Fabrication and Characterization of Hybrid Nanogenerators for Harvesting Energy System Applications

PhD Thesis

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DEPARTMENT OF ELECTRICAL ENGINEERING

FACULTY OF ENGINEERING AND TECHNOLOGY

INTERNATIONAL ISLAMIC UNIVERSITY, ISLAMABAD

DEDICATED TO

My Parents, Teachers, and Husband

CERTIFICATE OF APPROVAL

Title of Thesis: "Fabrication and Characterization of Hybrid Nanogenerators for harvesting Energy Systems Applications"

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ABSTRACT

Self-powered devices are necessary for the growing demand of sustainable energy as well as for portable devices. Numerous techniques and several piezo materials compositions have been investigated for energy harvesting. However, the composition of Zinc Oxide (ZnO) with Polyvinylpyrrolidone (PVP) for Piezoelectric Nanogenerator (PENG) using electrospinning technique has not been investigated for energy harvesting, to-date. In this study, multi solutions of ZnO and PVP were made in Dimethylformamide (DMF), varying the weight of both compositions. The electrospinning technique was used to produce the composite fibers of the solution. The parameters (Voltage, Feed rate, Needle Range, Distance, Time) were optimized. The Taylor cone nano fibers with good form were selected and PENG device have been made. Fabricated Piezoelectric Nanogenerator (PENG) effectively created V_{OC} of ~40-50 V and I_{SC} of 400 nA, which is promising power for wearable electronics, biosensors, light-up LEDs, and low power Internet of Things (IoT) devices. Powering wearable and portable devices, triboelectric nanogenerator (TENG) are considerably one of the promising technologies. Optimum efficiency and high output are always key concerns. This research addresses the ongoing challenge of raising efficient, flexible, and lightweight energy harvesting systems for recent wearable technologies. A triboelectric nanogenerator is proposed for harvesting the triboelectric effect. Using Polyurethane (PU), a bendable TENG that is in vertical contact-separation mode was developed. UV-curable PU forms the basis of TENGs. A sponge, repurposed from landfill waste, acts as a spacer to maintain a consistent air gap between the tribo-layers for enhanced triboelectrification. The triboelectric nanogenerators produced an open-circuit voltage approaching 500 V current of ~ 2 µA and also shows high performance with a power density of 8.53W/m^2. Proposed TENG provides a capable solution for sustainable, self-powered wearable electronics and has the potential for more development in energy-efficient and eco-friendly applications. To effectively combine a high output current of PENG and a high voltage of TENG, these two NGs are stacked upon each other, and separated by sponge spacers providing uniform air gap for triboelectric effect. This thesis aims to propose a hybrid type NG harvesting both piezoelectric and triboelectric effect at the same time. In the proposed hybrid NG, the piezoelectric NG (PENG) are fabricated by piezo type nanofibers and the triboelectric NG (TENG) are fabricated by self-healing polyurethane (PU). It also opens a potential route towards practical applications for powering electronic devices. Hybrid Nanogenerator has the potential to control small electronic devices powerfully with an impressive output of 650 volts and a current range of 3.5 to 4 µA. To analyse the functional and structural properties of materials used, characterization techniques such as SEM, Electrospinning and XRD were employed. This hybrid approach not only improves energy conversion efficiency but also ensures durability, mechanical flexibility and making it suitable for applications in self-powered sensors, wearable electronics, environmental monitoring systems and biomedical devices.

List of Publications and Submissions

[1]. Saba Ejaz, Imran Shah, Shahid Aziz, Gul Hassan, Ahmed Shuja, Muhammad Asif Khan and Dong-Won Jung. 2025 "Fabrication and Characterization of a Flexible Polyurethane-Based Triboelectric Nanogenerator for a Harvesting Energy System" in *MDPI Journal of Micromachines*, 16(2), 230; https://doi.org/10.3390/mi16020230 ***(Published)***.

[2]. Saba Ejaz, Gul Hassan, Ahmed Shuja. 2025 "Fabrication and Characterization of Piezoelectric Nanogenerator Based on ZnO and PVP for Harvesting Energy System Applications", in *Journal of Materials Science: Materials in Electronics* ***(Published)***.

[3]. Saba Ejaz, Muhammad Aamir, Muhammad Asif Khan and Babar Ashfaq. 2018 "Modeling and analysis of CPEC energy power projects using LEAP model" in International Conference on Computing, Mathematics and Engineering Technologies (iCoMET), DOI:10.1109/ICOMET.2018.8346410 ***(Published)***.

This thesis covers research work based on publications mentioned from 1 and 2.

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(Engr. Saba Ejaz)

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List of Abbreviations

AR-TENG	Adaptive rotating triboelectric nanogenerator
Al	Aluminium
ALD	Atomic Layer Depositions
BTO	Barium titanate
BCHNG	Bifilar-pendulum coupled hybrid nanogenerator
BPEH	Bio-piezoelectric energy harvesters
BP	British Petroleum
CU	Copper
DIL	Direct image lithography
EDL	Electric double layer
ES	Electrospinning
EMG	Electromagnetic generator
EC/TPU	Ethyl cellulose/thermoplastic polyurethane
FTO	Fluorine Tin Oxide
F-PU	Fluorinated polyurethane
FTL	Freestanding triboelectric layer
AuNPs	Gold nanoparticles
HNG	Hybrid Nanogenerator
IoT	Internet of Things
LED	Light-Emitting Diode
NGs	Nanogenerators
$ZnSnO_3$	Perovskite zinc stannite
PENG	Piezoelectric Nanogenerator
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PMMA	Poly Methyl Methacrylate
PVP	Polyvinylpyrrolidone
PU	Polyurethane
PTFE	Poly Tetra Fluor ethylene

PVDF	Polyvinylidene fluoride
PVDF–TrFE	Poly(vinylidene fluoride–trifluoroethylene)
PNG	Pyroelectric Nanogenerator
SEM	Scanning Electron Microscopy
ST-PSCs	Semi-transparent polymer solar cells
SCs	Solar cells
SCs	Supercapacitors
TiO_2	Titanium dioxide
ThEG	Thermoelectric generator
TENG	Triboelectric Nanogenerator
XRD	X-Ray Diffraction
ZnO	Zinc Oxide
ZnO NRs	Zinc oxide nanorods

Chapter 1

INTRODUCTION

In an era where the global demand for clean, sustainable, and portable energy is escalating rapidly, there is an urgent need to develop innovative technologies that can convert ambient mechanical energy into usable electrical power. Hybrid nanogenerators have emerged as a promising solution to this challenge, offering the advantage of combining multiple energy harvesting mechanisms—typically piezoelectric and triboelectric effects—into a single, compact device. These mechanisms work synergistically to enhance the energy conversion efficiency, making HNGs particularly suitable for powering low-energy electronic systems. Understanding the fabrication techniques, material selection, and structural design is crucial to optimizing the performance of these devices. Additionally, detailed characterization using tools such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and Electrospinning (ES) provides deep insights into the morphology, crystallinity, and chemical bonding of the materials involved, which directly influence the output behaviour of the nanogenerator. By delving into this foundational knowledge, researchers and engineers can better comprehend how to tailor nanostructures and device architectures to meet the specific requirements of applications such as wearable electronics, biomedical implants, remote sensing, and environmental monitoring. Ultimately, this introduction lays the groundwork for understanding how hybrid nanogenerators can play a transformative role in developing next-generation, self-powered energy systems.

1.1. Motivation

Most steady essential of present and future time is energy and key requirement in almost everything, i.e. in cell phones, laptops, sensors, transmission and receiving devices and many other daily life usable things [2]. The process of development is grooming faster and faster, as well as the population are increasing rapidly, so, the demand of energy is also increasing and tend to domineering consumption of fossil fuels, which are indirectly decreasing the fuel reserving. As industries and other developing are taking place which are causing global warming which is indirectly effective to the reserved sources. Extending the reserved energy to overcome the energy deficiencies and crises led to think about other solutions [3].

The speedy development in portable electronics devices, sensors network and wireless communication system are the mature interests in the current period [4]. As the size of electronic devices are decreasing aggressively and the requirement to have a stable source of power in regard to that size are major concern. Decreasing or shrinking the size of formal batteries lead to compromise in life time, and long lifetime source for powering them are the essential requirements [5]. So, the formal battery installation is not a suitable solution because of the lifetime and replacement issue in portable electronics devices and sensors network, especially in wireless systems. The focus of present era nanotechnology and Nano electronics researchers are to make electronic devices and sensors network system self-powered [6] i.e. capabilities to produce the required electrical energy themselves for performing all their functionalities.

Renewable energy resources are the most abundant and most probably free available resources i.e. solar sun, wind wave, sea wave, biomass and many other [7]. Utilization of these renewable energy resource are the major concern of researchers and scientists. One of the abundant and most reliable renewable energy resources are the ambient mechanical energy [8], the keen interest and a new approach for researcher and scientists to utilize theses free sources in a positive way for electrical power generation, leading toward the research in sustainable and renewable energy sources and are taking aggressive interest in nano-energy research. According to BP Energy Outlook 2018, renewable energy is the fastest growing source and makes up 40% of the total energy growth are shown in Figure 1.1 [9].

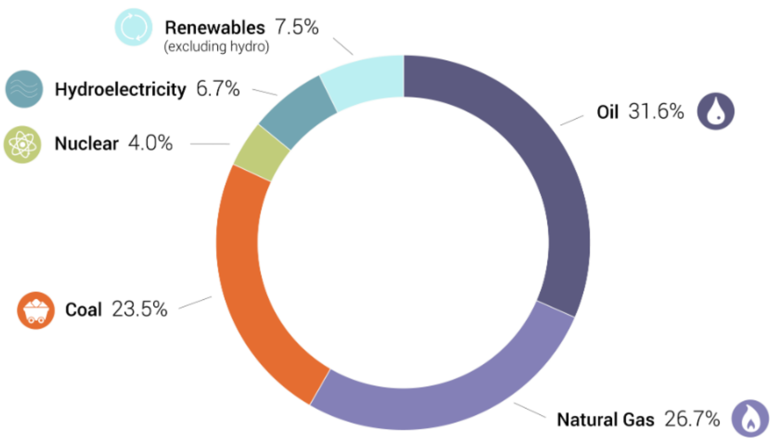

Figure 1.1: Global Energy consumption by fuel type (2022) [2]

1.2. Nanotechnology

The concept of nanoscience and nanotechnology were developed with the talk entitle "There's plenty of room in the bottom" by one of well-known American physicist Richard Feynman in December 1959 at California institute of technology (CIT). Richard Feynman declared the process by which scientist would able to utilize and characterize single atoms and molecules. In 1981, progress of Scanning electron microscopy (SEM) strengthens the concept of modern nanotechnology. So, Nano-technology is detail training and utilization of very tiny stuffs in different field of sciences i.e. in physics, chemistry, bioscience, material science and engineering [10].

1.3. Nano-energy Research

Nano-energy researches are the booming research field. Which are focusing and targeting to generate electric power by utilizing the surrounding ambient energy [2]. Among which the ambient mechanical and thermal energies are included. The focus of Nano-energy research is to improve maintainable Electrical control generation sources, that can be use energies then make portable electronic and sensors network system self-powered [11].

The present and future research are targeting to combine multi-functional Nano devices and developed Nano-systems for the purpose to operate like a living organism which have capabilities of sensing, communicating, controlling and performing multitasks [12]. So, it is obvious that for such Nano-system a Nano power source is required and the size of formal battery storage is high comparable to Nano-system, shrinking the size need to compromise on life time of battery which is highly inacceptable in wireless application and many other application-like biomedical sensors network system etc. The need of self-powered system is highly keen requirement of biomedical applications, which are impossible with formal battery sources because of life time and replacement issues [13] [14].

To overcome such issues and provide an alternate solution for such systems to be self-powered the nanotechnology and Nano-energy researchers are moving toward Nanogenerators. Nanogenerators (NGs) have been recently developed electricity generating devices, and are considered a great achievement in renewable and Nano-energy research and highly preferable solution for self-powered electronics [2].

1.4. Nanogenerators

Nanogenerators (NGs) are electronic devices or system, which have capabilities of generating electrical power from ambient mechanical or thermal energies. The concept of nanogenerators was developed in 2006 by one of famous researcher and scientist Zhang Lin Wang and J. Song [15]. Summarize basic and general concept of nanogenerators are shown in Figure 1.2.

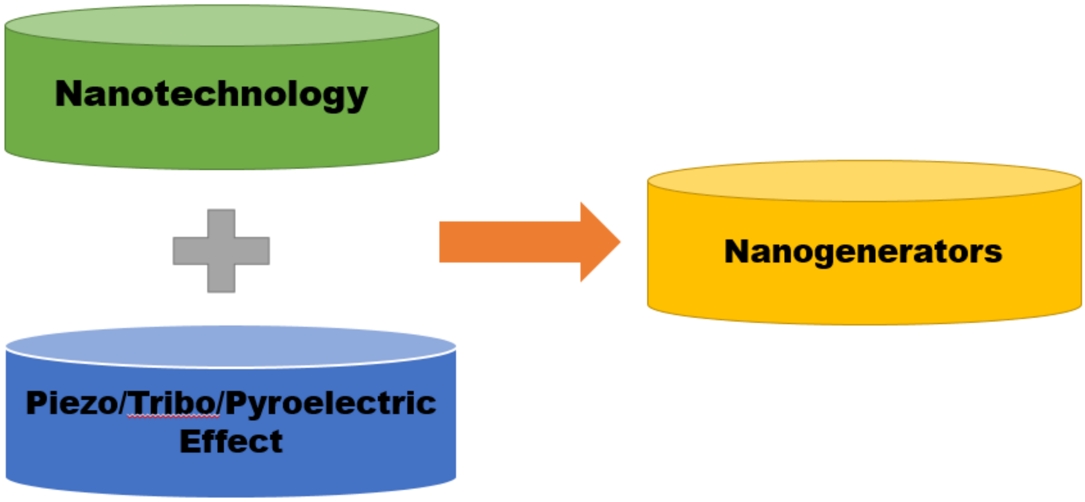

Figure 1.2: General basic concept of nanogenerators

Here are mainly three kinds of nanogenerators, a) Piezoelectric Nanogenerator (PENG), b) Pyroelectric Nanogenerator (PNG), c) Triboelectric Nanogenerator (TENG).

1.4.1. Piezoelectric Nanogenerator

Piezoelectric nanogenerators or in short PENGs are the first one developed nanogenerators, which are based on piezoelectric effect with combine properties of semiconductors and nanotechnology. PENGs are devices that generate electricity by turning small and uneven mechanical energy, like pressure or force, into electrical power [16]. The basic schematic illusion of PENG is shown in Figure 1.3 [4].

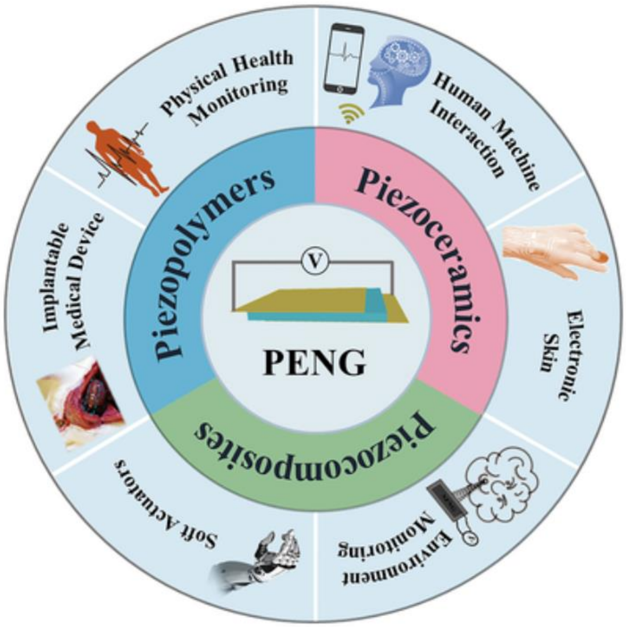

Figure 1.3: Figure show PENG applications and types of piezoelectric materials.

1.4.1.1.Piezoelectric effect

Piezoelectric materials, which can covert powered energy i.e. machine strain into electrical energy [17]. Basic phenomena of piezoelectric effect are shown in Figure 1.4. Working mechanism is simple, due to apply force/stress the crystal structure of material disturbed, and random orientation of polarized dipoles are changed. As the dipole are no more randomized and now crystal have equal charge distribution on both faces as shown in Figure 1.4b and create electrical potential as a result, which is drawn through electrodes. Piezoelectric effect occurs in piezo materials in different way by applying stress or voltage, these all produce piezoelectric phenomena depend upon the structure and releasing stress. Like bending, stretching, shrinking, pressing, or applying external geometry of concern piezoelectric nanogenerators.

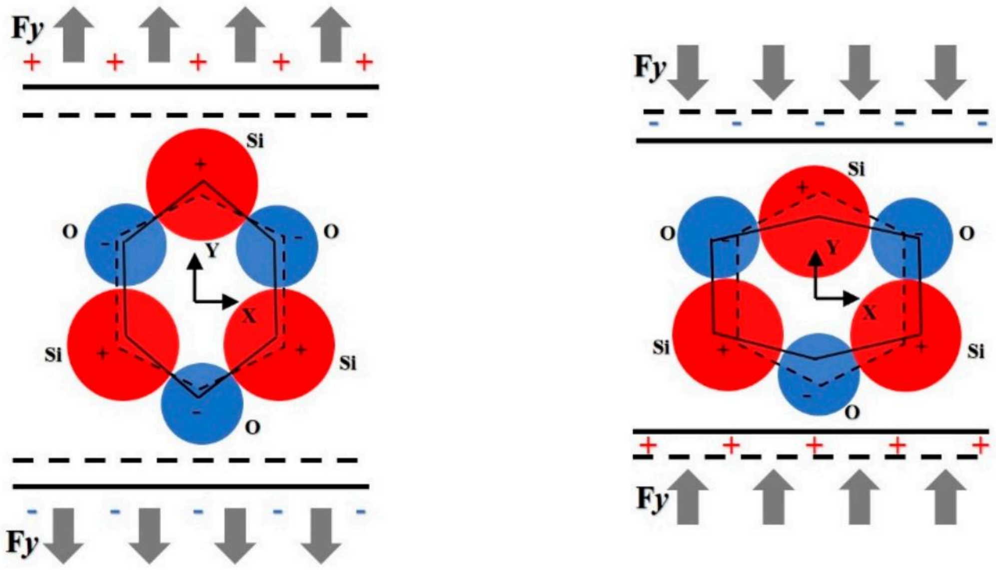

Figure 1.4: Schematic diagram illustrating the piezoelectric effect.

1.4.2. Triboelectric Nanogenerators

Triboelectric nanogenerators or in short TENGs are a type of electric power generator based on combine principal of electrostatic induction and triboelectric effect [18].

1.4.2.1. Triboelectric Effect and Electrostatic Induction

In everyday life we most probably face triboelectric effect whenever double unlike resources encounter each other. In general perspective triboelectric effect are considered negative effect in industries because the electrostatic charges produced in it can become a source of turmoil, breakdown phenomena in dielectrics and damages of device etc. But thinking in energy point of view the electrostatic charge produces by triboelectric effect create capacitive storage device on separation of triboelectric surfaces [18], which became the source of electrostatic generator like Van De Graaff generator and Friction Machine [19]. So, utilizing the coupling effects of triboelectric effect and. electrostatic induction, Wang group developed first triboelectric nanogenerator in 2012 to yield ambient powered energy [20]. Schematic then theoretical equalling modal of TENG is shown in Figure 1.5.

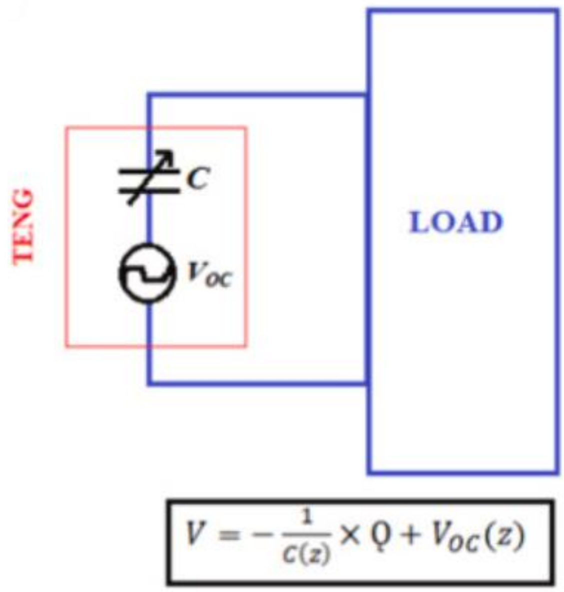

Figure 1.5: Design of TENG's equivalent electrical circuit model

TENG have basically four type of operating/working modes. Which include free-standing mode, single electrode mode, linear sliding mode and contact separation mode. The basic requirements for these all modes are two different triboelectric materials required with connection of proper electrodes, as well as proper insulation layer between them. For these all modes the basic principle is same which are whenever there is displacement accrued in any tribo layers, the electrostatic status disturbed due to electrostatic charge movements and thus electrostatic potential create between two electrodes. So, continuing to the mechanical push and relaxing process, both negative and positive peaks are produced and so we get AC signals from our concern TENG device.

1.4.2.2. Contact Separation mode

This mode of TENG is very simple, it can be between dielectric- dielectric layers or dielectric- metal layer, the schematic is shown in Figure 1.6a. This mode of operation has advantages because of simple erection and easy manufacture procedure. That mode has capability by combining stack of layers.

1.4.2.3. Linear sliding mode

As shown in Figure 1.6b, in this mode of operation one layer of TENG is slide over other and so charge generate. This mode of operation is favourable in comparison to contact separation mode because of the issue of displacement to maintain but have advantages is in this mode more charge density can be produced due to high area of contact.

1.4.2.4. Single electrode mode

This mode of working is very simple in comparison due sliding and contact separation mode but produce very low output comparatively. It consists of single electrode, meanwhile charges are driven to external load using single electrode, the basic schematic is illustrated in Figure 1.6c.

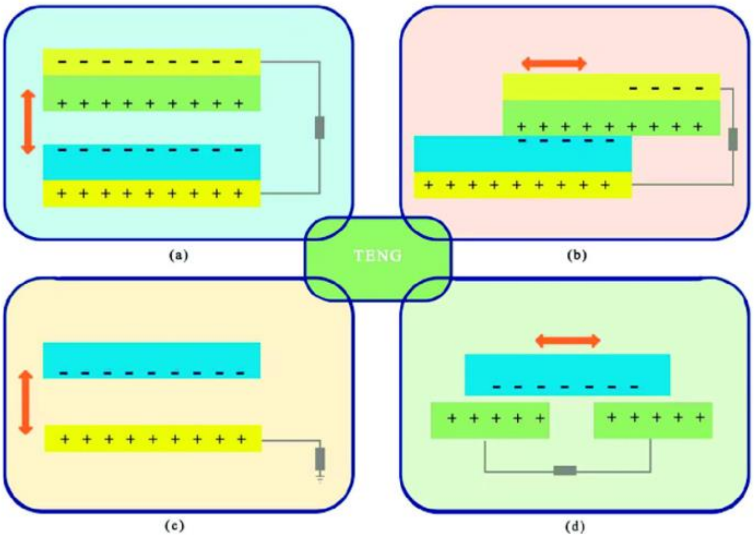

Figure 1.6: Four working modes of TENG: (a) vertical contact separation (b) horizontal sliding (c) single electrode and (d) independent layer mode.

1.4.2.5. Free Standing Mode

This mode of operation has high efficiency comparatively the basic mechanism is illustrated in Figure 1.6d, in this mode the electrodes or triboelectric layer without electrode are free to move over the static triboelectric with electrodes layers. The fabrication of such device is easy and are considering good for real time application.

1.4.3. Pyroelectric Nanogenerators

Pyroelectric nanogenerator (PNG) are power generators which have capabilities to utilize the ambient current energy and transform it to electrical energy. The PNGs are based on pyroelectric effect [21].

1.4.3.1. Pyroelectric Effect

The pyroelectric effect happens in certain materials when their temperature changes over time, causing sudden polarization. This effect is usually seen in materials that don't have the same properties in all directions. Uneven heating creates stress, which can lead to polarization through the piezoelectric effect [2]. Such as, temperature rises the impulsive polarization of pyroelectric material drops and decreasing in temperature increases the spontaneous polarization. So, using cycling temperature (increase and decrease) produce alternating current which are collected through electrodes. Basic mechanism of pyroelectric generator is shown in Figure 1.7 [22].

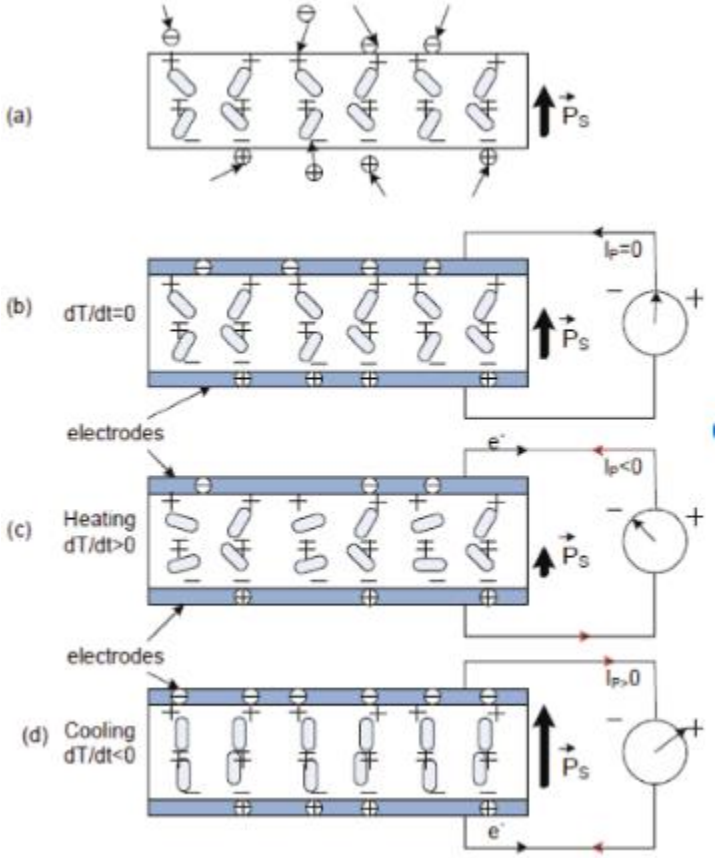

Figure 1.7: Diagram of pyroelectric film: (a) impulsive polarity, (b) constant temperature, (c) warming, (d) freezing [17]

1.4.4. Tendency Toward Hybrid Nanogenerators

TENGs are high voltage generator but low current producer in comparison to PENGs. And PENGs are high current generators [2]. So as high efficiency and high-power generation is the key requirement and demand from every power generating devices or systems. So, to achieve high power, Researchers are working in improving the structure and synthesizing material for best results. The tendency toward hybrid NGs are emerging research field these days. Hybrid NGs are more efficient and high-power generating device than single alone type of nanogenerators (i.e., PENG, TENG).

1.4.5. Hybrid Nanogenerators

Hybrid nanogenerators are hybrid structure nanogenerators by combining both PENG and TENG phenomena in single device. The working mechanism are simple and straight forward. The hybrid nanogenerators are structured that both piezoelectric effect and triboelectric effect occur at a same time and generate high power with comparison to single type NGs. Hassan, Khan, A. Hassan et al., [23] developed a hybrid nanogenerator that is flat panel type it reported that at 1MΩ load it produce power density of 10.41 mW/cm^2. The schematic of developed hybrid nanogenerators are shown in Figure 1.8.

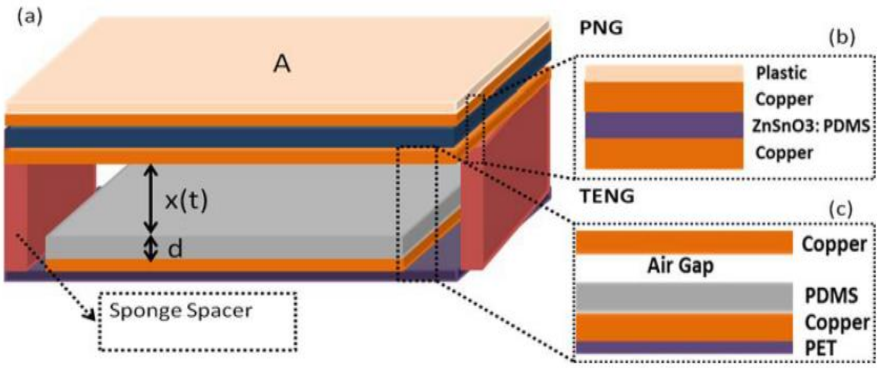

Figure 1.8: Schematic of flat type hybrid NG [23].

Nanogenerators are the efficient solution for portable electronics and consider best suitable solution for self-powered devices and sensor networks, especially in systems, where it is difficult to replace the commercial batteries and are consider disposable after the batter life time. The nanogenerators are cost efficient and have simple structure to design and fabricate. So, my current research works are to focus on developing hybrid nanogenerators for harvesting energy systems that can be used for different application purposes.

1.5. Thesis Goals

This thesis covers the problem statement of this project, as well as explain the objectives of this research project. Apart of that this thesis also describe the significant of the obtained results and impact of the project in nano-energy.

1.5.1. Problem Statement

A viable power source to come across the needs of energy necessity is very much needed in modern world as the conventional sources are draining. The new technologically advanced Nanogenerators (Hybrid) offer a tremendous approach to convert mechanical energy into electricity. Hybrid Nanogenerators based on nano materials are the nascent technology that assist self-powered systems, smart sensors, and flexible and portable electronics in the growing era of IoT (Internet of Things). The development of Nanogenerators is a revolution in the arena of ambient energy-harvesting technology as they are light-weight, easily to fabricated, viable and care-free systems.

Recently, many researchers are paying attention to Nanogenerators (NGs) as energy source in self-powered micro-nano system, and studying how to achieve their higher power generation. Hence, Hybrid nanogenerator was proposed for harvesting both piezoelectric and triboelectric effect at the same time. To effectively combine a high output current of PNG and a high voltage of TENG, these two NGs are stacked upon each other, and separated by sponge spacers providing uniform air gap for triboelectric effect. Especially, this manufactured structure has a low young's modulus for piezoelectricity. In the proposed hybrid NG, the piezoelectric NG (PNG) are fabricated by piezo type nanofibers and the triboelectric NG (TENG) are fabricated by self-healing polyurethane (PU). It also opens a potential route towards practical applications for powering electronic devices.

1.5.2. Objectives of Research

The primary aim of this research is to explore and develop an efficient hybrid nanogenerator system capable of harvesting sustainable energy for practical applications. To achieve this aim, the study is designed with the following specific objectives:

- To develop a hybrid nano-generator that will harvest many forms of energy vibrational energy, human body motion, mechanical triggering of tire rotation.
- A comprehensive review on the state-of-the-art of hybrid Nano-generators in which the triboelectric Nano generator (TENG) and piezoelectric Nano generator (PENG) are two recently developed technologies that are used for effective harvesting of ambient mechanical energy for the creation of self-powered systems. The advantages of TENGs and PENGs which include large open-circuit output voltage,

low cost, ease of fabrication, and high conversion efficiency enable their application as new flexible sensors, wearable devices, soft robotics, and machines. This perspective provides an overview of the current state of the art in triboelectric and piezoelectric devices that are used as self-powered sensors and energy harvesters for soft robots and machines; hybrid approaches that combine the advantages of both mechanisms are also discussed.

- A development of hybrid Nano-generator would develop that have aim to combine several diverse nanogenerators into a single unit, which can utilize numerous energy sources individually or simultaneously, enabling the use of any available ambient forms of energy at any time
- Different characterization and fabrication technique would be used to investigate the electrical and other characteristics and properties of the proposed nano-generator efficiently.
- All the experimental and characterization data will be manipulated and a detail written report will be prepared for the concern research work and millstones achieved.

1.5.3. Significance of Research

Energy harvesting has emerged as one of the fastest advancing technologies, entering a stage where hybrid and multi-source systems are becoming the focus of research and development. In this era, innovative material designs and integrated structures are enhancing energy conversion efficiency while allowing devices to utilize multiple sources of energy at the same time. The field encompasses the transformation of various ambient energies—such as solar and optical radiation, mechanical vibrations and motion, wind and fluid flow, magnetic fields, and thermal gradients—into usable electrical power. These conversions are achieved through diverse mechanisms, including photovoltaic, piezoelectric, electromagnetic, electrostatic, triboelectric, magnetostrictive, thermoelectric, and pyroelectric effects.

