

- 6.11 Physiological signal monitoring performance of HyNG (a) FEM 207 simulation-based eye deflection (b) simulated output voltage corresponding to deflection (c) schematic illustration of strain generation when eye lids open/close due to contraction and release phenomenon. Experimental output voltage response when HyNG is fixed at three different locations (d) temple, (e) lower eyelids and (f) upper eyelids.
- 6.12 Physiological signal monitoring of human movement (a) elbow 208 bending, (b) knee bending and (c) finger bending.

List of Tables

Table	Title	Page
1.1	The 32 crystal classes with/without piezoelectric properties	11
2.1	The degree of crystallinity estimated from PXRD pattern	57
2.2	Binding energies of PVDF fragments within PVDF/Ag ₂ CO ₃ complexes in	60
	DMF	
2.3	Performance of piezoelectric nanogenerator with different processing	71
	conditions	
3.1	Comparative table for piezoelectric coefficient (d_{33})	115
5.1	Lattice parameter (a), thickness (d), space group and bond length of α -Te	168
	monolayer, bilayer and trilayer	
5.2	In-plane and out-of-plane Born effective charges (e) of each atom of α -Te and	183
	trilayer and PZT	
6.1	Electroactive phase content in PVTe nanocomposite films	

Abbreviations & Symbols

PNG	Piezoelectric nanogenerator
FPNG	Flexible piezoelectric nanogenerator
PyNG	Pyroelectric nanogenerator
IoT	Internet of thing
PVDF	Poly(vinylidene fluoride)
FEM	Finite element method
AFM	Atomic force microscopy
PFM	Piezoresponse force microscopy
KPFM	Kelvin probe force microscopy
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
FE-SEM	Field emission scanning electron microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
UPS	Ultraviolet photoelectron spectroscopy
DMF	N, N-dimethylformamide
STFT	Short-time Fourier transform processed spectrograms
NWs	Nanowires
V _{OC}	Open circuit voltage
I _{SC}	Short circuit current
η	Piezoelectric energy conversion efficiency
Sacou	Acoustic sensitivity
S_m	Mechano-sensitivity
NPs	Nanoparticles
PET	Polyethylene terephthalate

List of publications

(a) Included in the thesis

- <u>H. K. Mishra</u>, D. Sengupta, A. Babu, B. Masood, R. Sarkar, S. Boddu, T. K. Kundu, D. Mandal, PVDF/Ag₂CO₃ nanocomposites for efficient dye degradation and flexible piezoelectric mechanical energy harvester, *Sustainable Energy Fuels* 2022, 6, 1625.
- <u>H. K. Mishra</u>, V. Gupta, K. Roy, A. Babu, A. Kumar, D. Mandal, Revisiting of δ– PVDF nanoparticles via phase separation with giant piezoelectric response for the realization of self-powered biomedical sensors, *Nano Energy* 2022, 95, 107052.
- H. K. Mishra, A. K. Gill, V. Gupta, P. Malik, T. Sinha, D. Patra, D. Mandal, All organic aqueous processable piezo-phototronic ink for strain modulated photoresponse, *Adv. Mater. Technol.* 2022, 8, 2201350.
- 4. <u>**H. K. Mishra**</u>, A. Jain, D. Saini, B. Mondal, C. Bera, D. Mandal, Enhanced pyroelectric throughput in two-dimensional manoelemental material (Under communication).
- 5. <u>**H. K. Mishra**</u>, U. Sarkar, B. Mondal, S. Naskar, D. Saini, D. Mandal, Ultra-flexible hybrid Nanogenerator for efficient mechanical and thermal energy harvesting. (Under communication).

(b) Not included in the thesis

- S. K. Ghosh, K. Roy, <u>H. K. Mishra</u>, M. R. Sahoo, B. Mahanty, P. N. Vishwakarma, D. Mandal, Rollable magnetoelectric energy harvester as a wireless IoT sensor, *ACS Sustainable Chem. Eng.* 2020, 8, 864.
- V. Gupta, A. Babu, S. K. Ghosh, Z. Mallick, <u>H. K. Mishra</u>, D. Saini, D. Mandal, Revisiting δ-PVDF based piezoelectric nanogenerator for self-powered pressure mapping sensor, *Appl. Phys. Lett.* 2021, *119*, 252902.

- K. Maity, U. Pal, <u>H. K. Mishra</u>, P. Maji, P. Sadhukhan, Z. Mallick, S. Das, B. Mondal, D. Mandal, Piezo-phototronic effect in highly stable CsPbI₃-PVDF composite for self-powered nanogenerator and photodetector, *Nano Energy* 2022, *92*, 106743.
- B. Mondal, <u>H. K. Mishra</u>, D. Sengupta, A. Kumar, A. Babu, D. Saini, V. Gupta, 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* 2022, *38*, 12157.
- P. Malik, V. Gupta, <u>H. K. Mishra</u>, A. Kumar and D. Mandal, Long term retention in δ-PVDF thin film prepared by rapid ice quenching technique, *J. Appl. Polym. Sci.* 2023, e53714.
- D. Saini, A. Kumar, <u>H. K. Mishra</u>, V. Gupta, D. Mandal, Real-time Smartphone Charging from Recycled Aluminium Foil-based Electromagnetic Energy Harvester, *Energy Technol*. 2023, 2300084.
- N. Ghosh, J. Kumar, A. Babu, <u>H. K. Mishra</u>, S. Naskar, D. Mandal, Surface functionalization of hair with clay: An ancient practice of hair clarifier (Under communication).
- 8. <u>**H. K. Mishra**</u>, D. Mandal, Mechanically induced large hydrogen evolution in 2D material (Under preparation).
- 9. <u>**H. K. Mishra**</u>, U. Sarkar, D. Mandal, Flexible piezo,- and pyro-electric nanogenerator based on electrospun fiber for efficient energy harvesting (Under preparation).
- D. Saini, A. Kumar, <u>H. K. Mishra</u>, V. Gupta, B. Mondal, Z. Mallick, D. Mandal, 3D Printed thermoelectret with giant piezoelectric coefficient for self-powered wearable pressure sensor and on-spot bone injury (Under communication).

Conferences/Workshops

- 33rd AGM of MRSI and 4th Indian Material Conclave, International Union of Materials Research Society-International Conference in Asia (IUMRS-ICA 2022), 19th-23rd December 2022, Indian Institute of Technology, Jodhpur, India; Prospective Applications of Piezoelectric Nanogenerator and Strain Modulated Piezo-phototronic Effect (Poster).
- International Conference on Advance Physics (IEMPHYS), 22 to 24th September 2022, Institute of Engineering and Management, Kolkata, India; Piezo-phototronic Effect in Piezoelectric Nanocomposite (PVDF/Ag₂CO₃) as a Self-powered Nanogenerator and Photodetector (Oral).
- Second Symposium on Physics of Nanomaterials-II (PNM-II), 7-8th July 2022, Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Mohali, India; Giant Piezoelectricity in Electroactive PVDF Nanoparticles (Poster).
- 2nd Research Scholar Day (RSD), 31-1st April 2022, Institute of Nano Science and Technology, Mohali, India; Electroactive δ-PVDF nanoparticles as an Aqueous Dispersed Piezoelectric Ink (Poster).
- 29th CRSI National Symposium in Chemistry & CRSI-ACS Symposium Series in Chemistry, 7-9th July 2022, Indian Institute of Science Education and Research, Mohali, India; Interfacial Nanostructuring of δ-PVDF Nanoparticles with Giant Piezoelectricity and Piezoelectric Ink (Poster).
- Advanced Energy Materials & Devices (AEMD), 3rd March 2022, CSIR-Central Glass & Ceramic Research Institute, Kolkata, India; Piezoelectric Polymer Nanocomposites for Removal of Organic Pollutant (Poster).

- International E-Conference on Nanomaterials & Nanoengineering APA Nanoforum, 24-26th February 2022, India; Polymer Nanocomposite Film with High Dielectric Constant and Piezo-catalysis Performance (Poster).
- 65th DAE Solid State Physics Symposium (DAE SSPS-2021), 15- 19th December 2021, Bhabha Atomic Research Centre, Mumbai, India; Electro-active δ-phase of PVDF Based Mechanical Energy Harvester (Poster).
- 9. International Symposium on Materials of the Millennium: Emerging Trends and Future Prospects (MMETFP-2021), 19-21th November 2021, Pandit Deendayal Energy University, Gujarat, India; Piezoelectric Polymer Nanocomposites for High Energy Storage Density (Poster).
- 10. International E-Conference on Physics of Materials & Nanotechnology (ICPN-2021),
 28-30th October 2021, Mangalore University, India; Nano-piezocatalyst Driven Organic Dye Degradation (Poster).
Table of Content

Abstract	i-iii
List of Figures	iv-xvi
List of Tables	xvii
Abbreviations & Symbols	xviii
List of Publications	xix-xxii
Chapter 1	1-48
Introduction and Objectives	
1.1. Energy harvesting: Self-powered & wearable technology	1
1.1.1 Overview	1
1.1.2 Energy Harvesting	2
1.1.3 Self-powered and wearable technology	5
1.2 Development of nanogenerators	8
1.2.1 Piezoelectric nanogenerator (PNG)	10
1.2.2 Theoretical background of piezoelectricity	12
1.2.3 Materials and types of piezoelectric nanogenerators (PNG	s) 13
1.2.4 Piezo/Pyro/Ferro-electric polymer: Poly(vinylidene fluorid	le) 17
1.2.5 Applications of piezoelectricity	20
1.2.5.1 Piezo-catalysis	20
1.2.5.2 Photodetector as a piezo-phototronic effect	24
1.2.5.3 Healthcare sector 27	
1.2.5.4 Piezoelectric ink as a printable technology	29
1.2.6 Pyroelectric nanogenerator (PyNG) and applications	32
1.3 Outline of the thesis	34
1.4 Materials characterizations	37
1.5 References	39

Chapter 2

Polymer Nanocomposite (PVDF/Ag₂CO₃) as a Flexible Piezoelectric Mechanical Energy Harvester and Organic Dye Degradation

Chapter 3	87-124
2.5 References	78
2.4 Conclusions	77
2.3.7 Piezo-catalysis dye degradation	75
2.3.6. Mechanical energy harvesting performance	72
2.3.5 Performance of FPNG	66
2.3.4 Room temperature dielectric properties of PNC films	62
2.3.3 Optical properties of PNC films	62
2.3.2 Surface morphology of PNC films	60
2.3.1 Electroactive phase nucleation in PNC films	53
2.3 Results and discussion	53
2.2.4 Fabrication of flexible piezoelectric nanogenerator (FPNG)	53
2.2.3 Preparation of PVDF/Ag ₂ CO ₃ nanocomposite films	52
2.2.2 Synthesis of Ag_2CO_3	51
2.2.1 Materials	51
2.2 Experimental section	51
2.1 Introduction	49

Electroactive δ -PVDF Nanoparticles with Giant Piezoelectric Throughput and Self-powered Biomedical Sensors

3.1 Introduction	87
3.2 Experimental section	89

All Organic Aqueous Processable δ-PVDF Nanoparticles for Piezoelectric Ink and Strain		
Chapter 4 12		
3.5 References		
3.4 Conclusions		
3.3.7 Healthcare signal monitoring	113	
3.3.6 Mechanical energy harvesting performance of FPNG	109	
3.3.5 Finite element method-based simulation	106	
3.3.4 Output performance of FPNG	104	
3.3.3 Nanoscale piezo-and ferro-electricity	98	
3.3.2 Electroactive phase nucleation in PVDF	92	
3.3.1 Mechanism of PVDF nanoparticles formation	90	
3.3 Results and discussion		
3.2.3 Fabrication of flexible piezoelectric nanogenerator (FPNG)	90	
3.2.2 Piezoresponse force microscopy measurement	90	
3.2.1 Synthesis of PVDF nanoparticles	89	

Modulated Photoresponse

4.1 Introduction		125	
4.2	Experir	nental section	127
	4.2.1	Preparation of PVDF nanoparticles	127
	4.2.2	Formulation of piezoelectric ink	128
	4.2.3	Fabrication of flexible piezoelectric nanogenerator (FPNG)	128
4.3	Results	and discussion	129
	4.3.1	Surface morphology	129
	4.3.2	Crystallographic phase analysis	132
	4.3.3	Mechanism of surface coating of PVDF NPs	133

4.3.4	Rheological properties of piezoelectric ink	136
4.3.5	Surface characterization	137
4.3.6	Piezo- and ferro- electric properties of piezoelectric ink	139
4.3.7	Piezoelectric performance of ink-based FPNG	145
4.3.8	Cyclic bending and releasing piezoelectric response	151
4.3.9	Photodetection properties and strain modulation of piezoelectric ink	153
4.4 Conclu	isions	158
4.5 Refere	nces	
Chapter 5	5	165-190
Ultrahigh	Pyroelectricity in 2D Monoelemental Tellurium	
5.1 Introdu	uction	165
5.2 Experi	mental section	166
5.2.1 H	Preparation of tellurium nanosheets	166
5.2.2 H	Fabrication of pyroelectric nanogenerator (PyNG)	167
5.2.3 Theoretical simulation		167
5.3 Result	s and discussion	168
5.3.1	Theoretical study of Tellurium nanosheets	168
5.3.2 0	Characterization of 2D Te nanosheets	170
5.3.3 H	Electrical output performance of PyNG	174
5.3.4 H	EM-based simulation for thermal strain distribution	180
5.3.5 N	Mechanism of ultrahigh pyroelectric response	184
5.4 Conclu	isions	186
5.5 Refere	nces	187

Chapter 6

Flexible Mechanical and Thermal Energy Harvesting Based Hybrid Nanogenerator

6.1 Introduction	
6.2 Experimental section	
6.2.1 Chemicals	193
6.2.2 Synthesis of Tellurium nanoflakes	193
6.2.3 Preparation of nanocomposite film	194
6.2.4 Fabrication of HyNG	195
6.3 Results and discussion	
6.3.1 Material and characterization	196
6.3.2 Electroactive phase nucleation in PVTe film	197
6.3.3 Surface morphology	199
6.3.4 Dielectric properties of PVTe film	200
6. 3.5 Electrical output performance of HyNG	201
6.3.5.1Piezoelectric output performance	201
6.3.5.2 Pyroelectric energy harvesting	203
6.3.6 Human gesture sensing performance	206
6.4 Conclusions	
6.5 References	
Chapter 7	
Summary and Future Outlook	
7.1 Summary	
7.2 Future outlook	

Chapter 1

Introduction and Objectives

1.1 Energy harvesting: Self-powered & wearable technology

1.1.1 Overview

Over the past few years, there has been a rapid increase in the demand for sustainable and renewable energy sources, as the adverse impacts of relying on fossil fuels for energy production have become more apparent. Fossil fuels such as coal, oil, and gas are finite resources that are being depleted at an alarming rate. Additionally, the combustion of these fuels releases greenhouse gases into the atmosphere, contributing to climate change and environmental pollution. Renewable energy sources, on the other hand, are replenished, more environmentally friendly and are not subjected to any depletion. These sources derived from rain, wind, sunlight, geothermal heat wave, tides and biomass have been extensively studied as alternate energy sources for sustainable energy to replace non-renewable sources (nuclear, natural gases, crude oils and coals).

The history of energy harvesting can be outlined back to the late 1800s when the first hydroelectric power plant was built in Wisconsin, USA. Since then, the world has witnessed several significant milestones in the development and investment in the renewable and sustainable energy sector. In the 1990s, severe climate change and global warming evoked alarming concerns that significantly accelerated the investment in renewable energy sources. In 1992, the United Nations Framework Convention on Climate Change (UNFCCC) was signed, which paved the way for the creation of the Kyoto Protocol in 1997. The protocol established objectives to decrease the emission of greenhouse gases. Therefore, renewable energy technologies played a vital role in transitioning from traditional, carbon-intensive energy sources to cleaner and more sustainable opportunities. By integrating these renewable energy technologies into wearable devices, we can reduce or eliminate the need for traditional batteries

or frequent charging from conventional power sources. This not only reduces environmental impact but also offers greater convenience and autonomy to users by extending the operational lifespan of these devices. Thus, renewable energy technologies enable the development of smaller and more compact power sources that are suitable for wearable electronic devices. It promotes the development of wearable technology by providing sustainable and reliable power solutions. In the early 2000s, countries such as Germany, Denmark, Switzerland and Spain became leaders in renewable energy investment, offering attractive incentives for renewable energy development. This led to a significant increase in the deployment of wind and solar power, as well as the development of new technologies such as mechanical and thermal energy based on piezo and pyro-electric materials for commercial applications. In this regard, the global energy harvesting market has experienced significant growth, driven by the increasing demand for clean energy solutions and the growing number of Internet of Things (IoT) devices and wireless sensor networks. The global piezoelectric energy harvesting market is expected to grow from USD 2.5 billion in 2023 to USD 5.0 billion by 2028, at a CAGR of 10.0%. The market is driven by the increasing demand for energy-efficient and sustainable solutions, the growing adoption of IoT devices, and the rising focus on wearable electronics. The technologies for scavenging energy from ubiquitous and abundant sources of mechanical and thermal energy can be converted into electrical energy. Therefore, it is expected that these forms of energy must be integrated to run low-power electronic devices where power is required in the μW range [1–3].

1.1.2 Energy harvesting

Energy harvesting technology is a promising field of study that focuses on capturing and converting ambient energy from the surrounding environment (renewable energy sources) into usable electrical energy. This technology offers a sustainable and efficient solution to power

wireless and self-powered wearable electronic devices (such as smart watches, mobile phones, tablets, sensors and actuators) that are becoming increasingly common in modern-day life [4–6]. It allows for the generation of power without the need for traditional power sources like batteries or some external power sources. The concept of energy harvesting has been well known for decades, but recent advancements in materials science and electronic engineering have made it more accessible and practical for real-time applications. Energy harvesting has the potential to revolutionize in various sectors such as healthcare, transportation, and environmental monitoring, sensors and actuators. There are various forms of energy harvesting (as shown in Figure 1.1) with sustainable and renewable energy sources as following [2].

i. Piezoelectric energy harvesting

This involves the conversion of mechanical energy into electrical energy through the use of piezoelectric materials. These materials generate electricity when they are subjected to mechanical pressure or vibration, and that can be used to power small electronic devices.

ii. Thermal energy harvesting

This involves the conversion of temperature differences into electrical energy through the use of thermoelectric and pyroelectric materials. It can be used in various sectors such as fire alarms, IR detectors and thermal imaging.

iii. Solar energy harvesting

This involves the conversion of sunlight into usable electrical energy through the use of the most common way of photovoltaic cells. Solar panels are commonly used to harvest solar energy, which can be utilized further to power up several potential electronic gadgets of daily life uses.

iv. Wind energy harvesting

It is the process of conversion of the kinetic energy of wind into electrical energy. The most common use of this energy harvesting is through wind turbines. These turbines are often found in wind farms and can produce large amounts of electricity because of the huge amount of kinetic energy.

v. Hydropower energy harvesting

It is the process of conversion of the kinetic energy of running water to generate electricity. Particularly, water droplet energy harvesting can be achieved by utilizing the energy from falling water or the kinetic energy present in ocean waves.



Figure 1.1 Demonstration of various types of renewable energy sources. Adopted from ref. [2].

vi. Geothermal energy harvesting

Geothermal power plants use the heat from the Earth's core to generate electricity. This can be done through the use of geothermal heat pumps, which extract heat from the ground and convert it into electricity.

vii. Biomass energy harvesting

Biomass energy harvesting refers to the process of utilizing organic matter, such as plant and animal waste, to generate energy. It can be obtained through different methods such as combustion, anaerobic digestion, gasification, or pyrolysis.

1.1.3. Self-powered and wearable technology

Self-powered and wearable technology rely on energy harvesting to enable them to operate without the need for an external power source such as a battery. There are several potential real-time technological applications such as following

i. Wireless sensors

Energy harvesting technology is widely used to power wireless sensors to monitor different parameters such as temperature, humidity, air quality, pressure, and vibration. These sensors can harvest energy from the surrounding environment to power their sensors and wireless communication systems, eliminating the need for batteries or wired power sources.

ii. Wearable electronics

Energy harvesting technology is also used to power wearable electronics such as smartwatches, fitness trackers, and biomedical devices. These devices are designed to be low-powered and energy-efficient, making them ideal for energy harvesting technology. The continuous advancement of technology will undoubtedly open up new possibilities and applications for wearable devices.

iii. Internet of things (IoT) devices

Energy harvesting technology is also used in IoT devices, which are designed to collect and transmit data from various sensors and devices to the receiver. These devices can be powered by energy harvesting technology, eliminating the need for batteries or external power sources.

iv. Smart buildings

Energy harvesting can power the sensors and control systems in smart buildings that regulate lighting, heating, and cooling systems. These systems can harvest energy from solar panels, wind turbines, and other renewable energy sources to power their operations.



Figure 1.2. Schematic diagram of wearable and portable self-powered devices and their applications. Adopted from ref. [10].

In the past few decades, the rapid growth of IoTs, electronic gadgets such as sensors, actuators and wireless transmitters have been an integral part of the world for the advancement of society such as security & protection, biomedical healthcare sector, wireless data acquisition system as shown in Figure 1.2 [7–12]. Each of these devices requires a very small power scale from nanowatt (nW) to microwatt (μ W) order. Therefore, the technologies that can harvest energy from renewable and sustainable energy sources are the possible way for self-powered and wearable electronics at micro/nano scale. The requirement of power for the large grid depends on the usable equipment or sector including from gigawatt (GW) to terawatt (TW) as shown in Figure 1.3 [6].



Figure 1.3 Magnitude of power and its corresponding applications. Macroscale energy is for powering a city and even a country; nanoscale energy is to power tiny small electronics. Both applications are measured by different characteristics. Adopted from ref. [6].

1.2 Development of nanogenerators

Traditional approaches for electrical power generation are well-known for the use of electromagnetic generators (EMGs) based on Faraday's law of electromagnetic induction, which was discovered in 1831. However, there exists some limitations of this technology which includes requirements of high-frequency mechanical energies. Most of technologies need a huge amount of infrastructure and expensive equipment in order to power electronic gadgets, smart sensors, and wearable devices [13]. There are various abundant and ubiquitous sources of mechanical and thermal energies such as walking, running, singing, human body movements, water waves, breathing and vehicle exhaust, that cannot be effectively harvested through EMGs. In turn, nanogenerator (NG) is the best-known eco-friendly alternative technology that can convert various abundant mechanical and thermal energies from the natural environment and artificial sources into electrical energy. NGs have several advantages over conventional energy harvesting devices like EMGs. Firstly, they are highly efficient, with conversion efficiencies ranging from ~ 20 % to 80 %. Secondly, they are robust, scalable and can be produced in large quantities at low cost. Thirdly, it contributes to sustainable power generation by utilizing renewable energy sources and reducing reliance on fossil fuels. They offer a clean and environmentally friendly alternative to traditional power generation methods, contributing to the overall goal of reducing carbon emissions and promoting sustainable development. Additionally, NGs have light-weight, cost-effectiveness, simple operation, easy signal processing and biocompatible. These nanogenerators may able to power various electronic components and wearable devices used in a variety of applications such as telecommunications, medical sector, defense technology and automotive industries, human-machine interfaces, MEMS and internet of things (IoT) devices (as shown in Figure 1.4) [14,15].

In order to harvest small-scale mechanical energy into electrical energy, first and foremost, NG was developed by Z. L. Wang in 2006, where, zinc oxide (ZnO) nanowire was used as a piezoelectric material. Towards the advancements of NGs researchers made significant attention has been paid to explore various materials, including zinc oxide, lead zirconate titanate (PZT), and other piezoelectric materials, to improve power output and efficiency. Techniques such as electrode modifications, nanostructuring, and device optimization were also investigated to enhance performance. Since then, various types of NGs are developed such as piezoelectric nanogenerator (PNG), pyroelectric nanogenerator (PyNG), triboelectric nanogenerator (TENG) [16,17].



Figure 1.4 Schematic view of nanogenerators, classified into three major areas, namely, self-powered sensor/system, blue energy and micro/nano energy systems with their representative applications. Adopted from ref. [13].

1.2.1 Piezoelectric nanogenerator (PNG)

Piezoelectric nanogenerators work on the piezoelectric effect to convert very tiny mechanical vibrations into electricity. Piezoelectricity originates from the Greek word "piezen" which means squeeze or to press. The phenomenon of piezoelectricity was first discovered in 1880 by Jacques and Pierre Curie. Piezoelectricity is the ability of certain materials to generate an electric charge in response to mechanical stress or pressure (i.e., electromechanical conversion). When a piezoelectric material is subjected to mechanical force or pressure, such as bending, stretching, or compressing, its internal structure is distorted, causing positive and negative charges to accumulate on opposite sides of the material. This charge generation results in an electric potential difference, or voltage, across the material [18].

Firstly, the Curie brothers have observed that certain crystals, such as quartz and tourmaline, could produce electric charges when subjected to mechanical deformation/stress. Since then, a wide range of materials, including ceramics, polymers, composites and twodimensional (2D) transition metal dichalcogenides (TMDCs) have been found to exhibit excellent piezoelectric properties [19,20]. There are two types of piezoelectric effects, namely, direct piezoelectric effect and reverse piezoelectric effect. When piezoelectric material is subjected to a mechanical stress, electric charges proportional to the applied stress are produced in the material. This phenomenon is known as the direct piezoelectric effect. On the other hand, when the same material is subjected to an external electric field, mechanical strain proportional to the applied electric field is generated which is known as the converse (indirect) piezoelectric effect. Figure 1.5, demonstrates the performance of quartz material as direct and indirect piezoelectricity [21]. The occurrence of the piezoelectric effect is explained better using the crystalline solid and the array of the dipoles/ions within the unit cell where the positive and negative charges are non-centrosymmetric within the planes of the unit cell under no external stress. The piezoelectricity of a material fundamentally depends on its crystallography. Among the total 32 crystal classes, 21 crystal classes are non-centrosymmetric, which do not have a center of symmetry (e.g., the net dipole moment (μ) per unit cell is non-zero). The remaining crystal classes have a center of symmetry ($\mu = 0$). But not all of them have piezoelectricity. In these non-centrosymmetric crystal classes, 20 crystal classes, except the cubic class, exhibit piezoelectric properties, as shown in Table 1.1.



Figure 1.5 Schematic representation of (a) direct piezoelectric effect and (b) indirect piezoelectric effect. Adopted from ref. [21].

 Table 1.1 The 32 crystal classes with/without piezoelectric properties.

Crystal system	Piezoelectric	Non-piezoelectric
Triclinic	1	1
Monoclinic	2, m	$\frac{4}{m}$
Trigonal	3, 32, 3 m	3 , 3 m
Hexagonal	6, 6 , 622, 6 mm, 6 2 m	$\frac{6}{m}, \frac{6}{m}$ mm
Orthorhombic	222, 2 mm	mmm
Tetragonal	4, 4 , 422, 4 mm, 4 2 m	$\frac{4}{m}, \frac{4}{m}$ mm
Cubic	23, 4 3 m	m3, m3m, 432

1.2.2 Theoretical background of piezoelectricity

The constitutive equation of the fundamental physics for piezoelectric nanogenerators are governed by the following Maxwell equations

$$\nabla . \mathbf{D} = \rho_f \quad (\text{Gauss's Law}) \tag{1.1}$$

$$\nabla \cdot \boldsymbol{B} = 0 \quad (\text{Gauss's Law for magnetism}) \tag{1.2}$$

$$\Delta \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial T} \text{ (Faraday's Law)}$$
(1.3)

$$\Delta \times \boldsymbol{H} = \boldsymbol{J}_f + \frac{\partial \boldsymbol{D}}{\partial \tau}$$
 (Ampere's circuital Law and Maxwell's addition) (1.4)

where the electric field **E**; the magnetic field **B**; magnetizing field **H**; the free electric charge density ρ_f ; the free electric current density J_f ; displacement field **D**,

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \tag{1.5}$$

and polarization field **P**, and permittivity in vacuum ε_0 . As for an isotropic media, $D = \varepsilon E$, where ε is the permittivity of the materials.

In Eq. (1.4), the second term is Maxwell's displacement current defined as

$$J_D = \frac{\partial D}{\partial T} = \varepsilon_0 \frac{\partial E}{\partial T} + \frac{\partial P}{\partial T}$$
(1.6)

For piezoelectric materials, which is anisotropic in nature, then the polarization tensor and direct and indirect equations are defined by

$$P_i = (\boldsymbol{e})_{ijk} \, (\boldsymbol{s})_{jk} \tag{1.7}$$

$$D = es + kE$$
 (Direct piezoelectric) (1.7a)

$$T = c_E s - e^T E$$
 (Indirect piezoelectric) (1.7b)

where s is the mechanical strain; the third order tensor $(e)_{ijk}$ is the piezoelectric tensor; T and c_E are the stress tensor and the elasticity tensor, respectively; k is the dielectric tensor. The displacement current with the variable polarization is as following

$$J_{Di} = \frac{\partial \boldsymbol{P}_i}{\partial T} = \boldsymbol{e}_{ijk} \left(\frac{\partial \boldsymbol{s}}{\partial T}\right)_{jk}$$
(1.8)

This equation (5) is responsible for piezoelectric current output generation for PNGs.

1.2.3 Materials and types of piezoelectric nanogenerators (PNGs)

Piezoelectric materials are classified into two main categories: lead containing and lead-free piezoelectric materials. Firstly, Lead-containing piezoelectric materials mainly include lead zirconate titanate (Pb_xZr_{1-x}TiO₃, abbreviated as PZT) and various dop ed modified versions, which exhibits excellent piezoelectric properties. However, due to the harmful effects of Pb-elements on the human-being and environment, Pb-based materials are limited for wearable electronic and healthcare sector. Therefore, it is very urgent to explore environment-friendly (Pb-free) materials and their performances. Recently, many types of lead-free piezoelectric materials such as barium titanate (BaTiO₃), zinc oxide (ZnO), and polyvinylidene fluoride (PVDF) and its co-polymers have been explored which show many advantages, including good piezoelectricity, simple structure, easy synthesis, low production cost, and suitability for mass production and application. Thus they are gradually replacing lead-containing piezoelectric materials [22–27].

The first PNG was investigated by Prof. Z. L. Wang and co-workers in 2006 with ZnO nanowire (NW) for efficiently low mechanical energy harvesting. These NWs were deformed by weak forces via atomic force microscope with platinum-coated silicon tip in contact mode. Due

to this deformation, the piezoelectric potential was generated at the upper and lower ends of the nanowires. A notable output voltage peak can be observed in each scan of the tip. The coupling between piezoelectric and semiconducting properties in ZnO nanowire leads to charge separation across the nanowire as a result of the applied strain. The corresponding output voltage image of the ZnO nanowire array was recorded when the AFM tip scans over the nanowire. The estimated output voltage and piezoelectric energy conversion efficiency was 6 to 9 mV and 17 to 30 %, respectively (Figure 1.6a). This method of using NWs to generate electrical energy under the action of external forces embodies the power generation function of materials at the nanometerscale and provides an experimental and theoretical basis for the design of self-generating nanodevices [28]. Further, in order to improve the power generation capabilities, AFM tip was replaced by an ultrasonic wave. Therefore, in continuation of earlier work, ZnO nanowire-based PNG was again fabricated by the same research group in 2007, which was driven by ultrasonic waves. This work laid the foundation for the technical transformation and application of nanogenerators and was a milestone in the field of nanomaterials. It has been demonstrated in four possible configurations of contact between NWs and the zigzag electrode as shown in Figure 1.6 (b–e). The typical structure of an ultrasonically driven nanogenerator was consists of a zigzag electrode, ZnO nanowires, a fixed substrate, and an external load (Figure 1.6b). NWs I and II are being deflected towards the left and right sides, respectively, by the electrode. Regardless of their deflection directions, the currents produced by NWs I and II constructively add up (Figure 1.6c and 1.6d). NW III was chosen to elaborate the vibration induced by an ultrasonic wave. As shown in Figure 1.6e, when the compressive side of NW III is in contact with the electrode, the same discharge process as for NW I occurs, resulting in the flow of current from the electrode into the NW. Further, NW IV short in height was under compressive

strain by the electrode without any bending. In such a case, the generated piezoelectric voltage at the top of the NW was negative. Across the electrode-ZnO interface, a positively biased Schottky barrier was formed; hence, the electrons can freely flow across the interface. As a result, electrons flow from the NW into the top zigzag electrode as the deformation occurs. Therefore, output current was a sum of those NWs that actively contribute in output power, but the voltage of the NG is determined by a single NW because all of the NWs were "in parallel" [29].



Figure 1.6 Piezoelectric nanogenerator based on ZnO NW array (a) mechanical deflection given by atomic force microscopy enabled conducting tip. Adopted from ref. [28]. (b) schematic demonstration of nanogenerator design, (c) zig-zag electrode and four types of nanowires, (d) generation of piezoelectric potential when NW I and II realizes the mechanical deflection and (e) when NWs touch the surface of adjacent teeth. Adopted from ref. [29].

Since 2006, there are substantial efforts have been paid for the PNGs in the research and development of sensing devices based on multifunctional piezoelectric materials. Figure 1.7, demonstrated the historical achievements in past few years for PNGs. Furthermore, there are

various piezoelectric materials that have been successfully employed based on inorganic materials such as GaN, ZnSnO₃, CdS, InN, (Na, K)NbO₃, PbZr_{0.52}Ti_{0.48}O₃ for large piezoelectric output performances. But all these materials have limitations due the difficult synthesis route, brittleness, non-biocompatibility and difficult to fabricate large area device.



Figure 1.7 Schematic demonstration of rapid development of piezoelectric nanogenerators in last few-years. Adopted from ref. [20].

Moreover, the primary focus of PNGs lies in their ability to provide flexibility and stretchability, which is crucial for applications in wearable and portable electronics. These applications encompass a wide range of functionalities, including arterial pulse detection for blood pressure monitoring, clinical diagnosis, drug delivery systems, tissue engineering, reactive oxygen species

(ROS) generation, and sensors. In this regard, the organic piezoelectric materials have centered very crucial attention because of their inherent properties such as light weight, flexibility, large area device fabrication capability, biocompatibility and excellent sensitivity with mechanical/thermal stimuli. In particular, the well-known piezoelectric polymers such as poly (vinylidene fluoride), synthetic polypeptide, poly(L-lactic acid) PLLA, nylon-11 and cellulose are the potential candidates for various real-life applications.

1.2.4 Piezo/Pyro/Ferro-electric polymer: Poly(vinylidene fluoride)

Poly(vinylidene fluoride, abbreviated as PVDF) is a semicrystalline fluoropolymer with a simple monomer unit structure (- CH_2 - CF_2 -) exhibits excellent piezo/pyro/ferro-electric properties. It has different polymorphic phases such as α (TGTG), β (TTTT), γ (TTTGTTTG) and δ (TG`TG`) depending on their stereochemical chain conformation, where T and G representing the trans and gauche conformations, respectively (Figure 1.8a). Among them, α -phase is non-polar and most thermally stable because of antiparallel packing of dipoles, therefore, the net dipole moment per unit cell is to be zero. However, the β -phase is most electroactive in nature due to its arrangements of dipoles in a particular direction, which leads to the highest dipole moment $(\mu = 8 \times 10^{-30} C.m)$ along the perpendicular c-axis. Meanwhile, γ -phase is also exhibiting electroactive nature but less than β -phase because of interruption in polymeric chain. Further, δ phase has been found to be electroactive in nature and it exhibits almost similar piezo/ferroelectric properties β -phase and even superior in some cases (unit cell of all these polymorphs are demonstrated in Figure 1.8b) [30,31]. Moreover, due to the semicrystalline nature of PVDF, it typically organizes into crystalline lamella as well as amorphous region. The piezo/ferro-electric properties are mainly govern by the crystalline part of polymer. Now, in order to get the electroactive phase in PVDF, several techniques have been adopted so far (as illustrated in Figure 1.9a). Moreover, Figure 1.9b, shows the increasing research trend of piezoelectric

nanogenerator since first discovery of PNG in 2006. The merits of PVDF-based ferroelectric polymers make them ideal candidates for these applications including robotics, human-machine interaction, e-skin based sensors, non-volatile memories, acoustic signal detection and biomedical sector.



Figure 1.8 Schematic representation of PVDF polymer (a) polymeric chain and (b) corresponding unit cells of polymorphs. Adopted from ref. [30].

The fabrication of polymer nanocomposite is a widely used approach to induce the electroactive phase to investigate better piezo/pyro/ferro-electric properties. By adding nanofillers (NFs) into the organic polymer matrix, one can prepare nanocomposites with high piezoelectric properties, good flexibility, and long service life. Polymer nanocomposites exhibits the better insights of the intermolecular interactions such as hydrogen bonding and ion–dipole interactions between PVDF dipoles (-CH₂-/-CF₂-) and nanofillers. It mainly categorized in organic, inorganic, organic–inorganic hybrid, carbon based and 2D materials (as shown in Figure 1.9c) [32–37].



Figure 1.9 (a) Schematic illustration to achieve electroactive phase from non-polar α -phase in PVDF and (b) current state-of-art of piezoelectric nanogenerator based research publications. (c) schematic of materials, structures and applications of flexible piezoelectric nanogenerators (PNGs). Adopted from ref. [32-37].

These polymer nanocomposites are the suitable approach to overcome the issue of brittleness and fragility of inorganic or ceramic based materials, and may provide the enhanced piezoelectric output performance. Moreover, PNGs made comprising of polymer nanocomposites provide a promising avenue for self-powered electronic and energy harvesting systems, enabling the development of wearable devices, wireless sensors and autonomous system.

1.2.5 Applications of piezoelectricity

Piezoelectric materials have enormous applications for our society, particularly, water and air purification by piezo-catalysis, optical properties such as photodetectors as a piezo-phototronic effect.

1.2.5.1 Piezo-catalysis

Environmental degradation and energy scarcity have sparked widespread concern in last few decades. Among various pollution (organic or inorganic), waste water has attracted substantial attention due to the shortage of clean water resource. The waste water pollutants such as common pesticides, herbicides, organic dyes and biological contaminants such as DNA, proteins, lipids, bacteria, virus, spores etc., present a serious and persistent threat to human health. Hence, the development of sustainable technology is essential to combating both the energy problem and environmental degradation. This has led to the development of several sophisticated water cleanup and disinfection treatments that use reactive oxygen species (ROS). The ROS are highly reactive molecules such as hydroxyl radicals (•OH), superoxide (\cdot O₂⁻), and singlet oxygen (1 O₂), are among the strongest aqueous redox species, and their effective and efficient production is desired in biological, chemical, and environmental fields [38–42]. In this regard, piezo-catalysis has recently emerged as a promising approach for generating ROS, that play an important role in various chemical and biological processes.



Figure 1.10 (a) Schematic view of piezo-catalysis mechanism of PVDF/MoS₂ film (b) corresponding degradation of organic dyes (Acridine Orange (AO), Ethidium Bromide (ET), Eosin Y (EO) and Rhodamine B (RHO)) with time under ultrasonic bath mechanical vibration. Adopted from ref. [41] (c) principal diagram of dye degradation with zinc oxide nanorods (ZnO) and (d) UV-visible absorbance spectra for dye degradation with time under mechanical vibration. Adopted from ref. [40] (e) probable mechanism of organic dye degradation and ROS generation in the presence of piezoelectric material BaTiO₃/PDMS, (f) UV-vis absorbance spectra for Rhodamine B dye degradation and (g) digital image representing the color of dye changes from pink to complete transparent after 120 min due to piezo-catalysis. Adopted from ref. [48].

The piezo-catalysis has been demonstrated as a new advanced oxidation process where low frequency vibration or high-frequency ultrasound waves induces the polarization and establish built-in electric field in piezo catalysts. As a result, electrons and holes can be continuously separated and attracted on the opposite surface for piezo catalytic redox reactions. In an aqueous solution, these surficial charge carriers can undergo oxidation and reduction reactions with water or dissolved species yielding homogeneous ROS that may have a range of applications in various fields such as environmental remediation, microbial inactivation, and cancer treatment.

