

**A study on nature-inspired multifunctional polymeric
composites for piezoelectric energy harvester, real time
triboelectric sensors and lead-free ultrasound transducer**

Thesis submitted to
Jadavpur University



By
Namrata Das

In partial fulfillment of the requirements for the degree of
Doctor of Philosophy (Ph.D.) in Science

**Department of Physics
Jadavpur University
Kolkata-700032
India**

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যাদবপুর বিশ্ববিদ্যালয়
কলকাতা-৭০০০৩২, ভারত



JADAVPUR UNIVERSITY
KOLKATA-700 032, INDIA

FACULTY OF SCIENCE : DEPARTMENT OF PHYSICS

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Partha Pratim Ray
Prof. Partha Pratim Ray 10/07/25

Department of Physics,
Jadavpur University,
Kolkata - 700032



Dr. Partha Pratim Ray
Professor
Department of Physics
Jadavpur University

Sukhen Das
Prof. Sukhen Das 10.07.2025

Department of Physics,
Jadavpur University,
Kolkata - 700032



Prof. Sukhen Das
Department of Physics
Jadavpur University
Kolkata - 700 032

* Established on and from 24th December, 1955 vide Notification No.10986-Edu/II-42/55 dated 6th December, 1955 under Jadavpur University Act, 1955 (West Bengal Act XXXIII of 1955) followed by Jadavpur University Act, 1981 (West Bengal Act XXIV of 1981)

ফোন : +৯১ ৩৩-২৪১৩-৮৯১৭
ফ্যাক্স : +৯১ ৩৩-২৪১৩-৮৯১৭

Website : www.jadavpur.edu

Phone : + 91-33-2413-8917
Fax : + 91-33-2413-8917

যাদবপুর বিশ্ববিদ্যালয়
কলকাতা-৭০০ ০৩২, ভারত



JADAVPUR UNIVERSITY
KOLKATA-700 032, INDIA

FACULTY OF SCIENCE : DEPARTMENT OF PHYSICS

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Partha Pratim Ray
Prof. Partha Pratim Ray 10/07/25

Department of Physics,
Jadavpur University,
Kolkata - 700032



Dr. Partha Pratim Ray
Professor
Department of Physics
Jadavpur University

Sukhen Das 10.07.2025
Prof. Sukhen Das

Department of Physics,
Jadavpur University,
Kolkata - 700032



Prof. Sukhen Das
Department of Physics,
Jadavpur University
Kolkata - 700 032

* Established on and from 6th December, 1955 vide Notification No.10986-Edn/1U-42/55 dated 6th December, 1955 under Jadavpur University Act, 1955 (West Bengal Act XXXIII of 1955) followed by Jadavpur University Act, 1981 (West Bengal Act XXIV of 1981)

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Website : www.jadavpur.edu

Phone : + 91-33-2413-8917
Fax : + 91-33-2413-8917

Declaration

I, hereby declare that the work embodied in the present thesis has been carried out by me under the supervision of Prof. Partha Pratim Ray and Prof. Sukhen Das at the Department of Physics, Jadavpur University, Kolkata-700032, India. Neither this thesis nor any part thereof has been submitted for any degree whatsoever.

Namrata Das
10.07.2025

Namrata Das

Research Scholar
Department of Physics
Jadavpur University
Kolkata-700032



Dedicated to
My parents,
who always kept me in their prayers
and
taught me the values of love, strength
and commitment.

Abstract

A study on nature-inspired multifunctional polymeric composites for piezoelectric energy harvester, real time triboelectric sensors and lead-free ultrasound transducer

Namrata Das

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With the growing energy crisis, there is a rising global interest in using renewable energy sources like solar, tidal, wind, rainwater and various biomechanical movements to cut carbon emissions and achieve carbon neutrality. Regarding green energy production, self-powered energy harvesting devices using multifunctional polymeric composites have attracted significant attention in recent years. The main goal of this research is to design polymeric composite based, self-powered devices by utilizing piezoelectric and triboelectric effects, either through the use of naturally available materials or by designing a bio-inspired device structure. Many studies explored piezoelectric nanogenerators (PENGs), but few have examined natural dopants in polymers for multifaceted nanocomposites. With this in concern, naturally available mud volcano clay from the Andaman and Nicobar Islands, India, was used to develop two cost effective and biocompatible PENGs for mechanical energy harvesting and body motion sensing. Clay nanoparticles (NPs) of two different sizes were produced through nano-structuring using mortar-pestle and ball milling methods and then incorporated into electroactive PVDF. A comparative study was done to evaluate the characteristics of the composites and output performance of PENGs made with each type of NPs. The PENGs showed high power densities and notable piezoelectric coefficients under hand-applied force, where PENG with ball-milled clay delivered better performance due to their smaller NP size.

Ultrasound transducers (USTs), also operating on piezoelectric effect, have traditionally relied on lead based single crystals, posing environmental risks while polymer composite-based USTs remain largely underexplored. Owing to this fact, a study was conducted on developing a lead free, high frequency UST using PVDF-TrFE based piezoelectric composite combined with a transition metal hydroxide. Using a pulse-echo test, a peak-to-peak output voltage of 5.19 V was obtained, along with a notable -6 dB bandwidth of 51.22 MHz (102.4%) with a high central frequency. Thus, the UST broadens the scope of non-invasive medical diagnostics and non-destructive testing in industrial applications.

Rainfall is one of the most widely explored renewable energy sources, offering a valuable form of mechanical energy by converting the waste kinetic energy of falling raindrops into electricity before they reach the ground. Based on this concept a real-time, bio-inspired triboelectric acid rain sensor has been fabricated, operating through solid-liquid interface contact electrification. Drawing inspiration from the micro-patterns on petunia flower petals, a template-sacrifice technique was employed to create the micro structured triboelectric polymeric membrane. The microstructures enhanced charge transfer, hydrophobicity and contact-separation, resulting in a high sensitivity of 34.4 V/kPa and a high contact angle of 135.8°. The improved hydrophobicity of the triboelectric nanogenerator (TENG) due to its rough surface has been explained by the Wenzel wetting model. Besides harvesting energy from raindrops, the TENG also enabled real-time pH monitoring of rainwater, allowing early warning of potential environmental hazards. In today's use-and-throw culture, developing sustainable and reusable technologies has become challenging. Therefore, a waste-based TENG was designed utilizing polystyrene (non-biodegradable polymer) from packaging waste and cellulose fibre from discarded banana pseudostems, promoting the waste-to-energy concept. This TENG with unique butterfly shape, can capture energy from irregular breezes in the environment, including wind gusts generated by passing vehicles and can also detect over-speeding of vehicles, assisting in road safety. It was found to generate an output voltage of 389 V (under an 11.7 N periodic force), with high stored energy during capacitor charging and excellent sensitivity.

The developed polymeric composite based self-powered nanogenerators, provide sustainable green energy harvesting and wearable sensor abilities. Meanwhile, the lead-free piezoelectric UST pave the way for accurate, non-invasive medical diagnostics, enhancing healthcare outcomes. Together, these three types of devices deliver comprehensive harvesting, sensing and diagnostic solutions, aligning with the advancements in the human-machine interface era.

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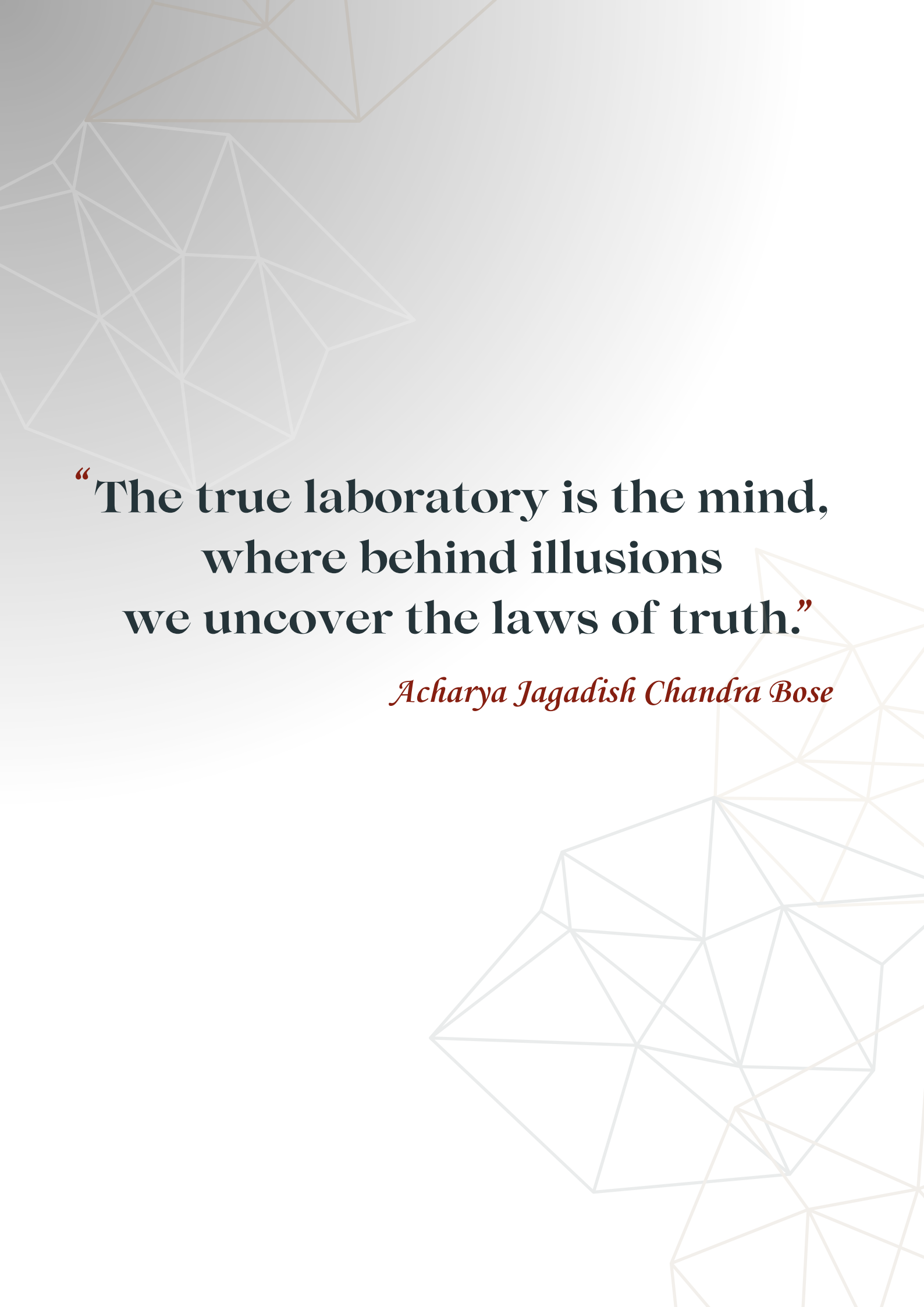
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**“The true laboratory is the mind,
where behind illusions
we uncover the laws of truth.”**

Acharya Jagadish Chandra Bose

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Namrata Das
10.07.2025
(Namrata Das)

Jadavpur University, Kolkata

Preface

Growing environmental concerns and the ongoing energy crisis have significantly increased global interest in renewable energy sources to reduce carbon emissions. To address this, self-powered devices are being explored as they can independently convert mechanical energy into electrical energy. In the field of sustainable energy generation, self-powered devices with multifunctional polymeric composites have been a popular research topic. Among the various energy harvesting methods, piezoelectric effect is quite efficient technology with wide range of applications in both nanogenerators and ultrasound transducers. Additionally, mechanical energy from natural energy sources like rainfall and wind presents a valuable renewable resource with significant potential to be harnessed through the triboelectric effect by converting the futile kinetic energy into usable electricity.

Chapter 1: In the context of sustainable development and advanced energy harvesting techniques, the chapter offers an outline of the historical evolution of energy harvesting globally and in India. It also introduces the fundamental principles of the piezoelectric and triboelectric effects. The background, working mechanisms and recent advancements in the field of piezoelectric nanogenerators, piezoelectric ultrasound transducers and triboelectric nanogenerators have also been discussed in this chapter.

Chapter 2: This chapter outlines the core methodology of the entire research, detailing the synthesis of lead-free organic and inorganic nanoparticles through chemically extracted methods and nano-structuring techniques. It describes four distinct polymeric film fabrication procedures along with innovative device designing techniques. Additionally, the chapter provides a detailed discussion of the characterization procedures and software used to demonstrate the real-time sensing applications of the developed devices.

Chapter 3: Naturally available, biodegradable mud volcano clay from Andaman and Nicobar Islands, India was used to develop two biocompatible PENGs for mechanical energy harvesting and body motion sensing. Clay NPs of two different sizes were produced through nano-structuring using two methods and then incorporated into electroactive PVDF. A comparative study was done to evaluate the characteristics of the polymeric composites and the output performances of PENGs made with each type of NPs. The PENGs showed high power densities and demonstrated various real-life

applicability. They effectively harvested energy from body movements, instrument vibrations and airflow. With further development, the nanogenerators could power self-charging portable devices for everyday use and for biomedical applications.

Chapter 4: Piezoelectric composite based high-frequency ultrasound transducers have become key tools in non-invasive medical diagnosis and non-destructive testing. In this chapter, a lead-free, high-frequency UST, having a simple and unique assembly procedure, have been presented. To achieve this, PVDF-TrFE based piezoelectric composite was integrated with a transition metal hydroxide. The impact of piezoelectric property on UST's output has been well explained using Maxwell's equations. By conducting a pulse-echo test, a high peak-to-peak output voltage was obtained that surpassed the output voltage magnitude of any previously reported UST in this field.

Chapter 5: The fabrication of a bio-inspired, raindrop energy-powered single electrode triboelectric nanogenerator has been presented in this chapter. The TENG was employed as a real-time acid rain sensor, working under solid-to-liquid interface contact electrification. Inspired by micro-motifs of petunia flower petal surface, an innovative 'replication' method utilizing template-sacrifice technique was applied to develop the triboelectric membrane. Hydrophobicity of the TENG due to introduction of rough surface topography has also been theoretically described using Wenzel model of wetting.

Chapter 6: This chapter describes the fabrication of a waste-derived TENG that produces electrical energy from futile kinetic energy of natural wind gusts. The spacer-less, butterfly-structured TENG features a wedge-shaped air gap that ensures full contact between triboelectric layers. For the tribonegative layer, microporous polymer film was fabricated using polystyrene packaging waste. Tribopositive layer included cellulose microfibers with microskeleton architecture, extracted from discarded banana pseudostems. A real-time vehicle speed monitoring and wireless on-road over-speed surveillance system was developed, using this TENG.

Chapter 7: This chapter summarizes the key outcomes of the research and highlights the potential future prospects in this field, based on current research trends.

All the references in this thesis are presented in the format given below:

Surname, Initial of the authors., Year. *Journal name*, *Volume*, Page number(s).

Example: Das, N., Sarkar, D., Saikh, M.M., Biswas, P., Das, S., Hoque, N.A. and Ray, P.P., 2022. *Nano Energy*, 102, p.107628.

Abbreviations

Abbreviation	Expansion
NPs	Nanoparticles
PENG	Piezoelectric nanogenerator
UST	Ultrasound transducer
TENG	Triboelectric nanogenerator
L-S TENG	Liquid-solid triboelectric nanogenerator
PVDF	Poly(vinylidene fluoride)
P(VDF-TrFE)	Poly(vinylidene fluoride-Trifluoroethylene)
PTFE	Polytetrafluoroethylene
PDMS	Polydimethylsiloxane
PLA	Polylactic acid
PVA	Polyvinyl alcohol
EPS	Expanded polystyrene
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
V _{oc}	Open circuit voltage
I _{sc}	Short circuit current
EDL	Electrical double layer
DSC	Differential scanning calorimetry
TGA	Thermal gravimetric analysis
AFM	Atomic force microscopy
PFM	Piezo force microscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
EDS	Energy dispersive spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
DSO	Digital storage oscilloscope
UTM	Universal Testing Machine
FEA	Finite Element Analysis

MCU	Microcontroller unit
LEDs	Light emitting diodes
NDT	Non-destructive testing
d_{33}	Piezoelectric coefficient
FWHM	Full width at half maximum
$F(\beta)$	β -phase content
dB	decibel
rpm	Revolutions per minute
RF	Radio frequency
FFT	Fast Fourier Transform
WCA	Water contact angle

List of Publications

This thesis is based on the following publications

[1] Piezoelectric activity assessment of size dependent naturally acquired mud volcano clay nanoparticles assisted highly pressure sensitive nanogenerator for green mechanical energy harvesting and body motion sensing.

Namrata Das, Debmalya Sarkar, Md Minarul Saikh, Prosenjit Biswas, Sukhen Das, Nur Amin Hoque, Partha Pratim Ray.
Nano Energy 102 (2022) 107628.

[2] Development of a lead-free, high-frequency ultrasound transducer with broad bandwidth and enhanced pulse-echo response, employing β -Ni(OH)₂/PVDF-TrFE piezoelectric composite.

Namrata Das, Debmalya Sarkar, Nitin Yadav, Asfak Ali, Sukhen Das, Partha Pratim Ray, Nur Amin Hoque.
Chemical Engineering Journal 475 (2023) 146322.

[3] Wenzel model motivated, superwetttable micro-motified membrane for droplet-driven, real-time acid rain sensor via sequential contact electrification strategy.

Namrata Das, Debmalya Sarkar, Souvik Sau, Asfak Ali, Sayoni Mandal, Sukhen Das, Partha Pratim Ray, Nur Amin Hoque.
Materials Today Energy (2025) 101812.

[4] Upcycling agricultural and packaging waste: A spacer-free, all-fibrous triboelectric sensor for bidirectional breeze energy harvesting and real-time on-road vehicular over-speed surveillance.

Namrata Das, Debmalya Sarkar, Nur Amin Hoque, Md. Minarul Saikh, Sukhen Das, Partha Pratim Ray.
(Under review)

Additional Publications

[5] Development of a sustainable and biodegradable sonchus asper cotton pappus based piezoelectric nanogenerator for instrument vibration and human body motion sensing with mechanical energy harvesting applications.

Debmalya Sarkar, **Namrata Das**, Md Minarul Saikh, Prosenjit Biswas, Solanky Das, Sukhen Das, Nur Amin Hoque, Ruma Basu.

ACS omega ACS Omega 6 (2021), 28710–28717.

[6] Self-Polarized ZrO₂/Poly(vinylidene fluoride-cohexafluoropropylene) nanocomposite-based piezoelectric nanogenerator and single-electrode triboelectric nanogenerator for sustainable energy harvesting from human movements.

Md Minarul Saikh, Nur Amin Hoque, Prosenjit Biswas, Wahida Rahman, **Namrata Das**, Sukhen Das, and Pradip Thakur.

Physica Status Solidi A 218 (2021), 2000695.

[7] Natural clay-based reusable piezo-responsive membrane for water droplet mediated energy harvesting, degradation of organic dye and pathogenic bacteria.

Dhananjoy Mondal, Souravi Bardhan, **Namrata Das**, Jhilik Roy, Saheli Ghosh, Anupam Maity, Shubham Roy, Ruma Basu, Sukhen Das.

Nano Energy 104 (2022) 107893.

[8] High β -crystallinity comprising nitrogenous carbon dot/PVDF nanocomposite decorated self-powered and flexible piezoelectric nanogenerator for harvesting human movement mediated energy and sensing weights.

Debmalya Sarkar, **Namrata Das**, Md Minarul Saikh, Prosenjit Biswas, Shubham Roy, Sumana Paul, Nur Amin Hoque, Ruma Basu, Sukhen Das.

Ceramics International 49 (2023), 5466–5478

[9] Elevating the performance of nanoporous bismuth selenide incorporated arch-shaped triboelectric nanogenerator by implementing piezo-tribo coupling effect: Harvesting biomechanical energy and low scale energy sensing applications.

Debmalya Sarkar, **Namrata Das**, Md Minarul Saikh, Shubham Roy, Sumana Paul, Nur Amin Hoque, Ruma Basu, Sukhen Das.

Advanced Composites and Hybrid Materials 6 (2023) 232.

[10] Micropatterned BaTiO₃@Ecoflex nanocomposite assisted self-powered and wearable triboelectric nanogenerator with improved charge retention by 2D MoTe₂/PVDF nanofibrous layer.

Debmalya Sarkar, **Namrata Das**, Souvik Sau, Ruma Basu, Sukhen Das.

Journal of Materials Chemistry C 12.3 (2024): 984-1001.

List of Conferences/ Seminars Attended

[1] Oral presentation at ANVESHAN: National Student Research Convention: 2019-2020 (East Zone), entitled 'Cotton pappus based Piezoelectric nanogenerator and touch sensor', organized by Association of Indian Universities (AIU), held in February 2020 at Jadavpur University, Kolkata.

[2] Oral presentation at ANVESHAN: National Student Research Convention: 2019-2020 (National Level), entitled 'Cotton pappus based Piezoelectric nanogenerator and touch sensor', organized by Association of Indian Universities (AIU), held in February 2020 at Rajiv Gandhi Proudhyogiki Vishwavidyalaya, Bhopal.

[3] Poster presentation at the National seminar on New Directions in Physical Sciences 2020, entitled 'Piezoelectric nanogenerator mediated energy harvesting' held in February 2020 at Jadavpur University in association with Indian Photobiology Society.

[4] Attended the DST-SERB Sponsored One Day Workshop on Material Synthesis & Characterization Techniques, held in February, 2020 at Jadavpur University, Kolkata.

[5] Poster presentation at 33rd AGM of MRSI and 4th Indian Material Conclave IUMRS-ICA 2022, entitled 'An eco-friendly naturally acquired triboelectric nanogenerator employing cellulose nanofibrous paper and mud volcano clay nanoparticles/PVDF mat for harvesting energy from human body motion' held in December 2022 at IIT Jodhpur, India.

[6] Oral presentation at 67th DAE solid state physics symposium, entitled 'Water Drop-mediated Triboelectric Nanogenerator Employing Microporous Polymeric Film, using Single-step Microwave Irradiation', held in December 2023 at Gitam University, Visakhapatnam, India.

[7] Oral presentation at European Materials Research Society (E-MRS) 2024 Spring Meeting, entitled 'Water Drop-mediated Triboelectric Nanogenerator Employing Microporous Polymeric Film, using Single-step Microwave Irradiation', held in May 2024 at Exhibition & Convention Center, Strasbourg, France.

[8] Poster presentation at Young Scientists' Colloquium 2024 (MRSI), entitled 'Microwave Irradiation Aided Fabrication of Microporous Polymeric Composite for Water Drop-Driven Triboelectric Nanogenerator', held in December 2024, at Ramakrishna Mission Vidyamandira, Belur Math, Howrah, India.

[9] Oral presentation at the 7th Regional Science & Technology Congress 2024-25, entitled 'Water Drop-mediated Triboelectric Nanogenerator Employing Microporous Polymeric Film, using Single-step Microwave Irradiation', held in January 2025 at Presidency University, Kolkata.

[10] Poster presentation at International Conference on Energy Conversion and Storage (IECS-2025), entitled 'Development of Microporous Polymeric Composite Aided by Single-step Microwave Irradiation for Water Drop-Driven Triboelectric Nanogenerator', held in January 2025, at IIT Madras, Tamil Nadu.

Awards/ achievements

[1] First position under Basic Science category at ANVESHAN: National Student Research Convention: 2018-2019 (East Zone), AIU, India.

[2] Best poster award at International Conference on Energy Conversion and Storage (IECS-2025), IIT Madras, Tamil Nadu.

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Chapter 1



Introduction

1.1. Energy harvesting technology

1.1.1. Fundamentals of energy harvesting

Energy plays a fundamental role in human life, as evidenced by the anticipated 25% increase in per capita energy consumption by 2040. With the world's energy dependence growing rapidly, there is a pressing need to explore alternative sustainable energy solutions. Energy harvesting refers to the technique of collecting energy from the environment around a system and transforming it into usable electrical energy [1]. The process is also commonly referred to as energy scavenging or power scavenging. Undoubtedly, this technology is highly appealing for a diverse range of self-powered systems. Research in the field of energy harvesting has been exploded in the past several years. Modern developments in wireless and low powered electronics such as micromechanical systems have prompted this surge. Mechanical vibrations which are commonly present in the environment, offer a viable source for energy generation. Numerous techniques have been developed to capture and convert this ambient vibrational energy into usable power. Typically, an energy harvester comprises of three primary components: the energy harvesting unit - that transforms ambient energy to electrical energy, a conditioning electrical circuit (voltage amplifier or rectifier) - that boosts and stabilizes the output voltage. The resulting output voltage is either directly

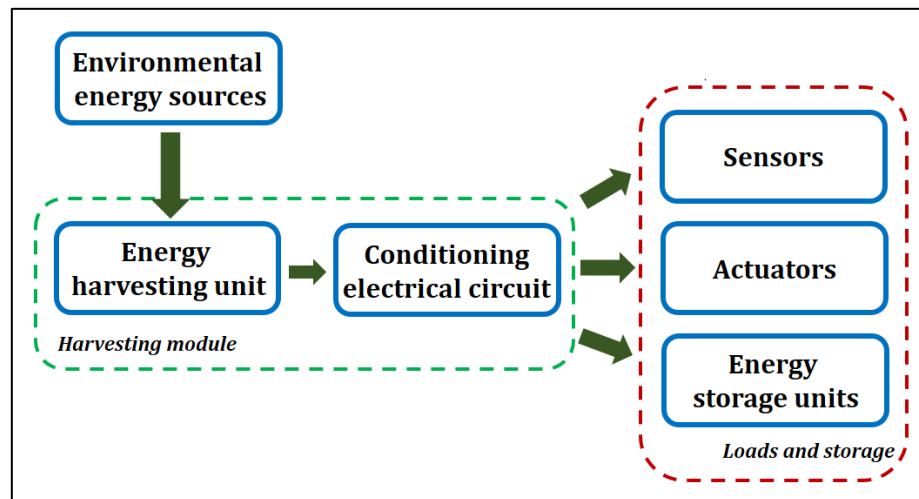


Figure 1.1. Simplified representation of energy harvesting process

supplied to sensors, actuators and other electronic devices or transferred to energy storage units such as batteries or supercapacitors for later use. Figure 1.1 illustrates a simple energy harvesting system in flowchart form, designed to capture ambient energy and converting it into electrical energy for further use and for storage. The specific

purpose and the natural environment in which a device is to be utilized, determine which energy harvesting source is optimal and each energy source has its own set of advantages and disadvantages. Windmills, turbines, solar cells and other forms of macro-energy collecting systems have existed for ages, but they are not innovatory since the ultimate design objective is to create a compact, long-lasting device [2]. Due to the advancements in energy harvesting technology, complex electronic systems are now smaller in size and consume less power. These improvements have paved the way for new computing paradigms and electronic applications, where numerous compact devices operate together or maintain strong communication links [3, 4]. The combination of ultralow-power microelectronics and advancements in micro-energy harvesting has led to the realization of truly self-powered devices by significantly reducing the need for frequent battery recharging cycles. Given the constraints of limited battery capacity and the frequent need for recharging, energy harvesting offers an effective solution to address the challenge of balancing energy demands with battery limitations [5, 6].

1.1.2. Brief history of energy harvesting

Majority of the energy used before the starting of Industrial Revolution in the 19th-century, were of renewable form. Energy harvesting in the form of wind power was first utilized as early as 3200 BC, when the ancient Egyptians used it to navigate the Nile

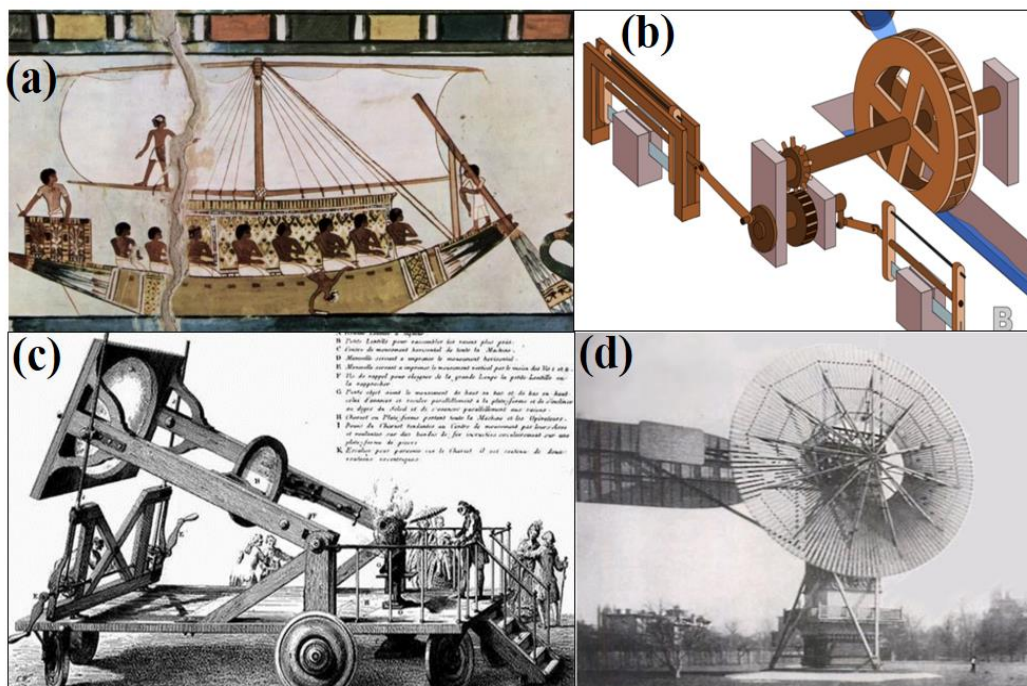


Figure 1.2. Energy harvesting techniques in ancient times [7]

River [7] as can be seen from figure 1.2(a). By around 200 BC, basic windmills were being employed in China and the Middle East for water pumping [8, 9]. Even before the windmills, the watermills consisting of rods and cranks operated as dual saws for cutting stone [7], as shown in figure 1.2(b). The Romans utilized solar and geothermal energy to warm their homes and public baths, while the ancient Greeks invented the earliest waterwheels, using hydropower to mill wheat into flour [10]. Sunlight began to be used as an energy source after wood, wind and water currents. According to historians, Archimedes used parabolic mirrors to ignite Roman ships, while Antoine Lavoisier later conducted experiments with lenses that focused sunlight intensely enough to melt metal [7], as shown in figure 1.2(c). During the medieval period, hydropower emerged as a key energy source. By around 19th century, with the discovery of the theory of electricity, scientists started exploring methods to produce electricity from renewable sources. The first modern turbine with 144 blades was constructed in 1888, and its generated electricity was stored in batteries, as can be seen in figure 1.2(d).

Therefore, it can be suggested that ancient civilizations were likely far more technologically advanced than they are often credited for. Archaeologists are now revealing some remarkable technologies from thousands of years ago, indicating that ancient civilizations might have already understood how to harness renewable energy. It has been found that terracotta pots from the Parthian era (250 BC to 224 AD) may have worked as early electrochemical cells used for electroplating, as suggested by their internal metal components and evidence of gold coated silver artifacts [11]. The unique construction and the celestial alignments of the Great Pyramid, Egypt have led researchers to theorize that it functioned as an ancient power plant, utilizing the piezoelectric effect, hydrogen and electromagnetic resonance [11].

The Industrial Revolution marked the beginning of an era dominated by fossil fuels, which were both inexpensive and easily accessible. Following that, a significant milestone for wind power occurred during the 1970s US energy crisis, which prompted researchers to seek for alternative energy sources. In 1980, U.S. Wind power established the world's first wind farm, featuring 20 turbines each with a capacity of 30 kilowatt [12-14]. The first wind farm in the world which was offshore was constructed in Denmark in 1991, consisting of 11 turbines each generating 450 kW, with a combined capacity of 5 megawatts (MW).

1.1.3. Energy harvesting in India

In ancient India, a variety of techniques were employed for harvesting energy, particularly water, along with sophisticated irrigation systems [15]. Historical records reveal the existence of numerous water canals, dams and water bunds that were used for irrigation, water storage and distribution [16, 17]. These systems were remarkably well-organized and constructed with great scientific precision as can be seen from figure 1.3(a) and (b), effectively serving large populations. Stepwells were innovative structures

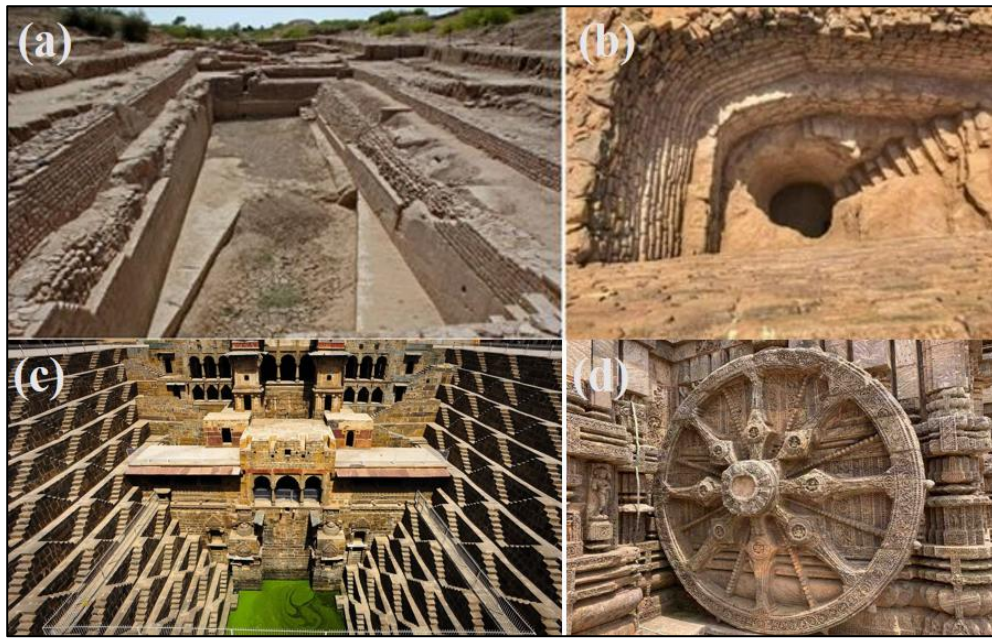


Figure 1.3. Ancient energy harvesting techniques in India [obtained from

built with staircases that provided convenient access to water throughout the year with passive cooling technology [18, 19] as can be seen from figure 1.3(c). Their design accounted for seasonal variations in groundwater levels, allowing people to reach water easily during both the monsoon when levels were high, and in summer when water level dropped drastically. The Konark Sun Temple in Odisha, as shown in figure 1.3(d) and the Modhera Sun Temple in Gujarat, are remarkable examples of ancient Indian architecture that reflect an understanding of solar principles. Although they were not intended for solar energy harvesting solely, their designs were strategically aligned to make the most of sunlight and natural heating [20].

India, with a population of approximately 1.46 billion and growing at an annual rate of 1.58%, is likely to encounter serious energy challenges in the coming decades. Since fossil fuel resources become increasingly scarce, the country may experience

energy shortages driven by rising energy costs and growing concerns over energy security [21]. India's growing energy demand is largely met by non-renewable sources like coal, imported oil and petroleum, which are both environmentally harmful and non-sustainable in the long term. To ensure energy security without hindering economic growth, it is crucial to transition from these conventional sources to renewable energy alternatives. Renewable energy harvesting presents a viable way to meet this growing demand [22, 23]. At present, renewable energy harvesting contribute around 33% to India's primary energy consumption. India is progressively adopting sustainable energy initiatives, exemplified by major projects such as the Bhadla solar park in Rajasthan, Gujarat's wind-solar hybrid cluster and various other green energy corridors. Additionally, our country has set an ambitious target of achieving 30 GW of offshore wind energy capacity by 2030. These efforts are focused on reducing carbon emissions, enhancing air quality and fostering a sustainable future. Harnessing energy from human footfall is particularly valuable for densely populated country like India, where places such as railway stations, footpaths and temples remain crowded throughout the day. By integrating piezoelectric, triboelectric or other energy harvesting technology into flooring, the pressure generated by footsteps can be detected by embedded sensors. These sensors, could convert the mechanical energy into electrical energy, which can then be stored and utilized as a power source [21]. India is emerging as a global leader in renewable energy harvesting sector, driven by government support and favourable economic conditions [24].

1.2. Background and motivation

The excessive use of non-renewable energy resources and the rising demand for power have become major concerns and pressing issues for humanity in recent years. The world today faces major energy challenges such as over dependence on fossil fuels, grid instability, pollution, global warming and the underutilization of environmental energy. If these trends continue, they are likely to result in the depletion of most fossil fuels within the next few decades [25-27]. In relevance to today's world, sustainability holds the key to securing a better future for all of us. 'Sustainable development' refers to using resources at a rate that meets the needs of the present without compromising the ability of future generations to meet their own needs [28]. This term was first introduced by Eva Balfour and Wes Jackson and the idea was later expanded and formalized by the

World Commission [29]. According to the definition, sustainable development encompasses three key dimensions: economic, social and environmental aspects. Therefore, meeting the growing energy demands has become essential for achieving sustainable development, which involves enhancing individuals' quality of life, ensuring adequate production for societal needs and reducing the environmental impact of the resources utilized in these practices. In the quest for sustainable alternatives and innovative energy harvesting methods, researchers are drawing inspiration from ancient energy harvesting techniques and combining them with modern technologies to develop advanced solutions.

To overcome several environmental challenges, the idea of "self-powered" systems has been introduced and has gained significant interest. The rising demand for energy and the need to reduce environmental pollution have motivated researchers and scientists to develop biocompatible, portable, cost-effective and self-powered nanogenerators. These nanogenerators convert mechanical energy into electrical energy, playing a crucial role in powering self-sustaining electronic devices [30-32]. These nanogenerators can harvest mechanical energy from a variety of life activities, including walking, jogging, touching, heartbeat and other human movements. They can also directly harness energy from natural energy sources like rainfall, wind, ocean waves, geothermal heat and sunlight [33-35]. Thus, in this age of the Internet of Things (IoTs), energy harvesters are good options to be used as alternative energy sources because of these benefits. Two of the latest advancements in energy harvesting technologies are piezoelectric and triboelectric nanogenerators, which are specifically developed to efficiently convert ambient mechanical energy into electrical energy for self-sustaining systems [36]. The history of piezoelectricity dates back to the 1880s, when two French scientists Pierre and Jacques Curie first discovered the piezoelectric effect. The term "piezoelectricity" comes from a Greek word 'piezein', meaning 'to press' or 'to squeeze' [37]. The Curie brothers found that applying mechanical stress to certain crystals such as quartz, tourmaline, topaz, Rochelle salt etc., caused them to generate electrical polarization. The first piezoelectric material to be used for commercial applications was quartz crystal. When a non-conducting and non-symmetric crystal like quartz gets stretched, it generates a small electrical voltage across its opposite surfaces. If the tension (T) on the crystal gets changed to compression (C), opposite voltage gets generated [91], as can be seen from figure 1.4(a). If the quartz crystal heats up, it becomes more

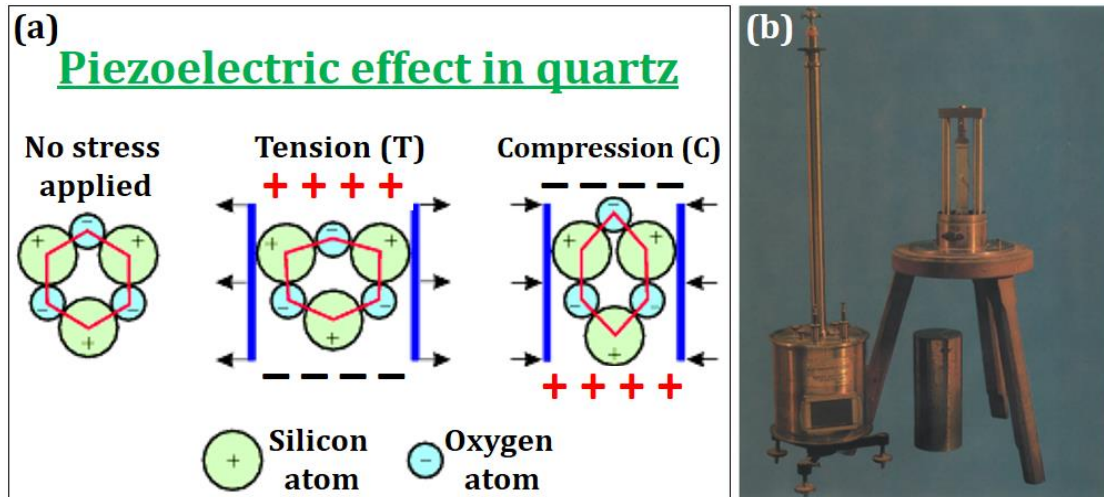


Figure 1.4. (a) Piezoelectric effect of quartz crystal [91], (b) Piezoelectric electrometer and piezoelectric quartz (right) [37]

deformable, enhancing its piezoelectric properties. However, once the temperature reaches 573°C , this piezoelectric behaviour of the crystal ceases entirely. Based on this discovery, Curie brothers developed the first piezoelectric quartz electrometer as displayed in figure 1.4(b). It was also found that the effect was reversible, which means that applying an electric field to these crystals could cause them to deform, mimicking the effect of physical pressure. These extraordinary experiments opened the door to numerous scientific and technological innovations, including the creation of piezoelectric sensors which can be used in medical imaging, fuel injection systems, ultrasound transducers and various other applications [39].

In 2006, Prof. Zhong Lin Wang and his team developed the first nanogenerator utilizing the piezoelectric effect. The primary goal of this pioneering work was to convert mechanical energy into usable electrical energy [40]. In the past, the piezoelectric effect had already been applied in large-scale devices through the use of bulk piezoelectric materials. However, over the past decade, advancements in the synthesis of piezoelectric nanomaterials have significantly contributed to the miniaturization of piezoelectric nanogenerators (PENGs). Following the development of the PENG, Professor Wang and his team explored the triboelectric properties of materials and in 2012 utilized this phenomenon to create a new type of nanogenerator known as the triboelectric nanogenerator (TENG) [41]. TENGs offer several benefits including high output power, low production cost, ease of fabrication and excellent energy conversion efficiency. With the increasing demand for flexible electronic devices like wearable gadgets, foldable

displays and electronic skin, flexible TENGs have become a major focus of research as potential power sources. The choice of appropriate materials and the optimized design of structures are crucial factors that influence both the energy output and mechanical durability of these flexible TENGs.

1.3. Piezoelectricity

1.3.1. Piezoelectric effect

The piezoelectric effect is the generation of electric charge in specific solid materials like certain crystals, polymers or any biological substances, when they are subjected to mechanical strain or stress. This process results in the polarization of the electric dipole moments, as shown in figure 1.5(a) [42, 43]. Piezoelectric materials typically function in one of three main working modes, represented by the following coefficients [63]:

- ❖ d_{33} mode, also referred to as the transverse configuration,
- ❖ d_{31} mode, known as the longitudinal configuration and
- ❖ The piezotronic mode.

The coefficients d_{33} and d_{31} reflect how effectively a material generates electrical charge in a specific direction when subjected to mechanical deformation and a schematic diagram of d_{33} mode (transverse mode) and d_{31} mode (longitudinal mode) have been shown in figure 1.5(b).

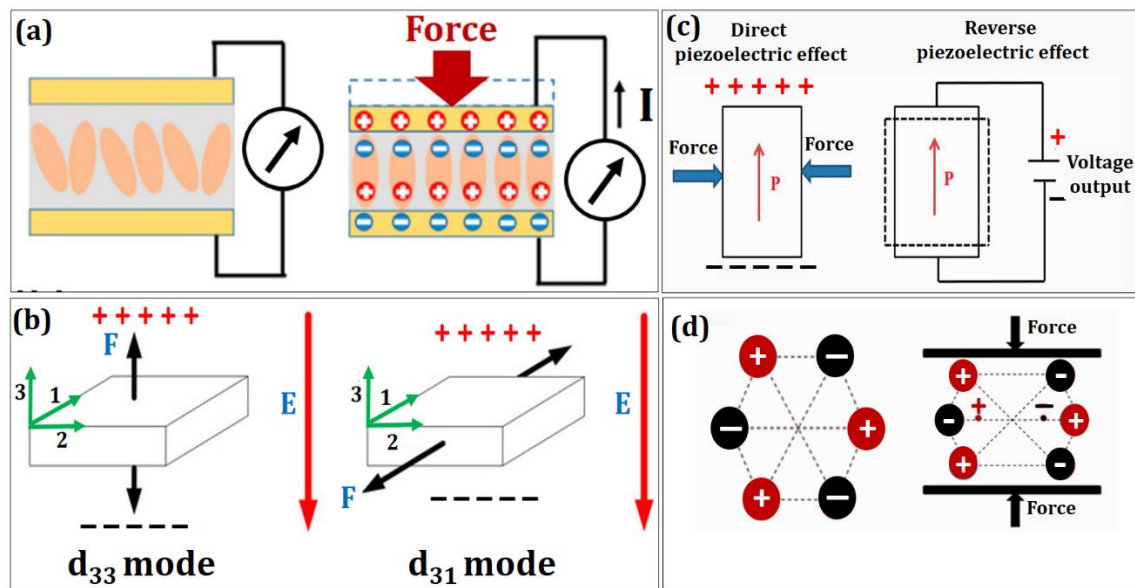


Figure 1.5. (a) Working principle of PENG [43], (b) d_{33} and d_{31} working mode, (c) Direct and reverse piezoelectric effect, (d) Structural orientation in piezo-polymers

The piezoelectric effect has a reversible character, meaning that materials exhibiting this effect also demonstrate the reverse piezoelectric effect, where the application of an electric field causes the material to undergo internal mechanical strain. Therefore, when an electric field is applied to a piezoelectric material, it can cause the material to either contract or expand due to the phenomenon known as the reverse piezoelectric effect [44, 45]. This effect was theoretically inferred using the thermodynamic principles. The direct and reverse piezoelectric effect have been illustrated in figure 1.5(c). These two effects were initially discovered in crystals lacking a centre of symmetry and later numerous other ceramic materials were also found to possess piezoelectric properties. The polarization characteristics of these materials depend on the atomic composition and the structural arrangement of the crystals. In nanocrystals, all dipoles align along a single polar axis, giving the crystal a symmetrical structure. In contrast, polycrystalline materials contain multiple regions, each with dipoles oriented along different polar axes [44, 46]. The equations describing any linear piezoelectric substance can be expressed as follows [44]:

$$\text{For direct piezoelectric effect: } \mathbf{D}_m = \mathbf{d}_{mi} \boldsymbol{\sigma}_i + \boldsymbol{\beta}_{ik}^{\sigma} \mathbf{E}_k \quad (1)$$

$$\text{For reverse piezoelectric effect: } \boldsymbol{\varepsilon}_i = \mathbf{S}_{ij}^E \boldsymbol{\sigma}_j + \mathbf{d}_{mi} \mathbf{E}_m \quad (2)$$

Here, the indices i and j range from 1 to 6, while m and k range from 1 to 3, representing various directions within the material's coordinate system. $\mathbf{D}$ is the electric displacement vector, $\mathbf{d}$ is the piezoelectric strain constant, $\boldsymbol{\sigma}$ is the stress vector, $\boldsymbol{\beta}$ is the permittivity, $\boldsymbol{\varepsilon}$ is strain vector, $\mathbf{E}$ is the applied electric field and $\mathbf{S}$ is the matrix of compliance coefficients. In contrast to piezoelectric ceramics and crystals where the piezoelectric effect arises from the material's non-centrosymmetric property, piezoelectric behaviour in polymers is primarily attributed to the alignment of molecular chains and their structural orientation in the solid phase, as illustrated in figure 1.5(d). When mechanical stress is applied, it shifts the charge centres of positive and negative ions, resulting in a change in polarization that generates electric field [47]. Therefore, presence and organization of polar groups within polymers are crucial in influencing the piezoelectric properties [48].

1.3.2. Piezoelectric materials

Approximately 200 materials exhibiting piezoelectric behaviour have been identified for the use in energy harvesting technologies [49]. Many different materials demonstrate piezoelectric behaviour, which include ceramics such as lead zirconate

titanate (PZT), barium titanate (BaTiO_3) and lithium niobate, polymers like polyvinylidene fluoride, naturally occurring substances such as quartz, Rochelle salt and topaz as well as organic materials including silk, clay and wood, . Natural piezoelectric substances generally possess low electromechanical coupling and thus exhibit weaker piezoelectric responses [50]. Among the piezoelectric ceramics, particularly PZT and BaTiO_3 have gained significant interest because of their superior piezoelectric performance in comparison to other available materials [51, 52]. Due to the harmful and toxic character of lead, scientists are increasingly turning their attention toward lead-free perovskite materials. These eco-friendly piezoelectric ceramics are polycrystalline in form, composed of unevenly arranged microscopic grains and are commonly produced via solid-state synthesis followed by sintering. Their piezoelectric properties are significantly influenced by the temperature at which the phase transitions occurs, which leads to the polarization vectors shift and finally enhance the piezoelectric response. These lead-free perovskites are generally represented by the chemical structure ABO_3 , where A and B are different metal cations forming a class of oxide compounds. Various types of piezo-ceramics, including thin films based on PZT and lead-free alternatives, have been explored for their potential in transducer applications and energy harvesting systems. Single crystals typically consist of a well-ordered arrangement of positive ions and negative ions, which strengthens the overall dipole moment. Commonly used single crystal materials include quartz, lithium tantalate, langasite, gallium orthophosphate and lithium niobate [53-54].

Currently, polymer based composites incorporated with different types of electroactive fillers are extensively used because of their flexibility and enhanced piezoelectric characteristics. Among the piezoelectric polymers, polyvinylidene fluoride (PVDF), which was discovered in 1969 by Dr. Heiji Kawai at the Kobayashi Institute of Physical Research in Tokyo [61], is considered the most widely used organic piezoelectric substance due to its notable piezoelectric constant, strong chemical stability, high mechanical strength and impressive dielectric characteristics. Classified as highly non-reactive thermoplastic fluoropolymer, PVDF is synthesized through the repeated polymerization of the vinylidene fluoride monomer ($\text{CH}_2\text{-CF}_2$) as can be seen in figure 1.6(a), consisting of approximately 59% fluorine and 3% hydrogen by weight. It is recognized as a semi-crystalline material with a glass transition temperature near -35°C . Compared to other commercial fluoropolymers, PVDF has a relatively low density of

1.78 g/cm³. The presence of huge switchable dipole moments within the fluorocarbon chains of PVDF imparts its ferroelectric characteristics, when subjected to an electric field [62]. PVDF has been employed in the fabrication of piezoelectric nanogenerators, ultrasound transducers, wearable sensors and other sensing systems [55, 56]. PVDF has several copolymers such as poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), poly (vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) and poly (vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (PVDF-TrFE-CFE), all of which show excellent piezoelectric performance [57, 58]. PVDF and its copolymers have gained recognition as some of the most efficient electroactive, semi-crystalline thermoplastic

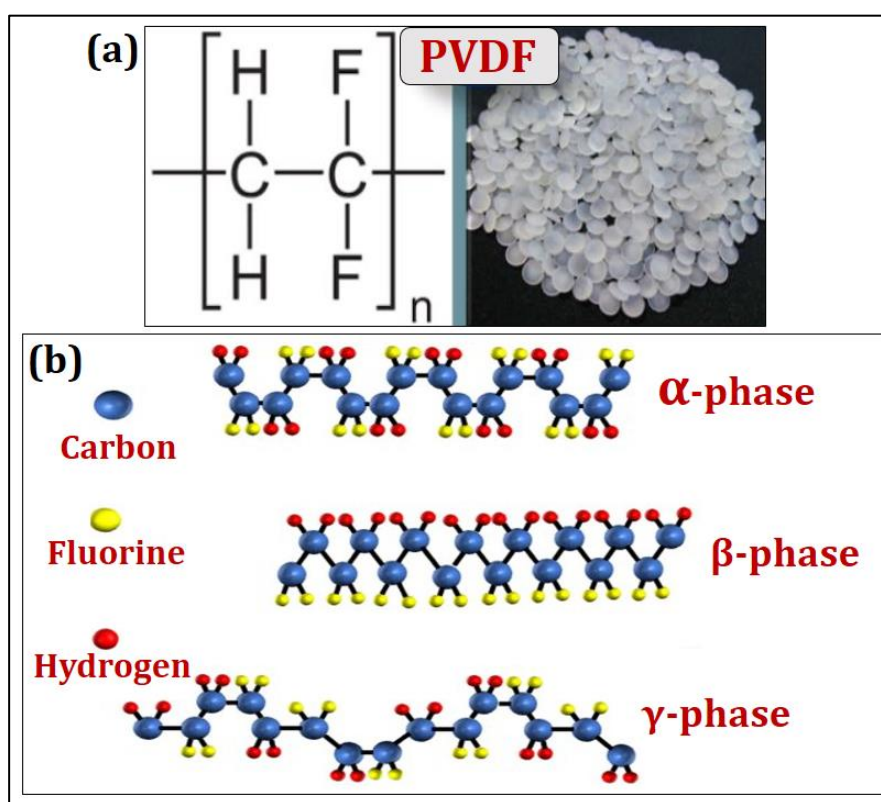


Figure 1.6. (a) Polymerization of $(\text{CH}_2\text{-CF}_2)$ monomer and digital image of PVDF, (b) Schematic diagram of different phases of PVDF (α , β and γ) [125]

polymers for producing advanced, affordable, flexible and biocompatible piezoelectric nanogenerators. PVDF is composed of five primary crystalline phase α , β , γ , δ and ϵ which are distinguished by the orientation of $-\text{CH}_2$ and $-\text{CF}_2$ dipoles. Among these, α , β and γ phases are the most frequently observed and the schematic diagram of these three phases have been shown in figure 1.6(b). When melted, PVDF predominantly forms the nonpolar α -phase (TG $\overline{\text{TG}}\text{G}'$ dihedral structure), known for its higher thermodynamic stability [39]. The γ -phase (TTTGT $\overline{\text{TG}}\text{G}'$ structure) exhibits moderate piezoelectric behaviour due to its

partial polarity. Of the polar β , γ and δ phases, the β -phase (TTTT conformation) is particularly significant, as it delivers superior piezoelectric, pyroelectric and ferroelectric characteristics along with excellent dielectric performance and suitable elasticity [59,60].

1.3.3. Piezoelectric nanogenerator (PENG)

1.3.3.1. Working principle and mechanism of PENG

Since its development, the piezoelectric nanogenerator has gained significant interest due to its ability to transform small, irregular forms of ambient mechanical energy into electrical power using piezoelectric nanomaterials [33]. PENGs generate electrical energy by transforming mechanical motion using the principles of the piezoelectric effect. PENGs operates on some fundamental equations which are [64]:

$$\sigma_p = c_{pq}\epsilon_q - e_{kp}E_k \quad (3)$$

$$D_i = e_{iq}\epsilon_q + \kappa_{ik}E_k \quad (4)$$

Here, σ_p is the stress tensor, c_{pq} is the elastic modulus tensor, ϵ_p is strain tensor, e_{kp} is piezoelectric tensor, E_k represents electric field, D_i is electric displacement and κ_{ik} is the dielectric tensor. The basic working mechanism of PENGs can be described as follows: when an external force is applied on a piezoelectric nanogenerator, the resulting internal and surface charges within the piezoelectric material create a potential difference across the device's electrodes. When the PENG is connected to an external circuit, this potential difference causes electron movement, thereby producing electrical output. The electrical output produced by a PENG can be theoretically interpreted using Hooke's law. The corresponding electrical response is expressed as follows:

$$D = \epsilon E \quad (5)$$

Here, D is electric displacement, ϵ is dielectric permittivity and E is the electric field strength. Now based on strain and the piezoelectric tensor, it can be written as [64]:

$$D_{Ri} = e_{ip}\epsilon_p \quad (6)$$

$$\rho^R = \frac{\partial D_{Ri}}{\partial x_i} \quad (7)$$

$$\Sigma^R = n_i D_{Ri} \quad (8)$$

Here, D_{Ri} denotes the residual electric displacement, ρ^R is the body charge which has been generated, Σ^R represents the surface charge of the piezoelectric material. As indicated by equation (6), the residual electric displacement is influenced by the strain and the piezoelectric tensor. Based on equation (7) and (8), when the strain is evenly distributed throughout the piezoelectric material, only residual surface charges remain [64]. The

equations pertaining to a PENG having a linear isotropic piezoelectric material, on the application of mechanical strain are [33]:

$$\mathbf{P}_i = (\mathbf{e})_{ijk} (\mathbf{S})_{jk} \quad (9)$$

$$\mathbf{T} = \mathbf{C}_E \mathbf{S} - \mathbf{e}^T \mathbf{E} \quad (10)$$

$$\mathbf{D} = \mathbf{e} \mathbf{S} - \mathbf{k} \mathbf{E} \quad (11)$$

Here, $\mathbf{P}$ is the polarization, $\mathbf{S}$ is mechanical strain; $(\mathbf{e})_{ijk}$ is piezoelectric third order tensor, $\mathbf{T}$ represents stress tensor and $\mathbf{C}_E$ is elasticity tensor, $\mathbf{k}$ is dielectric tensor and $\mathbf{E}$ is electric field. The displacement current for a linear polarizing medium can be represented as:

$$\mathbf{J}_{Di} = \frac{\partial \mathbf{P}_i}{\partial t} \quad (12)$$

Here $\mathbf{J}_{Di}$ represents the displacement current. Thus, it is evident from the equations that the output current density and the piezoelectric effect are linearly related to the rate at which the strain or stress acting on the PENG changes. In the absence of an external electric field, the displacement current of a dielectric material is entirely determined by its polarization, as indicated by equation (12). Assuming that $\mathbf{P}$ is oriented in the z -direction, it can be appropriately expressed as:

$$\mathbf{D}_z = \mathbf{P}_z = \sigma_p(z) \quad (13)$$

Here, $\sigma_p(z)$ represents piezoelectric polarization charge density for the dielectric material. Putting this term in equation (12), we obtain the displacement current term as:

$$\mathbf{J}_{Dz} = \frac{\partial \mathbf{P}_z}{\partial t} = \frac{\partial \sigma_p(z)}{\partial t} \quad (14)$$

Therefore, based on equation (14), it can be inferred that the displacement current has a direct relationship with the surface charge density resulting from piezoelectric polarization within the material. Finally, the PENG's open circuit voltage (V_{oc}) will be:

$$V_{oc} = d \frac{\sigma_p(z)}{\epsilon} \quad (15)$$

Here, d represent the width of the used piezoelectric media. Hence the above equations indicate that the output voltage of a piezoelectric nanogenerator is highly influenced by the polarization charges, which are henceforth dependent on the piezoelectric coefficient of the piezoelectric material used for the fabrication of the PENG [65].

1.3.3.2. Recent advances of piezoelectric nanogenerators

As technology continues to evolve in the electronics sector and the Internet of Things (IoT) expands rapidly, interest in energy harvesting has grown considerably in the recent years. Traditionally, most wearable systems relied on rechargeable batteries

and electrochemical capacitors for energy storage. However, these conventional methods come with several limitations including short lifespan, need for regular recharging, potential safety hazards and restricted energy capacity. These characters make them unsuitable for the next generation of power generating and wearable technologies. Since the development of piezoelectric nanogenerator in 2006, it has found applications across various fields such as energy harvesting, sensing, monitoring systems, human-machine interaction and various biomedical technologies. Despite lead zirconate titanate (PZT) demonstrating exceptional piezoelectric performance (with d_{33} value around 304 pC/N), its practical use is constrained due to its high lead content (reaching up to 60%) and due to its inherent stiffness [66]. Although there is a growing interest in PVDF and its copolymers due to their flexibility, biocompatibility, ease of fabrication and non-toxic nature, they exhibit relatively low piezoelectric coefficient (d_{33} value of approximately -33 pC/N) as compared to ceramic based piezoelectric materials. As a result, enhancing the piezoelectric response of PVDF is essential to advance the effectiveness of flexible PENGs constructed from this polymer. Recently, numerous investigations have focused on improving the piezoelectric performance of flexible PENGs with PVDF based multifunctional composites. Researchers have explored various fabrication techniques for producing piezoelectric films, including methods like melt spinning [67], spin coating, solution casting [68], electrospinning [67], 3D printing [69] etc., to understand the impact on the composite's efficiency.

Numerous researches have been going on for boosting the piezoelectric effect by introducing different structural modifications to the surface of the multifunctional composites. Gad et al. proposed an innovative method to improve the energy harvesting capability of composite nanofibrous membranes made from PVDF and ZnS by employing femtosecond laser-based surface modification technique [70]. Fotoukian et al. investigated how modifying the surface of titanium with a bioactive piezoelectric fiber, made from electrospun PLLA combined with different concentrations of hydroxyapatite filler, influences its properties [71]. As the β -polymorph of PVDF is well known for its superior piezoelectric characteristics, numerous studies have focused on improving the electrical output of PENGs by incorporating various fillers or additives into PVDF based flexible composite films, to boost the formation of the β -phase. Studies have shown that applying an electric field of about 150 MV/m at a temperature of 95 °C can convert the nonpolar α -phase crystals into the polar β -phase. This transformation indicates that

polarization treatment plays a crucial role in modifying the structural properties of the composite films [72, 73]. Oflaz et al. documented the development of flexible PVDF based composite films incorporated with graphene, boron nitride and silicon dioxide fillers. Subsequent thermal processing and polarization techniques contributed to a notable improvement in the β -phase content within the resulting composite film [72]. Joshi et al. introduced a scalable method involving supersonic spraying to fabricate flexible piezoelectric composites composed of PVDF and synthesised ZnSnO_3 , aiming to improve β -phase crystallinity [74]. Investigating environmental friendly green energy harvesters composed of readily available, safe and biodegradable resources has become essential to offer a viable answer to the growing need for sustainable energy solutions. Therefore, incorporating natural fillers or additives into the polymer matrix of piezoelectric nanocomposites has gained significant attention. Singh et al. developed a sustainable piezoelectric nanogenerator and a piezoelectric separator aimed to create a self-charging flexible supercapacitor using an eco-friendly bio-hydrogel derived from eatable *Mimosa pudica* seeds [75]. Sarkar et al. showcased the development and practical uses of a PENG constructed from polydimethylsiloxane (PDMS) and *Sonchus asper*, a widely available and eco-friendly natural fiber [76].

Nano/microfibers produced through solution or melt spinning methods can be utilized to create woven or knitted fabrics designed for PENGs. Incorporating these textile-based harvesters into everyday garments is expected to play a crucial role in advancing future smart wearable electronic devices [77]. Another recent advancement in the use of PENGs involves their application in personalized healthcare sector, where they support diverse clinical functions such as self-powering sensors, targeted drug delivery and tissue healing processes [78]. Park et al. developed a self-powered sensor utilizing a piezoelectric PZT film, for monitoring pulses. The PENG was attached to the wrist and throat area to detect pulse signals. These signals were then wirelessly transmitted to a smartphone for real-time health tracking [79]. Deng et al. designed a piezoelectric nanogenerator using PVDF-ZnO nanofibers aimed at recognizing human gestures, which was then employed to operate a robotic hand, enabling a human-machine interaction system [80].

1.3.4. Piezoelectric ultrasound transducer (UST)

1.3.4.1. Background of UST

Until the early 20th century, piezoelectric effect was primarily studied within research labs and had not been implemented in practical applications. During First World War, first real life use of piezoelectric technology emerged with the development of sonar systems [81]. Operating at ultrasonic frequencies, these devices demonstrated greater efficiency and effectiveness compared to the earlier Fessenden oscillator, leading to their widespread adoption. In 1917, Paul Langevin created the earliest ultrasound transducer based on the piezoelectric effect, aimed at locating enemy U-boats through the reflection of ultrasonic echoes [82]. He is regarded as the 'Father of ultrasonics' for discovering that quartz's piezoelectric characteristics could be harnessed to produce and detect ultrasonic waves [83-85]. This discovery sparked further research on the practical applications of piezoelectric effect, eventually contributing to the broad adoption of ultrasound technology in the field of underwater applications, non-invasive medical diagnostics and non-destructive testing. Langevin utilized quartz resonators and high-frequency ultrasound waves to detect underwater submarines. Together with his team, he developed an ultrasonic detection system that included a transducer made from a thin quartz crystals sandwiched between two metal plates along with a piezoelectric hydrophone. The hydrophone amplified the signal using a vacuum tube and the good acoustic impedance observed in the piezoelectric materials made them ideal for underwater transducer applications. The same quartz element could generate sound pulses when driven by electrical oscillators. The transducer sent out a pulse of very high frequency into the water and the reflected echo was detected by the hydrophone. By calculating the time interval between the emission and reception of the echo, the depth could be accurately determined [83]. The cross sectional image of the first piezoelectric ultrasound transducer designed by Paul Langevin has been shown in figure 1.7(a). Widely recognized as a pioneer in ultrasonic testing, Sergei Y. Sokolov introduced the concept of using ultrasonic wave transmission method to identify defects and internal irregularities in metals, as can be seen from figure 1.7(b). In his work, Sokolov explained the construction of quartz-based signal generators and techniques for effectively coupling these generators to the test object, to optimize energy transfer and various ways to detect ultrasonic waves after they passed through the material. He also invented the first "ultrasonic camera," capable of generating visual representations of the internal defects

of the solid structures. This approach relied on a large piezoelectric transducer, which retained the electric charges produced by the incoming ultrasound waves. A mechanical contact or scanning beam would then move across the transducer's surface, gradually forming an image of the detected flaw [86]. In 1957, Joseph Holmes and his team

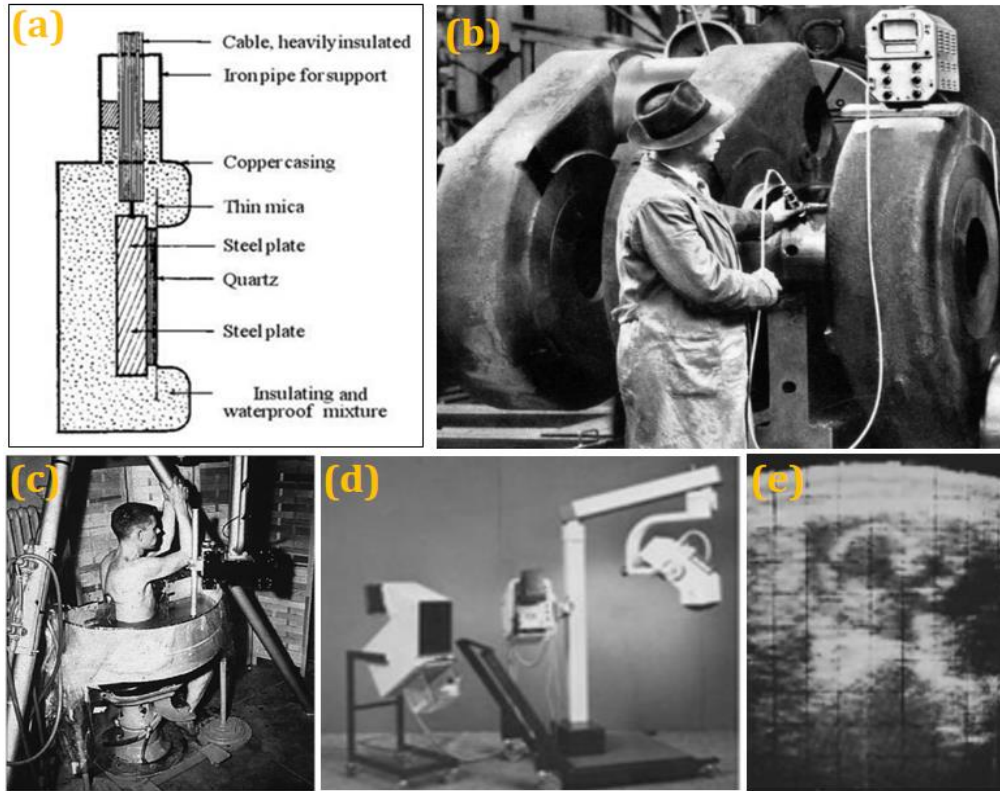


Figure 1.7. (a) Cross-sectional image of first piezoelectric UST [83], (b) Sergei Y. Sokolov using UST to identify defects in metals [86], (c) UST based Pan-scanner for clinical sonography [89], (d) First real-time UST scanner [86] and (e) Real-time scanned image using the UST

developed the Pan-scanner, which demonstrated a feasible approach to clinical ultrasonography. This device featured a dental chair where the patient was seated, with a plastic window connecting to a curved pan filled with saline solution. A piezoelectric transducer moved automatically in a circular motion through the liquid [88, 89], as can be seen in figure 1.7(c). Walter Krause and Richard Soldner constructed the first real-time UST scanner and the first ultrasonic scanner [86, 90] as can be seen in figure 1.7(d). Figure 1.7(e) shows a real-time scanned picture of a foetus hand and face using the UST.

1.3.4.2. Working principle of UST

Ultrasound, operating within the frequency spectrum of 20 kHz to several GHz, has demonstrated vast significance across various domains. High-frequency ultrasound offers great potential as an imaging technique for capturing finer details of anatomical

features such as skin, eyes, muscles and blood vessels. Based on the piezoelectric effect, the ultrasound transducer transforms electrical signals into sound waves and capture back the reflected signals. An ultrasound transducer comprises of five core components as can be seen from figure 1.8(a). They are [91-93]:

❖ **Piezoelectric crystal/ceramic or piezoelectric polymeric films:**

- Might consist of single element like PZT or with numerous elements for broadband transducers.
- PVDF based polymeric composites are useful for high frequency and high bandwidth USTs. PVDF has a low acoustic impedance which is almost similar to that of water, which makes it helpful for producing ultrasonic pulses with high resolution.
- Higher frequency oscillations are produced by thinner elements, whilst lower frequency oscillations are produced by thicker elements.

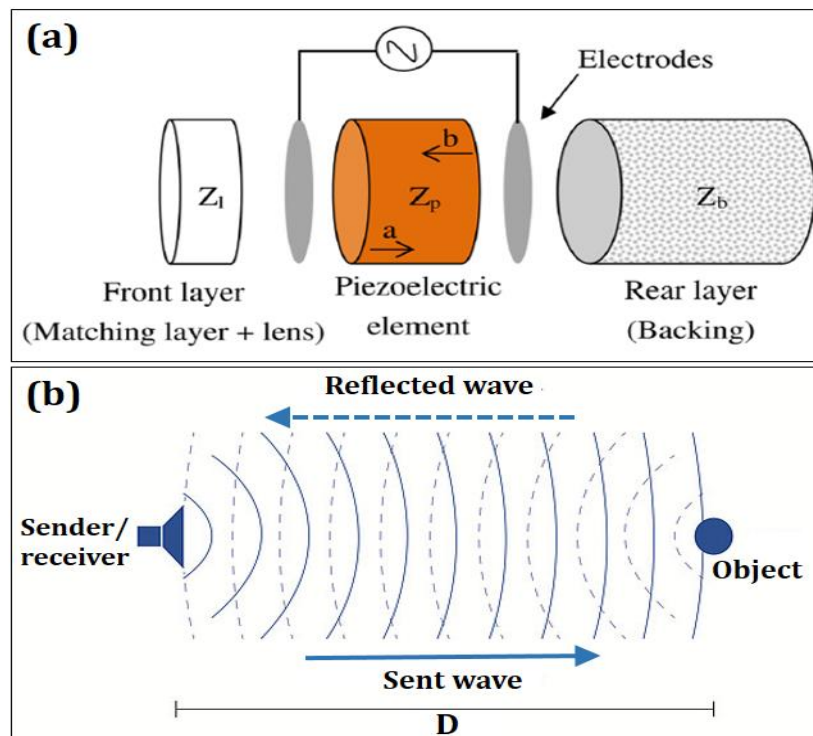


Figure 1.8. (a) A piezoelectric UST showing the core components [96], (b) Travelling of ultrasound waves from and to UST

❖ **Electrodes placed on both the surfaces of the piezoelectric material:**

- These enable electrical connections.

❖ **Damping or backing layer:**

- Attached at the back of piezoelectric layer, rear to the electrode.

- It absorbs ultrasound waves reflected in the reverse direction and reduces unwanted signals coming from the transducer casing.
- Dampens the piezoelectric material's resonant vibrations, resulting in a decreased length of spatial pulse.

❖ **Matching layer:**

- Acts as an interface in between the piezoelectric material and the testing object.
- Enables nearly complete transmission of ultrasound waves from the UST to the testing material by reducing reflections caused by differences in acoustic impedance between materials.

❖ **Housing or casing:**

- Provides protection and electrical insulation.

