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FABRICATION OF SnO_2 /MXENE/PVDF BASED EFFICIENT FLEXIBLE BIO MECHANICAL ENERGY HARVESTING DEVICE

**A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of**

DOCTOR OF PHILOSOPHY

**by
GAGAN SHARMA
(2K21/PHDAP/02)**

**Under the Supervision of
DR. DESHRAJ MEENA
Assistant Professor**



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JULY, 2026

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DEDICATION

This dissertation is dedicated to my family and supervisor.

ACKNOWLEDGEMENT

First and foremost, I express my sincere gratitude to the Almighty for granting me the strength, patience, and perseverance to complete my thesis. I would like to sincerely thank my supervisor, **Dr Deshraj Meena** for his constant guidance, encouragement, and support throughout my research. His valuable suggestions, constructive feedback, and continuous motivation have played a significant role in shaping this thesis and bringing it to completion. I am truly grateful for their mentorship. I am also thankful to **Prof. Prateek Sharma**, Hon'ble Vice-Chancellor of DTU, for providing a supportive research environment and necessary facilities. I would also like to extend my gratitude to **Prof. Rinku Sharma, Dean (Academic-PG)**, and **Prof. Vinod Singh, Head of the Department of Applied Physics**, as well as to all the faculty and staff members, for their cooperation and support during my research tenure. I would like to acknowledge my fellow research lab mates of CERL members **Ms. Shivani Sangwan, Mr. Mohit Kumar, Mr. Bhagat Singh, Ms. Mona Devi and Ms. Richa**, for their guidance, encouragement, cooperation, helpful discussions, and support throughout this journey.

A special thanks to my close friend **Dr. Yash Pathak, Mr. Anurag Bhandari and Mr. Kunal Madan**, whose anchor during challenging times, filling my days with laughter, warmth, and positivity. Thank you for standing by me through every high and low, for cheering on my successes, and for lifting my spirits whenever I felt overwhelmed. Furthermore, I wish to express my gratitude to my friends at DTU, including **Dr. Komal Verma, Mr. Aman Kumar, and Mr. Anurag Bhardwaj** for their unwavering technical guidance, valuable suggestions, and support throughout this journey. I am deeply thankful for the enriching discussions and invaluable guidance they provided throughout our research endeavours. I am incredibly fortunate to have friends like you, and I will always cherish the memories we've created together during this journey.

I would like to dedicate this memorable day of my life to the loving memory of my beloved grandparents, Late **Shri Om Parkash Sharma** and Late **Smt. Paaso Devi**. I remain deeply grateful for their blessings, which have been a constant source of hope,

strength, and inspiration throughout my life. I would like to express my deepest respect, love, and gratitude to my parents, **Shri Madan Lal Sharma** and **Smt. Rani Devi**, whose unconditional love, endless sacrifices, and constant blessings have been the greatest source of strength and inspiration throughout my life. I am deeply grateful to my beloved brother, **Shri Deepak Sharma**, for his unwavering love, constant support, and continuous encouragement throughout this journey. I extend my heartfelt thanks to my wife, **Mrs. Indu Sharma**, my sister-in-law, **Mrs. Sandhya Sharma**, and my brother-in-law, **Mr. Lakshay Sharma**, for their constant support, understanding, encouragement, and belief in me. Their presence and support have made this journey easier and more meaningful. A special note of love and appreciation goes to my daughters, **Gora** and **Aaru**, who have filled my life with happiness, love, and positivity. Their innocent smiles, affection, and cheerful presence have often given me renewed strength and motivation during difficult moments. They have been a constant source of joy throughout this journey, and I am deeply grateful to have them in my life.

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CANDIDATE'S DECLARATION

I, Mr. Gagan Sharma (2K21/PHDAP/02), hereby declare that the work which is being presented in the thesis entitled “Fabrication of SnO₂/MXene/PVDF based Efficient Flexible Bio Mechanical Energy Harvesting Device” in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy, submitted in the Department of Applied Physics, Delhi Technological University is an authentic record of my own work carried out during the period from August 2021 to June 2026 under the supervision of Dr. Deshraj Meena, Department of Applied Physics, Delhi Technological University. The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

Candidate's Signature

This is to certify that the student has incorporated all the corrections suggested by the examiners in the thesis and the statement made by the candidate is correct to the best of our knowledge.

Dr. Deshraj Meena
(Supervisor)

Dr.

(External Examiner)



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CERTIFICATE BY THE SUPERVISOR

Certified that **Mr. Gagan Sharma (2K21/PHDAP/02)** has carried out her research work presented in this thesis entitled “**Fabrication of SnO₂/MXene/PVDF based Efficient Flexible Bio Mechanical Energy Harvesting Device**” for the award of Doctor of Philosophy from Department of Applied Physics, Delhi Technological University, Delhi, under my supervision. The thesis embodies results of original work, and studies are carried out by the student himself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

Dr. Deshraj Meena

(Supervisor)

Assistant Professor
Department of Applied Physics
Delhi Technological University
Delhi-110042, India

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ABSTRACT

Fabrication of SnO₂/MXene/PVDF based Efficient Flexible Bio Mechanical Energy Harvesting Device

The escalating global energy demand, compounded by the environmental imperatives associated with the continued dependence on conventional fossil fuel resources, necessitates the urgent development and deployment of sustainable energy solutions. In this context, ambient mechanical energy harvesting technologies have garnered considerable scientific interest as viable alternatives, offering the capacity to transduce ubiquitous mechanical stimuli into exploitable electrical power. The present thesis investigates the potential of piezoelectric and triboelectric nanogenerators (PENGs and TENGs) as high-efficiency platforms for mechanical-to-electrical energy transduction, with particular emphasis on their applicability in self-sustaining, battery-free microelectronic systems. These nanogenerator architectures exploit the distinctive physicochemical properties of polymeric matrices and polymer-based nanocomposite materials to recuperate energy dissipated through routine anthropogenic activities, thereby establishing a renewable and decentralized power paradigm. Accordingly, this thesis presents a systematic and comprehensive investigation encompassing the rational design, controlled synthesis, and functional application of high-performance nanogenerators directed toward sustainable energy harvesting and environmental remediation.

In the first investigative phase, the influence of hydrothermally synthesized SnO₂/MXene (SNMX) nanocomposite fillers, introduced at low loading levels of 0.25, 0.50, and 0.75 wt%, on the electroactive phase content and dielectric behaviour of polyvinylidene fluoride (PVDF) was systematically examined. Morphological and structural characterization revealed a modified spherulitic microstructure indicative of a substantial phase transformation, with the non-polar α -phase fraction decreasing from 52% to yield a predominant polar ($\beta + \gamma$) phase content of 86%. Temperature- and frequency-dependent dielectric spectroscopy, conducted over 20 Hz to 1 MHz,

disclosed that at 25°C and 20 Hz, the relative dielectric permittivity of the 0.75 wt% SNMX/PVDF composite film was elevated approximately 25-fold relative to the pristine polymer, albeit accompanied by a high loss tangent of 2.2. A monotonic enhancement of dielectric permittivity with increasing operating temperature was observed across all composite formulations. The observed dielectric improvements are mechanistically attributed to: (a) the augmentation of the electroactive phase, which facilitates molecular dipolar reorientation under applied fields; and (b) the semiconductive SnO₂ interfacial layer on MXene flake surfaces, which suppresses the formation of percolative conductive pathways while concurrently enhancing interfacial polarization via the Maxwell–Wagner–Sillars (MWS) mechanism, in addition to conventional dipolar polarization contributions. A flexible device fabricated from the 0.75 wt% SNMX/PVDF nanocomposite film demonstrated a remarkable maximum peak-to-peak output voltage of 105 V, underscoring the exceptional energy harvesting efficacy of this nanocomposite system and its significant promise for next-generation self-powered electronic applications.

The second phase of this research is dedicated to the synthesis and physicochemical optimization of SnO₂/MXene/PVDF ternary composite films with the objective of enhancing their structural, optical, mechanical, dielectric, and electrical characteristics. Composite films comprising 2 wt% MXene nanosheets and varying concentrations of SnO₂ nanoparticles ($x = 0.0, 2.0, 4.0, 6.0,$ and 8.0 wt%) were fabricated via the solution casting technique and systematically characterized. X-ray diffraction (XRD) analysis confirmed a phase transformation from the non-polar α phase to the electroactive polar β phase within the PVDF matrix. Fourier-transform infrared spectroscopy (FTIR) quantified an enhancement in β -phase content from 65% in pristine PVDF to 80% in the optimized 6S-MP composite film. Field-emission scanning electron microscopy (FESEM) corroborated the formation of SnO₂ nanoparticles and the characteristic accordion-like morphology of the synthesized MXene, while also revealing that nanofiller incorporation induced significant morphological modifications attributable to disruption of matrix uniformity. Tauc plot analysis demonstrated a systematic reduction in both direct and indirect optical bandgap energies from 5.36 eV to 4.88 eV and from 5.11 eV to 4.61 eV, respectively,

as a function of increasing nanofiller concentration. Mechanical characterization further confirmed improvements in tensile strength and elastic modulus. Broadband dielectric spectroscopy conducted over the frequency range of 10^2 to 10^7 Hz revealed a fivefold enhancement in relative dielectric permittivity at 1 kHz for the 6S-MP composite relative to pristine PVDF, accompanied by a comparatively low loss tangent ($\tan \delta = 0.10$). Analysis of AC electrical conductivity in accordance with Jonscher's universal power law indicated a progressive increase with nanofiller loading and confirmed non-Debye relaxation behaviour. Collectively, these results establish that the 6S-MP composite film, incorporating 6 wt% SnO_2 and 2 wt% MXene, achieves an optimal balance of functional properties attributable to its elevated β -phase content, homogeneous nanofiller dispersion, and enhanced charge transport mechanisms, rendering it a promising candidate for the fabrication of flexible piezoelectric energy harvesting devices.

In the subsequent phase, the optimized 6S-MP composite film was employed in the fabrication of a Flexible Composite Piezoelectric Energy Harvester (FCPEH) device utilizing a conventional electrode-composite-electrode stack architecture. Under periodic palm tapping excitation, the FCPEH device yielded a maximum open-circuit voltage (V_{oc}) of 65 V and a peak power density of $43.8 \mu \text{W}/\text{cm}^2$, performance enhancements attributed to: (a) the uniformly distributed MXene network providing an expansive interfacial area conducive to efficient charge transfer; (b) the role of SnO_2 nanoparticles as heterogeneous nucleating agents promoting α to β phase transition; and (c) augmented interfacial polarization arising from the synergistic interaction of SnO_2 and MXene within the PVDF matrix. The device demonstrated sustained and stable average output voltage over a continuous operational period of 1000 seconds, affirming its mechanical robustness and long-term electrical stability. The practical utility of the optimized FCPEH device was validated through its successful application in: (1) real-time biomechanical motion detection, including heel strike, toe flexion, digital bending, pinching, and multi-finger tapping; (2) capacitive charging of $1 \mu \text{F}$ and $2.2 \mu \text{F}$ capacitors to 2.1 V and 1.3 V, respectively, within 80 seconds; and (3) simultaneous illumination of an eleven-LED array via palm tapping.

At the last phase, the PVDF-based composite films and ITO-coated PET substrates were employed as the triboelectric friction layers for device fabrication. The output performance of the TENG device increased progressively with increasing SnO₂ content, reaching an optimum at a filler concentration of 6 wt%. Among the investigated compositions, the composite containing 6 wt% SnO₂ and 2 wt% MXene exhibited the highest performance, generating a peak-to-peak open-circuit voltage of 210 V and a maximum power density of 1.01 mW cm⁻² at an optimal load resistance of 7 MΩ. This enhancement is primarily attributed to the increased dielectric constant, which promotes the formation of an effective microcapacitor network within the PVDF matrix, thereby increasing the surface charge density. Furthermore, the fabricated device demonstrated excellent operational stability over 500 contact-separation cycles. The practical applicability of the TENG was further validated through its successful operation in powering 31 LED and charging a capacitor.

These demonstrations collectively establish the above work as a meaningful advancement toward the realization of high-performance of flexible devices for biomechanical energy harvesting in self-powered wearable electronic applications.

LIST OF PUBLICATIONS

Publications included in this thesis:

1. **Gagan Sharma, and Deshraj Meena. “Substantial enhancement of the electroactive phase and dielectric properties at low loading levels of SnO₂/MXene nanocomposite as a novel nanofiller in the PVDF matrix”. *Materials Science in Semiconductor Processing* 195 (2025): 109607. [Impact factor-5.2]**
2. **Gagan Sharma and Deshraj Meena. “Optimization of SnO₂/MXene/PVDF Composites Films to Enhance Structural, Optical, Mechanical, Dielectric, and Electrical Characteristics Towards Next-Generation Flexible Optoelectronic and Energy Storage Devices” *Ceramic International* 52 (2026) 9125–9136. [Impact factor-6.0]**
3. **Gagan Sharma, Aman Kumar, Shivani Sangwan, Richa Sharma and Deshraj Meena. “Design and Development of a High-Performance PVDF based Flexible Composite Piezoelectric Energy Harvesting Device for Wearable Electronics”. *Surface and Interfaces* 95(2026)109748. [Impact factor-6.0]**
4. **Gagan Sharma, Deshraj Meena, Mohit Kumar, Aman Kumar, and Richa Sharma “Flexible Triboelectric Nanogenerators Based on SnO₂/MXene/PVDF Composite Films for Biomechanical Energy Harvesting” (Communicated).**

Publications not included in this thesis:

1. Shivani Sangwan, Aman Kumar, **Gagan Sharma**, Vinod Singh, Richa Sharma and Deshraj Meena “Heterostructured MXene@Ta₂O₅ Reinforced Based Flexible PENG for Efficient Mechanical Energy Harvesting”. *Applied Physics A* (2026) 132:617.
2. Yoshita Katiyar, Shivani Sangwan, **Gagan Sharma**, Mohit Kumar, Anshika Goyal, Manish Jain, and Deshraj Meena. “Ag@ SnO₂/g-C₃N₄ Ternary

Nanocomposite as an Efficient Acetone Vapors Sensor”. Chemistry Select 10, no. 23 (2025): e04081.

3. **Gagan Sharma**, Deshraj Meena. “Synthesis and characterization of C_3N_4 coupled SnO_2 and CNT nanocomposites as potential photoelectrode material”, Springer Nature’s Springer Proceedings in Physics.
4. Shivani Sangwan, **Gagan Sharma**, Manish Jain, M. C. Bhatnagar, and Deshraj Meena. “Sensing Influencing Factors of Semiconductor Metal Oxides Nanostructures based Resistive Gas Sensors: A Review”. (Under Review in Journal of Electronic Materials JEMS-D-25-01280)

LIST OF INTERNATIONAL CONFERENCES

Conference Contributions-Poster

- 1) Presented a Poster paper in the **International Conference On Atomic, Molecular, Material, Nano and Optical Physics with Applications (ICAMNOP)** organized by the Department of Applied Physics, **Delhi Technological University, Delhi, India** from **20th-22th Dec, 2023**.
- 2) **Presented** a Poster paper in the **International Conference on Thin Films and Nanotechnology - Knowledge, Leadership and Commercialization** organized by the Department of Physics, Indian Institute of Technology (IIT) Madras from 06th to 08th July, 2023.
- 3) **Presented** a Poster paper in the **International Conference on Advanced Materials for Emerging Technologies (ICAMET- 2023)**, held during May 4th-6th, 2023, at Netaji Subhas University of Technology New Delhi, India.

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LIST OF ABBREVIATIONS

Abbreviation	Full Form
IoT	: Internet of Things
SnO ₂	: Tin oxide
Ti ₃ C ₂ T _x	: Titanium carbide MXene
Ti ₃ AlC ₂	: Titanium aluminium carbide (MAX phase)
NPs	: Nanoparticles
PVDF	: Polyvinylidene fluoride
PENG	: Piezoelectric nanogenerator
TENG	: Triboelectric nanogenerator
Voc	: Open circuit voltage
TGTG'	: Trans-gauche-trans-gauche
TTTT	: All-trans
MWS	: Maxwell-Wagner-Sillars
AC	: Alternating current
DC	: Direct current
DMF	: N, N di-methyl formamide
wt%	: Weight percentage
RT	: Room temperature

CHAPTER 1

INTRODUCTION

This chapter presents a comprehensive and systematic examination of contemporary energy harvesting technologies, with particular emphasis on their multidisciplinary applications across various domains. It offers a rigorous and detailed discourse on mechanical energy harvesting methodologies, with concentrated focus on piezoelectric and triboelectric nanogenerators as prominent transduction mechanisms. The chapter is oriented toward addressing the critical and escalating demand for sustainable energy alternatives, with the overarching objective of mitigating dependence on finite fossil fuel reserves and accelerating the advancement of technologies capable of capturing and converting ubiquitous ambient energy into utilizable electrical output. Through a thorough investigation of the fundamental operating principles, inherent technical challenges, and recent scientific advancements in the field of energy harvesting, this chapter delineates a coherent and progressive trajectory toward the realization of an energy-efficient technological paradigm. Furthermore, it critically reviews and evaluates methodological strategies aimed at enhancing nanogenerator performance efficiency, encompassing optimized material selection and systematic structural engineering. The chapter culminates with a precise articulation of the research objectives, underscoring the imperative development of high-performance nanogenerator systems, and presents a structured delineation of the overall thesis framework.

1.1 Overview

The escalating global demand for energy has emerged as a critical challenge in contemporary society, largely attributable to the rapid proliferation of internet technologies, micro-electro-mechanical systems (MEMS), the Web of Things (WoT), and diverse sensor and actuator architectures. In this context, energy harvesting technologies capable of converting ambient mechanical energy into electrical energy have garnered considerable attention as a reliable and autonomous strategy for sustaining continuous power supply to low-power electronic systems[1-4]. The harvested electrical energy can be utilized both to augment the operational efficiency of existing devices and to power wireless sensor nodes or small-scale electronic systems.

The significance of energy harvesting has been further amplified by the progressive depletion of conventional fossil fuel reserves, compounded by the severe environmental degradation associated with their combustion. Concurrently, the past decade has witnessed substantial miniaturization in electronic device architecture, aimed at enhancing portability, operational efficiency, and user accessibility. However, this trend has necessitated a proportional reduction in battery dimensions, thereby constraining energy storage capacity. The predominant external power sources currently employed in portable electronics Li-ion batteries suffer from inherent limitations, including finite operational lifespans and adverse environmental implications upon disposal[5, 6]. Consequently, there exists an urgent and pressing demand for the development of efficient, environmentally sustainable, and durable alternative energy sources.

Furthermore, advances in nanotechnology have facilitated a substantial reduction in power consumption by microelectronic components, transitioning from the mW to the microwatt μ W regime[7, 8]. Nevertheless, the growing prevalence of nanoscale wireless systems encompassing wireless sensor networks, implantable biomedical devices, and related nano enabled platforms has intensified the demand for reliable micro power sources. Conventionally, these miniaturized wireless systems have been dependent on small-scale batteries that require periodic recharging, a constraint that

underscores the imperative to explore novel energy harvesting modalities with minimal environmental impact.



Figure 1.1: Various renewable energy sources present in world such as Solar, Wind, Hydropower, Biomass, Geothermal, Ocean energy (created using ChatGPT/DALL.E AI tool).

Figure 1.1 presents multiple types of renewable energy sources that can be harnessed from our world. Among the most widely investigated ambient energy sources are solar and wind energy[9]. Solar energy, abundantly available in the form of electromagnetic radiation and thermal flux, can be effectively transduced into electrical energy via photovoltaic cells. However, its energy output is inherently contingent upon the orientation of the harvesting surface relative to the sun, as well as prevailing atmospheric conditions; under overcast conditions or during nocturnal periods, photovoltaic efficiency is markedly diminished or entirely suppressed. Despite its high energy conversion potential, solar harvesting technology is fundamentally ill-suited for powering mobile and wearable electronic devices, given its requirement for fixed, stationary installation. Complementary solar thermal technologies, including thermal collectors and concentrating solar panels, enable the direct utilization of solar heat or its conversion into alternative energy forms. Similarly, wind energy facilitates electricity generation through the rotational actuation of turbines, which, when deployed in wind farms across hilly or remote

terrains, offer a viable and non-polluting energy generation mechanism. Nevertheless, both solar and wind energy systems are inherently subject to environmental variability and remain highly unpredictable, rendering them unsuitable as sole, dependable power sources for critical electronic applications[10, 11].

In contrast, mechanical vibration energy represents an abundantly available and environmentally independent form of ambient energy that remains largely underutilized. Mechanical vibrations span a broad spectrum of amplitudes and frequencies; biologically induced vibrations such as those arising from human motion typically occur in the frequency range of 1–10 Hz, whereas machine induced vibrations fall within the 10–100 Hz range [12, 13]. The harvesting of mechanical vibration energy encompassing sources from irregular airflow and ultrasonic waves to tidal forces and human body movement constitutes a particularly attractive approach owing to its ubiquitous availability and inherently ecofriendly nature.

In light of the aforementioned considerations, the present thesis systematically investigates novel strategies for the harvesting of mechanical energy through the exploitation of piezoelectric and triboelectric transduction mechanisms. Primary emphasis has been directed toward elucidating the underlying working mechanisms of these phenomena and toward the rational design of flexible energy harvesting devices capable of enhancing overall energy conversion efficiency in a cost-effective, structurally robust, and environmentally benign manner.

1.2 Mechanical Energy Harvesting Using Nanogenerators

A nanogenerator is defined as a micro to nanoscale energy transduction device capable of converting ambient mechanical energy into electrical energy through well-established electromechanical principles. The operational framework of nanogenerators is predominantly governed by two distinct physical mechanisms: the piezoelectric effect and the triboelectric effect. In piezoelectric based nanogenerators, electrical energy is generated through the application of mechanical stress to a piezoelectric material, which induces charge displacement and the development of an electric potential across the material. Triboelectric nanogenerators, in contrast, produce electrical output through the coupled mechanisms of contact electrification

and electrostatic induction during the cyclic contact and separation of dissimilar material surfaces.

Beyond their fundamental energy transduction capabilities, nanogenerators demonstrate considerable potential for seamless integration into wearable electronic platforms including smart biosensors and smartwatches enabling the continuous harvesting of electrical energy from the biomechanical motion of the human body as shown in Figure 1.2. The energy thus harvested can be effectively utilized to power the host device, substantially reducing dependence on conventional electrochemical batteries and extending operational autonomy. Consequently, nanogenerators represent a highly promising technological framework for the realization of self-powered electronic systems and the efficient utilization of ubiquitous ambient mechanical energy. Their multifunctional potential and adaptability across diverse application domains have firmly established nanogenerators as a dynamic and rapidly advancing research frontier within the broader field of sustainable energy harvesting technologies.



Figure 1.2: Different applications of the flexible nanogenerator (created using ChatGPT/DALL.E AI tool).

1.2.1 Piezoelectric Nanogenerator

Piezoelectric nanogenerator (PENG) operate on the principle of converting ambient mechanical energy into electrical power via the piezoelectric effect, a phenomenon intrinsic to non-centrosymmetric materials that generate surface charge accumulation in response to applied mechanical stress or strain. Figure 1.3 illustrate the working mechanism of PENG in different states. External stimuli including compressive pressure, bending deformation, vibrational excitation, or kinetic motion induce structural distortion within the piezoelectric lattice, resulting in dipole displacement, charge separation, and the establishment of a measurable electric potential. The resultant induced charges are subsequently harvested through electrode configurations, rendering mechanical energy from the surrounding environment into a viable electrical energy source[14].

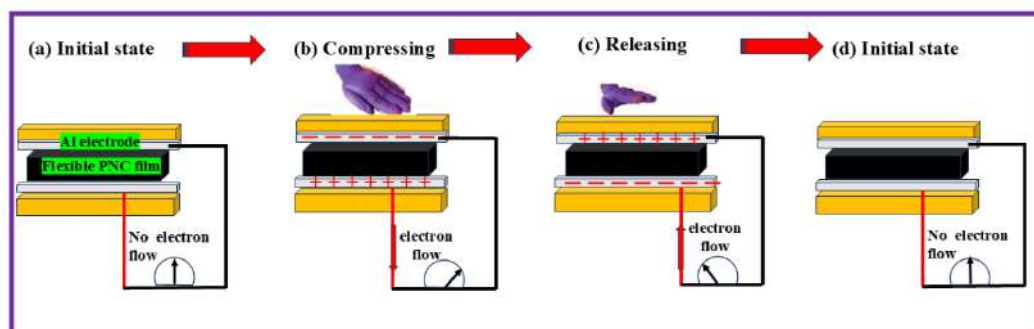


Figure 1.3: A schematic showing the working mechanism of PENG at different conditions.

The piezoelectric effect was originally identified in 1880 by Pierre and Jacques Curie, whose foundational experiments demonstrated that mechanical stress applied to certain crystalline materials could induce electrical polarization. This seminal discovery laid the groundwork for subsequent advancements in the field. Nearly a century later, in 1969, Kawai and Kureha reported appreciable piezoelectric activity in polyvinylidene fluoride (PVDF), documenting a piezoelectric coefficient superior to that of other known polymeric materials. A landmark development was realized in 2006, when the research group led by Zhong Lin Wang fabricated the first ZnO nanowire-based piezoelectric nanogenerator. By employing a conductive atomic force microscope (AFM) tip to apply localized mechanical force to individual ZnO nanowires, the study provided compelling experimental evidence that piezoelectric

nanostructures are capable of generating electrical energy, thereby establishing a new paradigm in nanoscale energy harvesting[15].

Subsequent investigations have concentrated on refining device architecture and enhancing output performance. Vertically aligned ZnO nanowire arrays integrated with zigzag electrode configurations were developed to facilitate continuous direct-current generation from ultrasonic wave stimulation. To address the structural limitations associated with vertically oriented configurations, laterally packaged ZnO fine-wire nanogenerators were introduced, demonstrating improved mechanical stability, manufacturability, and operational resilience under adverse environmental conditions. These architectures additionally yielded output voltages exceeding those of earlier fiber based and direct-current nanogenerator designs. More recently, high-performance direct-current PENGs incorporating lithium (Li)-doped ZnO nanosheets have been reported, wherein p-type doping effectively reduced free electron concentration, mitigated piezoelectric screening effects, and substantially elevated the piezoelectric output power density.

From a fundamental standpoint, the piezoelectric effect is reversible in nature and manifests through two complementary mechanisms: the direct piezoelectric effect and the converse piezoelectric effect. The direct effect, which constitutes the operative principle underlying energy harvesting, describes the generation of an electric potential in a non-centrosymmetric material subjected to mechanical stress. Conversely, the converse piezoelectric effect refers to the mechanical deformation induced within such materials upon the application of an external electric field, forming the functional basis for actuator and acoustic transducer technologies. In the absence of external mechanical perturbation, the internal molecular dipoles of piezoelectric materials maintain a symmetric arrangement, yielding zero net polarization at the macroscopic level[16]. Upon the application of mechanical stress, this structural symmetry is disrupted, precluding complete charge cancellation and resulting in the emergence of surface polarization and a measurable electrical potential.

The density of electric dipoles inherent to a piezoelectric material is a determining factor governing its functional performance and electromechanical response

characteristics. To maximize dipole density, these materials are subjected to an intense external electric field in proximity to the Curie temperature a process formally designated as poling. This procedure induces a net remnant polarization within the material matrix, which exhibits a measurable dependence on applied mechanical stress, thereby augmenting the overall piezoelectric response. It is well established that the majority of ferroelectric materials demonstrate piezoelectric behaviour however, this relationship is not reciprocally valid, as piezoelectricity does not necessarily imply ferroelectricity. The piezoelectric effect fundamentally represents an electromechanical coupling phenomenon, characterizing the interaction between the electrical and mechanical properties of the material. The electrical constitutive behaviour of the material is expressed as

$$D_i = \sum_{j=1}^3 \epsilon_{ij} E_j \text{ or } D = \epsilon E \quad 1.1$$

Where ϵ_{ij} is electric permittivity, D_i is electric displacement, E_j is electric field.

The relation between stress and strain

$$S_{ij} = \sum_{k,l=1}^3 S_{ijkl} T_{kl} \quad 1.2$$

Where S_{ij} is elastic compliance of the material. The reduced tensor equation of piezoelectric material as

$$D_i = E_j \epsilon_{ij}^T + d_{ij} T_j \quad 1.3$$

$$S_I = T_j S_{IJ}^E + d_{IJ} E_j \quad 1.4$$

Where the T and E the coefficients at constant stress and electric and d_{ij} is the strain constant respectively.

Device is said to work in d_{33} mode after applying stress in the same direction of polarization, and then

$$Q_{PENG} = A \sigma d_{33} \quad 1.5$$

6

where σ is the stress along the direction of applied force, A is the area of the piezoelectric material, d_{33} is the piezoelectric charge coefficient. The piezoelectric potential

$$V_{PENG} = t\sigma g_{33} \quad 1.6$$

where t and g_{33} is the thickness of the piezoelectric material and piezoelectric voltage coefficient respectively.

PENGs present several compelling attributes, including compact form factors, structural flexibility, low power consumption thresholds, and the capacity to harvest energy from ubiquitous ambient sources such as human biomechanical motion, wind, and hydrodynamic wave action. These characteristics render PENGs particularly well-suited for integration into wearable electronics, self-powered sensing platforms, and distributed micro-energy systems. To further augment device performance and facilitate scalable deployment, a range of optimization strategies have been pursued, encompassing material-level approaches such as compositional doping, ferroelectric poling, and nanostructure engineering, as well as fabrication techniques including electrospinning, hot pressing, and 3D printing, complemented by advanced structural and device-level engineering. Collectively, these methodologies have yielded substantial improvements in power density and energy conversion efficiency, thereby accelerating the translational potential of piezoelectric nanogenerators toward practical and commercially viable applications[17, 18].

1.2.2 Triboelectric Nanogenerators

In 2012, Professor Zhong Lin Wang and his research group introduced the Triboelectric Nanogenerator (TENG), a groundbreaking energy harvesting technology premised upon the triboelectric effect[19]. Since its initial conceptualization, TENG technology has undergone substantial developmental progression in terms of both device architecture and functional applicability. The widespread scientific interest in TENGs is attributed to a confluence of favourable characteristics, including cost-effective fabrication, relatively straightforward manufacturing processes, mechanical resilience, minimal gravimetric density, and inherent scalability[20]. Given the

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pervasive availability of mechanical energy in natural and anthropogenic environments encompassing wind, oceanic wave motion, human biomechanical activity, and industrial machine vibrations TENGs provide an effective and sustainable mechanism for capturing energy that would otherwise be irreversibly dissipated in the form of thermal radiation, acoustic emissions, or unutilized kinetic movement. In addition to powering low-consumption electronic devices, TENGs have demonstrated considerable utility as self-powered sensing platforms, thereby extending their operational relevance to real-time monitoring and diagnostic applications.

Fundamentally, TENG operation is governed by the triboelectric effect, wherein electrical charges are generated at the interface of two materials possessing dissimilar electron affinities upon contact and subsequent separation. This well-documented electrostatic phenomenon commonly observed in macroscopic contexts such as hair combing or balloon friction produces surface charges whose magnitude and polarity are dictated by intrinsic material parameters, including surface morphology, polarity, and susceptibility to mechanical deformation. These material-dependent charge transfer tendencies are systematically categorized within the triboelectric series, which ranks materials according to their relative propensity to donate or acquire electrons. Long regarded primarily as an electrostatic hazard or nuisance in industrial settings, the triboelectric effect has been recently reconceptualized as a powerful and exploitable mechanism for micro and nanoscale energy harvesting, enabling the practical implementation of functional TENG devices[21].

The operational principle of a TENG integrates two interdependent electrostatic mechanisms: contact electrification and electrostatic induction. Upon mechanical contact between two dissimilar material surfaces, charge transfer occurs at their shared interface as a consequence of differences in electron affinity as shown in Figure 1.4. As the surfaces undergo separation, the resulting spatial redistribution of charges establishes a potential difference between the connected electrodes, thereby driving electron flow through an external circuit and generating an electrical current. The cyclic repetition of contact and separation events produces an AC output. Relative to alternative mechanical energy harvesting technologies, TENGs exhibit a

notable capability to generate elevated output voltages even at low operational frequencies, complemented by advantages including straightforward fabrication protocols, structural flexibility, and versatile compatibility with diverse mechanical energy inputs.

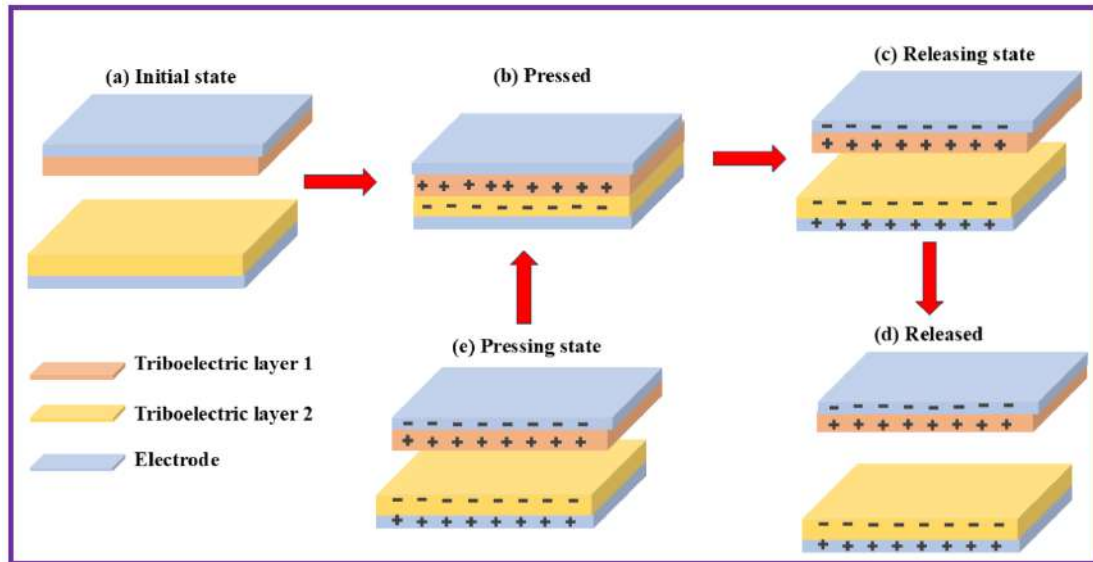


Figure 1.4:A schematic showing the working mechanism of TENG at different conditions.

The output voltage generated by TENG given by

$$V = -\frac{Q}{C(x)} + V_{OC}(x) \quad 1.10$$

This relationship is commonly referred to as the $V-Q-x$ relationship and describes the intrinsic capacitive behavior of the TENG. Here V_{OC} denotes the open-circuit voltage, $C(x)$ represents the capacitance between the two electrodes as a function of the separation distance (x), and (Q) corresponds to the amount of charge transferred between the electrodes[22].

TENGs are broadly classified into four principal operational modes: contact-separation, lateral sliding, single-electrode, and freestanding triboelectric-layer modes. These distinct configurations afford considerable design flexibility, enabling customization for targeted applications and specific mechanical excitation inputs. A conventional TENG architecture comprises two triboelectric layers equipped with appropriate electrode assemblies and insulating interlayers, arranged in either

dielectric or metal dielectric configurations. The selection of dielectric materials further influences the effective dielectric constant of the device, thereby modulating its energy storage capacity and charge transfer efficiency.

Under the application of external mechanical stimuli including compressive pressure, flexural deformation, or vibrational excitation the triboelectric layers undergo repeated contact and separation cycles, progressively disrupting the electrostatic equilibrium at the material interface and generating alternating potential differences across the electrode assembly. This dynamic electrostatic process enables sustained and continuous charge generation, which is subsequently collected by the electrodes as harvestable electrical energy. By virtue of their compact dimensions, high electromechanical conversion efficiency, mechanical durability, and low fabrication cost, TENGs are uniquely positioned for integration into wearable electronic systems, self-powered sensing networks, and distributed energy harvesting infrastructures, firmly establishing them as a technologically promising platform for the advancement of sustainable and self-sufficient electronic devices.

1.3. Polymers for the Flexible Nanogenerators

The fabrication of nanogenerators, encompassing both piezoelectric and triboelectric variants, has increasingly leveraged flexible polymeric materials owing to their superior vibration absorption capacity, environmental compatibility, and long-term mechanical durability. In this context, electroactive polymers have garnered considerable scientific attention for their multifunctional applicability in sensing, actuation, and mechanical energy harvesting, collectively designating them as smart materials.

Historically, piezoelectric behaviour was considered an exclusive characteristic of ceramic materials. However, in 1963, piezoelectric activity was first identified in two synthetic polymers, namely poly (methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC), marking a pivotal advancement in polymer science[23, 24]. Subsequently, Kepler reported piezoelectric behaviour in polyvinylidene fluoride (PVDF), while the ferroelectric properties of PVDF were formally established by Kepler and Anderson in 1978[25, 26]. Additional polymers documented to exhibit

piezoelectric characteristics include nylon-11, poly(L-lactic acid) (PLLA), poly(lactic-co-glycolic acid) (PLGA), polyamide, parylene-C, among others.

Among the known piezoelectric polymers, PVDF and its copolymers demonstrate the highest piezoelectric coefficients; however, their piezoelectric response remains comparatively lower than that of piezoceramic counterparts[27]. Despite their superior electromechanical performance, piezoceramics are inherently limited by their geometric rigidity and susceptibility to microcrack formation under repeated mechanical loading, which critically compromises their structural integrity and functional lifespan. Consequently, contemporary research efforts have increasingly shifted toward the development of flexible piezoelectric polymer-based nanogenerators, which offer enhanced mechanical compliance, broader substrate compatibility, and superior resistance to cyclic stress-induced degradation. Within this domain, PVDF has been extensively investigated due to its notable environmental stability, biocompatibility, and intrinsic piezoelectric response. The subsequent chapters of this thesis provide a comprehensive discussion of the structural characteristics and functional properties of PVDF and the relevant nanostructures investigated herein.

1.3.1 Polyvinylidene fluoride (PVDF)

PVDF is a semicrystalline homopolymer composed of repeating $(-\text{CH}_2-\text{CF}_2-)$ monomer units, wherein the molecular backbone incorporates electropositive hydrogen atoms and electronegative fluorine atoms. The spatial arrangement of these CH_2-CF_2 dipolar units gives rise to several distinct crystalline phases in PVDF, most notably the α , β , γ , and δ phases, each characterized by a unique molecular conformation and corresponding electromechanical response[28, 29]. Figure 1.5 shows a schematic image of the conformation of α , β , and γ phase in PVDF. Among these polymorphic phases, the β phase represents the most polar and electroactive crystalline configuration. In the α -phase, the molecular chain adopts an all-trans (TTTT) conformation, wherein hydrogen and fluorine atoms are arranged in an alternating fashion along the backbone[30]. This symmetric disposition of dipoles

results in mutual cancellation, yielding a net zero electric dipole moment across the polymeric chain[31, 32].

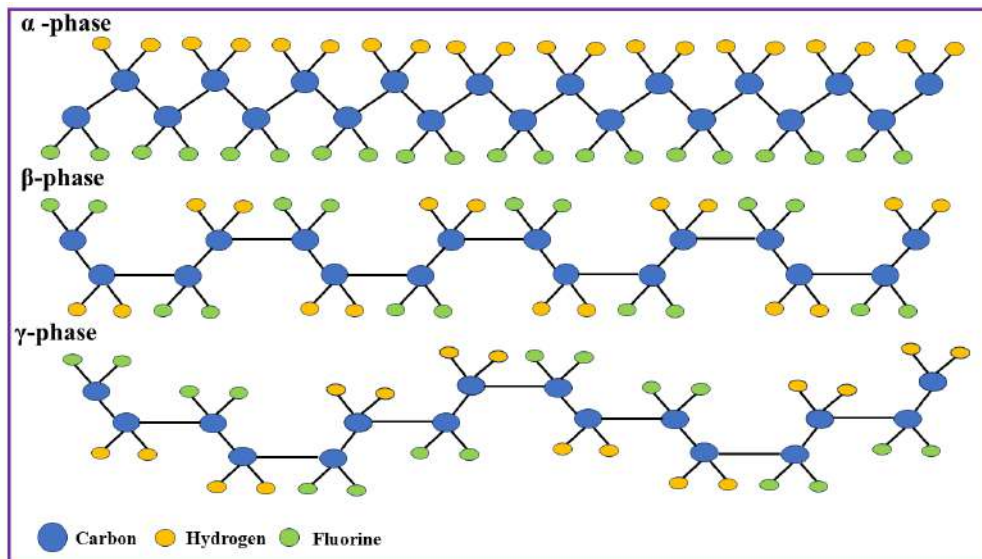


Figure 1.5: A schematic of conformation of α , β , and γ phase in PVDF.

In contrast, the β -phase adopts an alternating trans-gauche (TGTG') conformation, in which the hydrogen and fluorine atoms are segregated to opposing sides of the chain. This asymmetric arrangement generates a substantial net electric dipole moment, conferring strong piezo- and pyroelectric activity upon the material[33]. The γ -phase, which exhibits a T₃GT₃G' conformation, similarly possesses a net electric dipole moment attributable to the directional arrangement of hydrogen and fluorine substituents however, the magnitude of this dipole is comparatively lower than that observed in the β -phase[34]. Given these structural distinctions, maximizing the β -phase content within PVDF is of paramount importance for enhancing its piezoelectric and pyroelectric performance. The piezoelectric response of PVDF is directly correlated with the proportion of the electroactive polar β -phase present within the polymeric matrix, thereby underscoring the critical role of phase engineering in optimizing the functional properties of PVDF-based devices.

1.3.2 Strategies for Enhancing the Performance of PVDF-Based Nanogenerators

The nucleation of the electroactive β -phase polymorph within PVDF constitutes a fundamental prerequisite for the fabrication of high-performance piezoelectric energy harvesting devices. The preferential crystallization of PVDF into its β phase configuration can be accomplished through a encompassing mechanical stretching-induced chain alignment (formation of a necking region during stretching), melt crystallization conducted under conditions of minimal supercooling (melt-crystallized at high supercooling temperatures), ultrafast thermal quenching (non-isothermal mode at ultra-high cooling rates ranging between 30–3000 K), controlled melt annealing protocols (melting re-crystallization of a phase), and the deliberate incorporation of extrinsic filler materials into the polymer matrix[35-39]. Among the aforementioned strategies, the integration of external fillers has garnered considerable scientific attention owing to the precise and tunable control it affords over β -phase nucleation kinetics and crystallographic orientation.

Consequently, the development and augmentation of the β phase content within PVDF is a critical objective for advancing its suitability in efficient flexible devices. The impregnation of nanofillers having inherent high piezoelectric properties within the PVDF matrix is the good approach to increase its polar phase fraction. However, these nanofillers often demonstrate poor compatibility with the PVDF matrix due to a propensity for agglomeration within flexible composite.

1.3.3 Nanofiller Materials and Their Role

The choice of nanofiller also influences phase transitions within the polymer. A variety of nanofillers have been incorporated into PVDF matrices to enhance their electrical and dielectric performance. The incorporated nanofillers can be classified into three main categories: inorganic, organic, and hybrid composites combining inorganic and organic nanofillers. Incorporating inorganic nanofillers into the polymer matrix enhances the dielectric properties of PVDF while preserving the benefits of both components. SnO₂ nanostructures have been established as an efficient inorganic nanofiller. For example, Zhe et al. reported a high dielectric constant of approximately 300 at 10 kHz for SnO₂/PVDF nanocomposites with a high nanofiller concentration of 0.16 vol%. Adding nanostructure of inorganic materials significantly

elevates specific surface interactions, which improves PVDF's electroactivity thus the dielectric properties[40].

However, the independent use of inorganic nanofillers, such as TiO₂, SnO₂, BaTiO₃, etc., often results in trade-offs, such as increased dielectric loss, reduced mechanical flexibility and crystallinity of the PVDF. This is primarily attributed to the high nanofiller concentrations and the larger dielectric gradient. To address the limitations of inorganic nanofillers, organic/conductive nanofillers such as reduced graphene oxide (rGO), MXene, and multi-walled carbon nanotubes (MWCNTs) have been incorporated into polymer matrices. These nanofillers have proven effective in substantially enhancing the dielectric constant, reducing the optical energy band gap and electrical conductivity even at low concentrations, without compromising the flexibility of PVDF. Ti₃C₂T_x MXene has gained attention as an effective conductive filler due to its exceptional electrical conductivity of approximately 6500 S/cm and an elastic modulus of around 0.33TPa. MXene-based polymer nanocomposites are capable of achieving high dielectric constants with low percolation thresholds. However, as the filler loading approaches the percolation threshold, there is a significant boost in dielectric constant, dielectric loss, and electrical conductivity[41-43]. This underscores the necessity for surface modifications, such as the incorporation of insulating or semiconductive layers, to optimize the material's performance. However, these nanofillers are often associated with relatively high dielectric loss due to the nanofiller agglomeration, which leads to the formation of conductive networks at higher nanofiller concentrations. This phenomenon reduces the break down strength of the material, thereby lowering its energy storage density and limiting its practical applicability in energy storage devices.

Nowadays, the incorporation of the dual nanofillers into PVDF matrix have emerged as an efficient approach to improve its polar phase without disturbing the crystallinity and flexibility. In this regard, the combination of 2D conducting materials (like as graphene oxide, hexagonal boron nitride (h-BN), MXene etc.) with ceramics (BaTiO₃, ZnO, TiO₂ etc) is gaining interest among the researchers [22, 30-32]. This unique combination of 2D conducting and ceramics nanoparticles offers synergistic advantages. The high conductivity, large specific surface area, and excellent

flexibility of the 2D materials which facilitate β -phase nucleation by promoting the alignment of polymer chains, enabling interfacial interactions that orient molecular dipoles, and inducing crystallisation within the PVDF matrix. Whereas the ceramic nanoparticles serve as nucleating agents for polar phase transformation of the PVDF. Thus, the optimized combination of the 2D materials and ceramic dual fillers in PVDF matrix improves its piezoelectric behaviour.