One key advantage of piezo-catalysis is that it offers a simple and environmentally friendly approach to ROS generation, as it does not require the use of harsh chemicals or highenergy sources. There are various piezoelectric materials such as lead zirconate titanate (PZT), barium titanate (BaTiO₃), and zinc oxide (ZnO) have been employed to generate ROS by piezocatalysis. There are some other materials also with composite form such as $PVDF/MoS_2$, TiO₂/PbTiO₃ and Ag@LiNbO₃/PVDF have been well explored for piezo-catalysis as documented in Figure 1.10 [41,43–48]. Among them, MoS_2 -PVDF nanocomposite film of dimension 2 cm \times 2 cm and thickness 50 μ m was immersed in 10 mL of 10 ppm solutions of each dye (i.e., Acridine Orange (AO), Eosin Y (EO), Ethidium Bromide (ET) and Rhodamine B (RHO) in deionized water. The nanocomposite film was placed in a bath sonicator and subjected to pulsed ultrasonic vibrations for 20 min in dark condition as shown in Figure 1.10a. The percent degradation over time is presented in Figure 1.10b, where the MoS₂-PVDF film shows excellent catalytic activity in dark with >90% degradation achieved for each dye. Further, Jiangping Ma et al. have explored the hydrothermally-synthesized ZnO nanorods for piezo and photo catalysis dye degradation. The principle schematic (Figure 1.10c) for piezo-catalysis mechanism consists of external vibration that can bend ZnO nanorods to induce the occurrence

of piezoelectric potential and a large amount of electric charges via the piezoelectric effect, which can further induce the generation of reactive oxygen species to decompose dye molecule. The piezo-catalysis with the addition of ZnO catalyst for the decomposition of acid orange 7 (AO7) dye is depicted in Figure 1.10d, where the UV absorption peak intensity of dye solution decreases continuously with the increase of vibration time. Degradation of AO7 dye is estimated ~31.8% after undergoing vibration for 100 min. Weiqi Qian et al. have investigated the efficient organic dye (Rhodamine B; RhB) degradation with barium titanate (BaTiO₃, BTO) -polydimethylsiloxane composite porous foam catalyst. A schematic of the BTO-PDMS composite porous foam catalyst under ultrasonic vibration is displayed in Figure 1.10e. An SEM picture of BTO-PDMS composite material is shown in the inset, indicating that the porous structure has an average diameter of 300 µm. While extremely large or very small pores are inferior, pore sizes in the 300 µm range are ideal for piezo-catalysis and provide the benefits of less secondary pollution and enough interaction of materials with solutions. Under the Under the application of an ultrasonic stress, the BTO-PDMS composite porous foam is thought to create separated electron-hole pairs that react with OH^- and O_2 to generate 'OH and ' O_2^- radicals for organic dye degradation, respectively. The UV-visible absorbance (at 554 nm peak) of RhB is found to decreases and then completely disappear after 120 min, indicating that the RhB dye solution had been completely degraded ~ 94 % (Figure 1.10f). Digital photograph of the piezocatalytic decomposition of the dye in the presence of the BTO-PDMS composite catalyst before and after piezo-catalysis is shown in Figure 1.10g. The solution is initially pink, but the colour disappears after 120 min and becomes optically clear due to piezo-catalysis mechanism. After undergoing piezo-catalysis, the RhB solution turns transparent without suspended solids due to hardly any loss of BTO particles.

1.2.5.2 Photodetector as a piezo-phototronic effect

Optoelectronic sensors have attracted the attention of researchers in many fields because of their wide applications in modern electronics. The realization of optoelectronic sensing can further open up new avenue in wearable devices, healthcare sectors, and environmental monitoring. This is highly dependent on the performance of photodetectors, which work as photo-sensing components. To fulfill the growing demands of high-performance photo-sensing devices, tremendous efforts have been devoted to this and the third-generation semiconductor is believed to be a potential candidate to optimize the performance. In this regard piezo-phototronic might be considered as the suitable choice to fulfill the requirement of optical properties. Piezophototronic is the coupling of piezoelectric, photoexciting and semiconducting material. It was first proposed by Z. L. Wang in 2010. The study of the coupling between semiconductor and piezoelectric properties has formed the field of piezotronics. In addition, the well-known field of optoelectronics studies the coupling of semiconductor properties with photoexcitation properties. The study of the coupling between piezoelectric characteristics and photoexcitation characteristics has formed the field of piezophotonics (as shown in Figure 1.11) [49,50]. In particularly, piezo-phototronic effect is based on the piezoelectric effect. When a piezoelectric material is subjected to mechanical stress, it generates a potential difference across its surface due to the built-in-electric field because of separation of positive and negative charges. This potential difference can affect the optical properties of the material by modulating the separation and recombination of photo-generated electron-hole pairs. In the presence of a piezoelectric potential, the separation and recombination of electron-hole pairs are modulated by the mechanical strain induced by the piezoelectric effect [51–55].





Specifically, the piezo-phototronic effect works by modifying the band structure of the semiconductor material. The applied mechanical stress creates a deformation potential that affects the energy levels of the semiconductor's valence and conduction bands, leading to a change in the bandgap energy. This change in the bandgap energy affects the separation and recombination of photo-generated electron-hole pairs, which leads to a change in the optical properties of the material.[56–59]. The piezo-phototronic effect is used to modify the charge carrier separation and transport process at the Schottky contact in order to improve the performance of photodetectors.



Figure 1.12 Representation of experimental set used to measure the performance of photodetector based on ZnO micro/nanowire. The I-V characteristics of photodetector (b) under dark and various light illumination with excitation intensity of 2.2×10^{-5} Wcm⁻². (c) with various compressive strains under dark condition (d) with light illumination under variable strains from ~ -0.36 % to 0.36 % (e) variation in photocurrent with variable strains and (f) responsivity under different strains and illumination intensities.

O. Yang et al. have investigated piezo-phototronic effect with single ZnO micro/nanowire photodetector, and the experimental setup is depicted schematically in Figure 1.12a. A hightemperature thermal evaporation procedure was used to create the ZnO micro/nanowire. Using silver paste, the Schottky contact was formed at both ends of the ZnO nanowire [60]. The typical I-V characteristics of the fabricated device in the dark and under varied UV light (372 nm) irradiation intensities are shown (Figure 1.12b). Further, the symmetric I-V curve demonstrate the formation of the Schottky contact at both ends of the ZnO nanowire. The I–V curves of the ZnO wire photodetector under various strains in dark conditions and under UV illumination with 2.2×10^{-5} Wcm⁻² excitation light intensity are shown in Figure 1.12c and 1.12d, respectively. The photo- current increases gradually with the external strain differing ~ - 0.36% to 0.36% (Figure 1.12d) at a positive bias, while the dark current remains unchanged under strain (Figure 1.12c). Further, the large photocurrent was observed at a low illumination intensity (Figure 1.12e). At high-level illumination, the large amount of photogenerated charge carriers can partly screen the piezo-potential. With the piezo-phototronic effect, the responsivity of the device increased rapidly to sub μ Wcm⁻² (Figure 1.12f). That shows the excellent piezo-phototronic effect in nanowire, when UV light is illuminated.

1.2.5.3 Healthcare sector

The next generation of smart, flexible and wearable electronics for healthcare, robotics, and cyber-physical systems are essential for energy autonomy and conformability. In the past years, various configurations of flexible piezoelectric nanogenerators have been explored for human healthcare signal monitoring including heart rate, arterial pulse detection, and cardiovascular diseases (CVD). A perfect example is next-generation biomedical devices for accurate monitoring of physiological and vital parameters that can be conformably attached to human skin

or, in some cases, can even be implanted inside the body. In prospect, these flexible sensing devices could be used widely in future wearable/portable health monitoring system for remote medicine.[61-65] In particular, PVDF and its co-polymer are interesting material for physiological signal monitoring due to its excellent flexibility, stretchability and biocompatibility. Andreas Petritz et al. have explored the several healthcare possibilities with ultraflexible ferroelectric polymer transducers (UFPTs) from P(VDF:TrFE)_{70:30} co-polymer of PVDF. The UFPTs was fabricated on 1-µm thin parylene diX-SR substrate (Figure 1.13a). Further, the ultra-flexible pressure sensors (UFPTs) were integrated with a compact wireless module, resulting in a small and portable device. Moreover, UFPT device was directly attached to the skin surface without the need for adhesiveness, which has shown the capability of realtime healthcare signal detection. This e-health patch device can monitor vital signs such as pulse rate, human pulse wave, and respiratory rate. A photograph of the wireless patch in operation is displayed in Figure 1.13b, which shows a virtually imperceptible neck-mounted sensor (~2 mg without wiring) connected to a very compact and lightweight (~ 5.6 g) wireless module. This in turn was attached to the skin beneath the collarbone. Since the transducer is ultraflexible and the electronic module is light-weight therefore as fabricated e-health patch is comfortable to wear. This setup was used to monitor the human pulse wave in real time and determine the rate of the pulse wave in a 32-year-old woman at rest condition. pulse rate of 54 min^{-1} and an artery augmentation index (AI) of 56% from the recorded and wirelessly transmitted data. The AI value (AI (%) = $P_2/P_1 \times 100$) was determined from the shape of the human pulse wave, which is shown in Figure 1.13b and 1.13c. Figure 1.13d shows the pulse wave measurements from two ultraflexible ferroelectric sensors attached to the neck of a 34- year-old man. Thus, the UFPT sensor technology excels for real-time pulse wave monitoring.


Figure 1.13 Schematic demonstration of ultraflexible piezoelectric energy harvesting devices integrated on 1- μ m thin parylene substrate. (a) Ultraflexible ferroelectric polymer transducer (UFPTs) are used for various parameters of physiological signal monitoring for healthcare when attached to the human skin. (b) attachment of UFPTs device when attached to human body for pulse wave measurement (c) demonstration of an arterial pulse detection with important feature of signal (P₁ and P₂) of heart rate (54 min⁻¹ for 32-year-old women). (d) the blood pressure measurement of human arteria in the neck by the pulse wave velocity (PWV). Adopted from ref. [64].

1.2.5.4 Piezoelectric ink as a printable technology

Considering the rapid technological advances and the need for low cost, simple processing, and large area applications, additive manufacturing technologies are becoming increasingly interesting for applications including sensors, light-emitting devices, flat panel displays, solar cells, printable technology, and batteries, among others. These applications require materials with specific properties, being piezoelectric materials particularly relevant for sensor and actuator applications [66–68], For instances, the fields of organic and printed electronics have

attracted increased research interest within the past few years due to their abilities of costeffective manufacturing material deposition on large areas. In particular, piezoelectric ink is an important material for printable and flexible devices because it allows for the fabrication of electronic components that can be easily and inexpensively printed onto flexible substrates, such as plastics or paper. The current status of printable piezoelectric pressure sensors involves the fabrication of piezoelectric inks that can be used with various additive manufacturing technologies such as spray-printing, screen-printing, and doctor blade as illustrated in Figure 1.14a. Piezoelectric inks are used in the fabrication of an all-printed touch screen, demonstrating the effectiveness and viability of this approach.[69–71]. Figure 1.14b and 1.14c shows a schematic representation of the implemented layout, comprising the screen-printed piezoelectric film and electrodes on both surfaces of the film. Figure 1.14d shows the output voltage (V_{out}) of the amplifying circuit when sensor 3 is pressed and then released. Further, the repeatability of output signal was demonstrated in Figure 1.14e. The signal averages on 2.5 V as expected and develops a negative peak when being pressed, and then a positive peak when released. The existence of cross-talking sensor matrix array is showing the piezoelectric nature due to vibration when sensor 4 is touched and corresponding output signal (Figure 1.14f). Thus, Figure 1.14 shows that the piezoelectric sensors present an excellent response without hysteresis, therefore, the developed inks can be applied for the development of touch panels produced by additive manufacturing techniques.



Figure 1.14 Schematic representation of the different additive manufacturing techniques and procedures (a) Spray-coating, Screen Printing and Doctor blade. (b) layout of the all-printed touch screen sensors, (c) digital photograph of touch screen. (d) touch pad response upon finger pressing and release, (e) piezoelectric sensor under cycling pressing and releasing events, and (f) sensor matrix on touch event in one of the sensors and corresponding signals for each sensor.

1.2.6 Pyroelectric nanogenerator (PyNG) and applications

The phenomenon of pyroelectricity has been known for thousands of years ago when the Greek philosopher Theophrastus noticed that a stone, called lyngourion in Greek or lyncurium in Latin, that had the property of attracting straws and bits of wood. Then, he realized that this attraction was strongly dependent on the generation of electrostatic charge under temperature fluctuation [72,73]. The origin of pyroelectricity is related to the crystal structure of certain materials. It is a property of crystals that have a non-centrosymmetric crystal structure, which means that their crystal lattice does not have a center of symmetry. When a non-centrosymmetric crystal is heated or cooled, the atoms within the crystal vibrate and orient, causing a change in the dipole moment of the crystal. Therefore, pyroelectricity is referred as the change in spontaneous polarization when temperature oscillation (ΔT) is applied. Quantitatively it is defined as $\Delta P_S = p \Delta T$, where, $\Delta P_{\rm s}$, p are the change in the spontaneous polarization and pyroelectric coefficient. Further, the applicability of pyroelectric materials in energy harvesting devices, such as pyroelectric nanogenerators (PyNG), is a relatively recent development. The first demonstration of a PyNG was reported in 2012 by Z. L. Wang since then, PyNG have attracted significant research interest and are considered as a promising technology for sustainable energy harvesting. There are various materials that possesses the excellent pyroelectricity such as ZnO, PZT, BaTiO₃, KNbO₃, LiTaO₃, PVDF and its co-polymers have been explored so far. Traditional, PyNG consists of metal/pyroelectric material/metal like parallel plate capacitor geometry in which metal electrode used for collection of generated polarization due to change in temperature fluctuation.[74–80] Yang et al. have proposed a PyNG based on KNbO₃-NW/PDMS polymer composite with excellent pyroelectric response (as shown in Figure 1.15). As fabricated pyroelectric device mainly consists of three layers as top and bottom electrode with Ag film and indium tin oxide (ITO) electrode and third layer is NW-composite structure in between the two electrodes (Figure 1.15a). The diameter of synthesized KNbO₃ is 150 nm along the growth direction of [011] as shown in Figure 1.15a. Further, the electrical output response of pyroelectric device is obtained as 2 mV of voltage and 20 pA of current, respectively, under the periodic turn on and off temperature fluctuation from 295 to 298 K as shown in Figure 1.15b.



Figure 1.15 Experimental measurement of PyNG based on KNbO₃ NW (a) schematic demonstration of PyNG, TEM image and corresponding SAED pattern and HRTEM images of the NW (b) the electrical response of PyNG under periodic turn on and off cycle of temperature fluctuation. (c) schematic view of PyNG mechanism for electrical output generation based on electric dipoles orientations under heating and cooling cycle. Adopted from ref. [79].

The responsible mechanism for electrical signal generation is described in Figure 1.15c. The spontaneous electric dipoles in KNbO₃ NWs originate from Nb⁵⁺ ion movement in NbO₆ octahedra, where there are six possible orientations along the <001> directions. Due to thermal fluctuations, the electric dipoles will randomly oscillate within a degree from the respective

aligning axis. In the first case, under a fixed temperature (dT/dt = 0), the net spontaneous polarization of dipole movement is constant and hence there is no electrical output (Figure 1.15c). Next, in the middle layer at dT/dt > 0, the electric dipoles oscillate with a wider range from their alignment axis. Then the net spontaneous polarization is decreases due to decrease in dipole moment because of larger oscillation angle. Thus, induced charged at the electrodes started the flow electrons in the circuit. In the last case, when pyroelectric device is cooled i.e., dT/dt < 0, the induced spontaneous polarization is maximum due to the oscillation of electric dipoles in smaller degree (Figure 1.15c). Therefore, under cooling cycle net magnitude of spontaneous polarization is increases and thus electrons will flow in the opposite direction.

1.3 Outline of the thesis

This thesis aims to explore the current state-of-the-art in energy harvesting technology, including various techniques, materials, and applications. It also evaluates the challenges and future prospects of this technology, including its integration into real-life existing systems such as healthcare sector, dynamic pressure sensors, temperature sensor, cost-effectiveness, and scalability. Thus, the present thesis is organized in the following manner.

Chapter 2: We have prepared polymer nanocomposite based on PVDF and silver carbonate (Ag_2CO_3) with the predominant electroactive γ -phase that exhibits the high dielectric constant and mechanical energy harvesting performance. We have also demonstrated the formation of γ -phase in nanocomposite via C-C bond rotation to attain a stable conformation, which is driven by Ag charge nucleation. In addition to that we have also investigated the inter-fragment, non-covalent, intermolecular interactions between PVDF and the silver carbonate filler (Ag_2CO_3) via density functional theory (DFT) based on the linear combination of atomic orbitals (LCAO) approach. Further, fabricated flexible piezoelectric nanogenerator (FPNG) has shown excellent

electrical output signal such as open circuit voltage (V_{OC}), short circuit current (I_{SC}) and electrical power density (P) found to be more than 15 V, 6 mA and ~ 7 µW cm⁻², respectively. FPNG has shown various energy harvesting properties e.g., human gestures (such as finger bending, walking and acoustic signal detection) due to its excellent mechano-sensitivity (45 mV/kPa). In addition to that, under continuous ultrasound mechanical vibration, the piezocatalysis dye degradation of methyl orange (MO) is estimated to be approximately 80% with the nanocomposite film. Due to applied mechanical vibration to the nanocomposite film a piezopotential is generated on its surface which resulted in several redox reactions on the nanocomposite's surface in aqueous solution. Therefore, PVDF/Ag₂CO₃ nanocomposite is a promising material for both effective dye degradation and mechanical energy harvesting applications.

Chapter 3: First time, we have introduced the nanoprecipitation technique to machinate PVDF nanoparticles (diameter ~ 200 nm) with the predominant electroactive δ -phase (which is least studied so far) at the interface of solvent and non-solvent media. The remarkable piezo- and ferro-electric properties of the δ -phase in PVDF are similar with those of the extensively studied β -phase. It is noteworthy to mention that δ -phase has received limited attention due to the challenging processing conditions that require ultra-high electric fields (MV/m) and pressure (MPa). In this regard, the solvent-based phase separation method stands out as an exceptionally convenient approach, which has shown immense technological and commercial benefits for energy harvesting based applications. Further, giant piezoelectric coefficient i.e., d₃₃ ~ - 43 pm/V is estimated via piezo-response microscopy at a very low DC bias ± 5 V, that, confirms the exceptional switching dynamics of δ -PVDF dipoles. In addition to that, the fabricated FPNG with δ -PVDF NPs exhibits power density of 2µWcm⁻² and 24 % instantaneous piezoelectric

energy conversion efficiency. Moreover, due to the excellent mechano-sensitivity (S \sim 107 mV/kPa), FPNG promises physiological signal monitoring (arterial pulse detection) that shows the capability for self-powered sensors and actuators.

Chapter 4: In continuation of earlier work, as fabricated δ -PVDF NPs are further functionalized with semiconducting polydopamine-polyethylenimine (PDA-PEI) to make sure the well aqueous dispersion is possible. Further, these functionalized NPs have shown the excellent ability of printable piezoelectric ink due to the hydrophilic nature, which is proven by the written abilities on different substrates. In addition to that, we have also fabricated FPNG which shows a promising electrical output performance and speech signal detection ability. Besides it, FPNG exhibits the excellent photodetection ability as a strain modulated piezo-phototronic effect. The remarkable spectral parameters of photodetector are noticed as fast photo-response (0.43 s) and, responsivity 24 μ A/ W and specific detectivity ~ 1.4 × 10¹⁰ Jones, which promises the ideal choice for optoelectronic devices.

Chapter 5: In this work, we have considered two-dimensional (2D) monoelemental tellurium (Te) due to their emerging piezo- and ferro-electric properties. Here, we have demonstrated an ultrahigh pyroelectric response in 2D Te nanosheets (thickness ~ 4 to 6 nm) under the periodic turn-on and off temperature oscillations due to changes in spontaneous polarization. The exceptionally high pyroelectric coefficient ($p \sim 3000 \ \mu Cm^{-2}K^{-1}$) of 2D Te nanosheets exhibits the better performance than conventional pyroelectric materials such as PZT ($p \sim 347 \ \mu Cm^{-2}K^{-1}$) and PVDF ($p \sim 40 \ \mu Cm^{-2}K^{-1}$) by ~ eightfold. This substantial enhancement in pyroelectric coefficient underscores the excellent figure of merits (FoMs) exhibited by the 2D Te nanosheets. Further, theoretical calculations predict the important parameters such as born effective charges, piezoelectric coefficients and thermal expansion coefficients which are responsible for ultrahigh

pyroelectricity in 2D Te nanosheets. Thus, the newly explored 2D Te nanosheets show a new paradigm of their potential applicability and technological merits for futuristic thermal energy harvesting-based flexible electronics.

Chapter 6: As a consequence of earlier work, 2D tellurium nanoflakes are incorporated into the polymer matrix of PVDF for the hybrid flexible piezo- and pyro-electric nanogenerator (HyNG). As prepared nanogenerator exhibits the excellent electrical output performance as ~ 7.5 V and ~ 4 μ A of V_{oc} and I_{sc} under a continuous imparted mechanical force of 12 N. Similarly, we have also recorded the pyroelectric response of HyNG as V_{oc} ~ 100 mV and I_{sc} ~ 400 pA, respectively, under periodic temperature oscillation ($\Delta T = 7K$). The quantified piezoelectric and pyroelectric coefficients of HyNG are 81 pC/N and 300 μ Cm⁻²K⁻¹, respectively. Further, the excellent mechano-sensitivity (Sm ~ 148 mV/kPa) suggests the potential utility of HyNG to detect subtle physiological signal of human body movements such as eye blinking, elbow bending, finger bending and knee bending. Therefore, HyNG have the capability to convert efficient mechanical and thermal energy into usable electrical energy, which can be further used for several low power electronic devices such as wearable and implantable medical sensors.

Chapter 7: Describes the summary of present thesis work and prospective research planning in this field.

1.4 Material characterizations

In the present thesis materials characterization is performed with the following analytical instruments:

Fourier transform infrared spectra were recorded in ATR mode with 4 cm⁻¹ resolution and 64 scans using an IR spectrophotometer (VERTEX70 Bruker, Germany). Powder X-ray diffraction

(PXRD) patterns were measured using an X-ray diffractometer (D-8 Advance Bruker, Germany) with Cu-K α radiation (wavelength ~ 0.154 nm). The quantitative elemental analysis was carried out via X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Fisher Scientific, USA). The ultraviolet photoelectron spectroscopy (UPS) was performed using the He I (hv = 21.22 eV) UV source under ultrahigh vacuum ($\approx 10^{-9}$ mBar) for measurement of the work function. The selected area electron diffraction (SAED) pattern high resolution surface imaging was obtained by transmission TEM (JEM-2100, JEOL, Japan). The field emission scanning electron microscopy (FE-SEM) (JSMIT-300, JEOL, Japan) was employed to obtain the surface morphology. The surface topography and piezo-response force microscopy was recorded via atomic force microscopy (AFM) (Core AFM, Nanosurf, Switzerland). UV-visible-NIR transmittance spectra were recorded on a spectrophotometer (G9825A Cary Agilent, USA) and UV-visible absorbance spectra were recorded with a UV-2600 SHIMADZU, Japan. The dielectric study was performed using an impedance analyzer (E4990A Keysight Technology, USA). Water contact angle (WCA) were measured by drop shape analyzer (DSA25E Krussscientific, Germany). The rheology properties were collected with modular compact rheometer (MCR 302, Anton Paar, Austria). The electrical output performance of the FPNG, i.e., open circuit voltage (V_{OC}) and short circuit current (I_{SC}), were measured using an oscilloscope (DSOX1102G Keysight, USA) and source meter (B2902A, Keysight, USA), respectively.

1.5 References

- M.H. Ahmadi, M. Ghazvini, M.A. Nazari, M.A. Ahmadi, F. Pourfayaz, G. Lorenzini, T. Ming, Renewable energy harvesting with the application of nanotechnology: A review, Int. J. Energy Res. 43 (2019) 1387–1410.
- [2] R. Avtar, N. Sahu, A.K. Aggarwal, S. Chakraborty, A. Kharrazi, A.P. Yunus, J. Dou, T.A. Kurniawan, Remote Sensing and GIS A Review, Resouces 8 (2019) 23.
- [3] O. Ellabban, H. Abu-Rub, F. Blaabjerg, Renewable energy resources: Current status, future prospects and their enabling technology, Renew. Sustain. Energy Rev. 39 (2014) 748–764.
- [4] Y. Hu, Z.L. Wang, Recent progress in piezoelectric nanogenerators as a sustainable power source in self-powered systems and active sensors, Nano Energy 14 (2014) 3–14.
- [5] Y. Qin, X. Wang, Z.L. Wang, Microfibre-nanowire hybrid structure for energy scavenging, Nature 451 (2008) 809–813.
- [6] Z.L. Wang, Triboelectric nanogenerators as new energy technology and self-powered sensors Principles, problems and perspectives, Faraday Discuss. 176 (2014) 447–458.
- [7] C. Xu, Y. Song, M. Han, H. Zhang, Portable and wearable self-powered systems based on emerging energy harvesting technology, Microsyst. Nanoeng. 7 (2021) 1–14.
- [8] L. Dong, A.B. Closson, M. Oglesby, D. Escobedo, X. Han, Y. Nie, S. Huang, M.D. Feldman, Z. Chen, J.X.J. Zhang, In vivo cardiac power generation enabled by an integrated helical piezoelectric pacemaker lead, Nano Energy 66 (2019) 104085.
- [9] H. Zhang, X.S. Zhang, X. Cheng, Y. Liu, M. Han, X. Xue, S. Wang, F. Yang, S. A S, H. Zhang, Z. Xu, A flexible and implantable piezoelectric generator harvesting energy from the pulsation of ascending aorta: In vitro and in vivo studies, Nano Energy 12 (2015) 296–304.

- [10] Q. Shi, T. He, C. Lee, Progress in wearable electronics/photonics Moving toward the era of artificial intelligence and internet of things, InfoMat 2 (2020) 1131–1162.
- [11] Y. Hu, Y. Zhang, C. Xu, L. Lin, R.L. Snyder, Z.L. Wang, Self-powered system with wireless data transmission, Nano Lett. 11 (2011) 2572–2577.
- B. Shi, Z. Liu, Q. Zheng, J. Meng, H. Ouyang, Y. Zou, D. Jiang, X. Qu, M. Yu, L. Zhao,
 Y. Fan, Z.L. Wang, Z. Li, Body-integrated self-powered system for wearable and implantable applications, ACS Nano 13 (2019) 6017–6024.
- [13] M. Ma, Z. Kang, Q. Liao, Q. Zhang, F. Gao, X. Zhao, Z. Zhang, Y. Zhang, Development, applications, and future directions of triboelectric nanogenerators, Nano Res. 11 (2018) 2951–2969.
- [14] Z.L. Wang, On Maxwell's displacement current for energy and sensors : the origin of nanogenerators, Biochem. Pharmacol. 20 (2017) 74–82.
- [15] Z.L. Wang, On the first principle theory of nanogenerators from Maxwell's equations, Nano Energy 68 (2020) 104272.
- [16] Y. Zi, Z.L. Wang, Nanogenerators: An emerging technology towards nanoenergy, APL Mater. 5 (2017).
- P. Basset, S.P. Beeby, C. Bowen, Z.J. Chew, A. Delbani, R.D.I.G. Dharmasena, B. Dudem, F.R. Fan, D. Galayko, H. Guo, J. Hao, Y. Hou, C. Hu, Q. Jing, Y.H. Jung, S.K. Karan, S. Kar-Narayan, M. Kim, S.W. Kim, Y. Kuang, K.J. Lee, J. Li, Z. Li, Y. Long, S. Priya, X. Pu, T. Ruan, S.R.P. Silva, H.S. Wang, K. Wang, X. Wang, Z.L. Wang, W. Wu, W. Xu, H. Zhang, Y. Zhang, M. Zhu, Roadmap on nanogenerators and piezotronics, APL Mater. 10 (2022).

- [18] Z. Zhao, Y. Dai, S.X. Dou, J. Liang, Flexible nanogenerators for wearable electronic applications based on piezoelectric materials, Mater. Today Energy 20 (2021) 100690.
- [19] S. Rana, V. Singh, B. Singh, Recent trends in 2D materials and their polymer composites for effectively harnessing mechanical energy, IScience 25 (2022) 103748.
- [20] D. Hu, M. Yao, Y. Fan, C. Ma, M. Fan, M. Liu, Strategies to achieve high performance piezoelectric nanogenerators, Nano Energy 55 (2019) 288–304.
- [21] W. Wang, Y. Jiang, P.J. Thomas, Structural design and physical mechanism of axial and radial sandwich resonators with piezoelectric ceramics: A review, Sensors 21 (2021) 1–24.
- [22] X. Niu, W. Jia, S. Qian, J. Zhu, J. Zhang, X. Hou, J. Mu, W. Geng, J. Cho, J. He, X. Chou, High-Performance PZT-Based Stretchable Piezoelectric Nanogenerator, ACS Sustain. Chem. Eng. 7 (2019) 979–985.
- [23] G.G. Park, E.J. Lee, S. Jung, S. Jeong, H.S. Kim, Y. Choi, S.Y. Lee, Double Nanocomposites-Based Piezoelectric Nanogenerators for High-Performance Energy Harvester, ACS Appl. Energy Mater. 5 (2022) 8835–8843.
- [24] B. Mondal, H.K. Mishra, D. Sengupta, A. Kumar, A. Babu, D. Saini, V. Gupta, D. Mandal, Lead-free perovskite Cs₃Bi₂I₉-derived electroactive PVDF composite-based piezoelectric nanogenerators for physiological signal monitoring and piezo-phototronic-aided strained modulated photodetectors. Langmuir 38 (2022) 12157.
- [25] Z. Mallick, D. Saini, R. Sarkar, T.K. Kundu, D. Mandal, Piezo-phototronic effect in highly stable lead-free double perovskite Cs₂SnI₆-PVDF nanocomposite: Possibility for strain modulated optical sensor, Nano Energy 100 (2022) 107451.
- [26] L. Gu, J. Liu, N. Cui, Q. Xu, T. Du, L. Zhang, Z. Wang, C. Long, Y. Qin, Enhancing the

current density of a piezoelectric nanogenerator using a three-dimensional intercalation electrode, Nat. Commun. 11 (2020) 1–9.

- [27] A. Sood, M. Desseigne, A. Dev, L. Maurizi, A. Kumar, N. Millot, S.S. Han, A Comprehensive Review on Barium Titanate Nanoparticles as a Persuasive Piezoelectric Material for Biomedical Applications: Prospects and Challenges, Small 19 (2022) 1–29.
- [28] Z. Lin, J. Song, Piezoelectric nanogenerators based on zinc oxide nanowire arrays science 312 (2006) 242–246.
- [29] X. Wang, Direct-Current Nanogenerator, Science 102 (2007) 102–105.
- [30] Q. Li, J. Zhao, B. He, Z. Hu, Solution processable poly(vinylidene fluoride)-based ferroelectric polymers for flexible electronics, APL Mater. 9 (2021).
- [31] R.G. Kepler, R.A. Anderson, Ferroelectric polymers, Adv. Phys. 41 (1992) 1–57.
- [32] X. Yuan, X. Gao, J. Yang, X. Shen, Z. Li, S. You, Z. Wang, S. Dong, The large piezoelectricity and high power density of a 3D-printed multilayer copolymer in a rugby ball-structured mechanical energy harvester, Energy Environ. Sci. 13 (2020) 152–161.
- [33] C. K. Jeong, C. Baek, A. I. Kingon, K.-I. Park, S. H. Kim, Lead-free perovskite nanowireemployed piezopolymer for highly efficient flexible nanocomposite energy harvester. Small 14 (2018) 1704022.
- [34] E.J. Lee, T.Y. Kim, S.W. Kim, S. Jeong, Y. Choi, S.Y. Lee, High-performance piezoelectric nanogenerators based on chemically-reinforced composites, Energy Environ. Sci. 11 (2018) 1425–1430.
- [35] D. Wang, G. Yuan, G. Hao, Y. Wang, All-inorganic flexible piezoelectric energy harvester enabled by two-dimensional mica, Nano Energy 43 (2018) 351–358.
- [36] S. Ippili, V. Jella, J. Kim, S. Hong, S.G. Yoon, Unveiling predominant air-stable organotin

bromide perovskite toward mechanical energy harvesting, ACS Appl. Mater. Interfaces 12 (2020) 16469–16480.

- [37] H. Pei, S. Shi, Y. Chen, Y. Xiong, Q. Lv, Combining solid-state shear milling and fff 3dprinting strategy to fabricate high-performance biomimetic wearable fish-scale pvdf-based piezoelectric energy harvesters, ACS Appl. Mater. Interfaces 14 (2022) 15346–15359.
- [38] S. Tu, Y. Guo, Y. Zhang, C. Hu, T. Zhang, T. Ma, Piezocatalysis and piezophotocatalysis : catalysts classification and modification strategy reaction mechanism and practical application, Adv. Funct. Mater. 2005158 (2020) 1–31.
- [39] Y. Wang, Y. Xu, S. Dong, P. Wang, W. Chen, Z. Lu, B. Pan, D. Wu, C.D. Vecitis, G. Gao, Ultrasonic activation of inert poly(tetrafluoroethylene) enables piezocatalytic generation of reactive oxygen species Nat. Commun. 12 (2021) 3508.
- [40] J. Ma, J. Ren, Y. Jia, Z. Wu, L. Chen, N.O. Haugen, H. Huang, Y. Liu, Nano Energy High efficiency bi-harvesting light/vibration energy using piezoelectric zinc oxide nanorods for dye decomposition, Nano Energy 62 (2019) 376–383.
- [41] B. Bagchi, N.A. Hoque, N. Janowicz, S. Das, M.K. Tiwari, Re-usable self-poled piezoelectric/piezocatalytic films with exceptional energy harvesting and water remediation capability, Nano Energy 78 (2020) 105339.
- [42] C. Jin, D. Liu, J. Hu, Y. Wang, Q. Zhang, L. Lv, F. Zhuge, The role of microstructure in piezocatalytic degradation of organic dye pollutants in wastewater, Nano Energy 59 (2019) 372–379.
- [43] J. Liu, W. Qi, M. Xu, T. Thomas, S. Liu, M. Yang, Piezocatalytic Techniques in Environmental Remediation, Angew. Chem. Int. Ed. 62 (2023) e202213927.
- [44] D. Liu, C. Jin, F. Shan, J. He, F. Wang, Synthesizing BaTiO₃ nanostructures to explore

morphological influence, kinetics, and mechanism of piezocatalytic dye degradation, ACS Appl. Mater. Interfaces. 12 (2020) 17443–17451.

- [45] G. Singh, M. Sharma, R. Vaish, Flexible Ag@LiNbO₃/PVDF Composite Film for Piezocatalytic Dye/Pharmaceutical Degradation and Bacterial Disinfection, ACS Appl. Mater. Interfaces. 13 (2021) 22914–22925.
- [46] X. Chen, L. Liu, Y. Feng, L. Wang, Z. Bian, H. Li, Z.L. Wang, Fluid eddy induced piezopromoted photodegradation of organic dye pollutants in wastewater on ZnO nanorod arrays/3D Ni foam, Mater. Today. 20 (2017) 501–506.
- [47] X. Ning, A. Hao, Y. Cao, J. Hu, J. Xie, D. Jia, Effective promoting piezocatalytic property of zinc oxide for degradation of organic pollutants and insight into piezocatalytic mechanism, J. Colloid Interface Sci. 577 (2020) 290–299.
- [48] W. Qian, K. Zhao, D. Zhang, C.R. Bowen, Y. Wang, Y. Yang, Piezoelectric materialpolymer composite porous foam for efficient dye degradation via the piezo-catalytic effect, ACS Appl. Mater. Interfaces. 11 (2019) 27862–27869.
- [49] Z. L. Wang, Progress in Piezotronics and Piezo-Phototronics, Adv. Mater. 24 (2012)4632–4646.
- [50] Z.L. Wang, Piezotronic and piezophototronic effects, J. Phys. Chem. Lett. 1 (2010) 1388– 1393.
- [51] Z.L. Wang, Nanogenerators, self-powered systems, blue energy, piezotronics and piezophototronics – A recall on the original thoughts for coining these fields, Nano Energy 54 (2018) 477–483.
- [52] P. Lin, L. Zhu, D. Li, L. Xu, C. Pan, Z. Wang, Piezo-phototronic effect for enhanced flexible mos₂/wse₂ van der waals photodiodes, Adv. Funct. Mater. 28 (2018) 1–8.

- [53] Z.L. Wang, W. Wu, Piezotronics and piezo-phototronics: Fundamentals and applications, Natl. Sci. Rev. 1 (2014) 62–90.
- [54] C. Pan, J. Zhai, Z.L. Wang, Piezotronics and piezo-phototronics of third generation semiconductor nanowires, Chem. Rev. 119 (2019) 9303–9359.
- [55] X. Han, M. Chen, C. Pan, Z.L. Wang, Progress in piezo-phototronic effect enhanced photodetectors, J. Mater. Chem. C. 4 (2016) 11341–11354.
- [56] L. Zhu, Q. Lai, W. Zhai, B. Chen, Z.L. Wang, Piezo-phototronic effect enhanced polarization-sensitive photodetectors based on cation-mixed organic–inorganic perovskite nanowires, Mater. Today. 37 (2020) 56–63.
- [57] S. Veeralingam, S. Badhulika, Enhanced carrier separation assisted high-performance piezo-phototronic self-powered photodetector based on core-shell ZnSnO₃@In₂O₃ heterojunction, Nano Energy 98 (2022) 107354.
- [58] D.Q. Zheng, Z. Zhao, R. Huang, J. Nie, L. Li, Y. Zhang, High-performance piezophototronic solar cell based on two-dimensional materials, Nano Energy 32 (2017) 448.
- [59] L. Zhu, Z.L. Wang, Recent Progress in Piezo-Phototronic Effect Enhanced Solar Cells, Adv. Funct. Mater. 29 (2019) 1–18.
- [60] Q. Yang, X. Guo, W. Wang, Y. Zhang, S. Xu, D.H. Lien, Z.L. Wang, Enhancing sensitivity of a single ZnO micro-/nanowire photodetector by piezo-phototronic effect, ACS Nano 4 (2010) 6285–6291.
- [61] C. Dagdeviren, B.D. Yang, Y. Su, P.L. Tran, P. Joe, E. Anderson, J. Xia, V. Doraiswamy,
 B. Dehdashti, X. Feng, B. Lu, R. Poston, Z. Khalpey, R. Ghaffari, Y. Huang, M.J. Slepian,
 J.A. Rogers, Conformal piezoelectric energy harvesting and storage from motions of the heart, lung, and diaphragm, Proc. Natl. Acad. Sci. 111 (2014) 1927–1932.