Hybrid nanogenerators are particularly attractive because they combine different harvesting principles into a single platform, enabling the capture of energy from more than one source either concurrently or selectively, depending on environmental availability. This flexibility ensures that the device can operate continuously by switching to whatever energy form is present at a given moment. Consequently, hybrid systems not only contribute to the efficient utilization of renewable energy but also help achieve stable and reliable electrical outputs. Such advancements are paving the way for sustainable, self-powered technologies that can support a wide range of modern applications.

1.6. Summary

"This chapter presents a comprehensive overview of the motivation and foundational aspects of the research on hybrid nanogenerators for energy harvesting applications. With the rapid depletion of conventional energy sources and the increasing demand for sustainable and self-powered micro/nano devices, the development of alternative energy solutions has become imperative. Hybrid nanogenerators, which combine piezoelectric and triboelectric mechanisms, offer a promising route to convert mechanical energy from ambient sources into usable electrical power efficiently.

The motivation behind this study lies in addressing the limitations of individual energy harvesting technologies by integrating them into a single, more effective hybrid system. Materials such as zinc oxide (ZnO), polyvinylpyrrolidone (PVP), and polyurethane have been selected for their superior piezoelectric and triboelectric properties. The fabrication process and material selection aim to enhance energy output, durability, and cost-effectiveness. The primary goal of this thesis is to fabricate and optimize a hybrid nanogenerator capable of efficiently harvesting mechanical energy and evaluate its performance through detailed material and device-level characterization. The objectives include designing the device architecture, selecting suitable materials, optimizing fabrication parameters, and analyzing output performance under various conditions.

The significance of this research lies in its potential to contribute to the development of next-generation energy harvesting systems for wearable electronics, remote sensing devices, and other low-power applications. This work lays the foundation for scalable and eco-friendly solutions in the field of energy sustainability and smart device integration."

1.7. Outline of Thesis

The flow of the thesis as under:

CHAPTER 1: This chapter of thesis include the motivation, Nano-energy research, thesis goal, problem statement and significance of the project.

CHAPTER 2: Briefly explain the thoughts and theories behind Hybrid Nanogenerators.

CHAPTER 3: Describe and present the current literature survey of nanogenerators and applications.

CHAPTER 4: Explain the experimental techniques used during fabrication and characterization throughout this research.

CHAPTER 5: Describe the material characteristics and device process during fabrication.

CHAPTER 6: Comprise the Results and discussion of overall fabricated hybrid NG.

CHAPTER 7: This chapter of the thesis include the conclusion of this project as well as suggestion and ideas for improvement for future work.

Chapter 2

BACKGROUND THEORY

2.1. Origin of Nanogenerators

Nanogenerators (NGs) use piezoelectricity, triboelectricity, and pyroelectricity. Initially, an atomic force microscope tip triggered a single ZnO nanowire in the nano-generator, transforming microscopic mechanical energy into electric power. With better physics knowledge and development, NGs are now called a field that uses displacement current to transform mechanical energy into electric power/signal, regardless of nanomaterials. The concepts and theories to understand nanogenerators, it is essential to understand Maxwell's equations for electromagnetics. The piezoelectric Nanogenerator (the first Nanogenerator) was developed in 2006, which was based on piezoelectric effect [15]. In PENG the piezoelectric materials are became polarized when mechanical stress is applied to that materials and thus produces piezo potential for PENG. In 2012, Triboelectric Nanogenerator (TENG) was initially suggested, which based on combine effect of electrostatic induction and triboelectric effect [20]. In TENG electrostatic charges are produced on the surface of materials, when two materials having changed electron attractions are led into contact. Then on separation of these two-material voltage are developed which compel the electron to flow toward electrodes and thus AC current produces for TENG. For better understanding the variance among nanogenerators and electromagnetic generators, consider the following equation to declare the basic concepts and relation between the results of nanogenerators and Maxwell's displacement current [4], [5].

$$\nabla \times H = J + \frac{\partial D}{\partial t} \qquad (2.1)$$

In equation (2.1), displacement field is D and magnetic field is H, where D is

$$D = \varepsilon_o E + P \qquad (2.2)$$

In equation (2.2), P represent the polarization field and E represent Electric field. So, using equation (2.3), The Maxwell's displacement current JD can be written as given in equation (2.3) below.

$$J_D = \varepsilon \frac{\partial E}{\partial t} + \frac{\partial P_s}{\partial t} \quad (2.3)$$

So, in this above equation (2.3), the $\frac{\partial P}{\partial t}$ represents the output of nanogenerators and $\varepsilon \frac{\partial E}{\partial t}$ represents the generation of Electromagnetic wave. In the occurrence of no peripheral electric field, if the charges density on surface of PENG is represented by σP, then the displacement current can be represented as shown in equation (2.4) [24].

$$\frac{\partial D}{\partial t} = \frac{\partial p}{\partial t} = \frac{\partial \sigma_p}{\partial t} \quad (2.4)$$

Equation (2.4) is the mathematical modelling equation of output current for PENG. Similarly, the displacement current equation of TENG can be denoted as given below [24].

$$\frac{\partial D}{\partial t} = \sigma_c \frac{\partial x}{\partial t} = \frac{\partial \sigma_1(z,t)}{\partial t} \quad (2.5)$$

For better understanding of Theoretical concepts, Schematic of hybrid PENG-TENG are shown in Figure 2.1, which include and present all necessary parameters required to model a nanogenerator.

In equation (2.5), $\partial x/\partial t$ is the representation the speed at which both layers, TENG and Electrode 2 contact with each other. The first theoretical modelling of hybrid nanogenerator (PENG-TENG) was presented in 2017 by Song, Gao, Tao et al., [25] and onward it was extended to analytical approach by declaring three main conditions. a) TENG and PENG are not combined a single unit, but they are single units, b) Charges are consistently spread on TENG layer, and c) The Electric potential is the resultant of closed loop in the circuit. So, keeping above three conditions and Figure 2.1, we can conclude that,

$$V_a + V_T + V_1(t) = 0 \; and \; V_P + V_2(t) = 0 \quad (2.6)$$

In equation (2.6), V_a, V_T, V_P represent voltage across air gap, TENG and PENG layers. And V_1 and V_2 are the external load voltages as shown in Figure 2.1.

2.1.1. Introduction to Hybrid Nanogenerators

Hybrid nanogenerators are innovative energy harvesting devices that integrate multiple energy conversion mechanisms to increase performance as well as widen potential of application. These systems synergistically combine piezoelectric and triboelectric effects, enabling efficient transformation of mechanical into electrical energy. The hybrid configuration leverages the unique strengths of each mechanism to overcome individual limitations, making them perfect for self-powered systems, IoT applications and wearable electronics.

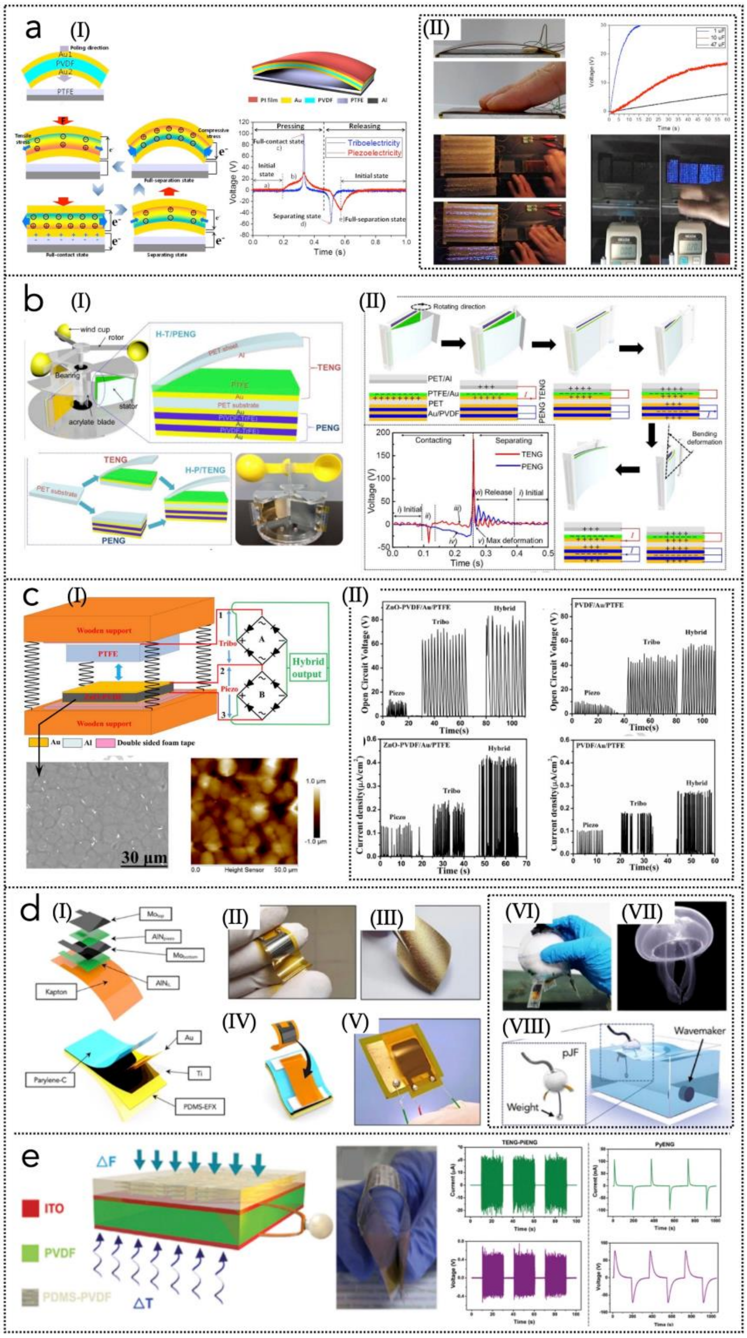

Figure 2.1: (a) High-output HBNG using PVDF/PTFE (b) HBNG for stable rotational energy harvesting (c) Flexible ZnO–PVDF/PTFE HBNG; ZnO boosts piezo & tribo effects (d) AlN–PDMS/parylene HBNG for wave energy; pJF with 3 units scavenging buoy energy (e) Piezo–Tribo–Pyro HBNG for combined mechanical & thermal energy harvesting [26]

Hybrid energy generators integrate diverse energy exchange methods to optimize output performance, which has enormous application potential. Energy complementation involves gathering mechanical energy using various methods, combining it with additional hygienic energy harvesters, and turning mechanical energy or other energy sources into hydrogen energy [27]. By taking part more transducing mechanisms in a single combined microsystem, hybridization can improve device performance. The potential results of signal augmentation in addition immediate flexibility to varied working situations have sparked study attention [26].

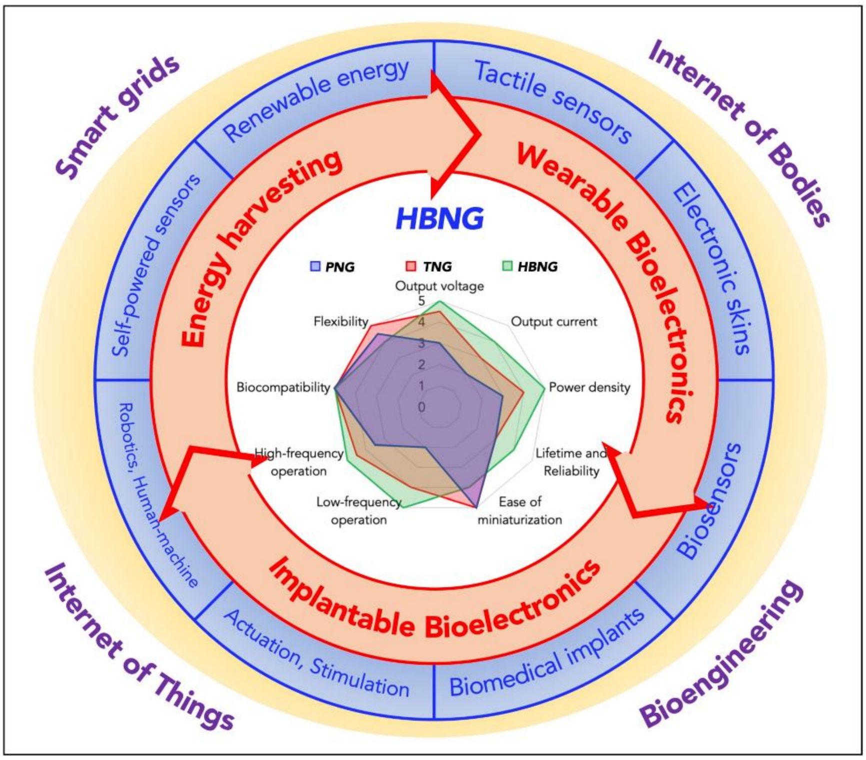

Figure 2.2: Illustration of HBNG applications**.** Central radar chart compares PNGs**,** TNGs, and HBNGs on: Flexibility**,** Voltage**,** Current**,** Power Density**,** Lifetime/Reliability**,** Miniaturization**,** Low-/High-Frequency Response**,** Biocompatibility [26].

2.2. Piezoelectric Nanogenerators (PENGs)

2.2.1. Principle of Piezoelectricity

In 1880, Pierre and Jacques Curie developed piezoelectricity. They observed in what way force affects quartz and tourmaline electrical charge production. They found that mechanical stress on these crystals generates electricity, also these electric charges have voltage that is proportionate to pressure. Gabriel Lippmann demonstrated the theory's mathematics in 1881. Inverse piezoelectric and Piezoelectric properties come after the Greek term "piezein," meaning pushing otherwise enfolding. During WWI, first use of piezoelectric ultrasonic transducers occurred. Today, they constantly employ piezoelectricity. An electrical signal comes from vehicle's airbag sensor provides to detect acceleration changes and activate the airbag [28].

When subjected to mechanical stress, Piezoelectricity is the generation of electrical charge in certain resources. This conclusion rises from the alignment of dipoles contained by the material, leading to a net polarization and subsequent charge generation on the material's surface. The fundamental relation governing piezoelectricity is:

where:

- ✓ Electric displacement vector
- ✓ Permittivity of the material
- ✓ Electric field
- ✓ Piezoelectric coefficient
- ✓ Applied mechanical stress

Piezoelectric nanogenerators (PENG) turn environmental and biomechanical energy into electricity. They are a promising substitute to rechargeable batteries for powering low-energy moveable electronics. Piezoelectric materials became necessary as PENGs gained popularity in robots, wearables, medical equipment, and other industries. This analysis covers elementary material, structure, characteristics, also preparation approaches of barium titanate, a key PENG, and its recent advancement, and development in the direction of high energy generation[28].

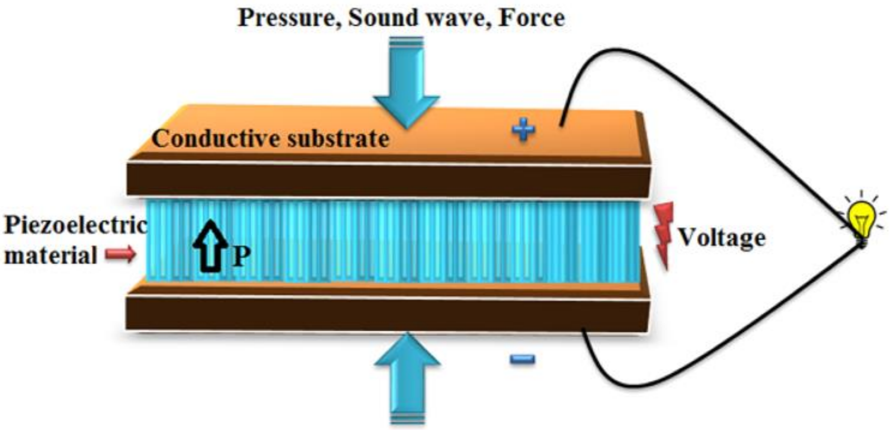

Figure 2.3: Working principle of Piezoelectric Energy Harvesting Nanogenerators (PENG); polarization (P) conditions and directions[28]

2.2.2. ZnO and PVP-Based Piezoelectric Nanogenerators

In piezoelectric nanogenerators the material usually used in it is Zinc oxide (ZnO) because of high mechanical flexibility, its outstanding piezoelectric properties, as well as ease of synthesis. Piezoelectric ZnO has a 3.37 eV band gap semiconductor. Biocompatible and nontoxic, it is highly transparent to visible light. It can be found in cubic (rock salt), hexagonal (wurtzite), and cubic (zinc blende) structures. With the Zn^{2+} cation surrounded by four O^{2-} anions, the hexagonal structure is the utmost predominant, and vice versa [29].

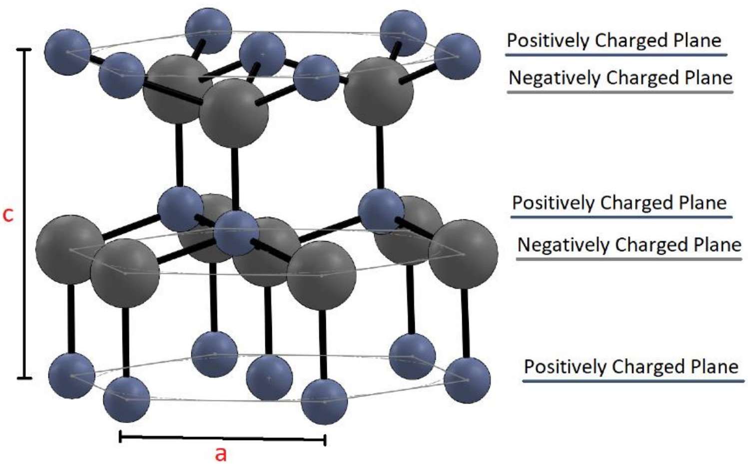

Figure 2.4: With Zinc in blue and Oxygen in grey ZnO hexagonal crystal structure is shown and lattice factors a and c are also shown[29].

When combined with Polyvinylpyrrolidone (PVP), ZnO forms a composite matrix that enhances the mechanical stability and process ability of the nanogenerator. Key characteristics include:

- **ZnO Nanostructures**: Nanowires, nanorods, or thin films provide high surface area and improved piezoelectric response.
- **PVP as a Binder**: Enhances material flexibility and ensures uniform distribution of ZnO particles.

The worldwide energy problem and environmental pollution caused by non-renewable energy usage motivated researchers to seek alternative energy devices that gather ambient energy. The most common ambient energy that can convert into electricity is mechanical energy. The most common mechanical energy harvesting procedure is Piezoelectric transduction because of its high electromechanical coupler factor and piezoelectric aspect. Thus, scientists are highly interested in piezoelectric energy harvesting [30].

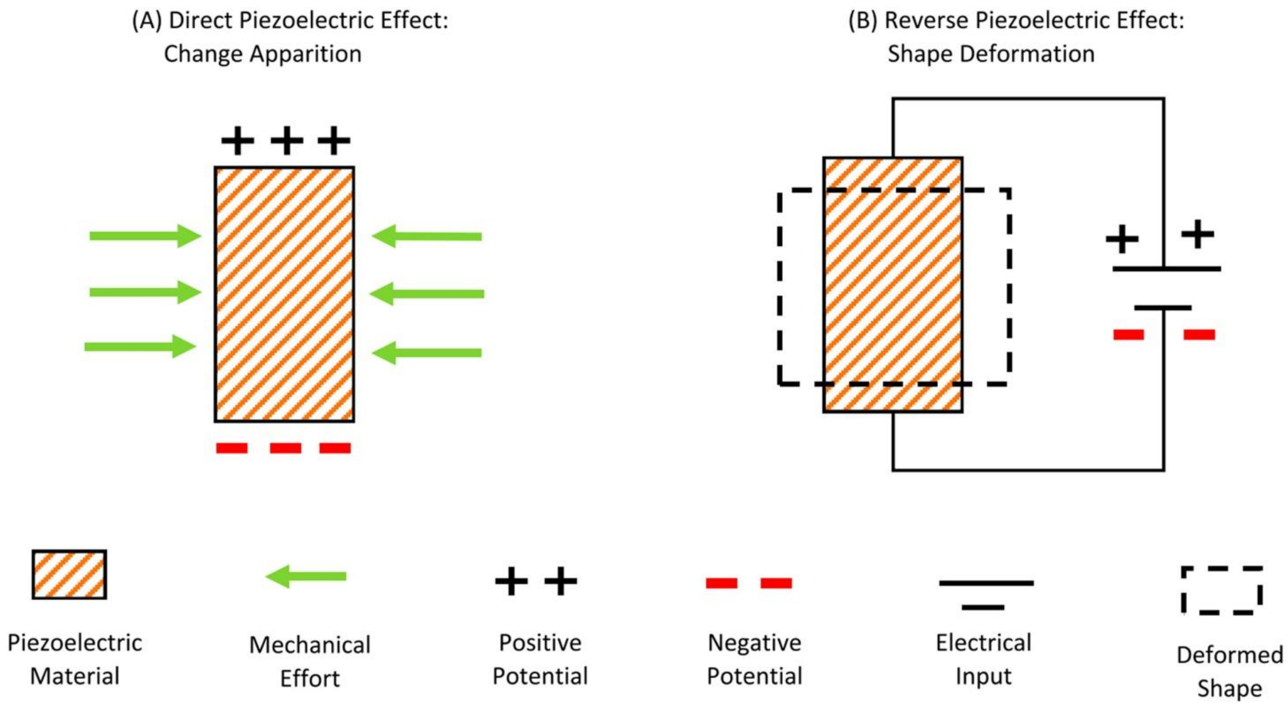

Figure 2.5: Electromechanical conversion of piezoelectric phenomena[30]

By capturing mechanical energy from the environment, nanofiber-based piezoelectric energy generators could power mountable electrical devices and systems. The main focus is on piezoelectric nanogenerators made from PVDF or PZT, which are created using electrospinning methods. By means of XRD, FTIR, SHG, PFM, and Raman spectroscopy it also describe mechanical and material analyses on made-up nanofibers to illustrate piezoelectric nanofibers [31].

Under applied mechanical pressure, leading to the generation of electrical potential The working mechanism involves the deformation of ZnO structures. This potential is harvested through electrodes attached to the composite.

2.3. Triboelectric Nanogenerators (TENGs)

The increasing growth of the Internet of Things has made powering gadgets and sensors difficult. The most promising alternative to standard battery technology is the triboelectric nanogenerator (TENG), which converts mechanical energy from the environment into electricity. Environmental mechanical energy is abundant in nature and can help TENGs create a clean, distributed energy network that can support wireless device innovation. For recent advancements in blue energy harvesting using TENG technology, compare EMG and TENG physics and engineering design. Maxwell's displacement current underlies nanogenerators' mechanism. Which introduce liquid-solid contact electrification TENG methods for water wave energy collection [32]. The designs and improvements of fully enclosed TENGs are studied, and a TENG network is suggested for collecting large amounts of blue energy from ocean waves. TENG also harvests energy from water waves, human motion, and vibration, etc., which is novel and relevant to the current era – the era of internet of things.

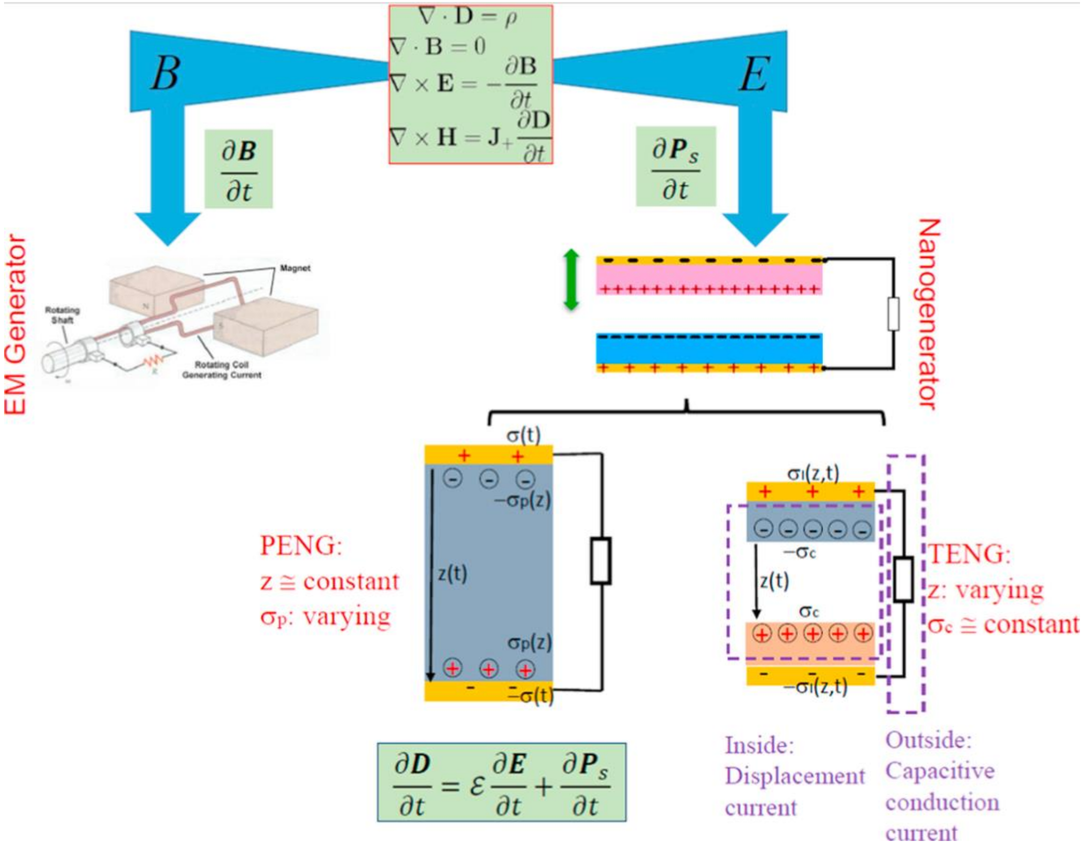

Figure 2.6: Theoretical comparison of EMG vs. Nanogenerators**.** EMG: $\partial B/\partial t$ (magnetic induction); Nanogenerators: $\partial P_s/\partial t$ (polarization change). PENG & TENG mechanisms shown; based on Maxwell's displacement current.[32]

2.3.1. Principle of Triboelectricity

When two different materials rub against each other, Triboelectricity occurs and therefore, they interchange electric charges. To become positively charged one material loses some electrons, although to become negatively charged the other material gains those electrons. This creates an electric potential difference that can drive current flow in an external circuit. The governing equation for triboelectric potential is:

where:

- ✓ Potential difference
- ✓ Surface charge density
- ✓ Separation distance

- ✓ Permittivity of free space

The triboelectric effect has been studied for thousands of years, yet its induced electrostatic charges can produce dust explosions, ignition, electronic damage, dielectric breakdown, and more in industrial applications. In 2012, Wang and co-workers first utilized this effect to create the TENG mechanical energy harvesting system. Wang and co-workers designed TENG to gather ambient mechanical energy, which is abundant yet lost in daily life, using CE and electrostatic induction. Figure 2.7 illustrates the operation of the contact-separation mode TENG. No charge is created or induced in the initial state (Figure 2.7 I). When two materials touch, triboelectric charges form (Figure 2.7 II). Once the two surfaces are pulled apart, a difference in electric charge can be created, leading to a quick movement of electrons from the bottom electrode to the top electrode. Once the surfaces completely separate, we can achieve equilibrium (Figure 2.7 IV). Through the external load, when the surfaces pull apart, charges created by static electricity will move back to even up the electric potential difference after that the surfaces are pressed together again. Figure 2.7 shows the generated current signal in the top right corner throughout this operating cycle.

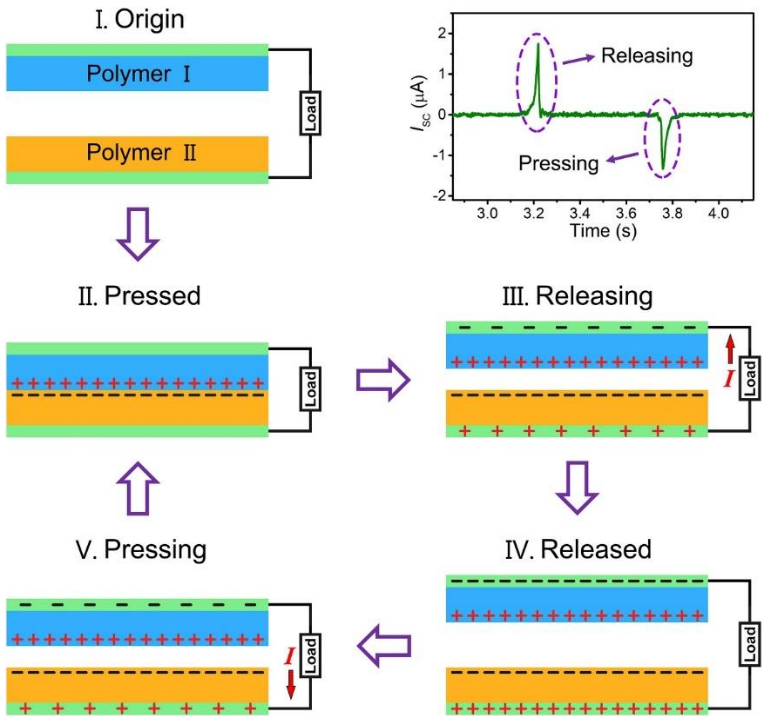

Figure 2.7: Schematics illustrating the working principle of the TENG in contact-separation mode

2.3.2. Polyurethane-Based Triboelectric Nanogenerators

In TENGs, Polyurethane is an effective material because of its high elasticity, durability, and favourable triboelectric properties. During contact and separation, material's ability to lose or gain electrons makes it suitable for energy harvesting. Key features include:

- **Surface Modification**: Enhanced surface roughness increases charge density.
- **Durability**: Polyurethane's mechanical robustness ensures long-term operation.

Self-healing TENGs reduce replacement waste and extend device life. Next-generation green energy technology requires self-healable TENGs made of degradable materials that disintegrate when damaged or utilized. Triboelectric nanogenerators (TENGs) could power wearable devices and sensors, according to human-oriented technology. New TENGs must be resilient, stable, biodegradable, and self-healing after mechanical damage. We present a customized ionic polyurethane TENG that heals, degrades, and performs well. Polycaprolactone-based PU was biodegradable, while imidazolium ionic liquids diol (IL) self-healed via ion-dipole contact. The electric double layer (EDL) of imidazolium ionic liquid diol increases capacitance and triboelectricity, resulting in a stronger output. These findings suggest a high-performance TENG design method for next-generation soft electronics [33]. Triboelectric nanogenerator (TENG) is widely explored due to its potential uses, but systematic studies on its performance in the presence of environmental factors are needed. They build a piston-structured TENG and one-way valve gas line test system using the contact–separation mode. In various atmospheres, Kapton-based TENG exhibits the most significant differences, with PET and PTFE following closely behind. A microscale discharge process explains the above phenomena. QSC has a negative linear relationship with static gas pressure above 1 atm. This study is crucial for future high-performance TENG configurations and device packing [34].

The working principle involves repeated contact and separation between polyurethane and another triboelectric material, generating alternating current in the external circuit.

2.4. Hybrid Nanogenerators: Synergistic Integration

Hybrid nanogenerators combine the piezoelectric and triboelectric effects into a single device to capitalize on their complementary characteristics:

- **Enhanced Output**: Simultaneous harvesting of piezoelectric and triboelectric energy increases overall efficiency.
- **Material Selection**: ZnO and PVP contribute to piezoelectric energy generation, while polyurethane serves as the triboelectric active layer.
- **Design Integration**: Layers of piezoelectric and triboelectric materials are strategically arranged to maximize energy harvesting under mechanical deformation.

The rapid rise in global energy demand, coupled with the urgent need for renewable and sustainable solutions, has driven significant research into energy harvesting technologies. Among the most promising approaches are nanogenerators (NGs) and solar cells (SCs), both offering distinct mechanisms for converting ambient energy into electricity. When integrated, hybrid NG-SC systems provide reliable power sources for applications such as self-powered electronics, wearable devices, environmental sensing, and wireless sensor networks. These advanced systems hold great potential to address practical energy requirements while paving the way toward sustainable and autonomous technologies. Finally, this analysis shows advanced hybrid systems and their many uses by pointing out the latest improvements in integrating NGs and SCs [35].

Hybrid energy generators integrate diverse energy exchange methods to optimize output performance, which has enormous application potential. Energy complementation involves gathering mechanical energy using various methods, combining it with other clean energy harvesters, and turning mechanical energy or other energy sources into hydrogen energy. The mechanism of single devices and the structural design of integrated units for different application scenarios are summarized for multitype energy harvesters. The hybrid TENG's improved energy harvesting efficiency makes it possible and essential for self-charging units in smart mobile devices and self-powered sensor networks [27].

Figure 2.8: Schematic illustrations of the hybrid triboelectric nanogenerator (TENG) with different energy harvesters [27].