Whether measuring the irregularities or detecting any object, the piezoelectric layer acts as both a transmitter as well as a receiver during its operation. During the runtime of a UST, the piezoelectric material initially sends out an ultrasound pulse. These ultrasound waves travel through the medium, strike the object of our interest and are then reflected back. While some waves are partially absorbed, the same piezoelectric material captures the reflected ultrasound waves [94], as can be seen from figure 1.8(b). The time interval Δt between the emission and the reception of the ultrasound waves helps to determine the distance between the UST and the object. If the sound velocity in the transmitting medium is (s), distance (D) between ultrasound source and the object can be calculated by [95]:

$$2.D = s.\Delta t \quad (16)$$

Ultrasound transducers operating above 30 MHz provide enhanced image clarity and high resolution. The clarity of the ultrasound image is influenced by the bandwidth of the ultrasound pulse, which affects axial resolution (R_{axial}) and by the width of the ultrasound beam, which impacts lateral resolution ($R_{lateral}$). R_{axial} and $R_{lateral}$ at -6dB can be expressed using the equations [96]:

$$R_{axial} = \frac{\lambda}{2BW} = \frac{s}{2f_c B} \quad (17)$$

$$R_{lateral} = \lambda F = \frac{s}{f_c} F \quad (18)$$

Here, f_c represents the central frequency of UST, B represents the bandwidth, F represents ratio of the focal length to aperture and λ represents wavelength. Therefore, if the number of cycles in each pulse remains constant, increasing the frequency leads to a shorter

wavelength and a decreased pulse length, while the bandwidth becomes broader. In ultrasound imaging for medical purposes, transducers having broad bandwidth and minimal signal loss are ideal. To enhance efficiency of a transducer mechanical matching is very important, which involves both front matching as well as rear backing. When a single electric pulse is applied to the piezoelectric material, it generates pressure waves in both forward as well as backward directions which labelled as 'a' and 'b' in figure 1.8(a). The forward moving pressure wave 'b' travels and eventually reaches the front face of the piezoelectric component. Then this pressure transmits to the front layer with normal incidence and the transmission coefficient can be represented as [96]:

$$T = \frac{2Z_t}{Z_t + Z_p} \quad (19)$$

Here Z_t and Z_p represent the acoustic impedance of the testing medium and that of the piezoelectric material, respectively.

1.3.4.3. Application of piezoelectric USTs and the recent advances

Piezoelectric ultrasound transducers, particularly those developed with lead-free piezoelectric layers, play a vital role in the field of emerging micro or nano devices. These USTs enable accurate sensing and detection in medical diagnosis and various industrial applications. These piezoelectric USTs are well suited for integration into compact systems because of their energy efficiency, versatile functionality and compatibility with limited-space environments. Some of the key applications of piezoelectric ultrasound transducers along with recent developments have been mentioned below.

❖ **Biomedical ultrasound imaging:** Due of the excellent acoustic energy to electric energy conversion efficiency, piezoelectric ultrasonic transducers have demonstrated significant potential in medical use. The USTs can create a very narrow beam owing to the focusing process, which significantly increases the sensitivity and resolution of the images. In the field of medical diagnostics, intravascular ultrasound (IVUS) serves as a vital technique for identifying cardiovascular conditions. Ultrasound transducers aid in the evaluation of blood circulation and the identification of issues like clots and arterial blockages within the blood vessels [97]. Yoon et al. [98] introduced a single crystal UST probe designed to overcome challenges related to the limited lumen area in cases of intravascular blockage. Operating at a central frequency of 45 MHz, the transducer demonstrated R_{axial} and $R_{lateral}$ of 25 μm and 120 μm respectively, enabling high-resolution images of vascular regions. Caronti et al. conducted a study showcasing the

pulse-echo performance of 10.7 MHz flexible piezoelectric UST, designed to offer the flexibility and the required curvature needed for a convex endocavity ultrasound probe. These probes were used for internal examinations such as rectal or vaginal scans, where a broad field of view and small penetration depth are essential [99].

❖ **Targeted ultrasound ablation:** Focused or targeted ultrasound ablation is a non-invasive technique that employs concentrated ultrasonic radiation to precisely burn and destroy specified unwanted tissue [100]. It is frequently used to treat malignancies, Parkinson's disease and various kinds of tumours. This non-invasive therapy intends to deliver targeted treatments with no damage caused to the nearby tissues. Choi et al. [100] developed an innovative concave piezoelectric transducer using theoretical simulations. This toroid like shape of the UST allowed for precise focusing of ultrasound beam, while minimizing surrounding effects and reducing the risk of harming the nearby tissues. Zhou et al. investigated the use of ultrasound echo from a focused ultrasound transducer as an innovative technique to examine the coagulation triggered by focused ultrasound ablation surgery (FUAS) [101]. This method presented multiple benefits such as lower acoustic signal loss, improved ability to penetrate tissue located deep within the body and higher focusing efficiency.

❖ **Fingerprint Sensing:** Among the most promising strategies used by large electronic corporations are biometric verification systems and ultrasonic fingerprint imaging technologies utilizing piezoelectric materials. Chen et al. [102] presented an array based UST utilizing PZT aimed at fingerprint imaging applications, operating at 24.82 MHz resonant frequency. The array demonstrated high electromechanical coupling and good mechanical quality factor, indicating strong potential for the use in large fingerprint sensing systems.

❖ **Ultrasonic energy transmission:** Conventional inductive coupling methods for wireless energy transfer is not much effective in meeting the evolving demands of implantable medical devices due to significant energy loss and limited safety. In contrast, ultrasound induced wireless power transmission has recently emerged as a good alternative [97]. This approach involves the transfer of mechanical energy via ultrasound waves from a transmitting UST to a receiving UST, which then supplies power to other connected devices.

1.4. Triboelectric nanogenerator

1.4.1. Triboelectric effect and triboelectric series

Triboelectrification is a common, long-known phenomenon for over 2600 years since Greek civilization. This phenomenon occurs universally across all states of matter, whether solid, liquid or gas and is the first electrical concept taught in school. Contact electrification is the scientific term for triboelectrification, which is the process by which two distinct materials, even that are chemically identical, develop electric charges when separated after coming into direct physical contact [103]. Triboelectric nanogenerators (TENGs) are innovative devices that harness mechanical energy from the environment and transform it into electrical energy. Developed by Professor Z.L. Wang's research team, TENGs have emerged as a leading option for next-generation energy solutions, largely due to the widespread and universal nature of the triboelectric effect. Operating through the principles of contact electrification along with electrostatic induction, TENGs represent a rapidly emerging technology for mechanical energy harvesting, offering a range of significant benefits. As also mentioned earlier, triboelectric effect refers to the contact electrification in which two different materials acquire electric charges after being brought into contact and then separated. In contrast, electrostatic induction enables the conversion of mechanical motion into electrical energy by altering the electric potential as a result of mechanically driven separation between the triboelectric materials. During this process charges get transferred via electron transfer between the materials and the charge transfer direction is determined by the inherent properties of the two materials. Maxwell's displacement current serves as the main driving mechanism of contact electrification. TENGs are very efficient at converting low frequency irregular mechanical vibrations into electrical energy, making them highly suitable for capturing energy from everyday activities [104]. Though triboelectric nanogenerators were initially discovered by accident during an experiment, it quickly sparked global interest due to their impressive performance, simple designing process, wide material compatibility, affordability and broad range of potential uses. TENGs offer an energy conversion efficiency ranging from 50% to 85%, with power densities reaching as high as 500 W/m² [108].

It is a common natural phenomenon that when two different materials come into physical contact, they become oppositely charged. The magnitude of the charge varies depending on the type of materials involved and this is a typical cause of the electrostatic

Positive 	Polyamide 11	Triboelectric series	Polyester	 Negative
	Polyamide 6-6		Polyurethane flexible sponge	
	Melanimel formol		Polychlorobutadiene	
	Wool		Nature rubber	
	Silk		Polybisphenol carbonate	
	Aluminum		Polychloroether	
	Paper		Polystyrene	
	Cotton		Polyethylene	
	Steel		Polypropylene	
	Wood		Polyimide	
	Hard rubber		Polyvinyl chloride	
	Nickel		Polydimethylsiloxane (PDMS)	
	Brass		Polytetraflouroethylene	
	Silver		Polytetraflouroethylene	

Figure 1.9. Triboelectric series showing tribopositive and tribonegative materials [106]

effect. The triboelectric series is the only existing tool that describes the triboelectrification behaviour of any material. It presents a list indicating the general tendency of materials to gain or lose charge and the materials in the list have been ordered with respect to their triboelectric polarization [105]. When specific materials are rubbed together, excess positive or negative charges are created on the surface of the material, resulting in static electricity. The effectiveness of this charge transfer is influenced by the materials' position within the triboelectric series. When choosing materials for TENG designing, this series is particularly helpful in minimizing static charging, which helps to avoid electrostatic discharge or attraction. Figure 1.9 illustrates the triboelectric series, showing the electron-donating and electron-accepting characteristics of triboelectric materials.

1.4.2. Working principle of TENG

Contact electrification and triboelectrification is a very prevalent physical phenomenon that takes place between any states of matter, such as solid-solid or solid-liquid or liquid-liquid or liquid-gas or gas-gas or gas-solid interactions. Understanding the fundamental mechanisms of contact electrification is crucial for advancing the design and performance of highly efficient triboelectric nanogenerators. In recent studies, it has been discovered that electron transfer is the primary mechanism behind contact electrification in solid-solid interactions. When a dielectric material interacts with a

metal, the phenomenon can be effectively explained using the model of surface states for dielectric materials and the model of Fermi level for metals [107]. When two materials are separated on an atomic level by a distance greater than their bonding length, the adjacent atoms generally exhibit attractive forces, as illustrated in figure 1.10(a). Experimental evidence shows that contact electrification happens only when interatomic distance is less than their bonding length, making the atoms repulsive in nature as depicted in figure 1.10(b).

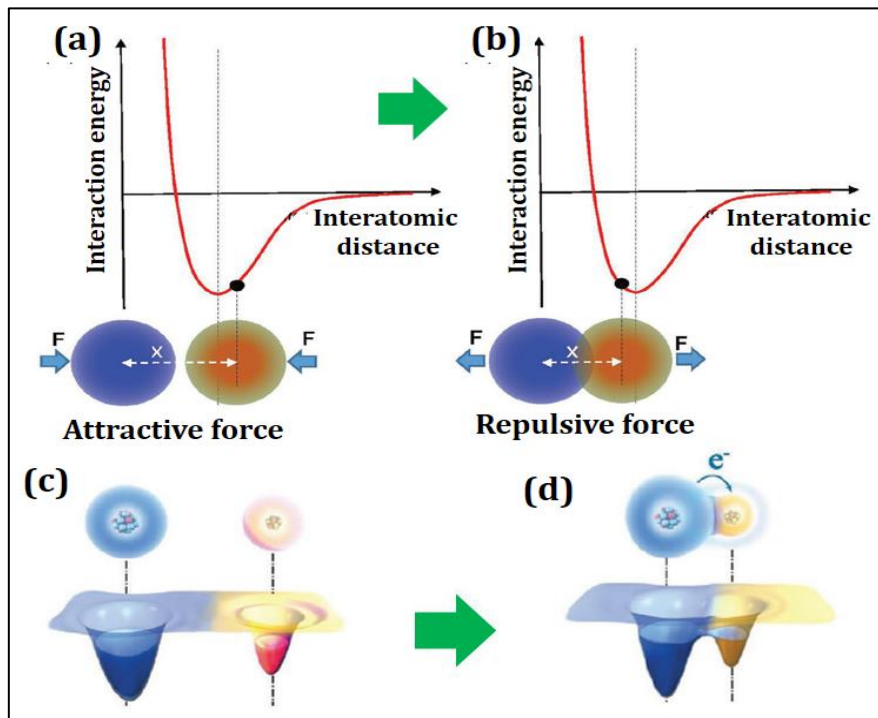


Figure 1.10. *Overlapping of electron clouds, illustrating charge transfer during contact electrification between the two atoms [107]*

As shown in figure 1.10(c), before atomic-level contact, both the material's electron clouds do not overlap. Once the atoms approach and make contact, the stress causes strong overlap of their electron clouds. This reduces the potential barrier and enables electron transition amongst them, as illustrated in figure 1.10(d). Mechanical force is essential to decrease the distance between atoms and maximize the electron cloud overlapping.

Triboelectrification between a solid and a liquid interface leads to the creation of an electrical double layer (EDL). When water or any other liquid comes into contact with the dielectric materials of TENG, the interface is primarily governed by the formation of electric double layer. The EDL generates intense electric field and stores a significant

amount of energy [108]. The formation of EDL generally occurs in two stages. Initially, electrons are exchanged between the solid surface and the liquid through contact electrification, causing atoms on the solid to become ionized. In the next phase, these surface ions interact with the ions present on the liquid surface, leading to the formation of a gradient of positive and negative ions at the interface [109].

1.4.3. Theoretical approach

The theory behind the operation of TENG can be described using Maxwell's equations, where the displacement current term arises from the time-dependent change in the electric field along with a polarization term for the dielectric medium. The Ampere's circuital law with Maxwell's correction can be written as:

$$\nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} \quad (20)$$

Here, the magnetizing field is represented as $\mathbf{H}$, free electric current density inside a material is represented as $\mathbf{J}_f$ and the electric displacement field is represented as $\mathbf{D}$. The term $\frac{\partial \mathbf{D}}{\partial t}$ in equation (20) represents the displacement current. In the context of energy generation, this polarization includes a contribution from strain related effect like contact electrification. To account for the impact of electrostatic charges generated through contact electrification in Maxwell's equations, Professor Wang introduced an extra term denoted as $\mathbf{P}_s$ to the displacement vector $\mathbf{D}$, which can be represented as [107]:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} + \mathbf{P}_s \quad (21)$$

Here, $\mathbf{P}$ represents the polarization vector, which is caused by the electric field present, $\mathbf{P}_s$ represents the existing surface charges that are not dependent on the electric field. If we substitute equation (21) in the standard Maxwell's equations then we shall obtain:

$$\mathbf{D}' = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (22)$$

Hence on the basis of the above equations, Maxwell's equations can be reframed as [107]:

$$\nabla \cdot \mathbf{D}' = \rho' \quad (23)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (24)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (25)$$

$$\nabla \times \mathbf{H} = \mathbf{J}' + \frac{\partial \mathbf{B}}{\partial t} \quad (26)$$

Here, ρ' and $\mathbf{J}'$ denotes the volume charge density and the current density respectively and can be mathematically represented as:

$$\rho' = \rho - \nabla \cdot P_s \quad (27)$$

$$J' = J + \nabla \cdot \frac{\partial P_s}{\partial t} \quad (28)$$

With the help of Maxwell's equations along with equation (21) and (22), the revised displacement current term (J_D) can be written as:

$$J_D = \frac{\partial D}{\partial t} \quad (29)$$

$$\text{Or, } J_D = \epsilon \frac{\partial E}{\partial t} + \frac{\partial P_s}{\partial t} \quad (30)$$

Here, the initial term $\epsilon \frac{\partial E}{\partial t}$ represents the displacement current which is determined by the time dependent electric field, while the next term $\frac{\partial P_s}{\partial t}$ is known as the Wang term. The Wang term signifies the part of the displacement current which is not generated by any electric field but is caused due to an external mechanical strain [107]. This concept laid the foundation for the creation of nanogenerators, which are now recognized as a key energy solution for the modern age.

1.4.4. Operational modes of TENG

A standard triboelectric nanogenerator includes a pair of dielectric materials, selected carefully from the triboelectric series based on their tendencies to gain or lose charge according to their triboelectric nature. Either one or both the dielectric surfaces are coated with electrodes, which are then connected through an external load using a metallic conductive wire. The TENG operates through four fundamental working modes, along with one combined mode. The working modes are [108]:

❖ **Vertical contact-separation mode:** The most fundamental operating mode of a TENG is the vertical contact-separation mode, as shown in figure 1.11(a), where two dielectric surfaces repeatedly come into contact and then move apart. This motion generates a time dependent, changing electric potential between the electrodes, prompting electron movement from one electrode to the other to compensate for the electrostatic potential difference caused by the triboelectric charges. This working mode functions based on relative movement of the triboelectric layers that occurs perpendicular to the interface of the materials. The change in distance between the material surfaces influences the potential difference across the electrodes. This variation in potential drives the current flow in the external circuit.

❖ **Lateral sliding mode:** In the lateral sliding configuration, one triboelectric layer moves horizontally across the surface of another, as shown in figure 1.11(b). This mode

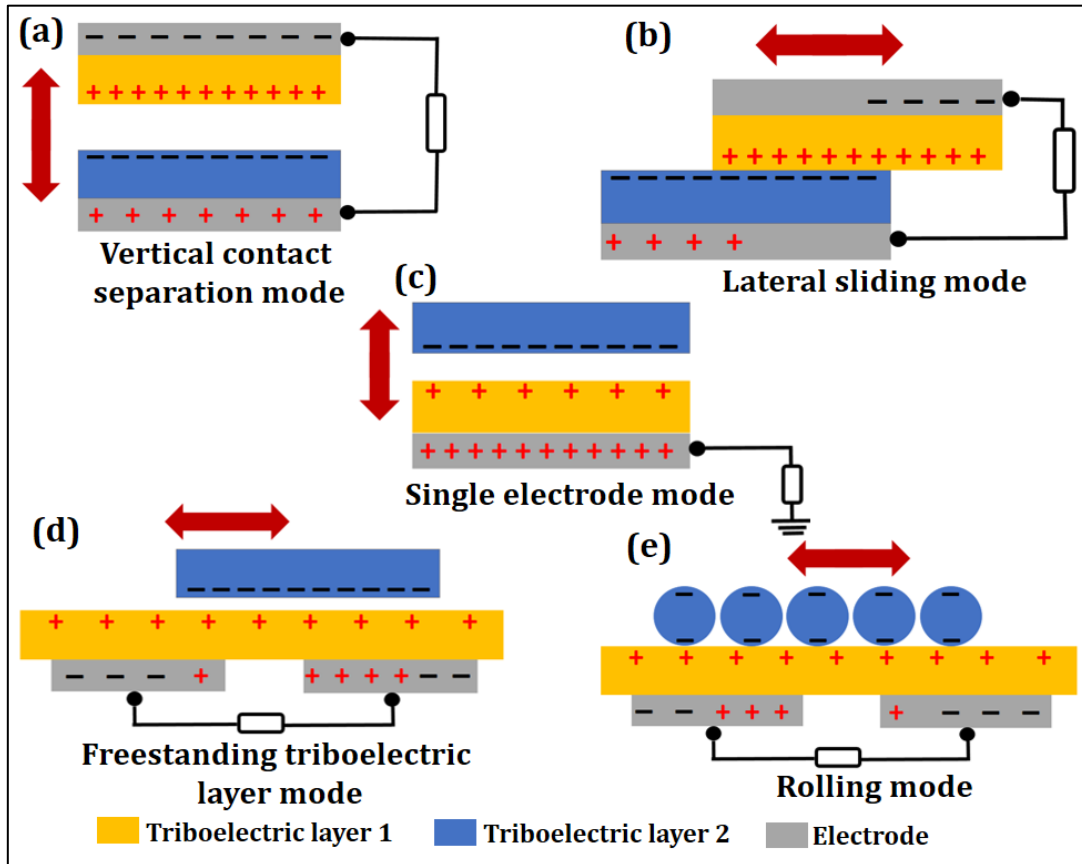


Figure 1.11. Working modes of triboelectric nanogenerators

relies on the combination of sliding electrification and in plane charge separation in the lateral direction of the two triboelectric materials. This in turn drives electron flow between the electrodes, generating an alternating current. This working mode can be made in a compact design through sliding motion generated by rotation.

❖ **Single electrode mode:** As illustrated in figure 1.11(c), the single-electrode mode involves one triboelectric layer moving toward another layer, which has a metal electrode attached behind it. The time dependent electric potential generated between the two triboelectric surfaces causes electrons to transfer between the electrode and the ground. In this mode, the ground serves as the reference electrode, making it highly adaptable for harvesting mechanical energy from various moving objects without needing any connected conductor [110]. This mode is suitable for situations like finger tapping, walking or motion from vehicles.

❖ **Freestanding triboelectric layer mode:** In the freestanding triboelectric-layer mode, a dielectric material oscillates between and over two separate electrodes, as shown in

figure 1.11(d). This motion causes electrons to move alternately between the electrodes, producing an alternating current. This working mode of TENG is essentially an advancement of the single-electrode mode. However, rather than relying on the ground as the reference electrode, it uses two symmetrical electrodes. The electrical output is generated due to an uneven charge distribution that occurs as the freely moving triboelectric layer shifts its position.

❖ **Rolling mode:** The operational mode illustrated in figure 1.11(e) represents a hybrid mode, often referred to as the rolling mode. It primarily integrates features of all the four basic working modes of TENG [110]. In this working mode, rolling spheres move across a dielectric surface which leads to the electron transfer amongst the two electrodes and thereby generates electrical power.

1.4.5. Applications and recent advances

TENG applications are generally classified into two main types. First is the energy harvesting applications and second category includes self-powered sensor systems. Functioning as micro/nano-scale energy harvesters, TENGs can supply continuous power to miniature devices like flexible wearable devices, electronic skin, health trackers, implantable medical tools etc. When used as self-sustaining sensors or systems, TENGs enable applications such as biological sensing, human-machine interfaces, environmental surveillance, infrastructure protection and various other smart applications [111]. In triboelectric nanogenerators, surface charge density is the key for the increment of output efficiency. The output signal is inherently constrained by air breakdown occurring between the two triboelectric surfaces, especially for parallel surface TENGs. Research has shown that by reducing the thickness of the triboelectric layer, increasing its dielectric constant or operating under lower air pressure can enhance the maximum achievable surface charge density. As a result, various methods such as surface modification of the triboelectric layer, ion injection and methods like external charge pumping are being explored to boost charge density [112]. These developments are primarily aimed at advancing the commercialization of self-powered systems that utilize TENGs. The rapid progress in artificial intelligence (AI) has opened up new opportunities for data interpretation using machine learning (ML), enhancing the role of TENGs in Internet of Things (IoT). ML algorithms aids in real-time signal processing for various AI-

driven tasks such as gesture detection, health monitoring, surface texture identification, virtual reality integration etc. [113, 114].

Triboelectric nanogenerators are designed to capture mechanical energy from multiple sources, with human motion being a sustainable and renewable energy option for powering healthcare devices. Several leading researchers are exploring the integration of real-time biomechanical energy harvesting of TENGs into implanted drug delivery for advanced healthcare systems. Targeted drug delivery through wearable as well as embedded devices offers enhanced treatment efficiency, minimized side effects and reduced overall medical expenses. Over the years, film-based medical patches have been utilized for treating skin conditions and aiding wound healing, precise site-specific action and sustained drug release for optimal therapeutic results. Liu et al. designed a TENG based self-powered sensing device and applied it within a joint wear simulation system. Their findings demonstrated the sensor's capability to detect wear debris in real time, highlighting its potential impact on the advancement of intelligent medical technologies [115]. Kim et al. developed a triboelectric nanogenerator using marine-derived materials, including catechol, chitosan and diatom-based hydrogel [116]. The TENG was capable of harvesting energy from human physical activity and could be integrated with self-powered tremor detection systems to assess the condition of Parkinson's patients using machine learning techniques. Shi et al. designed a fully recyclable, self-powered triboelectric nanogenerator made entirely from lignocellulosic materials and implemented it in a disposable patient health monitoring system [117]. The device was environmentally friendly, as it was both easily recycled and naturally decomposed after use. Additionally, they developed a self-powered intelligent ward system and a contactless medical monitoring setup aimed at enhancing patient convenience and minimizing the chance of cross-infection.

Flexible sensor technology provides major benefits for gesture detection and human machine interaction, enabling a wide range of intelligent applications. Wang and his research team developed a pioneering smart glove that combines identity recognition and gesture-based control. The glove features a triboelectric sensor constructed with a polyvinyl alcohol based hydrogel electrode, demonstrating excellent sensitivity and quick response. It enables non-contact detection of unique fingertip motion paths, allowing for user identification and access to a drone control interface [118]. An integrated TENG-driven counter has been proposed by Kang et al. for real-time tracking of product

quantities by utilizing LED flashes powered by a TENG [119]. This system was combined of a sliding-mode based TENG, a PENG and a wireless transmission module. This system had a self-powering counting setup with wireless data transfer for smart manufacturing and supply chain systems. Smart homes, which incorporate numerous electronic appliances, have become a significant focus in modern living. Within these systems, TENGs are crucial especially for their easy fabrication, ability to generate high voltages and excellent energy conversion performance. Ma et al. introduced a single-electrode TENG entirely derived from wood, where a porous structure was created through a delignification process, resulting in a flexible triboelectric friction layer [120]. The TENG was capable of capturing mechanical energy from environmental sources and human movement to power electronic devices within a smart home setting. To showcase its real-life application, they also developed a sensor array for tracking locations and transmitting signals for monitoring humidity. Introducing smart agriculture is very important for sustainable development in today's world. Since large number of sensors are being used in agricultural IoT systems, it becomes harder to provide a steady and long-lasting power supply for all these sensors. To solve this problem, Gao et al. developed an active biochemical sensor using a TENG [121]. This self-powered urea sensor showed excellent sensitivity and strong selectivity. The biochemical sensor effectively tracked changes in urea levels during crop development, detecting very low concentrations of about 4 μM . Its performance remained stable and was not noticeably affected by typical fertilizers used for farming.

Triboelectric nanogenerators have many other diverse applications which include micro and nanoscale energy harvesting, droplet energy harvesting, ocean energy harvesting, breeze energy harvesting and interface probes at liquid–solid interfaces. Nature has always inspired human progress, especially by imitating features like the water-repellent surfaces found in nature. Recently, growing interest has emerged in using liquid-solid interactions to capture energy from water coming in contact with TENGs. However, the high deformability of water presents difficulties in studying its output behaviour. To address this challenge, Sriphan et al. introduced a circuit model along with governing equations to simulate the electrical output of a droplet-based energy harvester with dual electrodes. This model thoroughly captures the dynamic behaviour of liquid-solid contact and serves as a theoretical foundation, enabling advancements in high-efficiency power supply systems and sensing technologies utilizing

the liquid-solid interface [122]. Wind energy harvesting using TENG has drawn growing interest because of its pollution free nature and wide availability of wind. Qu et al. designed a wind-driven film vibration based TENG having a stacked dual-blade design which was developed to efficiently harvest energy from gentle breeze (2–5 m/s) while delivering high power output [123]. Super hydrophobic bio inspired triboelectric surfaces are gaining attention for their strong water-repelling ability, excellent resistance to moisture and high electrical output. Liang et al. developed a biomimetic triboelectric layer based on poly(dimethylsiloxane), taking inspiration from lotus leaves [124]. The structure was formed using PMMA templates shaped through femtosecond laser processing and a single-step moulding technique. This method produced a highly water-repellent surface, achieving a contact angle of 150.6°. Compared to flat surfaces, the resulting TENG demonstrated a notable improvement in power output, attributed to increased surface charge density and elevated aspect ratio.

TENGs have demonstrated strong potential in various fields such as biomechanical energy harvesting, health monitoring, AI-driven smart technologies, capturing low-grade wind or water energy and incorporating recycled materials into device fabrication. Compared to the extensive efforts required to discover entirely new materials, modifying the triboelectric surface structure especially through physical, chemical or nature-inspired methods could be more affordable and practical approach. Additionally, effective power management and optimizing the structure of TENG helps to reduce output impedance, greatly boosting energy conversion efficiency. However, several challenges must still be overcome before TENGs can be widely adopted in industries. Future research should focus on further optimizing device architecture, increasing sensitivity, enhancing resistance to external disturbances and improving long-term stability.

1.5. Objectives and scope

Based on the above literature review on recent advancements in various types of energy harvesters, it is evident that growing environmental concerns and energy shortage have led to a surge in global interest toward adopting renewable energy sources as a means to reduce carbon emissions and move towards carbon neutrality. Therefore, these real-life challenges can be tackled by utilizing self-powered, multifunctional devices that not only convert mechanical energy into electrical power independently but also

serve as various types of sensors, simultaneously. In the field of green energy generation, self-powered energy harvesters based on multifunctional polymeric composites have gathered considerable attention in recent years. As one of the most efficient and eco-friendly methods for harvesting energy, the piezoelectric effect could be widely used for both nanogenerators as well as ultrasound transducers. Mechanical energy from natural sources such as rainfall and wind could be extensively explored as a renewable energy resource, providing valuable means of converting waste kinetic energy into electricity through the triboelectric effect. In today's throwaway culture, creating sustainable and reusable technologies poses a significant challenge. Hence, waste-based self-powered sensors present a favourable solution for promoting reusability and sustainability. Moreover, nature has always served as a source of inspiration for human innovation, particularly through the imitation of features such as naturally water-repellent surfaces and device designs.

Considering all the above facts and recent advances, it is evident that while numerous studies have focused on piezoelectric nanogenerators (PENGs), limited attention has been given to the use of natural fillers in polymers for developing multifunctional nanocomposites. Additionally ultrasound transducers (USTs) which also operate based on the piezoelectric effect, predominantly utilize lead-based single crystals, raising environmental concerns. In contrast, lead-free polymer composite based USTs remain significantly unexplored. Furthermore, the development of self-powered triboelectric sensors, particularly those incorporating waste materials or highlighting bio-inspired designs to harvest futile environmental energy also remains relatively rare. With these considerations, this thesis focuses on the development of biocompatible, multifunctional and lead-free nanocomposites. Various characterisations of these composites were done, along with a comprehensive investigation of their potential device applications.

1.6. Organization of the thesis

To present each stage of the research in a structured manner, the thesis is divided into seven chapters. A concise overview of the subsequent chapters is provided below.

Chapter 1 provides a brief overview of the global and Indian history of energy harvesting, along with an introduction to the fundamentals of the piezoelectric and triboelectric effect.

Chapter 2 outlines the core methodology of the entire study, describing the synthesis processes of lead-free organic and inorganic nanoparticles as well as nanocomposites. It also presents a detailed discussion of the comprehensive characterization techniques and software used for the study.

Chapter 3 focuses on mechanical energy harvesting and body motion sensing through the piezoelectric effect, utilizing naturally available clay nanoparticles of two distinct sizes synthesized through nano-structuring techniques.

Chapter 4 highlights a different application of the piezoelectric effect by presenting the design of a lead-free polymer composite-based ultrasound transducer, suitable for non-invasive medical diagnostics and non-destructive industrial testing.

Chapter 5 presents another very efficient energy harvesting approach based on the triboelectric effect, where the developed nature inspired device harvests unused kinetic energy from raindrops while simultaneously serving as a real-time acid rain sensor.

Chapter 6 investigates an additional application of the triboelectric effect for harvesting low-intensity wind gusts and detecting vehicle over-speeding by utilizing waste-derived raw materials to promote the waste-to-energy concept.

Chapter 7 summarizes the key findings of the entire research and also outlines the potential direction for future work.

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Chapter 2



Methodology

2.1. Synthesis procedure of nano/microfillers

Numerous approaches have been investigated for synthesizing or extracting nanofillers and microfillers, which are then integrated into polymer matrices. These fillers were utilized either to boost the piezoelectric response by enhancing the β -phase content in PVDF or to modify the surface of polymeric membranes for improved triboelectric performance. Some of the key synthesis and extraction methods of these fillers have been outlined below.

2.1.1. Ball milling process

Ball milling is a green, non-combusting and efficient technology that uses kinetic energy to grind fine powders into particles below micrometer range. For natural particles, ball milling is preferred over chemical treatments to maintain their natural characteristics. It has a very simple operational technique, low grade reaction conditions and requires no solvent or no particular temperature. This mechanical technique is a much energy saving and environment friendly process in comparison to other chemical treatment, by causing least contamination. It increases the surface area of the particles and the oxygen-comprising functional groups on the surface of the particles, leading to a high adsorption capacity [1].

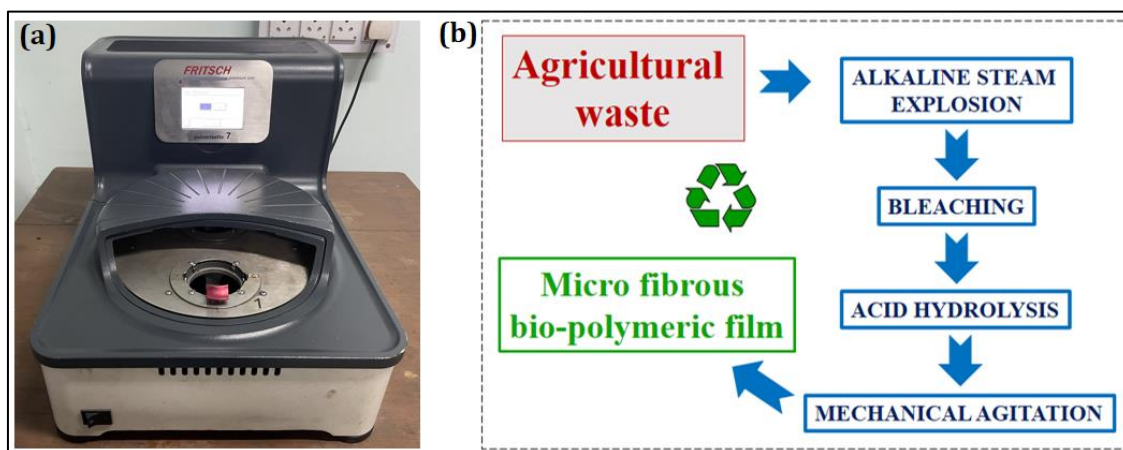


Figure 2.1. (a) Fritsch Pulverisette 7 ball mill instrument, (b) Extraction process of microfibers from agricultural waste

2.1.2. Bio-polymeric microfiber extraction from agricultural waste

Microfibers were extracted from agricultural waste through a sequence of chemical treatments including alkaline steam explosion, bleaching, acid hydrolysis and mechanical processing. These steps collectively yielded a microfibrinous bio-polymeric film. The complete extraction process has been illustrated in figure 2.1(b).

2.1.3. Hydrothermal treatment

Hydrothermal synthesis procedure is used to crystallize chemical compounds directly from the aqueous solutions by precisely regulating thermodynamic parameters such as temperature of the solution, pressure and solution composition [2]. This method was employed to produce nanoparticles of metal hydroxides and sulphides in this work.

2.2. Fabrication procedure of polymeric composites

This thesis has been focused on the development of multifunctional polymeric composite films through three widely used fabrication techniques: solution casting method, spin coating method and electrospinning method.

2.2.1. Solution casting method

Solution casting is a simple method for fabricating flexible polymer thin films, as shown in the flowchart in figure 2.2(a). It is based on Stokes' law, which describes the behaviour of solid particles moving through a liquid medium [3]. Polymers such as PVDF

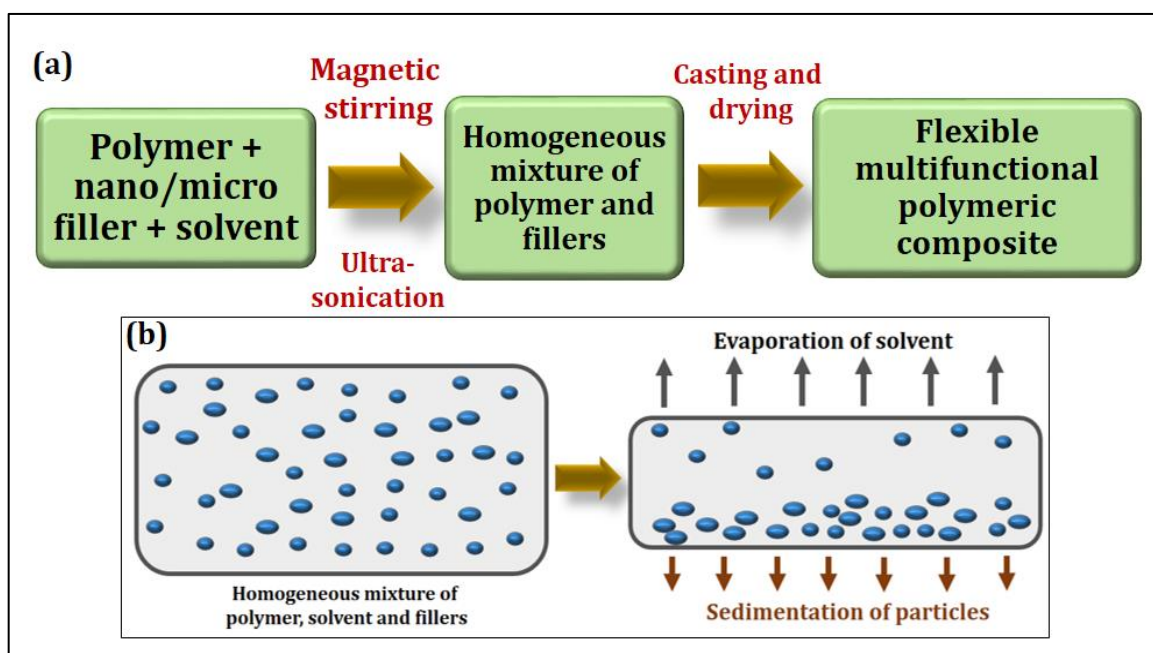


Figure 2.2. (a) Fabrication of polymer composite by solution casting technique, (b) Mechanism of solution casting method

and its co-polymer PVDF-TrFE, along with the desired synthesized nanoparticles were uniformly dispersed in suitable solvents like DMSO or DMF using mechanical stirring. Once a homogeneous mixture was achieved, the solution was poured onto a petri dish

and placed in a hot air oven at an appropriate temperature to form the desired multifunctional composite. Figure 2.2(b) shows that the filler particles were initially well dispersed on the glass surface, then gradually settled down due to gravity as the solvent evaporated, forming a thin polymer composite.

2.2.2. Spin-coating technique

Spin coating is an easy technique employed to create ultra-thin polymeric composite, promoting significant β -phase nucleation in the PVDF based composites. In this method, a PVDF copolymer was first dissolved in a polar organic solvent such as dimethylformamide (DMF) or dimethylsulfoxide (DMSO) and then nanoparticles were incorporated and mixed thoroughly. Key parameters like substrate temperature, spinning speed and ambient humidity were carefully optimized and the heat-assisted spin coating was performed at a specific rotation speed to obtain a thin and uniform film [4]. In this work, the programmable Spin Coater SpinNXG-P1 from Apex Instruments was used. The schematic diagram of this method is shown in figure 2.3.

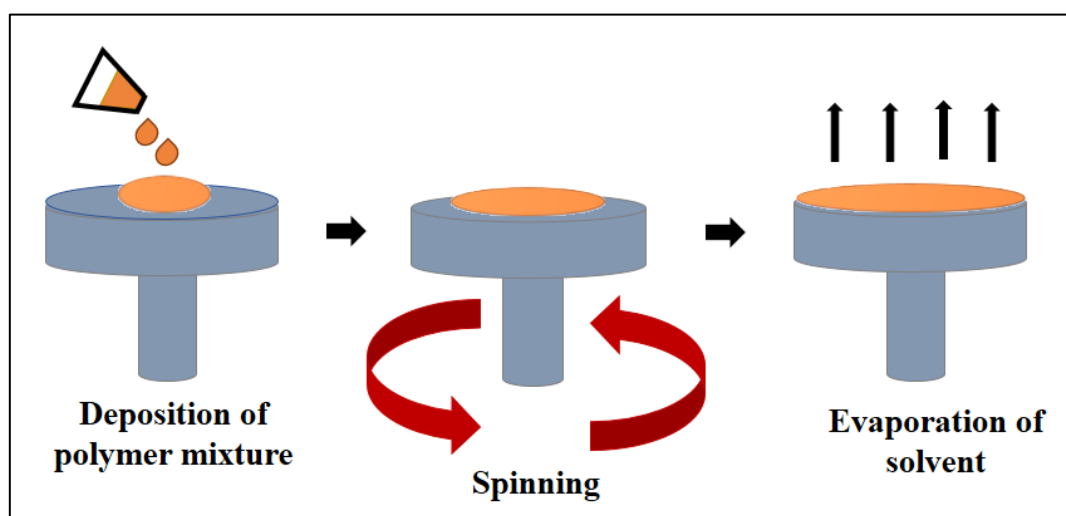


Figure 2.3. Schematic diagram of spin-coating technique

In this work, electropoling process of the spin coated composite was used to reorient the crystals within the polymer (PVDF-TrFE), for enhancing the β phase along with its piezoelectric properties. Firstly, the film was annealed by gradually increasing the temperature of the composite from room temperature to about 80 °C over the course of 1 hour, with a controlled rate of around 1 °C per minute. Following this, the composite was carefully positioned between two electrodes and DC voltage was applied.

2.2.3. Electrospinning technique

Polymeric nanofibers were produced using a high voltage electrospinning technique for designing a TENG, as nanofibrous film offers a large surface area in the triboelectric layer, thereby amplifying the triboelectric effect. To prepare the nanofibers, the polymer was dissolved in a solvent by vigorous stirring and then acetone was added to the solution. This prepared solution was then loaded into a plastic syringe followed by

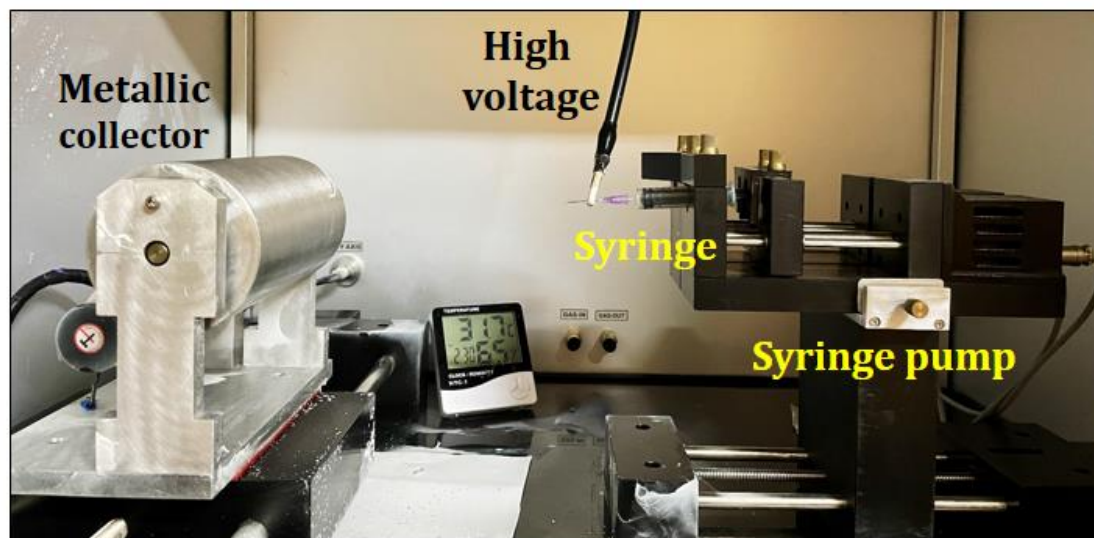


Figure 2.4. Digital image of the electrospinning setup

configuring certain parameters like temperature and humidity inside the electrospinning unit. To extract the solution using a pump, the flow rate and the position of the syringe needle was adjusted with respect to the metallic collector plate. The electrospinning process was carried out at a very high voltage and as a result nanofibers accumulated over the collector which was later peeled off. This setup has been shown in figure 2.4.

2.2.4. Template sacrifice method

Drawing inspiration from the surface microstructures of leaves and flower petals, a cost-effective replication technique was employed to fabricate multifunctional polymer composite containing nano-in-micro architecture. Initially, PVA was dissolved in DI water and the resulting solution was spread onto a clean, flat natural micro structured template (a flower petal) followed by heating. The natural template was removed and a structured PVA layer remained, serving as a negative template. Next, a water insoluble polymer, cross-linking agent and the desired nanoparticles were mixed to form a uniform blend, which was applied onto the patterned PVA template and was then cured. The final step involved immersing the composite in a heated water bath to dissolve PVA entirely,

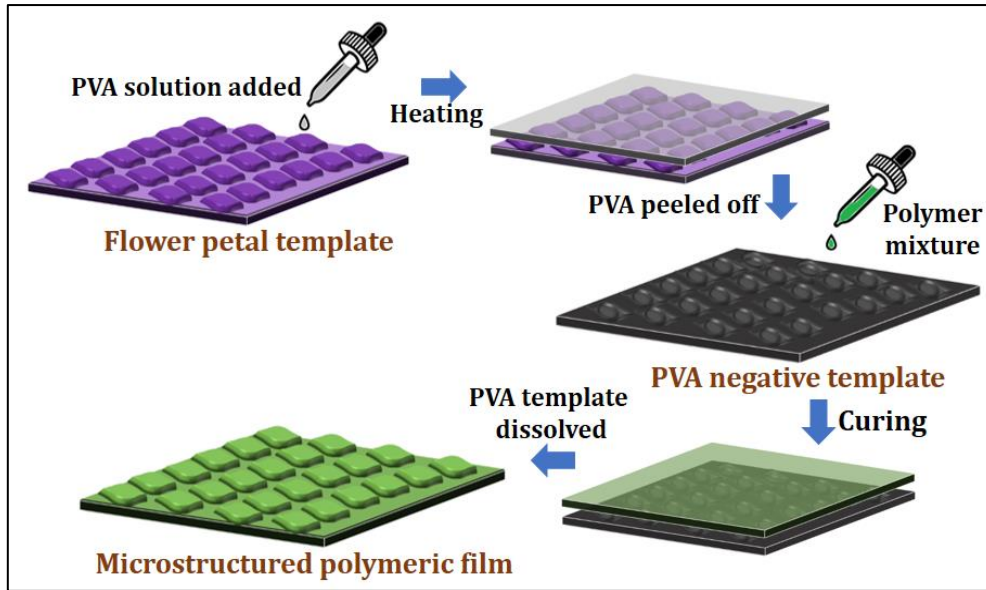


Figure 2.5. Schematic diagram showing the fabrication process of polymeric film via template sacrifice method

leaving behind the polymeric film with micro structured surface replicating those of the original natural template as can be seen from figure 2.5.

2.3. Device designing procedure

Utilizing the developed multifunctional polymeric composites, a nanogenerator and an ultrasound transducer were fabricated operating through the piezoelectric effect, while water-driven and wind-powered sensors were designed based on the principles of triboelectric effect.

2.3.1. Designing of piezoelectric nanogenerator

Rectangular piece of a solution-casted composite thin film was taken and two aluminium electrodes of suitable thickness were affixed to both sides of the film. Copper wires were then connected to the setup to enable electrical characterization. Subsequently, the entire assembly was encapsulated in a layer of polydimethylsiloxane (PDMS), serving as a protective coating. The encapsulated structure was then placed in a vacuum oven for curing, resulting in the finalized piezoelectric nanogenerator (PENG).

2.3.2. Designing of piezoelectric ultrasound transducer

In this work, a lead-free polymeric composite film based ultrasound transducer was developed with a simple yet distinctive design, setting it apart from traditional USTs containing lead based piezoelectric crystals.

A custom-designed cylindrical aluminium substrate was first fabricated and its surface was precisely levelled into a smooth plane using a CNC milling machine. This aluminium layer worked as the backing layer of the UST. A thin, uniform layer of gold was then sputter-coated onto the polished aluminium surface, acting as the bottom electrode. Following this, a composite thin film was spin-coated over the gold coated substrate, forming the matching layer of the UST. A PVDF-TrFE based composite was chosen due to its acoustic impedance being closely matched with that of biological tissues and water, eliminating the need for an additional matching layer for the UST [5]. The composite film was electrically poled to enhance its piezoelectric properties. Another thin gold layer was sputtered on top of the poled film, serving as the top electrode. The complete four-layer assembly was then securely connected to the central pin of an RF coaxial connector. To insulate the aluminium substrate from the outer conductive part of the connector, a separator was inserted, giving the UST its final tubular configuration.

2.3.3. Designing of droplet-driven triboelectric nanogenerator

A bio-inspired, single-electrode triboelectric nanogenerator was fabricated using a hydrophobic PDMS-based micro patterned triboelectric membrane. This TENG was designed for efficient water droplet energy harvesting and precise monitoring of water pH levels.

A flexible, rectangular substrate was first fabricated using Ecoflex polymer. A rectangular strip of carbon tape was then attached to this substrate to serve as the electrode. Additionally, a small rectangular triboelectric membrane with microstructured surface was attached onto the Ecoflex base. A connecting wire was connected between the membrane and the electrode to facilitate electrical measurements. This process led to the successful development of a highly sensitive TENG.

2.3.4. Designing of wind-driven triboelectric nanogenerator

To harness irregular wind gusts, a TENG was developed with a simple, spacer-free butterfly design that enabled energy harvesting even from gentle breeze. Two rectangular pieces of carbon tape (electrodes) were affixed to two PET sheets (outer support). On top of the electrodes, bio-polymeric microfibers extracted from agricultural waste and electrospun fibrous films were attached. Connecting wires were placed between these layers to allow electrical output measurements. A small rubber tube served as the central support, into which the two triboelectric layers were inserted

breadthwise through adjacent slits and secured at an angle. This resulted in a lightweight, spacer-free, wind-driven TENG.

2.4. Characterization of nano/microfillers and polymeric films

After the synthesis of materials, a critical step involves analyzing their physical and chemical characteristics. It is essential to examine aspects such as structure, morphology, crystallinity, phase, surface charge, chemical composition etc. In this study, a range of scientific instruments were employed to examine the structural, physical, chemical and electrical characteristics of the synthesized nanoparticles, microfibers and polymeric composites. Detailed descriptions of these instruments are provided below.

2.4.1. X-ray Diffractometer (XRD)

X-ray powder diffractometer (XRD) (Model-D8, Bruker AXS Inc., Madison, WI) was used to examine the crystallographic properties of the synthesized nanoparticles, microfibers and polymeric films, as shown in figure 2.6. The analysis was conducted with monochromatic Cu-K α radiation at 40 kV and 40 mA with a target of 1.5418 Å. This

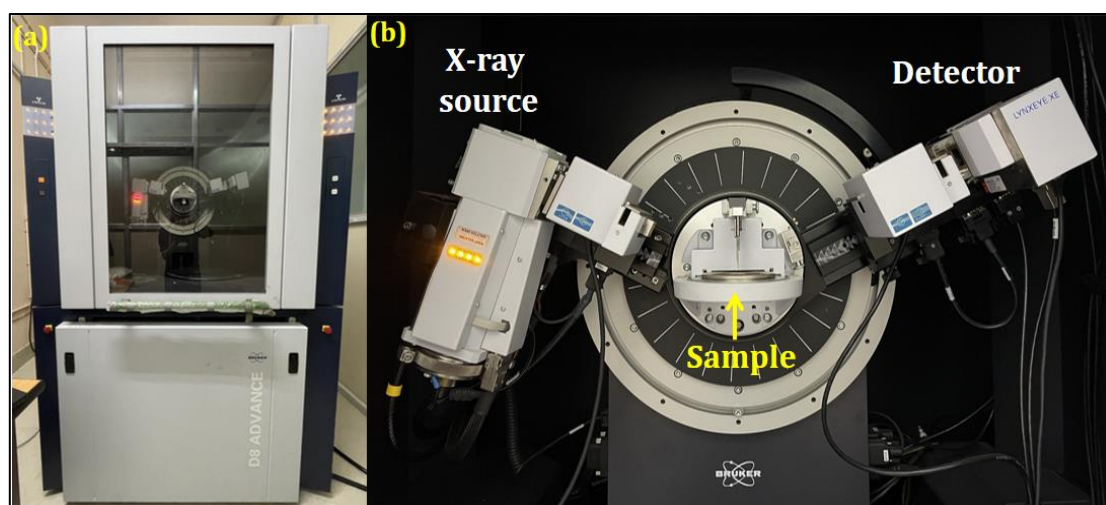


Figure 2.6. Digital image of Bruker D8 Advance XRD machine

technique is valuable for assessing a material's crystallinity and detecting crystalline defects. When X-rays interact with the orderly lattice planes of a crystalline sample, a distinct diffraction pattern is produced. In this study, a highly stabilized Bruker X-ray generator is utilized and the well-collimated X-ray beam is directed onto the sample, where it is diffracted by the structured three-dimensional lattice planes. The detector captures and processes the X-ray signals and the experimentally obtained diffraction

patterns are then compared with standard reference patterns from the JCPDS database for analysis.

When monochromatic X-rays incident upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of the wavelength of incident x-rays (λ). This condition is called Bragg's law and is given by the equation:

$$2d \sin\theta = n\lambda \quad (1)$$

Here, d represents the interplanar spacing and θ represents the glancing angle. The average grain size of the samples can be calculated from the XRD analysis using the Debye-Scherrer equation [6]:

$$\langle D \rangle = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

Here, β is the full width at half maximum intensity in radians. While this equation was applied to determine the crystallite sizes of the synthesized nanoparticles, it was not enough to study various other microstructural parameters. Therefore, Rietveld refinement was employed, where the XRD patterns were refined using the MAUD software (version 2.9), enabling the calculation of lattice parameters and other detailed crystallographic properties of the nanoparticles.

2.4.2. Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique used to obtain the infrared absorption, emission or transmission spectra of a material to identify the corresponding frequencies and detect the presence of specific

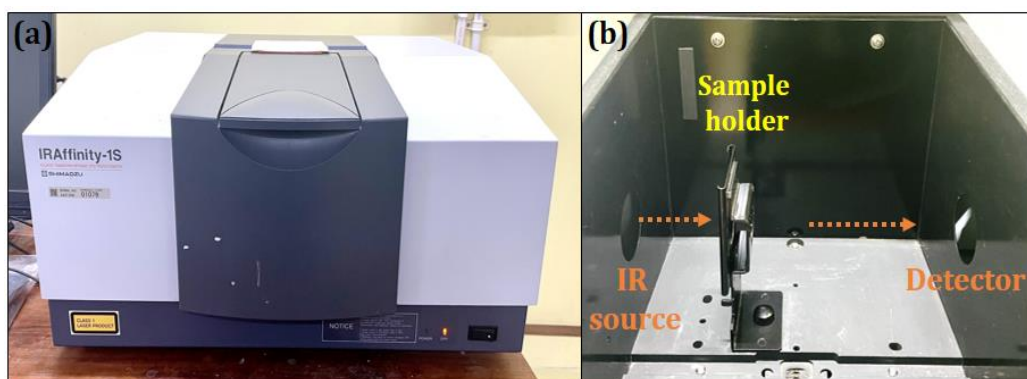


Figure 2.7. Digital image of FTIR Spectrometer (FTIR-8400S, Shimadzu)

chemical bonds within the sample. The powder and polymeric samples were analyzed at room temperature using FTIR spectroscopy (FTIR-8400S, Shimadzu) spanning a spectral range of 400 cm^{-1} to 4000 cm^{-1} . The FTIR analysis was carried out using Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR).

2.4.3. Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscopy (FESEM; INSPECT F50, Netherlands) with a bias voltage of 10 kV to 30 kV was used to examine the structural morphologies including their structure, shape and size of the synthesized nanoparticles and the prepared polymeric samples. For FESEM analysis, the dried samples were placed on carbon grids and sputter-coated with a thin layer of gold using Q150T Turbo Pumped Sputter Coater, to prevent charge accumulation during imaging. These gold-coated samples were then observed using the scanning electron microscope operated under a minimum chamber pressure of $2 \times 10^{-3}\text{ Pa}$.

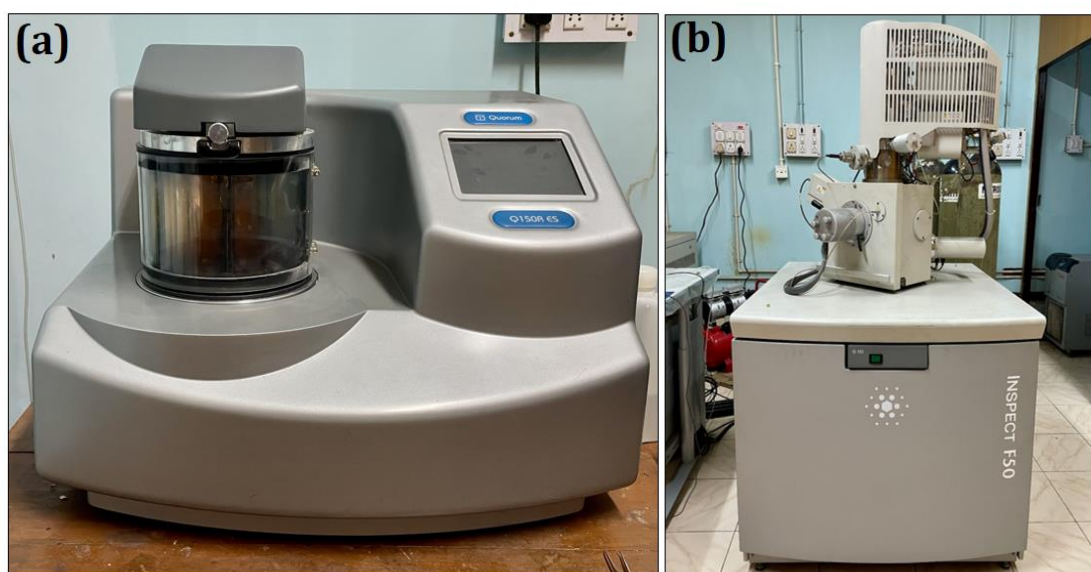


Figure 2.8. (a) Q150T Turbo Pumped Sputter Coater for gold coating, (b) Digital image of FESEM with EDX attachment

In addition to analyzing structure and morphology, determining the elemental composition of a sample is crucial before proceeding with any application. Energy Dispersive X-ray Analysis (EDX) is a widely used technique for this purpose. Elemental mapping along with energy dispersive spectroscopy (EDS) of the samples were analysed to estimate the EDX data with the help of Bruker Quantax EDS analyzer integrated with FESEM machine.

2.4.4. Atomic force microscopy (AFM) and piezo force microscopy (PFM)

To confirm the enhancement of the piezoelectric and the ferroelectric properties of the spin-coated polymeric composite, piezo force microscopy analysis was performed using the Piezo force module of the Piezoresponse Force Microscopy (PFM). The instrument used was Asylum MFP-3D AFM, Oxford Instruments, Asylum Research, as can be seen in figure 2.9. AFM system software was integrated in the PFM imaging and spectroscopy module, which was used to carry out AFM analysis for evaluating the surface roughness and topographical features of the composite thin films. For PFM analysis, the composite was subjected to a dual signal with a DC bias voltage ranging from -7 V to +7 V, applied across its thickness.

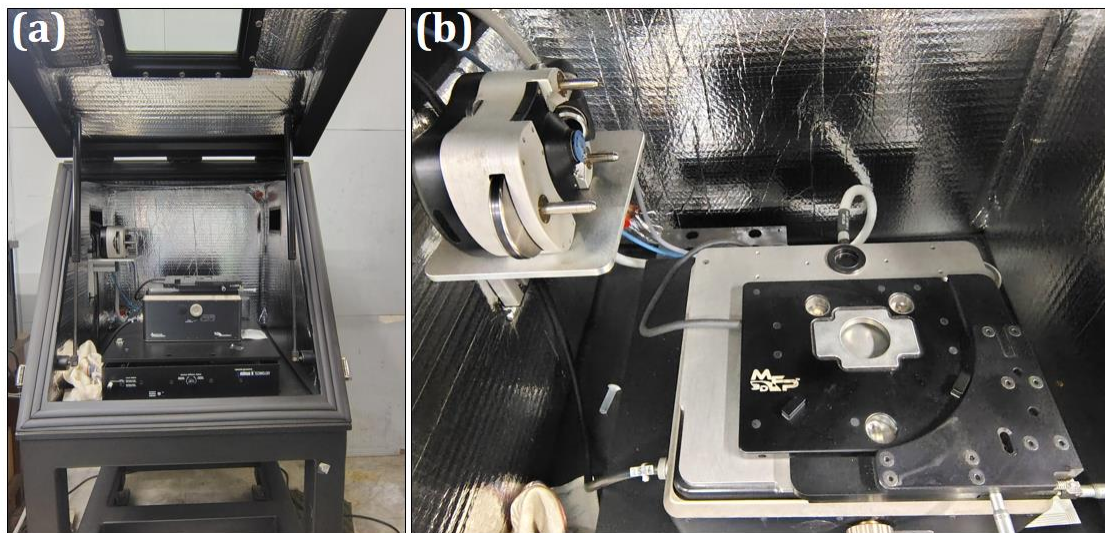


Figure 2.9. (a) Asylum MFP-3D AFM, (b) Interior view of the instrument

Gwyddion 2.63 software was employed to generate three-dimensional AFM images of the film surface and to determine surface roughness parameters, including the average height deviation from the mean plane and the root mean square of height deviations for the composite thin film.

2.4.5. Thermo gravimetric analyzer (TGA) and differential scanning calorimetry (DSC)

To study the temperature dependent mass changes and to evaluate the thermal stability of the samples, thermo gravimetric analysis and differential scanning calorimetry were conducted. A DTG-60H, Shimadzu was utilized over a wide temperature range, operating at a heating rate of 5–10 °C per minute. The data were obtained under a

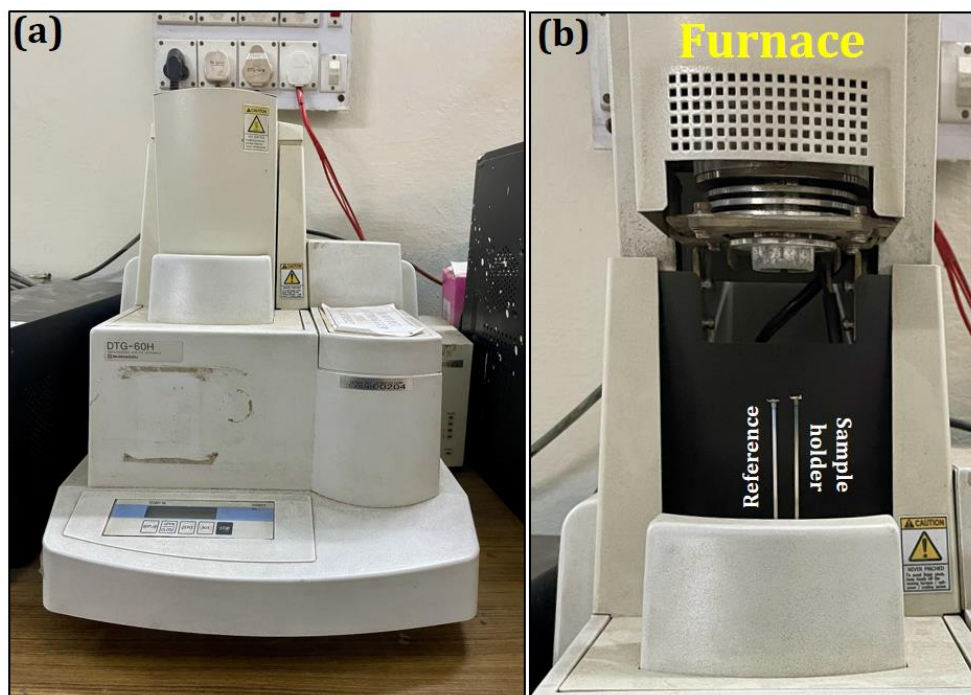


Figure 2.10. (a) DTG-60H instrument for thermal analysis, (b) Internal chamber showing the furnace, reference and the sample stages

nitrogen atmosphere with a flow rate of 50 cc/min. Small quantities of the samples were placed on platinum holders and the resulting mass loss along with the corresponding differential data were recorded using the TA-60 software integrated with the instrument.

2.4.6. Electrostatic meter

The relative surface potentials produced on the polymeric films were measured using a surface potential meter USSVM2, AlphaLab, Inc., where the sensor head was

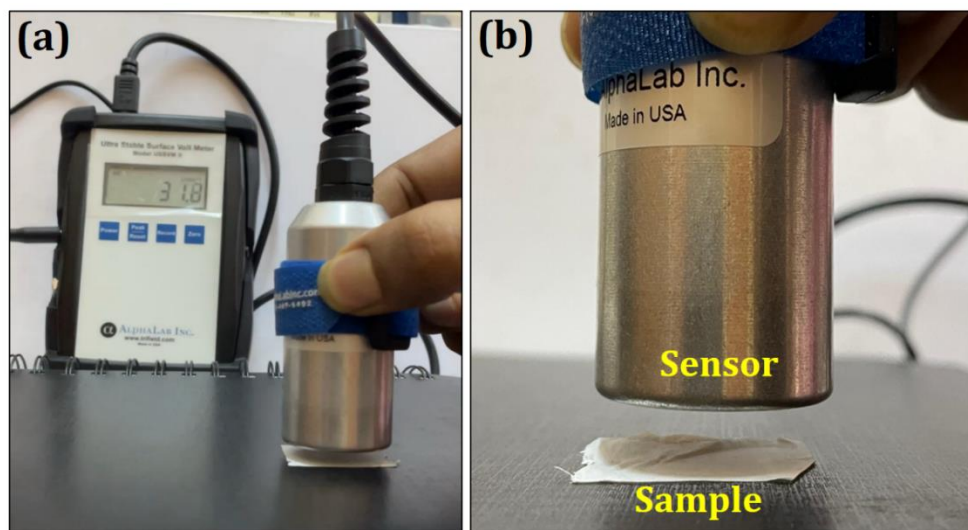


Figure 2.11. (a) Electrostatic meter USSVM2, (b) Closer image of sensor head and the sample

positioned 5 mm above the sample surface being analysed. This is a highly stable surface voltmeter which has been used to measure both the magnitude and polarity of static charges present on surface of the films without any physical contact.

2.4.7. Universal Testing Machine (UTM)

The tensile strength and Young's modulus of the polymeric nanocomposites were measured using a universal testing machine (UTM), Tinius Olsen model: H50KS, UK. For the tests, nanocomposite samples were prepared with dimensions of 1 cm × 5 cm and a constant strain rate of 5 mm/min was applied during the measurements.

2.4.8. LCR Meter

LCR meter is a multifunctional electronic testing instrument used to measure the inductance (L), capacitance (C) and resistance (R) of a sample. To determine the piezoelectric coefficient (d_{33}) of the PENGs, capacitance measurements were conducted across a range of frequencies using a digital LCR meter (Agilent E4980A). The piezoelectric coefficient of a PENG can be determined at a specific frequency using the following mathematical expression [7]:

$$d_{33} = V.C/F \quad (3)$$

Here, V represents the output voltage, F is the applied force and C denotes the device's capacitance. Therefore, by determining the capacitance using the LCR meter, the piezoelectric coefficient can be conveniently calculated.

2.4.9. Piezo-tribo imparting machine

A custom-designed piezo-tribo imparting machine was employed to apply a consistent, periodic mechanical force to the fabricated nanogenerators in the vertical direction, for electrical output measurement. In this setup, mechanical stimulation is delivered through a tapping motion by a metallic tapping head onto the device, as can be seen from figure 2.12(a) and (b). The frequency and magnitude of the applied force are adjustable based on experimental requirements.

2.4.10. Digital storage oscilloscope (DSO)

For electrical characterization of the fabricated nanogenerators, a digital storage oscilloscope (DSO) was used by connecting the PENG/TENG to the DSO while applying a continuous mechanical force, as shown in figure 2.12(c). The open circuit voltage was

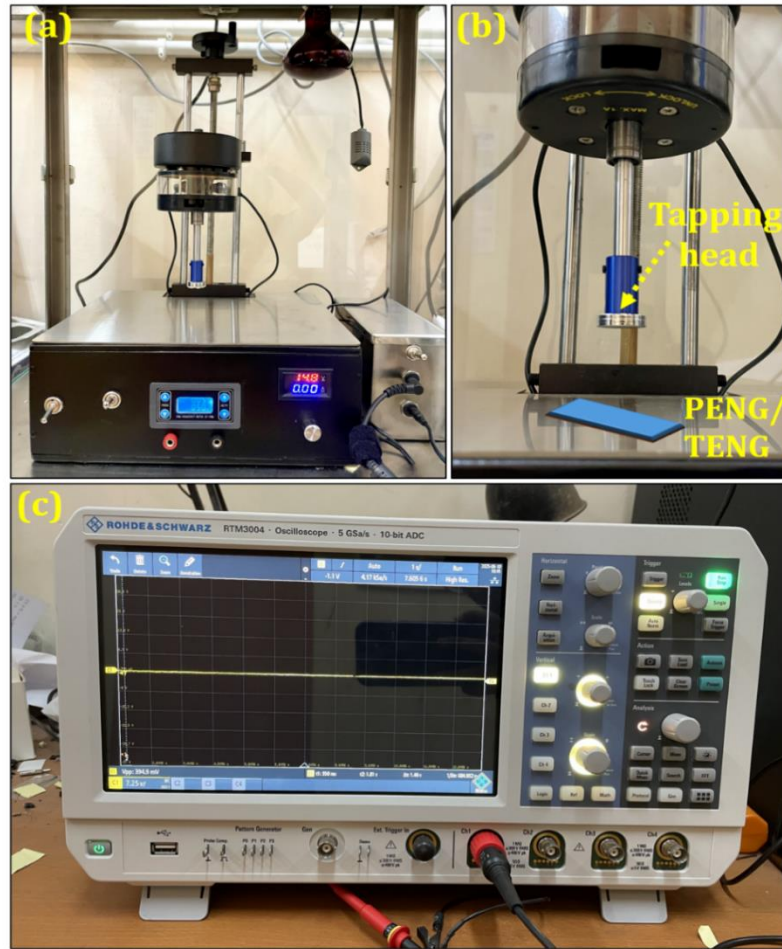


Figure 2.12. (a) Piezo-tribo imparting machine, (b) Closer image of tapping head imparting vertical force on nanogenerator, (c) Digital image of digital storage oscilloscope (DSO)

measured using Keysight Oscilloscope DSO-X 3012A while vertical mechanical energy was applied.

2.4.11. High resistance electrometer

The high resistance electrometer (Keysight Electrometer B2985) is a graphical instrument capable of measuring even extremely small output currents. During the application of mechanical force to the nanogenerators, this electrometer was used to measure the short-circuit current obtained.

2.4.12. Finite element analysis and wireless sensing system

To gain a more precise quantitative analysis of the operation and power generation mechanism of the designed TENG on the application of mechanical force, Finite Element Analysis (FEA) was employed using COMSOL Multiphysics. This analysis

simulates the potential distributions at varying separation distances between triboelectric layers of a TENG.

In order to setup wireless sensor systems, Arduino Mega or Arduino UNO system were used through a laptop to send the output signal produced by the self-powered nanogenerator. Next the data was collected, processed and analysed after the produced output data from the nanogenerator was passed through a microcontroller unit (MCU) module. LED indicators were integrated into the circuit to provide real-time signal feedback. This wireless sensing setup enabled real-time monitoring of the output data of nanogenerator on a mobile device or laptop.

2.5 References

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Chapter 3

Piezoelectric Assessment of Size-Dependent Mud Volcano Clay for Pressure-Sensitive Nanogenerators



3.1 Introduction

In the recent years, numerous systematic and effective research efforts have been underway, focusing on the development of high-performance, sustainable and non-toxic energy-harvesting nanogenerators [1-3]. These nanogenerators can capture electrical energy from mechanical vibrations generated by human activities and can also harness energy directly from natural sources like rainfall, wind, ocean waves, waterfalls, geothermal heat and sunlight [4, 5]. Human life involves several multifunctional and advanced electronic gadgets which operates on batteries or other power supplies [11-18]. Among the non-conventional alternatives, piezoelectric nanogenerators (PENGs) have emerged as one of the propitious mechanisms to harvest electrical energy through the direct conversion of mechanical energy procured from the basic daily activities into electrical energy [19-25]. The modeling and performance enhancement of efficient PENGs using materials like ZnO, BaTiO₃, PZT, ZnSnO₃ and PMN-PT have gained significant research attention [26-31].

Poly (vinylidene fluoride) (PVDF) and its copolymers have come to light for being one of the most effectual electroactive, semi-crystalline, thermoplastic polymers for fabricating piezoelectric nanogenerators [32-34]. PVDF mainly consists of five crystalline polymorphs which are α , β , γ , δ and ϵ , classified on the basis of bond orientation of $-\text{CH}_2$ and $-\text{CF}_2$ dipoles. Among the polar β , γ and δ forms of PVDF, β polymorph (TTTT conformation) is of prime importance among all the crystallite forms of PVDF, since it yields optimal piezoelectricity, pyroelectricity, ferroelectricity and adequate dielectric properties with desired elasticity [35, 36]. Customarily, 'poling' was done with the help of an external high electric field and mechanical stretching on α -PVDF to nucleate to β -polymorph. A more effective approach to boost harvested energy and dielectric properties is by fabricating nanocomposites using nanofillers, metal nanoparticles [37], agro-industrial bio wastes [38], salts [39, 40] and clays [41-44a] etc., which enhance electric dipoles via interfacial polarization. Recent research shows significant progress in enhancing dielectric and thermal properties using various nanocomposites incorporating clay-based materials. Previous studies include Bhattacharya et al. showing effective utilization of waste red mud for high-performance supercapacitor electrodes and Hardjito et al. studying the Pozzolanic Activity Assessment of LUSI (Lumpur Sidoarjo) Mud in Semi High Volume Pozzolanic Mortar. The usage of clay or mud waste is

much attractive since they are pollution-free, cost-effective and are easily extractable from the environment.

Mud volcano eruptions are a geothermal phenomenon that mainly spews out mud, sediments, mineral deposits, water and different types of gases. The mud volcano by-product which has been put into use in this study has been obtained from Baratang region in Andaman and Nicobar Islands, India. The raw material used in this work is not very scarce and is much easy on the pocket. The mud volcano contains different metal oxides and some biomaterials, which makes it completely eco-friendly in nature and the quantity of raw material used to fabricate a PENG is also minimal [42, 43]. The clay particles enhance the durability and the lifetime of piezoelectric nanogenerators which eventually increases the electromechanical breakdown strength. The close interaction of the nano-sized clay particles and PVDF chains results in highly piezoelectric β -polymorphs in the clay NPs/PVDF nanocomposite thin film due to the alignment of the polymer chains in all-trans conformation (TTTT), i.e., effective nucleation of the electroactive β -phase takes place.