- [62] Y. Zang, F. Zhang, C.A. Di, D. Zhu, Advances of flexible pressure sensors toward artificial intelligence and health care applications, Mater. Horizons 2 (2015) 140–156.
- [63] T.S. Dinh Le, J. An, Y. Huang, Q. Vo, J. Boonruangkan, T. Tran, S.W. Kim, G. Sun, Y.J. Kim, Ultrasensitive anti-interference voice recognition by bio-inspired skin-attachable self-cleaning acoustic sensors, ACS Nano 13 (2019) 13293–13303.
- [64] A. Petritz, E. Karner-Petritz, T. Uemura, P. Schäffner, T. Araki, B. Stadlober, T. Sekitani, Imperceptible energy harvesting device and biomedical sensor based on ultraflexible ferroelectric transducers and organic diodes, Nat. Commun. 12 (2021) 2399.
- [65] R. Wang, L. Mu, Y. Bao, H. Lin, T. Ji, Y. Shi, J. Zhu, W. Wu, Holistically engineered polymer–polymer and polymer–ion interactions in biocompatible polyvinyl alcohol blends for high-performance triboelectric devices in self-powered wearable cardiovascular monitorings, Adv. Mater. 32 (2020) 1–10.
- [66] E. Gutiérrez-Fernández, J. Cui, D.E. Martínez-Tong, A. Nogales, Preparation, physical properties, and applications of water-based functional polymer inks, Polymers 13 (2021) 1–17.
- [67] S. Gonçalves, J. Serrado-Nunes, J. Oliveira, N. Pereira, L. Hilliou, C.M. Costa, S. Lanceros-Méndez, Environmentally Friendly Printable Piezoelectric Inks and Their Application in the Development of All-Printed Touch Screens, ACS Appl. Electron. Mater. 1 (2019) 1678.
- [68] M. Franco, R. Alves, N. Perinka, C. Tubio, P. Costa, S. Lanceros-Mendéz, Water-Based Graphene Inks for All-Printed Temperature and Deformation Sensors, ACS Appl. Electron. Mater. 2 (2020) 2857–2867.
- [69] B. Nan, S. Olhero, R. Pinho, P.M. Vilarinho, T.W. Button, J.M.F. Ferreira, Direct ink

writing of macroporous lead-free piezoelectric Ba_{0.85} Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃, J. Am. Ceram. Soc. 102 (2019) 3191–3203.

- [70] M. Berggren, D. Nilsson, N.D. Robinson, Organic materials for printed electronics, Nat. Mater. 6 (2007) 3–5.
- [71] S. Emamian, B.B. Narakathu, A.A. Chlaihawi, B.J. Bazuin, M.Z. Atashbar, Screen printing of flexible piezoelectric based device on polyethylene terephthalate (PET) and paper for touch and force sensing applications, Sens. Actuator A Phys. 263 (2017) 639– 647.
- [72] R.W. Whatmore, Pyroelectric devices and materials, Reports Prog. Phys. 49 (1986) 1335– 1386.
- [73] S.B. Lang, Pyroelectricity: From ancient curiosity to modern imaging tool, Phys. Today.58 (2005) 31–36.
- [74] S. Korkmaz, A. Kariper, Pyroelectric nanogenerators (PyNGs) in converting thermal energy into electrical energy: Fundamentals and current status, Nano Energy 84 (2021) 105888.
- [75] G. Velarde, Pyroelectric thin films Past , present , and future Pyroelectric thin films Past , present , and future, APL Mater. 9 (2021) 010702.
- [76] S. Jachalke, E. Mehner, H. Stöcker, J. Hanzig, M. Sonntag, T. Weigel, T. Leisegang, D.C. Meyer, J. Hanzig, M. Sonntag, T. Weigel, S. Jachalke, E. Mehner, H. St, How to measure the pyroelectric coefficient?, Appl. Phys. Rev. 4 (2017) 021303.
- [77] C.R. Bowen, J. Taylor, E. Leboulbar, D. Zabek, A. Chauhan, R. Vaish, Environmental Science Pyroelectric materials and devices for energy harvesting applications, Energy Environ. Sci. 7 (2014) 3836.

- [78] D. Zabek, J. Taylor, E. Le Boulbar, C.R. Bowen, Micropatterning of flexible and free standing polyvinylidene difluoride (PVDF) films for enhanced pyroelectric energy transformation, Adv. Energy Mater. 5 (2015) 1–6.
- [79] Z.L. Wang, G. Zhu, Y. Yang, S. Wang, C. Pan, Progress in nanogenerators for portable electronics, Mater. Today 15 (2012) 532–543.
- [80] Y. Zi, L. Lin, J. Wang, S. Wang, J. Chen, X. Fan, P.K. Yang, F. Yi, Z.L. Wang, Triboelectric-pyroelectric-piezoelectric hybrid cell for high-efficiency energy-harvesting and self-powered sensing, Adv. Mater. 27 (2015) 2340–2347.

Chapter 2

Polymer Nanocomposite (PVDF/Ag₂CO₃) as a Flexible Piezoelectric

Mechanical Energy Harvester and Organic Dye Degradation



2.1 Introduction

The demand for flexible, lightweight, and portable electronic devices along with high energy density is increasing rapidly, particularly for sensors and actuators. To meet these requirements, flexible piezoelectric polymer nanocomposites are gaining widespread attention due to their exceptional piezo-, pyro-, and ferro-electric properties. These nanocomposites offer several promising applications, ranging from environmental remediation, high-density energy storage, superior mechanical energy harvesting, to various biomedical sectors, such as physiological signal monitoring, tissue engineering, drug delivery, as well as sensors and actuators for defense systems and artificial intelligence [1-6]. In particular, polymer nanocomposites have been considered as a promising candidate for high dielectric constant (ε_r), electric breakdown strength (E_b) , low loss tangent (tan δ), easy fabrication process, low cost, excellent flexibility in advancement of market electronics [7–10]. Therefore, we have selected poly(vinylidene fluoride, i.e., PVDF) as potential polymer matrix due to its exceptional piezo-, pyro-, and ferro-, electric applications and high breakdown strength for energy storage [11–15]. In order to nucleate the electroactive phase in PVDF polymer we have incorporated silver carbonate (Ag₂CO₃) as a filler. In polymer nanocomposites, polymers usually act as the matrix and a very small amount of inorganic/organic filler can be used as a reinforcement, which can enhance the dielectric and ferroelectric properties. Recently, the development of self-powered electronic devices has made these polymer nanocomposites of high interest. Furthermore, due to the rapid rise of industrialization, the issue of environmental pollution is a major concern globally, resulting in the deterioration of air and water quality due to the presence of organic and inorganic contaminants. Pesticides, chemical colors, and biological contaminants such as bacteria, lipids, viruses, DNA, and proteins regularly affecting water quality [16]. Both air pollution and wastewater are regarded as severe threats to human health. As a result, it is critical to address environmental degradation as soon as possible. In this context, it is necessary to develop sustainable technology using reactive oxygen species (ROS) [17]. ROS are highly reactive molecules including superoxide radicals ('O2-), hydroxyl radicals ('OH), and hydrogen peroxide (H_2O_2) that degrades the pollutants in wastewater [18]. In this regard, photocatalysis has been widely investigated for more than a half-century due to its applications in efficient energy conversion and environmental purification via ROS generation. Additionally, heterojunction structuring, [19–21] doping (metal and non-metal), [22, 23] adding polymers and co-catalysts, [24, 25] and other techniques can improve the degradation activity and charge carrier separation of materials. Despite the fact that photocatalysis has shown very promising applications, there are a few difficulties, such as low efficiency and difficult catalyst separation, that limit its practical application [16, 26]. Recently, piezoelectric-based catalysts have gained significant attention due to their high charge separation efficiency. Furthermore, in the presence of mechanical stress (i.e., either low frequency vibration or high frequency ultra-sound vibration), piezoelectric materials (i.e., non-centrosymmetric in nature) generate a piezo-potential due to spontaneous polarization. The generated electric field is capable of producing adequate voltage for water electrolysis, which leads to the generation of ROS [27]. The above-mentioned phenomena can result in effective charge separation and transportation to establish a superior catalytic process. Basically, there are two processes involved in the charge transfer mechanism in piezoelectric-based catalysis, as follows: (i) tuning the surface charge energy from piezopotential and (ii) forming composites of piezoelectric and semiconducting materials [26]. It is noteworthy to mention that several piezoelectric materials have shown outstanding piezocatalytic properties thus far, such as MoS₂, ZnO and the perovskite family (BaTiO₃, BiFeO₃, and

(Na, K)NbO₃) [17, 28–32]. However, they are limited by their complex synthetic procedures and other drawbacks. In particular, MoS_2 only exhibits piezoelectricity in monolayers due to its noncentrosymmetric nature, whereas the piezoelectricity disappears in the bulk owing to the opposite orientations of its atomic layers. Similarly, the perovskite family require complex processing conditions, are brittle in nature and toxic. In contrast, Ag_2CO_3 is a semiconducting material (band gap of ~ 2.65 eV), demonstrating photocatalytic activity for the removal of organic pollutants [33]. It is expected that the combination of PVDF polymer and Ag_2CO_3 semiconducting material may display superior piezo-catalytic activity for the removal of organic pollutants.

2.2 Experimental section

2.2.1 Materials

PVDF ($M_w \sim 1,80,000$ GPC) pellets were purchased from Sigma Aldrich and analytical grade N, N-dimethylformamide (DMF) was purchased from Merck, India. Silver nitrate (AgNO₃, 99.5 %) and sodium hydrogen carbonate (NaHCO₃, 99.8 %) were purchased from Merck, India.

2.2.2 Synthesis of Ag₂CO₃

 Ag_2CO_3 nano/microrods were synthesized by the co-precipitation method. Firstly, 2.5 mmol of NaHCO₃ was dissolved in 30 ml of deionized water to form a transparent solution. In this solution, 20 ml of another solution containing 5 mmol AgNO₃ was added very slowly dropwise [33]. After that, the complete reaction setup was put in an ice bath under dark condition for 8 h and then centrifuged at 2000 rpm in ethanol to obtain the nanorods. The sample was kept in oven at 70 °C overnight to remove moisture content.

2.2.3 Preparation of PVDF/Ag₂CO₃ nanocomposite films

PVDF pellets were dissolved in DMF to prepare 12 (w/v) % transparent solution under continuous stirring at 60°C and 400 rpm for 6 h. Thereafter, different concentrations (0, 0.25, 0.50 and 1.0) wt % of Ag₂CO₃ nanorods were dispersed in PVDF/DMF solution under vigorous stirring in the same condition until its color changed from pale yellow to greenish. Then PVDF/Ag₂CO₃ solution was degassed for 30 min. Thereafter, nanocomposite films are prepared on clean glass substrate by solution casting method at 120 °C for 8 h to complete evaporation of solvent. The prepared films of PVDF/Ag₂CO₃ were peeled off from glass substrates for further characterization (Figure 2.1). As prepared PVDF/Ag₂CO₃ films were designated as PNC# where # represents the concentration of Ag₂CO₃ nanorods in the PVDF/DMF solution.



Figure 2.1 Schematic demonstration of preparation of PVDF/Ag₂CO₃ nanocomposite (PNC) film and FPNG.

2.2.4 Fabrication of flexible piezoelectric nanogenerator (FPNG)

PNC nanocomposite film was prepared in $4\times 2 \text{ cm}^2$ dimension, and then silver electrode were made on the both sides (top and bottom) of PNC nanocomposites film. Thereafter, connections were established by copper wires on both sides for electrical measurements. Then. FPNG was encapsulated with polydimethylsiloxane (PDMS). The PDMS (sylgard184, silicon elastomer) solution was prepared by using elastomer and curing agent in 10:1 ratio and then dried for 40 min at 60 °C followed by FPNG was corona poled at 60 kV and 80 °C for 30 min (Figure 2.1).

2.3 Results and discussion

2.3.1 Electroactive phase nucleation in PNC films

FTIR spectroscopy (in ATR mode) is employed for the identification of electroactive phase formation in PNC films as shown in Figure 2.2a. It is observed that in the case of PNC0 *i.e.*, neat PVDF film, non-electroactive α -phase is predominant at vibrational bands 486, 532, 613, 764, 796, 975 cm⁻¹, while by the incorporation of Ag₂CO₃ filler into PVDF matrix, the electroactive phase content gradually increases as concentration increases in Figure 2.2a. The complete conversion of α -phase (non-electroactive) to γ -phase (semi-electroactive) is observed in PNC0.50 film from the vibrational bands at 814, 837 and 1233 cm⁻¹ respectively and previously mentioned vibrational bands of the α -phase disappear completely [34,35]. Meanwhile, as the filler concentration increases further *i.e.*, PNC1.0 film the characteristics vibrational bands related to α -phase are increasing again along with the γ -phase. It is predicted that, when higher concentration is added into the PVDF matrix then the possible interaction between -CH₂-/-CF₂dipoles of PVDF and Ag₂CO₃ filler decrease in unit volume. Besides it, there are few chances with increasing the filler concentration into the PVDF matrix, filler density increases which results the decrease in specific surface area that promotes increase of the crystallization "transgauche" conformation which is the signature of α -phase at vibrational band 764 cm⁻¹. Thus, it can be concluded that in the PNC1.0 film, the γ -phase reduces and again α -phase starts appearing [36]. The results infer that very small amount of Ag₂CO₃ filler can hinder the dipole moment of PVDF (-CH₂-/-CF₂-) and induces the semi-polar γ -phase (TTTGTTT). Further, relative proportion of electroactive phase (F_{EA}) content in PNC films is estimated by

$$F_{EA} = \frac{A_{\gamma}}{\left(\frac{K\gamma}{K\alpha}\right)A_{\alpha} + A_{\gamma}}$$
(2.1)

where A_{α} and A_{γ} are the absorbance at wavenumber 764 and 837 cm⁻¹ respectively and K_{γ} and K_{α} are the absorption coefficients at 837 and 764 cm⁻¹ respectively [35]. The variation of electroactive fraction of γ -phase (F(γ) %) with increasing amount of Ag₂CO₃ fillers are shown in Figure 2.2b. As the Ag₂CO₃ filler amount increases, the F(γ) % also increases. At higher concentration of PNC1.0, due to the dual phases (α and γ -phase) content of semi-electroactive γ -phase fraction reduces in comparison to PNC0.50. As a result, maximum semi-electroactive γ -phase (F(γ) ~ 93 %) content is observed in PNC0.50 film and it shows the complete conversion of α to γ - phase. Moreover, the shifting of the vibrational bands of -CH₂- stretching in asymmetric (v_{as}) and symmetric (v_{s}) bands towards lower energy in comparison to pure PVDF film resembles the interfacial interaction between Ag₂CO₃ and -CH₂-/- CF₂- dipoles of PVDF matrix (Figure 2.2c) [37–42]. The shift in frequency towards lower wavenumber shows the damping oscillations due to the increase in effective mass of -CH₂- dipoles. The damping factor (2r_{dc}) can be calculated as

$$\bar{\nu}_{int} = \left[\bar{\nu}_0^2 - \left(\frac{r_{dc}}{2\pi c}\right)^2\right]^{1/2}$$
(2.2)

where $\bar{\nu}_{int}$ is the wavenumber of CH₂ damping vibration due to Ag₂CO₃ doped PVDF films and

 \bar{v}_0 is the damping free vibration of neat PVDF film (PNC0) and c is the velocity of light. Moreover, the variation of absorbance intensity of 837 cm⁻¹ (strong β/γ -phase confirmation) and 764 cm⁻¹ (strong α -phase confirmation) are shown in Figure 2.2d [37-40].



Figure 2.2 (a) ATR-FTIR spectra of PNC film, (b) variation of electro-active fraction ($F(\gamma)$ %) with Ag₂CO₃ content and damping factor variation, (c) variation of -CH₂- region of stretching in and (d) the intensity variation of 837 (for γ -phase) and 764 (for α -phase) in PNC films.

The calculated results of 2rdc values are shown in Figure 2.2b. Moreover, the variation of absorbance intensity of 837 cm⁻¹ (strong β/γ -phase confirmation) and 764 cm⁻¹ (strong α -phase confirmation) are shown in Figure 2.2d. The formation of Ag₂CO₃ has been confirmed by XRD pattern and it is well matched with the reported results as shown in Figure 2.3a [33]. Crystallographic phase of the PNC films was identified by the XRD pattern which is shown in Figure 2.3b. The XRD pattern of PNC0 film reveals the complete α -phase of PVDF at 2 θ value 17.9° (100), 18.4° (020), 19.9° (110) and 26.8° (021) respectively [35,43]. Thus, PNC0 film exhibits predominant α -phase. By the increase of Ag₂CO₃ filler concentration in PVDF matrix, α phase start to reduce. Although, the distinct peak analysis gets difficult due to the overlapping peak positions of PVDF (at 17.9° (100), 18.3° (020), 18.5° (020) and 19. 9° (110) and 20.4° (110/200) respectively) and Ag₂CO₃ filler (17.6° (101), 18.4° (020), 18.6° (020) and 20.6° (110)). Therefore, the characteristics peaks of Ag₂CO₃ are marked as (*) in XRD pattern. In PNC0.50, peaks at $2\theta = 18.6^{\circ}$ (020) and 20.1° (110) are the characteristics of γ -phase of PVDF and the peak at 17.9° (100) corresponding to α -phase diminished. The peak at 2 θ values 20.6° (110) are present due to Ag₂CO₃ filler [44]. In PNC1.0 the α -phase peak at 17.9° (100) again induces, which is attributed to the co-existence of both α and $\gamma\text{-}$ phase. The reappearance of peak 17.9 $^\circ$ (100) in the PNC1.0 film is due to the solubility limit of Ag₂CO₃ filler into PVDF matrix. The XRD results are consistent with FTIR results (Figure 2.2a). The degree of crystallinity (γ_c) can be calculated by using the equation

$$\chi_c = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{amr}} \times 100 \%$$
(2.3)

where $\sum A_{cr}$ and $\sum A_{amr}$ are the summation integral area under the crystalline and amorphous peaks respectively [34]. It indicated that the crystallinity of Ag₂CO₃ doped PVDF film changes

drastically as the Ag_2CO_3 concentration increases and the estimated crystallinity is 51 %, 47 %, 41% and 42% for PNC0, PNC0.25, PNC0.50 and PNC1.0 respectively as shown in Table 2.1.



Figure 2.3 PXRD pattern of (a) as prepared Ag₂CO₃ nano/micro rods, (b) PNC films and symbol (*) marked for the peaks of Ag₂CO₃.

Table 2.1 The degree of crystallinity estimated from PXRD pattern.

Sample	Crystallinity (%)
PNC0	51
PNC0.25	47
PNC0.50	40
PNC1.0	42

Further, the nucleation of γ -phase in PNC film can be understand by two mechanism (i) the electrostatic interaction of negative surface charge of Ag₂CO₃ and PVDF dipoles -CH₂-/-CF₂-. The interaction of PVDF and Ag₂CO₃ semiconducting material shows a strong electroactive phase nucleation from non-polar α -phase (*TGTG*[^]) to semi-polar γ -phase (*TTTGTTT*) and (ii) in

presence of heat, Ag₂CO₃ decomposes to form silver nanoparticles (Ag NPs) [37]. Then oxygen molecule in air may forms a charged species (Ag-O-O⁻) with Ag NPs, due to electron demanding characteristics of the silver nanoparticles. Such species supposed to bind successively with the F and H atoms parallelly of the α -PVDF, where the fluorine interacts with the Ag and the H associate with the electron rich oxygen as shown in Figure 2.4a(i). Such feasible interaction leads to severe steric crowding within the α -PVDF molecule. In consequence, the α -PVDF may reorient through C-C bond rotation to form less strained γ -conformation, as depicted in Figure 2.4a(ii) and subsequent oxygen removal additionally stabilizes the γ -conformation by effective charge nucleation on F atoms by Ag NPs in Figure 2.4(iii) and Figure 2.4(iv), respectively [38].



Figure 2.4 The interaction mechanism of electro-active γ -phase formation in PNC film (a) Ag₂CO₃ decompose to form Ag NPs and oxygen molecules in air forms Ag-O-O⁻ with Ag NPs (b) α -phase reorient through C-C bond rotation to form less strained γ -conformation (c, d) oxygen removal and effective charge nucleation stabiles the γ -conformation.

Further, intermolecular interactions between Ag₂CO₃ and PVDF is studied via DFT calculations based on the linear combination of atomic orbitals (LCAO) approach, implementing implicit solvent model calculations for DMF solvent. Optimized structure of γ -PVDF/Ag₂CO₃ within DMF is shown in Figure 2.5. Ag₂CO₃ molecules form Ag...F and O...H type noncovalent bonds with the PVDF chains. From the binding energy values, it was found that the formation of γ -PVDF/Ag₂CO₃ is more feasible (as the binding energy is the most negative) compared to α -PVDF/Ag₂CO₃ and β -PVDF/Ag₂CO₃ complexes (as shown in Table 2.2). This justifies the formation of γ -PVDF without forming β -PVDF after the addition of Ag₂CO₃ filler into neat PVDF (which is predominantly in α -phase) [39,40].



Figure 2.5 The optimized structure of γ -PVDF/Ag₂CO₃ in DMF showing Ag...F and O...H distances.

PVDF/filler complexes	Binding energy (kcal/mol) in DMF
a-PVDF/Ag ₂ CO ₃	-3.01
β -PVDF/Ag ₂ CO ₃	-9.93
γ -PVDF/Ag ₂ CO ₃	-10.22

Table 2.2 Binding energies of PVDF fragments within PVDF/Ag₂CO₃ complexes in DMF.

2.3.2 Surface morphology of PNC films

Scanning electron microscope (SEM) is employed to obtain the surface morphology of PNC0.50 film as shown in Figure 2.6a, showing the uniform distribution of Ag₂CO₃ filler rod like structure (white color) throughout the polymer matrix *i.e.*, on the PVDF spherulites and the enlarge region in inset describes the uniform distribution. Figure 2.6b, justifies the uniform rod shape morphology of the as prepared Ag₂CO₃ filler. Furthermore, the softness and flexibility of PNC0.50 film is demonstrated in bending and rolling condition as shown in Figure 2.6c and 2.6d. As a result, the PNC film can be seamlessly attached to human skin and it can be also further utilized as a FPNG. In order to get the clear idea of spherulite size, we have performed the surface topography of PNC films by atomic force microscopy (AFM). The AFM topography of neat i.e., PNC0 film and PNC0.50 reveals the formation of several boundaries due to the impingement of spherulites when their radial growths are taking place from the nuclei as shown in Figure 2.6e, f respectively. The distribution of spherulite size in both cases PNC0 and PNC0.50 can be examined by histogram plot as shown in the inset of Figure 2.6e, f, respectively. In the case of PNC0, the size of the spherulites varies from 25 to 30 μ m (with a standard deviation $\pm 0.5 \,\mu m$) and the average size is 28 μm as shown in Figure 2.6e. Similarly, for

PNC0.50 film, the size of spherulites varies from 10 to 15 μ m (with a standard deviation $\pm 0.3 \,\mu$ m) and the average size is 12 μ m as shown in Figure 2.6f which is relatively lower than neat PVDF film.



Figure 2.6 (a) SEM surface morphology of PNC0.50 film and inset shows the enlarged region of Ag_2CO_3 distribution within PVDF matrix, (b) as synthesized Ag_2CO_3 nanorod like surface morphology, (c, d) flexibility of as prepared PNC film in bending and rolling condition. AFM topography of PNC film and inset shows the variation of spherulites size of (e) PNC0 and (f) PNC0.50 film. The spherulite size is estimated by considering maximum length from one edge to other edge of the spherulite.

2.3.3 Optical properties of PNC films

The UV-visible absorbance spectra of PNC films are shown in Figure 2.7a. There are no strong absorption peaks in the UV-region for PNC0 film, however for PNC film with Ag₂CO₃ filler, there are sharp peaks at 425 nm, 419 nm, and 414 nm for PNC0.25, PNC0.50, and PNC1.0, respectively. This blue shift in absorbance spectra is caused by a possible alteration associated with an electronic transition in the material, which varies depending on the shape and size of the synthesized Ag₂CO₃. These are the characteristics peaks of Ag₂CO₃ filler and it is evident that the presence of Ag₂CO₃ filler in PVDF matrix and also suggesting the good dispersion into the matrix. The optical band (E_g) gap of PNC films (Figure 2.7b) and Ag₂CO₃ filler (E_g = 2.65 eV) is also investigated using the Tauc plot. The absorption coefficient (α) of PNC films can be estimated using the following equation to determine their energy band gap [45]

$$\alpha = 2.303 \times \left(\frac{Absorbance}{Thickness}\right)$$
(2.4)

where thickness is taken into account for PNC films. The assessed E_g of PNC films are 5.20 eV, 2.54 eV, 2.57 eV, and 2.62 eV for PNC0, PNC0.25, PNC0.50, and PNC1.0, respectively as shown in Figure 2.7b. Furthermore, UV-visible transmittance spectra of PNC films are shown in Figure 2.7c. Now, it can be observed that the film transparency reducing as the filler concentration of Ag_2CO_3 increases in PVDF matrix, which is also reflected from digital photograph of PNC films as shown in Figure 2.7d.

2.3.4 Room temperature dielectric properties of PNC films

The variation of dielectric constant (real permittivity *i.e.*, ε_r) and loss tangent (*i.e.*, $\tan(\delta)$) as a function of frequency are shown in Figure 2.8a and 2.8b respectively. During the dielectric operation there is an energy loss in material which is related to dielectric constant of material.


Figure 2.7 (a) UV-visible absorption spectra of PNC films and (b) corresponding energy band gap (Tauc plot) and the marked region highlighted in inset is due to Ag_2CO_3 filler. (c) UV-visible transmission spectra to demonstrate the transparency in PNC film and (d) corresponding digital photographs of PNC film (scale bar 0.5 mm).

The complex dielectric permittivity $\varepsilon^*(\omega)$, are correlated with real dielectric constant $\varepsilon'(\omega)$ and imaginary dielectric constant $\varepsilon''(\omega)$ as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{2.5}$$

Moreover, these two parameters *i.e.*, real and imaginary dielectric constants are related with loss tangent and defined as

$$\tan(\delta) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}$$
(2.6)

Now, it is found that at lower frequency (1 kHz) the dielectric constant gradually increases from 6.6 to 16.3 for PNC0 to PNC0.50 respectively which is \sim 2.4 times than PNC0 film as shown in Figure 2.8a and very low loss tangent for PNC0.50 *i.e.*, $(tan(\delta) \sim 0.037)$ in Figure 2.8b. It is noteworthy to mention that, the large change in $\varepsilon'(\omega)$ is due to the increase in interfacial polarization due to Maxwell-Wagner-Sillers (MWS) approximation theory.[46-48] However, further increase in concentration of filler Ag₂CO₃ *i.e.*, PNC1.0 film the $\varepsilon'(\omega)$ decreases. It might be due to two reasons (i) the interaction of PVDF dipole -CH₂-/-CF₂- and Ag NPs and (ii) the growth of PVDF spherulites formation or the possible number of interfaces. These two reasons can affect the dielectric constant. For lower concentration, the formation of spherulites size is very small up o PNC0.50, so the possible number of interactions in the unit volume of film increases, resulting the large interface polarization. Hence, the maximum dielectric constant achieved for PNC0.50. However, PNC1.0 shows the large amount of filler Ag_2CO_3 which means that there are less number of interactions possible in the unit volume, so interface polarization decreases which results the decrease in dielectric constant. [49-53] Thus, PNC0.50 composites film shows the highest dielectric constant among all the concentrations and loss tangent at 1 kHz (Figure 2.8c). Therefore, PNC0.50 is suitable for energy storage and mechanical energy harvester applications which is already verified from ATR-FTIR spectra because of the highest electroactive phase content $F(\gamma) \sim 93$ %. In polymer composites, generally two types of relaxation mechanism occur first one is dipole segmental relaxation which is associated with micro-Brownian motion of polymer chain *i.e.*, α -relaxation and second is localized motion of small groups and unit chains which is associated as β - and γ - relaxations respectively at lower frequencies [53-56]. The non-linear variation of frequency dependent loss tangent of PNC film is responsible for the relaxation mechanism due to the PVDF chain movement. Since the crystallinity of PNC films are decreasing compared to neat PVDF film *i.e.*, PNC0, thus PVDF chain becomes more migratory at lower frequencies, which results the increase in dielectric loss tangent at lower frequencies.



Figure 2.8 (a, b) Variation of dielectric constant and tangent loss of PNC film at room temperature. (c) dependance of dielectric constant and loss tangent 1 kHz frequency with Ag_2CO_3 concentration, (d) the relaxation time of PNC films corresponding to the frequency of lowest dielectric loss.

Furthermore, the relaxation time (τ_{rel}) can be calculated using $\tau_{rel} = \frac{1}{f_{min}}$, where f_{min} is the frequency at lowest tan(δ) value. The respective plots of relaxation time (τ_{rel}) versus Ag₂CO₃ content are shown in Figure 2.8d [11,14]. It dictates the dipolar orientation in PNC films.

2.3.5 Performance of FPNG

When an external mechanical force is applied to a piezoelectric material, the center of symmetry in the crystal structure is broken, resulting in the formation of dipoles. The fabrication method of flexible piezoelectric nanogenerator (FPNG) is schematically represented in Figure 2.9a. The open circuit voltage (V_{OC}) and the short circuit current (I_{SC}) are examined on continuous finger (covered with nitrile gloves) imparting as shown in Figure 2.9b and 2.9c, respectively. The FPNG exhibited more than 15 V of V_{OC} and 6 μ A of I_{SC} on the repetitive mechanical force of 6 N. In the electrical output response asymmetry arises in peak amplitude due to the pressing and releasing state of external force because of different straining rate applied and another reason is the damping effect occurring due to change in pressing state to the releasing state (Figure 2.9b and 2.9c). Thus, this behavior shows the piezoelectricity in the FPNG. Further, the working mechanism of FPNG is explained in Figure 2.9d-f. Initially, when no mechanical stress is applied to FPNG the dipole moments are in equilibrium (the center of charge of cations and anions are in the same locations) and resulting zero piezo-potential through the FPNG (Figure 2.9d). Further, when stress is applied to the FPNG then volume decreases, and a negative strain is developed. Accordingly, the center of charge for the cations and anions changes that forms the dipoles. These dipoles undergo the mechanical stress which induces the net surface charge due to the polarization effect and generates piezo-potential between the two electrodes and creates a new balance state (Figure 2.9e). In this case maximum current flows in the circuit. Finally, when

mechanical stress is removed the electrons flow back to return to the state prior to the applied stress. As a result, a reversed piezoelectric electric current is observed (Figure 2.9f).



Figure 2.9 Performance of FPNG (a) schematic representation of fabricated FPNG, (b, c) the electrical output response, open circuit voltage (V_{OC}) and short circuit current (I_{SC}) under continuous hand imparting of force. Working mechanism of FPNG (d) no stress, (e) under stress and (f) when stress is removed.

In addition, to confirm this, 2D finite element method (FEM) based simulation conducted by the application of three different stress e.g., 30, 60 and 100 kPa. In FEM based theoretical model Figure 2.10(i-iii), we can see the distribution of stress within the FPNG increases as the externally applied stress increases, and the highest stress is induced when 100 kPa stress is

applied due to the stress confinement effect. From Figure 2.10(iv-vi), we observed that as the applied stress is increasing, the generated piezo-potential increases which shows the polarization effect in the FPNG. When stress is applied then the individual molecular dipoles are aligned in the particular direction and give rise the net resultant dipole moment (non-zero). As an outcome, the maximum generated piezo-potential are ~ 13 , 18 and 27 V noticed upon the application of 30, 60 and 100 kPa of stress respectively. The results infers that the experimentally observed piezopotential (~20 V peak to peak) is slightly lower than the simulated results (~27 V). This deviation arises due to the voltage drop through internal leakage path and charge loss in the device structure [57]. The magnitude of charge (|Q|) was calculated as $Q = \int I dt$, where I is the short circuit current and the magnitude of charge is evaluated 384 pC. Then the magnitude of piezoelectric charge coefficient $|d_{33}|$ can be estimated as $|d_{33}| = \frac{Q}{F} = 64$ pC/N. Moreover, the comparative list for the performance of piezoelectric nanogenerator is shown in Table 2.3). The performance of FPNG is examined with the variation of external load resistance from $10^5 \Omega$ to $10^8 \Omega$. It is observed that the amplitude of the output voltage across the external load resistance increases as resistance increases and saturated at infinitely high resistance of 5 MQ. Similarly, the variation of current with external load resistance is also measured and the amplitude of output current is noticed, which decrease as load resistance increases (Figure 2.11a). At nanoscale level, the electrical output power is very important for electronic devices and nanogenerators, so the variation of electrical power density (P) with load resistance is examined and depicted in Figure 2.11b where it is found to get saturated at 5 M Ω of resistance. Then, electrical power density can be estimated by

$$P = \frac{V^2}{(R_L \times A)} \tag{2.7}$$

where, V, R_L are the output voltage and load resistance and A is the effective area during imparting of force on FPNG. The maximum power density is found to be ~7 μ W/cm² at 5 M Ω of resistance.



Figure 2.10 FEM simulation-based theoretical model of FPNG (i-iii) the stress distribution into the FPNG upon the application of three different stress 30, 60 and 100 kPa and it can be observed by a scale (0.3 to 1 MPa range) and (iv-vi) corresponding to different stress the piezo-potential generation through the FPNG and value can be evaluated by a scale (ranges from 5 to 35 V).

To check the feasibility of the FPNG in energy storage, the capacitor charging was performed with three different capacitors 1μ F, 2.2 μ F and 10 μ F using a full wave bridge rectifier. The output voltage across these capacitors on continuous hand imparting is obtained 1.34 V, 1.05 V and 0.57 V respectively, the capacitor is charged in a very short time of 50 s thereafter it is

saturated as shown in Figure 2.11c. The maximum energy stored in a capacitor was calculated as $\frac{1}{2}CV^2$ and it is estimated to be ~1.6 µJ through 10 µF capacitor.



Figure 2.11 Variation of electrical output of FPNG with the of external load resistance (a) voltage and current, (b) electrical output power density and inset shows an equivalent circuit, (c) capacitor charging of FPNG under continuous imparting force with three different capacitors (1, 2.2 and 10) μ F and inset shows the bridge rectifier circuit (d) the mechano-sensitivity of FPNG by using free fall of force.

Moreover, the mechanical sensitivity of the FPNG is examined by using free falling of mass (weight box of different masses) from a constant height (7 cm). In mechanical sensitivity plot (Figure 2.11d), as the pressure is increasing the output voltage of FPNG is also increasing and

after the certain pressure the plot become non-linear. So, we can see the linear pattern of curve upto 47 kPa pressure after appropriate linear fitting ($R^2 \approx 0.9991$). Further, the mechanosensitivity (S) of FPNG is quantified by using the formula $Sm = \frac{\Delta V_{OC}}{\Delta \sigma_a}$, where ΔV_{OC} and

 $\Delta \sigma_a$ are the change in output voltage in the linear region and change in the applied pressure respectively. The estimated value of *S* of the FPNG is 45 mVkPa⁻¹.

Table 2.3 Performance of piezoelectric nanogenerator with different processing conditions.

Materials	Method of	Open	Short	Power	References
	Preparation	circuit	circuit	density	
		voltage	current	(µW/cm ²)	
		(V)	(µA)		
BaTi _(1-x) Zr _x O ₃ /	Solution casting	11.9	1.35	0.14	ACS Appl. Mater.
PVDF					Interfaces, 2015, 7,
					9831–9840
Ag-pBT/PVDF	SLS technique	10	0.14	-	Nano Energy, 2020,
					74, 104825
ZnO/PVDF	Solution casting	11	9.8	0.44	Adv. Energy
					Mater., 2014, 4, 1
Polydopamine/	Electrospinning	6	1.5	0.85	Nano Energy, 2020,
BaTiO ₃ /P(VDF					78, 105251
-TrFE)					
PMN-	Tape casting	10.3	0.04	-	Nanomaterials,
PT/PVDF					2016, 6, 1–9
Graphene/	Electrospinning	7.9	4.5	-	Compos. Sci.
					Technol., 2017,

PVDF					138, 49–56
Ag-	Solution casting	14	0.96	0.98	Appl. Energy,
BaTiO ₃ /PVDF					2018, 230, 865–874
MAPbBr ₃ /	Electrospinning	5	0.06	0.28	Nano Energy, 2018,
PVDF					49, 380–392
NaNbO ₃ /	Solution casting	3.34	0.53	-	Mater. Res.
PVDF					Express, 2019, 6,
					0–9
Tri-layer of	Spin coating	10	2.5	0.72	Appl. Surf. Sci.,
BTO/PVDF					2017, 405, 420–426
Ag ₂ CO ₃ /PVDF	Solution casting	15	6	7	this work

2.3.6. Mechanical energy harvesting performance

FPNG has shown excellent mechanical energy harvesting properties. In this context, the gesture sensing performance of as prepared FPNG is demonstrated in Figure 2.12a. The FPNG is placed under the sole (inset of Figure 2.12b) and then under pressing and releasing conditions the electrical output response (more than 1 V) is recorded as shown in Figure 2.12a. It is very interesting to note that several other significant gesture sensing features has been also observed during different oscillations. Thus, in the enlarge region (Figure 2.12b) the small peaks marked by A, G are due to the oscillation in air, and very sharp acceleration peaks B, H are due to the upward heel strike (contact phase). Another oscillation peak *i.e.*, C after heel strike at B. Next, stance phase in static condition is observed and marked by D and then followed by a downward acceleration at heel strike F. These different conditions (A to H) show the gesture sensing performance of human motion monitoring system. Furthermore, to represent this type of

oscillations in an alternative way, the 3D spectrogram processed short time Fourier transform (STFT) model is prepared as shown in Figure 2.12c which displays the color contour plot with three parameters (time, amplitude and frequency). The amplitude change corresponding to several oscillations can be detected by this type of plot. Thus, FPNG is able to identify the human motion gestures [58]. Moreover, mechanical energy harvesting from sound wave of FPNG has also been examined. In the experiment, when music is turn on (pop music) the peakto-peak open circuit voltage increases as the frequency of sound pressure level (SPL) increasing and it get saturated at 80 dB of SPL and generates the output voltage of ~ 2.7 V (Figure 2.12d). When the music is on, sound wave propagates to the air medium and interact with surface of FPNG and then FPNG can convert sound energy into electrical energy. Saturation occurs at 80 dB of SPL and thereafter the output signal gets decrease as SPL is increasing. This suggest that the FPNG is able to recognize the sound wave in the range of 40 dB to 110 dB range. It is indicating that there are ubiquitous sources of mechanical vibrations in terms of noise that is arising due to traffic, industries, airports, music, and many public places. Thus, it is expected that as prepared FPNG can work very efficiently in those areas. The quantification of acoustic sensitivity (S_{acou}) is estimated by the equation [59]

$$S_{acou} = \frac{V}{P} = \frac{V}{P = P_0 \times 10^{L_P/20}}$$
(2.8)

where, P, V is the sound pressure and output voltage of the FPNG, P_0 is the reference sound pressure at 0.00002 Pa and L_P is the sound pressure level (SPL) in decibel respectively. The estimated sensitivity (S_{acou}) of the FPNG is ~13 V/Pa.



Figure 2.12 The human gesture sensing performance of FPNG (a) electrical output voltage when mounted below the sole, (b) the enlarged region of a single peak of different oscillation and inset shows during pressing and releasing motion (c) the STFT model of gesture sensing to examine the signals at different oscillations, (d) acoustic sensing response of FPNG at different SPL and saturated at 90 dB of SPL, (e, f) electrical output signal for flexibility of FPNG when attached to the index finger and its bending movement at different angles.

Furthermore, in order to prove the flexibility and utility of the FPNG, it is attached to the human skin (index finger) as illustrated in Figure 2.12e. Then by continuous movement of finger at different angles (0° (straight), 30° , 45° and 90°) electrical output voltage has been collected (Figure 2.12f). The output voltage is increasing as the finger movement angle is increasing and reached maximum output at 90° as shown in Figure 2.12f.