Recently, incorporation of inorganic nanomaterials/MXene nanocomposites as nanofillers have attracted considerable interest among researchers due to their notable advantages. Specifically, the dispersion of semiconductive layer of inorganic nanomaterials on MXene nanosheets obstruct the establishment of conductive pathways. Thereby suppressing the electrical conductivity and enhances the charges at surfaces, thus improves the dielectric properties. Like as Feng et al. synthesized BaTiO₃/MXene/PVDF composites, incorporating 8 wt % BaTiO₃ and 2 wt% MXene, which exhibited a dielectric constant of 77 and a loss of 0.15 at 100 Hz[44]. Similarly, at 1 kHz, the MXene/TiO₂/MoS₂/P(VDF-HFP) nanosheet-loaded nanocomposite films, with an optimal loading of 8.0 wt%, demonstrated a high dielectric constant of 944 while maintaining a low dielectric loss of 0.19[43]. Similarly, the incorporation of filler into the PVDF matrix has proven to be highly effective in enhancing the piezoelectric performance of PVDF. For instance, Kumari P. et al. Reported the improved output power 0.14 mW/cm² of PVDF films upon the addition of BaTiO₃ nanofillers[45].

Thus, MXene and metal oxide nanostructures have emerged as an excellent nanofiller for the PVDF matrix, significantly enhancing its structural, optical, mechanical, dielectric, and electrical conductivity properties. The key advantages of incorporating metal oxide nanostructures with MXene as nanofillers include: (1) reduced leakage conduction in the composites, and (2) lower dielectric loss, which enhances the breakdown strength of the composite, thereby leading to a higher energy storage density. Recent reports on the incorporation of TiO₂, MnO₂, and similar nanostructures along with MXene as nanofillers have revealed notable enhancements in the properties of PVDF. However, according to the available literature, detailed information on the optimal wt% of SnO₂ and MXene in PVDF for achieving

maximum structural, optical, mechanical, and electrical properties is still lacking. Additionally, the eco-friendly and easily synthesized nature of SnO_2 , along with its versatile optical and electrical properties, makes it a suitable choice as a nanofiller

For example, Yousaf et al. achieved an open-circuit voltage ($V_{oc} = 16.3 \text{ V}$) and maximum power density ($170 \mu\text{W}/\text{cm}^2$) using optimised MXene/ ZnO /PVDF composite NG device. The obtained results are attributed to the piezoelectric behaviour of ZnO and MXene's high conductivity, helping better charge separation and transportation[46]. Similarly, Chauhan et al. demonstrated highest β -phase content (85.6 %) in PVDF by incorporating the carbon nanofiber (CNF) and ZnO nanorods (NR) in PVDF matrix. The dual nanofillers PVDF composite film based piezoelectric device yield a V_{oc} of 80 V and power density of $20 \text{ mW}/\text{cm}^3$ under periodic palm tapping[47]. The improved performance of the device is due to (a) CNF forms charge transfer networks at an optimized loading, (b) ZnO NR act as efficient nucleating agents, promoting polar phase transformation.

In the framework of the present thesis, intrinsically piezoelectric nanostructures were deliberately selected and systematically integrated into PVDF polymer matrices, with a focused investigation into the underlying physicochemical and crystallographic mechanisms governing the enhancement of piezoelectric properties within the resulting nanocomposite systems. Furthermore, the applicability of these engineered PVDF based flexible piezoelectric nanocomposites as active functional materials in PENG and TENG architectures were rigorously explored, with the objective of broadening their utility in the domain of multifunctional mechanical energy harvesting technologies.

1.4 Nanofillers

1.4.1 Tin Oxide (SnO_2)

Metal oxide semiconductors constitute a broadly significant and continually expanding class of functional materials, owing to their inherently tuneable energy band gaps, exceptional chemical inertness, and robust mechanical stability properties that have collectively driven their integration into an increasingly diverse range of technological applications. The progressive maturation of advanced fabrication

methodologies, enabling the controlled synthesis of metal oxides in various nanostructured morphologies including thin films, nanoparticles, nanowires, and nanorods has substantially broadened their functional utility, extending well beyond conventional semiconductor electronics into domains such as chemical sensing, optoelectronics, heterogeneous catalysis, and energy harvesting and storage systems. Within this expansive materials landscape, Tin oxide (SnO₂) has garnered considerable and sustained research interest as a prominent transparent conducting oxide (TCO), a distinction that has been extensively documented and reviewed across the scientific literature[24].

A particularly noteworthy characteristic of tin dioxide is its capacity to form oxides of varying valence states, which endows the material with a remarkable versatility to participate in both catalytic reaction pathways and electrochemical charge storage processes. As the thermodynamically most stable oxide of tin, SnO₂ has established itself not merely as a high-performance TCO, but also as a multifunctional material of considerable relevance to sustainable development objectives. Its earth-abundant availability, inherent non-toxicity, and wide optical band gap collectively render SnO₂ a highly attractive candidate for deployment across a spectrum of applications, encompassing chemical sensing, catalytic systems, and electrochemical energy harvesting and storage technologies thereby positioning it as a material of both fundamental scientific interest and significant practical consequence [22].

1.4.2 MXene

Considerable and sustained research efforts have been devoted to the identification and development of suitable materials capable of efficiently capturing diverse forms of ambient energy, with the ultimate objective of realizing high-performance miniaturized energy harvesting modules.

In this context, 2D materials have attracted substantial scientific attention as compelling candidates for extending the applicability of Moore's law within the domain of microscale energy harvesting. Among the expanding family of 2D materials, MXene a class of 2D transition metal carbides, nitrides, and carbonitrides have emerged as particularly promising functional materials for ambient energy

harvesting, owing to a distinctive combination of physicochemical attributes that collectively facilitate the efficient transduction of multiple energy forms into electrical energy as shown in Figure 1.6.

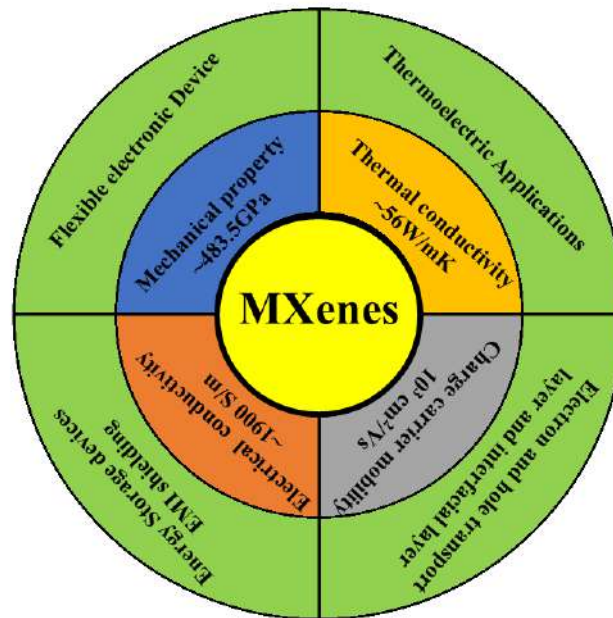


Figure 1.6: Various characteristics of MXene.

Specifically, the advantageous properties of MXene in this regard may be delineated as follows: (1) MXene inherently exhibit metallic-level electronic conductivity, which minimizes resistive energy dissipation during charge transport and current flow upon conversion to electrical energy; (2) the intrinsic 2D morphology of MXene confers an exceptionally high specific surface area and elevated aspect ratio, enabling nanostructures derived therefrom to achieve a large effective active area within a compact geometric footprint; (3) relative to other solution-processable 2D materials, MXene demonstrate superior mechanical stability, thereby ensuring enhanced durability and operational reliability in energy harvesting applications subjected to cyclic mechanical loading; (4) the abundance of surface functional groups endows MXene with pronounced hydrophilicity and a distinctive surface charge distribution, which are particularly conducive to electrokinetic current generation in aqueous operating environments; and (5) the highly tuneable physicochemical properties of MXene achievable through systematic variation of elemental composition and surface

termination chemistry render them adaptable to a broad spectrum of targeted energy harvesting scenarios[48-51].

Capitalizing on these multifaceted advantages, a diverse array of MXene-based nanostructures has been explored for ambient energy harvesting since the material's first synthesis in 2011, yielding consistently encouraging results[52]. To date, MXene-based architectures have demonstrated the capability to harvest an extensive range of energy sources, encompassing solar energy, thermoelectric energy, triboelectric energy, piezoelectric energy, salinity-gradient energy, electrokinetic energy, ultrasonic energy, and humidity-driven energy, each mediated through its respective and mechanistically distinct energy transduction pathway. Collectively, these exceptional properties position MXene as highly effective and multifunctional nanofillers within PVDF based nanogenerator systems, supporting the realization of efficient, mechanically flexible, and durable device platforms with broad applicability in sustainable energy harvesting, wearable electronic systems, and self-powered sensing technologies.

1.5 Research Gap

A significant knowledge gap persists concerning the intrinsic nanofiller properties that govern energy conversion efficiency. Although PVDF exhibits remarkable mechanical flexibility, its inherent piezoelectric and triboelectric outputs remain inadequate for large-scale applications. Thus, systematic optimization of the polymer matrix via the strategic incorporation of a well-designed nanofiller combination is critically needed. The mechanisms by which nanofillers modulate molecular crystallization, surface charge density, and interfacial polarization remain poorly understood. Furthermore, minimizing filler weight fraction while preserving maximum flexibility and environmental compatibility constitutes a principal challenge in material design.

Notwithstanding notable progress in nanogenerator design and fabrication for mechanical energy harvesting, a substantial research gap persists regarding the comprehensive understanding of material properties governing the operational efficiency of both piezoelectric and triboelectric nanogenerators. Additionally,

inadequate mechanical robustness, poor stability, and performance degradation under real operating conditions remain critical limitations. Rapid advancements in nanotechnology, however, offer a viable pathway to enhance piezoelectric performance through precise manipulation of material properties at the nanoscale.

To substitute toxic lead-based piezoceramics and brittle fillers, efficient metal oxide alternatives are actively pursued. While SnO₂ and MXenes have been independently studied, their synergistic coupling as SnO₂ nanoparticles with conductive MXene nanosheets remains largely unexplored for mechanical energy harvesting. Composites with varying SnO₂ and fixed MXene weight fractions offer a strategic approach to overcome existing material limitations. Additionally, the influence of the SnO₂/MXene heterostructure on the piezoelectric performance of the PVDF matrix is systematically examined.

1.6 Thesis Scope

This thesis aims to improve the output performance of the fabricated PENG and TENG devices using PVDF based composite flexible films. The detail investigation has been done on how SnO₂ and MXene nanofillers at relatively lower concentration enhances the dielectric, structural and mechanical properties of the heterostructure of SnO₂ and MXene contribute to enhancing overall device efficiency across a broad spectrum of applications. Such incorporated nanofillers approach opens new avenues for deploying nanogenerators in wearable electronics, IoT devices, and biomedical sensors where compact design, high efficiency, and reliable power output are essential requirements.

1.6.1 Research Aims and Objectives

The main objective of the thesis is the synthesis, characterization and exploring potential application of SnO₂ and MXene based on PVDF composite film. And to construct a Flexible composite piezoelectric energy harvesting device based on above synthesized PVDF nanocomposite films for multipurpose applications, particularly by utilizing piezoelectric and triboelectric phenomena to capture ambient mechanical energy. The following is a summary of the primary goals of this study:

- To synthesize tin oxide (SnO_2) nanoparticles and MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) via the hydrothermal method and selective etching of aluminum layers from Ti_3AlC_2 MAX phase using hydrofluoric acid (HF) as an etchant, respectively followed by comprehensive characterization of the synthesized materials.
- To synthesize a SnO_2 /MXene (SNMX) heterostructure embedded within the PVDF matrix and to investigate its dielectric properties as a function of temperature variation, along with assessing the piezoelectric output performance of the corresponding flexible composite devices.
- To optimize of SnO_2 /MXene/PVDF composites films to enhance their structural, optical, mechanical, dielectric, and electrical characteristics towards next-generation flexible optoelectronic and energy storage devices
- To design and construct Flexible Composite devices using the fabricated composite films and to evaluate their piezoelectric and triboelectric output performance by applied mechanical force.
- To explore and demonstrate the practical applicability of the constructed all flexible devices for sustainable mechanical energy harvesting applications, with emphasis on performance optimization and real-world utility.

1.6.2 Thesis Structure and Organization

The present thesis is organized into seven chapters. In the first chapter, a brief overview, working principle, material requirement, motivation, objectives, and thesis outlines are described. In the second chapter, the experimental method with different characterization techniques and electric measurement of energy harvesting device. In chapter third, fourth, fifth and sixth, synthesis of nanomaterial and PVDF composites film and their piezoelectric and triboelectric performance are presented. Finally in chapter seven, thesis conclusion and future perspective of the present research work are presented. The thesis is organized in the following chapters:

Chapter 1: Introduction

This chapter provides a succinct overview of the need for sustainable energy solutions, highlighting the significance of energy harvesting technology in meeting

global energy demands. Additionally, as we enter the smart era, wearable and portable electronics are becoming commonplace across various industries, including wireless sensor networks, healthcare, artificial intelligence, and IoT. However, one of the biggest challenges with modern electronic devices remains their power supply. To address this issue, wearable and portable devices must be powered by cleaner, renewable energy sources. Consequently, a variety of energy harvesting devices based on electromagnetic, piezoelectric, triboelectric, and pyroelectric phenomena have been developed over time. Among these, mechanical energy harvesters are particularly significant, as they utilize piezoelectric and triboelectric nanogenerators to convert ambient mechanical energy such as vibrations, movements, and slight pressure variations into electricity. Owing to their capabilities, these systems are ideal for powering smart systems and distributed IoT devices that require low-power, continuous energy sources without relying on traditional power networks or frequent battery replacements. This chapter further explores how piezoelectric and triboelectric nanogenerators, as advanced technologies, are especially well-suited to meet these energy demands due to their efficiency, scalability, and potential for integration into a wide range of applications. Moreover, they offer a promising pathway toward a more sustainable and energy-efficient future by addressing the energy challenges posed by the rapid growth of smart devices and systems.

Chapter 2: Synthesis and characterization techniques

Chapter 2 provides a comprehensive overview of the experimental methodologies employed for the synthesis and characterization of the samples, along with the relevant theoretical foundations underlying each technique. A detailed discussion of various synthesis approaches is presented, including the hydrothermal method, thermal polymerization, and other relevant techniques. This chapter further describes the characterization methods used to investigate the as-prepared nanomaterials and nanocomposites. The fundamental principles, advantages, and limitations of key analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), UV–visible spectroscopy, are critically examined. In addition, the fabrication of a flexible composite-based piezoelectric energy harvesting device, designed for both triboelectric and piezoelectric measurements, is described.

Chapter 3: Substantial enhancement of the electroactive phase and dielectric properties at low loading levels of SnO₂/MXene nanocomposite as a novel nanofiller in the PVDF matrix

Chapter 3 presents the hydrothermal synthesis of a nanocomposite consisting of SnO₂ nanoparticles combined with 20 wt% Ti₃C₂T_x MXene nanosheets. The resulting SNMX nanocomposite was incorporated as a nanofiller into PVDF composite films at three different loadings (0.25, 0.50, and 0.75 wt%). The SNMX nanocomposite demonstrated a strong tendency to promote the formation of electroactive β and γ phases within the PVDF matrix. Furthermore, the composite films exhibited remarkable improvements in dielectric performance, with the 0.50 wt% and 0.75 wt% SNMX/PVDF films achieving relative dielectric permittivity (ϵ_r) values of 150 and 165, and loss tangent ($\tan\delta$) values of 0.8 and 2.1 at 20 Hz, respectively. Temperature-dependent analysis revealed that the relative dielectric permittivity of the 0.75 wt% SNMX/PVDF film rises to 250 at 100°C. The combination of enhanced electroactive behavior, superior dielectric properties, and outstanding mechanical durability positions these SNMX/PVDF films as promising candidates for flexible energy-harvesting applications in piezoelectric-based portable electronics. Of particular significance, the piezoelectric flexible nanogenerator (PENG) fabricated from the 0.75 wt% SNMX/PVDF nanocomposite film delivers an impressive peak-to-peak output voltage of 105 V.

Chapter 4: Optimization of SnO₂/MXene/PVDF composites films to enhance structural, optical, mechanical, dielectric, and electrical characteristics towards next-generation flexible optoelectronic and energy storage devices

Chapter 4 presents a PVDF composite film were developed by incorporating a distinctive combination of SnO₂ nanoparticles and MXene nanosheets as nanofillers, aimed at enhancing structural, morphological, optoelectronic, mechanical, dielectric, and electrical characteristics. The composite films were prepared via the solution casting technique and thoroughly evaluated using multiple characterization methods. The results demonstrate that the 6S-MP composition (6 wt% SnO₂ and 2 wt% MXene) yields the most favorable performance, exhibiting the highest β phase

content, a narrowed energy band gap, superior tensile strength, enhanced dielectric response, and improved electrical conductivity. With its cost-effectiveness, environmental compatibility, and ease of scalability, the 6S-MP composite film holds significant promise for driving advancements in next-generation optoelectronic and energy storage applications.

Chapter 5: Design and Development of High Performance PVDF based Flexible Composite Piezoelectric Energy Harvesting Device towards Wearable Electronics

Chapter 5 present, a dual nanofiller system comprising MXene nanosheets and SnO₂ nanoparticles was introduced into a PVDF matrix to develop flexible composite films via the solution-casting method, with MXene concentration held constant while SnO₂ loading was systematically varied. The β phase crystallization behavior and surface morphology of the fabricated composite films were examined through various characterization techniques. Among all compositions, the optimized 6S-MP formulation (2 wt% MXene and 6 wt% SnO₂) delivered the best piezoelectric performance as a flexible composite piezoelectric energy harvesting (FCPEH) device, achieving a peak open-circuit voltage (V_{oc}) of 65 V and an outstanding output power density of 43.8 μ W/cm². The 6S-MP FCPEH device further demonstrated its practical viability by successfully powering 11 commercial LEDs and charging capacitors of 1 μ F and 2.2 μ F through periodic palm tapping. These compelling results, driven by the device's superior energy harvesting efficiency, establish it as a strong candidate for integration into self-powered wearable sensors and next-generation energy harvesting systems.

Chapter 6: Conclusion, Future Scope & Social Impact

This chapter presents a thorough overview of the principal findings of the thesis, with particular emphasis on mechanical energy harvesting technologies, encompassing both piezoelectric and triboelectric nanogenerators. It further outlines potential directions for future research that could accelerate progress toward self-sustaining energy systems, ultimately broadening the practical applicability of nanogenerators in real-world scenarios.

Chapter 1

CHAPTER 2

EXPERIMENTAL DETAILS AND CHARACTERIZATION TECHNIQUES

This chapter outlines the experimental procedures employed for the synthesis of filler particles within the PVDF matrix and the subsequent fabrication of composite films. The hydrothermal and etching methods were utilized for the preparation of filler materials, both of which are discussed in detail throughout the chapter. Flexible composite films were fabricated using the drop casting method. A comprehensive overview of the working principles of the various characterization techniques and instruments employed in this study is also provided to facilitate a thorough understanding of the analytical approach. Phase formation and morphological analysis of the prepared powders and flexible films were carried out using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), UV-Visible Spectroscopy, Universal Testing Machine (UTM), and Fourier Transform Infrared Spectroscopy (FTIR). The dielectric properties of the fabricated composite films were evaluated using an impedance analyzer. To assess the energy harvesting performance, mechanical force was applied to the surfaces of the fabricated PENG and TENG devices through finger tapping, and the resulting open-circuit voltage was recorded using a digital storage oscilloscope.

2.1 Introduction

Considerable emphasis has recently been directed toward the advancement of nanotechnology, particularly within the scientific, industrial, and research sectors. This rapidly evolving field presents numerous unexplored opportunities with substantial potential to enhance both human life and the surrounding environment. Over the course of the last decade alone, a diverse array of multifunctional nanoscale inorganic building blocks including nanoparticles, nanotubes, nanowires, and nanorods have been successfully synthesized, exhibiting a broad spectrum of remarkable mechanical, optical, electrical, and structural properties.

In the pursuit of developing superior and high-performance materials, both sample preparation and characterization constitute indispensable procedural steps. Comprehensive material characterization encompasses compositional analysis, phase analysis, surface characterization, and structural as well as microstructural analysis, all of which exert a significant influence on the resultant material properties. Consequently, the characterization of material features at the nanoscale has catalyzed the emergence of numerous advanced methodologies within the field of materials science.

Among these, sophisticated characterization and measurement techniques such as X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, and impedance spectroscopy have proven instrumental in uncovering novel and compelling physicochemical phenomena that would otherwise remain inaccessible through conventional analytical approaches (Fig 2.1). In light of the above, the present chapter provides a comprehensive overview of the synthesis methods and characterization techniques employed for SnO₂ nanoparticles, 2D MXene nanosheets, and PVDF nanocomposite films. Furthermore, the fabrication of a flexible composite piezoelectric energy harvesting device, along with the corresponding electrical measurements and performance evaluation, is systematically described.

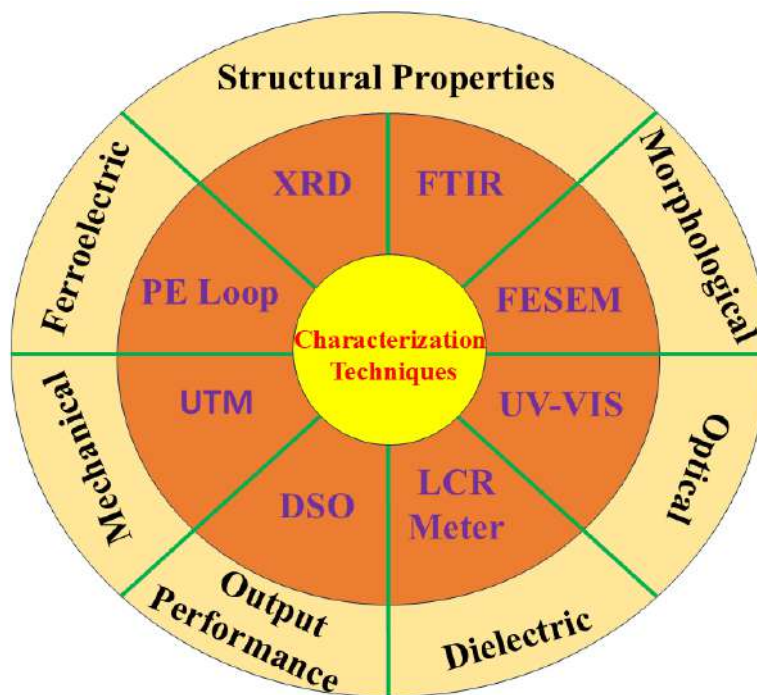


Figure 2.1: Various technique for characterization and output performance.

2.2 Synthesis method

In the present thesis work, we have synthesized SnO_2 particle by using hydrothermal method and MXene using HF etching method. Also, the $\text{SnO}_2/\text{MXene}$ (SNMX) nanocomposite synthesized using hydrothermal method. The synthesis of PVDF composite using solution casting method.

2.2.1 Hydrothermal Method

The term “hydrothermal” is derived from two components: “hydro,” meaning water, and “thermal,” meaning heat. The first report on crystal formation using the hydrothermal method was presented by Karl Emil von Schafhäütl in 1845[53].

The hydrothermal technique employs an aqueous solution as the reaction medium within a specially designed sealed vessel, where elevated temperature and pressure are generated either through external heating or the autogenous vapor pressure of the system. Figure 2.2 shows a digital photograph and schematic of hydrothermal autoclave set-up. This approach enables the creation of a high-temperature, high-pressure reaction environment suitable for material synthesis. Nanomaterials

synthesized via this method typically exhibit high purity, uniformity, well-defined crystal symmetry, and distinctive physicochemical properties[54, 55]. In addition to facilitating synthesis at relatively low temperatures and shorter reaction times, the hydrothermal method provides enhanced control over the size, composition, and density of the final products. Crystal formation under hydrothermal conditions primarily involves the dissolution of reactants in the aqueous medium, followed by the transport and separation of ionic or molecular species driven by a temperature gradient within the vessel[56].

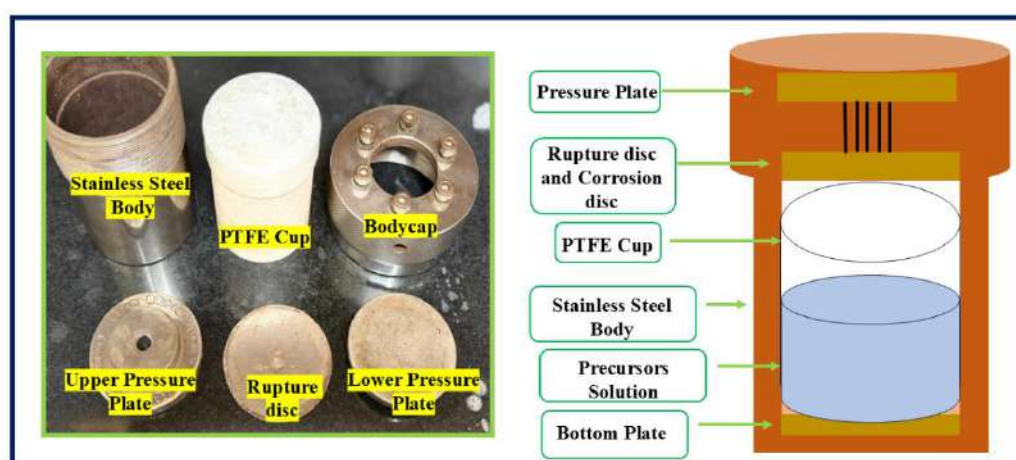


Figure 2.2: A digital photograph and schematic of hydrothermal autoclave set-up used in hydrothermal synthesis.

As these species migrate toward regions of lower temperature, a supersaturated solution is formed, promoting nucleation and growth on seed crystals. At the growth interface, processes such as adsorption, decomposition, and desorption occur, leading to the crystallization of the dissolved species and the formation of the desired product. The morphology of the resulting crystals is strongly influenced by the growth conditions; thus, variations in hydrothermal parameters can yield diverse morphologies for the same material.

2.2.2 Etching Method

MXene are synthesized through the selective chemical etching of the A-layer from the corresponding MAX phase precursor, wherein M denotes an early transition metal, A represents a group IIIA or IVA element, and X signifies carbon and/or nitrogen. The removal of the A-layer via this etching process induces a fundamental transformation

in the structural morphology of the MAX phase, yielding layered 2D materials that bear a strong structural resemblance to graphene an analogy that served as the conceptual basis for the designation "MXene." The resulting MXene compounds adopt the general chemical formula $M_{n+1}X_nT_x$, where n assumes integer values ranging from 1 to 4, and T denotes the diverse surface functional groups predominantly hydroxyl ($-OH$), fluorine ($-F$), and oxygen ($-O$) terminations that are spontaneously introduced onto the MXene surface as a direct consequence of the chemical etching process[57]. These surface terminations play a critical role in governing the physicochemical properties of MXene, including their hydrophilicity, electrochemical behavior, and interfacial interactions with surrounding matrices, thereby rendering the precise control of surface chemistry a key parameter in the functional optimization of MXene-based materials for advanced applications[52].

HF etching represents the most widely employed and technically efficient methodology for the synthesis of MXene; however, the inherent limitations and considerable safety hazards associated with this approach have necessitated the exploration and development of alternative synthetic routes. Specifically, HF-based etching is predominantly applicable to MAX phases containing Al as the A-layer element, thereby constraining the compositional diversity of MXene accessible through this method as shown in Figure 2.3. Furthermore, the etching process conducted in an HF environment invariably results in MXene nanosheets bearing predominantly fluorine ($-F$) surface termination groups, which restricts the tunability of surface chemistry and may adversely influence the functional performance of the resulting materials in certain applications[58]. The acute toxicity, corrosive nature, and stringent handling requirements associated with HF additionally impose significant practical and safety-related constraints on its large-scale utilization in laboratory and industrial settings. Collectively, these limitations underscore the critical imperative to develop safer, more versatile, and compositionally inclusive alternative methodologies for MXene synthesis, capable of yielding materials with controlled surface functionalization and expanded structural diversity beyond those achievable through conventional HF-based etching protocols.

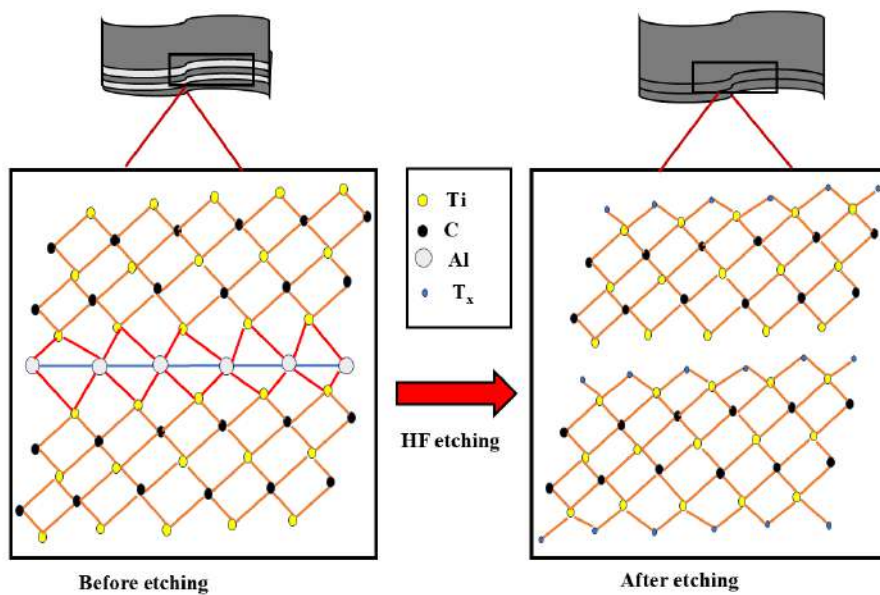


Figure 2.3: Removal of Al layer by using HF etching.

2.2.3 Synthesis of Flexible Composite Films: Drop Casting Method

As Drop casting is a simple and efficient technique widely employed for the fabrication of thin films with controlled thickness and composition. In the present study, this method was utilized to prepare flexible films based on polymer and polymer nanocomposite materials. The technique is particularly advantageous in applications requiring precise control over film characteristics. The drop-casting process begins with dissolving the solutes in a suitable solvent at a predetermined concentration. The solution is thoroughly mixed using a magnetic stirrer, followed by ultrasonication in an ultrasonic bath to ensure complete homogeneity. The selection of solvent and solute concentration plays a critical role in achieving the desired film properties. Figure 2.4 shows the schematic diagram for the synthesis of flexible PVDF and PVDF composite films via drop casting method, a predefined concentration of the prepared solution is then dispensed onto a glass substrate using a micropipette. Subsequently, the substrate is placed in an oven maintained at a constant temperature to facilitate solvent evaporation, leading to the formation of a film with the desired thickness.

This method is favoured due to its simplicity, cost-effectiveness, and ability to control film thickness and composition by adjusting the solution concentration and deposition volume. However, variations in film thickness may occur, and factors such as solvent

evaporation rate and substrate surface characteristics can influence the final film properties. Therefore, careful optimization of these parameters is essential to obtain smooth, uniform films with consistent thickness.

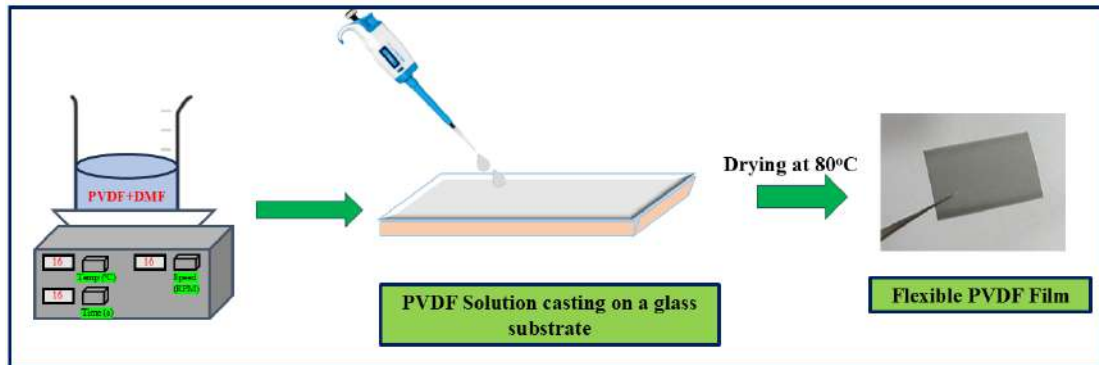


Figure 2.4: The schematic diagram for the synthesis of flexible PVDF and PVDF composite films via drop casting method.

2.2.4 Fabrication of Flexible Composite Energy Harvesting Device

Synthesized flexible composite films were cut into small pieces of area $(2.5 \times 2.5) \text{ cm}^2$ for the fabrication of PENG and TENG device.

The composite-based PENG device was fabricated by typical electrode composite electrode stack technique. To prevent electrode shorting at any endpoint, the device was fabricated by sandwiching the composite films between two metallic (aluminium) electrodes, which served as the top and bottom charge collecting layers. The electrode areas were slightly smaller ($2.2 \text{ cm} \times 2.2 \text{ cm}$) than the film area. Bipolar copper wiring connected to the electrodes for getting voltage output. Kapton tape, known for its neutral piezoelectric effect, was used to enclose the entire prototype. This encapsulation not only offers enhanced protection against wear, mechanical agitation, and other potential losses during energy-harvesting measurements but also minimizes charge carrier exchange between the surrounding air and the electrode layers. Similarly, for TENG device was assembled using the PVDF composite film as the active triboelectric layer and PET film as the counter triboelectric layer. Aluminium adhesive tape was applied to the PVDF film surface as the bottom electrode, while PET film served as the top electrode, completing the sandwich-type structure. Copper wire was used to establish electrical interconnections for device characterization.

2.3 Characterization Techniques

Several characterization techniques such as X-ray diffraction, Field Emission scanning electron microscopy, UV-vis absorption spectroscopy, and Universal Testing Machine, are utilized to confirm the successful synthesis of SnO₂, MXene and its heterostructure together with their polymer nanocomposite films.

2.3.1. X-ray Diffraction

The crystal structure of materials can be determined using X-ray diffraction (XRD), a powerful analytical technique. In this method, a crystalline sample is irradiated with an X-ray beam, and the intensity of the scattered X-rays is measured. Analysis of the resulting diffraction pattern provides information about the atomic arrangement within the crystal lattice[59].

When a monochromatic X-ray beam of wavelength λ is incident on a crystalline material at an angle θ , constructive interference (diffraction) occurs only when the path difference between X-rays reflected from successive lattice planes satisfies Bragg's condition (Fig 2.5)[60].

$$2d \sin \theta = n\lambda \quad 2.1$$

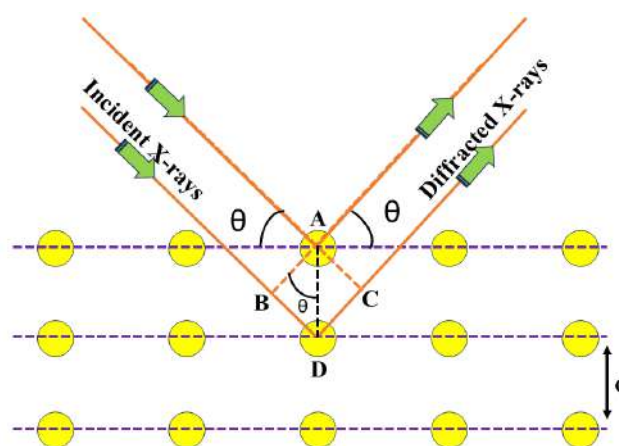


Figure 2.5: A Schematic showing the diffraction of X-rays obeying Brags law.

Figure 2.6 shows the experimental configuration for XRD measurements. The setup primarily consists of four components: an X-ray source, a sample holder, a goniometer, and an X-ray detector. The X-ray source typically comprises a cathode

ray tube, in which a high voltage is applied to heat the filament (cathode), resulting in the emission of electrons. These electrons are accelerated toward a copper target (anode). Upon impact, the high-energy electrons eject inner-shell electrons from the copper atoms, leading to the generation of characteristic X-rays. These X-rays are then directed onto the sample, where they are diffracted by the periodic arrangement of atoms in the crystal lattice. The diffracted X-rays are subsequently detected, and the recorded diffraction pattern is used to identify and analyze the crystal structure of the sample. To characterize the structural properties of the synthesized materials, X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV diffractometer equipped with Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

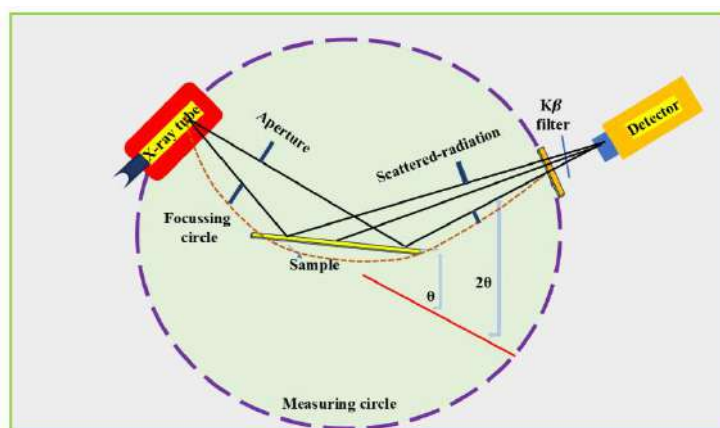


Figure 2.6: A Schematic showing the components of XRD diffractometer

2.3.2 Field Emission Scanning Electron Microscopy

A field emission scanning electron microscope (FESEM) employs a high-energy electron beam to image the surface morphology of a sample. Unlike optical microscopes, which use light for image formation, FESEM utilizes electrons to generate highly magnified and high-resolution images.

In its fundamental operation, an electron beam is generated and focused onto the sample surface using a series of electromagnetic lenses. Upon interaction with the sample, secondary electrons are emitted from the surface[61]. These emitted electrons are collected by a detector, and the resulting signal is processed to form an image of the sample. A typical FESEM system comprises several essential components,

including a specimen stage for mounting the sample, a secondary electron (SE) detector for collecting secondary electrons, a backscattered electron (BSE) detector, an image display unit, a control system for instrument operation, and an electron optical column for generating and focusing the electron beam (Fig 2.7).

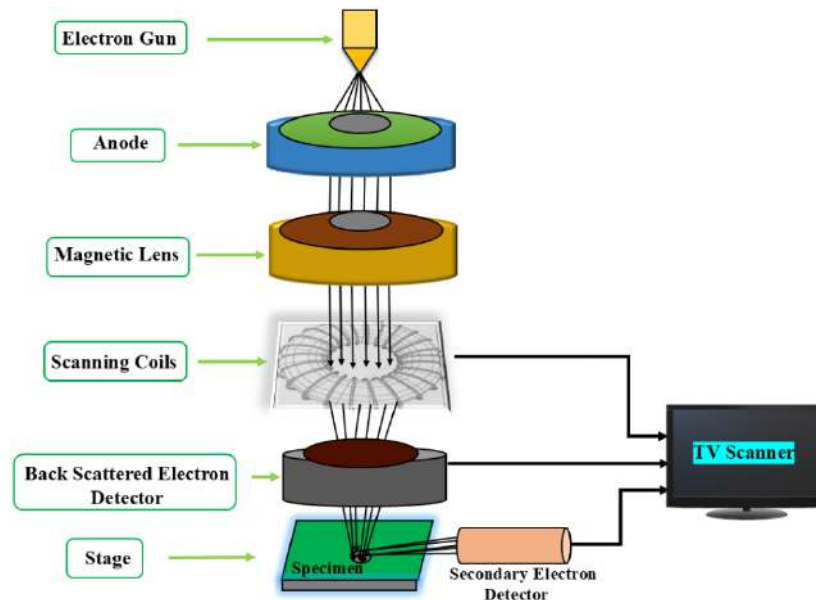


Figure 2.7: Schematic illustrating the components of FESEM.

Compared to conventional thermionic emission sources, the field emission source often based on lanthanum hexaboride (LaB6) or similar materials produces a significantly finer and more coherent electron beam, resulting in improved spatial resolution. Under a high electric field gradient, electrons are extracted from the field emission source and accelerated toward the sample. These primary electrons are focused and scanned across the sample surface by electromagnetic lenses within a high-vacuum column[62]. When the primary electrons interact with the atoms of the sample, they excite the valence electrons, leading to the emission of secondary electrons. Due to their low energy, only secondary electrons generated near the surface can escape and be detected, while those produced deeper within the material are reabsorbed. Consequently, secondary electrons are highly sensitive to surface features and are primarily used for topographical imaging of the sample. Backscattered electrons, in contrast, are high-energy electrons that are elastically scattered and reflected back from the sample. These electrons originate from deeper regions within the material and carry compositional information. The intensity of

backscattered electrons depends strongly on the atomic number of the constituent elements; regions with higher atomic numbers appear brighter in BSE images. Therefore, backscattered electron imaging is particularly useful for distinguishing compositional variations within the sample. The signals obtained from both secondary electron and backscattered electron detectors are converted into electrical signals, processed, and displayed as grayscale or false-color images on a computer monitor. The surface morphology of the synthesized particles was examined via field emission scanning electron microscopy (FESEM, JEOL JSM-7800F Prime).

2.3.3 Energy Dispersive X-ray Spectroscopy

An effective method for determining the elemental composition and chemical compounds present in a sample is energy-dispersive X-ray spectroscopy (EDS). An EDS system is typically integrated with a scanning electron microscope (SEM), which provides the appropriate region of the sample for analysis. During measurement, a focused electron beam strikes the sample, interacts with its atoms, and ejects electrons from the inner (K) shell. When an electron is excited to a higher energy state, a vacancy is created in the inner shell. Electrons from higher energy levels, such as the L, M, and N shells, then transition to fill the K-shell vacancy, releasing excess energy in the form of X-rays[63].

After being emitted from the sample, the generated X-rays enter the detector, where they produce electrical pulses. These pulses carry information about the elemental composition of the sample and are subsequently converted into digital signals. After the measurement is complete, a characteristic X-ray spectrum is obtained, in which the primary peaks correspond to the elements present in the specimen. Elemental composition and spatial elemental distribution of the films were determined using energy-dispersive X-ray spectroscopy (EDX, SWIFT ED 3000).

2.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is an indispensable analytical technique for investigating the vibrational characteristics of functional groups present in organic and semi-organic compounds. The analysis is conducted by exposing the sample to electromagnetic radiation within

the spectral range of 400-4000 cm^{-1} . Upon absorption of infrared radiation, the vibrational energy levels of molecular bonds undergo transitions that manifest in two primary modes: stretching and bending vibrations. This technique is particularly effective for identifying organic molecules containing polar bonds and strong dipole moments, such as N-H, O-H, and C-H functional groups[64].

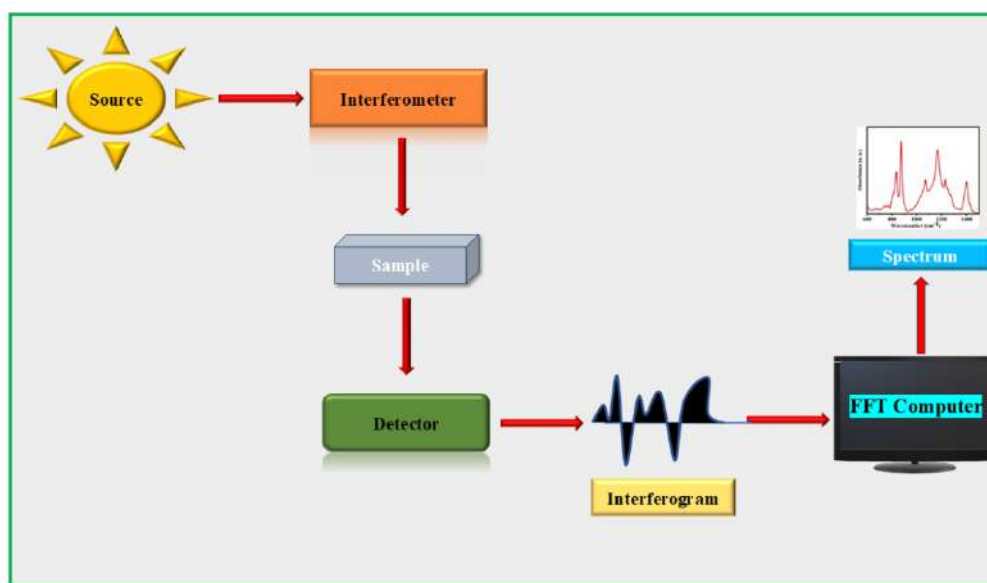


Figure 2.8: Basic layout of the component of FTIR

Among the principal advantages of FTIR spectroscopy are its rapid scanning capability relative to conventional dispersive techniques and its versatility in analyzing samples across all three physical states solids, liquids, and gases. The fundamental basis of this approach lies in the characteristic vibrational behaviour of molecular bonds, which is governed by the nature of the constituent atoms. When a sample is irradiated with infrared light, its molecules absorb energy and undergo transitions to higher vibrational energy states (excited states). Upon relaxation to their ground (deexcited) states, the molecules emit radiation corresponding to the energy difference between the excited and ground states. Each material selectively absorbs specific infrared wavelengths from the incident radiation, thereby generating a unique spectral fingerprint. The resonant vibrational frequencies are influenced by several parameters, including atomic masses, vibronic coupling, and molecular potential energy surfaces[65].

Consequently, a direct relationship exists between bond types and their corresponding vibrational frequencies. Simple diatomic molecules, for instance, exhibit only a single stretching vibration, whereas more complex polyatomic compounds display multiple vibrational modes, including both stretching and conjugate (coupled) vibrations. These interactions give rise to characteristic infrared absorption frequencies associated with specific chemical groups. Since each functional group possesses a distinct vibrational energy, IR spectroscopy yields a unique spectral fingerprint that facilitates unambiguous identification[66].

FTIR spectroscopy enables the identification of materials and their bonding characteristics through measurement of the wavelengths absorbed by the sample. The resulting spectrum is conventionally presented with wavenumber (cm^{-1}) along the x-axis and either transmittance or absorbance along the y axis. The number and position of absorption peaks are determined by the chemical composition of the sample. Precise identification of functional groups is achieved by carefully analyzing and comparing these peaks against reference infrared spectra of known bonds and compounds.

The sequential stages of the FTIR process are depicted in Figure 2.8. In this optical configuration, infrared radiation emitted from the source is directed through a collimator before reaching a beam splitter. The beam splitter divides the incident beam into two equal components; each directed toward a separate mirror one of which undergoes continuous translational movement. This motion introduces an optical path difference between the two beams, thereby modulating the wavelengths of the incident radiation at varying frequencies. Upon reflection from their respective mirrors, the two beams recombine to produce a complex interference pattern known as an interferogram.