2.4.1. Working Mechanism

The hybrid nanogenerator operates through a coordinated process:

1. **Mechanical Deformation**: External forces cause simultaneous deformation of ZnO-PVP composites and contact-separation of polyurethane.
2. **Charge Generation**: Piezoelectric charges are generated within ZnO-PVP, while triboelectric charges are induced at the polyurethane interface.
3. **Charge Harvesting**: Both charges are collected through a shared electrode system, resulting in higher energy output.

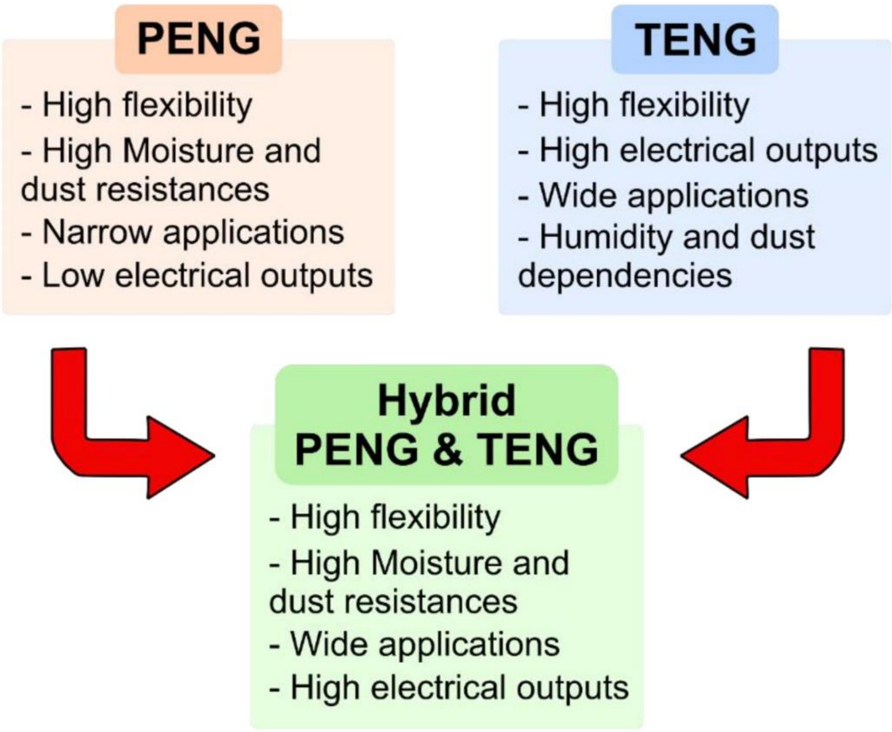

Figure 2.9: Advantages of using the hybrid PENG and TENG concept [36].

2.5. Advantages of Hybrid Nanogenerators

1. **High Efficiency**: Combined mechanisms ensure more effective energy conversion.
2. **Broadband Response**: Effective under a wide range of mechanical stimuli.
3. **Material Compatibility**: Flexible materials like PVP and polyurethane enable wearable and portable applications.
4. **Scalability**: Suitable for mass production using low-cost fabrication techniques.

2.6. Challenges and Future Directions

- **Material Optimization**: Enhancing the piezoelectric and triboelectric performance through material engineering.
- **Device Integration**: Developing compact, lightweight, and robust hybrid systems.
- **Stability**: Addressing degradation of materials under prolonged operation.
- **Applications**: Expanding the use cases for hybrid nanogenerators in real-world energy harvesting scenarios.

2.7. Summary

The chapter begins with an overview of energy harvesting technologies, highlighting their relevance in powering small-scale electronic devices, especially in remote or inaccessible locations. The focus then shifts to two primary mechanisms: piezoelectric and triboelectric effects. The piezoelectric effect is explained as the generation of electrical charge in certain materials, like ZnO, when subjected to mechanical stress. Its key advantages include high voltage output and suitability for nanoscale applications. Similarly, the triboelectric effect, which occurs due to contact electrification between different materials (such as polyurethane and PVP), is described in detail. It is noted for its simplicity, broad material choice, and capability to generate electricity from various forms of motion.

The chapter further explores how combining these two effects into a hybrid nanogenerator significantly enhances overall performance, output voltage, and reliability. The synergy between the two mechanisms allows for efficient energy conversion over a wider range of frequencies and mechanical inputs.

In addition, the chapter reviews material properties, device structures, and previous advancements in nanogenerator research. This includes a critical discussion on the advantages and limitations of individual systems and the motivation behind hybrid designs. Theoretical models, output behavior, and the importance of material morphology and surface properties are also addressed. Overall, this chapter provides a strong conceptual framework that supports the fabrication and experimental approach discussed in later chapters. It sets the stage for understanding how scientific principles are applied to design and optimize nanogenerators for practical, real-world energy harvesting applications.

Chapter 3

LITERATURE REVIEW

3. Literature Survey

This section of the thesis enlists the research and studies taken up in fabrication and characterization of Hybrid Nanogenerators for harvesting energy systems applications. Whereas Piezoelectric nanogenerator is based on ZnO: PVP and Triboelectric nanogenerator is based on Polyurethane. The increasing demand for sustainable and self-powered systems has driven significant research interest in nanogenerators (NGs) for energy harvesting applications. Hybrid nanogenerators, which combine piezoelectric and triboelectric effects, have emerged as promising solutions to scavenge mechanical energy from the environment. This chapter critically reviews the current state of research on piezoelectric nanogenerators (PENGs) based on Zinc Oxide (ZnO) and Polyvinylpyrrolidone (PVP), as well as triboelectric nanogenerators (TENGs) utilizing polyurethane. The synergistic integration of these mechanisms is discussed in the context of materials, structural design, and device performance. Extensive review of such studies is provided in the following subsections:

3.1. Literature Survey of PENG

Researchers are studying PENGs for their wearable and flexible applications. These devices generate energy from body heat or movement, making them suitable for incorporation into garments, shoes, or other wearables. Recent work has improved these devices' strength, flexibility, and efficiency [38]. Traditional PENGs has poor power output, making them unsuitable for many applications. Power output has been the focus of recent device improvements[39]. Researchers have developed novel materials, designs, and methods for making PENGs that are more powerful, efficient, and versatile [40]. PENGs can power sensors without external power [41]. Researchers are developing self-powered PENG sensors for monitoring environmental, healthcare, and structural health [42]. Researchers are investigating PENGs as multifunctional devices that may sense mechanical motion, harvest energy, and more [43]. PENGs can detect wave motion and gather energy for environmental monitoring. PENGs are complicated and precise because of additive manufacturing and nanofabrication. These methods provide PENGs with better performance and usefulness. These PENG advancements will enable new sensing, energy harvesting, and self-powered gadgets. They discuss the latest PENG investigations from human action that use piezoelectric materials to gather inactive biomechanical energy [44].

Piezoelectric ceramic exhibits exceptional dielectric permittivity and piezoelectric coefficient [44]. However, the rigid and tough skeleton of ceramic inhibits the potential for easy fabrication into energy harvesting devices attributing to the absence of design flexibility. Among the various piezoelectric materials, polyvinylidene fluoride (PVDF) is a flexible, biocompatible polymer with piezoelectric properties [45].

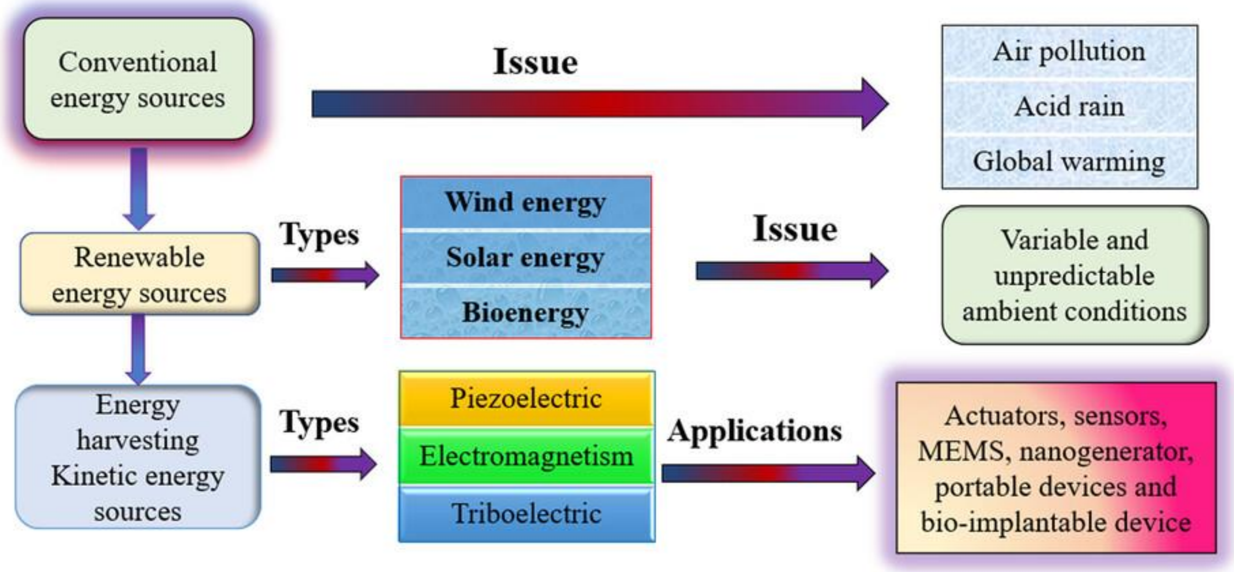

Figure 3.1: Schematic representation of the evolution of piezoelectricity[45].

Wearable applications need flexible, inexpensive, compact, and accessible power sources. Traditional power electronics are too heavy and inflexible [46]. External power sources and batteries have limited uses and lifecycles, making wearable devices and embedded that need regular energy difficult. These issues have led to 1D energy-related innovations, with nanogenerators as a promising power source [47]. They change energy from muscle movements and heartbeats into electrical signals that can be used for detecting biological indicators, helping the heartbeat, stimulating nerves, and repairing tissues [48]. Bio-piezoelectric energy harvesters (BPEH) that have high piezoelectric coefficients because of their nanomaterial structure and composition are interesting. This technique boosts energy conversion efficiency regardless of external sources or device settings [49].

The structural design of PENGs also plays a critical role in energy harvesting efficiency. Multilayer stacking, core–shell structures, and aligned nanowire arrays have been used to increase the contact area and mechanical robustness [50]. Flexible and wearable PENGs have been developed using substrates like PET, Kapton, and textile-based fibers, making them suitable for applications in biomedical sensors, electronic skin, and smart garments [51].

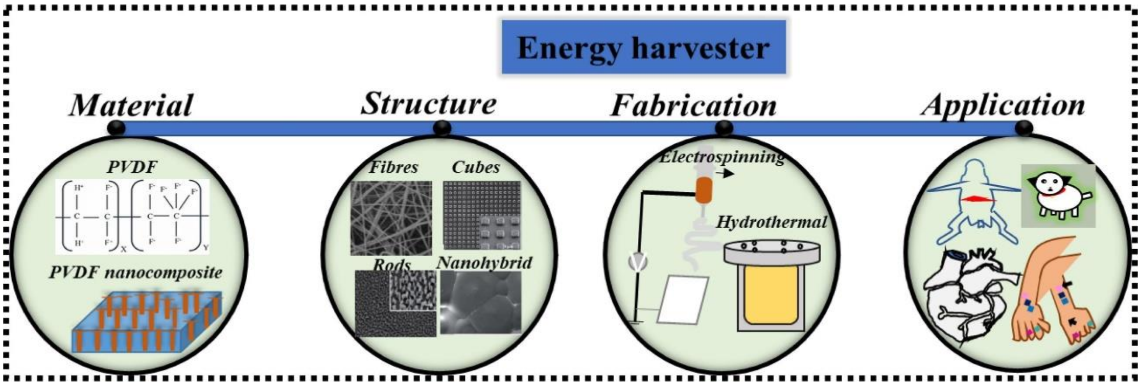

Figure 3.2: Material structure and design schematic [48].

For next generation of wearable electronics, flexible piezoelectric nanogenerators are important because for smart device setup they have a high power thickness and can produce self-powered devices [52]. On behalf of flexible piezoelectric nanogenerators, Poly(vinylidene fluoride–trifluoroethylene) (PVDF–TrFE) created mixtures that have outstanding potential. A big difference in permittivity among matrix and filler decreases the dielectric strength of polymer composites with piezoelectric fillers, making it hard to create strong electric fields needed for poling [53]. Due to its flexibility and electroactive phase, polyvinylidene fluoride (PVDF) thin films have promising energy harvesting applications. PVDF-based thin films have limited piezo responsiveness; hence, commercial applications are rare despite considerable research [54]. Adding titanium dioxide (TiO_2) tiny particles to the thick PVDF solution using a casting method boosts the voltage produced by the PVDF films when they respond to pressure. PVDF-TiO_2 nanocomposite films outperformed pure PVDF in storing modulus, flexible strength, and elastic modulus [55]. As compared to pure PVDF, PVDF-TiO_2 films increased dielectric constant (ε) by 143% and AC conductivity (σac) by 214%. PVDF-TiO_2 layers had higher residue polarity (Pr) standards, representing better piezoelectric presentation [56]. Modern approaches have used piezoelectric materials more in recent decades. Researchers focus on developing materials with desirable qualities. Since 2010, utilizing piezoelectric materials by adding sensing capabilities and energy harvesting into textile configurations has been researched [57].

During electrospinning, electricity and stretching pull apart twisted PVDF chains, lining them up along the fiber, which improves piezoelectric properties and β phase [58]. Electrospinning can produce fibers with highly aligned nanostructures for sensor and energy uses by regulating operation parameters [59]. The needle's jet becomes wider, called a Taylor cone. Through electrospinning, Taylor cone shape forms when polymer solution hits a key point everywhere push from electric forces matches the pull from surface tension [60]. The cone-shaped polymer jet has a unique nozzle tip angle. Through electrospinning, on the droplet surface charges create a hideous force that faces its external stiffness. Electrospinning feasibility depends on this interaction between the two forces [61].

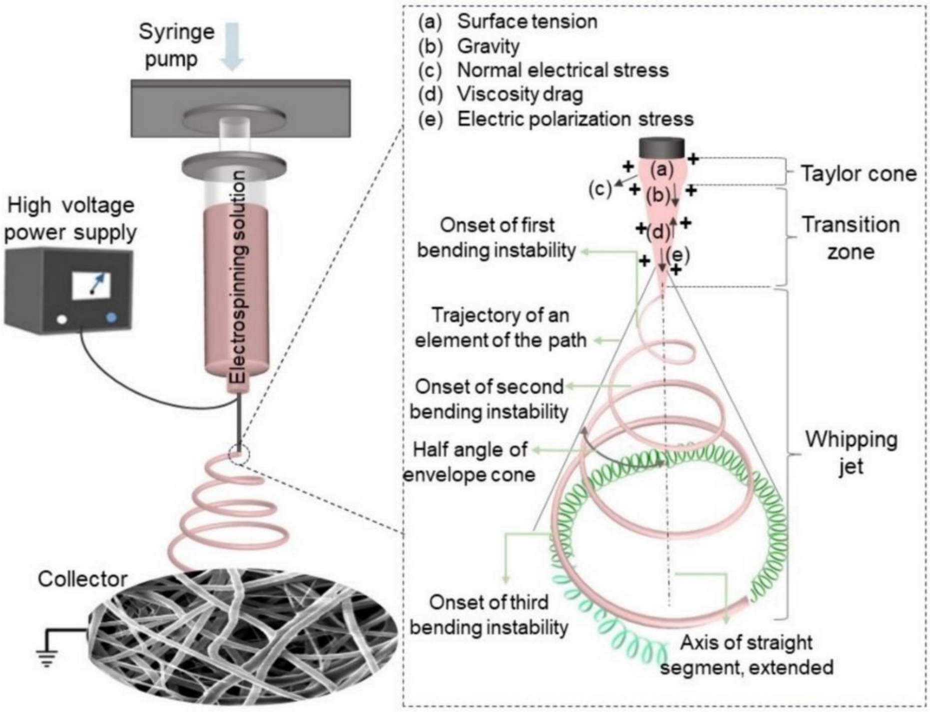

Figure 3.3: Schematic of electrospinning process, Jet forms via Taylor cone**,** transition**,** whipping, and fiber region under combined forces (e.g., surface tension, gravity, electric stress), shows bending instabilities post-transition. [61]

Figure 3.4 shows how PENGs work: With the dipoles, piezoelectric material is shoved with largely line up out-of-plane. Charges build at surface to offset the bound charge. Compressing the piezoelectric material discharges excess surface charge and decreases out-of-plane polarity because of certain charge losses [62]. To counteract polarization, stretchable tension binds extra superficial charge. Under external forces, piezoelectric material connected to loads generates current flow and electric potential [63].

Moreover, integration of PENGs into hybrid nanogenerators—where piezoelectric modules are coupled with triboelectric nanogenerators (TENGs)—has been shown to overcome the limitations of low power density and discontinuous output [64]. These hybrid devices take advantage of both contact electrification and piezoelectricity, providing a more stable and higher energy output suitable for powering microelectronic devices [65]. Such systems demonstrate the potential for self-powered energy solutions in remote or inaccessible areas.

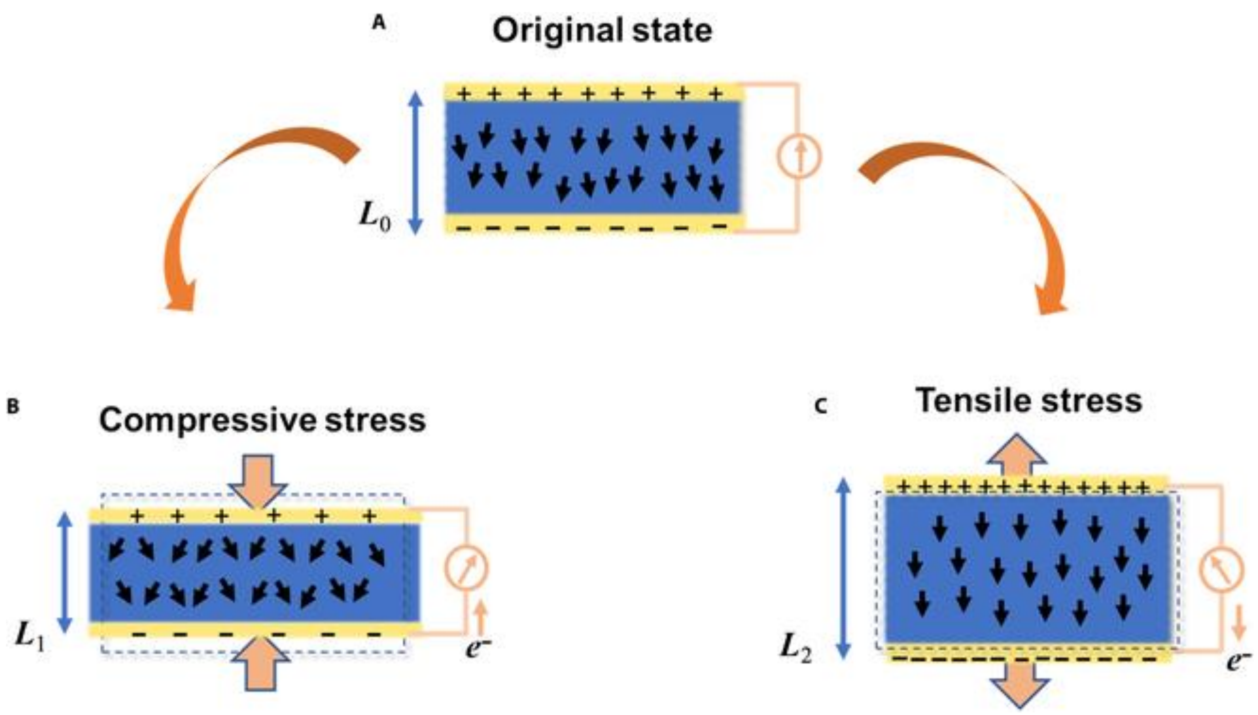

Figure 3.4: Schematic illustration of working mechanism of a PENG. (A) Original state. (B) Compressive stress. (C) Tensile stress [63].

Azimi, Golabchi, Nekookar et al. presented that Additionally, PENGs can replace batteries in self-powered biomedical devices. It reduces electronics size and battery replacement concerns [66] Zhang, Zhou, Liu et al. developed ZnO nanoparticles, and concentrated graphene oxide using PVDF, an elastic energy harvester to power a battery-free heart pacemaker. In the human heart, each beating generates 0.487 μJ of electric energy, bettering the pacemaker's verge energy [67]. Adjusting the piezocomposite's (K, Na)NbO_3 (KNN) nanoparticle distribution created a new energy harvester. An all-in-one energy harvester can power a pacemaker with a cardiac pulse. Apart from the foregoing applications, PENGs can charge capacitors, brighten LEDs, power digital watches, etc. Piezocomposites provides lightweight, sustainable electricity for all low-power and tiny electronics [68].

With the rapid growth of portable electronics and wireless sensor networks, the demand for sustainable and self-powered energy sources has intensified. Among various energy harvesting technologies, piezoelectric nanogenerators (PENGs) have emerged as a promising solution for converting ambient mechanical energy into electrical energy [69]. First introduced by Wang and Song in 2006 using ZnO nanowires, PENGs harness the intrinsic piezoelectric properties of certain materials at the nanoscale, thereby enabling efficient mechanical-to-electrical energy conversion from sources such as vibrations, human motion, and ambient noise [70].

Piezoelectric materials such as zinc oxide (ZnO)**,** barium titanate ($BaTiO_3$)**,** and polyvinylidene fluoride (PVDF) have been widely studied due to their high piezoelectric coefficients, flexibility, and ease of synthesis [71]. ZnO, in particular, has received significant attention because of its non-toxicity, low cost, and the ability to form diverse nanostructures including nanowires, nanorods, and nanobelts [72]. Studies have shown that vertically aligned ZnO nanowires embedded in polymer matrices such as PVP or PDMS can enhance the output voltage and current due to the increased deformation under stress [73]. Recent advancements in material engineering have focused on hybrid composites to further improve the performance of PENGs [74]. For instance, incorporating conductive fillers like graphene, carbon nanotubes (CNTs), or silver nanowires into the polymer matrix enhances the dielectric properties and charge mobility, which significantly boosts the power output [75] Additionally, surface modifications and doping of ZnO with elements like Al or Ga have been explored to optimize its crystal quality and piezoelectric response [76].

3.2. Literature survey of TENG

Polymers' lightweight, facile process ability in addition strength, formability, and robustness, adjustable surface, also antimicrobial qualities offer many material uses. For storage and energy generation, polymer applications have risen steeply over the past era for examples triboelectric nanogenerators (TENGs) [77]. TENGs alter friction into electrical energy. For thousands of years Triboelectricity have occurred, but then its low energy conversion efficiency prevented its practical application. In 2012, researchers introduced triboelectric nanogenerators, but their efficiency proved too low for practical use [78]. However, with future progress they showed potential for harvesting low level machine-driven energy. With growing energy requirement and the fast emergence of the Internet of Things (IoT), there is a greater need for the sensors to be used in the IoT systems which is estimated to exceed 200 billion by 2025 [79]. Therefore, there is a huge requirement for the energy deliveries without replacement and restoring of the charge storing device for their sustainable performance. Due to its high instantaneous output power, Triboelectric Nanogenerator (TENG) is the market leader, recyclable, wide range of materials, modified working modes and cheap manufacture method [80].

Every year, manufacturers produce more portable energy harvesting, communication, patient monitoring, and biosensor gadgets. Fuelling, maintaining, and disposing of each device sounds nearly impossible [81]. Next-generation wearable and portable electronics use flexible and elastic triboelectric nanogenerators (TENGs). For biomechanical identifying and energy harvesting, they presented an all nanofiber TENG. They made PVDF and TPU nanofiber (NF) membranes using force spinning (FS) to create the TENG [82]. With consistently sputtered gold Nano film, TPU nanofiber films were interfaced. Tests on the PVDF-TPU or Au NF-TENG revealed that a 254 V open-circuit voltage and an 86 μA short-circuit current produced the part of TPU fiber membrane that was in contact with gold at a load frequency of 240 bpm, which is 112 and 87% higher than the regular TENG [83].

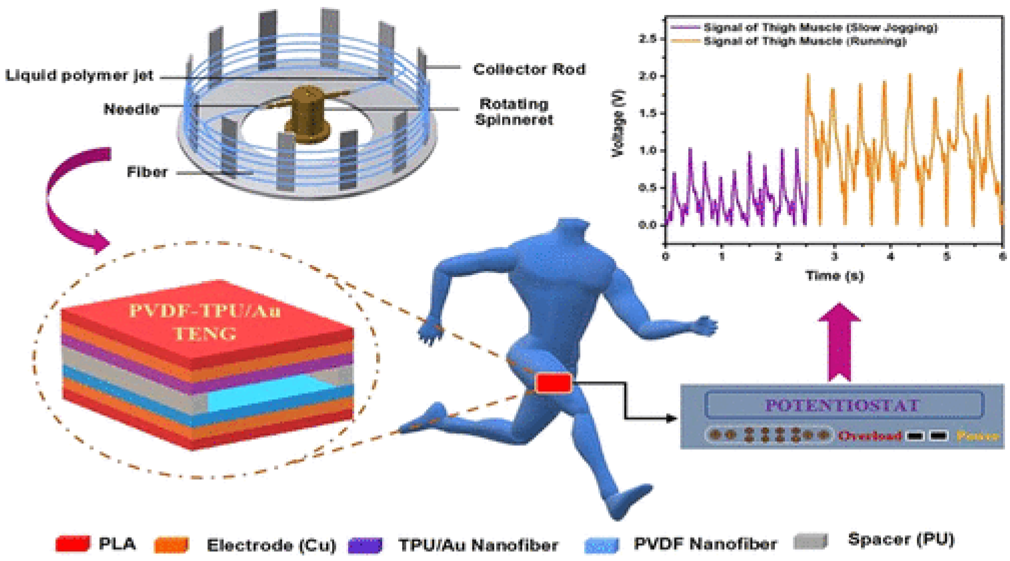

Figure 3.5: Graphical Abstract of TENG [83]

TENGs can generate electricity for devices using renewable energy. A sustainable power TENG can power vibration sensors, environmental monitors with multidirectional vibration mechanisms, and electronic devices [84]. Since their invention, People have used TENGs for industrial use, lighting, off-shore and on-shore situations, power grid integration and self-powered devices. These nanogenerators have proven suitable for renewable energy applications [85]. Figure 3.6 shows a range of uses, including sensors, bio systems, checking systems, human healthcare, self-powered systems, industrial applications, smart homes, ecological sensors, healing applications and industrial systems [86]. For AI applications, TENGs can be self-powered devices similar IoT and machine learning [87], helping build monitoring oceanic bionetworks and supportable ocean monitoring systems, with self-powered TENG sensors, and supportive chemical and biological sensor uses. TENGs are used in soft robotics, self-powered wind speed, vibration, and gas sensors; industrial monitoring systems, saving and protection[88]. They are used in smart suitability systems, healing applications, industrial freezing water monitoring, reveal intertwining, human healthcare monitoring, medical electronic devices, bio systems, accuracy medicine in cancer treatment, smart factories and smart home applications [89]. Additionally, TENGs contribute to smart grid applications. Recent advances have focused on improving the output performance and durability of TENGs. Techniques such as surface patterning, Nano structuring, and composite material engineering have been explored to increase surface charge density and enhance contact area

[90]. Incorporating materials like graphene**,** MXenes**,** and ZnO nanostructures into triboelectric layers has shown significant enhancement in the electrical output and mechanical stability [91]. Furthermore, encapsulation strategies using elastomers like PDMS have been employed to improve the longevity and robustness of TENGs under harsh conditions.

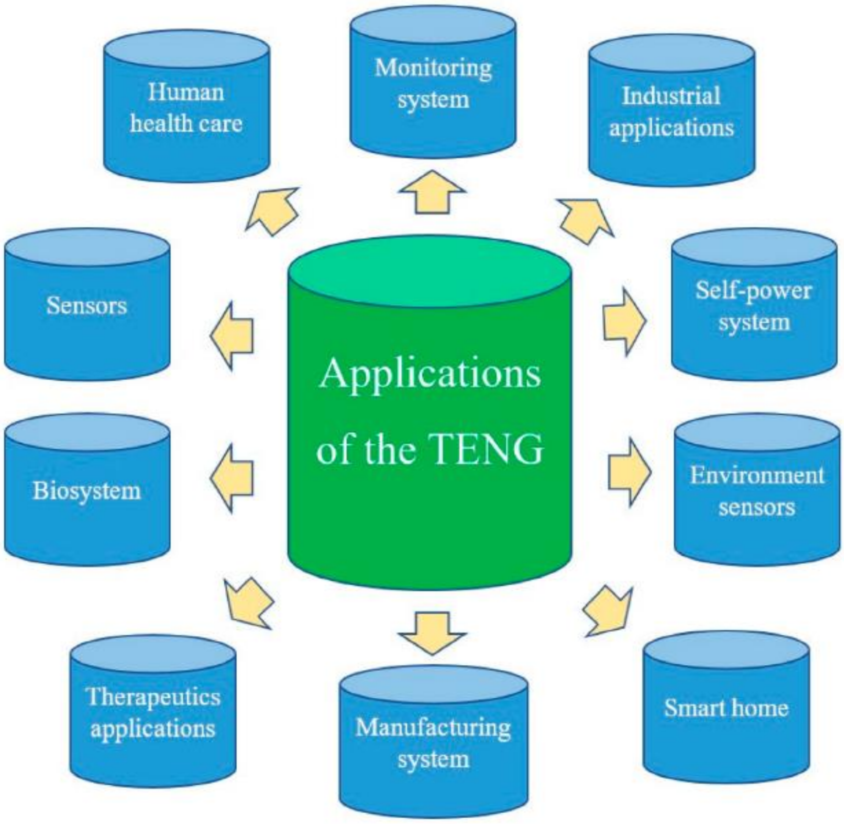

Figure 3.6: Numerous applications of TENGs [89].

Triboelectric nanogenerators boosted energy-harvesting devices. Without greenhouse emissions they can efficiently generate electricity from underwater waves and surface to power marine apparatus [92]. This project suggests a pendulum-like TENG and adjusts a commercial sustain for harvesting energy from marine waves. We used PU foam and PDMS as triboelectric couples [93]. Simulations in a trend flume showed with a maximum power output of 1.1 W/m², current values of 8.9 µA and maximum voltage of 145 V respectively. We recorded no performance decrease after 1200 stability measurement cycles [94]. We carefully examine the newest techniques in TENG for sensing, generating power, collecting signals, making decisions, connecting, and wireless communication to give a complete overview, unlike earlier reviews that only looked at sensing or energy generation [95]. We introduce TENG technology after discussing the components of wearable sensing systems. In depth research on wearable TENG architectures focuses on their use as some of their energy harvesting applications and self-powered sensors in soft wearable sensing systems [96]. We talk over origami or kerygma structures, fabric based schemes (woven, fiber, 2D/3D knits, and interwove structures and yarn types), e-skins (thin sheets and films), and nanocomposites. Thus, data collection, power organization, decision making behaviour and data analysis, of TENG based wearable devices are examined, followed by this technology's viewpoints [97].

Wearable sensing is popular with textile TENGs because they can easily integrate into everyday apparel. Textile TENGs' wear, flexibility, and stretch qualities allow them to measure a variety of unstructured body movements without sensing element blockage [98]. Some textile TENGs are washable and have improved moisture management to prevent TENG performance loss due to moisture. Many textile TENG designs have been built utilizing industrial textile manufacturing methods, indicating their scalability [99]. Recovery and therapeutic insoles are available; however, sensor systems are still cumbersome and limited to indoor or clinical settings. Our flexible, portable, and multi-functional insole monitoring technology uses Archimedean algorithmic spiral TENG-based power systems constructed from biopolymers like bacterial cellulose, PDMS, PEDOT:PSS, and others [100]. The soft, portable, and IoT-compatible smart insole system provides biomechanical study of gait, posture, and other podiatry-related variables with good mechanical and electrical performance (JSC = 40-50 $\mu A/cm^2$ and PD ≈ 500-600 $\mu W/cm^2$) [101].