2.3.7 Piezo-catalysis dye degradation

The PVDF/Ag₂CO₃ nanocomposite film ($2 \times 2 \text{ cm}^2$ area) is kept in dye solution (methyl orange in deionized water by keeping the 10 mg/l of concentration) under dark condition. We have prepared methyl orange dye solution in deionized water. The mechano-degradation of dye in the presence of nanocomposite film is shown in Figure 2.13a. When piezoelectric nanocomposite PNC film is placed under the continuous ultrasound mechanical vibration the piezo-potential is generated. This piezo-potential serves as a charge separation mechanism at the interface of material inducing several redox reactions. The UV-visible absorbance spectra (Figure 2.13b) describe the degradation in intensity with time and inset shows the change in dye color. The internal electric field in the PVDF is generated by the piezoelectric polarization and separates electron-hole pairs (e^{-} - h^{+}) in the PNC film equation 2.9. According to equation 2.9a the generated h⁺ converts hydroxyl ion (OH⁻) into hydroxyl radical (•OH), which is a crucial reactive oxygen species (ROS) for methyl orange (MO) dye degradation.[18] Meanwhile, a superoxide anion radical ((O_2)) is formed by the ultrasound-driven electron by oxygen reduction (equation 2.9b) [60]. There is a chance to form another ROS *i.e.*, hydrogen peroxide (H_2O_2) by coupling with the protons (H^+) with $\bullet O_2^-$ (equation 2.9c) [61]. The strongly oxidative $\bullet O_2^-$, OH• and $H_2O_2^$ are responsible for the degradation reactions of the dyes in solution. The probable steps showing the generation of the oxidative species are likewise.

Ultrasound + PVDF/Ag₂CO₃ = e^{-} + h^{+} (2.9)

$$OH^{-} + h^{+} = \bullet OH \tag{2.9a}$$

$$O_2 + e^{-} = \bullet O_2^{-} \tag{2.9b}$$

•
$$O_2^- + e^- + 2H^+ = H_2O_2$$
 (2.9c)

Further, the percentage of mechano-catalytic dye degradation (D) has been calculated by using the equation

$$D = {(A_0 - A_t)} / _{A_0} \times 100 \%$$
 (2.10)

where, A_0 and A_t are the maximum absorption peaks of MO at 464 nm at 0 and t time respectively. The estimated mechano-catalytic dye degradation (D) after 100 min is found to be ~ 80 % as shown in Figure 2.12c.



Figure 2.13 (a) Schematic illustration of ROS generation under continuous ultrasound frequency (b) UV-visible absorbance spectra of MO dye degradation treated with ultrasound frequency at different times (0 to 100 min) and (c) the percentage of dye degradation due to piezo-catalysis at different time.

2.4 Conclusions

In this work, we have prepared polymer nanocomposite (PVDF/Ag₂CO₃) with pure γ -phase (F(γ) ~93 %). The formation of γ -phase is confirmed by the FTIR spectroscopy and the probable mechanism behind α - to γ - phase formation is further illustrated via favorable C-C bond rotation to attain stable conformation which is driven by Ag charge nucleation. Further, we have investigated the inter-fragment non-covalent intermolecular interactions between PVDF and silver carbonate fillers (Ag₂CO₃) via density functional theory (DFT) based on the linear combination of atomic orbitals (LCAO) approach. Thereafter, FPNG is fabricated that shows an excellent electrical output performance. The open circuit voltage (V_{OC}), short circuit current (I_{SC}) and electrical power density (P) is found to be more than 15 V, 6 μ A and \sim 7 μ W/cm² respectively. Moreover, the FPNG have shown the mechanical sensitivity of 45 mVkPa⁻¹ and very high acoustic sensitivity of 13 V/Pa respectively. The FPNG have also shown several gesture sensing performances and human skin bending as a mechanical energy harvester. Furthermore, the piezo-catalysis dye degradation (~ 80 %) of methyl orange (MO) is realized under continuous ultra-sound mechanical vibration in the presence of PNC0.50 film. When mechanical vibration is applied to the nanocomposite film, the piezo-potential generated on the surface due to the spontaneous polarization. This piezo-potential can power to generate several redox reactions on the surface of the nanocomposite under the aqueous solution. Thus, PVDF/Ag₂CO₃ are suitable choice of material for efficient dye degradation and mechanical energy harvesting application.

2.5 References

- C. Yang, H. Wei, L. Guan, J. Guo, Y. Wang, X. Yan, X. Zhang, S. Wei, Z. Guo, Polymer nanocomposites for energy storage, energy saving, and anticorrosion, J. Mater. Chem. A 3 (2015) 14929–14941.
- [2] M. Guo, J. Jiang, Z. Shen, Y. Lin, C.-W. Nan, Y. Shen, High-energy-density ferroelectric polymer nanocomposites for capacitive energy storage: enhanced breakdown strength and improved discharge efficiency, Mater. Today 29 (2019) 49–67.
- [3] F. R. Fan, W. Tang, Z. L. Wang, Flexible Nanogenerators for Energy Harvesting and Self-Powered Electronics, Adv. Mater. 28 (2016) 4283–4305.
- [4] M. Sun, Z. Li, C. Yang, Y. Lv, L. Yuan, C. Shang, S. Liang, B. Guo, Y. Liu, Z. Li, D. Luo, Nanogenerator-based devices for biomedical applications, Nano Energy 89 (2021) 106461–106486.
- [5] Q. Shi, T. He, C. Lee, More than energy harvesting Combining triboelectric nanogenerator and flexible electronics technology for enabling novel micro-/nanosystems, Nano Energy 57 (2019) 851–871.
- [6] J. Yan, M. Liu, Y. G. Jeong, W. Kang, L. Li, Y. Zhao, N. Deng, B. Cheng, G. Yang, Performance enhancements in poly(vinylidene fluoride)-based piezoelectric nanogenerators for efficient energy harvesting, Nano Energy 56 (2019) 662–692.
- [7] H. Li, F. Liu, B. Fan, D. Ai, Z. Peng, Q. Wang, Nanostructured ferroelectric-polymer composites for capacitive energy storage, Small Methods 2 (2018) 1700399-1700417.
- [8] S. H. Kim, H. S. Kang, E. H. Sohn, B. J. Chang, I. J. Park, S. G. Lee, High discharge energy density and efficiency in newly designed PVDF@SiO₂–PVDF composites for energy capacitors, ACS Appl. Energy Mater. 3 (2020) 8937–8945.

- [9] L. Persano, C. Dagdeviren, Y. Su, Y. Zhang, S. Girardo, D. Pisignano, Y. Huang, J.A. Rogers, High performance piezoelectric devices based on aligned arrays of nanofibers of poly(vinylidenefluoride-co-trifluoroethylene), Nat. Commun. 4 (2013) 1633–1643.
- [10] J. H. Bae, S. H. Chang, PVDF-based ferroelectric polymers and dielectric elastomers for sensor and actuator applications: a review, Funct. Compos. Struct. 1 (2019) 012003– 012022.
- [11] A.J. Lovinger, Ferroelectric Polymers, Science 220 (1983) 1115–1121.
- [12] D. Hu, M. Yao, Y. Fan, C. Ma, M. Fan, M. Liu, Strategies to achieve high performance piezoelectric nanogenerators, Nano Energy 55 (2019) 288–304.
- [13] Z. M. Dang, J. K. Yuan, S. H. Yao, R. J. Liao, Flexible nanodielectric materials with high permittivity for power energy storage, Adv. Mater. 25 (2013) 6334–6365.
- [14] S. K. Ghosh, W. Rahman, T. R. Middya, S. Sen, D. Mandal, Improved breakdown strength and electrical energy storage performance of γ-poly(vinylidene fluoride)/unmodified montmorillonite clay nano-dielectrics, Nanotechnology 27 (2016) 215401–215410.
- [15] W. Li, Q. Meng, Y. Zheng, Z. Zhang, W. Xia, Z. Xu, Electric energy storage properties of poly(vinylidene fluoride), Appl. Phys. Lett. 96 (2010) 192905–192908.
- [16] B. Bagchi, N. A. Hoque, N. Janowicz, S. Das, M. K. Tiwari, Re-usable self-poled piezoelectric/piezocatalytic films with exceptional energy harvesting and water remediation capability, Nano Energy 78 (2020) 105339–105350.

- [17] J. Ma, J. Ren, Y. Jia, Z. Wu, L. Chen, N. O. Haugen, H. Huang, Y. Liu, High efficiency bi-harvesting light/vibration energy using piezoelectric zinc oxide nanorods for dye decomposition, Nano Energy 62 (2019) 376–383.
- [18] Y. Wang, Y. Xu, S. Dong, P. Wang, W. Chen, Z. Lu, D. Ye, B. Pan, D. Wu, C. D. Vecitis, G. Gao, Ultrasonic activation of inert poly(tetrafluoroethylene) enables piezocatalytic generation of reactive oxygen species, Nat. Commun. 12 (2021) 3508–3516.
- [19] F. Guo, M. Li, H. Ren, X. Huang, W. Hou, C. Wang, W. Shi, C. Lu, Fabrication of p-n CuBi₂O₄/MoS₂ heterojunction with nanosheets-on-microrods structure for enhanced photocatalytic activity towards tetracycline degradation, Appl. Surf. Sci. 491 (2019) 88– 94.
- [20] S. Bai, L. Wang, X. Chen, J. Du, Y. Xiong, Chemically exfoliated metallic MoS₂ nanosheets: A promising supporting co-catalyst for enhancing the photocatalytic performance of TiO₂ nanocrystals, Nano Res. 8 (2015) 175–183.
- [21] Y. Wang, Q. Wang, X. Zhan, F. Wang, M. Safdar, J. He, Visible light driven type II heterostructures and their enhanced photocatalysis properties: a review, Nanoscale 5 (2013) 8326–8339.
- [22] J. Choi, H. Park, M. R. Hoffmann, Effects of single metal-ion doping on the visible-light photoreactivity of TiO₂, J. Phys. Chem. C. 114 (2010) 783–792.
- [23] R. Marschall, L. Wang, Non-metal doping of transition metal oxides for visible-light photocatalysis, Catal Today. 225 (2014) 111–135.

- [24] S. L. Lee, C. J. Chang, Recent Developments about conductive polymer based composite photocatalysts, Polymers 11 (2019) 206–227.
- [25] C. Cheng, A. Amini, C. Zhu, Z. Xu, H. Song, N. Wang, Enhanced photocatalytic performance of TiO₂-ZnO hybrid nanostructures, Sci. Rep. 4 (2014) 4181–4186.
- [26] S. Tu, Y. Guo, Y. Zhang, C. Hu, T. Zhang, T. Ma, H. Huang, Piezocatalysis and piezophotocatalysis: Catalysts classification and modification strategy, reaction mechanism, and practical application, Adv. Funct. Mater. 30 (2020) 2005158–2005189.
- [27] Y. Zhang, Z. Ma, Y. Zhang, B. Li, M. Feng, Y. Zhao, Q. An, Biofriendly molecular and protein release substrate with integrated piezoelectric motivation and anti-oxidative stress capabilities, Nanoscale 13 (2021) 8481–8489.
- [28] J. H. Lin, Y. H. Tsao, M. H. Wu, T. M. Chou, Z. H. Lin, J. M. Wu, Single- and fewlayers MoS₂ nanocomposite as piezo-catalyst in dark and self-powered active sensor, Nano Energy 31 (2017) 575–581.
- [29] C. Jin, D. Liu, J. Hu, Y. Wang, Q. Zhang, L. Lv, F. Zhuge, The role of microstructure in piezocatalytic degradation of organic dye pollutants in wastewater, Nano Energy 59 (2019) 372–379.
- [30] Y. L. Liu, J. M. Wu, Synergistically catalytic activities of BiFeO₃/TiO₂ core-shell nanocomposites for degradation of organic dye molecule through piezophototronic effect, Nano Energy 56 (2019) 74–81.
- [31] H. You, X. Ma, Z. Wu, L. Fei, X. Chen, J. Yang, Y. Liu, Y. Jia, H. Li, F. Wang, H. Huang, Piezoelectrically/pyroelectrically-driven vibration/cold-hot energy harvesting for

mechano-/pyro- bi-catalytic dye decomposition of NaNbO₃ nanofibers, Nano Energy 52 (2018) 351–359.

- [32] D. Yu, Z. Liu, J. Zhang, S. Li, Z. Zhao, L. Zhu, W. Liu, Y. Lin, H. Liu, Z. Zhang, Enhanced catalytic performance by multi-field coupling in KNbO₃ nanostructures: Piezophotocatalytic and ferro-photoelectrochemical effects, Nano Energy 58 (2019) 695–705.
- [33] B. M. Pirzada, Pushpendra, R. K. Kunchala, B. S. Naidu, Synthesis of LaFeO₃/Ag₂CO₃ Nanocomposites for Photocatalytic Degradation of Rhodamine B and *p* -Chlorophenol under Natural Sunlight, ACS Omega 4 (2019) 2618–2629.
- [34] S. Garain, T. K. Sinha, P. Adhikary, K. Henkel, S. Sen, S. Ram, C. Sinha, D. Schmeißer,
 D. Mandal, Self-Poled Transparent and Flexible UV Light-Emitting Cerium Complex–
 PVDF Composite: A High-Performance Nanogenerator, ACS Appl. Mater. Interfaces 7 (2015) 1298–1307.
- [35] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, Prog. Polym. Sci. 39 (2014) 683–706.
- [36] S.F. Mendes, C.M. Costa, C. Caparros, V. Sencadas, S. Lanceros-Méndez, Effect of filler size and concentration on the structure and properties of poly(vinylidene fluoride)/BaTiO₃ nanocomposites, J Mater Sci. 47 (2012) 1378–1388.
- [37] B. Dong, G. Liu, J. Zhou, J. Wang, R. Jin, Transformation of silver ions to silver nanoparticles mediated by humic acid under dark conditions at ambient temperature, J. Hazard. Mater. 383 (2020) 121190–121199.

- [38] T. K. Sinha, S. K. Ghosh, R. Maiti, S. Jana, B. Adhikari, D. Mandal, S. K. Ray, Graphene-Silver-Induced Self-Polarized PVDF-Based Flexible Plasmonic Nanogenerator Toward the Realization for New Class of Self Powered Optical Sensor, ACS Appl. Mater. Interfaces. 8 (2016) 14986–14993.
- [39] R. Sarkar, T.K. Kundu, Hydrogen bond interactions of hydrated aluminum nitrate with PVDF, PVDF-TrFE, and PVDF-HFP: A density functional theory-based illustration, Int.
 J. Quant. Chem., 120 (2020) e26328.
- [40] R. Sarkar, T.K. Kundu, Density functional theory studies on PVDF/ionic liquid composite systems, J. Chem.Sci., 130 (2018) 115–133.
- [41] George C. King, Vibrations and Waves, The University of Manchester, Manchester, UK.
- [42] S. K. Ghosh, M. M. Alam, D. Mandal, The in situ formation of platinum nanoparticles and their catalytic role in electroactive phase formation in poly(vinylidene fluoride): a simple preparation of multifunctional poly(vinylidene fluoride) films doped with platinum nanoparticles, RSC Adv. 4 (2014) 41886–41894.
- [43] R. Gregorio, Determination of the α , β , and γ crystalline phases of poly(vinylidene fluoride) films prepared at different conditions, J. Appl. Poly. Sci. 100 (2006) 3272–3279.
- [44] A. C. Lopes, C. M. Costa, C. J. Tavares, I. C. Neves, S. Lanceros-Mendez, Nucleation of the Electroactive γ Phase and Enhancement of the Optical Transparency in Low Filler Content Poly(vinylidene)/Clay Nanocomposites, J. Phys. Chem. C. 115 (2011) 18076– 18082.

- [45] E. A. Falcao, L. W. Aguiar, R. Guo, A. S. Bhalla, Optical absorption of Nd₂O₃-Doped polyvinylidene fluoride films, Mater. Chem. Phy. 258 (2021) 123904–123909.
- [46] R. McKenzie, W. Zurawsky, J. Mijovic, A molecular interpretation of Maxwell–Wagner– Sillars processes, J. Non-Cryst. Solids 406 (2014) 11–21.
- [47] P. Pissis, D. Fragiadakis, A. Kanapitsas, C. Delides, Broadband Dielectric Relaxation Spectroscopy in Polymer Nanocomposites, Macromol. Symp. 265 (2008) 12–20.
- [48] S. Sarkar, S. Garain, D. Mandal, K. K. Chattopadhyay, Electro-active phase formation in PVDF–BiVO₄ flexible nanocomposite films for high energy density storage application, RSC Adv. 4 (2014) 48220–48227.
- [49] Prateek, R. Bhunia, A. Garg, R. K. Gupta, Poly(vinylpyrrolidone)/Poly(vinylidene fluoride) as Guest/Host Polymer Blends: Understanding the Role of Compositional Transformation on Nanoscale Dielectric Behavior through a Simple Solution–Process Route, ACS Appl. Energy Mater. 2 (2019) 6146–6152.
- [50] Prateek, V. K. Thakur, R. K. Gupta, Recent Progress on Ferroelectric Polymer-Based Nanocomposites for High Energy Density Capacitors: Synthesis, Dielectric Properties, and Future Aspects, Chem. Rev. 116 (2016) 4260–4317.
- [51] M. Yang, H. Zhao, D. He, J. Bai, Largely enhanced dielectric properties of carbon nanotubes/polyvinylidene fluoride binary nanocomposites by loading a few boron nitride nanosheets, Appl. Phys. Lett. 109 (2016) 072906–072911.
- [52] K. S. Hemalatha, G. Sriprakash, M. V. N. Ambika Prasad, R. Damle, K. Rukmani, Temperature dependent dielectric and conductivity studies of polyvinyl alcohol-ZnO

nanocomposite films by impedance spectroscopy, J. App. Phys. 118 (2015) 154103-154117.

- [53] H. Yin, A. Schönhals, Broadband Dielectric Spectroscopy on Polymer Blends, Polymer Blends Handbook, Springer Netherlands, Dordrecht, (2014) 1299–1356.
- [54] I. S. Elashmawi, E. M. Abdelrazek, H. M. Ragab, N. A. Hakeem, Structural, optical and dielectric behavior of PVDF films filled with different concentrations of iodine, Phys. B: Condens. Matter 405 (2010) 94–98.
- [55] V. Sencadas, S. Lanceros-Méndez, R. Sabater i Serra, A. Andrio, J.L. Gomez Ribelles, Relaxation dynamics of poly(vinylidene fluoride) studied by dynamical mechanical measurements and dielectric spectroscopy, Eur. Phys. J. E 35 (2012) 41–52.
- [56] T.A. Hanafy, Dielectric relaxation and alternating current conductivity of lanthanum, gadolinium, and erbium-polyvinyl alcohol doped films, J. Appl. Phys. 112 (2012) 034102–0.34112.
- [57] S. K. Ghosh, T. K. Sinha, B. Mahanty, S. Jana, D. Mandal, Porous polymer composite membrane based nanogenerator: A realization of self-powered wireless green energy source for smart electronics applications, J. Appl. Phys. 120 (2016) 174501–174512.
- [58] L. Moro, D. Benasciutti, Harvested power and sensitivity analysis of vibrating shoemounted piezoelectric cantilevers, Smart Mater. Struct. 19 (2010) 115011–115023.
- [59] C. Lang, J. Fang, H. Shao, X. Ding, T. Lin, High-sensitivity acoustic sensors from nanofibre webs, Nat. Commun. 7 (2016) 11108–11115.

- [60] V. Vighetto, A. Ancona, L. Racca, T. Limongi, A. Troia, G. Canavese, V. Cauda, The Synergistic Effect of Nanocrystals Combined with Ultrasound in the Generation of Reactive Oxygen Species for Biomedical Applications, Front. Bioeng. Biotechnol. 7 (2019) 374–384.
- [61] J. F. Turrens, Mitochondrial formation of reactive oxygen species, J. Physiol. 552 (2003) 335–344.

Chapter 3

Electroactive δ -PVDF Nanoparticles with Giant Piezoelectric

Throughput and Self-powered Biomedical Sensors



3.1 Introduction

Over the past few years, there has been a significant increase in demand for portable electronic devices, mainly driven by the rapid growth in the market value of mobile electronics [1,2]. To efficiently harvest the energy from mechanical vibrations, several strategies have been proposed which are abundant in our surroundings through activities such as running, bending, twisting, and stretching of the human body [3], as well as singing, breathing [4], and respiratory motion [5]. In this regard, tremendous approaches have been made to fabricate portable power-driven electronic devices by using several piezoelectric and ferroelectric inorganic materials such as lead zirconate titanate (PZT), barium titanate (BTO), alkali niobates (MNbO₃ (M = K, Na, Li)) and zinc stannate (ZnSnO₃) [6–12]. However complex chemical synthesis route, brittleness, and insufficient bio-compatibility limits its wide range of applications, particularly when direct contact to human body or living organ is concerned. In this context, piezoelectric polymers have achieved immense attention because of their bio-compatibility, stretchability, flexibility, easy processability, shape adaptation, large area processing, higher electrical breakdown strength and also low cost [13]. In this connection, poly(vinlyidene fluoride) (PVDF, chemical formula: (-CH₂–CF₂–)n) and its co-polymer P(VDF-TrFE) have been widely studied due to their excellent piezo-, ferro- and pyro-electric properties which are required for sensors, electromechanical actuators, and energy harvesters [14–16]. It is a semi-crystalline polymer where crystalline parts are mainly responsible for electroactive behavior as discussed in chapter 1 (section 1.2.4). Among the different polymorphs of PVDF, δ -phase is analogous to non-polar α -phase, however, it is a polarized form of α -phase, also known as α_p -phase which is electroactive in nature. So far it was known that β -phase exhibits highest dipole moment per unit cell, that is fully electroactive in nature. In contrast, γ -phase possess lesser dipole moment than β -phase and known as semi-

electroactive phase. The physiochemical properties of δ -phase are not well explored since its discovery. For instance, several prime parameters, e.g., net dipole moment per unit cell, remnant polarization (P_r), coercive field (E_c) and piezoelectric coefficient (d_{33}) are not yet conclusively studied. Further, recent studies have suggested that the electroactive properties of δ -phase in PVDF are almost similar to those of the well-established β -phase [18-20]. Therefore, there is a growing interest in developing technological applications that include the superior electroactive nature of δ -phase. However, δ -phase is mainly observed under very high electrical fields of ~ MV/m [18,21]. The β -phase (form I) has an orthorhombic unit cell structure with a space group of Cm2m $(c^{14}{}_{2\nu})$, where each monomer unit's dipole moment is parallel to each other and oriented perpendicular to the chain axis [22,23]. On the other hand, α -phase (form II) has a monoclinic unit cell structure with a space group $(P2_1/c)$, where adjacent dipoles are antiparallel to the chain axis [24]. The γ -phase (form III) has a monoclinic unit cell structure with a space group of C2cm, and disordered planar zig-zag chain conformations [25,26]. Lastly, δ -phase (form IV) possess an orthorhombic unit cell with a space group of $P2_1cn$, and one of the chain axes is rotated 180° in such a way so that the resultant dipole moment has a non-zero value, despite having similar d-spacing and lattice constants to the α -phase [27]. Martin et.al [20] have reported the solid-state phase transformation of the δ -phase as an alternative to the electric poling assisted process. It is worth mentioning that a significant amount of research has been conducted on electroactive β - and γ -phase PVDF films and fibers due to their superior piezoelectric properties [28-32]. Additionally, researchers have observed a growing interest in versatile shapes such as ribbons, flakes, and particles, which exhibit synergistic properties that enhance the overall performance of sensors, actuators, and energy harvesters [33-38]. For instance, spherical particles in nano-dimension are more advantageous due to large surface to volume ratio, thus

electroactive δ -PVDF nanoparticles (NPs) fabrication with spherical shape is an outmost challenge.

In this work, very first time we have introduced a novel approach using solvent-antisolvent mediation in the process of nanoprecipitation technique to prepare PVDF NPs (diameter ~220 nm) with a predominant electroactive δ -phase. The Piezoresponse force microscopy (PFM) has confirmed both piezoelectric and ferroelectric properties in δ -NPs. The unprecedented high piezoelectric coefficient i.e., $d_{33} \sim -43 \text{ pm/V}$ is noticed that attributed to the nanostructured spherical shape of NPs, which promises its technological applications comparable to or even much superior as that of β -phase of PVDF. As a consequence, we anticipate that the device employing these δ -PVDF NPs will exhibit significant electromechanical sensitivity, rendering it an ideal candidate for the fabrication of effective flexible sensors suitable for non-invasive biosignal detection, such as monitoring of pulse rate, voice signals, and respiration detection.

3.2 Experimental section

3.2.1 Synthesis of PVDF nanoparticles

 δ -PVDF nanoparticles were synthesized by a phase separation induced nanoprecipitation method using two different polarity solvents. Firstly, PVDF powder was dispersed in acetone (good solvent) with a concentration of 5 mg/ml in a centrifuge tube by gentle shaking and named as solution A. Thereafter, a blend solution of DI water and methanol (non-solvent) in 1:1 volume ratio was prepared named as solution B. Then solution B was injected very slowly from bottom end into solution A. PVDF nanoparticles were formed at the interface of two different solvents and congregated at the bottom end of the test tube due to gravity. It was then collected by using centrifugation with ethanol 3 times at 4000 rpm. Then the PVDF nanoparticles are heat treated at 80 °C for 6 h and used for further characterization.

3.2.2 Piezoresponse force microscopy measurement

Piezoresponse force microscopy (PFM) in contact mode was employed to quantify random dipole switching and piezoelectric performance at the nanoscale level. For the measurement, δ -PVDF NPs were transferred on a clean glass substrate coated with indium tin oxide (ITO) along with a conducting tip coated with platinum/iridium (Pt/Ir) as a spring constant (k) of 3 N/m and a frequency (ω) of 75 kHz.

3.2.3 Fabrication of flexible piezoelectric nanogenerator (FPNG)

FPNG was fabricated by the incorporation of δ -PVDF nanoparticles into a PDMS (Sylgard 184, a silicone elastomer) polymer matrix with various concentrations of PVDF NPs (0 wt% for pure PDMS, and 10, 20, 30, and 40 wt%). The resulting PVDF/PDMS solutions were casted onto 2×2 cm² clean glass slides and heat treated at 60 °C for 40 min. Subsequently, composite films were removed from the glass substrate for device fabrication. Copper electrode was placed on the top and bottom sides of the films, and two copper wires were established to the top and bottom electrodes of FPNG to collect the electrical signals. At last, as fabricated FPNG was corona poled at 30 kV of electric field and 60 °C temperature for 40 min.

3.3 Results and discussion

3.3.1 Mechanism of PVDF nanoparticles formation

The method used for synthesizing of δ -PVDF NPs through the nanoprecipitation technique is schematically demonstrated in Figure 3.1. This process involves the formation of nanoparticles at

the interface between a solvent (acetone) and a non-solvent (water:methanol) of PVDF as shown in Figure 3.1a [35]. The digital image (Figure 3.1b) of nanoprecipitation have been captured at various time intervals (0, 10, 20, 40, and 60 min), indicating that the functionalization of nanoparticles at the interface occurs first, then they settle down at the bottom of the tube via a diffusion-driven precipitation process.



Figure 3.1. Schematic representation of δ -PVDF nanoparticles preparation by nanoprecipitation method (a) the solvent and non-solvent interface is marked with rectangular region, where arrows are indicating the accumulated nanoparticles precipitated at the bottom of the tube (b) photograph of mechanism at 0, 10, 20, 40 and 60 m of solvent and non-solvent interfaces.

Nano-assembly of nanoparticles occurs at the interface due to the hydrophobic interaction between water molecules and the -CF₂- dipoles of PVDF, which self-fold its macromolecular chains, as illustrated in Figure 3.2 [39]. Essentially, the hydrophobic interaction arises from the disruption of hydrogen bonds between water molecules due to the presence of a non-polar solute like acetone, leading to the formation of a cavity resembling a cage [40]. The newly formed hydrogen bonded network between neighboring water molecules, which resembles ice-like clathrate hydrate, surrounds and assembles a reduced number of polymeric chains into voids. Consequently, the surface area available for the formation of PVDF nanoparticles is decreased, causing them to diffuse through the interface and precipitate at the bottom of the test tube. The reduction in the number of PVDF chains during nanoparticle nucleation may also affect the size of the particles, which suggests that particle size can be tuned by optimizing the amount of PVDF in the solvent system. The yield of the as-synthesized PVDF nanoparticles is estimated to be 80 %.



Figure 3.2 Schematic view of hydrophobic interaction of water molecules with –CF₂– dipoles of PVDF polymer.

3.3.2 Electroactive phase nucleation in PVDF

Further, transmission electron microscopy (TEM) image and histogram plot, (as depicted in Figure 3.3a) confirm the uniform spherical shape of as-synthesized NPs with average diameter of ~ 220 nm (inset of Figure 3.3a). The selected area electron diffraction (SAED) pattern (Figure 3.3b) confirmed that the interplanar spacing (d-values) corresponded to the δ -PVDF crystalline phase [27]. For instances, two planes, *i.e.* (110) and (111) having d-values of 0.44 nm and 0.32

nm respectively, observed in SAED image as well matched with its XRD pattern (Figure 3.4). Next, (041), (141) and (310) planes are indexed in SAED pattern, these are low intensity peaks attribute to higher 2θ values corresponding to very small d-spacing values *e.g.*, 0.21 nm, 0.19 and 0.17 nm respectively as comparison to the (110) and (111) planes. Similar reflection planes are also identified as δ-phase PVDF film by Bachmann et.al. [27].



Figure 3.3 (a) TEM image of spherical δ -PVDF nanoparticles with the histogram (inset) for particles diameter distribution (b) SAED pattern of δ -PVDF nanoparticles.

In addition to that, the complementary evidence of formation of δ -PVDF nanoparticles is further confirmed from XRD pattern. For the better understanding, a PVDF sample in the α -phase is prepared by subjecting the as-prepared δ -PVDF nanoparticles to a high temperature of 170°C. It's important to note that a temperature higher than the melting point of the current phase is necessary to obtain the non-polar α -phase from any crystalline phase of PVDF [41,42]. The XRD pattern depicted in Figure 3.4 illustrates that the α -phase displays three distinct diffraction peaks before the 20 angle of 21° at 17.8° (100), 18.5° (020), and 20.1° (110), followed by three additional peaks at 25.7° (120), 26.7° (021), and 27.5° (111). In contrast, the δ -phase shows only two peaks before the 2 θ angle of 21° at 18.5° (020) and 20.1° (110), and two more peaks appear after 21° at 26.7° (021) and 27.9° (111). The reflection planes and peak positions serve as complementary supporting evidence for the PVDF δ -phase characteristics, in addition to the observations derived from the SEAD pattern [43, 44]. Based on the subsequent analysis, it can be inferred that the disappearance of two peaks at 17.8° (100) and 25.7° (120) in the δ -phase can be attributed to the alteration in crystal symmetry from the α -phase. The emergence of a distinct peak at 17.8° is a fundamental characteristic feature that validates the formation of the non-polar α -phase in PVDF, as the remaining peaks have overlapping features with either the β - or γ -phase [45]. Another significant disparity can be observed in the $2\theta \sim 25^{\circ}$ to 28° region, where an asymmetrical Gaussian-like broad diffraction pattern is evident in the combination of two crystalline peaks from (021) and (111) planes and one amorphous halo in δ -PVDF nanoparticles. In contrast, the XRD pattern ($2\theta \sim 25^{\circ} - 28^{\circ}$) of α -PVDF displays a relatively symmetric Gaussian diffraction pattern that arises due to the presence of three crystalline planes, namely, (120), (021), (111) and one amorphous halo.

Further, the crystallite size ($t_{\chi_c} = 8 \text{ nm}$) of δ -PVDF NPs is estimated from the Debye-Scherrer equation, *i.e.*,

$$t_{\chi_c} = \frac{k\lambda}{\beta \cos\theta} \tag{3.1}$$

where k (~ 0.9) is the dimensionless shape factor, β is the full width at half maxima (FWHM) in radians, θ is the Bragg's angle. It is worth noting that the recrystallization process, similar to the phase conversion from $\delta \rightarrow \alpha$ -phase, causes an increase in t_{χ_c} up to 10 nm under heat treatment at 170 °C.



Figure 3.4 XRD pattern of (a) δ -PVDF NPs in upper panel and (b) PVDF α -phase film prepared by heating of δ -PVDF NPs at high temperature 170 °C in lower panel. The region between $2\theta \sim$ 24° to 30° has been magnified 6-fold to provide a clearer representation and facilitate the differentiation of characteristic features of both the δ - and α -phases in the XRD pattern within this range.

Moreover, the degree of crystallinity (χ_c) of δ -PVDF nanoparticles ($\chi_c(\delta) \sim 43$ %), can be determined by

$$\chi_c = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{amr}} \times 100 \%$$
(3.2)

The total area under the sharp diffraction peaks in the crystalline and amorphous halo regions are denoted by $\sum A_{cr}$ and $\sum A_{amr}$ respectively. It should be noted that the recrystallization process,

involving the conversion from $\delta \rightarrow \alpha$ -phase, leads to a remarkable enhancement in the degree of crystallinity up to 51%.

It is noteworthy to mention that the most commonly used technique i.e., Fourier transform infrared (FTIR) spectroscopy for PVDF crystalline phase identification cannot identify or requires careful analysis. Because the vibrational bands that appear due to the α - and δ -phase share identical features owing to their similar stereochemical chain conformations and respective unit cell of δ -phase. Hence, XRD pattern analysis has become an invaluable technique, as it offers detailed features ranging from peak positions, number of peaks to line shape analysis, and is crucial for distinguishing between different crystalline phases of PVDF. While laboratorybased XRD is commonly employed, although synchrotron-based XRD is also attempted in some cases due to its high resolution. In this context, it has been realized that the combination of XRD and FTIR spectrum is conclusive in distinguishing all four crystalline phases of PVDF (i.e., α , β , γ , and δ). However, several distinguishing features have been observed in ATR-FTIR spectroscopy, Raman spectroscopy, DSC thermogram for differentiating between the $\delta \rightarrow \alpha$ phase. A distinct shifting of the vibrational band position between α - to δ -phase is noticed in the ATR-FTIR spectra (Figure 3.5a), such as 870 shifted to 875 cm⁻¹ and 761 shifted to 763 cm⁻¹ (Figure 3.5b and 3.5c). Despite having almost similar chain conformations, this shifting demonstrates one of the key differences between the electroactive δ -phase and non-polar α phase. The vibrational bands in the FTIR spectra of the δ - and α -phases appear to be almost similar due to the identical chain conformations (i.e., TGTG'), which restricts the ability to identify the phases with ease similar other phases like the β (TTTT) and γ (TTTG). Additionally, Raman spectroscopy was conducted to determine if there were any distinguishing features between the δ - and α -phases (as shown in Figure 3.5d). In both cases (α and δ), similar
vibrational band positions were observed at 287, 613, 796, 842, 883, and 1200 cm⁻¹ respectively. Nevertheless, a significant difference in intensity was noted in between two bands at 883 and 842 cm⁻¹. Particularly, peak intensity ratio between the 883 and 842 cm⁻¹ (i.e., I_{883}/I_{842}) is observed to decrease (~ 12%) in the δ -phase as compared to the α -phase due to the symmetric stretching of the –CF₂– group. Furthermore, it was observed that the peak intensity at 842 cm⁻¹ was much more prominent in the δ -phase, while only a small shoulder is evident in the α -phase. This difference in intensity could be attributed to the orientation difference between these two-unit cells.



Figure 3.5 The ATR-FTIR spectra of (a) δ - and α -phase of PVDF and enlarge view of spectra in the region (b) 758 cm⁻¹ to 767 cm⁻¹ and (c) 860 cm⁻¹ to 890 cm⁻¹, (d) Raman spectra and (e) thermal DSC thermogram of PVDF both δ - and α -phase.

From thermal study as displayed in Figure 3.5e, it has been observed that the δ -phase exhibits two endothermic peaks at 157 °C and 164 °C, whereas the α -phase shows only a single broad peak centered at 160 °C. The two dominant peaks that appear at 164 °C and 162 °C are related to the melting behavior of the α -phase. This suggests that the conversion from the δ -phase to the α -phase occurs at 157 °C in the δ -PVDF nanoparticles containing sample. However, a slight difference is observed in the melting temperature of 2-5 °C between the δ - and α -phase, which makes it very clear to differentiate between the two exiting phases during the melting process from δ - to α -phase.

3.3.3 Nanoscale piezo-and ferro-electricity

To investigate the piezo-and ferro-electricity at the nanoscale we have employed scanning probe microscopy (SPM) based atomic force microscopy (AFM) and the corresponding measurement scheme is demonstrated in Figure 3.6a. The 3D AFM surface topography of δ -PVDF NPs is displayed in Figure 3.6b, indicating the average diameter of NPs are ~ 220-230 nm which is consistence with the observation under TEM (Figure 3.3a). To study the ferroelectric switching and piezoelectric response of the sample, an AC signal of 4 V amplitude (V₀) was applied between the conducting tip and ITO coated substrate. A dual signal of DC bias (V_{DC}) ± 11 V with the superimposed AC signal $V_{tip} = (V_{DC} + V_0 \cos (\omega t))$ was then applied to the samples throughout the scan under the piezoresponse force microscopy (PFM) mode of AFM, resulting in the acquisition of ferroelectric (phase) and piezoelectric (amplitude) hysteresis loops. Ferroelectric phase response is shown (Figure 3.6c), where an increase in positive DC bias voltage causes the dipoles inside the δ -PVDF nanoparticles in the particular crystalline lamella (domain) to reorient themselves in the direction of the applied bias voltage, resulting in a positive phase change response. The maximum dipole orientation occurs when it crosses the positive

coercive voltage ($V_C \sim 1V$), after which it achieves phase change saturation at bias voltage ($V_r \sim 5$ V). Similarly, when the bias voltage switches to the negative cycle, the individual dipoles reorient themselves in the direction of the electric field until the coercive voltage ($V_C \sim 1V$) is reached that saturate their orientations completely at -5 V of DC bias voltage (V_r). This behavior indicates the achievement of complete ferroelectric-like behavior and $\approx 180^{\circ}$ orientation of dipoles under the application of an external DC bias voltage, which is directly governed by the direction of the localized polarization of dipoles. Therefore, the hysteretic phase response serves as evidence of localized ferroelectricity attributed to the electroactive δ -PVDF nanoparticles. The very low V_C and V_r values in the ferroelectric hysteresis loop provide strong evidence for the superior electroactive nature of the δ -phase, which is expected to exhibit notable piezoelectric response as well. Furthermore, to monitor the piezoelectric response, the amplitude hysteresis response (also known as the butterfly loop) recorded within the range of ± 11 V of DC bias voltage, as illustrated in Figure 3.6d. Upon increasing the positive DC bias voltage (i.e., 0 to 11 V), there is a crystal lattice expansion of ~ 0.45 nm takes place, after it surpasses the coercive voltage (V_C ~1V) when subjected to an electric field. Similarly, the PVDF NPs undergo contraction when the bias voltage decreases from +11 V to 0 V as evidenced by the amplitude response. Likewise, when the DC bias is increased in the negative direction (i.e., from 0 to -11 V), the dipoles within the nanoparticles expand and reach maximum deformation of ~ 0.25 nm at -5 V. Conversely, when the voltage is decreased the dipoles contract and return to their initial position at 0 V, resulting in a fully closed butterfly loop for the δ -PVDF NPs. Additionally, the PFM measurement was conducted in the vertical mode, allowing for the evaluation of the localized microscopic piezoelectric coefficient (d_{33}) for the δ -PVDF NPs from the butterfly loop.



Figure 3.6 SPM based AFM analysis of δ -PVDF NPs (a) schematic view of measurement setup for the local piezo- and ferro-electricity, (b) 3D surface topography (3 × 3 μm^2). Piezo-response force microscopy (PFM) spectroscopic (c) phase (ferroelectric hysteresis loop) and (d) amplitude (piezoelectric hysteresis loop) under the application of ± 10 V DC bias voltage.