The resulting interferogram is subsequently transmitted through the sample, which selectively absorbs specific wavelengths from the incident spectrum, as previously described. A detector records the intensity of the transmitted radiation as a function of wavelength. The collected signal is then processed using a mathematical Fourier transform algorithm, which converts the raw interferogram into an interpretable

spectral dataset. The final spectrum obtained through this transformation provides a comprehensive basis for the identification of multiple functional groups within the analyzed sample. In the present thesis work, identification of electroactive phases in both PVDF and composite films was conducted using Fourier-transform infrared spectroscopy (FTIR, Nicolet 5700).

2.3.5 UV-Visible Spectroscopy

A quantitative method called UV-Vis Spectroscopy quantifies the amount of light that a sample absorbs or transmits in relation to a reference sample (Fig. 2.9). To do this, the quantity of light passing through a sample is compared to the amount of light passing through a reference sample. A number of variables, including sample concentration and composition, affect light intensity. Beer-Lambert's law states that the absorbance of light is directly proportional to both the concentration of the sample and the path length.

The Beer-Lambert law is[67]

$$A = \epsilon l C \quad 2.2$$

where, l is the length covered by the light through the sample, C is the concentration, ϵ is the molar extinction coefficient, and A is the amount of light absorbed[68]. The bandgap of the material is estimated by tauc's equation[69]

$$(\alpha h\nu)^n = (h\nu - E_g) \quad 2.3$$

where, E_g , α , and $h\nu$ is the energy band gap of sample, absorption coefficient, and energy of the incident photon, respectively, and $n=1/2$ is used for indirect bandgap and $n=2$ for direct bandgap. By extrapolating the linear region of the plot $(\alpha h\nu)^n$ on the Y-axis versus the photon energy ($h\nu$) on the X-axis, the E_g value obtained.

In a spectrophotometer that uses two lamps, the visible light source is usually a tungsten or halogen lamp, while the UV light source is usually a deuterium lamp. Light is divided into a narrow range of wavelengths using a monochromator.

Typically, absorption filters are composed of coloured glass that is intended to absorb particular wavelengths of light.

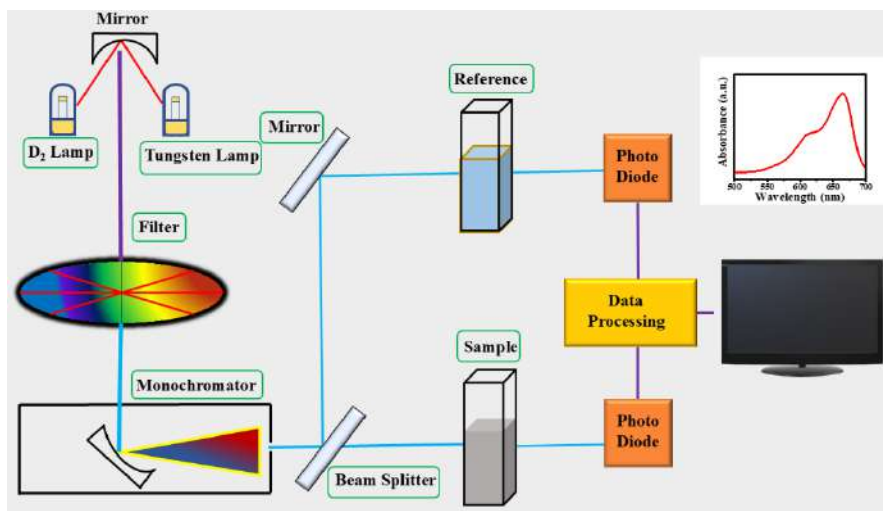


Figure 2.9: Schematic diagram of UV-visible spectrophotometer used to analyze the optical properties[70].

By causing destructive interference, these filters can be employed as a wavelength selector to remove undesirable wavelengths. The light then travels through a sample using the spectrophotometer's chosen wavelength selection. A CCD detector is used to transform light into a readable electrical signal once it has passed through the sample. The output is sent to a computer or screen once the signal has been recognized. The schematic diagram of the UV-vis apparatus used for optical absorption analysis is displayed in Fig. 2.9. In the present study the optical bandgap of the samples was estimated through UV-Visible absorption spectroscopy using a PerkinElmer Lambda-1050 spectrophotometer. .

2.3.6 Dielectric/Impedance Analyser

In William Whewell initially used the term "dielectric." The ratio of the capacitance of a capacitor containing the material to that of the same capacitor in vacuum is known as the dielectric property, and it describes a material's capacity to store electrical energy. It is represented as follows:

$$\epsilon_r = \frac{C}{C_0} \quad 2.4$$

where, ϵ_r is the dielectric constant, C is the capacitance of the dielectric material and C_0 is the capacitance in vacuum.

Two parallel conducting plates spaced apart by a distance (d) make up a parallel plate capacitor. The capacitance C_0 of a parallel plate capacitor that is vacuum-sandwiched between its two plates is displayed as

$$C_0 = \frac{A\epsilon_0}{d} \quad 2.5$$

where, ϵ_0 ($= 8.854 \times 10^{-12}$ F/m) is the permittivity of free space, A is the area of the plates of capacitor.

On combining equation 2.4 and 2.5,

$$\epsilon_r = \frac{Cd}{A\epsilon_0} \quad 2.6$$

For an alternating electric field, dielectric constant is given by

$$\epsilon^* = \epsilon_r - j\epsilon_r'' \quad 2.7$$

where, (ϵ_r) is real component of dielectric constant and (ϵ_r'') is an imaginary component of dielectric constant.

The dissipation factor, or dielectric loss ($\tan \delta$), is computed as the ratio of the complex permittivity's imaginary and real parts, as shown by:

$$\tan \delta = \frac{\epsilon_r''}{\epsilon_r} \quad 2.8$$

In the present work, the dielectric constant of the prepared samples was measured using an Impedance Analyzer (Model: KEYSIGHT E4990A). Instrument consists of a sample holder, PID temperature controller unit, Vacuum chamber, and Impedance Analyzer.

2.4 Electrical Measurements of Nanogenerators

The electrical characterization of both the PENG and TENG devices was systematically conducted by affixing aluminum electrodes onto the PVDF and PVDF

composite films. Copper interconnects were subsequently drawn from the designated electrode terminals to establish the requisite electrical circuit connections. The mechanical tapping method was employed to quantify the output performance of the frequency-coupled piezoelectric energy harvester (FCPEH) devices. A high-precision digital storage oscilloscope (Tektronix MDO 500) was utilized to acquire and record the open-circuit output voltage signals generated by the FCPEH devices under varying mechanical stimuli and human-body-induced biomechanical motions. Furthermore, a full-wave bridge rectifier integrated circuit (DB107) was incorporated into the measurement configuration to characterize the rectified electrical output performance of the fabricated nanogenerators, enabling the quantitative assessment of both the rectified voltage and current parameters under the aforementioned excitation conditions.

CHAPTER 3

SUBSTANTIAL ENHANCEMENT OF THE ELECTROACTIVE PHASE AND DIELECTRIC PROPERTIES AT LOW LOADING LEVELS OF SnO₂/MXENE NANOCOMPOSITE AS A NOVEL NANOFILLER IN THE PVDF MATRIX

In this chapter, we investigate the impact on electroactive phase and dielectric properties of polyvinylidene fluoride (PVDF) on addition of hydrothermally synthesized SnO₂/MXene (SNMX) nanocomposite with different concentration (0.25wt%, 0.50wt%, 0.75wt%) as nanofillers. The pure and SNMX/PVDF composite films were fabricated using solution casting method. Morphological and structural analyses revealed a modified spherulitic structure, indicating a transformation from the non-polar phase (52%) to the polar ($\beta + \gamma$) phase (86%). The dielectric measurements were conducted over a frequency range of 20 Hz to 1 MHz at different operating temperature to examine the various relaxations occurring in the polymer. At 25°C and an applied field frequency of 20 Hz, the relative dielectric permittivity of the SNMX/PVDF composite film (0.75 wt%) elevates approximately 25-fold relative to the pristine PVDF film, with a concomitant reduction in loss tangent. Further, the relative dielectric permittivity of all films intensifies with rising operating temperature. At 100°C, the relative dielectric permittivity amplifies from 165 to 250 compared to room temperature for the 0.75 wt% nanofiller concentration. The increment in dielectric properties with addition of SNMX are attributed to a) the enhancement of the electroactive phase, which favours molecular reorientation, b) the presence of SnO₂ semiconductive layer on the surface of MXene flakes that prevent formation of conductive pathways, thus improves the interfacial polarization through the Maxwell–Wagner–Sillars (MWS) effect in addition to dipolar polarization. A piezoelectric flexible nanogenerator (PENG) fabricated from the 0.75wt% SNMX/PVDF nanocomposite film generated a maximum peak to peak voltage is 105 V.

3.1 Introduction

In recent years, flexible dielectric materials have garnered significant interest due to their potential applications in the rapidly developing field of flexible nanoelectronics. In this context, dielectric polymers have attracted considerable attention because of their desirable physical and chemical properties [31, 71, 72]. However, polymers generally exhibit lower dielectric constants compared to inorganic materials. For instance, polyvinylidene fluoride (PVDF), a prototypical dielectric polymer, has a dielectric constant of approximately 6.8 and a loss of about 0.0184 at 1 kHz, owing to its fluorinated structure [73]. In contrast, inorganic materials such as ZnO, TiO₂ and BaTiO₃ demonstrate much higher dielectric constants at room temperature [74-76]. Despite excellent dielectric properties, inorganic ceramics possess limitations, including brittleness, limited tunability, susceptibility to dielectric breakdown, and low toughness. As a result, their use in flexible nanoelectronics is constrained [77].

In contrast, PVDF offers strong flexibility, and excellent mechanical strength which make it suitable for flexible nanodevices. However, due its low dielectric constant than the inorganic materials hinder its application to nanoelectronics devices. Thus, researchers are trying to improve the dielectric constant and electroactive phase of PVDF. It exists in three phases: α , β , and γ with the β and γ phases being electroactive [29]. In recent times, polymer nanocomposites, incorporating inorganic nanofillers into the polymer matrix, enhancing PVDF's dielectric properties while retaining the advantages of both materials. However, increasing the filler content raises the dielectric constant, but it also leads to higher dielectric loss, reduced flexibility and crystallinity [72, 78].

The choice of nanofiller also influences phase transitions within the polymer. SnO₂ nanostructures have been established as an efficient inorganic nanofiller [40, 79]. For example, Zhe et al. reported a high dielectric constant of approximately 300 at 10 kHz for SnO₂/PVDF nanocomposites with a high nanofiller concentration of 0.16 vol% [40]. Adding nanostructure of inorganic materials significantly elevates specific surface interactions, which improves PVDF's electroactivity thus the dielectric properties [79].

Similarly, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene has gained attention as an effective conductive filler due to its exceptional electrical conductivity of approximately 6500 S/cm and an elastic modulus of around 0.33 TPa [41, 42]. MXene-based polymer nanocomposites are capable of achieving high dielectric constants with low percolation thresholds. However, as the filler loading approaches the percolation threshold, there is a significant boost in dielectric constant, dielectric loss, and electrical conductivity. This underscores the necessity for surface modifications, such as the incorporation of insulating or semiconductive layers, to optimize the material's performance [41-43].

5 Recently, incorporation of inorganic nanomaterials/MXene nanocomposites as nanofillers have attracted considerable interest among researchers due to their notable advantages. Specifically, the dispersion of semiconductive layer of inorganic nanomaterials on MXene nanosheets obstruct the establishment of conductive pathways. Thereby suppressing the electrical conductivity and enhances the charges at surfaces, thus improves the dielectric properties [43, 44, 80]. Like as Feng et al. synthesized $\text{BaTiO}_3/\text{MXene}/\text{PVDF}$ composites, incorporating 8 wt% BaTiO_3 and 2 wt% MXene, which exhibited a dielectric constant of 77 and a loss of 0.15 at 100 Hz [44]. Similarly, at 1 kHz, the MXene/ $\text{TiO}_2/\text{MoS}_2/\text{P(VDF-HFP)}$ nanosheet-loaded nanocomposite films, with an optimal loading of 8.0 wt%, demonstrated a high dielectric constant of 944 while maintaining a low dielectric loss of 0.19 [43]. 20 Similarly, the incorporation of filler into the PVDF matrix has proven to be highly effective in enhancing the piezoelectric performance of PVDF. For instance, Kumari P. et al. reported the improved output power 0.14 mW/cm² of PVDF films upon the addition of BaTiO_3 nanofillers [81].

Interestingly, to the best of our knowledge, the impact of SNMX nanocomposite fillers on dielectric behaviour of PVDF films has not been previously reported. Additionally, the most studies focus on higher filler concentrations, typically exceeding 5 wt%, which can reduce crystallinity, alter electroactive properties, and form networks within the polymer matrix [31]. These changes can affect electrical conductivity and augments dielectric loss. To overcome these challenges, this study employs a very low filler concentration of SNMX nanofillers, demonstrating high dielectric constant and low loss at lower filler loading [78]. The reduced filler content

did not compromise the transparency, flexibility, or crystallinity of the nanocomposite films.

In this study, we have synthesized a nanocomposite of SnO₂ nanoparticles with 20 wt% of Ti₃C₂T_x MXene nanosheets using hydrothermal method. The synthesized SNMX nanocomposite was used as nanofiller for the fabrication of PVDF composite films with three different weight concentrations (0.25 wt%, 0.50 wt%, and 0.75 wt%). Notably, the SNMX nanocomposite has been shown to preferentially induce the electroactive β and γ phases in PVDF. Additionally, significant improvements in the dielectric properties have been observed, with relative dielectric permittivity (ϵ_r) of 150 and 165 and loss tangent ($\tan \delta$) of 0.8 and 2.1 at 20 Hz for the 0.50 wt% and 0.75 wt% SNMX/PVDF composite films, respectively. Temperature-dependent studies indicate that at 100°C, the relative dielectric permittivity of the 0.75 wt% SNMX/PVDF composite film reaches 250. The enhanced electroactive behaviour and dielectric properties, coupled with the exceptional durability of the SNMX/PVDF films, suggest their potential application as flexible power sources in portable electronic devices employing piezoelectric technology. Notably, the piezoelectric flexible nanogenerator (PENG) made from the 0.75 wt% SNMX/PVDF nanocomposite film produces a peak-to-peak voltage of 105 V.

3.2 Experimental Section

3.2.1 Materials

All reagents used in the experiment were of analytical grade and were employed without any modifications, as received. MAX phase Ti₃AlC₂ ($\geq 90\%$, particle size of $\leq 100 \mu\text{m}$), hydrofluoric acid (HF, 40 wt%), stannic chloride pentahydrate (SnCl₄.5H₂O), sodium hydroxide (NaOH), N-dimethylformamide (DMF), Urea (CH₄N₂O) and hydrochloric acid (HCl) were purchased from Sigma-Aldrich Chemical Co. Ltd. The used polyvinylidene fluoride (PVDF) powder was purchased from Alfa Aesar.

3.2.2 Synthesis of Tin Oxide nanostructure (SnO₂)

A low-cost hydrothermal method was used to synthesize SnO₂ nanoparticles as shown in Figure 3.1 (a). 4 g of SnCl₄.5H₂O was dissolved in 30 ml ethanol and magnetically stirred to obtain a clear solution. Subsequently 1.095 g of citric acid was added into

the solution and further stirred for 2 hours. The resultant white solution was transferred to an autoclave filled with 70% capacity and treat it hydrothermally for 8 hours at 160 °C. After the reaction time, the precipitates were centrifuged and washed multiple times with DI water and ethanol. The collected precipitate was dried at 60 °C for 12 hours.

3.2.3 Synthesis of MXene

Ti₃C₂T_x sheets were produced by selectively etching the Al layer from the MAX phase Ti₃AlC₂ and then delaminating it using an intense layer delamination method [42]. First, 1 g of MAX phase powder was mixed with 48% concentrated hydrogen fluoride (HF) for 24 hours at room temperature using a magnetic stirrer. The mixture was filtered and the obtained precipitates washed multiple times with deionized water and centrifuged until the pH reached 7. Finally, the filtered black slurry was dried for 6 hours at 80°C and grinded into a fine powder to obtain Ti₃C₂T_x MXene sheets. The used synthesis process is depicted in Figure 3.1 (b).

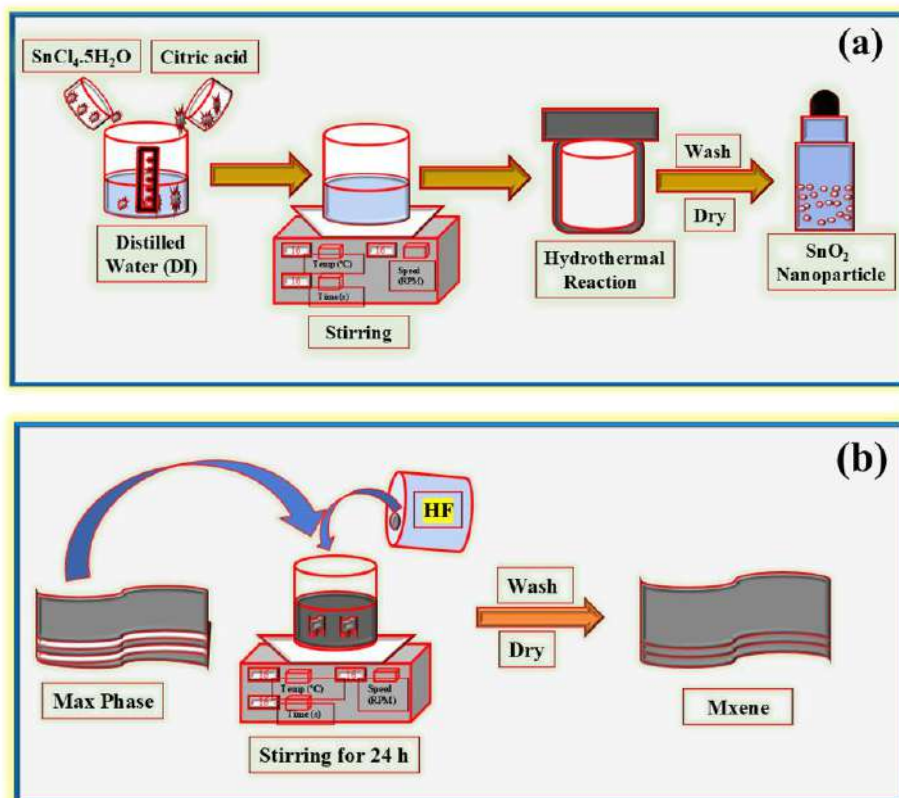


Figure 3.1: A stepwise depiction of the synthesis processes for (a) SnO₂ nanoparticles and (b) MXene flakes.

3.2.4 Synthesis of SnO₂/MXene (SNMX) nanocomposite

The SnO₂/MXene nanocomposite was synthesized using the hydrothermal method. This process involved sonicating SnO₂ and Ti₃C₂T_x (20 wt%) in 100 mL of distilled water, followed by the addition of 0.32 g of urea and dropwise addition of 40 μ L of HCl. The resulting solution was then sealed in an autoclave and heated at 120 °C for 8 hours. The resulting powder was extracted, centrifuged, and then sequentially cleaned with ethanol and deionized water. It was then allowed to dry overnight at 60°C in an oven. The produced SnO₂/MXene nanocomposite are referred to as SNMX nanocomposite.

3.2.5. Synthesis of PVDF film

PVDF powder was dissolved in a 10 wt% solution of N-dimethylformamide (DMF) to produce the flexible, free-standing PVDF films. The mixture was stirred at ambient temperature for a duration of 4 hours. The resulting solution was then applied to cleaned glass slides and annealed at 80°C in a microwave oven for 2 hours. Subsequently, the films were detached to yield flexible, free-standing films.

3.2.6. Synthesis of SNMX/ PVDF composite films

Polyvinylidene fluoride (PVDF), SNMX powder, and DMF were used in the preparation of flexible composite films. PVDF powder was first dissolved in DMF for 1 hour at room temperature using a magnetic stirrer, resulting in a homogeneous and clear solution. On the other hand, SNMX powder was added to DMF in varying concentrations (0.25 wt%, 0.50 wt%, and 0.75 wt%) and ultrasonically agitated for 1 hour at room temperature. The PVDF solution was then combined with the synthesized different wt% SNMX solutions and stirred for 40 hours at room temperature to get a slurry type solution of SNMX/PVDF composite. The resulting solution was then applied to cleaned glass slides and annealed at 80°C in a microwave oven for 2 hours. Subsequently, the films were detached to obtained flexible, free-standing films. Further, the thickness of the synthesized films was measured using digital vernier calliper and the measured thickness values of the synthesized composite films are tabulated in Table 3.1.

Table 3.1: Thickness values of Pure PVDF and composite films.

Sample	Pure PVDF	0.25wt% SNMX	0.50wt% SNMX	0.75wt% SNMX
Thickness(mm)	0.19	0.23	0.20	0.25

3.2.7 Fabrication of the piezoelectric flexible generator

The flexible composite films were sectioned into small pieces, each measuring 2.5 cm × 2.5 cm, and aluminium tape was applied to both surfaces to function as the top and bottom electrodes for the piezoelectric flexible nanogenerator (PENG). Copper wires were then attached to the aluminium tape using copper tape to measure the output signals when pressure was applied and the device was connected to an external circuit. Figure 3.2 (a & b) illustrates both the schematic diagram of the fabricated PENG device and a digital photograph of the prepared PENG devices.

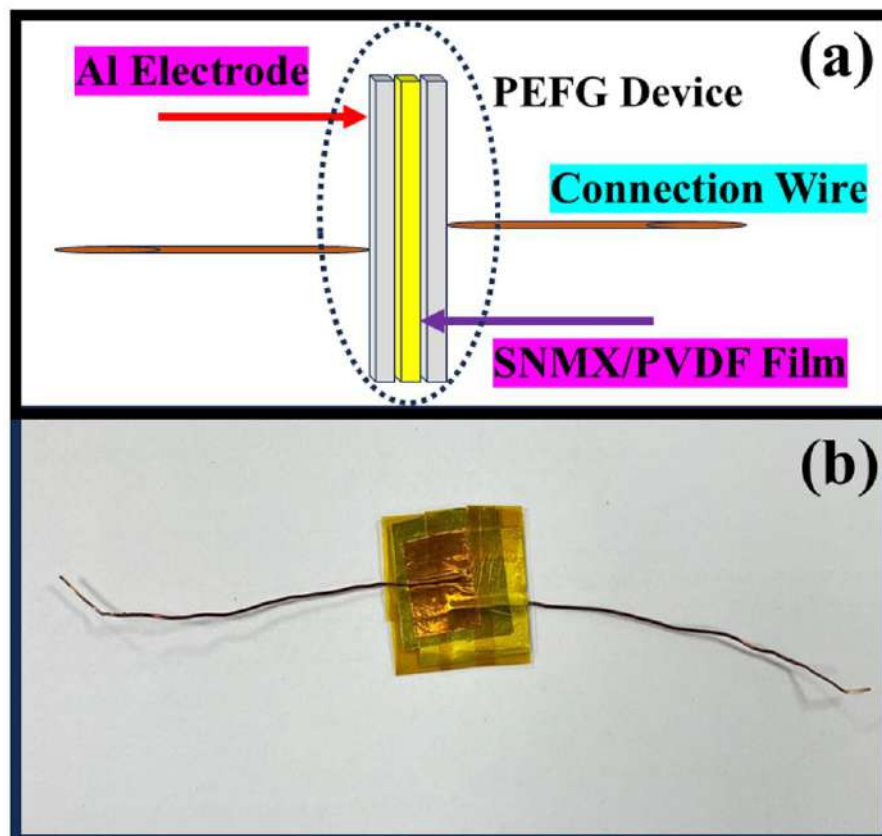


Figure 3.2: (a) Schematic representation of the structure of the PENG device and (b) digital image of the fabricated PENG device.

3.2.8 Characterizations

The crystal phases of the synthesized samples were determined using a Rigaku Ultima IV X-ray diffractometer (XRD) equipped with a $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation source. The scans were performed at a rate of 2° per minute across a 2θ range of 5° to 70° . An energy-dispersive X-ray spectroscopy (EDX) system (SwiftED3000, Oxford) was used for elemental mapping and compositional analysis, and an FEI Quanta 200 field emission scanning electron microscope (FESEM) was used to analyse the surface morphology of the samples. Fourier transform infrared (FTIR) spectroscopy (NICOLET 5700) was used to analyse the electroactive phases of the PVDF and composite films. The dielectric characteristics were measured using an impedance analyzer (E4990A), with a frequency range of 20 Hz to 10 MHz.

3.3 Results and Discussion

3.3.1 X-ray Diffraction

Structural characterization of the MAX phase Ti_3AlC_2 (before HF etching) and synthesized MXene $\text{Ti}_3\text{C}_2\text{T}_x$ (after HF etching) were performed using X-ray diffraction (XRD), as shown in the Figure 3.3(a).

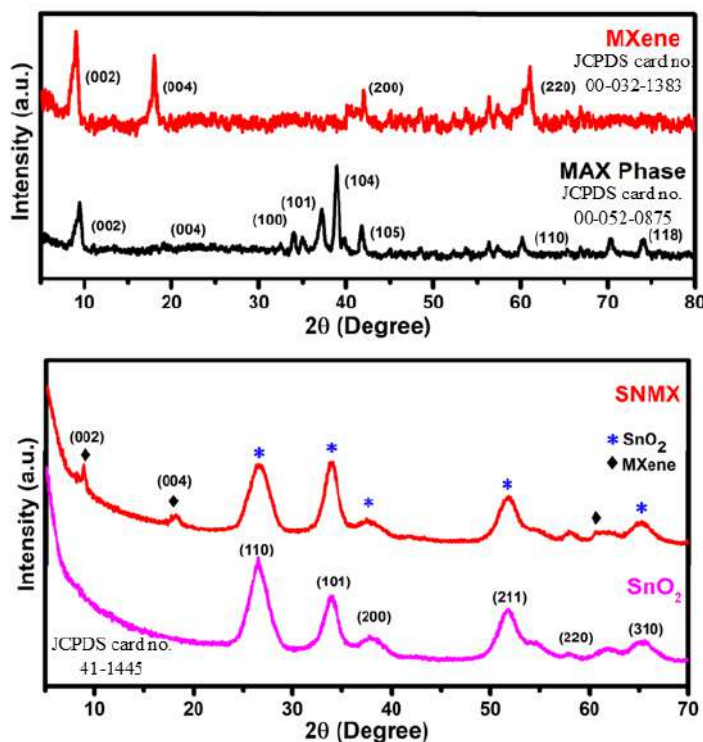


Figure 3.3: XRD patterns of (a) MAX powder (Ti_3AlC_2) compared to MXene, and (b) comparison between SnO_2 nanoparticles and SNMX nanocomposite.

XRD pattern of the MAX phase is in good agreement with the data presented in JCPDS card no. 00-052-0875. A characteristic sharp peak corresponding to the Al layer is observed in the MAX phase at $2\theta = 38.92^\circ$ along the preferred (104) direction, which needs to be fully etched out during the synthesis process. The other prominent peaks at $2\theta = 9.4^\circ$, 38.04° , 41.74° , 60.2° , and 74.2° correspond to the (002), (101), (105), (110), and (118) planes, respectively. After HF treatment, the characteristic diffraction peak at $2\theta = 38.92^\circ$ (104) corresponding to Al disappears in the XRD pattern of MXene $\text{Ti}_3\text{C}_2\text{T}_x$, confirming the complete removal of Al from the MAX phase. Most notably, the diffraction peak for the (002) plane shifts backward after HF etching, from $2\theta = 9.4^\circ$ in the MAX phase to $2\theta = 9.02^\circ$ in the MXene. This peak shift is attributed to the intensify in the c-lattice parameter of the MXene and indicates the formation of an interlayer gap in the layered structure. The XRD peaks match well with JCPDS card no. 00-032-1383, confirming the successful synthesis of MXene $\text{Ti}_3\text{C}_2\text{T}_x$ sheets from the MAX phase by HF etching [41-44, 80-82].

Figure 3.3(b) displays the XRD pattern of nanocrystalline SnO_2 nanoparticles (NPs). The strong diffraction peaks indicate excellent crystallinity and tetragonal rutile phase of the SnO_2 . The diffraction peaks at $2\theta = 26.58^\circ$, 33.94° , 38.02° , 51.80° , 54.75° , 58.09° , and 65.87° are well indexed to (110), (101), (200), (211), (220), (002), and (310) planes, respectively, according to JCPDS Card No. 41-1445 [31, 40]. The SNMX composite exhibited almost all of the distinct peaks of both MXene and SnO_2 , suggesting successful synthesis of SNMX nanocomposite [83]. The modest broadening of the peaks, is attributed to an increase in d-spacing and a rise in the orderliness of the crystal planes.

Figure 3.4(a) presents the X-ray diffraction (XRD) patterns for all the films under investigation, spanning a 2θ range from 10° to 50° . The α , β , and γ phases constitute the majority of the PVDF and SNMX/PVDF composite films at varying concentrations. The diffraction peaks at 18.4° , 20.0° and 26.6° which can be

indexed to the (020), (110), and (021) planes, respectively, correspond to the α phase of PVDF. The XRD pattern displays two moderate peaks at approximately 18.5° and 39.0° , and a strong peak at 20.3° , which can be affiliated to the γ phase. These diffraction peaks correspond to the (110/101), (020), and (211) planes, respectively. In contrast, a weak peak at 38.8° , corresponding to the (002) plane, and at 20.6° , corresponding to the (110/200) plane, are predominantly associated with the β phase. Figure 3.4(b) is the magnified version of the XRD within the range of 15° to 25° . The pattern reveals a noticeable decrease in the intensity of peaks associated with the α phase, while the intensities of peaks corresponding to the β and γ phases elevate significantly with the rising concentration of SNMX. The intensifies in intensity of the ($\beta + \gamma$) phase suggesting the phase transition in the composite films due to the presence of nanofiller [29, 78, 84].

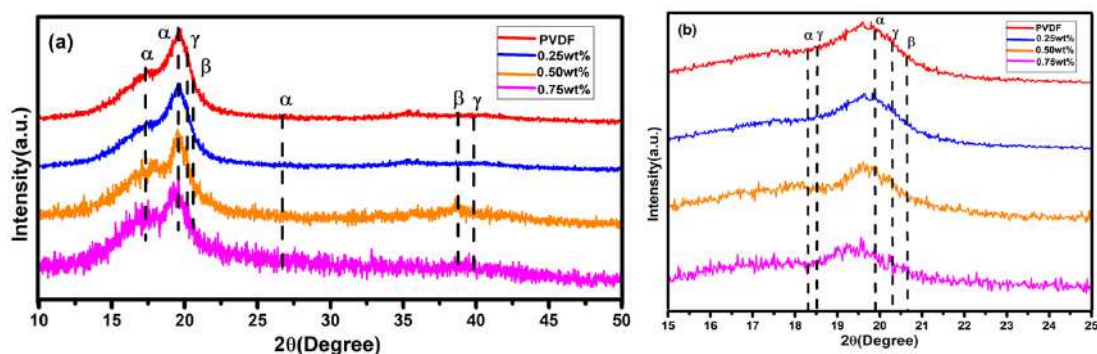


Figure 3.4: XRD pattern of (a) representative samples and (b) magnified view highlighting the phases.

Further, the intensity ratio of the EA ($\beta + \gamma$) phase to the α phase has been estimated, and it was found that the electroactive (EA) phase of the highest 0.75 wt% SNMX/PVDF films is 1.3 times greater than that of the pure PVDF film. The obtained EA phase ratio corresponding to PVDF, 0.25wt% SNMX/PVDF, 0.50wt% SNMX/PVDF and 0.75wt% SNMX/PVDF are 0.58, 0.62, 0.73, and 0.80 respectively. It is also important to highlight that the crystallinity of the PVDF films progressively decreases as the concentration of the nanofiller increases. This decrement in the crystallinity may be due to formation of new nucleation sites. However, as the concentration of nanofiller is very low so decrement in the crystallinity is very low as

compared to reported data [43]. Thus, the obtained XRD results confirms that EA phase of the films increases without significant loss the crystallinity of the polymer.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.5 (a) displays a plot of the FTIR spectrum of pure PVDF and SNMX/PVDF films in the range of 400–1500 cm^{-1} . The spectra show peaks that correspond to the different phases (α , β and γ) of the PVDF. The exclusive peaks for the α phase are at approximately 488, 534, 616, 764, 976 and 1207 cm^{-1} ; for the β phase, they are at 473 and 1275 cm^{-1} ; and for the γ phase, they are at 482, 811 and 1234 cm^{-1} . The absorbance for the $\beta + \gamma$ phases is notably stronger than that of the α phase, as indicated by the peaks at 837 and 511 cm^{-1} . Consequently, the electroactive β and γ phases can be characterized by the presence of these two peaks. Several studies suggest that the peaks at 1431 and 1429 cm^{-1} can be used as characteristic bands for the β and γ phases, respectively [29, 78, 84]. To clearly observe how the loading of SNMX affects the intensity of the unique peaks, magnified spectra in the ranges of 740 cm^{-1} to 860 cm^{-1} and 1140 cm^{-1} to 1320 cm^{-1} have been plotted and are shown in Figure 3.5 (b & c). It can be seen that the intensity of the α phase peaks at 764 cm^{-1} and 976 cm^{-1} decreases, while the intensity of the $\beta + \gamma$ phase (837 cm^{-1}) and γ phase (1235 cm^{-1}) increases with the increment in the percentage of SNMX in the PVDF matrix, suggesting transformation of α phase into β and γ phases. The absorption peak at 764 cm^{-1} can be attributed to the bending of the CF_2 skeleton, whereas that at 837 cm^{-1} originates from the rocking of the CH_2 , the stretching of the C-C skeleton and CF_2 , these two peaks correspond to the non-polar α - and polar β -phases [74].

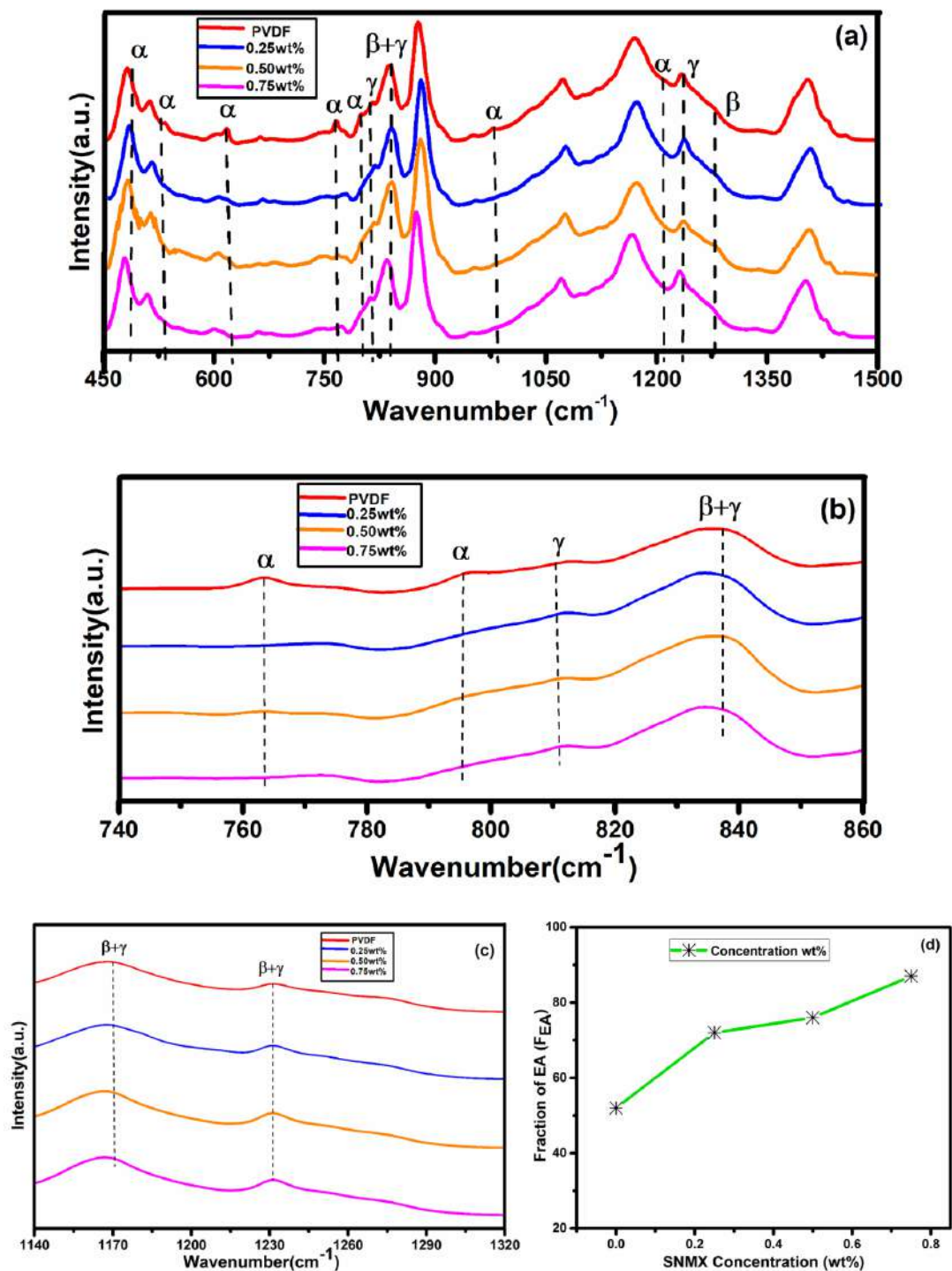


Figure 3.5: FTIR spectra of all samples across different ranges: (a) 400–1500 cm⁻¹, (b) 740–860 cm⁻¹, (c) 1140–1320 cm⁻¹, and (d) plot of the fraction of EA versus SNMX concentration (wt%).

In fact, for the 0.75 wt% film, the α phase peaks nearly disappear due to the incorporation of SNMX in PVDF matrix. The relative fraction (F_{EA}) of the EA phases

(β and γ) in terms of crystalline components has been calculated using equation 1 for all the films [45].

$$F_{EA} = \frac{I_{837}}{\left(\frac{K_{837}}{K_{764}}\right)I_{764} + I_{837}} \times 100\% \quad 3.1$$

In this context, F_{EA} represents the fraction of the electroactive phase, while I_{837} and I_{764} denote the peak intensities at wavenumbers 837 cm^{-1} and 764 cm^{-1} , respectively. The values of K_{837} ($7.7 \times 10^4 \text{ cm}^2/\text{mol}$) and K_{764} ($6.1 \times 10^4 \text{ cm}^2/\text{mol}$) correspond to the molecular absorption coefficients at these respective wavenumbers.

The fraction formula indicates that when SNMX nanofiller incorporated into the PVDF matrix, the F_{EA} intensifies. The calculated F_{EA} values for various samples have been plotted in Figure 5(d). The F_{EA} of the 0.75 wt% film (86%) is 1.5 times higher compared to that of the pure film (52%). These results align with the XRD results, which showed a decrease in the α content of the composite films and an increase in their EA phase. The rise in the electroactive phase suggests that the molecules have reoriented [78]. In this case, the polarization induced by the SNMX nanofillers promotes this reorientation. The material's elevates dielectric constant, which will be discussed subsequently, further illustrates this reorientation and the associated enhancement of the electroactive (EA) content.

3.3.3 Morphological and compositional analysis

FESEM analysis was employed to investigate the morphology and structure of exfoliated MXene, SnO_2 nanoparticles (NPs) and the SNMX nanocomposite.

Figure 3.6 (a-f) shows the obtained images at low and high magnification. After the HF treatment of the MAX phase (which exhibited an uneven surface and tightly packed structure), transformed into an accordion-like morphology of MXene, as depicted in Figure 3.6 (a & b). Additionally, the parallel arrangement of MXene layers resulted from the specific etching direction of "Al" [82]. The nanocrystalline morphology of SnO_2 nanoparticles (NPs) is shown in Figure 3.6 (c & d).

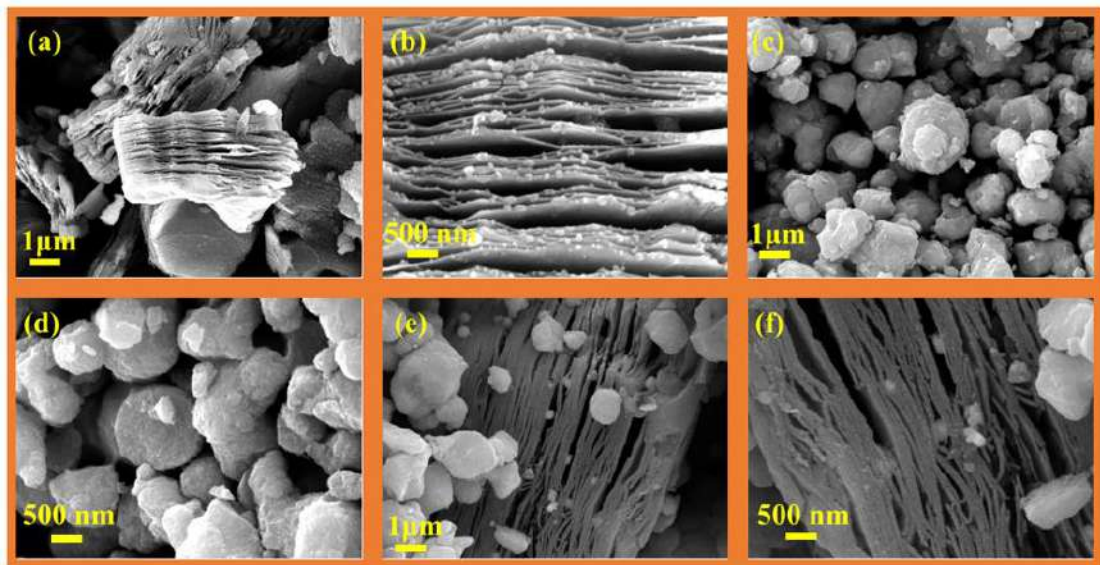
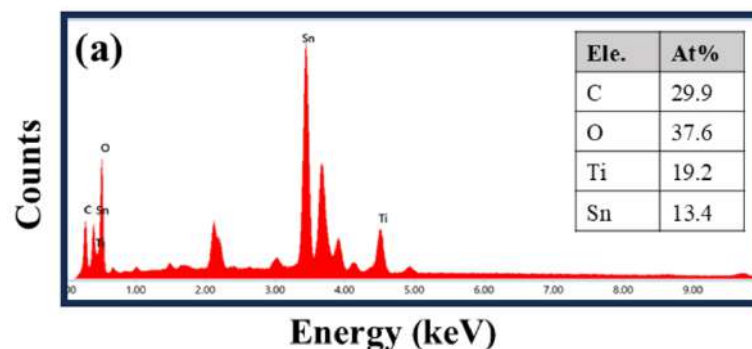


Figure 3.6: FESEM images showing (a & b) the accordion-like morphology of exfoliated MXene, (c & d) SnO₂ nanoparticles, and (e & f) MXene flakes functionalized with SnO₂ nanoparticles.

Further, the FESEM analysis confirmed the composite synthesis by the high dispersion of NPs among the MXene flakes. It can be clearly observed that the SnO₂ NPs are integrated in between the MXene layers preventing their restacking. However, some aggregated SnO₂ NPs are dispersed on top of the MXene sheets. EDX was employed to verify the elemental composition of the SNMX composite. The peaks for Sn, Ti, C, and O are observed in the EDS spectra within the 1–10 keV region as shown in Figure 3.7(a). The atomic percentages of the SNMX nanocomposite are listed in the Table in the spectra [83]. The distribution of SnO₂ nanoparticles across the MXene is confirmed by the elemental mapping of the SNMX nanocomposite, which shows the presence of mixed elements of SnO₂ and MXene in the characterized area and represented in Figure 3.7(b–g).



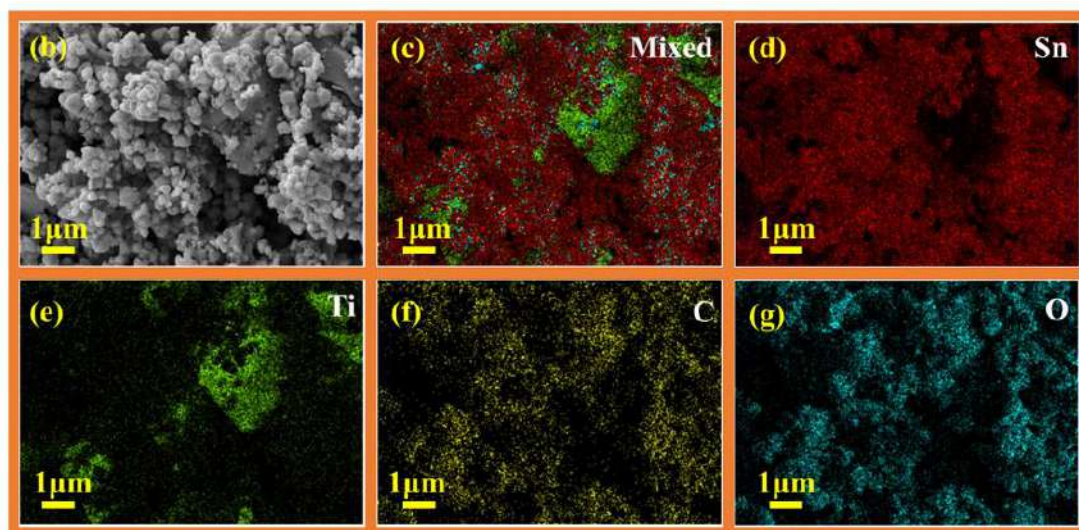


Figure 3.7: (a) EDX analysis, and (b to g) elemental mapping of the SNMX nanocomposite.

FESEM images of pure PVDF and the SNMX/PVDF composite films are presented in the Figure 3.8 (a-d).