The use of mud volcano clay nanoparticles as dopants in the PVDF matrix to enhance β -nucleation and to develop high-performance PENGs has not yet been explored. Therefore the present work includes the fabrication of two PVDF/mud volcano clay nanoparticles (NPs) based PENGs, which were capable of harvesting electrical energy from light mechanical vibrations. The output performance of PENGs was also compared using clay nanoparticles prepared by grinding clay with a mortar-pestle and ball milling. Normal mortar pestle ground NPs have relatively greater size in comparison to the NPs obtained from ball mill process. This difference in sizes of NPs led to a larger surface area in case of ball mill processed NPs. Ball milling is a green, economical and efficient technology that uses kinetic energy to grind fine powders into particles below micrometer range [44b]. It increases the surface area of the particles and the oxygen-comprising functional groups on the surface of the particles, leading to a high adsorption capacity [44c]. The present work mainly reveals the fabrication of clay NPs incorporated, self-poled piezoelectric nanocomposites and involves a comparison between the characterization and output performances of the thin films and PENGs. The enhancement of β -crystallinity, improvement of thermal stability due to strong electrostatic interaction and interfacial polarization have been elaborated via various experimental procedures.

3.2 Experimental section

3.2.1 Processing of raw clay for obtaining pure clay nanoparticles

The as-received mud volcano clay from the site was washed and made free of any biological impurities. Primarily 100 g of clay mixed with 200 ml Millipore water was kept under constant stirring for 8 hours, then the excess water was drained out and this process was repeated 2 to 3 times. Thereafter, 3% H₂O₂ and 300 ml DI water were mixed with the previously prepared mixture and kept at rest for 24 hours. This mixture was then centrifuged and washed with distilled water several times to remove any biological impurities present in the clay. Finally, the clean clay was dried at 80°C and divided into the following two parts:

- (i) One half of the dried sample was ground properly in a clean mortar pestle to get a fine powder of nanoparticles.
- (ii) The other half was mechanically milled with the help of the ball milling technique for 8 hours to obtain uniform mud volcano clay nanoparticles.

3.2.2 Composite thin film synthesis

Mortar pestle ground clay NPs/PVDF and ball mill ground clay NPs/PVDF thin films were prepared by a simple solution casting method. Firstly, 250 mg of PVDF pellets (Sigma-Aldrich, Germany; M: 180 000 GPC; Mn: 71 000) was made to dissolve in 5 mL of dimethyl sulfoxide (DMSO) (Merck) at 60 °C under continuous magnetic stirring to obtain a clear solution. Then mortar pestle ground and ball mill ground clay NPs were added to the previously prepared clear solution in 1, 5, 10 mass % and 0.5, 1, 1.5 mass % and kept on the magnetic stirrer for 12 hours under uniform lab condition. Solutions were then kept for ultrasonication for 30 minutes to obtain homogeneous mixtures. The final solutions were then cast on clean glass petri dishes and kept in a dust-free oven for 12 hours at 80°C for complete drying of DMSO and eventually, the composite thin films were obtained. By the same procedure, pure PVDF thin film (without any dopant) was prepared. Therefore, 7 films in total were obtained. Three among them contained 1, 5, 10 mass % of mortar pestle ground clay NPs (named as MP1, MP5, MP10 respectively) and the other three films had 0.5, 1, 1.5 mass % of ball mill ground clay NPs (named as BM0.5, BM1.0, BM1.5 respectively) loaded in them and one pure PVDF film (PP). With the use of the above made two types of doped PVDF films, two PENGs were fabricated and named MPENG and BPENG, using a film having mortar

pestle and ball milled clay as dopant, respectively. The various amounts of NPs, processed by mortar-pestle and ball milling methods and their notations are presented in table 3.1.

Table 3.1. Amount of nanoparticles added to PVDF matrix with their respective notations

Notations	Mass percentage of clay nanoparticles	Mass of clay NPs (gram)	Mass of PVDF (gram)	Amount of DMSO (mL)
PP	0.0	0.0000	0.2500	5.000
MP1	1.0	0.0025	0.2500	5.000
MP5	5.0	0.0125	0.2500	5.000
MP10	10.0	0.0250	0.2500	5.000
BM0.5	0.5	0.00125	0.2500	5.000
BM1.0	1.0	0.00250	0.2500	5.000
BM1.5	1.5	0.00375	0.2500	5.000

3.2.3. Fabrication of piezoelectric nanogenerators MPENG and BPENG

A rectangular portion of the composite films, with the dimension of 2.7 cm x 2.4 cm x 51 μm were cut from MP5 and BM1.0 thin films. Two aluminium electrodes of slightly smaller dimension of 2.6 cm x 2.3 cm (to avoid short circuit) and of around 63 μm thick, were attached on both sides of each cut film. Two wires were also connected on both sides of each film to measure the output performance of the PENGs. This whole setup was properly compressed to eliminate any air gap and then encapsulated in polydimethylsiloxane (PDMS) gel (Sylgard 184, Dow Corning, ratio of 1:10). It was dried in a vacuum desiccator for 15 minutes and for 30 minutes in a hot air oven at 60°C for the complete removal of any trapped air bubbles in the gel mixture. This insulating coating made the devices robust and helped to eliminate triboelectricity during relative movement between the devices and the contacted objects while pressing. Finally, two flexible PENGs (MPENG and BPENG) of the dimension of 4.9 cm x 3.0 cm x 0.2 cm were fabricated successfully. In this work, PENGs were fabricated using the most electroactive films (MP5 and BM1.0). Figure 3.1(a) shows the schematic diagram of PENGs and the digital images of MPENG and BPENG are shown in figure 3.1(f) and (g) respectively.

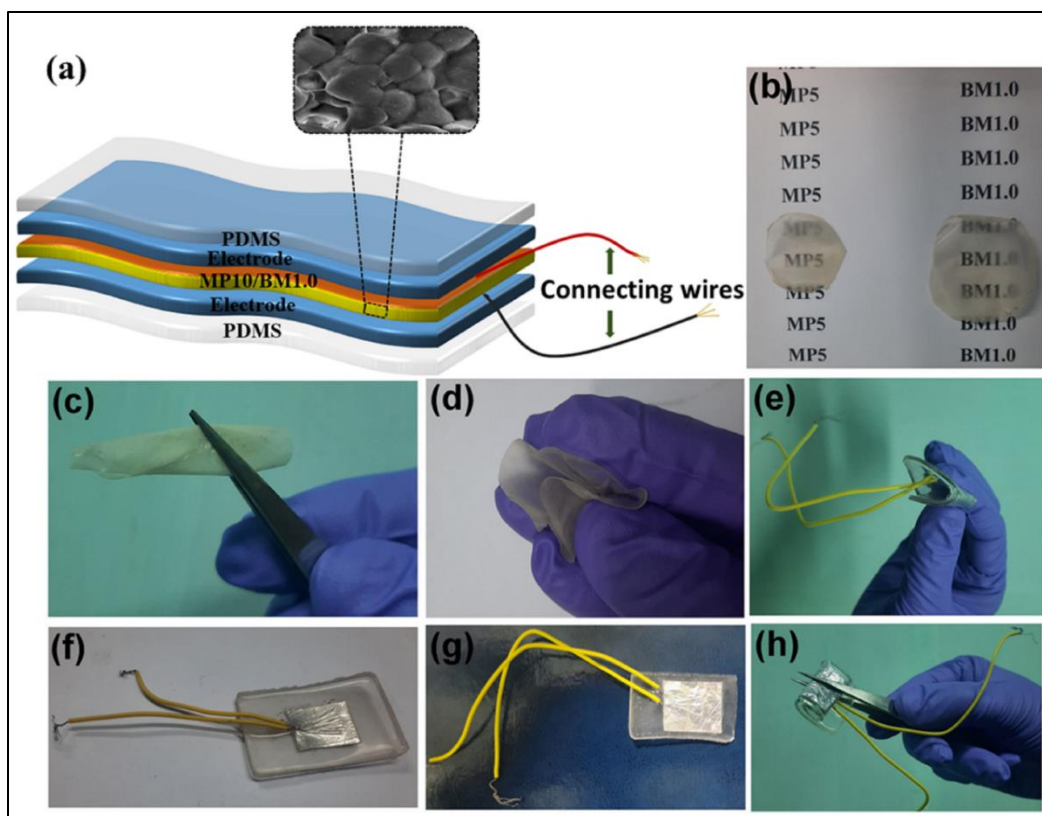


Figure 3.1. (a) Schematic figure of PENG, (b) Transparency of MP5 and BM1.0, (c) and (d) Flexibility test of composites, (e) and (h) Flexibility test of PENGs, (f) and (g) Digital image of MPENG and BPENG

Owing to their highest β crystallinity, these two films have been chosen to fabricate the PENGs for showcasing the highest piezoelectric response and piezo sensitivity. Figure 3.1(b) shows how transparent the nanocomposite films were. Figure 3.1(c) and (d) demonstrate the flexibility of the fabricated thin films. They can be easily folded or rolled without causing any disfigurement of the films.

3.4. Results and discussion

3.4.1. Morphological analysis

The surface morphologies of the mortar pestle and ball mill ground clay nanoparticles are shown in figure 3.2(a) and (b) respectively and the average size of clay NPs ground by mortar pestle was around 600-700 nm and for ball mill ground NPs the average size was 200-300 nm, as seen from the images. The FESEM images of pure PVDF and the clay-loaded PVDF samples are shown in figure 3.2(c) and 3.2(d)-(i) respectively. The surface morphologies of the mortar pestle ground clay NPs doped PVDF thin films (MP1, MP5, MP10)

and ball mill ground clay NPs doped PVDF thin films (BM0.5, BM1.0, BM1.5) show the formation of clear spherulites with an average diameter of 5 μm and 3 μm respectively. This confirms the nucleation of electroactive β -crystals in the composite samples. The spherulites

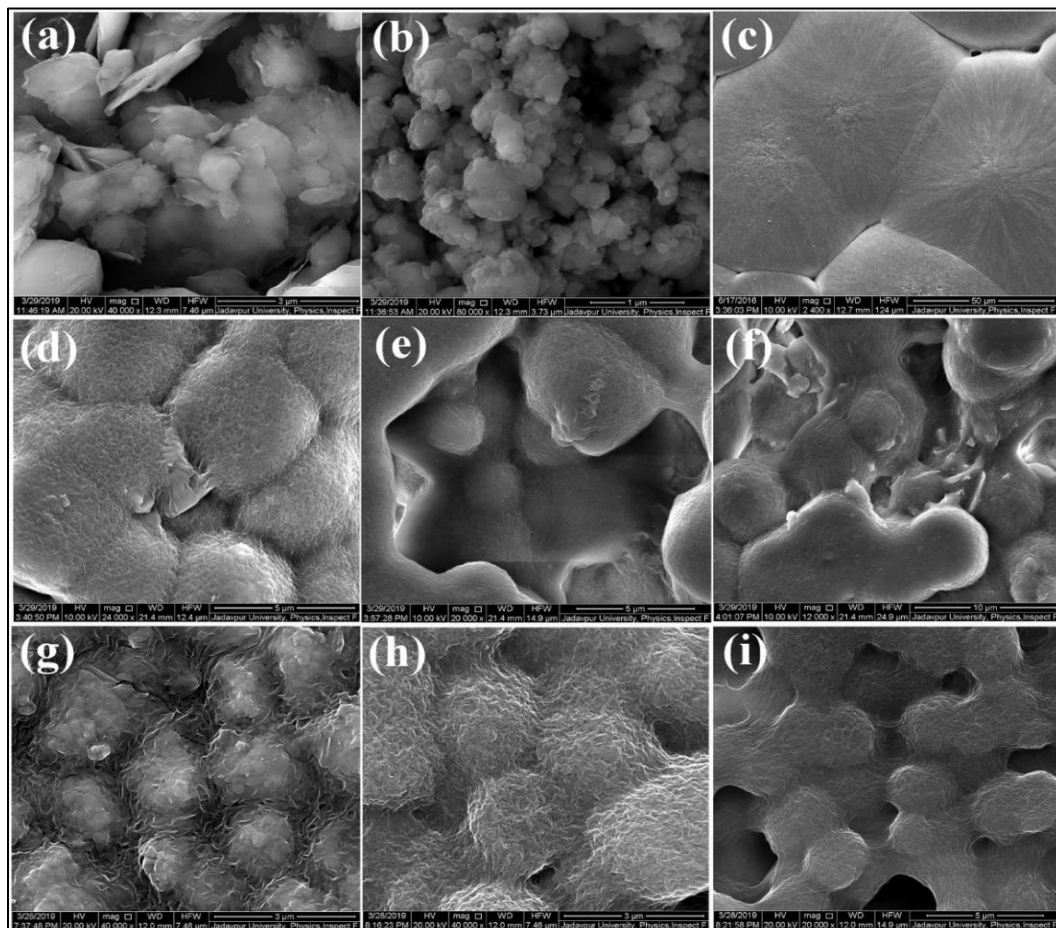


Figure 3.2. FESEM image of (a) Pure mortar pestle ground clay NPs, (b) Pure ball mill ground clay NPs, (c) Pure PVDF thin film, (d) MP1, (e) MP5, (f) MP10 and (g) BM0.5, (h) BM1.0, (i) BM1.5

in the pure PVDF film has a diameter of $\sim 40 \mu\text{m}$, which confirms the presence of nonpolar α -crystals in pure PVDF film. The samples MP5 and BM1.0 show the maximum dispersion and the distribution properties of NPs in the PVDF matrix. Homogeneous and even distribution of clay NPs have been clearly observed in the mortar pestle ground and ball mill ground clay NPs doped PVDF thin films up to 5 mass% loading (MP5) and 1 mass% (BM1.0) loading respectively as shown in figure 3.2(e) and 3.2(h). On further addition of NPs to the PVDF matrix for both cases, agglomeration of the NPs takes place. FESEM images of agglomerated clay NPs in PVDF in MP10 and BM1.5 have been shown in figure 3.3(a) and (b) respectively.

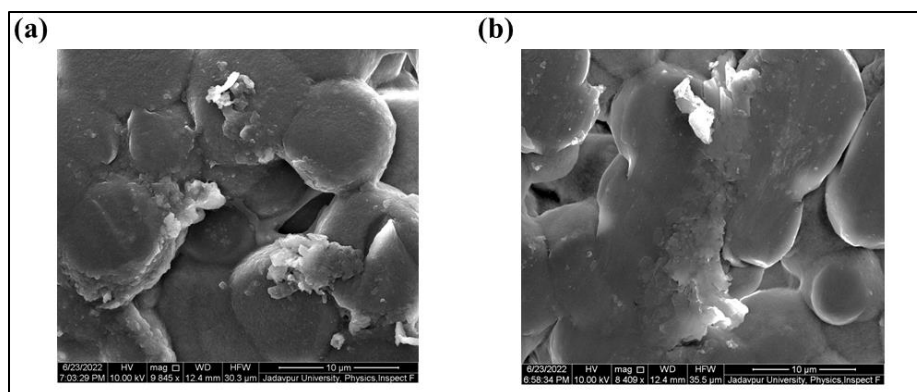


Figure 3.3. Agglomeration of NPs in PVDF matrix in (a) MP10 and (b) BM 1.5

3.4.2. X-Ray Diffraction (XRD) analysis

The confirmation for the nucleation of electroactive β -crystals in the composite thin films was obtained from XRD analysis. Figure 3.4(a) and (b) exhibit the XRD pattern of pure PVDF and clay-loaded PVDF composites. As seen from the XRD graphs, the diffraction peaks were obtained at $2\theta = 17.6^\circ$ (100), 18.3° (020), 19.9° (021) and 26.6° ((201), (310)) for pure PVDF thin film, which clearly suggests the presence of nonpolar α -crystalline phase [45]. All the diffraction peaks corresponding to α and γ crystalline phases disappear on the addition

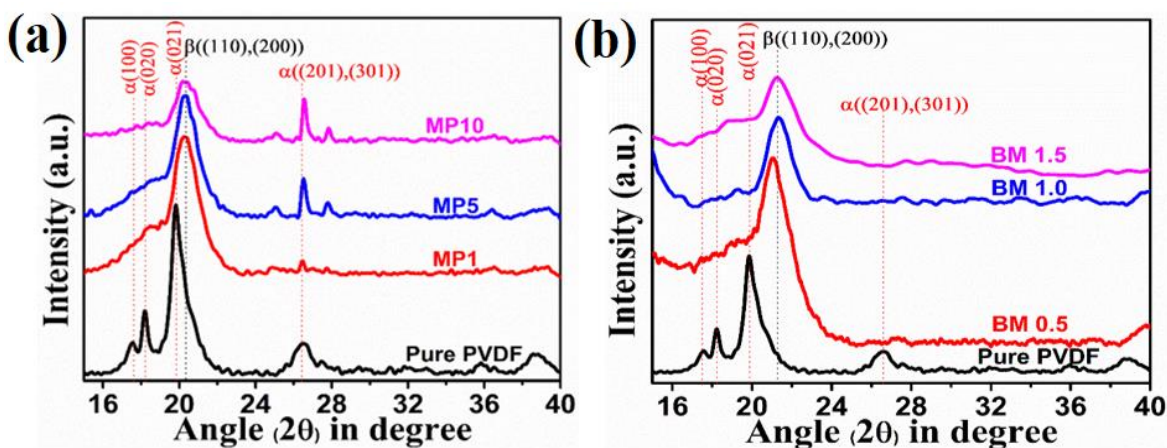


Figure 3.4. XRD spectra of (a) PVDF, MP1, MP5 and MP10, (d) PVDF, BM0.5, BM1.0 and BM1.5

of clay NPs into the PVDF matrix and a sharp, prominent peak at $2\theta = 20.5^\circ$ ((110), (200)) is spotted. From this sharp characteristic peak, it can be fairly concluded that the addition of clay nanoparticles to the PVDF has led to the nucleation of electroactive, polar β -crystals in the clay loaded PVDF composite films and waived off the α and γ crystallinity from it. The XRD patterns of pure mortar pestle and ball mill ground clay NPs are shown in appendix 1,

figure A1.1.(a) and (b) respectively. After a further detailed study of the XRD graphs, it was noticed that the diffraction peak at $2\theta = 20.5^\circ$ (maximum β crystallinity) for both the fabricated composite films. The highest β crystallinity was observed for MP5 and BM1.0, as confirmed from XRD patterns. This occurs because, on further loading of the NPs, agglomeration takes place leading to a decrease in the interfacial surfaces between the NPs and the PVDF matrix which eventually decrease the β -phase nucleation in the thin film. Quantitative analysis of β phase nucleation can be done by calculating the ratio $I_{20.5}/I_{18.3}$, where $I_{20.5}$ and $I_{18.3}$ are the intensities of the peak at 20.5° ((110), (200)) and 18.3° (020) for both the films respectively. The value of the ratio was 3.85 for MP5 and 11.24 for BM1.0, which clearly indicate a sharp increase in the value for ball mill ground clay doped thin film leading to a greater β crystallinity as shown from figure 3.5(c). This value obtained from the calculation evidently proves that the ball mill ground clay NPs have a greater ability to increase the β phase nucleation in the polymer composite thin films which can be due to the smaller size of the NPs.

3.4.3. Fourier transform infrared (FTIR) spectroscopy analysis

Apart from XRD analysis, the nucleation of electroactive β -crystals in the composite thin films was further validated by FTIR study of pure PVDF thin film and the composite thin films in the range of 400 cm^{-1} to 1350 cm^{-1} , as presented in figure 3.5(a) and (b) respectively. Pure PVDF film showcased its non-polar α -phase through the characteristic absorbance bands in the finely packed spectrum at 488 cm^{-1} (for CF_2 wagging), 532 cm^{-1} (for CF_2 bending), 615 cm^{-1} and 764 cm^{-1} (for CF_2 bending and skeletal bending) and 796 cm^{-1} and 976 cm^{-1} (for CH_2 rocking) [46]. These peaks (in the absorption band of pure PVDF thin film) clearly signify that it has mostly non-polar α -phase with negligible part of polar β or γ phases. Prominent characteristic peaks of the absorbance band at 840 cm^{-1} (for CH_2 rocking, CF_2 stretching and skeletal C-C stretching) and 813 cm^{-1} (for CF_2 asymmetric stretching) were obtained in the case of NPs doped thin films, which can validate some alignment in the PVDF polymer chain in the form of TTTT, confirming the presence of polar β polymorphs. The absorption peaks for the electroactive β phase were observed at 445 cm^{-1} (for CF_2 rocking and CH_2 rocking), 479 cm^{-1} (for CF_2 deformation) 510 cm^{-1} (for CF_2 stretching), 600 cm^{-1} (for CF_2 wagging) and 840 cm^{-1} (for CH_2 rocking, CF_2 stretching and skeletal C-C stretching) [46, 47]. The most

prominent peak was obtained at 840 cm^{-1} confirming the enhancement of the β phase and the absence of absorbance peaks agreeing to the α -phase, proving complete fading away of any α phase properties of the composite thin films. Thus, it can be concluded that there is a huge enhancement of β phase crystallinity in the MP/BM nanocomposites, which is possibly due to the nucleation of clay NPs with the polymer matrix [48].

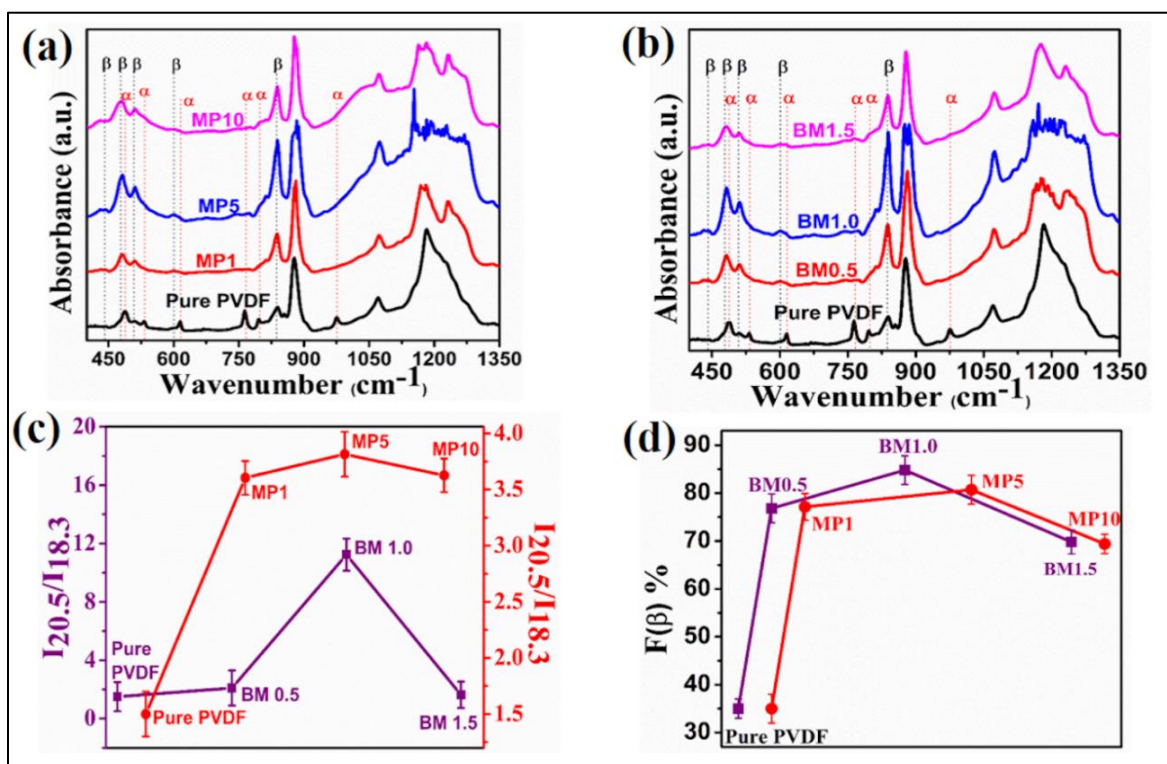


Figure 3.5. (a) FTIR spectra of PVDF, MP1, MP5 and MP10, (b) FTIR spectra for PVDF, BM0.5, BM1.0 and BM1.5, (c) Ratio of $I_{20.5}$ and $I_{18.3}$, (d) β -phase content of PVDF and composites

In the FTIR spectra, closer examination of the graphs reveal that MP5 and BM1.0 have maximum intensity for the main β phase characteristic peak of the absorption band, which confirms maximum β phase crystallinity. Therefore, it can be said that the FTIR analysis is in accordance with the XRD analysis. A quantitative analysis was also performed to check the improvement of β -phase fraction ($F(\beta)$) from the FTIR spectra, using Lambert-Beer law. This fraction gives us the knowledge about the quantity of β polymorph present in composite thin films, which henceforth helps in the analysis of the piezoelectric, ferroelectric and dielectric properties of the samples. The β -phase fraction content ($F(\beta)$), from the IR spectra, was calculated with the help of Lambert–Beer law, which states [47, 49]:

$$F(\beta) = \frac{A_{\beta}}{\left(\frac{K_{\beta}}{K_{\alpha}}\right)A_{\alpha} + A_{\beta}} \quad (1)$$

Where A_{α} is the absorbance at 764 cm^{-1} , A_{β} is the absorbance at 840 cm^{-1} and the value of K_{β} is $7.7 \times 10^4\text{ cm}^2\text{ mol}^{-1}$, and the value of K_{α} is $6.1 \times 10^4\text{ cm}^2\text{ mol}^{-1}$ are the absorption coefficients at 840 cm^{-1} and 764 cm^{-1} , respectively. From figure 3.5(d) it can be seen that the β -phase fraction ($F(\beta)$) increases with the increasing clay NPs loading content and attains a maximum value for MP5 (5 mass% of mortar pestle ground clay NPs) having a value of $F(\beta) = 80.7\%$ and for BM1.0 (1 mass% of ball mill ground clay NPs) having a value of $F(\beta) = 84.8\%$, whereas that for pure PVDF thin film $F(\beta) = 35\%$. It is experimentally seen that on further increasing the mass% of clay, $F(\beta)$ also increases but up to a certain limit and then starts decreasing, since any further doping of clay reduces the β -crystal formation by demolishing the free chain movements of the PVDF matrix [34, 50].

To optimize the content of clay nanoparticles in the composites MP1, MP5 and MP10 two more composite films with 2.5% of mortar pestle ground NPs (MP2.5) (intermediate of 1% and 5%) and using 7.5% of NPs (MP7.5) (intermediate of 5% and 10%) were prepared. FTIR analysis of all the films and the β -phase fraction have been provided in appendix 1, figure A1.2. (a) and (b). It can be seen that the β phase increases on loading of clay into PVDF from 1% to 5%, attains a maximum β phase at 5% and then gradually decreases from 5% to 10%. The mass of nanoparticle loading was optimized by the fact that loading of 5% of mortar pestle ground clay NPs in PVDF exhibits the highest piezoelectric response. Beyond 5%, β -phase of the composites decrease due to the agglomeration of the clay NPs in the polymer matrix and the surface to mass ratio declines. The β -phase fraction content of all the five composites clearly indicate the relation of β -phase nucleation with the mass% of nanoparticles.

3.4.4. Differential scanning calorimetry (DSC) analysis

In addition to XRD and FTIR analysis, the confirmation of the β phase crystallinity was moreover obtained from differential scanning calorimetry (DSC) analysis of the thin films. Figure 3.6(a) and (b) represent the DSC thermographs for the phase crystallization and melting behavior of pure PVDF and the composites. From the thermograph of neat PVDF, it can be observed that the melting point is at 163.14°C which clearly indicates the presence of

non-polar α polymorph in the film [50, 51]. For the composite thin films, as it can be seen, the melting points have been increased to a greater temperature, with MP5 and BM1.0 showing greatest value among all of them. From these experimental observations, it can be said that this enhancement of melting temperature on the addition of clay NPs to the polymer

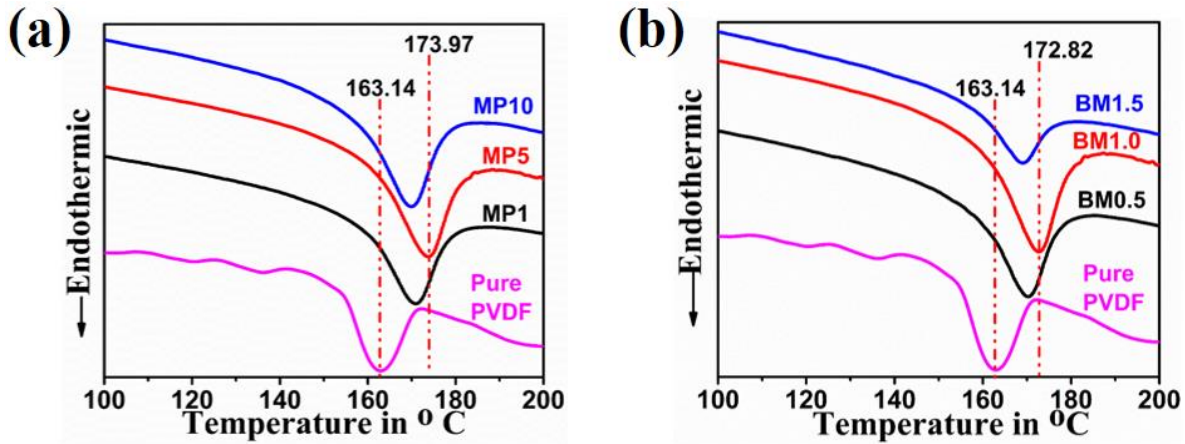


Figure 3.6. (a) DSC curve for pure PVDF, MP1, MP5 and MP10, (b) DSC curve for pure PVDF, BM0.5, BM1.0 and BM1.5

matrix has occurred due to some morphological changes in the polymer matrix leading to the change in the crystallinity of PVDF. The nonpolar α crystal morph in pure PVDF has been transformed into β crystal morph yielding a good β phase in the composite thin films. A considerable amount of increase to 173.97°C (for MP5) and 172.82°C (for BM1.0) was seen due to the doping of clay NPs into the PVDF matrix. These experimental results evidently suggest that the clay nanoparticles play a vital role as a nucleating agent leading to the formation of β polymorphs. This fact is in accordance with the previous FTIR and XRD experimental results.

3.5. Working principle of composite thin film and mechanism of the PENG

In electrodynamics, Maxwell's equations are always consistent with local invariance or conservation of charges. This can be written in the form of the equation of continuity as:

$$\nabla \cdot \vec{J} + \frac{\partial}{\partial t} (\nabla \cdot \vec{D}) = 0 \quad (2)$$

$$\text{Or, } \frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0 \quad (3)$$

From the continuity equation charge density can be defined as:

$$\rho = \rho_f + \rho_b \quad (4)$$

Where ρ , ρ_f and ρ_b are total, free and bound charges respectively. Hence, current density can be defined as:

$$\mathbf{J} = \mathbf{J}_f + \mathbf{J}_b \quad (5)$$

Where, $\mathbf{J}$, $\mathbf{J}_f$ and $\mathbf{J}_b$ are total, free and bound currents respectively. For any dielectric material, the ancillary fields that take part during the dipole formation can be represented as:

$$\mathbf{D}(\mathbf{r}, t) = \epsilon_0 \mathbf{E}(\mathbf{r}, t) + \mathbf{P}(\mathbf{r}, t) \quad (6)$$

$$\mathbf{H}(\mathbf{r}, t) = \mathbf{1}/\mu_0 \mathbf{B}(\mathbf{r}, t) - \mathbf{M}(\mathbf{r}, t) \quad (7)$$

Where, $\mathbf{D}$ is the displacement field, ϵ_0 is the permittivity of free space, $\mathbf{E}$ is electric field, $\mathbf{P}$ is the polarization, $\mathbf{H}$ is the magnetic field, μ_0 is the permeability of free space, $\mathbf{B}$ is the magnetic induction and $\mathbf{M}$ is the magnetization.

Here in this work, for the fabricated nanocomposite thin film, Maxwell's macroscopic equations or Maxwell's equations in matter have been used, considering only free charges and current. The equations are as follows:

$$\nabla \cdot \vec{\mathbf{D}} = \rho_f \quad (\text{Gauss's Law of electrostatics}) \quad (8)$$

$$\nabla \cdot \vec{\mathbf{H}} = 0 \quad (\text{Gauss's law magnetostatics}) \quad (9)$$

$$\nabla \times \vec{\mathbf{E}} = -\frac{\partial \vec{\mathbf{B}}}{\partial t} \quad (\text{Faraday's law}) \quad (10)$$

$$\nabla \times \vec{\mathbf{H}} = \vec{\mathbf{J}}_f + \frac{\partial \vec{\mathbf{D}}}{\partial t} \quad (\text{Ampere's circuital law with Maxwell's addition}) \quad (11)$$

where, $\vec{\mathbf{E}}$ is the electric field; $\vec{\mathbf{D}}$ is the displacement electric field; $\vec{\mathbf{B}}$ is the magnetic induction; $\vec{\mathbf{H}}$ is the magnetic field; ρ_f is the volume charge density of free electron and $\vec{\mathbf{J}}_f$ is the current density due to free electron flow. From electrodynamics, it is known that the displacement current for an electric field and the polarization current for an electric polarization are obtained from the following two equations respectively:

$$\mathbf{J} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (12)$$

$$\mathbf{J}_p = \frac{\partial \mathbf{P}}{\partial t} \quad (13)$$

Therefore, for a linear isotropic medium it can be clearly articulated that the second term $(\frac{\partial \vec{\mathbf{D}}}{\partial t})$ in equation (11) (Maxwell's fourth equation) is the total displacement current $\vec{\mathbf{J}}_D$ and can be represented as:

$$\vec{\mathbf{J}}_D = \frac{\partial \vec{\mathbf{D}}}{\partial t} = \epsilon_0 \frac{\partial \vec{\mathbf{E}}}{\partial t} + \frac{\partial \vec{\mathbf{P}}}{\partial t} \quad (14)$$

The total displacement current being a time-dependent term, depend not only on the electric field but also on the electric polarization of the dielectric medium. For an electromagnetic wave, the first term of equation (14) $(\epsilon_0 \frac{\partial \vec{E}}{\partial t})$ gives rise to the magnetic field H. The enhancement of this term is taken under consideration for the better output performance of wireless communication systems like broadcast radios, mobile communications, Wi-Fi, televisions, RADAR etc. From the second term $(\frac{\partial \vec{P}}{\partial t})$, the enhancement of piezoelectric effect can be effectively done by increasing P, since it is dependent on the strain or force applied to the piezoelectric material. For a linear isotropic piezoelectric material, piezoelectric equations on the application of mechanical strain are [53a]:

$$\vec{P}_i = (e)_{ijk}(\vec{S})_{jk} \quad (15)$$

$$\vec{T} = C_E \vec{S} - e^T \vec{E} \quad (16)$$

$$\vec{D} = e \vec{S} - k \vec{E} \quad (17)$$

where $\vec{S}$ is the mechanical strain; $(e)_{ijk}$ is the piezoelectric third order tensor, $\vec{T}$ is the stress tensor and C_E is the elasticity tensor and k is the dielectric tensor. For a linear polarizing medium the displacement current is represented as:

$$\vec{J}_{Di} = \frac{\partial \vec{P}_i}{\partial t} \quad (18)$$

Therefore it can be clearly said that the piezoelectric effect and the output current density is linearly proportional to the rate of change of the strain or force applied to the material. It can be said that the attained output result from the PENGs on the application of force is at par with the theoretical formulas. When no external electric field E is applied on the dielectric medium, the displacement current solely depends on the polarization P, as can be seen from equation (18). Taking P along the z direction, it can be written:

$$D_z = P_z = \sigma_p(z) \quad (19)$$

where, $\sigma_p(z)$ is piezoelectric polarization surface charges density of the material. Therefore the remaining displacement current term shall be:

$$J_{Dz} = \frac{\partial P_z}{\partial t} = \frac{\partial \sigma_p(z)}{\partial t} \quad (20)$$

Hence from equation (20), it can be concluded that the displacement current is directly proportional to the piezoelectric polarization surface charge density of the material. Therefore, smaller the size of the clay NPs, greater will be the surface charge density, leading

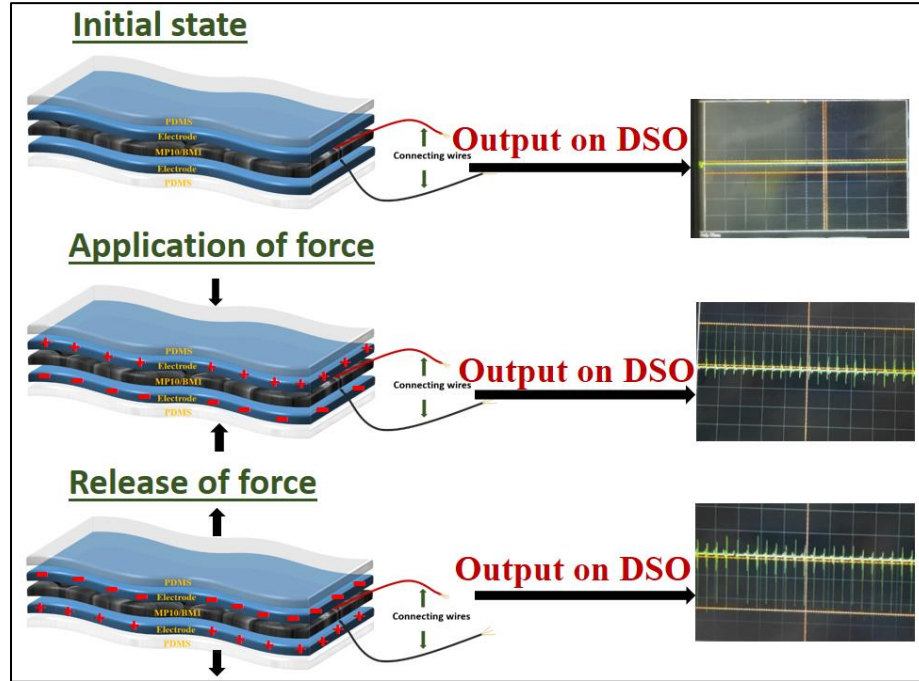


Figure 3.7. Working mechanism of PENG for voltage generation

to greater polarization. The theoretical facts can be affirmed by the experiment on the devices, that is BPENG shows higher output performance than MPENG. Ball mill can grind any material more finely than mortar pestle, which is operated manually. Therefore, the NPs obtained from the ball mill has a much smaller size in comparison to the latter, leading to a high surface area. Consequently, the ball mill ground NPs have a larger surface area for a very small mass%, which leads to the device which has been designed using them, to yield higher output results in comparison to the device making use of mortar pestle ground NPs. The mechanical energy to electrical energy conversion mechanism of the fabricated nanogenerator is illustrated in figure 3.7. As stated earlier, the β -phase enhancement occurs due to the addition of clay NPs to the PVDF matrix. It can be assuredly stated that there is a formation of some strong electrostatic interaction between the clay NPS and the $-\text{CH}_2/\text{CF}_2$ dipoles of PVDF due to mechanical stress and the interfacial surface charge. When an external force is applied on the composite, opposite electrical charge separation occurs and

hence the opposite polarity is formed at the two opposite sides, which leads to the formation of electric dipole [54a, 54b, 55]. A schematic diagram has been provided for the ion dipole

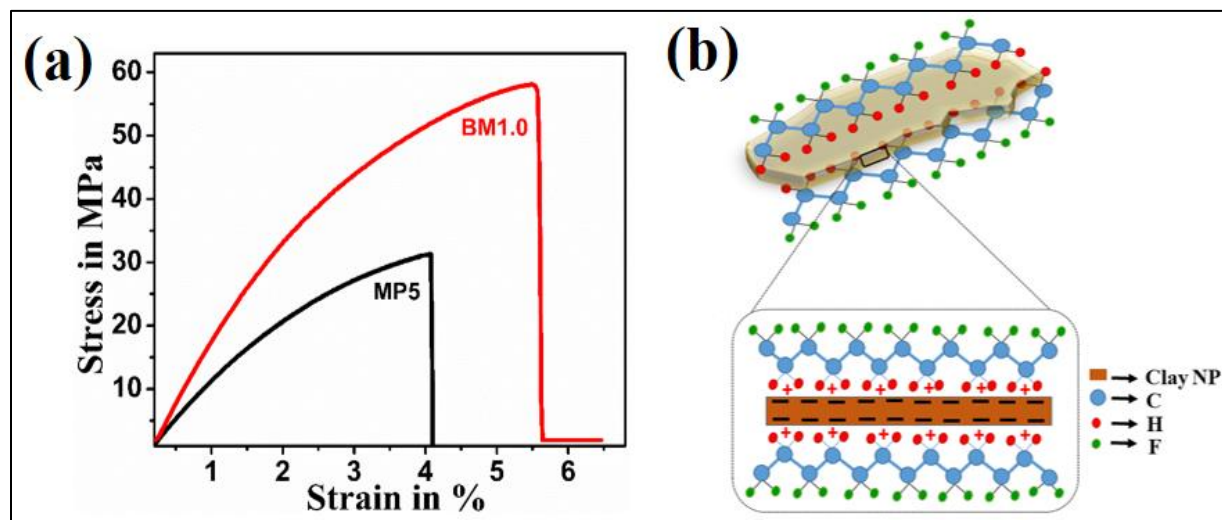


Figure 3.8. (a) Stress-strain curve of MP5 and BM1.0, (b) Schematic diagram of ion-dipole interaction between clay NPs and PVDF polymer chain

interaction mechanism between clay NPs and PVDF polymer chain in figure 3.8(b). The molecular dipoles and piezoelectric effect caused by the strong electrostatic interaction between the clay NPs and the dipoles of PVDF, leads to an all-trans configuration causing induced self-polarization. On the application of an external force on the device, displacement and redistribution of the dipoles in the self-poled polymer matrix takes place yielding higher output voltage [34]. This increase of self-polarization effect due to the induced charge production in the electrodes and the alignment of dipoles in the crystal in the direction of applied mechanical force leads to a higher output result. On the application of a vertical force on the device, a positive polarization charge gets accumulated on the top electrode and simultaneously an equal amount of induced negative charge accumulates on the bottom electrode [53a]. Therefore, a potential difference is obtained between the two electrodes that is directly proportional to the magnitude of the applied force and frequency of force, which henceforth leads to the flow of electrons through an external load. On the withdrawal of the vertical force, the accumulated charges on both the electrodes start retracing back to their initial state, which can be experimentally confirmed by the negative signal obtained in the voltage versus time graphs. This occurs since the dipoles instantaneously return back to their original state and electrons flow in the opposite direction, leading to a sharp decrement

of piezoelectric potential. This entire process repeats itself in a similar manner on the application of a continuous vertical periodic compression and relaxation, yielding a good output performance of MPENG and BPENG.

3.6. Output performance of PENGs

3.6.1. Electrical characterization of PENGs

Owing to the high flexibility of the composite films, the tensile strength of the films were examined. MP5 and BM1.0 revealed a maximum of 32 MPa and 56 MPa tensile strength with Young's modulus of 1408 N/mm² and 2150 N/mm² respectively. Therefore, it can be easily concluded that the elasticity of the composites have been increased on the addition of NPs into PVDF, since the Young's modulus of pure PVDF [53b] is around 700 N/mm². A stress versus strain curve of MP5 and BM1.0 is provided in figure 3.8(a).

Figure 3.9(a) and (b) show the open circuit output voltage versus time graph for MPENG and BPENG respectively. This output voltage was obtained by constant periodic application of force by human fingers and the output was detected using a DSO. A magnified

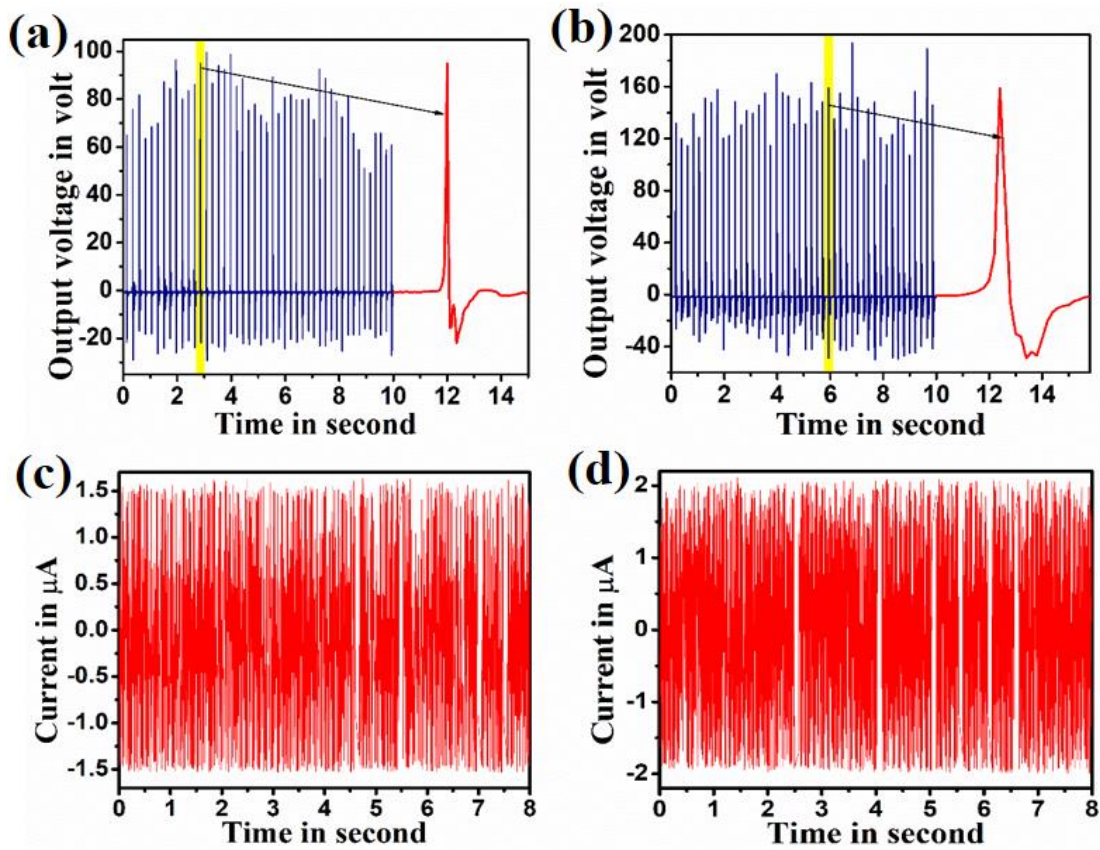


Figure 3.9. V_{oc} of (a) MPENG and (b) BPENG, I_{sc} of (c) MPENG and (d) BPENG

view of a single peak of the open circuit voltage is represented in figure 3.9(a) and (b) itself, showing a tiny second peak along with the main voltage peak which might be due to the damping effect of the applied force present in the device layers, that is some residual force still remains even after the withdrawal of the hand. The short circuit current for both the devices was also measured by an electrometer and the output results are presented in figure 3.9(c) and (d) for MPENG and BPENG respectively. MPENG yields an open-circuit voltage (V_{oc}) of $\sim 85V$ and short-circuit current (I_{sc}) of $\sim 1.6 \mu A$, leading to a power density of $\sim 4115 \mu W/cm^3$. BPENG shows a V_{oc} of $\sim 125V$ and $I_{sc} \sim 1.9 \mu A$, giving a power density of $\sim 7187 \mu W/cm^3$, under a periodic force by hand of $F \sim 13.3 N$ and $12.7 N$ for MPENG and BPENG respectively. The power densities of the nanogenerators have been calculated using the following equation:

$$\text{Power density} = \text{Power (IV)} / \text{Operative volume of nanogenerator} \quad (21)$$

$$(i) \text{ For MPENG: } I_{sc} = 1.6 \mu A, V_{oc} = 85 V. \text{ Hence, power density} = 4115 \mu W/cm^3$$

$$(ii) \text{ For BPENG: } I_{sc} = 1.9 \mu A, V_{oc} = 125 V. \text{ Hence, power density} = 7187 \mu W/cm^3$$

The amount of force imparted on the nanogenerators by various striking objects can be easily obtained from the laws of conservation of energy. It is known that:

$$mgh = \frac{1}{2} mv^2 \quad (22)$$

Where, m = mass of striking object, v = velocity of striking object, h = height of the object from where it fall, g = acceleration due to gravity. From here the velocity of the object can be found and calculated value of velocity for the case of imparting force by hand is $v = 1.3 ms^{-1}$. Now, the momentum gained by the body can be represented as:

$$mv = (F - mg) \Delta t \quad (23)$$

Therefore, the applied force F would be:

$$F = m (v/\Delta t + g) \quad (24)$$

where, Δt = time interval between two successive positive or negative peak of the output voltage vs time graph. On imparting force by hand, $m = 0.80 kg$, $v = 1.3 ms^{-1}$, $h = 0.09 m$, and $g = 9.8 m/s^2$, $\Delta t = 0.19 s$ (for MPENG) and $0.21 s$ (for BPENG). Putting these values into the formula, the applied force on MPENG = $13.3 N$ and on BPENG = $12.7 N$.

To examine the triboelectric contribution, output voltage of fabricated PENGs have been tested in bending mode, showing a very low output voltage of $0.6 V$ and $0.8 V$ for MPENG and BPENG respectively. A 'polarity switching' test was also performed for the two PENGs to

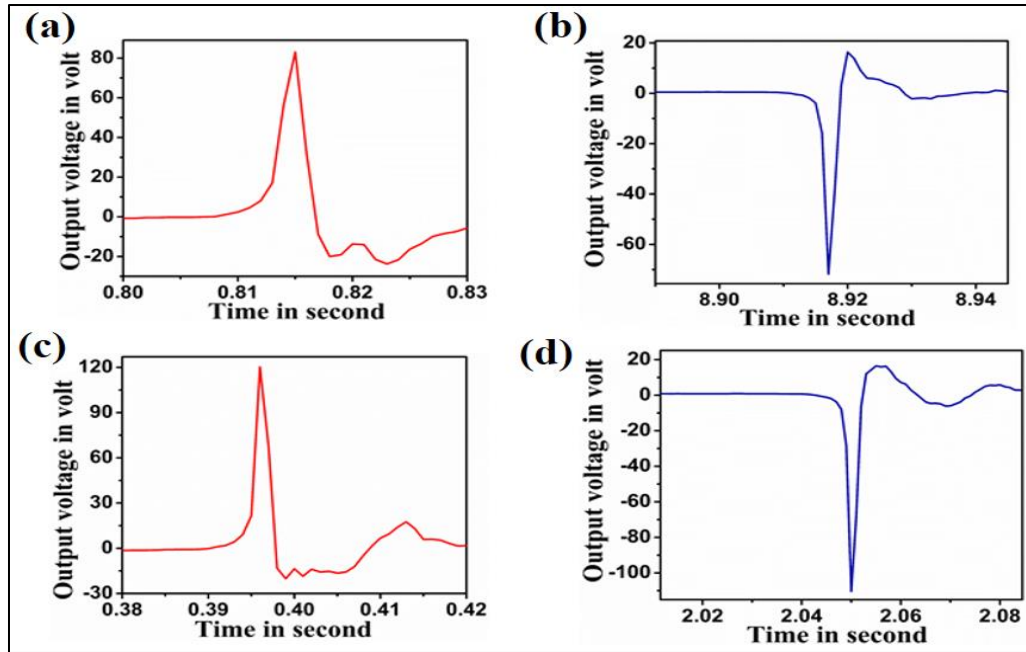


Figure 3.10. Polarity switching test for MPENG in (a) Forward connection and (b) Reverse connection, and for BPENG in (c) Forward connection and (d) Reverse connection

exclude the triboelectric interference and to confirm that the output electric signals are obtained from the piezoelectric effect entirely, as shown in figure 3.10(a)-(d). Output voltage of the designed devices with varying frequency of 2Hz – 12 Hz of force (applied force ~ 5 N) by a self-designed device (from Ocean college, Zhejiang University, PR China) was also experimentally analyzed and the maximum voltage was obtained at 10Hz, as shown in figure 3.11(a). This gradual increment of output voltage with frequency was primarily due to an improved equivalence of the impedance in the system, leading to an amplification of current.

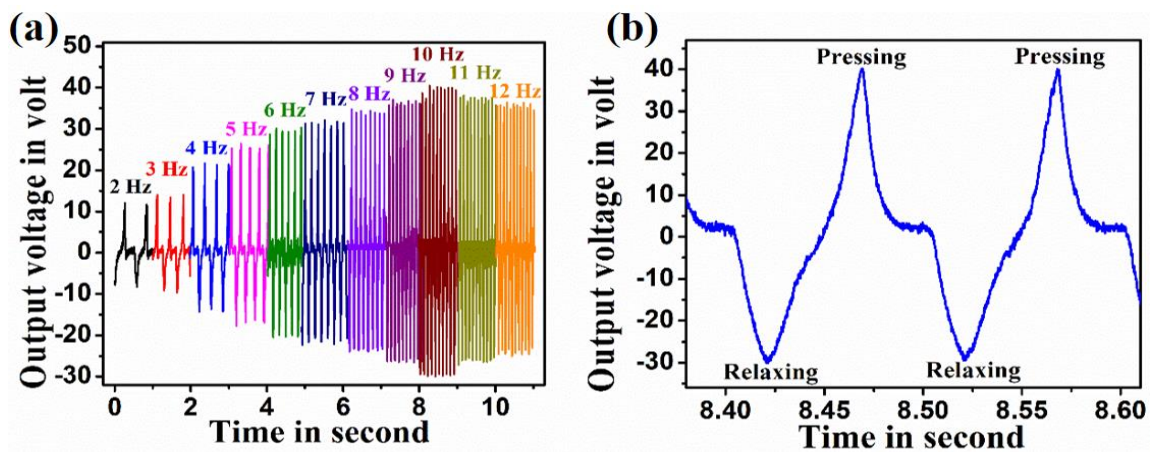


Figure 3.11. (a) Frequency dependent V_{OC} for 2 to 12 Hz, (b) Magnified view of 2 cycles of V_{OC} for 10 Hz frequency under application of 5 N force

This increment does come to a saturation point at a particular frequency where the impedance equivalence decreases, hence a decrease in the output voltage was experienced [5, 52]. Herein, beyond 10 Hz the output voltage gradually started to decrease at 11 Hz and 12 Hz and the reason behind this decrement of voltage is that, at higher frequency of force the compression cycles become very small and the device takes more time to come back to its original state. This infers that the frequency of the saturation point was 10Hz, after which there is a gradual decrease in the impedance equivalence. Figure 3.11(b) demonstrates the magnified view of two cycles of V_{OC} corresponding to 10 Hz frequency. This study was carried out under same applied force of 5N and same frequency of 5Hz and yielded an output voltage of 29 V and 47 V respectively, for MPENG and BPENG. The power densities for the PENGs were calculated using the formula:

$$P = \frac{V^2}{R_L v} \quad (25)$$

Where, P is the power density, V is the output voltage, R_L is the load resistance and v is the operative volume of the nanogenerator. The maximum power density for MPENG at a load resistance of 46 M Ω was 641 $\mu\text{W}/\text{cm}^3$ and BPENG yielded a maximum power density of 1232 $\mu\text{W}/\text{cm}^3$ at a load resistance of 58 M Ω . The comparison of the output voltages and power densities obtained from the two devices have been provided in figure 3.12(a) and (b). The output voltage and the power density acquired from the PENGs were far superior as compared to various previously reported biodegradable material or clay-based prototype

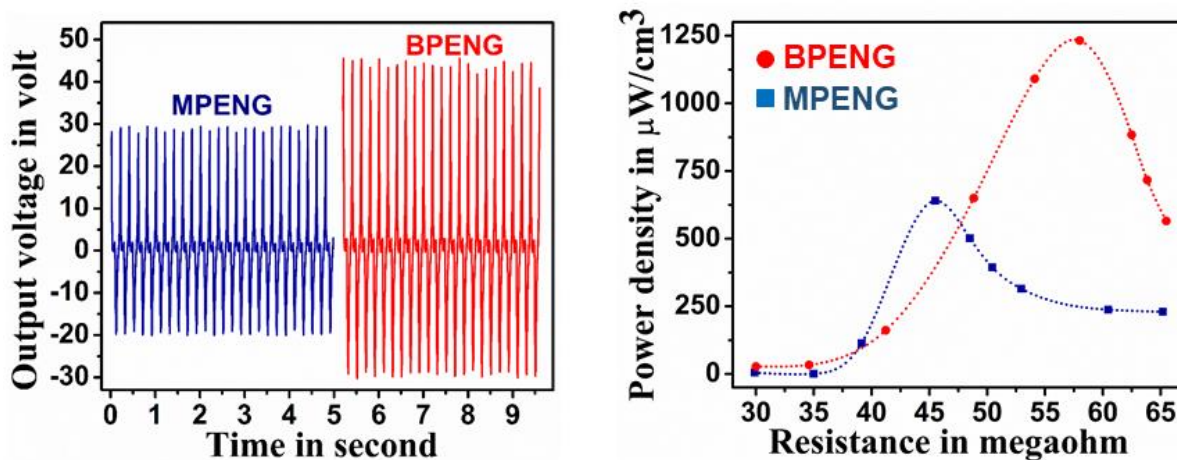


Figure 3.12. (a) Output voltage vs time graph and (b) Power density vs resistance graph at 5N force and 5Hz frequency for MPENG and BPENG

PENGs which indicates the novelty of this work based on its biodegradability of the dopant and performance of the device. The ability of the devices to convert other forms of biomechanical energy to electrical energy was also analyzed by recording the output voltage obtained from foot pressing. A considerable voltage of 32 V and 41 V were obtained from MPENG and BPENG, when the nanogenerators were pressed gently by heel as illustrated in figure 3.13(a) and (b). An appreciable output voltage of 5 V and 9 V was seen when jogging was performed on the PENGs as shown in figures 3.13(c) and (d) for MPENG and BPENG.

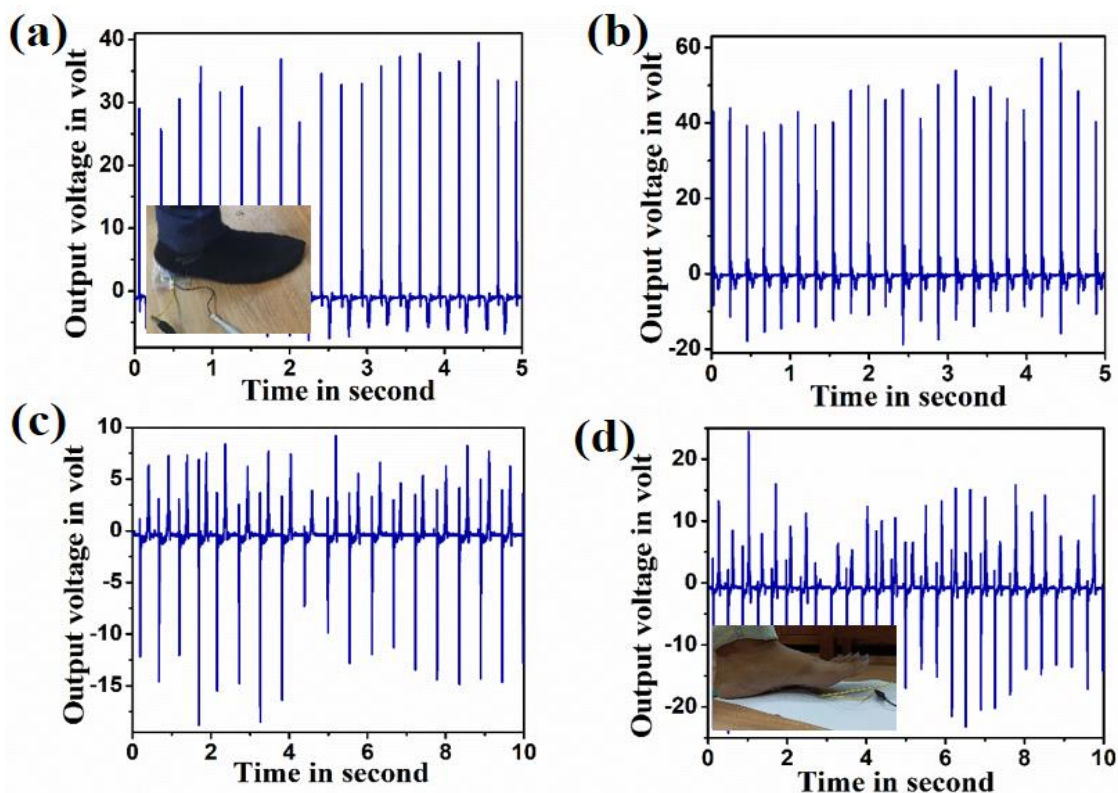


Figure 3.13. Open circuit voltage (V_{oc}) obtained by heel pressing on (a) MPENG and (b) BPENG, V_{oc} obtained from jogging on (c) MPENG and (d) BPENG

The output voltage obtained for the case of heel pressing was relatively greater than the case of jogging since the contact area between foot and nanogenerator and the force imparted were relatively higher in comparison to the case of jogging. This concept can easily be utilized for designing self-powering wearable devices.

Furthermore, MPENG and BPENG were attached to the body of a vortex machine to check the output voltage generated from the vibration of the machine, as shown in figure 3.14(a) and (b) respectively. The experiment was done for two different speed settings of

low and high for the vortex machine. A voltage of 1.5 V and 2.3 V (for low and high speed) were obtained for MPENG and 6.5 V and 9.0 V (for low and high speed) were obtained for BPENG. Output voltage was also obtained when air was blown on the nanogenerators by a

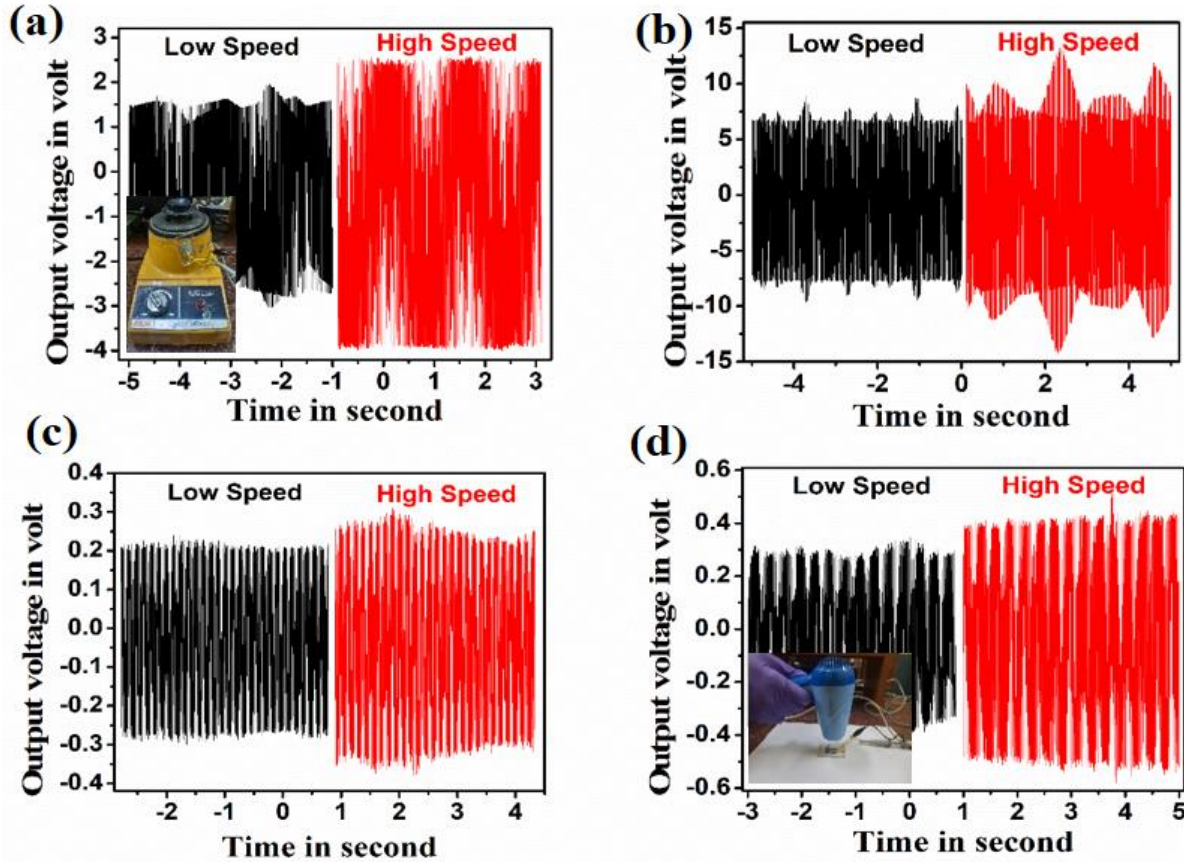


Figure 3.14. V_{oc} obtained the vibration of vortex machine for (a) MPENG and (b) BPENG, V_{oc} obtained from air blown on (c) MPENG and (d) BPENG

hair dryer from a distance, for two speed settings. Observed voltage values were 0.18 V and 0.25 V (for low and high speed) for MPENG and 0.29 V and 0.38 V (for low and high speeds), as illustrated in figure 3.14(c) and (d) respectively. The proposed nanogenerators pave a simple way for the prospective applicability in self-chargeable portable gadgets, in various biomedical applications or can be used as body motion sensors. The piezoelectric responses for the devices have been investigated by calculating the piezoelectric coefficient d_{33} of MP5 and BM1.0. For MP5, d_{33} was 39.75 pC/N at 50 Hz and for BM1.0 d_{33} was 50.10 pC/N at 50 Hz. The capacitance with varying frequency for MPENG and BPENG were measured using digital LCR meter (Agilent, E4980A). The detailed calculation for d_{33} and the graph is given

below. The piezoelectric coefficient d_{33} of MPENG and BPENG were calculated at 50Hz using the following mathematical equation:

$$d_{33} = V.C/F \quad (26)$$

where, V is the output voltage, F is the imparted force and C is the capacitance of the device.

(i) For MPENG, the calculated d_{33} was 39.75 pC/N at 50 Hz, where $F = 13.3$ N, $V = 85$ V and $C = 6.22$ pF.

(ii) For BPENG, the calculated d_{33} was 50.10 pC/N at 50 Hz, where $F = 12.7$ N, $V = 125$ V and $C = 5.09$ pF. The graph for capacitance with varying frequency for the two devices has been shown in figure 3.15.

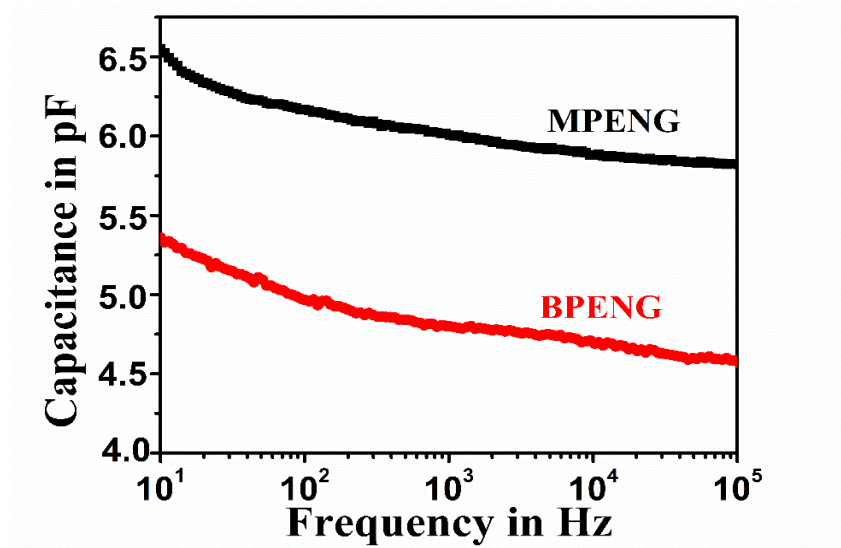


Figure 3.15. Capacitance vs frequency graph of MPENG and BPENG

By comparing with the recent works [54c], the proposed MPENG and BPENG were by far the most superior clay nanoparticle based PENG reported so far. A comparative study for output performances of the fabricated MPENG and BPENG with previously reported flexible PENGs have been done in table 3.2 below.

Table 3.2. Comparative study for output performances of MPENG and BPENG with previously reported flexible PENGs

Title of the article	Force or pressure	V _{oc}	I _{sc}	Power or power density
LiTaO ₃ -Based Flexible Piezoelectric Nanogenerators for Mechanical Energy Harvesting [6]	4N	18V	1.2μA	25 mW/m ²
Enhanced energy harvesting ability of polydimethylsiloxane-BaTiO ₃ -based flexible piezoelectric nanogenerator for tactile imitation application [7]	35 N	39 V	2.9 μA	24.2μW
Highly-flexible piezoelectric nanogenerators with silver nanowires and barium titanate embedded composite films for mechanical energy harvesting [8]	3 N	14 V	0.96 μA	9.86 mW/m ²
Physico-chemical and piezoelectric characterization of electroactive nanofabrics based on functionalized graphene/talc nanolayers/PVDF for energy harvesting [9]	0.4 MPa	12.9 V	-	1.72 μW/cm ²
Flexible piezoelectric nanogenerator in wearable self-powered active sensor for respiration and healthcare monitoring [10]	37 N	1.5 V	200 nA	-
Present work	13.3 N, 12.7 N	85 V, 125 V	1.6 μA, 1.9 μA	4115 μW/cm³, 7187 μW/cm³

3.6.2. Practical applications of MPENG and BPENG

The nanogenerators can also be used as a storage device. To prove this proficiency of the devices, a 2.2 μF capacitor was charged up to 3.1 V and 3.5 V in 16 s using MPENG and BPENG respectively by making proper electrical connection and a four-probe full wave rectifier, as shown in figure 3.16(a). The exponential charging graph of output voltage versus time for the capacitor suggests the high energy-storage ability of the fabricated PENGs, as illustrated in figure 3.16(b). To check the novelty and the practicality of the two PENGs in real life, a number of commercially available LEDs were lighted up with the help of the devices, to check their energy conversion competency. With proper electrical connections

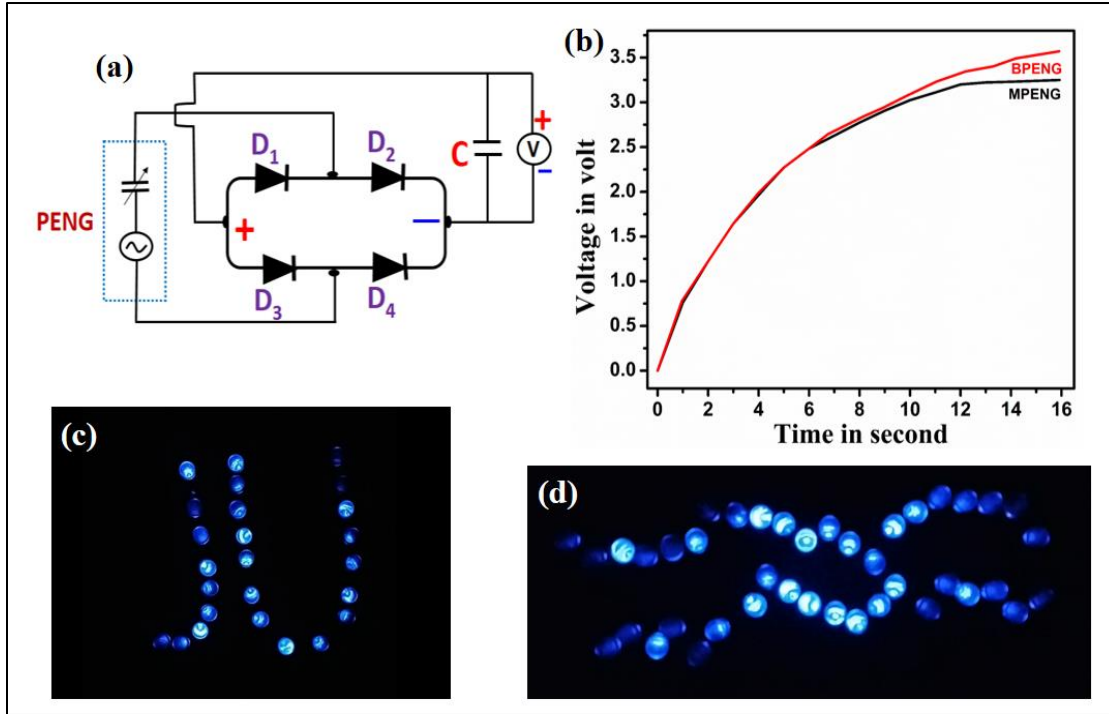


Figure 3.16. (a) Circuit diagram for capacitor charging (b) Charging graph for MPENG and BPENG, (c) and (d) snapshot of the illumination of blue LEDs by MPENG and BPENG

and by using a full wave rectifier, MPENG and BPENG were able to lighten up 25 and 40 number of blue LEDs when connected in series, on the application of periodic force, as shown in figure 3.16(c) and (d) respectively.

To check the longevity and the stability of the PENGs, the output performances were frequently checked for 15 weeks (one cycle of 300 second per week) and it was observed that the output performances for both the devices remained stable and nearly the same. On the periodic application of force by hand, the durability or the endurance test for MPENG and BPENG for more than 15000 periodic cycles was performed, generating a stable and continuous output voltage with very low deviation as shown in figure 3.17(a) and (b) respectively. The output voltages for MPENG and BPENG on the periodic application of force of 4 Hz by hand, for 3 consecutive weeks exhibited nearly the same value and maintained no less than 94% of the initial output voltage, throughout. The consistency and the stability of MPENG and BPENG at same frequency (4 Hz) are shown in figure 3.17(c) and (d).