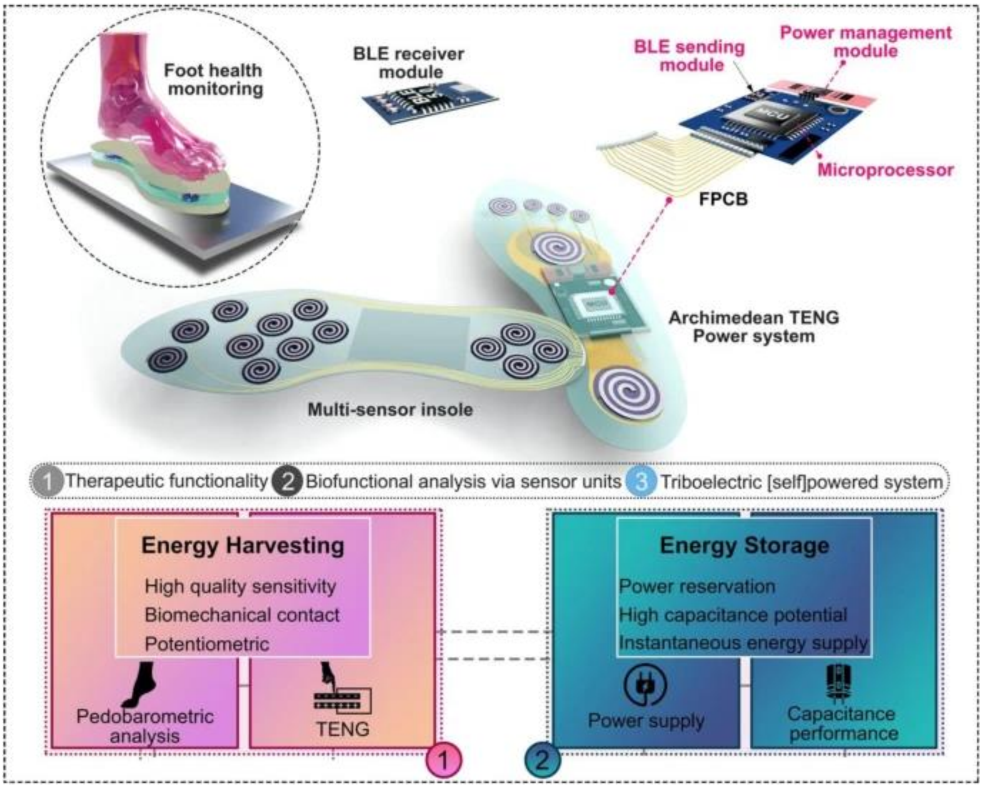

Figure 3.7: Graphical Abstract [101]

They will demonstrate the fabrication and characterization of low cost, power-efficient TENG with copper (Cu), Aluminum (Al), gold nanoparticles (AuNPs) as a metal layers and Poly Methyl Methacrylate (PMMA), Poly Tetra Fluor ethylene (PTFE) and Polyimide as a polymer layers [102]. Fluorine Tin Oxide (FTO) and glass has been used as a non-flexible substrate on which layers have been deposited using DC Magnetron sputtering and Spin-Coating techniques. These metal-polymer thin layers were then joined together to fabricate different TENG devices using polyurethane (PU) as a spacer [103]. Comparative study of various TENG was conducted using SDS1022-DSO which shows AC sine voltages on pressing and releasing these devices. AC sine voltages of all TENG show different characteristics that are time-varying waveforms [104]. The all-recyclable TENG (AR-TENG) is made from a special plastic with tiny holes, generates a power density of 1.547 W m^{-2} (with a peak output voltage of 360 V and a current of 22 μA), and continues to work well even after being in seawater or after 1,000,000 uses [105]. This AR-TENG powers a buoy-type ocean monitoring system and an intelligent life jacket, is recyclable, and can be used in other devices. This technique enables effective renewable energy harvesting without e-waste manufacturing, reducing global warming and ozone depletion [106].

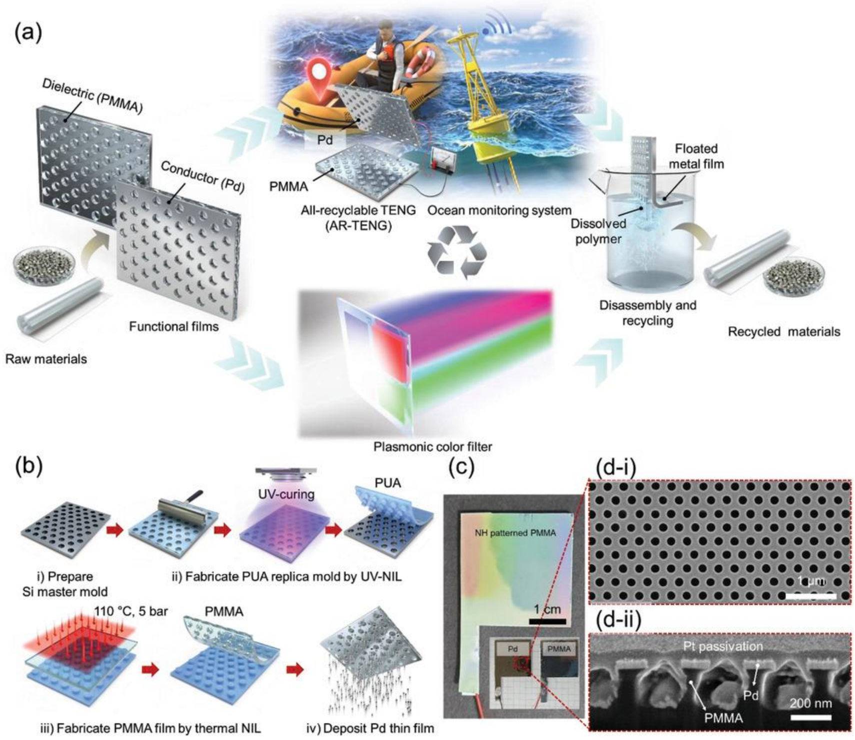

Figure 3.8: **(a)** AR-TENG recycling & **(b)** film fabrication via UV/thermal NIL, **(c–d)** Images & SEM of AR-TENG showing nanostructured Pd/PMMA layers [106].

For high-performance TENGs, electrospun EC/TPU nanofiber membranes create rough surfaces for better friction, and piezoelectric BTO nanoparticles increase electric output by working together with both piezoelectricity and triboelectricity [107]. Thus, the composite membrane had a stress of 9.25 MPa and a strain of 275.2% when the BTO nanoparticle content was 8 wt % in EC/TPU (1:4 weight ratio) nanofibers. Thus, the composite membrane had a stress of 9.25 MPa and a strain of 275.2% when the BTO nanoparticle content was 8 wt % in EC/TPU (1:4 weight ratio) nanofibers. The TENG produces larger electric outputs that is voltage of 125.8 V, current of 34.1 μA, and power density of 1.68 W/m² than individual piezoelectric nanogenerators. TENGs can power microelectronics and commercial LEDs and to measure human physical training they act as self-powered sensors [108]. TENGs offer numerous advantages including lightweight design**,** low-cost fabrication**,** environmental friendliness, and high power density [109]. These features make them highly suitable for powering small-scale electronics, wearable devices, and self-powered sensors [110]. The performance of TENGs largely depends on the selection of materials and surface microstructures. Typically, dielectric polymers such as polytetrafluoroethylene (PTFE), polyimide (PI), and polyurethane (PU) are used due to their excellent triboelectric properties and flexibility [111]. Researchers have also investigated the use of biocompatible and biodegradable materials to make TENGs suitable for biomedical and environmental applications [112].

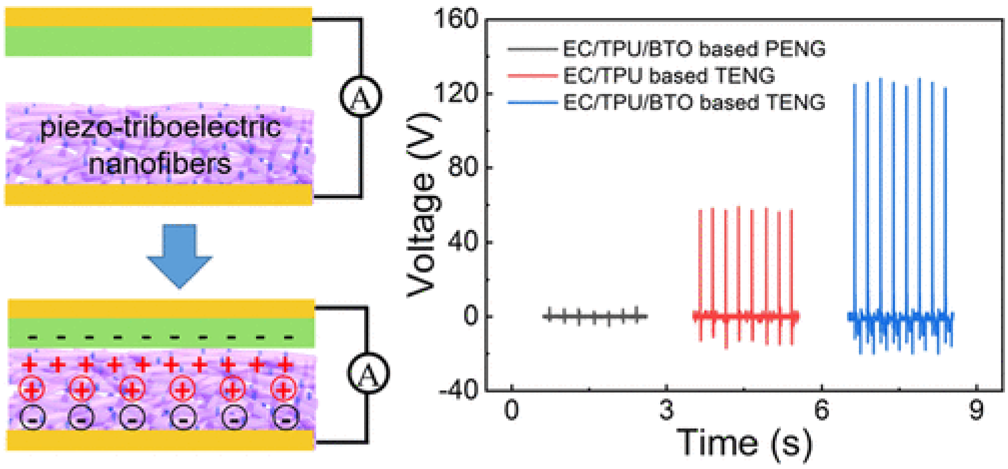

Figure 3.9: Flexible EC/TPU-BTO nanofiber layer for high-performance TENGs. [108]

We created a new TENG that uses an electrostatic double layer, similar to how electrical double layers and supercapacitors (SC) work, by having electrostatic charges stick to the dielectric layer on the electrodes [113]. We mimicked SC's structure and mechanism to build three-dimensional electrodes from polyurethane sponge and silver nanowires. Electrochemical polarization or corona charging increased output power thirteen fold. Additionally, a compressible self-charging power system using TENG and SC was created to sustainably power electric gadgets [114]. The ever-increasing global demand for sustainable and portable energy sources has directed significant research interest toward energy harvesting technologies [115]. Among various approaches, Triboelectric Nanogenerators (TENGs) have emerged as a promising solution due to their ability to convert low-frequency mechanical energy into usable electrical energy [116]. Originally conceptualized by Wang et al. in 2012, TENGs exploit the principles of triboelectrification and electrostatic induction to harvest energy from ambient mechanical sources such as human motion, vibrations, wind, and water waves [117].

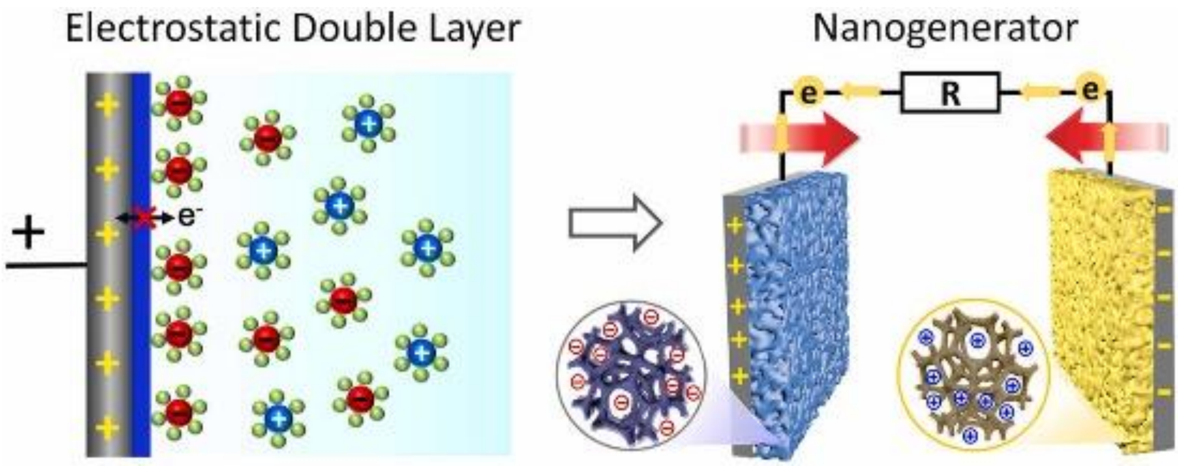

Figure 3.10: 3D PU sponge/AgNW-based TENG using electrostatic double layer for efficient energy harvesting.

To improve the contact electrification area, mask less direct image lithography (DIL) was utilized to produce polyurethane (PU) layers with surface micro cones in 3 min. DIL is precise and fast [118]. Chemical treatment with trichloro (1H,1H,2H,2H-perfluorooctyl) silane (FOTS) gas increases the interaction region and electron attraction because it makes the surface rougher at a tiny scale and adds fluorine [119]. In the TENG, PU and F-PU layers using micro cones obtain a high current of 22 μA, and five times greater than F-PU and flat PU layers [120]. Surface roughened morphology, Fluorine, and micro cones boost electric output. TENG can be shaped to capture mechanical energy from human motions Owing to flexibility of F-PU and PU layers, customizability of DIL technique and strength [121].

3.3. Literature survey of Hybrid Nanogenerators

A single hybrid device and a grid of four hybrid devices connected in parallel can charge various capacitors. The suggested setup of energy harvesters was designed to take advantage of both triboelectric and piezoelectric effects to boost performance by using both methods at the same time when water waves hit, all in one simple push and release action. It was also shown that such a grid of energy harvesters can power small electronic devices that would enable future battery-less, self-powered marine sensing platforms for environmental monitoring [122]. PV-derived hybrid power systems can boost dispatch able renewable energy and reduce weather-dependent electricity production. This article introduces monolithic hybrid devices that integrate high-performance ST-PSCs and liquid-solid triboelectric nanogenerators. We achieve PSCs with 17.4% stiff and 15.7% flexible efficiency. Extra changes to the electrodes and clear TENGs improve light capture and see-through quality across a wide range of wavelengths (380-1000 nm) but lower the amount of light that passes through in the near-infrared range (1000-2500 nm) for hybrid devices [123]. These hybrid devices offer outstanding visible light transparency, color accuracy, heat resistance, and integration on rigid and flexible substrates. On sunny days, hybrid devices achieve 10.1% solar conversion efficiency using one sun, resulting in a maximum electrical power output of 101 W m^{-2}. Hybrid devices may generate 2.62 W m^{-2} of electricity by converting the energy of water drops, providing green electricity on rainy days [124].

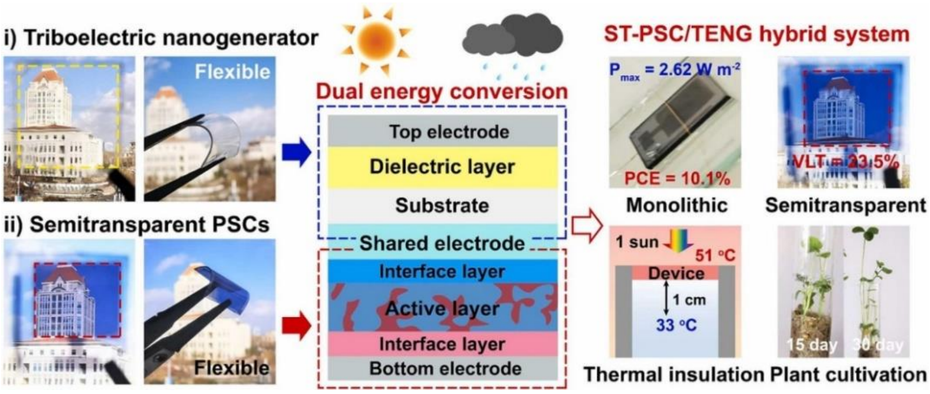

Figure 3.11: Graphical Abstract of Hybrid Nanogenerator [124]

PV-derived hybrid power systems can boost dispatch able renewable energy and reduce weather-dependent electricity production. This article introduces monolithic hybrid devices that integrate high-performance ST-PSCs and liquid-solid triboelectric nanogenerators [125]. We achieve PSCs with 17.4% stiff and 15.7% flexible efficiency. Extra changes to the electrodes and clear TENGs improve light capture and see-through quality across a wide range of wavelengths (380-1000 nm) but lower the amount of light that passes through in the near-infrared range (1000-2500 nm) for hybrid devices. These hybrid devices offer outstanding visible light transparency, color accuracy, heat resistance, and integration on rigid and flexible substrates. On sunny days, hybrid devices achieve 10.1% solar conversion efficiency using one sun, resulting in a maximum electrical power output of 101 W m^{-2}. Hybrid devices may generate 2.62 W m^{-2} of electricity by converting the energy of water drops, providing green electricity on rainy days [126]. We combine the water-wave triboelectric nanogenerator (TENG) and evaporation generator to create a hybrid nanogenerator that better uses water energy. In calm water, this hybrid nanogenerator can boost water wave TENG production. Optimized water-wave TENG peak power is 0.62 mW at 2.5 Hz, and TENG charges a 0.33 μF capacitor to 15 V in 80 s during genuine waves. Wood block-based evaporation generators generate direct currents during spontaneous water evaporation. The evaporation generator converts 84.2% of solar energy into vapor, producing a current density of 3.2 $\mu A \cdot cm^{-2}$ and an output power density of 1.4 $mW \cdot m^{-2}$ when connected to a 10 kΩ load at 23 ℃ and 30% humidity [127]. To show the evaporation generator's application potential, we construct a multi-stage boost circuit with pulse charging to improve voltage output and reduce charging time. The suggested hybrid nanogenerator might harvest water wave and steam evaporation energy, expanding TENG energy harvesting technologies [128].

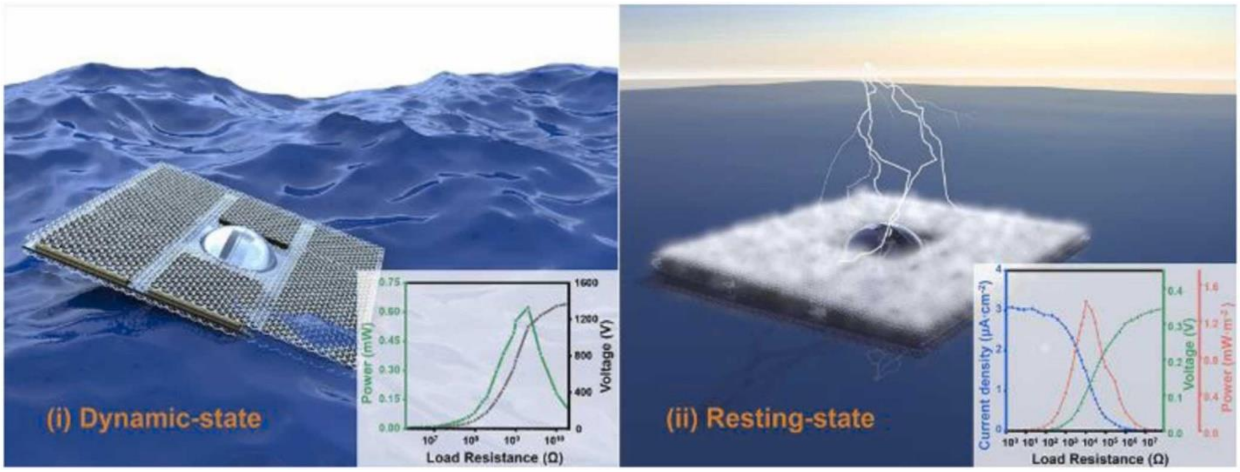

Figure 3.12: Novel hybrid nanogenerator is proposed based on a water-wave triboelectric nanogenerator (TENG) [128]

A platform that collects energy from waves uses a special module called a bifilar-pendulum coupled hybrid nanogenerator (BCHNG) along with an electromagnetic generator (EMG), two piezoelectric nanogenerators (PENGs), and two layered triboelectric nanogenerators (TENGs) [129]. The combination of lightweight TENG with heavy PENG and EMG can increase power take-off's ability to gather water wave energy, improve BCHNG module area usage, and simplify floating wave energy collecting device design. The bifilar pendulum's two degrees of swing flexibility allow the BCHNG module to capture the water wave's kinetic and gravitational potential energy simultaneously [130]. Hybrid nanogenerators have demonstrated considerable promise in various configurations. One common approach involves stacking or integrating TENG and PENG layers into a single flexible device, which can simultaneously generate electricity through both triboelectric and piezoelectric effects [131]. This synergy has resulted in significantly enhanced power densities and responsiveness under low-frequency vibrations and irregular mechanical stimuli, such as those generated by human motion or environmental disturbances. Additionally, the co-existence of different transduction mechanisms ensures energy harvesting from both macro- and micro-scale mechanical sources [132].

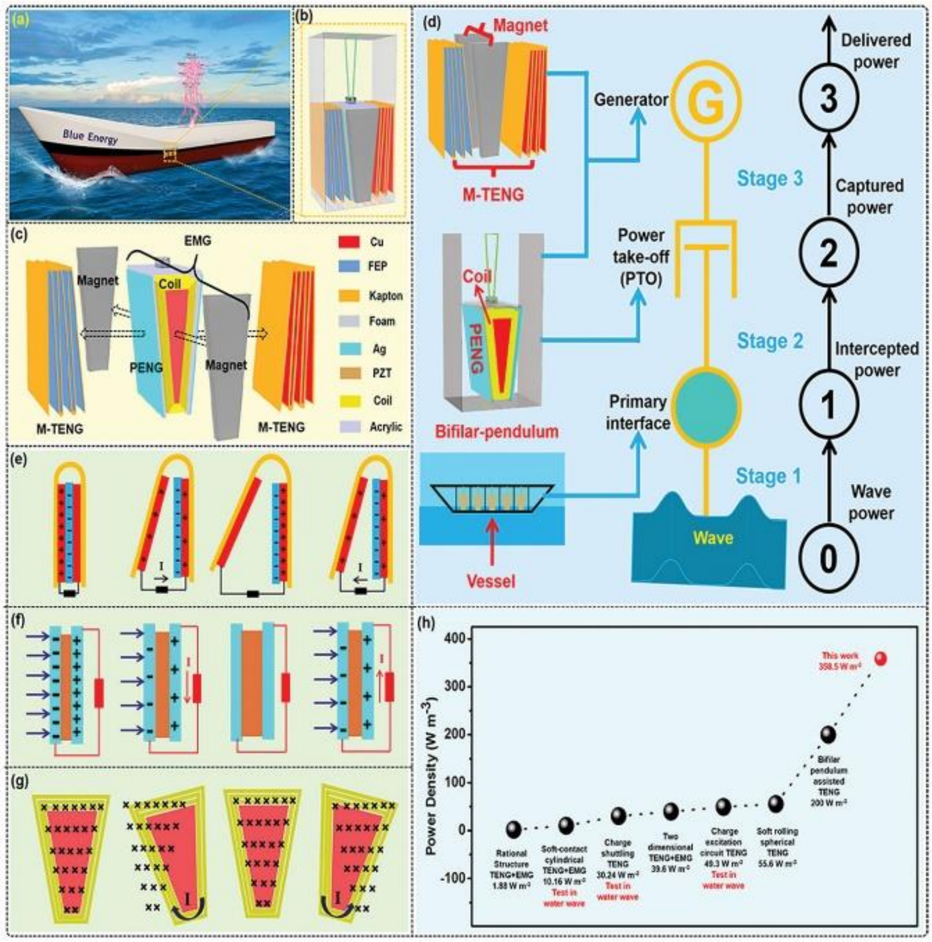

Figure 3.13: BCHNG-integrated vessel structure and operation. BCHNG module-equipped vessel configuration. b) Expanded BCHNG module schematic. c) Three-generator BCHNG structural components. d) Vessel power transfer chain using harvesting ocean-wave energy BCHNG modules. TENG, PENG, and EMG functional principles. h) Device structure performance with wave energy harvesting at the cutting edge [130].

To collect energy, Adaptive rotating triboelectric nanogenerator (AR-TENG) corresponding transformers circuit and connection of a thermoelectric generator (ThEG) is used. AR-TENG reduces friction due to dielectric layer flexibility, and ThEG reuses heat via the Seebeck effect. Additionally, the AR-TENG transformer circuit's maximum output conversion efficiency is 96.4%. Thus, the total device charging supercapacitors stores energy 28 times faster than AR-TENG alone. This study offers a way to improve TENG energy-harvesting efficiency and a wide range of IoT applications [133]. Doctors and nurses utilize disposable surgical face masks, but the COVID-19 outbreak has increased their use. Their tight attachment to the face constantly exposes them to facial expressions, breathing, and speech. Electromechanical transducers can use these motional forces to power mask-integrated sensors thanks to their peculiar mechanical energy source [134]. The procedure is usually done with piezoelectric and triboelectric nanogenerators; however, most of them are excessively wide or dense or, humidity sensitive and not conformable, to embed in a mask and skin. This mask contains a wearable energy harvester that can be reused, unlike recent smart energy-harvesting cloth masks [135]. The soft biocompatible hybrid piezoelectric nanogenerator (hPENG) is metal-free. Ecoflex and skin-conformable elastomeric blend of poly(dimethylsiloxane) (PDMS), they both are linked with laser-ablated polyimide flexible substrate to electrospun with pure PVDF membranes and a biobased plasticizer (cardanol oil, CA) [136]. An electromagnetic generator and triboelectric nanogenerator form a wearable noncontact free-rotating hybrid nanogenerator (WRG). This nanogenerator achieves continuous production in 2 seconds with one external force, outperforming existing wearable nanogenerators by two orders of magnitude due to its mechanical energy storage design. The WRG can be fitted into shoes to generate 14.68 mJ per step, enough to power most personal information gadgets. WRG powers wireless sensors, GPS, and smartphones throughout [137]. The integration of hybrid nanogenerators with energy storage devices such as capacitors, supercapacitors, or thin-film batteries has paved the way for self-powered electronics [138]. Such configurations are especially valuable in powering Internet of Things (IoT) devices, wearable sensors**,** medical implants**,** and remote environmental monitoring systems [139]**.** Research has shown that hybrid nanogenerators can operate in self-charging power units, where the harvested energy is stored and used continuously without the need for external charging, thereby extending the operational lifetime of portable and wearable devices [140].

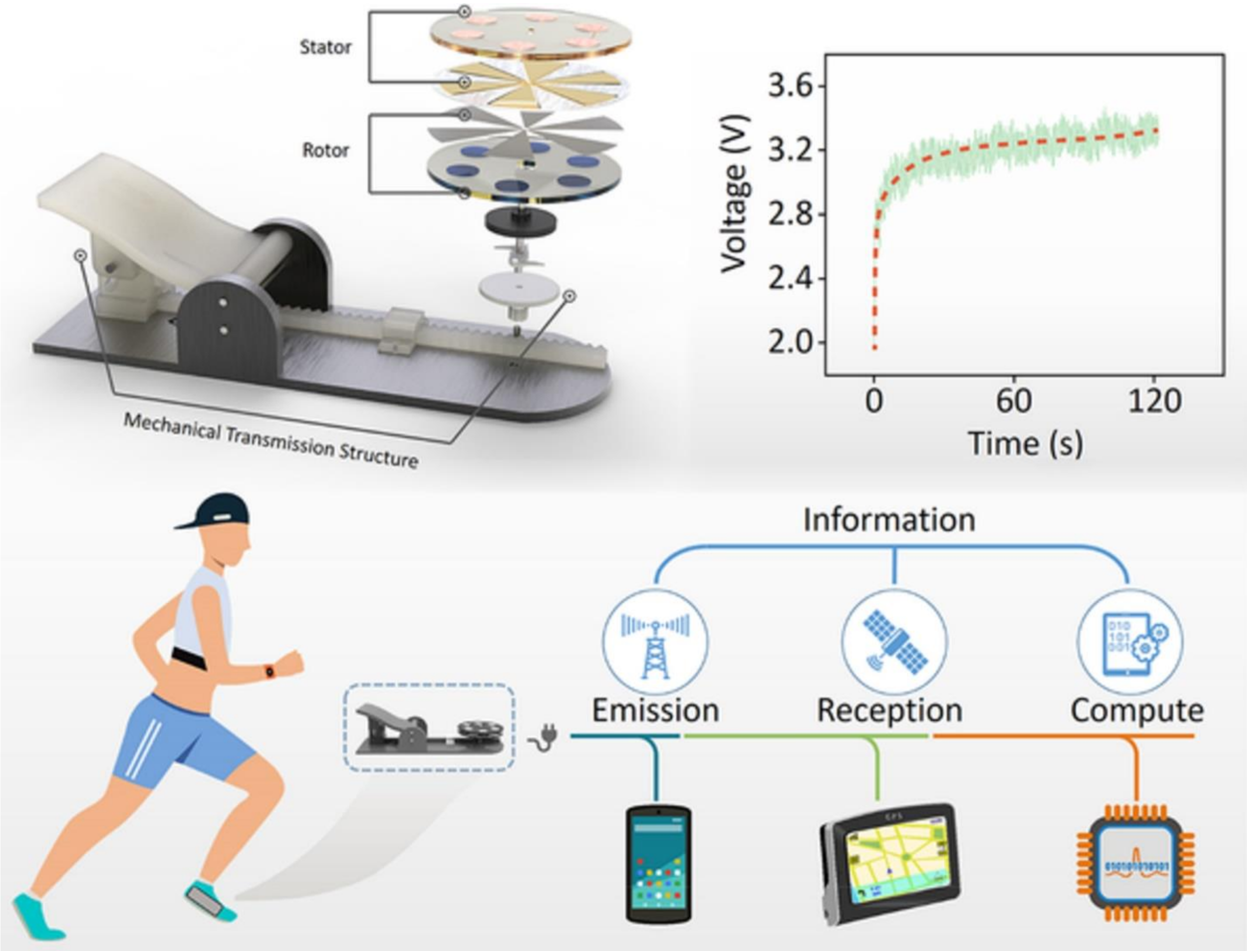

Figure 3.14: Wearable noncontact free-rotating hybrid nanogenerator for self-powered electronics [137]

Hassan, Khan, A. Hassan et al., introduced a hybrid nanogenerator (NG) capable of simultaneously harvesting energy through both piezoelectric and triboelectric mechanisms. In their design, the piezoelectric nanogenerator (PNG) was fabricated using a composite of polydimethylsiloxane (PDMS) and perovskite zinc stannate ($ZnSnO_3$) nanocubes, which provided a high charge polarization of 59 $\mu C/cm^2$. Meanwhile, the triboelectric nanogenerator (TENG) was developed using UV-treated PDMS. To optimize performance, the PNG and TENG were vertically stacked with sponge spacers in between, ensuring a uniform air gap essential for enhancing triboelectric interactions. The structure also exhibited a low Young's modulus, which is particularly favourable for efficient piezoelectric response. As a result, the hybrid NG demonstrated a remarkable open-circuit voltage of 300 V, a maximum power density of 10.41 mW/cm² under a 1 MΩ load, and a peak short-circuit current density of 16 mA/cm² at a 50 Ω load. These outcomes confirm the device's strong potential as a reliable power source for a wide range of self-powered electronic systems [141]. Despite their impressive potential, hybrid nanogenerators still face technical challenges. These include mechanical wear and fatigue, energy loss during transduction, complex fabrication processes, and issues with material compatibility and stability [142]. Addressing these concerns requires a multidisciplinary approach involving nanomaterials engineering, device modelling, and microfabrication technologies [143]. Moreover, scalable and cost-effective fabrication methods such as 3D printing, roll-to-roll processing, and solution-based synthesis are being explored to bring hybrid nanogenerators closer to commercial deployment [144].

After these developments and background theory it was noted that the integration of self-powered energy harvesting systems into modern electronics has become a focal point in sustainable technology research. Over the past decade, numerous studies have explored the design and optimization of piezoelectric nanogenerators (PENGs) and triboelectric nanogenerators (TENGs) for applications ranging from wearable electronics to biomedical devices. Literature shows significant advancements in material selection, fabrication techniques, and performance enhancement strategies for individual PENGs and TENGs. In particular, various piezoelectric materials such as lead zirconate titanate (PZT), barium titanate (BTO), polyvinylidene fluoride (PVDF), and zinc oxide (ZnO) have been extensively examined, alongside triboelectric materials including PDMS, PTFE, and polyurethane.

Despite these developments, several limitations persist. Most studies on ZnO-based PENGs focus either on pure ZnO nanostructures or ZnO composites with PVDF, cellulose, or other polymeric matrices, leaving the potential of ZnO blended with polyvinylpyrrolidone (PVP) largely unexplored. The electrospinning of ZnO–PVP composite nanofibers for energy harvesting applications has not been systematically studied, particularly in terms of parameter optimization to achieve uniform fiber morphology and enhanced electrical performance. Additionally, the reported PENG devices in literature often produce modest output voltages and currents, which limits their capability for directly powering practical electronic devices.

Similarly, in the field of TENGs, substantial research has been devoted to material innovation and structural design; however, there is limited exploration into the use of self-healing polyurethane in vertical contact–separation mode configurations. Moreover, while some works have incorporated porous or sponge-based spacers to improve air-gap stability, the reuse of landfill-derived sponge material as a sustainable and cost-effective structural component for TENGs has received minimal attention. The concept of integrating environmental waste recycling into nanogenerator design thus remains an underdeveloped domain with high potential for green energy solutions.

Another critical gap in the literature is the combined operation of PENG and TENG units in a single hybrid configuration. Although hybrid nanogenerators have been proposed in certain studies, these often rely on planar stacking without precise air-gap control, leading to inconsistent triboelectric contact and sub-optimal energy conversion efficiency. Furthermore, very few reports have demonstrated hybrid devices capable of simultaneously delivering both high voltage (from TENG) and high current (from PENG) in a structurally flexible, durable, and lightweight format suitable for wearable integration. The optimization of structural parameters for both components within the hybrid system remains insufficiently addressed.