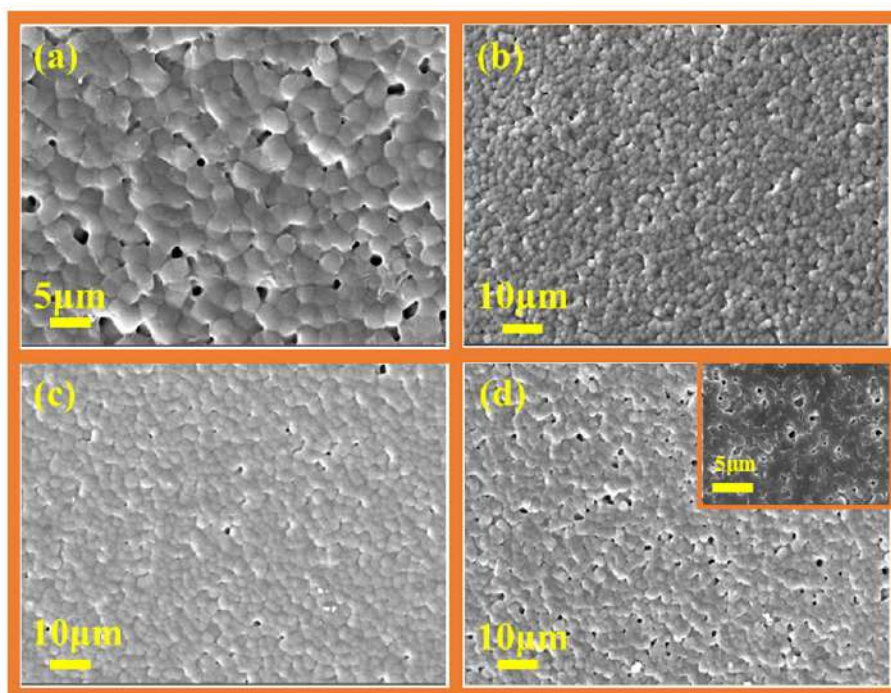


Figure 3.8: FESEM images of (a) pure PVDF, (b) 0.25 wt% SNMX/PVDF, (c) 0.50 wt% SNMX/PVDF, and (d) 0.75 wt% SNMX/PVDF.

The porous and spherulitic microstructure observed in both pure and SNMX/PVDF composite films. The morphologies of all the composite films are nearly identical. It can be observed as the SNMX filler concentration increases the surface of the films

become more porous thereby suggesting uniform dispersion of SNMX nanocomposite within the PVDF matrix. Which facilitates the migration of charges within the composite film and aids in aligning the dipoles in a specific direction [45, 85]. Additionally, the increment in the number of pores further indicates that incorporation of SNMX nanocomposite enhances the surface roughness of the composite films.

3.3.4 Impedance spectroscopic: Dielectric parameters

Dielectric spectroscopy has been employed to investigate the dielectric behaviour of the prepared films. The dielectric properties of bulk or nanoscale solid materials are influenced by the spatial distribution and alignment of the local electric field within the system. Consequently, the temperature dependence and frequency-dependent relative dielectric permittivity and loss tangent offer valuable insights into the defect behaviour, structural changes and transport mechanisms within the solid [86-88].

The dielectric constant exhibits a complex nature and can be expressed as Equation 3.2:

$$\epsilon^* = \epsilon_r - j\epsilon_r'' \quad 3.2$$

The real part of the complex dielectric constant (ϵ^*), also known as the relative dielectric permittivity (ϵ_r), measures the electrical energy stored in the material when a necessary alternating electric field is applied. In contrast, the imaginary part (ϵ_r''), the dielectric loss, describes the energy dissipated in the material, as the molecules undergoing polarization are unable to match the rate of oscillation of the external electric field [89].

The relative dielectric permittivity (ϵ_r'') and loss tangent for the materials were determined using Equation (3.3) and (3.4), respectively.

$$\epsilon_r = \frac{Cd}{A\epsilon_0} \quad 3.3$$

$$\tan\delta = \frac{\epsilon_r''}{\epsilon_r} \quad 3.4$$

where A is the electrode area, ϵ_0 is the permittivity of free space (8.85×10^{-12} F/m), d is the sample thickness, C is the capacitance [85-88].

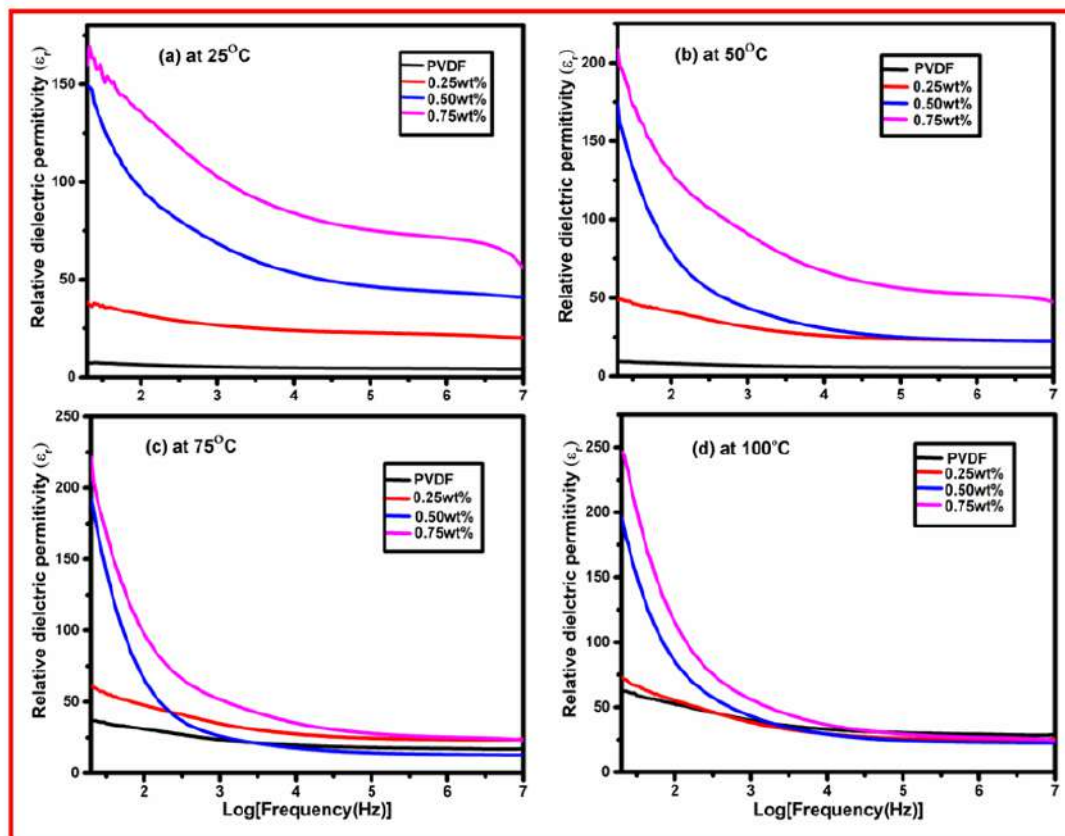


Figure 3.9: Relative dielectric permittivity ϵ_r spectra of PVDF and SNMX/PVDF composites films at (a) 25°C, (b) 50°C, (c) 75°C, and (d) 100°C.

Figure 3.9 (a-d) shows the variation of the relative dielectric permittivity with frequency (20 Hz - 10 MHz) of the applied electric field at different operating temperatures for all the films. It is evident that the relative dielectric permittivity (ϵ_r) intensifies with temperature across the entire frequency range, while it diminishes with higher frequency. Furthermore, the incorporation of the SNMX nanocomposite into the PVDF matrix significantly enhances the relative dielectric permittivity of the films. At room temperature and 20 Hz, the relative dielectric permittivity elevates from 7 for pristine PVDF to 35 with 0.25 wt%, 147 with 0.50 wt%, and 165 with 0.75 wt% SNMX/PVDF composite films. Increase in relative dielectric permittivity with the addition of SNMX may be attributed to enhanced Maxwell–Wagner–Sillars (MWS) interfacial polarization and easy charge migration at lower applied frequency [86-88]. As the nanofiller concentration increases, polarization driven by the alignment of interfacial charges between the polymer and the SNMX nanofiller intensifies. Furthermore, as β and γ phases of PVDF are known to exhibit the

highest spontaneous polarization. Thereby, the enhancement in EA phase means increment in the polar phase with loading of SNMX nanofillers favouring the reorientation of the molecules in applied external electric field. Thus, the film with high EA content demonstrates the maximum dielectric constant [78, 85].

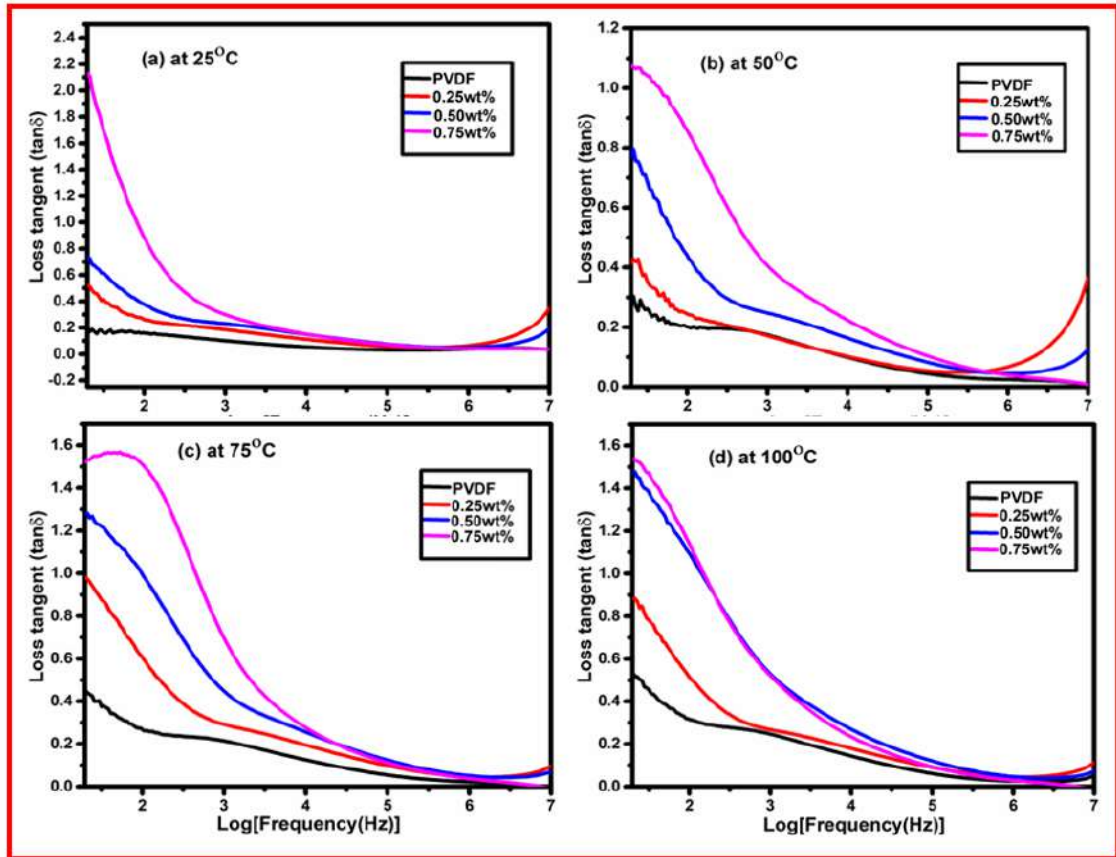


Figure 3.10: Loss tangent spectra of PVDF and SNMX/PVDF composite films at (a) 25°C, (b) 50°C, (c) 75°C, and (d) 100°C

At higher operating temperatures, ϵ_r continues to proliferate, reaching approximately 250 at 100°C and 20 Hz, while the relative dielectric permittivity of pure PVDF increases to 60 under the same conditions. At room temperature, the dielectric constant boosts by about 25 times, whereas at 100°C, it increases approximately 4 times compared to pure PVDF films. These results indicate that even a small amount of SNMX nanocomposite as nanofillers significantly improves the relative dielectric permittivity of PVDF at room temperature. The observed escalation in the relative dielectric permittivity with rising operating temperature can be ascribed to the enhanced segmental motion of the molecular chains in PVDF [85, 90].

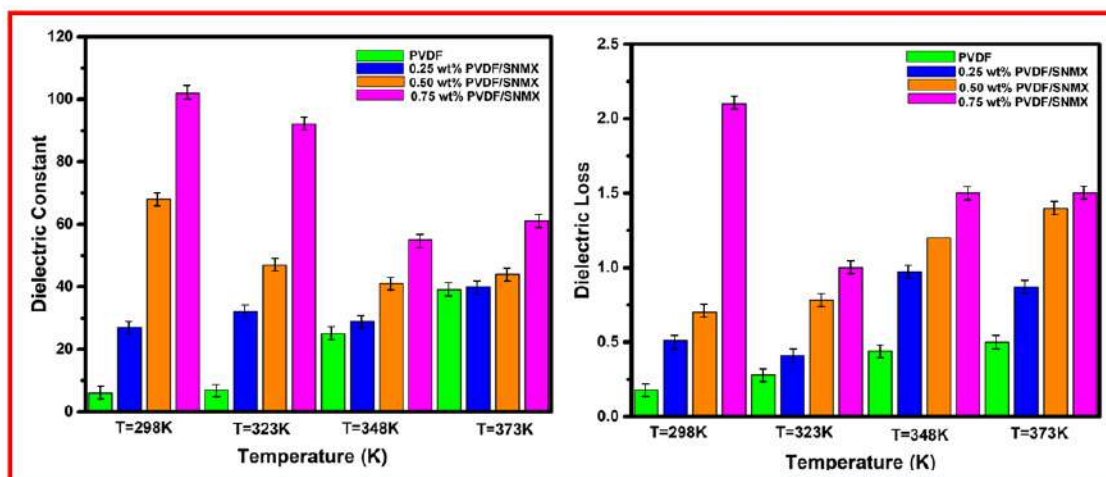


Figure 3.11: Relative dielectric permittivity and loss tangent values at various temperatures measured at a frequency of 20 Hz

While additional nanofiller would likely increase the relative dielectric permittivity, it would also result in higher dielectric loss. The variation of the loss tangent ($\tan\delta$) with applied frequency (20 Hz - 10 MHz) is plotted for all the films at different working temperature and displayed in Figure 3.10 (a-d). It has been observed that the loss tangent amplifies as the nanofiller SNMX concentration grows in the PVDF. At 20 Hz and room temperature, the loss tangent of the nanocomposite films with 0.25 wt%, 0.50 wt% and 0.75 wt% SNMX is approximately 0.5, 0.75 and 2.3, respectively, while that of pure PVDF is around 0.2 under the same conditions. The frequency-dependent changes in loss tangent may attributed to different relaxation mechanisms within the materials. One is the α -relaxation in the crystalline region, accounts for the loss tangent at low frequencies. The increase in dielectric loss at higher frequencies suggests a second relaxation peak corresponding to α -relaxation in the amorphous region, occurring in the 1MHz–10 MHz range [85]. It is interesting to note that the obtained losses are significantly lower with enhanced relative dielectric permittivity as compare to the previous reported data [40, 78]. The lower losses are attributed to significant enhancement in the EA phase with low concentration of the SNMX fillers without reducing the crystallinity of the PVDF. For lower filler loadings, up to the percolation threshold, the filler is encapsulated within the PVDF matrix, acting as small, individual capacitors that collectively enhance both ϵ_r and $\tan\delta$ [43]. The reduced relative dielectric permittivity and loss tangent of

SNMX/PVDF nanocomposites, as compared to PVDF, can be attributed to mobility constraints. The presence of nanoparticles hinders the movement of polymer chains, resulting in an increase in relaxation time and a shift of the relaxation process to lower frequencies. As a result, nanocomposites with a SNMX content exhibit a decrease in dielectric loss[85].

Further, the temperature-dependent loss tangent behaviour suggests that the losses increase with elevated operating temperatures for all films, except for the 0.75 wt% SNMX nanocomposite film. The 0.75wt% film demonstrate highest loss tangent (~ 2.3) at room temperature and lowest loss tangent (~ 1.1) at 50 °C. However, on further increment in the operating temperature (75 and 100 °C) the loss increases to ~ 1.5 and remains same. Also, the losses of 0.25wt% and 0.50wt% films at 100°C becomes twice that of the at room temperature. The obtained relative dielectric permittivity and loss tangent values at different operating temperature at a frequency of 20 Hz is demonstrated in Figure 3.11 (a and b).

Table 3.2: A comparative analysis of the dielectric parameters with PVDF composite films at room temperature.

S.No.	Nanofiller/PVDF Composite	Nanofiller Conc.	Dielectric Parameters		Freq.	Ref.
			Dielectric constant	Dielectric loss		
1.	BaTiO ₃ /SnO ₂ /PVDF	60 vol%	145	0.8	10 kHz	[91]
2.	SnO ₂ /PVDF	0.16vol%	300	0.82	10 kHz	[40]
3.	SnO ₂ /PVDF	15wt%	40	0.34	40 Hz	[31]
4.	DA@SnO ₂ /PVDF	1wt%		6	1 kHz	[92]
5.	SnO ₂ /PVDF	0.1wt%	145	0.8	10 Hz	[78]
6.	BaTiO ₃ /MXene/PVDF	8wt%	77	0.14	100 Hz	[44]
7.	MnO ₂ /MXene/PVDF	7wt%	37	0.2	1 kHz	[93]
8.	CaCu ₃ Ti ₄ O ₁ /MXene/PVDF	30vol%	28	0.061	10 kHz	[80]
9.	SnO ₂ @MXene/PVDF	0.25wt%	38	0.7	20 Hz	This work
10.	SnO ₂ @MXene/PVDF	0.50wt%	150	0.6	20 Hz	This work
11.	SnO ₂ @MXene/PVDF	0.75wt%	165	2.1	20 Hz	This work

A comparison of recent studies on the enhancement of the relative dielectric permittivity of PVDF using different nanofillers is provided in the Table 3.2.

Although, some reports demonstrate high relative dielectric permittivity with higher loss tangent at substantial wt% of nanofillers. That leads to degradation in crystallinity and flexibility of the PVDF films.

Thus, the obtained dielectric results and findings enhance our understanding the influence of SNMX nanofillers in PVDF matrix. The results suggest that the synthesized films have the potential to act as flexible dielectric material in various industries, including electronics, energy storage, and telecommunications.

3.4 Piezoelectric flexible nanogenerator (PENG) studies

An oscilloscope was used to measure the generated voltage output after constructing the piezoelectric flexible nanogenerator (PENG) device using the synthesized SNMX/PVDF flexible composite films. The graphs in the Figure 3.12(a-d) display the open-circuit voltage produced by the devices with different concentrations of SNMX nanocomposites in the PVDF matrix when force was applied using a manual taper. The plots demonstrate that the open-circuit voltage intensifies as the SNMX content in the PVDF matrix rises. The observed peak-to-peak voltage (PPV) outputs for the composite films are 65 ± 1.5 V, 97 ± 1.5 V and 105 ± 1.5 V, corresponding to 0.25 wt%, 0.50 wt% and 0.75 wt% SNMX nanofillers in the PVDF matrix, respectively. While the virgin PVDF film PPV output is 32 ± 1.5 V. The voltage output from the PENG device follows an alternating voltage waveform [31, 78, 81].

The range of load resistances influences the resulting power density. Therefore, power density of 0.75wt% SNMX/PVDF composite films were investigated across the load resistances from 500 k Ω to 10 M Ω . The obtained variations in power density as a function of load resistance is presented in Figure 3.13. The formula used to calculate the output power density of the PENG device is given in Equation (3.5). Where V is the voltage across the load resistance R and A is the effective area of electrodes.

$$P = \frac{V^2}{R \times A} \quad 3.5$$

The power density increases up to 3 M Ω , reaching a maximum of 0.44 μ W/cm², after which it decreases as the load resistance continues to increase. According to the

maximum power transfer theorem, maximum power is achieved when the internal impedance of the source matches the external load resistance [45].

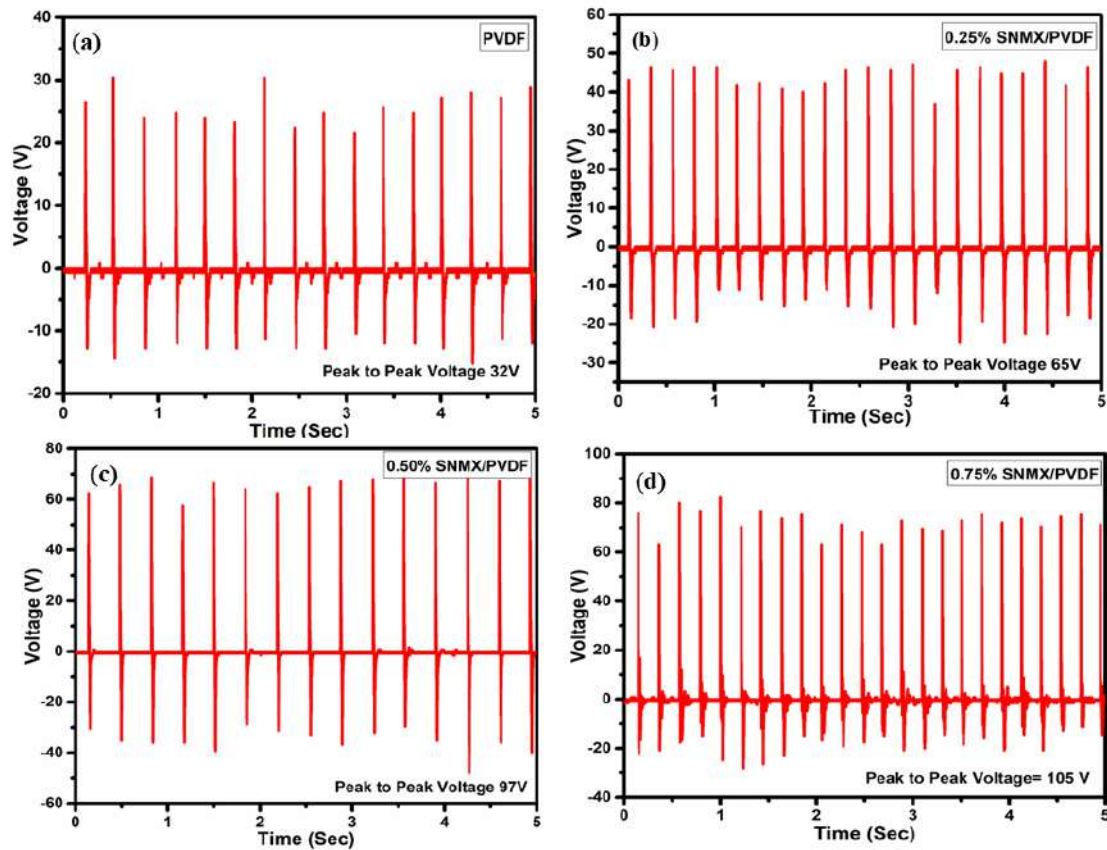


Figure 3.12: Peak to Peak Voltage output characteristics of (a) pure PVDF, (b) SNMX (0.25 wt%), (c) SNMX (0.50 wt%), and (d) SNMX (0.75 wt%) composites films.

The PPV output of 0.75 wt% SNMX/PVDF composite film is enhanced by more than three times than that of the pristine PVDF film. It has been reported that boosting the dielectric constant, reducing the film thickness, and improving the surface roughness of the active material are highly effective in improving the performance of the PENG [86, 90, 94]. Further, the nanofillers are commonly incorporated into polymer matrices to enhance the dielectric constant and the surface roughness of polymers. Thus, this enhancement in PPV output may be attributed to increased relative dielectric permittivity and improved surface roughness of the 0.75 wt% SNMX/PVDF film as suggested by the FESEM. The energy harvested by the PENG can be used to power small circuits, functioning as a nanogenerator.

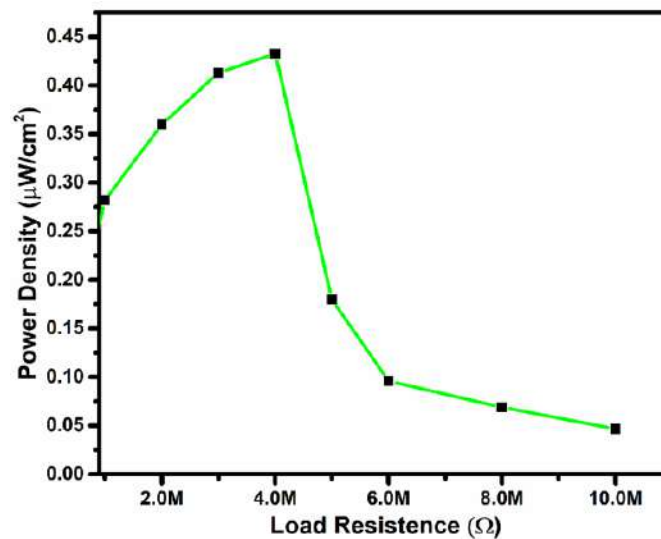


Figure 3.13: Variation of power density of the 0.75 wt% SNMX/PVDF composite film as a function of load resistance.

3.5 Conclusion

SNMX/PVDF composite films, made of PVDF and SNMX nanocomposites, have been studied for their electroactive phase formation and significant enhancement of dielectric characteristics over a wide frequency range (20 Hz to 1 MHz). When 0.75wt% SNMX is added to the PVDF matrix, the SNMX/PVDF composite film exhibits the maximum electroactive phase yield (FEA = 86%). FTIR and XRD analyses confirm that the electroactive phases in the SNMX/PVDF films have nucleated. In particular, the SNMX/PVDF films loaded with 0.50 wt% and 0.75 wt% SNMX nanocomposite at 20 Hz and room temperature exhibit the high relative dielectric permittivity, 150 and 165, respectively, with notably low loss tangent. The temperature-dependent dielectric characteristics of the manufactured films shows that the relative dielectric permittivity of composite films increase rapidly as compare to pure PVDF. The largest peak-to-peak voltage produced by a piezoelectric flexible nanogenerator (PENG) made from 0.75 weight percent SNMX/PVDF nanocomposite film is 105 V. Therefore, the SNMX/PVDF composite films with increased electroactive phase, superior dielectric properties and enhanced PPV as PENG suggest that they may/can meet the needs of next-generation electronic components, such as power conditioning, flexible film capacitors, and pulsed power generators.

CHAPTER 4

OPTIMIZATION OF SnO₂/MXENE/PVDF COMPOSITES FILMS TO ENHANCE STRUCTURAL, OPTICAL, MECHANICAL, DIELECTRIC, AND ELECTRICAL CHARACTERISTICS TOWARDS NEXT-GENERATION FLEXIBLE OPTOELECTRONIC AND ENERGY STORAGE DEVICES

In this chapter, we synthesized PVDF composite films consisting of 2 wt% MXene nanosheets and x wt% of SnO₂ nanoparticles (x = 0.0, 2.0, 4.0, 6.0, 8.0) using the solution casting method and characterized them using different techniques. Interestingly, the 6S-MP composite film, containing 6 wt% SnO₂ and 2 wt% MXene, exhibits optimized optical, mechanical, dielectric, and electrical conductivity properties. X-ray diffraction (XRD) analysis indicated the transformation of the non-polar phase to the polar phase in the PVDF composite film. FTIR measurements revealed an enhancement in the β phase content from 65% in pristine PVDF to 80% in the 6S-MP composite film. FESEM micrographs confirm the formation of SnO₂ nanoparticles and the characteristic accordion-like structure of the synthesized MXene. Additionally, the introduction of nanofillers disrupted the uniformity of the PVDF matrix, resulting in distinct morphological changes in the composite films. The Tauc plot analysis revealed that as the nanofiller content increased, the calculated direct and indirect bandgap energies decreased from 5.36 eV to 4.88 eV and from 5.11 eV to 4.61 eV, respectively. Furthermore, the addition of nanofillers enhanced the tensile strength and elasticity of the composite films. Dielectric measurements (102 to 107 Hz) showed that at 1 kHz, the relative dielectric permittivity of the 6S-MP composite film increased fivefold compared to pristine PVDF, with relatively low loss tangent ($\tan \delta$) of 0.10. According to Jonscher's rule, the AC electrical conductivity of the composite films increased with the nanofiller concentration and exhibited non-Debye type behaviour. The optimized optical, mechanical, dielectric, and electrical conductivity properties of 6S-MP film are due to its highest β phase content, better dispersion of SnO₂ nanoparticles and increased charge transport. Thus, the optimized film can be used for fabricating next generation flexible optoelectronic devices with enhanced charge-storage capabilities.

4.1 Introduction

With the rapid advancement of the Internet of Things, flexible polymer composites based on low-dimensional nanomaterials exhibiting superior energy storage and energy harvesting capabilities have garnered increasing interest for integration into wearable and flexible electronic systems. The development of lightweight, flexible, and easily synthesizable polymer-based composite films has received tremendous attention due to their unique combination of high mechanical strength, excellent flexibility, superior electrical breakdown strength, enhanced relative dielectric permittivity, and low dielectric loss[7, 95-97]. Therefore, these materials are becoming increasingly essential for next-generation flexible nanoelectronics and storage devices.

Among various polymer composites, polyvinylidene fluoride (PVDF)-based composites have been extensively studied owing to their remarkable electroactive phases, desirable mechanical stability, and relatively high dielectric strength. Moreover, PVDF composites offer environmentally friendly processing methods and facile synthesis, further supporting their applicability in flexible electronic devices[7, 97, 98]. Recent studies have reported significant improvements in energy storage density, energy conversion efficiency, sensitivity, and biocompatibility for PVDF-based composites, highlighting their potential for a broad spectrum of applications [97-100]. A variety of nanofillers have been incorporated into PVDF matrices to enhance their electrical and dielectric performance. The incorporated nanofillers can be classified into three main categories: inorganic, organic, and hybrid composites combining inorganic and organic nanofillers [86, 101, 102].

Incorporating inorganic nanofillers into the polymer matrix enhances the dielectric properties of PVDF while preserving the benefits of both components. However, the independent use of inorganic nanofillers, such as TiO_2 , SnO_2 , BaTiO_3 , etc., often results in trade-offs, such as increased dielectric loss, reduced mechanical flexibility and crystallinity of the PVDF [31, 86, 103]. This is primarily attributed to the high nanofiller concentrations and the larger dielectric gradient. To address the limitations of inorganic nanofillers, organic/conductive nanofillers such as reduced graphene

oxide (rGO), MXene, and multi-walled carbon nanotubes (MWCNTs) have been incorporated into polymer matrices [77, 104, 105]. These nanofillers have proven effective in substantially enhancing the dielectric constant, reducing the optical energy band gap and electrical conductivity even at low concentrations, without compromising the flexibility of PVDF. However, these nanofillers are often associated with relatively high dielectric loss due to the nanofiller agglomeration, which leads to the formation of conductive networks at higher nanofiller concentrations. This phenomenon reduces the breakdown strength of the material, thereby lowering its energy storage density and limiting its practical applicability in energy storage devices [77, 104-106].

Consequently, developing effective strategies to modify the structural, optical, morphological, dielectric, and electrical properties of PVDF-based composites has emerged as a highly active and promising area of research [98, 107]. To achieve this goal, researchers have widely focused on precisely engineering the nanofillers composition, optimizing loading concentration ensuring uniform dispersion and strengthening intermolecular interaction contact within PVDF matrices.

In this context, introducing a third insulating phase (inorganic) into the conductive/polymer system to disrupt continuous conductive pathways and promote uniform nanofiller dispersion has emerged as an efficient approach to enhance the PVDF properties. Additionally, the incorporation of inorganic nanofillers has been shown to effectively balance the conductive nanofillers and polymer matrix, offering a promising pathway for tuning the dielectric, optical, and mechanical behaviour of flexible PVDF composites for high-performance energy-related applications [44, 93]. For instance, R. Behera et al. demonstrated an enhancement in the dielectric and electrical properties of PVDF upon the incorporation of TiO₂ nanoparticles (inorganic) and MXene (conductive) as nanofiller. The composite containing 2 wt% MXene and 10 wt% TiO₂ exhibited a dielectric constant of 18.45 and a dielectric loss of 0.05 at 1 kHz [103].

Thus, MXene and metal oxide nanostructures have emerged as an excellent nanofiller for the PVDF matrix, significantly enhancing its structural, optical, mechanical,

dielectric, and electrical conductivity properties. The key advantages of incorporating metal oxide nanostructures with MXene as nanofillers include: (1) reduced leakage conduction in the composites, and (2) lower dielectric loss, which enhances the breakdown strength of the composite, thereby leading to a higher energy storage density [44, 108]. Recent reports on the incorporation of TiO_2 , MnO_2 , and similar nanostructures along with MXene as nanofillers have revealed notable enhancements in the properties of PVDF [74, 93]. However, according to the available literature, detailed information on the optimal wt% of SnO_2 and MXene in PVDF for achieving maximum structural, optical, mechanical, and electrical properties is still lacking. Additionally, the eco-friendly and easily synthesized nature of SnO_2 , along with its versatile optical and electrical properties, makes it a suitable choice as a nanofiller [31, 109].

Therefore, in the present work, we have synthesized nanofiller and composite films of PVDF with unique composition of SnO_2 nanoparticle and MXene nanosheet as nanofillers to provide better structural, morphological, optoelectronic, mechanical, dielectric, and electrical properties. The PVDF composite films were fabricated using the solution casting technique and characterized by several characterization techniques. This study shows that the 6S-MP (6 wt% SnO_2 and 2 wt% MXene) composite film exhibits highest β phase content, a reduced energy band gap, maximum tensile strength, improved dielectric properties, and enhanced conductivity. The proposed 6S-MP composite film provides a cost-effective, environmentally friendly, and scalable solution for advancing next-generation optoelectronic and energy storage devices.

4.2. Experimental section

4.2.1. Materials

Polyvinylidene fluoride (PVDF) powder with molecular weight 534000 g/mol was procured from Sigma Aldrich, USA. Dry N,N dimethyl formamide (DMF, Merck India), Stannic chloride hydrated 98% ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, MW= 350.58 g/mol, Sigma-Aldrich), Titanium aluminium carbide (Ti_3AlC_2) ($\geq 90\%$, particle size of $\leq 100 \mu\text{m}$, Sigma-Aldrich), Sodium hydroxide pellets (NaOH, Merck India), Hydrogen fluoride

acid 48% concentrated (HF, Mw= 20.1 g/mol, Sigma-Aldrich), Citric acid (Thermo scientific chemicals), Ethanol (Merck, Germany) were used in this work without any further purification. All the materials were of analytical grade. Additionally, deionized water is available in our laboratory.

4.2.2. Preparation of SnO₂ nanoparticle

Tin oxide nanoparticles were synthesized by the modified hydrothermal method. In this method, initially, 8 g of SnCl₄·5H₂O was mixed with 60 ml of anhydrous ethanol under vigorous stirring for 1h. Then, 2 g of citric acid was added to the stirred solution and further stirred for an additional 2h to ensure homogeneity. Next, the obtained solution was transfer into a Teflon-lined stainless-steel autoclave and properly sealed. The autoclave was heated at 160 °C for 24 h in a vacuum oven. Following the reaction, the system was allowed to cool spontaneously to room temperature. The obtained solution from autoclave was centrifuged (5000 rpm) for 30 minutes. The as-obtained product was thoroughly washed multiple times using absolute ethanol and distilled water to remove any residual impurities. Finally, the collected precipitates were dried at 80 °C for 8 h to obtain the SnO₂ nanoparticles. After that the sample was kept in a vacuum desiccator to ensure complete removal of residual solvents.

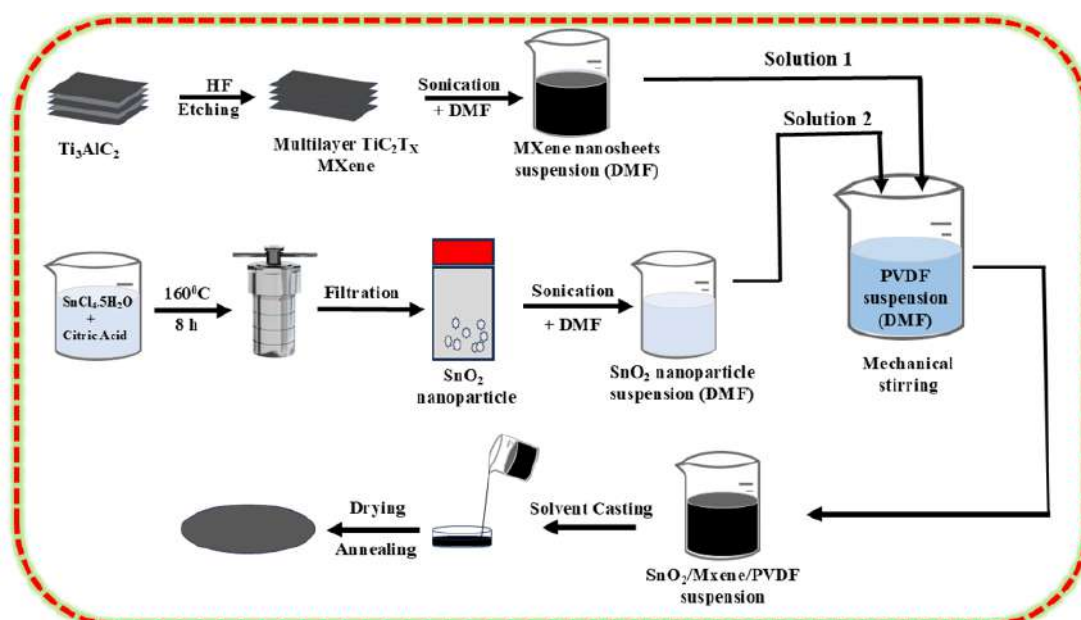
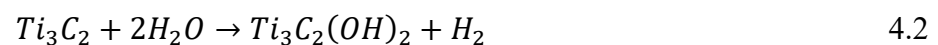
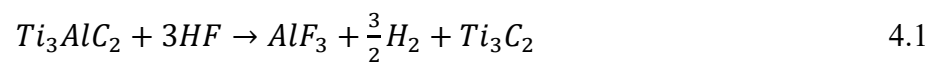


Figure 4.1: A stepwise depiction of the synthesis processes for SnO₂ nanoparticles/MXene nanosheets/PVDF composite films.

4.2.3. Preparation of $Ti_3C_2T_x$ MXene nanosheets

$Ti_3C_2T_x$ was synthesized via the delamination method. Hydrogen fluoride (HF) acid was employed to selectively etch the aluminium layers from the MAX phase, thereby producing MXene. A schematic representation of the entire synthesis process is provided in the Figure 4.1. 2 g of MAX phase powder was gradually added to 30 mL of 48% concentrated HF solution and stirred for 24 hours at room temperature using a magnetic stirrer. Following this, the resulting multi-layered MXene suspension was centrifuged six times at 3500 rpm for 10 minutes each, using deionized water (DI water), until the pH of the supernatant reached 6. Finally, the mixture was dried for 12 hours at $70^\circ C$ in a vacuum oven for further use. The possible chemical reactions involved in the synthesis of MXene nanosheets are proposed as follows[110]:



4.2.4. Preparation of SnO_2 / MXene/PVDF composite films

To prepare the bare PVDF film, 1 g of as procured PVDF powder was dissolved in 15 ml of DMF under magnetic stirring for 4 h to obtain uniform and transparent solution. The as obtained slurry solution was casted in a clean dried glass petri-dish and the solvent was evaporated at $90^\circ C$ using a hot air oven for overnight. To prepare the PVDF composite films, the weight fraction of MXene was maintained at 2 wt%, while the weight fractions of SnO_2 were set at 0 wt%, 2 wt%, 4 wt%, 6 wt%, and 8 wt%. Then uniform suspensions of MXene nanosheets and SnO_2 nanoparticles were individually prepared by dispersing them in DMF and sonicated for 1h. The obtained uniform suspension of the SnO_2 nanoparticle and MXene nanosheets were poured in the PVDF solution and stirred for 30 h using magnetic stirrer (400 rpm). The as obtained mixture was casted in a clean dried glass petri-dish and the solvent was evaporated at $90^\circ C$ using a hot air oven for overnight. Table 4.1 represents the codes assigned to the as synthesized composite films for ease of discussion. Further, the

thickness of the prepared composite films was measured using a digital vernier calliper and tabulated in Table 4.2.

Table 4.1: Codes assigned to the synthesized composite films.

Film Code	Composition of synthesized films
PVDF	PVDF
MP	MXene (2wt%)/PVDF
2S-MP	SnO ₂ (2wt%)/MXene (2wt%)/ PVDF
4S-MP	SnO ₂ (4wt%)/MXene (2wt%)/ PVDF
6S-MP	SnO ₂ (6wt%)/MXene (2wt%)/ PVDF
8S-MP	SnO ₂ (8wt%)/MXene (2wt%)/ PVDF

4.2.5. Material Characterization

To characterize the structural properties of the synthesized materials, X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV diffractometer equipped with Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The surface morphology of the synthesized particles was examined via field emission scanning electron microscopy (FESEM, JEOL JSM-7800F Prime). Elemental composition and spatial elemental distribution of the films were determined using energy-dispersive X-ray spectroscopy (EDX, SWIFT ED 3000). The identification of electroactive phases in both PVDF and composite films was conducted using Fourier-transform infrared spectroscopy (FTIR, Nicolet 5700). The optical bandgap of the samples was estimated through UV-Visible absorption spectroscopy using a PerkinElmer Lambda-1050 spectrophotometer. Dielectric properties were measured at room temperature using an impedance/material analyser (Keysight E4990A) over a frequency range of 20 Hz to 10 MHz. For electrical measurements, the samples were cut into square shapes with dimensions of approximately $5 \text{ mm} \times 5 \text{ mm}$. Mechanical properties, including tensile strength and elastic modulus, were evaluated using a 10 kN universal testing machine (Instron Dynamic UTM 8801) at a strain rate of 1 mm/min. Sample preparation for mechanical testing adhered to the ASTM D882 standard.

4.3. Results and discussion

4.3.1. Structural and Morphological Analysis of the Nanofillers

4.3.1.1. XRD Analysis

X-ray diffraction analysis was employed to assess the crystalline quality and phase purity. The obtained XRD patterns of the synthesized SnO₂ nanoparticles, Ti₃AlC₂

(MAX phase), and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene are shown in Figure 4.2. The presence of distinct sharp diffraction peaks confirms the rutile tetragonal phase and polycrystalline nature of the synthesized SnO_2 nanoparticles. The diffraction peaks at $2\theta = 26.48^\circ, 33.74^\circ, 37.80^\circ, 51.56^\circ, 54.54^\circ$, and 65.68° . are attributed to the crystallographic planes (110), (101), (200), (211), (220) and (310), respectively, and are in accordance with the standard JCPDS card no. 041-1445 [31, 40].

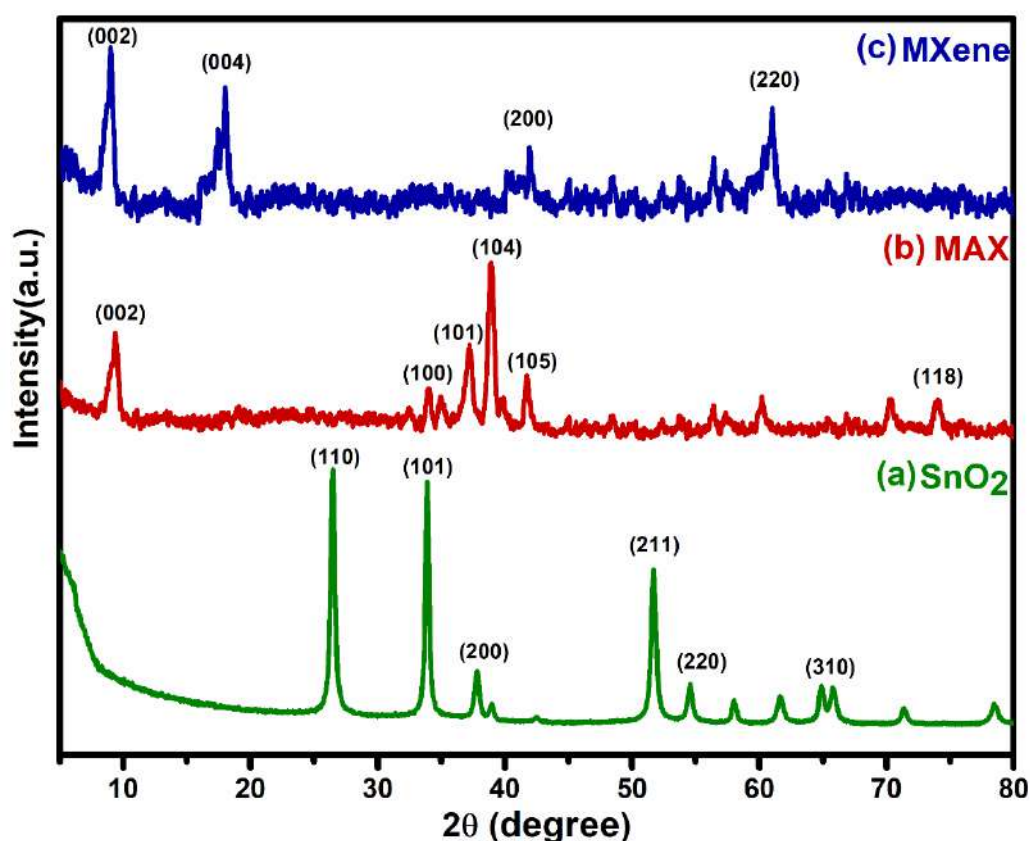


Figure 4.2: XRD patterns of (a) SnO_2 nanoparticles (b) MAX powder (Ti_3AlC_2) and (c) MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) nanosheets.

Further the XRD pattern of Ti_3AlC_2 , where peaks at $2\theta = 9.58^\circ, 34.01^\circ, 36.62^\circ, 38.92^\circ, 41.84^\circ$ and 73.56° correspond to the (002), (100), (101), (104), (105), and (118) planes, respectively (JCPDS card no. 52-0875), indicating a hexagonal phase with space group $P6_3/m\ m\ c$. Upon etching Ti_3AlC_2 with HF, the XRD pattern of $\text{Ti}_3\text{C}_2\text{T}_x$ displayed peaks at $2\theta = 9.03^\circ, 17.93^\circ, 41.52^\circ$ and 60.31° , corresponding to the (002), (004), (200), and (220) diffraction planes [82]. Notably, the peak at $2\theta = 9.58^\circ$ (002) in Ti_3AlC_2 was shifted to $2\theta = 9.03^\circ$ in $\text{Ti}_3\text{C}_2\text{T}_x$, signifying the

formation of $\text{Ti}_3\text{C}_2\text{T}_x$. This shift is attributed to the etching of the Al layers from Ti_3AlC_2 and the introduction of surface functional groups on $\text{Ti}_3\text{C}_2\text{T}_x$ (e.g., $-\text{O}$, $-\text{OH}$, and $-\text{F}$). The absence of the Ti_3AlC_2 peak at $2\theta = 38.92^\circ$ (104) in the $\text{Ti}_3\text{C}_2\text{T}_x$ XRD pattern further suggests the complete etching of the Al layers [111].