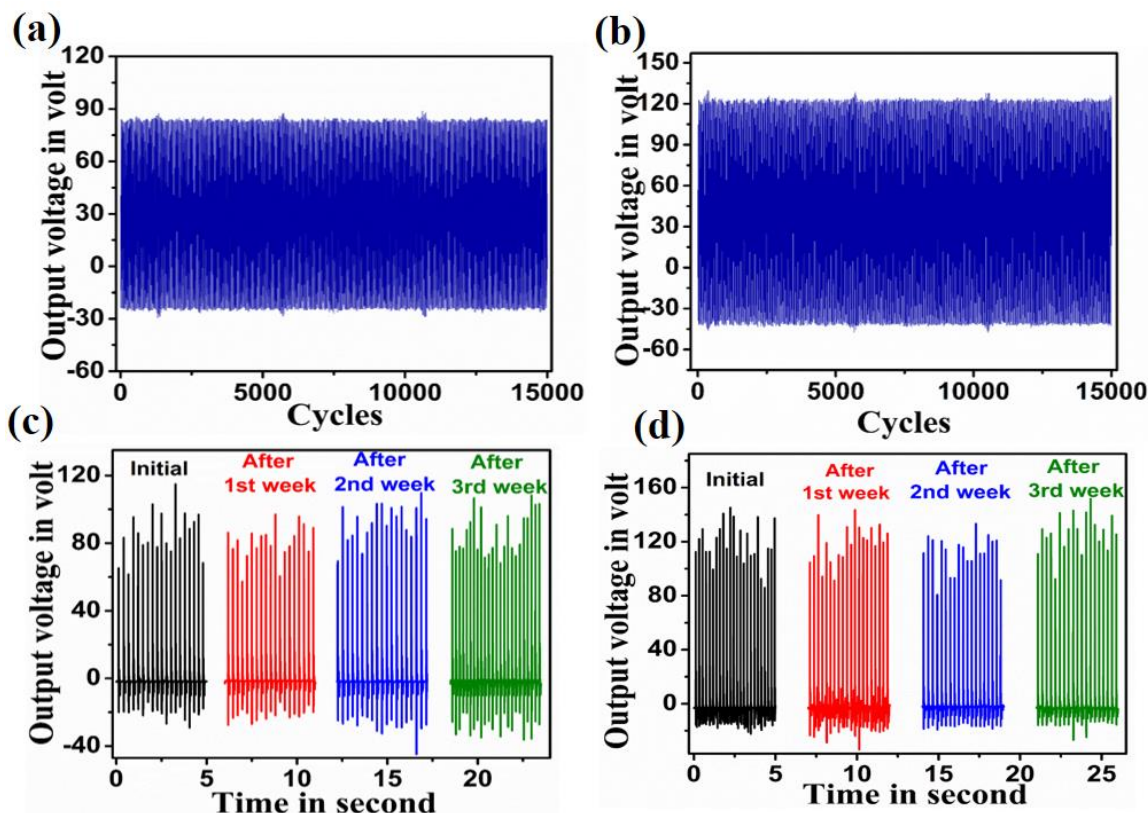


Figure 3.17. Durability test for 15000 cycles for (a) MPENG and (b) BPENG, Stability test for 3 weeks for (a) MPENG and (b) BPENG

3.7. Summary

To recapitulate the entire work, the influence of clay NPs on the electroactive β -phase enhancement of PVDF in the clay modified nanocomposites was primarily inspected. From FESEM micrographs, homogeneous and even distribution of clay NPs has been clearly observed with an average size of 600-700 nm for mortar pestle ground NPs and for ball mill ground NPs the average size was 200-300 nm, with samples MP5 and BM1.0 showing maximum dispersion properties of NPs in the PVDF matrix. On the addition of mortar pestle ground and ball mill ground clay NPs to the polymer, the maximum β -phase crystallization accomplished is $\sim 80.7\%$ and $\sim 84.8\%$ respectively. This considerable increase from 35% (for pure PVDF) to the previously mentioned value was due to the good electrostatic ion-dipole interaction and high interfacial polarization. The thermal stability of both types of clay NPs incorporated films were improved with the highest melting point of 173.97°C (for MP5) and 172.82°C (for BM1.0). The output performances for the devices were also checked using the most effective nanocomposites using both the kind of clay NPs. MPENG exhibits a large value

of $V_{oc} = 85$ V and short circuit current $I_{sc} = 1.6$ μ A with power density ~ 4115 μ Wcm⁻³ and BPENG provided $V_{oc} = 125$ V and $I_{sc} = 1.9$ μ A, with power density ~ 7187 μ Wcm⁻³ under a periodic force by hand. By applying the same magnitude of force MPENG and BPENG were capable to glow 25 and 40 blue LEDs respectively and can charge a 2.2 μ F capacitor within 16 s. The calculated results of piezoelectric coefficient d_{33} of MP5 and BM1.0 were 39.75 pC/N and 50.10 pC/N, at 50Hz frequency. Therefore, it can be concluded that the designed PENGs make the use of eco-friendly dopants, exhibiting good output performances. Body movement sensing was also an important attribute of the PENGs. Thus, the PENGs can be used in several self-powered electronic gadgets and power storage devices by converting mechanical energy from daily activities to electrical energy, without causing any harm to the environment. Therefore, MPENG and BPENG can be utilized in various biomedical fields or can be used as body motion sensor, if improvised properly and put under industrial scale.

3.8. References

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Chapter 4

Lead-Free Ultrasound Transducer Using Piezoelectric Composite with Enhanced Pulse-Echo Response



4.1 Introduction

Ultrasound, which lies in the frequency range of 20 kHz up to a few GHz has proved itself extremely useful in fields like medical science, testing, navigation, etc. [1, 2]. Ultrasound imaging is widely used today for medical diagnosis due to its non-invasive nature [3] and ability to reduce background interference. Ultrasound transducers (USTs) use piezoelectric materials to convert mechanical energy into electrical signals, offering broad bandwidth and high sensitivity for effective diagnosis [4]. Conventional USTs use piezoelectric single crystals or piezoceramics like PZT [5] with high electromechanical coupling, but they suffer from acoustic impedance mismatch, narrow bandwidth, low energy efficiency and aperture design challenges. Hence, thin-film based ultrasound transducers are highly promising for biomedical imaging [6], offering excellent impulse reception as they transmit and receive pulses reflected from living tissue surfaces. This reflected pulse having various acoustic impedances, is carried back to the transducer and eventually, physiological information about the tissues are obtained. Beyond biomedical use, thin-film ultrasound transducers are valuable in nondestructive testing (NDT) [7], which uses ultrasound to assess material thickness, internal structure and damage in concrete and other structures. Compared to conventional methods, thin-film based USTs offer better flaw detection by effectively penetrating multiple layers. Among the recent advancements in polymer film-based USTs, Du et al. demonstrated the use of polymer-based optoacoustic transducers for ultrasound imaging by employing a lead halide perovskite material [5]. Petritz et al. worked on ferroelectric transducers employing spin-coated PVDF-TrFE polymer [8].

Poly (vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), a copolymer of PVDF, is a widely studied piezopolymer due to its high polarization, thermal stability, low mechanical and electrical losses [4, 8]. Furthermore, various acoustic impedances of the reflected pulse from PVDF-TrFE based UST almost match with that of the living cells or tissues and with water, producing high-resolution images [14]. Hence, PVDF-TrFE operates within the desired frequency range and its properties make it well suited for ultrasound transducer designing. There have been scarce reports on the development of UST using polymer nanocomposites incorporated with transition metal hydroxide nanoparticles. Nickel hydroxide (Ni(OH)_2) (a transition metal hydroxide) has improved physiochemical

properties and is a popular semiconducting metal hydroxide [10]. It has also been experimentally proven that a small amount of Ni(OH)_2 in the polymer matrix significantly enhances polarization and increases the composite's breakdown strength. There are primarily two polymorphic states of nickel hydroxide, $\alpha\text{-Ni(OH)}_2$ and $\beta\text{-Ni(OH)}_2$, which get transformed into $\gamma\text{-NiOOH}$ and $\beta\text{-NiOOH}$ respectively, when the formers get charged up. Among these two polymorphs, $\beta\text{-Ni(OH)}_2$ possesses greater stability in comparison to the α -polymorph [12]. This is because, $\beta\text{-Ni(OH)}_2$ possesses a layered structure that enables easy ion movement. Here, in this work, a lead-free UST using the synthesized ultrafine β -nickel hydroxide nanoplates incorporated polymeric nanocomposite has been designed. The thin nanocomposite composed of $\beta\text{-Ni(OH)}_2$ nanoplates and the piezoelectric polymer PVDF-TrFE (30-70%) was prepared by a simple spin coating method. Upon characterization of the composite, a high crystallization with an extremely high β phase content of 90.04% and high piezoelectric coefficient (d_{33}) of 50.22 pm/V has been obtained, which indicates that the nanoplates possess favorable piezoelectric characteristics. Moreover, the UST which was capable of both generating and receiving pulse signals, exhibited exceptional performance showcasing a remarkable peak-to-peak output voltage of 5.19 V. Notably, the transducer demonstrated an exceptionally broad -6 dB bandwidth of 51.22 MHz (102.4%) having a central frequency of 50.01 MHz, which shall lead to significantly high-resolution ultrasound images. Considering the superior output voltage, ultra-broad bandwidth and remarkably high central frequency, the designed transducer shows immense potential for successful implementation on an industrial scale. Lead-free diagnostics are widely recognized as safer for medical use, particularly in procedures with prolonged or direct human body contact, as they eliminate the risk of lead exposure. Hence, this lead-free transducer design holds promise for applications in the photoacoustic field, enabling the acquisition of high-resolution ultrasound images in medical domains which enables the precise detection of abnormal tissues in living bodies, offering a nontoxic advancement in medical imaging. The polymer composite film-based ultrasound transducers have also effectively overcome the challenges encountered with piezoelectric crystal-based transducers. This is attributed to the significantly reduced thickness and smaller size of the composite. These exceptional characteristics, combined with the innovative design of the ultrasound transducer, contribute to its robustness, compactness and portability.

4.2 Experimental section

4.2.1. Materials

PVDF-TrFE powder (M.W. gm/mol, Sigma-Aldrich, USA), N, N dimethylformamide (DMF), (Merck, India), nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) (Merck, India) and lithium hydroxide (LiOH) (Merck, India).

4.2.2. Synthesis of nickel hydroxide nanoplates

A simple hydrothermal process was employed for the synthesis of β -nickel hydroxide nanoplates with the help of nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and lithium hydroxide (LiOH). These chemicals were AR grade and were used without any further purification. 0.3 M nickel acetate tetrahydrate salt was dissolved in 60 mL of double distilled water and the prepared salt solution was kept under vigorous stirring on a magnetic stirrer. After thorough mixing for about 30 minutes, the pH of the solution was brought to 12 by gradual addition of 1 M lithium hydroxide to the salt solution. This prepared solution was then transferred to a teflon-lined stainless steel autoclave setup (80 mL in volume), filling it up to 80% of its capacity. The setup was then kept in a clean, dry hot air oven at 150 °C for 12 hours. The light green coloured precipitate obtained was then centrifuged and washed with double distilled water several times to bring the pH of the precipitate to 7. Eventually, the precipitate was collected, dried at 80 °C for 12 hours and ground into a fine powder with the help of a mortar pestle to obtain β -nickel hydroxide nanoplates [11]. β -form of $\text{Ni}(\text{OH})_2$ was prepared as it is the most stable form [12].

4.2.3. Composite thin film fabrication

Nickel hydroxide based thin film was prepared by a simple spin coating method. To fabricate the polymer composite NTr5, the widely used solution blending method was employed. This method is particularly effective in producing composite films with stable and homogeneous dispersions. First, 0.15 g of PVDF-TrFE powder was added to 3 mL of dimethylformamide (DMF) and kept under stirring at 60 °C. Then 5 mass% of β - $\text{Ni}(\text{OH})_2$ nanoplates were added to the already prepared clear polymer solution and stirred continuously for 12 hours. To achieve a uniform blend, the solution underwent additional ultrasonication for a duration of 30 minutes. Subsequently, 200 μL of this solution was casted

onto an aluminium substrate, which had a gold coating on it. The coating process involved spinning the substrate at 300 revolutions per minute (r.p.m.) for a period of 60 second, utilizing a Programmable Spin Coater SpinNXG-P1 from Apex Instruments. As a subsequent step, another 200 μL of the solution was applied onto the previously deposited film. This spin coating process was carried out at 700 r.p.m. for a duration of 120 second which allowed for the uniform distribution of the solution. Finally, it was dried in a clean dry hot air oven at 60 $^{\circ}\text{C}$ for 15 minutes, to form a uniform $\text{Ni}(\text{OH})_2$ incorporated nanocomposite (named NTr5). For the comparison of β -phase nucleation content in the composite thin film, a pure PVDF-TrFE thin film (PTr) was also synthesized as a control setup. The schematic diagram illustrating the fabrication process of NTr5 with the help of the simple spin coating method is shown in figure 4.1(a).

4.3. Composite thin film-based ultrasound transducer (P-UST) designing

For designing the ultrasound transducer (named P-UST), firstly a cylindrical aluminium substrate was taken, having a diameter of 9 mm. The backing layer substrate of aluminium was tailor-made to specific requirements and the surface of the aluminium substrate was perfectly levelled to a smooth plane by the milling process with the help of a CNC machine, forming a T-like appearance. It was then properly washed several times with ethyl alcohol and was made free of any undesired impurities on the substrate. This layer acted as the backing layer of the ultrasound transducer. On this clean and smooth aluminium surface, gold was uniformly sputtered to form a thin uniform gold coating of approximately 20 nm in thickness with the help of Quorum Q150R Plus - Rotary Pumped Coater. This gold layer on the aluminium surface served as the bottom electrode of the ultrasound transducer. Thereafter, the composite thin film was spin coated onto the gold sputtered aluminium substrate according to the above-mentioned procedure in section 4.2.3, forming the matching layer of P-UST. PVDF-TrFE-based composites are particularly effective in this regard since their acoustic impedance closely align with that of living cells or tissues as well as water, resulting in the production of high-resolution images by the USTs, hence a separate matching layer was not required. Furthermore, these composite films exhibit a relatively low insertion loss, making it easier to match their acoustic impedance to that of human tissues [14]. The thickness of the composite NTr5 film was approximately 26 μm . Not only does the

gold coating plays the role of an electrode (bottom electrode) in the transducer setup but also help in the proper binding of the polymer composite thin film to the aluminium substrate. Electrical poling of composite thin film was done by first annealing NTr5 at 80 °C

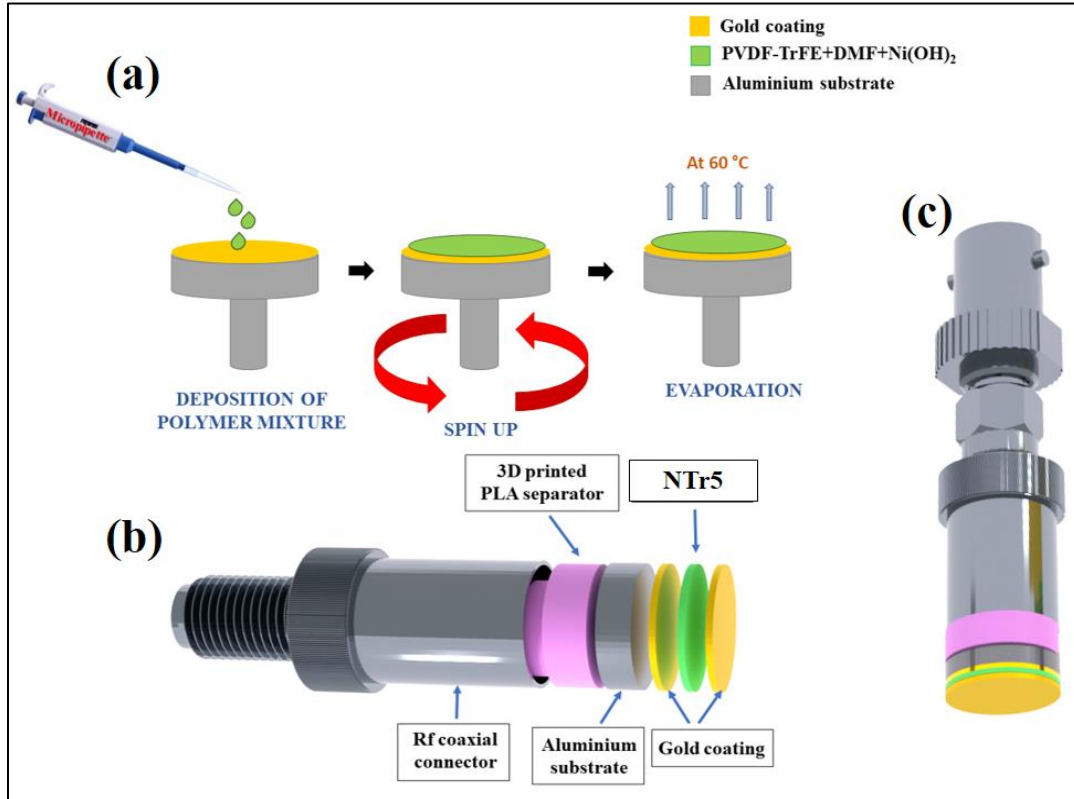


Figure 4.1. (a) Fabrication process of NTr5 via spin coating method, (b) Assembly of P-UST, exhibiting all the layers separately, (c) Schematic diagram of P-UST after assembly

for over the course of 1 hour and then a slowly increasing DC voltage was applied from 0 kV to 32 kV, from a height of 13 mm. The detailed description and the various conditions maintained during the poling procedure has been added in the appendix 2 file. Subsequently, another layer of gold of about the same thickness as the former layer (~ 20 nm) was again sputtered over the piezoelectric composite thin film, serving as the second electrode (top electrode) of the transducer. Thereafter, the daintily assembled four layers were securely attached to the central pin of an RF (radio frequency) coaxial connector. The assembly concept of the UST, exhibiting all the layers separately has been shown in figure 4.1(b). To prevent the T-shaped substrate from coming into contact with the outer conducting part of the RF coaxial connector, a 3D-printed PLA (polylactic acid) separator was added. This separator served as a protective barrier, ensuring that there was no direct contact between

the T-shaped substrate and the outer conducting component of the RF coaxial connector, as can be seen from the schematic diagram of P-UST in figure 4.1(c). When all the aforementioned components were combined, the UST acquired a tubular shape with an approximate length of 6 cm. To establish the complete circuit, a copper wire was utilized to connect the RF connector and the top electrode. This connection ensured the completion of the circuit when the transducer (P-UST) was connected to a pulser-receiver setup. The digital image of the self-assembled ultrasound transducer P-UST is illustrated in figure 4.2. This idea of using Ni(OH)_2 stands out as there has been limited research on utilizing transition metal hydroxides in transducer designing also making it lead-free in nature.

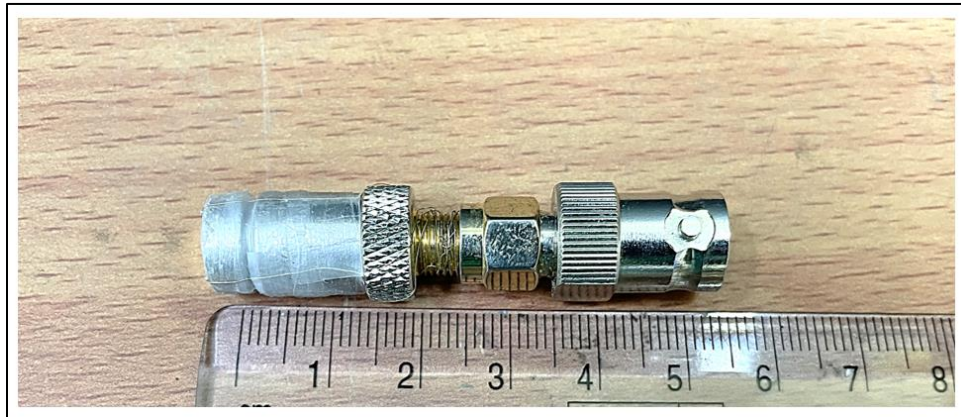


Figure 4.2. Digital image of assembled P-UST

Herein, the assembly procedure for the UST is very unique and innovative, that sets it apart from conventional designs of ultrasound transducers. This new approach ensures that the UST is exceptionally compact, portable and user-friendly, making it highly convenient to use in practical life.

4.4. Experimental setup for the operation of P-UST

The designed ultrasound transducer (P-UST) was attached to a pulser-receiver (OLYMPUS-5073PR) setup with 75 MHz and -3 dB of ultrasonic bandwidth. The receiver is characterized by a maximum bandwidth (-3 dB, $R_L = 50 \text{ ohm}$) ranging from 1 kHz to 75 MHz. Subsequently, the output of the ultrasound transducer was captured and monitored by connecting it to a digital storage oscilloscope (Keysight Oscilloscope DSO-X 3012A). The pulse echo output data was acquired by operating P-UST over an aluminium block with a generous layer of ultrasound gel on it. The application of the gel enhanced the ultrasound's

velocity, leading to an improved transmission. To analyze the pulse and echo responses, the transducer was positioned 5 mm away from the aluminium target block. During operation, great care was taken to ensure optimal contact between the transducer and the gel, with the objective of eliminating any air gaps between the contacting surface of the transducer and the aluminium block. This careful approach aimed to enhance the efficiency and accuracy of the transducer's performance for the transmission of pulses and the reception of echoes. Since, P-UST not only generated an ultrasound signal but also acted as a receiver itself, therefore no separate pulse receiver was further required. The schematic diagram of the whole operating setup of P-UST has been demonstrated in figure 4.3 and this setup facilitated the detection and recording of the ultrasound signals, enabling further analysis and observation of the transducer's output.

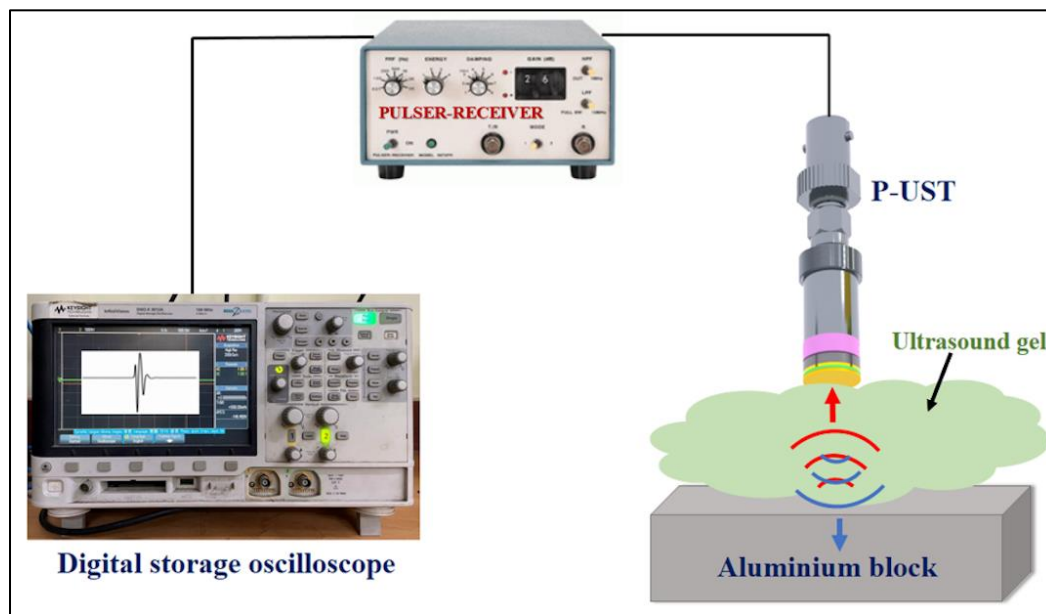


Figure 4.3. Schematic diagram of the operating setup of P-UST

4.5. Results and discussion

4.5.1. Morphological and microstructural analysis

The morphologies of the synthesized $\text{Ni}(\text{OH})_2$ nanoparticles and the thin films were analysed using Field Emission Electron Microscopy (FESEM). Figure 4.4(a) shows the formation of distinct, uniform nanoplates of $\text{Ni}(\text{OH})_2$ with an average size of 70-170 nm. It can also be seen that the nanoplates have a flaky pattern with a flat and smooth surface.

These morphological characteristics can increase the breakdown strength of the composite thin film [11]. Furthermore, the very small size of the nanoplates also increased the overall surface area of $\text{Ni}(\text{OH})_2$ nanoparticles, which in turn has increased the β -phase nucleation in the composite thin film due to enhanced polarization and high surface charge density [9].

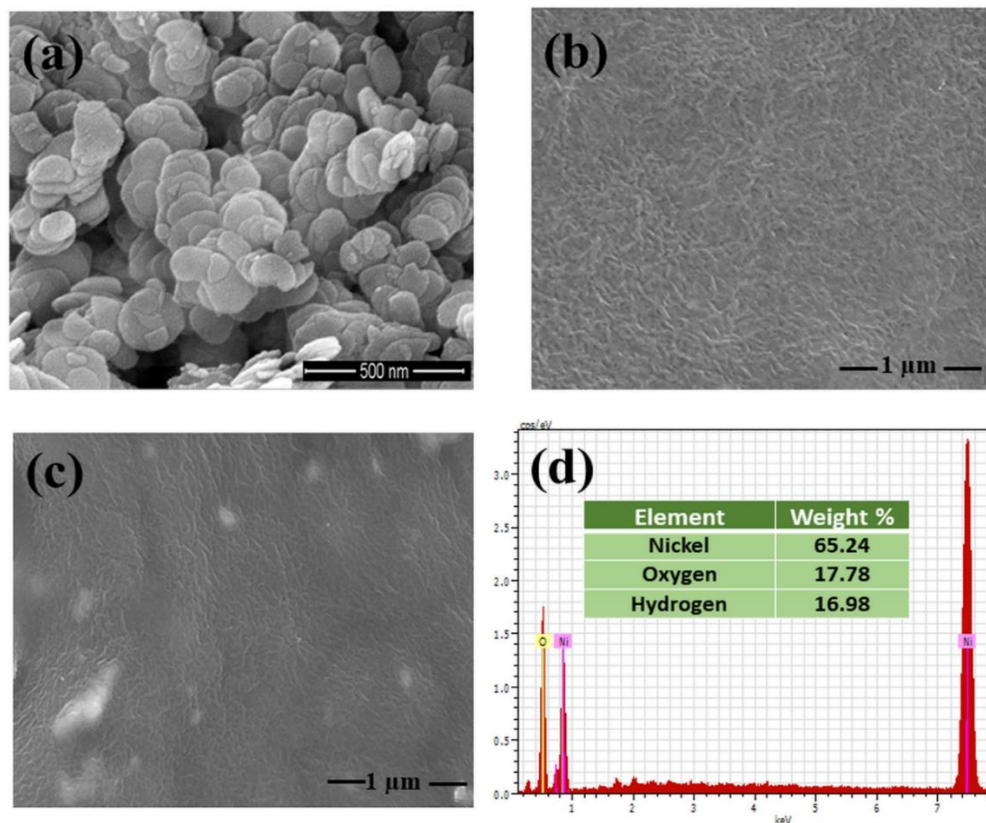


Figure 4.4. FESEM image of (a) Pure $\text{Ni}(\text{OH})_2$ nanoplates, (b) PTr and (c) NTr5, (d) EDS spectrum of $\text{Ni}(\text{OH})_2$ and inset shows the weight% of various elements present in the $\text{Ni}(\text{OH})_2$

The FESEM images of pure PVDF- TrFE thin film (PTr) and the composite thin film (NTr5) are represented in figure 4.4(b) and (c) respectively. Both the micrographs displayed roughened and non-uniform surfaces, composed of tiny grains which are randomly ordered [15]. The surface of the pure and the composite thin films showcases a crystalline laminar pattern over the entire area [16]. Figure 4.4(c) clearly shows the homogeneous distribution and dispersion of $\text{Ni}(\text{OH})_2$ nanoplates over the entire surface of the polymer.

The EDS spectroscopy was employed to analyse the distribution of the various elements in $\text{Ni}(\text{OH})_2$, showcasing the various proportions of nickel (Ni), oxygen (O) and hydrogen (H) within the compound, as shown in figure 4.4(d). The inset of this figure exhibits atomic weight percentage of the various elements in the nanoparticles. This characterisation

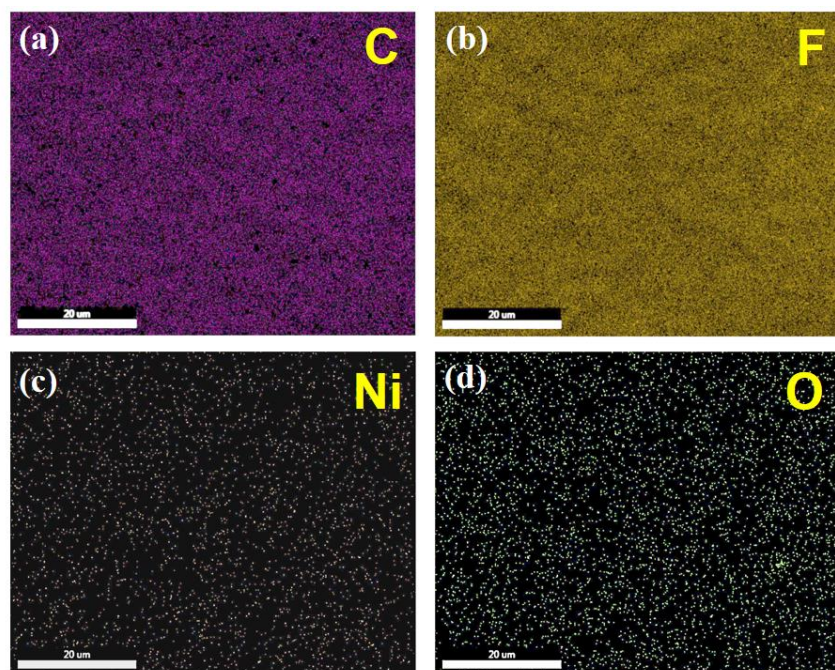


Figure 4.5. Elemental mapping images of NTr5 with various volume fractions of (a) Carbon, (b) Fluorine, (c) Nitrogen and (d) Oxygen in the composite

technique also confirms the successful synthesis of $\text{Ni}(\text{OH})_2$ nanoplates. To experimentally confirm the uniform dispersion of $\beta\text{-Ni}(\text{OH})_2$ nanoplates within the PVDF-TrFE matrix, elemental mapping for NTr5 was conducted, as illustrated in the figure 4.5. This elemental mapping visually represented the homogeneous distribution of the effective dispersion of carbon (C), fluorine (F), nickel (Ni) and oxygen (O) within the NTr5 composite. The results clearly indicated that the $\text{Ni}(\text{OH})_2$ nanoplates have been evenly distributed throughout the polymer matrix, demonstrating a random dispersion pattern.

4.5.2. Structural study of nanoparticles and electroactive β -phase analysis of composite (X-ray diffractogram)

The X-ray diffractogram pattern of $\beta\text{-Ni}(\text{OH})_2$ nanoplates, provides an overview about the purity and the well crystalline structure formation. The characteristic peaks in the diffraction pattern of $\text{Ni}(\text{OH})_2$ shows the reflection at the 2θ values of 19.52° (001), 33.01° (100), 38.57° (101), 52.12° (102), 58.98° (110), 62.69° (111), 70.48° (103), 72.71° (201). These peaks correspond to the hexagonal phase of $\beta\text{-Ni}(\text{OH})_2$ [17], confirming the formation of nickel hydroxide nanocrystals [JCPDS, file No. 14-0117] [11]. For detailed information about the crystal parameters and microstructure, Rietveld refinement was performed for the

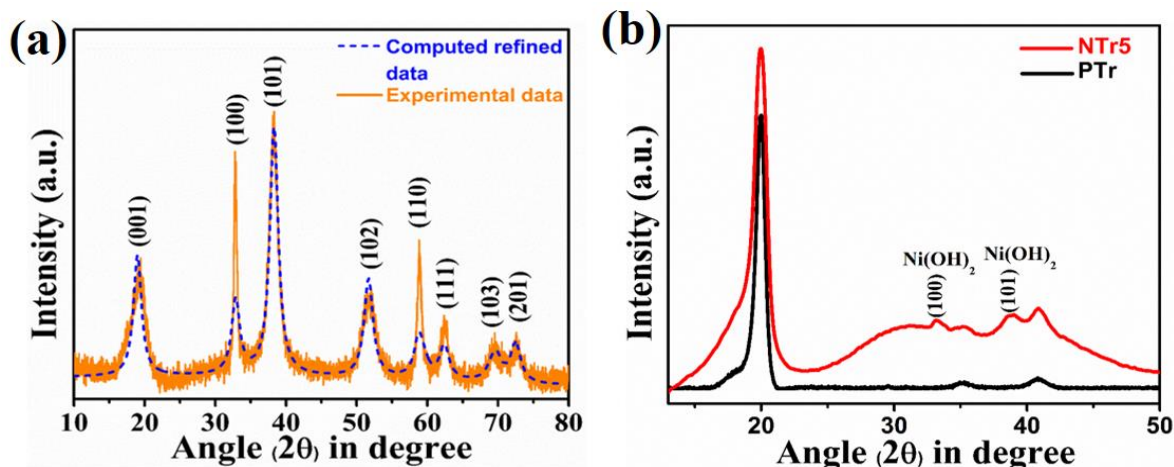


Figure 4.6. (a) Experimental and computed refined X-ray diffractogram of $\text{Ni}(\text{OH})_2$ nanoplates, (b) X-ray diffractogram of PTr and NTr5

curve better fitting. Refinement of the experimental X-ray diffractogram was executed with the help of Maud v2.94 software. Figure 4.6(a) illustrates the experimental and the computed refined X-ray diffractogram of $\text{Ni}(\text{OH})_2$. The parameters for the refined computed XRD data at the end of the final cycle are represented in table 4.1. Figure 4.6(b) shows the diffractogram of pure PVDF-TrFE thin film (PTr) and the composite thin film (NTr5). As seen from the XRD pattern, a prominent diffraction peak at 18.5° corresponding to the plane (020)

Table 4.1. Crystallographic parameters for the refined XRD data of $\text{Ni}(\text{OH})_2$ nanoparticles

Parameters	Value for $\text{Ni}(\text{OH})_2$ nanoparticles
a (Å)	3.13
b (Å)	3.13
c (Å)	4.63
α (°)	90.00
β (°)	90.00
γ (°)	120.00
V (Å ³)	45.36
Crystallite size (nm)	7.665058
R _p (%)	8.09
R _{wp} (%)	11.13
χ^2	1.37
Microstrain	5.2135977×10^{-7}

is present in the case of PTr [20]. This peak is indicative of the presence of α -phase in pure PVDF-TrFE. For NTr5, the diffractogram displays a prominent peak at 19.9° corresponding to ((110), (200)) lattice planes [16]. This sharp peak clearly indicates the presence of crystalline β -phase in the composite due to the nucleation of the electroactive polar phase. The polar β -crystals in the composite are formed due to the addition of the $\text{Ni}(\text{OH})_2$ nanoplates to the pure polymer and furthermore it waived off any α or γ crystallinity from NTr5. Herein, the X-ray analysis conducted on the β - $\text{Ni}(\text{OH})_2$ nanoplates determined their average crystalline size to be approximately 7.66 nm, thus providing valuable insights into the structural characteristics of the nanoplates. The values of these salient parameters can also be obtained by calculations, using some renowned formulas as mentioned below. Using the Debye-Scherrer equation, the average crystalline size of β - $\text{Ni}(\text{OH})_2$ can be predicted from the characteristic diffraction peaks with high intensities. According to this equation [18]:

$$D = \frac{K\lambda}{\beta_{1/2} \cos\theta} \quad (1)$$

Where, D represents the crystalline size of the nanoparticles, K represents the Scherrer constant (0.98), λ represents the wavelength of the incident monochromatic Cu-K α beam (1.54 Å), β denotes the full width at half maximum (FWHM) and θ represents the respective Bragg's angle. With the help of Bragg's equation, the distance between the atomic layers or interplanar spacing (d) of the crystal can be easily obtained. The equation is represented as:

$$2d \sin\theta = n\lambda \quad (2)$$

Where, n represents the order of diffraction in the form of an integer. Since the β - $\text{Ni}(\text{OH})_2$ has a hexagonal structure, the lattice parameters (a, b, c) of the nanoparticles can be easily calculated using the formula:

$$\frac{1}{d^2} = \frac{4}{3a^2} (h^2 + hk + k^2) + \frac{l^2}{c^2} \quad (3)$$

Where, h, k and l represent the Miller indices and for hexagonal structure: $a = b \neq c$. The calculated average values of the lattice parameters are $a = 3.13 \text{ Å}$, $b = 3.13 \text{ Å}$, and $c = 4.63 \text{ Å}$. These values are well matched with the theoretical value of lattice parameters from literature review [12, 19]. Subsequently, using these calculated values of a, b and c the volume of a unit cell was calculated with the help of the equation:

$$V = a \times b \times c \quad (4)$$

The volume of a unit cell of the nanoparticle, denoted as V , was determined to be $45.35 \text{ \AA}^3$. The value of the dislocation density can be obtained using the formula:

$$\rho = \frac{1}{D^2} \quad (5)$$

Where, ρ is the dislocation density. This parameter indicates the number of defects present in the nanoparticle, determined by the length of the dislocation lines present in each unit

Table 4.2. Assessment of salient parameters from XRD analysis of Ni(OH)_2 nanoplates

2θ (in degree)	Miller indices (h k l)	FWHM (β)	Interplanar spacing (d) (in $\text{\AA}$)	Crystallite size of Ni(OH)_2 (D) (in nm)	Dislocation density (ρ) (in nm^{-2})
19.52	(001)	2.434	4.54	3.310	0.0912
33.01	(100)	0.574	2.71	14.422	0.0048
38.57	(101)	1.736	2.33	4.844	0.0426
52.12	(102)	2.242	1.75	3.938	0.0644
58.98	(110)	0.770	1.56	11.840	0.0071
62.69	(111)	1.121	1.48	8.289	0.0145
70.48	(103)	1.189	1.33	8.147	0.0150
72.71	(201)	1.357	1.29	7.263	0.0189

volume of the sample crystal. The dislocation density value of nanoparticles is influenced by the presence of defects and hence it exhibits variation depending on the number of defects present in the NPs [18]. The calculated values of all the above-mentioned parameters have been represented in a tabular form in table 4.2 for all the sharp distinct peaks.

4.5.3. Investigation of β -phase nucleation (FTIR spectroscopy analysis)

For proper knowledge about the dynamics of the samples and for further confirmation of the nucleation of electroactive β -crystals in the composite, Fourier transform infrared spectroscopy analysis of PTr and NTr5 was carried out in the range of 500 cm^{-1} to 1350 cm^{-1} , as displayed in figure 4.7(a). The spin coated composite film, with $\beta\text{-Ni(OH)}_2$ nanoplates incorporated in PVDF-TrFE exhibited the well packed characteristic absorbance

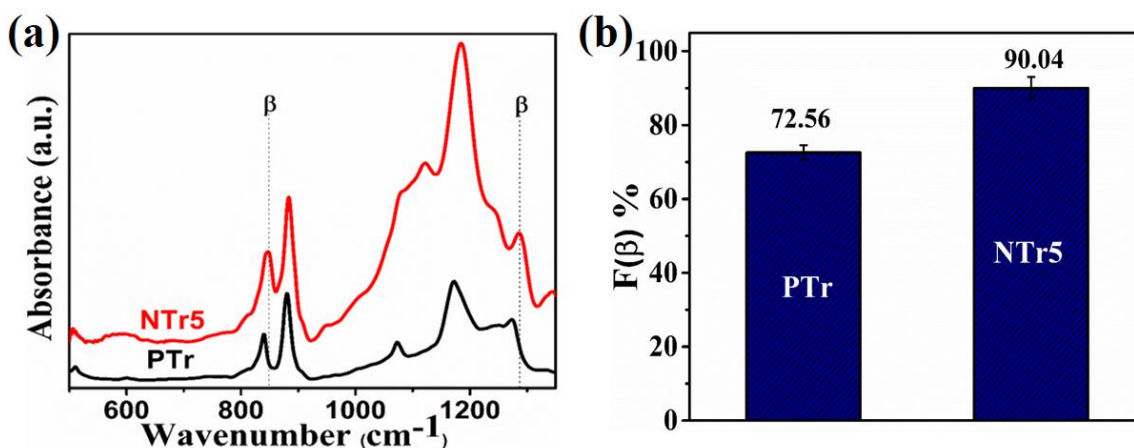


Figure 4.7. (a) FTIR analysis of PTr and NTr5, (b) Comparison of β -phase content of PTr and NTr5

bands at 840 cm⁻¹ and 1275 cm⁻¹, which is indicative of the formation of well-defined polar crystalline β -crystals [9]. No significant band at 1234 cm⁻¹ was observed for NTr5, concluding the transformation into TTTT form and no γ crystallization took place. A small band at 840 cm⁻¹ has been observed in pure PVDF-TrFE, which infers that there must be a trivial number of β -crystals in PTr. The absorption peaks at 763 cm⁻¹ and 978 cm⁻¹ can be attributed to in-plane bending motions, specifically indicative of the TGTG conformation characteristic of the alpha-phase [21]. The peak at 840 cm⁻¹ corresponds to the β -phase of PVDF-TrFE, which is due to CH₂ rocking, CF₂ stretching and skeletal C-C stretching, with this band being highly responsive to dipole orientation under an electric field [22]. Moreover, the 1275 cm⁻¹ peak represented C-C symmetric stretching, CCC scissoring vibration, and CF₂ asymmetric stretching vibration in the beta-phase [23]. Notably, the ferroelectric crystallinity was greatly influenced by the C-F asymmetric stretch [24]. Therefore, it can be confirmed that the addition of Ni(OH)₂ nanoplates to the pure polymer has led to the huge enhancement of the electroactive β -crystals in NTr5, primarily due to the nucleation of the nanoplates with the PVDF-TrFE matrix and effective ion-dipole interaction in the composite. Hence, the spectroscopy analysis of the electroactive β -phase nucleation is in agreement with the diffractogram analysis of the films. More details about the FTIR spectra of PTr and NTr5 have been included in appendix 2, figure A2.1. To measure the amount of electroactive β -polymorph present in the films, a quantitative analysis of the FTIR spectra was also carried out. The fraction of electroactive β -phase content $\{F(\beta)\}$ was calculated from the FTIR spectra using the Lambert–Beer law. This law was stated as [9]:

$$F(\beta) = \frac{A_{\beta}}{\left(\frac{K_{\beta}}{K_{\alpha}}\right)A_{\alpha} + A_{\beta}} \times 100\% \quad (6)$$

Where A_{α} is the absorbance at the band 764 cm^{-1} (for CF_2 and skeletal bending), A_{β} is the absorbance at the band 840 cm^{-1} (for CH_2 rocking, CF_2 stretching and skeletal C-C stretching). The value of K_{β} is $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and the value of K_{α} is $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, which are the absorption coefficients at the bands 840 cm^{-1} and 764 cm^{-1} respectively. From figure 4.7(b) it can be seen that PTr has a $F(\beta)$ value of 72.56% and NTr5 has a highly enhanced $F(\beta)$ value of 90.04%. To show the effect of poling on the composite, FTIR analysis

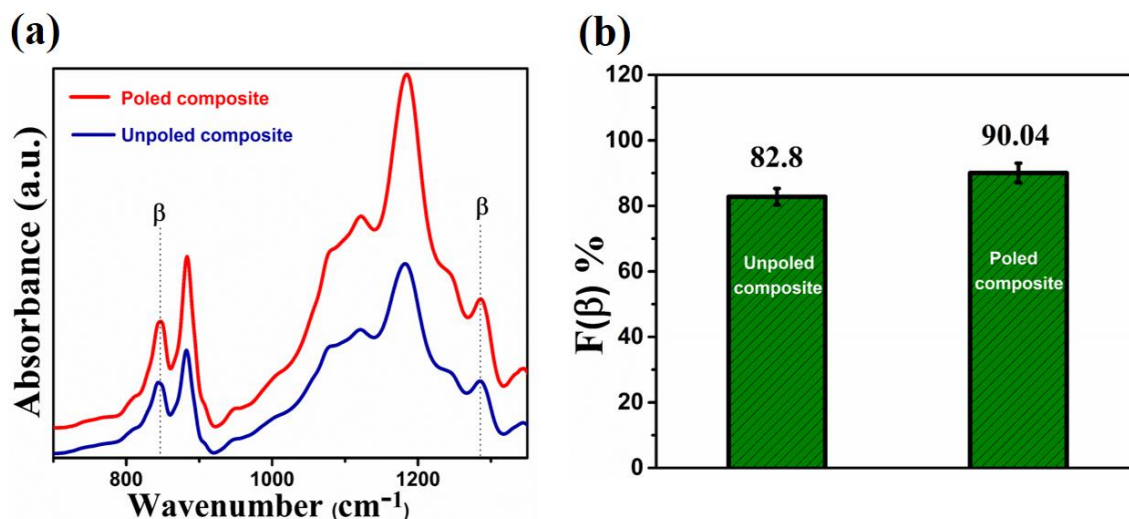


Figure 4.8. (a) FTIR spectra and (b) β phase content of the unpoled and poled composites

of an unpoled composite has been done which demonstrated a $F(\beta)$ value of 82.8%, are represented in figure 4.8(a), which is much lower than $F(\beta)$ value of poled NTr5. As can be seen from figure 4.8(b), the β phase content of the composite increased from 82.8% to 90.4% for unpoled and poled composite films respectively.

4.5.4. Thermo-gravimetric analysis of β -Ni(OH) $_2$ nanoplates, PTr and NTr5

To analyze the thermal properties of β -Ni(OH) $_2$ nanoplates TGA (Thermogravimetric Analysis) was conducted, where thermographs revealed a three-step degradation process for the nanoparticles. To verify the mass percentage loading of the nanoparticles in the composite film NTr5, the thermal analysis (TGA) of the composite was done, which almost matches with the actual mass% loading done. Figure 4.9(a) shows the TGA thermographs of Ni(OH) $_2$ nanoparticles spanning from 25 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$. The first degradation step occurs

around 100 °C, primarily attributed to the elimination of adsorbed water from the sample. The second phase of mass degradation falls within the temperature range of 286 °C to 322 °C, signifying the initiation of the thermal decomposition process of $\text{Ni}(\text{OH})_2$ into NiO .

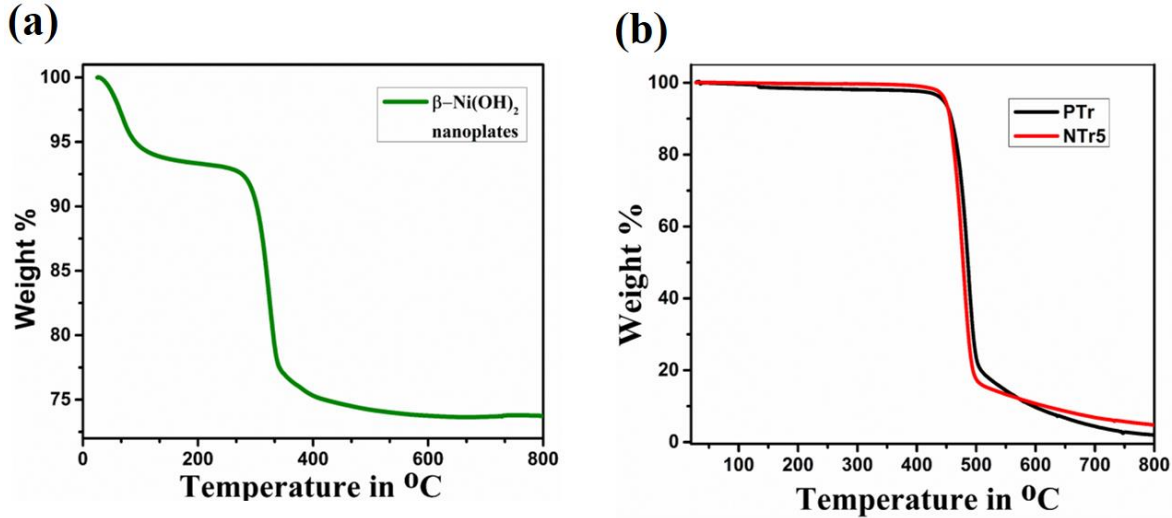


Figure 4.9. (a) TGA curve of $\beta\text{-Ni}(\text{OH})_2$ nanoplates, (b) TGA curve of PTr and NTr5

The thermal stability and the mass percentage of nanoparticles in the nanocomposite were as well assessed through TGA. Figure 4.9(b) illustrates the TGA results, indicating that NTr5 and PTr exhibit similar one-step degradation pattern. This suggests that the inclusion of $\text{Ni}(\text{OH})_2$ did not significantly alter the thermal stability of PVDF-TrFE and both films initiated degradation at around 449°C. To estimate the approximate mass content of $\beta\text{-Ni}(\text{OH})_2$ nanoplates within the NTr5 composite, the following equation was employed [25]:

$$\omega_{\text{np}} = C_{\text{PTr}} - C_{\text{NTr5}} \quad (8)$$

Where C_{PTr} represents the weight loss percentage of pure PVDF-TrFE film, C_{NTr5} represents the weight loss percentage of $\beta\text{-Ni}(\text{OH})_2$ nanoplates incorporated nanocomposite and ω_{np} represents the content of $\beta\text{-Ni}(\text{OH})_2$ nanoplates in NTr5. As can be seen in figure 4.9(b), C_{PTr} and C_{NTr5} are about 98.76% and 94.14%, respectively. Therefore, the calculated mass content of $\beta\text{-Ni}(\text{OH})_2$ nanoplates within the NTr5 composite (ω_{np}) is about 4.62 %. This mass content obtained from TGA analysis is less than the actual mass loading percentage (5 mass%) because some mass has been lost due to the conversion of $\text{Ni}(\text{OH})_2$ to NiO , as already seen from figure 4.9(a).

4.6. Surface investigation, piezoelectric and ferroelectric study of NTr5

4.6.1. Surface roughness analysis by AFM analysis

AFM analysis was done to analyze the surface roughness and topography of the composite thin film NTr5, the image of which is shown in figure 4.10(a). As can be seen from the image, the high surface roughness is due to the incorporation of $\text{Ni}(\text{OH})_2$ nanoplates in the PVDF-TrFE matrix. Furthermore, the composite thin film exhibits nanoparticles that are

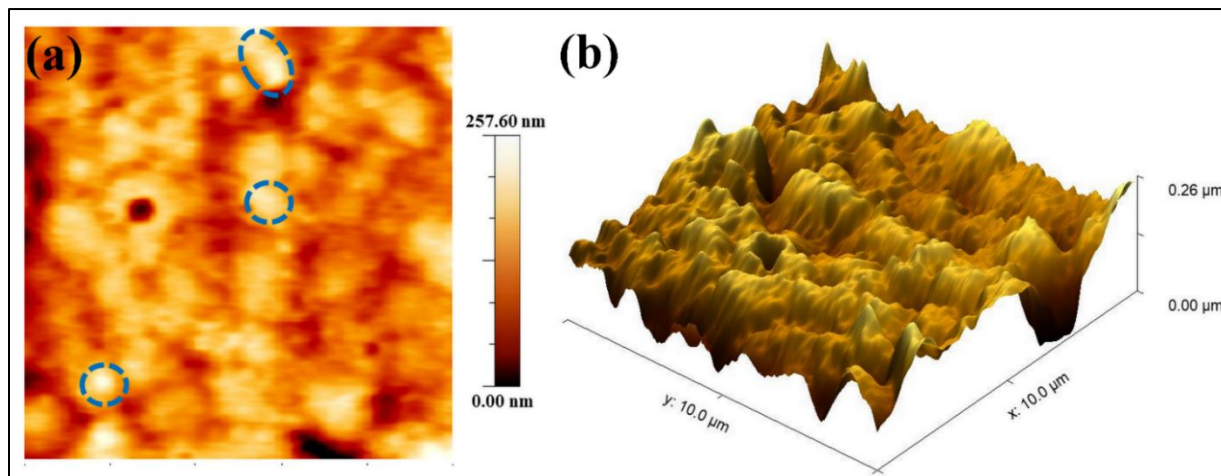


Figure 4.10. (a) AFM topography image of NTr5 composite film, (b) 3D AFM image of NTr5 to analyze the surface roughness

evenly dispersed throughout its surface, indicating a well-distributed arrangement. Additionally, the film demonstrated a smaller spherulite size, suggesting the potential nucleation of an electroactive phase. Upon closer examination of the AFM topography, the presence of crystalline ellipsoidal lamellas [26] was clearly observed in the NTr5 film, which indicates the formation of an electroactive phase. Gwyddion 2.63 software was utilized to obtain three-dimensional AFM image of the film surface as illustrated in figure 4.10(b). The average height deviation from the mean plane (R_a) and the root mean square of the average height deviation from the mean plane (R_q) for the composite thin film was also obtained. The analysis revealed that the value of R_a for NTr5 was approximately 31.28 nm, while the R_q value was approximately 38.47 nm. Using the mentioned software, the average roughness of the NTr5 film was estimated to be approximately 158.117 nm and the overall thickness of the polymer composite was approximately 260 nm. The thickness of the composite has also been visually depicted on the scale of figure 4.10(a) and also corresponds to the z-axis of

figure 4.10(b). These observations serve as a strong indication of the formation of an electroactive phase within the film. As the surface roughness increases, the effective area available for charge accumulation within the composite matrix also increases. Consequently, this results in a higher surface charge density of the NTr5 film when it comes into contact with other materials. Therefore, it is evident that the $\text{Ni}(\text{OH})_2/\text{PVDF-TrFE}$ nanocomposite film with its higher surface roughness, exhibited greater piezoelectric effect compared to the bare PVDF-TrFE film. This is due to the larger contact area available for charge generation and accumulation on the composite's surface.

4.6.2. Analysis of piezoelectric and ferroelectric properties (PFM analysis)

Piezo force microscopy analysis of the composite thin film NTr5 was performed for the confirmation of the enhancement of localized piezoelectric and ferroelectric properties when an external electric field was applied. The PFM technique allowed us to investigate and analyze the film's piezoelectric and ferroelectric response in terms of both amplitude and phase. In this switching spectroscopy analysis, an external voltage was applied to the composite, across its thickness with the help of a conducting tip. Thenceforth, the local deformation of the composite was measured, and the piezoelectric butterfly loop and the ferroelectric hysteresis response were recorded. A dual signal of DC bias voltage spanning from -7 V to +7 V was applied across the thickness of the composite. This applied bias voltage caused the film to undergo strain, which was then detected by a cantilever attached to the PFM tip. A detailed description about the DC bias voltage applied has been included in the

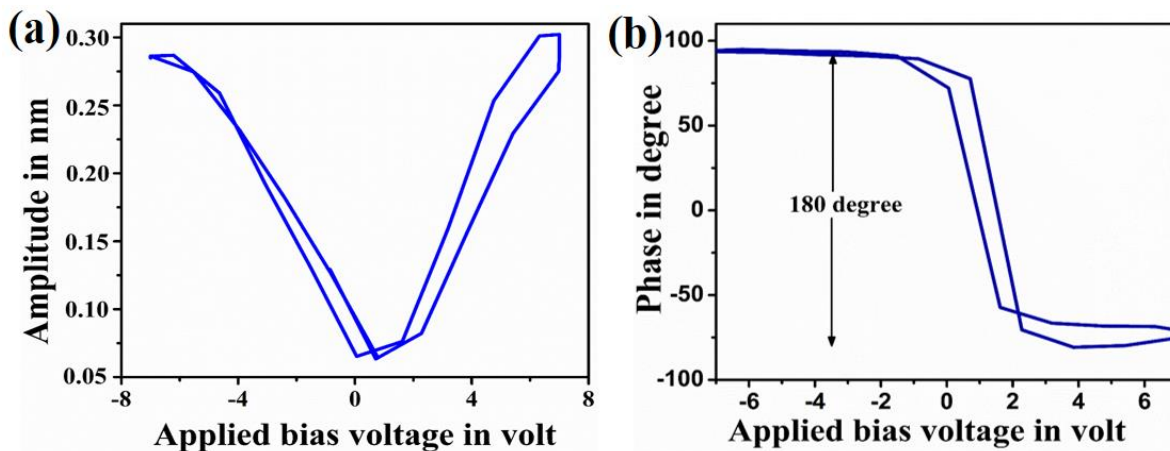


Figure 4.11. (a) Piezoelectric displacement response of NTr5 for bias voltage from -7 V to +7 V via PFM analysis, (b) PFM phase change hysteresis of NTr5 showing 180° of phase reversal

appendix 2 file. In figure 4.11(a), the impact of applying the DC bias voltage on the strain amplitude can be observed. Increasing the positive DC bias voltage led to a crystal lattice expansion, resulting in a maximum deformation of 0.3 nm at approximately 7 V, as can be seen from the graph. Subsequently, as the applied bias voltage was reduced back to 0 V, the lattice started to contract and returned to its initial state. Likewise, when a negative DC bias was applied, the crystal lattice underwent expansion and contraction, forming a comprehensive piezoelectric butterfly loop during the entire process. This butterfly loop established the presence of the converse piezoelectric effect in the composite thin film NTr5 [26]. Since this plot represented the relationship between the amplitude of deformation formed in the composite and the applied bias voltage, by examining the slope of the linear region of the loop, the piezoelectric coefficient d_{33} could be determined [42]. The obtained value of d_{33} from the graph was 50.22 pm/V. A comparative study for maximum piezoelectric

Table 4.3. Comparative study for maximum d_{33} of NTr5 with previously reported polymer composites

Title of the article	Polymer composite	Maximum d_{33} value
Piezoelectric effect and electroactive phase nucleation in self-standing films of unpoled PVDF nanocomposite films [27]	Hexahydrate metal salts/PVDF nanocomposite film	13.49 pm/V
PFM characterization of PVDF nanocomposite films with enhanced piezoelectric response [28]	Modified graphene nanoplatelets and zinc-oxide nanorods/ PVDF nanocomposite films	7.5 pm/V,
Evaluation of piezoelectric behavior and biocompatibility of poly(vinylidene fluoride) ultrafine fibers with incorporated talc nanosheets [29]	Talc nanosheets (TNS)/PVDF composites	43.3 pm/V
Electrospun poly(vinylidene fluoride-trifluoroethylene) based flexible magnetoelectric nanofibers [30]	Nd _{0.05} Bi _{0.95} Fe _{0.95} Co _{0.05} O ₃ /PVFF-TrFE composite	35.0 pm/V
Printed recyclable and self-poled polymer piezoelectric generators through single-walled carbon nanotube templating [31]	Single-walled carbon nanotubes/ PVDF-TrFE composite	12.0 pm/V
Local mechanical and electromechanical properties of the P(VDF-TrFE)-graphene oxide thin films [32]	PVDF-TrFE-graphene oxide thin films	38.0 pm/V
Present work	β-Ni(OH)₂/PVDF-TrFE composite	50.22 pm/V

coefficient (d_{33}) of the fabricated composite NTr5 with the previously reported polymer composites has been shown in table 4.3.

By analyzing the hysteresis loop [33] in figure 4.11(b), it can be said that NTr5 exhibited a complete ferroelectric hysteresis loop in terms of phase, with approximately 180° of phase reversal. This behavior can be attributed to the orientation of dipoles induced by the application of the DC bias voltage. This phase transition arose from the polarization reversal in the composite due to swapping of the local electric domains from an antiparallel configuration to a parallel one or vice versa. This swapping is well consistent with the electrical domain of the tip of PFM, when the bias voltage was applied. Importantly, the incorporation of $\text{Ni}(\text{OH})_2$ into the PVDF-TrFE matrix led to a nanoscale enhancement of piezoelectric and ferroelectric properties.

4.7. Theoretical analysis of the working of P-UST

From the knowledge of electrodynamics, the working principle of the composite thin film NTr5 can be analyzed, which is dielectric in nature. It is known that the displacement electric field D for any dielectric medium that participates in the dipole formation can be expressed as:

$$\mathbf{D}(\mathbf{r}, t) = \epsilon_0 \mathbf{E}(\mathbf{r}, t) + \mathbf{P}(\mathbf{r}, t) \quad (9)$$

where, ϵ_0 is permittivity of free space, E is the electric field and P is the polarization. Considering only the free charges in the composite film, Maxwell's equation in matter can be expressed as [34]:

$$\nabla \times \vec{H} = \vec{J}_f + \frac{\partial \vec{D}}{\partial t} \quad (\text{Ampere's circuital law with Maxwell's addition}) \quad (10)$$

Where, $\vec{H}$ is the magnetic field, and $\vec{J}_f$ represents the current density due to the flow of free electron. For the case of a linear isotropic medium, $\frac{\partial \vec{D}}{\partial t}$ can be represented as:

$$\frac{\partial \vec{D}}{\partial t} = \epsilon_0 \frac{\partial \vec{E}}{\partial t} + \frac{\partial \vec{P}}{\partial t} \quad (11)$$

Herein, $\frac{\partial \vec{P}}{\partial t}$ is associated with the enhancement of the piezoelectric effect by effectively increasing the value of P . On the application of no external electric field E , the increment of surface charge leads to better polarization. When the polarization works in the z direction, it can be written [9]:

$$\frac{\partial P_z}{\partial t} = \frac{\partial \sigma_p(z)}{\partial t} \quad (12)$$

where, $\sigma_p(z)$ represents surface charge density of the piezoelectric material. From the above equation, it can be articulated that the surface charge density is directly proportional to the change of piezoelectric polarization of the piezoelectric material. Therefore, the noteworthy small size of Ni(OH)_2 nanoplates has led to the increment of the polarization and surface charge density. Now to understand the relation between the increase in surface charge or polarization and the performance of UST, the electromechanical coupling coefficient k needs to be analysed, which indicates the effectiveness with which a piezoelectric material converts electrical energy into mechanical vibrations and vice versa. Electromechanical coupling coefficient k can be represented as [35]:

$$k^2 = \frac{\text{stored mechanical energy}}{\text{input mechanical energy}} = e_{33}^2 / (c_{33}^D \epsilon_{33}^S) \quad (13)$$

Where, e_{33} is the piezoelectric stress constant, c_{33}^D is the elastic constant, ϵ^S is the clamped dielectric permittivity. Now, the polarization term is related to the piezoelectric stress constant e_{33} by the relation [36]:

$$P = \sum e_{ij} \epsilon_j \quad (14)$$

Where, ϵ represents the strain tensor. Now, the resonant frequency and the acoustic impedance of a material are primarily determined by the inherent property of the material, namely the speed of sound within it. An appropriate match in acoustic impedance between the ultrasound transducer and the medium through which the ultrasound waves propagate is of paramount importance for optimizing transducer's performance. Relevant parameters for achieving this impedance match are outlined below [35]:

$$\omega_0 = 2\pi c_p \quad (15)$$

$$Z_a = \rho c_p \quad (16)$$

Where, ω_0 represents the resonant frequency, c_p represents the speed of sound inside the piezoelectric material, Z_a represents the acoustic impedance and ρ represents the density. In order to optimize power transmission, it is crucial that the input electrical impedance of the ultrasound transducer, specifically at the designated frequency is real and that its input resistance aligns with the electrical impedance of the power source. The electromechanical coupling coefficient 'k' serves as a crucial metric for evaluating how efficiently a piezoelectric

material can convert electrical energy into mechanical energy and vice versa. In the context of transducer design, a higher k value is much desirable as it signifies superior energy conversion capabilities and results in a broader bandwidth, thereby enhancing overall performance of the ultrasound transducer. The efficiency of a transducer represents the effectiveness of the device to convert the mechanical energy into electrical signals. The efficiency η can be mathematically represented as:

$$\eta = P_{\text{out}} / P_{\text{in}} \quad (17)$$

Where, P_{out} represents the electrical output power and the mechanical input power is represented by P_{in} . From this equation it can be inferred that a material with a superior piezoelectric effect (high piezoelectric coefficient) leads to a higher output electrical power, yielding superior transducer efficiency. This in turn increases the sensitivity of the ultrasound transducer as well, since the higher piezoelectric effect, which is characterized by a high value of piezoelectric coefficient, increases the change in electric polarization for a particular change in mechanical strain.

The signal-to-noise ratio (SNR) measures the fraction of strength of the anticipated signal to the unwanted background noise. On the increment of output voltage, the desired signal turns out to be more prominent in comparison to the noise. This leads to an enhancement of the SNR, allowing better detection and analysis of the preferred signals from the UST. The presence of Ni(OH)_2 nanoparticles helps in mitigating the electrical and thermal noises, which results in an improved SNR ratio. This feature is very noteworthy in ultrasound imaging applications where there is a demand for high-quality and low-noise signals, crucial for accurate medical diagnosis.

4.8. Output performance of P-UST (Pulse-echo test)

Herein, an intrinsic bidirectional ultrasound signal transmission performance has been demonstrated by utilizing a single transducer, to both generate and receive ultrasound pulse signals. The received pulse signals provided evidence of the successful transmission process and validated the transducer's capability to effectively capture back the ultrasound signals. Using the setup depicted in figure 4.3, where the transducer P-UST was operated over an aluminium block with a liberal layer of ultrasound gel on the block, a pulse-echo test was conducted to assess the output performance of the UST. Figure 4.12 demonstrates the

pulse-echo signal which was obtained by P-UST. The amplitude of the voltage signal of the fabricated transducer surpasses that of any commercial ultrasound transducer available in the market, showcasing exceptional performance. Notably, it achieved an impressive peak-to-peak output voltage of 5.19 V, as can be seen from figure 4.12(a). To verify the effect of nanoparticles in the polymer matrix, output data was also acquired from a UST employing pure polymeric film. The data regarding this have been included in the appendix 2 file, in figure A2.2. The output voltage magnitude of P-UST exceeds that of any previously reported ultrasound transducer in the field. To optimize the echo amplitude, the tilt angle between the transducer and the aluminium target block was adjusted accordingly.

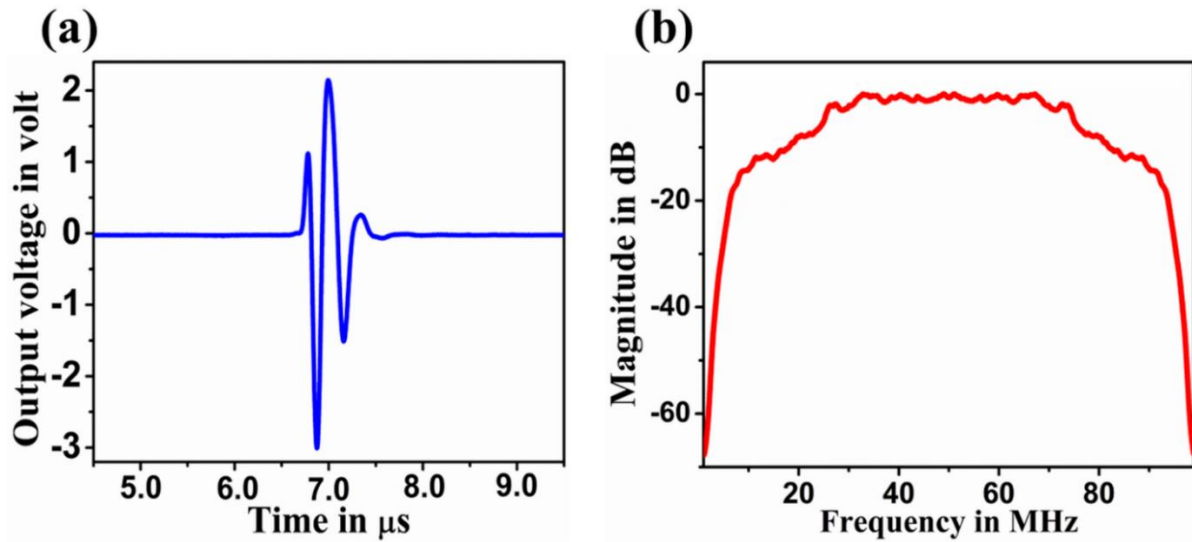


Figure 4.12. (a) Experimental pulse echo signal received by P-UST, (b) Fast Fourier Transformed output of the voltage pulse echo signal

Subsequently, a comparison between the time-domain waveform of the output voltage and its corresponding spectrum in the frequency domain was conducted. By subjecting the voltage versus time output signal to a Fast Fourier Transform (FFT) [13], the acquired voltage data was transformed into the frequency domain, obtaining the amplitude in decibels, plotted against frequency in MHz as shown in figure 4.12(b). To obtain the output signal in amplitude vs frequency format, the Fourier Transform formula was utilized:

$$\text{Amplitude (dB)} = 20 \times \log_{10} (|X(f)|) \quad (16)$$

where $|X(f)|$ represents the Fourier Transform of the magnitude of the signal in the frequency domain. When we take the absolute value of the Fourier Transform and apply the

logarithmic transformation, the amplitude in decibels can be expressed relative to the reference level. The fabricated transducer, incorporated with β -nickel hydroxide and PVDF-TrFE, consistently demonstrated robust and prominent signal strength within the frequency range of 24.41 MHz to 75.63 MHz. The detection performance of P-UST exhibited an ultra-broad bandwidth with a central frequency of 50.01 MHz. Upon analysis of the magnitude vs frequency graph, it was determined that the ultrasound wave exhibited a -6 dB bandwidth of 51.22 MHz. Remarkably, the measured -6 dB percentage bandwidth was significantly wider, approximately of 102.4%. This value of wide bandwidth suggested that the output signal could cover a broader frequency range, along with its noteworthy high central frequency emphasizes the transducer's competence to capture a widespread spectrum of ultrasound frequencies efficiently. The exceptionally high central frequency achieved by P-UST is expected to result in significantly enhanced resolution of ultrasound images compared to those obtained from commercially available ultrasound transducers. A comparative study has been performed in table 4.4, showing output performances of P-UST, with previously reported piezoelectric composite based ultrasound transducers.

Table 4.4. Comparative study of the output performance of P-UST, with previously reported piezoelectric composite based USTs

Title of the article	Piezoelectric composite used	Maximum output voltage of UST
3D printing of piezoelectric element for energy focusing and ultrasonic sensing [37]	Piezoelectric-composite slurry with BaTiO ₃ nanoparticles	0.301V
A KNN composite-based piezoelectric helix for ultrasonic transcutaneous energy harvesting [38]	KNN composite-based piezoelectric helix	1.70 V
KNNS-BNZH lead-free 1–3 piezoelectric composite for ultrasonic and photoacoustic imaging [39]	(KNNS-BNZH)/epoxy 1–3 composite	0.78 V
Flexible piezoelectric micro ultrasonic transducer array integrated on various flexible substrates [40]	PVDF based composite	75 mVpp
High-performance potassium sodium niobate piezoceramics for ultrasonic transducer [41]	KNN-BNZ-AS-Fe/epoxy 1–3 composite	0.80 V
Our present work	β-Ni(OH)₂/PVDF-TrFE composite	5.19 V

Upon implementation, P-UST has the potential to detect abnormalities in living tissues on the basis of the density disparities between normal and abnormal tissues. By exploiting this distinction, the transducer can generate high-resolution images that facilitate accurate identification and diagnosis of abnormalities in tissues. Thus, the improved resolution resulting from the ultra-high central frequency, opens up new possibilities for precise and reliable diagnosis, monitoring and treatment of medical conditions using the transducer's high-quality imaging capabilities. Furthermore, the output voltage data obtained from the novel P-UST significantly surpasses the voltage values achieved by any other piezoelectric film-based ultrasound transducer in previous studies within this field. This remarkable distinction sets P-UST apart as an innovative advancement in the realm of ultrasound transducers in terms of voltage generation too.

4.9. Summary

In summary, the main focus was to investigate how β -Ni(OH)₂ nanoplates affected the enhancement of the electroactive β -phase in PVDF-TrFE within the fabricated composite thin film. Additionally, this work introduces a novel approach by integrating highly piezoelectric transition metal hydroxide into the polymer matrix for the development of transducer that demonstrates exceptional performance. The fabrication process of the β -Ni(OH)₂ nanoplates-modified composite involved the spin coating method. Notably, the achieved maximum crystallization of the β -phase in the composite was 90.04%, which was very high. The significant increase in crystallization, rising from a $F(\beta)$ value of 72.56% in pure PVDF-TrFE to the aforementioned value for the composite, can be attributed to the favorable electrostatic ion-dipole interaction and strong surface polarization within the polymer composite structure. To investigate and analyze the piezoelectric and ferroelectric response of the composite thin film NTr5, PFM analysis was also conducted which yielded a d_{33} value of 50.22 pm/V. The effect of piezoelectric property on the output of the UST has been well explained theoretically with the help of Maxwell's equations, which is in accordance with the experimental data. Herein, the bidirectional transmission of ultrasound signals was evaluated by utilizing P-UST, which was capable of both generating and receiving pulse signals. A remarkable peak-to-peak output voltage of 5.19 V was achieved. The FFT graph revealed a significant frequency range from 24.41 to 75.63 MHz. P-UST showed an

exceptionally wide -6 dB bandwidth of 51.22 MHz (102.4%) centered at 50.01 MHz. Hence, it can be concluded that the designed ultrasound transducer which is lead-free, non-toxic and cost-effective, holds great potential for the utilization across a range of construction and biomedical applications. Given its high output voltage, ultra-broad bandwidth and high central frequency, the designed transducer is a good option for medical diagnostics, offering potential for significantly improved ultrasound image resolution. This noteworthy feature paves the way for new opportunities in accurate diagnosis, monitoring and treatment of serious medical conditions.