Further, change in amplitude (ΔZ) at the alteration of bias voltage (ΔV) is used to calculate the magnitude of d_{33} , which was estimated to be approximately 43 pm/V.

$$d_{33} = \frac{\Delta Z}{\Delta V} \tag{3.3}$$

That indicates the giant piezoelectric response resembles from highly electroactive nature of the spherical shape PVDF NPs with δ -phase. For instances, the normal component of electric field induces in-plane stress, which is directly related with the normal deformation in the sample because of compact adhesion between nanoparticles and substrate (like one dimensional nature). This interaction is further explained by the following equation

$$S_3 = s^{E}{}_{13}(T_1 + T_2) + S^{E}{}_{33}T_3 + d_{33}E_3$$
(3.4)

where, T, S, E and s^{E}_{13} are the stress tensor, strain tensor, electric field and elastic compliance component respectively. To clarify, we assume one-dimension interaction of nanoparticles with substrate. Therefore, in the absence of applied stress $T_2 = T_3 = 0$ (along the lateral direction) and T_1 (along the vertical direction) will remains non-zero, which gives the giant effective d_{33} . It is worth noting that the piezoelectric properties and spherical shape of the δ -PVDF NPs make them highly promising for use in the biomedical sectors.

It has the potential to be utilized in several applications such as tissue engineering, drug delivery, inhibition of Alzheimer's growth, and neuron recovery. In fact, studies have shown that these nanoparticles can generate reactive oxygen species (ROS) in response to external stimuli such as ultrasound frequencies or normal shaking [47-49]. In addition, we conducted PFM writing and erasing experiment to investigate the dipole switching properties of the δ -PVDF NPs (as shown in Figure 3.7). To carry out the measurement, an AC oscillation frequency of 12 kHz and a voltage amplitude of 6 V is applied to the conducting probe. This allowed us to observe significant changes in the ferroelectric properties during the writing and erasing process. A DC bias voltage of +14 V was applied between the conducting tip and ITO coated substrate where δ -PVDF NPs were written in a triangular pattern (Figure 3.7a and 3.7b). The written pattern over the nanoparticles was then read using a 0 V of DC bias between the conducting

probe and the sample. It is observed that the PFM amplitude and phase response of the written area shows a significant domain switching with bright contrast in the amplitude image (Figure 3.7a) and corresponding phase change (Figure 3.7b). The switching of the dipoles led to a dark contrast in the PFM phase image, which is due to the switching of the dipoles in the opposite direction to the applied field. The line profile analysis over the selected region reveals that after domain writing, the amplitude changed to $\Delta Z \approx 330 \ \mu V$ (Figure 3.7a(i)) with a corresponding phase change of $\Delta \phi \approx 180^{\circ}$ (Figure 3.7b(i)). The equivalent dipole orientation is schematically demonstrated in Figure 3.7b(ii).



nm

nm



Figure 3.7 PFM writing a bit image $(3.6 \times 3.6 \,\mu m^2)$ over to δ -PVDF NPs from right panel (a) the amplitude images and corresponding change in amplitude ($\Delta Z \approx 330 \,\mu V$) with line profile of marked triangular area in (a, i), (b) phase image and corresponding change in phase ($\Delta \varphi \approx 180^\circ$) along with the dipole switching in (b, i, ii). PFM erasing a bit illustrated in the right panel (c) amplitude and corresponding change in amplitude ($\Delta Z \approx 0 \,\mu V$) in (c, i), (d) phase image and corresponding change in phase ($\Delta \varphi \approx 0^\circ$) along with the dipole switching in (d, i, ii).

Furthermore, to erase the written area over the δ -PVDF NPs, a negative bias of -14 V was applied to the selected region. The amplitude and phase patterns over the previously written domains after erasing are displayed in Figure 3.7c and 3.7d. The line profile over the erased region shows an amplitude change of $\Delta Z \sim 0 \ \mu V$ (Figure 3.7c(i)) with a corresponding phase change of $\Delta \phi \sim 0^{\circ}$ (Figure 3.7d(i)). The schematic orientation of the dipoles is also displayed in

Figure 3.7d(ii). It indicates that the dipoles within the written domain switched back to their initial position after erasing. Therefore, the prompt domain switching response under the application of low voltage provides excellent evidence that δ -PVDF NPs exhibit superior ferroelectric switching kinetics, which has direct linear relevance to their corresponding piezoelectric properties.

3.3.4 Output performance of FPNG

The flexible piezoelectric nanogenerator (FPNG) was fabricated as mentioned in the experimental section and schematically demonstrated in the inset of Figure 3.8a. The crystal structure of the δ -phase undergoes deformation when an external mechanical force is applied to it, causing a flow of charge carriers over the surface (in close proximity to the top and bottom electrodes) due to effective changes in polarization [50]. By continuously hand imparting force, the open circuit voltage (V_{OC}) (Figure 3.8a) and short circuit current (I_{SC}) (Figure 3.8b) responses were recorded. The generated V_{OC} and I_{SC} were more than 7 V and 1.5 µA respectively, under a continuous force amplitude of 6 N at a frequency of ~ 5 Hz. It is important to mention that FPNG were prepared using five different concentrations (0 wt % (control i.e., only PDMS), 10 wt %, 20 wt %, 30 wt %, and 40 wt %) of δ -PVDF nanoparticles into polydimethylsiloxane (PDMS) matrix. Then, it has been noted that there is a remarkable enhancement in the electrical output when the concentration of δ -PVDF NPs increases in the PDMS matrix. The maximum response was recorded with 40 wt% of FPNG, which can be attributed to the piezoelectric nature of δ -PVDF NPs.



Figure 3.8 Electrical output performance of FPNG as (a) open circuit voltage (V_{OC}) and inset shows the schematic view of FPNG preparation, (b) short circuit current (I_{SC}), the repeatability and stability response of FPNG as short circuit current over 3000 cycles on (c) day 1 and (d) day 30.

Additionally, PDMS serves as an effective mechanical impact absorber, facilitating the propagation of the generated strain throughout the FPNG and resulting in a significant increase in electrical output response. Furthermore, we conducted tests to assess the stability and repeatability of FPNG. We recorded the short circuit current response over the course of 3000

cycles on both day 1 and day 30, as illustrated in Figure 3.8c and 3.8d, respectively. The results indicate that even after 30 days and 3000 cycles, the peak-to-peak current amplitudes remain consistent, indicating that FPNG exhibits excellent stability and repeatability over the prolonged period of time.

3.3.5 Finite element method-based simulation

To gain insight into the mechanism behind the generation of piezo-potential, a theoretical simulation is conducted using the finite element method (FEM). Two different models were prepared for comparison: one consisting of nanoparticles and the other a planar film based on PVDF geometry, both subjected to a constant applied pressure of 100 kPa. The theoretical simulation model for the distribution of piezo-potential has been investigated with variable concentrations of PVDF nanoparticles (10, 20, 30 and 40 wt %) in the PDMS matrix, considering the possible distribution of nanoparticles (as shown in Figure 3.9 (a-d) in the PDMS matrix). The results indicate that the piezo-potential increases as the concentration of PVDF nanoparticles in the PDMS matrix increases. The optimal piezo-potential ~ 10 V is observed when the PDMS matrix comprised of 40 wt % PVDF nanoparticles due to the well-dispersed and interconnected nature of the nanoparticles in the PDMS matrix (as shown in Figure 3.9d). The results indicate that the nanoparticles generate a higher piezo-potential ~ 10 V, whereas the planar film generates only ~ 2.5 V (Figure 3.9e). This significant difference in piezo-potential can be attributed to the structural change from nanoparticles to planar film because of the stress confinement within the matrix of δ -PVDF nanoparticles is greater than in the planar film, leading to a larger piezopotential (as shown in Figure 3.10a and 3.10b).



Figure 3.9 2D FEM based theoretical simulation model for piezo-potential generation upon the application of 100 kPa stress (a-d) with varying concentration of δ -PVDF nanoparticles in the PDMS matrix, (e) planer PVDF film-based geometry.

Moreover, the relative displacement within the δ -PVDF nanoparticles is much higher (~ 4 nm) than in the planar film (~1 nm) when the same amount of stress is applied (as displayed in Figure

3.10c and 3.10d). Experimental and theoretical simulated results show a slight deviation, which can be attributed to the presence of leakage paths in the device arrangement.



Figure 3.10 2D FEM based theoretical simulation model for piezo-potential generation (a) δ -PVDF nanoparticles comprising system, (b) planer PVDF film-based geometry. The stress confinement under the application of 100 kPa of pressure (c) δ -PVDF nanoparticles and enlarged image of rectangular marked region shows the distribution on nanoparticles (d) stress distribution in the planer PVDF film.

Further, it should be emphasized that the simulated results adhere to the classical piezoelectric theory of the interaction mechanism between structural and electrical output, as described by the following equations

$$T = c^E \cdot S - e^T \cdot E \tag{3.5}$$

$$D = e.S + \varepsilon_0 \varepsilon_{rs}.E \tag{3.6}$$

where *S* is the mechanical strain, $(e)_{ijk}$ is the piezoelectric tensor, e^T and c^E are stress and elasticity tensor respectively. ε_0 , ε_{rs} are the dielectric tensors and *E* is the electric field [51].

3.3.6 Mechanical energy harvesting performance of FPNG

Piezoelectric response in FPNG can be evaluated by determining the piezoelectric coefficient (d_{33}) , which is given $d_{33} = \frac{Q}{F}$, $(Q = \int_{t_1}^{t_2} I \, dt)$ where Q represents the charge generated and I

denote short circuit current under the applied mechanical force (F = 6 N) within the current limits t_1 and t_2 . The calculated d_{33} value is approximately ≈ -61 pC/N. Notably, the obtained d_{33} value differs slightly from that determined by piezoresponse force microscopy (PFM) because here we examined resultant response of the entire device (macroscopic level) where large number of δ -PVDF NPs have been considered into account while in the case of PFM, we evaluated only localized response (microscopic level) from δ -PVDF NPs. It is worth noting that the piezoelectric coefficient obtained in our study (-61 pC/N) is relatively higher than that reported results in other studies, which is summarized in Table 3.1. It suggests the exceptional piezoelectric properties of the nano precipitated δ -PVDF nanoparticles. Moreover, we have also investigated the performance of FPNG by analyzing the voltage and current variation with external load resistance (R_L) ranging from 10⁵ to 10⁸ Ω under continuous hand imparting of

force as shown in Figure 3.11a. We observed that the output voltage increases with an increase in resistance and saturates at a high resistance of 5 M Ω due to the impedance matching phenomenon, where the external load resistance is equivalent to the internal resistance of the FPNG. Conversely, the output current shows the opposite behavior to that of the output voltage, where it is maximum at low resistance and then decreases at higher resistance. Furthermore, the variation of the instantaneous power density (*P*) is evaluated with an effective imparting area (*A*) of FPNG by the following equation

$$P = \frac{V^2}{(R_L \times A)} \tag{3.7}$$

The maximum power density of the flexible piezoelectric nanogenerator (FPNG) is determined to be 2 μ W/cm² as shown in Figure 3.11b which allows it to successfully power up five blue LEDs when pressure is imparted by hand (inset of Figure 3.11b). To determine the feasibility of FPNG for various electronic applications, capacitor charging and discharging responses were examined with 1 and 2.2 μ F. It indicates that the FPNG can charge the capacitors in a very short span of time and eventually reached a steady state, as demonstrated in Figure 3.11c. Further, FPNG demonstrated an exceptional mechano-sensitivity (Sm ~ 107 mV/kPa), which opens up possibilities for its use in physical motion sensing of the human body (as displayed in Figure 3.11d) [52]. Additionally, mechanical energy harvesting capability of FPNG was tested during running on treadmill. The FPNG was placed under the treadmill machine, and its piezoelectric response was recorded as output voltage while running on the treadmill (as shown in Figure 3.12a). It indicates that the FPNG can generate an electrical output voltage of more than 6 V under running conditions (as illustrated in Figure 3.12b).



Figure 3.11 Performance of FPNG with external load resistance (a) voltage and current variation (b) electrical power density under the load resistance ranging from $10^5 \Omega$ to $10^8 \Omega$ and inset shows 5 blue LED lightening by FPNG, (c) capacitor charging and discharging of FPNG with an equivalent circuit diagram in the inset and (d) mechano-sensitivity of FPNG by using free fall force of different weights from a constant height of 10 cm.

Furthermore, δ -PVDF NPs comprised FPNG has registered the superior piezoelectric figure of merit

 $(FOM)_P$, defined as

$$(FOM)_P = d_{33} \times g_{33} = \frac{d^2{}_{33}}{\epsilon_0 \times \epsilon_r}$$
 (3.8)

where, d_{33} is the piezoelectric coefficient, and g_{33} is the voltage coefficient ($g_{33} = \frac{d_{33}}{\varepsilon_0 \times \varepsilon_r}$) where ε_0 and ε_r are the permittivity of free space and material respectively [53]. The estimated value of $(FOM)_P$ is 44.25 × 10⁻¹² Pa⁻¹ which is much higher than the reported results [54,55].

In addition to that, piezoelectric energy conversion efficiency i.e., conversion of mechanical energy into electrical energy of FPNG is determining by the ratio of electrical energy to the applied mechanical energy. The output electrical energy (E_{ele}) for one cycle is obtained using the equation

$$E_{ele} = \int_0^t \frac{V^2}{R} dt \tag{3.9}$$

where V is the output voltage across a load resistance (R) of 5 M Ω . The mechanical energy can be determined as $E_{mech} = F \times \Delta L$, where F is the applied force, and ΔL can be estimated as $\epsilon \times L$, where ϵ is the strain constant and L is the thickness of the device. The fabricated FPNG showed an instantaneous piezoelectric energy conversion efficiency of 24%, which is significantly greater than the efficiency reported in previous studies [56–58].



Figure 3.12 Schematic illustration of human running during exercise on treadmill machine and then device was placed in the shoe to record the electrical output response (b) corresponding output voltage signal.

3.3.7 Healthcare signal monitoring

The flexible and wearable FPNG serves as an effective sensor capable of detecting the arterial blood pressure wave, which corresponds to the dynamic pressure changes in blood flow [59]. Further, arterial pulse rate signal was recorded when FPNG was attached to the human wrist and it demonstrated a regular and repeatable pulse (~66 beats per minute (bpm) under normal rest conditions (as shown in Figure 3.13a). The enlarged view of a single waveform (inset of Figure 3.13a) indicates three distinguishable peaks named as P1 (early systolic), P2 (late systolic), and P3 (diastolic), which is typical nature of the arterial pulse waveform [60]. By analyzing these three peaks, essential parameters such as the time delay ($\Delta \tau = t_2 - t_1$), radial augmentation index (*AI_r*) e.g., the ratio of P_2/P_1 , and diastolic augmentation index (DAI) the ratio of P_3/P_1 are estimated. These parameters provide important information for physiological health care

monitoring signals such as vascular aging, ventricular load, arterial stiffness and myocardial infarction. For instance, the calculated values of $\Delta \tau$, AI_r and DAI are 0.43s, 0.62, and 0.65, respectively, indicating the physiological parameters of healthy persons. Therefore, the FPNG has the potential to be used as a biomedical sensor for clinical diagnosis, continuous monitoring of pulse wave and IoT-based remote healthcare clouds [61-63]. To understand the variation in amplitude vs frequency, the 2D short-time Fourier transform (STFT) is presented in Figure 3.13b, which reveals that different amplitude pressure signals within the 0-70 Hz frequency range attributed to the characteristics of arterial pulse responses.



Figure 3.13 Physiological signal monitoring as (a) arterial pulse detection and inset shows enlarged view of a single peak with the typical nature of blood pressure wave (d) 2D-STFT processed spectrogram of an arterial pulse signal.

Material	Manufacturing Process	Reported d ₃₃	References
		Magnitude	
		(pC/N, pm/V*)	
PVDF	Phase inversion in spin coated	49.6	Chem. Commun. 51
	film followed by melt		(2015) 8257-8260
	quenching		
PVDF	Electrospinning fiber with	38	ACS Appl. Mater.
	naturally sugar assisted		Interfaces 10 (2018)
			44018-44032.
P(VDF-TrFE)	Vertically aligned P(VDF-TrFE)	35*	Sci. Rep. 5 (2015)
	nanotubes arrays with Al matrix		09790-09797
P(VDF-	Solution casting at 90 °C	15	Mater. Chem. Phys.
HFP)/ZnO			186 (2017) 327–332
PVDF/CNT	Spin coating	13*	ACS Appl. Mater.
			Interfaces 10 (2018)
			13092–13099
P(VDF-	Spin coating thin films	34.7 <u>±</u> 2.4	Appl. Surf. Sci. 463
TrFE)/ZnO			(2019) 626–634
P(VDF-	Electrospinning fiber	50	ACS Appl. Mater.
TrFE)/BTO			Interfaces 11 (2019)
			7379–7386
PVDF	nanoporous structure in film	32	Nano Lett. 11 (2011)
	followed by dry etching		5142–5147
PVDF	Produced by iterative thermal	58*	ACS Nano 8 (2014)
nanoribbons	size reduction techniques		9311–9323
P(VDF-TrFE)/Ag	Ag/PVDF-TrFE films prepared by	20.23	Sci. Rep. 5 (2015)
	tape casting		13209–13216
PVDF	δ-nanoparticles prepared by	61	this work
	nanoprecipitation technique		

Table 3.1 Comparative table for piezoelectric coefficient (d_{33}) .

3.4 Conclusions

In summary, we have fabricated PVDF NPs via nanoprecipitation technique with predominant δ phase. Noteworthy to mention that, this method is advantageous compared to the traditional process which requires high electric fields for δ -phase conversion. Further, as fabricated PVDF NPs have shown excellent piezo- and ferro-electric properties which is evident by PFM. The δ -PVDF NPs have demonstrate a remarkable localized piezoelectric coefficient (d_{33}) ~ -43 pm/V. Additionally, the switching kinetics of the ferroelectric dipoles during writing and erasing under external voltage in PFM further indicate their superior ferroelectric behavior, which could be applicable in scanning probe-based memory applications. Moreover, we have fabricated FPNG with the δ -PVDF NPs which exhibits excellent piezoelectric output performance. The FPNG demonstrated a V_{OC} (open-circuit voltage) of more than 7 V and an I_{SC} (short-circuit current) of 1.5 μ A, with a power density of 2 μ W/cm². Furthermore, the FPNG exhibits a mechanosensitivity of 107 mV/kPa and an instantaneous piezoelectric energy conversion efficiency (η_{piezo}) of 24%. These exceptional properties of δ -PVDF NPs make them suitable for a range of applications, spanning from biomedical sectors to mechanical energy harvesters for self-powered portable electronics.

3.5 References

- N. Sezer, M. Koç, A comprehensive review on the state-of-the-art of piezoelectric energy harvesting, Nano Energy 80 (2021) 105567-105592.
- [2] V. Jella, S. Ippili, J. H. Eom, J. Choi, S. G. Yoon, Enhanced output performance of a flexible piezoelectric energy harvester based on stable MAPbI₃-PVDF composite films, Nano Energy 53 (2018) 46–56.
- [3] F. R. Fan, W. Tang, Z.L. Wang, Flexible Nanogenerators for energy harvesting and selfpowered electronics, Adv. Mater. 28 (2016) 4283–4305.
- [4] X. Chen, X. Li, J. Shao, N. An, H. Tian, C. Wang, T. Han, L. Wang, B. Lu, Highperformance piezoelectric nanogenerators with imprinted P(VDF-TrFE)/BaTiO₃ nanocomposite micropillars for self-powered flexible sensors, Small 13 (2017) 1604245– 1604257.
- [5] K. I. Park, J. H. Son, G. T. Hwang, C.K. Jeong, J. Ryu, M. Koo, I. Choi, S.H. Lee, M. Byun, Z.L. Wang, K.J. Lee, Highly-efficient, flexible piezoelectric PZT thin film nanogenerator on plastic substrates, Adv. Mater. 26 (2014) 2514–2520.
- [6] W. Wu, S. Bai, M. Yuan, Y. Qin, Z. L. Wang, T. Jing, Lead Zirconate Titanate nanowire textile nanogenerator for wearable energy-harvesting and self-powered devices, ACS Nano 6 (2012) 6231–6235.
- [7] A. Koka, H.A. Sodano, A Low-Frequency energy harvester from ultralong, vertically aligned BaTiO₃ nanowire arrays, Adv. Energy Mater. 4 (2014) 1301660–1301666.
- [8] J. Yan, Y.G. Jeong, High performance flexible piezoelectric nanogenerators based on BaTiO₃ nanofibers in different alignment modes, ACS Appl. Mater. Interfaces 8 (2016) 15700–15709.

- [9] M. R. Joung, H. Xu, I. T. Seo, D. H. Kim, J. Hur, S. Nahm, C. Y. Kang, S. J. Yoon, H. M. Park, Piezoelectric nanogenerators synthesized using KNbO₃ nanowires with various crystal structures, J. Mater. Chem. A 2 (2014) 18547–18553.
- [10] M. K. Gupta, S. W. Kim, B. Kumar, Flexible High-Performance Lead-Free Na_{0.47}K_{0.47}Li _{0.06}
 NbO₃ microcube-structure-based piezoelectric energy harvester, ACS Appl. Mater. Interfaces 8 (2016) 1766–1773.
- [11] D. B. Deutz, N. T. Mascarenhas, J. B. J. Schelen, D. M. de Leeuw, S. van der Zwaag, P. Groen, Flexible piezoelectric touch sensor by alignment of lead-free alkaline niobate microcubes in PDMS, Adv. Funct. Mater. 27 (2017) 1700728–1700735.
- [12] J. M. Wu, C. Xu, Y. Zhang, Y. Yang, Y. Zhou, Z.L. Wang, Flexible and transparent nanogenerators based on a composite of lead-free ZnSnO₃ triangular-belts, Adv. Mater. 24 (2012) 6094–6099.
- [13] Z. Xu, C. Jin, A. Cabe, D. Escobedo, N. Hao, I. Trase, A.B. Closson, L. Dong, Y. Nie, J. Elliott, M.D. Feldman, Z. Chen, J.X.J. Zhang, Flexible energy harvester on a pacemaker lead using multibeam piezoelectric composite thin films, ACS Appl. Mater. Interfaces 12 (2020) 34170–34179.
- [14] J. Yan, M. Liu, Y. G. Jeong, W. Kang, L. Li, Y. Zhao, N. Deng, B. Cheng, G. Yang, Performance enhancements in poly(vinylidene fluoride)-based piezoelectric nanogenerators for efficient energy harvesting, Nano Energy 56 (2019) 662–692.
- [15] C. Ribeiro, C. M. Costa, D. M. Correia, J. Nunes-Pereira, J. Oliveira, P. Martins, R. Gonçalves, V. F. Cardoso, S. Lanceros-Méndez, Electroactive poly(vinylidene fluoride)-based structures for advanced applications, Nat. Protoc. 13 (2018) 681–704.

- [16] L. Persano, C. Dagdeviren, Y. Su, Y. Zhang, S. Girardo, D. Pisignano, Y. Huang, J.A. Rogers, High performance piezoelectric devices based on aligned arrays of nanofibers of poly(vinylidenefluoride-co-trifluoroethylene), Nat. Commun. 4 (2013) 1633–1643.
- [17] A. J. Lovinger, Ferroelectric Polymers, Science 220 (1983) 1115–1121.
- [18] M. Li, H.J. Wondergem, M.-J. Spijkman, K. Asadi, I. Katsouras, P.W.M. Blom, D.M. de Leeuw, Revisiting the δ-phase of poly(vinylidene fluoride) for solution-processed ferroelectric thin films, Nat. Mater. 12 (2013) 433–438.
- [19] W. C. Gan, W. H. A. Majid, T. Furukawa, Ferroelectric polarization, pyroelectric activity and dielectric relaxation in Form IV poly(vinylidene fluoride), Polymer. 82 (2016) 156– 165.
- [20] J. Martín, D. Zhao, T. Lenz, I. Katsouras, D. M. de Leeuw, N. Stingelin, Solid-stateprocessing of δ-PVDF, Mater. Horiz. 4 (2017) 408–414.
- [21] G. T. Davis, J. E. McKinney, M. G. Broadhurst, S. C. Roth, Electric ☐ field □ induced phase changes in poly(vinylidene fluoride), J. Appl. Phys. 49 (1978) 4998–5002.
- [22] R. Hasegawa, Y. Takahashi, Y. Chatani, H. Tadokoro, Crystal Structures of Three Crystalline Forms of Poly(vinylidene fluoride), Polym. J. 3 (1972) 600–610.
- [23] K. Nakamura, Y. Wada, Piezoelectricity, pyroelectricity, and the electrostriction constant of poly(vinylidene fluoride), J. Polym. Sci. Part A-2 Polym. Phys. 9 (1971) 161–173.
- [24] I. V. Aleksandrov, Nuclear magnetic resonance and the structure of matter, Russ. Chem. Rev. 29 (1960) 535–540.
- [25] S. Weinhold, M. H. Litt, J. B. Lando, The Crystal Structure of the γ-Phase of Poly(vinylidene fluoride), Macromolecules 13 (1980) 1178–1183.

- [26] M. Kobayashi, K. Tashiro, H. Tadokoro, Molecular Vibrations of Three Crystal Forms of Poly(vinylidene fluoride), Macromolecules 8 (1975) 158–171.
- [27] M. Bachmann, W.L. Gordon, S. Weinhold, J.B. Lando, The crystal structure of phase IV of poly(vinylidene fluoride), J. Appl. Phys. 51 (1980) 5095–5099.
- [28] S. Maji, P. K. Sarkar, L. Aggarwal, S. K. Ghosh, D. Mandal, G. Sheet, S. Acharya, Selforiented β-crystalline phase in the polyvinylidene fluoride ferroelectric and piezosensitive ultrathin Langmuir–Schaefer film, Phys. Chem. Chem. Phys. 17 (2015) 8159– 8165.
- [29] D. Mandal, K. J. Kim, J. S. Lee, Simple synthesis of palladium nanoparticles, β-phase formation, and the Control of Chain and Dipole Orientations in palladium-doped Poly(vinylidene fluoride) thin films, Langmuir 28 (2012) 10310–10317.
- [30] Q. Li, J. Zhao, B. He, Z. Hu, Solution processable poly(vinylidene fluoride)-based ferroelectric polymers for flexible electronics, APL Mater. 9 (2021) 010902–010912.
- [31] Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Compos. Sci. Technol. 63 (2003) 2223–2253.
- [32] S. Koombhongse, W. Liu, D. H. Reneker, Flat polymer ribbons and other shapes by electrospinning, J. Polym. Sci. B Polym. Phys. 39 (2001) 2598–2606.
- [33] M. Kanik, O. Aktas, H. S. Sen, E. Durgun, M. Bayindir, Spontaneous high piezoelectricity in Poly(vinylidene fluoride) nanoribbons produced by iterative thermal size reduction technique, ACS Nano 8 (2014) 9311–9323.

- [34] N. Hussain, M.-H. Zhang, Q. Zhang, Z. Zhou, X. Xu, M. Murtaza, R. Zhang, H. Wei, G. Ou, D. Wang, K. Wang, J. F. Li, H. Wu, Large piezoelectric strain in sub-10 nanometer two-dimensional polyvinylidene fluoride nanoflakes, ACS Nano 13 (2019) 4496–4506.
- [35] C. Fu, H. Zhu, N. Hoshino, T. Akutagawa, M. Mitsuishi, Interfacial nanostructuring of Poly(vinylidene fluoride) homopolymer with predominant ferroelectric phases, Langmuir 36 (2020) 14083–14091.
- [36] D. Y. Park, D. J. Joe, D. H. Kim, H. Park, J. H. Han, C. K. Jeong, H. Park, J. G. Park, B. Joung, K. J. Lee, Self-powered real-time arterial pulse monitoring using ultrathin epidermal piezoelectric sensors, Adv. Mater. 29 (2017) 1702308–1702317.
- [37] T. S. Dinh Le, J. An, Y. Huang, Q. Vo, J. Boonruangkan, T. Tran, S. W. Kim, G. Sun, Y. J. Kim, Ultrasensitive anti-interference voice recognition by bio-inspired skin-attachable self-cleaning acoustic sensors, ACS Nano 13 (2019) 13293–13303.
- [38] H. Xue, Q. Yang, D. Wang, W. Luo, W. Wang, M. Lin, D. Liang, Q. Luo, A wearable pyroelectric nanogenerator and self-powered breathing sensor, Nano Energy 38 (2017) 147–154.
- [39] Z. Xiao, Q. Dong, P. Sharma, Y. Yuan, B. Mao, W. Tian, A. Gruverman, J. Huang, Synthesis and application of ferroelectric P(VDF-TrFE) nanoparticles in organic photovoltaic devices for high efficiency, Adv. Energy Mater. 3 (2013) 1581–1588.
- [40] M. Dong, M. Hafezi, Z. Tong, L. Qin, Preparation and oil lubrication of polyvinylidene fluoride (PVDF) nanospheres, Mater. Res. Express 6 (2019) 085093–085107.
- [41] T. Furukawa, Ferroelectric properties of vinylidene fluoride copolymers, Phase Transit. 18 (1989) 143–211.

- [42] B. Ince-Gunduz, R. Alpern, D. Amare, J. Crawford, B. Dolan, S. Jones, R. Kobylarz, M. Reveley, P. Cebe, Impact of nanosilicates on Poly(vinylidene fluoride) crystal polymorphism: Part 1. Melt-crystallization at high supercooling, Polymer 51 (2010) 1485–1493.
- [43] K. Tashiro, Y. Itoh, S. Nishimura, M. Kobayashi, Vibrational spectroscopic study on ferroelectric phase transition of vinylidene fluoride-trifluoroethylene copolymers: 2. Temperature dependences of the far-infrared absorption spectra and ultrasonic velocity, Polymer 32 (1991) 1017–1026.
- [44] V. Gupta, A. Babu, S. K. Ghosh, Z. Mallick, H. K. Mishra, D. Saini, D. Mandal, Revisiting δ-PVDF based piezoelectric nanogenerator for self-powered pressure mapping sensor, Appl. Phys. Lett. 119 (2021) 252902–252608.
- [45] P. Martins, A. C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications, Prog. Polym. Sci. 39 (2014) 683– 706.
- [46] Y. Y. Choi, T. G. Yun, N. Qaiser, H. Paik, H. S. Roh, J. Hong, S. Hong, S. M. Han, K. No, Vertically aligned P(VDF-TrFE) core-shell structures on flexible pillar arrays, Sci. Rep. 5 (2015) 10728–10736.
- [47] M. Hoop, X. Z. Chen, A. Ferrari, F. Mushtaq, G. Ghazaryan, T. Tervoort, D. Poulikakos, B. Nelson, S. Pané, Ultrasound-mediated piezoelectric differentiation of neuron-like PC12 cells on PVDF membranes, Sci. Rep. 7 (2017) 4028–4036.
- [48] Y. Zhang, Z. Ma, Y. Zhang, B. Li, M. Feng, Y. Zhao, Q. An, Biofriendly molecular and protein release substrate with integrated piezoelectric motivation and anti-oxidative stress capabilities, Nanoscale 13 (2021) 8481–8489.

- [49] Y. Wang, Y. Xu, S. Dong, P. Wang, W. Chen, Z. Lu, D. Ye, B. Pan, D. Wu, C. D. Vecitis, G. Gao, Ultrasonic activation of inert poly(tetrafluoroethylene) enables piezocatalytic generation of reactive oxygen species, Nat. Commun. 12 (2021) 3508–3516.
- [50] T. Ikeda, Fundamentals of piezoelectricity, Oxford University Press, Oxford; New York; 1996.
- [51] Z. L. Wang, On Maxwell's displacement current for energy and sensors: the origin of nanogenerators, Mater. Today 20 (2017) 74–82.
- [52] S. K. Ghosh, D. Mandal, High-performance bio-piezoelectric nanogenerator made with fish scale, Appl. Phys. Lett. 109 (2016) 103701–103706.
- [53] Y. Zhang, C. R. Bowen, S. Deville, Ice-templated poly(vinylidene fluoride) ferroelectrets, Soft Matter 15 (2019) 825–832.
- [54] S. K. Ghosh, M. Xie, C. R. Bowen, P. R. Davies, D. J. Morgan, D. Mandal, A hybrid strain and thermal energy harvester based on an infra-red sensitive Er3+ modified poly(vinylidene fluoride) ferroelectret structure, Sci. Rep. 7 (2017) 16703–16716.
- [55] Y. Zhang, M. Xie, J. Roscow, Y. Bao, K. Zhou, D. Zhang, C. R. Bowen, Enhanced pyroelectric and piezoelectric properties of PZT with aligned porosity for energy harvesting applications, J. Mater. Chem. A 5 (2017) 6569–6580.
- [56] C. Chang, V. H. Tran, J. Wang, Y. K. Fuh, L. Lin, Direct-Write Piezoelectric Polymeric Nanogenerator with High Energy Conversion Efficiency, Nano Lett. 10 (2010) 726–731.
- [57] G. Zhu, R. Yang, S. Wang, Z. L. Wang, Flexible high-output nanogenerator based on lateral ZnO nanowire array, Nano Lett. 10 (2010) 3151–3155.

- [58] S. K. Ghosh, D. Mandal, Synergistically enhanced piezoelectric output in highly aligned 1D polymer nanofibers integrated all-fiber nanogenerator for wearable nano-tactile sensor, Nano Energy 53 (2018) 245–257.
- [59] H. Ouyang, J. Tian, G. Sun, Y. Zou, Z. Liu, H. Li, L. Zhao, B. Shi, Y. Fan, Y. Fan, Z. L. Wang, Z. Li, Self-powered pulse sensor for antidiastole of cardiovascular disease, Adv. Mater. 29 (2017) 1703456–1703466.
- [60] J. Yang, J. Chen, Y. Su, Q. Jing, Z. Li, F. Yi, X. Wen, Z. Wang, Z. L. Wang, Eardruminspired active sensors for self-powered cardiovascular system characterization and throat-attached anti-interference voice recognition, Adv. Mater. 27 (2015) 1316–1326.
- [61] S. Munir, B. Jiang, A. Guilcher, S. Brett, S. Redwood, M. Marber, P. Chowienczyk, Exercise reduces arterial pressure augmentation through vasodilation of muscular arteries in humans, Am. J. Physiol. Hear. Circ. Physiol. 294 (2008) 1645-1650.
- [62] K. Roy, S. Jana, S. K. Ghosh, B. Mahanty, Z. Mallick, S. Sarkar, C. Sinha, D. Mandal, Three-dimensional MOF-assisted self-polarized ferroelectret: An effective autopowered remote healthcare monitoring approach, Langmuir 36 (2020) 11477–11489.
- [63] F. Ali, W. Raza, X. Li, H. Gul, K. H. Kim, Piezoelectric energy harvesters for biomedical applications, Nano Energy 57 (2019) 879–902.

Chapter 4

All Organic Aqueous Processable $\delta\mbox{-PVDF}$ Nanoparticles for

Piezoelectric Ink and Strain Modulated Photoresponse



4.1 Introduction

Organic piezoelectric materials have emerged as a promising alternative to their inorganic counterparts, owing to their numerous advantages such as low cost, lightweight, and biocompatibility. In particular, organic piezoelectric inks have attracted significant attention due to their ability to convert mechanical energy into electrical energy, making them suitable for various applications such as sensors, energy harvesters, and actuators [1-6]. The development of all organic piezoelectric inks has opened up new avenues for the manufacturing of flexible and stretchable devices, enabling their use in a wide range of fields, including wearable electronics, biomedical sensors, and soft robotics. In this context, all organic functional polymers have drawn crucial attention due to their inherent flexibility, lightweight, surface potential tunability and easy processing for different additive manufacturing techniques (e.g., spray coating, screen printing and inkjet printing, etc.) [7]. Besides, the use of all organic piezoelectric inks towards energy harvesting from mechanical vibration to electrical energy and printable electronics, it also exhibits the excellent properties of optoelectronic devices for the next generation of wearable electronic gadgets. In particular, the piezo-phototronic properties are promising since the induced piezo-potential at the junction can possibly to use to modulate the generation, separation and recombination of charge carriers at the interface of electrode and material [8]. Thus, a novel approach towards piezotronics and piezo-phototronics has emerged by integrating the piezoelectric, semiconducting, and photoresponsive materials altogether [9]. Ongoing research in this field is expected to lead to the development of new and innovative applications which further expand the potential of piezo-phototronics. Over the past few years, there has been extensive research on the piezo-phototronic effect of various inorganic piezoelectric semiconducting materials. These materials include zinc oxide (ZnO), gallium nitride (GaN), zinc stannate (ZnSnO₃), cadmium selenide (CdSe), cesium lead bromide (CsPbBr₃), and twodimensional chalcogenides like molybdenum disulfide (MoS_2), tin selenide (SnSe), and indium selenide (InSe) [10-17]. Despite their potential, these materials have several limitations due to their challenging synthesis process, steep cost, brittleness, difficulties in large-area device fabrication, and limited scalability. In this concern, organic electroactive polymers, such as polylactide, odd nylons, poly(lactic-co-glycolic acid) (PLGA), poly(vinylidene fluoride) (PVDF) and its co-polymers are attracting for smart active materials [18]. Among them, PVDF and its copolymers are regarded as a suitable alternative because of their outstanding piezo-, pyro-, and ferro-electric properties attributing from electroactive phase(s) as discussed earlier in chapter 3 [19,20]. In the continuation of previous work based on δ -PVDF NPs, we noticed that piezoelectric large area device fabrication is challenging due to its nanoparticles-based geometry. Moreover, the spherical shape of nanoparticles is very important for the giant piezoelectricity, therefore, to retain the original shape is also utmost challenging. Since the surface of PVDF shows a strong hydrophobic nature, so, aqueous processable PVDF nanoparticles (NPs) based device fabrications are rarely reported. As a result, it becomes a glaring disadvantage for printable electronic devices. Therefore, the necessity to make aqueous dispersible PVDF NPs is of utmost importance for all organic-based device fabrication perspective. Thus, we have taken serious efforts to functionalize the surface of nanoparticles that turn from hydrophobic to hydrophilic. It might be one of the suitable alternatives to make an aqueous dispersible in order to use for diverse areas such as biomedical sectors (e.g., tissue engineering, drug delivery systems), sensors/actuators and printable electronic devices [21-23]. For instance, we have employed polydopamine and polyethylenimine i.e., PDA-PEI to coat the surface of PVDF NPs, which ensures the well aqueous dispersion. Noteworthy to mention that the polydopamine (PDA) emerged as a promising material due to its universal adhesiveness, easy functionalization, simple

preparation route, biocompatibility, and free radical scavenging properties. Dopamine, a molecule with both abundant catechol and amino groups can self-polymerize to form a conformal coating on the surface of PVDF NPs in ambient conditions [24-27]. In this chapter, we have fabricated PVDF NPs with an electroactive δ-phase, via a simple solution processing technique where the requirement of electric field is absolutely not required. Then these NPs surface is coated via in-situ copolymerization with PDA-PEI to make it highly dispersive in aqueous medium. It enables the formulation of piezoelectric ink that can be used to fabricate flexible piezoelectric nanogenerators (FPNG) for various applications such as voice recognition system, mechanical energy harvesting, and photodetection. Furthermore, we have demonstrated the piezo-phototronic effect of PDA-PEI coated PVDF NPs under external mechanical stimuli and light exposure. The obtained spectral parameters of the resulting photodetector, including responsivity, specific detectivity, and fast response, suggest that aqueously processable PVDF NPs could be used as a piezoelectric ink and have the potential to be utilized in the development of flexible and wearable organic electronic devices in the futuristic applications.

4.2 Experimental section

4.2.1 Preparation of PVDF nanoparticles

PVDF pellets ($M_w \sim 1,80,000$ GPC), dopamine hydrochloride (DA) and polyethylenimine (PEI, Mn ~ = 600 g/mol) were purchased from Sigma-Aldrich, USA and analytical grade N, Ndimehtylformamide (DMF) was purchased from Merck, India. They are used without any further purification. Then, PVDF pellets were dissolved in DMF at very low concentration of 1 wt (w/v) % under the magnetic stirring at 60°C and 500 rpm overnight until the transparent solution is obtained. Then PVDF/DMF solution was loaded into a disposal syringe (10 ml of volume). The syringe pump was used to control flow rate of PVDF solution so that it passes into a beaker containing de-ionized water dropwise, which is kept under a continuous magnetic stirring at 1000 rpm as shown in Figure 4.1. Thereafter, the solution was centrifugated at 2000 rpm and washed with ethanol and de-ionized water then the obtained nanoparticles were dried in a vacuum oven at 60°C for 5 h.