4.3.1.2. FESEM Analysis

Figure 4.3 (a&b) present the general and partially enlarged FESEM images of the synthesized SnO_2 nanoparticles revealing their uniform growth and three-dimensional spherical morphology. Furthermore, the bar histograms presented in Figure 4.3(c) for SnO_2

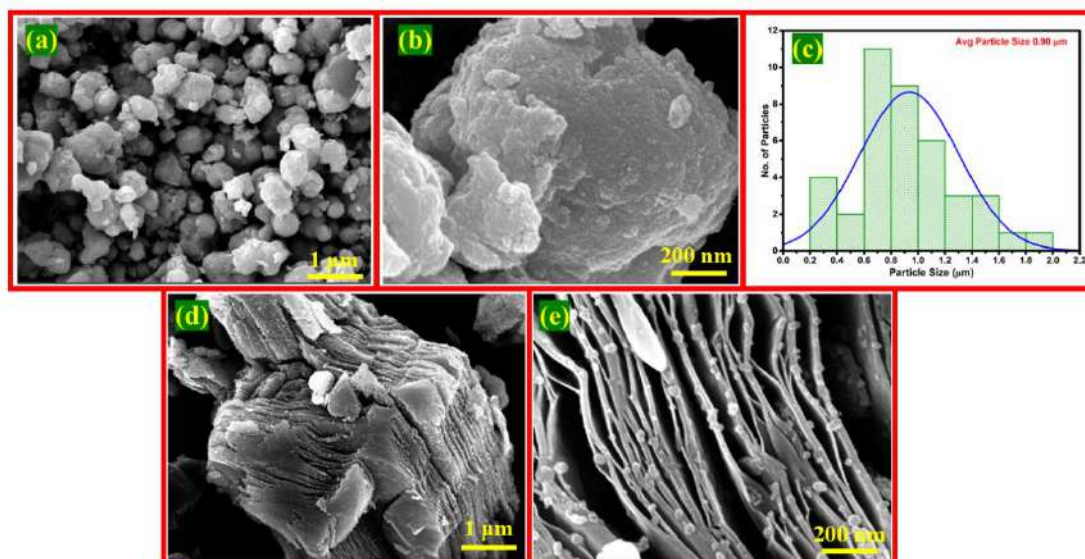


Figure 4.3: FESEM images showing (a & b) SnO_2 nanoparticles, (c) particle size distribution (d & e) the accordion-like morphology of exfoliated MXene.

particles depict the frequency versus particle size distribution, which was used to calculate the average particle size using ImageJ software. FESEM images of the MXene sheets at 1 μm and 200 nm scale are displayed in the Figures 4.3 (d&e). Illustrating an accordion-like structure with a large specific surface area. The well-defined two-dimensional morphology and observable interlayer spacing confirm the successful etching of the Al layer from Ti_3AlC_2 . The exothermic reaction between HF and aluminium generates a substantial amount of hydrogen gas, which facilitates

the expansion of the intercalated layers. Moreover, the formation of these layers enhances the surface activity, thereby contributing to a highly reactive surface [112].

4.3.2. Structural Analysis of PVDF Composite Films

4.3.2.1. XRD Analysis

Figure 4.4(a) display the XRD patterns of PVDF and PVDF composite films within the 2θ range of 10° to 80° . The non-polar (α) and polar (β) phases constitute the predominant crystalline phases in all composite films across different concentrations.

Diffraction peaks observed at 18.4° and 19.5° , corresponding to the (020) and (110) planes respectively, are attributed to the α -phase of PVDF. Conversely, the peaks at 20.6° and 38.8° , indexed to the (110/200) and (002) planes respectively, are characteristic of the β -phase. Additionally, the SMP composite films exhibit distinct peaks of the SnO_2 nanofiller at $2\theta = 26.2^\circ$, 33.4° , 51.6° , and 65.2° , corresponding to the (110), (101), (211), and (301) planes, respectively. The intensity of these peaks increases with rising SnO_2 content, indicating enhanced incorporation of SnO_2 nanoparticles. Diffraction peaks corresponding to MXene are not observed, likely due to its low concentration in the composite films [93, 113].

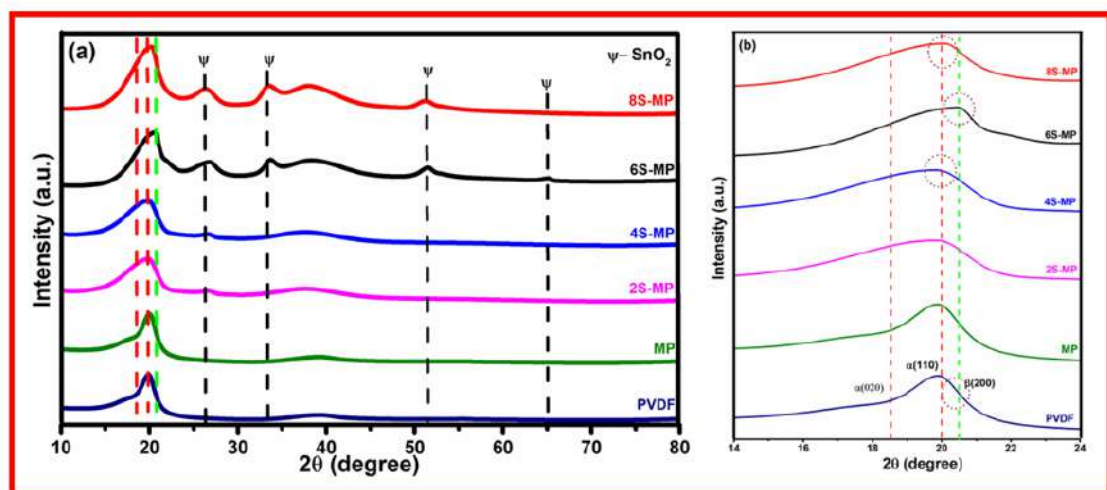


Figure 4.4: XRD pattern (a) Range 10° to 80° PVDF and PVDF composite films and (b) magnified from 14° to 24° for highlighting the phases.

Figure 4.4(b) provides a magnified view of the XRD patterns in the 2θ range of 14° to 24° . This close-up reveals a notable reduction in the intensity of α -phase-related

peaks, while the intensity of β -phase peaks increases significantly with increasing the nanofiller concentration. At a nanofiller concentration of 6 wt%, the intensity of the α -phase peak at 19.5° (110) almost disappears. Meanwhile, the 20.6° peak corresponding to the β -phase shows a remarkable increase in intensity compared to the pristine sample, indicating an enhancement in the electroactive β -phase upon the addition of SnO_2 nanoparticles as fillers. Interestingly, on further increase in the nanofiller concentration to 8 wt%, the XRD peaks shifts towards the α -phase (110), indicating reduction in the β -phase. Thus, 6 wt% SnO_2 nanofillers demonstrate maximum enhancement in the electroactive β -phase of PVDF composite film.

Furthermore, the overall crystallinity of the PVDF films is observed to decrease progressively with increasing nanofiller content. This reduction in crystallinity is likely due to the formation of additional nucleation sites introduced by the nanofillers [29, 84, 114].

4.3.2.2. FTIR Analysis

The β -phase content in the synthesized pristine PVDF and composite films were analysed using FTIR absorption spectroscopy. The β -phase in PVDF contributes significantly to the piezoelectric response of self-powered devices. An increased β -phase content correlates with a higher dipole moment, thereby enhancing the piezoelectric performance [31].

The obtained FTIR absorption spectra shown in Figure 4.5 reveal that all the composite films exhibit the presence of both α - and β -phases. The characteristic absorption peaks at 835 cm^{-1} , 1279 cm^{-1} , and 1400 cm^{-1} are indicative of the β -phase, whereas the peaks observed at 763 cm^{-1} , 795 cm^{-1} , 974 cm^{-1} , and 1382 cm^{-1} correspond to the α -phase in the synthesized pristine PVDF film. Qualitative analysis of the FTIR spectra has been done on the basis of the relative intensities of peaks associated with both α and β phases. The incorporation of MXene and SnO_2 nanofillers into the PVDF matrix is anticipated to induce a higher number of dipole moments, thereby promoting the formation of the β -phase. This is evidenced by the reduction in α -phase peak intensities upon the addition of nanofillers, providing

strong support for the enhanced β -phase content. Also, similar type of behaviour in β -phase content has been observed in XRD pattern [29]. The enhancement in β -phase content is primarily associated with the formation of an all-trans (TTTT) conformation of the CH_2 and CF_2 segments along the PVDF backbone, facilitated by electrostatic interactions between the polymer chains and the abundant surface charges present on the MXene nanosheets [74].

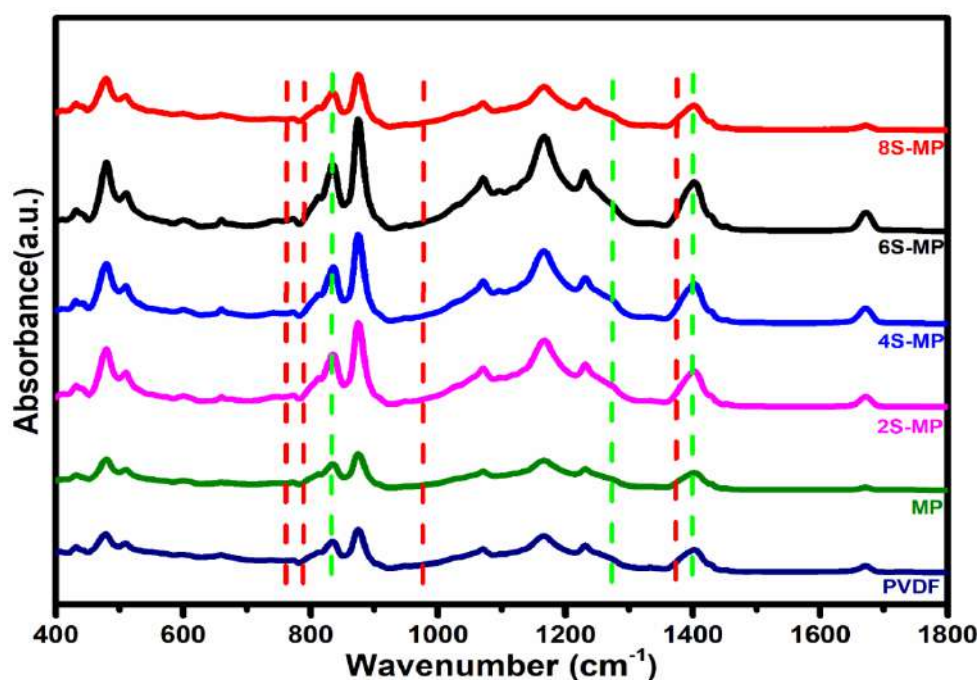


Figure 4.5: FTIR spectra of PVDF and PVDF composite films ranges from 400–1800 cm^{-1} .

Quantitative analysis of β -phase content in the synthesized PVDF matrices was performed using the Lambert–Beer law [114]. The relative fraction of the β -phase in the films was calculated based on absorbance values using Equation (4.4).

$$F_{\beta} = \frac{A_{\beta}}{1.26 A_{\alpha} + A_{\beta}} \times 100\% \quad 4.4$$

The ratio of absorption coefficients k_{β} / k_{α} is taken as 1.26, where $k_{\beta} = 7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $k_{\alpha} = 6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, corresponding to the characteristic absorption at 835 cm^{-1} (β -phase) and 763 cm^{-1} (α -phase), respectively. Here, A_{α} and A_{β} represent the absorbance intensities at 763 cm^{-1} and 835 cm^{-1} , and F_{β} denotes the fraction of the β -phase content in the PVDF matrix.

The pristine PVDF film exhibits a β -phase content of 65%. As the SnO₂ loading increases, $F\beta$ also increases, reaching a maximum of 80% at a SnO₂ concentration of 6 wt%. However, at a higher nanofiller concentration of 8 wt%, $F\beta$ decreases to 73%. This decline is attributed to the excessive nanofiller content leading to nanoparticle agglomeration, which introduces structural defects into the PVDF matrix and perturbs the potential energy landscape of the polymer chains, thereby hindering β -phase formation[45, 74]. The trend observed in $F\beta$ closely follows the variation in the dielectric constant of the composite films.

4.3.3. Morphological Analysis of Composite Films

FESEM was employed to investigate the surface morphology of pure PVDF and PVDF based composite films. The incorporation of nanofillers into the PVDF matrix induced notable morphological alterations in the composite films structure. Figure 4.6 (a-r) presents the FESEM micrographs of PVDF films both with and without nanofillers at different magnifications. The micrographs of the pure PVDF film (a, b & c) reveal predominantly fibrillar structures, which are characteristic of α -phase spherulites (indicated by the blue circle). These morphological features are absent in the PVDF nanocomposite films. The introduction of nanofillers disrupts the uniformity of the PVDF matrix, leading to distinct morphological changes.

The surface micrographs of the nanocomposite films demonstrate the presence of spherulitic structures; however, a noticeable reduction in spherulite size is observed upon the addition of MXene and SnO₂ nanoparticles (highlighted by the red circle). The size of the spherulites is indicative of the polymer's crystallization kinetics, which are governed by both the nucleation ability of the nanofillers and the subsequent growth rate of the spherulites [115]. Furthermore, the composite exhibits a porous morphology, attributed to phase transitions in the polymer matrix induced by the inclusion of nanofillers.

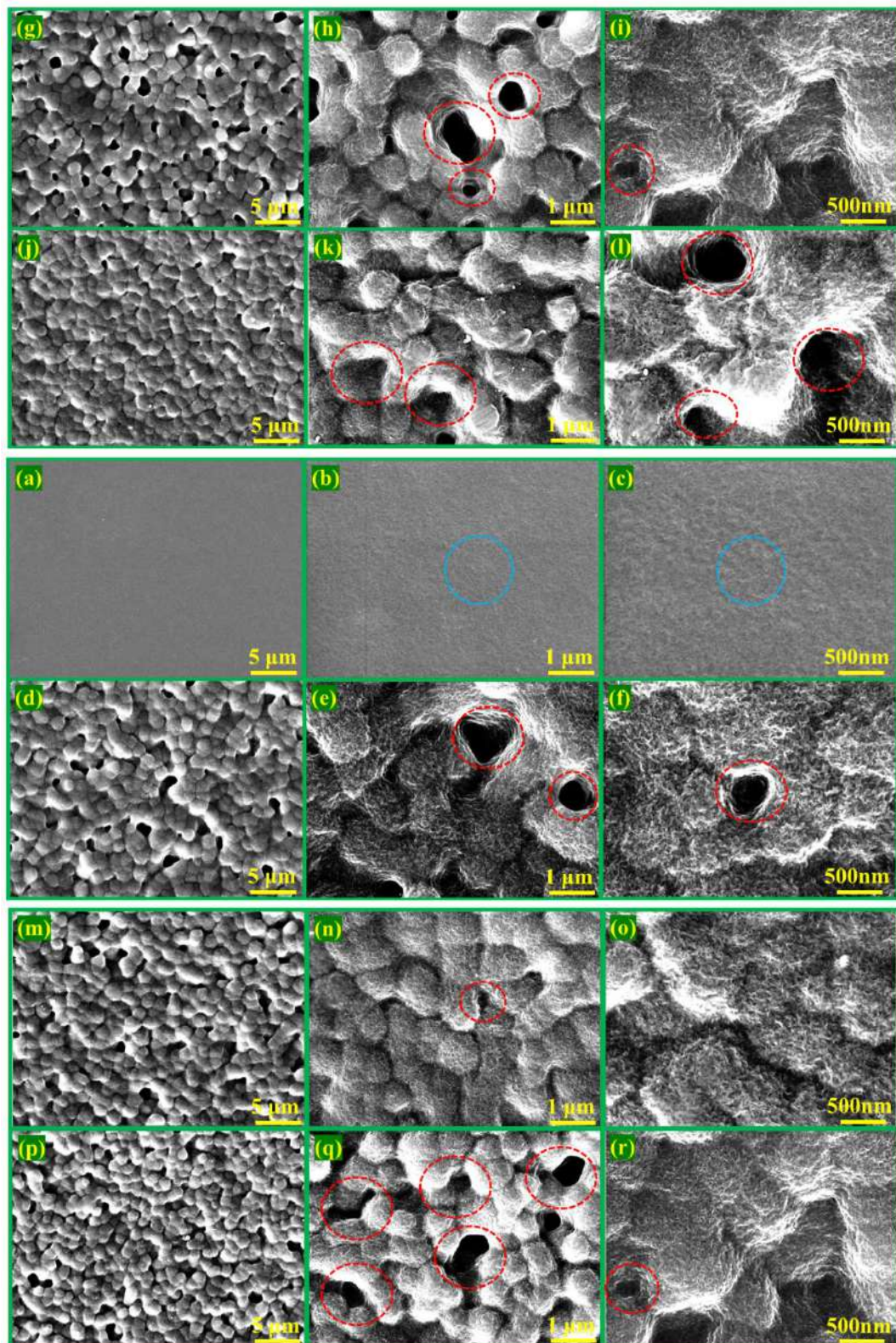


Figure 4.6: FESEM images of (a to c) pure PVDF, (d to f) MP, (g to i) 2S-MP (j to l) 4S-MP (m to o) 6S-MP (p to r) 8S-MP composite film.

Interestingly, a decrease in the α / β phase ratio correlates with a reduction in spherulite size. In this study, to validate the modifications in crystalline morphology upon the incorporation of 6 wt% SnO₂ evidenced through FTIR and XRD analysis corresponding changes in nucleation-related physical properties were examined. These observations further support the role of nucleation in promoting the β -phase. Accordingly, the 6S-MP sample, which exhibits the highest β -phase content, also displays the smallest spherulite size.

Elemental mapping analysis confirmed the presence of the incorporated nanofillers and their homogeneous distribution throughout the PVDF matrix, as illustrated in Figures 4.7 and 4.8. Figure 4.7 depicts the uniform dispersion of MXene within the PVDF matrix of the MP composite film, while Figure 4.8 demonstrates the distribution of both MXene and SnO₂ nanofillers in the 6S-MP sample. This uniform distribution can be attributed to the effective sonication and stirring processes employed during the preparation of the composite films.

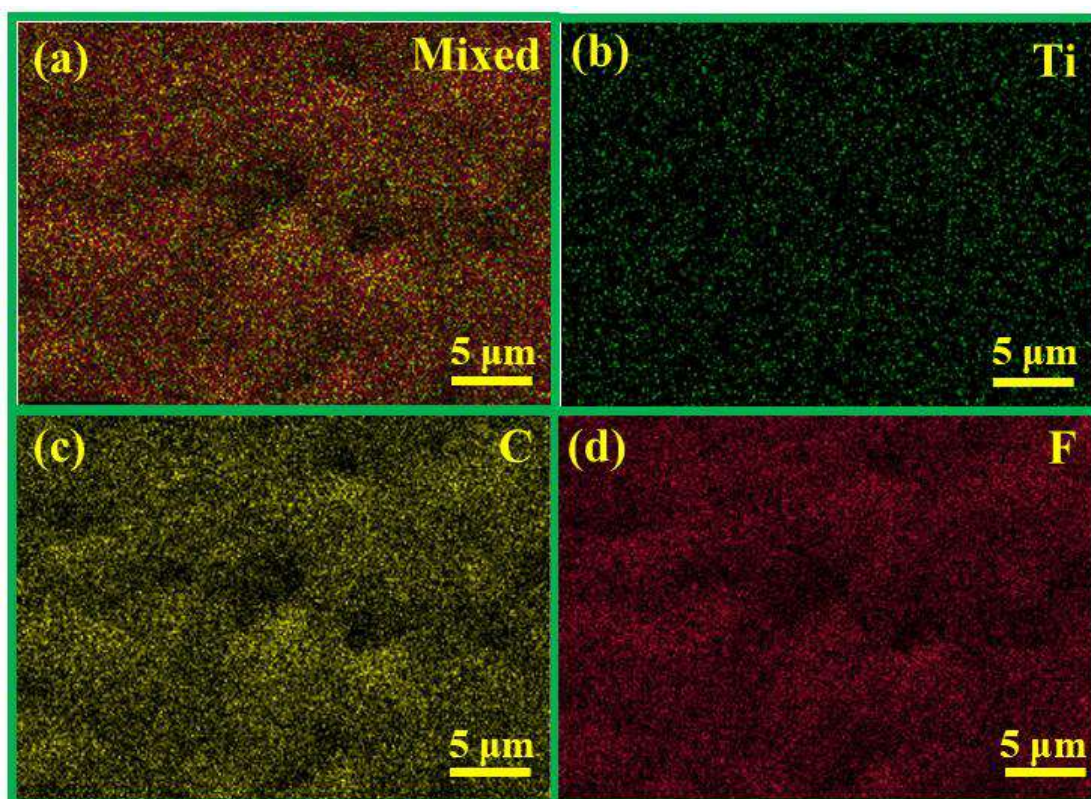


Figure 4.7. (a to d) Elemental mapping of the MP composite film.

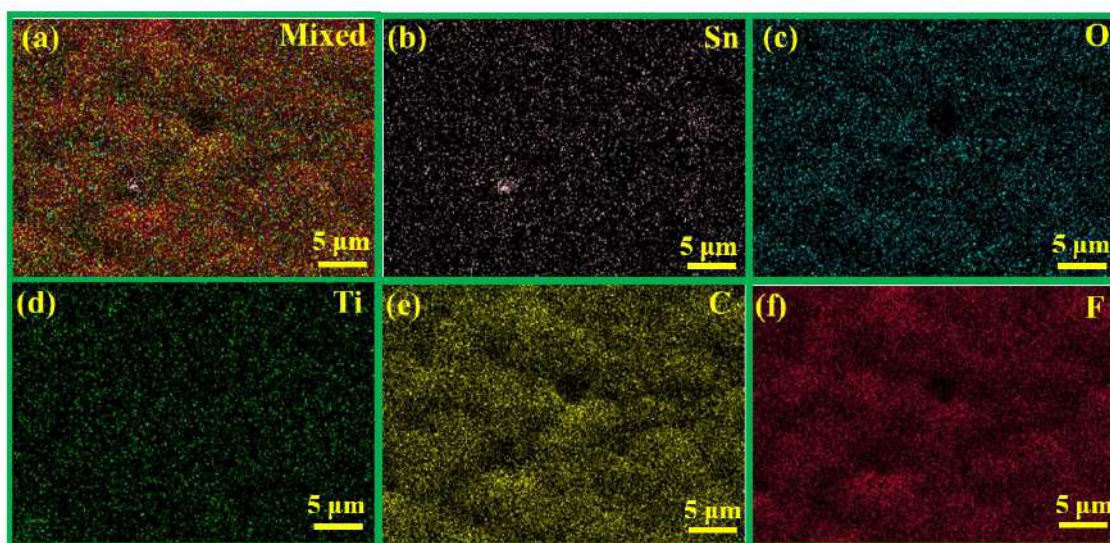


Figure 4.8. (a to f) Elemental mapping of the 6S-MP composite film.

4.3.4. Optical Properties of Composite Films

4.3.4.1. UV-Visible Absorbance Spectroscopy

The optical properties of PVDF and its composite films were analysed using UV–Visible absorbance spectroscopy in the wavelength range of 200–800 nm and the absorbance spectrum is illustrated in Figure 4.9.

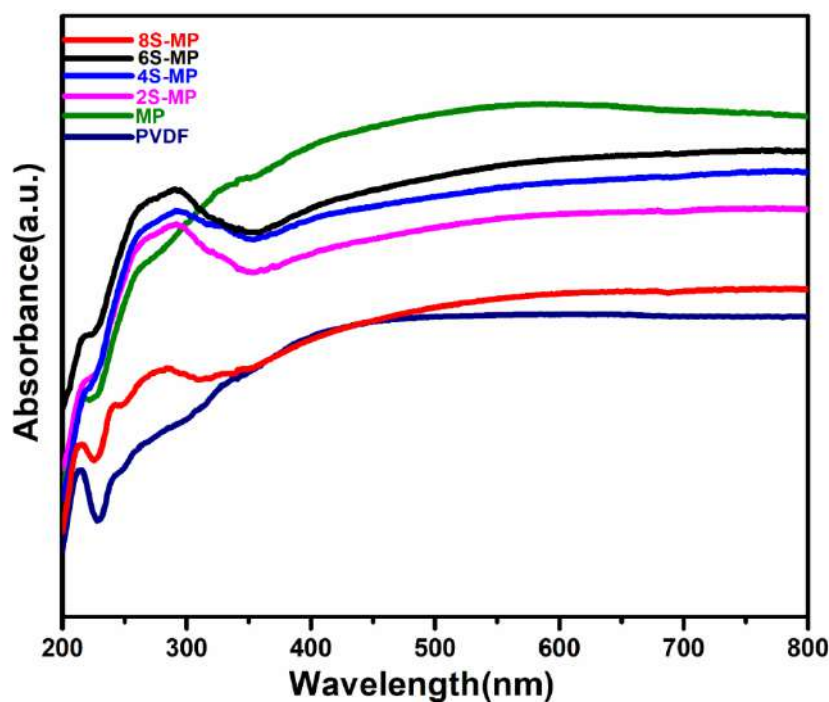


Figure 4.9: UV-Vis absorption spectra of PVDF and PVDF composite film.

It is evident that the absorbance of pristine PVDF is significantly lower than that of the composite films within the visible spectrum. Among all samples, the MP composite film exhibits the highest absorbance in visible region. In the ultraviolet (UV) region, the PVDF film displays an absorbance band at 215 nm, which can be attributed to the CF₂ vibrational modes of PVDF [74, 105]. The intensity of this UV absorption band decreases in the composite films; however, an increase in intensity is observed for the 8S-MP film.

Table 4.2: Thickness, Energy band gap (E_{gin}, E_{gd}), Conductivity (σ_{dc}), Frequency exponent (s), Mechanical strength, Relative dielectric constant (ϵ_r') and Loss tangent ($\tan\delta$) of the PVDF and PVDF composite film.

Sample	Thickness (μm)	E_{gin} (eV)	E_{gd} (eV)	$\sigma_{dc} * 10^{-7}$ (Sm^{-1})	s	Stress MPa	ϵ_r' (kHz)	$\tan\delta$ (kHz)
PVDF	110	5.35	5.11	4.0	0.79	25	6	0.01
MP	130	5.17	4.83	8.6	0.89	30	10	0.01
2S-MP	100	5.07	4.73	7.9	0.82	-	12	0.03
4S-MP	110	5.06	4.70	10.6	0.83	33	15	0.04
6S-MP	120	4.88	4.61	11.3	0.84	46	30	0.1
8S-MP	100	5.26	4.98	7.38	0.81	26	18	0.08

Additionally, the SMP composite films exhibit an absorption band at 295 nm (4.2 eV), which can be ascribed to the incorporated SnO₂ nanoparticles. The intensity of this band increases with SnO₂ content up to 6 wt% in the PVDF matrix. Moreover, a redshift in the band position accompanied by band broadening is observed [116]. This broadening and shift are likely due to changes in the crystallinity of the composite films induced by the addition of SnO₂. Notably, the film containing 8 wt% SnO₂ shows a reduction in band intensity, which may be attributed to nanoparticle agglomeration. Optical properties of these polymer nanocomposite films make them promising candidates for use as UV shielding materials in future optical technologies.

4.3.4.2. Energy Band Gap Analysis

The optical energy band gap of the synthesized films has been calculated using the obtained UV-visible absorbance spectrum. The indirect and direct energy band gap of the films have been calculated using Equation (4.5).

$$\alpha(\nu) = \frac{(h\nu - E_g)^n}{h\nu} \quad 4.5$$

Here $h\nu(\text{eV}) = \frac{1240}{\lambda}$ denotes the photon energy, E_g is the energy band gap, $\alpha = 2.303 * \frac{A_b}{d}$ is the absorbance coefficient, A_b is the absorbance, d is the thickness of the prepared sample and the exponent $n = 2$ corresponds to an allowed indirect electronic transition, and $n=1/2$ pertains to a direct transition [73].

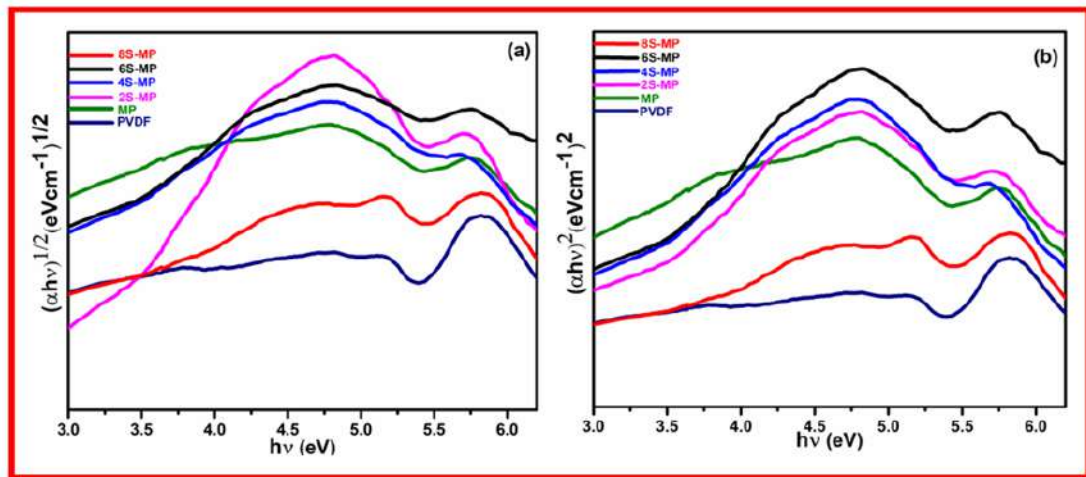


Figure 4.10: Tauc plots of (a) indirect (b) direct band gap of PVDF and PVDF composite film.

The plotted Tauc plots between $(\alpha h\nu)^{1/2}$ versus $(h\nu)$, and $(\alpha h\nu)^2$ versus $(h\nu)$, for determining the indirect (E_{gin}) and direct optical energy band gap (E_{gd}), respectively, of pure PVDF, MP, and SMP composite films are presented in Figure 4.10 (a & b). The optical band gap energies were estimated from the intercept of the extrapolated linear portion of the curve with the photon energy axis at $\alpha = 0$. The calculated E_{gin} and E_{gd} values for all the films are tabulated in Table 2.

The E_{gin} and E_{gd} values of the pristine PVDF film are found to be 5.11 eV and 5.35 eV, respectively which are in close agreement with their literature values[73, 74]. The incorporation of MXene into PVDF reduced the E_{gin} and E_{gd} from 5.11 to 4.83 eV and from 5.35 to 5.17 eV, respectively. Furthermore, on progressive incorporation of SnO_2 nanoparticles into the PVDF matrix leads to a systematic reduction in the both (E_{gin} and E_{gd}) optical band gap upto 6 wt% of SnO_2 nanoparticles. This reduction is attributed to the generation of structural defects and localized electronic states near

the band edges, which effectively lower the Fermi level in the composite films. These defect states facilitate charge carrier transitions, thereby modulating the electronic structure and optical properties of the composites [73, 105]. This trend is ascribed to defect-induced localized states, enlargement of grain size, and the corresponding increase in charge carrier density within the conduction band. This reduction in the energy band gap raises the electrical conductivity along with modulation in optical characteristics of the composite films [73, 117].

Interestingly, on further increasing the SnO₂ concentration (8 wt%) in PVDF matrix values of the both optical energy gap increases. At this concentration the nanofillers start forming clusters/agglomeration within the PVDF matrix as evident from FESEM result. This clustering of the nanofillers leads to reduction in the interactions between nanofiller and the PVDF matrix, which obstruct charge transport, resulting in increase in energy band gap. This energy band gap engineering of the composite's films is fascinating towards many flexible optoelectronic applications including organic light-emitting diodes, flat panel displays, and photovoltaics [73, 74, 105, 117].

4.3.5. Mechanical Properties of Composite Films

4.3.5.1. UTM Analysis

The mechanical performance of pure PVDF, MP and SMP composite films were determined using the UTM data. The stress strain curve of the films is plotted in Figure 4.11 (a). The tensile strength values for pure PVDF, MP, 4S-MP, 6S-MP and 8S-MP films are found 25, 30, 33, 46 and 26 MPa, respectively. The composite film containing 6 wt.% SnO₂ exhibited the highest tensile strength with enhancements of 82% relative to the pristine PVDF. However, beyond this optimal concentration, a decline in mechanical properties was observed. This reduction is attributed to the increased SnO₂ content which impairs uniform dispersion and promotes particle agglomeration. The formation of agglomerates introduces structural defects and stress concentration points within the matrix, thereby compromising the mechanical integrity of the composites [118, 119].

Further, to obtain the elastic modulus, slope of the linear part of the stress strain curve is measured. The measured elastic modulus values of the films are plotted in

histogram shown in Figure 4.11 (b). The MP composite film has lowest strain compare to SMP films. The observed pattern of elastic modulus and strain values are in accordance with the reported data [37].

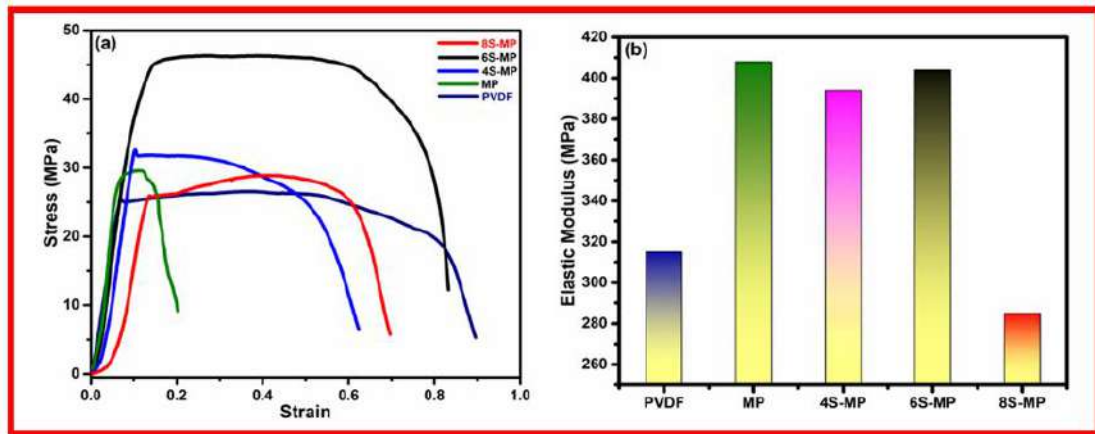


Figure 4.11: (a) Stress vs. strain curve and (b) elastic modulus variation of PVDF and PVDF composite films.

4.3.6. Dielectric properties of Composite Films

For device applications like supercapacitors and batteries, enhancing a material's charge storage capacity is essential for improving its dielectric properties [109]. Dielectric measurements provide valuable insights into the material's relaxation mechanisms and their dependence on frequency. Two important physical parameters derived from these measurements are dielectric constant and loss tangent.

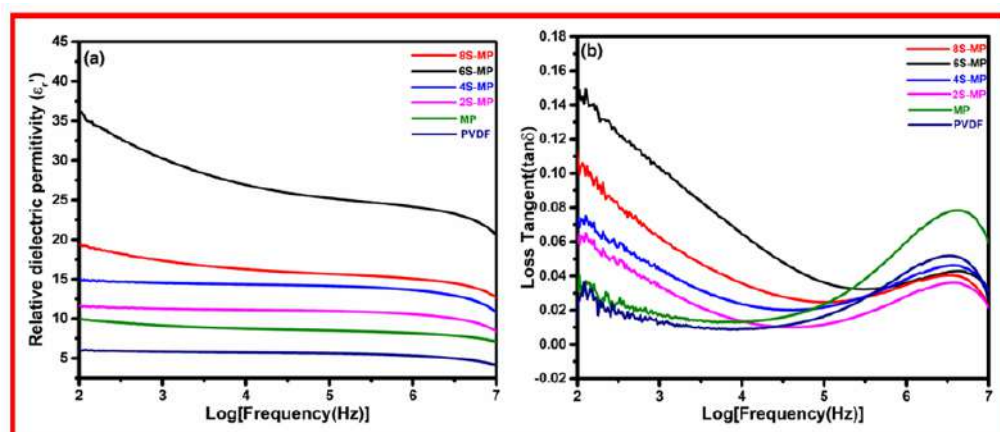


Figure 4.12: Frequency dependent (10^2 to 10^7) dielectric properties of PVDF and PVDF composite film (a) Relative dielectric permittivity, (b) loss tangent.

Several factors influence a material's relative dielectric permittivity including applied frequency, temperature, molecular orientation, applied pressure, and molecular structure [86, 88]. Thus, frequency dependent study of the dielectric properties was investigated of the synthesized films at room temperature. Figure 4.12 (a&b) presents the variations in ϵ_r' , and $\tan \delta$ as functions of frequency ranges from 10^2 Hz to 10^7 Hz for the PVDF, MP and SMP composite films. The ϵ_r' , of PVDF and MP films remains almost constant with applied frequency whereas the SMP films exhibit a gradual decrease with increasing frequency. The variation in ϵ_r' , is more at lower frequencies (100 Hz to 1kHz) than that of in higher frequency range. This phenomenon is primarily attributed to the inability of dipoles to fully align with the oscillating electric field at higher frequencies. At lower frequencies, dipoles can effectively track the changes in the electric field, whereas at higher frequencies, the rapid oscillations hinder the dipoles from aligning with the field, leading to a diminished and delayed polarization response, which consequently results in a reduction in the ϵ_r' [92, 93].

It is expected that the relative dielectric permittivity of the composite films will enhance due to their increased β phase content as compared to the pristine PVDF film. Therefore, the composite film (6S-MP) with highest β phase content has shown maximum ϵ_r' at room temperature. At 1 kHz, the ϵ_r' of the 6S-MP composite film increases five times than that of pristine PVDF. However, the composite film (8S-MP) with 8 wt% SnO_2 shows decrement in the dielectric constant. At room temperature and 1 kHz, the values of ϵ_r' and $\tan \delta$ of PVDF and composite films are tabulated 4.2. The observed ϵ_r' behaviour is explained using the Maxwell-Wagner-Sillars (MWS) interfacial polarization and β phase content of the films. The SMP composite films comprises three distinct interfacial interactions: SnO_2/PVDF , MXene/PVDF , and $\text{SnO}_2/\text{MXene}$. These interfaces facilitate charge accumulation and interfacial polarization arising from the distinct electrical properties of SnO_2 , MXene, and PVDF [93, 120]. An increase in SnO_2 content up to 6 wt% results in a greater number of interfaces within the composite through homogenous dispersion throughout the macromolecular chain, thereby enhancing interfacial polarization and significantly increasing the ϵ_r' . Additionally, the enhanced polar β -phase further contributing to the improved ϵ_r' [74, 121].

Loss tangent ($\tan \delta$) of the composite films initially decreases and then increases with frequency. $\tan \delta$ is influenced by factors, including conductivity loss and polarization loss. At lower frequencies, $\tan \delta$ is predominantly attributed to interfacial polarization loss and the orientation polarization of PVDF molecules. While at higher frequencies, dielectric relaxation becomes the dominant factor due to the increased movement of polymer chains within the PVDF matrix [77, 120]. It can be observed the $\tan \delta$ of the composite films at low frequencies increases with increasing SnO_2 content up to 6 wt%, yet remains relatively low.

Furthermore, the composite films with 8 wt% SnO_2 content shows reduction in the ϵ_r and $\tan \delta$. The reduced ϵ_r and $\tan \delta$ of the 8S-MP composite film is due to the forming the cluster of nanoparticles within the PVDF. That clustering of nanoparticles in the PVDF matrix leads to increases the number of immobile charge carriers in the matrix resulting in a decrease in ϵ_r and $\tan \delta$ [85, 122]. Table 4.3 compares the dielectric properties of this work with other reported polymer composites.

Table 4.3: Comparative analysis of dielectric properties of $\text{SnO}_2/\text{MXene}/\text{PVDF}$ composite films with other reported PVDF composites.

S.No	Composites	Filler concentration	f(kHz)	ϵ_r	$\tan \delta$	Ref.
1	$\text{MnO}_2/\text{MXene}/\text{PVDF}$	MnO_2 : 7 wt% MXene: 13 wt%	1	37.3	0.05	[93]
2	$\text{BaTiO}_3/\text{MXene}/\text{PVDF}$	BaTiO_3 : 8 wt% MXene: 2 wt%	0.1	77	0.15	[44]
3	$\text{Ta}_2\text{O}_5/\text{PVDF}$	Ta_2O_5 : 1.25 wt%	1	40	0.262	[123]
4	$\text{SrTiO}_3/\text{MXene}/\text{PVDF}$	SrTiO_3 : 30 wt% MXene: 12 wt%	1	117.8	0.169	[124]
5	$\text{CCTO}/\text{MXene}/\text{PVDF}$	CCTO: 30 vol% MXene: 5 wt%	10	26	0.063	[80]
6	SnO_2/PVDF	SnO_2 : 15 wt%	1	27	0.2	[31]
7	$\text{MnO}_2 \text{ NW}/\text{CNT}/\text{PVDF}$	CNT: 3.0 wt% MnO_2 : 4.5 wt%	0.1	50.6	0.7	[125]
8	$\text{SnO}_2/\text{MXene}/\text{PVDF}$	SnO_2 : 6 wt% MXene: 2 wt%	1	30	0.1	This Work

4.3.7. AC Conductivity of Composite Films

The total conductivity originates from the combined contributions of free charge carriers and bound charge carriers. Decrease in conductivity with increasing frequency is indicative of dominant free carrier transport, whereas an increase in conductivity with frequency implies a predominance of bound charge carrier contribution [88]. Therefore, the AC conductivity ($\sigma(\omega)$) of the all the synthesized films has been studied as function of applied field frequency and represented in Figure 4.13. The $\sigma(\omega)$ was calculated using the Equation (4.6).

$$\sigma(\omega) = \omega \varepsilon_0 \varepsilon_r' \tan \delta \quad 4.6$$

where $\omega = 2\pi f$ is the angular frequency, ε_0 is the permittivity of free space, ε_r' is the relative permittivity, and $\tan \delta$ is the loss tangent [88, 126].

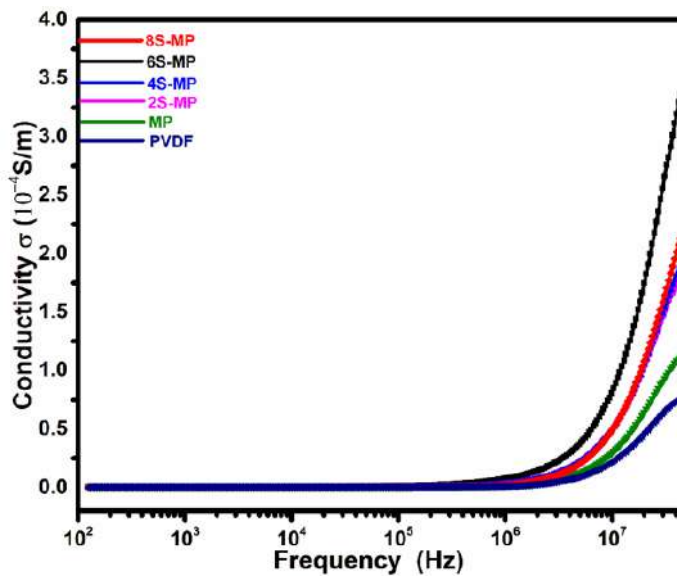


Figure 4.13: Frequency dependent dielectric AC conductivity of PVDF and PVDF composite film.

Across all samples, conductivity increases with frequency, confirming that the conduction mechanism is primarily governed by bound charge carriers. In lower frequency region (10^2 - 10^5) the variation in $\sigma(\omega)$ is negligible. The observed variation can be described by the Funke jump relaxation model, which suggests that charge carriers engage in successful hopping over prolonged durations, leading to long-range translational movement that results in frequency-independent conductivity [127]. However, at higher frequencies the films show greater variation in $\sigma(\omega)$ with

frequency as well as with nanofiller concentration. This sudden rise in conductivity is attributed to dipole relaxation and short-range ion mobility [109].

The increment in $\sigma(\omega)$ of PVDF with nanofiller concentration above 10^5 Hz can be attributed to the electronic polarization. The increase in conductivity with rising frequency is attributed to enhanced charge carrier mobility and the ionic hopping mechanism involved in the conduction process [128]. The highest conductivity is observed for 6S-MP composite film, suggesting optimal nanoparticle-polymer interaction at these loadings. At higher nanoparticle content (8S-MP), agglomeration leads to a reduction in interfacial interaction between the polymer and nanofiller particles. This aggregation favours particle-particle rather than particle-polymer interactions, thereby obstructing charge transport pathways and causing a slight reduction in conductivity relative to the 8S-MP composite film [44, 128].

The frequency dependence of the AC conductivity was analysed using Jonscher's universal power law, expressed as (Equation (4.7)):

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \quad 4.7$$

where σ_{dc} represents the frequency-independent (DC) conductivity, and $A\omega^s$ corresponds to the frequency-dependent part. Here, A is a pre-exponential factor indicating the degree of polarization, and s ($0 < s < 1$) is the power law exponent reflecting the extent of interaction between mobile ions and the lattice, which varies with frequency [44, 129].

The calculated values of σ_{dc} and s are tabulated in Table 4.2. The MP and SMP composite films exhibit higher σ_{dc} conductivity compared to pure PVDF due to the inherently conductive nature of SnO₂ and MXene. Furthermore, the s values range between 0 and 1 for a perfect Debye dielectric dipolar material and an ionic-type material, respectively. All the composite films exhibit a non-Debye relaxation phenomenon, as indicated by s values approaching 1 [109, 129].