4.10. References

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Chapter 5

Micro-Motified and Droplet-Driven Triboelectric Sensor for Real-Time Acid Rain Monitoring



5.1. Introduction

Amid the global energy crisis, renewable sources like solar, tidal and liquid flow energy have gained attention for their potential to reduce carbon emissions and support carbon neutrality [1]. Rainfall is a significant supply of fresh water and it is highly advantageous to convert the kinetic energy of randomly falling raindrops into electrical energy before they contact the ground. Triboelectric nanogenerators (TENGs) have proved to be a viable energy technology for harvesting erratic, randomly falling and low-frequency water drop energies. Droplet based TENGs [2] emerge as highly effective technology for renewable energy conversion since it can function in situations involving a limited water supply. TENG operates on the principles of triboelectric effect [3] and electrostatic induction to transform mechanical energy into electrical energy. When two materials with different triboelectric polarities come into periodic contact and separation, they create electric potential differences. This drives the flow of electrons through an external load, enabling the generation of continuous electrical output. In the context of TENG, output performance is significantly influenced by the surface roughness of the dielectric layer [4]. The most practical method to enhance the sensitivity of the TENG is by optimizing the effective contact area between the triboelectric layers. A textured or rough triboelectric surface containing micro or nanostructures exhibits a greater specific surface area, leading to a substantial enhancement in charge transfer density. Diverse micro or nano structure designing technologies [5, 6] including lithographic technology, self-assembled layers, chemical deposition and template dissolution method have been employed in numerous studies to enhance surface roughness. However, these conventional fabrication methods are intricate and expensive. This suggests a need for a simple structural design that employs a versatile and cost-effective fabrication method.

By taking inspiration from various architectures in nature, bio-inspired TENG [7, 8] designs that mimic biological structures have been widely applicable since they are more efficient and surface patterns are easily tunable depending on the intended output results. Drawing inspiration from the petal surface structure of petunia flower (*Petunia x atkinsiana*), a flexible PDMS composite membrane (tribonegative layer) was developed with well-defined microstructures by imitating petunia petal surface. This replication process was achieved through the template sacrifice method. Among the recent works on bio inspired templates used, Zhu et al. developed a triboelectric electronic skin for

sensitive tactile sensing which was inspired by the microstructures of a rose petal [7]. Wang et al. fabricated a low cost bionic triboelectric nanogenerator for health monitoring inspired by the microstructures on lotus leaf [8]. A few more research works have been done on bio inspired template based triboelectric nanogenerators but a very few works have been done using metal chalcogenide nanoparticles (NPs). Silver sulfide (Ag_2S), a metal chalcogenide, exhibits intriguing characteristics including a monoclinic crystal structure, a relatively narrow band gap [9] ranging from 0.9 eV to 1.05 eV, a considerable absorption coefficient, good optical properties and noteworthy chemical stability. Since, Ag_2S has a high chemical stability and comparatively narrow band gap, it facilitates effective charge transfer and charge separation during triboelectric operations.

Liquid-solid interacting triboelectric nanogenerators [11] (L-S TENGs) are attracting interest for their practical applications, as they harness energy through the interaction between liquid droplets and solid surfaces [6]. In order to further increase the hydrophobicity of the polymeric composite membrane, PTFE was added to it due to its extremely hydrophobic nature and its remarkable resistance to both acid and alkali solutions [12]. In this study, a highly hydrophobic, compact single electrode triboelectric nanogenerator (b-STNG) comprised of the PDMS based triboelectric layer (b-APC) with bio-mimetic boat shaped micro motifs was designed, that can harvest mechanical energy from water droplets as well as from basic finger touch. To verify that b-STNG can harness electrical energy from raindrops, droplet energy harvesting abilities of this hydrophobic TENG with varying parameters was examined, also showing notable sensitivity to both the pH and ion concentration of liquid. The potential of L-S TENGs for pH measurement of aqueous solutions have been demonstrated by a number of earlier research works [35]. Microstructures exhibit synergistic enhancement of charge transfer, hydrophobicity and contact-separation between triboelectric layer and water drop with high contact angle. Owing to this, the raindrop-powered TENG was implemented as a pH sensor to detect acid rain. Since acid rain can lead to skin and respiratory illnesses, early detection of acid rain can be beneficial for public health and well-being. Numerous architectural structures made of calcareous materials like limestone and marbles are also greatly affected by acid precipitation. The growth and productivity of plants are also directly impacted by acid rain to a large extent. Hence, b-STNG was able to accurately detect pH value of rainwater in real-time with the help of coloured LED indicator system, decreasing ecological impact by enabling prompt protection against acid rain in the environment.

5.2. Experimental section

5.2.1. Materials

Silver nitrate (AgNO_3) (99.9% Sigma–Aldrich), sodium sulfide (Na_2S) (98% Sigma Aldrich), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (99% SRL chemical), ammonia solution (NH_3) (25% indiaMART), polydimethylsiloxane (PDMS) gel (Sylgard 184, Dow Corning), Polyvinyl alcohol (PVA) (Loba Chemie), polytetrafluoroethylene (PTFE) (Sigma–Aldrich) and de-ionized (DI) water were used. The reagents utilized in the experiments were of analytical grade and of highest purity and the chemicals were employed in their as-received state without undergoing additional purification.

5.2.2. Synthesis of silver sulfide nanoplates

The synthesis of silver sulfide nanoplates was carried out using a simple hydrothermal method. Firstly, 2.5 mmol of AgNO_3 was combined with 50 mL of DI water and was subjected to vigorous stirring on a magnetic stirrer for 2 hours. Simultaneously, in a second solution, 10 mL of ethylene glycol was added to 1.25 mmol of Na_2S and stirred for 1 hour. The second solution was then combined with the first solution, undergoing continuous stirring and heating at 70°C for 2 hours. 10 mL of ammonia solution was gradually added to it drop-wise while maintaining constant stirring and heating. The prepared solution was carefully poured into 80 mL teflon-lined stainless steel autoclave setup, filling it up to 80% of its volume. This setup was placed in a clean, dry hot air oven and was heated at 160°C for 12 hours. The resulting precipitate exhibited a blackish colour. After the precipitate cooled to room temperature, it was subjected to centrifugation and thorough washing with double-distilled water multiple times to adjust the pH to 7. The collected precipitate was then dried at 60°C for 48 hours and was ground into fine black-coloured powder, yielding silver sulfide nanoplates.

5.2.3. Fabrication of micro-structured PVA mould based on petunia petal (Negative replica)

The initial step involved cleaning a fresh petunia flower with deionized water for a few times, followed by cutting the petal into rectangular shape. This was dried using air blow and securely fixed onto a glass slide. A 15 wt% polyvinyl alcohol (PVA) solution was prepared by dissolving PVA in deionized (DI) water at 80°C , by continuously stirring it for a duration of 5 hours. Then, the PVA polymer solution underwent a 20-minute ultrasonic

treatment to effectively eliminate any bubbles present. The prepared PVA solution was then carefully poured on the flat rectangular flower petal mould using coating method. The mould with the PVA solution underwent a 2-hour heating process at a temperature of 70°C. Following this, the petunia petal was detached from the dried PVA using adhesive tape, providing the micro-patterned negative PVA template.

5.2.4 Fabrication of Ag₂S incorporated, micro-structured PDMS composite (Positive replica)

1 g of PDMS (Sylgard 184, Dow Corning, ratio of 10:1) was thoroughly mixed and was made bubble-free by keeping the mixture under vacuum for 10 minutes. To it, 0.5 mass% of Ag₂S NPs were added and mixed thoroughly for 15 minutes, to obtain a homogeneous mixture. The micro patterned negative PVA template was then coated with this mixture and pre-cured for 35 minutes at 30°C. Next, PTFE particles with an amount of 1 mg/cm² were coated onto the mixture by mechanical sieving and the composite was

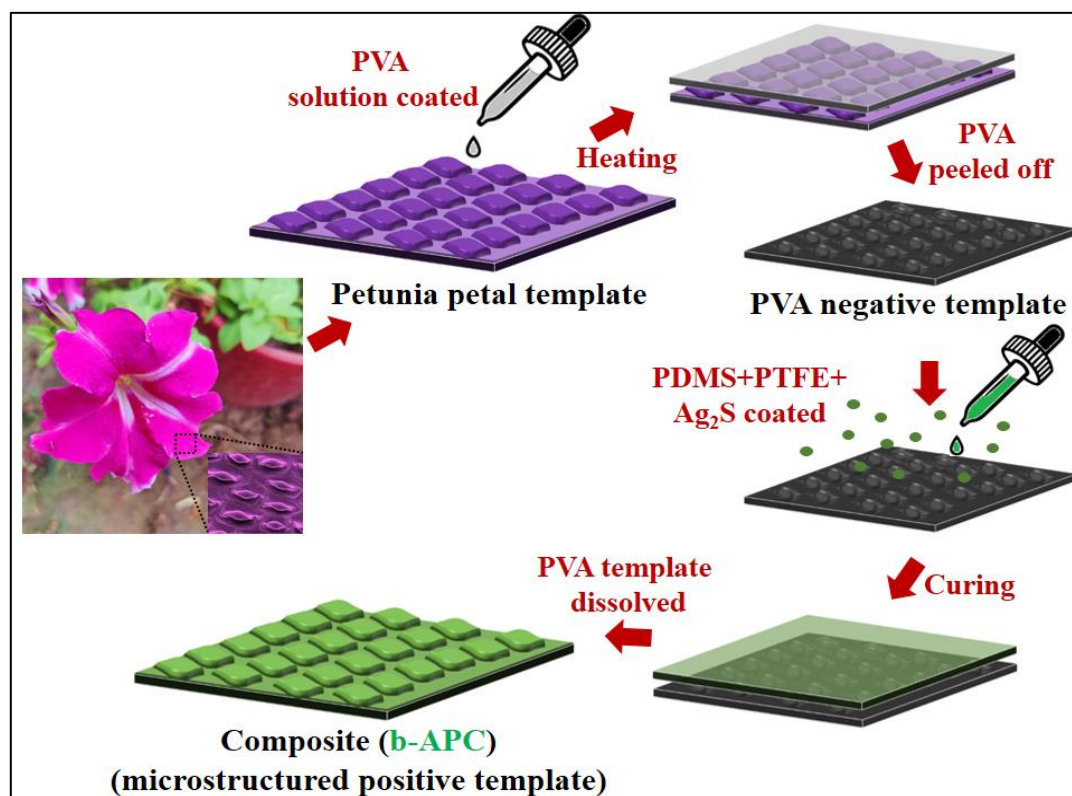


Figure 5.1. Schematic diagram of b-APC fabrication via template sacrifice technique

cured at room temperature. Subsequently, it underwent a 3 hour heating process in a 80°C water bath, leading to the complete dissolution of the PVA template. This resulted in the formation of a bio-mimetic PDMS composite membrane incorporated with Ag₂S

nanoplates and PTFE (named b-APC), exhibiting micro motifs identical to those of the petunia flower petal surface, as can be seen in figure 5.1. The embedded PTFE particles bonded on to the triboelectric layer resulted in a stretchable and highly hydrophobic triboelectric layer of the TENG. Figure 5.2(a) represents the digital photograph of the triboelectric layer b-APC and figure 5.2(b) shows how highly flexible the composite is.

5.2.5 Designing of the bio-inspired, single electrode triboelectric nanogenerator (b-STNG)

Firstly, for the preparation of a stretchable substrate, two components of Ecoflex 00–30, namely 0.5 gram each of Ecoflex A and Ecoflex B were thoroughly mixed in a petri dish. Then this mixture was uniformly spread onto a rectangular plate and allowed to cure at room temperature. After the curing process, the substrate was carefully peeled off, yielding a thin and flexible substrate. A rectangular piece of carbon tape was affixed to the substrate, which acted as the electrode. Along with this, a small rectangular portion with the dimension of 3.6 cm x 2.6 cm x 0.08 cm was cut from b-APC and was affixed on the Ecoflex substrate. A connecting wire was attached between b-APC and the electrode

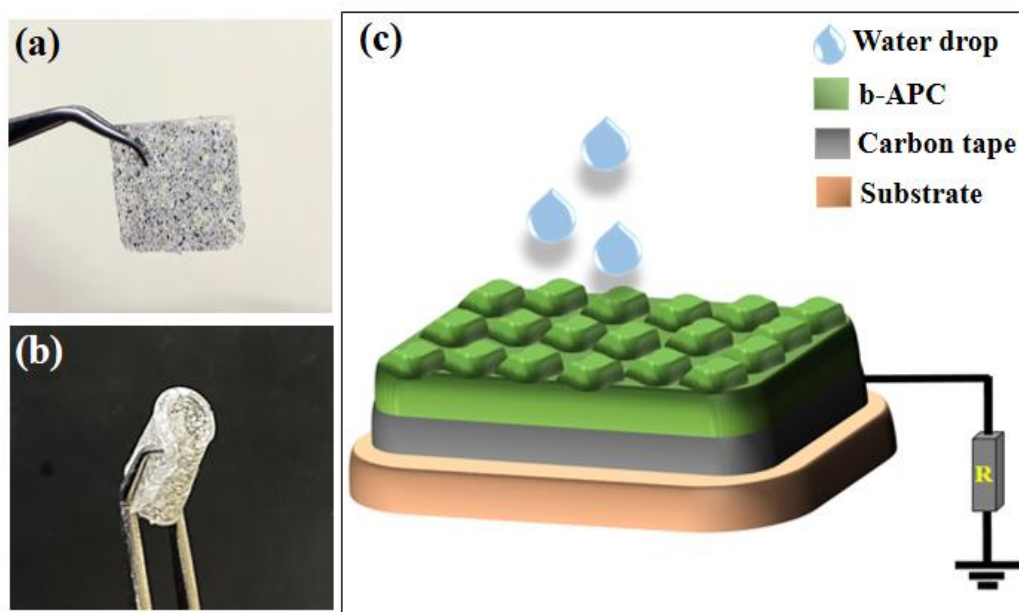


Figure 5.2. (a) Digital photograph of b-APC, (b) Photograph showing the flexibility of b-APC, (c) Assembled b-STNG showing all its layers and components

for obtaining electrical measurements. Finally the highly flexible and hydrophobic bio-inspired, single electrode triboelectric nanogenerator named b-STNG was designed successfully. The surface modification and the incorporation of PTFE not only boosted the electrical performance but also provided b-STNG with excellent mechanical and chemical

stability. Raindrops normally possess kinetic energy during their descent and electrostatic energy is produced when they come into contact with air. Herein, the water drop energy harvesting capability of the hydrophobic b-STNG was investigated to confirm that it can harness electrical energy from randomly falling raindrops. The assembled TENG showing all its components have been demonstrated in figure 5.2(c).

5.3. Result and discussion

5.3.1. Morphological analysis

The structural analysis of the synthesized Ag_2S nanoparticles and the micro structured composite membrane b-APC was done using Field Emission Electron Microscopy. Figure 5.3(a) clearly shows distinct and uniformly shaped plate-like structures of the Ag_2S nanoparticles. The Ag_2S particles range in size from 85 to 170 nm and exhibit a smooth, flat polyhedral structure. This nano-polyhedron structure of Ag_2S was chosen for synthesis via the hydrothermal process due to its ease of operation, high yield and good reproducibility. A full bloom magenta coloured petunia flower, as displayed in figure 5.1(a), was chosen carefully for examination. The FESEM image of a petal section from this flower was taken to study the microstructures on it. Figure 5.3(b)

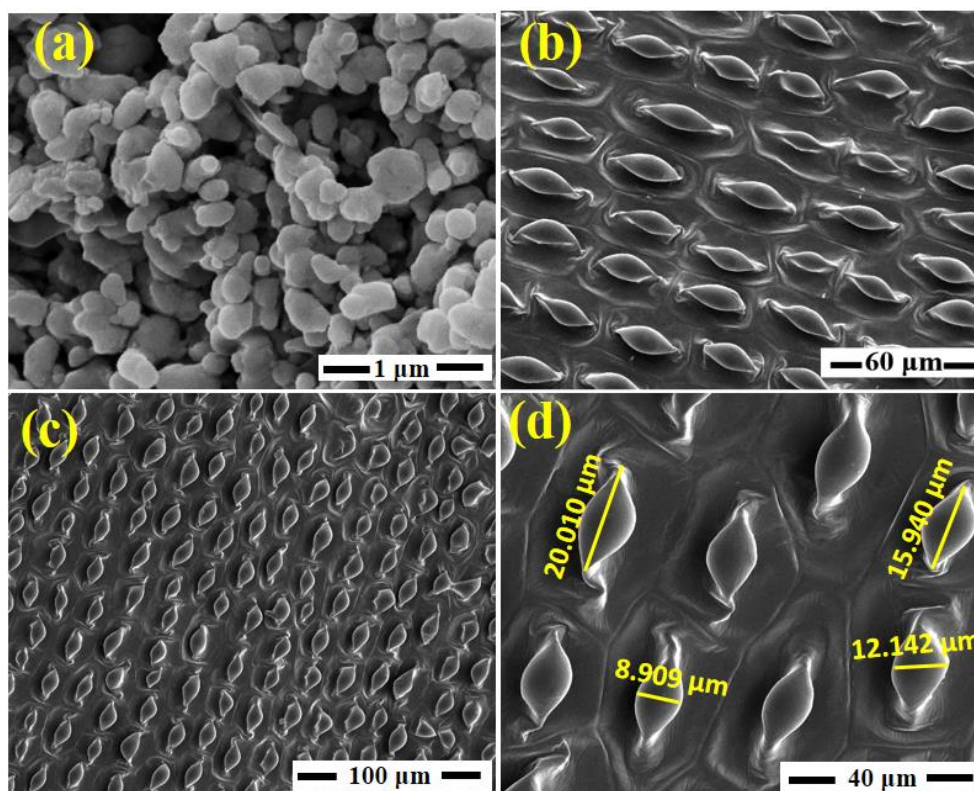


Figure 5.3. (a) FESEM image of Ag_2S nanoplates, (b) FESEM image of petunia petal surface, (c) FESEM image of b-APC with micro-boat structures, (d) Enlarged FESEM image of b-APC surface

represents the FESEM images of the microstructure of the petunia petal, which is composed of extremely organized and aligned boat like patterns. These 3D micro motifs, termed 'micro-boats' measured approximately 15-21 μm in length and 7-13 μm in width. In figure 5.3(c), the FESEM image of b-APC also clearly showed 'micro-boats' that exhibit a prominent similarity in shape, pattern and arrangement to those found in the petunia petal. This similarity highlights a remarkable resemblance between the petal micro motifs and that of the fabricated bio-mimetic positive replica (b-APC), indicating successful bio-mimicking of the petunia petal surface structures. To further examine the size and shape of the micro-boats, figure 5.3(d) displays an enlarged FESEM image of the b-APC surface. This configuration forms a nano-in-micro structure within the composite, significantly enhancing the sensitivity of the triboelectric nanogenerator [16].

The EDS spectroscopy of Ag_2S was employed to analyse the distribution of the various elements in the NPs, showcasing the various proportions of silver (Ag) and sulfur (S), as shown in figure 5.4(a). Moreover, EDS spectroscopy to analyze the distribution of

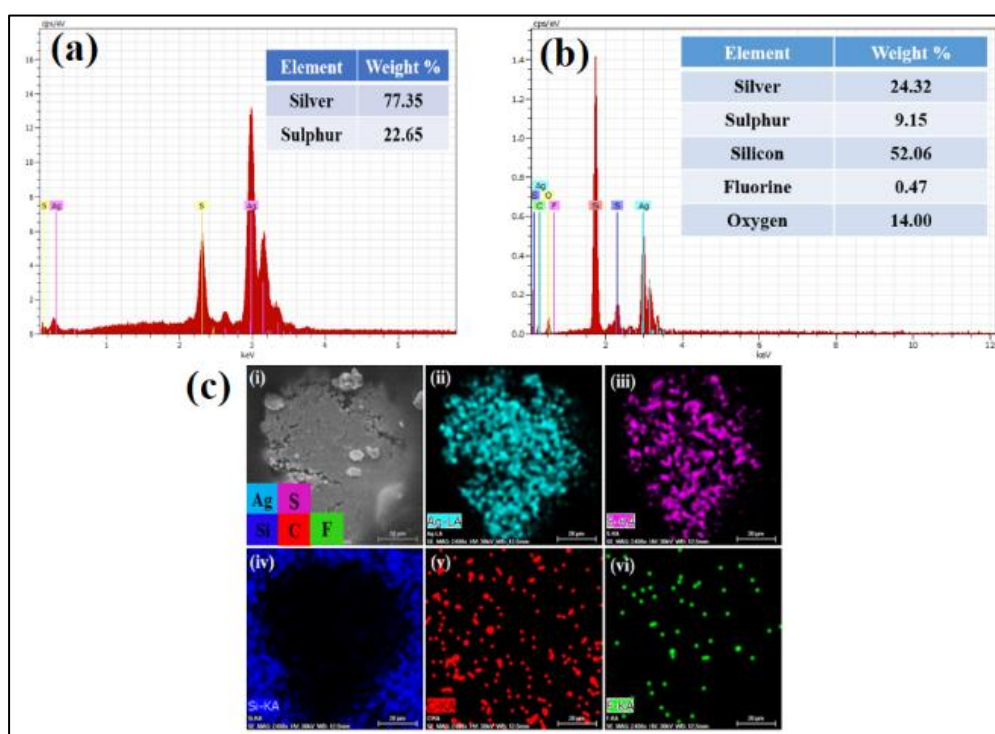


Figure 5.4. EDS spectrum of (a) Ag_2SNPs and (b) b-APC, (c) Elemental mapping for b-APC

the various elements of Ag_2S , PTFE and PDMS in b-APC composite was also done. This study revealed the various proportions of silver (Ag), sulfur (S), silicon (Si), fluorine (F) and oxygen (O) within the composite, as can be seen from figure 5.4(b). The inset of figure 5.4(b) displays the atomic weight percentages of the various elements in b-APC. As shown

in figure 5.4(c), elemental mapping for b-APC was carried out in order to experimentally verify the distribution of Ag_2S nanoplates and PTFE particles within the PDMS matrix. According to the results, there was a random dispersion pattern and an even distribution of Ag_2S nanoplates and PTFE particles throughout the polymer matrix.

5.3.2. Structural analysis of Ag_2S and b-APC composite (X-ray diffractogram)

To obtain a more detailed structural information about the nanoparticle and the polymeric composite, X-ray diffractogram pattern of Ag_2S and b-APC was analyzed. The XRD pattern of Ag_2S demonstrated the purity of the nanoparticles and the highly crystalline structure of Ag_2S nanoplates. The characteristic peaks of Ag_2S in the diffraction pattern, as can be seen from figure 5.5(a), were very sharp and distinct, indicating well-formed crystalline structure of Ag_2S . The prominent peaks of Ag_2S corresponded 2θ values of 26.189° (111), 29.063° (012), 31.820° (120), 33.660° (121), 34.743° (112),

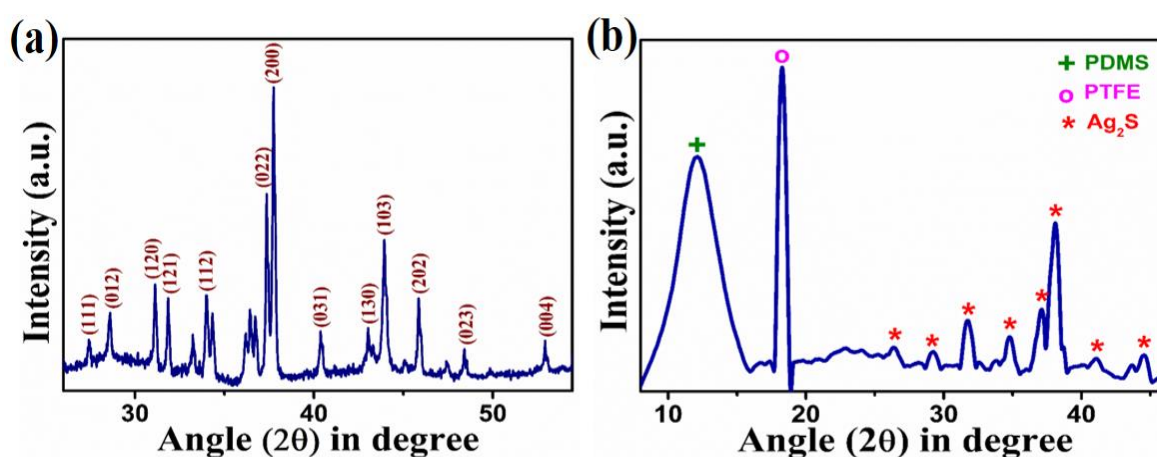


Figure 5.5. X-ray diffractogram of (a) Ag_2S nanoplates, (b) b-APC composite

36.806° (022), 37.934° (200), 40.798° (031), 43.473° (130), 44.140° (103), 46.284° (202), 47.560° (023) and 53.212° (004). The XRD peaks are indicative of orthorhombic structure of Ag_2S , thereby confirming the successful synthesis of silver sulfide nanoplates [13]. This conclusion is supported by matching the observed peaks with the standard reference (JCPDS file No. 003-0844). The X-ray diffractogram of the bio-inspired, Ag_2S and PTFE incorporated PDMS composite (b-APC) was also studied, as shown in figure 5.5(b). The XRD graph exhibited a diffused broad peak at $2\theta = 12^\circ$, indicating the presence of PDMS with amorphous structure [15]. A sharp and well-defined diffraction peak appeared at approximately $2\theta = 18^\circ$, corresponding to the PTFE powder [16] used in the composite. This significant XRD peak corresponds to the (100) crystal plane of PTFE,

aligning with the JCPDS reference pattern 00-045-1594. Prominent peaks between $2\theta = 25^\circ$ to 45° , corresponding to NPs were also prominently visible in the X-ray diffractogram of b-APC. Structural analysis of PDMS film and PTFE particles has been included in the appendix 3 file in figure A3.1(a) and (b).

Moreover to obtain comprehensive information about the crystal parameters of Ag_2S and its microstructure, some calculations were done to determine the values of several important parameters. Firstly, the full width at half maximum (FWHM), denoted as $\beta_{1/2}$, was calculated from the XRD graph corresponding to the prominent peaks. It is known that using Bragg's equation, the distance between the atomic layers or the interplanar spacing (d) of the Ag_2S crystal can be easily determined. Bragg's equation can be represented as:

$$2d \sin \theta = n\lambda \quad (1)$$

Here, θ represents the corresponding Bragg's angle, n signifies the order of diffraction as an integer and λ signifies the wavelength of the incident monochromatic Cu-K α beam which had a value of $1.54 \text{ \AA}$. The average crystalline size of Ag_2S can be predicted using the Debye-Scherrer equation, based on the characteristic diffraction peaks that exhibit high intensities. Debye-Scherrer equation can be represented as [14]:

$$D = \frac{K\lambda}{\beta_{1/2} \cos \theta} \quad (2)$$

Here, D signifies the crystalline size of the nanoparticles and K is the Scherrer constant (0.98). Given the orthorhombic structure of Ag_2S , the lattice parameters (a , b , c) of the nanoparticles can be determined using the specific formula:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (3)$$

Here, h , k and l signify the Miller indices for orthorhombic structure and the lattice parameters are related as $a \neq b \neq c$. The average values of the lattice parameters were calculated and the values were found to be $a = 4.74 \text{ \AA}$, $b = 6.98 \text{ \AA}$ and $c = 6.82 \text{ \AA}$. These values were consistent with those found in the crystallographic database for nanocrystalline orthorhombic silver sulfide. The axial angle α , β and γ of orthorhombic silver sulfide are related as $\alpha = \beta = \gamma = 90^\circ$. Using the calculated values of a , b and c the volume (V) of the nanoparticle's unit cell was determined from the equation:

$$V = a \times b \times c \quad (4)$$

The volume of the unit cell for the Ag₂S nanoparticle was found to be 225.64 Å³ using the above formula. The respective macrostrains (ε) of the nanocrystalline orthorhombic silver sulfide nanoparticles were also determined using the formula:

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan \theta} \quad (5)$$

Table 5.1. Assessment of crystal parameters of Ag₂S and its microstructure

2θ (degree)	Miller indices (hkl)	FWHM β _{1/2} (rad)	Interplanar spacing d (Å)	Crystallite size (D)(nm)	Macrostrain ε (×10 ⁻³)	Dislocation density δ (×10 ¹⁵ m ⁻²)
31.820	(120)	0.002846	2.8089	50.629	2.496086	0.3901
34.743	(112)	0.003618	2.5789	40.139	2.891302	0.6206
36.806	(022)	0.002942	2.4390	49.639	2.211058	0.4058
37.934	(200)	0.003134	2.3690	46.754	2.280150	0.4574
44.140	(103)	0.004386	2.0492	34.099	2.704415	0.8600
46.284	(202)	0.003584	1.9592	42.045	2.096909	0.5656

The dislocation density (δ) values were calculated with the help of the formula [14]:

$$\delta = \frac{1}{D^2} \quad (6)$$

Dislocation density of a crystal reflects the quantity of defects within the nanoparticle. It is assessed by the length of dislocation lines per unit volume in the crystal sample. The corresponding values of all the above mentioned parameters have been represented in a tabular form in table 5.1.

5.3.3. FTIR spectroscopy analysis of the composite membrane b-APC

To accurately understand the dynamics of b-APC and to confirm the presence of PDMS, PTFE and Ag₂S in the composite b-APC, FTIR spectroscopy in absorbance mode was employed. A pure PDMS film was prepared and subjected it to FTIR spectroscopy as well. This film was fabricated to compare and verify the incorporation of 0.5 weight percentage of the synthesized Ag₂S nanoparticles and PTFE in b-APC by highlighting the characteristic bands of both materials, as displayed in figure 5.6(a). For both polymeric films, vibrational absorption peaks at 690 cm⁻¹ and 790 cm⁻¹ were observed which were associated to CH₃ rocking and Si-C stretching vibrations. It is known that the absorption peaks about 950 - 1300 cm⁻¹ were attributed to the Si-O-Si asymmetric vibration [15].

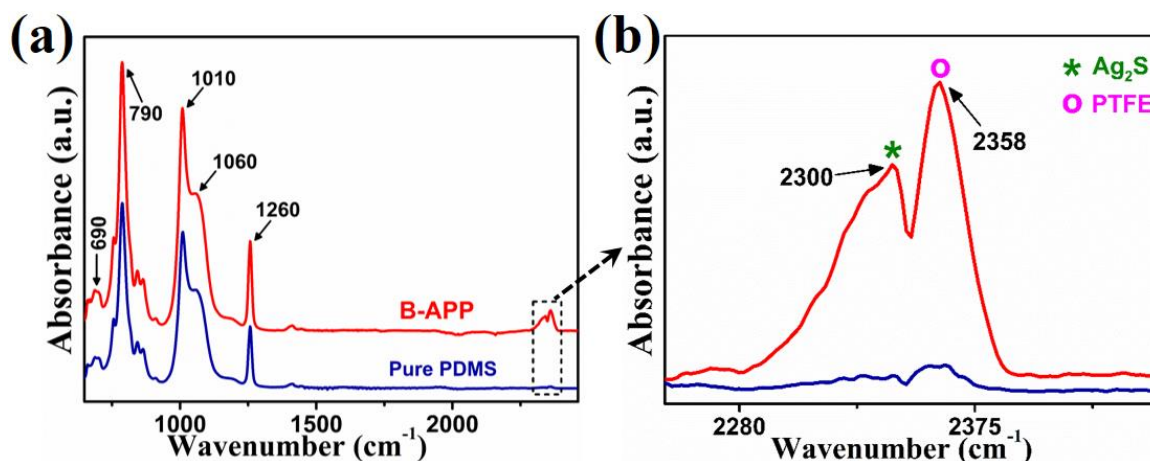


Figure 5.6. (a) FTIR analysis of pure PDMS film and b-APC composite, (b) Magnified view of FTIR graph from 2280 cm^{-1} to 2380 cm^{-1}

The peaks at 1010 cm^{-1} and 1060 cm^{-1} corresponded to Si-O-Si stretching vibrations, which were indicative of siloxane structures. The prominent peak at 1260 cm^{-1} represented the symmetric deformation of CH_3 in Si- CH_3 and also CH_2 wagging [17]. Furthermore, the absorption peaks at 2904 cm^{-1} and 2962 cm^{-1} were linked to CH-stretching vibrations in the methyl groups (CH_3). Small absorption peaks were also observed between 2280 cm^{-1} to 2380 cm^{-1} for b-APC exclusively, as can be seen from the figure 5.6(b). The absorption peak at 2300 cm^{-1} , confirmed the presence and incorporation of silver sulfide nanoparticles in b-APC [18]. This specified the complete cleavage of it by the reaction mechanism. A medium peak at 2358 cm^{-1} was also observed in the FTIR spectroscopy of b-APC which corresponded to the $-\text{CF}_2-$ backbone vibrations of PTFE [19]. The absorption peaks which have been indicated in figure 5.6(b) were only present in b-APC and were absent in the pure PDMS film. Intensities of absorption peaks for Ag_2S NPs and PTFE are considerably low in comparison to that of PDMS, since the weight percentage of these two materials added to PDMS were very less in quantity.

5.3.4. Surface wettability analysis of the composites

The water contact angle (WCA) of the micro-structured triboelectric layer b-APC was studied, along with the WCA of three other polymer films: (i) pure PDMS film, (ii) film composed of PDMS and PTFE and (iii) film containing PDMS, PTFE and Ag_2S . All of the three films had a smooth and non-structured surfaces. The physical properties of a liquid droplet are primarily determined by the surface tension of the solid surface it interacts with. The shape taken by a droplet upon contacting a solid surface is directly influenced by the surface tensions of the three interfaces [20]: (i) liquid/gas interface

(γ^{LG}), (ii) liquid/solid interface (γ^{LS}) and (iii) solid/gas interface (γ^{SG}). All of these interfaces significantly contribute to this interface-induced surface tension, as can be seen from figure 5.7(a). All of the three interfaces are extremely necessary to determine the equilibrium shape of the droplet. The contact angle that a liquid droplet forms on a solid surface depends upon the three interface induced surface tension terms, influencing the overall shape of the droplet. As illustrated in figure 5.7(a), at the 'triple line point' where all the three forces converge, the net force is zero. This signifies an equilibrium state and can be represented by the Young's law [20]:

$$\gamma^{LG} \cos\theta = \gamma^{SG} - \gamma^{LS} \quad (7)$$

This equation is used for characterizing the behaviour of the solid surface based on the angle θ , where θ represents the Young's contact angle. Young's equation is based on the assumption that the surface is homogeneous and has a smooth topography. When

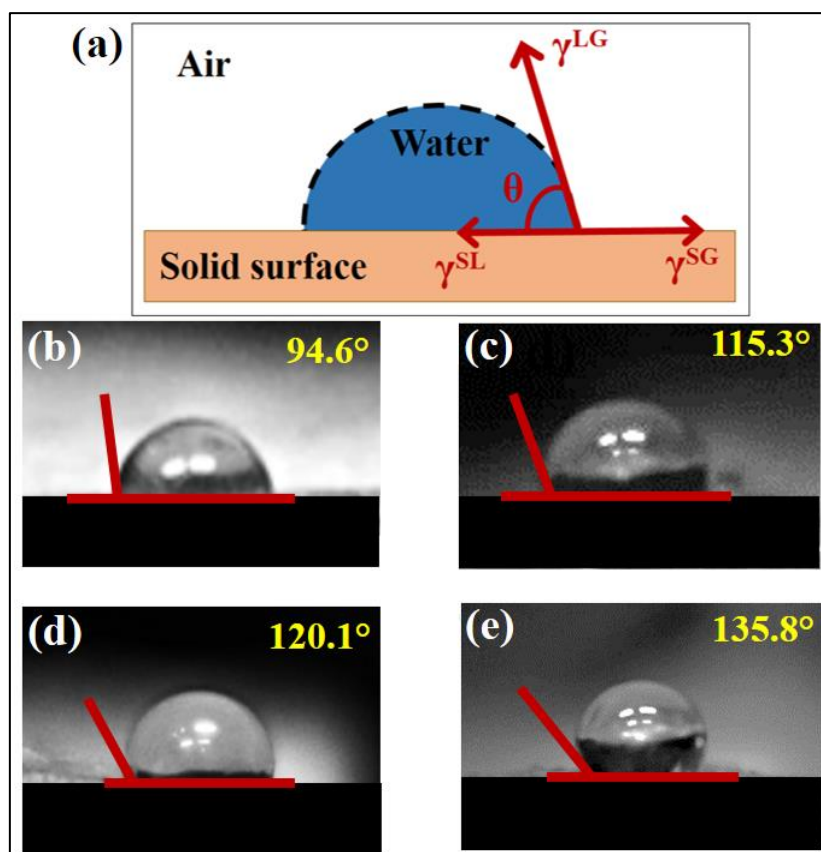


Figure 5.7. (a) Schematic diagram showing surface tension forces at solid-liquid-gas interface, WCA of (b) Smooth PDMS film surface, (c) Smooth surfaced film with PDMS and PTFE, (d) Smooth surfaced composite with PDMS, PTFE and Ag_2S , (e) Micro-structured b-APC

(i) θ is less than 90° , the solid surface exhibits hydrophilic characteristics and when (ii) θ is greater than 90° , the solid surface exhibits hydrophobic characteristics.

Herein, a water droplet of 15 μL was taken for the water contact angle (WCA) measurements. The water contact angle of the pristine, smooth PDMS film surface was found to be 94.6° . This indicates that pure PDMS film exhibits low hydrophobic characteristics [21] as can be seen from figure 5.7(b). The smooth surfaced film made of PDMS and PTFE had a WCA of 115.3° , as shown in figure 5.7(c). Upon addition of PTFE, there has been a notable improvement in the WCA compared to that of pure PDMS polymer. This is because PTFE is highly hydrophobic in nature [2] and thus it adds to the hydrophobicity of this composite membrane. The third composite resembled b-APC in composition but differed by having a smooth surface. The WCA of this composite was 120.1° , as can be seen in figure 5.7(d). Incorporation of Ag_2S nanoplates enhanced the surface roughness of the polymeric composite membrane to some extent and this led to the increment of the WCA of polymeric composite. According to Cassie-Baxter effect, the micro and nanoscale roughness of Ag_2S surfaces increased the hydrophobicity [22]. The presence of Ag_2S NPs induced some air pockets to develop between the water drop and the composite surface, which decreased the area of contact and thus increased the hydrophobicity of the surface. Finally for the bio-mimetic microstructured b-APC, the WCA was 135.8° , as shown in figure 5.7(e). This value was significantly higher compared to the other polymeric films, indicating a noteworthy increase in WCA due to the combined effect of the bio-inspired micro motifs and the presence of PTFE and Ag_2S in b-APC. This property consequently enhanced the efficiency of contact-separation between water droplets and the triboelectric layer, reducing the contact-separation time.

To analyze the impact of roughness over a particular surface qualitatively, the surface wettability of both hydrophilic and hydrophobic surfaces is needed to be examined. On a rough or structured hydrophilic surface, a droplet fills the gaps of the roughness and wets the entire solid surface area, as depicted in figure 5.8(a)[i]. In contrast, on a rough or structured hydrophobic surface, the droplet rests elevated on the irregularities. This results in the droplet contacting only a portion of the total solid surface area with air pockets remaining underneath, as depicted in figure 5.8(a)[ii].

When a liquid droplet reaches equilibrium on a solid surface (hydrophilic or hydrophobic), some external work is required to shift the contact line across the surface. Hence, the net force should be zero where the surface tensions of the three interfaces meet together. To qualitatively characterize a surface's hydrophilic and hydrophobic properties, the following equation can be used:

$$\cos \theta_r = r \cos \theta \quad (8)$$

Where, θ_r is the measured contact angle and r is the roughness factor.

Equation (8) is referred to as the Wenzel model of wetting [23], proposed by Wenzel in 1936, which establishes the relationship between surface roughness and wettability. The roughness factor (r) can be represented as:

$$r = \frac{\text{actual wetted area of the rough surface}}{\text{projected area}} \quad (9)$$

According to this equation, it is evident that the roughness factor $r \geq 1$ always ($r = 1$ for perfectly smooth surface and $r > 1$ for rough surfaces). Therefore, it can be said that the roughness factor always exceeds unity in practical scenarios, as can be easily concluded from figure 5.8(a). For a hydrophilic surface $\theta < 90^\circ$ and thus $\cos \theta > 0$. Given that $r > 1$ for real life scenario, it follows that $\cos \theta_r > \cos \theta$, which means that θ_r is smaller than θ i.e., much less than 90° . Therefore, if any smooth surface is hydrophilic in nature, then it will

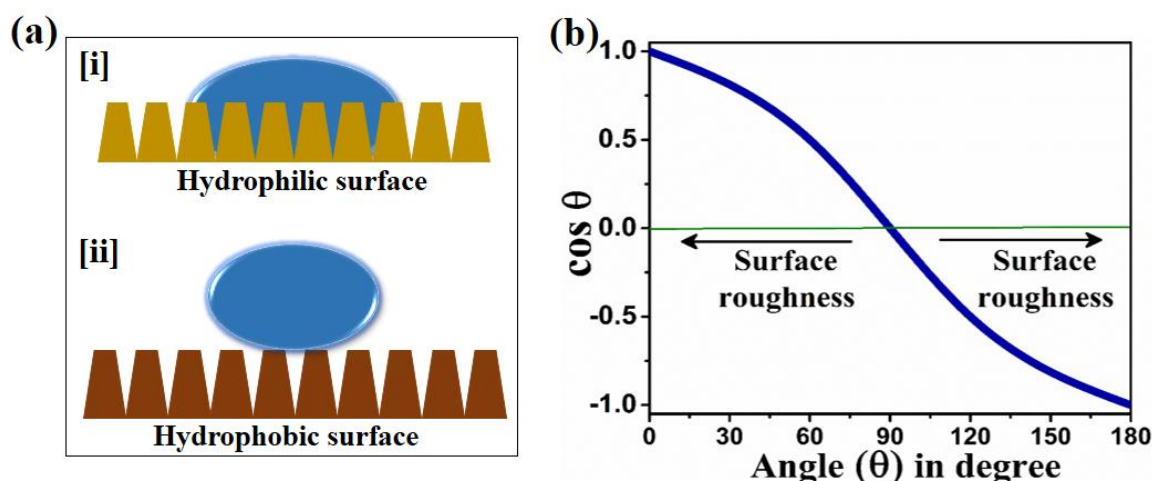


Figure 5.8. Impact of roughness on water drop (a)[i] For hydrophilic surface, [ii] For hydrophobic surface, (b) Graphical plot representing Wenzel model of wetting

become more hydrophilic in nature when roughened or structured. Conversely, for any hydrophobic surface, $\theta > 90^\circ$ by its inherent property. Further when this hydrophobic surface is roughened more, its hydrophobicity is increased significantly since $\theta_r > \theta$. This relation according to the Wenzel model of wetting has been well explained graphically in figure 5.8(b). This implies that roughening a smooth surface intensifies its inherent hydrophobicity or hydrophilicity, making hydrophobic surfaces more hydrophobic and hydrophilic surfaces more hydrophilic in nature. For this reason, the composite surface was designed to have a rough topography by incorporating bio-inspired micro motifs on b-APC. PDMS is naturally hydrophobic in nature and the addition of PTFE and Ag_2S had

further increased this property. Hence, the microstructured surface additionally enhanced the inherent hydrophobicity of b-APC, making b-STNG highly suitable for water drop-based energy harvesting and sensing applications.

In liquid-solid interacting triboelectric nanogenerators (L-S TENGs), when a liquid drop comes into contact with a solid surface, the phenomenon of sequential liquid-solid contact electrification occurs and results in the creation of an electric double layer (EDL). L-S TENG finds widespread use in droplet energy harvesting [24] where the hydrophobic property of the triboelectric layer plays a fundamental role in enhancing the output performance and its durability. The hydrophobic nature of PTFE particles also significantly improved the contact separation efficiency between water droplets and the triboelectric layer. Additionally, the strong electronegativity of PTFE particles enhanced the charge transfer between the water droplet and the tribonegative layer [2]. Thus, the electrical performance of b-STNG could be greatly enhanced by the inclusion of PTFE particles and the microstructures, in contrast to TENG without these modifications. For the two triboelectric nanogenerators as stated above, a study on water repellence was

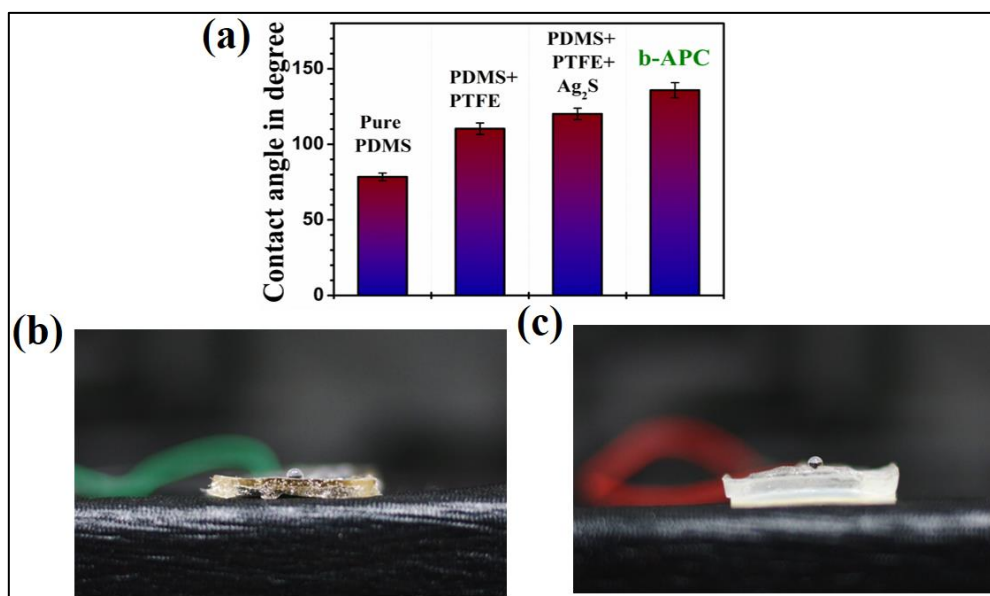


Figure 5.9. (a) Bar graph showing WCA of fabricated films, (b) Image showing surface wettability for smooth surfaced TENG, (c) Image showing surface wettability for b-STNG

also conducted to analyse the shape of the water drop on the TENGs' surfaces. The water contact angle (WCA) was measured for: (i) pristine, smooth surfaced PDMS film, (ii) smooth surfaced film composed of PDMS and PTFE, (iii) smooth surfaced film comprised of 0.5% Ag₂S NPs, PDMS and PTFE and (iv) b-APC. A bar graph representing the WCA of the four fabricated films has been done, as shown in figure 5.9(a). Figure 5.9(b) depicts

the digital image showing the surface wettability for smooth surfaced TENG, having same composition as that of b-STNG. A drop of water took a semi-circular shape when it was placed on the TENG surface lacking microstructures. However, when a drop of water was applied on b-STNG, it displayed exceptional water repellence and it took a spherical shape on the surface, as can be seen from figure 5.9(c). Thus, b-STNG has higher hydrophobicity because of the surface micro-motifs on b-APC.

5.3.5 Output performance of b-STNG (from finger tapping motion)

The bio-inspired single-electrode triboelectric nanogenerator (b-STNG) harvested mechanical energy from finger tapping motions by utilizing the principles of contact electrification and electrostatic induction [25]. According to the triboelectric series, the tribo-electrification phenomenon resulted from negative charges on the surface of b-APC (due to the presence of PDMS and PTFE) and positive charges on the human skin surface. Initially, at equilibrium, when the b-APC was in complete contact with human fingers, oppositely polarized triboelectric charges were induced and there was a charge transfer between these two layers. When b-APC and fingers were separated, the negative charges on the surface of b-APC induced positive charges on the carbon electrode, causing free electrons to flow from the electrode to the ground [26]. This generated an output voltage signal, which gradually decreased as the negative triboelectric charges on b-APC nearly cancelled out the induced positive charges on the electrode. As the human fingers gradually approached b-APC again, induced positive charges on the carbon electrode decreased, causing electrons to flow in the opposite direction. This continued until the human skin and b-APC became fully contacted, resulting in a reversed output signal. To analyze the effect of microstructures on the tribonegative layer, the results of b-STNG were compared with the output of smooth-surfaced TENG. The open circuit voltage (V_{oc}) was investigated by connecting the TENGs to a digital storage oscilloscope and applying a constant periodic axial force of 12.3 N with fingers. The calculations for the imparting force [27] have been shown in appendix 3 file. The TENG with a smooth-surfaced tribonegative layer exhibited a voltage of 267 V, while the b-STNG produced a significantly higher output voltage of 374 V, as shown in figure 5.10(a). Upon application of same amount of force, the short circuit current (I_{sc}) of the devices were measured using an electrometer. The TENG with the smooth-surfaced tribonegative layer showed a short circuit current of 8.84 μ A, while the micro-structured b-STNG showed a considerably

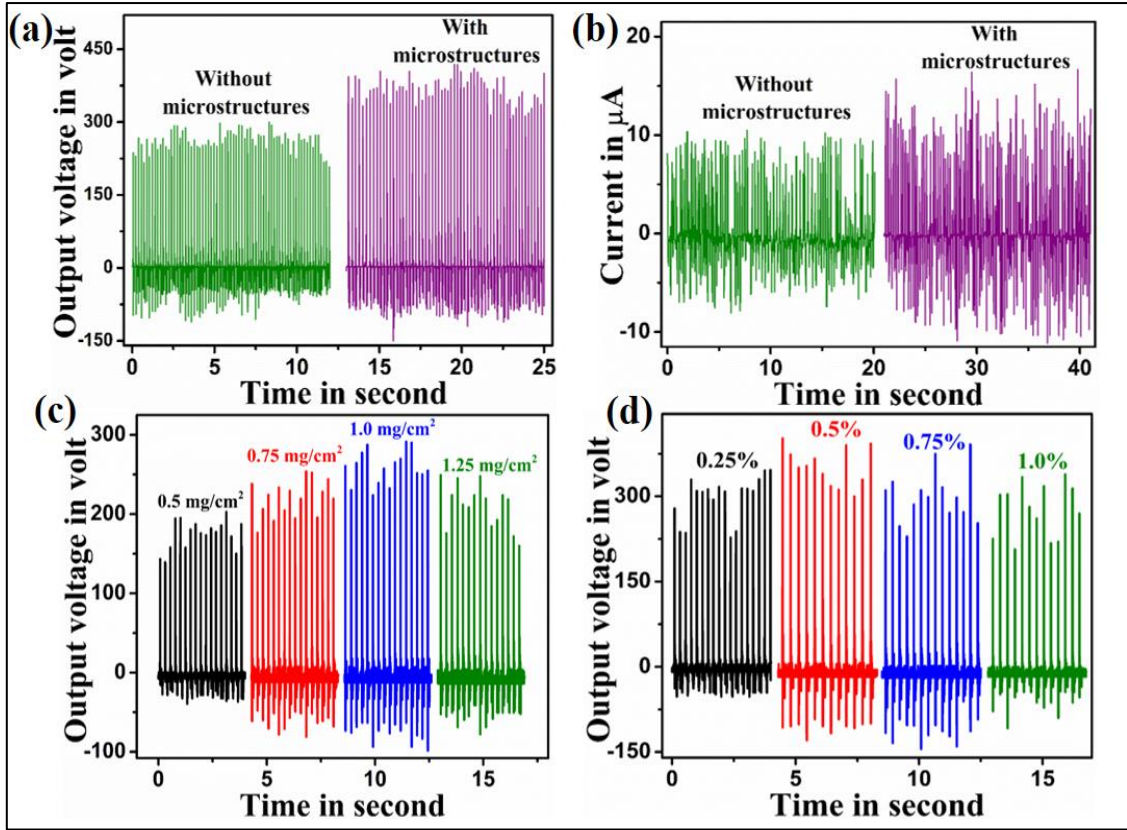


Figure 5.10. (a) V_{oc} and (b) I_{sc} of TENG with smooth-surface and of b-STNG, V_{oc} for devices with (c) varying PTFE content and (d) varying content of Ag_2S

higher current of 11.44 μA , as can be seen in figure 5.10(b). It is evident that the output voltage of a TENG improves with increased effective surface area [25].

To explore the impact of Ag_2S and PTFE concentration mixed with PDMS, four bio-mimetic triboelectric nanogenerators were designed following the same procedure as b-APC but incorporating varying amounts of PTFE particles (0.5 mg/cm², 0.75 mg/cm², 1 mg/cm² and 1.25 mg/cm²). Figure 5.10(c) illustrates the output voltage of the devices with varying PTFE concentrations. The figure shows that as the amount of PTFE particles increases the output voltage also increases, reaching a peak output voltage of 252 V at 1 mg/cm². However, further increasing the concentration resulted in a decline in the output voltage. Fluorine, which is contained in PTFE is known to have higher electronegativity compared to other elements. This makes it easier for the negative charges to be absorbed by particles that contain a higher proportion of fluorine. Hence, with the increase of PTFE amount, amount of negative charge getting stored within the composite film also increases. [28]. Moreover, from 1 mg/cm² to 1.25 mg/cm², the PTFE concentration in the composite becomes sufficiently high, resulting in lesser interfaces between PDMS and

PTFE in the triboelectric surface region of the composite. Hence, beyond 1 mg/cm², the output performance of the triboelectric nanogenerator starts to decrease [28].

Since the device with 1 mg/cm² PTFE showed maximum output, four more TENGs were designed containing PDMS+1 mg/cm² PTFE particles and 0.25%, 0.5%, 0.75% and 1.0% Ag₂S NPs. Figure 5.10(d) demonstrates that output voltage reaches a peak of 368 V when the NP content reaches 0.5%. This is due to the fact that the dielectric constant rises as the Ag₂S weight% increases [29]. Output voltages begin to drop as the concentration of Ag₂S NPs in composites increase gradually beyond 0.5%. This occurs because of agglomeration of NPs in composites, leading to a decrease in surface charge density [29].

To investigate the load capacity of b-STNG, multiple load resistances were used with varying values, ranging from 10³ to 10⁹, as displayed in figure 5.11(a). b-STNG exhibited varying instantaneous power density values for varying load resistances and the power density (P) was calculated using the formula [25]:

$$P = \frac{V^2}{R_L \times A} \quad (10)$$

Here, V is the output voltage of b-STNG, R_L represents the load resistance value and A represents the effective surface area of b-STNG (3.6 cm x 2.6 cm). The maximum power density for b-STNG was obtained to be 3.25 W/m² at 10⁷ Ω. Figure 5.11(a) shows that,

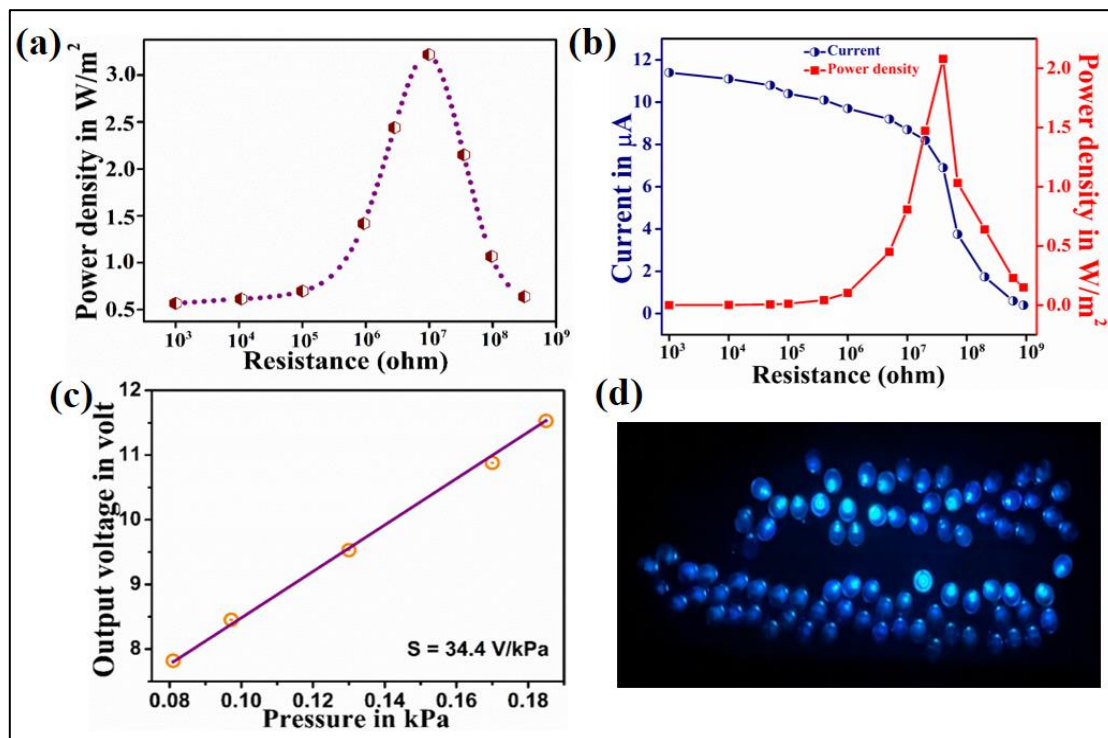


Figure 5.11. (a) Power density of b-STNG, (b) Dependence of I_{sc} and power density with varying load resistances for b-STNG, (c) Sensitivity plot for b-STNG, (d) Digital image of lighting up of LEDs

with the increase of load resistances the power density primarily increases, attains a maximum value of 2.08 W/m^2 at a $40 \text{ M}\Omega$ and then gradually decreases. To further investigate the load capacity of b-STNG, the relationship between short-circuit current and peak power density was analyzed across $10^3 \Omega$ to $10^9 \Omega$. The graph in figure 5.11(b) also illustrates that the short circuit current of b-STNG has a maximum value of $11.30 \mu\text{A}$ at $10^3 \Omega$ and then gradually decreases with the increase of load resistances. To show that b-STNG can produce a considerable voltage from small mechanical vibrations, the sensitivity of the device was calculated. To obtain this, five types of Indian currency coins were used with varying masses (₹1, ₹2, ₹5, ₹10 and ₹20). These coins were dropped onto the from a height of 8 cm, giving varying output voltages. Using the pressure values for each case, a linear graph of output voltage vs pressure was plotted, as shown in figure 5.11(c) and the sensitivity (S) of the device was finally obtained to be 34.4 V/kPa upto an external pressure of 0.185 kPa , using the formula [25]:

$$S = \frac{\Delta V}{\Delta P} \quad (11)$$

Here, ΔV and ΔP represent the change in output voltage and applied external pressure respectively. As shown in figure 5.11(d), by making proper electrical circuit connection and using a full-wave rectifier, b-STNG was able to instantly light up 93 blue LEDs connected in series.

Output voltage performance of b-STNG with varying frequency of 1 Hz to 7 Hz of force (applied force of 5 N) by a customised piezo-tribo impart testing machine was also experimentally analyzed and the maximum voltage was obtained at the highest frequency of 7 Hz, as shown in figure 5.12(a). It is evident from the graph that the maximum output voltage (179.6 V) at 7 Hz frequency has increased by almost 2.3 times than the output

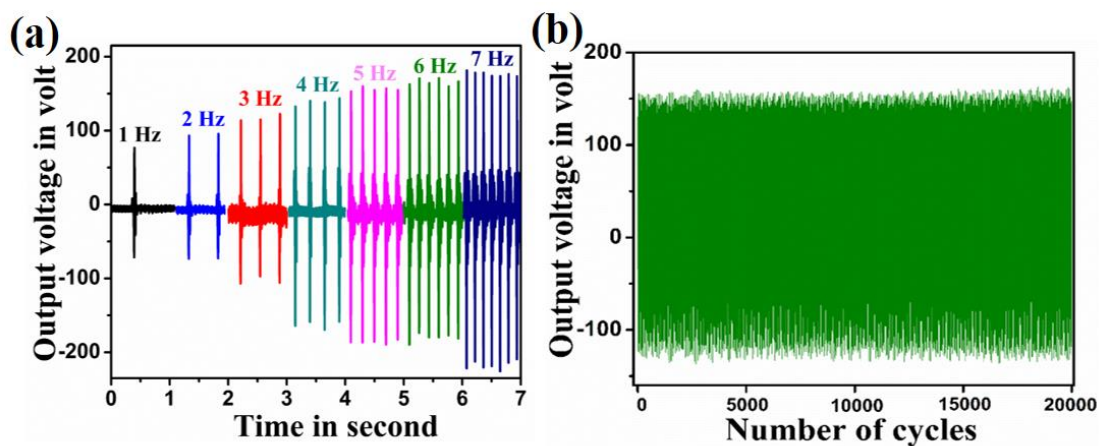


Figure. 5.12. (a) V_{oc} of b-STNG with varying frequency of force, (b) Stability test of b-STNG

voltage at 1 Hz frequency (77.3 V). To evaluate the long term stability of b-STNG, its output performance was tested for over 20,000 periodic cycles on application of 5 N force using the piezo-tribo imparting machine. It was observed that the output voltage remained steady and continuous with minimal deviation, as shown in figure 5.12(b).

To gain a more precise quantitative analysis of the power generation mechanism of b-STNG from finger tapping motion, Finite Element Analysis (FEA) has been employed using COMSOL Multiphysics. This analysis simulates the potential distributions at varying separation distances between the triboelectric layer and human skin. The constructed

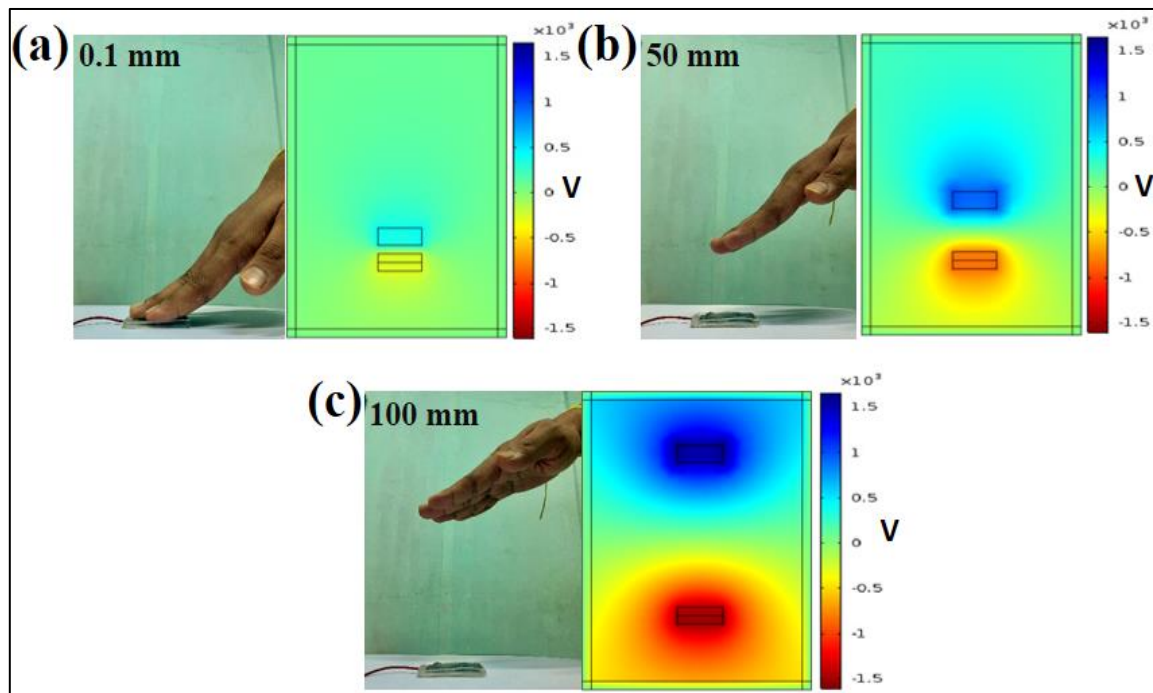


Figure 5.13. Finite Element Analysis based on COMSOL software when fingers: (a) Completely touch b-STNG, (b) Are 50 mm from b-STNG and (c) Are 100 mm from b-STNG

model was based on human skin, the triboelectric layer b-APC consisting of PDMS, PTFE and Ag_2S , along with a grounding carbon electrode, all layers with dimensions of $40 \times 40 \text{ mm}^2$. The thicknesses were assumed to be 1 mm for the human skin, 0.5 mm for the triboelectric layer and 0.5 mm for the carbon electrode. The skin surface was assumed to have a uniform charge density of $+5 \mu\text{C}/\text{cm}^2$ while the b-APC surface was assumed to have a charge density of $-5 \mu\text{C}/\text{cm}^2$. Figure 5.13(a)-(c) represent the simulation outcomes of the potential distribution in b-STNG for varying separation distances of 0.1 mm, 50 mm and 100 mm respectively, between human skin and the triboelectric layer b-APC. When the human skin was in full contact with b-APC surface, the electric potential value became nearly zero on both surfaces. As the separation distance increased, the electric potential

difference between the two surfaces gradually increased. When the layers were separated by 100 mm, the electric potential on the skin surface reached 1.5 kV, while the triboelectric layer exhibited a negative electric potential of nearly -1.5 kV, as shown in figure 5.13(c). Thus, based on the Finite Element Analysis results of b-STNG, it was evident that the potential difference between human skin and the negative triboelectric layer increased gradually as the separation distance between them increased [30].

5.3.6. Working mechanism of water drop based b-STNG

Raindrops normally possess kinetic energy during their descent and electrostatic energy is produced when they come into contact with air. Herein, the water drop energy harvesting capability of the hydrophobic b-STNG has been investigated to confirm that the device can harness electrical energy from randomly falling raindrops. The schematic representation of working principle of b-STNG based on liquid-solid interaction has been illustrated in figure 5.14. For harvesting water drop energy from b-STNG, working on L-S interaction, it was inclined at an angle of 45° . The electrode of the device was linked to an external load resistance (R) and then was grounded. When a water drop first made contact with the negatively charged triboelectric layer, there was charge transfer that took place at the liquid-solid interface.

Step: 1- When water drop and triboelectric layer are separated, that is they are not in contact, an equal quantity of positive charge is induced on carbon tape (electrode)

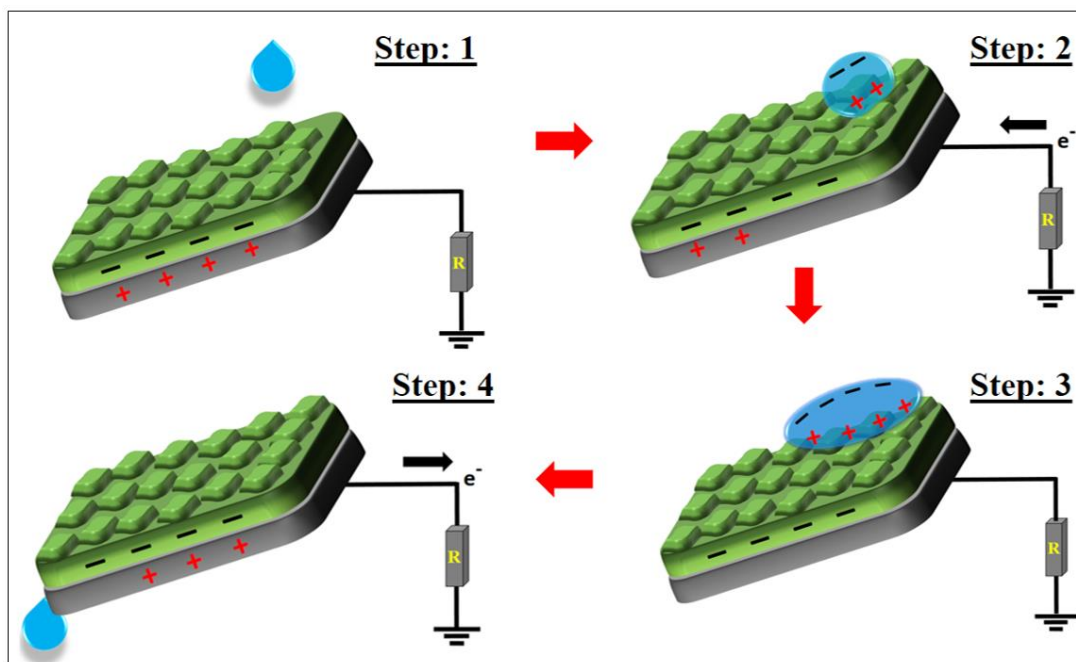


Figure 5.14. Working principle of b-STNG based on liquid-solid interaction

by the negatively charged triboelectric layer. This leads to an electrostatic equilibrium condition between these two layers.

Step: 2- When a water drop comes into contact with the negatively charged triboelectric layer, electrons starts to flow from the ground towards the electrode. This leads to the formation of charge shielding between these surfaces and hence the electrostatic equilibrium condition breaks [31].

Step: 3- In this step, electrons continues to flow up from ground up to the carbon tape until the water drop spreads adequately on the micro-structured triboelectric layer.

Step: 4- Finally, when the water drop slides off the hydrophobic triboelectric layer, the electrostatic equilibrium condition again occurs. This also diminishes the charge shielding which had been created. In this step, the electrons starts to flow from the electrode to the ground.

To summarize all the four steps, the transition of a water drop from contact to separation leads to the generation of an alternating current. Continuous electrical energy was produced as droplets kept falling and with repeated contact and separation with the water drops, the triboelectric layer continued to accumulate negative charges. It is also very essential to examine the factors influencing the output performance of b-STNG. The underlying principle of b-STNG depends upon Maxwell's displacement current and its output voltage (V_{oc}) can be represented using the following equation [31]:

$$V_{oc} = R \left(C \frac{dV}{dt} + V \frac{dC}{dt} \right) \quad (12)$$

Here, R is the load resistance, C is the capacitance of triboelectric layer, t is the contact time between the water drop and the triboelectric layer and V represents the potential difference between the electrode and ground. The short circuit output current (I_{sc}) can be represented using the following equation:

$$I_{sc} = \frac{dQ}{dt} = A \frac{d\sigma_i(x,t)}{dt} \quad (13)$$

$$\text{Or, } I_{sc} = C \frac{dV}{dt} + V \frac{dC}{dt} \quad (14)$$

Here, Q represents the amount of charge transferred, A represents the spreading area of the water drop, σ_i represents free charge density in the electrode. Therefore, it can be concluded that both V_{oc} and I_{sc} are positively associated with the capacitance, the potential difference between the electrode and ground and the free charge density in the electrode. Conversely, they are inversely proportional to the contact time between the water drop and the triboelectric layer. Moreover, a larger contact area between the water

drop and the triboelectric layer results in greater capacitance, thereby increasing the output voltage and current. Therefore, some other important parameters were examined to further optimize the output performance of b-STNG.

5.3.7 Output performance of b-STNG (for falling water drop)

The following parameters were considered to determine the impact of external conditions on the output voltage and short-circuit current of the b-STNG: angle of inclination (θ), height of descent (H), frequency of descent and volume of water drop. Additionally, the output of our device was also tested for water drops from various water sources along with salt and sugar solution. Figure 5.15(a)-(c) illustrate the influence of inclination (angle between the triboelectric layer and the horizontal base) on the output voltage and short-circuit current of b-STNG. The voltage and current data were taken for 0° (5 V, 0.1 μ A), 15° (9 V, 0.6 μ A), 30° (10 V, 0.7 μ A), 45° (19 V, 1.3 μ A) and 60° (15 V, 1.1 μ A) as displayed in figure 5.15(b) and 5.15(c) and it can be seen that maximum output was obtained at an angle of 45° . As the inclined angle was progressively raised from 0° to 45° , the uneven distribution of the water drops along the slope was highlighted. The front end of the drop spread faster and the change of contact area improved, leading to a rise in the charge transfer speed. Consequently, the electrostatic induction was increased and the output performance was improved. When the inclination angle was increased above 45° , the water drops shrunk and the spreading over the inclined plane promptly reached

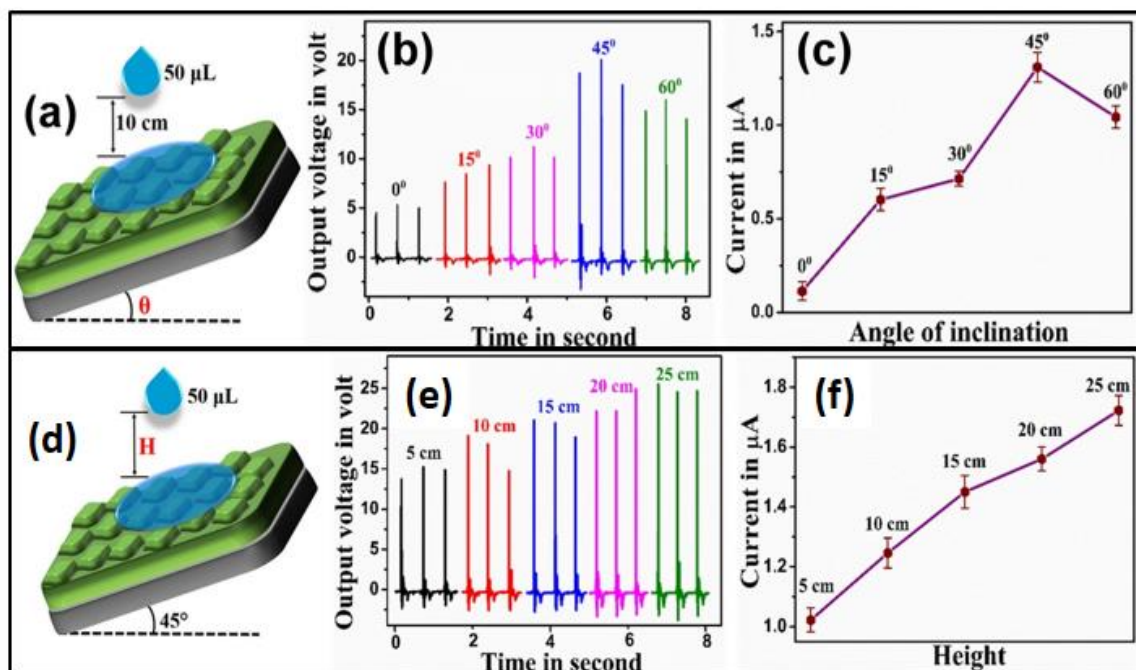


Figure 5.15. Schematic diagram, V_{OC} and I_{SC} based on (a)-(c) Angle of inclination, (d)-(f) Height

its highest value. Hence, the output data deteriorated as a result of restricted horizontal spreading and reduced spreading area of the water droplets [32]. For this experiment water drop volume was 50 μL and was dropped from 10 cm.