The absence of systematic research into electrospun ZnO–PVP nanofibers for PENG fabrication, the application of self-healing polyurethane with recycled sponge spacers in TENG design, and the synergistic stacking of these two technologies into a high-performance hybrid nanogenerator forms the primary gap addressed in this thesis. The proposed work aims to overcome these limitations by:

- Synthesizing and optimizing ZnO–PVP nanofibers via electrospinning for improved piezoelectric performance.
- Designing a vertical contact–separation mode TENG using UV-curable self-healing polyurethane and environmentally reclaimed sponge spacers for enhanced durability and sustainability.

- Integrating both devices into a hybrid configuration with precise mechanical alignment to achieve a balanced output of high voltage and high current, enabling direct powering of low-power electronic devices.

By addressing these gaps, the research seeks to contribute a scalable, eco-friendly, and mechanically robust hybrid nanogenerator platform capable of meeting the rising demands of self-powered wearable electronics, portable biosensors, environmental monitoring systems, and biomedical applications. This approach not only advances the energy harvesting capabilities of nanogenerators but also introduces sustainable design elements, bridging the gap between performance optimization and environmental responsibility.

3.4. Summary

The fabrication and characterization of hybrid nanogenerators, integrating piezoelectric and triboelectric effects, have emerged as promising approaches for energy harvesting applications. These systems synergistically combine the advantages of piezoelectric nanogenerators (PENGs) and triboelectric nanogenerators (TENGs), enabling efficient conversion of mechanical energy into electrical energy. PENGs leverage the piezoelectric properties of ZnO, which exhibits a high piezoelectric coefficient, environmental stability, and non-toxicity. Polyvinylpyrrolidone (PVP) is employed as a stabilizing and film-forming agent, enhancing the fabrication process and material integrity. ZnO-PVP-based PENGs are utilized in low-power devices, biomedical sensors, and self-powered systems. Advances focus on nanostructure engineering and composite optimization to improve energy output. TENGs operate on the triboelectric effect, with polyurethane being a key material due to its excellent dielectric properties, flexibility, and compatibility for surface modification. Charge generation is amplified through micro/nanostructured surface designs. Polyurethane-based TENGs find applications in wearable electronics, environmental monitoring, and mechanical energy harvesting, with ongoing research aimed at improving efficiency through material innovations and structural designs. Hybrid nanogenerators combine the PENG and TENG mechanisms to achieve higher energy output and broadened functionality. The integration of ZnO-PVP for piezoelectric response and polyurethane for triboelectric performance ensures complementary energy harvesting. Innovations focus on optimizing structural design and combining these materials in multi-layered or composite forms to maximize output voltage and current density. Hybrid nanogenerators are being explored for large-scale energy harvesting, IoT devices, and smart grids. Hybrid nanogenerators based on ZnO-PVP and polyurethane offer a sustainable and efficient solution for energy harvesting applications. By addressing current challenges and leveraging advancements in material science, these systems hold immense potential for powering future technologies in an energy-conscious world.

Chapter 4

EXPERIMENTAL TECHNIQUES

4.1. Fabrication Technique

This section includes all techniques and tools used during designing and fabrication process.

4.1.1. Spin Coater

By spinning a substrate at high speeds, spin coating deposits thin layers of material. There are various uses for this decades-old method. Fast and simple spin coating deposits thin coats on flat substrates. Spinning the coating solution onto the substrate spreads it and leaves a very uniform coating of the chosen material. In summary, spin coating has four stages: fluid dispense, spin-up, stable fluid outflow (spin-off), and evaporation-dominated drying. Stages 3 (flow controlled) and 4 (evaporation controlled) affect coating thickness most. This evidence shows that viscous flow and evaporation must always occur simultaneously [145].

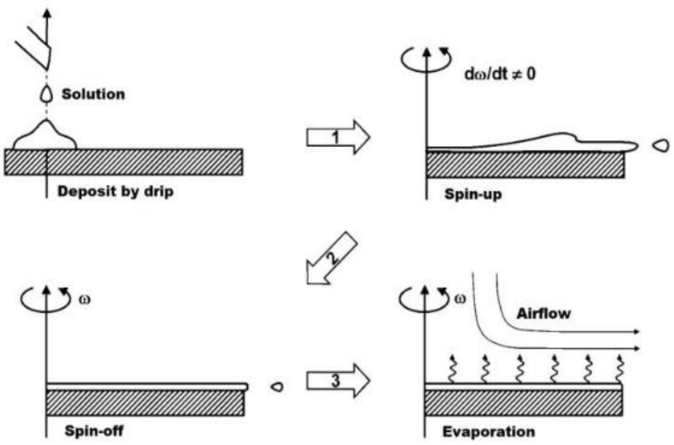

Figure 4.1: Stages of thin film deposition by the spin-coating method [146]

First, a pipette casts the solution onto the substrate. The solution will spread across the substrate, whether it is spinning before or after deposition (dynamic or static spin coating). After spreading at a lower speed, the substrate approaches the appropriate rotation speed. The majority of the fluid exits the substrate at this point. The fluid will level when drag balances rotational accelerations, even if it spins faster than the substrate. Because of viscous forces, the fluid thins. When we throw off the fluid, interference effects frequently modify the film colour. If the colour stops changing, the film is mostly dried. As fluid forms droplets near the edge to be thrown off, edge effects may occur. After fluid flow ends, solvent evaporation dominates thinning. Vapour pressure, solvent volatility, and environmental variables affect solvent evaporation. When the evaporation rate is uneven, like near a substrate's edge, the film will be uneven [147].

$$h_f \propto \frac{1}{\sqrt{\omega}} \qquad \text{………………… (4.1)}$$

Equation 4.1: Spin coating thickness equation

The equation shown below must be contented, when viscous and centrifugal forces are in balance,

$$-\eta \frac{\partial^2 v}{\partial z^2} = \rho \omega^2 r \text{ …………………… (4.2)}$$

In cylindrical coordinates, v is the fluid speed in revolutions per second (going outward), r and z that tie the revolution of the substrate, ρ is the fluid's density in grams per cubic centimeter, ω is how fast it rotates in radians per second, and η is the thickness of the fluid in poise [148]. The film width as a function of time, h(t), is given with suitable flow and velocity boundary conditions, and subsequently a film that is initially uniform,

$$h = \frac{h_o}{\sqrt{1+4Kh_o^2 t}} \text{ …………………………….. (4.3)}$$

At time zero, where h_o is the film viscosity (on the other hand not actually significant because of first stage of unstable solution exclusion at early time), and K is a system constant defined by

$$K = \frac{\rho \omega^2}{3\eta} \quad \text{…………………………… (4.4)}$$

This can be thought of as the fluid-dynamical “set” point of the coating process [148]. When these assumptions are made, the final coating thickness, h_f is predicted by

$$h_f = C_o \left(\frac{e}{2(1-C_o)K}\right)^{\frac{1}{3}} \text{ ………………………… (4.5)}$$

These techniques can be used for depositing PENG and TENG layer during our experimentation so that can develop our proposed hybrid nanogenerator. Basic Schematic and working principle are showed in Figure 4.2.

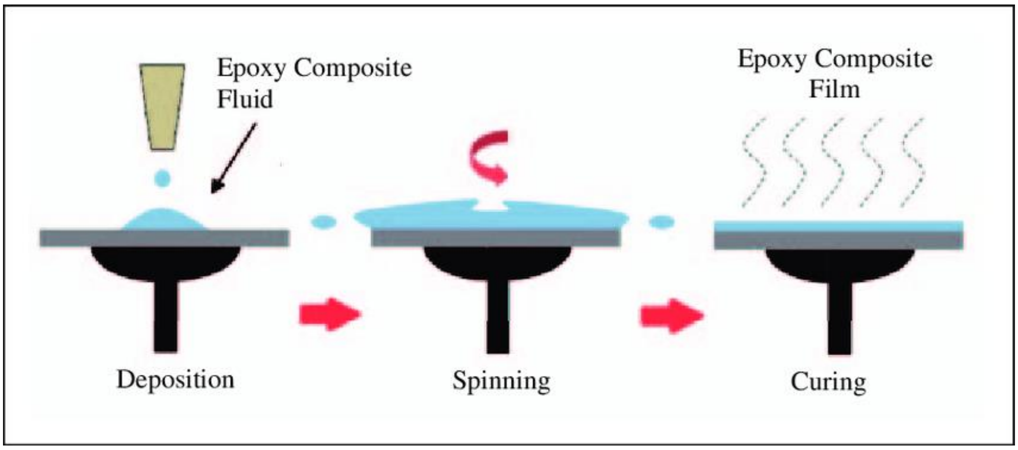

Figure 4.2: Spin Coating Process [149]

4.1.2. Magnetic Stirrer and Hot Plate

Magnetic stirrer and hot plate are laboratory instruments that mixes and heats solutions using a magnetic field and a heating element. In many scientific fields, it is used, together with biology, chemistry, and materials science. Hot plate magnetic stirrer is used to keep the liquid circulating with heating capability to obtain homogenous mixture. It is a simple laboratory equipment and increases the speed, reliability and safety for reactions. It includes a hot plate and magnetic stirrer as shown in Figure 4.3. It has dual control which allows the users to set stirring speed and set heat output independently. The Hot plate temperature can be varied up to 550 °C. The magnetic stirrer consists of a rotating or stationary magnet whose speed can be adjusted from zero to 1500 rpm. Design of devices determines the nature and intensity of mixing. Magnetic stirring can be done with a chemical agent in closed or open system [150]. Due to small size of stirring bar it is easily be cleaned and sterilized. They don't require any lubricants for cleaning which could contaminate the product or reaction. The devices are inserted in a liquid to spin very quickly to give homogenous mixture.

Figure 4.3: Hot plate and magnetic stirrer

4.1.3. UV Lamp

UV curing, or ultraviolet curing, is a photochemical process that uses ultraviolet (UV) light to harden inks, adhesives, and coatings. It's a solvent less, high-speed, low-temperature process that's used in many industries. UV Curing uses UV lamps to spark a chemical reaction or physical activity that makes a bond or substance stronger, tougher, or more stable. Recent decades have seen remarkable UV curing technology growth. Since it can be processed and packaged in seconds, instant curing technology has extended beyond printing [151]. Some materials are UV curable and they get harden or soften by passing through UV light. Sun is major source of UV radiation. Our grown PENG and TENG layer are passed through UV light to get harden and reduce the adhesiveness. These both are used Sun Light as well as artificial UV lamp for completing this process.

4.1.4. Electrospinning (ES)

The electrospinning method uses a high electric potential between opposite-polarity electrodes. High voltage can break through the surface tension in a polymer solution or melt, allowing the solvent to evaporate and the fibers structure to form [152]. From a polymer solution, a voltage driven fabrication technique called electrospinning produces small fibers using electro hydrodynamics. This process requires usually a syringe, a reservoir, a pump, a blunt needle (for needle-based electrospinning), a collector and a high-voltage power source.

Starting the spinning process, a determined voltage produces an electric field among the collector and needle tip. Though the pump keeps the solution flowing, on the liquid's surface charges build up. When electrostatic repulsion exceeds surface tension, the liquid meniscus warps into a Taylor cone. At the needle tip, the movement transforms from soaked to a charged cone-shaped structure [153].

Figure 4.4: Taylor cone formation with and without a potential difference [153].

When the Taylor cone forms, the charged liquid jet ejects to the collector. Different geometrical configurations of collectors include flat plates, revolving drums, mandrels, and disks, among others. As solvent evaporates, the process forms solid fibers if the solution's viscosity is above a certain threshold. Violent whipping between the cone and collector deposits a non-woven fiber mat on the collector [154]. This technique can be used in the fabrication process of PENG which is based on ZnO and PVP. And achieved very good Taylor cone and fibers from electrospinning. How electrospinning works it is shown below in Figure 4.5.

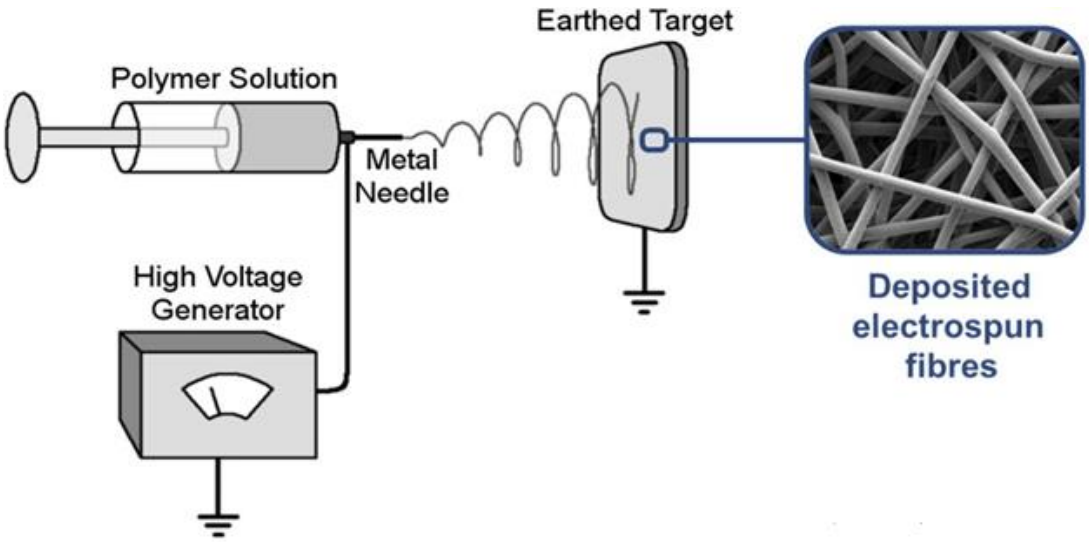

Figure 4.5: Working mechanism of Electrospinning

4.2. Characterization Technique

In this section of the chapter some basic characterization technique and tools are presented. Including Surface morphology technique, Oscilloscope, Picoammeter, X-ray diffraction and I-V Characterization technique.

4.2.1. I-V Characterization

Current-voltage Analysis is done to accurately map the characterization and efficiency of the nanogenerators that helped in accessing the quality of the nanogenerators material and film. This is also important to see the impact of the contacts and the device assembly on to the performance. Current voltage analysis relationship is given by equation.

$$I = \frac{V}{R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.6)$$

Where I is current, V is voltage and R is resistance. This technique is used to evaluate the effect of electric field with respect to the movement of charges. Different voltage levels are applied and accordingly current can be measured with respected to them, applied voltage can be either AC or DC depending on the requirement. Using copper contacted anode and cathode, characterizations are performed using Current and Voltage (I-V) analysis with two probe technique [155]. At several ambient conditions, Current and voltage tests are conducted to examine sustainability of the ultra-capacitor and the thermal stability. I-V characteristics of nanogenerator is found by connecting one probe to anode and other probe to cathode of the nanogenerator [156]. Applying voltage to the nanogenerator and measuring the current behaviour during charging and discharging can tell us the performance of nanogenerator.

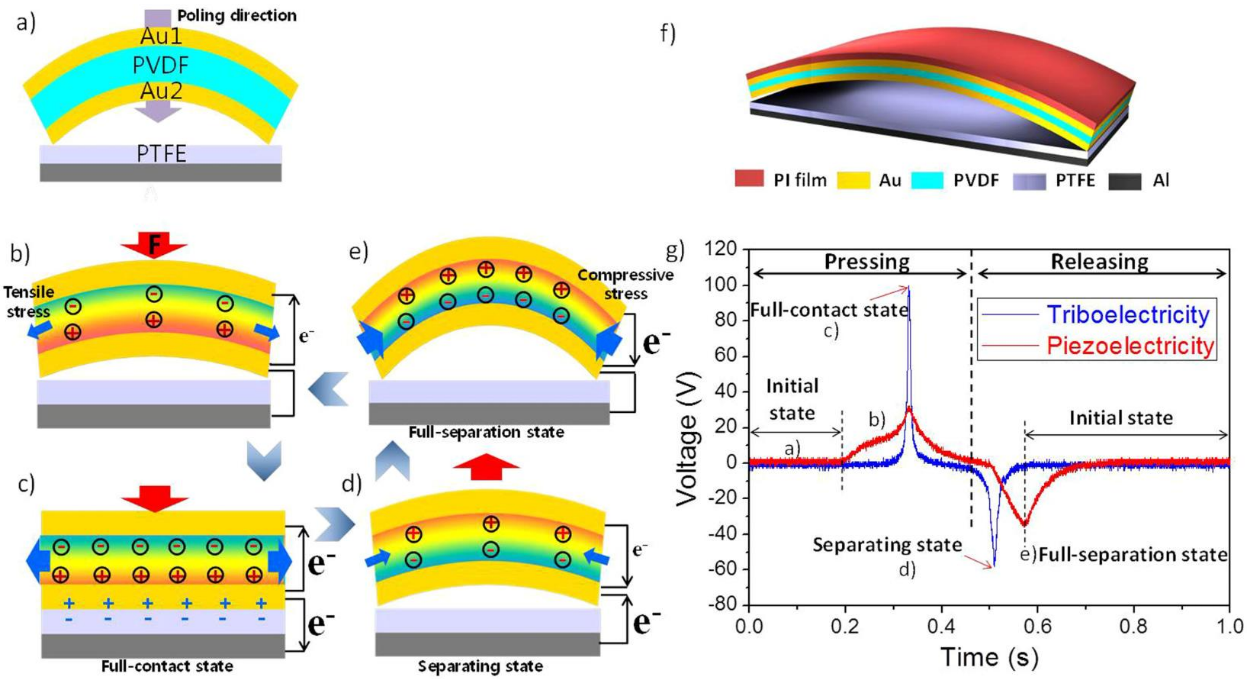

Figure 4.6: I-V characteristics of Hybrid Nanogenerator [157]

4.2.2. Digital Oscilloscope

A digital oscilloscope, also known as a digital storage oscilloscope (DSO), is a device that measures and records electrical signals. It converts analogue signals into digital data, which can then be stored, analysed, and displayed. Digital Oscilloscope is one of the common characterizations and voltage/current measurement tool found in every Electronic related laboratory [158]. From our developed hybrid nanogenerator, to measure the produce current and voltage, digital oscilloscope is used and recorded different measured value to optimize and analyse the developed Hybrid NG. By digital storage oscilloscope, open circuit voltage (V_{oc}) of the nanogenerator was measured,

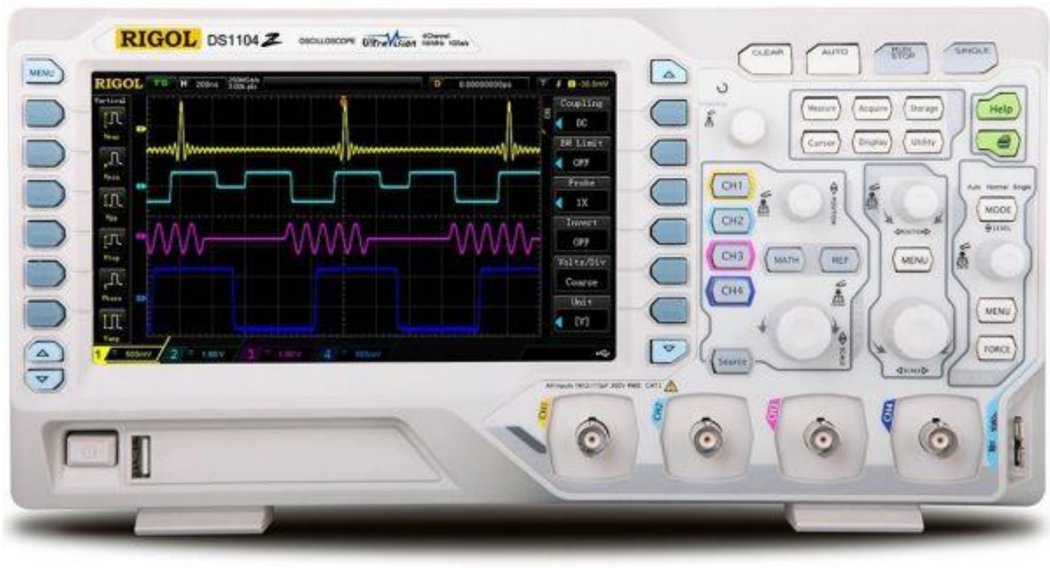

Figure 4.7: Oscilloscope

4.2.3. Picoammeter/Femtometer

A Picoammeter is a device that measures extremely small electric currents, or pico amps (pA)**.** They are used in experiments and other applications that require high sensitivity. In hybrid nanogenerators, for current measurements it can be used. It gives current value probably in micro ampere’s (uA) and in nano ampere’s (nA). Here, Figure 4.8 shows Picoammeter.

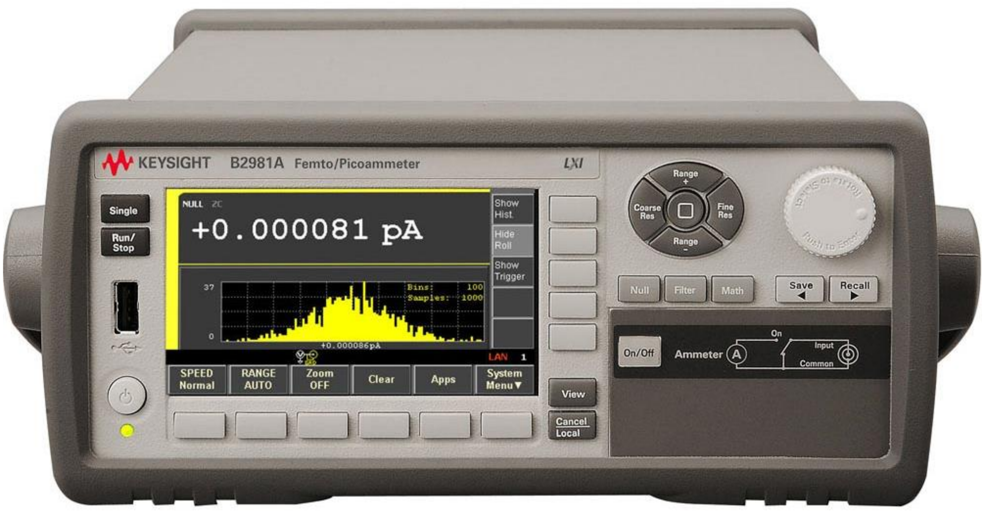

Figure 4.8: Picoammeter/Femtometer

4.2.4. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) employs X-rays to diffract light into multiple directions to define groupings of atoms or the precise places in a crystal or amorphous material. XRD is the one research laboratory technique that non-destructively and accurately measures crystal structure, chemical composition, orientation, lattice strain, crystallite size, layer thickness and preferred alignment. XRD is used to study powders, solids, thin films, and nanomaterials by materials researchers [159]. Tiny crystallites make up many materials. 'Phase' of these crystals is their structural and chemical makeup. Materials can be multiphase or single phase mixtures of non-crystalline and crystalline components. Different crystalline stages yield different X-ray diffraction patterns. X-ray diffraction patterns from unknown substances can be compared to orientation databases to identify phases. The process is like comparing crime scene fingerprints [160]. This technique is used in both PENG and TENG. Here, shown in Figure 4.9., the working mechanism of X-ray diffraction technique.

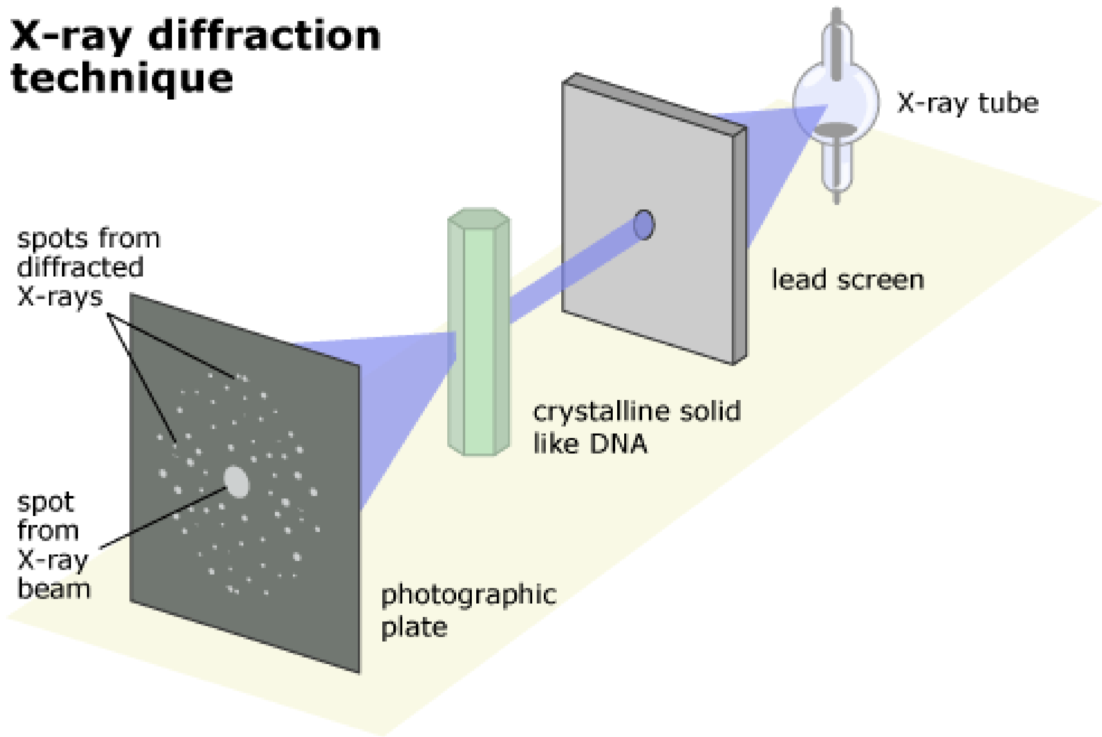

Figure 4.9: X-ray Diffraction Technique

4.2.5. Scanning Electron Microscopy

Scanning electron Microscopy (SEM) is one of the most important instrument available for the investigation and analysis of the chemical composition and microstructure morphology of sample. Light microscopy has been, and continues to be, of great importance to scientific research. Using electron beams on surface of sample, SEM is used to produce images of a sample. Surface composition and topography is obtained by the interaction of electronic beams with the sample surface giving signals that contain information. It is effective for analysing organic and inorganic materials on micrometre and nanometre scale. The magnification of SEM reaches to 300,000x and even above than that in modern models. The SEM probes surface morphology with a high-energy electron beam. In an electron gun, Tungsten filament having parameters 100 microns and 2700 K, functions by means of a cathode, and electron beam in a vacuumed chamber emitting a high energy that is 30 keV and current approximately ~3 A. SEM machines have an electron gun, scan coils for refraction, two or more electromagnetic lenses, a backscattered electron detector and a sample chamber, secondary electron, and to view scanned images a computer system with show screens and to control the electron beam a keyboard is used. SEM may reveal micro- and Nano spaces. SEM reveals details and intricacy that optical microscopy cannot [161].

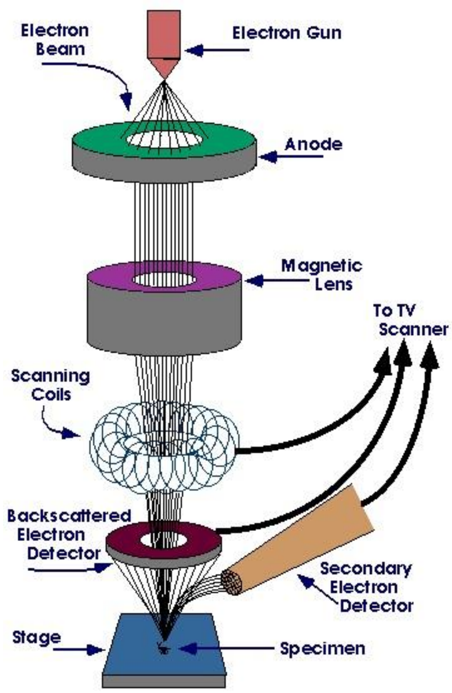

Figure 4.10: Different Parts of SEM [162]

4.3. Summary

Chapter 4 provides a detailed account of the experimental methodologies employed in the fabrication and characterization of the hybrid nanogenerator designed for energy harvesting applications. The fabrication process begins with spin coating, a widely used technique to deposit uniform thin films of polyvinylpyrrolidone (PVP) and other active materials onto substrates, ensuring controlled thickness and surface uniformity. This is followed by hot plate treatment, which aids in the thermal curing of the coated layers, enhancing their adhesion and stability. Electrospinning is then utilized to fabricate Nano fibrous structures of zinc oxide (ZnO) or polymer composites, contributing to the piezoelectric component of the hybrid system by increasing surface area and mechanical responsiveness. For material characterization**,** X-ray diffraction (XRD) is employed to analyse the crystalline structure of the synthesized materials, verifying phase purity and structural integrity. Scanning electron microscopy (SEM) is used to study surface morphology, particle distribution, and nanostructure alignment, offering crucial insights into how material characteristics influence device performance. Furthermore, current-voltage (I-V) measurements are conducted to evaluate the electrical output behaviour of the device under various mechanical stimuli, enabling the assessment of energy harvesting efficiency. Together, these techniques form an integrated approach to both optimize the structural design and validate the functional capabilities of the nanogenerator. This experimental framework establishes a strong foundation for achieving high-performance, scalable, and application-ready energy harvesting systems.

Chapter 5

MATERIAL CHARACTERISTICS AND DEVICE PROCESSES

[1]. **Saba Ejaz**, Gul Hassan, Ahmed Shuja. 2025 “Fabrication and Characterization of Piezoelectric Nanogenerator Based on ZnO and PVP for Harvesting Energy System Applications”, in *Journal of Materials Science: Materials in Electronics* ***(Published)***.

[2]. **Saba Ejaz**, Imran Shah, Shahid Aziz, Gul Hassan, Ahmed Shuja, Muhammad Asif Khan and Dong-Won Jung. 2025 “Fabrication and Characterization of a Flexible Polyurethane-Based Triboelectric Nanogenerator for a Harvesting Energy System” in *MDPI Journal of Micromachines*, 16(2), 230; **https://doi.org/10.3390/mi16020230** ***(Published)***.

Both works contribute directly to the hybrid nanogenerator processes presented in this chapter. This chapter describe the brief overview of materials properties, which are used to develop the proposed device. Furthermore, this chapter also include the process followed during fabricating and designing the device. By consideration of such material properties, different application can be retrieved, such as energy harvesting and sensing etc.

5.1. Overview of Zinc Oxide

Zinc oxide (ZnO), a semiconductor, is used in luminescent, solar cells, acoustic, electrical, and chemical sensors [163]. Zinc Oxide (ZnO) is a powdery, white, water unsolvable inorganic substance. The earth's crust contains zincite, which is also available for marketable manufacture. ZnO nanoparticles (NPs) can be synthesized through chemical and green methods. ZnO is an II–VI semiconductor since it contains oxygen which is in 6th group and zinc which is in 2nd group, of Periodic Table. ZnO semiconductors have a broad bandgap and 3.3 eV of energy at ambient temperature [164]. Zinc Oxide (ZnO) is a widely used material in nanogenerators due to its piezoelectric properties, meaning it can generate electricity when mechanical stress is applied, making it a promising candidate for harvesting energy from ambient vibrations; its key advantages include being readily available, low cost, biocompatible, and having well-established synthesis techniques, allowing for the creation of efficient nanogenerators in various forms like nanorods or nanowires.

5.2. Properties of Zinc Oxide

5.2.1. Piezoelectric Nature

The crystal structure of ZnO (typically wurtzite) lacks a centre of symmetry, allowing for charge separation when mechanical strain is applied, generating an electrical potential. Zinc is initiate in rock salt which is cubic in configuration, in wurtzite which is hexagonal in structure, and in zinc blende which is also cubic in structure. Four O^{2-} anions surrounded by Zn^{2+} cation it shows that it has hexagonal structure which is the utmost dominant. The tetrahedral shape, with measurements of (a) which is rock salt that is 0.3296nm and (c) which is wurtzite that is 0.52065 nm, causes wurtzite ZnO to lack a center of symmetry. The ZnO tetrahedron has four different bond lengths. Other than three structures the c-axis bond which is wurtzite that is longer [165]. Therefore, leading to divergence along the axis of the unit cell, dipoles do not nullify, as shown in Figure 5.1.