4.4. Conclusion

Using a solution casting technique, PVDF composite films with different wt% of SnO₂ and 2wt% MXene as nanofillers were effectively synthesized. Assessment of their different characterization suggests that the 6 wt% SnO₂ and 2 wt% MXene (6S-MP film) is the optimized nanofiller concentration in PVDF matrix towards improvement in its structural, optical, mechanical, dielectric, and electrical properties. XRD and FTIR analyses confirmed the enhancement of the electroactive phase in the composite. FESEM micrograph of the pure PVDF film reveal predominantly fibrillar structures, which are characteristic of α -phase spherulites which are absent in the PVDF composite films. Tauc plots revealed a decrease in direct and indirect band gaps from 5.36 and 5.11 eV to 4.88 and 4.61 eV, respectively. The 6S-MP composite film showed an 82% improvement in tensile strength over pristine PVDF. At 103 Hz, it exhibited a dielectric constant of 30 with a relatively low loss tangent of 0.1. Interestingly when the nanofiller content is increased to 8 wt% of SnO₂, the properties of composite film (8S-MP) start deteriorating. The increase in electroactive phase, reduction in energy band gap, and enhancement in dielectric properties indicate that optimized composite film is well-suited for applications in energy harvesting, UV shielding, and energy storage devices, respectively. So the next chapter is described the mechanical energy harvesting properties (PENG and TENG) of these flexible composite films by the fabrication of Flexible Composite Energy Harvesting Device.

CHAPTER 5

DESIGN AND DEVELOPMENT OF A HIGH PERFORMANCE PVDF BASED FLEXIBLE COMPOSITE PIEZOELECTRIC ENERGY HARVESTING DEVICE FOR WEARABLE ELECTRONICS

Dual nanofillers designed for polymer nanocomposites are expected to obtain excellent biomechanical energy harvesting performance by virtue of hybrid morphologies, charge transfer capability and interaction with surface charge. In this study, a dual nanofillers MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) nanosheets and tetragonal tin oxide (SnO_2) nanoparticles are incorporated into a PVDF matrix. At a fixed concentration of 2 wt% MXene and varying concentrations of SnO_2 nanoparticles (2 wt%, 4 wt%, 6 wt%, and 8 wt%), composite PVDF flexible films were fabricated using the solution-casting method. FTIR analysis identified an optimal composition of 2 wt% MXene and 6 wt% SnO_2 (6S-MP), which shows a maximum β phase content of 80% due to uniform distribution of the nanofillers as confirmed by the FESEM images. The 6S-MP flexible composite piezoelectric energy harvester (FCPEH) device generated maximum open circuit voltage (V_{oc}) of 65 V and a power density of $43.8 \mu\text{W}/\text{cm}^2$ under periodic palm tapping. The improved results of the device attributed to (a) the uniformly distributed MXene provides a large surface area for efficient charge transfer, (b) the SnO_2 nanoparticles act as nucleating agent to promote the α to β phase transition (c) the improved interfacial polarization due to synergistic effect of SnO_2 and MXene into PVDF Matrix. The FCPEH device maintained a stable average output voltage during 1000 seconds on periodic palm tapping, which indicate the robustness and stability of the device. The optimized 6S-MP FCPEH device was employed to (1) efficiently detect biomechanical motion such as heel movement, toe movement, bending, pinching and different finger tapping, (2) charge the $1 \mu\text{F}$ and $2.2 \mu\text{F}$ capacitor to 2.1 V and 1.3 V, respectively, within only 80 seconds, and (3) glowing the 11 LED Pannel through periodic palm tapping. Thus, this work is significant step towards the development of efficient FCPEH device for high performance biomechanical energy harvesting towards self-powered wearable electronics.

5.1 Introduction

As smart technologies become increasingly integrated into everyday life, their dependence on batteries and electrochemical cells presents significant challenges. These conventional power sources often suffer from short lifespans, environmental hazards, high maintenance costs, and the constant need for recharging[1-3]. To overcome these limitations, developing self-powered devices has become crucial not only to reduce dependence on fossil fuels but also to minimise their environmental impact[4]. In this context, emerging technologies are being developed to efficiently harness, low-frequency, and disordered mechanical energy abundant in ambient environment for electrical energy generation[130].

In order to scavenge energy from ambient environmental and biomechanical sources, particularly from body movement or tapping, triboelectric and piezoelectric energy harvesting devices have been thoroughly studied in recent years[1, 31, 73, 131]. These devices are suitable for flexible, portable electronics that operate at low frequencies. Compared to other unconventional energy sources, triboelectric and piezoelectric energy-harvesting devices are relatively inexpensive[17]. However, triboelectric devices have several major drawbacks, including complex construction, poor stability, low durability, industrial-scale packaging challenges in humid environments. Also, their high output voltages that may damage electronic circuits or pose fire hazards especially in applications where only low power is required for general electronic circuitry[17, 31, 73, 132-134].

In contrast, piezoelectric device offers advantages over triboelectric device in terms of easier integration into electronic devices, simpler fabrication, and more straightforward structural design. For flexible piezoelectric device the researchers have explored various polymers[130, 135]. Among these polymers, Polyvinylidene fluoride (PVDF) has emerged as a pivotal material for flexible piezoelectric devices, owing to its exceptional thermal stability, mechanical durability, and pronounced electroactive characteristics. However, the pristine PVDF based piezoelectric devices usually have low output power density which limits their practical application for real

time flexible devices. Thus, the current research is focused on strategies to enhance their output power density[114].

It is widely established that the piezoelectric response of the PVDF within a piezoelectric device, and thus its performance, can be effectively tailored through incorporation of the different nanofillers. PVDF can crystallise into several distinct polymorphs α , β , γ , δ , and ϵ phases[136]. Among which β phase are polar and has remarkable properties such as excellent dielectric and piezoelectric properties, high thermal stability, enhanced mechanical strength, increased energy density with intrinsic flexibility. These properties of the β phase are attribute to its all-trans (TTTT) zigzag chain conformation. As the TTTT conformation possesses high microscopic dipoles due to the arrangement of hydrogen and fluorine atoms in opposite directions[30-32, 114].

Consequently, the development and augmentation of the β phase content within PVDF is a critical objective for advancing its suitability in efficient flexible piezoelectric devices. The impregnation of nanofillers having inherent high piezoelectric properties within the PVDF matrix is the good approach to increase its polar phase fraction. However, these nanofillers often demonstrate poor compatibility with the PVDF matrix due to a propensity for agglomeration within flexible composites[30, 118].

Nowadays, the incorporation of the dual nanofillers into PVDF matrix have emerged as an efficient approach to improve its polar phase without disturbing the crystallinity and flexibility. In this regard, the combination of 2D conducting materials (like as graphene oxide, hexagonal boron nitride (h-BN), MXene etc.) with ceramics (BaTiO₃, ZnO, TiO₂ etc) is gaining interest among the researchers[46, 47, 137-139]. This unique combination of 2D conducting and ceramics nanoparticles offers synergistic advantages. The high conductivity, large specific surface area, and excellent flexibility of the 2D materials which facilitate β -phase nucleation by promoting the alignment of polymer chains, enabling interfacial interactions that orient molecular dipoles, and inducing crystallisation within the PVDF matrix. Whereas the ceramic nanoparticles serve as nucleating agents for polar phase transformation of the PVDF.

Thus, the optimized combination of the 2D materials and ceramic dual fillers in PVDF matrix improves its piezoelectric behaviour[46, 47, 139].

For example, Yousaf et al. achieved an open-circuit voltage ($V_{oc} = 16.3$ V) and maximum power density ($170 \mu\text{W}/\text{cm}^2$) using optimised MXene/ZnO/PVDF composite NG device. The obtained results are attributed to the piezoelectric behaviour of ZnO and MXene's high conductivity, helping better charge separation and transportation[46]. Similarly, Chauhan et al. demonstrated highest β -phase content (85.6 %) in PVDF by incorporating the carbon nanofiber (CNF) and ZnO nanorods (NR) in PVDF matrix. The dual nanofillers PVDF composite film based piezoelectric device yield a V_{oc} of 80 V and power density of $20 \text{ mW}/\text{cm}^3$ under periodic palm tapping. The improved performance of the device are due to (a) CNF forms charge transfer networks at an optimized loading, (b) ZnO NR act as efficient nucleating agents, promoting polar phase transformation[47].

In this context, present work uses the combination of MXene nanosheets (2D) with SnO_2 nanoparticles as nanofillers to improve the piezoelectric properties of the PVDF. The MXenes ($\text{Ti}_3\text{C}_2\text{T}_x$) nanosheets have inherent abundance of surface terminations (e.g., $-\text{O}$, $-\text{OH}$, $-\text{F}$), high electrical conductivity, and large specific surface area, enabling direct interaction with PVDF without necessitating additional processing[52, 140, 141]. While the surface charge of tin oxide (SnO_2) nanoparticles plays the key role in the β -phase nucleation procedure[31, 142, 143]. Therefore, this novel combination of the nanofillers is supposed to improve the energy conversion efficiency of PVDF due to the synergistic effect of MXene and SnO_2 . The MXene nanosheets are expected to improve the mechanical strength, charge transfer and dipole alignment via hydrogen bonding[144-146]. While the SnO_2 nanoparticles acts as a nucleating agent through electrostatic interactions thus promoting β -phase formation. To produce such high-performance PVDF-based composites, solution casting is one of the best methods of choice due to its notably straightforward, cost-effective, and versatile approach. In our previous work [147], we focused on the optimization of structural, dielectric, and mechanical properties of SnO_2 /MXene/PVDF composite films. However, that study did not address device

fabrication and energy harvesting performance. The present work extends this material system towards the development of a flexible piezoelectric energy harvesting device with real-time performance evaluation.

Therefore, in this work, a dual nanofillers MXene nanosheets and SnO₂ nanoparticles are incorporated into a PVDF matrix. At a fixed concentration of MXene and varying concentrations of SnO₂ nanoparticles, composite PVDF flexible films were fabricated using the solution-casting method. The β phase crystallization and surface morphology of the synthesized composite films were investigated using the different characterization tools. The optimized 6S-MP (2 wt% MXene and 6 wt% SnO₂) flexible composite piezoelectric energy harvesting (FCPEH) device demonstrated the highest V_{oc} 65 V and the superior output power density 43.8 μ W/cm². The fabricated 6S-MP FCPEH device is capable of illuminating 11 commercial LEDs and charging capacitors (1 μ F and 2.2 μ F) using periodic palm tapping. The improved energy harvesting efficiency of the optimised fabricated device make it a promising candidate for self-powered wearable sensors and next-generation energy-harvesting technologies.

5.2 Materials and Experimental Methods

5.2.1 Materials

All the materials were of analytical grade and used without any further purification.

5.2.2 Synthesis of Nanofillers

SnO₂ nanoparticles were synthesized via a modified hydrothermal method employing SnCl₄·5H₂O and citric acid, followed by purification through centrifugation and washing, and subsequent thermal drying[114, 147, 148]. MXene was synthesized through the selective etching of Al from a MAX phase precursor using concentrated hydrofluoric acid (HF), followed by iterative centrifugation for purification and delamination. The synthesized samples were stabilized in a vacuum desiccator to ensure complete solvent removal[52, 82, 114].The detailed synthesis process has been described in our previous study [147].

5.2.3 Material Characterization

The details of the characterization techniques used are reported in our previous report [147]. The tapping method was used to evaluate the performance of the FCPEH devices. A digital storage oscilloscope (Tektronix MDO 500) was utilized to measure the output voltage generated by the FCPEH devices under mechanical and human-body-induced motions.

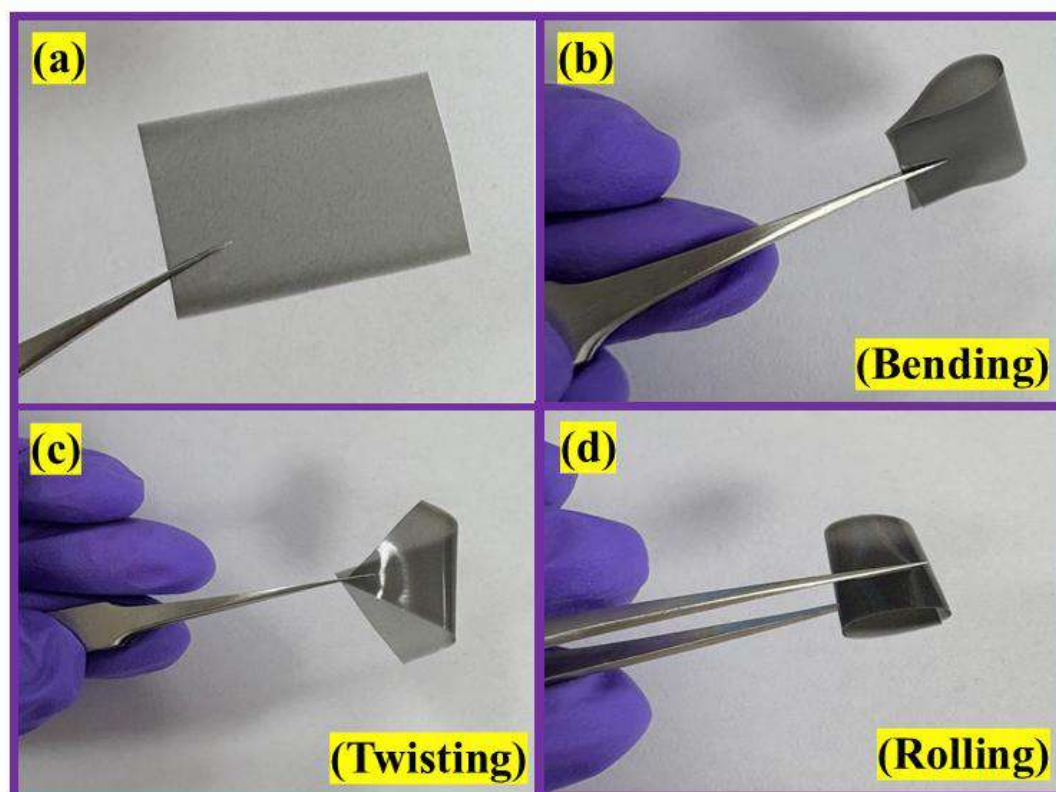


Figure 5.1: Digital images of (a) Flexible composite film (b) Bending, (c) Twisting and (d) Rolling of the 6S-MP composite film.

5.2.4 Fabrication of FCPEH Device

PVDF composite film synthesized by the efficient and facile solution casting method. The detailed synthesis process has been described in our previous work [147]. The resulting nanocomposites are denoted as PVDF, MP (2 wt% MXene), 2S-MP (2 wt% MXene and 2wt% SnO₂), 4S-MP (2 wt% MXene and 4wt% SnO₂), 6S-MP (2 wt% MXene and 6wt% SnO₂), and 8S-MP (2 wt% MXene and 8wt% SnO₂). The digital photograph of the 6S-MP flexible composite film is shown in Figure 5.1(a). Self-

standing flexible composite film can be easily bended, twisted and rolled as shown in Figure 5.1(b-d).

Synthesized flexible composite films were cut into small pieces of area $(2.5 \times 2.5) \text{ cm}^2$ for the fabrication of Flexible Composite Piezoelectric Energy Harvesting (FCPEH) device. The composite-based energy harvester device was fabricated by typical electrode composite electrode stack technique. To prevent electrode shorting at any endpoint, the device was fabricated by sandwiching the composite films between two metallic (aluminium) electrodes, which served as the top and bottom charge collecting layers. The electrode areas were slightly smaller $(2.2 \text{ cm} \times 2.2 \text{ cm})$ than the film area. Bipolar copper wiring connected to the electrodes for getting voltage output. Kapton tape, known for its neutral piezoelectric effect, was used to enclose the entire prototype. This encapsulation not only offers enhanced protection against wear, mechanical agitation, and other potential losses during energy-harvesting measurements but also minimizes charge carrier exchange between the surrounding air and the electrode layers.

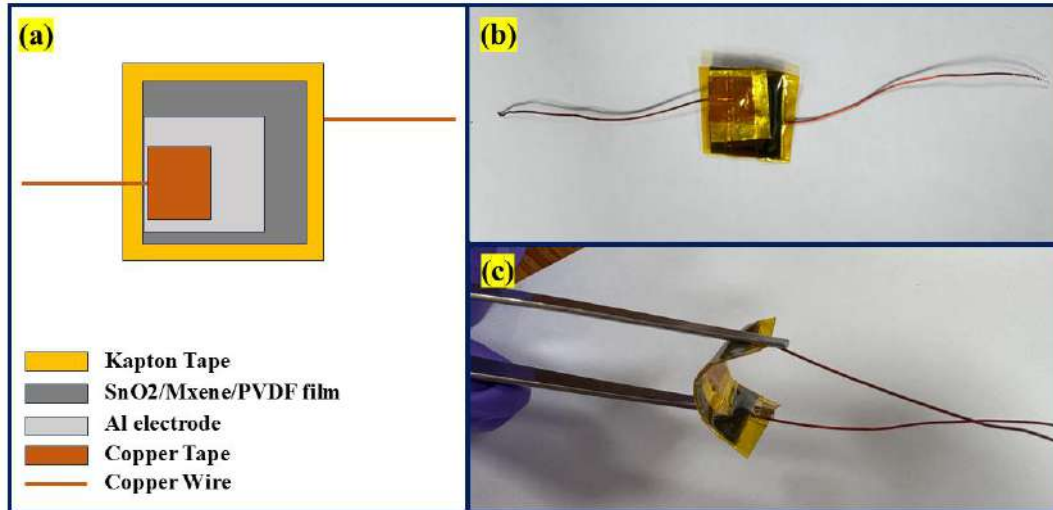


Figure 5.2: (a) Schematic diagram of the FCPEH device (b) Digital image of the FCPEH device (c) Flexibility representation of the FCPEH device

A schematic diagram and a digital photograph of flexible composite piezoelectric energy harvesting (FCPEH) device is also shown in Figure 5.2(a&b). The FCPEH device can be bend comfortably as shown in Figure 5.2(c). The fairly FCPEH device could be suitable for embedded and wearable electronic.

5.3. Result and Discussion

5.3.1 Characterization of the nanofillers and the composite films

The obtained XRD pattern confirm the successful etching of Al layers from Ti_3AlC_2 , resulting in the formation of $\text{Ti}_3\text{C}_2\text{T}_x$ and tetragonal rutile structure of the synthesized SnO_2 nanoparticles [147]. FESEM image of the synthesized SnO_2 nanoparticle is presented in Figure 5.3(a), which reveals their spherical morphology. Figure 5.3(b) depicts the MXene morphology, revealing a multilayered, sheet-like structure. In the high-resolution inset image, the presence of thin, well-stacked layers, indicating that the Al layer was successfully etched[52, 82, 147].

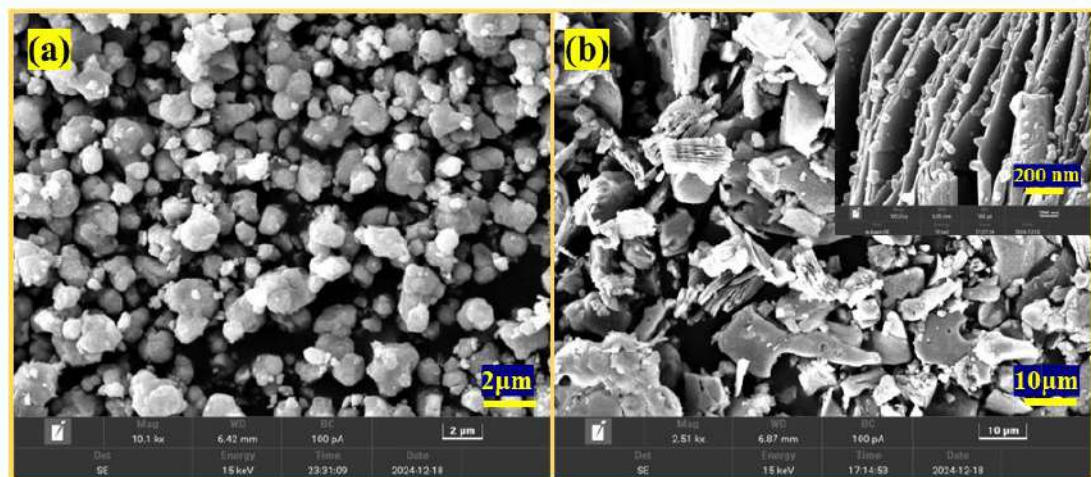


Figure 5.3: The FESEM image of (a) SnO_2 nanoparticles (b) MXene nanosheets, inset (enlarged view of nanosheets).

FESEM images of the synthesized PVDF composite films is presented in Figure 5.4(a–f). Figure 5.4(a) reveals that the pristine PVDF film exhibits a uniform, smooth, and densely packed morphology. The film surface is devoid of wrinkles, fractures, porosity, folds, and granular features. This absence of structural defects indicates the formation of a homogeneous matrix, attributable to the use of a polar solvent during the blending process, which consequently yields a flexible and consistent film.

The incorporation of nanofillers perturbs the homogeneity of the PVDF matrix, inducing distinct morphological alterations. Surface micrographs of the nanocomposite films confirm the presence of spherulitic structures, albeit with a conspicuous reduction in spherulite size subsequent to the addition of MXene and

SnO₂ nanoparticles. As exemplified by the FESEM image of the 6S-MP composite film in Figure 5.4(e), a highly compact and uniform surface morphology is attained, which is devoid of pin-hole cracks. Notably, the film containing 8 wt% SnO₂ shows increment in spherulitic structures, which may be attributed to agglomeration of the nanofillers. FESEM analysis further corroborate the role of nucleation in promoting the β phase, as confirmed by FTIR analysis. The addition of SnO₂ nanoparticles with 2 wt% MXene into the PVDF matrices progressively enhanced the β -phase content, peaking at 80% for the 6S-MP composite film [147].

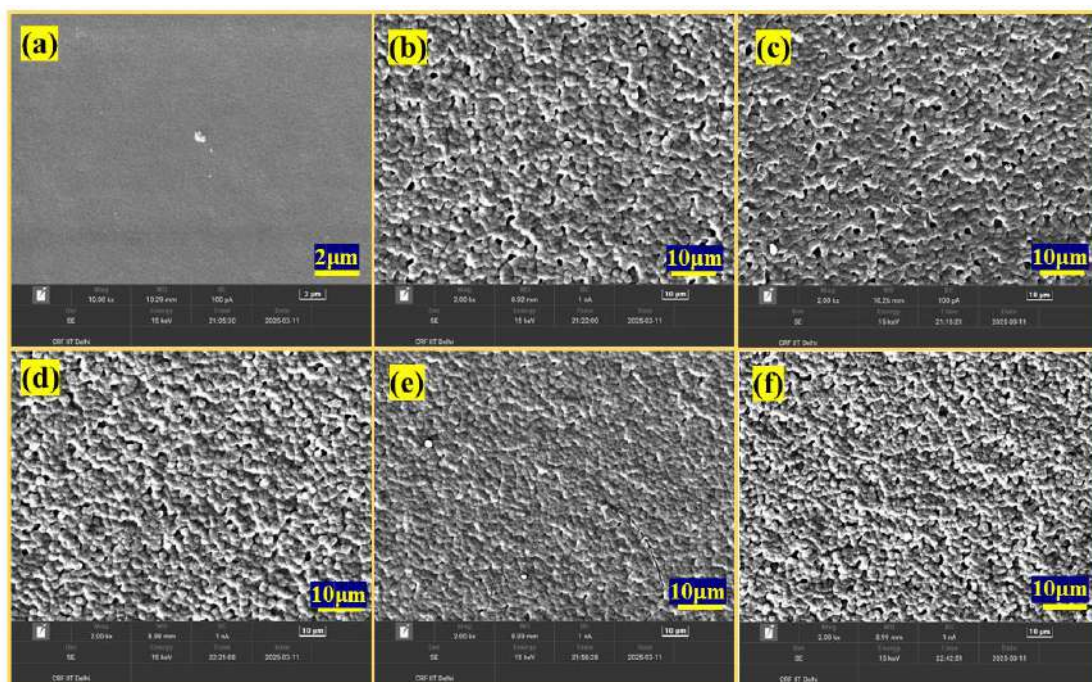


Figure 5.4: FESEM Images of (a) Pristine PVDF (b) MP (c) 2S-MP (d) 4S-MP (e) 6S-MP and (f) 8S-MP Films.

5.3.2 Piezoelectric Mechanism

A cyclic process (1) initial state, (2) compressive state, (3) release state, and (4) return to the initial state can be used to illustrate the functioning of the FCPEH device, as shown in Figure 5.5(a-d). The piezoelectric response of the FCPEH device is influenced by several factors, including induced polarization, dipole strength, flexibility, and mechanical integrity[17, 32]. According to surface morphological and structural characterization, the incorporation of SnO₂ and MXene into the PVDF matrix significantly increases the β phase content while reducing the spherulitic

structure, thereby enhancing the mechanical robustness and overall piezoelectric performance of the PVDF composite films.

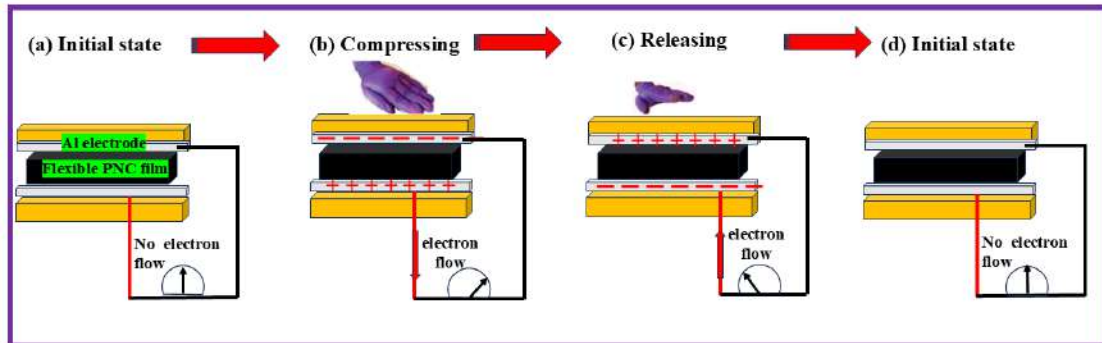


Figure 5.5: (a-d). A schematic representation of the Flexible Composite Piezoelectric Energy Harvester (FCPEH) device working mechanism during loading and unloading.

Figure 5.5(a) depicts the FCPEH device in its initial state, characterised by a random spatial distribution of electrical charges. This disordered dipole configuration results in a net zero piezoelectric potential, and consequently, no electrical output is generated by the FCPEH device. Figure 5.5(b) illustrates the FCPEH device under compressive mechanical stress. After apply an external force induces deformation, which aligns the internal dipoles through stress induced polarization. This effect generates a piezoelectric potential. Concurrently, the mechanical compression reduces the inter-electrode distance. The coupled effect of dipole alignment and reduced electrode separation establishes distinct positive and negative terminals at the top and bottom surfaces of the composite, respectively, facilitating a continuous flow of electrical charge. Figure 5.5(c) presents the release state of the FCPEH device after remove of the external mechanical force. The device exhibits a rapid signal dissipation phenomenon. As the elastic composite reverts towards its original geometry, the inter electrode distance increases. The weak internal polarization strength is insufficient to maintain dipole alignment, leading to the randomization of dipoles. This process disrupts charge migration and terminates the electrical signal output. Figure 5.5(d) shows the FCPEH device upon remove the complete mechanical force, defined as its initial state. The internal charges have fully back to their initial, randomized positions, resulting in the complete dissipation of the piezoelectric potential and a cessation of charge migration, thereby no output voltage.

5.3.3 Energy Harvesting Performance Study

5.3.3.1 Open Circuit Voltage of the Fabricated FCPEH Device

Prior to operational voltage output, the fabricated devices were subjected to an electrical neutrality test. The absence of a detectable electrical signal between the device electrodes in the absence of an external stimulus confirmed a negligible offset voltage and background noise. The piezoelectric output performance of all the fabricated FCPEH devices were characterized by measuring the open circuit voltage (V_{oc}) under palm tapping, applied with a force of approximately 20 N. The obtained V_{oc} for all the FCPEH devices is shown in Figure 5.6(a-f). The PVDF, MP, 2S-MP, 4S-MP, 6S-MP, and 8S-MP FCPEH devices yielded an average V_{oc} of approximately 18 V, 27 V, 38 V, 52 V, 65 V, and 37 V, respectively.

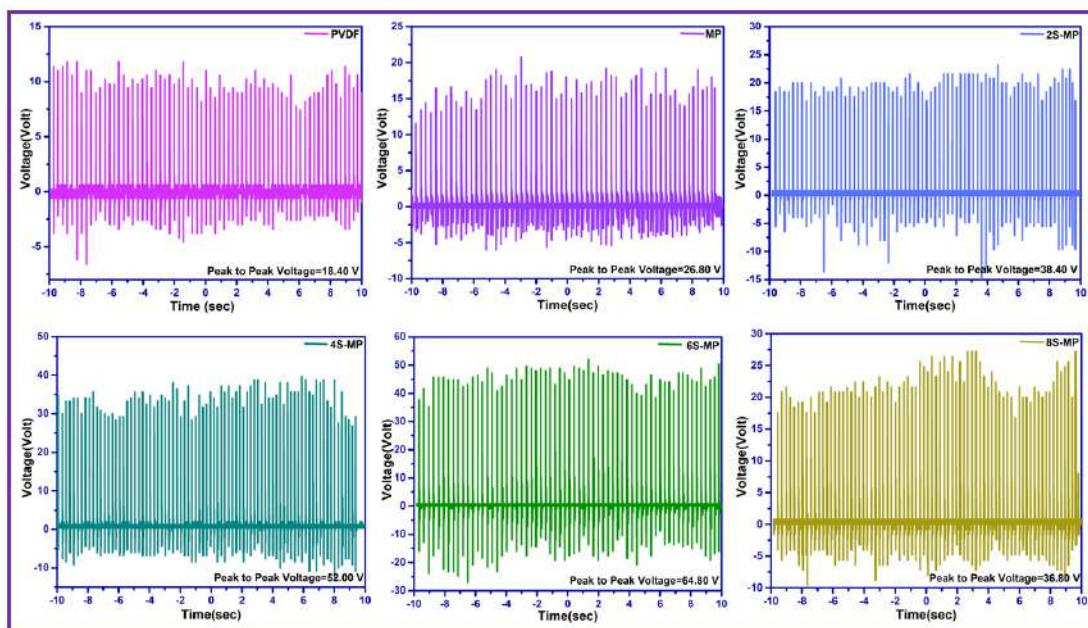


Figure 5.6: Piezoelectric output voltage performance by periodic palm tapping (a) PVDF (b) MP (c) 2S-MP (d) 4S-MP (e) 6S-MP and (f) 8S-MP FCPEH device.

The piezoelectricity of PVDF originates from the molecular dipole moment within its $[-CH_2-CF_2-]$ repeat unit, arising from the disparity in van der Waals radius and electronegativity between fluorine and hydrogen atoms[149]. The highest piezoelectric response is exhibited by the β phase, which features an all trans (TTT) chain conformation[140, 150]. The arrangement of the repeated units for alpha and β phase of PVDF are shown in Figure 5.7 (a).

The obtained enhanced piezoelectric output voltages of the 6S-MP FCPEH device underscore the efficacy of incorporating optimized concentration of SnO₂ and MXene nanofillers. The enhanced output is principally due to pronounced interfacial polarization arising from the multi component interactions between the MXene nanosheets, SnO₂ nanoparticles, and the PVDF polymer chains.

The incorporation of MXene (Ti₃C₂T_x) nanosheets, surface functionalized with Oxide(=O), Hydroxyl (–OH), and Fluorine (–F) groups, promotes β phase crystallization via hydrogen bonding with PVDF [–CH₂–CF₂–] groups and electron dipole interactions with polymer chains, which will help in the arrangement of fluorine atoms on one side[51, 140, 141, 145, 151].

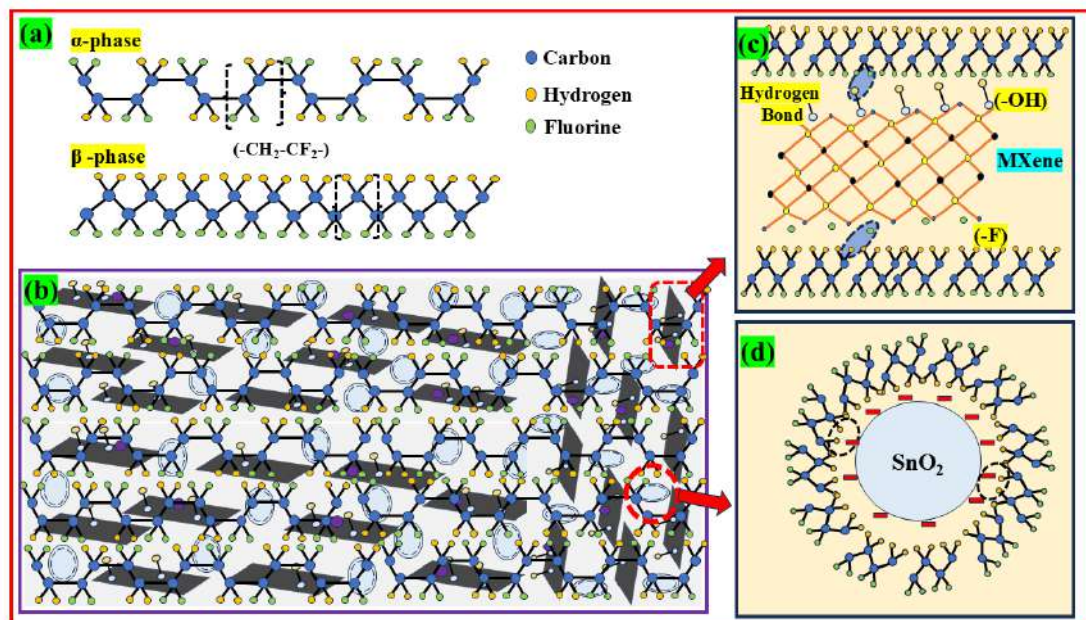


Figure 5.7: Schematic of the (a) α , and β conformations of PVDF (b) surface electrostatic interaction of the SnO₂ nanoparticle, MXene nanosheets and [–CH₂–CF₂–] repeated unit of PVDF chain (c&d) enlarged view of the interaction of SnO₂ nanoparticles, MXene nanosheets and [–CH₂–CF₂–] repeated unit of PVDF chain.

Additionally, the incorporation of SnO₂ nanoparticles in to 2 wt% MXene PVDF, provides extra nucleation sites. The essential factor for the nucleation is the static electric interaction between the negative surface charged SnO₂ nanoparticle and the [–CH₂–] groups of PVDF having a positive charge density. The positive –CH₂– charge density of the PVDF chains suffers strong interactions with the negatively charged surface nanoparticle that led the polymer chains to align on the surface of the nanoparticle in the

extended TTTT conformation and therefore resulting in the enhanced β phase[31, 143]. The schematic representation of the nanofillers inside the PVDF matrix along with described feasible interaction is shown in Figure 5.7 (b-d).

The synergistic presence of conductive MXene and SnO_2 within the insulating PVDF matrix induces significant Maxwell-Wagner-Sillars (MWS) interfacial polarization. Charge carrier mobility is facilitated by this significant interfacial polarization, which also increases the charge density at the contact[152]. Consequently, charge carriers accumulate rapidly at the contact, forming space charge regions that reduce charge recombination. Under an applied load, the conductive and flexible nature of PVDF composite films further facilitates dipole alignment towards the electrodes and enhances the induced electric field. Consequently, this synergistic effect of improved interfacial polarization, efficient charge separation and increased induced electric field significantly boosts the piezoelectric output of the FCPEH devices.

The output voltage increases with SnO_2 concentration up to an optimal loading of 6 wt.% and 2 wt% of MXene, beyond this concentration, a decrease in voltage is observed. This decline is likely attributable to a reduction in the β phase content, as corroborated by FTIR analysis. At higher filler concentrations, SnO_2 nanoparticles may impede β phase formation and promote defect generation within the polymer matrix, thereby compromising piezoelectric performance. Furthermore, the aggregation of MXene sheets at elevated SnO_2 loadings diminishes the availability of surface functional groups for interaction with PVDF, contributing to the observed performance reduction.

The piezoelectricity of the FCPEH device confirmed by the consistent observation of a negative peak voltage of lower magnitude than the positive peak voltage, a phenomenon resulting from the difference in strain rate within the composite film. Figure 5.8 (a) represents a magnified view of one complete cycle of the output voltage, revealing two distinct sets of responses corresponding to positive and negative piezoelectric potentials. In both sets, a pronounced asymmetry is observed between the magnitudes of the positive and negative voltage peaks. The larger positive peak is generated by the applied mechanical load. The subsequent negative

7

peak related to the release phase, occurring during the transition from a compressed to a relaxed state following the removal of the applied force. The second set of piezoelectric outputs is attributable to the damping effect inherent to the FCPEH device.

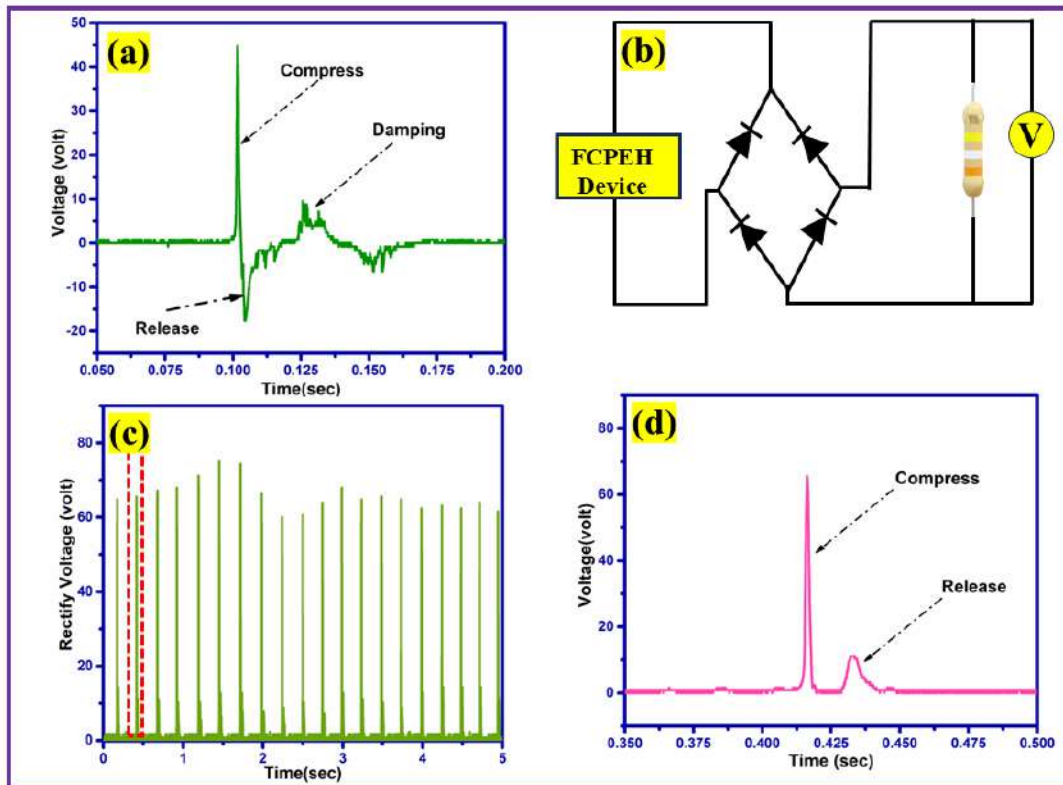


Figure 5.8: (a) Enlarged view show one cycle of the peak-to-peak output voltage of the 6S-MP FCPEH device. (b) Required circuit of the rectify piezoelectric performance for FCPEH device (c) Rectified output voltage of 6S-MP FCPEH device (d) Enlarged view show one cycle of the rectified output voltage of 6S-MP FCPEH device.

The rectified circuit connection and rectified output voltage cycles of the FCPEH device are presented in Figure 5.8(b&c). The 6S-MP FCPEH device demonstrates a notable output performance, achieved without an external poling. A magnified view of a single cycle of the rectified signal reveals a profile comprising two peaks corresponding to compress and release (Figure 5.8(d)). This behaviour originates from the successive compression and relaxation cycles of the composite film under applied mechanical stress. The process initiates with the generation of a piezoelectric potential across the electrodes, a consequence of stress-induced polarization that aligns the

electric dipoles of the PVDF phase unidirectionally. Subsequently, this potential decays rapidly upon the removal of the external pressure.

The operational stability of the 6S-MP device was assessed over approximately 1000 seconds consecutive palm tapping cycles. As shown in Figure 5.9, the device maintained a stable average V_{oc} of ~ 65 V without significant degradation under consistent tapping force. The $\text{SnO}_2/\text{MXene}/\text{PVDF}$ composite structure thus yields a flexible and durable device with enhanced piezoelectric response. Given its superior performance among all fabricated devices, the 6S-MP FCPEH device was selected for subsequent characterization.

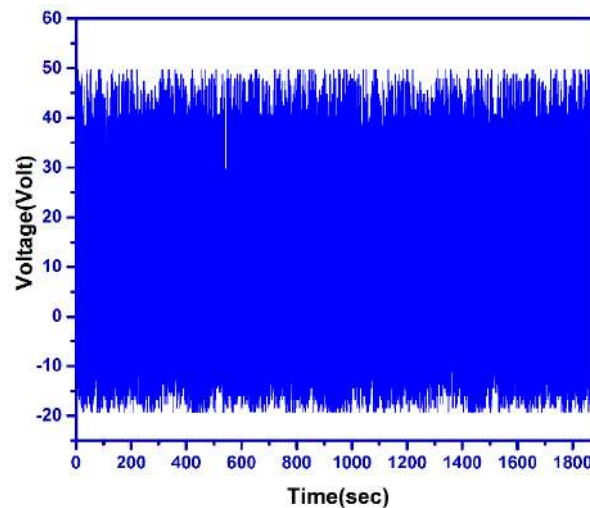


Figure 5.9: The stability test of FCPEH device under finger tapping force for ~ 1900 consecutive cycles.

Table 5.1: Comparison of open circuit peak to peak voltage and power density of the 6S-MP FCPEH device from various PVDF-based piezoelectric device reported in literature.

S.No.	Piezoelectric Energy Harvesting Device	Synthesis Technique	Open circuit voltage (V_{oc})	Power Density (P)	Ref.
1	PVDF/MWCNT/ZnO	Electrospinning Method	10 V	$0.33 \mu\text{W}/\text{cm}^2$	[153]
2	PVDF/KNNLTS/MWCNT	Solution Casting	87.2V	$145.4 \mu\text{W}/\text{cm}^2$	[154]
3	PVDF/MWCNT/BaTiO ₃	Electrospinning Method	11.4V	$1.16 \mu\text{W}/\text{cm}^2$	[30]
4	PVDF/SnO ₂	Solution Casting	45 V	$4900 \mu\text{W}/\text{cm}^3$	[31]
5	MXene/ZnO/PVDF	Electrospinning Method	16.3V	$170 \mu\text{W}/\text{cm}^2$	[46]
6	SnO₂/MXene/PVDF	Solution Casting	65V	$43.8 \mu\text{W}/\text{cm}^2$	This Work

5.3.3.2 Power Density of the Fabricated 6S-MP FCPEH Device

To evaluate the practical applicability of the fabricated 6S-MP FCPEH device for real world electronic applications, its power generation performance was characterized. Since the output power of a FCPEH is a function of external load resistance, the output voltage was measured across a series of load resistances, as illustrated in the circuit schematic inset in Figure 5.10(a&b). The instantaneous output power density was calculated by $[P = \frac{V^2}{R_L \cdot \text{Area}}]$ where V is the measured output voltage across the load resistance R_L , and the effective FCPEH device surface area ($\sim 6.25 \text{ cm}^2$) [31, 114, 155]. Analysis of the resulting power curve (Figure 5.10(a)) revealed a maximum instantaneous power density of $\sim 43.8 \mu\text{W/cm}^2$ at an optimal load resistance of $5 \text{ M}\Omega$. The output voltage was observed to increase monotonically with increasing load resistance, achieving saturation at approximately $30 \text{ M}\Omega$ (Figure 5.10(b)). Furthermore, the short circuit current was calculated using the equation $[I = \sqrt{\frac{P \cdot \text{Area}}{R_L}}]$ for each load resistance [155]. As anticipated, the current exhibited an inverse relationship with load resistance (Figure 5.10(b)), consistent with Ohm's law, wherein higher impedances restrict charge flow within the circuit. Table 5.1 compare the piezoelectric output performance of the fabricated 6S-MP FCPEH device with the previously reported PVDF based devices in the literature. Consequently, the 6S-MP FCPEH device demonstrates optimal power transfer for driving electronic components with an equivalent input impedance.

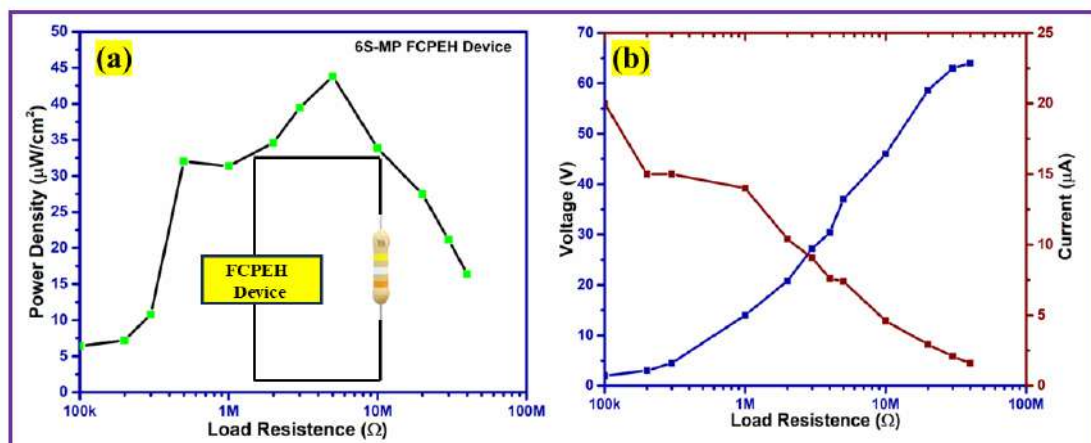


Figure 5.10: (a) Output Power Density of the 6S-MP FCPEH device across a series of load resistances. (inset required circuit) (b) Variation of piezoelectric output voltage and current density of the 6S-MP FCPEH device with load resistance.

5.4. Application of the Fabricated 6S-MP FCPEH device

The flexible device is gaining significant interest due to their real time application in driving energy to the electronic components of the different devices. Thus, here we report the actual use of the optimized 6S-MP FCPEH devices towards different applications [31, 155].