4.2.2 Formulation of piezoelectric Ink

Firstly, dopamine-HCl (5 mg/ml) and PEI (0.25 wt. %, 125 mg) were dispersed in 50 ml of deionized water and stirred for 16 h at room temperature. The colour of the solution was changed from colourless to dark brown indicating the formation of PDA-PEI. Then PVDF NPs (5 mg) were dispersed into 25 ml of PDA-PEI solution followed by probe sonication (power ~100 W) for 45 min to prepare PDA-PEI@PVDF NPs. The mass ratio of PDA:PEI:PVDF is used 1:0.5:1.15 in the final composite system. For the sake of simplicity, only PDA-PEI is designated as a control sample and functionalized PVDF NPs with PDA-PEI as a PVDF@f Ink which is further used as a piezoelectric ink.

4.2.3 Fabrication of flexible piezoelectric nanogenerator (FPNG)

The FPNG was prepared by using piezoelectric ink i.e., PVDF@f Ink. Firstly, aluminium (Al) interdigital electrode (IDE) with 5 mm of channel width and 500 μ m of channel separation over $3 \times 2 \ cm^2$ area is prepared on poly (ethylene terephthalate) (PET) substrate by shadow mask assisted electron beam deposition technique. Then piezoelectric ink solution containing film is prepared on the IDE electrode consisting of PET substrate and then vacuum dried at 50°C for 2 h. External electrical connection were established by taking two copper wires from each corner of IDE. Then it was used further for optical properties measurements. Thereafter, to avoid direct contact with PVDF@f Ink surface and to make it robust, FPNG was encapsulated with thin PDMS coating (layer thickness ~260 μ m) (Sylgard 184, 10:1 ratio of silicon elastomer and

curing agent is used). Further, the FPNG was corona poled with 30 kV of needle voltage, 7 kV of grid plate voltage for the uniform field distribution and 60 °C temperature of sample mounting stage for 30 min. It should be noted that FPNG is fabricated with PDA-PEI coated PVDF NPs based piezoelectric ink while for control FPNG there are no PVDF NPs. Thereafter, it was used for the electrical signal collection when a continuous mechanical pressure was applied to the as-fabricated FPNG by the linear actuator motor. Similar corona poling conditions were applied for PVDF NPs coating with PDA-PEI (named as PVDF@f (P) and for unpoled case designated as PVDF@f (UP)) to perform the Kelvin probe microscopy (KPFM) and Ultraviolet photoelectron spectroscopy (UPS) study.

4.3 Results and discussion

4.3.1 Surface morphology

The δ -phase comprising PVDF nanoparticles is prepared using a phase separation method, as illustrated in Figure 4.1. It involves the use of a solvent (DMF) and a non-solvent (water) to induce phase separation at the interface to form of the nanoparticles shape of PVDF [28]. The self-folding process of the PVDF macromolecular chain leads to the formation of nanoparticles at the interface of the ternary system of PVDF-DMF-water, due to the hydrophobic interaction between -CF₂- dipoles and water molecules [29]. It's worth noting that external agitation, such as magnetic stirring, was applied during the nanoparticle formation to ensure the monodispersion of the PVDF NPs. At a low concentration of PVDF-DMF (1 wt%), monodisperse spherical PVDF nanoparticles with an average size between 180 to 245 nm were successfully synthesized. However, as the concentration was increased the nanoparticles became inhomogeneous due to particle coagulation, as evident from FE-SEM imaging (Figure 4.2).



Figure 4.1 Schematic demonstration of fabrication method of δ -PVDF nanoparticles via phase separation technique at ternary phase system i.e., PVDF-DMF-water.



Figure 4.2 The surface morphology of PVDF nanoparticles when different w/v % of PVDF/DMF are considered, in particular FE-SEM images of (a) 1 w/v %, (b) 2 w/v % and (c) 4 w/v % of PVDF/DMF cases.

Further, transmission electron microscopy (TEM) image confirms the surface coating (Figure 4.3a-d) i.e., PDA-PEI coating on the δ -PVDF nanoparticles, which can be observed at the periphery of the nanoparticles as marked with dotted lines. The size of nanoparticles after the coating is found to be ~245 nm (Figure 4.3c and 4.3d).


Figure 4.3 TEM image of PVDF NPs coated with PDA-PEI, i.e., PVDF@f Ink at (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min of reaction time and the symbol (#) represent the unmarked nanoparticles surface to visualize the coating layer (e) The plot illustrates the variation of PDA-PEI coating (layer thickness) with reaction time.

In addition to that we have also optimized the optimal surface coating with the reaction time (as illustrated in Figure 4.3a-d). In order to investigate the optimal coating of PDA-PEI layer on PVDF NPs surface, we have recorded the TEM images with different reaction time. It is observed that the thickness of the layer increases as the reaction time increases i.e., 15 min, 30 min, 45 min, and 60 min as shown in Figure 4.3a-d, respectively. After 15 min of reaction time, the PVDF NPs are not uniformly coated, and some of the places less than \sim 10 nm of layer

thickness were noticed. While a further increase in reaction time, layer thickness gradually increases and after an optimal coating there is no significant effect on reaction time is evident (as shown in Figure 4.3e). So, we found the optimal time for uniform coating of PVDF NPs is 45 min.

4.3.2 Crystallographic phase analysis

The electroactive δ -phase has been confirmed from powder X-ray diffraction pattern (PXRD). It is observed from Figure 4.4a, diffraction peaks are found at 20 value of 18.5° (020), 20.1° (110), 26.7° (021) and 27.9° (111) attributed to δ -phase of PVDF [30,31]. The selected area electron diffraction (SAED) pattern (Figure 4.4b) confirms the electroactive δ -phase as evidenced from three planes i.e., (110), (111) and (041) with d-values 0.43, 0.32 nm and 0.21 nm, respectively, which is consistent with XRD pattern (Figure 4.4a) as well. Among them (041) plane could not be observed in XRD pattern because of very low intensity at a high 20 value with respect to the main diffraction peak from (110) plane [30]. Noteworthy to mention that, the formation of an electroactive δ -phase in PVDF is responsible for the interfacial crystallization and hydrogenbonding interaction. It is attributing the interaction between -CH₂-/-CF₂- dipoles of PVDF and C=O moieties of DMF [32,33]. Therefore, PVDF-solvent interaction is leading to the rotation of C-F bonds around the main carbon backbone (i.e., C-C chain) so that the electroactive δ - phase is induced during the crystallization process [34]. Further, the crystallite size (~8 nm) of δ -PVDF NPs has been estimated from Debye-Scherrer equation similar to the previous chapter 3 and section 3.3.2.



Figure 4.4 (a) PXRD pattern (b) SAED pattern of as fabricated δ -PVDF nanoparticles.

4.3.3 Mechanism of surface coating of PVDF NPs

The super hydrophobic nature of the PVDF surface makes it challenging to use PVDF as an active component in devices, especially for fabricating all organic flexible devices that require organic electrodes to be placed on the surface of PVDF [35]. To overcome this issue, as synthesized δ -PVDF nanoparticles surface were modified with a PDA-PEI copolymer in an aqueous medium, resulting in PVDF@f Ink. The PDA-PEI contains abundant polar functional groups (-NH-, -OH, and >C=O) that make it highly dispersible in water, mainly through hydrogen bonding interactions with water molecules, and have a high possibility of exhibiting strong electrostatic interaction with the PVDF functionalities [36]. It is assumed that the polar functionalities of PDA-PEI, which are mainly composed of electron-donating groups, will interact with the electropositive hydrogen of PVDF. The structure of the PDA-PEI coated PVDF nanoparticles along with the plausible molecular interaction is schematically represented in Figure 4.5. The coating of polar functional groups on the PVDF nanoparticles by PDA-PEI made

them hydrophilic and thus well-dispersed in water. Because of the coating was accompanied with polar functional groups, the coated NPs became hydrophilic and thus well dispersed in the water.



Figure 4.5 Schematic demonstration for surface coating of δ -PVDF with PDA-PEI.

Further, water contact angle (WCA) measurement was used to examine the hydrophilicity of the PVDF@f Ink-coated thin film. It can be observed that the WCA on the surface of the PVDF@f Ink coverage thin film is approximately 15° (Figure 4.6a), indicating a strong hydrophilic nature compared to the bare PVDF film with a WCA > 90° (as shown in Figure 4.6b). To demonstrate the printability and good adhesion behavior of the as-prepared piezoelectric ink on different substrates, we have written the word "INST" on various substrates such as glass, PET sheet, and glossy paper, and the corresponding digital images are shown in Figure 4.6 (i), (ii), and (iii), respectively. This indicates that the PVDF@f Ink exhibits good adhesion to different types of substrates, which is a prerequisite for printable device fabrications.



Figure 4.6 Digital image of water contact angle (WCA) measurement of a deionized water droplet on (a) PVDF@f Ink layer, (b) bare PVDF NPs (c) Digital photographs of word "INST" written by using piezoelectric ink on different substrates (i) Glass, (ii) PET sheet and (iii) Glossy paper.

Further, we have also examined the dispersibility of PDA-PEI coated δ -PVDF NPs in aqueous medium. It is found that the Zeta (ζ) potential distribution is stable till 30 days (Figure 4.7) that promises the long term dispersibility which is utmost important parameter for the polymer ink that is suitable for device fabrication. Thus, it can be concluded that PVDF@f Ink can be regarded as a superior aqueous based piezoelectric ink due to strong hydrophilic nature.



Figure 4.7 Zeta (ζ) potential distribution with respect to time (days).

4.3.4 Rheological properties of piezoelectric ink

Furthermore, we have also investigated the rheological characteristics of this piezoelectric ink. The observations indicate that the control sample, namely the PDA-PEI solution, displays a linear relationship between shear stress (as shown in Figure 4.8a) and viscosity (as shown in Figure 4.8b) with the applied shear rates, which corresponds to the behavior of Newtonian fluids. Conversely, when shear rates are applied to PVDF@f Ink, a non-linear relationship is noticed in the shear stress (Figure 4.8a). Additionally, the viscosity varies with the shear rate and displays two distinct regimes, one following the Power-law model ($\tau = k\dot{\gamma}^n$) in the higher shear rate region (marked in purple), and the other following the Herschel-Bulkley (HB) model ($\tau = \tau_0 + k\dot{\gamma}^n$) in the lower shear rate region (highlighted in blue in Figure 4.8b). Therefore, the rheological parameters, i.e., viscosity and shear stress of PVDF@f Ink exhibit the typical behavior of ink types, as described in references [7,37].



Figure 4.8 Rheological properties of piezoelectric ink (PVDF@f Ink) and control solution (PDA:PEI) (a) shear stress and (b) viscosity vs strain.

4.3.5 Surface characterization

X-ray photoelectron spectroscopy (XPS) was conducted to verify the chemical state of functionalized PVDF NPs with PDA-PEI. The high-resolution C 1s spectra (Figure 4.9a) of PVDF@f Ink was analyzed and deconvoluted into five peaks centered at 284.8 eV, 285.7 eV, and 287.9 eV, which were attributed to C-NH₂, C-O/C-N, and C=O species, respectively. This suggests that PVDF NPs were effectively functionalized with PDA-PEI, as evidenced by the TEM image. The C 1s spectra of -CH₂- and -CF₂- moieties of PVDF NPs also displayed two more peaks at 285.5 and 290.5 eV (Figure 4.9a). The O 1s spectra showed two distinguishable peaks at 531.2 eV and 533.4 eV, which were consisting of C=O and C-O chemical species of PDA as shown in Figure 4.9a. In addition, N 1s spectra (Figure 4.9c) confirmed the amine functional groups, including primary R-NH₂ at 402 eV, secondary R-NH-R at 400.2 eV, and

tertiary =NR at 398.5 eV, thereby demonstrating the presence of PEI and PDA [38,39]. The F 1s signal (Figure 4.9d), on the other hand, was attributing to the PVDF NPs core of PVDF@f ink.



Figure 4.9 The high-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) N 1s and (d) F 1s for functionalized PVDF nanoparticles with PDA-PEI i.e., PVDF@f Ink.

4.3.6 Piezo- and ferro- electric properties of piezoelectric ink

To verify the piezo- and ferro-electric properties of functionalized PVDF@f Ink, atomic force microscopy (AFM) with piezo-response force microscopy (PFM) is used for further characterization. The AFM topography of the control (PDA-PEI) displayed the presence of uniform distribution of particle-like structures with an average diameter of ~ 70 nm (Figure 4.10a). Some larger particles were also observed, which were attributed to the aggregation of a few nanoparticles, as seen in the FE-SEM image (Figure 4.2). The topography of the PVDF@f Ink layer surface (Figure 4.10b), where nanoparticles with an average diameter of 180 to 245 nm were also uniformly distributed, with some coagulated particles marked with circular and elliptical rings. The larger particle size suggests that the surface of PVDF NPs were effectively coated with PDA-PEI, indicating good functionalization. The measurement setup and experimental conditions for PFM testing are similar to the previous work (Chapter 3, section 3.2.2 and 3.3.3 respectively). Therefore, the complete ferroelectric (phase) hysteresis loop is observed from PVDF@f Ink layer with ~180° of phase reversal due to the orientation of dipoles under the application of DC bias voltage (Figure 4.10c). Similarly, the amplitude hysteresis loop (Figure 4.10d) of PVDF@f Ink layer is evident for piezoelectricity. The hysteresis loop observed in the phase and amplitude response of the PVDF@f Ink layer demonstrates the ferroelectric and piezoelectric properties even at extremely low DC bias voltages of \pm 7 V. This is significant because it indicates that PVDF nanoparticles with the δ -phase in the piezoelectric ink have the potential to be utilized in various applications where large area devices can be printed, such as pressure sensors, mechanical and thermal energy harvesters, nonvolatile memory, and actuators.



Figure 4.10 AFM topography of (a) Control (PDA-PEI), (b) δ -PVDF nanoparticles functionalized sample with PDA-PEI i.e., PVDF@f Ink and the marked region shows the presence of δ -PVDF nanoparticles into the PDA:PEI matrix. Piezoresponse force microscopy (PFM) response of piezoelectric ink (PVDF@f Ink) (c) Phase hysteresis loop and (d) Amplitude response upon the application of DC bias voltage of \pm 7 V.

In addition to that, we have performed the Kelvin probe force microscopy (KPFM) on surface of piezoelectric ink coating layer to further confirm the change in surface potential before and after corona poling, since it has direct relevance with piezoelectric properties. The surface potential distribution of both samples before (Figure 4.11a, b) and after (Figure 4.11c, d) electrical poling is examined by KPFM imaging. It is worth noting that both samples exhibit a negative surface potential (Sp), but PVDF@f Ink shows a relatively higher Sp (~ -0.2 V) than the control sample (Sp ~ -0.1 V) when unpoled. In contrast, a significant change in Sp is observed in PVDF@f Ink $(Sp \sim -2.6 \text{ V})$ after corona poling, while the control sample shows no notable changes $(Sp \sim -0.12)$ V). This clearly indicates that the ferroelectric dipoles of PVDF are aligned in PVDF@f Ink through the application of an electric field in the corona poling process. Further, the work function (Φ) of PVDF@f Ink and the control sample can be determined using the formula Φ_{Sample} $= \Phi_{tip} - eV$, where Φ_{Sample} and Φ_{tip} are the work function of the sample and conducting tip (Pt/Ir), respectively. The work function in the unpoled case for the control and PVDF@f Ink layer was estimated to be 5.05 and 4.94 eV, respectively. It is observed that there is a significant change in work function in PVDF@f Ink layer (2.17 eV) after electrical poling, but no noticeable change is observed in the control sample (5.03 eV). Therefore, the change in work function indicates that the Fermi level (E_F) is shifting towards the LUMO level, which corresponds to the increase in Sp. as shown in the energy band diagram (Figure 4.11e-h), and is responsible for the ferroelectric-induced polarization [40,41].



Figure 4.11 Kelvin probe force microscopy (KPFM) response of both control and piezoelectric ink i.e., PVDF@f Ink samples, firstly the surface topography of (a, c) control sample before and after poling respectively, (b, d) piezoelectric ink before and after poling. Schematic representation of electronic energy band diagram based on the work function measured by KPFM and corresponding shift in Fermi level (E_F) of control (e and g) and PVDF@f Ink (f and h) in unpoled and poled cases, respectively.

Besides, KPFM we have also performed the ultraviolet photoelectron spectroscopy (UPS) to clarify the real shifting of Fermi level (E_F) as demonstrated in Figure 4.12a and 4.12b, respectively. Since work function (Φ) and electron affinity (χ) are important parameters that define the optoelectronic properties and device performance at the metal-semiconductor interface [42]. Therefore, we analyzed the UPS data (Figure 4.12a) and found that the secondary electron (SE) edge significantly shifts in the PVDF@f ink sample after poling, whereas SE shift is

marginal in control sample. It is indicating a large number of dipoles are aligned in the direction of the applied electric field [43]. The work function is estimated from UPS data as $\Phi = hv - E_{cut off}$, where, hv is the photon energy of He-I source (hv = 21.22 eV) and $E_{cut off}$ is the SE cut off points [42]. Then, work function is evaluated to be 4.94 and 4.71 eV for control (UP) and control (P), respectively and for the PVDF@f Ink (P) and PVDF@f Ink (UP) is 4.42 and 2.52 eV, respectively.

The work function estimated from UPS and KPFM showed good agreement (Figure 4.12b) and confirmed the band alignment. We also analyzed the valence band region to estimate the valence band maximum (VBM) position and found a clear shifting of Fermi level (E_F) and change in electron affinity (χ) [44]. It is obtained by extrapolating the UPS data near the Fermi edge (E_F) as shown in Figure 4.12a. The VBM positions are found to be 0.42 and 1.15 eV for the PVDF@f Ink (UP) and PVDF@f Ink (P), respectively. The energy band diagram (as shown in Figure 5k) shows the clear shifting of Fermi level (E_F) and also the change in electron affinity (χ) from 2.71 to 1.17 eV. The energy band diagram demonstrated the mechanism of Schottky barrier height (SBH) and charge transport mechanism. The optical energy band gap was estimated from UV-visible absorbance spectra and Tauc's plot (as shown in Figure 4.13a and 4.13b). Therefore, the work function and electron affinity play a crucial role in defining optoelectronic properties and device performance, and their analysis provides a deeper understanding of the underlying mechanisms.



Figure 4.12 Ultraviolet photoelectron spectroscopy (UPS) is performed to measure the (a) work function under poled (P) and unpoled (UP) conditions, (b) comparison plot of work function obtained from both KPFM and UPS study and (c) energy band diagram and shifting of Fermi level (E_F) based on UPS results under poled and unpoled conditions.



Figure 4.13 (a) UV-visible absorbance spectra under poled (P) and unpoled (UP) condition and (b) Tauc's plot for band gap (Eg) of PVDF@f Ink.

4.3.7 Piezoelectric performance of ink-based FPNG

The FPNG is fabricated as mentioned in the experimental section and the schematically demonstrated in Figure 4.14a. To investigate the energy harvesting performance, a compressive stress is applied to the FPNG that convert the mechanical force into electricity due to the presence of δ -PVDF NPs in piezoelectric ink. The amplitude of pressure is gradually increased from ~3 to 11 kPa, and the resulting electrical output response is measured in terms of open circuit voltage (V_{OC}) and short circuit current (I_{SC}). The maximum (peak to peak) electrical output response of 6 V V_{OC} and 2 μ A I_{SC} is recorded when the FPNG is subjected to 11 kPa of pressure at a frequency of 5 Hz (Figure 4.14b and 4.14c). During the piezoelectric performance testing we have taken suitable precautions to avoid triboelectric artifacts such as the imparting linear probe was being isolated from any living origin or any other objects [45,46].



Figure 4.14 (a) Schematic demonstration of (i) FPNG preparation (ii) encapsulation with PDMS, (b) open circuit voltage (V_{OC}) and (c) short circuit current (I_{SC}) on continuous mechanical impart with different amplitude of pressure (3, 6 and 11 kPa).

On the other hand, FPNG is also prepared with pristine PDA-PEI, i.e., without PVDF NPs. In this context, the V_{OC} and I_{SC} is found to be 800 mV and 600 nA, respectively (as shown in Figure 4.15a and 4.15b) under the similar input conditions e.g., imparted by pressure amplitude of 11 kPa and 5 Hz frequency. This output is anticipated as a result of the corona poling-induced trap charges or ionized air molecules existing on the surface of FPNG.



Figure 4.15 Electrical output response of as prepared control FPNG (i.e., only PDA-PEI) (a) open circuit voltage (V_{OC}) and (b) short circuit current (I_{SC}) under the application of 5 Hz frequency and imparting pressure amplitude, *e.g.*, 3, 6 and 11 kPa, respectively.

Furthermore, it has been observed that after 90 days, the piezoelectric performance i.e., V_{OC} (Figure 4.16a) and I_{SC} (Figure 4.16b) signals from control f-PNG has disappeared (~ 90 % reduction is noted). It assures that the permanent polarized charges are not present in control FPNG, however, noticeable changes of V_{OC} (Figure 4.17a) and I_{SC} (Figure 4.17b) signals (due to the presence of permanent polarized charges) are not observed from PVDF@f Ink-based FPNG. Thus, the electrical output response obtained from FPNG with piezoelectric ink has shown very high output voltage and current response than control FPNG. It clearly indicates that the piezoelectric ink exhibits superior mechanical energy harvesting properties.



Figure 4.16 The piezoelectric output performance of control FPNG (i.e., only PDA-PEI) as (a) open circuit voltage (V_{OC}) and (b) short circuit current (I_{SC}) when the measurement is performed on day 0 and day 90.



Figure 4.17 The piezoelectric performance of as-fabricated f-PNG with PVDF@f Ink as (a) open circuit voltage (V_{OC}) and (b) short circuit current (I_{SC}) when the measurement is performed on day 0 and day 90.

Additionally, we have also investigated the behavior of FPNG under different external load resistance (R) values ranging from 10^5 to $10^8 \Omega$ with continuous pressure of 11 kPa. The results show that the output voltage of FPNG increases with increasing load resistance and get saturated at a high resistance of 5 M Ω , indicating impedance matching between the external load resistance and the internal load resistance of FPNG, due to the typical nature of piezoelectric nanogenerator (Figure 4.18a). Furthermore, the performance of electrical output power density $(0.5 \text{ }\mu\text{W/cm}^2)$ of FPNG with the variation of external load resistance has been also examined as represented in Figure 4.18a. To showcase the practical application of our FPNG, we performed capacitor charging under continuous mechanical force using three different capacitors (1 µF, 4.7 μ F, and 10 μ F), and the corresponding transient charging response is shown in Figure 4.18b. The results demonstrate that the FPNG can charge the capacitor within a short time of 50 seconds and then reached to steady state. Furthermore, we have also evaluated the stability and repeatability of our FPNG by subjecting it to short circuit current over 24,000 cycles on day 0 and day 60 (as shown in Figure 4.18c and Figure 4.18d, respectively) under continuous mechanical pressure (11 kPa) using a linear actuator with a frequency of 30 Hz. The results indicate that the current amplitude remains stable without any significant degradation or deviation. This mechanical fatigue test demonstrates that the FPNG is capable of operating for long periods under mechanical stress.



Figure 4.18 Performance of FPNG with variable external load resistance (a) V_{OC} and power density, (b) capacitor charging with three different capacitors (1, 4.7 and 10) μ F. The stability and repeatability of FPNG is examined by short circuit current (I_{SC}) over 24000 cycles in (c) day 0 and (d) day 60.

4.3.8 Cyclic bending and releasing piezoelectric response

In order to demonstrate the piezoelectric response of FPNG, cyclic bending and releasing strain was applied. Then electrical output voltage (Figure 4.19) is recorded under three different bending radii (r_1 , r_2 and $r_3 = 12$, 19 and 28 mm, respectively). In this scenario, the tensile strain is developed along the thickness direction (parallel to the dipole orientation of FPNG i.e., ε_y) during bending of the FPNG into arc shape and it is defined as $\varepsilon_y = \frac{L}{2r} = 0.92$ %, where L and r is the thickness (260 µm) and bending radius (28 mm), respectively. Similarly, the strain developed in the length direction i.e., perpendicular to the dipole orientation, i.e., $\varepsilon_x = 0.40$ % by using the Poisson's ratio $v = \left|\frac{\varepsilon_y}{\varepsilon_x}\right| = 0.44$ of PVDF [47,48]. Therefore, the piezoelectric output voltage is found to be increased as the bending radii is increasing and the maximum output voltage (130 mV) is recorded at $r_3 = 28$ mm of bending radius.



Figure 4.19 Cyclic bending and unbending response of FPNG with three different arc radii (r₁, r₂ and r₃).

In addition, to monitor the sensitivity, FPNG is attached to the throat of human skin by using an adhesive tape. It is observed that, FPNG can able to recognize distinct alphabetical characters. For instances, when different alphabet, e.g., "N", "A", "N" and "O" and "H", "E", "L", "L", and "O" are pronounced and corresponding output response are recorded (Figure 4.20a). It indicates the response from each alphabet is different from another since it involves different acoustic frequency modulation while speaking. Thus, FPNG can able to sense the different pressure change due to vocal cord vibration under different acoustic frequency involve during pronunciations. Furthermore, the short time Fourier transform (STFT) processed 2D spectrogram is shown in Figure 4.20b and 4.20c that clearly reveals the distribution of frequency for each distinct alphabet. These results clearly indicate its wide applications in voice recognition, low frequency vibration and acoustic energy harvesting.



Figure 4.20 The human physiological signal (acoustic sensitivity of FPNG) recorded during pronunciation of alphabet (a) "N-A-N-O" and "H-E-L-L-O" independently and (b, c) corresponding STFT processed 2D spectrogram (i, ii).

4.3.9 Photodetection properties and strain modulation of piezoelectric ink

In order to explore the photodetection capabilities of PVDF@f Ink, we used light with a wavelength of 405 nm (shown in Figure 4.21a) as it has a broad range of UV-absorbance (as depicted in Figure 4.13a) with variable power intensities of 0.64 mW/cm² and 1.30 mW/cm². When the light was periodically turned on and off, the photodetector (PD) displayed an enhanced photocurrent response under unbiased conditions, with the magnitude of the photocurrent response increasing as the intensity of the light increased 0.64 mW/cm² and 1.30 mW/cm², respectively (as shown in Figure 4.21b). Noteworthy to mention that increase in photocurrent (I_P) suggests that the generation of the large number of charge carriers with increment of light intensity [49]. Further, as a quantified detection sensitivity of photodetector (PD) \sim 1380 % is recorded which is defined as the ratio of photo to dark current (I_d) , i.e., $S = \Delta I / I_d \times 100\%$, where, $\Delta I = I_p - I_d$. The fast response, i.e., 0.43 s rise and decay time is noticed (Figure 4.21c) which is significant since it is realized without any external bias. This fast photoresponse and the switching dynamics of PD could be an ideal choice for piezo-photodetectors. Under the equilibrium condition, the flow of majority of charge carriers are restricted due to the formation of a larger Schottky barrier height (SBH) between the aluminum electrode and PVDF@f interface (Figure 4.21d). Therefore, the Fermi level of metal electrode align with the Fermi level of PVDF@f when no light is illuminated and thus low current is observed. On the other hand, when light is illuminated the significant increase in photocurrent is observed due to the generation of electron-hole $(e^{-} - h^{+})$ pairs and their separation followed by the collection by two electrodes. The large accumulation of electrons at the interface reduces the SBH (Figure 4.21e) and thus, the Fermi level of PVDF@f reduces that leads to the increase in photocurrent as shown in Figure 4.21b. It also demonstrated that photocurrent increases with increasing light intensity,





Figure 4.21 Schematic demonstration of as prepared photodetector (PD), (b) switching response of photocurrent vs time under periodically turn on and off cycles at different light illumination intensities (c) rise and decay time of single cycle of photoresponse. Energy band diagram representing the working mechanism of photodetector (d) at equilibrium under dark and (e) under light illumination.

Further, the responsivity (R) and detectivity (D) of PD are examined as [50]

$$R = \frac{I_P}{P^* \times A} \tag{4.1}$$

where, I_P is photocurrent and P^* and A represents the light intensity and effective area of PD. The evaluated R is 24 μ A/W at 0.64 mW/cm² of intensity. Additionally, the specific detectivity of PD which is the ability that can detect very lowest possible signals and it is expressed as

$$D^* = \frac{R\sqrt{A}}{\sqrt{2qI_d}} \tag{4.2}$$

where, *R* and *A* are responsivity and Area of PD, *q* and I_d are the elementary charge and dark current respectively. The value of *D** for the as fabricated PD is evaluated ~ 1.4×10^{10} Jones. Thus, these spectral parameters and photoresponse of PD attributed to the strong optical absorption due to the semiconducting nature of PDA-PEI which is covered to PVDF NPs.

In addition to that we have also investigated the piezo-phototronic effect i.e., coupled effect of piezoelectric polarization, semiconductor material and their charge transport mechanism under the light illumination as well as external mechanical stimuli. To quantitatively analyze the performance of the PVDF@f ink photodetector, current-voltage (I-V) characteristics were measured by sweeping the bias voltage from -10 V to +10 V under different conditions such as no strain, compressive strain (accomplished by simple finger pressing from the top side), and tensile strain (by bending the device into a curved shape) under a constant light illumination of 0.64 mW/cm² (shown schematically in the inset of Figure 4.22a and 4.23a and 4.23c, respectively). The I-V characteristics were obtained under both dark and light illumination conditions (Figure 4.22a), and a non-linear I-V curve indicates the formation of a Schottky barrier at the interface of the metal contact and PVDF@f Ink. It was observed that the photocurrent decreased when the device was illuminated with light (Figure 4.22a). This can be attributed to the generation of a large number of excitons (e⁻ - h⁺) upon light illumination, which

subsequently recombine and reduce the current, as shown in the corresponding energy band diagram in Figure 4.22b.



Figure 4.22 Current-voltage (I-V) characteristics of PD under (a) without strain, with dark and light illumination and (b) corresponding schematic of energy band diagram.

When a compressive strain (CS) was applied under the same light illumination and sweeping voltage, an increase in photocurrent was observed in the I-V characteristics (Figure 4.23a) due to the generation of a piezo-potential and subsequent decrease in the SBH at the interface (as illustrated in Figure 4.23b). It results in an enhanced photocurrent under compressive force. However, when a tensile strain was applied in the positive direction (i.e., $\Delta \varepsilon > 0$) to PD, a decrease in current was observed (Figure 4.23c) compared to the compressive strain due to the faster recombination rate of excitons and the generated positive piezo-potential at the interface. As a result, the SBH increased, which restricted charge carrier transportation (as mentioned in the energy band diagram Figure 4.23d). Therefore, the maximum excitons were trapped at the interface of the metal and PVDF@f Ink layer, leading to a decrease in current as the tensile strain

increased ($\Delta\epsilon$ from 0 to 3.1%). Hence, it can be concluded that the fabricated PD exhibits a negative piezo- phototronic effect when illuminated with light due to the faster recombination rate.



Figure 4.23 Current-voltage (I-V) characteristics of PD under (a) under compressive force, (c) tensile strain upon illumination of 0.64 mW/cm² light and corresponding insets shows the schematic illustration of PD under external mechanical stimuli. The corresponding energy band diagram represents the charge carrier transportation upon (c) compressive strain, (d) tensile strain ($\Delta \varepsilon > 0$) at constant illumination intensity of 0.64 mW/cm².

4.4 Conclusions

In summary, we have synthesized PVDF NPs with electroactive δ -phase via phase separation technique due to the interfacial crystallization at the ternary phase system i.e., PVDF-DMF-water in ambient condition. Further, these δ -PVDF NPs were functionalized with PDA-PEI to make it as an aqueous dispersible which facilitates the piezoelectric ink properties. Besides it, the surface coating of PVDF NPs is responsible for the change in surface charge (which is accountable for piezoelectricity) and corresponding work function as attributed from KPFM and UPS measurements, respectively. Thus, the functionalized NPs (i.e., PVDF@f Ink) are displaying excellent piezo and ferro- electric properties. Furthermore, FPNG is prepared with piezoelectric ink to demonstrate the device fabrication possibilities, and thereafter mechanical energy harvesting properties are recorded. It promises the capability to generate a V_{OC} of 6 V and short circuit current (I_{SC}) 2 µA. The FPNG is also found as an acoustic sensor due to its excellent voice signals distinguishable abilities. Moreover, as fabricated self-powered PD comprising of PVDF@f ink possesses remarkable optical properties and piezo-phototronic effect, upon the illumination of light and mechanical stimuli. Thus, δ -PVDF NPs can be used as a several potential applications such as piezoelectric ink for various electronic device fabrications, mechanical energy harvesting, biomedical signals recording, speech signal recognition system, and piezo-phototronic effect.

4.5 References

- K. Dong, X. Peng, Z.L. Wang, Fiber/Fabric-Based Piezoelectric and Triboelectric Nanogenerators for Flexible/Stretchable and Wearable Electronics and Artificial Intelligence, Adv. Mater. 32 (2020) 1902549.
- [2] L. Lu, W. Ding, J. Liu, B. Yang, Flexible PVDF based piezoelectric nanogenerators, Nano Energy. 78 (2020) 105251.
- [3] A. Laudari, A.R. Mazza, A. Daykin, S. Khanra, K. Ghosh, F. Cummings, T. Muller, P.F.
 Miceli, S. Guha, Polarization Modulation in Ferroelectric Organic Field-Effect
 Transistors, Phys. Rev. Applied. 10 (2018) 014011.
- [4] Z.L. Wang, W. Wu, Piezotronics and piezo-phototronics: fundamentals and applications, Nat. Sci. Rev. 1 (2014) 62–90.
- [5] D. Rus, M.T. Tolley, Design, fabrication and control of soft robots, Nature. 521 (2015) 467–475.
- [6] S.K. Ghosh, D. Mandal, Envisioned strategy for an early intervention in virus-suspected patients through non-invasive piezo- and pyro-electric-based wearable sensors, J. Mater. Chem. A. 9 (2021) 1887–1909.
- [7] S. Gonçalves, J. Serrado-Nunes, J. Oliveira, Nelson. Pereira, L. Hilliou, C.M. Costa, S. Lanceros-Méndez, Environmentally Friendly Printable Piezoelectric Inks and Their Application in the Development of All-Printed Touch Screens, ACS Appl. Electron. Mater. 1 (2019) 1678–1687.
- [8] K. Maity, U. Pal, H.K. Mishra, P. Maji, P. Sadhukhan, Z. Mallick, S. Das, B. Mondal, D. Mandal, Piezo-phototronic effect in highly stable CsPbI3-PVDF composite for self-powered nanogenerator and photodetector, Nano Energy. 92 (2022) 106743.

- [9] Z. Pan, W. Peng, F. Li, Y. Cai, Y. He, On the Piezo- Phototronic Effect in Si/ZnO Heterojunction Photodiode: The Effect of the Fermi- Level Difference, Adv. Funct. Mater. 30 (2020) 2005996.
- [10] X. Han, W. Du, R. Yu, C. Pan, Z.L. Wang, Piezo-Phototronic Enhanced UV Sensing Based on a Nanowire Photodetector Array, Adv. Mater. 27 (2015) 7963–7969.
- [11] R. Yu, W. Wu, Y. Ding, Z.L. Wang, GaN Nanobelt-Based Strain-Gated Piezotronic Logic Devices and Computation, ACS Nano. 7 (2013) 6403–6409.
- [12] J.M. Wu, C.-Y. Chen, Y. Zhang, K.-H. Chen, Y. Yang, Y. Hu, J.-H. He, Z.L. Wang, Ultrahigh Sensitive Piezotronic Strain Sensors Based on a ZnSnO₃ Nanowire/Microwire, ACS Nano. 6 (2012) 4369–4374.
- [13] F. Xiao, K.Liu, Y. Bie, J. Zhao, F. Wang, Absorption spectroscopy of individual cadmium selenide nanowire, Appl. Phys. Lett. 101 (2012) 093106.
- [14] L. Zhu, Y.-C. Wang, D. Li, L. Wang, Z.L. Wang, Enhanced Spin–Orbit Coupled Photoluminescence of Perovskite CsPbBr₃ Quantum Dots by Piezo-Phototronic Effect, Nano Lett. 20 (2020) 8298.
- [15] W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T.F. Heinz, J. Hone, Z.L. Wang, Piezoelectricity of single-atomic-layer MoS₂ for energy conversion and piezotronics, Nature 514 (2014) 470–474.
- [16] H. Wang, S. Zhang, T. Zhang, J. Liu, Z. Zhang, G. Yuan, Y. Liang, J. Tan, Y. Ren, W. Lei, SnSe Nanoplates for Photodetectors with a High Signal/Noise Ratio, ACS Appl. Nano Mater. 4 (2021) 13071–13078.
- [17] M. Dai, H. Chen, R. Feng, W. Feng, Y. Hu, H. Yang, G. Liu, X. Chen, J. Zhang, C.-Y. Xu, P. Hu, A Dual-Band Multilayer InSe Self-Powered Photodetector with High

Performance Induced by Surface Plasmon Resonance and Asymmetric Schottky Junction, ACS Nano 12 (2018) 8739–8747.

- [18] R.I. Haque, R. Vié, M. Germainy, L. Valbin, P. Benaben, X. Boddaert, Inkjet printing of high molecular weight PVDF-TrFE for flexible electronics, Flex. Print. Electron. 1 (2015) 015001.
- [19] A.J. Lovinger, Ferroelectric Polymers, Science 220 (1983) 1115–1121.
- [20] H.K. Mishra, V. Gupta, K. Roy, A. Babu, A. Kumar, D. Mandal, Revisiting of δ–PVDF nanoparticles via phase separation with giant piezoelectric response for the realization of self-powered biomedical sensors, Nano Energy 95 (2022) 107052.
- [21] J. Sumerel, J. Lewis, A. Doraiswamy, L.F. Deravi, S.L. Sewell, A.E. Gerdon, D.W. Wright, R.J. Narayan, Piezoelectric ink jet processing of materials for medical and biological applications, Biotechnol J. 1 (2006) 976–987.
- [22] J. Zhang, M. Ahmadi, G. Fargas, N. Perinka, J. Reguera, S. Lanceros-Méndez, L. Llanes,
 E. Jiménez-Piqué, Silver Nanoparticles for Conductive Inks: From Synthesis and Ink
 Formulation to Their Use in Printing Technologies, Metals 12 (2022) 234.
- [23] S.J. Kang, Y.J. Park, I. Bae, K.J. Kim, H.-C. Kim, S. Bauer, E.L. Thomas, C. Park, Printable Ferroelectric PVDF/PMMA Blend Films with Ultralow Roughness for Low Voltage Non-Volatile Polymer Memory, Adv. Funct. Mater. 19 (2009) 2812–2818.
- [24] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-Inspired Surface Chemistry for Multifunctional Coatings, Science 318 (2007) 426–430.
- [25] Z. Wang, H.-C. Yang, F. He, S. Peng, Y. Li, L. Shao, S.B. Darling, Mussel-Inspired Surface Engineering for Water-Remediation Materials, Matter. 1 (2019) 115–155.