Figure 5.15(d)-(f) represent the schematic representation and the output data of b-STNG with the increase of the falling height (H) of water drop on b-STNG. The output voltage and current data were taken for 5 cm (15 V, 1.2 μA), 10 cm (18 V, 1.3 μA), 15 cm (21 V, 1.5 μA), 20 cm (22 V, 1.6 μA) and 25 cm (25 V, 1.7 μA). The maximum output voltage and current were observed for 25 cm, keeping the drop volume at 50 μL and $\theta = 45^\circ$. Here, it was observed that the output performance improved with an increase in falling height. This is because the friction between water drop and the air generates more free charges in the drop before it contacted the triboelectric film. Therefore greater falling height led to more duration of contact between water drop and air, leading to improved output results. Simultaneously, the spreading area on the triboelectric surface increased as height increased. This increment of the output performance with height can be explained with the help of the following equation [32]:

$$W_e = \frac{\rho v^2 d}{\sigma} \quad (15)$$

Here, W_e represents the Weber number, ρ represents the fluid density, v represents fluid velocity, d represents drop radius and σ represents the surface tension of the fluid. When the diameter and surface tension of water drop are fixed, the Weber number rises with the velocity. This means that greater the ratio of inertial force to surface tension, greater will be the spreading area and velocity under the influence of inertial force. Due to the micro-structured and rough surface of triboelectric layer, the inertial force increases the interface pressure among the triboelectric film surface and the water drop, consequently expanding the effective contact area. As a result, the surface of b-APC becomes a larger diffusion region for water drops, leading to a greater amount of friction charge between the water drops and the film surface.

Figure 5.16(a)-(c) display the schematic depiction and output performance of b-STNG on the basis of the frequency of individual droplet contact with b-APC. The output voltage and current data were taken for 2 Hz (13 V, 0.9 μA), 3 Hz (17 V, 1.2 μA), 4 Hz (21 V, 1.4 μA) and 5 Hz (18 V, 1.2 μA). The graphs show that the output voltage and current of the b-STNG increase with frequency up to 4 Hz, after which there was a drop in both

the voltage and current at 5 Hz. This is due to the fact that a higher frequency caused a faster

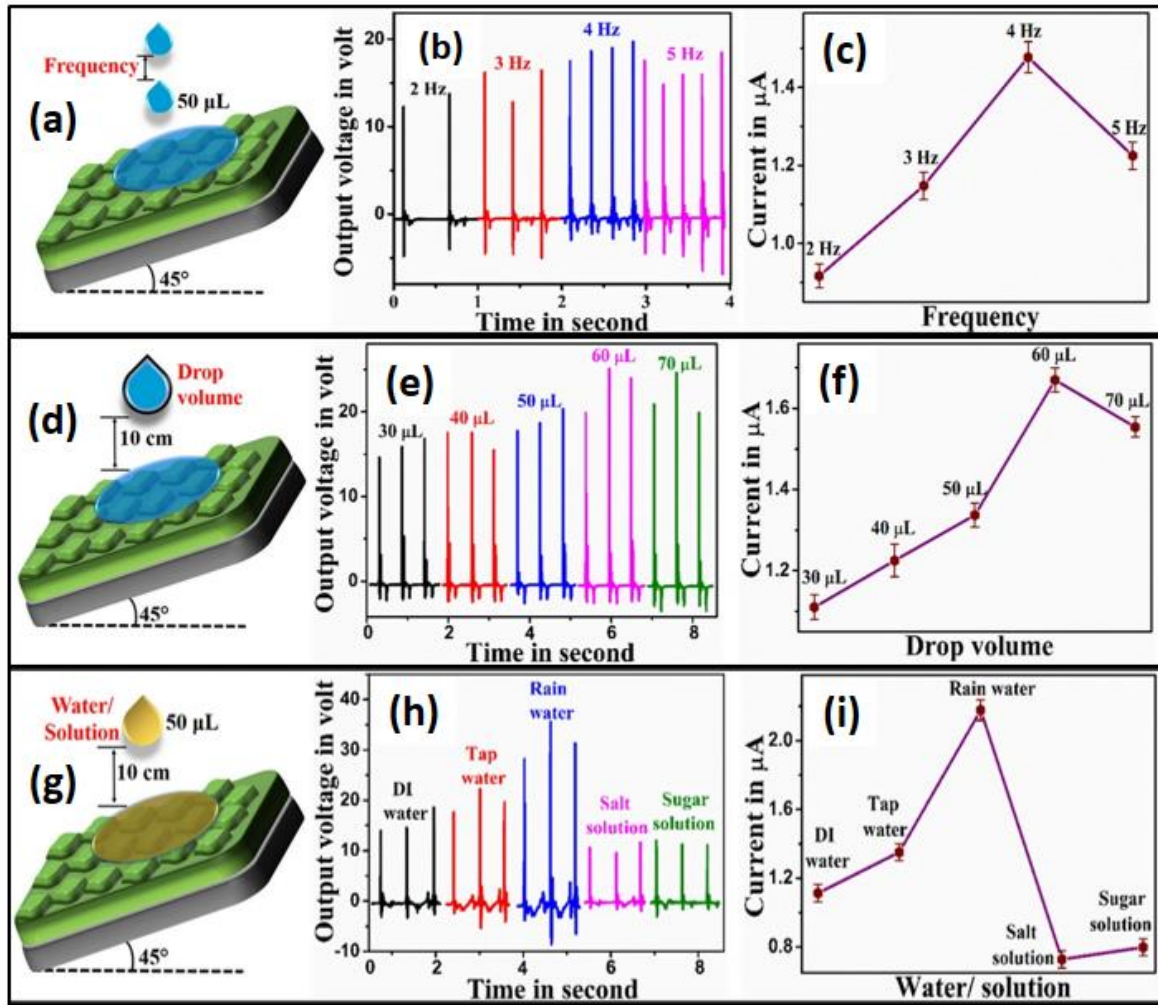


Figure 5.16. Schematic diagram, V_{oc} and I_{sc} depending on (a)-(c) Frequency, (d)-(f) Drop volume, (g)-(i) Influence of various liquids

injection of surface charges into the saturated state, increasing the number of transferred charges [33]. However, when the frequency was raised over a certain point, the discrete water drops became a continuous flow of water. Because of the constant impact of water, the surface charges could not be transmitted over time and hence the output performance decreased.

The relationship between the water drop volume and the output performances of b-STNG has been depicted in figure 5.16(d)-(f). The data for the voltage and current were taken for 30 μL (16 V, 1.1 μA), 40 μL (18 V, 1.2 μA), 50 μL (20 V, 1.3 μA), 60 μL (24 V, 1.7 μA) and 70 μL (22 V, 1.6 μA). The results indicated that the output data of the b-STNG initially increased, reaching a peak at 60 μL , and then decreased as the water droplet

volume continued to increase. This is because when the water drop volume was quite large, the induced charge between the water drop and the triboelectric layer was not transferred adequately [34].

b-STNG was tested for various water samples and aqueous solutions as can be seen in figure 5.16(g)-(i). Output voltages and current of the b-STNG were tested for DI water (16 V, 1.2 μ A), tap water (19 V, 1.4 μ A), rain water (31 V, 2.2 μ A), salt solution [solution of 0.90% w/v of NaCl; 9g/L saline] (10 V, 0.8 μ A) and sugar solution [5% w/v glucose solution; (50 g/L)] (11 V, 0.7 μ A). In contrast to DI water, the output from the tap water was larger but the output from the sugar and salt solutions was much smaller, as illustrated in figure 5.16(h) and 5.16(i). This is due to the fact that at low ion concentrations, the output values increase with increasing concentration. On the other hand at higher concentration of ions in the solution, the output decreases with the increase in ion concentration [24]. This occurs because the ions in the solution neutralize the charges on the PTFE and b-APC collectively at larger concentrations. Since DI water contains no ions and tap water has a low ion concentration, the output performance of b-STNG for tap water was significantly better than that of DI water. When rainwater was used, outputs were nearly twice that of DI water because the electrolyte concentration of rainwater closely matched the concentration at which triboelectric nanogenerators driven by electrolyte solutions achieve maximum outputs [24]. Water was gathered from natural rainfall by placing a beaker in open area, in order to conduct the experiment utilizing rainwater. It is known that triboelectric charges get created as raindrops fall from the sky because of contact electrification between the raindrops and airborne particles [35]. These charges are then retained in the collected rainfall. This is the reason that collected rainwater naturally has positive charges in it. This observation in the output results inspired us to utilize b-STNG as a rainwater harvester and an acid rain sensor. Given its high sensitivity to ion and electrolyte concentrations, b-STNG can effectively detect voltage and current fluctuations at different pH levels of acid solutions.

5.3.8. Output results of b-STNG for acidic solution

When moisture and other acidic compounds like sulfuric acid (H_2SO_4) and nitric acid (HNO_3) combine in the atmosphere, acid precipitation ($\text{pH} < 5.6$) with high hydrogen ion concentrations is created. Since the triboelectric device is highly sensitive to ions, it was used as a self-powered pH sensor that can be effectively used as an acid rain sensor.

Acid rain is mostly composed of H_2SO_4 and HNO_3 , thus in order to confirm the proof-of-concept, artificial acid rainwater was created by combining H_2SO_4 and HNO_3 separately to make two acid solutions. A water sprinkler was used to shower acid solutions on b-STNG to produce a simulated acid rainfall environment with raindrop flow rate of 100 mL/min. Figure 5.17(a) and (b) display V_{OC} and I_{SC} obtained from b-STNG by sprinkling

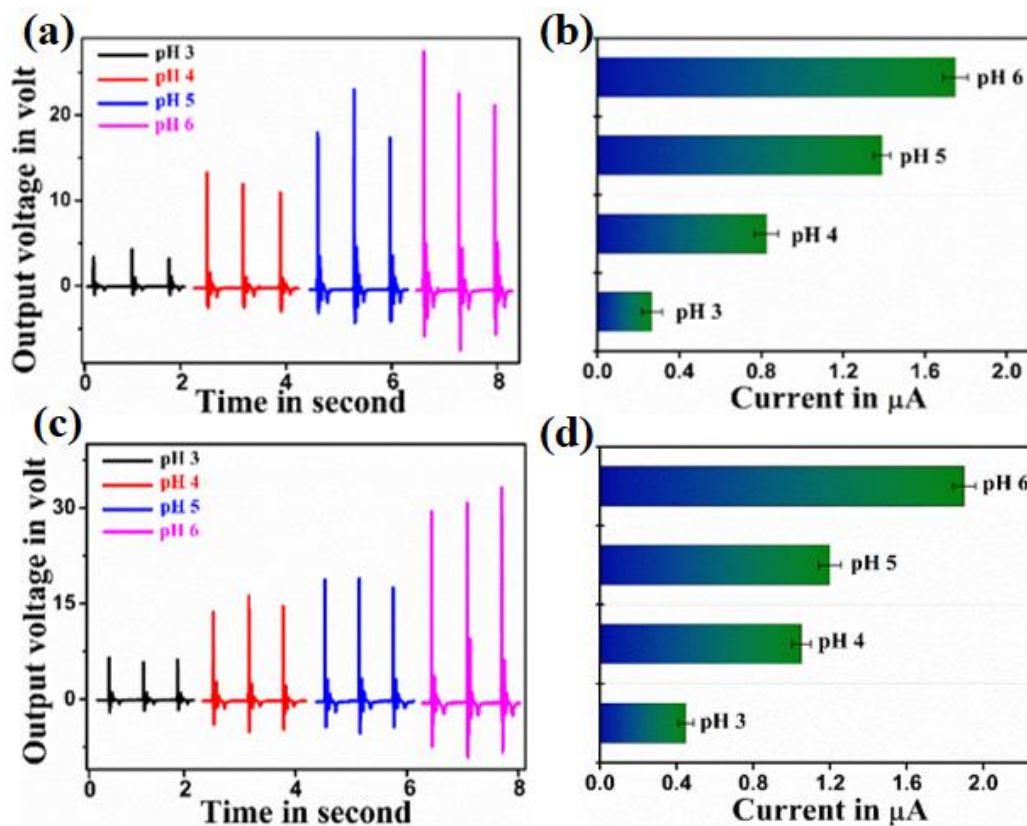


Figure 5.17. (a) V_{OC} and (b) I_{SC} obtained from H_2SO_4 solution with different pH, (c) V_{OC} and (d) I_{SC} obtained from HNO_3 solution with different pH gradients obtained from b-STNG

H_2SO_4 solution having different pH gradients. The output data for H_2SO_4 solution was obtained for pH 3 (4 V, 0.3 μA), pH 4 (12 V, 0.8 μA), pH 5 (20 V, 1.4 μA) and for pH 6 (25 V, 1.7 μA). Similarly, the output results were tested for HNO_3 solution with varying pH gradients, as can be seen from figure 5.17(c) and (d).

The data for the output voltage and current for HNO_3 solutions were taken for pH 3 (6 V, 0.5 μA), pH 4 (15 V, 1.1 μA), pH 5 (19 V, 1.2 μA) and for pH 6 (31 V, 1.9 μA). It is evident from the graphs that lower the pH of both acid solutions, lesser are the output results. This is because the contact electrification process is hindered by the H^+ ions found in acidic solutions, which results in a charge screening effect. When the pH falls, the conductivity of the artificial acid rain solution rises and it becomes greater than the conductivity of a regular raindrop. An increase in conductivity of a solution indicates an

increased concentration of ions in it, resulting in a screen effect and a reduction in electron transport at the liquid- solid interface, resulting in lesser output outcomes [35]. Another observation made from figure 5.17 was that, for a given pH, the output data for H_2SO_4 solution was less than that for HNO_3 solution. This is because HNO_3 produces only one H^+ ion per molecule but H_2SO_4 molecule create two H^+ ions, indicating that H_2SO_4 is more acidic in nature.

The influence of pH value and ion concentration of the solution, on the performance of b-STNG has been further elaborated on the basis of a schematic diagram. Figure 5.18 illustrates the mechanism which takes place during the contact separation of acidic solution with b-APC surface, on the basis of ion concentration of the solution. The ongoing processes are electron transfer, hydrogen ion adsorption and charge transfer.

Step 1: As can be seen in step 1 of figure 5.18, electron transfer and hydrogen ion

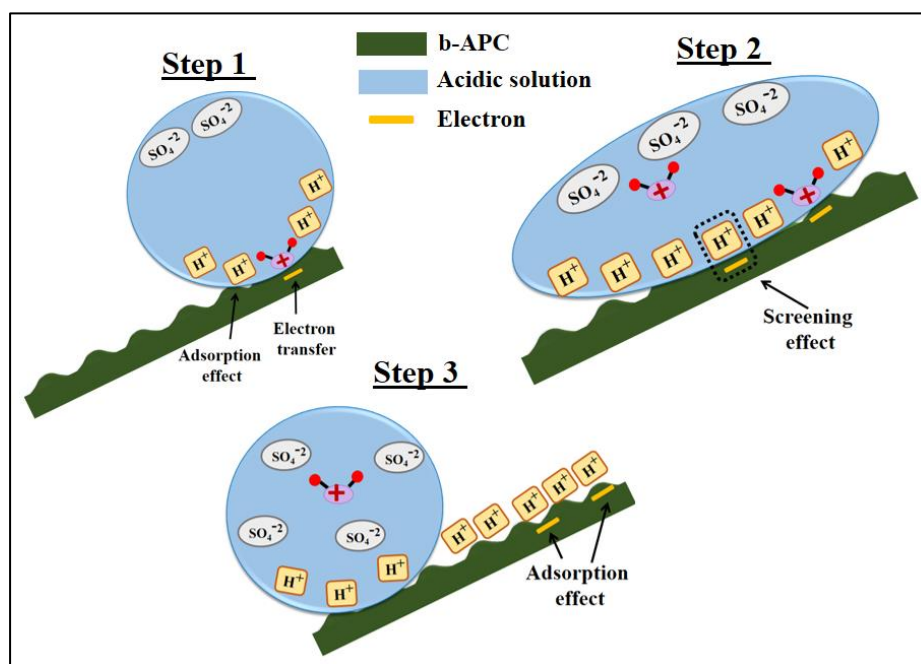


Figure 5.18. Contact electrification mechanism of acidic solution and b-APC surface

adsorption take place simultaneously when acid solution and b-APC come into contact. To inhibit electron transfer between the water molecules and the triboelectric layer, a large concentration of hydrogen ions get adsorbed on its surface. Moreover, small ions have a higher diffusion coefficient in aqueous solution than large ions, which cause hydrogen ions to reach to the liquid-solid interface more quickly [36].

Step 2: In this step, the solution is spread on a broader area on b-APC surface and the ions accumulate at the liquid-solid interface, hindering electron transfer process due

to the screening effect. The solution gets dispersed across a larger area of b-APC surface and the H^+ ions in the H_2SO_4 solution start accumulating at the liquid-solid interface. This phenomenon henceforth inhibit the electron transfer process because of the screening effect. Hydrogen ion adsorption on the b-APC surface is the dominant process, with only a minimal amount of electron transfer taking place. The reduction in the charge generated by contact electrification at higher ion concentrations can be attributed to the screening effect of the free ions.

Step 3: There are still some hydrogen ions adsorbed on the triboelectric surface after the acidic solution start falling off from b-APC surface. At the same time, electrostatic attraction causes certain H^+ ions to be adsorbed on the b-APC surface. In ionic solutions, these ions are physically adsorbed on the triboelectric surface instead of being chemically attached to it due to the electrostatic and ionic adsorption processes. In summary, it can be said that the output performance of b-STNG decreases as the solution becomes more acidic. Furthermore, compared to the output results for actual rainwater, the output voltage and current for acid solutions were substantially lower. This is because rainwater naturally has positive charges in it. A test was carried out to confirm the degree of stability of b-STNG even after prolonged contact with an acidic solution, as shown in appendix 3, figure A3.2.

5.3.9 Self-powered acid rain sensor for real time pH detection of rainwater

A self-powered acid rain sensor system was developed, utilizing the output data from b-STNG for a range of pH values to detect the pH acid rain as displayed in figure 5.19. Firstly, an Arduino Mega system was used through a laptop to send the output signal produced by sprinkling the artificial acid rain (mixture of HNO_3 and H_2SO_4 solutions in 1:1 ratio) on the TENG surface. Next the data was collected, processed and analysed after the produced output data from b-STNG was passed through the microcontroller unit (MCU) module. The output voltage corresponding to each pH value were brought under 5 V using a voltage divider. A low-pass filter and rectifier module, which were connected to the processing circuit for rectifying the signal, were used to filter the produced output signal. LEDs with varying colours were connected to the circuit that indicated the pH value of the acidic solution in real time. The output signal obtained was rectified and delivered to the Arduino Mega system and was also sent to the LEDs for pH indication. Acid rain in real life has a pH range of 3 to 6, thus coloured LEDs were chosen to

correspond with this range. In addition to detecting acid rain, a control setup was also taken indicating a pH of 7 which corresponded to normal water. The LEDs were colour coded according to the pH levels as follows - Red LED: pH 3, Yellow LED: pH 4, Blue LED: pH 5, White LED: pH 6, Green LED: pH 7 (Control setup). By adjusting HNO_3 and H_2SO_4

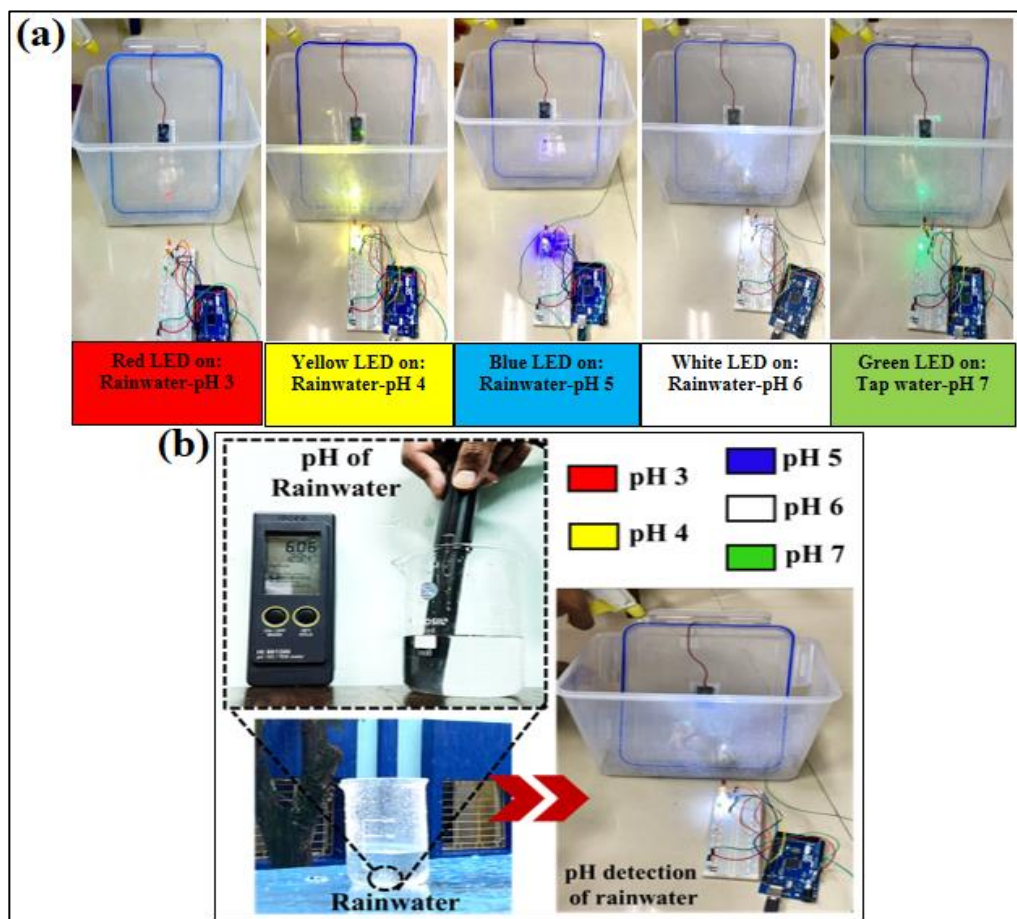


Figure 5.19. (a) pH sensing via coloured LED indicators, (b) Real time pH detection of rainwater

acid concentration, acidic solutions with different pH values were made to simulate artificial rains of different pH values. Figure 5.19(a) illustrates how upon sprinkling an acidic solution with a certain pH on b-STNG, LEDs matching that pH lighted up.

When a red or yellow LED lit up, it meant that the acidity of the rainwater was extremely high, which is dangerous and calls for caution. Significantly high level of acid rain was still indicated by the lighting up of blue LED, which represented a pH of 5. A white LED represented normal rainfall and signalled no threat to the environment. Additionally, when regular water was sprayed on the triboelectric device, the self-powered sensing system could react to it by promptly turning on the green LED, indicating a pH of 7.

After detecting the pH of the lab prepared artificial rainwater by b-STNG, a real-life model was designed to determine the unknown pH of collected natural rainwater. The primary motives for preparing this model were (i) real-time identification of the unknown pH of collected natural rainwater and (ii) displaying the value of matched pH with the help of coloured LED indicators. This proposed system could expand the practicality of the designed b-STNG in real-time self-powered acid rainwater monitoring applications. A beaker was placed in an open place to collect natural rainwater. The actual pH of collected rainwater was measured with a pH meter and the result showed that it had a pH of 6.06 as shown in figure 5.19(b). After that, the collected rainwater was poured into a water sprinkler and was showered on b-STNG to produce a simulated acid rainfall with flow rate of 100 mL/min. b-STNG generated output voltage signals corresponding to the particular pH value and were passed to the laptop through the ARDUINO Mega system to prepare a data set, which was further analysed by a MCU module. After analysing the data, the white LED lit up immediately, as depicted in figure 5.19(b) and continued glowing until the sprinkling of the collected rainwater was stopped. According to the list of coloured LED indicators of pH, glowing of white LED indicated pH 6 of the collected rainwater, which also matched with the result of the pH measured with a pH meter. Therefore, the prepared real-life model concluded that the fabricated b-STNG can successfully detect the unknown pH of rainwater in real-time. Real-time information on the pH properties of raindrops is crucial for determining the level of danger rainfall might cause to the environment. Thus, actual information on the pH properties of raindrops can be predicted to reduce possible harm by enabling prompt preparedness for acid rain in our daily lives.

Numerous health issues, including those related to the skin, heart, lungs and bones have been directly and indirectly linked to acid precipitation. Toxic metals can leach into groundwater and water bodies due to acid rain. These metals henceforth pollute drinking water and build up in the food chain leading to renal dysfunction, brain and blood disorders and various cancers. Acid rain also affect plants to quite an extent. These damages mainly include decreased growth and productivity owing to the damage to photosynthetic process and reproductive parts. Higher level of acid concentration in soil also modifies genes that are critical for their defence against abiotic stress. It can also causes soil acidification, modifies the microbial and enzymatic activity and the equilibrium of carbon and nitrogen metabolism. Therefore, it is crucial to promptly

determine whether the rainfall is acidic in nature and to take appropriate safeguards for the safety of all living things. Since many renowned architectural buildings which are part of cultural heritage are constructed of calcareous materials like marble and limestone. Acid rain harm these materials, highlighting the importance of conservation. Taj Mahal, one of the Seven Wonders of the World is an Indian marble mausoleum that reacts with acid rain, which has resulted in the monument developing pits, decolourization and becoming lustreless. The raindrop powered b-STNG might be used to promptly determine pH of rainwater and assist in the execution of preventive actions to save these historically significant buildings if implemented close to such architectural monuments.

5.4. Summary

In summary, a bio-inspired, highly hydrophobic, single electrode TENG was developed operating under liquid-solid contact electrification that could harvest mechanical energy not only from simple finger contact but also from water droplets. To create the negative triboelectric layer (b-APC), a unique 'replication' approach employing template sacrifice methodology was utilized. The triboelectric surface had micro motifs shaped like boats, inspired by the micro patterns on petunia flower petal surface. b-APC was fabricated using PDMS, PTFE particles and synthesized Ag₂S nanoplates. The hydrophobicity of b-APC increased significantly with the addition of PTFE particles and mostly due to the introduction of rough topography on the surface of the layer, which has also been theoretically described by the Wenzel model of wetting. With the use of finite-element analysis through COMSOL Multiphysics software, potential distributions at various stages of the b-STNG power production process were modelled. The water drop driven, contact electrification based b-STNG responded to rainwater exceptionally well, showing great sensitivity to the pH of the liquid as well as to its ion concentration, due to the shielding effect of H⁺ ions. A real-life model was designed to determine the unknown pH of collected natural rainwater. This model could identify the unknown pH of collected natural rainwater instantly and displayed the value of matched pH with the help of coloured LED indicators. Thus, in addition to harvesting energy from randomly falling raindrops, b-STNG was able to predict the pH of rainfall in real-time, reducing possible environmental impact and providing prompt precaution from acid rain.

5.5. References

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Chapter 6

Upcycled Waste-Based Triboelectric Sensor for Wind Harvesting and On-Road Speed Surveillance



6.1. Introduction

The Fourth Industrial Revolution, emerging in the mid-20th century, has progressed at an exponential pace, far surpassing the rate of change witnessed during the previous three industrial revolutions [1]. The primary cause behind this rapid development is the need to reduce excessive dependence on traditional fossil fuels, to harness energy from alternative sources and to recycle/reuse waste materials for energy conversion [2]. While large-scale industries offer alternatives [3] to fossil fuels, they require large infrastructure and investment, making them impractical for capturing small-scale mechanical energy from nature or human motions. To harness micromechanical energy from nature, triboelectric nanogenerators (TENGs) have gained popularity due to their remarkable efficiency, even at very low frequencies [4]. Introduced in 2012, TENGs operate on triboelectrification and electrostatic induction [5], using Maxwell's displacement current [6] to convert mechanical energy into electricity through four working modes. Wind energy harvesting has become a crucial element in the global quest for sustainable and renewable energy solutions [7]. According to research, the potential of global wind energy is about 5.3×10^{13} kWh annually [8]. TENGs can harvest energy from sporadic breezes from the environment, which include wind gusts produced by passing cars on the roads [9] as well. Recently, Jiang et al. fabricated a fur-brush dish triboelectric nanogenerator based on segmented structure, which could harvest low-speed wind energy for powering traffic light systems [10]. Sharma et al. reported a cylindrical spinning TENG for harvesting low-grade wind energy from highways, utilizing empirical analysis and theoretical modelling [11]. Most wind energy based TENGs use expensive materials, raising device costs. Further research is needed to reduce these expenses and enhance affordability.

Expanded polystyrene (EPS), a non-biodegradable plastic which is sold as thermocol or styrofoam, is widely used for disposable food containers and packaging. In today's throwaway culture, it often ends up in landfills or as marine debris. Waste polystyrene can be reused as a triboelectric layer in TENGs [12] due to its strong tribonegative properties, as indicated by the triboelectric series. Banana is world's second most produced fruit and India producing 31.5 million tons due to its suitable climate, becomes the leading producer. Banana pseudostems, making up over 60% of the plant [13], become major agricultural

waste after each harvest. Rich in carbon based organic components, pseudostem waste can take two years to decompose. Since it contains about 60–65% cellulose by dry weight, it can serve as a raw material for TENGs instead of ending up in landfills. Cellulose is the most abundant natural polymer on earth and can also be an interesting option as a triboelectric material due to its biocompatible nature. Natural cellulose has a tribopositive nature and facilitates effective charge transfer when paired with strong negative triboelectric materials [15]. Therefore, a waste based TENG was designed, utilizing polystyrene from packaging waste and cellulose from discarded banana pseudostems, highlighting the use of waste-derived raw materials. Nylon 66 was selected as the additional component for the tribopositive layer of the device due to its highly tribopositive nature, attributed to the presence of $-NH_2$ groups [15]. Electrospun nylon 66 nanofibers [16] were fabricated due to its large contact area which enhances the triboelectric effect.

The tribopositive layer of the TENG was fabricated by embedding extracted cellulose fibers structured in a micro-skeleton architecture, onto electrospun nylon 66 nanofibrous mat. For the tribonegative layer, discarded polystyrene pieces were sourced from a nearby crockery store and then recycled to create a free-standing, microporous polymeric film. The spacer-less w-TNG which was designed with a unique butterfly shape, features entirely porous and all-fiber components, making the device exceptionally lightweight. This is an important characteristic for efficient energy harvesting from light airflow as well as from simple finger touch. To validate the wind energy harvesting ability, the spacer-less, butterfly-shaped device was tested under varying parameters. Since w-TNG can effectively capture energy from irregular wind gusts, placing it near a passing vehicle enabled it to generate output signals driven by the air currents produced by the vehicle's motion. Based on this concept, w-TNG was utilized for detecting vehicle speeds on the road and issuing over-speed warnings via a red LED indicator through a wireless speed monitoring system, contributing to enhanced road safety. Therefore, the air current-based speed detection and wireless over-speed surveillance system proves especially beneficial in hilly regions, where roads are narrow and have numerous hairpin bends.

6.2 Experimental section

6.2.1. Materials required

Banana pseudostem was collected from a nearby banana plantation and waste polystyrene was obtained from discarded packaging materials. Sodium hydroxide solution NaOH (99.9% Sigma–Aldrich), glacial acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) ($\geq 99\%$ Sigma–Aldrich), sodium hypochlorite solution (NaOCl) (available chlorine 4.00–4.99 %, Sigma–Aldrich), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) ($\geq 99\%$ Sigma–Aldrich), nylon 66 pellets ($\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2$)_n (Otto Chemie), formic acid (HCOOH) (98% SRL chemicals), acetone (CH_3COCH_3) ($\geq 99.5\%$ Sigma–Aldrich) DMF (N,N-Dimethylformamide, $\text{HCON}(\text{CH}_3)_2$) ($\geq 99.8\%$ Sigma–Aldrich), Chloroform (CHCl_3) ($\geq 99.5\%$ Sigma–Aldrich) and de-ionized (DI) water. All reagents used were of analytical grade and maximum purity, which were used without further purification.

6.2.2. Microfibrous cellulose fabrication from pseudostem waste

Step 1: The banana plant pseudostem which was collected from a banana plantation site, was chopped into small fragments, washed with deionized water and dried at 60°C for 8 hours. To 80 g of dry pseudostem fragments, 2% NaOH solution was added and was subjected to vigorous stirring on a magnetic stirrer for 3 hours. After the alkali treatment,

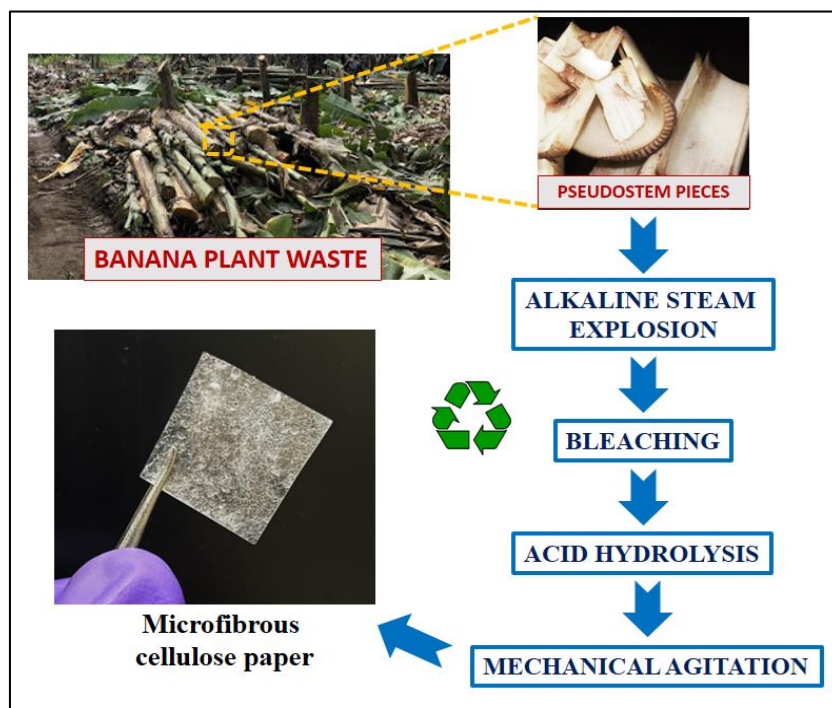


Figure 6.1. Extraction of microfibrous cellulose paper from waste banana pseudostem

this concoction was then transferred to a teflon-lined stainless steel autoclave setup and was heated at 120°C for 2 hours. It was allowed to cool to room temperature and after the autoclave's internal pressure decreased, the pseudostem fibers were collected. The fibers were then repeatedly cleaned with DI water until the solution reached pH 7 and then dried at 70°C for 2 hours. This process is known as alkaline steam explosion treatment.

Step 2: This step included the bleaching of the steam exploded fibers. A mixture of NaOH (27 g) and acetic acid (78.8 g) were added to the steam-exploded fibers and then subjected to stirring on a magnetic stirrer. In addition to this, a 1:3 volume ratio of sodium hypochlorite solution was also added. This bleaching procedure was carried out six times, taking one hour each time. Following the bleaching process, the discoloured fibers were thoroughly cleaned several times with DI water to eliminate the odor of the bleaching chemicals, before being dried completely.

Step 3: To the bleached fibers, 10 ml of oxalic acid was added and the mixture was heated in an autoclave setup at 120°C for 2 hours, to obtain high pressure. Next, it was cooled to room temperature to release the pressure and again, the mixture was subjected to heating in an autoclave at 120°C for 30 minutes. The fibers were then removed and washed thoroughly until the rinse water no longer decolorized the KMnO_4 solution. This step is called the acid hydrolysis process.

Step 4: This step included the mechanical agitation of the chemically treated fibers. The steam exploded, bleached and acid hydrolyzed fibers were suspended in DI water and was stirred for 4 hours using a mechanical homogenizer at 8000 rpm. The white-coloured suspension was then poured in a petri dish and was dried at 80°C, to obtain a white colour microfibrinous cellulose paper. The complete extraction process of cellulose is illustrated in the flowchart shown in figure 6.1.

6.2.3. Fabrication of freestanding nylon 66 fibrous mat

Nylon 66 nanofibers were fabricated using the electrospinning technique. To prepare the fibrous mat, nylon 66 pellets (20 wt./V %) were dissolved in formic acid by stirring it for 12 hours at 600 rpm. After the complete dissolution of nylon 66 pellets in formic acid, acetone was added to the solution. This prepared solution was then loaded in a syringe. Certain parameters were configured in the electrospinning unit, including the temperature

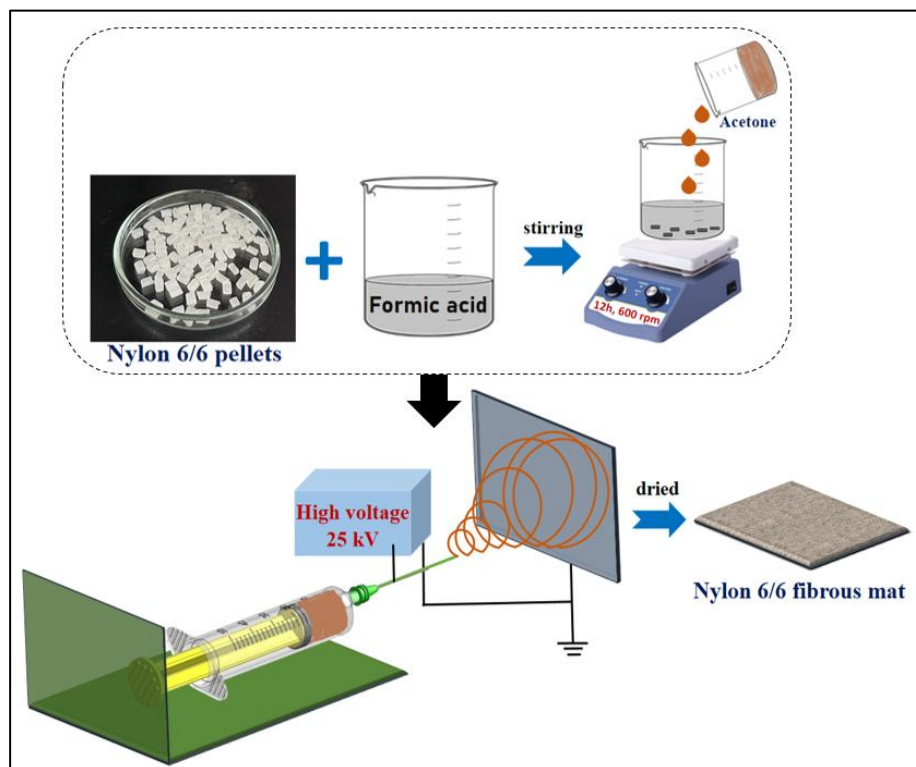


Figure 6.2. Electrospinning-based fabrication process of nanofibrous nylon 66 mat

of 25°C and the humidity not exceeding 40%. To extract the solution using a pump, the flow rate was set to 1.2 ml/hour, with the syringe needle positioned 12 cm from the fiber collector plate (aluminium foil). The electrospinning process was carried out at a very high voltage of 25 kV for 10 hours. As a result, nylon 66 nanofibers accumulated all over the aluminium foil, which was later peeled off and used as a nylon 66 fibrous mat. The electrospinning-based fabrication process has been illustrated in figure 6.2.

6.2.4. Fabrication of cellulose imbued nylon 66 mat (tribopositive layer)

For the preparation of the tribopositive layer, firstly a small portion (0.2 mg) of the microfibrillar cellulose paper was mixed with 2 ml of DMF and stirred vigorously on a magnetic stirrer at 50°C for 4 hours. The solution was then sonicated for 15 minutes to achieve a homogeneous suspension of cellulose microfibrils. Next, 0.5 ml of this suspension was evenly spread over a rectangular section (3.5 cm × 2.5 cm) of the nylon 66 fibrous mat. The coated mat was dried at 50°C for 6 hours. This process resulted in cellulose microfibrils

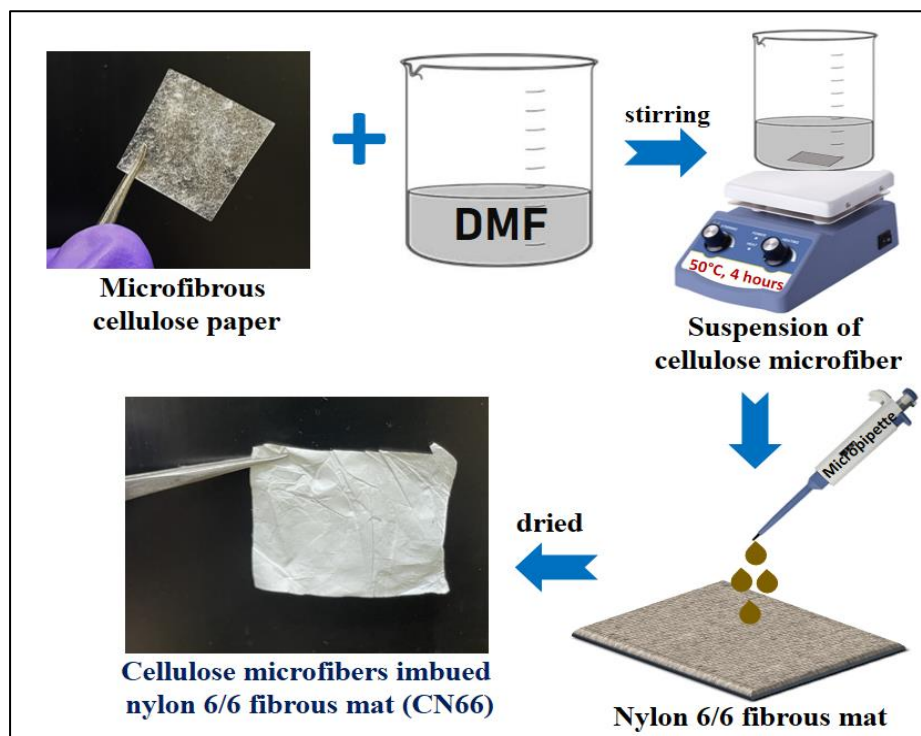


Figure 6.3. Fabrication of all-fibrous CN66 film using nylon 66 mat and cellulose paper

imbued nylon 66 fibrous mat, named as CN66, serving as the all-fibrous tribopositive layer of the triboelectric nanogenerator. The process of fabricating the all-fibrous CN66 film using nylon 66 mat and cellulose paper is depicted in figure 6.3.

6.2.5. Fabrication of microporous polystyrene film (tribonegative layer)

Firstly, some discarded polystyrene packaging boxes were collected from a nearby crockery store. Few pieces were taken and thoroughly cleaned with liquid soap and tap water multiple times to remove any remaining dirt and left to dry at room temperature. 400 mg of this dry and clean polystyrene was cut into tiny pieces and were mixed with 5 ml of chloroform in a clean vial. The vial was shaken a few times, resulting in the immediate formation of a clear polystyrene solution. This transparent solution was carefully poured onto a clean, dry glass petri dish and was gently tapped to ensure even distribution of the solution on the petri dish surface. It was left to dry overnight at room temperature, forming

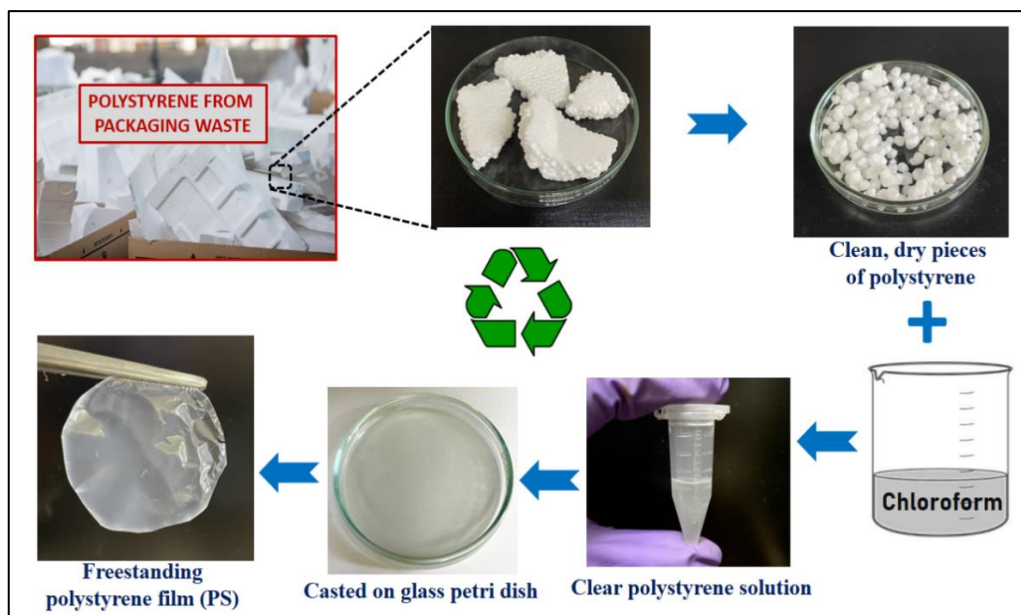


Figure 6.4. Fabrication steps of freestanding PS film derived from discarded packaging materials

a freestanding polystyrene film that was carefully peeled off from the glass petri dish. The steps for fabricating the porous polystyrene film named as PS from discarded packaging materials are illustrated in figure 6.4 and it served as the tribonegative layer of the TENG.

6.2.6. Butterfly-shaped triboelectric nanogenerator (w-TNG):

To capture erratic wind gusts, the TENG was designed with a simple butterfly structure, enabling it to harvest electrical energy even from a light breeze. The butterfly shaped w-TNG structure has been designed based on wind-driven fluttering CN66 and PS

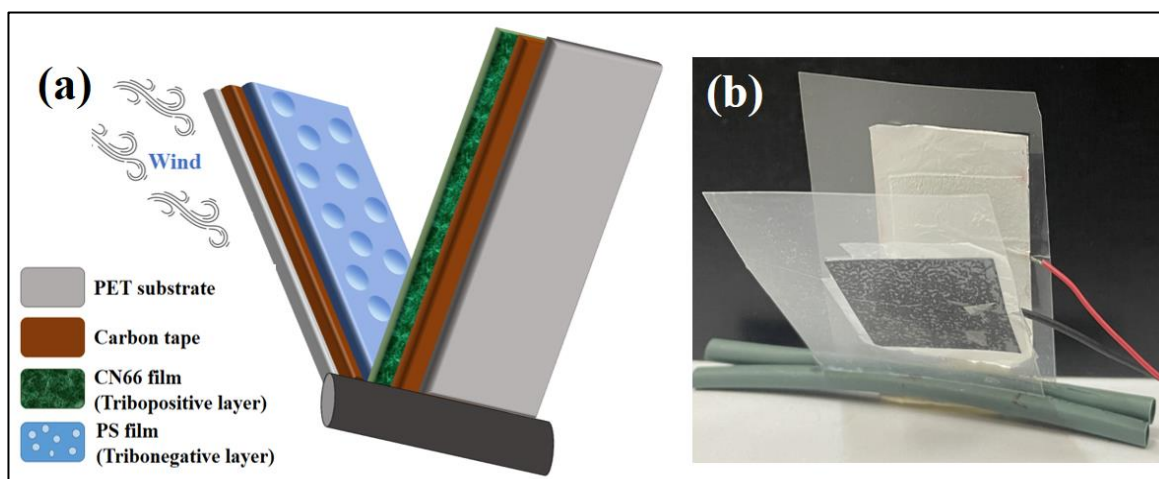


Figure 6.5. (a) Schematic diagram of the butterfly shaped w-TNG, (b) Digital photo of w-TNG

films along with two carbon tape layers attached on two polyethylene terephthalate (PET) sheets respectively. First, two rectangular PET pieces (3.6 cm × 2.6 cm) were used as the substrate to provide outer support for the device. Next, rectangular sections of carbon tape (3.5 cm × 2.5 cm) were then affixed to the substrates, which served as the two electrodes. CN66 (tribopositive layer) and PS film (tribonegative layer) sections of the same dimensions, were attached to the electrodes with connecting wires placed in between them to facilitate electrical measurements. A small rubber tube with a 6 mm diameter was used as the central support for the device. The two triboelectric layers were inserted breadthwise into the two adjacent slits of the rubber tube and affixed at an angle, giving the device a butterfly-like shape. The schematic diagram of the assembled w-TNG, with the components and design, has been illustrated in figure 6.5(a) and the digital image of w-TNG is shown in figure 6.5(b).

6.3. Working mechanism of wind driven w-TNG

The designed w-TNG operates based on contact electrification and electrostatic induction [17] between the two triboelectric layers CN66 and PS, generating high output voltage and moderate output current. TENGs produce electricity by periodically bringing two vertically separated dielectric materials into contact and then releasing them through an externally applied mechanical force. As a result, alternating current is produced between electrodes connected to the respective dielectric materials [18]. Figure 6.6 illustrates the schematic representation of the working principle of the designed w-TNG, under the influence of an external mechanical force.

Step I: Initially, the two triboelectric layers CN66 and PS are positioned at a fixed distance apart. When an external force is applied on w-TNG, the two triboelectric layers come into very close proximity, causing electron transfer from the surface of tribopositive CN66 to tribonegative PS, as can be seen from figure 6.6(I). The two triboelectric layers get oppositely charged as a result of contact electrification and if the triboelectric layers have very limited conductivity or insulation properties, these charges are bounded to the surfaces in the form of static charges. When two triboelectric materials come into close contact their electron clouds overlap, which allow electrons to move from one material to another if the distance between their atoms is smaller than that of their bond length [18,19]. Hence, this

overlapping of electron clouds can explain the charge transfer process between two triboelectric layers coming into contact, due to the application of force.

Step II: When the external force is removed, allowing the w-TNG to return to its original form, the CN66 and PS layers begin to separate. This separation reduces the electrostatic effect of surface charges comparative to each other. Consequently, due to electrostatic induction, opposite polarity charges get gradually generated on the electrodes connected to each triboelectric layer, leading to the formation of a potential difference between CN66 and PS. Hence, current flowing through the external circuit was obtained [20], as depicted schematically in figure 6.6(II).

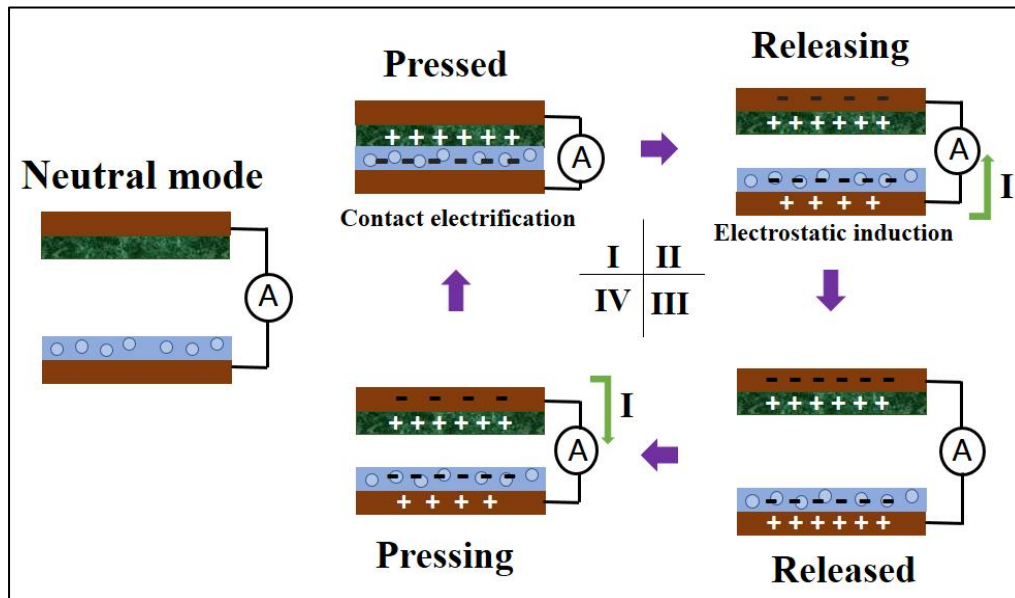


Figure 6.6. Working principle of w-TNG under the influence of an external mechanical force

Step III: At this stage, the external force is fully withdrawn, causing the induced charge density on the respective electrodes to reach its peak value, as can be seen from figure 6.6(III). This occurs because in this position the electrostatic effect of surface charges on each other is minimal [18]. When the potential difference between the electrodes reaches the peak value, an instant current flows through the external circuit connecting the two electrodes attached to the triboelectric layers. This flow of current takes place in order to equalize the potential difference between the two electrodes [20].

Step IV: When w-TNG is again compressed by an external force, that is the gap between CN66 and PS begins to decrease, the electrostatic interaction between the two

interacting surfaces of the respective triboelectric layers begins to increase. As a result, the density of the generated charge on the two electrodes steadily drops and approaches zero, leading to a flow of current in the opposite direction [18] as indicated by the arrow in figure 6.6(IV). Thus, the entire four-stepped process enables the conversion of mechanical energy into electrical energy on the application of periodic force. A continuous alternating electrical output is produced by w-TNG due to the repeated contact and separation between CN66 and PS films.

Recently, Dr. Wang has formally established the theories explaining the electrical output of triboelectric nanogenerators [21, 22] deriving them from Maxwell's equations. The Ampere's circuital law with Maxwell's correction can be written as:

$$\nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} \quad (1)$$

Here, the magnetizing field is represented as $\mathbf{H}$, free electric current density inside a material is represented as $\mathbf{J}_f$ and the electric displacement field is represented as $\mathbf{D}$. The term $\frac{\partial \mathbf{D}}{\partial t}$ in equation (1) represents the displacement current. The electric displacement field $\mathbf{D}$ can be represented as:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} + \mathbf{P}_s \quad (2)$$

Here, $\mathbf{E}$ represents the electric field, $\mathbf{P}$ represents the polarization of the medium which is induced by the electric field. The term $\mathbf{P}_s$, also known as the Wang term, refers to the polarization induced by electrostatic surface charges as a result of mechanical excitation. After incorporating this surface polarization term into the displacement vector, the Maxwell displacement current can be expressed as [23]:

$$\mathbf{J}_D = \epsilon \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}_s}{\partial t} \quad (3)$$

Considering the four-layer triboelectric nanogenerator w-TNG (with two dielectric layers denoted as 1 and 2; and two electrodes) operating in contact-separation mode. On the application of force on the TENG, the two dielectric layers come into contact and the electrostatic field generated by the triboelectric charges leads to electron flow through the external circuit. Due to this, the free electrons start to accumulate in the electrode, which depends on the distance $z(t)$ between the two dielectric layers. The electric fields for the dielectric layers 1, dielectric layers 2 and gap between them can be represented as $\mathbf{E}_z = \frac{\sigma_1(z,t)}{\epsilon_1}$,

$E_z = \frac{\sigma_1(z,t)}{\epsilon_2}$ and $E_z = \frac{\sigma_1(z,t) - \sigma}{\epsilon_0}$, respectively, where σ represents the surface charge density and $\sigma_1(z,t)$ is the surface charge density in the electrodes. Thus, between the two electrodes, the relative voltage drop can be represented as [22]:

$$V = \sigma_1(z,t) \left[\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2} \right] + z \left[\frac{\sigma_1(z,t) - \sigma}{\epsilon_0} \right] \quad (4)$$

It is known that in the case of a short circuit, $V = 0$, therefore:

$$\sigma_1(z,t) = \frac{z\sigma}{\frac{d_1\epsilon_0}{\epsilon_1} + \frac{d_2\epsilon_0}{\epsilon_2} + z} \quad (5)$$

The surface polarization (P) can be represented as $P = \sigma n$, where n denotes a unit normal to the corresponding surface. Therefore, it is possible to represent the displacement current density produced by surface polarization as [22]:

$$J_D = \frac{\partial P}{\partial t} = \frac{\partial \sigma_1}{\partial t} = \sigma \frac{\partial z}{\partial t} \frac{\frac{d_1\epsilon_0}{\epsilon_1} + \frac{d_2\epsilon_0}{\epsilon_2}}{\left[\frac{d_1\epsilon_0}{\epsilon_1} + \frac{d_2\epsilon_0}{\epsilon_2} + z \right]^2} \quad (6)$$

6.4. Results and discussion

6.4.1. Morphological characteristics and 3D surface profile analysis of the polymeric films

Field Emission Electron Microscopy (FESEM) was used to examine the surface morphology of chemically treated microfibrous cellulose extracted from banana pseudostem at different stages, focusing on micron scale features of the fibers. Figure 6.7(a) presents the FESEM image of untreated banana pseudostem fibers that were simply rinsed with deionized water and were dried. The surface of the chemically untreated fibers appears relatively smooth, with fiber diameters ranging from 9 μm to 15 μm . This suggests that in the untreated pseudostem, the cellulose fibers were bound together by ‘natural binders’ (cementing materials) such as pectin, hemicellulose and lignin. In this stage, many cellulose fibers remain bonded together as lignin functions as a binding agent by creating bridging bonds with the cellulose esters [24]. Figure 6.7(b) displays the FESEM image of cellulose fibers that have undergone steam explosion and bleaching procedures. The micrograph taken after the alkali treatment reveals defibrillation of the fibers, resulting from the steam explosion process. The fiber surfaces appear rough and broken, suggesting that the alkali treatment led

to the fractional dissolution of non-cellulosic substances like pectin, hemicellulose, lignin and other impurities [25]. The treatments also led to partial swelling of the cellulose fibers, causing them to start breaking apart and separating into individual fibers [24]. The morphological characteristics suggest that both intensive bleaching and as well as alkali

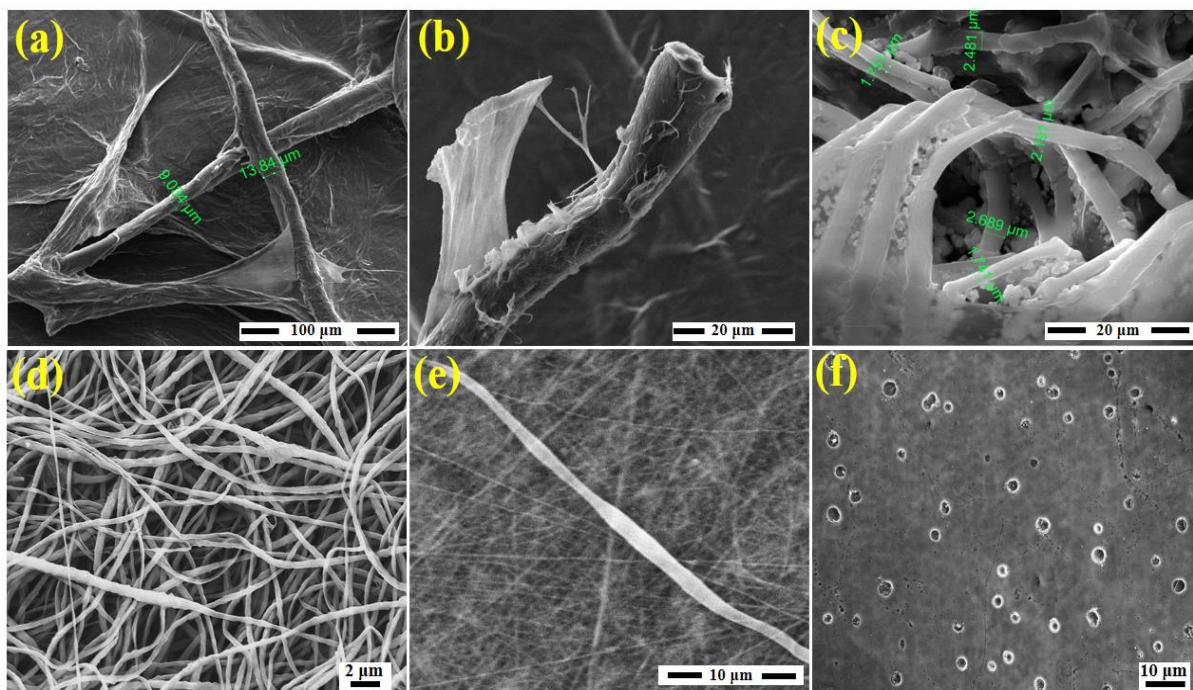


Figure 6.7. FESEM image of (a) Untreated fibers, (b) Defibrillated cellulose fibers after steam explosion and bleaching, (c) Acid-hydrolyzed cellulose fibers with microstructure, (d) Electrospun nylon 66 nanofibrous mat, (e) CN66, (f) Micrograph of microporous PS film

treatment are essential for effectively removing the non-cellulosic cementing materials (namely hemicellulose and lignin) upto a desired level. The fibers underwent mild acid treatment to reduce the fiber diameter even further. Figure 6.7(c) displays the FESEM image of acid-hydrolyzed cellulose fibers, clearly revealing the fibrous cellulose microstructure resulting from further removal of cementing materials. During the acid hydrolysis process, the fibers separate into individual fibrils, leading to a reduction in diameter from 9 μm -15 μm to approximately 1 μm -5 μm . However, the image shows that several cellulose microfibrils have aggregated due to water evaporation while drying the fibers, leading to the formation of larger fiber bundles.

The surface morphology of the nylon 66 fibrous mat was also analyzed using FESEM, which confirmed a nanofibrous structure, as illustrated in figure 6.7(d). The image validates

that highly uniform nanofibers with an average diameter of about 71 nm were successfully produced through the electrospinning process, which were free from any aggregation. The nano-architecture of the nylon 66 mat offered a large contact area between the active triboelectric friction surfaces. The nanofibers were produced as surface modifications, which significantly enhanced the generation of triboelectric surface charges, thereby boosting the overall electrical performance of the TENG. Figure 6.7(e) presents the FESEM image of the all-fibrous CN66, which consisted of a nylon 66 fibrous mat embedded with cellulose microfibers. The image reveals a cellulose microfiber, approximately 2 μm in diameter, integrated onto the surface of the nylon 66 nanofibrous layer. The polystyrene (PS) film exhibited a microporous structure as confirmed by figure 6.7(f) obtained using an optical microscope. The image reveals numerous microscopic pores evenly distributed throughout the film, with average pore diameters ranging from 2 μm to 5 μm .

The three-dimensional surface profiles of the polymeric films were reproduced using ImageJ analysis software, based on the FESEM images [15]. In accordance with the FESEM images, 3D surface profiles of the microfibrinous cellulose paper, CN66 polymeric film and PS

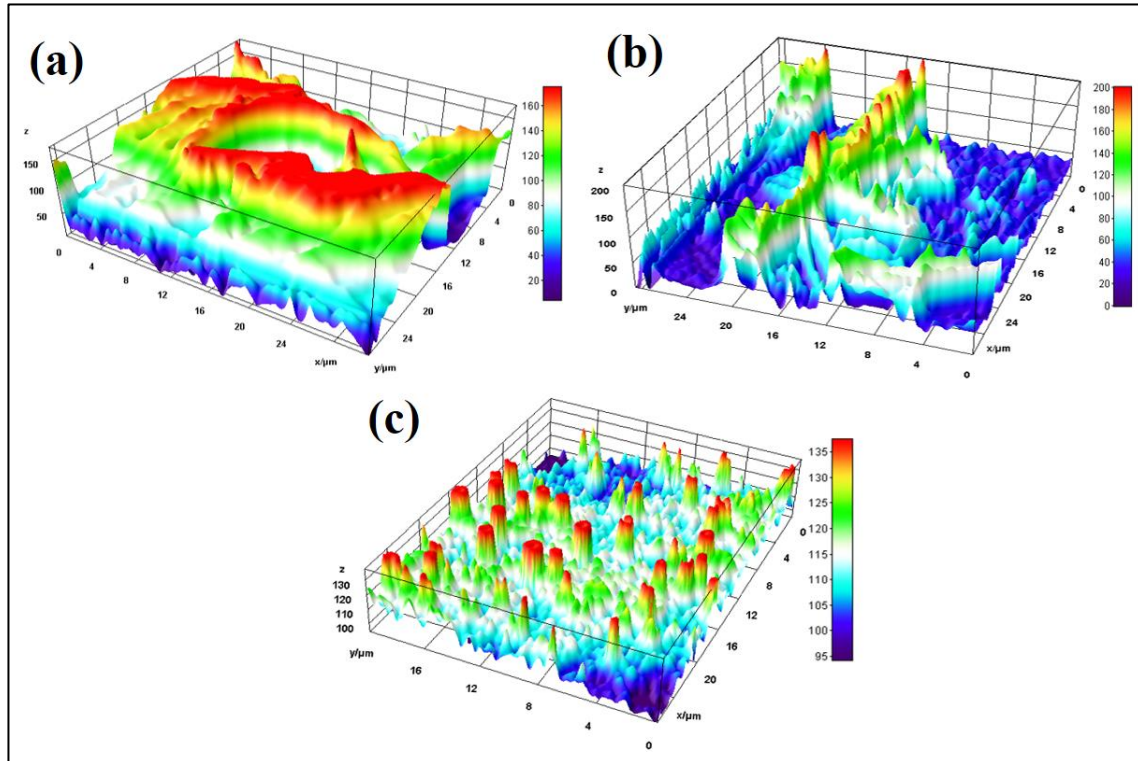


Figure 6.8. 3D surface profile analysis using ImageJ software from FESEM image

film have been created. The surface profile shown in figure 6.8(a) corresponds to the FESEM image of cellulose paper depicted in figure 6.7(c), revealing a microstructure like rough surface topology. The surface profile in figure 6.8(b) corresponds to the FESEM image of microfibrillar CN66 depicted in figure 6.7(e), illustrating the roughness of nylon 66 fibers and the presence of the cellulose fiber on the nylon 66 mat. The 3D surface profile of microporous PS has been depicted in figure 6.8(c) which was reproduced from the FESEM image in figure 6.7(f). This inverted surface plot of the PS film shows the depth of the pores present in it and their even distribution across the film. The 3D surface profiles of the polymeric films suggest that they have noteworthy surface roughness, providing a high contact area between the triboelectric layers during friction.

6.4.2. Structural analysis of CN66 and PS films (X-ray diffractogram)

To gain deeper insight into the structural characteristics, X-ray diffraction analysis was conducted on the polymeric films. Figure 6.9(a) presents the diffractogram of nylon 66, revealing four distinct patterns. Notably, three sharp reflection peaks appear at 2θ values of 13.4° , a doublet near 24° and another peak at 20° , corresponding to the (002), (010, 110) doublet and (100) planes, respectively. These peaks are characteristic of α -type nylon 66 crystals arranged in a triclinic unit cell [26]. Figure 6.9(b) presents the diffractogram of the extracted cellulose paper. The cellulose-I structure was indicated by the main diffraction peaks that were seen at $2\theta = 16^\circ$, 22.5° and 34.5° , which matched the crystallographic planes of (110), (200) and (040) respectively [27].

The prominent peaks observed in the diffraction pattern of CN66 correspond to those of cellulose and nylon 66, confirming the coexistence of both components within the CN66 film. In the CN66 diffraction pattern, peaks for nylon 66 are marked with a red star (*) and those for cellulose with a green plus (+). Two prominent diffraction peaks were detected at 2θ values of 22.5° and 34.5° , corresponding to the (200) and (040) crystallographic planes as can be seen in figure 6.9(c). These sharp and distinct characteristic peaks observed in CN66 signify that the extracted cellulose fibers from the banana pseudostem possess a highly crystalline cellulose-I structure [40]. The diffractogram of CN66 also confirms the presence of nylon 66 polymer in it. A prominent reflection peak appears at 2θ value of 13.4° , corresponding to (002) plane of α -type nylon 66 crystals, which are oriented in a triclinic

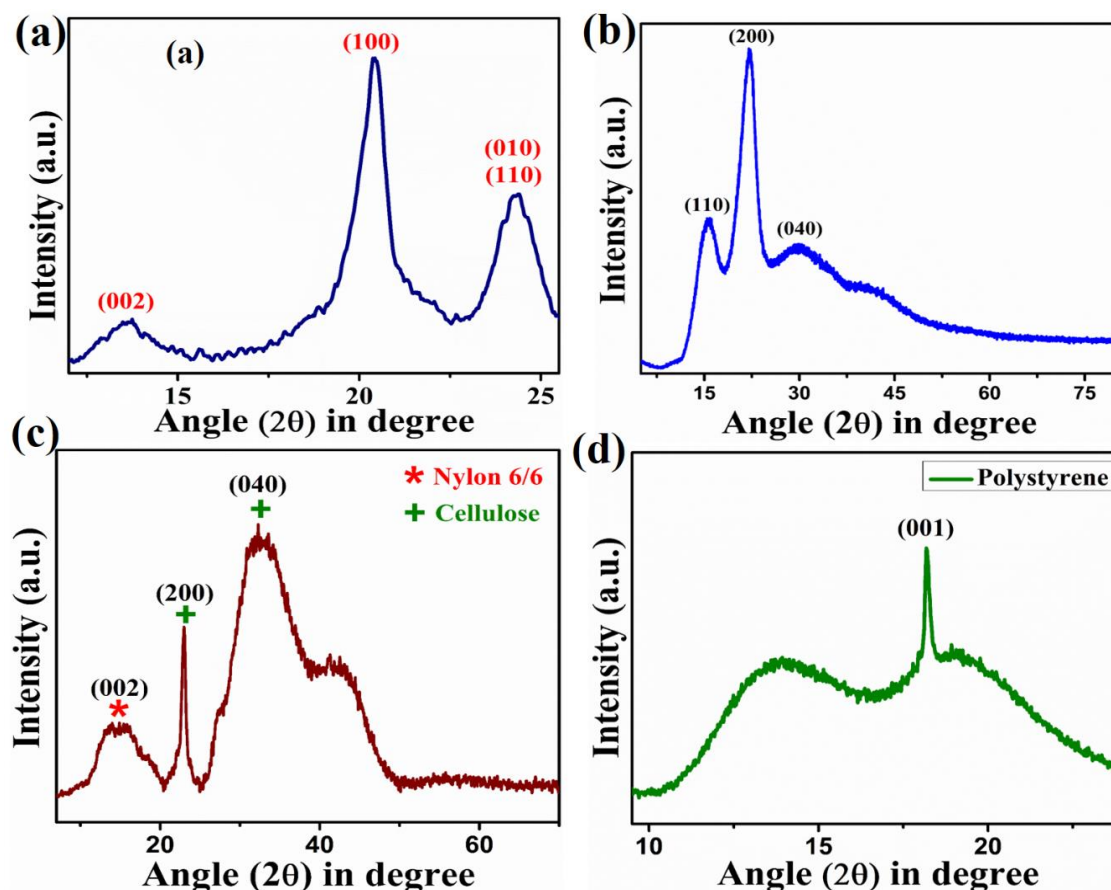


Figure 6.9. XRD of (a) pure nylon 66, (b) extracted cellulose paper, (c) CN66 film and (d) PS film

unit cell structure [28]. Figure 6.9(d) displays the XRD spectrum of the microporous PS film derived from waste packaging materials. The diffractogram features a broad peak around $2\theta = 19.33^\circ$, corresponding to the (001) reflective plane, suggesting a minor degree of local ordering within the polystyrene chains. This diffraction peak indicates the semicrystalline nature of the polystyrene film [29].

6.4.3. FTIR spectroscopy analysis of CN66 and PS films

Fourier Transform Infrared (FTIR) spectroscopy was conducted in transmittance mode to accurately comprehend the dynamics of the fabricated polymeric films. The FTIR spectra of nanofibrous nylon 66 electrospun mat has been represented in figure 6.10(a). Bands with wavenumbers of 3301 cm^{-1} and 2934 cm^{-1} were observed which corresponded to N–H stretching vibration and $-\text{CH}_2$ stretching vibration, respectively. Furthermore, the presence of $-\text{CH}$ symmetric stretching vibration, $-\text{C}=\text{O}$ stretching vibration and N–H bending vibration in the nylon 66 correspond to the bands seen at wavenumbers 2860 cm^{-1} , 1637

cm^{-1} and 1536 cm^{-1} , respectively [30]. Bands observed at 1354 cm^{-1} and 1149 cm^{-1} corresponded to amide III band/ CH_2 rocking vibration and CCH symmetric bending/ CH_2 twisting respectively. At 1128 cm^{-1} and 959 cm^{-1} , bands were also observed which corresponded to CCH symmetric bending and C–C stretching. A band at 549 cm^{-1} was also observed which corresponded to $\text{O}=\text{C}-\text{N}$ bending [31]. The FTIR spectra of the extracted microfibrinous cellulose paper has been represented in figure 6.10(b). The presence of bands at 1735 cm^{-1} , 1370 cm^{-1} , 1034 cm^{-1} , and 761 cm^{-1} , as shown in the graph correspond to cellulose. At 1640 cm^{-1} , the $-\text{OH}$ bending of adsorbed water was seen [32]. The FTIR signal at 1574 cm^{-1} , 1525 cm^{-1} (aromatic ring vibration) and 1245 cm^{-1} represent lignin residues that are present in cellulose paper [33].