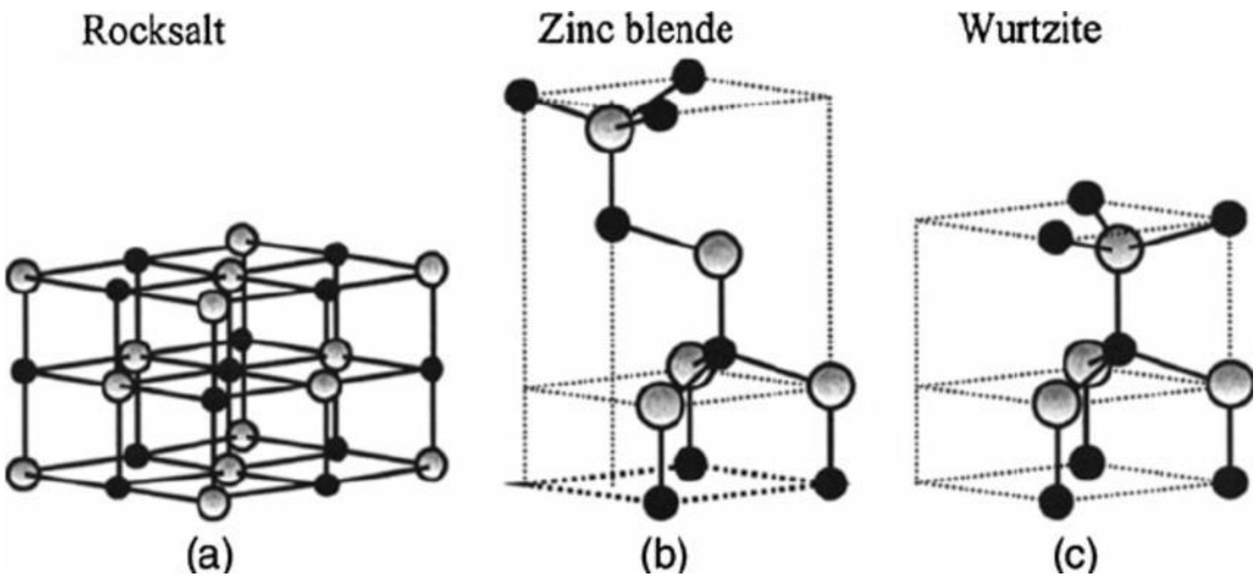

Figure 5.1: ZnO crystal structures: cubic rocksalt (a), cubic zinc blende (b) and hexagonal Wurtzite (c). The shaded gray and black spheres represent zinc and oxygen atoms[166].

5.2.2. Synthesis Methods

Over and done with numerous approaches, Zinc oxide (ZnO) can be produced, including the utmost common precipitation method where a zinc salt solution is reacted with a base to form a precipitate of ZnO, alongside other approaches like sol-gel synthesis, hydrothermal synthesis, microwave-assisted synthesis, and green synthesis using plant extracts or microbial organisms to produce environmentally friendly nanoparticles[167].

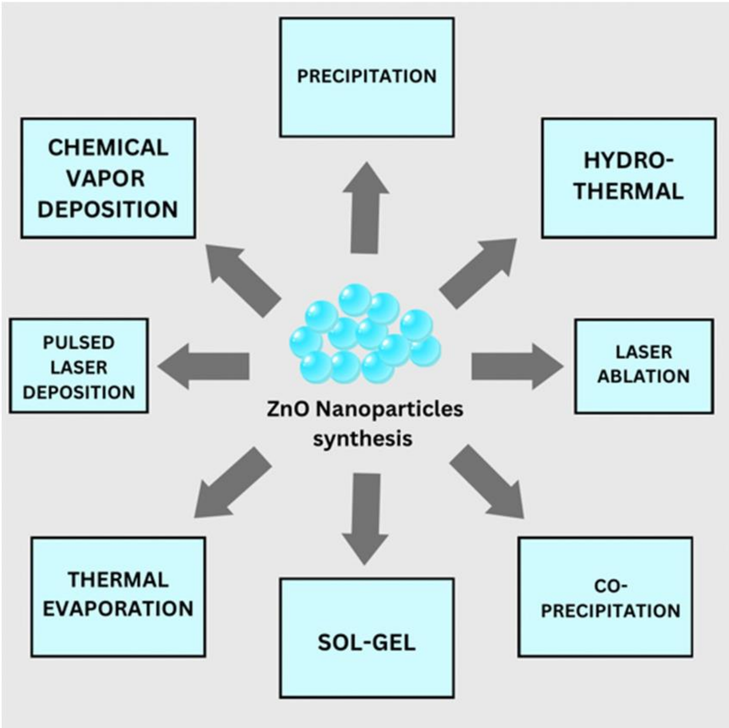

Figure 5.2. Synthesis methods for ZnO [168]

5.2.3. Mechanical Properties of ZnO

Mechanical properties of material are important and essential when materials are utilizing for electromechanical applications. Some of basic characteristics of material are softness, hardness, stiffness, young modulus etc. Apart of that one of the best properties of material is strain measurement, strain represent the deformation accrued due to any external force or stress etc. As the proposed work, are directly related to electromechanical applications and thus the investigation of mechanical properties of ZnO is essential part [169]. To deeply synthesis material for electromechanical application and achieve optimum results, deep knowledge of mechanical properties of any material is the key requirement. Single NW mechanical properties are challenging due to experiencing mechanical test as reported in [170]. Because of the incredibly popularity for ZnO-based piezoelectric nanogenerators (NGs), the study and understanding ZnO mechanical behaviour is indeed very essential. Structural characterization of NSs therefore plays a major role in developing effective and reliable piezo electrical devices and applications i.e., sensors etc.

5.2.4. Piezo Properties

Mechanical energy is converted to electrical energy by piezoelectricity. The direct piezoelectric effect is the material which has piezoelectric properties that has stress to generates electrical polarization. Stress is generated once electric fields are applied to piezoelectric materials. Piezoelectricity happens only in twenty out of thirty-two types of crystals that have hemimorphic unit cells and lack a center of symmetry [171].

Piezoelectric effect or in short Piezo effect was introduced by Pierre and Jacques in 1888. This effect is one of essential characteristics of some material by mean of which mechanical energy is directly convert to electrical energy. The concept and theories beyond piezoelectric effect are already discussed in previous chapters. So, till today it is observed and reported that the piezoelectric effect is found in those material which exhibit the non-centrosymmetric crystal structures [172]. As already discussed, that ZnO are one of those material which has non-centrosymmetric crystalline structure and thus piezoelectric effect accrued in ZnO on apply any external stress/force. Some other material like polyvinyl adenine fluoride (PVDF) etc. exhibit too such properties [173].

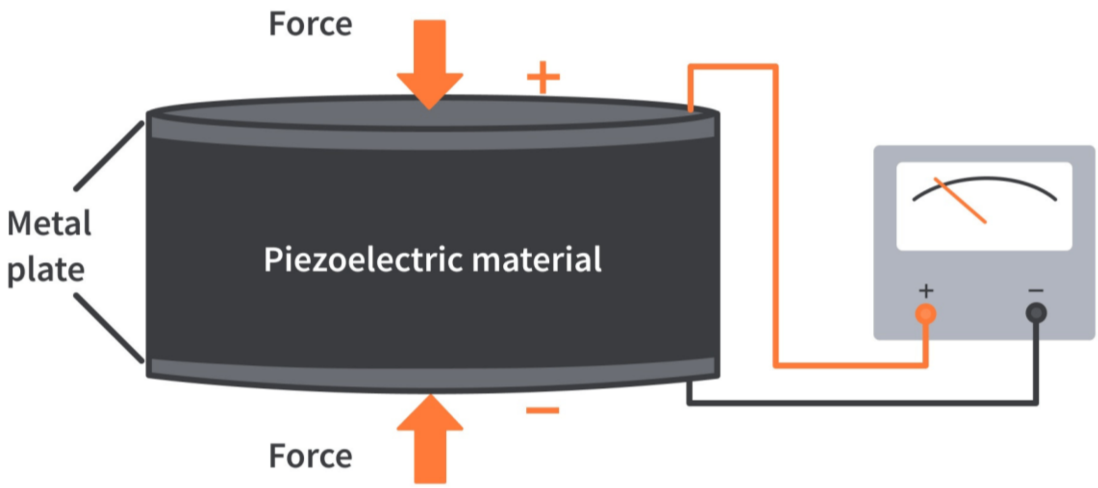

Figure 5.3. Piezoelectric material [174]

5.2.5. Electrical Properties of ZnO

As already discussed, that the bandgap is one of the most important and considerable features of material and a lot of applications are dependable on such feature. ZnO is wide bandgap substantial and thus it has huge quantity of uses in optoelectronics and electronics. It possesses comparatively high break down voltage in comparable to other similar bandgap material. Apart of that some other properties like, the high temp and low noise electrical applications, comparatively higher breakdown voltages etc. are also linked with wide bandgap in semiconducting materials. To tune the bandgap between 3-4 eV, the ZnO is alloyed with other material i.e. Cadmium Oxide or Magnesium Oxide [175].

The transport properties in ZnO can be alter by varying the strength of electric field. While having low electric field energy of electron is comparative lower than thermal energy electron. So, this conclude that in this case (low electric field) the variance in electron distribution is negligible. And thus, the mobility will remain same as well, in other words the rate of scattering unaffected too and so far, the Ohm's law proliferates [176]. In the presence of high electrical field than the thermal energy, the distributions mechanism of electron is differed from its stable state while the electron energy is more than thermal energy. Because none of energy is released into crystal structure, electron may have a very large drifting speed, which ensures that the materials can be useful in high frequencies applications. In n-type ZnO (intrinsic) the source conductivity is found to be due to O-vacancies and Zn interstitials. However, there will always be an open discussion upon these sources and the properties variance due to point defects [177].

5.3. Overview of Polyurethane (PU)

Polyurethane is a synthetic polymer that belongs to the plastic family and is widely used across various industries due to its versatility, durability, and resistance to wear and tear. It was first developed in 1937 by the German scientist Bayer, and since then, it has become an essential material in numerous applications. Polyurethane is known for its ability to be either flexible or rigid, making it suitable for a wide range of products [178].

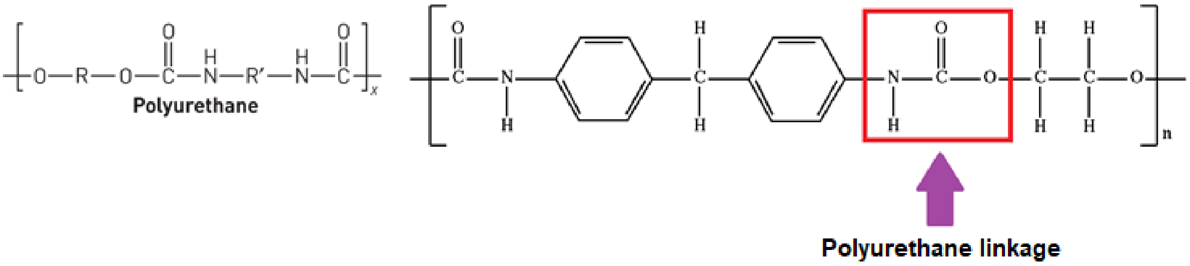

Figure 5.4. Polyurethane Structure

There are two main types of polyurethane: thermosetting and thermoplastic. Thermosetting polyurethane retains its shape once it has been moulded and hardened, whereas thermoplastic polyurethane can be reheated and reshaped. This polymer is found in different forms such as foams, coatings, adhesives, sealants, elastomers, and fibers [179]. Some of its most common applications include furniture, mattresses, footwear, automotive parts, construction materials, and insulation.

One of the key advantages of polyurethane is its waterproof, chemical-resistant, and abrasion-resistant properties. Despite being lightweight, it is highly durable and provides excellent structural support in various products. In its foam form, it is commonly used in cushions, bedding, and packaging, while in its rigid form, it is used for insulation in buildings, refrigerators, and industrial equipment [180]. With growing environmental concerns, researchers are now working on making polyurethane eco-friendlier and sustainable [181]. Traditional polyurethane is not biodegradable, which poses a challenge for waste management. Scientists are developing bio-based polyurethanes made from renewable resources, which could help reduce environmental impact and improve recyclability[182]. As technology advances, polyurethane is expected to become an even more sustainable and widely used material in the future.

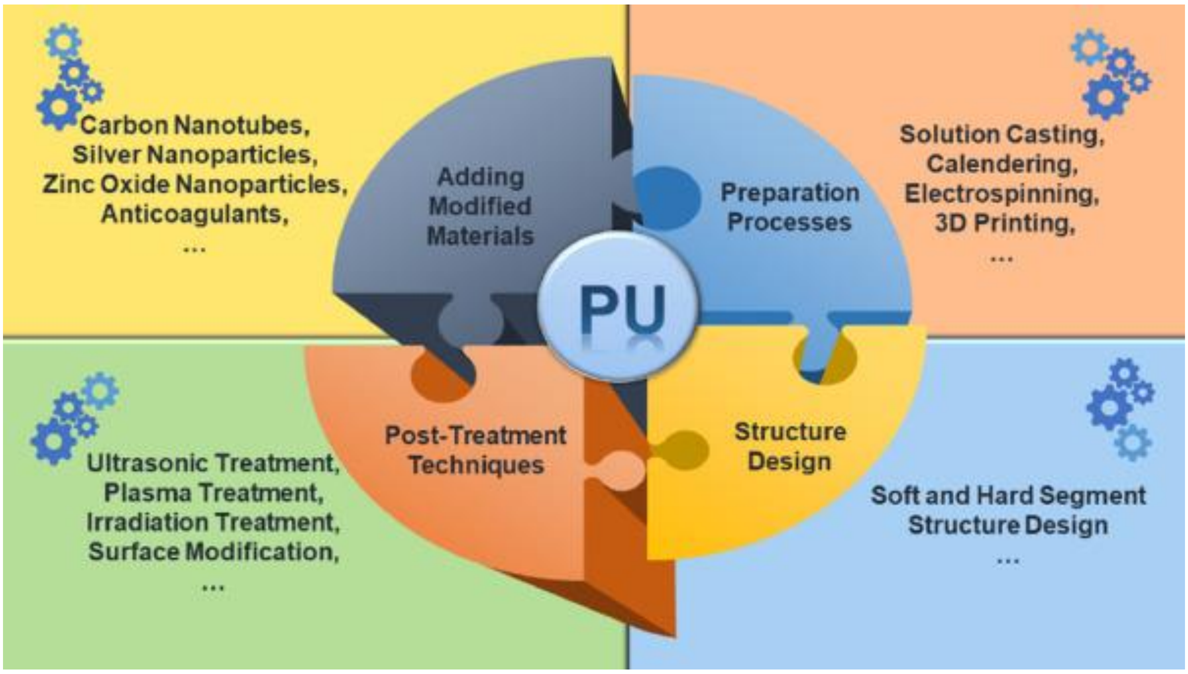

Figure 5.5. Methods for functionalizing PU materials

5.3.1. Application of Polyurethane (PU)

With a wide range of applications across multiple industries, Polyurethane is an extremely flexible material. One of its most common uses is in the furniture and bedding industry, where it is used to make cushions, mattresses, and upholstered furniture due to its excellent comfort, flexibility, and durability. The soft foam structure of polyurethane makes it ideal for providing support and pressure relief in seating and sleeping surfaces. In the construction industry, polyurethane is widely used for insulation purposes [183]. Rigid polyurethane foam is an excellent thermal insulator, by reducing heat loss which helps to improve energy efficiency in buildings. It is also used in sealants, adhesives, and coatings to provide protection against moisture, corrosion, and wear. Additionally, polyurethane-based paints and coatings enhance the durability and appearance of floors, walls, and wooden surfaces [184].

Another major application of polyurethane is in the automotive industry. It is used to manufacture car seats, headrests, interior panels, and insulation components. The lightweight yet strong nature of polyurethane helps improves vehicle fuel efficiency while maintaining safety and comfort. Additionally, polyurethane coatings and paints protect vehicles from harsh weather conditions and scratches [185].

In the footwear industry, polyurethane is used to make soles for shoes and sandals. It provides excellent shock absorption, flexibility, and wear resistance, making it an ideal choice for sports shoes, casual footwear, and work boots. Similarly, in the sports and recreation industry**,** polyurethane is used in making artificial sports tracks, swimming pool liners, and even protective gear like helmets and knee pads. Polyurethane is also essential in the electronics and appliance industry**,** where it is used as an insulating material for refrigerators, freezers, and air conditioners [186]. It helps maintain temperature efficiency and reduces energy consumption. Furthermore, polyurethane adhesives are commonly used in assembling electronic devices and components due to their strong bonding properties. With its remarkable properties, polyurethane continues to be a crucial material in modern manufacturing and daily life. Its durability, flexibility, and resistance to environmental factors make it indispensable in various sectors, and ongoing research is making it even more sustainable and efficient for future applications [187].

5.4. Device Fabrication processes

In this section of thesis, various steps are followed during the fabrication of proposed hybrid nanogenerator device.-A part of that packaging of complete device are also discussed and some photographs of fabricated device are also included to compare the proposed device schematic with the fabricated device.

5.4.1. PENG Development Process

For PENG development process, two materials are used one is Zinc Oxide and other is Polyvinylpyrrolidone. The ZnO powder (<100 nm particle size), PVP powder (average Mw ~55,000) and DMF (anhydrous, 99.8%) were procured from Sigma-Aldrich, USA. The other materials including Aluminum electrode were procured from China.

5.4.1.1. Synthesis of ZnO-PVP solution

ZnO has 60 meV of binding energy and 3.37 eV of an energy bandgap is chemically, electrically, and thermally stable. Moreover, it shows excellent optical, electrical and photocatalytic properties. However, PVP is a water-soluble polymer obtained from the monomer N-vinylpyrrolidone. It is available in a variety of molecular weights and corresponding viscosities and is suitable for piezoelectric applications. ZnO Powder mixed with PVP powder by weight at (1:0.5), (3.5:4), (3.5:6.5), (3.5:6.5), (3.5: 6.5 g) respectively in 6ml of DMF, by varying constraints for example (Needle Range, Voltage, Distance, Feed rate, Time) as shown in Table 5-1. The ZNO-PVP solution beaker kept place on magnetic stirrer, for 24 hours, set the temperature at 70^{o}, rpm at 380. Figure 5.6. shows, the schematic design of solution preparation.

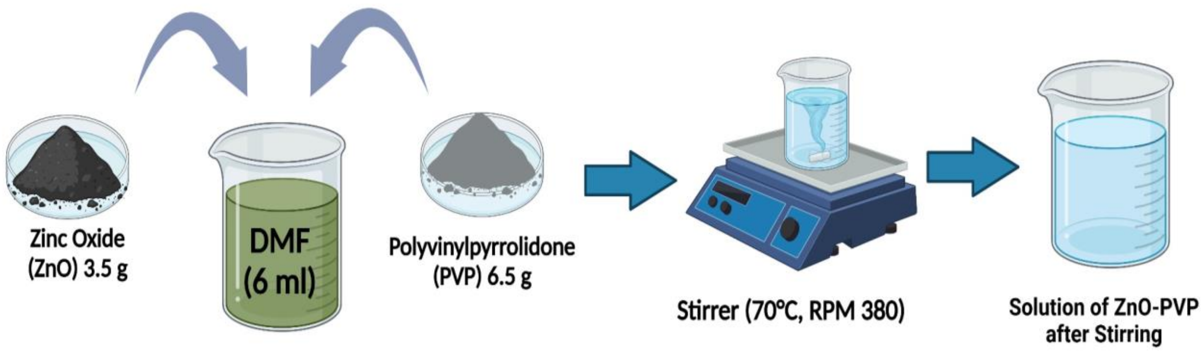

Figure 5.6: Schematic Design of ZnO-PVP solution

5.4.1.2. Electrospinning of ZnO-PVP Solution

Five different types of solution were prepared by considering different parameters. These five solutions were further feed to electrospinning process, to examine the quality of fibers. The prepared solutions were again passing from ultra-sonication for 30 minutes to ensure the homogeneity of the solution. The solution was to feed one by one to the electrospinning process, as shown in Figure 5.7. the parameters were changed for (Voltage, Feed rate, Needle Range, Distance, Time) as shown in Table 5-1 respectively and the fibers existence and quality were investigated.

Table 5-1: Parameters for solution preparation

Factors	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
ZnO + PVP+DMF	1g + 0.5g + 6ml	3.5g + 4g + 6ml	3.5g + 6.5g + 6ml	3.5g + 6.5g + 6ml	3.5g + 6.5g + 6ml
Voltage	9.13 kV	8.85 - 14.0 kV	8.44 kV	12.07 kV	8.07 - 9.45 kV
Feed rate	0.02	0.05	0.05	0.050	0.050
Needle Range	20	20	21	21	21
Distance	12 cm	12 cm	12 cm	12 cm	12 cm
Time	20 mins	30 mins	1 hour	1:30 hours	3 hours
Results	No fibers because the solution is dilute	No, fibers just spraying	Taylor cone fibers created.	Taylor cone fibers created	Taylor cone nano fibers created in a good form

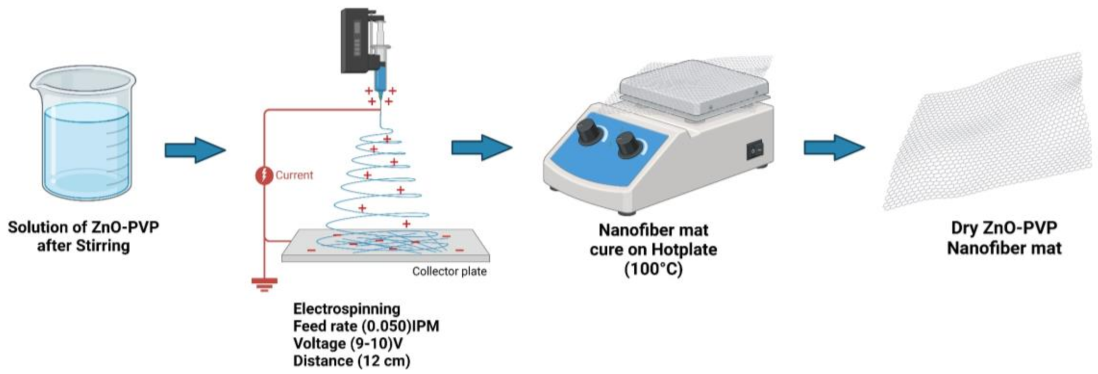

Figure 5.7: Schematic Illustration of ZnO-PVP fibers preparation

5.4.1.3. Response of ZnO-PVP solution in Electrospinning:

The five different types of solution were prepared by varying different parameters as mentioned in Table 5-1. These five solutions were loaded into a plastic syringe equipped with a needle. The ES process was proceeded by selecting parameters such as (Voltage, Feed rate, Needle Range, Distance, Time) as shown in Table 5-1. No fibers were produced in experiment 1-2, while in experiment 2-3 the fibers were produced in low quality, while in experiment no. 5 the fibers quality were good and Taylor cone nanofibers in good form were produced. The fibers mixture was deposited on Al sheet, by operating at 9.45 kV voltage and 0.050 feed rate, after ES the Al foil was placed on hot plate for 24 hours at 90^{o} C. The deposited layer of ZnO-PVP was peeled off as shown in Figure 5.8a and PENG device were made as shown in Figure 5.8b.

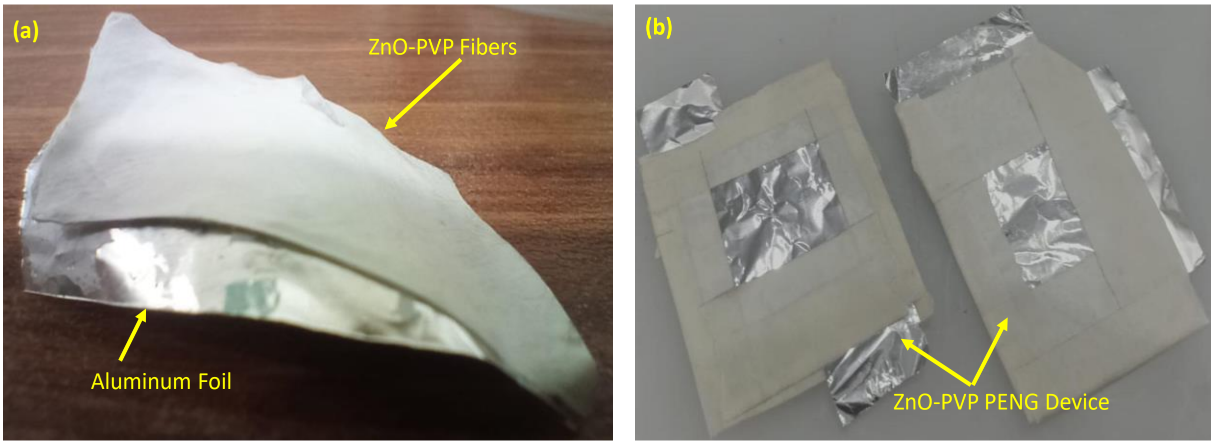

Figure 5.8: (a) deposited layer of ZnO-PVP (b) PENG Device

5.4.1.4. Fabrication of PENG Device, Mechanism and operation process

The ZnO-PVP composite fibers mat were folded and sandwiched with two Al foil as electrode. The mechanism and operation process of the fabricated PENG device are illustrated in Figure 5.9., which provides an overview of its working principles, operation, and output responses. Initially, the device remains in an unchanging state, with no external force exerted and no observable output voltage. To activate the device, an external force is applied using finger-tapping, as shown in Figure 5.9. During the pressing phase, the tapping force compresses the layers of the device, initiating charge accumulation at the interfaces due to the piezoelectric effect. This cyclic pressing and releasing action results in periodic changes in charge accumulation, reflected in the dynamic output voltage profile observed in oscilloscope. On PENG device with the help of finger tapping it can generate power, and output currents and voltages was examined using a Picoammeter and an oscilloscope respectively.

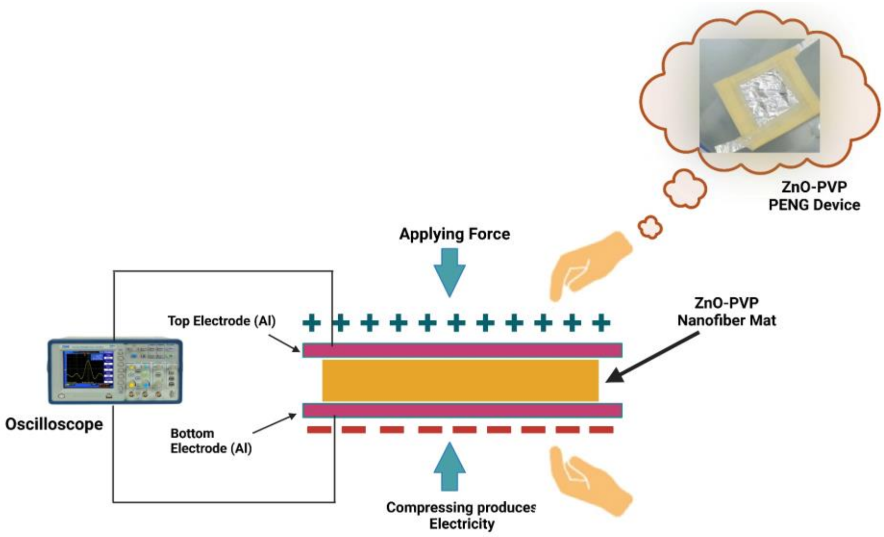

Figure 5.9: Mechanism and operation process of ZnO-PVP PENG Device

5.4.2. TENG Development Process

A nanogenerator was proposed for triboelectric effect harvesting. Bendable vertical contact separation mode TENGs were made from polyurethane (PU). UV-curable PU constitutes TENGs. For improved triboelectrification, to preserve an air gap among tribo-layers a landfill-recycled sponge functions such as a spacer. Triboelectric nanogenerators can monitoring systems by lighting LEDs, power Wi-Fi, portable devices, and charging capacitors. They could use the TENG to self-powered wearable electronics and develop ecological, for energy-efficient and eco-friendly applications. The PU-TENG undergoes tests with charge storage devices and many electrical loads to determine harvesting mechanical energy. Figure 5.10 illustrates the suggested TENG structure.

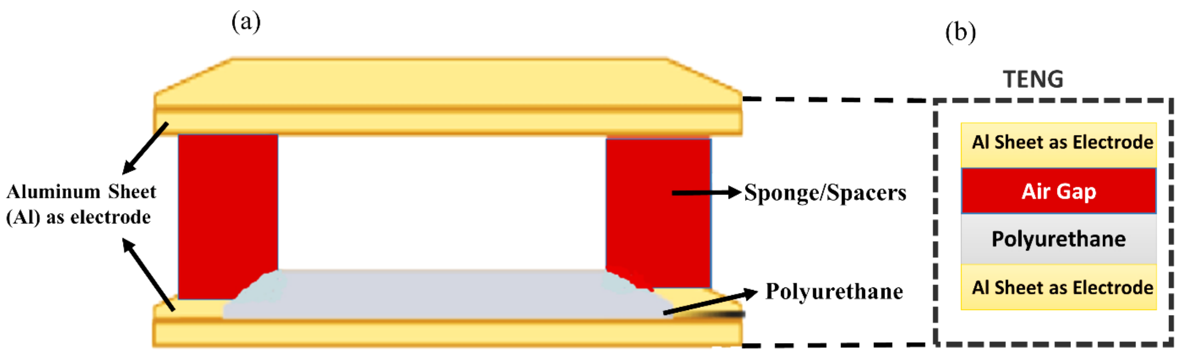

Figure 5.10: (**a**) Structure of the proposed TENG. (**b**) Zoomed-in structure of the TENG.

5.4.2.1. Methodology and Experimentation

This TENG has four main modes: self-supporting triboelectric layer, vertical contact separation, single electrode (SE), and in-plane contact sliding. For the TENG study, they work on vertical contact separation mode.

➢ ***Vertical Contact Separation Mode***

Figure 5.11a illustrates the TENG's operation and harvesting performance. Figure 5.11b illustrates Figure 5.11a's technique with TENG output voltages. The gadget starts consistently without effort, as seen in Figure 5.11a. Despite erroneous voltage generation due to environmental variables and illumination, Figure 5.11b shows noise. Explaining the mechanism by hand-tapping the device helps. Finger tapping and pushing begin in Step 2 (Figure 5.11a). The output curve changes as charges develop (Figure 5.11b). In Figure 5.11a, during step 3, the TENG peaked at 80 volts. PU and Al electrodes are fully contracted. Pressure is released, and the device stabilizes after compressing. Discharging during triboelectrification created a negative peak (Figure 5.11b). In the external circuit, that opposites triboelectric charges and modifies the electric field in Figure 5.11a. Negative peak and positive peaks are different, for the reason that the device's external force and the substrates or layers healing forces vary.

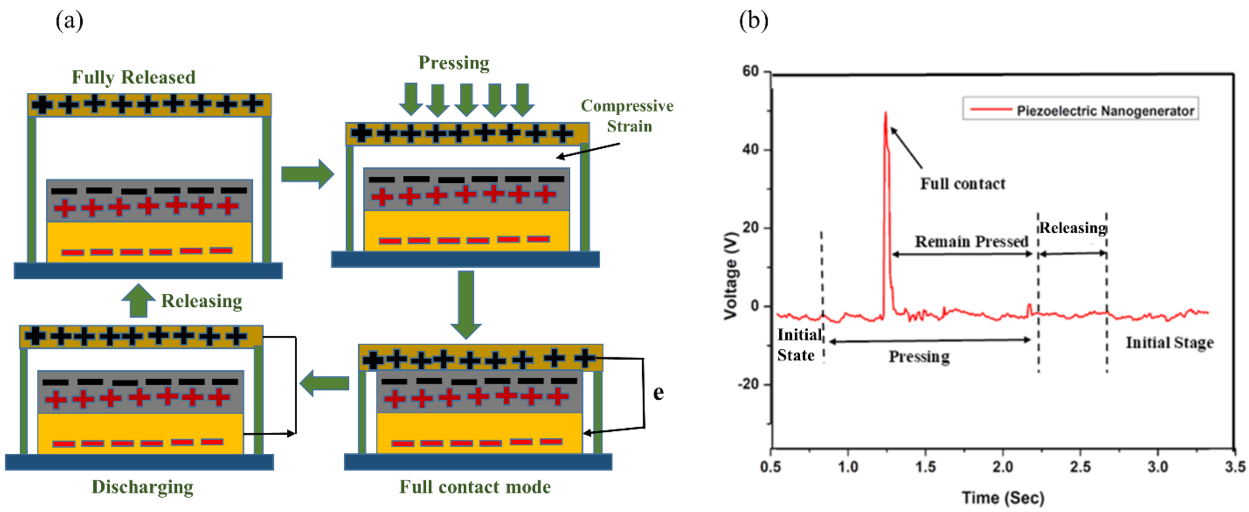

Figure 5.11: (a) Complete mechanism process of Proposed TENG, (b) Generated Output Voltage

5.4.2.2. Design Principle of TENG

The strategy to design a TENG which starts with Aluminum foil that is wrapped on PET sheet to show that it is an electrode. Due to its versatility, polyurethane (PU) is melted as a thin solution in the darkroom to manufacture triboelectric nanogenerators (TENGs) to produce energy. In the middle of the end electrode, a spatula is used to layer polyurethane to form a thin, smooth layer and cure the PU layers using UV light. The UV treatment cures and smooths the surface, as seen in Figure 5.12. Once it dries, a PET sheet and Aluminum foil form a new top electrode.