- [26] L. Shao, Z.X. Wang, Y.L. Zhang, Z.X. Jiang, Y.Y. Liu, A facile strategy to enhance PVDF ultrafiltration membrane performance via self-polymerized polydopamine followed by hydrolysis of ammonium fluotitanate, J. Membr. Sci. 461 (2014) 10–21.
- [27] A.K. Gill, Sk. Riyajuddin, M. Alam, K. Ghosh, D. Patra, Mussel-inspired UV protective organic coatings via layer-by-layer assembly, Eur. Poly. J. 124 (2020) 109455.
- [28] C. Fu, H. Zhu, N. Hoshino, T. Akutagawa, M. Mitsuishi, Interfacial Nanostructuring of Poly(vinylidene fluoride) Homopolymer with Predominant Ferroelectric Phases, Langmuir 36 (2020) 14083–14091.
- [29] Z. Xiao, Q. Dong, P. Sharma, Y. Yuan, B. Mao, W. Tian, A. Gruverman, J. Huang, Synthesis and Application of Ferroelectric P(VDF-TrFE) Nanoparticles in Organic Photovoltaic Devices for High Efficiency, Adv. Energy Mater. 3 (2013) 1581–1588.
- [30] M. Bachmann, W.L. Gordon, S. Weinhold, J.B. Lando, The crystal structure of phase IV of poly(vinylidene fluoride), J. Appl. Phys. 51 (1980) 5095–5099.
- [31] W.C. Gan, W.H.A. Majid, T. Furukawa, Ferroelectric polarization, pyroelectric activity and dielectric relaxation in Form IV poly(vinylidene fluoride), Polymer 82 (2016) 156– 165.
- [32] M. Benz, W.B. Euler, O.J. Gregory, The Influence of Preparation Conditions on the Surface Morphology of Poly(vinylidene fluoride) Films, Langmuir 17 (2001) 239–243.
- [33] W. Ma, J. Zhang, X.-L. Wang, Formation of poly(vinylidene fluoride) crystalline phases from tetrahydrofuran/N, N-dimethylformamide mixed solvent, J. Mater. Sci. 43 (2008) 398–401.
- [34] M. Benz, W.B. Euler, O.J. Gregory, The Role of Solution Phase Water on the Deposition of Thin Films of Poly(vinylidene fluoride), Macromolecules 35 (2002) 2682–2688.

- [35] R. Moradi, J. Karimi-Sabet, M. Shariaty-Niassar, M.A. Koochaki, Preparation and Characterization of Polyvinylidene Fluoride/Graphene Superhydrophobic Fibrous Films, Polymers 7 (2015) 1444–1463.
- [36] M.S. Grewal, H. Abe, Y. Matsuo, H. Yabu, Aqueous dispersion and tuning surface charges of polytetrafluoroethylene particles by bioinspired polydopamine– polyethyleneimine coating via one-step method, R. Soc. Open Sci. 8 (2021) 210582.
- [37] A. Glasser, É. Cloutet, G. Hadziioannou, H. Kellay, Tuning the Rheology of Conducting Polymer Inks for Various Deposition Processes, Chem. Mater. 31 (2019) 6936–6944.
- [38] R.A. Zangmeister, T.A. Morris, M.J. Tarlov, Characterization of Polydopamine Thin Films Deposited at Short Times by Autoxidation of Dopamine, Langmuir 29 (2013) 8619–8628.
- [39] T. Liu, K.C. Kim, B. Lee, Z. Chen, S. Noda, S.S. Jang, S.W. Lee, Self-polymerized dopamine as an organic cathode for Li- and Na-ion batteries, Energy Environ. Sci. 10 (2017) 205–215.
- [40] T. Huang, Y. Zhang, P. He, G. Wang, X. Xia, G. Ding, T.H. Tao, "Self-Matched" Tribo/Piezoelectric Nanogenerators Using Vapor-Induced Phase-Separated Poly(vinylidene fluoride) and Recombinant Spider Silk, Adv. Mater. 32 (2020) e1907336.
- [41] F.S. Shokr, The influence of dipoles orientation on the charge transport mechanism of Au/rr-P3HT/P(VDF-TrFE) heterojunction diode in the form of 1D-line grating nanostructure arrays, Results Phys. 12 (2018) 754.
- [42] G. Shao, Work Function and Electron Affinity of Semiconductors: Doping Effect and Complication due to Fermi Level Pinning, Energy Environ. Mater. 4 (2021) 273–276.
- [43] J.W. Lee, H. Cho, J. Chun, K.N. Kim, S. Kim, C. Ahn, I. Kim, J.-Y. Kim, S.-W. Kim, C. Yang, J. Baik, Robust nanogenerators based on graft copolymers via control of dielectrics for remarkable output power enhancement, Sci. Adv. 3 (2017) e1602902.

- [44] M. Peng, Y. Ma, L. Zhang, S. Cong, X. Hong, Y. Gu, Y. Kuang, Y. Liu, Z. Wen, X. Sun, All-inorganic cspbbr₃ perovskite nanocrystals/2d non-layered cadmium sulfide selenide for high-performance photodetectors by energy band alignment engineering, Adv. Funct. Mater. 31 (2021) 2105051.
- [45] A. Šutka, P.C. Sherrell, N.A. Shepelin, L. Lapčinskis, K. Mālnieks, A.V. Ellis, Measuring piezoelectric output—fact or friction?, Adv. Mater. 32 (2020) 2002979.
- [46] C. Chen, S. Zhao, C. Pan, Y. Zi, F. Wang, C. Yang, Z.L. Wang, A method for quantitatively separating the piezoelectric component from the as-received "Piezoelectric" signal, Nat. Commun. 13 (2022) 1391.
- [47] G. Ico, A. Showalter, W. Bosze, S.C. Gott, B.S. Kim, M.P. Rao, N.V. Myung, J. Nam, Size-dependent piezoelectric and mechanical properties of electrospun P(VDF-TrFE) nanofibers for enhanced energy harvesting, J. Mater. Chem. A 4 (2016) 2293–2304.
- [48] S.K. Ghosh, A. Biswas, S. Sen, C. Das, K. Henkel, D. Schmeißer, D. Mandal, Yb³⁺ Assisted Self-Polarized PVDF Based Ferroelectretic Nanogenerator: A Facile Strategy of Highly Efficient Mechanical Energy Harvester Fabrication, Nano Energy 30 (2016) 621–629.
- [49] X. Han, M. Chen, C. Pan, Z. Lin Wang, Progress in piezo-phototronic effect enhanced photodetectors, J. Mater. Chem. C 4 (2016) 11341–11354.
- [50] K.S. Pasupuleti, S.S. Chougule, N. Jung, Y.-J. Yu, J.-E. Oh, M.-D. Kim, Plasmonic Pt nanoparticles triggered efficient charge separation in TiO₂/GaN NRs hybrid heterojunction for the high performance self-powered UV photodetectors, Appl. Surf. Sci. 594 (2022) 153474.

Chapter 5

Ultrahigh Pyroelectricity in 2D Monoelemental Tellurium
5.1 Introduction

With the growing demand for renewable energy sources, researchers are more interested in obtaining energy from natural resources such as solar, biomass, geothermal, wind and hydrogen, etc [1]. This incentive has led to the development of materials for energy harvesting studies, including thermoelectrics, photovoltaics, and thermophotovoltaics. In this scenario, the ferroelectric materials a subclass of piezo/pyro-electrics are very attractive because of their excellent mechanical and thermal energy conversion ability as dynamic pressure and temperature sensors, transducers, actuators, and energy harvesters. Particularly, pyroelectricity referred to as a change in spontaneous polarization (P_s) with the function of temperature oscillation, is a promising route for thermal energy harvesting of untapped heat energy derived from rapidly increasing industrialization, vehicle exhausts, convention, and the human body [2,3]. Quantitively, the pyroelectric coefficient (p) and figure of merits (FOMs) are very essential to elucidate the selection of the materials for a realistic applications. According to the Born-Szigeti theory of pyroelectricity, the total pyroelectric coefficient (p) at constant mechanical stress (σ) is defined as

$$p = \left(\frac{dP_S}{dT}\right)_{\sigma} = p_1 + p_2 = \left(\frac{\partial P_S}{\partial T}\right)_{\varepsilon} + \sum_i \left(\frac{\partial P_S}{\partial \varepsilon_i}\right)_T \left(\frac{d\varepsilon_i}{dT}\right)_{\sigma}$$
(5.1)

Two terms named as p_1 and p_2 referred to the primary (at constant strain (ε)) and secondary part of pyroelectricity (depends on thermal expansion and piezoelectricity coefficient) [4]. In the last few decades, high pyroelectric response and FOMs are noticed for traditional inorganic pyroelectric materials e.g., triglycine sulphide (TGS), PbZrTiO₃, BaTiO₃ and lead magnesium niobate lead titanate (PMN-0.25PT) [5]. On the other hand, due to the difficult synthesis route, fragility, non-biocompatibility, and non-biodegradability, or even recyclability, they rarely meet the criteria of next-generation electronics. Owing to the large spontaneous polarization, 2D transition metal dichalcogenides (TMDCs) possess excellent piezo,- pyro,- and ferro,- electricity [6]. But they are restricted because of the very small out-of-plane piezoelectric response obtained so far for e.g., MoSSe. Therefore, to maximize the total pyroelectric coefficient and FOMs, inplane piezoelectricity, which contributes to the secondary pyroelectricity coefficient is very crucial. In turn, we have introduced a monoelemental chalcogenide i.e., tellurium (Te) of group-VI A element in the periodic table. It has a tunable band gap i.e., inversely proportional to the thickness layer ranging from 0.35 eV for bulk to 1.2 eV for a few layers [7]. Tellurium is a newly explored piezoelectric coefficient (~ 1 pm/V) for monolayer as experimentally reported by Apte et al [8]. For instance, tellurium has different polytopes depending upon the crystal structure like 1T (α), 2H (β) and rectangular (γ) forms where the atoms are arranged in tri-layers as octahedral, trigonal prismatic and rectangular, respectively [9].

5.2 Experimental section

5.2.1 Preparation of tellurium nanosheets

Bulk Tellurium (Te) powder (99.99 %) was purchased from Merck chemical (India) with 200 mesh sizes. Isopropanol (IPA) was purchased from Merck India. All chemicals were used further without any purification. Tellurium nanosheets were prepared by the liquid phase exfoliation (LPE) method (as reported by Xie et al.).¹⁰ IPA solvent is chosen for LPE of Te due to its low toxicity, excellent exfoliation efficacy and low boiling point. Firstly, Te powder was grounded in an agate mortar for 30 min to make sure the larger crystals are broken into smaller ones. Then, Te/IPA slurry was transferred to a 50 mL plastic tube for ultrasonic probe sonication followed by bath sonication for 6 h. The temperature of ~ 20 °C was maintained during sonication. keeping a

5 mgmL⁻¹ concentration of Te/IPA. The resultant suspension was centrifuged at 4000 rpm for 30 min followed by supernatant was collected for further study.

5.2.2 Fabrication of pyroelectric nanogenerator (PyNG)

A flexible interdigital electrode (IDE) was prepared with the electron beam (E-beam) evaporation technique with Au/Cr coating of 50/20 nm thickness on a flexible PET substrate. Then, as exfoliated Te nanosheets were gently transferred to the IDE followed by the electrical connections (copper wire) were established in order to conduct the electrical measurements (demonstrated in Extended Data Fig. 1). Further, we have purchased lead zirconate titanate (PZT)-based disc sensor (15 mm, Piezo Elements Sensor) and poly(vinylene difluoride) (PVDF) based sensor Mikuni-UAE, DT1-028K).

5.2.3 Theoretical simulation

All first-principles calculations are performed within the density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP).11 The projector augmented wave (PAW) method and the exchange-correlation interaction is described within the Perdew-Burke-Ernzerhof (PBE) formulation [12,13]. The electronic wave functions are expanded in a plane-wave basis with a kinetic energy cut-off of 500 eV for the trilayer of α -Te. Generalized Gradient Approximation (GGA)[14] functional was used with a Gamma grid k-point mesh of 8×8×1. The crystal structure is relaxed with the total energy convergence criterion of 10–8 eV. Phonon dispersion is calculated with 3×3×1 supercells and total 81 atoms using PHONOPY [15]. Piezoelectric coefficients and Born effective charges are calculated using density functional perturbation theory (DFPT).

5.3 Results and discussion

5.3.1 Theoretical study for Tellurium nanosheets

In order to get the large piezo and pyro-electricity the non-centrosymmetric crystal structure is essential. First-principles calculations based on density functional theory (DFT) confirmed the optimized crystal structure for α -Te monolayer, bilayer and trilayer and corresponding lattice parameters are shown in Table 5.1 with their respective space groups.

Table 5.1 Lattice parameter (a), thickness (d), space group and bond length of α -Te monolayer, bilayer and trilayer

No. of layers	Lattice parameters (Å)	Thickness (Å)	Space group	θ ₁ (°)	θ ₂ (°)
Monolayer	4.21	3.6	P-3m1	88.17	88.17
Bilayer	4.23	10	C2	87.98	87.82
				87.82	87.98
Trilayer	4.25	15.96	C2	88.10	87.78
				88.34	87.34
				87.78	88.10

It is found that the monolayer is centrosymmetric having P-3m1 space group (Figure 5.1a). While the trilayer structures of α -Te (Figure 5.1b) exhibit the identical space group as a monolayer (Figure 5.1a), however, it is not in the energetically lowest ground state ($E = E_{Total}^{P-3m1} - E_{Total}^{C2} = 14.2 \text{ meV}$). Noteworthy to mention that the optimized and energetically most stable crystal structure of α -Te trilayer exhibits C2 space group (Figure 5.1c).



Figure 5.1 Geometric structure of α -Te (a) monolayer with side-view and top-view, (b) and (c) side-view of P-3m1 space group, and C2 space group of trilayer. The unit cells of α -Te are highlighted in light green color. The phonon dispersion curve of α -Te (d) monolayer and (e) trilayer.

Further, as the number of layers increases α -Te becomes non-centrosymmetric due to the change in the internal bond angles (θ_1 and θ_2) and van der Waals interaction among the layers. It is found that for monolayer $\theta_1 = \theta_2 = 88.17^\circ$, whereas for trilayer case $\theta_1 \neq \theta_2$. Because of the minor twist in the internal bond angles (see Table 5.1), the structure with space group C2 becomes a noncentrosymmetric which is the prime factor for high in-plane piezoelectricity in 2D Te nanosheets. This becomes the cause of the breaking of inversion symmetry in the case of monolayer and trilayer. Therefore, it is expected that the large in-plane piezoelectricity will effectively enhance the secondary pyroelectric coefficient (p_2). Further, the phonon dispersion curves with ZA, TA and LA modes are shown in Figure 5.1d and 5.1e for monolayer and trilayer, respectively. Since there are no imaginary modes at any high symmetry directions, so α -Te monolayer and trilayer are dynamically stable. It is observed that acoustic phonon frequency, particularly, the ZA mode decreases at Γ and M points for trilayer, which further indicate the softening of acoustic phonon modes that leads to the structural change from monolayer to trilayer in Te structure (Figure 5.1d and 5.1e).

5.3.2 Characterization of 2D Te nanosheets

The surface topography and thickness of tellurium is estimated from atomic force microscopy (AFM) as shown in Figure 5.2. The surface topography (Figure 5.2a) of bulk tellurium and corresponding average crystal thickness ~ 300 nm \pm 20 nm as demonstrated in colored line profile plot Figure 5.2b. Further, after the exfoliation of bulk tellurium by LPE approach, it turns into the 2D Te nanosheets which is confirmed by surface topography (Figure 5.2c). Then the average thickness ~ 4-6 nm (\pm 1.2 nm) of 2D Te nanosheets are estimated by marked color lines with highlighted rings as shown in Figure 5.2d.



Figure 5.2 AFM surface topography of (a) bulk tellurium (scale bar is 2 μ m) (b) corresponding height profile with three different colors marked line profiles (c) LPE exfoliated 2D tellurium nanosheets (scale bar is 2 μ m) and (d) corresponding height profile of marked rings with different colors.

Further, transmission electron microscopy (TEM) image confirmed the shape of exfoliated Telike nanosheets and the lateral size in the range of 3-5 nm as shown in Figure 5.3a. The histogram plot of TEM image (left side top inset of Figure 5.3a) is well-fitted with the Gaussian form which implies the uniformity of 2D Te nanosheets after exfoliation process. Further, the crystal lattice fringes in high-resolution transmission electron microscopy (HR-TEM) were

clearly identified with the lattice interplanar spacing of 0.32 nm and 0.24 nm which corresponds to the reflection planes of (101) and (102), respectively (right bottom inset of Figure 5.3a). The X-ray diffraction (XRD) pattern confirms the crystalline properties of bulk and exfoliated 2D Te nanosheets as shown in Figure 5.3b. Bulk and exfoliated Te nanosheets exhibit very similar diffraction peaks that correspond to the hexagonal crystalline structure which is in well agreement with the standard PDF database (JCPDF Card No: 36-1452) [10]. The XRD pattern indicates, there are no further changes noticed in the crystal structure due to the induced lattice strain after the exfoliation process. Moreover, the exfoliation was also confirmed from the XRD pattern with a diffraction peak at 23.1° that corresponds to the (100) facet plane of Te nanosheets. A very significant decrease in intensity has been observed in the (100) plane of 2D Te nanosheets than bulk Te, which leads to the anisotropy in the Te nanosheets which is also in well agreement as reported by Xiao et al. [17]. The Raman spectrum of 2D exfoliated nanosheets and bulk Te are shown in Figure 5.3c. It described basically three main Raman active vibrational modes i.e., A₁ which corresponds to the chain expansion where each atom moves in the basal plane. Whereas the E_1 and E_2 modes are attributed to the bond bending and asymmetric stretching along the helical chain direction (Figure 5.3d). Bulk Te (without exfoliation) exhibits three vibrational modes located at 90.5, 118 and 140 cm⁻¹ which are ascribed to the E_1 -TO, A_1 and E₂ modes of Raman active phonons, respectively [18]. In turn, the exfoliated Te nanosheets exhibit a slight blue shift in vibration modes of E_1 -TO, A_1 and E_2 at 99, 120 and 143 cm⁻¹, respectively compared to bulk Te (schematically demonstrated in Figure 5.3d). The observed blue shift is attributed to the helical chain-like structure and interlayer long-range coulombic interactions due to the Te-Te bond among the vibrational modes which is supported by earlier reports [19,20].



Figure 5.3 (a) TEM image of exfoliated Te nanosheets and corresponding inset in top left side for average nanosheet size distribution and right bottom inset (scale bar 2 nm) shows the SAED pattern with the reflection planes. (b) The XRD pattern, (c) Raman spectra and (d) corresponding Raman active vibration modes of tellurium.

Further, we have employed piezoresponse force microscopy (PFM) to confirm the nanoscale outof-plane piezo/ferro-electricity due to the non-centrosymmetric nature of Te nanosheets with the C2 space group. The PFM measurement conditions were used similar to section 3.1.2 and 3.2.3 of chapter 3. The spectroscopy response of the PFM phase (Figure 5.4a) and amplitude (Figure 5.4b) of 2D Te nanosheets has demonstrated the typical ferro and piezo-electric hysteresis upon the external DC biasing. Further, the net piezoelectric coefficient was estimated i.e., $d_{33} \sim 3.7$ pm/V by taking the slope from the amplitude response that can be enabled by the equation

$$Piezoelectric \ coefficient \ (d_{33}) = \frac{Net \ piezoeelctric \ amplitude}{Applied \ DC \ bias}$$
(5.2)



Figure 5.4 Piezoresponse force microscopy (PFM) spectroscopy of 2D tellurium nanosheets (a) ferroelectric phase reversal hysteresis and (b) amplitude hysteresis under the applied DC bias voltage of \pm 10 V.

5.3.3 Electrical output performance of PyNG

Pyroelectricity is the coupling of displacement vector (\vec{D}) and changes in temperature oscillations (ΔT) which is described by the relation $\vec{D} = \epsilon_0 \vec{E} + \vec{P}$, where, \vec{P} , \vec{E} and ϵ_0 are the net polarization, electric field vector and dielectric permittivity of free space. Then the net polarization is defined as $\vec{P} = \vec{P}_{ind} + \vec{P}_s$, where, \vec{P}_{ind} is the induced polarization upon the application of electric field and \vec{P}_s is the spontaneous polarization and displacement vector $\vec{D} = \epsilon_0 \epsilon_r \vec{E} + \vec{P}_s$, here, ϵ_r is the dielectric constant of the materials. In the absence of an electric field the displacement vector is defined as $\vec{D} = \vec{P}_s$. Thus, the pyroelectric coefficient at constant electric field and mechanical stress (σ) can be represented by [21,22]

$$\vec{p} = \left(\frac{d\vec{D}}{dT}\right) = \left(\frac{d\vec{P}_S}{dT}\right)_{E,\sigma}$$
(5.3)

Furthermore, in order to evaluate the pyroelectric response due to the time dependent temperature oscillations to drive the electrons flow in the circuit, pyroelectric nanogenerator (PyNG) is fabricated comprising of Te nanosheets (Figure 5.5).



Figure 5.5 Schematic demonstration of fabrication of pyroelectric nanogenerator (a) flexible PET substrate (b) preparation of inter digital electrode (IDE) on PET substrate with Gold (c) 2D tellurium nanosheets transferred over the IDE and (d) two terminal wire connection established for electrical output measurement.

Further, a pyroelectric measurement setup is customized for electrical measurements, where infrared (IR) radiation source is employed for the temperature fluctuation at a constant frequency of 0.1 Hz by a function generator (Figure 5.6). Then, PyNG is placed under the IR temperature source, and a periodic on-and-off temperature fluctuation is applied at the top surface, while the

bottom surface is connected to the peltier cooler to maintain the temperature difference (ΔT) (Figure 5.6). The output open circuit voltage (V_{OC}) and short circuit current (I_{SC}) is measured, when temperature increases from room temperature 297 K to 303 K (i.e., $\Delta T \sim 6$ K, as shown in Figure 5.7a) and corresponding first-order derivative dT/dt ~ 1.4 K/s, respectively (Figure 5.7b). It is observed that the current shows a positive pulse when 2D Te nanosheets are heated (dT/dt > 0) and a negative peak due to the convective cooling process (dT/dt < 0). Thus, PyNG exhibits the V_{OC} ~ 1 V and I_{SC} of 13 nA, respectively as depicted in Figure 5.7c and 5.7d.

According to the Lang-Steckel method, the output short circuit current is directly proportional to the rate of change of temperature with time as described by

$$I_{SC} = p.A.\frac{dT}{dt}$$
(5.4)

where, A is the effective electrode area and p is the pyroelectric coefficient respectively. However, for open circuit conditions it is expressed as

$$V_{OC} = \frac{p}{\epsilon} \cdot t. \, \Delta T \tag{5.5}$$

herein, ϵ , *t* and ΔT are the dielectric permittivity, thickness across the polarization direction and change in temperature respectively [23]. With our experimental data, the obtained pyroelectric coefficient (*p*) is ~ 3000 µCm⁻²K⁻¹. It is important to mention here that, it is ~ 8 times higher with well-known pyroelectric material like lead zirconate titanate (PZT) and ~ 1.5 times than the lead magnesium niobate lead titanate PMN-0.25PT, respectively [5].



Figure 5.6 Pyroelectric measurement set up for the electrical output measurement with periodic turn on and off temperature oscillation profile with the IR source and function generaor.



Figure 5.7 Pyroelectric thermal energy harvesting (a) acquired profile of temperature oscillation and (b) corresponding rate of change in temperature at a constant frequency of 0.1 Hz. The electrical output performance as (c) open circuit voltage and (d) short circuit current of pyroelectric nanogenerator comprising of Te nanosheets.

It is noteworthy to point out that, in order to corroborate our experimental findings, we have also collected pyroelectric response from a well-known pyroelectric material such as PVDF and PZT disc-based sensor that is commercially available (as mentioned in the experimental section). The pyroelectric signals of PZT (Figure 5.8) and PVDF (Figure 5.9) sensor in terms of V_{OC} and I_{SC} are recorded with the similar experimental conditions and measurements setup as used for Te

based device mentioned above. Then, the estimated pyroelectric coefficients are ~ 347 and 40 μ Cm⁻²K⁻¹ for PZT and PVDF, respectively, which is in well agreement with the reported results [5]. Thus, it can be inferred that Te nanosheets-based PyNG shows the excellent pyroelectric response and further it can be utilized for a variety of potential applications for thermal energy harvesting.



Figure 5.8 Pyroelectric electrical output performance of commercial PZT disc sensor (a) acquired temperature oscillation profile, (b) first order derivative of heat transfer and corresponding (c) open circuit voltage and (d) short circuit current.



Figure 5.9 Pyroelectric electrical output performance of commercial PVDF sensor (a) acquired temperature oscillation profile, (b) first order derivative of heat transfer and corresponding (c) open circuit voltage and (d) short circuit current.

5.3.4 FEM-based simulation for thermal strain distribution

Furthermore, to understand the origin of large pyroelectricity in our fabricated PyNG, we have performed the finite element method (FEM) based theoretical simulation by using an experimentally obtained temperature fluctuation ($\Delta T = 6 K$) as shown in Figure 5.10. It has been observed that when temperature fluctuation is applied to the Te device, that temperature difference is confined between the adjacent electrodes and also at the top and bottom surfaces of

the device (Figure 5.10a and 5.10c). The enlarged view of the temperature distribution profile for Te nanosheets is shown in Figure 5.10b. Further, the thermal strain distribution is ~ 0.4 and which can be observed from enlarge in Figure 5.10d and 5.10e, respectively. It enables the thermal energy harvesting performance by the synergistic effect of thermal strain confinement within the Te nanosheets.



Figure 5.10 FEM based theoretical simulation of (a) temperature profile acquired for simulation $(\Delta T \sim 6 \text{ K})$ (b) enlarged view for heat rate transfer (c) bottom surface of device when temperature oscillation is applied. Further, thermal strain distribution in 2D tellurium nanosheets with the same temperature profile and (e) enlarged of thermal strain induced in nanosheets.

Furthermore, we have also investigated the impact of temperature variation with Te pyroelectric device signal generation e.g., open circuit voltage (V_{OC}) and short circuit current (I_{SC}) as shown in Figure 5.11a and 5.11b, respectively. It can be observed that V_{OC} and I_{SC} decreases as the distance between IR source and PyNG increases. It is observed that at a very lower distance of 3 cm the maximum electrical output generated because of large heat rate transfer to the nanosheets.



Figure 5.11 The variation of electrical output performance of (a) open circuit voltage and (b) short circuit current with respect to distance from IR source to the pyroelectric device.

Since pyroelectricity originates from a permanent spontaneous polarization (P_s) of the unit cell in the crystal structure, which is possible to tune by the heating and cooling of temperature. The experimentally obtained high pyroelectric coefficient in comparison to the well-known pyroelectric materials is validated from first principle based theoretical approach. The trilayer Te belongs to 3-point group, which have a unique polar axis and generates net electric dipole moment [24]. Thus, estimated in-plane spontaneous polarization $P_{sp,a}$ and $P_{sp,b}$ are -1.89 C/m² and -0.93 C/m², respectively of Te nanosheets, which are relatively ~ 10³ times higher than MoSSe monolayer [25] (14.15 × 10⁻⁴ C/m²) and ~ 2 times than Lead Zirconate Titanate (PZT) (0.78 C/m²). It is found that in α -Te trilayer, the in-plane piezoelectric coefficient ($e_{22} = 16.33 \times 10^{-10}$ C/m) is five times higher compared to MoSSe monolayer [26] ($e_{22} = 3.74 \times 10^{-10}$ C/m). Since, pyroelectric coefficient is directly proportional to Born effective charges (BEC), piezoelectric coefficient (e_{ij}), and thermal expansion coefficient (α_a) as described in reference [27]. Therefore, for better understanding we have investigated BEC for trilayer as well as for each atom of tellurium and also for lead zirconate titanate (PZT) which is summarized in Table 5.2.

Table 5.2 In-plane and out-of-plane Born effective charges (e) of each atom of α -Te and trilayer and PZT

Materials	Atom	1	2	3	4	5	6	7	8	9
α-Te	$Z^*_{\chi\chi}$	-5.30	-6.22	-8.64	-8.66	-6.23	-5.31	13.18	14.11	13.18
	Z^*_{yy}	-5.31	-6.23	-8.66	-8.64	-6.22	-5.30	13.18	14.11	13.18
	Z_{zz}^*	-0.30	0.04	3.31	3.31	0.04	-0.30	1.93	0.21	1.93
	Average	-3.44	-4.13	-4.66	-4.66	-4.13	-3.44	9.43	9.48	9.43
	Atom	Pb	Pb	Zr	Ti	O ₁	O ₃	O_4	O ₆	
PZT ⁷	Z^*_{xx}	3.77	3.87	5.56	5.99	-2.55	-2.34	-2.85	-2.06	
	Z_{yy}^*	3.77	3.87	5.56	5.99	-4.22	-2.34	-4.97	-2.06	
	Z_{zz}^*	3.46	2.63	5.95	5.27	-2.33	-4.65	-1.86	-4.28	
	Average	3.66	3.45	5.69	5.75	-3.11	-3.11	-3.22	-2.8	

The average BEC of 7th, 8th, and 9th atoms of α -Te trilayer are ~ 3 times higher than Pb atoms and ~ 2 times higher than Zr and Ti atoms of PZT. Moreover, the average BEC of the other Te atoms are higher than the oxygen atoms of PZT. Thus, in-plane BECs are relatively higher than well-known pyroelectric material i.e., PZT as shown in Table 5.2. Further, the estimated thermal

expansion coefficient (α_a) is 15.94 which is more than 2 times higher than MoSSe ($\alpha_a \sim 7.09$). Therefore, all these parameters reveal the high in-plane pyroelectricity in α -Te nanosheets and also validated the experimental results.

5.3.5 Mechanism of ultrahigh pyroelectric response

It is noteworthy to mention that to enhance the pyroelectric coefficient the device geometry is very essential because in the case of conventional pyroelectrics i.e., out-of-plane, the thermodynamic process results in a very small temperature change (ΔT) and also corresponding the first-order derivative of temperature (dT/dt). It directly affects spontaneous polarization and electrical output performance [2]. In contrast, the in-plane geometry plays a vibrant role for high pyroelectric response due to excellent BEC, piezoelectricity and thermal expansion coefficient. Then a mechanism of pyroelectricity based on dipoles orientation and corresponding change in spontaneous polarization depending on temperature fluctuations is shown in Figure 5.12. In the first case when rate of temperature is constant i.e, (dT/dt = 0) then random oscillation of electrical dipoles occurs which results the net polarization to be zero (as illustrated in Figure 5.12a). In the next case, when rate of heat transfer is large i.e., dT/dt > 0, then heat is transferred in both direction (i.e., x-y plane) that prolongs the large thermal variations in the nanosheets (Figure 5.12b). Thus, there is a wider expansion of dipoles from their alignment axis which leads to decrease in net polarization due to decrease in dipole moment per unit cell in the system as following

Polarization (P) =
$$\frac{Dipole\ moment\ (p)}{Area}$$
 and dipole moment ((p) = q. d = qdcos φ) (5.6)

where, q, d and φ are the charge, vector distance from origin of dipole and the angle of dipole orientation, respectively. In the last case, when rate of heat transfer is less i.e., dT/dt < 0, then there is a very small expansion of dipoles that leads to maximum polarization in the system which can be observed by the strength of polarization direction (Figure 5.12c).



Figure 5.12 Schematic demonstration of pyroelectric mechanism of 2D tellurium nanosheets based nanogenerator on dipole orientation from their alignment axis when (a) temperature is constant i.e., dT/dt = 0, (b) dT/dt > 0 and (c) dT/dt < 0, (d) the comparative illustration of pyroelectric coefficient, current and voltage figure of merits, marked red color rectangle represent the 2D tellurium nanosheet (this work).

Further, we have also evaluated current (F_i) and voltage (F_v) pyroelectric figure of merits (FOMs) by following equations [22]

$$F_i = \frac{p}{c_E} = \frac{p}{\rho c_p} \tag{5.7}$$

$$F_{\nu} = \frac{p}{c_E \varepsilon_{33}^{\sigma}} = \frac{p}{\rho c_p \varepsilon_{33}^{\sigma}}$$
(5.8)

where, p, c_p , ρ , are pyroelectric coefficient (μ Cm⁻²K⁻¹), specific heat capacity (Jkg⁻¹K⁻¹), density (kgm⁻³), respectively. The c_E and $\varepsilon_{33}^{\sigma}$ are the volume specific heat capacity (Jm⁻³K⁻¹) and dielectric constant at constant stress, respectively [28]. Then the estimated pyroelectric coefficient and FOMs of 2D tellurium nanosheets are compared with well-known pyroelectric materials as demonstrated in Figure 5.12d.

5.4 Conclusions

In conclusion, we have synthesized 2D tellurium nanosheets by LPE process and then fabricated a pyroelectric nanogenerator for thermal energy harvesting. Further, we demonstrated an unprecedented ultrahigh pyroelectric coefficient ($p \sim 3000 \ \mu Cm^{-2}K^{-1}$) and corresponding FOMs from 2D Te nanosheets under periodic on and off temperature oscillations at a constant frequency of 0.1 Hz. This giant pyroelectric response was further explained by a first-principles calculation based on density functional theory. The estimated spontaneous polarization, BEC, thermal expansion coefficient and in-plane piezoelectricity of 2D tellurium nanosheets shows a several order high magnitudes than well-known traditional pyroelectric materials like PZT and PVDF. As a result, this astonishing pyroelectric response in 2D tellurium nanosheets open a new avenue for thermal energy harvesting and its practical applicability for next generation of flexible electronic technologies.

5.5 References

- D. Zhang, H. Wu, C.R. Bowen, Y. Yang, Recent Advances in Pyroelectric Materials and Applications, Small 17 (2021) 2103960–2103983.
- Y. Zhou, T. Ding, J. Guo, G. Xu, M. Cheng, C. Zhang, X.-Q. Wang, W. Lu, W.L. Ong, J. Li, J. He, C.-W. Qiu, G.W. Ho, Giant polarization ripple in transverse pyroelectricity, Nat. Commun. 14 (2023) 426–437.
- [3] S.B. Lang, Pyroelectricity: From ancient curiosity to modern imaging tool, Phys. Today. 58 (2005) 31–36.
- [4] J. Liu, S.T. Pantelides, Mechanisms of Pyroelectricity in Three- and Two-Dimensional Materials, Phys. Rev. Lett. 120 (2018) 207602–207609.
- [5] C.R. Bowen, J. Taylor, E. Leboulbar, D. Zabek, A. Chauhan, R. Vaish, Environmental Science Pyroelectric materials and devices for energy harvesting applications, Energy Environ. Sci. 7 (2014) 3836–3856.
- [6] G. Rao, H. Fang, T. Zhou, C. Zhao, N. Shang, J. Huang, Y. Liu, X. Du, P. Li, X. Jian, L. Ma, J. Wang, K. Liu, J. Wu, X. Wang, J. Xiong, Robust Piezoelectricity with Spontaneous Polarization in Monolayer Tellurene and Multilayer Tellurium Film at Room Temperature for Reliable Memory, Adv. Mater. 34 (2022) 2204697–220707.
- [7] G. Qiu, A. Charnas, C. Niu, Y. Wang, W. Wu, P.D. Ye, The resurrection of tellurium as an elemental two-dimensional semiconductor, npj 2D Mater. Appl. 6 (2022) 17–27.
- [8] A. Apte, S. Kouser, F. Safi Samghabadi, L. Chang, L.M. Sassi, D. Litvinov, B.I. Yakobson, A.B. Puthirath, P.M. Ajayan, Piezo-response in two-dimensional α-Tellurene

films, Mater. Today. 44 (2021) 40-47.

- [9] P.K. Sachdeva, S. Gupta, C. Bera, Large piezoelectric and thermal expansion coefficients with negative Poisson's ratio in strain-modulated tellurene, Nanoscale Adv. 3 (2021) 3279–3287.
- [10] Z. Xie, C. Xing, W. Huang, T. Fan, Z. Li, J. Zhao, Y. Xiang, Z. Guo, J. Li, Z. Yang, B. Dong, J. Qu, D. Fan, H. Zhang, Ultrathin 2D Nonlayered Tellurium Nanosheets: Facile Liquid-Phase Exfoliation, Characterization, and Photoresponse with High Performance and Enhanced Stability, Adv. Funct. Mater. 28 (2018) 1705833–1705844.
- [11] G. Kresse, J. Furthmiiller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 (1996) 15–50.
- [12] P. E. Blöchl, O. Jepsen, & O. K. Andersen, Improved tetrahedron method for Brillouinzone integrations. Phys. Rev. B 49 (1994) 16223–16233.
- [13] M. Ernzerhof, G.E. Scuseria, Assessment of the Perdew–Burke–Ernzerhof exchangecorrelation functional. J. Chem. Phy. 110 (1999) 5029–5036.
- [14] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [15] I. Tanaka, Scripta Materialia First principles phonon calculations in materials science, Scr. Mater. 108 (2015) 1–5.
- [16] Z. Wu, H. Krakauer, First-principles calculations of piezoelectricity and polarization rotation in Pb(Zr_{0.5}Ti_{0.5})O₃ Phys. Rev. B 68 (2003) 014112–014119.
- [17] Q. Xiao, X.Y. Li, Z.Q. Zhang, C.X. Hu, G.H. Dun, B. Sun, Y. Peng, Q. Wang, Z. Zheng,

H.L. Zhang, Facile Fabrication of Highly Uniform Tellurium Nanorods for Self-Powered Flexible Optoelectronics, Adv. Electron. Mater. 6 (2020) 2000240–2000249.

- [18] Y. Wang, G. Qiu, R. Wang, S. Huang, Q. Wang, Y. Liu, Y. Du, W.A. Goddard, M.J. Kim, X. Xu, P.D. Ye, W. Wu, Field-effect transistors made from solution-grown twodimensional tellurene, Nat. Electron. 1 (2018) 228–236.
- [19] J.K. Qin, P.Y. Liao, M. Si, S. Gao, G. Qiu, J. Jian, Q. Wang, S.Q. Zhang, S. Huang, A. Charnas, Y. Wang, M.J. Kim, W. Wu, X. Xu, H.Y. Wang, L. Yang, Y. Khin Yap, P.D. Ye, Raman response and transport properties of tellurium atomic chains encapsulated in nanotubes, Nat. Electron. 3 (2020) 141–147.
- [20] Y. Du, G. Qiu, Y. Wang, M. Si, X. Xu, W. Wu, P.D. Ye, One-Dimensional van der Waals Material Tellurium: Raman Spectroscopy under Strain and Magneto-Transport, Nano Lett. 17 (2017) 3965–3973.
- Y. Yang, W. Guo, K.C. Pradel, G. Zhu, Y. Zhou, Y. Zhang, Y. Hu, L. Lin, Z.L. Wang, Pyroelectric Nanogenerators for Harvesting Thermoelectric Energy, Nano Lett. 12 (2012) 2833–2838.
- [22] S. Jachalke, E. Mehner, H. Stöcker, J. Hanzig, M. Sonntag, T. Weigel, T. Leisegang, D.C. Meyer, J. Hanzig, M. Sonntag, T. Weigel, S. Jachalke, E. Mehner, H. St, How to measure the pyroelectric coefficient ?, Appl. Phys. Rev. 4 (2017) 021303–021320.
- [23] S.K. Ghosh, T.K. Sinha, M. Xie, C.R. Bowen, S. Garain, B. Mahanty, K. Roy, K. Henkel,
 D. Schmeißer, J.K. Kim, Temperature-Pressure Hybrid Sensing All-Organic Stretchable
 Energy Harvester, ACS Appl. Electron. Mater. 3 (2021) 248–259.

- [24] X. Zhang, Q. Liu, J. Luo, A.J. Freeman, A. Zunger, Hidden spin polarization in inversionsymmetric bulk crystals, Nat. Phys. 10 (2014) 387–393.
- [25] C. Xia, W. Xiong, J. Du, T. Wang, Y. Peng, J. Li, Universality of electronic characteristics and photocatalyst applications in the two-dimensional Janus transition metal dichalcogenides, Phys. Rev. B 98 (2018) 165424–165432.
- [26] L. Dong, J. Lou, V.B. Shenoy, Large In-Plane and Vertical Piezoelectricity in Janus Transition Metal Dichalchogenides, ACS Nano 11 (2017) 8242–8248.
- [27] J. Liu, M. V. Fernández-Serra, P.B. Allen, First-principles study of pyroelectricity in GaN and ZnO, Phys. Rev. B. 93 (2016) 081205–081211.
- [28] W. Li, G. Tang, G. Zhang, H.M. Jafri, J. Zhou, D. Liu, Y. Liu, J. Wang, K. Jin, Y. Hu, H. Gu, Z. Wang, J. Hong, H. Huang, L.Q. Chen, S. Jiang, Q. Wang, Improper molecular ferroelectrics with simultaneous ultrahigh pyroelectricity and figures of merit, Sci. Adv. 7 (2021) eabe3068.