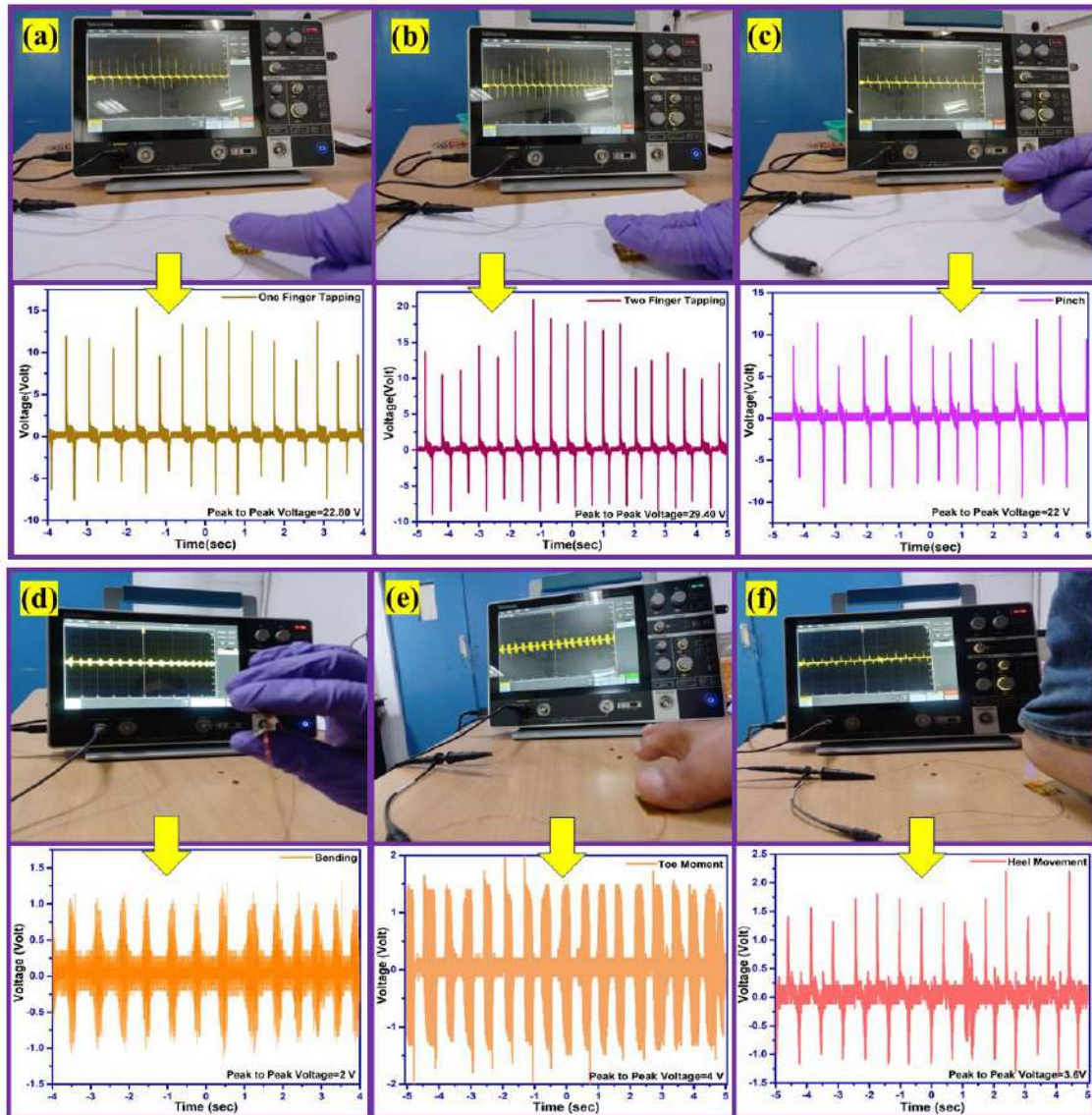


Figure 5.11: Output voltage performance of the 6S-MP FCPEH device when subjected to various human body motions: (a) One finger tapping, (b) Two finger tapping, (c) Pinch the device (d) Bending the device, (e) Toe tapping, and (f) Heel tapping respectively.

Sensitivity, flexibility, wearability, and biomechanical energy conversion efficiency of the 6S-MP FCPEH device, the device was tested by human body motions. Table 5.2

present the energy harvesting capability of the FCPEH with data across various movements: one finger tapping (pressing), two finger tapping, pinching, bending, heel movement, and toe tapping (pressing) with their corresponding open-circuit voltage outputs.

Table 5.2: Open circuit voltage of the 6S-MP FCPEH device from various Biomechanical Motion

S.No.	Human body- 6S-MP FCPEH Device Interaction	Open Circuit Voltage (Voc)	Represented Figure
1	One Finger Tapping	22.80 V	5.11 (a)
2	Two Finger Tapping	29.40 V	5.11 (b)
3	Pinch the Device	22 V	5.11 (c)
4	Bending the Device	2 V	5.11 (d)
5	Heel Movement	3.6 V	5.11 (e)
6	Toe Moment	4 V	5.11 (f)

To evaluate the energy-producing capability of the 6S-MP FCPEH device, two capacitors (1 and 2.2 μ F) were charged using mechanical input energy supplied by human finger tapping, as shown in Figure 5.12(a). The voltages across the 1 μ F and 2.2 μ F capacitors reached 2.1 V and 1.3 V, respectively, within only 80 seconds (Figure S2). This performance demonstrates the device's ability to efficiently charge energy storage units within a short duration. A panel comprising 11 commercial blue, red, and yellow LEDs was directly and instantly powered by the 6S-MP FCPEH device, without the use of any capacitor or external storage element, using gentle human palm tapping. Digital images of the illuminated LEDs are shown in Figure 5.12(b).

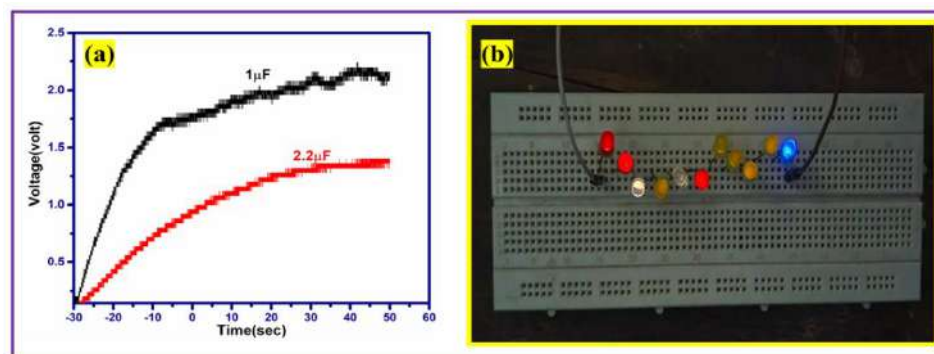


Figure 5.12: (a). 6S-MP FCPEH device Applications (a) Charging of the capacitors (1 μ F and 2.2 μ F) (b) Glowing 11 LED Panel

5.5 Conclusion

In summary, SnO₂ and MXene were successfully prepared using hydrothermal method and etching treatment respectively, then incorporated into a PVDF matrix to develop flexible composite films via the solution casting method. Structural (XRD and FTIR) and morphological (FESEM) analyses confirm the synthesis of nanofillers and enhancement of polar phase with the successful integration of SnO₂ and MXene within the PVDF matrix. All the prepared FCPEH device exhibited higher open circuit voltage as compared to the PVDF FCPEH device when applied to mechanical force. The maximum output voltage and power density of the 6S-MP FCPEH device can reach up to 65 V and 43.8 μ W/cm². The fabricated FCPEH device can efficiently harvest human motion based mechanical energy arising from finger tapping, heel and toe movement. Furthermore, FCPEH Device demonstrated efficient energy storage capabilities, successfully charging 1 μ F and 2.2 μ F capacitors to 2.1 V and 1.3 V respectively within 80 s through finger tapping. This device also powers 11 glowing LED panels using the mechanical force. This study opens a new avenue for the development of eco-friendly advanced flexible composite for energy devices, emphasizing long-term stability and practical utility.

CHAPTER 6

FLEXIBLE TRIBOELECTRIC NANOGENERATORS BASED ON SnO₂/MXENE/PVDF COMPOSITE FILMS FOR BIOMECHANICAL ENERGY HARVESTING

This study systematically investigates the effects of varying SnO₂ and MXene concentrations within the PVDF matrix on the output characteristics of the fabricated triboelectric nanogenerators (TENGs) devices. The PVDF-based composite films and indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrates were employed as the triboelectric frictional layers for the device fabrication. The TENG output improved progressively with increasing SnO₂ content, reaching an optimum at 6 wt%. The composite containing 6 wt% SnO₂ and 2 wt% MXene exhibited superior performance, delivering a peak-to-peak open-circuit voltage of 210 V and a maximum power density of 1.01 mW cm⁻² at an optimal load resistance of 7 MΩ. This upgrading is mainly ascribed to the increased dielectric constant, which facilitates the formation of an effective micro capacitor network within the PVDF matrix, thereby enhancing surface charge density. The device also demonstrated excellent stability over 500 contact separation cycles. The practical viability of the device was substantiated through its direct application in powering 31 light-emitting diodes (LEDs) and charging a capacitor. Thereby highlighting its considerable potential for integration into self-powered electronic systems and energy harvesting applications.

6.1 Introduction

Wearable triboelectric nanogenerators (TENGs) have garnered considerable attention as a highly promising approach for converting human biomechanical motion into electrical power, operating through the synergistic effects of triboelectric induction and contact electrification [21, 156, 157]. TENGs have been designed in diverse configurations and offer notable advantages with respect to lightweight construction, facile fabrication, mechanical durability, portability, and cost-effectiveness [158]. Nevertheless, although TENGs have demonstrated significant potential for energy harvesting their performance still requires further optimization to enhance the device's energy conversion efficiency for practical applications[159].

In that context, PVDF-based composite materials have attracted significant research interest towards the efficient, flexible, and eco-friendly construction of TENG devices. This is primarily due to their excellent mechanical flexibility and facile processability. However, a persistent challenge confronting PVDF based flexible TENGs has been their characteristically low output power density [160]. The output performance of PVDF-based TENGs can be effectively enhanced by incorporating judiciously selected hybrid organic–inorganic nanofillers. Organic fillers such as CNTs, or rGO, or MXenes combined with metal oxides (e.g., TiO_2 , BaTiO_3 , Ta_2O_5 , SnO_2 , etc.) synergistically improve the piezoelectric properties of PVDF composites by promoting β -phase formation and interfacial polarization[161-165].

Building on chapter 4 that optimized the structural, dielectric, mechanical, and piezoelectric properties of $\text{SnO}_2/\text{MXene}/\text{PVDF}$ composite films[147]. The present chapter systematically extends the investigation to triboelectric performance with comprehensive real-time evaluation of the fabricated composite films based TENG devices. The optimized 6S-MP TENG delivers a high open-circuit voltage of 210 V and a power density of 1.01 mW cm^{-2} , and is capable of directly illuminating 31 commercial LEDs and charging 2.2 μF and 4.7 μF capacitors within a short duration under periodic palm tapping.

6.2 Result and discussion

PVDF composite films were cut into $2.5 \times 2.5 \text{ cm}^2$ pieces for TENG device fabrication. The device was assembled using the PVDF composite film as the active triboelectric layer and PET film as the counter triboelectric layer. Aluminium adhesive tape was applied to the PVDF film surface as the bottom electrode, while PET film served as the top electrode, completing the sandwich-type structure. Copper wire was used to establish electrical interconnections for device characterization. A digital image of 6S-MP TENG device is presented in Figure 6.1(a). To induce mechanical vibrations that facilitate periodic contact and separation between the two triboelectric layers, the tapping method was employed.

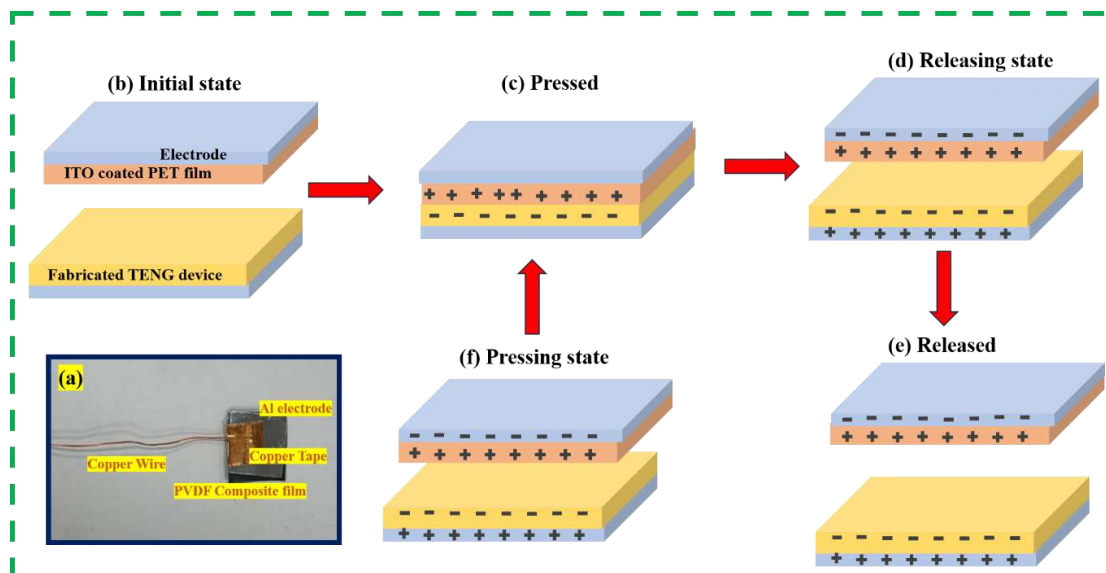


Figure 6.1: (a) Digital image of 6S-MP TENG device (b-f) A schematic representation of working mechanism of TENG device in vertical contact separation mode.

The operating mechanism of the TENG in vertical contact-separation mode is shown in Figure 6.1(b–f). In the initial state, no surface charges are present and the system is electrically neutral. When an external compressive force is applied, the two triboelectric layers make physical contact, and the triboelectrification effect generates equal and opposite surface charges on the ITO-coated PET and PVDF composite films. These charges are retained at the interfaces due to the insulating nature of the film materials. Upon force withdrawal, the layers separate, creating a potential difference between the electrodes that drives electron flow from the bottom to the top

electrode through the external circuit via electrostatic induction, partially restoring electrical equilibrium. At full separation, charge flow ceases and a new electrostatic equilibrium is reached. When the force is reapplied, the layers contact again, reversing the potential distribution and driving electrons in the opposite direction, generating an alternating electrical output. This periodic contact-separation cycle produces a continuous AC signal [161].

To examine the impact of increasing the concentration of SnO₂ nanofillers on the output performance of TENG device, a systematic electrical characterization is carried out using the manual palm tapping method. Prior to the acquisition of operational voltage outputs, all the fabricated devices underwent baseline electrical characterization to verify electrical neutrality.

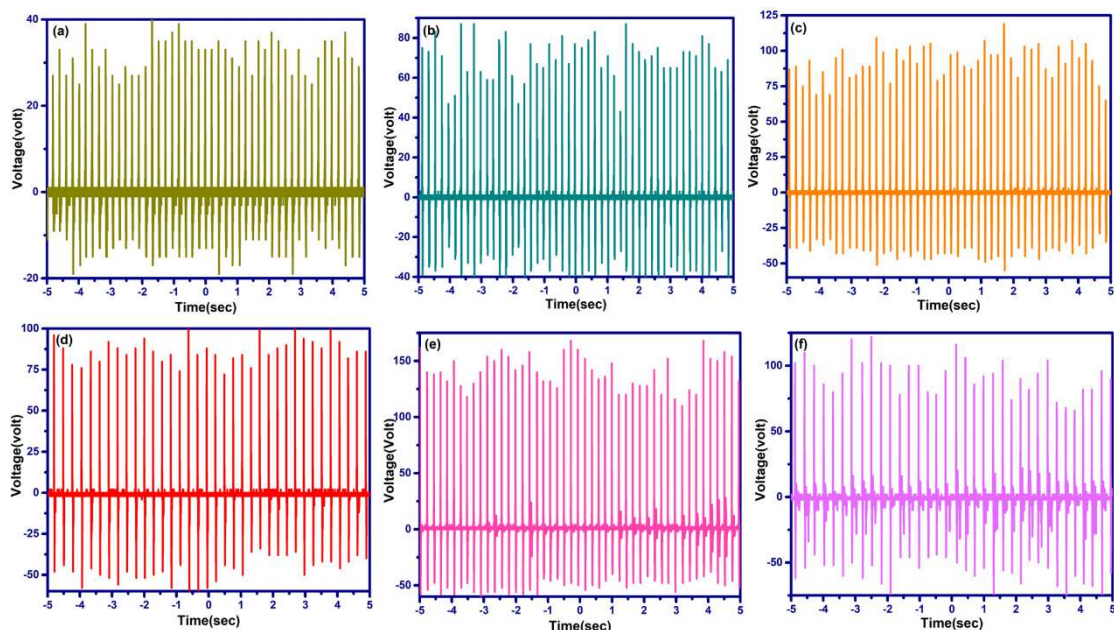


Figure 6.2: Output voltage performance by periodic tapping (a) PVDF (b) MP (c) 2S-MP (d) 4S-MP (e) 6S-MP and (f) 8S-MP TENG device.

The absence of any measurable electrical signal across the device electrodes under stimulus-free conditions confirmed a negligible offset voltage and minimal background noise levels, thereby validating the integrity of the measurement setup. The triboelectric energy harvesting performance of the fabricated all TENG devices were systematically evaluated through open-circuit voltage measurements. The corresponding peak to peak voltage profiles for all TENG devices are presented in

Figure 6.2. The pure PVDF, MP, 2S-MP, 4S-MP, 6S-MP, and 8S-MP composite films based TENG device configurations yielded mean open-circuit voltages of approximately 50 V, 70 V, 110 V, 145 V, 210 V, and 150 V, respectively, demonstrating a systematic dependence of the output voltage on the structural configuration of the active layers.

The output performance of a TENG is fundamentally contingent upon three principal parameters: the triboelectric surface charge density of the active layers (σ), the interlayer separation distance between the two opposing triboelectric surfaces, and the relative velocity of mechanical displacement between the triboelectric layers during operation[131]. Among these, the triboelectric surface charge density (σ), intrinsically linked to the capacitance of the TENG system, plays a important role in determining the open circuit voltage V_{oc} of the device. The V_{OC} , is given by equations (6.1)

$$V_{oc} = \frac{\sigma x(t)}{\epsilon_0} = \frac{C \Delta V x(t)}{A \epsilon_0} = \frac{\epsilon_r \Delta V x(t)}{d} \quad 6.1$$

Where surface charge density is defined as equations (6.2)

$$\sigma = \frac{C \Delta V}{A} = \frac{\epsilon_0 \epsilon_r \Delta V}{d} \quad 6.2$$

Here, ϵ_r is the relative dielectric constant, ΔV is the potential difference and C is capacitance of the triboelectric system.

Accordingly, the optimization of device performance necessitates the maximization of the effective capacitance (C) of the triboelectric system, which is primarily determined by the dielectric constant (ϵ_r) of the constituent triboelectric materials and the effective frictional contact area at the triboelectric interface[131].

It can therefore be rigorously inferred from the aforementioned theoretical framework that the output voltage of the TENG will exhibit a systematic enhancement with increasing dielectric permittivity of the active materials. As documented in chapter 4, with systematic increments in SnO_2 filler concentration (0, 2, 4, 6, and 8 wt%) incorporated within the PVDF matrix, the measured ϵ_r at a frequency of 1 kHz underwent a progressive enhancement, increasing from 6 to 10, 12, 15, 30, and 18, respectively[147]. This enhanced ϵ_r is leads to the spontaneous formation of a micro

capacitor network architecture, accompanied by the generation of localized microscopic dipole moments distributed throughout the composite matrix [161]. Consequently, the film possessing the maximum ϵ_r have enhanced effective capacitance, which leads to the highest output voltage.

Figure 6.3(a) represents a enlarge view of a complete output voltage cycle of the TENG device. The triboelectric behaviour of the device is confirmed by the consistent appearance of a negative voltage peak with a lower magnitude than the corresponding positive peak, which is attributed to differences in the strain rate within the composite film. The positive and negative rectified output voltage cycles of the TENG device are shown in Figures 6.3(b) and 6.3(c), respectively

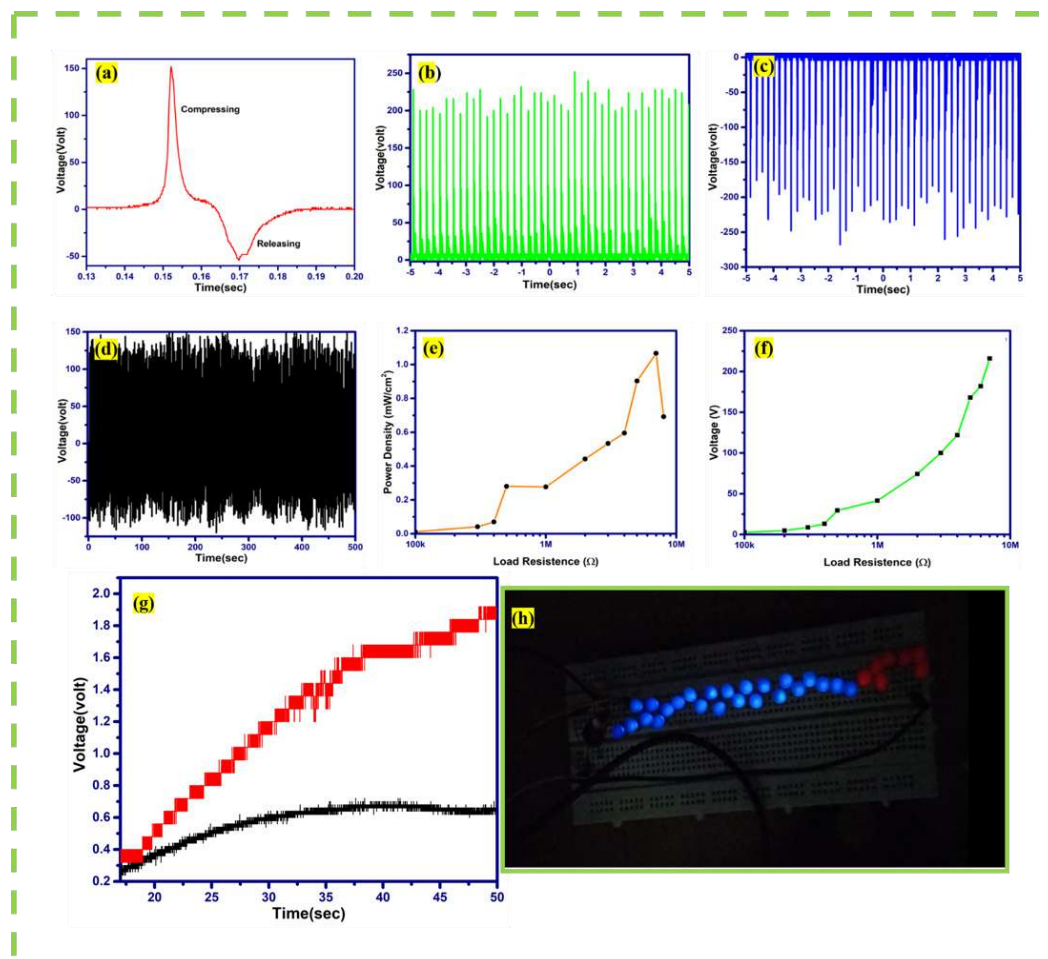


Figure 6.3: (a) Magnified plot of peak to peak of TENG in single contact-separation cycle. (b) Positive rectified output voltage (c) Negative rectified output voltage (d) Stability test under repetitive tapping force for ~ 500 consecutive cycles (e) Output Power Density across a series of load resistances (f) Variation of triboelectric output voltage of 6S-MP TENG device (g) Capacitor charging curves of various capacitors 2.2 μF (Red curve) and 4.7 μF (Black curve) (h) Glowing 31 LED Pannel.

Further, the operational stability of the TENG device was assessed over approximately 500 seconds consecutive manual palm tapping cycles. As shown in Figure 6.3(d), the device maintained a stable average Voc of approximately 210 V without significant degradation under consistent tapping force. The 6S-MP composite film thus yields a flexible and durable TENG device with enhanced triboelectric response even in the absence of an external poling. Consequently, the 6S-MP TENG device electrical power generation performance was evaluated.

The output power delivered by a TENG device is intrinsically dependent upon the magnitude of the externally coupled load resistance. Thus, the corresponding output voltage was measured across a systematically varied series of discrete load resistances. The instantaneous output power density was calculated using equation (6.3).

$$P = \frac{V^2}{R_L * \text{Area}} \quad 6.3$$

Here, V represents the output voltage measured across the external load resistance RL, while the effective contact area of the fabricated TENG device is approximately 6.25 cm²[166]. The corresponding power density plot (Figure 6.3(e)) indicates that the device attained a peak instantaneous power density of approximately 1.01 mW/cm² at an optimal load resistance of 7 MΩ. Furthermore, as illustrated in Figure 6.3(f), the output voltage exhibited a continuous increase with increasing load resistance throughout the investigated range.

To evaluate the energy-harvesting capability of the 6S-MP TENG, two capacitors of capacitance 2.2 μF and 4.7 μF were charged under mechanically induced repetitive tapping, as shown in Figure 6.3(g). Within 50 s, the terminal voltages of the 2.2 μF and 4.7 μF capacitors reached 1.76 V and 580 mV, respectively, demonstrating efficient transfer of harvested mechanical energy to capacitive storage over a short duration. Additionally, the TENG directly and instantaneously powered an array of 31 commercially available blue and red LEDs under low-amplitude tapping, without any external or auxiliary energy storage. The corresponding luminescent states of the LED array are shown in Fig. 6.3(h).

6.3 Conclusion

In summary, the TENG device fabricated using a SnO₂/MXene/PVDF composite film paired with ITO coated PET electrode exhibited substantially improved electrical output compared with bare PVDF based device prepared by solution casting method. Among all the fabricated TENG devices, the 6S-MP TENG device achieved the maximum output voltage of 210 V along with a maximum power density of approximately 1.01 mW/cm². In addition, the device demonstrated excellent energy storage capability by charging 2.2 μ F and 4.7 μ F capacitors to 1.76 V and 580 mV, respectively, within 50 seconds under repeated manual tapping. The harvested mechanical energy was also sufficient to illuminate 31 LED panels simultaneously. These findings provide a deeper understanding of the factors responsible for the enhanced triboelectric performance of the developed TENG while highlighting its potential as an efficient and practical solution for sustainable mechanical energy harvesting applications.



CHAPTER 7

CONCLUSIONS, FUTURE SCOPE AND SOCIAL IMPACT

The main goal of this chapter is to highlight the key findings, significant observations, results and discussions arising from our current research work. In addition, this chapter presents the salient outcomes of the thesis, along with how the limitations of our current research study have opened pathways for future research.

7.1 Summary of Research Work

The key contributions discussed in the various chapters of the present thesis are summarised as follows:

Chapter 1- This chapter presents a comprehensive overview of the growing demand for sustainable energy solutions, emphasizing the pivotal role of energy harvesting technologies in addressing the increasing global energy requirements. With the rapid proliferation of wearable electronics, portable devices, and smart systems, there is an urgent need to replace conventional power sources with clean, renewable, and sustainable alternatives. Mechanical energy harvesters have attracted considerable attention owing to their ability to convert ambient mechanical energy, including vibrations, human motion, and low-pressure fluctuations, into usable electrical energy through piezoelectric and triboelectric nanogenerators. These nanogenerators provide an efficient and sustainable power solution for low-power electronic systems by enabling continuous energy generation without dependence on conventional power grids or frequent battery replacement. Consequently, they have emerged as promising candidates for powering next-generation wearable electronics, self-powered sensors, and distributed IoT devices. Furthermore, this chapter discusses the fundamental operating principles, recent advancements, and application potential of piezoelectric and triboelectric nanogenerators. Owing to their high energy conversion efficiency, mechanical flexibility, scalability, and ease of integration into diverse electronic platforms, these technologies represent viable alternatives for self-powered systems. Their continued development is expected to play a significant role in addressing the escalating energy demands associated with the widespread deployment of smart devices, thereby contributing to the realization of a sustainable, energy-efficient, and environmentally friendly future.

Chapter 2- In this chapter, a comprehensive description of the experimental methodologies employed for the synthesis and characterization of SnO₂ and MXene nanomaterials, as well as their heterostructures. It provides a detailed of the solution-casting method utilized for the fabrication of PVDF-based composite films. A thorough overview of the characterization techniques is also included, comprising X-

ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) for structural analysis and phase identification, field-emission scanning electron microscopy (FESEM) for detailed morphological and microstructural investigations, and UV–Visible spectroscopy and a Universal Testing Machine (UTM) for evaluating the optical band gap and mechanical properties, respectively. Furthermore, the dielectric characteristics of the fabricated composite films were investigated using an impedance analyzer. The piezoelectric and triboelectric performance of the all-fabricated devices was assessed by applying a mechanical force through manual finger tapping, while the generated open-circuit voltage was recorded using a digital storage oscilloscope. In addition, external load resistances were connected to the fabricated devices to evaluate the output power generated by the fabricated energy-harvesting systems.

Chapter 3- In this chapter, SNMX/PVDF composite films were successfully fabricated by incorporating SNMX nanocomposites into a PVDF matrix and systematically investigated for electroactive phase formation, dielectric behavior, and piezoelectric energy harvesting performance. The incorporation of SNMX nanocomposites significantly enhanced the electroactive phase content and dielectric properties of PVDF over a broad frequency range (20 Hz–1 MHz). Among the investigated compositions, the composite film containing 0.75 wt% SNMX exhibited the highest electroactive phase fraction, indicating its optimum filler concentration for maximizing functional performance. FTIR and XRD analyses confirmed the effective nucleation and growth of electroactive crystalline phases within the SNMX/PVDF composite films. Dielectric studies revealed a substantial enhancement in relative dielectric permittivity upon SNMX incorporation. Specifically, the films containing 0.50 wt% and 0.75 wt% SNMX exhibited high dielectric constants of 150 and 165, respectively, at 20 Hz and room temperature while maintaining comparatively low dielectric loss values. Temperature-dependent dielectric measurements further demonstrated a pronounced increase in dielectric permittivity for the composite films relative to pristine PVDF, highlighting the positive influence of the nanocomposite filler on polarization mechanisms. Furthermore, the piezoelectric energy harvesting performance of the fabricated films was evaluated through flexible piezoelectric

nanogenerator (PENG) devices. The PENG based on the 0.75 wt% SNMX/PVDF composite film generated the highest peak-to-peak output voltage of 105 V, demonstrating its superior electromechanical energy conversion capability. The simultaneous enhancement in electroactive phase content, dielectric characteristics, and piezoelectric output performance suggests that the optimized SNMX/PVDF composite films are promising candidates for advanced electronic and energy-related applications, including power conditioning systems, flexible dielectric capacitors, self-powered devices, and pulsed power generation technologies.

Chapter 4- In this chapter, PVDF-based composite films incorporating varying concentrations of SnO₂ nanoparticles and a fixed content of 2 wt% MXene were successfully fabricated via the solution-casting technique. Comprehensive characterization revealed that the composite containing 6 wt% SnO₂ and 2 wt% MXene (6S-MP) represents the optimum nanofiller composition for enhancing the structural, optical, mechanical, dielectric, and electrical properties of the PVDF matrix. XRD and FTIR analyses confirmed a significant increase in the electroactive β -phase content within the composite films. FESEM micrographs of pristine PVDF exhibited predominantly fibrillar morphologies associated with α -phase spherulites, whereas such structures were absent in the composite films, indicating a notable modification in the crystalline phase and morphology upon nanofiller incorporation. Optical investigations based on Tauc plot analysis demonstrated a reduction in both direct and indirect optical band gaps from 5.36 and 5.11 eV for pristine PVDF to 4.88 and 4.61 eV, respectively, for the optimized composite film. Mechanical characterization revealed that the 6S-MP composite exhibited an approximately 82% enhancement in tensile strength compared to pure PVDF. Furthermore, the optimized composite displayed a dielectric constant of 30 at 10³ Hz while maintaining a relatively low dielectric loss tangent of 0.1, indicating its suitability for energy storage applications. Notably, a further increase in SnO₂ concentration to 8 wt% resulted in a deterioration of the composite properties, suggesting the existence of an optimal filler loading beyond which agglomeration and interfacial defects may adversely affect performance. The enhanced electroactive phase content, reduced energy band gap, and improved dielectric characteristics

collectively demonstrate the potential of the optimized 6S-MP composite film for advanced applications in piezoelectric energy harvesting, ultraviolet shielding, and high-performance energy storage devices.

Chapter 5- In this chapter, the fabricated flexible composite piezoelectric energy harvesting (FCPEH) devices exhibited significantly higher open-circuit voltage outputs compared to the pristine PVDF-based FCPEH device under identical mechanical excitation conditions. Among the developed devices, the 6S-MP FCPEH device demonstrated the highest performance, achieving a maximum output voltage of 65 V and a power density of $43.8 \mu\text{W cm}^{-2}$. The fabricated FCPEH devices effectively harvested biomechanical energy generated from various human motions, including finger tapping, heel movement, and toe movement. Furthermore, the FCPEH device exhibited excellent energy storage capability, successfully charging 1 μF and 2.2 μF capacitors to voltages of 2.1 V and 1.3 V, respectively, within 80 s under periodic finger-tapping excitation. The harvested energy was also sufficient to illuminate 11 LED panels, demonstrating the practical applicability of the device for self-powered electronic systems. .

Chapter 6- In this study, TENG device fabricated using a $\text{SnO}_2/\text{MXene}/\text{PVDF}$ composite film paired with an ITO-coated PET electrode exhibited significantly enhanced electrical output compared with the bare PVDF-based device fabricated via the solution-casting method. Among all the fabricated TENG devices, the 6S-MP TENG demonstrated the highest performance, delivering a maximum output voltage of 210 V and a peak power density of approximately 1.01 mW cm^{-2} . Furthermore, the device exhibited excellent energy-storage capability, charging 2.2 μF and 4.7 μF capacitors to 1.76 V and 580 mV, respectively, within 50 s under repeated manual tapping. The harvested mechanical energy was also sufficient to simultaneously illuminate 31 LED panels, thereby demonstrating the practical feasibility of the fabricated TENG for self-powered energy-harvesting applications.

These findings provide a promising pathway for the development of environmentally sustainable and high-performance flexible composite materials for next-generation

energy harvesting applications, with particular emphasis on long-term operational stability and real-world functionality

7.2 Future Perspective

The material design strategies and device architectures developed in this thesis provide a robust foundation for the advancement of next-generation flexible electronic systems. Furthermore, the findings of this research establish a framework for future investigations and open several promising avenues for continued exploration and technological development.

Material Design Strategies and Morphological Engineering

The synthesized nanofiller systems and the nanogenerators developed in this study provide a versatile platform for the rational design and engineering of advanced nanofiller architectures. Future research may focus on exploring a wider range of hybrid nanofiller systems by integrating conductive materials with inorganic metal oxides exhibiting superior dielectric properties, such as MXene combined with various high-permittivity metal oxides. Furthermore, systematic investigations into different crystallographic phases and structural morphologies of SnO₂, including nanorods, nanowires, nanofibers, and mesoporous nanospheres, may provide deeper insights into interfacial polarization mechanisms and the nucleation of the electroactive β -phase, thereby facilitating the development of high-performance piezoelectric nanocomposites.

In addition to compositional optimization, advanced physical surface engineering strategies, such as controlled ion irradiation for precise modulation of the surface roughness and electron affinity of polymer matrices, offer significant potential for enhancing the triboelectric and piezoelectric performance of nanocomposite systems. Furthermore, the integration of machine learning and data-driven optimization approaches could facilitate the prediction of optimal nanofiller concentrations, filler morphologies, and triboelectric material pairings. Such computational frameworks would accelerate material discovery, minimize experimental trial-and-error, and enable the rational design of high-performance energy harvesting nanocomposites.

Large-Scale Industrial Fabrication

Flexible PVDF-based nanocomposite films and the corresponding nanogenerators developed in this study exhibit exceptional performance under laboratory-scale conditions, their successful translation to industrial-scale production remains a critical challenge. Future research should therefore prioritize the development of scalable fabrication strategies, including continuous roll-to-roll printing and other high-throughput manufacturing techniques, to facilitate cost-effective, large-area production and accelerate the commercial deployment of these flexible energy-harvesting devices.

The developed PVDF-based nanocomposite films hold significant potential for application as high-performance flexible dielectric materials and energy-harvesting nanogenerators in next-generation microelectronic and smart wearable systems requiring continuous, self-sustained power. Their integration into wearable platforms, such as smartwatches, biometric textiles, and intelligent footwear, would enable the efficient conversion of biomechanical energy into electrical energy, thereby providing a sustainable, battery-free power source for remote IoT sensors, wireless electronics, and real-time healthcare monitoring systems. Such capabilities highlight their promise for advancing self-powered wearable technologies and intelligent sensing applications.

7.4 Social impact

Ecological Sustainability and Mitigation of Electronic Waste Generation

Conventional wearable electronic devices have historically been reliant upon chemical-based battery systems, which inherently incorporate hazardous lithium and lead along with toxic compounds that are known to infiltrate terrestrial and aquatic ecosystems through leachate contamination. The cumulative annual disposal of such battery systems has precipitated a global electronic waste crisis of significant environmental concern. The PENG and TENG device developed in the present investigation adopt an environmentally conscientious fabrication methodology through the deliberate selection of lead-free PVDF, SnO₂, and MXene. Moreover,

through the effective transduction of ambient mechanical energy into a renewable electrical energy supply, these devices represent a net zero-emission energy conversion technology. The substitution of conventional electrochemical batteries with mechanical energy harvesting systems, as demonstrated in this thesis, constitutes a direct and meaningful contribution toward the substantial reduction of toxic electronic waste and the environmental degradation attributable to heavy-metal extraction and processing.

Enhancement of Quality of Life and Advancement of Healthcare Technologies

Contemporary society exhibits an escalating dependence on compact, wearable electronic devices encompassing smartwatches, physiological fitness monitors, and continuous biomedical surveillance systems. Nevertheless, the practical constraint imposed by the necessity of periodic battery recharging has emerged as a considerable technological limitation. The flexible PENG and TENG nanogenerators engineered within the scope of this thesis demonstrate considerable potential to enable complete self-sufficiency in small-scale electronic systems. Through the harvesting of pervasive biomechanical energy generated by routine human physiological activity including ambulation, upper-limb movement, and cardiac vibrations these devices are capable of sustaining uninterrupted and autonomous operation of wearable electronic platforms. This recharge-independent operational capability substantially elevates the quality of daily life by enabling the seamless assimilation of electronic technology into routine human activity. Furthermore, such systems hold the potential to provide life-critical operational reliability for implantable medical devices and continuous patient health monitoring applications.

Technological Democratization in Geographically Underserved Regions

A persistent sociotechnological disparity in developing nations arises from the inadequate or absent centralized electrical grid infrastructure in rural and geographically isolated communities. Given that the proposed nanogenerator systems function with complete independence from centralized power distribution networks, they embody substantial potential to facilitate the democratization of technological access. Specifically, these devices are capable of supplying localized electrical power

to essential low-power instrumentation including agricultural soil condition sensors, remote meteorological monitoring units, and point-of-care diagnostic systems thereby ensuring that geographically marginalized communities are not systematically excluded from ongoing digital and healthcare advancements.

Congruence with Strategic National Missions of the Government of India

The scientific outcomes and technological contributions of this research demonstrate strong alignment with several active national policy frameworks. The Perform, Achieve and Trade (PAT) scheme, the national action plan on climate change, Make in India , and Aatmanirbhar Bharat initiatives underscore the imperative for the development of indigenously conceived technologies and the strengthening of domestic manufacturing capabilities. Through the development of scalable, high-performance nanogenerators for flexible electronic applications, this research actively reinforces national technological self-sufficiency while simultaneously reducing dependency on imported electronic components and critical raw material supply chains.

REFERENCES

- [1] S. Bairagi, M. Shahadat, D.M. Mulvihill, W. Ali, Mechanical energy harvesting and self-powered electronic applications of textile-based piezoelectric nanogenerators: A systematic review, *Nano Energy*, 111 (2023) 108414.
- [2] F. Lv, Z. Hong, Z. Ahmad, H. Li, Y. Wu, Y. Huang, Design of flexible piezoelectric nanocomposite for energy harvesters: a review, *Energy Material Advances*, 4 (2023) 0043.
- [3] H.H. Singh, N. Khare, Flexible ZnO-PVDF/PTFE based piezo-tribo hybrid nanogenerator, *Nano Energy*, 51 (2018) 216-222.
- [4] J. Park, Y. Lee, M. Ha, S. Cho, H. Ko, Micro/nanostructured surfaces for self-powered and multifunctional electronic skins, *Journal of Materials Chemistry B*, 4 (2016) 2999-3018.
- [5] Z.L. Wang, Triboelectric nanogenerators as new energy technology for self-powered systems and as active mechanical and chemical sensors, *ACS nano*, 7 (2013) 9533-9557.
- [6] S.K. Ghosh, T.K. Sinha, B. Mahanty, D. Mandal, Self-poled efficient flexible "Ferroelectric" nanogenerator: a new class of piezoelectric energy harvester, *Energy Technology*, 3 (2015) 1190-1197.
- [7] X. Zhang, X. Huang, C. Li, H. Jiang, Dye-sensitized solar cell with energy storage function through PVDF/ZnO nanocomposite counter electrode, *Advanced Materials (Deerfield Beach, Fla.)*, 25 (2013) 4093.
- [8] W. Seung, H.J. Yoon, T.Y. Kim, H. Ryu, J. Kim, J.H. Lee, J.H. Lee, S. Kim, Y.K. Park, Y.J. Park, Boosting power-generating performance of triboelectric nanogenerators via artificial control of ferroelectric polarization and dielectric properties, *Advanced Energy Materials*, 7 (2017) 1600988.
- [9] M.D.P. Emilio, *Microelectronic circuit design for energy harvesting systems*, Springer, 2017.
- [10] R. Tiwari, N.R. Babu, Recent developments of control strategies for wind energy conversion system, *Renewable and Sustainable Energy Reviews*, 66 (2016) 268-285.
- [11] A.M. Abdullah, A.R. Chowdhury, Y. Yang, H. Vasquez, H.J. Moore, J.G. Parsons, K. Lozano, J.J. Gutierrez, K.S. Martirosyan, M.J. Uddin, Tailoring the viscosity of water and ethylene glycol based TiO₂ nanofluids, *Journal of Molecular Liquids*, 297 (2020) 111982.
- [12] C. Wei, X. Jing, A comprehensive review on vibration energy harvesting: Modelling and realization, *Renewable and Sustainable Energy Reviews*, 74 (2017) 1-18.
- [13] L. Wu, Z. Ren, Y. Wang, Y. Tang, Z.L. Wang, R. Yang, Miniaturized and high volumetric energy density power supply device based on a broad-frequency vibration driven triboelectric nanogenerator, *Micromachines*, 15 (2024) 645.
- [14] F. Zamanpour, L. Shooshtari, M. Gholami, R. Mohammadpour, P. Sasanpour, N. Taghavinia, Transparent and flexible touch on/off switch based on BaTiO₃/silicone polymer triboelectric nanogenerator, *Nano Energy*, 103 (2022) 107796.
- [15] Z.L. Wang, J. Song, Piezoelectric nanogenerators based on zinc oxide nanowire arrays, *science*, 312 (2006) 242-246.
- [16] C. Wan, C.R. Bowen, Multiscale-structuring of polyvinylidene fluoride for energy harvesting: the impact of molecular-, micro-and macro-structure, *Journal of Materials Chemistry A*, 5 (2017) 3091-3128.
- [17] J. Briscoe, S. Dunn, Piezoelectric nanogenerators—a review of nanostructured piezoelectric energy harvesters, *Nano Energy*, 14 (2015) 15-29.
- [18] X.-Q. Fang, J.-X. Liu, V. Gupta, Fundamental formulations and recent achievements in piezoelectric nano-structures: a review, *Nanoscale*, 5 (2013) 1716-1726.
- [19] F.-R. Fan, Z.-Q. Tian, Z.L. Wang, Flexible triboelectric generator, *Nano energy*, 1 (2012) 328-334.
- [20] A. Baburaj, S. Jayadevan, A.K. Aliyana, N.K. Sk, G.K. Stylios, AI-Driven TENGs for Self-Powered Smart Sensors and Intelligent Devices, *Advanced Science*, 12 (2025) 2417414.
- [21] U.K. Khanapuram, G.M. Rani, S. Panda, T. Charoonsuk, K. Mistewicz, S. Hajra, K.R. Kaja, R. Umapathi, S. Sriphan, J. Jala, Harvesting Energy from Friction: The Revolutionary Decade of Triboelectric Nanogenerators, *Advanced Powder Materials*, (2025) 100373.
- [22] S. Rana, H. Sharma, R. Bokolia, K. Bhatt, R. Singh, R. Meena, B. Singh, PVDF/N-rGO nanofibers based sustainable triboelectric nanogenerator for self-powered wireless motion sensor, *Carbon*, 234 (2025) 119926.