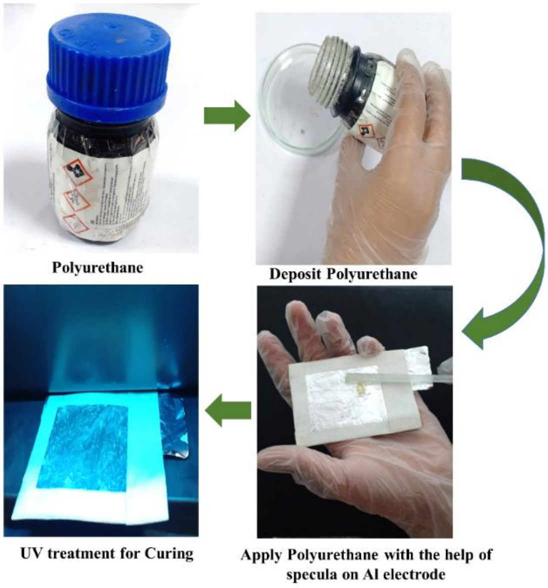

Figure 5.12: Design Principle of TENG

5.4.2.3. Manufacturing Process of TENG

Triboelectric Nanogenerator manufacturing process is shown in Figure 5.13a. Photopolymer Pts Ltd. supplied UV-curable polyurethane (PU) polymer for the device. Electromagnetic wavelengths like ultraviolet can quickly cure, dry, and harden sticky films, polymer resins, paints and dyes, a UV nail lamp (Model LN-818P) can curing with toughens and lowers connection and layer becomes dry. For 10 minutes, exposed the constructed devices to UV ozone in a transparent glass cylindrical container that is vacuum-packed. TENG layer is manufactured on aluminium foil as shown below in Figure 5.13a.

Manufacturing begins on TENG gadget. Triboelectric Nanogenerator devices exclusively utilize polyurethane. To ensure triboelectricity, a sponge spacer separates the TENG, among PU layer and Aluminum electrode. Proposed Triboelectric Nanogenerator applies

PU to two Aluminum electrodes, one on bottom and one on top. TENGs that gather ambient mechanical energy like human motion are adaptable, cost-effective, and high-performance. As tribo layers, TENG gadget recycles recyclable materials and garbage with Kapton tape and UV-curable polyurethane (PU). As a spacer, for improved triboelectrification a sponge from landfill unused functions to keep an air gap in the middle of tribo layers, however aluminium foil which is reprocessed used as electrodes. TENG that is generated has a power density of 8.53 W/m² and can reuse aluminium foil and garbage sponge materials. For 30 min, coating was treated below UV light to dry completely. For the triboelectric effect, by sponge spacers, layered electrodes that are separated to generate a homogenous air gap. TENG performance is improved by sponge spacers for contact separation in the proposed design. Figure 5.13b shows how this configuration produces the generators perpendicular pressure during push-up or pressure.

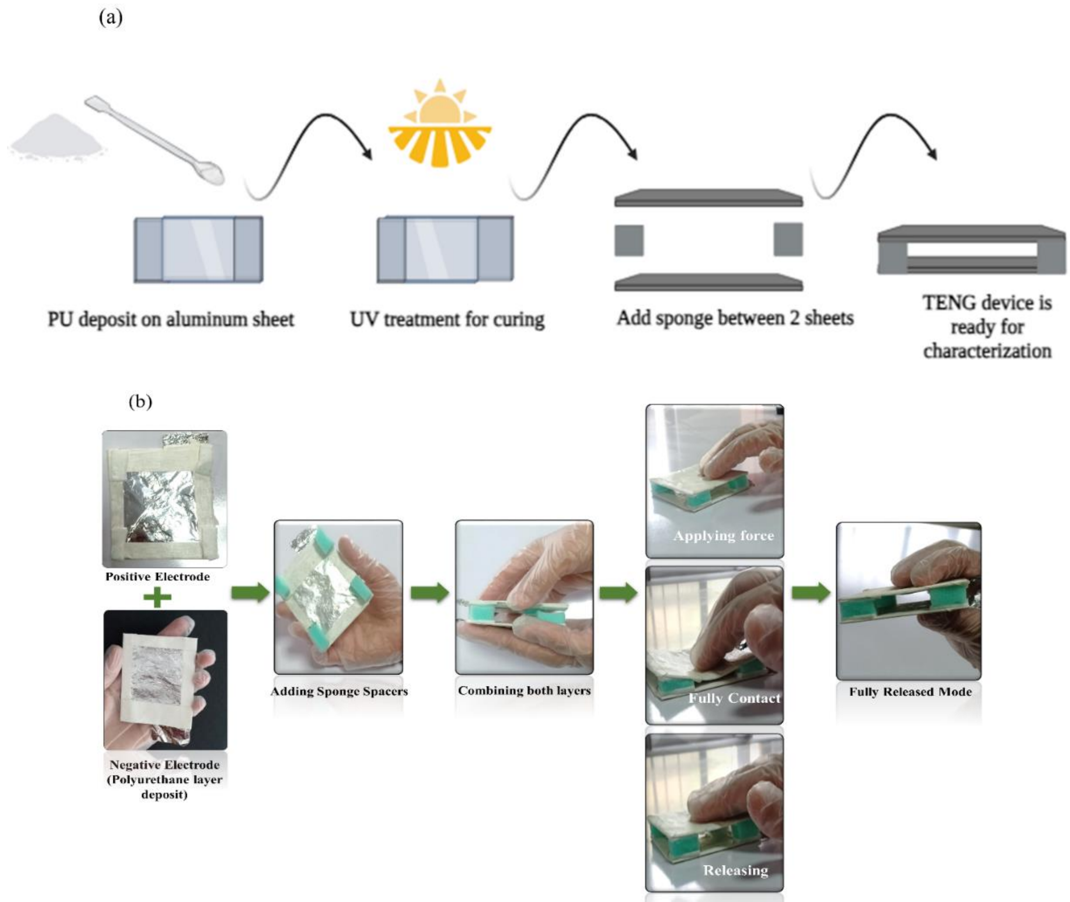

Figure 5.13: Schematic Design, (b) Fabrication process of TENG

5.4.3. Hybrid Nanogenerator Development Process

Main focused in this research was to developed a Hybrid Nanogenerator. Hybrid Nanogenerators (HNGs) are an innovative harvesting energy technology that integrates multiple energy conversion mechanisms to enhance power generation. The combination of Triboelectric Nanogenerators (TENGs) and Piezoelectric Nanogenerators (PENGs) is one of best effective methods for maximizing energy output. In this Hybrid Nanogenerator (HNG), which combines PU-based Triboelectric Nanogenerator (TENG) and ZnO-based Piezoelectric Nanogenerator (PENG) offers an effective way to harvest mechanical energy. By utilizing ZnO nanostructures in a PVP matrix for piezoelectricity and polyurethane (PU) for triboelectricity, this HNG provides enhanced power output, flexibility, and efficiency. The circuit diagram of proposed hybrid NG is shown below in figure 5.14, in which bridge rectifier is used to provide the rectified output. The TENG and PENG are separated by a spacer and combined to make certain electrostatic induction and triboelectric occurrence. As shown below in Figure 5.15, which includes TENG device which has PU layer (Tribo layer) and PENG device they both are separated by sponge. The designed hybrid NG consist of three electrodes. Upper layer of PENG, lower layer of PENG which has nanofibers of ZnO and PVP, then it is attached with TENG device with the help of double tape. The one common electrode which is working as 2nd layer for TENG combine with PU layer and a part of that is the 2nd electrode for PENG device as well. The Schematic of proposed hybrid NG and image of fabricated device are shown in Figure 5.15.

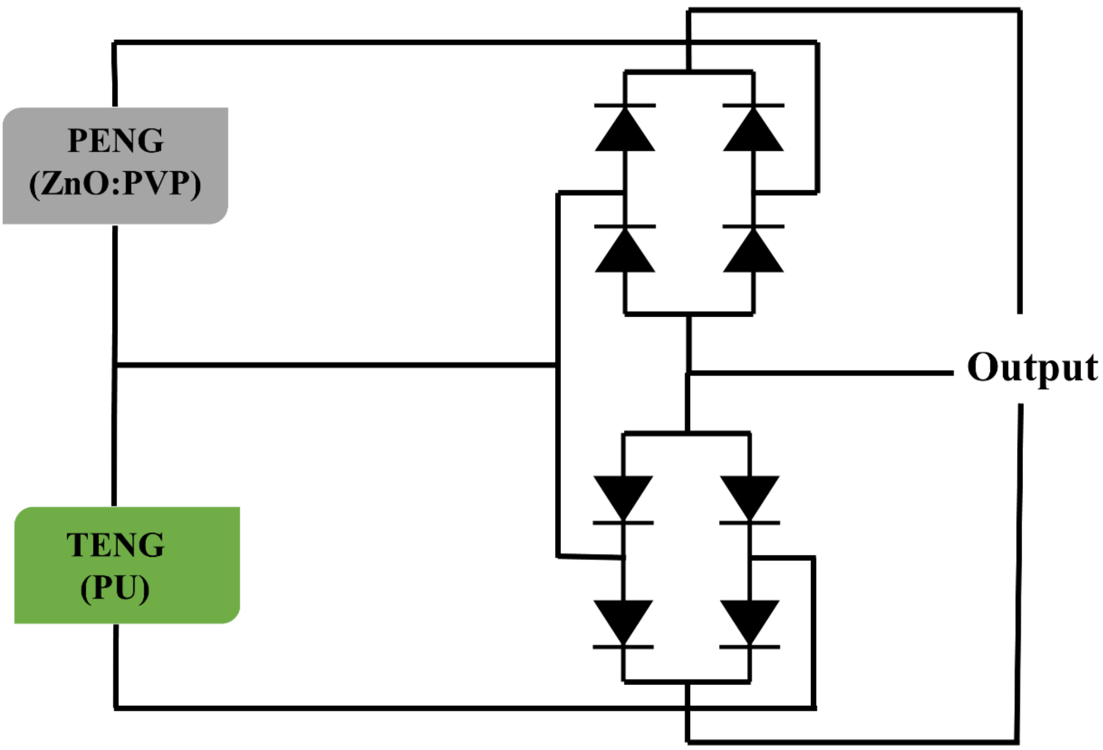

Figure 5.14: Circuit Diagram of proposed Hybrid Nanogenerator

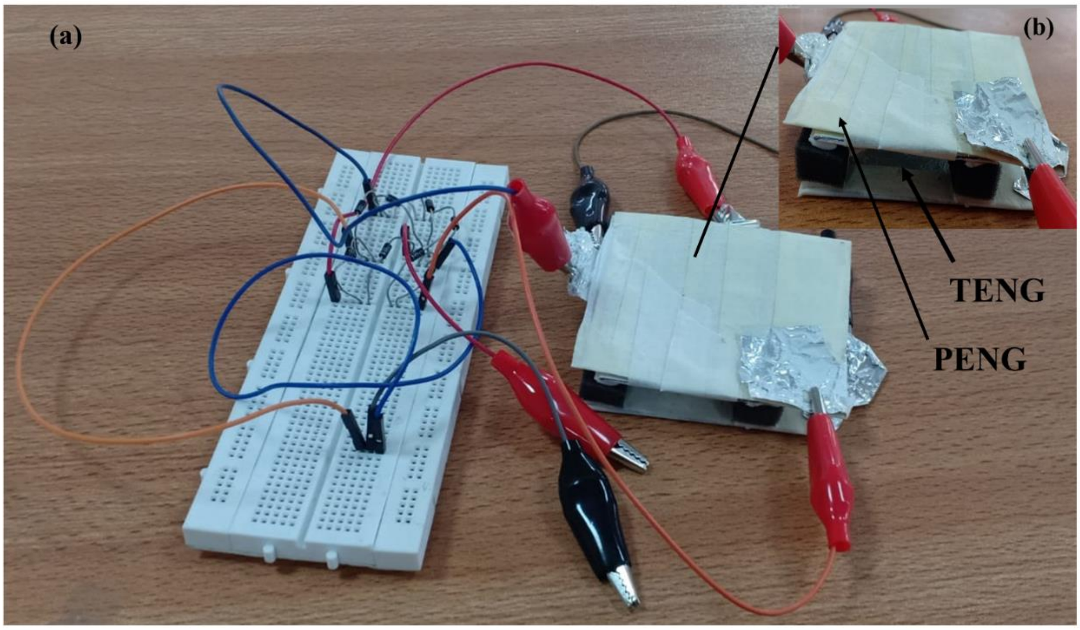

Figure 5.15: (a) Schematic of proposed Hybrid NG, (b) Image taken from fabricated hybrid NG

5.5. Summary

Chapter 5 presents a systematic overview of the material synthesis, structural design, and fabrication processes involved in developing the hybrid nanogenerator. The chapter begins with the fabrication of the piezoelectric component**,** where electrospinning is utilized to synthesize Nano fibrous structures of zinc oxide (ZnO) blended with polyvinylpyrrolidone (PVP). This technique enables the formation of uniform, high-surface-area fibers that enhance the mechanical-to-electrical energy conversion efficiency. The synthesis process is carefully optimized to ensure proper alignment and crystalline quality of the piezoelectric nanomaterial. Following this, the triboelectric device is developed using polyurethane films, selected for their strong triboelectric properties and flexibility. Surface modification and layering techniques are employed to improve charge generation during contact-separation motions. Both devices undergo material characterization using techniques such as SEM for morphological analysis and XRD for structural confirmation, ensuring the integrity and functionality of each layer. The chapter culminates with the integration of both systems into a single hybrid nanogenerator, where a custom-designed circuit is implemented to harness and rectify the generated electrical signals. The hybrid device is assembled through a carefully sequenced process, aligning the piezoelectric and triboelectric layers to operate synergistically. This integration not only enhances the output performance but also broadens the operational bandwidth, making the device more suitable for real-world mechanical energy harvesting. Overall, this chapter establishes a strong foundation for the development of a high-efficiency, flexible, and scalable hybrid energy harvesting system.

Chapter 6

RESULTS AND DISCUSSION

[1]. Saba Ejaz, Gul Hassan, Ahmed Shuja. 2025 "Fabrication and Characterization of Piezoelectric Nanogenerator Based on ZnO and PVP for Harvesting Energy System Applications", in *Journal of Materials Science: Materials in Electronics* ***(Published)***.

[2]. Saba Ejaz, Imran Shah, Shahid Aziz, Gul Hassan, Ahmed Shuja, Muhammad Asif Khan and Dong-Won Jung. 2025 "Fabrication and Characterization of a Flexible Polyurethane-Based Triboelectric Nanogenerator for a Harvesting Energy System" in *MDPI Journal of Micromachines*, 16(2), 230; **https://doi.org/10.3390/mi16020230** ***(Published)***.

This chapter involve the details discussion of characterizations and results discussion of the developed Hybrid nanogenerator which is based on piezoelectric and triboelectric nanogenerators. Different devices are developed to better synthesis the device and achieve optimum results. The synthesis is carried out based on ratio of amount of ZnO and PVP nano-powder and UV curable liquid polyurethane, as well as the thickness of grown layers for TENG and PENG and space between PENG and TENG layers (spacer). At the end of this chapter, some applications are included, which are experimented during characterization, i.e. glowing of LEDs.

6.1. Characterization of PENG

Various strategies and techniques were investigated to improve and achieve the harvest power of PENG devices. Primary objective of this research is to achieve electrical energy through converting the mechanical energy by investigating the piezo properties of ZnO-PVP composition, using electrospinning technique. Using XRD and SEM, characterization of ZnO-PVP mat was achieved and the output voltages and current were examined using an oscilloscope Pico ammeter respectively.

6.1.1. SEM and XRD results of PENG

Using Scanning electron microscopy, the model number is (SEM, Model: KYKYEM6900) surface morphology of the ZnO-PVP mat was evaluated at the Centre for Advanced Electronics and Photovoltaic Engineering (CAEPE), IIUI. The analysis was conducted at an accelerating voltage of 29 kV, utilizing a tungsten filament operated at 2.6 A. On a

Bruker D8 Advance diffractometer X-ray diffraction (XRD) examination was carried out that has some parameters like $\lambda = 1.5406$ Å, Cu-Kα radiation, current is 30 mA and voltage is 40 kV. Range of scanning was step size = 0.02°, 2θ = 10°–80°, scanning speed = 1°/min. Crystallite size was calculated based on Scherrer's equation while phase configuration was investigated with X'Pert High-Score software.

The morphology of ZnO-PVP mat were examined using SEM, at 30 µm, and 60 µm as shown below in Figure 6.1. The surface morphology confirmed the uniform distribution of ZnO-PVP nanofibers and a robust composite structure. The SEM Images also demonstrate the successful synthesis of the ZnO-PVP composite, highlighting its potential for innovative material applications.

The crystalline nature of the composite was more examined using X-Ray Diffraction (XRD). In Figure. 6.2, the XRD graph features distinct peaks at angles 32.4°, 35.1°, and 36.9°, corresponding to the hexagonal wurtzite structure of ZnO. The dominant peak at (101) confirms the preferential alignment of ZnO crystals, indicative of effective crystallization within the composite. The stabilizing and dispersing properties of the material are due to the combination of crystalline ZnO properties and PVP's role as a supportive, nanocrystalline matrix. The SEM and XRD results collectively demonstrate the ZnO-PVP composite's suitability for piezoelectric applications, emphasizing its uniform morphology and robust crystallinity. These structures create the composite a capable applicant for advanced PENG designs.

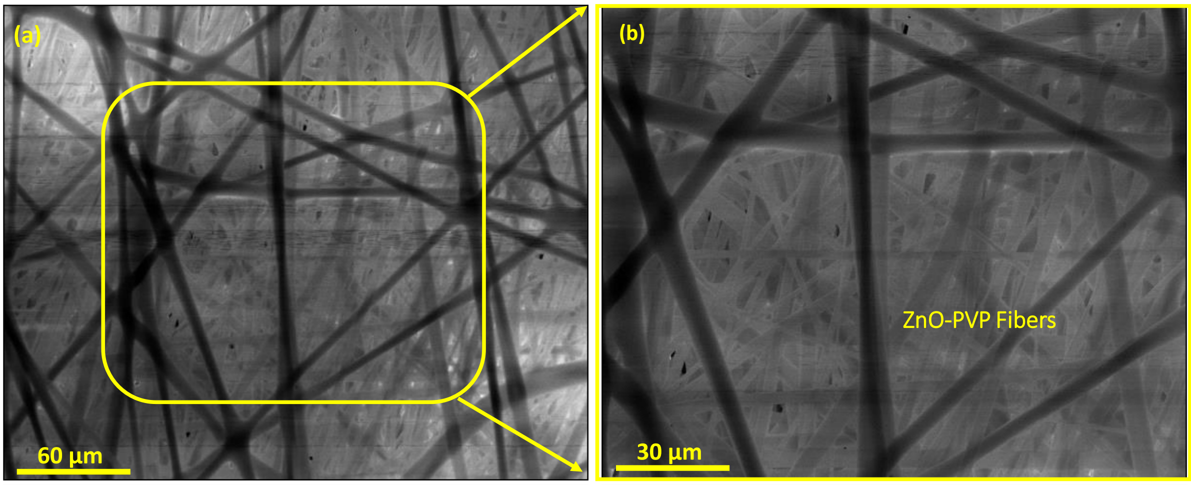

Figure 6.1: SEM Images of ZnO-PVP (a) at 60µm (b) at 30 µm

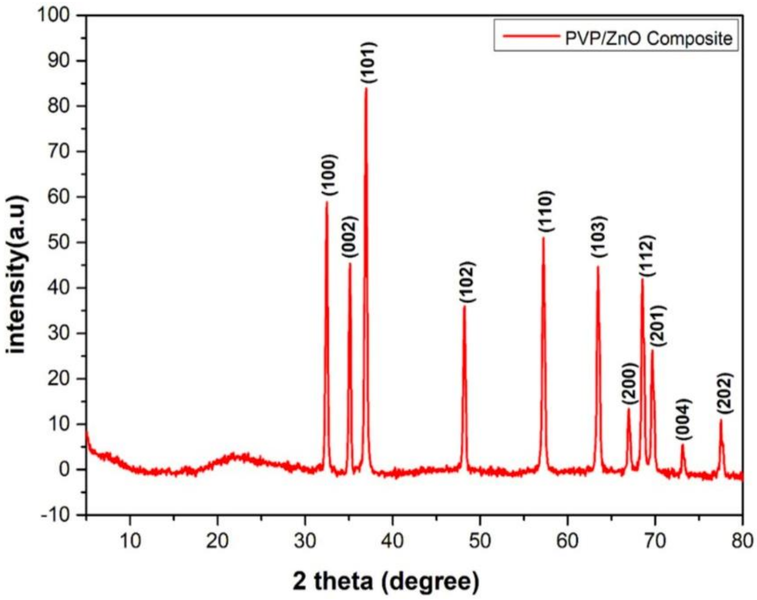

Figure 6.2: XRD of ZnO-PVP (the standard XRD pattern of ZnO/PVP (JCPDS No. 36-1451))

6.1.2. Piezoelectricity of the PENG Device

The ZnO-PVP-based PENG shows promising piezoelectric properties, effectively produce electrical energy through converting mechanical energy. The fabricated device consists of ZnO-PVP nanofibers sandwiched between Al foil sheets, which work by means of the bottom and top electrodes. This simple and low-cost design approach validates the efficiency of the PENG, generating a peak output voltage of approximately 40–50 V under hand tapping, as shown in Figure 6.3. This performance underlines its suitability for harvesting energy and self-powered electronic uses.

In the piezoelectric effect, working principle of the PENG is fixed, where an electric charge is generated by applying mechanical pressure across the device. The generated output is observed to be constant and reproducible. Under mechanical stimuli, such as hand tapping, the ZnO-PVP layer accumulates charge, producing a I_{SC} of ~400 nA and V_{OC} of ~45 V. These results are illustrated in Figure 6.3., where the periodic tapping corresponds to well-defined output peaks.

Capability of the device to harvest energy is further validated through its application to power a light emitting diode (LED). As depicted in Figures 6.3 (c) and 6.3 (d), slow tapping fails to illuminate the LED, while continuous tapping produces sufficient energy for illumination, confirming the device’s practical utility.

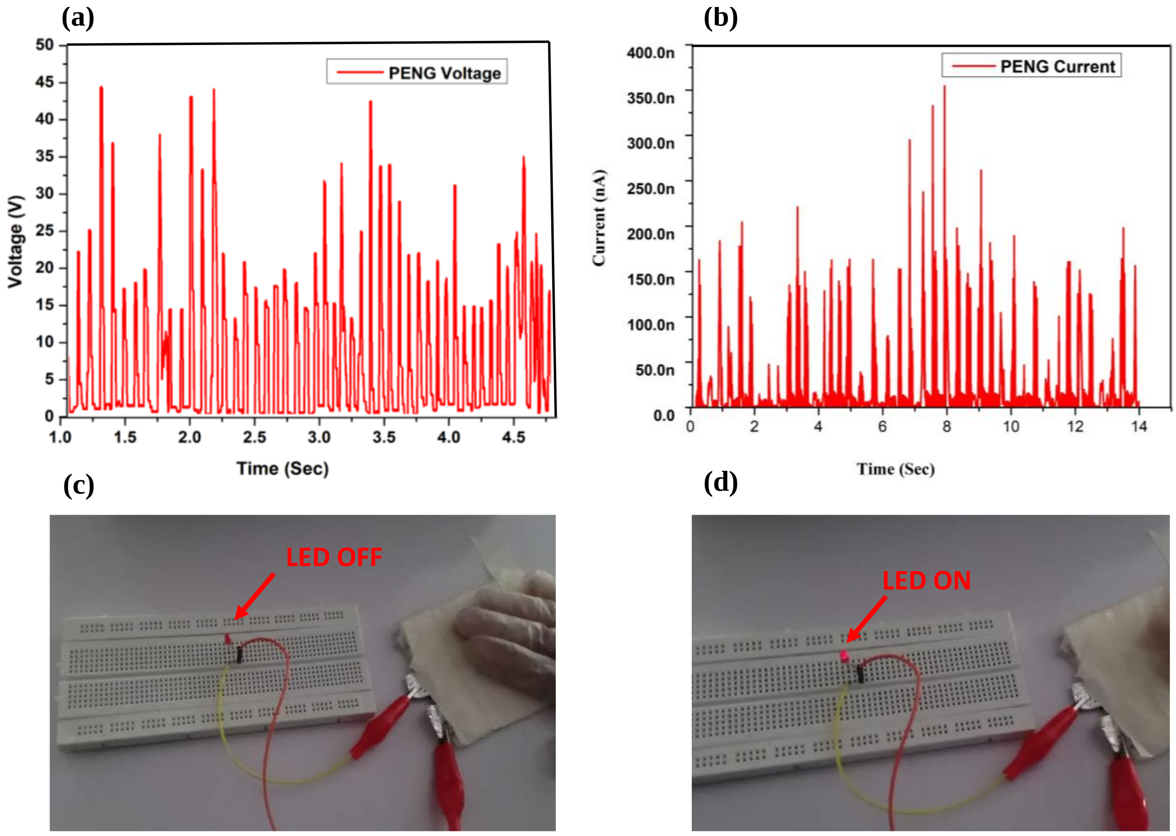

Figure 6.3: (a) PENG Voltage Output (b) PENG Output Current (c) LED OFF (d) LED ON

The electrical characteristics of the PENG are analysed through the resistance equation (Equation 6.1) [141]:

$$R_{png} = \frac{d_o}{A\varepsilon_{png} f} \qquad (6.1)$$

In Equation (6.1), d_o is the width of PENG grown layer, while the ε_{png} and A are permittivity and area of PENG correspondingly and f is frequency. Compared to triboelectric nanogenerators (TENG), the PENG exhibits significantly lower impedance, which enhances its efficiency for sustained energy harvesting. Unlike TENGs, which depend on capacitive mechanisms and air gaps, the PENG offers a simpler design with lower resistance and consistent output. The relationship between current and voltage is further expressed by Ohm's Law (Equation 6.2)[188]:

$$I = \frac{V}{R}\, Ampere \qquad (6.2)$$

This indicates that the current is inversely proportional to the resistance and directly proportional to the voltage, allowing the PENG to maintain stable performance across varying mechanical inputs. Results are highlighted the prospective of the ZnO-PVP PENG for various applications, including energy harvesting for supercapacitors, biomedical devices, and human gesture monitoring. Its consistent output, low corresponding resistance, and sustainable performance make it a viable candidate for integration into hybrid nanogenerators and other energy-harvesting systems.

6.2. Characterization of TENG

A dark-field electron microscope can show PU domain morphology. Note the PU SEM picture in Figure 6.4a. This picture was SEM-characterized. Wide PU material is 18.3–18.8 mm. Normal PU diameter is confirmed at 10 µm. TENGs benefit from the increased surface area of PU's contact layer for triboelectrification. Figure 6.4b displays the XRD of PU. As with other polyurethane materials, they detect a large diffraction peak at 20°. The tear-resistant polyurethane cuts well. Aircraft, cars, and eyeglasses use it.

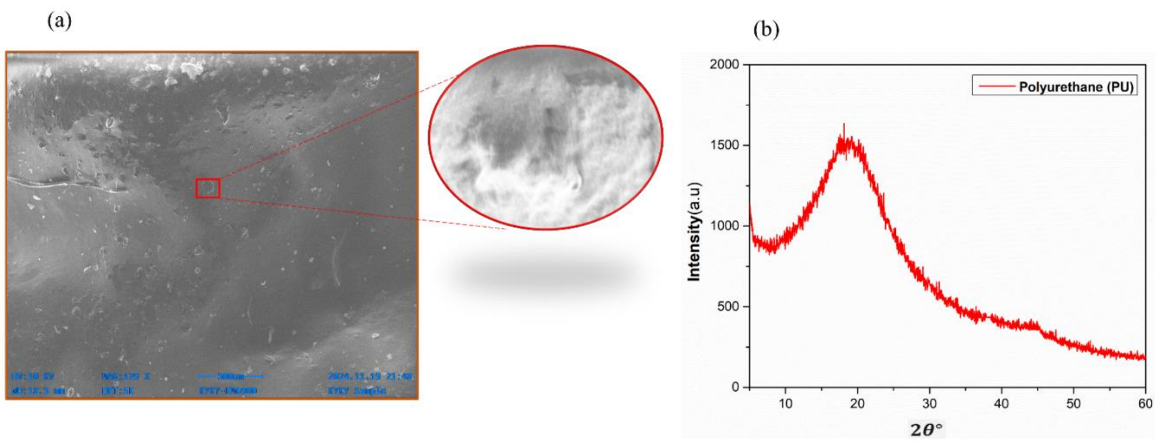

Figure 6.4: (**a**) SEM image of PU. (**b**) X-ray Diffraction (XRD) Results.

Figure 6.5. shows how a few geometrical factors affect device performance. V_{teng} fluctuates with x(t) and d as shown in Fig. 6.5a. This figure shows TENG geometry synthesis options that affects the performance of device. Study of vertical contact separation mode of TENG that perform the changing the triboelectric surface thickness and the air gap can increase the voltage output V_{teng}.

$$V_{teng} = -\frac{q}{A\varepsilon_0}\left(\frac{d}{\varepsilon_r} + x(t)\right) + \frac{\sigma x(t)}{\varepsilon_r} \tag{6.3}$$

Equation (6.3) employs surface area interaction that is Area = Width × Length, where transferred charges among electrodes is represented by q. ε_r shows the tribo material relative permittivity and ε_0 shows the air permittivity. Changing d from 0 to 300 μm and x(t) from 0 to 20 mm correspondingly, significantly affected V_{teng}. Fig. 6.5 shows V_{teng} fluctuation from 0 to 20 mm for x(t) and 0 to 300 μm for (d), with little d-dependent changes. Theoretical analysis that facilitates non-uniform electric field of coupled triboelectric surfaces. For hybrid nanogenerator, a 6 mm air gap yields the best results. Triboelectric layer that has the thickness, we looked at the depths of UV-curable PU made with a spin coater in hybrid mode (Figure 6.5).

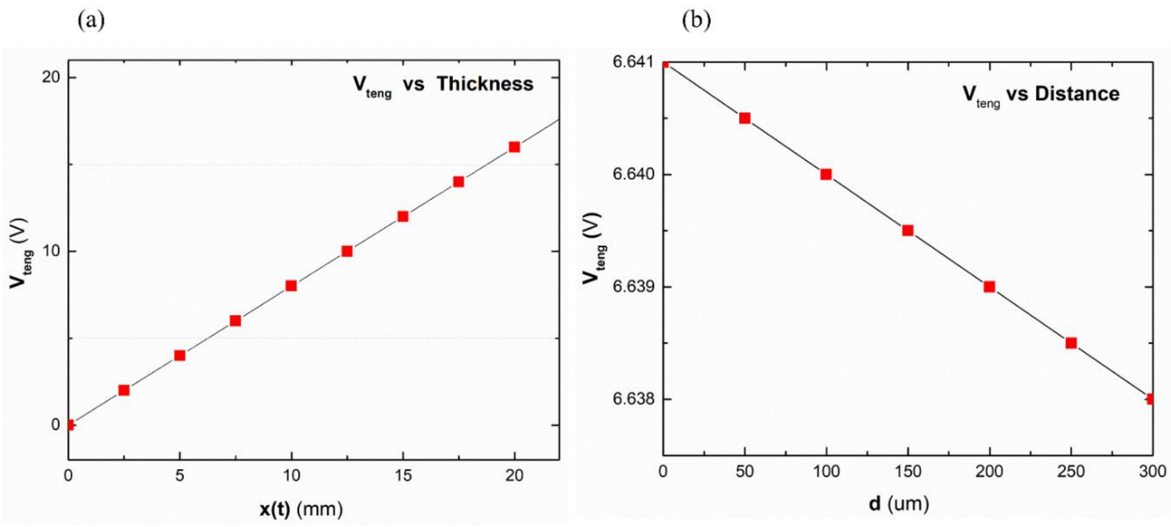

Figure 6.5: (**a**) Variation of the V_{teng} by the varied x(t). (**b**) Variation of the V_{teng} by the varied d.