Chapter 6

Flexible Mechanical and Thermal Energy Harvesting Based Hybrid

Nanogenerator

6.1 Introduction

There has been significant progress in the development of wearable and implantable electronics (WIEs), making them increasingly attractive to our social lives. These devices have become ubiquitous in our daily lives, improving efficiency and convenience across a wide range of activities. Particularly, mobile sensors, Internet of things (IoTs), which are essential components of WIEs, need to be easily integrated with accessories and fabrics, including bracelets, watches, eyeglasses, and necklaces, or implanted directly into the human body [1,2]. Therefore, the need for more sustainable and reliable power sources for personal electronic devices has led to a growing interest in converting waste energy into usable electrical energy. The waste energy which is particularly available in our surrounding such as mechanical vibrations (e.g., human motion including blood flow, heartbeat, contraction of blood vessels, muscle stretching or eye blinking and music, water flow) and thermal energy (e.g., vehicle exhaust, solar radiation, during breathing, rapid growth of industrialization) [3]. In this context, energy harvesting is carried out by converting scattered or wasted energy from the surrounding, which is not used but should be used, into electrical energy. In turn, nanogenerators (NGs) have emerged as a promising method for effectively harvesting local untapped energy from the environment into electricity, particularly for self-powered WIEs systems. In particular, piezoelectric and pyroelectric materials are commonly used in NGs to convert mechanical vibrations and thermal fluctuations, respectively, into electrical energy and are commonly known as hybrid NGs [4,5]. Piezoelectric materials generate electrical charges in response to mechanical stress, while pyroelectric materials generate electrical charges due to changes in spontaneous polarization in response to temperature fluctuation. The most important part of NGs is efficiency which depends on several factors, including the properties of the materials used, the design of the device, and the environmental conditions in which it operates.

Single-cell hybrid NGs that can simultaneously harvest mechanical and thermal energies have become an active area of research in the field of energy harvesting. These devices can capture multiple forms of energy from their surroundings, leading to a higher overall energy conversion efficiency. In this scenario, Lee et al. have investigated a single-cell hybrid NG device that uses a micropatterned poly(vinylidene fluoride trifluoroethylene) [P(VDF-TrFE)] material. The micropatterning of the material allows for greater control over the strain and thermal oscillations applied to the device, leading to a more efficient energy conversion efficiency [6]. Similarly, Ko et al. reported a hybrid NG using Pb(Zr_{0.52}Ti_{0.48})O₃ film and LaNiO₃/Pt electrodes, which promises excellent piezoelectric coefficient of 140 pC/N and pyroelectric coefficient 50 nC/cm²K, respectively [7]. While the developed hybrid NGs have shown great potential for energy-harvesting applications, however, the fabrication process of these devices is difficult and cumbersome. This presents challenges for their mass production and practical application. However, there are still many challenges to overcome in their fabrication procedures, such as lightweight, large-area device fabrication, flexibility, and cost-effectiveness. To improve the efficiency of NGs, researchers are working to develop new materials with enhanced piezoelectric and pyroelectric properties, as well as innovative device structures that can capture and convert more energy. Therefore, ferroelectric polymers have been widely used in hybrid NGs, they may not be suitable for harvesting energy in more extreme environments due to their relatively small piezoelectric and pyroelectric coefficients than some state-of-the-art piezo and pyroelectric-based inorganic materials such as PbZrTiO₃, BaTiO₃, LiTaO₃ etc. In spite of the high response of inorganic materials, they have been limited because of their rigidity, steep cost, and nonbiocompatibility. In turn, ferroelectric polymers are highly considered for energy harvesting applications due to their inherent properties (such as low cost, biocompatibility, flexibility) [8].

Therefore, to increase the electrical output response in hybrid NGs some nanocomposites are considered [9]. For example, in our previous work based on the 2D monoelemental chalcogenide (i.e., Tellurium) we have realized very unprecedented ultra-high piezo and pyro-electricity. Thus, as a consequence of previous work, we have prepared a nanocomposite thin film comprising of PVDF and Te by a spin coating method. It induces an electroactive β and γ -phase in the PVDF. Further, we have fabricated flexible hybrid piezoelectric and pyroelectric NG (HyNG) that promises an excellent electrical output performance as ~ 7.5 V and ~ 4 µA of open circuit voltage (V_{oC}) and short circuit current (I_{SC}) under a continuous imparted mechanical force of 12 N. After that we have also recorded the excellent pyroelectric response of HyNG as ~ 100 mV and 400 pA of V_{oC} and I_{SC} under periodic temperature oscillation i.e., $\Delta T \sim 7 K$. The quantified piezoelectric and pyroelectric coefficients of fabricated HyNG are 81 pC/N and 300 µCm⁻²K⁻¹, respectively. Thus, it suggests the viability of fabricated HyNG to use further in realistic applications such as harvesting of very minute mechanical vibration from human eye blinking.

6.2 Experimental section

6.2.1 Chemicals

Analytical grade Sodium Tellurite (Na₂TeO₃), polyvinylpyrrolidone (PVP), aqueous ammonia solution (NH₃·H₂O) and hydrazine hydrate (N₂H₄·H₂O) were purchased from Sigma Aldrich, India. PVDF (Mw ~ 2,75,000) and dimethylformamide (DMF) were also purchased from Sigma Aldrich, India. All the chemicals were used further without any purification.

6.2.2 Synthesis of Tellurium nanoflakes

The hydrothermal method was used to synthesize tellurium nanoflakes as per the earlier report [10,11]. In a typical procedure, a homogeneous solution was prepared by mixing analytical-grade

Na₂TeO₃ (0.00045 mol) and PVP in double-distilled water (33 ml) at room temperature under magnetic stirring. This solution was then transferred to a Teflon-lined stainless-steel autoclave containing an aqueous ammonia solution (25%, wt/wt%) and hydrazine hydrate (80%, wt/wt%). The autoclave was sealed tightly and maintained at 180°C for 36 h, after which it was cooled to room temperature naturally. The resulting solid silver-grey products were precipitated by centrifugation at 5000 RPM for 5 min and washed three times with distilled water to eliminate any remaining ions in the final product as schematically demonstrated in Figure 6.1.



Figure 6.1 Schematic illustration of tellurium nanoflakes preparation.

6.2.3 Preparation of nanocomposite film

Firstly, we have prepared PVDF/DMF (12 w/v %) solution under continuous magnetic stirring of 400 RPM 60 °C temperature till homogeneous solution. Then, different concentrations of tellurium 0.15, 0.25 and 0.50 wt % are dispersed in the PVDF/DMF solution and continuously

stirred again for a long time (5 h) and then bath sonication is employed to make the homogenous dispersion of tellurium in the solution. After that, films were prepared on the clean ITO-coated PET substrate by a spin coating method (1000 RPM, 60 s, and 80°C in-situ temperature) as shown in Figure 6.2. The thickness of the film is optimized ~ 10 μ m. As prepared nanocomposite films are designated as NPV, PVTe15, PVTe25 and PVTe50 depending on the concentration of tellurium such as 0, 0.15, 0.25 and 0.50 wt %, respectively in PVDF/DMF.

6.2.4 Fabrication of HyNG

The copper electrode deposition was accomplished over the as-prepared PVTe50 film by a sputtering technique. Then, two electrical wires were established from the copper side and the ITO substrate to record the electrical output signals (Figure 6.2). Then, HyNG was sealed with Kapton tape to avoid any other artifacts on the surface. Thereafter, HyNG was further used for piezoelectric and pyroelectric-based electrical measurements.



Figure 6.2 Schematic demonstration of PVTe nanocomposite film preparation.

6.3 Results and discussion

6.3.1 Material and characterization

Firstly, we have employed the powder X-ray diffraction (PXRD) pattern to confirm the crystalline structure of pure tellurium (Te) nanoflakes (NFs) as shown in Figure 6.3a. The peaks in the XRD pattern are in good agreement with the earlier reported results and also with the JCPDS file No. 36-1452 [11]. The scanning electron microscopy (SEM) images exhibit the surface morphology of Te NFs, it has the length of tens of microns with an irregular shape (Figure 6.3b). The presence of Te nanowires alongside Te nanoflakes in the SEM image suggests that both types of nanostructures are existing in the growth solution. The high-resolution transmission electron microscopy (HR-TEM) image shows the continuous crystal lattice fringe pattern of the Te nanoflakes, and the measured lattice spacing is ~ 0.38 nm (Figure 6.3c), which is assignable to the (100) planes of the Te NFs. This plane also matched with the XRD pattern (Figure 6.3a) [12,13]. Further, the Raman spectra of Te NFs exhibit the presence of three main vibrational modes, which are Raman-active and located at 96 cm⁻¹ (E₁ transverse (TO) phonon mode), 120 cm⁻¹ (A₁ mode) and 140 cm⁻¹ (E₂ mode) as shown in Figure 6.3d. These vibrational modes correspond to specific structural features of the Te NFs. Among these vibrational modes, one of the modes is called the A-mode and is associated with the expansion of the chains in the basal plane of the Te NFs. While other two modes are E-modes, which correspond to bondbending around the $[121\overline{0}]$ direction and asymmetric stretching mainly along the helical chains oriented along the [0001] direction, respectively [10]. The presence and characteristics of these vibrational modes provide valuable information about the crystal structure and properties of the Te NFs. Therefore, as mentioned characterization explicit the proof of concept for highly





Figure 6.3 (a) PXRD pattern, (b) SEM surface morphology, (c) SAED pattern and (d) Raman spectra of as-synthesized tellurium NFs.

6.3.2 Electroactive phase nucleation in PVTe film

In order to get an in-depth understanding of electroactive phase formation in PVTe nanocomposite film, we have carried out FTIR measurements as shown in Figure 6.4a. It can be observed that in the case of NPV where no filler is incorporated in the PVDF matrix, paraelectric α -phase is dominated which is assigned to the vibration bands at 764, 975, 1383 cm⁻¹,

respectively. Besides the α -phase in NPV, there is also very least content of electroactive β (vibrational band present at 837, 1275 cm⁻¹) and γ -phase which is evidenced by the presence of a vibrational band at 812, 837 and 1237 cm⁻¹, respectively. Further, as tellurium NFs (0.15, 0.25 and 0.50 wt %) are added in the PVDF matrix then electroactive phase (β and γ) induces more significantly than NPV while the α -phase starts to disappear completely in PVTe50 film. In the case of PVT50, the maximum amount of electroactive (β and γ) phase nucleated which can be observed from the intensity of vibrational bands 1275 and 1237 cm⁻¹, respectively [16]. The estimated fraction of electroactive content (F_{EA}), fraction of β -phase ($F(\beta)$) and γ -phase ($F(\gamma)$) of PVTe nanocomposite film is shown in Table 6.1.



Figure 6.4 Electroactive phase nucleation in PVDF nanocomposite film as (a) FTIR spectra and (b) XRD pattern, symbol (*) shows the respective peaks of Tellurium.

In order to get in depth analysis of electroactive phase nucleation we have also employed the powder X-ray diffraction (PXRD) pattern of nanocomposite film as shown in Figure 6.4b. In the XRD pattern of NPV film, three diffraction peaks are present at 17.9° (100), 18.5° (020) and 20.1° (110) which is ascribed to the predominant α -phase and some part of γ -phase. However, as
the concentration of Te NFs increased in PVDF then the electroactive phase induces which can be observed from the disappearance of major peak of α -phase at 17.8° (100). There are very small peak present at 18.5 (020) in nanocomposite film which endorsed the existence of γ -phase, a similar trend is also found from FTIR spectra [17]. Noteworthy to mention here that as the concentration of Te NFs increases in the polymer matrix then the intensity of that particular peaks 23.2° (100) and 27.7° (101) also increases (Figure 6.4b), which indicates the presence of Te NFs in the nanocomposite system.

Sample	Total	β-phase content	γ-phase content
	electroactive	(F (β))	(F (γ))
	phase (F _{EA})		
NPV	49	20	29
PVTe15	75	30	45
PVTe25	91	44	47
PVTe50	97	48	49

 Table 6.1 Electroactive phase content in PVTe nanocomposite films.

6.3.3 Surface morphology

The surface morphology of as prepared nanocomposite film was obtained by field-emission scanning electron microscopy (FE-SEM) as shown in Figure 6.5. The FE-SEM image of neat PVDF film shows the fibril structure like spherulite formation with large spherulite size of ~ 11 \pm 1.5 µm (Figure 6.5a). However, PVTe50 nanocomposite film reveals the uniform distribution of spherulites with diameter ranging from 2 to 4 \pm 0.4 µm as shown in Figure 6.5b. The homogenous dispersion of Te NFs in the PVDF matrix is confirmed by the uniform distribution

of spherulites. Spherulites formation for PVTe50 are smaller than those for neat PVDF (NPV), which indicates that the nucleation kinetics of the PVTe50 nanocomposite film due to the presence of Te NFs. Further, the increase of β/γ -phase fraction in the nanocomposite film may be accomplished due to the existence of large number of favorable nucleation centers.



Figure 6.5 FE-SEM surface morphology of (a) neat PVDF and (b) PVTe50 nanocomposite film.

6.3.4 Dielectric properties of PVTe film

Frequency-dependent room temperature dielectric properties of PVTe nanocomposite films are investigated at room temperature as shown in Figure 6.6. It can be observed that the dielectric constant increases when the concentration of Te NFs increased in the PVDF matrix (Figure 6.6a). This large dielectric constant (PVTe50 \sim 30) at a lower frequency (1 kHz) regime is attributed to the interfacial interaction of PVDF dipoles because of the Maxwell-Wagner -Sillers approximation theory of two dissimilar dielectric media as we discussed in section 2.3.4 of Chapter 2. Furthermore, a non-linear trend is noticed for the frequency-dependent loss tangent of nanocomposite film at room temperature as shown in Figure 6.6b. The maximum loss tangent is found for PVTe 50 film which exhibits the energy dissipation in a dielectric material. This behavior is the ideal nature due to the relaxation process of the PVDF polymeric chain [18].



Figure 6.6 Frequency-dependent dielectric performance of PVTe nanocomposite film (a) variation of the real part of dielectric constant and (b) dielectric loss at room temperature.

6. 3.5 Electrical output performance of HyNG 3

6.3.5.1 Piezoelectric output performance

The fabrication process of the present hybrid nanogenerator is schematically shown in Figure 6.7a. Under a continuous mechanical force, the crystal lattice structure undergoes deformation, resulting in the generation of piezo potential at the surface of HyNG due to the change in polarization state. When a mechanical force is varied from 3 to 12 N at a constant frequency of 5 Hz, the electrical output open circuit voltage (V_{OC}) and short circuit current (I_{SC}) is increasing. Maximum V_{OC} and I_{SC} is found to be ~ 7.5 V and 4 μ A, respectively at 12 N of force for PVTe50 comprising HyNG. In order to get in depth understanding of excellent piezoelectric output generation, we have estimated the magnitude of piezoelectric coefficient ($|d_{33}| = \frac{Q}{F} = 81 \ pC/N$), where Q and F are generated charge and applied force respectively. This large piezoelectric coefficient shows the practical use of fabricated HyNG for self-powered sensors.



Figure 6.7 Piezoelectric output performance of HyNG (a) schematic demonstration of HyNG fabrication and (b) open circuit voltage and (c) short circuit current under variable mechanical force from 3 to 12 N at 5 Hz of frequency.

Further, to the better comparison we have also prepared HyNG with bare PVDF where no filler was incorporated then it exhibits the V_{OC} and $I_{SC} \sim 0.8$ V and 400 nA, respectively under similar force of 12 N (Figure 6.8a, b). Thus, the recorded output V_{OC} and I_{SC} is 9 and 10 times higher than bare PVDF. Therefore, this large piezoelectric output signal for the PVTe50 HyNG is anticipated that due to change in stress induced polarization in the nanocomposite system [19].



Figure 6.8 Piezoelectric response of HyNG prepared by bare PVDF film (a) open circuit voltage and (b) short circuit current under the 12 N of force and 5 Hz frequency.

Further, we have also estimated the performance of HyNG with external load resistance as shown in Figure 6.9a, as resistance increases then output voltage is also increases and get saturated at high resistance due to the impedance matching of internal load resistance of device with external load resistance. Further, we have also estimated the electrical power density (*P*) similar to the section 2.3.5 of chapter 2 as shown in Figure 6.9a. The estimated *P* is recorded to be $\sim 4.5 \,\mu\text{W/cm}^2$.

Moreover, to demonstrate the practical application of HyNG as a pressure sensor we have applied variable pressure ranging from 0.25 to 70 kPa. In the Figure 6.9b, it is noticed that HyNG have two regions linear and non-linear. The linear region is well fitted with corresponding equation and then mechano-sensitivity ($Sm = \frac{\Delta V_{OC}}{\Delta \sigma_a}$), where ΔV_{OC} and $\Delta \sigma_a$ are the change in output voltage and mechanical pressure, is estimated to be ~ 148 mVkPa⁻¹. Due to its excellent mechano-sensitivity, HyNG could be used as a pressure sensor.



Figure 6.9 Piezoelectric output performance of HyNG (a) variation of output voltage and power density and (b) pressure sensing performance of HyNG.

In order to realize the thermal energy harvesting, the HyNG was subjected to a periodic temperature oscillation with a similar pyroelectric measurement setup as mentioned in section 5.3.3 of chapter 5. In the consequence of our earlier work based on 2D tellurium nanosheets (chapter 5), we found unprecedented pyroelectricity. Therefore, to make it a flexible and large-area device we have fabricated PVDF and tellurium nanocomposite. In particular, due to the highest electroactive nature in PVTe50-based nanocomposite film, it is considered for pyroelectric measurement. Due to the temperature fluctuation, the spontaneous polarization changes which result in the pyroelectric open circuit voltage and short circuit current generation as per our earlier discussion in chapter 5 [20–22]. From Figure 6.10, under temperature fluctuation ($\Delta T \sim 7 K$) and heat rate transfer dT/dt = 1.5 K/s as shown in Figure 6.10a and 6.10b, respectively, the measured repeated and periodic pyroelectric voltage ~100 mV (Figure 6.10c) and current ~ 400 pA (Figure 6.10d) signal is recorded in PVTe50-based HyNG.



Figure 6.10 Pyroelectric output performance of HyNG (a) acquired temperature oscillation profile (b) corresponding first order derivative of temperature, (c) open circuit voltage with single enlarge peak in inset and (d) short circuit current with single enlarged peak in the inset.

However, this pyroelectric response is very high compared to pure PVDF (NPV)-based HyNG i.e., 14 mV and 60 pA of voltage and current, respectively (Figure 6.10c and 6.10d). Thus, this excellent pyroelectric response is attributed due to the presence of tellurium nanoflakes in the nanocomposite system. Further, we have quantified the pyroelectric coefficient (p) of HyNG by using the similar expression of section 5.3.3 of chapter 5. The estimated $p \sim 300 \,\mu \text{Cm}^{-2}\text{K}^{-1}$ which is more than ~ 7 times higher than pure PVDF (40 $\mu \text{Cm}^{-2}\text{K}^{-1}$) based HyNG. Due to this excellent pyroelectric response of PVTe based HyNG nanocomposite could be considered a better option for thermal energy harvesting.

6.3.6 Human gesture sensing performance

Due to excellent flexibility and excellent mechano-sensitivity (Sm) of HvNG, it has been realized that it can capture very minute deflection from human physiological signals. In order to perform this, firstly we have calculated the mechanical deflection of human eve movement by the finite element method (FEM)-based simulation [23,24]. Then, it has been noticed from the contour plot of deflection sensitivity (6.11a) that when position of the sensor is far from the center of eye movement then deflection is less and corresponding to that deflection the electrical output was estimated based on the theoretical approach (Figure 6.11b). Further, we have prepared HyNG with a 1×1 cm² area and placed at three places around the eye i.e., upper eyelid, lower eyelid, and temple, respectively. During the eye movement, the mechanical deflection arises i.e., contraction and release phenomenon occurs (Figure 6.11c) and consequently the electrical output voltage signal is generated as shown in Figure 6.11d-f. The recorded electrical output signal at three different locations (inset of Figure 6.11d-f) are in well agreement with numerically simulated results. Thus, as fabricated HyNG has the capability to capture small deflections of human eye blinking of muscles and skins caused by eyelid and eyeball movements based on numerical simulation which is further validated by experimental demonstration to measure normal eye blinking.



Figure 6.11 Physiological signal monitoring performance of HyNG (a) FEM simulation-based eye deflection (b) simulated output voltage corresponding to deflection (c) schematic illustration of strain generation when eye lids open/close due to contraction and release phenomenon. Experimental output voltage response when HyNG is fixed at three different locations (d) temple, (e) lower eyelids and (f) upper eyelids.

Moreover, the HyNG is affixed to various human movement areas, including elbow bending, knee bending, and finger bending (different angles), to monitor the physiological signals (Figure 6.12). The HyNG is initially attached to the human elbow and knee, where mechanical stress is generated and transferred to the device through flexion and extension. Consequently, the electrical output voltage is recorded ~ 7.5 mV and 6 mV for elbow and knee bending and releasing motion as shown in Figure 6.12a and 6.12b, respectively. Additionally, HyNG is fixed on the index finger and then during cyclic bending and releasing, the electrical output signals is recorded to be ~ 2.5 mV to 5 mV depending on the bending angles (30 ° to 90 °) (Figure 6.12c).



Figure 6.12 Physiological signal monitoring of human movement (a) elbow bending, (b) knee bending and (c) finger bending.

6.4 Conclusions

In summary, we have prepared PVDF and Te nanoflakes-based nanocomposite film via spin coating method with an electroactive β - and γ -phase. Then we fabricated flexible hybrid piezoand pyro-electric nanogenerator (HyNG), which exhibits very excellent electrical response. The collected output piezoelectric response V_{OC} and I_{SC} is found to be ~ 7.5 V and 4 μ A, respectively. Further, HyNG promises an excellent electrical power density (*P*) ~ 4.5 μ W/cm² and piezoelectric coefficient (d₃₃) ~ 81 pC/N, respectively. Moreover, HyNG has demonstrated to capture very small mechanical deflection of human eye movement. In addition to that, we have also realized the pyroelectric response in HyNG under temperature periodic temperature ($\Delta T = 7K$) oscillations. The pyroelectric voltage and current response were recorded to be 100 mV and 400 pA, respectively. Further, the estimated pyroelectric coefficient (p) ~ 300 μ Cm⁻²K⁻¹ is observed in PVTe50 nanocomposite based HyNG compared to pure PVDF based HyNG (~ 40 μ Cm⁻²K⁻¹). Thus, HyNG has promises an excellent piezo- and pyro-electric performance for self-powered flexible electronic devices and human physiological signal monitoring.

6.5 References

- C. Jiang, X. Li, S.W.M. Lian, Y. Ying, J.S. Ho, J. Ping, Wireless Technologies for Energy Harvesting and Transmission for Ambient Self-Powered Systems, ACS Nano 15 (2021) 9328.
- [2] X. Wang, S. Niu, F. Yi, Y. Yin, C. Hao, K. Dai, Y. Zhang, Z. You, Z.L. Wang, Harvesting Ambient Vibration Energy over a Wide Frequency Range for Self-Powered Electronics, ACS Nano 11 (2017) 1728.
- [3] M. Satthiyaraju, T. Ramesh, Effect of annealing treatment on PVDF nanofibers for mechanical energy harvesting applications, Mater. Res. Express. 6 (2019) 105366.
- [4] R.A. Surmenev, R. V. Chernozem, I.O. Pariy, M.A. Surmeneva, A review on piezo- and pyroelectric responses of flexible nano- and micropatterned polymer surfaces for biomedical sensing and energy harvesting applications, Nano Energy 79 (2021) 105442.
- [5] D. Zhang, H. Wu, C.R. Bowen, Y. Yang, Recent Advances in Pyroelectric Materials and Applications, Small 17 (2021) 2103960.
- [6] J.H. Lee, K.Y. Lee, M.K. Gupta, T.Y. Kim, D.Y. Lee, J. Oh, C. Ryu, W.J. Yoo, C.Y. Kang, S.J. Yoon, J.B. Yoo, S.W. Kim, Highly stretchable piezoelectric-pyroelectric hybrid nanogenerator, Adv. Mater. 26 (2014) 765.
- Y.J. Ko, D.Y. Kim, S.S. Won, C.W. Ahn, I.W. Kim, A.I. Kingon, S.H. Kim, J.H. Ko, J.H. Jung, Flexible Pb(Zr_{0.52}Ti_{0.48})O₃ Films for a Hybrid Piezoelectric-Pyroelectric Nanogenerator under Harsh Environments, ACS Appl. Mater. Interfaces 8 (2016) 6504.
- [8] L. Yang, Q. Zhao, K. Chen, Y. Ma, Y. Wu, H. Ji, J. Qiu, PVDF-Based Composition-Gradient Multilayered Nanocomposites for Flexible High-Performance Piezoelectric Nanogenerators, ACS Appl. Mater. Interfaces 12 (2020) 11045.

- [9] D. Bhattacharya, S. Bayan, R.K. Mitra, S.K. Ray, 2D WS₂ embedded PVDF nanocomposites for photosensitive piezoelectric nanogenerators with a colossal energy conversion efficiency of ~25.6%, Nanoscale 13 (2021) 15819.
- Y. Wang, G. Qiu, R. Wang, S. Huang, Q. Wang, Y. Liu, Y. Du, W.A. Goddard, M.J. Kim,
 X. Xu, P.D. Ye, W. Wu, Field-effect transistors made from solution-grown twodimensional tellurene, Nat. Electron. 1 (2018) 228.
- [11] M. Amani, C. Tan, G. Zhang, C. Zhao, J. Bullock, X. Song, H. Kim, V.R. Shrestha, Y. Gao, K.B. Crozier, M. Scott, A. Javey, Solution-Synthesized High-Mobility Tellurium Nanoflakes for Short-Wave Infrared Photodetectors, ACS Nano 12 (2018) 7253.
- [12] C. Zhao, C. Tan, D.H. Lien, X. Song, M. Amani, M. Hettick, H.Y.Y. Nyein, Z. Yuan, L. Li, M.C. Scott, A. Javey, Evaporated tellurium thin films for p-type field-effect transistors and circuits, Nat. Nanotechnol. 15 (2020) 53.
- [13] G. Qiu, A. Charnas, C. Niu, Y. Wang, W. Wu, P.D. Ye, The resurrection of tellurium as an elemental two-dimensional semiconductor, Npj 2D Mater. Appl. 6 (2022) 1–10.
- [14] Z. Shi, R. Cao, K. Khan, A.K. Tareen, X. Liu, W. Liang, Y. Zhang, C. Ma, Z. Guo, X. Luo, H. Zhang, Two-Dimensional Tellurium: Progress, Challenges, and Prospects, Nano-Micro Lett. 12 (2020) 99.
- [15] J.K. Qin, P.Y. Liao, M. Si, S. Gao, G. Qiu, J. Jian, Q. Wang, S.Q. Zhang, S. Huang, A. Charnas, Y. Wang, M.J. Kim, W. Wu, X. Xu, H.Y. Wang, L. Yang, Y. Khin Yap, P.D. Ye, Raman response and transport properties of tellurium atomic chains encapsulated in nanotubes, Nat. Electron. 3 (2020) 141.
- [16] H.K. Mishra, D. Sengupta, A. Babu, B.M. Pirzada, R. Sarkar, B.S. Naidu, T.K. Kundu, D.Mandal, PVDF/Ag₂CO₃ nanocomposites for efficient dye degradation and flexible

piezoelectric mechanical energy harvester, Sustain. Energy Fuels, 6 (2022) 1625.

- [17] P. Martins, A.C. Lopes, S. Lanceros-mendez, Progress in Polymer Science Electroactive phases of poly (vinylidene fluoride): Determination, processing and applications, Prog. Polym. Sci. 39 (2014) 683.
- [18] V.K. Thakur, R.K. Gupta, Recent Progress on Ferroelectric Polymer-Based Nanocomposites for High Energy Density Capacitors: Synthesis, Dielectric Properties, and Future Aspects, Chem. Rev. 116 (2016) 4260.
- [19] X. Chen, X. Li, J. Shao, N. An, H. Tian, C. Wang, T. Han, L. Wang, B. Lu, High-Performance Piezoelectric Nanogenerators with Imprinted P(VDF-TrFE)/BaTiO₃ Nanocomposite Micropillars for Self-Powered Flexible Sensors, Small 13 (2017) 1–12.
- [20] G. Velarde, S. Priya, J. Karthik, D. Pesquera, L. W. Martin, Pyroelectric thin films-Past, present, and future, APL Mater. 9 (2021) 010702.
- [21] Y. Yang, S. Wang, Y. Zhang, Z.L. Wang, Pyroelectric nanogenerators for driving wireless sensors, Nano Lett. 12 (2012) 6408.
- [22] S. Korkmaz, A. Kariper, Pyroelectric nanogenerators (PyNGs) in converting thermal energy into electrical energy: Fundamentals and current status, Nano Energy 84 (2021) 105888.
- [23] J. Chen, H. Liu, W. Wang, N. Nabulsi, W. Zhao, J.Y. Kim, M. Kwon, High Durable, Biocompatible, and Flexible Piezoelectric Pulse Sensor Using Single-Crystalline III-N Thin Film, Adv. Funct. Mater. 29 (2019) 1903162.
- [24] N.I. Kim, J. Chen, W. Wang, M. Moradnia, S. Pouladi, M.K. Kwon, J.Y. Kim, X. Li, J.H.
 Ryou, Highly-Sensitive Skin-Attachable Eye-Movement Sensor Using Flexible
 Nonhazardous Piezoelectric Thin Film, Adv. Funct. Mater. 31 (2021) 2008242.

Chapter 7

Summary and Future Outlook

7.1 Summary

In this chapter, the essential findings of the Ph.D. research work are summarized. The research work presented in various chapters throughout the thesis, aimed to address energy harvesting of untapped mechanical and thermal energy from the surrounding to usable electrical energy. Moreover, it also provides valuable insights and contributions to the field of mechanical and thermal energy harvesting. This final chapter serves as a culmination of the research and highlights the key outcomes and implications of the study. The following sections provide an overview of the main findings from each chapter.

Chapter 1: This chapter describes a pedagogical introduction to renewable energy sources as an alternative approach to emphasize the importance of transitioning away from fossil fuels (e.g., coal, gases, and oil) and highlights energy harvesting as a potential solution. A broad overview of fundamentals and different applications of nanogenerator (NG) based on mechanical and thermal energy sources i.e., piezoelectric and pyroelectric, respectively, are discussed. In particular, poly(vinylidene fluoride) i.e., PVDF has been selected in research work due to its intrinsic characteristics such as flexibility, biocompatibility, cost-effectiveness and remarkable piezo/pyro-electricity.

Chapter 2: First and foremost, we have given special emphasis to engineering the polymer nanocomposite with PVDF and silver carbonate (Ag₂CO₃) which has a majorly electroactive γ -phase. The nucleation of electroactive phase has been elucidated through the interaction of Ag₂CO₃ filler and molecular dipoles of PVDF based on silver charge nucleation. In addition to that, it has been also evident from inter-fragment, non-covalent, intermolecular interaction based on the linear combination of atomic orbitals LCAO approach. Moreover, the fabricated flexible piezoelectric nanogenerator (FPNG) has exhibited remarkable electrical output performance,

including a high open circuit voltage (V_{OC}) ~15 V, a short circuit current (I_{SC}) ~ 6 μ A, and an electrical power density (*P*) of ~7 μ Wcm⁻². The FPNG has demonstrated its capability to harvest energy from various sources, such as human gestures (e.g., finger bending, walking) owing to its exceptional mechano-sensitivity (Sm) of 45 mV/kPa. Additionally, when the PVDF/Ag₂CO₃ nanocomposite film was exposed to continuous ultrasound mechanical vibrations, it displayed a notable piezo-catalytic effect. This effect was evident in the degradation of methyl orange (MO) dye ~ 80% in an aqueous media. The mechanical vibrations applied to the nanocomposite film generate a piezo-potential on its surface which leads to several redox reactions that facilitated the degradation process. These findings highlight the potential of the PVDF/Ag₂CO₃ nanocomposite as a highly promising material for efficient dye degradation and mechanical energy harvesting applications.

Chapter 3: In the second phase of work, we have fabricated PVDF nanoparticles (NPs) with a predominant electroactive δ -phase, which has been relatively less explored compared to other phases of PVDF. The remarkable piezoelectric and ferroelectric property is noticed from δ -phase of PVDF nanoparticles, which is comparable or even superior to the extensively studied β -phase. However, the δ -phase has received limited attention in research due to the challenging processing conditions adopted so far, mainly it requires ultra-high electric fields (~ MV/m) and pressure (~ MPa). In this context, the solvent-based phase separation method is undertaken which emerges as an exceptionally convenient approach, offering significant advantages for energy harvesting applications. This method has demonstrated immense technological and commercial benefits. Additionally, we have estimated a giant piezoelectric coefficient i.e., d₃₃ ~ -43 pm/V, through piezo-response microscopy under a very low DC bias of ± 5 V. This measurement confirms the exceptional switching dynamics of the δ -phase PVDF comprising molecular dipoles. In addition

to that, fabricated FPNG with PVDF nanoparticles exhibits excellent piezoelectric energy conversion efficiency (η) ~ 24 % and mechano-sensitivity (Sm) of 107 mV/kPa. Indeed, the exceptional mechano-sensitivity of the FPNG makes it capable of detecting and monitoring physiological signals, such as arterial pulse detection in humans. This capability holds great potential for the development of self-powered sensors and actuators that can be seamlessly integrated into wearable devices or healthcare applications as a self-powered device.

Chapter 4: In addition to earlier work, we have given efforts to make δ -PVDF nanoparticles as a piezoelectric ink. In this regard, we have engineered the hydrophobic surface of PVDF NPs by co-polymerization with polydopamine-polyethylenimine (PDA-PEI) conjugates to make it an aqueous dispersible. The printability of the piezoelectric ink, comprising the functionalized δ -PVDF NPs, has been successfully demonstrated by writing the alphabets on various substrates. This showcases the capability of the ink to adhere and form a well-defined pattern on different surfaces. Further, the FPNG prepared by piezoelectric ink has displayed excellent piezoelectric output performance and photodetection ability. It also exhibits the piezo-phototronic effect under simultaneous light illumination and mechanical stimuli.

Chapter 5: We have explored the 2D material (monoelemental Tellurium) due to its emerging piezo/ferro-electric properties. In this work, we have demonstrated ultrahigh pyroelectric response and corresponding figure of merits (FoMs) in 2D tellurium (Te) nanosheets under periodic temperature oscillations. The superior pyroelectric response of 2D Te nanosheets holds promise for their futuristic integration into advanced thermal energy harvesting devices, paving the way for innovative applications in the field of flexible electronics.

Chapter 6: In consequence of previous work, we have synthesized highly crystalline tellurium nanorods via hydrothermal method. Then, a flexible piezo and pyro-electric-based hybrid

nanogenerator i.e., HyNG fabricated with PVDF and tellurium nanocomposite-based spin-coated film. Subsequently, HyNG has shown promising electrical output performance as a piezoelectric coefficient ($d_{33} \sim 81$ pC/N) and pyroelectric coefficient ($p \sim 300 \ \mu \text{Cm}^{-2}\text{K}^{-1}$), respectively. In addition to that, mechano-sensitivity (Sm) ~ 148 mV/kPa is noticed for HyNG which has the potential utility to detect very minute mechanical vibration. To showcase the capabilities of HyNG, we have successfully monitored physiological signals related to human eye deflections caused by eye movement at different locations. The ability of HyNG to detect and monitor such subtle mechanical movements opens up possibilities for applications in several potential sectors like human-machine interfaces, wearable devices, and healthcare monitoring.

7.2 Future outlook

The global demand for sustainable energy sources has led to extensive research in the field of mechanical and thermal energy harvesting-based nanogenerators and their practical applications. Therefore, this thesis has presented some appealing applications of piezo- and pyro-electric nanogenerators, it merely provides a glimpse into their vast potential applications. Undoubtedly, there are still several areas that require dedicated focus and continuous investigation to address the remaining challenges and further advancement in the field. To facilitate future research endeavors, the following topics could be considered as potential areas of further investigation:

 The primary aim is to improve the energy conversion efficiency and overall performance of piezo-and pyro-electric nanogenerators with new advanced materials that includes 2D materials and their composite structures, along with utilizing nanoscale structures. Further, the integration of these materials into flexible substrates, textiles, and wearable electronics will enable the generation of energy from ambient mechanical and thermal sources in a wide range of applications, including smart clothing, healthcare monitoring, and Internet of Things (IoT) devices.

- ii. Recently some initiatives have been made in the development of nanogenerators (NGs) where *in-vivo* applications such as self-powered implantable devices are facilitated. However, the successful integration of NGs into in vivo environments, particularly implanted and wearable bio-devices, remains a considerable challenge. Thus, one can work on the key requirements for such applications, such as biocompatibility, long-term reliability, and performance of nanogenerators so as to capable to harvest biomechanical energy within the human body.
- iii. The power requirements of electronic devices can vary depending on their energy consumption. To meet the demand for high-power applications, triboelectric nanogenerators (TENGs) hold great promise as a futuristic option due to their potential to generate large power densities.
- iv. Piezo-phototronics is indeed a fascinating field of research that explores the three-way coupling effect among piezoelectric, semiconductor, and photonic properties of materials. This phenomenon enables the manipulation of electronic and optical behaviors in materials by applying mechanical strain or stress. The integration of piezo-phototronic effects in wearable electronic devices holds great promise for advancements in various applications. Moreover, the introduction of the piezoelectric potential at the interface of the semiconducting material could possible to modulate the charge carrier dynamics. This modulation can lead to an increase in the photogeneration and separation of charge carriers, improving the overall efficiency of solar cells. By effectively utilizing the mechanical

strain applied to the device, the piezo-phototronic effect could enhance the optoelectronic performance of wearable devices.

v. Piezoelectric materials can be considered a promising candidate for environmental cleaning and remediation. It can be further utilized for hydrogen generation which involves the piezoelectric effect to generate electrical charges that will drive water-splitting reactions or enhance the catalytic activity for hydrogen evolution. Therefore, it is presumed that piezoelectric materials could have the potential for the development of efficient and sustainable hydrogen production technologies.

Curriculum vitae

Hari Krishna Mishra

Affiliation: Institute of Nano Science and Technology (INST), Knowledge City, Sector-81, Mohali-140306, India & Indian Institute of Science Education and Research (IISER), Knowledge City, Sector-81, Mohali-140306, India Email-Id: hari.ph18208@inst.ac.in Alt. Email-Id: harikrishnamishraphysics@gmail.com



Mr. Hari Krishna Mishra (Reg. No. PH18208) joined the Institute of Nano Science and Technology (INST), Mohali, in July 2018 for his doctoral dissertation and registered at the Indian Institute of Science Education and Research (IISER), Mohali for the award of the degree of Doctor of Philosophy. He is working on designing of functional biocompatible polymer-based nanomaterials and 2D chalcogenides of piezo-, pyro-, and ferro-electric properties for mechanical and thermal energy harvesting. As fabricated devices have been successfully utilized in various applications including self-powered electronic devices, energy storage, acoustic signal detection and the healthcare sector (e.g., arterial pulse detection and human body part movement). In addition to that, some applications have been intended to utilize the piezo potential in piezo-catalysis and hydrogen evolution reaction (HER).

Hari Krishna Mishra