In the FTIR spectra of CN66, nylon 66 bands are marked with a red star (*) and cellulose bands with a green plus (+). As depicted in figure 6.10(c), for CN66 notable bands were detected at wavenumbers of 3301 cm^{-1} and 2934 cm^{-1} , corresponding to N–H stretching vibration and $-\text{CH}_2$ stretching vibration respectively, which corresponded to nylon 66 fibers. Moreover, the peaks observed at wavenumbers 2860 cm^{-1} , 1637 cm^{-1} and 1536 cm^{-1} are associated with the presence of $-\text{CH}$ symmetric stretching vibration, $-\text{C}=\text{O}$ stretching vibration and N–H bending vibration associated to nylon 66, respectively. A few bands appearing in the 1475 cm^{-1} to 1275 cm^{-1} range are associated with the bending vibrations of CH_2 . At 936 cm^{-1} , the crystalline phase of the amide stretching mode ($\text{C}-\text{C}=\text{O}$) was also observed, followed by a band at 1200 cm^{-1} was seen corresponding to the carbonyl wagging mode [35]. The existence of nylon 66 fibers in the CN66 polymer matrix is confirmed by these distinctive bands on the infrared spectrum. In figure 6.10(c), peaks were observed in the range of 1830 cm^{-1} to 1730 cm^{-1} , attributed to functional groups like methoxyl ($-\text{O}-\text{CH}_3$), C–O–C linkages, and aromatic C=C bonds, indicating the presence of cellulose within the polymeric film CN66. The existence of C=O linkage, a distinctive group of lignin and hemicellulose at 1765 cm^{-1} - 1715 cm^{-1} may be the cause of the peak at 1736 cm^{-1} in the spectrum that corresponds to the cellulose fiber in CN66. This band may also indicate carboxyl or aldehyde absorption, which might result from the oxidation of the C-OH groups or from the opening terminal of glycopyranose rings. When cellulose is treated with alkali during the extraction process, the hydroxyl groups get removed by the reaction with

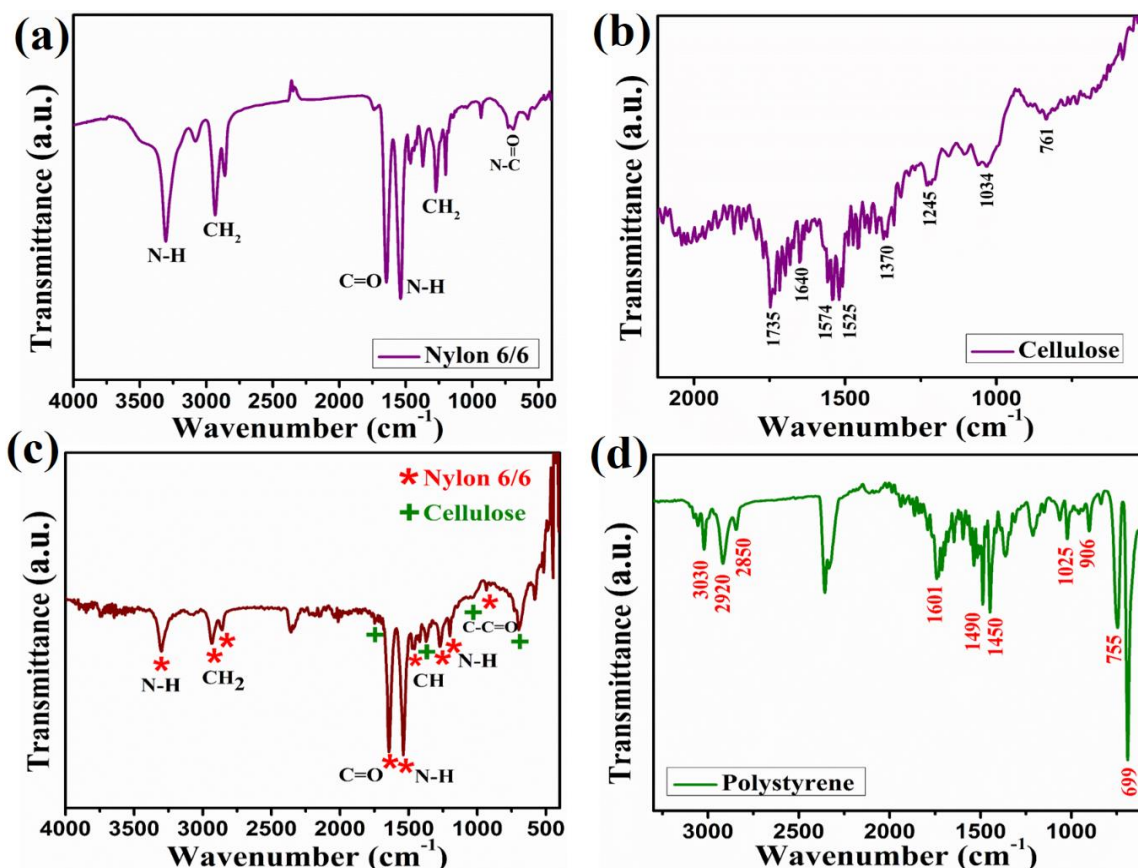


Figure 6.10. (a) FTIR spectra of pure nylon 66, (b) FTIR spectra of extracted cellulose paper, (c) CN66 film and (d) PS film

sodium hydroxide, which decreases hydrogen bonding. As a result, the concentration of -OH bonds in the spectrum rises [36]. The bands obtained at 1370 cm^{-1} correspond to the C-H stretching mode of cellulose. Previous studies show that the xyloglucan fractions linked to non-hydrolyzed hemicelluloses firmly bonded inside the cellulose microfibrils were responsible for the peak that appeared at around 1034 cm^{-1} in the spectrum. The band observed at 761 cm^{-1} corresponded to the C-H strains due to the presence of some lignin in the cellulose microfibrils [37].

Figure 6.10(d) shows the FTIR spectrum of the porous polystyrene polymeric film in transmittance mode. In the spectra, aromatic C-H stretching vibration is responsible for the bands observed at wave numbers 3030 cm^{-1} , whereas aromatic C=C stretching vibration represented the existence of benzene rings and has been responsible for the bands observed at wave numbers 1490 cm^{-1} and 1450 cm^{-1} . The presence of only one substituent on the benzene ring has been indicated by the band that emerged at wave numbers of around 750

cm^{-1} and 700 cm^{-1} , which corresponded to the C-H out-of-plane bending vibration [38]. The existence of bands with wave numbers of around 2920 cm^{-1} and 2850 cm^{-1} indicated the presence of methylene. The aromatic C=C stretching vibration has been identified as the source of the IR transmission band at 1601 cm^{-1} . The in plane =C-H deformation is represented by the band at 1025 cm^{-1} , however the out of plane =C-H deformation is represented by the bands at 906 cm^{-1} and 755 cm^{-1} . Moreover, the peak at 699 cm^{-1} indicates the out-of-plane aromatic deformation, as can be seen from FTIR spectra [39].

6.4.4. Surface potential measurements of the polymeric films

The relative surface potentials produced on the pristine nylon 66 fibrous mat, microfibrillar cellulose paper, tribopositive friction layer CN66 and tribonegative friction layer PS were measured following the contact-separation between the tribopositive and tribonegative surfaces. Measurements were taken over the course of 80 cycles, with data collected immediately after every 20 cycles, under a constant applied force of 5 N and at a frequency of 5 Hz. The probe of the surface potential meter was positioned 5 mm above the sample surface which was being analyzed. While evaluating the surface potential of the tribopositive materials nylon 66 mat, cellulose paper and CN66, the PS film was used as the counter tribonegative material to facilitate the contact-separation process. At the initial stage (without any friction cycles) and immediately following the contact-separation after 20, 40, 60 and 80 number of friction cycles, the pristine nylon 66 fibrous mat showed positive surface potentials of +82 V, +115 V, +189 V, +226 V and +280 V, respectively, as illustrated in figure 6.11(a). The cellulose fibrous paper exhibited surface potentials of +8 V, +42 V, +78 V, +102 V and +128 V at the initial stage and after 20, 40, 60 and 80 number of friction cycles with PS film. The initial and subsequent surface potential values of the cellulose surface were lower than those of nylon 66, due to its relatively lower tribopositive nature as indicated by the triboelectric series. As shown in the graph in figure 6.11(a), the positive surface potential of CN66 was recorded at +96 V initially and increased to +185 V, +264 V, +392 V and +540 V after 20, 40, 60 and 80 friction cycles, respectively. The comparison of the positive surface potential values of the individual triboelectric materials (cellulose and nylon 66) with that of CN66 motivated the incorporation of cellulose microfibers onto the nylon 66 fibrous mat, aiming to enhance the triboelectric nature of the tribopositive layer in w-TNG. The graph

also illustrates that surface potential values rise with an increasing number of friction cycles. This is attributed to the enhanced charge transfer between the triboelectric surfaces, resulting from a greater number of contact electrification and electrostatic induction events during repeated contact-separation cycles. Similarly, for varying contact separation cycles, the negative surface potentials of the PS film were measured using the CN66 film as the counter tribopositive material. As shown in the graph in figure 6.11(b), the negative surface potential of the porous PS film was recorded at -950 V initially and got increased to -1267 V, -1442 V, -1702 V and -1845 V after 20, 40, 60 and 80 friction cycles, respectively. The initial and subsequent negative surface potential values of the PS film indicate that polystyrene is inherently highly tribonegative.

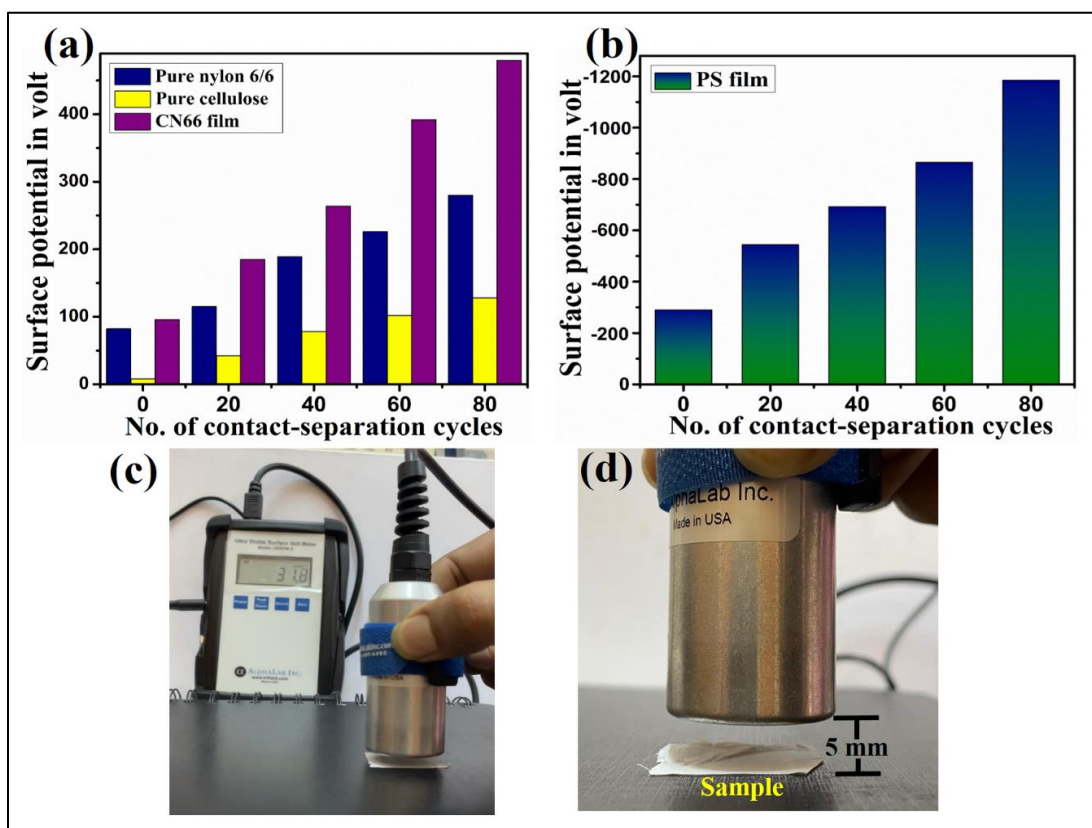


Figure 6.11. Surface potential of (a) Tribopositive materials, (b) Tribonegative PS film, (c) Experimental setup, (d) Closer image of the distance between the sample and the probe

Furthermore, repeated contact-separation cycles significantly amplified the negative potential on its surface. Figure 6.11(c) shows the experimental setup for the measurement of the surface potential value. A closer image of the distance kept between the sample and the probe during data collection, has been shown in figure 6.11(d).

6.4.5 Electrical characterization of the w-TNG

The w-TNG efficiently harvested mechanical energy from finger tapping via contact electrification and electrostatic induction. With both triboelectric layers being porous, w-TNG remained exceptionally lightweight while effectively converting minimal mechanical energy into electricity. To evaluate the impact of cellulose microfibers alongside nylon 66 microfibers on the performance of the triboelectric nanogenerator, another TENG was fabricated using the same designing procedure but utilising only electrospun nylon 66 fibers (not including cellulose fibers) as the tribopositive layer. The output results were compared with those of w-TNG. The open-circuit voltage (V_{oc}) of w-TNG on the application of constant periodic axial force, was measured by connecting it to a DSO. The periodic axial force was imparted on the TENG using fingers and it measured 11.6 N. The detailed calculation of the imparted force [41] has been provided in the appendix 4 data file. As illustrated in figure 6.12(a), w-TNG generated an output voltage of 389 V. In contrast, when subjected to the same applied force, the TENG without cellulose microfibers produced a considerably lower output voltage of 215 V, as shown in the appendix 4 data file in Figure A4.1(a). This phenomenon is clearly supported by the increase in surface potential with enhanced tribopositivity of CN66 compared to pure nylon 66 due to the incorporation of cellulose, as shown in figure 6.11(a). An electrometer was used to measure the short circuit current (I_{sc}) of the TENGs on applying the same amount of constant periodic axial force. As shown in figure 6.12(b), w-TNG showed a high short circuit current of 12.61 μA , while the TENG lacking cellulose microfibers in the tribopositive layer displayed a reduced short circuit current of 7.11 μA , as displayed in the appendix 4 data file in figure A4.1(b). The increase in output voltage and current for w-TNG with the inclusion of cellulose microfibers could be readily anticipated by examining the relative surface potential values presented in Section 6.4.4. It is evident from the graph in figure 6.11(a) that the surface potential of nylon 66 fibers embedded with cellulose microfibers was nearly twice that of pure electrospun nylon 66 fibers. The high output voltage and current observed are mainly attributed to the increased tribopositivity of the cellulose-infused nylon 66 layer, likely due to a combination of factors [15], resulting from the superior ability of cellulose to lose electrons and the enhanced positive polarity of the triboelectric layer due to the presence of $-NH_2$ groups in nylon 66.

Another contributing factor is the enhanced real contact area of the electrospun nanofibers, resulting from increased surface roughness. As the surface roughness of the triboelectric layer increases, the effective area available for charge accumulation within the polymeric triboelectric layer also expands [42]. Additionally, the contact area is likely to increase due to significantly higher areal fiber contact density and the improved ability of the nanofibers to conform to the counter-surface.

The output voltage of the w-TNG was further tested at different frequency ranges of 1 to 7 Hz under periodic axial force of 5 N as can be seen in figure 6.12(c), using a customized

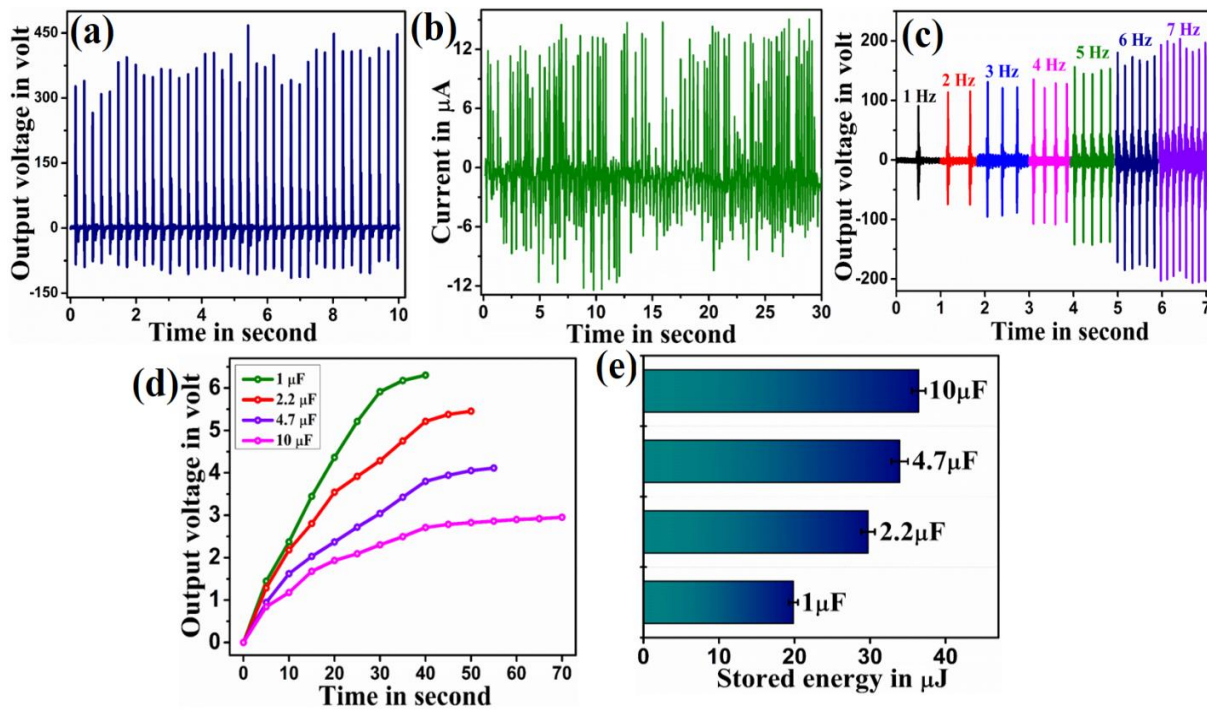


Figure 6.12. (a) V_{oc} and (b) I_{sc} of w-TNG, (c) Frequency dependent V_{oc} , (d) Capacitor charging graph of w-TNG, (e) Total energy stored in the capacitors within 40 second

piezo-tribo impart testing machine. The maximum output voltage (~ 192 V) was obtained at 7 Hz which was more than twice the output voltage obtained at 1 Hz (91 V). Output voltage of w-TNG can be determined using the following equations [41]:

$$V_{oc} = \frac{\sigma \cdot x(t)}{\epsilon_0} \quad (7)$$

$$\text{Where, } x(t) = v \cdot t, \left(t < \frac{x_{\max}}{v} \right) \quad (8)$$

Here, V_{oc} represents the output voltage, σ represents the charge density of the triboelectric surface, $x(t)$ represents the gap between the two triboelectric layers, ϵ_0 represents the permittivity of free space, v represents the average velocity, x_{max} represents the maximum gap between the triboelectric layers. It is known that the velocity of the applied force rises as the frequency of force application increases. Therefore, it can be concluded from equation (7) that as frequencies rise, so does the output voltage for w-TNG. To demonstrate the efficiency of the fabricated w-TNG, appropriate electrical connections were established to charge various capacitors using a four-probe full-wave bridge rectifier under continuous finger-applied force. Figure 6.12(d) demonstrates the capacitor charging curves, signifying that under contact separation mode w-TNG can charge up 1 μ F, 2.2 μ F, 4.7 μ F, and 10 μ F capacitors to 6.30 V, 5.45 V, 4.11 V and 2.95 V within 40, 50, 55 and 70 seconds respectively. These exponential capacitor charging curves of output voltage versus time indicate the high energy storage capability of w-TNG. It can also be observed from the graph that larger capacitors retain the charges for a longer time while capacitors with lower value reach greater voltages and saturation owing to their lower time constant [28]. The stored energy in various capacitors during the charging process can be determined using the given equation [14]:

$$E = \frac{1}{2} CV^2 \quad (9)$$

Here E represents the stored energy, C represents the capacitance value and V represents the voltage obtained by the capacitor. In this study, the voltage values reached by each capacitor at 40 seconds were used to calculate the stored energy. As shown in figure 6.12(e), the total energy stored in the 1 μ F, 2.2 μ F, 4.7 μ F, and 10 μ F capacitors within 40 seconds were 19.85 μ J, 29.74 μ J, 33.93 μ J and 36.45 μ J respectively. The graph also indicates that smaller capacitors stored lesser energy than large capacitors, mostly because of their lower charge storage capacity [28] and hence the highest energy stored was across 10 μ F capacitor.

The sensitivity of w-TNG was determined in order to demonstrate that the device was able to detect tiny mechanical vibrations and generate significant voltage. Five different kinds of Indian currency coins (₹1, ₹2, ₹5, ₹10 and ₹20) with different masses were used for the calculation of the sensitivity of w-TNG. The coins were individually dropped on w-TNG from 8 cm height, resulting in varying output voltages. A linear output voltage vs. pressure

graph was plotted with the help of the pressure values for each instance, as seen in figure 6.13(a). The sensitivity (S) of the device at a low-pressure region was ultimately determined to be 38.7 V/kPa up to an external pressure of 0.18 kPa with the help of the equation [21]:

$$S = \frac{\Delta V}{\Delta P} \quad (10)$$

Here, ΔV represents the change in output voltage and ΔP represent the change in applied external pressure respectively. Many load resistances with different values were employed, ranging from $10^3 \Omega$ to $200 \text{ M}\Omega$, to examine the load capacity of w-TNG. For different load resistances, w-TNG showed different instantaneous power density values as can be seen in figure 6.13(b) and the formula used to determine the power density (P) is as follows [17]:

$$P = \frac{V^2}{R_L \times A} \quad (11)$$

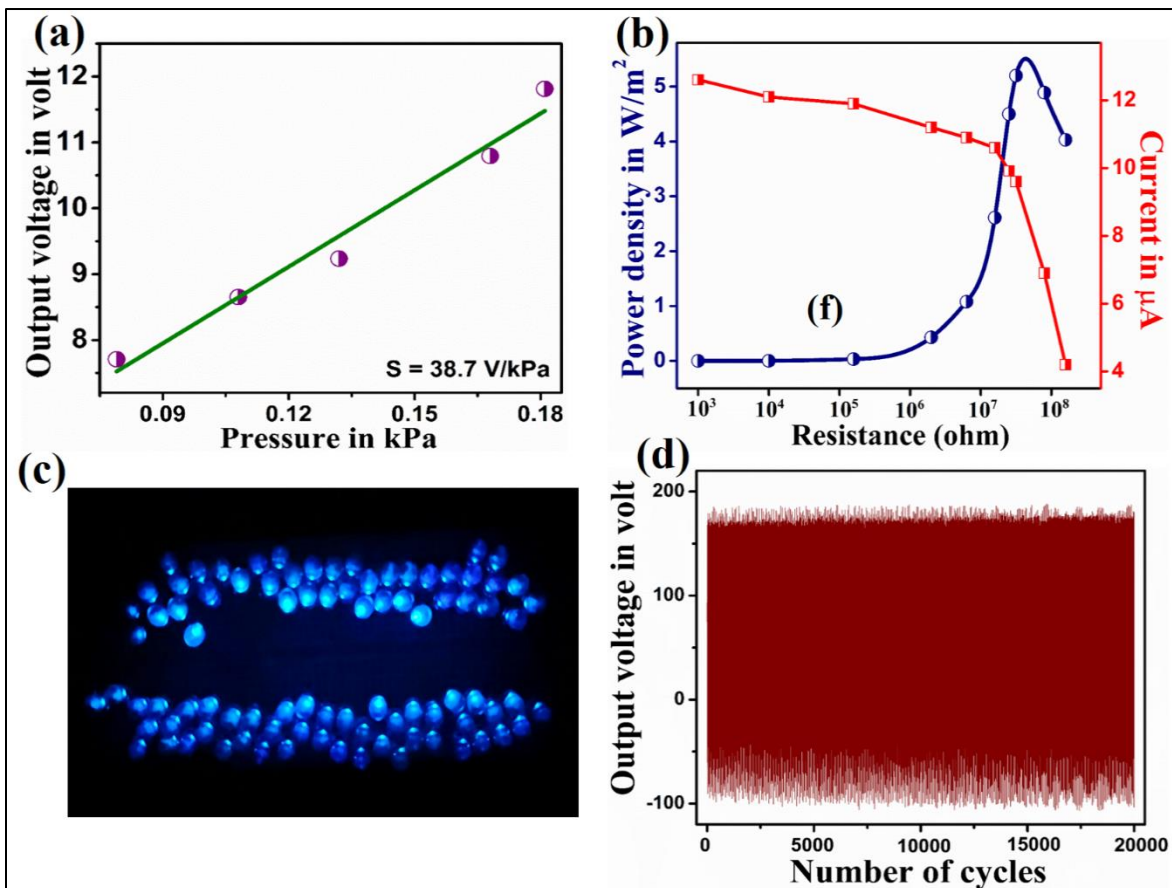


Figure 6.13. (a) Sensitivity of w-TNG, (b) Correlation of power density and I_{sc} of w-TNG, (c) Illumination of 98 blue LEDs, (d) Endurance test of w-TNG

Here, V represents the output voltage of w-TNG, R_L is the corresponding load resistance value and A denotes the effective surface area of the device (3.5 cm x 2.5 cm). The maximum power density value for w-TNG was calculated to be 5.2 W/m² at 50 M Ω . The graph depicted in figure 6.13(b) shows that as the load resistance increases, the power density initially rises, reaching a peak of 5.2 W/m² at a load resistance of 50 M Ω and then gradually declines. To further explore the load capacity of w-TNG, the correlation between short-circuit current and peak power density was examined across a range of load resistances from 10³ Ω to 200 M Ω . The short-circuit current of w-TNG reaches its maximum value of 12.61 μ A at 10³ Ω and steadily decreases as the load resistance increases.

To evaluate the energy conversion capability of w-TNG and to verify its practicality in real-life applications, multiple commercially available light-emitting diodes (LEDs) were powered. w-TNG successfully illuminated 98 blue LEDs connected in series when an axial periodic force was applied using fingers, as depicted in figure 6.13(c). This was achieved by utilizing a full-wave rectifier in a correct electrical circuit connection. Using the piezo-tribo imparting machine, the output performance of w-TNG was evaluated for more than 20,000 periodic cycles when 7 N of force was applied in order to determine its long-term stability and its endurance. As represented in figure 6.13(d), it was found that the output voltage of around 181 V stayed constant and continuous with very little deviation. This demonstrates the consistency and stability of w-TNG, making it a reliable energy harvester capable of long-term use without losing its high sensitivity.

6.4.6. Output performance of w-TNG (wind energy harvesting)

In this study, a contact separation mode-based freestanding, butterfly shaped triboelectric nanogenerator has been presented. To enable easy flapping of the device at lower wind speeds, a wedge-shaped air gap at the edge was incorporated. This rational device design enhanced the effect of triboelectrification and electrostatic induction by ensuring full contact between the triboelectric layers, with airflow acting as the operating force. The impacts of device structure angle, wind source distance, wind speed etc., have been systematically analyzed by evaluating the output data of w-TNG under varying parameters. This investigation aims to determine the optimal structure and ideal operating conditions for w-TNG. As illustrated in figure 6.14 and 6.15, various factors were taken into

account in order to determine how changing parameters affect the output voltage and short-circuit current of wind driven w-TNG. Output data were collected using air blown by a hair dryer, considering the following parameters: (i) distance between the air source and w-TNG (D), (ii) device structure angle (θ), (iii) temperature of the blown air (T), (iv) speed of the blown air (S), and (v) air blown from different sources. The hair dry was chosen as the standard source of air blown during all the parameter changing experiments except that with varying source. The speed of the air blown using hair dryer was about 2.5 m/s, which was measured using an anemometer.

Figure 6.14(a)-(c) illustrates the influence of distance between the air source and w-TNG on its output performance. The output voltage and current data were obtained for 5 cm (79 V, 2.3 μ A), 10 cm (70 V, 2. μ A), 15 cm (53 V, 1.7 μ A) and 20 cm (37 V, 1.2 μ A). The airflow speed was set to 2.5 m/s, the device angle was adjusted to 40° and the data were recorded at room temperature (27°C). Here, it can be observed that as the distance between the hairdryer and the device increases, the output voltage and current gradually decreases. This is because the air flow becomes diffused when the hair dryer (wind source) is removed farther from the device, which lowers the operating force acting on w-TNG. From previous reports, it is known that the output voltage and current of the triboelectric nanogenerator

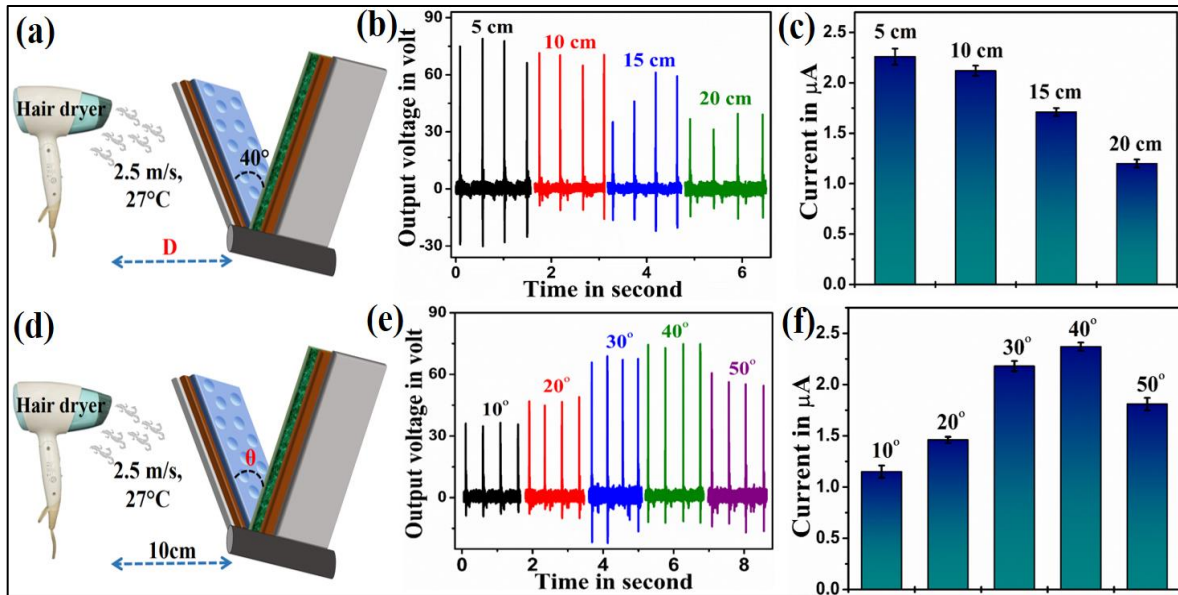


Figure 6.14. Schematic depiction, V_{OC} and I_{SC} of w-TNG with varying (a)-(c) Distance between air source and w-TNG, (d)-(f) Device structure angle

are proportional to the applied force up to a certain limit. This behavior may be attributed to the enhanced compressive force, which improves the contact area between the two triboelectric layers, leading to the generation of more number of electric charges [4]. Since the surfaces of the CN66 and PS layers are not completely smooth but have microscopic roughness, a lower contact force (caused by diffused air) leads to only partial contact between the triboelectric layers, resulting in minimal charge generation. As the contact force increases (for a smaller D value), the triboelectric charge generation steadily rises until full contact between the layers is achieved.

To examine the impact of different device angles (θ) on the output performance of the triboelectric nanogenerator, the angle between CN66 and PS layers of w-TNG was adjusted, while keeping all other parameters constant ($S = 2.5 \text{ m}^2/\text{s}$, $T = 27^\circ\text{C}$, $D = 10 \text{ cm}$). Output voltage and current data were recorded for 10° (35 V, $1.2 \mu\text{A}$), 20° (45 V, $1.5 \mu\text{A}$), 30° (67 V, $2.2 \mu\text{A}$), 40° (73 V, $2.4 \mu\text{A}$) and 50° (55 V, $1.8 \mu\text{A}$) as shown in figure 6.14(d)-(f). It is observed that the output voltage and current increase as the device angle gradually increases up to 40° . This can be explained using the following equation [14]:

$$V_{OC} = \Delta\sigma_{SC} \cdot S / C_{TENG} \quad (12)$$

Here, $\Delta\sigma_{SC}$ is the triboelectric charge density, S represents the effective contact area between the triboelectric layers and C_{TENG} represents the capacitance of the triboelectric device. For the above-mentioned scenarios with different device angles, $\Delta\sigma_{SC}$ and S remain the same, but the capacitance value varies since it depends on the device angle as follows [34]:

$$C_{TENG} \propto \epsilon \cdot l / \theta \quad (13)$$

Here, ϵ represents the permittivity, l represents the length of the triboelectric layers and θ represents the angle between the two triboelectric layers. Thus, at a larger structural angle, the capacitance value decreases, leading to an increase in the output voltage generated by the triboelectric device. However, as shown in figure 6.14(e) and (f), the output performance of w-TNG decreased beyond 40° . At a larger device angle, the triboelectric layers stay farther apart, resulting in unstable contact between them at a given airflow, which weakens the output signals. Additionally, as the device angle increases, the flapping motion of the w-TNG becomes more unstable. Therefore, device contact angle of 40° was taken as the optimum value for all the cases.

Figure 6.15(a)-(c) illustrates the schematic representation and output performance of w-TNG based on the temperature of the air blown onto the device. The output voltage and current data were measured for 40°C (68 V, 2.2 μ A), 50°C (70 V, 2.4 μ A), 60°C (64 V, 2.2 μ A) and 70°C (60 V, 2.1 μ A). The graphs indicate that the V_{OC} and I_{SC} of w-TNG remain nearly stable up to 50°C. However, a slight decrease in both voltage and current is observed at 60°C

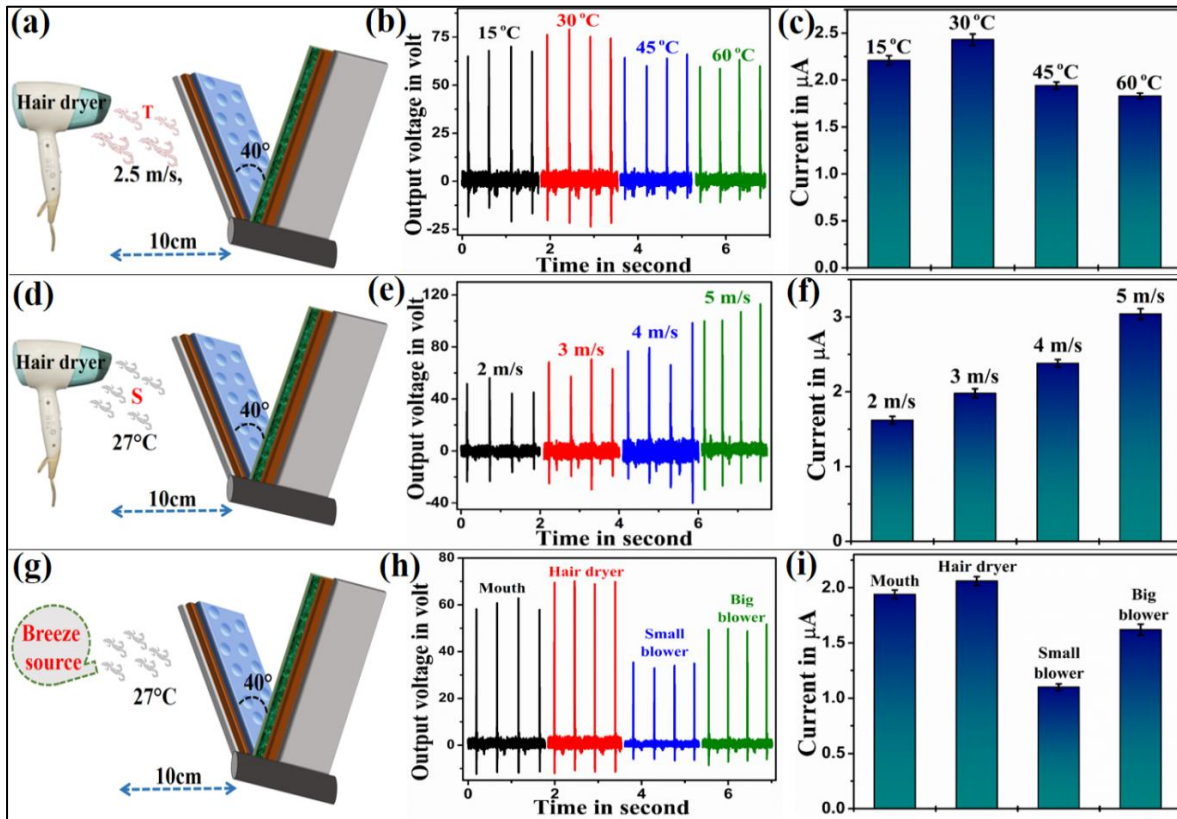


Figure 6.15. Schematic depiction, V_{OC} and I_{SC} of w-TNG with varying (a)-(c) Temperature of the blown air, (d)-(f) Speed of the blown air, (g)-(i) Source of the air blown

and 70°C. This decrement of the output performance is mainly caused because cellulose degrades more quickly around 50°C, which might cause de-polymerization, a possible loss of structural integrity and a weakening of the material's overall characteristics [25]. As nylon 66 and polystyrene, the materials used in the triboelectric layers are generally stable at this temperature, the decrease in w-TNG's output performance is not very significant. Therefore, all other experiments involving parameter variations were conducted using air blown at room temperature.

Figure 6.15(d)-(f) shows the relationship between the output performances of w-TNG and the simulated wind speeds. The data for V_{oc} and I_{sc} were obtained for 2 m/s (50 V, 1.6 μ A), 3 m/s (65 V, 1.9 μ A), 4 m/s (77 V, 2.4 μ A) and 5 m/s (106 V, 3.1 μ A). This demonstrates a steady enhancement in the output performance of w-TNG as the speed of the simulated wind increases. This occurs because, as wind speed increases the triboelectric layers experience higher dynamic pressure. This is due to the increased frequency and momentum of the flapping movement of the device, which enhances the effective contact area and the force between the friction layers.

To analyze the variation in w-TNG's output performance with different air sources, the device was tested using air blown from the mouth (61 V, 1.9 μ A), a hair dryer (69.6 V, 2.1 μ A), a small manual long-tip air blower (34 V, 1.1 μ A) and a large manual long-tip air blower (50 V, 1.6 μ A) as shown in figure 6.15(g)-(i). The air blown from the mouth had a speed of approximately 2.8 m/s, while the hair dryer produced air at 3.7 m/s, aligning well with the corresponding output measurements from both sources. The small blower generated a wind gust with a speed of 1.6 m/s per blow, while the large blower produced a gust at 2.3 m/s. The difference in speed and force for different air sources caused the variance in w-TNG's output performance with air blown from different sources. Since greater the force, greater will be the contact area between the triboelectric layers, the hair dryer produces the maximum output due to its highest speed among the four sources.

6.4.7. Real-time over-speed alert system for vehicles

It is known that a passing vehicle generates wind flow or air currents primarily due to the pressure difference created during its motion, with high pressure forming at the front and low pressure trailing behind it. When w-TNG was positioned near a single passing vehicle, it generated output data which was produced by the air current created due to the vehicle's motion. Based on this concept, w-TNG was applied for detecting on-road vehicle speeds and indicating over-speeding warnings through a RED LED indicator via a wireless speed monitoring system. Numerous studies on TENG-based traffic surveillance systems have been conducted in the recent past. These systems used commercially available materials to fabricate the TENGs, with defined locations for device installation and were usually associated with electromagnetic phenomena. Moreover, most TENGs in this sector operated

in contact-separation mode, requiring physical force to be applied to the device to generate an output. This force usually came from the pressure exerted by vehicles as they passed over the TENG. The repeated passing of vehicles over the TENG damages the device over time, gradually degrading its structure and significantly reducing its efficiency within just a few days. Since the wind-driven w-TNG operates without any direct physical force applied to it, its structural integrity is preserved and its high efficiency over an extended period is also maintained. Thus, the designed air current-based speed detection and wireless over-speed warning system is particularly valuable in hilly regions, where roads are narrow and have numerous hairpin bends. Due to the limited presence of traffic surveillance centers in such areas, the risk of accidents at these bends is significantly higher. Here, figure 6.16(a) illustrates a hairpin bend on a hilly road, featuring the installed w-TNGs, a speed limit sign and red LED for over speed warning purposes. The figure also depicts of how the monitoring and detection process is carried out using IoT-based wireless speed control system.

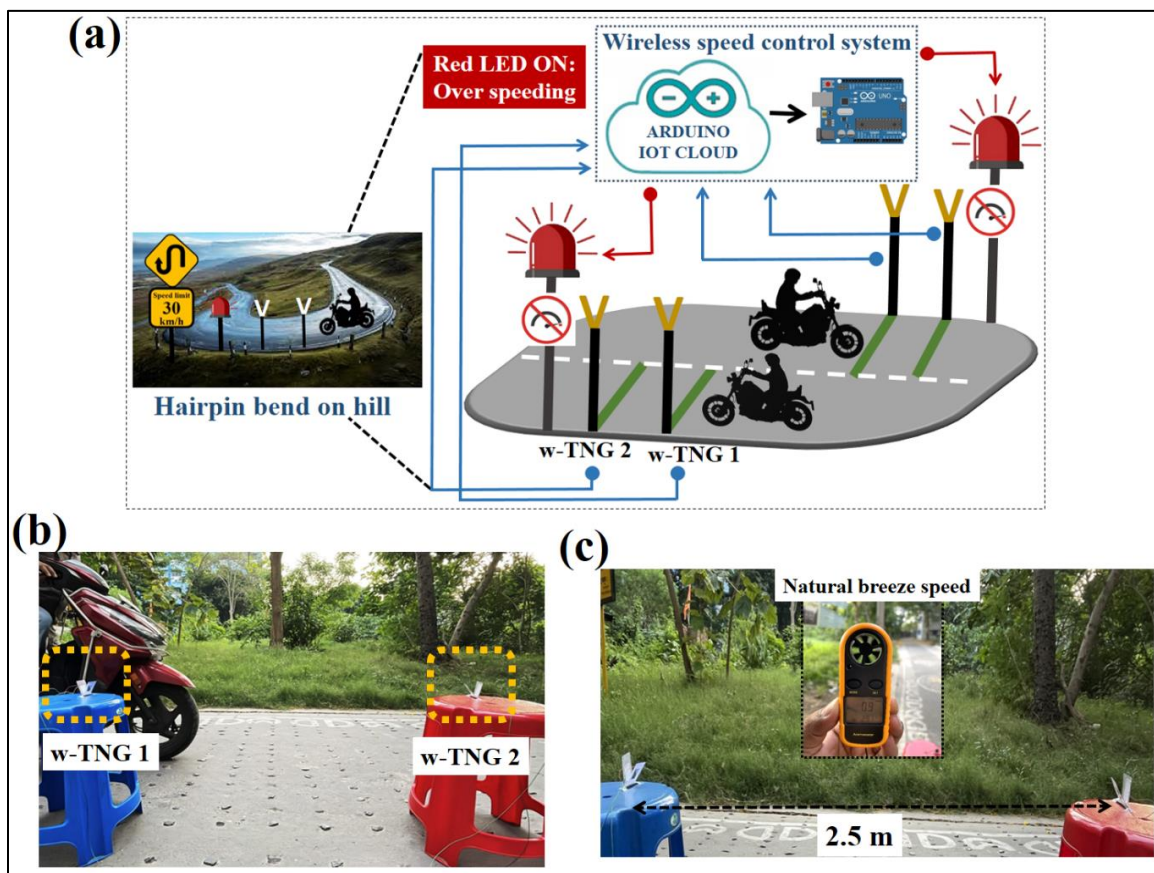


Figure 6.16. (a) Schematic diagram of IoT-based wireless, real-time speed control and warning system, (b) Real-time speed detection of motorbike, (c) Zoomed in view of speed sensor setup

To demonstrate real-time speed detection of a motorbike, two w-TNGs (w-TNG1 and w-TNG2) were placed on stools at a height of 100 cm, spaced 2.5 meter (length L) apart. Both TENGs were connected to a DSO for output signal detection and a motorbike was driven in the vicinity of 40-60 cm from the devices. The experimental setup showing real-time speed detection of a motorbike using two w-TNGs has been depicted in figure 6.16(b). The closer view of the butterfly shaped w-TNGs installed on the road, showing the distance between them has been depicted in figure 6.16(c). When the motorbike just crossed w-TNG1, an output voltage signal was obtained instantly, as shown in the graph in figure 6.17(a). The flapping movement of w-TNG1, which was triggered by the air current produced by the passing motorbike, was the cause of the voltage peak that was seen. Similarly, as the motorbike crossed by the second TENG (w-TNG2), positioned 2.5 meters away, an immediate second voltage peak was recorded, due to the flapping of w-TNG2, as illustrated in figure 6.17(b). As shown in the inset of figure 6.16(c), anemometer recorded a natural breeze speed of 0.9 m/s. This low velocity did not interfere with the output signals of the w-TNGs. If the voltage signal from w-TNG1 peaks at time t_1 and the signal corresponding to w-TNG2 peaks at time t_2 , then the time difference Δt can be represented as:

$$\Delta t = t_2 - t_1 \quad (8)$$

Hence, with the help of this time difference and the known distance between w-TNG1 and w-TNG2, the speed (S) of motorbike may be calculated using the standard speed equation:

$$S = \frac{L}{\Delta t} \quad (9)$$

From the graph in figure 6.17(a), the time interval Δt was determined to be 0.48 second, leading to a calculated motorcycle speed of 5.2 m/s (or 18.72 km/h). This calculated value was consistent with the speed shown on the motorcycle's speedometer during data verification. It is known that the most noticeable air current behind a motorbike occurs within a diameter of 0.5-1.5 meter, due to the immediate displacement of air. Beyond this range, air-current effects rapidly dissipate as the airflow get mixed with the natural breeze, making the flapping motion of w-TNGs less effective. Therefore, to prevent the interference between the air currents generated as the bike crossed w-TNG1 and w-TNG2 successively, the TENGs were spaced 2.5 meters apart, ensuring clear isolation of the voltage signals. The speed equation suggests that the time difference (Δt) between the output signals produced

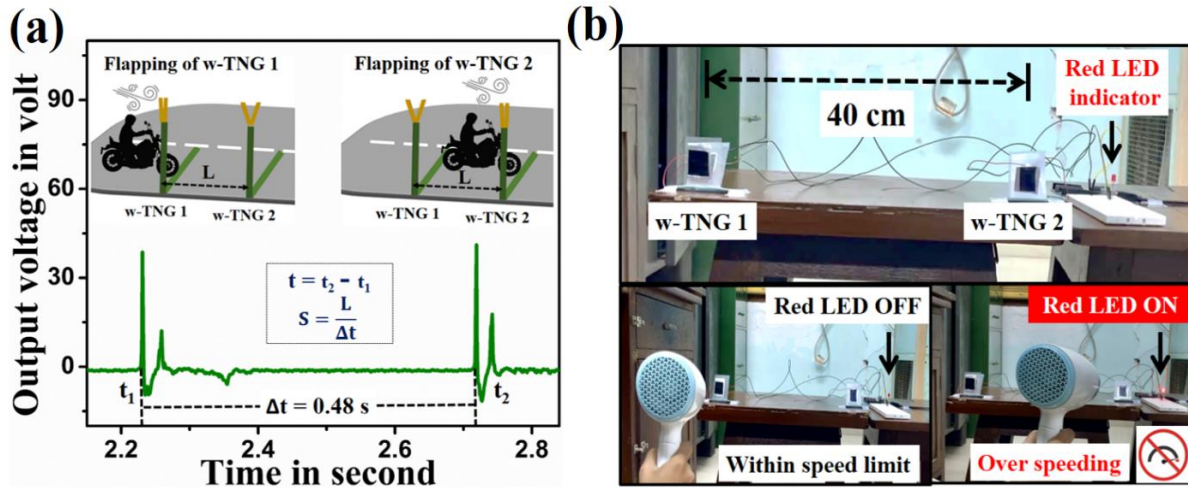


Figure 6.17. (a) Output voltage graph and schematic depiction of our proposed speed detection method, (b) Simulated traffic surveillance setup integrated in lab-scale

by the two TENGs has been taken into account to determine the motorbike's speed rather than the output voltage magnitude. Thus, using the two TENGs, the speed of any vehicle can be determined with high accuracy, as it depends solely on the time interval (Δt) between voltage peaks. Other variables such as vehicle size, direction of travel by the vehicle or load on the vehicle might influence the peak voltage magnitude but do not affect the speed calculation. Moreover, the integrity of the devices is preserved as the voltage signals are entirely airflow induced, with no physical contact or damage to the TENGs. Using w-TNGs that operate based on air currents, the output signals generated by passing vehicles can be effectively monitored, enabling the activation of warning lights for over-speeding. A self-powered over-speed detection and warning system was developed using output signals from two w-TNGs, using a simulated traffic surveillance setup integrated in lab-scale. Two w-TNG were placed 0.4 m apart and the air current produced by passing vehicles was simulated using a hand-held hairdryer, as can be seen from figure 6.17(b). Firstly, an Arduino UNO system was used through a laptop to send the voltage signal produced by airflow generated by the hairdryer from w-TNG1 and w-TNG2. Next, data from both devices were collected and analyzed to calculate the speed of the moving hairdryer. It is important to note that the speed of the hairdryer's movement was being monitored, and not the air blown from it. The airflow generated by the dryer, which causes the subsequent flapping of the devices, simulates the air current produced by a passing vehicle. The data were processed through a microcontroller unit (MCU), with the output voltage obtained from each device's flapping

reduced to below 5 V using a voltage divider. A low-pass filter and rectifier module connected to the processing circuit were employed to filter and rectify the output signals. The speed limit for the hairdryer movement was set at 3.5 km/h and if the speed exceeded the limit, a red coloured LED connected to the circuit was activated to indicate an over-speed warning signal. As shown in figure 6.17(b), when the hairdryer was moved at a speed exceeding 3.5 km/h (specifically 4.8 km/h), the red LED began blinking immediately, signaling an over-speed condition. Conversely, when the movement speed was reduced below 3.5 km/h, the red LED turned off, indicating that the speed was within the acceptable limit. When implemented on hairpin bends of hill roads, this over-speed detection and warning system based on the air gust-driven butterfly-shaped w-TNG, could serve as an effective solution for preventing accidents and enhancing road safety.

The graph below in figure 6.18 corresponds to the simulated vehicle speed detection using hairdryer. The time difference Δt here was 0.3 s and the distance between the two w-TNGs was 0.4 m. Therefore, the calculated speed was 4.8 km/h, which exceeded the speed limit = 3.5 km/h (set in the programming). Due to the over-speeding scenario, the red LED indicator lit up.

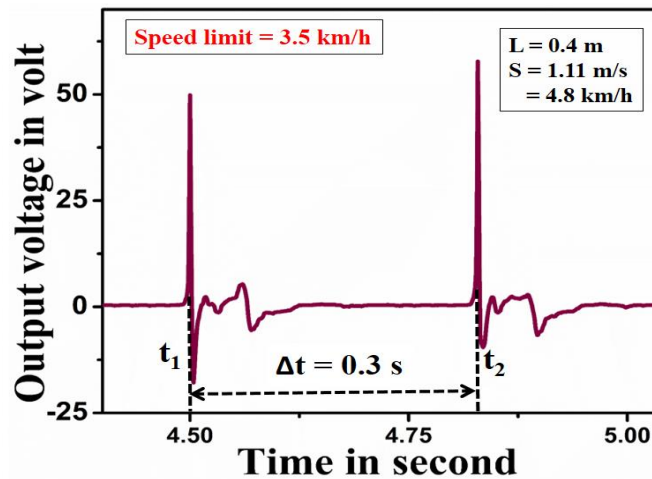


Figure 6.18. V_{oc} corresponding to simulated vehicle speed detection system using hairdryer

6.5. Summary

In order to promote the waste-to-energy concept, the current study suggests a waste-derived triboelectric nanogenerator (w-TNG), which generates electrical energy from the wasteful kinetic energy of natural wind gusts. For effective energy harvesting from mild

ambient breezes, the ultra-lightweight, spacer-less, butterfly-structured w-TNG has a wedge-shaped air gap that guarantees complete contact between triboelectric layers, improving triboelectrification and electrostatic induction. In order to create tribopositive layer, extracted cellulose fibers with micro-skeleton structure were embedded onto an electrospun nylon 66 nanofibrous mat and to make a free-standing, microporous polymeric film for the tribonegative layer, discarded polystyrene pieces were recycled. Using ImageJ software, 3D surface profiles of the polymeric films based on FESEM micrographs were created. The results showed significant surface roughness that increased the area of contact between the triboelectric layers during friction. Having completely porous components, the spacer-less w-TNG was incredibly lightweight, which was a significant benefit for effective energy harvesting from both mild airflow and simple finger touch. Under finger applied force, the w-TNG generated 389 V and 12.61 μA , achieving a peak power density of 5.2 W/m^2 at 50 $\text{M}\Omega$ and a sensitivity of 38.7 V/kPa up to 0.18 kPa. The w-TNG's high sensitivity enabled wind energy harvesting using wind gusts. Moreover, a real-time, self-powered vehicle speed monitoring and wireless over-speed surveillance system was developed using the w-TNG, featuring a red LED indicator for over-speed warnings. Thus, air current-based speed detection and wireless over-speed surveillance system is particularly effective for hilly areas, where narrow roads and frequent hairpin bends pose increased safety risks.

6.6. References

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Chapter 7



Conclusion and outlook

The global energy crisis and growing environmental concerns have increased the need for alternative and sustainable energy solutions. Traditional power stations require large infrastructure as well as high capital investment. These systems are not only inefficient at capturing small-scale environmental energy but also contribute to further waste generation. To address this, researchers have been developing innovative methods to capture energy from small-scale mechanical vibrations from the environment, drawing inspiration from nature and by recycling waste materials. Among these, the piezoelectric and triboelectric effects are particularly effective for converting mechanical energy into electricity, with wide applications in nanogenerators and ultrasound transducers. Hence, this thesis has been focused on the development of biocompatible, multifunctional and lead-free nanocomposites used to fabricate a piezoelectric nanogenerator, a piezoelectric ultrasound transducer and self-powered triboelectric sensors. Their energy harvesting performances and practical applications were thoroughly investigated.

Chapter 3 explores the effect of size-modified clay nanoparticles on enhancing the electroactive β -phase in PVDF based nanocomposites for designing piezoelectric nanogenerators. The addition of mortar-pestle ground and ball-milled clay NPs increased β -phase crystallinity to $\sim 80.7\%$ and $\sim 84.8\%$ respectively due to strong ion-dipole interactions and interfacial polarization. Thermal stability of the polymeric composites also improved. Device performance tests showed power densities of $\sim 4115 \mu\text{W}/\text{cm}^3$ for MPENG and $\sim 7187 \mu\text{W}/\text{cm}^3$ for BPENG under hand-applied force. These devices lit up 25 and 40 LEDs and charged a $2.2 \mu\text{F}$ capacitor in 16 second. The piezoelectric coefficients (d_{33}) were 39.75 pC/N (MP5) and 50.10 pC/N (BM1.0) at 50 Hz. These eco-friendly PENGs demonstrated strong energy output and body motion sensing, indicating their potential for self-powered electronics and sustainable energy harvesting.

Chapter 4 highlighted an additional application of the piezoelectric effect which included the designing of a lead-free, polymer composite based ultrasound transducer. β -Ni(OH)₂ nanoplates incorporated piezoelectric composite was fabricated using the spin coating method, which showed high β -phase crystallinity of 90.04% due to strong ion-dipole interactions and surface polarization. Piezo force microscopy confirmed a high piezoelectric coefficient value of 50.22 pm/V and theoretical analysis using Maxwell's equations aligned with the experimental data. The UST enabled bidirectional ultrasound signal transmission, with a peak-to-peak output voltage of 5.19 V that surpassed the output voltage magnitude of any previously reported polymeric composite based UST in

this field. FFT analysis showed a wide frequency response from 24.41 MHz to 75.63 MHz and an ultra-broad -6 dB bandwidth of 51.22 MHz (102.4%) centered at 50.01 MHz. These features made the lead-free transducer a good option for medical diagnostics and non-destructive testing, offering improved imaging resolution and diagnostic accuracy.

Chapter 5 presented another very efficient energy harvesting approach based on the triboelectric effect. A bio-inspired, hydrophobic single-electrode TENG was designed for droplet energy harvesting via the triboelectric effect at the liquid–solid interface. Using template sacrifice method, the triboelectric layer had boat-shaped microstructures inspired by petunia petal surface. The hydrophobicity of the TENG increased mostly due to the introduction of rough topography on the surface, which was theoretically described by the Wenzel model of wetting. The TENG effectively harvested energy from finger touch and raindrops and COMSOL simulations showed its potential distribution at various stages. Notably, the TENG also detected pH and ion concentration of liquids due to the H^+ ion shielding effect. A real-life model was designed which could identify the unknown pH of rainwater instantly and displayed the value of pH with the help of coloured LED indicators, to facilitate prompt precaution from acid rain in our daily life.

Chapter 6 presented one more application of the triboelectric effect for harvesting low-intensity environmental breeze energy through a lightweight, butterfly shaped TENG. The device was made spacer-free, which utilized a wedge-shaped air gap to ensure full contact between triboelectric layers, enhancing charge generation. The triboelectric layers were extracted from cellulose fibers (agricultural waste) with micro-skeleton structure and microporous polymeric films derived from discarded polystyrene (packaging waste). 3D surface profiles of the polymeric films based on FESEM micrographs were created. Owing to its fully porous structure, the TENG was light weight, allowing efficient energy harvesting from both gentle breeze and light finger taps. It delivered an output of 389 V and 12.61 μA under applied force, achieving a peak power density of 5.2 W/m^2 and the high sensitivity of 38.7 V/kPa made it highly responsive to even mild breezes. A practical application was demonstrated through a self-powered, real-time vehicle speed monitoring system with wireless over-speed alerts, using a LED indicator. This system is especially valuable in hilly regions with narrow roads and sharp turns, offering an eco-friendly solution for energy harvesting and road safety monitoring.



Appendices



Appendix 1: Supporting information of chapter 3

1. Details of XRD analysis of clay NPs

The XRD patterns of pure mortar pestle ground and ball mill ground clay NPs as shown in figure A1.1.(a) and (b) respectively display sharp peaks such as $2\theta = 25.3^\circ$, 26.8° and 27.8° , which were also seen in XRD patterns of composite thin films. This is conclusive of the fact that clay nanoparticles were present in the composite thin films.

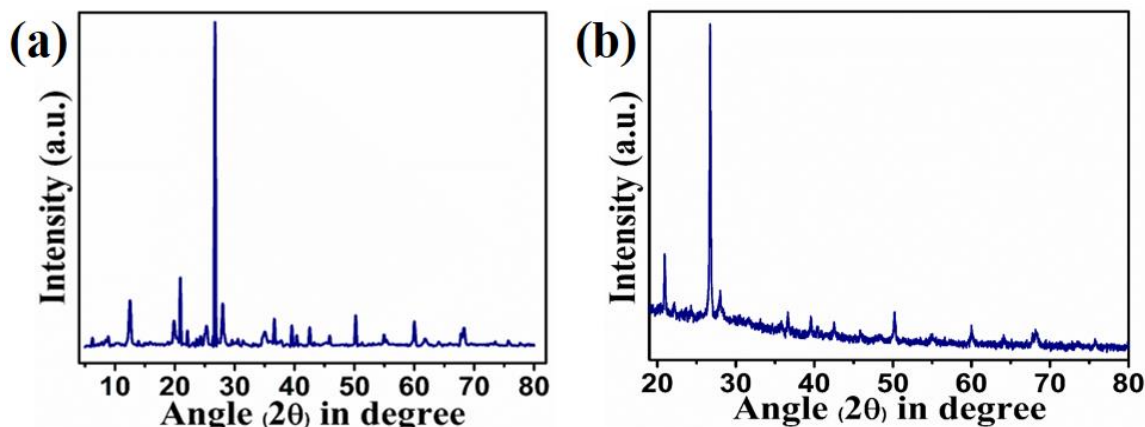


Figure A1.1. XRD spectra of (a) Mortar pestle ground clay NPs, (b) Ball mill ground clay NPs

2. Optimization of clay NP content in the composite thin films

From the FTIR analysis of MP2.5 and MP7.5, prominent peaks were observed at 445 cm^{-1} , 479 cm^{-1} , 510 cm^{-1} , 600 cm^{-1} and 840 cm^{-1} as shown in figure A1.2. (a). The β -phase fraction content $\{F(\beta)\}$ calculated reveals that MP2.5 has a β phase of 78.2% and MP7.5 has a β phase of 72.09%, as shown in figure A1.2. (b).

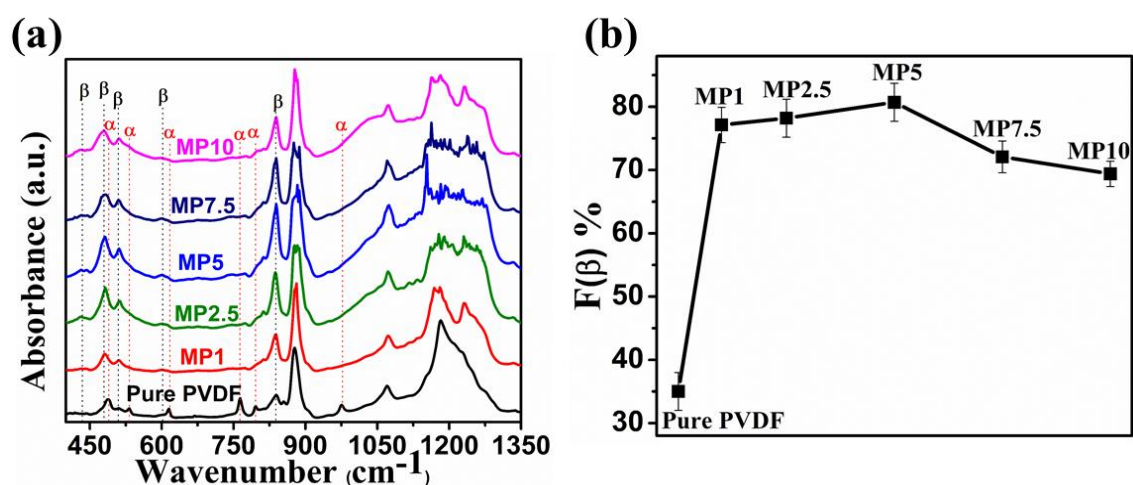


Figure A1.2. (a) FTIR spectra for pure PVDF, MP1, MP2.5, MP5, MP7.5 and MP10, (b) β -phase content of the 5 thin films

Appendix 2: Supporting information of chapter 4

1. Details of FTIR analysis of PTr and NTr5

The FTIR data from 800 cm^{-1} to 1300 cm^{-1} has been represented to show the change in the intensity of peaks at 840 cm^{-1} and 1275 cm^{-1} for the pure film and the composite. From figure A2.1, it is evident that the intensity at these two bands have increased for NTr5, leading to a high piezoelectric effect.

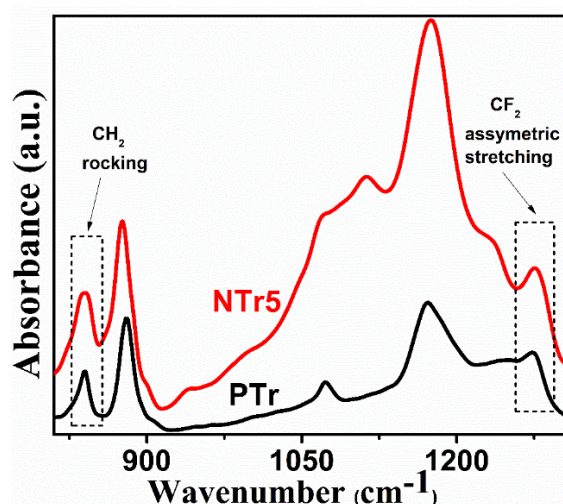


Figure A2.1. FTIR spectra of PTr and NTr5 showing the change in intensity of peaks at 840 cm^{-1} and 1275 cm^{-1} corresponding to β -phase

2. Description of the poling procedure done on the composite NTr5

Firstly, we annealed NTr5 by gradually increasing the temperature of the composite from room temperature to 80 ± 5 $^{\circ}\text{C}$ over the course of 1 hour, with a controlled rate of around 1 $^{\circ}\text{C}$ per minute. Following this, the composite was carefully positioned between two electrodes. As the temperature stabilized at 80 $^{\circ}\text{C}$, the DC voltage applied across the electrodes was slowly increased from 0 kV to 32 kV. This voltage level corresponded to a field strength of 1.23 GV/m across the sample, which was calculated using the equation:

$$E = \frac{U}{D} \quad (1)$$

Where E represents the electric field strength, U represents the applied DC voltage applied and D represents the thickness of the composite. A constant rate of 50 V per minute was maintained during the voltage increase to effectively prevent any electrical breakdown. The composite was maintained at this state for 2 hours before undergoing a controlled cooling process to return it to room temperature.

3. DC bias voltage description for PFM analysis

In the context of piezo force microscopy analysis conducted on a composite thin film, the examination of local piezoelectric and ferroelectric switching loops involved the application of pulsed voltage signals ranging from -7 V to +7 V. The amplitude of the signal exhibited a decline as the applied voltage swept from -7 V to 0 V, which attributed to the contraction of dipoles within the material. Conversely, as the applied voltage increased, the amplitude gradually rose due to the expansion of dipoles, reaching its peak at +7 V. During this phase, a reduction in the applied voltage (from +7 V to 0 V) led to a decrease in amplitude, accompanied by antiparallel field directions to the dipoles. Furthermore, it was observed that within the voltage bias range of -7 V to +7 V, there was a transition in the dipolar orientation, occurring gradually as the voltage increased. The combined signal, which involved a dual component of DC bias (V_{DC}) spanning from -7 V to +7 V, combined with the superimposed AC signal, allowed for the recording of both phase and amplitude hysteresis responses. This combined signal can be mathematically represented as:

$$V_{tip} = V_{DC} + V_0 \cos(\omega t). \quad (2)$$

To explore the piezoelectric properties of the films, a direct current (DC) voltage was applied across the film at levels exceeding its coercive voltage. As per the literature review, PVDF-TrFE possesses a relatively low coercive voltage, of around 4.6 V.

4. Effect of inclusion of β -Ni(OH)₂ nanoplates into PVDF-TrFE

Two more USTs were designed: (i) UST using a spin coated pure PVDF-TrFE film as the matching layer - peak to peak output voltage of 0.12 V as can be seen in figure A2.2., (ii) UST using thin coating of β -Ni(OH)₂ on aluminium substrate- No significant output.

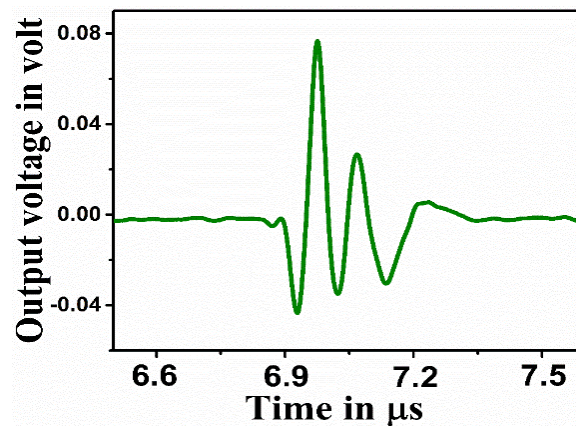


Figure A2.2. Experimental pulse echo signal received by the transducer using pure PVDF-TrFE film

Appendix 3: Supporting information of chapter 5

1. Structural analysis of PDMS film and PTFE particles

X-ray diffractogram of a pure PDMS film is shown in figure A3.1(a), displaying a peak at $2\theta = 12^\circ$ (amorphous nature). XRD pattern of PTFE particles in figure A3.1(b) shows peak at $2\theta=18^\circ$, while six other weak peaks can be observed between $2\theta=30^\circ$ and 70° . These diffraction peaks match (100), (110), (200), (210), (300), (220) and (310) crystal planes of PTFE, in correspondence to the reference pattern, 00-045-1594.

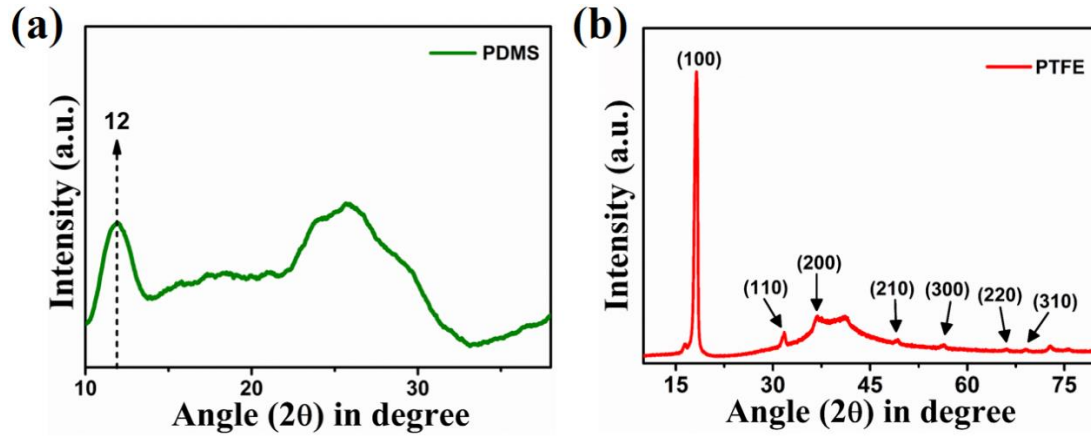


Figure A3.1. XRD analysis of (a) Pure PDMS film and (b) PTFE particles

2. Calculation of applied force by fingers on b-STNG

According to law of conservation of energy, we know:

$$mgh = \frac{1}{2} mv^2 \quad (1)$$

Here, m - mass of striking object, v - velocity of object, h - height of the object from where it drops, g - acceleration due to gravity. Calculated velocity was $v = 1.4 \text{ ms}^{-1}$. At this point, the momentum gained by the body may be represented as:

$$mv = (F - mg) \Delta t \quad (2)$$

Here F represents the applied force, which can be written as:

$$F = m (v/\Delta t + g) \quad (3)$$

Here, Δt represents the time gap between two consecutive positive or negative peaks on the output voltage vs. time graph.

When the force was imparted by fingers on b-STNG, $m = 0.70 \text{ kg}$, $v = 1.4 \text{ ms}^{-1}$, $h = 0.10 \text{ m}$, and $g = 9.8 \text{ m/s}^2$ and $\Delta t = 0.18 \text{ s}$. Using these values in formula (3), the force exerted by fingers on b-STNG is equal to 12.3 N.

3. Stability test of b-STNG in acidic solution

We carried out a test to confirm the degree of stability of b-STNG even after prolonged contact with an acidic solution. The output voltage data of the device was recorded after every two hours, by applying force with fingers, as can be seen from figure A3.2 As can be seen from the graph, the output data displayed no noticeable degradation even after 6 hours.

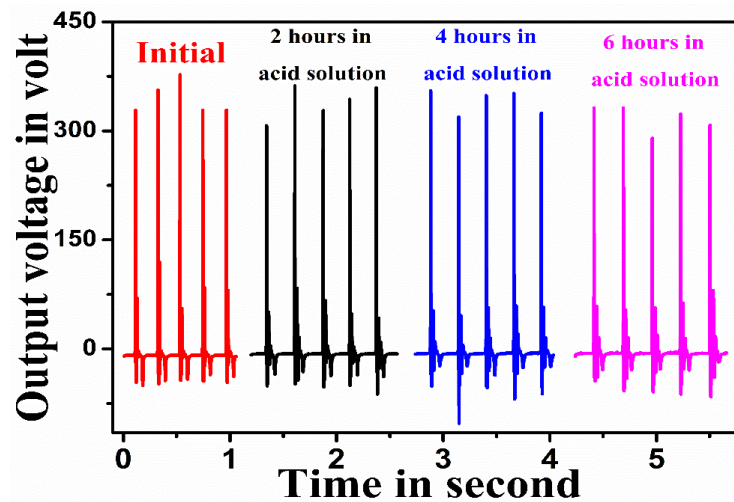


Figure A3.2 Stability test of b-STNG

Appendix 4: Supporting information of chapter 6

1. Calculation of applied force by fingers on w-TNG

The force that various striking items apply to the triboelectric nanogenerator may be readily determined using the law of conservation of energy. It is known:

$$mgh = \frac{1}{2} mv^2 \quad (1)$$

Here, m is the mass of striking item, v is the velocity of striking item, h is the height of the striking item from where it strikes, g represents the acceleration due to gravity. When force is applied by fingers, this equation enables us to calculate the velocity of the impacting item. The velocity (v) was calculated to be 1.3 ms^{-1} . Now, at this point, the momentum obtained by the body can be represented as:

$$mv = (F - mg) \Delta t \quad (2)$$

Here F is the applied force that can be written as:

$$F = m (v/\Delta t + g) \quad (3)$$

Here, Δt signifies the time gap between two successive positive or negative voltage peaks on the output voltage vs. time graph. When the force on w-TNG was imparted by fingers, $m = 0.70 \text{ kg}$, $v = 1.3 \text{ ms}^{-1}$, $h = 0.10 \text{ m}$, and $g = 9.8 \text{ m/s}^2$ and $\Delta t = 0.19 \text{ s}$. Using these parameters in formula (3), the force applied by fingers on w-TNG was equal to 11.6 N .