TENGs get input stress from finger-tapping mechanisms. Electrical categorization used a voltage divider circuit and full-bridge rectifier, and an oscilloscope detected the voltage that is open-circuit (V_{oc}) peaks which are rectified. A 30 N force at 3–5 Hz yielded a 500 V V_{OC} peak. The device handled high-resistance loads well, as voltage is increased through the load with load resistance. Power density peaked at 10 MΩ load resistance, perhaps owing to oscilloscope impedance matching. These results show that load impedance adjustment is crucial for peak power output. The Instek GDS-810C Digital Storage Oscilloscope that has 100-MHz measured the output voltage. TENG generates a current of 2 μA and a maximum output voltage of 500 V (Figure 6.6a and b). High output impedances are typical with TENGs due to capacitive modes and air gaps.

The proposed TENG has enormous potential for creating sensors and energy that use their power. See Figures 6.6a and b for voltage and current outputs. In contact separation vertical mode TENGs improve electrical output, as shown in Figure 6.6c, and used experimental frequencies to gather the best data for TENG device operation. An upgraded TENG device was built and tested for sensitivity under different frequencies and pressures and after optimizing structural and geometrical characteristics. Figure 6.6c shows that the gadget generated 184 V under a force of 7 ± 2 N. As applied force increased, output voltage peaked at nearly 550 V at 28 ± 2 N. Furthermore, at a constant force of 15 ± 2 N, impact of frequency on device performance was assessed. As frequency increased up to 12 Hz, output voltage increased significantly (Figure 6.6d). The device's frequency response reached saturation above this frequency, since output performance did not improve.

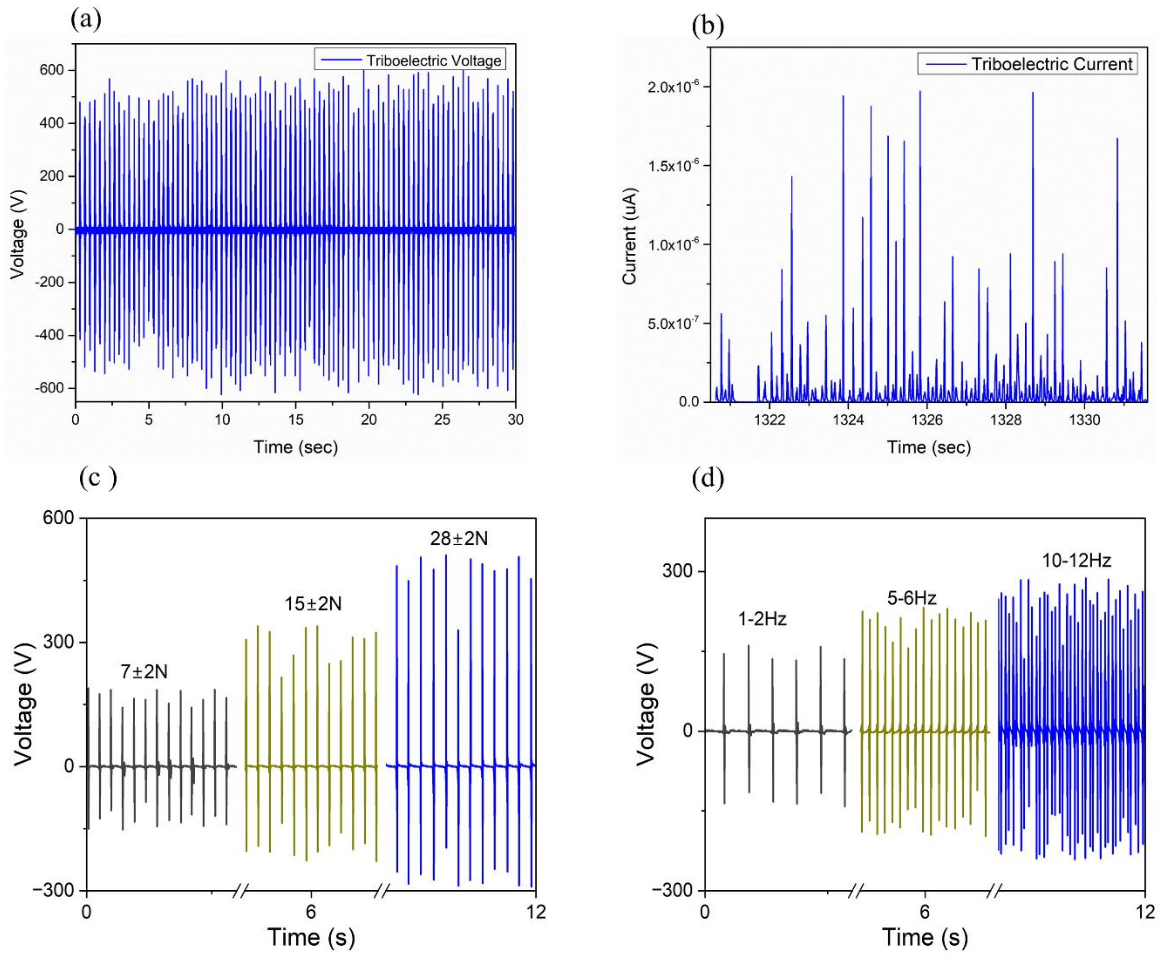

Figure 6.6: (a,b) TENG Voltage (V) and Current (μA) graphs with time (s). (c) Force-dependent voltage output. (d) TENG output behaviour by frequency.

Voltage across the load increased with load resistance, proving the gadget can manage high-resistance loads. At 10 MΩ load resistance, impedance equivalent with the oscilloscope led to the highest power density. Owing to low current and high voltage, TENGs have internal resistance that are in mega ohm's. Transfer of power is at its highest when the external load resistance is equal to device impedance. Many studies indicate that polyurethane-based TENGs generate significant power at load resistances ranging from 1 to 100 MΩ, with 10 MΩ being the optimal selection. At 10 MΩ, obtain greatest density of power by matching the external load to the internal impedance of TENG that is based on polyurethane. Figure 6.7b shows power–resistance charts using experimental data. These findings emphasize impedance of load adjustment for highest output power. We set a force applicator to 15 N at 3–5 Hz to test the stability and endurance of the TENG device. In Figure 6.7a, voltage output was verified before and after 2 hours of procedure.

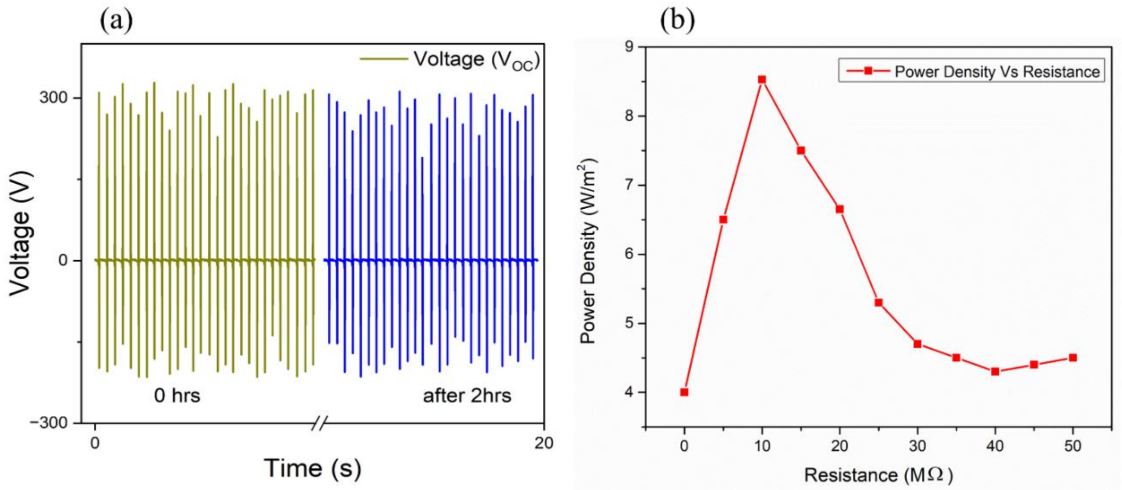

Figure 6.7: (**a**) Output voltage at 0 h and after 2 h of continuous operation. (**b**) Power Density vs. Resistance.

Figure 6.8 shows the intended TENG with the point denoting the aluminium bottom and top electrodes, polyurethane, and sponge spacers. On TENG, nonstop hand tapping charges the capacitor in Figure 6.8b. DMM displays a 3.53 V capacitor charge for LED illumination. The button toggles an LED in Figure 6.8c when the capacitor stores charges at 3.53 V. Figure 6.8c shows the LED glowing when the button is pressed.

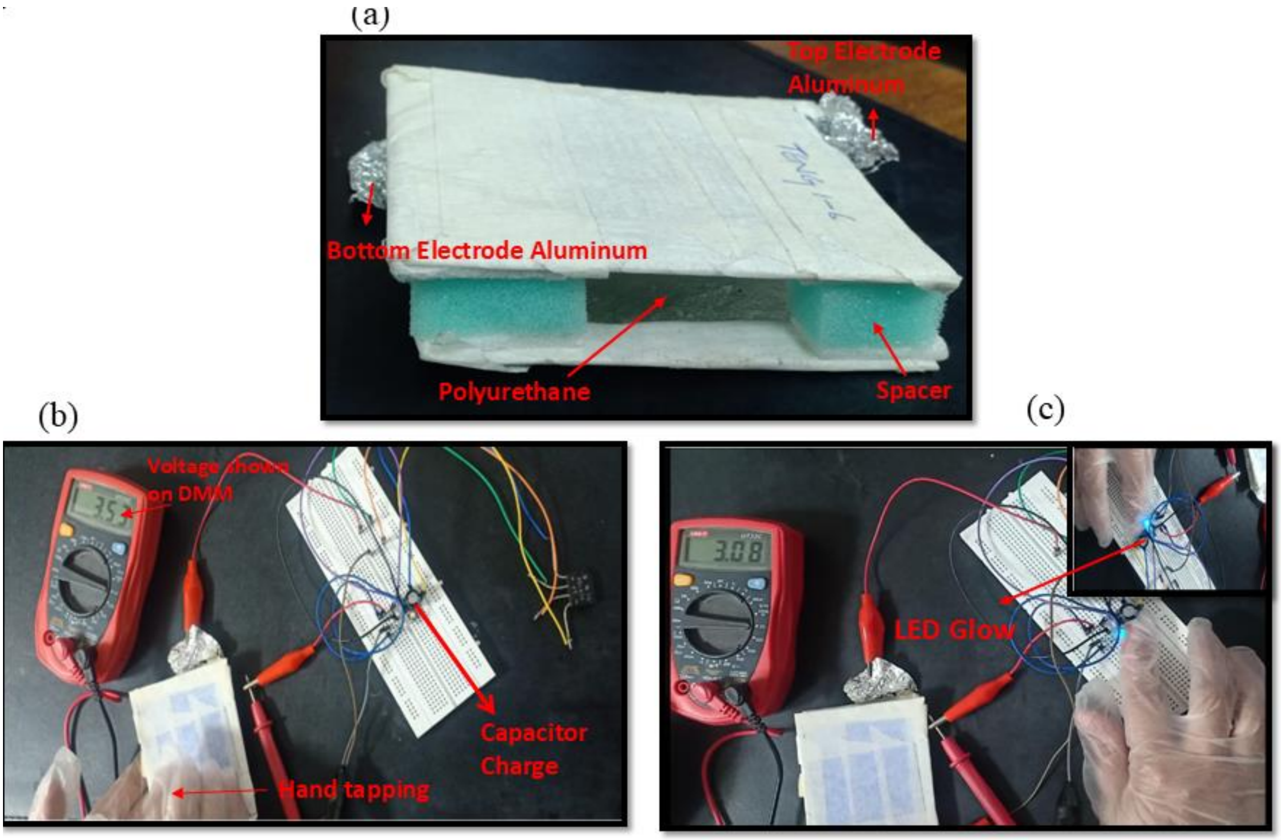

Figure 6.8: (**a**) Full image of the fabricated TENG. (**b**) Capacitor charging by the TENG device. (**c**) LED's glow after capacitor charging.

6.3. Rectified Output of Hybrid Nanogenerator

The device is in hybrid in structure and have two different devices which are functional at a same time. To combine the output and rectify the outputs, two bridge rectifiers are combined by combining one input common as shown in Figure 6.9. Two device PENG and TENG are shown and both have one common electrode, which is input to both bridge rectifiers. The output is measured from combing both of negative and positive terminals from both rectifier bridges as shown in Figure 6.9.

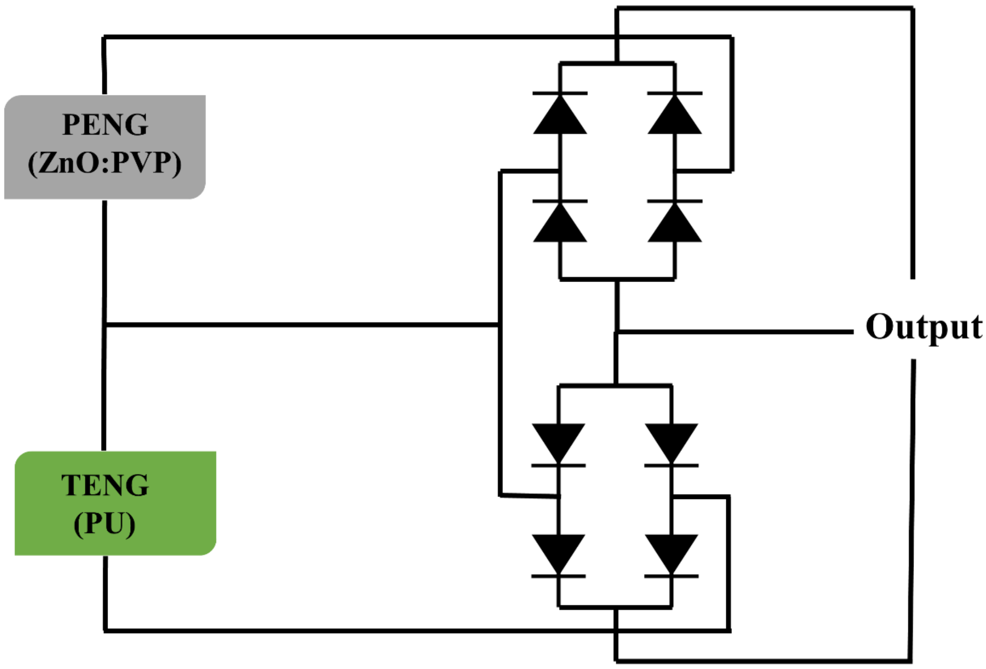

Figure 6.9: Bridge Rectifier designed for proposed Hybrid nanogenerator

6.4. Output Results of Hybrid Nanogenerator

A highly efficient hybrid nanogenerator has been developed by integrating two changed harvesting energy devices: PENG and TENG. The piezoelectric component of the nanogenerator is based on zinc oxide (ZnO) and Polyvinylpyrrolidone (PVP), materials known for their excellent piezoelectric properties, which enable the conversion of mechanical stress into electrical energy. On the other hand, the triboelectric component utilizes polyurethane, a material with strong charge transfer capabilities, allowing it to generate electrical energy through contact electrification and electrostatic induction when subjected to mechanical motion. By combining these two mechanisms, the hybrid nanogenerator is capable of significantly enhancing the overall energy output.

The peak rectified voltage for hybrid device is recorded up to 650V, while the PENG device single alone can only generate up to 40-50V without having in hybrid mode and TENG device can only generate up to 500 V without having in hybrid mode. The output voltage vs time curve of combine effect is also measured and recorded as shown in Figure 6.10. The combine peak output voltages after rectification are achieved up to 650V. In above two cases the output is measured by simple hand stabling mechanism. So as shown in Figure

6.10, the output boost up when both triboelectric and piezoelectric device effect are measured at the same time in hybrid mode.

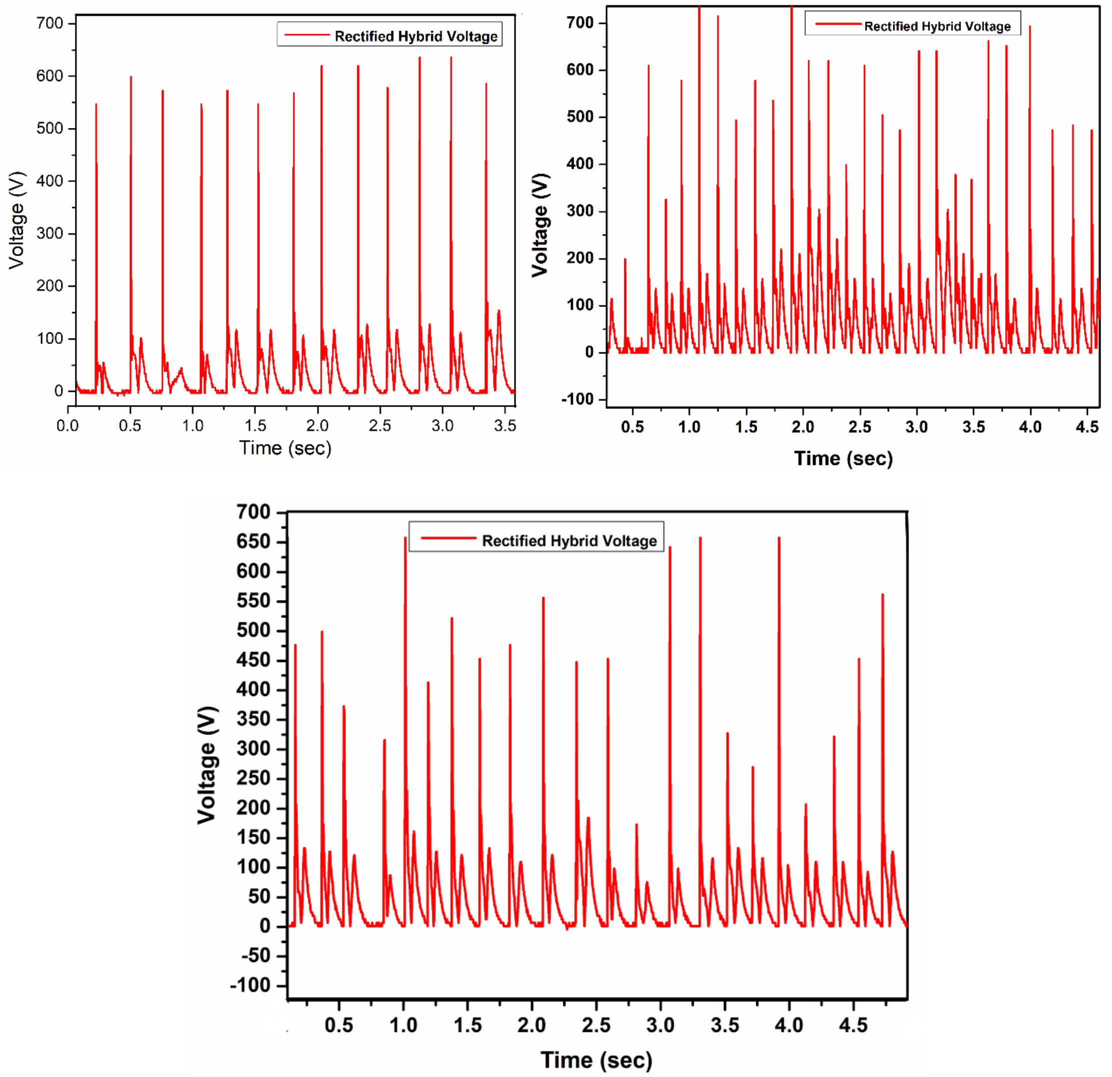

Figure 6.10: Rectified Hybrid Voltage Results

The output of measured current vs time of hybrid nanogenerator is illustrated in Figure 6.11. By combining both piezo and triboelectric nanogenerators we produce a Hybrid Nanogenerator that can generate current up to 3.5-4 µA as shown in Figure 6.11. Now collect only positive peaks in voltage results and currents results because of bridge rectifier.

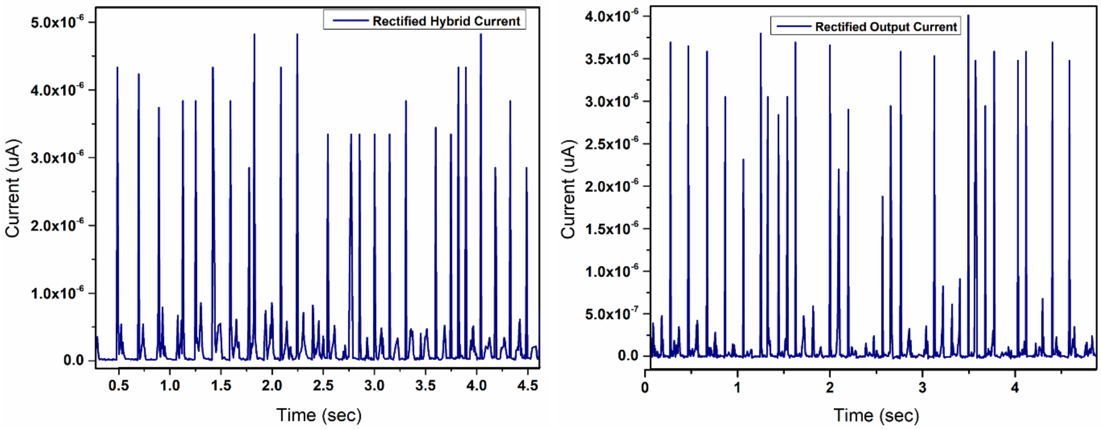

Figure 6.11: Rectified Hybrid Current Results

The experimental results demonstrate that this hybrid nanogenerator successfully generates a current of ~3.5 - 4 µA and a high output voltage of 650 V, showcasing its capability to powerfully exchange mechanical energy into functional electrical power. The synergistic effect of the piezoelectric and triboelectric components ensures that energy generation is maximized, making this device a promising solution for various self-powered applications. Such a hybrid system is particularly beneficial for powering low-energy electronic devices, wearable technology, and other applications requiring sustainable and renewable energy sources. The impressive voltage and current output suggest that this nanogenerator has the potential to be integrated into advanced harvesting energy systems, contributing to improvement of eco-friendly in addition self-sustaining power solutions. This research highlights the effectiveness of hybrid nanogenerators in improving energy conversion efficiency and paves the technique for future advancements in the self-powered devices and field of nanogenerators.

6.5. Application of Hybrid Nanogenerator (NG)

This hybrid nanogenerator, combining piezoelectric (ZnO and PVP) and triboelectric (polyurethane) mechanisms, is a ground-breaking energy harvesting system designed for self-powered applications. This nanogenerator has the potential to control small electronic devices powerfully with an impressive output of 650 volts and a current range of 3.5 to 4 microamperes. One of its key applications is lighting multiple LEDs, demonstrating its ability to transform mechanical into useful electrical energy for practical use as shown below in Figure 6.12.

This hybrid nanogenerator can be unified into biomedical sensors, wearable electronics, also IoT devices, enabling them to operate without traditional batteries. By harvesting energy from mechanical vibrations, human motion, or environmental forces, it provides a sustainable and eco-friendly power solution. In low power or remote applications, such as environmental monitoring systems and wireless sensor networks, our nanogenerator can serve as a continuous power source, reducing dependence on conventional energy sources.

Furthermore, this technology can be utilized in smart fabrics, where movement-generated energy can power small electronic circuits embedded in clothing. Additionally, in structural health monitoring, the nanogenerator can be installed in buildings, bridges, and vehicles to generate power from vibrations while simultaneously detecting mechanical stress and damage. These diverse applications highlight the potential of our hybrid nanogenerator in advancing energy sustainability and self-powered systems for next-generation technology.

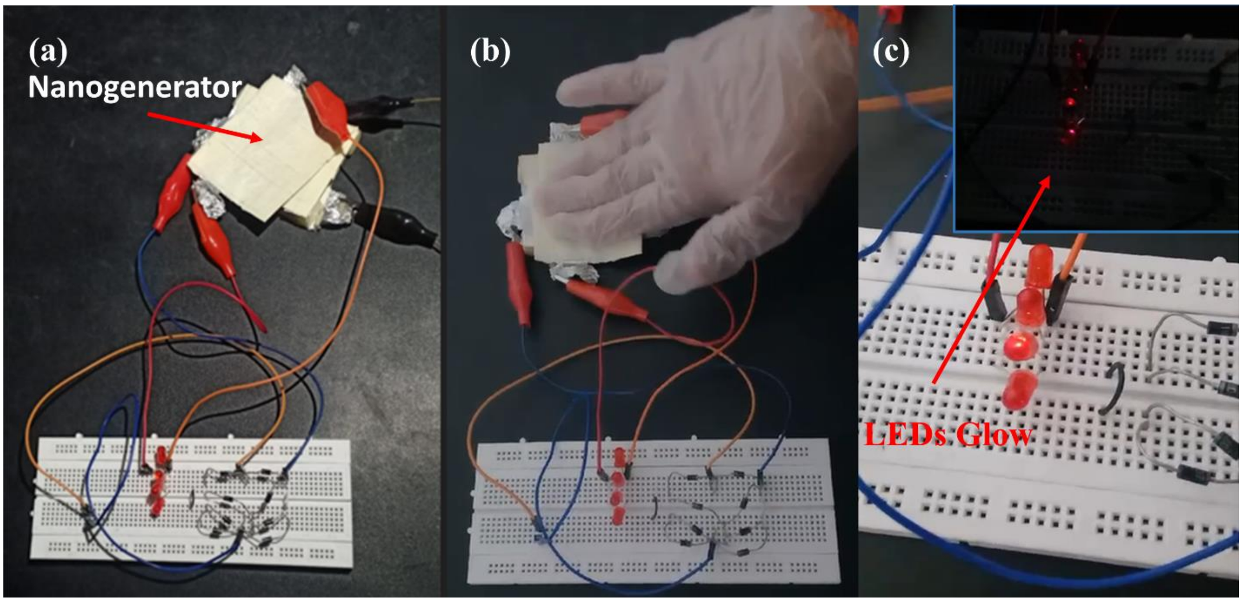

Figure 6.12: (a) Circuit diagram of Hybrid Nanogenerator (b) Testing hybrid nanogenerator by simple hand tapping (c) Glow LEDs with the help of hand tapping

6.6. Summary

Chapter 6 provides an in-depth analysis of the experimental results obtained from the fabrication and testing of piezoelectric, triboelectric, and hybrid nanogenerators. The chapter begins with the piezoelectric device, where current and voltage output graphs demonstrate a consistent and promising energy response under mechanical stress. The nanofibers synthesized via electrospinning were analyzed using Scanning Electron Microscopy (SEM), revealing well-aligned, uniform fiber morphology, while X-ray Diffraction (XRD) confirmed the crystalline structure of ZnO within the polymer matrix. The performance of the piezoelectric device was further validated through a practical demonstration in which a small array of LEDs was successfully illuminated, indicating sufficient voltage generation and real-world applicability.

Following this, the triboelectric nanogenerator was evaluated, where different polyurethane film thicknesses were tested to study their effect on energy output. Graphs depicting current and voltage responses showed that optimized film thickness significantly enhanced triboelectric efficiency. SEM imaging provided insight into surface roughness and texture, while XRD analysis confirmed the structural consistency of the triboelectric layers. This section also included a demonstration where mechanical tapping produced enough energy to glow LEDs, showcasing the triboelectric unit's functional capability.

The final section discusses the hybrid nanogenerator, which combines both piezoelectric and triboelectric components into a single device. The I–V characteristics of the hybrid system showed a marked improvement in output performance due to the synergistic effect of both energy harvesting mechanisms. A custom circuit was integrated for efficient power management, and the hybrid device was tested under mechanical motion, successfully powering multiple LEDs in a demonstration setup, validating its potential for self-powered systems. This chapter effectively highlights how the integration of individual nanogenerators enhances overall performance and strengthens the case for hybrid systems in next-generation energy harvesting applications.

Chapter 7

Conclusion and Future Work

7.1. Conclusion

The present research successfully demonstrates the fabrication and characterization of a Hybrid Nanogenerator (HNG) integrating both Piezoelectric Nanogenerator (PENG) based on ZnO–PVP composite nanofibers and Triboelectric Nanogenerator (TENG) based on polyurethane (PU). This work addresses the increasing demand for sustainable, self-powered systems that can operate independently of conventional energy sources, especially for applications in wearable electronics, biomedical devices, environmental monitoring, and portable Internet of Things (IoT) platforms.

In the piezoelectric part of this study, electrospinning was employed to fabricate ZnO–PVP nanofibers using Dimethylformamide (DMF) as a solvent, with various weight compositions of ZnO and PVP. Careful optimization of process parameters such as applied voltage, feed rate, needle-to-collector distance, and electrospinning duration resulted in uniform, well-aligned nanofibers exhibiting a clearly defined Taylor cone formation. The optimized PENG demonstrated promising electrical output, with an open-circuit voltage (VOC) in the range of 40–50 V and a short-circuit current (ISC) of ~400 nA. These performance levels are adequate for low-power and wearable electronics, light-emitting diodes, and small-scale sensing devices.

The triboelectric component was realized through a flexible, vertical contact–separation mode TENG using UV-curable polyurethane. The device incorporated a sponge spacer, repurposed from landfill waste, to maintain a uniform air gap and improve triboelectrification efficiency—offering an additional environmental benefit by recycling waste material. This TENG achieved an open-circuit voltage of nearly 500 V, a current of ~2 μA, and a power density of 8.53 W/m^2, demonstrating its capability as a high-output, eco-friendly power source for wearable and portable applications.

By stacking PENG and TENG together in a hybrid configuration separated by sponge spacers to preserve air gap integrity, the complementary properties of the two devices were synergistically combined. The hybrid nanogenerator leveraged the high voltage output of the TENG and the high current output of the PENG to achieve an impressive total output of ~650 V and a current range of 3.5–4 μA. This result clearly demonstrates the benefit of hybridization, overcoming the limitations of each individual device type and offering improved energy conversion efficiency.

Comprehensive characterization techniques such as Scanning Electron Microscopy (SEM), Electrospinning process analysis, and X-Ray Diffraction (XRD) were used to examine the structural, morphological, and crystallographic properties of the fabricated nanofibers and polyurethane films. These analyses confirmed the uniformity, crystallinity, and surface morphology necessary for efficient piezoelectric and triboelectric performance. The durability and flexibility of the hybrid structure make it suitable for repeated mechanical stress, which is crucial for long-term wearable and environmental monitoring applications.

Overall, the outcomes of this research not only validate the feasibility of ZnO–PVP and polyurethane-based hybrid nanogenerators for energy harvesting systems, but also open new pathways for practical, real-world implementations. The hybrid device's capability to generate substantial electrical output under simple mechanical stimuli positions it as a competitive candidate for powering self-sustained sensor nodes, health-monitoring wearables, low-power communication modules, and other distributed electronics without reliance on external power sources.

In conclusion, this thesis successfully establishes a robust, flexible, and high-performance hybrid nanogenerator platform capable of meeting the evolving demands of self-powered electronics. The combined piezoelectric–triboelectric approach not only enhances overall performance but also ensures versatility, mechanical resilience, and adaptability across a wide range of electrical engineering applications. This work thus contributes significantly to the growing field of nanogenerator technology, paving the way toward more autonomous, eco-friendly, and sustainable energy harvesting solutions.

7.2. Future Work

Building upon the promising results of the current research, several potential directions can be explored to further enhance the performance, reliability, and practical deployment of hybrid nanogenerators based on ZnO–PVP piezoelectric layers and polyurethane triboelectric layers:

- **Material Optimization:**

- Investigate doping of ZnO nanostructures (e.g., with Al, Ga, or rare-earth elements) to improve piezoelectric coefficient and charge generation.
- Explore surface modification of polyurethane for enhanced triboelectric polarity and durability.

- **Structural and Morphological Advancements:**

- Design nanostructured surface patterns (micro/nano-pillars, grooves) to increase contact area and triboelectric charge density.
- Optimize electrospinning parameters for PVP–ZnO fibers to achieve higher alignment and uniformity.

- **Hybrid Integration Strategies:**

- Develop multi-layer stacking configurations to maximize both voltage and current outputs.
- Incorporate flexible conductive interconnects to minimize energy loss during hybrid coupling.

- **Power Management and Storage Systems:**

- Integrate advanced rectification and impedance matching circuits to improve energy transfer efficiency.
- Couple the output with high-capacity supercapacitors or thin-film batteries for stable, continuous power delivery.

- **Long-Term Stability and Reliability Testing:**

- Conduct accelerated aging tests under varying humidity, temperature, and mechanical stress conditions.

- Study the fatigue resistance of ZnO–PVP and polyurethane layers under repeated mechanical deformation.

- **Application-Specific Prototyping:**

- Design wearable and implantable self-powered sensors for biomedical monitoring.
- Implement hybrid nanogenerators in low-power IoT nodes, wireless sensor networks, and structural health monitoring systems.

- **Scalability and Manufacturing:**

- Develop roll-to-roll or printing-based fabrication processes for large-scale production.
- Evaluate cost-effective synthesis routes without compromising device performance.

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