References

- [23] J. Liu, S. Li, S. Zhou, Z. Chen, J. Xu, N. Cui, M. Yuan, B. Li, L. Gu, A high-performance, biocompatible, and fully biodegradable piezo-triboelectric hybrid nanogenerator based on PVA/Glycine/PVA heterostructured piezoelectric film, *Nano Energy*, 122 (2024) 109310.
- [24] X. Zhang, J. Villafuerte, V. Consonni, J.-F. Capsal, P.-J. Cottinet, L. Petit, M.-Q. Le, Characterizing and optimizing piezoelectric response of ZnO nanowire/PMMA composite-based sensor, *Nanomaterials*, 11 (2021) 1712.
- [25] H.S. Nalwa, *Ferroelectric polymers: chemistry, physics, and applications*, CRC Press, 1995.
- [26] P. Costa, J. Nunes-Pereira, N. Pereira, N. Castro, S. Gonçalves, S. Lanceros-Mendez, Recent progress on piezoelectric, pyroelectric, and magnetoelectric polymer-based energy-harvesting devices, *Energy technology*, 7 (2019) 1800852.
- [27] R. Fu, S. Chen, Y. Lin, S. Zhang, J. Jiang, Q. Li, Y. Gu, Improved piezoelectric properties of electrospun poly (vinylidene fluoride) fibers blended with cellulose nanocrystals, *Materials Letters*, 187 (2017) 86-88.
- [28] Q. Zhang, V. Bharti, G. Kavarnos, Poly (vinylidene fluoride)(PVDF) and its copolymers, *Encyclopedia of smart materials*, (2002).
- [29] X. Cai, T. Lei, D. Sun, L. Lin, A critical analysis of the α , β and γ phases in poly (vinylidene fluoride) using FTIR, *RSC advances*, 7 (2017) 15382-15389.
- [30] X. Lin, F. Yu, X. Zhang, W. Li, Y. Zhao, X. Fei, Q. Li, C. Yang, S. Huang, Wearable piezoelectric films based on MWCNT-BaTiO₃/PVDF composites for energy harvesting, sensing, and localization, *ACS Applied Nano Materials*, 6 (2023) 11955-11965.
- [31] E. Kar, N. Bose, B. Dutta, S. Banerjee, N. Mukherjee, S. Mukherjee, 2D SnO₂ nanosheet/PVDF composite based flexible, self-cleaning piezoelectric energy harvester, *Energy conversion and management*, 184 (2019) 600-608.
- [32] M. Fahad, A. Waqar, D. Park, B. Kim, Flexible MXene/PVDF composite-based piezoelectric device (FPED) for dual applications in energy harvesting and smart IoT-driven gaming, *Journal of Industrial and Engineering Chemistry*, 149 (2025) 657-675.
- [33] J. Guo, M. Nie, Q. Wang, Self-poling polyvinylidene fluoride-based piezoelectric energy harvester featuring highly oriented β -phase structured at multiple scales, *ACS Sustainable Chemistry & Engineering*, 9 (2020) 499-509.
- [34] A.J. Lovinger, Unit cell of the γ phase of poly (vinylidene fluoride), *Macromolecules*, 14 (1981) 322-325.
- [35] A. Salimi, A.A. Yousefi, Analysis method: FTIR studies of β -phase crystal formation in stretched PVDF films, *Polymer Testing*, 22 (2003) 699-704.
- [36] B.S. 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 I. Melt-crystallization at high supercooling, *Polymer*, 51 (2010) 1485-1493.
- [37] A. Gradys, P. Sajkiewicz, S. Adamovsky, A. Minakov, C. Schick, Crystallization of poly (vinylidene fluoride) during ultra-fast cooling, *Thermochimica Acta*, 461 (2007) 153-157.
- [38] H. Pan, B. Na, R. Lv, C. Li, J. Zhu, Z. Yu, Polar phase formation in poly (vinylidene fluoride) induced by melt annealing, *Journal of Polymer Science Part B: Polymer Physics*, 50 (2012) 1433-1437.
- [39] P.K. Szewczyk, A. Gradys, S.K. Kim, L. Persano, M. Marzec, A. Kryształ, T. Busolo, A. Toncelli, D. Pisignano, A. Bernasik, Enhanced piezoelectricity of electrospun polyvinylidene fluoride fibers for energy harvesting, *ACS applied materials & interfaces*, 12 (2020) 13575-13583.
- [40] Z. Liu, F. Wang, H. Zhu, Enhanced dielectric properties of polyvinylidene fluoride with addition of SnO₂ nanoparticles, *physica status solidi (RRL)—Rapid Research Letters*, 10 (2016) 753-756.
- [41] A.D. Dillon, M.J. Ghidui, A.L. Krick, J. Griggs, S.J. May, Y. Gogotsi, M.W. Barsoum, A.T. Fafarman, Highly conductive optical quality solution-processed films of 2D titanium carbide, *Advanced Functional Materials*, 26 (2016) 4162-4168.
- [42] A. Lipatov, H. Lu, M. Alhabeb, B. Anasori, A. Gruverman, Y. Gogotsi, A. Sinitskii, Elastic properties of 2D Ti₃C₂T_x MXene monolayers and bilayers, *Science advances*, 4 (2018) eaat0491.
- [43] W. Ma, K. Yang, C. Zhou, H. Li, Enhanced dielectric constant and suppressed electrical conductivity in polymer nanocomposite films via loading MXene/TiO₂/MoS₂ nanosheets, *Ceramics International*, 48 (2022) 10447-10457.
- [44] Y. Feng, Q. Deng, C. Peng, Q. Wu, High dielectric and breakdown properties achieved in ternary BaTiO₃/MXene/PVDF nanocomposites with low-concentration fillers from enhanced interface polarization, *Ceramics International*, 45 (2019) 7923-7930.

References

- [45] A. Kumar, R. Sharma, Piezoelectric flexible generator based on Mn-doped ZnO/PVDF composite films for energy harvesting application, *Current Applied Physics*, 68 (2024) 159-168.
- [46] J. Yousaf, K. Hayat, S. Khan, J.U. Din, N. Ali, S. Ali, Y. Khan, S.K. Shah, Ti3C2–MXene/ZnO/PVDF Composite Fibers as Renewable Energy Materials for Piezoelectric Nanogenerator Applications, *Journal of Alloys and Compounds*, (2025) 183392.
- [47] D. Chauhan, A.K. Singh, S. Tyagi, P.I. Anand, S. Ramakrishna, M.K. Srivastava, Engineering of electrospun lead-free PVDF/Carbon Nanofiber-ZnO nanocomposites for enhanced piezoelectric energy harvesting and wearable sensing applications, *Composites Part B: Engineering*, (2025) 113039.
- [48] A. Sherryna, M. Tahir, Role of Ti3C2 MXene as prominent schottky barriers in driving hydrogen production through photoinduced water splitting: a comprehensive review, *ACS Applied Energy Materials*, 4 (2021) 11982-12006.
- [49] L.-f. Hong, R.-t. Guo, Y. Yuan, X.-y. Ji, Z.-s. Li, Z.-d. Lin, W.-g. Pan, Recent progress of two-dimensional MXenes in photocatalytic applications: a review, *Materials Today Energy*, 18 (2020) 100521.
- [50] P. Ganguly, M. Harb, Z. Cao, L. Cavallo, A. Breen, S. Dervin, D.D. Dionysiou, S.C. Pillai, 2D nanomaterials for photocatalytic hydrogen production, *ACS Energy Letters*, 4 (2019) 1687-1709.
- [51] A. Mankuni, S. Varghese, Flexible piezoelectric nanogenerator based on a poly (vinylidene fluoride)–Ti3C2 MXene film for underwater energy harvesting, *ACS Applied Electronic Materials*, 6 (2024) 4194-4203.
- [52] K.R.G. Lim, M. Shekhirev, B.C. Wyatt, B. Anasori, Y. Gogotsi, Z.W. Seh, Fundamentals of MXene synthesis, *Nature Synthesis*, 1 (2022) 601-614.
- [53] J. Li, Q. Wu, J. Wu, Synthesis of nanoparticles via solvothermal and hydrothermal methods. 12, in: *Synthesis of Nanoparticles via Solvothermal and Hydrothermal Methods 12*, Springer international publishing Switzerland, 2016.
- [54] S. Feng, R. Xu, New materials in hydrothermal synthesis, *Accounts of chemical research*, 34 (2001) 239-247.
- [55] G. Yang, S.-J. Park, Conventional and microwave hydrothermal synthesis and application of functional materials: A review, *Materials*, 12 (2019) 1177.
- [56] S.S. Khudiar, F.A.-H. Mutlak, U.M. Nayef, Synthesis of ZnO nanostructures by hydrothermal method deposited on porous silicon for photo-conversion application, *Optik*, 247 (2021) 167903.
- [57] J.A. Kumar, P. Prakash, T. Krithiga, D.J. Amarnath, J. Premkumar, N. Rajamohan, Y. Vasseghian, P. Saravanan, M. Rajasimman, Methods of synthesis, characteristics, and environmental applications of MXene: A comprehensive review, *Chemosphere*, 286 (2022) 131607.
- [58] Y. Wei, P. Zhang, R.A. Soomro, Q. Zhu, B. Xu, Advances in the synthesis of 2D MXenes, *Advanced materials*, 33 (2021) 2103148.
- [59] J. Epp, X-ray diffraction (XRD) techniques for materials characterization, in: *Materials characterization using nondestructive evaluation (NDE) methods*, Elsevier, 2016, pp. 81-124.
- [60] C.G. Pope, X-ray diffraction and the Bragg equation, *Journal of chemical education*, 74 (1997) 129.
- [61] M.A. Sutton, N. Li, D. Joy, A.P. Reynolds, X. Li, Scanning electron microscopy for quantitative small and large deformation measurements part I: SEM imaging at magnifications from 200 to 10,000, *Experimental mechanics*, 47 (2007) 775-787.
- [62] A. Ul-Hamid, *A beginners' guide to scanning electron microscopy*, Springer, 2018.
- [63] Y. Leng, *Materials characterization: introduction to microscopic and spectroscopic methods*, John Wiley & Sons, 2013.
- [64] W.M. Doyle, Principles and applications of Fourier transform infrared (FTIR) process analysis, *Process Control Qual*, 2 (1992) 11-41.
- [65] G.C. Schatz, R.P. Van Duyne, Electromagnetic mechanism of surface-enhanced spectroscopy, in, *Wiley: New York*, 2002, pp. 759-774.
- [66] D. Titus, E.J.J. Samuel, S.M. Roopan, Nanoparticle characterization techniques, in: *Green synthesis, characterization and applications of nanoparticles*, Elsevier, 2019, pp. 303-319.
- [67] D.F. Swinehart, The beer-lambert law, *Journal of chemical education*, 39 (1962) 333.
- [68] P. Glaister, Titration curve analysis: some observations, *Journal of Chemical Education*, 74 (1997) 744.
- [69] S. Kumar, S. Khanchandani, M. Thirumal, A.K. Ganguli, Achieving enhanced visible-light-driven photocatalysis using type-II NaNbO3/CdS core/shell heterostructures, *ACS applied materials & interfaces*, 6 (2014) 13221-13233.

References

- [70] F.S. Rocha, A.J. Gomes, C.N. Lunardi, S. Kaliaguine, G.S. Patience, Experimental methods in chemical engineering: Ultraviolet visible spectroscopy—UV-Vis, *The Canadian Journal of Chemical Engineering*, 96 (2018) 2512-2517.
- [71] A. Sengupta, S. Das, S. Dasgupta, P. Sengupta, P. Datta, Flexible nanogenerator from electrospun PVDF–polycarbazole nanofiber membranes for human motion energy-harvesting device applications, *ACS Biomaterials Science & Engineering*, 7 (2021) 1673-1685.
- [72] A. Thakur, J. Mandeep, S. Dam, N.C. Shekar, G. Amarendra, S. Hussain, P. Rajesh, A. Saha, Enhancing the electroactive phases in freestanding flexible films of MoS₂/PVDF, *Polymer Crystallization*, 4 (2021) e10164.
- [73] A. Anand, D. Meena, K.K. Dey, M.C. Bhatnagar, Enhanced piezoelectricity properties of reduced graphene oxide (RGO) loaded polyvinylidene fluoride (PVDF) nanocomposite films for nanogenerator application, *Journal of Polymer Research*, 27 (2020) 358.
- [74] N.D. Kulkarni, P. Kumari, Development of highly flexible PVDF-TiO₂ nanocomposites for piezoelectric nanogenerator applications, *Materials Research Bulletin*, 157 (2023) 112039.
- [75] M. Choi, G. Murillo, S. Hwang, J.W. Kim, J.H. Jung, C.-Y. Chen, M. Lee, Mechanical and electrical characterization of PVDF-ZnO hybrid structure for application to nanogenerator, *Nano Energy*, 33 (2017) 462-468.
- [76] N.H. Yusoff, R.A.M. Osman, M.S. Idris, K.N.D.K. Muhsen, N.I.M. Nor, Dielectric and structural analysis of hexagonal and tetragonal phase BaTiO₃, in: *AIP Conference Proceedings*, AIP Publishing LLC, 2020, pp. 020038.
- [77] J. Tang, H. Zhang, Z. Yang, Z. Mao, J. Zhang, Comparison of barium titanate and multi-walled carbon nanotubes modified PVDF composites: A perspective of dielectric, crystalline, rheological and mechanical properties, *Ceramics International*, 50 (2024) 1059-1068.
- [78] A. Thakur, M. Jangra, S. Dam, S. Hussain, Enhanced dielectric constant with addition of a low amount of SnO₂ nanoparticles as fillers in a PVDF matrix with low dielectric loss, *Nano-Structures & Nano-Objects*, 34 (2023) 100978.
- [79] S. Sarkar, S. Garain, D. Mandal, K. Chattopadhyay, Electro-active phase formation in PVDF–BiVO₄ flexible nanocomposite films for high energy density storage application, *RSC advances*, 4 (2014) 48220-48227.
- [80] A. Tsyganov, M. Vikulova, I. Zotov, I. Burmistrov, A. Gorokhovskiy, N. Gorshkov, Synergistic effect of CaCu₃Ti₄O₁₂ ceramic and Ti₃C₂T_x MXene nanoflakes on the dielectric properties of poly(vinylidene fluoride) composites, *Materials Chemistry and Physics*, 313 (2024) 128714.
- [81] M. Kumar, N.D. Kulkarni, P. Kumari, Piezoelectric performance enhancement of electrospun functionally graded PVDF/BaTiO₃ based flexible nanogenerators, *Materials Research Bulletin*, 174 (2024) 112739.
- [82] A. Mondal, M. Faraz, M. Dahiya, N. Khare, Double-layer electronegative structure-based triboelectric nanogenerator for enhanced performance using combined effect of enhanced charge generation and improved charge trapping, *ACS Applied Materials & Interfaces*, 16 (2024) 50659-50670.
- [83] S. Gasso, M.K. Sohal, A. Mahajan, MXene modulated SnO₂ gas sensor for ultra-responsive room-temperature detection of NO₂, *Sensors and Actuators B: Chemical*, 357 (2022) 131427.
- [84] T. Furukawa, Ferroelectric properties of vinylidene fluoride copolymers, *Phase Transitions: A Multinational Journal*, 18 (1989) 143-211.
- [85] S. Chen, V.K. Thakur, A.A. Skordos, Fluorine and nitrogen doping of zinc oxide to enhance dielectric storage of PVDF based particulate composites, *Materials Science and Engineering: B*, 302 (2024) 117244.
- [86] H. Parangusan, D. Al-Sowaidi, E.-H. Elhadrami, D. Ponnammma, J. Bhadra, Development of flexible PVDF/BaTiO₃-MoS₂ polymer nanocomposites for energy harvesting and gas sensing applications, *Journal of Materials Science: Materials in Electronics*, 35 (2024) 679.
- [87] P.L. Reddy, K. Deshmukh, T. Kovářík, D. Reiger, N.A. Nambiraj, L. R. K.P. SK, Enhanced dielectric properties of green synthesized Nickel Sulphide (NiS) nanoparticles integrated polyvinylalcohol nanocomposites, *Materials Research Express*, 7 (2020) 064007.
- [88] R. Meena, R.S. Dhaka, Dielectric properties and impedance spectroscopy of NASICON type Na₃Zr₂Si₂PO₁₂, *Ceramics International*, 48 (2022) 35150-35159.
- [89] S. Sangwan, R. Meena, R. Bokolia, V. Singh, D. Meena, Exploration of structural and dielectric properties of orthorhombic Ta₂O₅ nanoplatelets towards the potential optoelectronic devices, *Materials Today Communications*, 38 (2024) 108468.

References

- [90] R. Sahoo, S. Mishra, A. Ramadoss, S. Mohanty, S. Mahapatra, S.K. Nayak, Temperature-dependent dielectric properties of metal-doped ZnO nanofiller reinforced PVDF nanocomposites, *Materials Research Bulletin*, 132 (2020) 111005.
- [91] J.-W. Zha, X. Meng, D. Wang, Z.-M. Dang, R.K. Li, Dielectric properties of poly (vinylidene fluoride) nanocomposites filled with surface coated BaTiO₃ by SnO₂ nanodots, *Applied Physics Letters*, 104 (2014).
- [92] M.V. Paranjape, S.A. Graham, H. Patnam, P. Manchi, J.S. Yu, Dopamine treated SnO₂/PVDF composite films for hybrid mechanical energy harvester, *Composites Science and Technology*, 221 (2022) 109323.
- [93] L. Cao, Y. Chen, S. Feng, Y. Su, Reduced dielectric loss of MXene/PVDF composites with adding MnO₂ nanorods, *Ceramics International*, 50 (2024) 47655-47665.
- [94] N.D. Kulkarni, A. Saha, P. Kumari, The development of a low-cost, sustainable bamboo-based flexible bio composite for impact sensing and mechanical energy harvesting applications, *Journal of Applied Polymer Science*, 140 (2023) e54040.
- [95] H. Hu, F. Zhang, S. Luo, W. Chang, J. Yue, C.-H. Wang, Recent advances in rational design of polymer nanocomposite dielectrics for energy storage, *Nano Energy*, 74 (2020) 104844.
- [96] K. Dong, X. Peng, Z.L. Wang, Fiber/fabric-based piezoelectric and triboelectric nanogenerators for flexible/stretchable and wearable electronics and artificial intelligence, *Advanced Materials*, 32 (2020) 1902549.
- [97] P. Thakur, A. Kool, N.A. Hoque, B. Bagchi, F. Khatun, P. Biswas, D. Brahma, S. Roy, S. Banerjee, S. Das, Superior performances of in situ synthesized ZnO/PVDF thin film based self-poled piezoelectric nanogenerator and self-charged photo-power bank with high durability, *Nano Energy*, 44 (2018) 456-467.
- [98] P. Saxena, P. Shukla, A comprehensive review on fundamental properties and applications of poly (vinylidene fluoride)(PVDF), *Advanced Composites and Hybrid Materials*, 4 (2021) 8-26.
- [99] A. Mukherjee, S. Roy, P.K. Maji, B. Dasgupta Ghosh, Functionalized Cu-Doped ZnO/PVDF composite: an excellent energy storage material for wearable devices, *ACS Applied Energy Materials*, 7 (2024) 8903-8915.
- [100] S. Zhang, Y. Liu, J. Hao, G.G. Wallace, S. Beirne, J. Chen, 3D-printed wearable electrochemical energy devices, *Advanced Functional Materials*, 32 (2022) 2103092.
- [101] C. Xing, Y. Wang, X. Huang, Y. Li, J. Li, Poly (vinylidene fluoride) nanocomposites with simultaneous organic nanodomains and inorganic nanoparticles, *Macromolecules*, 49 (2016) 1026-1035.
- [102] T. Vijayakanth, D.J. Liptrot, E. Gazit, R. Boomishankar, C.R. Bowen, Recent advances in organic and organic-inorganic hybrid materials for piezoelectric mechanical energy harvesting, *Advanced Functional Materials*, 32 (2022) 2109492.
- [103] R. Behera, K. Elanseralathan, Improved electrical properties in three phase poly (vinylidene fluoride) nanocomposites with hybrid fillers of titanium dioxide and MXene, *Materials Today Communications*, 34 (2023) 105334.
- [104] S. Tu, Q. Jiang, X. Zhang, H.N. Alshareef, Large dielectric constant enhancement in MXene percolative polymer composites, *ACS nano*, 12 (2018) 3369-3377.
- [105] A. Ismail, M. Mohammed, S. Fouad, Optical and structural properties of polyvinylidene fluoride (PVDF)/reduced graphene oxide (RGO) nanocomposites, *Journal of Molecular Structure*, 1170 (2018) 51-59.
- [106] 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, *Materials Today*, 29 (2019) 49-67.
- [107] A. Ismail, F.G. El Desouky, Facile assembly of flexible quaternary SnO₂/SrSnO₃/Fe₃O₄/PVDF nanocomposites with tunable optical, electrical, and magnetic properties for promising magneto-optoelectronic applications, *Scientific Reports*, 13 (2023) 4997.
- [108] H.-Q. Wang, J.-W. Wang, X.-Z. Wang, X.-H. Gao, G.-C. Zhuang, J.-B. Yang, H. Ren, Dielectric properties and energy storage performance of PVDF-based composites with MoS₂@ MXene nanofiller, *Chemical Engineering Journal*, 437 (2022) 135431.
- [109] H.S. Alzahrani, H. Almaghami, S. Al-Balawi, A. Al Ojeery, Q.A. Alsulami, N. Algethami, A. Rajeh, Study of structural, optical, photoluminescence, dielectric, and conductivity properties of PVDF/PVP-SnO₂ nanocomposites for optoelectronics and micro-supercapacitors, *Journal of Energy Storage*, 102 (2024) 114034.

References

- [110] Q. Zhao, L. Yang, Y. Ma, H. Huang, H. He, H. Ji, Z. Wang, J. Qiu, Highly sensitive, reliable and flexible pressure sensor based on piezoelectric PVDF hybrid film using MXene nanosheet reinforcement, *Journal of Alloys and Compounds*, 886 (2021) 161069.
- [111] A.C. Khot, T.D. Dongale, J.H. Park, A.V. Kesavan, T.G. Kim, Ti3C2-based MXene oxide nanosheets for resistive memory and synaptic learning applications, *ACS Applied Materials & Interfaces*, 13 (2021) 5216-5227.
- [112] M. Okubo, A. Sugahara, S. Kajiyama, A. Yamada, MXene as a charge storage host, *Accounts of chemical research*, 51 (2018) 591-599.
- [113] A.M. Abd El-Aziz, M. Afifi, Influence the β -PVDF phase on structural and elastic properties of PVDF/PLZT composites, *Materials Science and Engineering: B*, 301 (2024) 117152.
- [114] G. Sharma, D. Meena, Substantial enhancement of the electroactive phase and dielectric properties at low loading levels of SnO2/MXene nanocomposite as a novel nanofiller in the PVDF matrix, *Materials Science in Semiconductor Processing*, 195 (2025) 109607.
- [115] A. Lopes, J.C. Ferreira, C. Costa, S. Lanceros-Méndez, Crystallization kinetics of montmorillonite/poly (vinylidene fluoride) composites and its correlation with the crystalline polymer phase formation, *Thermochimica Acta*, 574 (2013) 19-25.
- [116] A.P. Indolia, M. Gaur, Optical properties of solution grown PVDF-ZnO nanocomposite thin films, *Journal of Polymer Research*, 20 (2013) 43.
- [117] A.M. El Sayed, Boosting the optical and electrical properties of PVA/Na-CMC blend by Cr2O3 nanoparticles for photonic and energy storage applications, *Journal of Energy Storage*, 82 (2024) 110609.
- [118] S. Sangwan, V. Singh, D. Meena, Optimizing dielectric and mechanical characteristics of Ta2O5 reinforced PVDF flexible nanocomposite films for energy storage devices, *Ceramics International*, 51 (2025) 33010-33018.
- [119] N.D. Kulkarni, M. Kumar, P. Kumari, PVDF/RGO based piezoelectric nanocomposite films for enhanced mechanical and dielectric properties, *Materials Today: Proceedings*, 76 (2023) 81-87.
- [120] Y. Feng, C.-H. Wang, S.-X. Liu, Low dielectric constant of polymer based composites induced by the restricted polarizability in the interface, *Materials Letters*, 185 (2016) 491-494.
- [121] R. Mahdi, W.A. Majid, Piezoelectric and pyroelectric properties of BNT-base ternary lead-free ceramic-polymer nanocomposites under different poling conditions, *RSC advances*, 6 (2016) 81296-81309.
- [122] Q. Cao, W. Zhu, W. Chen, X. Chen, R. Yang, S. Yang, H. Zhang, X. Gui, J. Chen, Nonsolid TiO_x nanoparticles/PVDF nanocomposite for improved energy storage performance, *ACS applied materials & interfaces*, 14 (2022) 8226-8234.
- [123] S. Sangwan, V. Singh, D. Meena, Optimizing Dielectric and Mechanical Characteristics of Ta2O5 Reinforced PVDF Flexible Nanocomposite Films for Energy Storage Devices, *Ceramics International*, (2025).
- [124] H. Chen, Y. Li, J. Wang, T. Lu, H. Xu, D. Yang, L. Chen, MXene/SrTiO3/PVDF ternary composites with excellent dielectric properties and thermal stability, *Journal of Materials Science*, (2025) 1-11.
- [125] A. Shayesteh Zeraati, S.A. Mirkhani, U. Sundararaj, Enhanced dielectric performance of polymer nanocomposites based on CNT/MnO2 nanowire hybrid nanostructure, *The Journal of Physical Chemistry C*, 121 (2017) 8327-8334.
- [126] S.S. Jadaun, A.K. Panwar, Effects of heterogeneous structure on conduction mechanism and electrochemical performance of LiTa2PO8-fast lithium-ion conductor in quasi-solid-state lithium-ion batteries, *Journal of Energy Storage*, 115 (2025) 116030.
- [127] K. Funke, Jump relaxation in solid electrolytes, *Progress in Solid State Chemistry*, 22 (1993) 111-195.
- [128] P. Xu, W. Fu, X. Luo, Y. Ding, Enhanced dc conductivity and conductivity relaxation in PVDF/ionic liquid composites, *Materials Letters*, 206 (2017) 60-63.
- [129] A. Arya, A. Sharma, Structural, electrical properties and dielectric relaxations in Na⁺-ion-conducting solid polymer electrolyte, *Journal of Physics: Condensed Matter*, 30 (2018) 165402.
- [130] R. Yue, S.G. Ramaraj, H. Liu, D. Elamaram, V. Elamaram, V. Gupta, S. Arya, S. Verma, S. Satapathi, X. Liu, A review of flexible lead-free piezoelectric energy harvester, *Journal of Alloys and Compounds*, 918 (2022) 165653.

References

- [131] T. Bhatta, P. Maharjan, H. Cho, C. Park, S.H. Yoon, S. Sharma, M. Salauddin, M.T. Rahman, S.S. Rana, J.Y. Park, High-performance triboelectric nanogenerator based on MXene functionalized polyvinylidene fluoride composite nanofibers, *Nano Energy*, 81 (2021) 105670.
- [132] A.-M. Stamatellou, A.I. Kalfas, Experimental investigation of energy harvesting from swirling flows using a piezoelectric film transducer, *Energy Conversion and Management*, 171 (2018) 1405-1415.
- [133] C. Wang, S. Wang, Q.J. Li, X. Wang, Z. Gao, L. Zhang, Fabrication and performance of a power generation device based on stacked piezoelectric energy-harvesting units for pavements, *Energy Conversion and Management*, 163 (2018) 196-207.
- [134] P. Sagar, N. Sinha, M. Shukla, T. Yadav, B. Kumar, Flexible piezoelectric nanogenerator based on Nd-ZnS nanoplates for human body movements detection and wearable electronics, *Journal of Alloys and Compounds*, 1010 (2025) 178035.
- [135] M. Xu, Y. Wen, F. Niu, Q. Yang, C. Xiong, Z. Shi, Flexible piezoelectric generator based on PLLA/ZnO oriented fibers for wearable self-powered sensing, *Composites Part A: Applied Science and Manufacturing*, 169 (2023) 107518.
- [136] H.H. Singh, S. Singh, N. Khare, Enhanced β -phase in PVDF polymer nanocomposite and its application for nanogenerator, *Polymers for Advanced Technologies*, 29 (2018) 143-150.
- [137] M. Acosta, N. Novak, V. Rojas, S. Patel, R. Vaish, J. Koruza, G. Rossetti, J. Rödel, BaTiO₃-based piezoelectrics: Fundamentals, current status, and perspectives, *Applied Physics Reviews*, 4 (2017).
- [138] L.A. Shah, T. Malik, M. Siddiq, A. Haleem, M. Sayed, A. Naeem, TiO₂ nanotubes doped poly (vinylidene fluoride) polymer membranes (PVDF/TNT) for efficient photocatalytic degradation of brilliant green dye, *Journal of Environmental Chemical Engineering*, 7 (2019) 103291.
- [139] A. Anand, D. Meena, M. Bhatnagar, Synthesis and characterization of flexible PVDF/Bi₂Al₄O₉/RGO based piezoelectric materials for nanogenerator application, *Journal of Alloys and Compounds*, 843 (2020) 156019.
- [140] J. Kim, M. Jang, G. Jeong, S. Yu, J. Park, Y. Lee, S. Cho, J. Yeom, Y. Lee, A. Choe, MXene-enhanced β -phase crystallization in ferroelectric porous composites for highly-sensitive dynamic force sensors, *Nano Energy*, 89 (2021) 106409.
- [141] W. Wu, X. Li, Y. Liu, Z. Liu, Y. Wang, T. Jiao, Electrospun MXene-based nanofibrous membranes: Multifunctional integration, challenges, and emerging applications, *Progress in Organic Coatings*, 208 (2025) 109480.
- [142] N. Siedl, S.O. Baumann, M.J. Elser, O. Diwald, Particle networks from powder mixtures: generation of TiO₂-SnO₂ heterojunctions via surface charge-induced heteroaggregation, *The Journal of Physical Chemistry C*, 116 (2012) 22967-22973.
- [143] P. Martins, C. Caparros, R. Gonçalves, P. Martins, M. Benelmekki, G. Botelho, S. Lanceros-Mendez, Role of nanoparticle surface charge on the nucleation of the electroactive β -poly (vinylidene fluoride) nanocomposites for sensor and actuator applications, *The Journal of Physical Chemistry C*, 116 (2012) 15790-15794.
- [144] S. Sharma, A. Chhetry, M. Sharifuzzaman, H. Yoon, J.Y. Park, Wearable capacitive pressure sensor based on MXene composite nanofibrous scaffolds for reliable human physiological signal acquisition, *ACS applied materials & interfaces*, 12 (2020) 22212-22224.
- [145] M. Sebastian, A. Larrea, R. Gonçalves, T. Alejo, J. Vilas, V. Sebastian, P. Martins, S. Lanceros-Méndez, Understanding nucleation of the electroactive β -phase of poly (vinylidene fluoride) by nanostructures, *RSC advances*, 6 (2016) 113007-113015.
- [146] B. Nayak, S. Anwar, A. Roy, S. Anwar, Investigation of 2D-Ti₃C₂TX-loaded PVDF composites for a high-performance flexible piezoelectric energy harvester and wearable sensor, *ACS Applied Electronic Materials*, 5 (2023) 7045-7060.
- [147] G. Sharma, D. Meena, Optimization of SnO₂/MXene/PVDF Composites Films to Enhance Structural, Optical, Mechanical, Dielectric, and Electrical Characteristics Towards Next-Generation Flexible Optoelectronic and Energy Storage Devices, *Ceramics International*, (2026).
- [148] Z. Li, W. Shen, X. Zhang, L. Fang, X. Zu, Controllable growth of SnO₂ nanoparticles by citric acid assisted hydrothermal process, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 327 (2008) 17-20.
- [149] J.A. Howard, V.J. Hoy, D. O'Hagan, G.T. Smith, How good is fluorine as a hydrogen bond acceptor?, *Tetrahedron*, 52 (1996) 12613-12622.

References

- [150] J.-X. Chen, H.-H. Li, J.-W. Li, W.-Y. Tsai, L.-X. Lee, C.-C. Cheng, Y.-H. Tseng, C.-F.J. Kuo, C.-W. Chiu, High-performance triboelectric nanogenerator based on CNTs/PDA-modified BTO/PVDF nanohybrid films for wearable device applications, *Progress in Organic Coatings*, 210 (2026) 109677.
- [151] C. Jiang, L. Zeng, D. Tan, P. Yan, N. Sun, Q. Guo, Z. Zhang, Z. Tao, C. Fang, R. Ji, Piezoelectric behavior of single-layer oxidized-MXene for nanogenerators and piezotronics, *Nano Energy*, 114 (2023) 108670.
- [152] M. Samet, A. Kallel, A. Serghei, Maxwell-Wagner-Sillars interfacial polarization in dielectric spectra of composite materials: Scaling laws and applications, *Journal of Composite Materials*, 56 (2022) 3197-3217.
- [153] L. Xu, J. Lv, S. Yu, Piezoelectric properties of as-spun poly (vinylidene fluoride)/multi-walled carbon nanotube/zinc oxide nanoparticle (PVDF/MWCNT/ZnO) nanofibrous films, *Polymers*, 16 (2024) 2483.
- [154] K. Verma, R. Sharma, Development of KNNLTS–PVDF-based flexible piezoelectric generator for energy-harvesting application, *Bulletin of Materials Science*, 47 (2024) 38.
- [155] A. Kumar, R. Sharma, High output piezoelectric and triboelectric nanogenerators based on Y-doped ZnO for self-powered electronic devices, *Materials Science in Semiconductor Processing*, 199 (2025) 109814.
- [156] M.T. Rahman, M.S. Rahman, H. Kumar, K. Kim, S. Kim, Metal-organic framework reinforced highly stretchable and durable conductive hydrogel-based triboelectric nanogenerator for biomotion sensing and wearable human-machine interfaces, *Advanced Functional Materials*, 33 (2023) 2303471.
- [157] P. Gajula, I. Woo, J.W. Bae, Voltage-Switchable Janus-Inspired Triboelectric Nanogenerator with La-MOF@ GO–BaSrTiO₃ Hybrids for Self-Powered Smart School Bag and Directional Energy Harvesting, *Composites Part B: Engineering*, (2025) 113329.
- [158] S. Mishra, P. Supraja, D. Haranath, R.R. Kumar, S. Pola, Effect of surface and contact points modification on the output performance of triboelectric nanogenerator, *Nano Energy*, 104 (2022) 107964.
- [159] K. Ruthvik, A. Babu, P. Supraja, M. Navaneeth, V. Mahesh, K.U. Kumar, R.R. Kumar, B.M. Rao, D. Haranath, K. Prakash, High-performance triboelectric nanogenerator based on 2D graphitic carbon nitride for self-powered electronic devices, *Materials Letters*, 350 (2023) 134947.
- [160] P. Hajara, M. Shijeesh, K. Vijoy, T.P. Rose, K. Saji, Harnessing energy through ZnO-Based triboelectric nanogenerator: A comparative analysis of polymer materials, with emphasis on PVDF nanofibers, *Journal of Electronic Materials*, 53 (2024) 5617-5628.
- [161] S.S. Rana, M.T. Rahman, M. Salauddin, S. Sharma, P. Maharjan, T. Bhatta, H. Cho, C. Park, J.Y. Park, Electrospun PVDF-TrFE/MXene nanofiber mat-based triboelectric nanogenerator for smart home appliances, *ACS applied materials & interfaces*, 13 (2021) 4955-4967.
- [162] R.M. Habibur, U. Yaqoob, S. Muhammad, A.I. Uddin, H.C. Kim, The effect of RGO on dielectric and energy harvesting properties of P (VDF-TrFE) matrix by optimizing electroactive β phase without traditional polling process, *Materials Chemistry and Physics*, 215 (2018) 46-55.
- [163] G.M. Rani, C.-M. Wu, K.G. Matora, R. Umapathi, C.R.M. Jose, Acoustic-electric conversion and triboelectric properties of nature-driven CF-CNT based triboelectric nanogenerator for mechanical and sound energy harvesting, *Nano Energy*, 108 (2023) 108211.
- [164] S. Sangwan, A. Kumar, G. Sharma, V. Singh, R. Sharma, D. Meena, Heterostructured MXene@ Ta₂O₅ reinforced PVDF based flexible PENG for efficient mechanical energy harvesting, *Applied Physics A*, 132 (2026) 617.
- [165] G. Sharma, A. Kumar, S. Sangwan, R. Sharma, D. Meena, Design and development of a high performance PVDF based flexible composite piezoelectric energy harvesting device for wearable electronics, *Surfaces and Interfaces*, 95 (2026) 109748.
- [166] G. Tian, W. Deng, Y. Gao, D. Xiong, C. Yan, X. He, T. Yang, L. Jin, X. Chu, H. Zhang, Rich lamellar crystal baklava-structured PZT/PVDF piezoelectric sensor toward individual table tennis training, *Nano Energy*, 59 (2019) 574-581.



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Substantial enhancement of the electroactive phase and dielectric properties at low loading levels of SnO₂/MXene nanocomposite as a novel nanofiller in the PVDF matrix

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ABSTRACT

Herein, we investigate the impact on electroactive phase and dielectric properties of polyvinylidene fluoride (PVDF) on addition of hydrothermally synthesized SnO₂/MXene (SNMX) nanocomposite with different concentration (0.25 wt%, 0.50 wt%, 0.75 wt%) as nanofillers. The pure and SNMX/PVDF composite films were fabricated using solution casting method. Morphological and structural analyses revealed a modified spherulitic structure, indicating a transformation from the non-polar phase (52 %) to the polar (β + γ) phase (86 %). The dielectric measurements were conducted over a frequency range of 20 Hz to 1 MHz at different operating temperature to examine the various relaxations occurring in the polymer. At 25 °C and an applied field frequency of 20 Hz, the relative dielectric permittivity of the SNMX/PVDF composite film (0.75 wt%) deviates approximately 25-fold relative to the pristine PVDF film, with a concomitant reduction in loss tangent. Further, the relative dielectric permittivity of all films intensifies with rising operating temperature. At 100 °C, the relative dielectric permittivity amplifies from 165 to 250 compared to room temperature for the 0.75 wt% nanofiller concentration. The increment in dielectric properties with addition of SNMX are attributed to a) the enhancement of the electroactive phase, which favours molecular reorientation, b) the presence of SnO₂ semiconductive layer on the surface of MXene flakes that prevent formation of conductive pathways, thus improves the interfacial polarization through the Maxwell-Wagner-Sillars (MWS) effect in addition to dipolar polarization. A piezoelectric flexible nanogenerator (PENG) fabricated from the 0.75 wt% SNMX/PVDF nanocomposite film generated a maximum peak to peak voltage is 105 V.

1. Introduction

In recent years, flexible dielectric materials have garnered significant interest due to their potential applications in the rapidly developing field of flexible nanoelectronics. In this context, dielectric polymers have attracted considerable attention because of their desirable physical and chemical properties [1–3]. However, polymers generally exhibit lower dielectric constants compared to inorganic materials. For instance, polyvinylidene fluoride (PVDF), a prototypical dielectric polymer, has a dielectric constant of approximately 6.8 and a loss of about 0.0184 at 1 kHz, owing to its fluorinated structure [4]. In contrast, inorganic materials such as ZnO, TiO₂ and BaTiO₃ demonstrate much higher dielectric constants at room temperature [5–7]. Despite excellent dielectric properties, inorganic ceramics possess limitations, including brittleness, limited tunability, susceptibility to dielectric breakdown, and low

toughness. As a result, their use in flexible nanoelectronics is constrained [8].

In contrast, PVDF offers strong flexibility, and excellent mechanical strength which make it suitable for flexible nanodevices. However, due to its low dielectric constant than the inorganic materials hinder its application to nanoelectronics devices. Thus, researchers are trying to improve the dielectric constant and electroactive phase of PVDF. It exists in three phases: α, β, and γ with the β and γ phases being electroactive [9]. In recent times, polymer nanocomposites, incorporating inorganic nanofillers into the polymer matrix, enhancing PVDF's dielectric properties while retaining the advantages of both materials [1]. However, increasing the filler content raises the dielectric constant, but it also leads to higher dielectric loss, reduced flexibility and crystallinity [3, 10].

The choice of nanofiller also influences phase transitions within the

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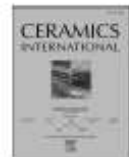
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Optimization of SnO₂/MXene/PVDF composites films to enhance structural, optical, mechanical, dielectric, and electrical characteristics towards next-generation flexible optoelectronic and energy storage devices

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ABSTRACT

In this report, we synthesized PVDF composite films consisting of 2 wt% MXene nanosheets and x wt% of SnO₂ nanoparticles (x = 0.0, 2.0, 4.0, 6.0, 8.0) using the solution casting method and characterized them using different techniques. Interestingly, the 6S-MP composite film, containing 6 wt% SnO₂ and 2 wt% MXene, exhibits optimized optical, mechanical, dielectric, and electrical conductivity properties. X-ray diffraction (XRD) analysis indicated the transformation of the non-polar phase to the polar phase in the PVDF composite film. FTIR measurements revealed an enhancement in the β phase content from 65 % in pristine PVDF to 80 % in the 6S-MP composite film. FESEM micrographs confirm the formation of SnO₂ nanoparticles and the characteristic accordion-like structure of the synthesized MXene. Additionally, the introduction of nanofillers disrupted the uniformity of the PVDF matrix, resulting in distinct morphological changes in the composite films. The Tauc plot analysis revealed that as the nanofiller content increased, the calculated direct and indirect bandgap energies decreased from 5.36 eV to 4.88 eV and from 5.11 eV to 4.61 eV, respectively. Furthermore, the addition of nanofillers enhanced the tensile strength and elasticity of the composite films. Dielectric measurements (10²–10⁷ Hz) showed that at 1 kHz, the relative dielectric permittivity of the 6S-MP composite film increased fivefold compared to pristine PVDF, with relatively low loss tangent (tan δ) of 0.10. According to Jonscher's rule, the AC electrical conductivity of the composite films increased with the nanofiller concentration and exhibited non-Debye type behaviour. The optimized optical, mechanical, dielectric, and electrical conductivity properties of 6S-MP film are due to its highest β phase content, better dispersion of SnO₂ nanoparticles and increased charge transport. Thus, the optimized film can be used for fabricating next generation flexible optoelectronic devices with enhanced charge-storage capabilities.

1. Introduction

With the rapid advancement of the Internet of Things, flexible polymer composites based on low-dimensional nanomaterials exhibiting superior energy storage and energy harvesting capabilities have garnered increasing interest for integration into wearable and flexible electronic systems. The development of lightweight, flexible, and easily synthesizable polymer-based composite films has received tremendous attention due to their unique combination of high mechanical strength, excellent flexibility, superior electrical breakdown strength, enhanced relative dielectric permittivity, and low dielectric loss [1–4]. Therefore, these materials are becoming increasingly essential for next-generation flexible nanoelectronics and storage devices.

Among various polymer composites, polyvinylidene fluoride (PVDF)-based composites have been extensively studied owing to their remarkable electroactive phases, desirable mechanical stability, and relatively high dielectric strength. Moreover, PVDF composites offer environmentally friendly processing methods and facile synthesis, further supporting their applicability in flexible electronic devices

[3–5].

Recent studies have reported significant improvements in energy storage density, energy conversion efficiency, sensitivity, and biocompatibility for PVDF-based composites, highlighting their potential for a broad spectrum of applications [4–7]. A variety of nanofillers have been incorporated into PVDF matrices to enhance their electrical and dielectric performance. The incorporated nanofillers can be classified into three main categories: inorganic, organic, and hybrid composites combining inorganic and organic nanofillers [8–10].

Incorporating inorganic nanofillers into the polymer matrix enhances the dielectric properties of PVDF while preserving the benefits of both components. However, the independent use of inorganic nanofillers, such as TiO₂, SnO₂, BaTiO₃, etc., often results in trade-offs, such as increased dielectric loss, reduced mechanical flexibility and crystallinity of the PVDF [10–12]. This is primarily attributed to the high nanofiller concentrations and the larger dielectric gradient. To address the limitations of inorganic nanofillers, organic/conductive nanofillers such as reduced graphene oxide (rGO), MXene, and multi-walled carbon nanotubes (MWCNTs) have been incorporated into polymer matrices

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Design and development of a high performance PVDF based flexible composite piezoelectric energy harvesting device for wearable electronics

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ABSTRACT

Dual nanofillers designed for polymer nanocomposites are expected to obtain excellent biomechanical energy harvesting performance by virtue of hybrid morphologies, charge transfer capability and interaction with surface charge. In this study, a dual nanofillers MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) nanosheets and tetragonal tin oxide (SnO_2) nanoparticles are incorporated into a PVDF matrix. At a fixed concentration of 2 wt% MXene and varying concentrations of SnO_2 nanoparticles (2 wt%, 4 wt%, 6 wt%, and 8 wt%), composite PVDF flexible films were fabricated using the solution-casting method. FTIR analysis identified an optimal composition of 2 wt% MXene and 6 wt% SnO_2 (6S-MP), which shows a maximum β phase content of 80% due to uniform distribution of the nanofillers as confirmed by the FESEM images. The 6S-MP flexible composite piezoelectric energy harvester (FCPEH) device generated maximum open circuit voltage (V_{oc}) of 65 V and a power density of $43.8 \mu\text{W}/\text{cm}^2$ under periodic palm tapping. The improved results of the device attributed to (a) the uniformly distributed MXene provides a large surface area for efficient charge transfer, (b) the SnO_2 nanoparticles act as nucleating agent to promote the α to β phase transition (c) the improved interfacial polarization due to synergistic effect of SnO_2 and MXene into PVDF Matrix. The FCPEH device maintained a stable average output voltage during 1000 seconds on periodic palm tapping, which indicate the robustness and stability of the device. The optimized 6S-MP FCPEH device was employed to (1) efficiently detect biomechanical motion such as heel movement, toe movement, bending, pinching and different finger tapping, (2) charge the 1 μF and 2.2 μF capacitor to 2.1 V and 1.3 V, respectively, within only 80 seconds, and (3) glowing the 11 LED Panel through periodic palm tapping. Thus, this work is significant step towards the development of efficient FCPEH device for high performance biomechanical energy harvesting towards self-powered wearable electronics.

1. Introduction

As smart technologies become increasingly integrated into everyday life, their dependence on batteries and electrochemical cells presents significant challenges. These conventional power sources often suffer from short lifespans, environmental hazards, high maintenance costs, and the constant need for recharging [1–3]. To overcome these limitations, developing self-powered devices has become crucial not only to reduce dependence on fossil fuels but also to minimise their environmental impact [4]. In this context, emerging technologies are being developed to efficiently harness, low-frequency, and disordered mechanical energy abundant in ambient environment for electrical energy generation [5].

In order to scavenge energy from ambient environmental and

biomechanical sources, particularly from body movement or tapping, triboelectric and piezoelectric energy harvesting devices have been thoroughly studied in recent years [1,6–8]. These devices are suitable for flexible, portable electronics that operate at low frequencies. Compared to other unconventional energy sources, triboelectric and piezoelectric energy-harvesting devices are relatively inexpensive [9]. However, triboelectric devices have several major drawbacks, including complex construction, poor stability, low durability, industrial-scale packaging challenges in humid environments. Also, their high output voltages that may damage electronic circuits or pose fire hazards especially in applications where only low power is required for general electronic circuitry [7–12].

In contrast, piezoelectric device offers advantages over triboelectric device in terms of easier integration into electronic devices, simpler

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