2. Electrical characterisation of TENG without cellulose

The output voltage vs time graph and the current vs time graph of the TENG not including cellulose microfibers in the tribopositive layer has been displayed in figure A4.1 (a) and (b) respectively.

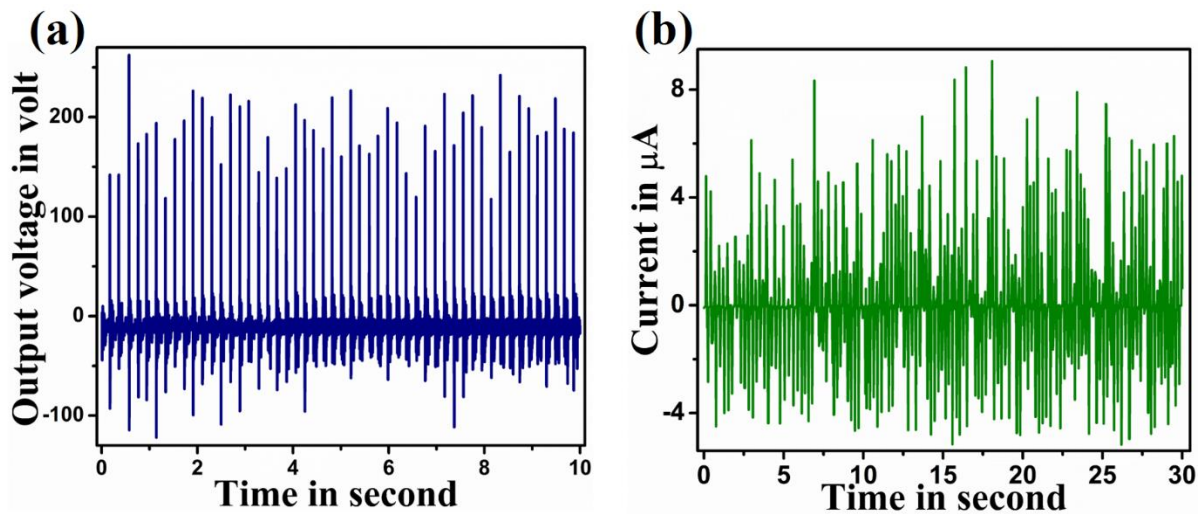
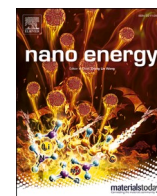


Figure A4.1. (a) V_{oc} and (b) I_{sc} of TENG not including cellulose microfibers in the tribopositive layer



Thesis publications





Piezoelectric activity assessment of size-dependent naturally acquired mud volcano clay nanoparticles assisted highly pressure sensitive nanogenerator for green mechanical energy harvesting and body motion sensing

Namrata Das^a, Debmalya Sarkar^a, Md. Minarul Saikh^{a,b}, Prosenjit Biswas^c, Sukhen Das^{a,*}, Nur Amin Hoque^{d,*}, Partha Pratim Ray^{a,*}

^a Department of Physics, Jadavpur University, Kolkata 700032, West Bengal, India

^b General Degree College at Pedong, Kalimpong 734311, West Bengal, India

^c Department of Physics, Kalimpong College, Kalimpong 734301, West Bengal, India

^d Department of Physics, IISER Mohali, Sahibzada Ajit Singh Nagar 140306, Punjab, India

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Body motion sensing

ABSTRACT

Over the last few years, there are several methodical and productive ongoing research based on the development of high performing, sustainable, non-hazardous energy harvesting nanogenerators. It is a substantial challenge to construct an energy harvester that has a superior output performance as well as an eco-friendly character. In this work, the utilization of naturally available, biodegradable mud volcano clay from Andaman and Nicobar Islands, India was done to design two simple, portable, cost-effective, biocompatible, eco-friendly piezoelectric nanogenerators (PENGs). In the first place, we developed two types of multifunctional poly-(vinylidene fluoride) (PVDF) thin film incorporated with mortar pestle ground clay nanoparticles (average size of 600–700 nm) for 3 mass% (MP1, MP5, MP10) and ball mill ground nanoparticles (average size of 200–300 nm) for 3 mass% (BM0.5, BM1.0, BM1.5), with large electroactive β crystallinity. The incorporation of clay NPs into the PVDF matrix led to notable nucleation of piezoelectric β crystallite {F(β)} of 80.7% and 84.8% for mortar pestle ground (5% doping) and ball mill ground (1% doping) clay NPs respectively. Using these two multifaceted composite thin films we designed two devices using MP5 (MPENG) and using BM1 (BPENG), which possess good energy harvesting potency, commendable power density values and very fast charging capability. Our MPENG and BPENG generate output voltage of ~ 85 V with a short circuit current of ~ 1.6 μ A and output voltage of ~ 125 V with a short circuit current of ~ 1.9 μ A, respectively and power densities of 4115 μ W/cm³ and 7187 μ W/cm³ respectively, on the application of periodic force by hand. The calculated piezoelectric coefficient d_{33} of MP5 and BM1.0 were 39.75 pC/N and 50.10 pC/N at 50 Hz, respectively. To check the real-life applications, MPENG and BPENG were used to lighten up 25 and 40 no. of blue LEDs when connected a series connection and we charged a 2.2 μ F capacitor within few seconds. These nanogenerators could also generate a notable voltage from various body movements like heel pressing, jogging or from vibrations or air flow from various instruments. On further advancement, our proposed devices can be used to power up various self-chargeable portable gadgets in our daily lives and in biomedical fields.

1. Introduction

Overexploitation of nonrenewable energy resources and increasing power demands have become great concerns as well as burning issues for mankind over the past few years, which in the coming few decades will eventually lead to the extinction of most of the fossil fuels. Hence, it has become a global area of interest for developing various energy

scavenging techniques and to lessen the usage of conventional power sources. The increasing power demand and the urge to minimize environmental pollution have triggered the researchers and scientists to develop robust, biocompatible, biodegradable, pollution-free, portable, lightweight, pocket friendly and self-powered nanogenerators by the effective conversion of mechanical to electrical energy, which is of pivotal importance for self-powered electronic devices [1–3] These

* Corresponding authors.

E-mail addresses: sdasphysics@gmail.com (S. Das), nuramin03@gmail.com (N.A. Hoque), parthapray@yahoo.com (P.P. Ray).

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nanogenerators are capable of harvesting electrical energy from various living systems which include mechanical forms like walking, jogging, touching, pushing, stretching, heart beat and other human activities or directly from any natural sources such as rainfall, airflow, sea waves, waterfalls, geothermal energy, solar energy etc. [4–10].

Human life involves several multifunctional and advanced electronic gadgets like mobile phones, wearable electronic devices, tablets, laptops, actuators, sensors, etc., which operates on batteries or other power supplies [11–18]. In recent times, piezoelectricity, pyroelectricity, triboelectricity etc. have emerged as effective, nonpolluting green energy sources which act as alternatives for the prevailing exhaustible resources. Among them, piezoelectric nanogenerators (PENGs) have emerged as one of the propitious mechanisms to harvest electrical energy through the direct conversion of mechanical energy procured from our basic daily activities into electrical energy [19–25]. The modeling and the advancing performance of several efficient piezoelectric nanogenerators, which make the use of staid piezoelectric materials or ceramics like ZnO, BaTiO₃, PZT, ZnSnO₃, PMN-PT etc. have received much attention of the researchers [13,26–31].

Poly(vinylidene fluoride) (PVDF) and its copolymers have come to light for being one of the most effectual electroactive semi-crystalline thermoplastic polymers for fabricating simple, sophisticated, cost-effective, flexible, lightweight and nonpolluting piezoelectric nanogenerators [5,32]. Modeling of innovative PVDF based self-charged power cells, using proper materials and techniques, has gained much importance in this field due to the high electrical energy storage capacity of PVDF and PVDF based nanocomposites (NCs) [5,6,33,34]. PVDF mainly consists of five crystalline polymorphs which are α , β , γ , δ , and ϵ , classified on the basis of bond orientation of $-CH_2$ and $-CF_2$ dipoles, out of which α , β and γ are the most common crystallite forms of PVDF. Melting of this polymer predominantly results in nonpolar α -crystalline phase (TG⁺GTG⁺ dihedral conformation), which is more thermodynamically stable, while the γ -crystalline phase (TTTGT⁺TTG⁺ conformation), for its polar character, gives average piezoelectricity. Among the polar β , γ , and δ forms of PVDF, β polymorph (TTTT conformation) is of prime importance among all the crystallite forms of PVDF, since it yields optimal piezoelectricity, pyroelectricity, ferroelectricity and adequate dielectric properties with desired elasticity [5,35,36].

Customarily, 'poling' was done with the help of an external high electric field and mechanical stretching on α -PVDF to nucleate to β -polymorph. As a better alternative, the gain in the harvested energy and dielectric properties (through enhancement of electric dipoles via large interfacial polarization) can be attained by infusing suitable nanocomposites (NCs), nanofillers, ceramics, metal oxides, metal nanoparticles [37], salts [39,40], nanotubes, organic matters [6,33], agro-industrial bio wastes [38,39], clays [41–43,44a] etc. From recent researches, we see that several works have been done on the improvement of dielectric properties, thermal properties or the development of supercapacitors have been done using various nanocomposites, even with different clay materials. Previous studies include Bhattacharya showing effective utilization of waste red mud for high-performance supercapacitor electrodes and Hardjito studying the Pozzolan Activity Assessment of LUSI (Lumpur Sidoarjo) Mud in Semi High Volume Pozzolan Mortar. The usage of clay or mud waste is much attractive since they are pollution-free, cost-effective and easily extractable from nature.

Mud volcano eruptions are geothermal phenomena that mainly spews out mud, sediments, mineral deposits, water, and different types of gases. The mud volcano by-product which has been put into use in our study has been obtained from Baratang in Andaman and Nicobar Islands, India. The raw material used in our work is not very scarce and is much easy on the pocket. The mud volcano contains different metal oxides and some biomaterials, which makes it completely eco-friendly in nature and the quantity of raw material used to fabricate a PENG is also less [42,43]. The clay particles enhances the toughness, durability and the lifetime of the nanogenerators which eventually increases the

electromechanical breakdown strength. The close interaction of the nano-sized clay particles and PVDF chains results in highly piezoelectric β -polymorphs in the clay NPs/PVDF nanocomposite thin film due to the alignment of the polymer chains in all-trans conformation (TTTT), i.e., effective nucleation of the electroactive β -phase takes place.

The development of PENG with high output performance using mud volcano clay nanoparticles which act as dopants in the PVDF matrix for the improvement of the β -nucleation has not been done yet. Therefore our present work includes the fabrication of two PVDF/ mud volcano clay nanoparticles (NPs) based piezoelectric nanogenerators, which are capable of harvesting electrical energy from light mechanical work - such as walking, finger imparting, foot-stamping, pulse vibration etc. We have also done a relative study of the output performance of PENGs designed with the help of clay NPs obtained by grinding the clay material (after proper treatment) through a normal mortar pestle and ball mill process. Normal mortar pestle ground NPs have relatively greater size in comparison to the NPs obtained from ball mill process. This inequality in size of NPs leads to a larger surface area in case of ball mill processed NPs. Ball milling is a green, economical and efficient technology that uses kinetic energy to grind fine powders into particles below micrometer range [44b]. It has a very simple operational technique, low grade reaction conditions and requires no solvent or no particular temperature. This mechanical technique is a much energy-saving and environment-friendly process in comparison to other chemical treatment for surface nanoparticle hydroxylation, by causing least contamination. It increases the surface area of the particles and the oxygen-comprising functional groups on the surface of the particles, leading to a high adsorption capacity [44c]. Our present work mainly demonstrates the fabrication of self-poled piezoelectric nanocomposite thin films involves a comparison between the characterization and output performances of the thin films and PENGs, using the two types of NPs. The enhancement of β -crystallinity, improvement of thermal stability due to strong electrostatic interaction and interfacial polarization have been elaborated via various experimental procedures. The average size of clay NPs ground by mortar pestle was around 600–700 nm and for ball mill ground NPs the average size was 200–300 nm. On analyzing the characteristics of the two types of composite thin films, ball mill ground clay NPs/PVDF film showed better β phase nucleation in comparison to mortar pestle ground clay NPs/PVDF thin film. Subsequently, two superior, high performing, portable PENGs were designed by incorporating mortar pestle ground clay NPs (named MPENG) and ball mill ground clay NPs (named BPENG). MPENG exhibits a large value of open circuit voltage (V_{oc} = 85 V) and short circuit current (I_{sc} = 1.6 μ A) with a power density = 4115 μ Wcm⁻³ and BPENG provides V_{oc} = 125 V and I_{sc} = 1.9 μ A, with power density = 7187 μ Wcm⁻³ under a periodic force by hand (F ~ 13.3 N and 12.7 N for MPENG and BPENG respectively.) These 2 devices could lighten up 25 and 40 no. of blue LEDs when connected a series connection and we charged a 2.2 μ F capacitor in 16 s. The nanogenerators generated significant voltage from various body movements like heel pressing, jogging or from vibrations or air flow from various instruments and thus can be efficiently applicable for next generation electronics (Table.1).

Table 1

Different amounts of nanoparticles, both by mortar pestle and ball milling process added to the PVDF matrix with their respective notations.

Notations	Mass percentage of clay nanoparticles	Mass of clay nanoparticles (gram)	Mass of PVDF (gram)	Amount of DMSO (mL)
PP	0.0	0.0000	0.2500	5.000
MP1	1.0	0.0025	0.2500	5.000
MP5	5.0	0.1250	0.2500	5.000
MP10	10.0	0.0250	0.2500	5.000
BM0.5	0.5	0.00125	0.2500	5.000
BM1.0	1.0	0.00250	0.2500	5.000
BM1.5	1.5	0.00375	0.2500	5.000

2. Experimental section

2.1. Composite thin film synthesis

The detailed procedure for the processing of raw clay for obtaining pure clay nanoparticles is described in the supporting file. Mortar pestle ground clay NPs/PVDF and ball mill ground clay NPs/PVDF thin films were prepared by a simple solution casting method. Firstly, 250 mg of PVDF pellets (Sigma-Aldrich, Germany; M: 180,000 GPC; Mn: 71,000) was made to dissolve in 5 mL of dimethyl sulfoxide (DMSO) (Merck) at 60 °C under continuous magnetic stirring to obtain a clear solution. Then mortar pestle ground and ball mill ground clay NPs were added to the previously prepared clear solution in 1, 5, 10 mass % and kept on the magnetic stirrer for 12 h under uniform lab condition, then it was kept for ultrasonication for 30 min to obtain a homogeneous mixture. The final solution was then cast on clean glass Petri dishes and kept in a dust-free oven for 12 h at 80 °C for complete drying of DMSO and eventually, the composite thin films were obtained. By the same procedure, pure PVDF thin film (without any dopant) was prepared. Therefore, 7 films in total were obtained. 3 among them contained 1, 5, 10 mass % of mortar pestle ground clay NPs (named as MP1, MP5, MP10 respectively) and the other 3 films had 0.5, 1, 1.5 mass % of ball mill ground clay NPs (named as BM0.5, BM1.0, BM1.5 respectively) loaded in them and 1 pure PVDF film (PP). With the use of the above made 2 types of doped PVDF films, 2 PENG were fabricated and named MPENG and BPENG, using a film having mortar pestle and ball mill ground clay as dopant, respectively. To optimize the content of clay nanoparticles in the composites MP1, MP5 and MP10 we prepared two films with 2.5% of mortar pestle ground clay NPs (MP2.5) (intermediate of 1% and 5%) and using 7.5% of NPs (MP7.5) (intermediate of 5% and 10%). From experimental results it was seen that the β phase increases on loading of clay into PVDF from 1% to 5%, attains a maximum β phase at 5% and then gradually decreases from 5% to 10%. The corresponding characteristic data have been provided in the [supporting information](#) file in [Fig. S7](#).

2.2. Fabrication of MPENG and BPENG

A small portion of the circular films, with the dimension of 2.7 cm $\times$ 2.4 cm $\times$ 51 μ m were cut from MP5 and BM1.0 thin films. Two aluminum electrodes of slightly smaller dimension of 2.6 cm $\times$ 2.3 cm (to avoid short circuit) and of around 63 μ m thick, were attached on both sides of each cut film. Two wires were also connected on both sides of each film to measure the output performance of the PENGs. These setups, including the film, electrodes and wire were properly compressed to eliminate any air gap, then encapsulated in polydimethylsiloxane (PDMS) gel (Sylgard 184, Dow Corning, ratio of 1:10) and dried in a vacuum desiccator for 15 min and for 1 h at 60 °C for the complete removal of any trapped air bubbles in the gel mixture. This insulating coating makes the devices robust and helps to eliminate triboelectricity during relative movement between the devices and the contacted objects during pressing. Finally, two flexible PENGs (MPENG and BPENG) of the dimension of 4.9 cm $\times$ 3.0 cm $\times$ 0.2 cm were fabricated successfully.

2.3. Characterization

2.3.1. Characterization of clay nanoparticles doped PVDF thin films and devices

A study of the electroactive β -phase nucleation was done by characterizing both types of doped thin films. The β -phase nucleation, microstructures, morphologies of the above synthesized thin films were studied with the help of Fourier transform infrared (FTIR) spectroscopy (FTIR-8400S, Shimadzu), using field emission scanning microscopy (FESEM; INSPECT F50), X-ray diffraction (XRD; Model-D8, Bruker AXS Inc., Madison, WI). Since this phase gives us an idea about the extent of piezoelectric, ferroelectric, and dielectric properties, the fraction

provides us with a notion about the amount of β polymorph present in composite samples.

The thermal stability of the doped PVDF and clay nanoparticle composite thin films were studied from the heating scan thermographs with the help of a differential scanning calorimeter (DSC-60, Shimadzu, Singapore).

3. Result and discussion

3.1. Field emission electron microscopy (FESEM) morphology

The surface morphologies of the mortar pestle and ball mill ground clay nanoparticles are shown in [Fig. 1](#) (a) and (b) respectively and the average size of clay NPs ground by mortar pestle is around 600–700 nm and for ball mill ground NPs the average size is 200–300 nm, as seen from the images. The FESEM images of pure PVDF and the clay-loaded PVDF samples are represented in [Fig. 1](#) (c) and 1(d)-(i) respectively. The surface morphologies of the mortar pestle ground clay NPs doped PVDF thin films (MP1, MP5, MP10) and ball mill ground clay NPs doped PVDF thin films (BM0.5, BM1.0, BM1.5) show the formation of clear spherulites with an average diameter of 5 μ m and 3 μ m respectively. This confirms the nucleation of electroactive β -crystals in the composite samples. The spherulites in the pure PVDF film has a diameter of $\sim$ 40 μ m, which confirms the presence of nonpolar α -crystals in pure PVDF film. The samples MP5 and BM1.0 show the maximum dispersion and the distribution properties of NPs in the PVDF matrix. Homogeneous and even distribution of clay NPs has been clearly observed in the mortar pestle ground and ball mill ground clay NPs doped PVDF thin films up to 5 mass% loading (MP5) and 1 mass% (BM1.0) loading respectively as shown in [Fig. 1](#) (e) and 1(h). On further addition of NPs to the PVDF matrix for both the cases, agglomeration of the NPs and the polymer matrix takes place. The FESEM images of agglomerated clay NPs in PVDF in MP10 and BM1.5 have been shown in [Fig. S2](#) (a) and (b) respectively. The formation of β phase and the thorough analysis of structural details were further studied by XRD analysis, FTIR spectra and DSC analysis.

3.2. X-ray diffraction (XRD) analysis

The confirmation for the nucleation of electroactive β -crystals in the composite thin films was further obtained from XRD analysis. [Fig. 2](#) (a) and (b) demonstrates the XRD pattern of pure PVDF and clay-loaded PVDF composites. As seen from the XRD graphs, the diffraction peaks are obtained at $2\theta = 17.6^\circ$ (100), 18.3° (020), 19.9° (021) and 26.6° ((201), (310)) for pure PVDF thin film, which clearly suggests the presence of nonpolar α -crystalline phase [45]. All the diffraction peaks corresponding to α and γ crystalline phases disappear on the addition of clay nanoparticles into the PVDF matrix and a sharp, prominent peak at $2\theta = 20.5^\circ$ ((110), (200)) is spotted. From this characteristic sharp peak, we can fairly conclude that the addition of clay nanoparticles to the PVDF has led to the nucleation of electroactive, polar β -crystals in the clay loaded PVDF composite thin films and waived off the α and γ crystallinity from it. From a further detailed study of the XRD graphs, we notice the maximum β crystalline diffraction peak at $2\theta = 20.5^\circ$ for both the fabricated films. The highest β crystallinity was observed for MP5 (5 mass percentage of mortar pestle ground clay NPs) and BM1.0 (1 mass percentage of ball mill ground clay NPs), as confirmed from XRD patterns. This happens because, on further loading of the NPs, agglomeration takes place leading to a decrease in the interfacial surfaces between the NPs and the PVDF matrix which eventually decrease the β -phase nucleation in the thin film. The FESEM images of agglomerated clay NPs in PVDF in MP10 and BM1.5 have been shown in [Fig. S2](#) (a) and (b) respectively. Quantitative analysis of β phase nucleation in the composite thin films can be done by calculating the ratio $I_{20.5}/I_{18.3}$, where $I_{20.5}$ and $I_{18.3}$ are the intensities of the peak at 20.5° ((110), (200)) and 18.3° (020) for both the films respectively. The value of the ratio is 3.85 for

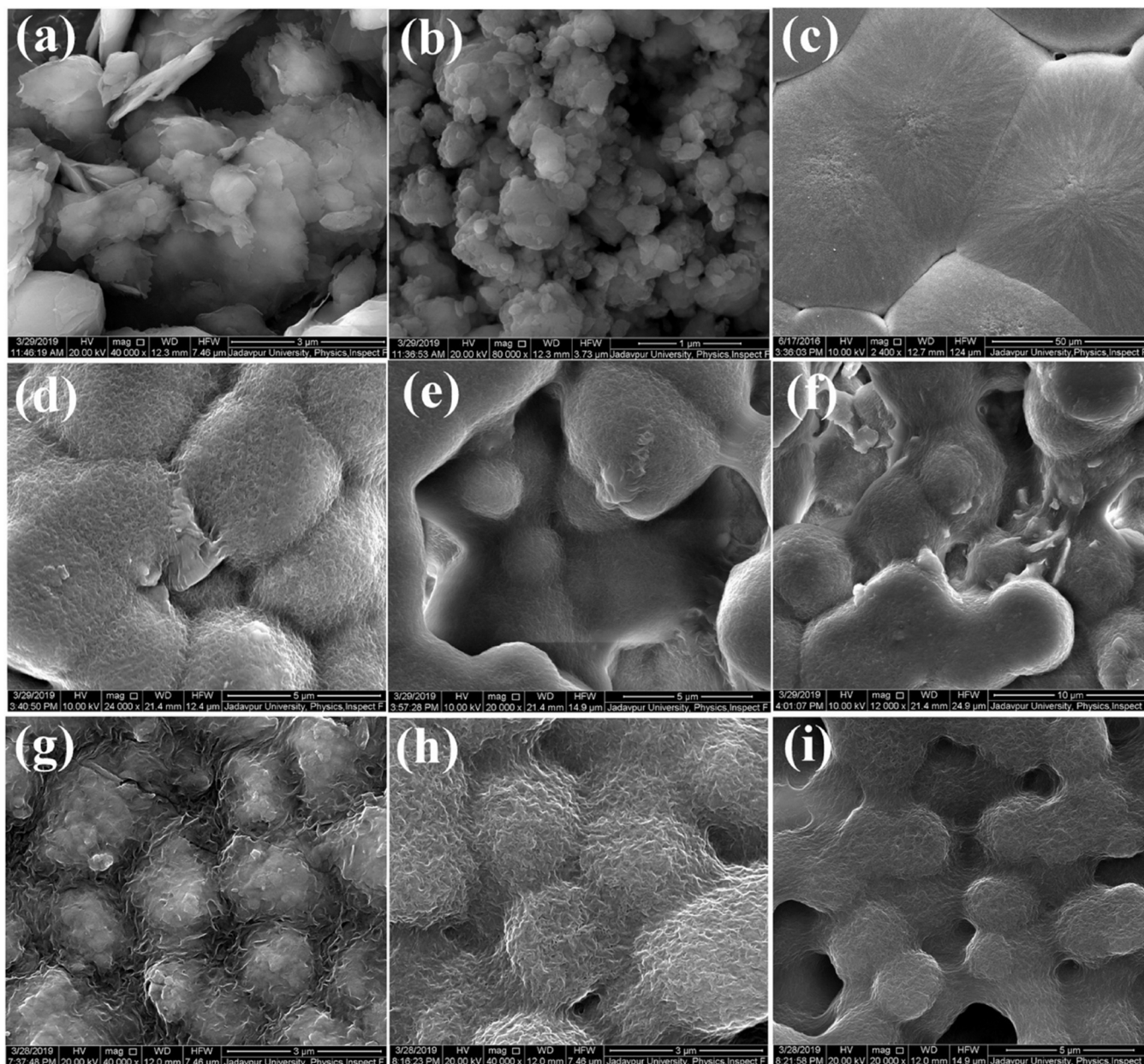


Fig. 1. FESEM image of (a) pure mortar pestle ground clay NPs, (b) pure ball mill ground clay NPs, (c) pure PVDF thin film, (d) MP1, (e) MP5, (f) MP10 thin films and (g) BM0.5, (h) BM1.0, (i) BM1.5 thin films.

MP5 and 11.24 for BM1.0, which clearly indicate a sharp increase in the value for ball mill ground clay doped thin film leading to a greater β .

crystallinity as shown from Fig. 2(c). This value obtained from the calculation evidently proves that the ball mill ground clay NPs have a greater ability to increase the β phase nucleation in the polymer composite thin films which can be due to the smaller size of the NPs.

3.3. Fourier transform infrared (FTIR) spectroscopy analysis

Apart from XRD analysis, the nucleation of electroactive β -crystals in the composite thin films was further validated and concluded by FTIR study of pure PVDF thin film versus mortar pestle/ball mill ground NPs aided thin films in the range of 400 cm^{-1} to 1350 cm^{-1} , as presented in Fig. 2(d) and (e). Pure PVDF film showcases its non-polar α -phase through the characteristic absorbance bands in the finely packed spectrum at 488 cm^{-1} (for CF_2 wagging) 532 cm^{-1} (for CF_2 bending), 615 cm^{-1} and 764 cm^{-1} (for CF_2 bending and skeletal bending), and

796 cm^{-1} and 976 cm^{-1} (for CH_2 rocking) [46]. These peaks (in the absorption band of pure PVDF thin film) clearly signify that it has mostly non-polar α -phase with negligible part of polar β or γ phases. Prominent characteristic peaks of the absorbance band at 840 cm^{-1} (for CH_2 rocking, CF_2 stretching and skeletal C-C stretching) and 813 cm^{-1} (for CF_2 asymmetric stretching) were obtained in the case of NPs doped thin films, which can validate some alignment in the PVDF polymer chain in the form of TTTT, confirming the presence of polar β polymorphs. The absorption peaks for the electroactive β phase were observed at 445 cm^{-1} (for CF_2 rocking and CH_2 rocking), 479 cm^{-1} (for CF_2 deformation) 510 cm^{-1} (for CF_2 stretching), 600 cm^{-1} (for CF_2 wagging) and 840 cm^{-1} (for CH_2 rocking, CF_2 stretching and skeletal C-C stretching) [46,47]. The most prominent peak was obtained at 840 cm^{-1} confirming the enhancement of the β phase and the absence of all the characteristic absorbance peaks agreeing to the α -phase proves complete fading away of any α phase properties of the composite thin films. Thus, we can effectively conclude that there is a huge enhancement of β phase

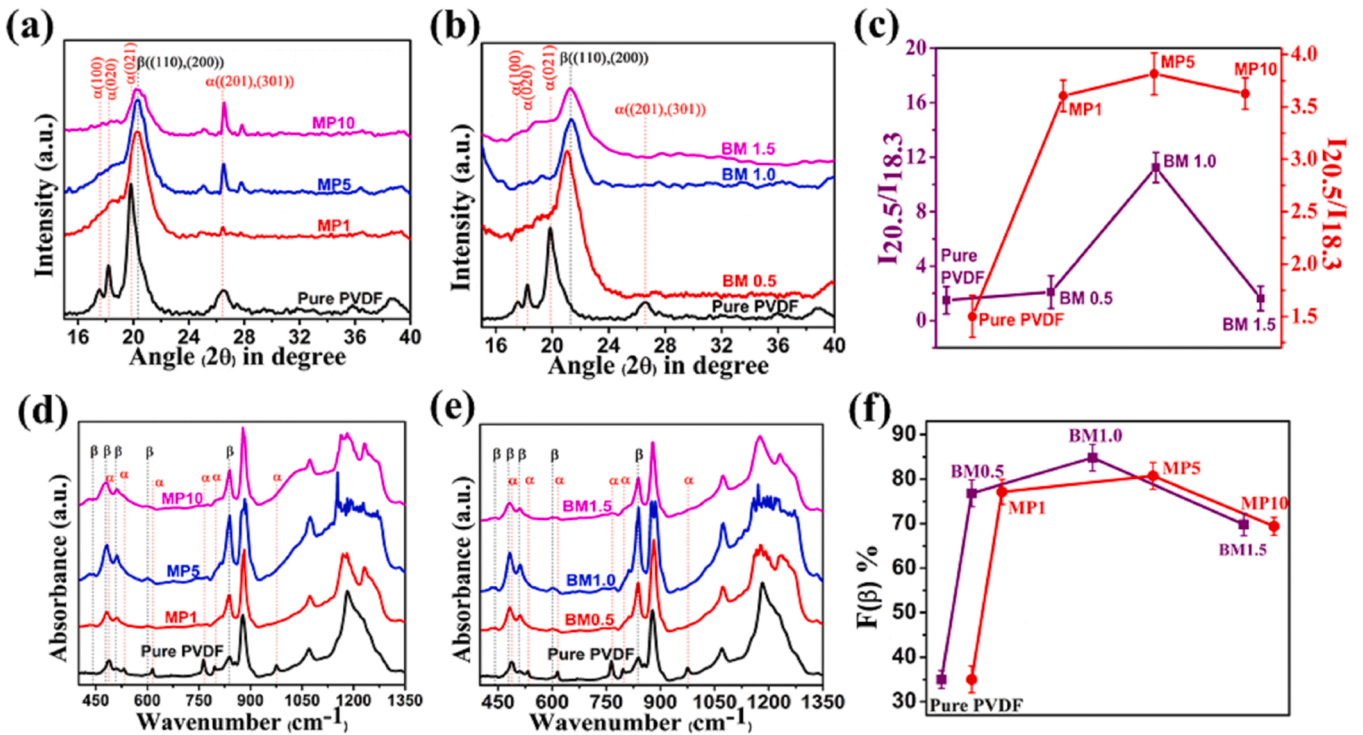


Fig. 2. (a) and (d) XRD spectra and FTIR spectra respectively for pure PVDF, MP1, MP5 and MP10 thin films, (b) and (e) XRD spectra and FTIR spectra for pure PVDF, BM0.5, BM1.0 and BM1.5 thin films, (c) Ratio of $I_{20.5}$ and $I_{18.3}$ for pure PVDF and composite thin films, (f) β -phase content of the thin films.

crystallinity in the MP/BM nanocomposites, which is possibly due to the nucleation of clay NPs with the polymer matrix [48]. In the FTIR spectra, closer examination of the graphs reveal that MP5 and BM1.0 have got maximum intensity for the main β phase characteristic peak of the absorption band, confirming maximum β phase crystallinity. Therefore, we can undoubtedly say that the FTIR analysis is in accordance with the XRD analysis. A quantitative analysis was also done to check the improvement of β -phase fraction ($F(\beta)$) from the FTIR spectra, using Lambert-Beer law. This fraction gives us knowledge about the quantity of β polymorph present in composite thin films, which henceforth helps in the analysis of the piezoelectric, ferroelectric, and dielectric properties of the samples. The β -phase fraction content $\{F(\beta)\}$, from the IR spectra, was calculated with the help of the Lambert-Beer law which states as [47,49]:

$$F(\beta) = \frac{A_{\beta}}{\left(\frac{K_{\beta}}{K_{\alpha}}\right)A_{\alpha} + A_{\beta}} \quad (1)$$

Where A_{α} is the absorbance at 764 cm^{-1} , A_{β} is the absorbance at 840 cm^{-1} , and the value of K_{β} is $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, and the value of K_{α} is $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ are the absorption coefficients at 840 cm^{-1} and 764 cm^{-1} , respectively. From Fig. 2(f) we see that the β -phase fraction ($F(\beta)$) increases with the increasing clay NPs loading content and attains a maximum value for MP5 (5 mass% of mortar pestle ground clay NPs) having a value of $F(\beta) = 80.7\%$ and for BM1.0 (1 mass % of ball mill ground clay NPs) having a value of $F(\beta) = 84.8\%$, whereas that for pure PVDF thin film $F(\beta) = 35\%$. It is experimentally seen that on further increasing the mass% of clay, $F(\beta)$ also increases, but up to a certain limit and then again decreases, since any further doping of clay reduces the β -crystal formation by demolishing the free chain movements of the PVDF matrix [34,50].

3.4. Differential scanning calorimetry (DSC) analysis

In addition to XRD and FTIR analysis, the confirmation of the β phase crystallinity was moreover obtained from differential scanning

calorimetry (DSC) analysis of the thin films. Fig. 3(a) and (b) represent the DSC thermographs for the phase crystallization and melting behavior of pure PVDF and clay-doped PVDF thin films. From the thermograph of neat PVDF, we observe that the melting point is at 163.14°C which clearly indicates the presence of non-polar α polymorph in the film [47,50,51]. For the composite thin films, as we can see, the melting points have been increased to a greater temperature, with MP5 and BM1.0 showing greatest value among all of them. From these experimental observations, we can say that this enhancement of melting temperature on the addition of clay NPs to the polymer matrix has occurred due to some morphological changes in the polymer matrix leading to the change in the crystallinity of PVDF. The nonpolar α crystal morph (TGTG conformation) in pure PVDF has been transformed into β crystal morph (TTTT conformation) yielding a good β phase in the composite thin films. A considerable amount of increase to 173.97°C (for MP5) and 172.82°C (for BM1.0) was seen due to the doping of clay NPs into the PVDF matrix. These experimental results evidently suggest that the clay nanoparticles play a vital role as a nucleating agent leading to the formation of β polymorphs. This fact is in accordance with the previous FTIR and XRD experimental results.

3.5. Working principle of composite thin film and mechanism of the PENG

In electrodynamics, Maxwell's equations are always consistent with the local invariance or conservation of charges. This can be written in the form of the equation of continuity as:

$$\nabla \cdot \vec{J} + \frac{\partial}{\partial t} (\nabla \cdot \vec{D}) = 0 \quad (2)$$

Or,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0 \quad (3)$$

From the continuity equation we can define charge density as:

$$\rho = \rho_f + \rho_b \quad (4)$$

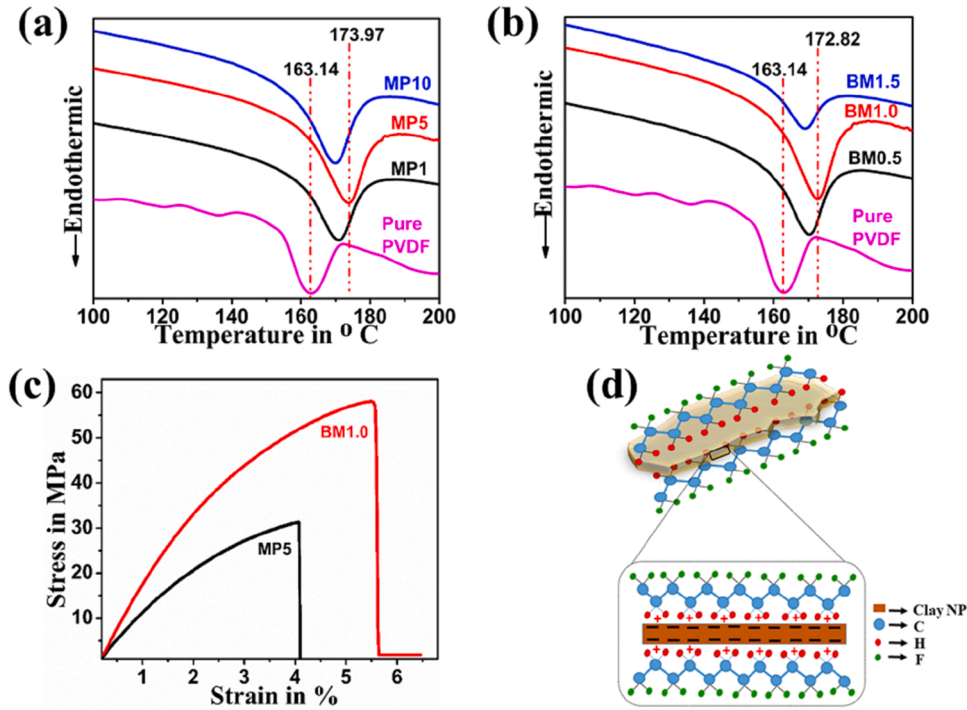


Fig. 3. (a) DSC curve for pure PVDF, MP1, MP5 and MP10 thin films, (b) DSC curve for pure PVDF, BM0.5, BM1.0 and BM1.5 thin films, (c) Stress-strain curve of MP5 and BM1.0, (d) Schematic diagram of ion-dipole interaction between clay NPs and PVDF polymer chain.

Where ρ , ρ_f and ρ_b are total, free and bound charges respectively.

Hence, we can define current density as:

$$J = J_f + J_b \quad (5)$$

Where, J , J_f and J_b are total, free and bound currents respectively.

For any dielectric material, the ancillary fields that take part during the dipole formation can be represented as:

$$D(r, t) = \epsilon_0 E(r, t) + P(r, t) \quad (6)$$

$$H(r, t) = 1/\mu_0 B(r, t) - M(r, t) \quad (7)$$

Where, D is the displacement field, ϵ_0 is the permittivity of free space, E is the electric field, P is the polarization, H is the magnetic field, μ_0 is the permeability of free space, B is the magnetic induction and M is the magnetization.

Here in our work, for the fabricated nanocomposite thin film, we shall make use of Maxwell's macroscopic equations or Maxwell's equations in matter, considering only free charges and current. The equations are as follows:

$$\nabla \cdot \vec{D} = \rho_f \quad (\text{Gauss's Law of electrostatics}) \quad (8)$$

$$\nabla \cdot \vec{H} = 0 \quad (\text{Gauss's law magnetostatics}) \quad (9)$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (10)$$

$$\nabla \times \vec{H} = \vec{J}_f + \frac{\partial \vec{D}}{\partial t} \quad (\text{Ampere's circuital law with Maxwell's addition}) \quad (11)$$

where, $\vec{E}$ is the electric field; $\vec{D}$ is the displacement electric field; $\vec{B}$ is the magnetic induction; $\vec{H}$ is the magnetic field; ρ_f is the volume charge density of free electron and $\vec{J}_f$ is the current density due

to free electron flow.

From electrodynamics, we know, displacement current for an electric field and the polarization current for an electric polarization are obtained from the following two equations respectively:

$$\vec{J} = \epsilon_0 \frac{\partial \vec{E}}{\partial t} \quad (12)$$

$$J_p = \frac{\partial \vec{P}}{\partial t} \quad (13)$$

Therefore, for a linear isotropic medium we can clearly articulate that the second term ($\epsilon_0 \frac{\partial \vec{E}}{\partial t}$) in Eq. (11) (Maxwell's fourth equation) is the total displacement current $\vec{J}_D$ and can be represented as:

$$\vec{J}_D = \frac{\partial \vec{D}}{\partial t} = \epsilon_0 \frac{\partial \vec{E}}{\partial t} + \frac{\partial \vec{P}}{\partial t} \quad (14)$$

The total displacement current being a time-dependent term, depend not only on the electric field but also on the electric polarization of the dielectric medium. For an electromagnetic wave, the first term of Eq. (14) ($\epsilon_0 \frac{\partial \vec{E}}{\partial t}$) gives rise to the magnetic field H . The enhancement of this term is taken under consideration for the better output performance of wireless communication systems like broadcast radios, mobile communications, Wi-Fi, televisions, RADAR etc. From the second term ($\frac{\partial \vec{P}}{\partial t}$), the enhancement of piezoelectric effect can be effectively done by increasing P , since it is dependent on the strain or force applied to the piezoelectric material. For a linear isotropic piezoelectric material, the piezoelectric equations on the application of mechanical strain, are [53a]:

$$\vec{P}_i = (e)_{ijk} (\vec{S})_{jk} \quad (15)$$

$$\vec{T} = C_E \vec{S} - e^T \vec{E} \quad (16)$$

$$\vec{D} = e \vec{S} - k \vec{E} \quad (17)$$

where $\vec{S}$ is the mechanical strain; $(e)_{ijk}$ is the piezoelectric third order tensor, $\vec{T}$ is the stress tensor and C_E is the elasticity tensor and k is the dielectric tensor.

For a linear polarizing medium the displacement current is represented as:

$$\vec{J}_{Di} = \frac{\partial \vec{P}_i}{\partial t} \quad (18)$$

Therefore we can clearly say that the piezoelectric effect and the output current density is linearly proportional to the rate of change of the strain or force applied to the material. We can now markedly say that our attained output result from our PENGs on the application of force is at par with the theoretical formulas.

When no external electric field E is applied on the dielectric medium, the displacement current solely depends on the polarization P , as can be seen from Eq. (18). Taking P along the z direction, we can rightfully write:

$$D_z = P_z = \sigma_p(z), \quad (19)$$

where, $\sigma_p(z)$ is piezoelectric polarization surface charges density of the material.

There we are left with the displacement current term as:

$$J_{Dz} = \frac{\partial P_z}{\partial t} = \frac{\partial \sigma_p(z)}{\partial t} \quad (20)$$

Hence from Eq. (20), we can conclude that the displacement current is directly proportional to the piezoelectric polarization surface charge density of the material. Therefore, smaller the size of the clay NPs, the greater will be the surface charge density leading to greater polarization. We can furthermore affirm this theoretical fact by our experiment on our devices, that is BPENG (using ball mill ground clay NPs) shows higher output performance than MPENG (using mortar pestle ground clay NPs). For BPENG, the clay nanoparticles used to fabricate the composite thin film were obtained by ball mill process. Ball mill can grind any material more finely than mortar pestle,

which is operated manually. Therefore, the NPs obtained from the ball mill has a much smaller size in comparison to the latter, leading to a high surface area. Consequently, The ball mill ground NPs have a larger surface area for a very small mass%, which leads to the device which has been designed using them to yield higher output results in comparison to the device making use of mortar pestle ground NPs.

The mechanical energy to electrical energy conversion mechanism of our fabricated nanogenerator is illustrated in Fig. 7(a). As stated earlier, the β -phase enhancement occurs due to the addition of clay NPs to the PVDF matrix, we can assuredly state that there is a formation of some strong electrostatic interaction between the clay NPs and the $-\text{CH}_2/\text{CF}_2$ dipoles of PVDF due to mechanical stress and the interfacial surface charge. When an external force is applied on the composite, opposite electrical charge separation occurs and hence the opposite polarity formed at the two opposite sides, which leads to the formation of electric dipole [54a–e]. We have provided a schematic diagram for the ion dipole interaction mechanism between clay NPs and PVDF polymer chain in Fig. 3(d). This phenomenon is purely due to the synergistic effect of the molecular dipoles and piezoelectric effect by the strong electrostatic interaction between the clay NPs and the dipoles of PVDF, leading to an all-trans configuration causing induced self-polarization. On the application of an external force on the device, redistribution and displacement of the dipoles in the self-poled polymer matrix takes place yielding higher the piezoelectric voltage production [34]. This increase of self-polarization effect due to the induced charge production in the electrodes and the alignment of dipoles in the crystal in the direction of applied mechanical force leads to a higher output result. On the application of a vertical force on the device, a positive polarization charge gets accumulated on the top electrode and simultaneously an

equal amount of induced negative charge accumulates on the bottom electrode [53a]. Therefore, a potential difference is obtained between the 2 electrodes that is directly proportional to the magnitude of the applied force and frequency of force, which henceforth leads to the flow of electrons through an external load. On the withdrawal of the vertical force, the accumulated charges on both the electrodes start retracing back to their initial state, which can be experimentally confirmed by the negative signal obtained in the voltage vs time graphs. This occurs since the dipoles instantaneously return back to their original state and electrons flow in the opposite direction, leading to a sharp decrement of piezoelectric potential. This entire process repeats itself in a similar manner on the application of a continuous vertical periodic compression and relaxation, yielding a good output performance of the MPENG and BPENG.

3.6. Output performance of PENGs

In this work, two piezoelectric nanogenerators have been fabricated using the most electroactive films (MP5 and BM1.0) and the detailed designing of the PENGs have been elaborated in the fabrication of MPENG and BPENG part under the Experimental section and Fig. 4(a) shows the schematic diagram of it. The digital images of MPENG and BPENG are shown in Fig. 4(f) and (g) respectively. Owing to their highest β crystallinity, these two films have been chosen to fabricate the PENGs for showcasing the highest piezoelectric response and piezo sensitivity. Fig. 4(b) shows how transparent the nanocomposite thin films are. Fig. 4(c) and (d) demonstrates the flexibility of our fabricated thin films. They can be easily folded or rolled without causing any disfigurement of the films. MP5 and BM1.0 revealed a maximum of 32 MPa and 56 MPa tensile strength respectively with Young's modulus of 1408 N/mm² and 2150 N/mm² respectively. Therefore, it can be easily concluded that the elasticity of the composites have been increased manifold on the addition of NPs into PVDF, since the Young's modulus of pure PVDF [53b] is around 700 N/mm². A stress vs strain curve of MP5 and BM1.0 is provided in Fig. 3(c). Fig. 4(e) and (h) show how thin and flexible the nanogenerators are and the portable nature of the PENGs. They can be easily bent, rolled or folded to quite an extent, without damaging the devices. Fig. 5(a) and (b) show the open circuit output voltage vs time graph for MPENG (PENG designed using MP5) and BPENG (PENG designed using BM1.0) respectively. This output voltage was obtained by constant periodic application of force by human fingers and the output was detected using a digital storage oscilloscope (Keysight, Oscilloscope DSO-X 3012 A). The short circuit current for both the devices was also measured by an electrometer (Keysight, Electrometer B2985) and the output results are graphically presented in Fig. 5(c) and (d) for MPENG and BPENG respectively. When periodic force was exerted using human fingers, our nanogenerators generate excellent output characteristics of open circuit voltage (Voc),

the short circuit current (Isc), and a superior power density. MPENG yields a positive open-circuit voltage (Voc) of ~ 85 V and short-circuit current (Isc) of ~ 1.6 μA , leading to a power density of ~ 4115 $\mu\text{W}/\text{cm}^3$. Under similar applied force, BPENG shows a voltage Voc of ~ 125 V and Isc ~ 1.9 μA , giving a power density of ~ 7187 $\mu\text{W}/\text{cm}^3$, under a periodic force by hand of $F \sim 13.3$ N and 12.7 N for MPENG and BPENG respectively. Output voltage of fabricated PENGs have been tested in bending mode, showing a very low output voltage (triboelectric contribution) of 0.6 V and 0.8 V for MPENG and BPENG respectively. A 'polarity switching' test was also performed for our PENGs to exclude the triboelectric interference and to confirm that the output electric signals are obtained from the piezoelectric effect entirely. The data regarding this has been included in the supporting file in Fig. S6. The calculations for force and power density have been included in the supporting file. A magnified view of a single peak of the open circuit voltage is represented in Fig. 5(a) and (b) itself, showing a tiny second peak along with the main voltage peak which might be due to the damping effect of the applied force present in the device layers, that is,

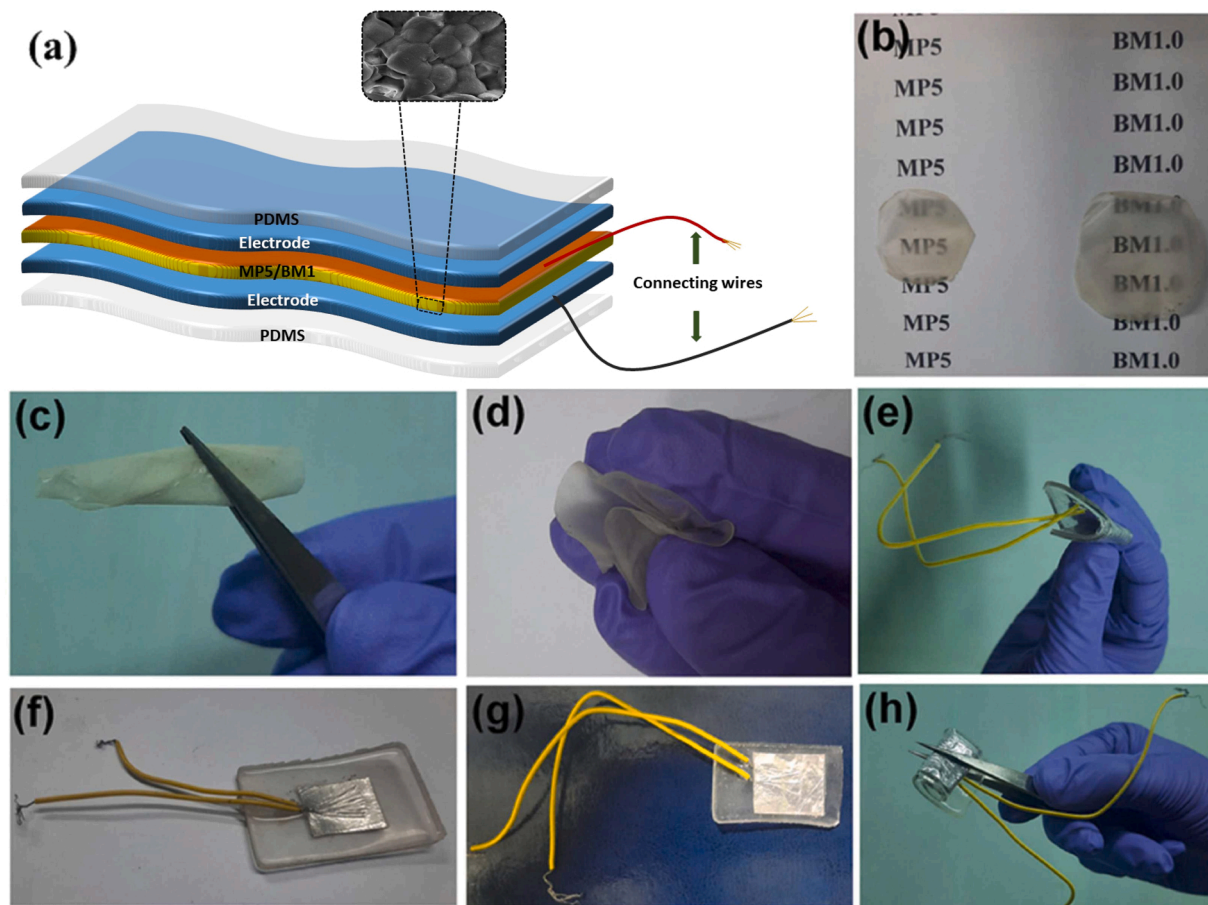


Fig. 4. (a) Schematic diagram of device layout, (b) Transparency assessment of MP5 and BM1.0 thin film, (c) and (d) Flexibility test of composite thin films, (e) and (f) Flexibility test of MPENG and BPENG respectively, (g) and (h) Digital image of MPENG and BPENG respectively.

some residual force still remains even after the withdrawal of the hand. Output voltage performance of our designed devices with varying frequency of 2–12 Hz of force (applied force ~ 5 N) by a self-designed device (from Ocean college, Zhejiang University, PR China) was also experimentally analyzed and the maximum voltage was obtained at 10 Hz, as shown in Fig. 5(e). This gradual increment of output voltage with frequency is primarily due to an improved equivalence of the impedance in the system, leading to an amplification of current. This increment does come to a saturation point at a particular frequency where the impedance equivalence decreases, hence we experience a decrease in the output voltage [5,52]. In our case, beyond 10 Hz the output voltage gradually started to decrease at 11 Hz and 12 Hz and the reason behind this decrement of voltage is that, at higher frequency of force, the compression cycles becomes very small and the device takes more time to come back to its original state. This infers that the frequency of the saturation point was 10 Hz and after which there is a gradual decrease in the impedance equivalence. Fig. 5(f) demonstrates the magnified view of 2 cycles of V_{OC} corresponding to 10 Hz frequency. A study of the output performances of MPENG and BPENG under the same applied force of 5 N and same frequency of 5 Hz was conducted and yielded an output voltage of 29 V and 47 V respectively. The power densities for our PENGs were calculated using the formula:

$$P = \frac{V^2}{R_L v} \quad (21)$$

Where, P is the power density, V is the output voltage, R_L is the load resistance and v is the operative volume of the nanogenerator. The maximum power density for MPENG at a load resistance of 46 M Ω was 641 $\mu\text{W}/\text{cm}^3$ and BPENG yielded a maximum power density of 1232

$\mu\text{W}/\text{cm}^3$ at a load resistance of 58 M Ω . The comparison of the output voltages and power densities obtained from the two devices have been provided in the supporting information file in Fig. S4. From Fig. 5(a) and (b) itself, we can see a negative open-circuit voltage of 20 V for both the fabricated nanogenerators, while is primarily caused during the releasing state of the force. The output voltage and the power density acquired from our fabricated PENGs were far superior to various previously documented biodegradable material or clay-based prototype PENGs which indicates the novelty of our work based on its biodegradability of the dopant and performance of the device. By comparing with the recent works [54e], our proposed MPENG and BPENG are by far the most superior clay nanoparticle based PENG reported so far. A comparative study for output performances our fabricated MPENG and BPENG with previously reported flexible PENGs have been done in table S2 in the supporting information file.

The ability of our devices to convert other forms of biomechanical energy to electrical energy was also analyzed by recording the output voltage obtained from foot pressing. A considerable voltage of 32 V and 41 V were obtained from MPENG and BPENG, when the nanogenerators were pressed gently by heel as illustrated in Fig. 6(a) and (b). An appreciable output voltage of 5 V and 9 V was seen when jogging was performed on our fabricated devices as shown in Fig. 6(c) and (d) for MPENG and BPENG. The output voltage obtained for the case of heel pressing was relatively greater than the case of jogging since the contact area between foot and nanogenerator and the force imparted were relatively higher in comparison to the case of jogging. This concept can easily be utilized for designing self-powering wearable devices. Furthermore, MPENG and BPENG were attached to the body of a vortex machine to check the output voltage generated from the vibration of the

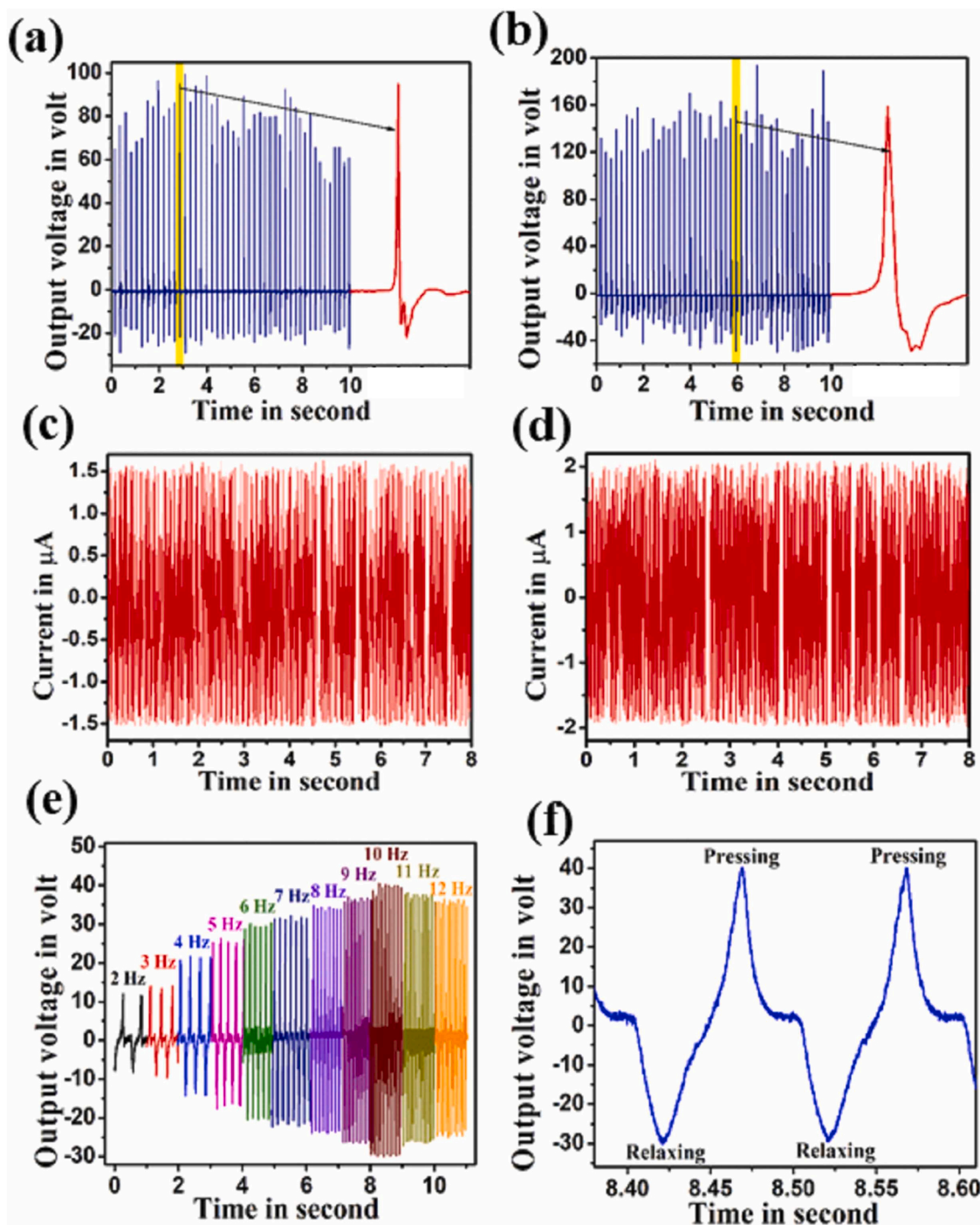


Fig. 5. Open circuit voltage (V_{oc}) of (a) MPENG and (b) BPENG, Short circuit current (I_{sc}) of (c) MPENG and (d) BPENG by imparting force by fingers, (e) Frequency dependent V_{oc} for a frequency of 2–12 Hz, (f) Magnified view of 2 cycles of V_{oc} corresponding to 10 Hz frequency under application of 5 N force.

machine, as shown in Fig. 6(e) and (f) respectively. The experiment was done for two different speed settings of low and high for the vortex machine. A voltage of 1.5 V and 2.3 V (for low and high speed) were obtained for MPENG and 6.5 V and 9.0 V (for low and high speed) were obtained for BPENG. Output voltage was also obtained when air was blown on the nanogenerators by a hair dryer from a distance, for two speed settings. Observed voltage values were 0.18 V and 0.25 V (for low and high speed) for MPENG and 0.29 V and 0.38 V (for low and high speeds), as illustrated in Fig. 6(g) and (h) respectively. The proposed nanogenerators paves a simple way for the prospective applicability in self-chargeable portable gadgets, in various biomedical applications or

can be used as body motion sensors. The piezoelectric responses for our devices have been investigated by calculating the piezoelectric coefficient d_{33} of MP5 and BM1.0. For MP5, d_{33} was 39.75 pC/N at 50 Hz and for BM1.0 d_{33} was 50.10 pC/N at 50 Hz. The capacitance with varying frequency for MPENG and BPENG were measured using digital LCR meter (Agilent, E4980A). The detailed calculation for d_{33} and the graph is provided in the supporting file, Fig. S3.

3.7. Practical applications of MPENG and BPENG

To check the novelty and the practicality of our 2 PENGs in real life,

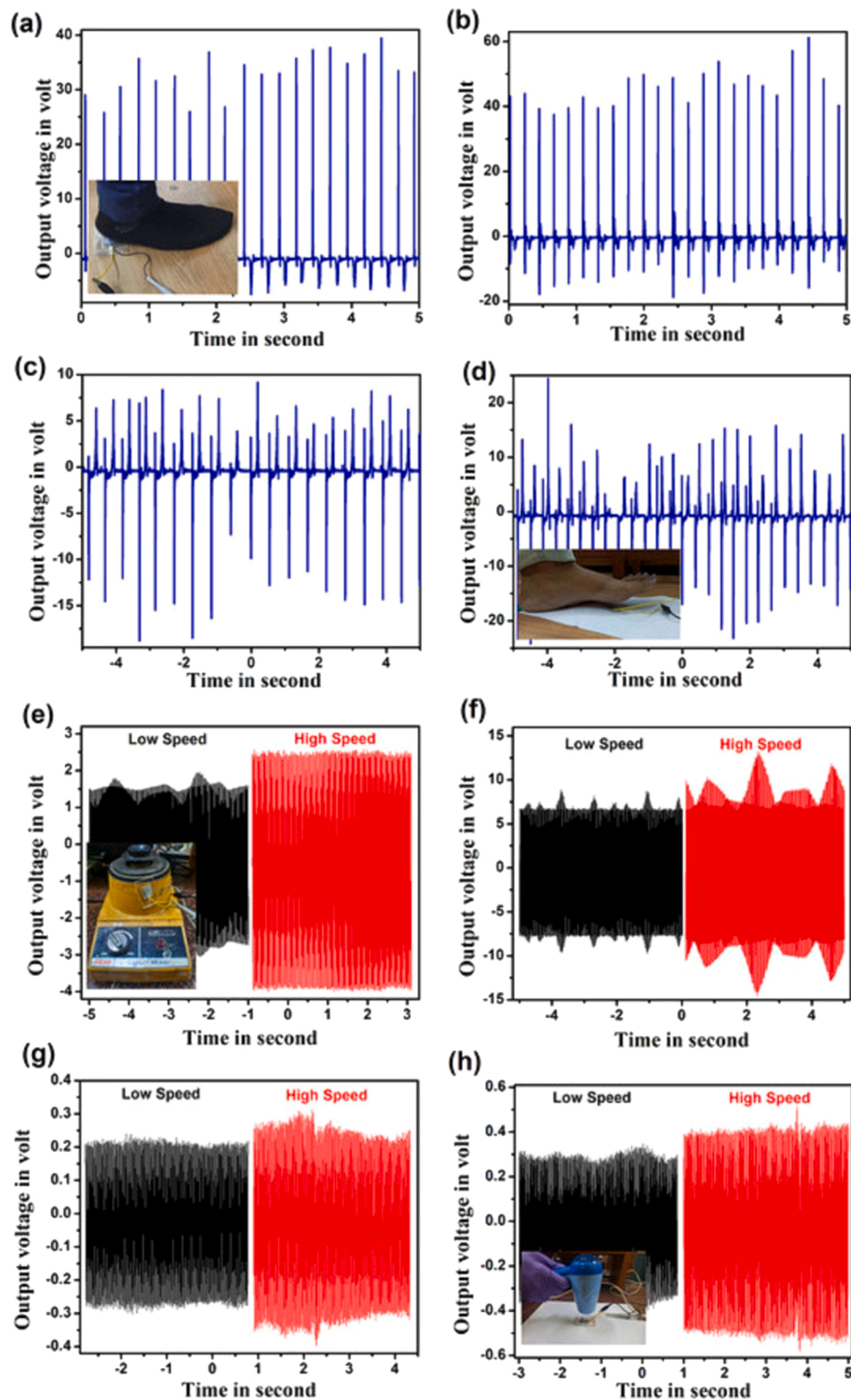


Fig. 6. Open circuit voltage (V_{oc}) obtained by heel pressing on (a) MPENG and (b) BPENG, V_{oc} obtained from jogging on (c) MPENG and (d) BPENG, V_{oc} obtained the vibration of vortex machine for (e) MPENG and (f) BPENG, V_{oc} obtained from air blown on (g) MPENG and (h) BPENG.

we lighted up a number of commercially available light-emitting diodes (LEDs) with the help of our devices (as shown in video VS1 and VS2 in [supporting information](#)), to inspect their energy conversion competency. On making proper electrical connections and by using a full wave rectifier, MPENG and BPENG were able to lighten up 25 and 40 no. of

blue LEDs when connected in series, on the application of periodic force, as shown in [Fig. 7\(c\)](#) and (d) respectively. Our designed nanogenerator can also be used as a storage device. To prove this proficiency of our devices, we charged a $2.2 \mu\text{F}$ capacitor up to 3.1 V and 3.5 V in 16 s using MPENG and BPENG respectively by making proper electrical

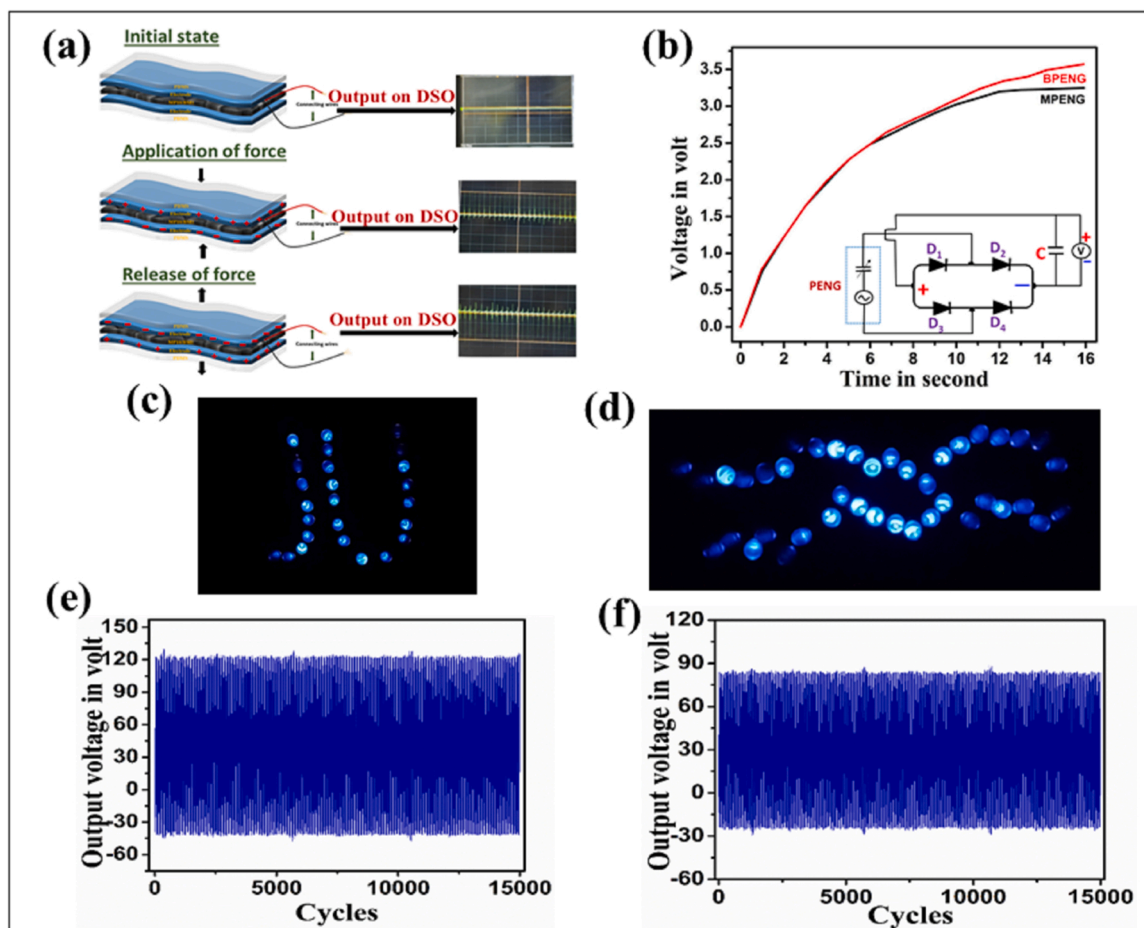


Fig. 7. (a) Possible mechanism of piezoelectric nanogenerator for voltage generation, (b) charging graph for MPENG and BPENG with required circuit diagram for charging capacitor, (c) and (d) snapshot of the blue LEDs at the time of light up by the MPENG and BPENG respectively, durability test for 15000 cycles for (e) MPENG and (f) BPENG.

connection and a four-probe full wave rectifier. The exponential charging graph of output voltage vs time for the capacitor suggests the high energy-storage ability of our fabricated PENGs, as illustrated in Fig. 7.

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To check the longevity and the stability of our fabricated PENGs, the output performances were frequently checked for 15 weeks (one cycle of 300 s per week) and it was observed that the output performances for both the devices remained stable and nearly the same. On the periodic application of force by hand, the durability or the endurance test for MPENG and BPENG for more than 15000 periodic cycles was performed, generating a stable and continuous output voltage with very low deviation as shown in Fig. 7(e) and (f) respectively. The output voltages for MPENG and BPENG on the periodic application of force of 4 Hz by hand, for 3 consecutive weeks exhibited nearly the same value and maintained no less than 94% of the initial output voltage, throughout. The consistency and the stability of MPENG and BPENG at same frequency (4 Hz) are shown in the supporting file information, Fig. S5.

4. Conclusion

To recapitulate the entire work, we primarily inspected the influence of clay NPs on the electroactive β -phase enhancement of PVDF in the clay modified nanocomposite thin films. From FESEM micrographs,

homogeneous and even distribution of clay NPs has been clearly observed with an average size of around 600–700 nm for clay NPs ground by mortar pestle and for ball mill ground NPs the average size was 200–300 nm, with samples MP5 and BM1.0 showing maximum dispersion properties of NPs in the PVDF matrix. On the addition of mortar pestle ground and ball mill ground clay NPs to the polymer, the maximum β -phase crystallization accomplished is $\sim 80.7\%$ and $\sim 84.8\%$ respectively. This considerable increase from 35% (for pure PVDF) to the previously mentioned value is due to the good electrostatic ion-dipole interaction and high interfacial polarization. The thermal stability of both types of clay NPs incorporated films were improved with the highest melting point of 173.97°C (for MP5) and 172.82°C (for BM1.0). We also checked the output performances for our fabricated devices using the most effective nanocomposite thin films using both the kind of clay NPs. MPENG exhibits a large value of open circuit voltage ($V_{oc} = 85\text{ V}$) and short circuit current ($I_{sc} = 1.6\text{ }\mu\text{A}$) with power density $\sim 4115\text{ }\mu\text{Wcm}^{-3}$ and BPENG provides $V_{oc} = 125\text{ V}$ and $I_{sc} = 1.9\text{ }\mu\text{A}$, with power density $\sim 7187\text{ }\mu\text{Wcm}^{-3}$ under a periodic force by hand ($F \sim 13.3\text{ N}$ and 12.7 N for MPENG and BPENG). By applying the same magnitude of force, and using a bridge rectifier MPENG and BPENG are capable to glow 25 and 40 blue LEDs respectively and can charge a $2.2\text{ }\mu\text{F}$ capacitor within 16 s. The calculated results of piezoelectric coefficient d_{33} of MP5 and BM1.0 were 39.75 pC/N and 50.10 pC/N , at 50 Hz frequency. Therefore, we can conclude that our designed PENGs make the use of eco-friendly dopants, exhibiting good output performances. Body movement sensing is also an important attribute of our PENGs. Thus, our devices can be used in several self-powered electronic gadgets

and various power storage devices by converting mechanical energy from our daily activities to electrical energy, without any harm to the environment. Therefore MPENG and BPENG can be utilized in various biomedical fields or can be used as body motion sensor, if can be improvised properly and can be put under industrial scale.

CRedit authorship contribution statement

Namrata Das: Conceptualization, Investigation, Methodology, Writing – original draft. **Debmalya Sarkar:** Conceptualization. **Md. Minarul Saikh:** Visualization. **Prosenjit Biswas:** Visualization. **Sukhen Das:** Supervision. **Nur Amin Hoque:** Supervision, Resources. **Partha Pratim Ray:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2022.107628](https://doi.org/10.1016/j.nanoen.2022.107628).

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Mr. Debmalya Sarkar, Ph.D research scholar. He has completed his Bachelor's degree and Master's degree in 2016 and 2018 respectively from Jadavpur University with Physics honors. Currently, he is a PhD research scholar in Jadavpur University. His main research topics are fabricating nanocomposites and harvesting energy with the help of piezoelectric, triboelectric nanogenerator by using natural and functional nanoparticles.



Md. Minarul Saikh, Assistant Professor and Ph.D research scholar. He is an Assistant Professor and former Head of the Department (HOD) in the Department of Physics at the Government General Degree College at Pedong, Kalimpong, India. He obtained his B.Sc. and M.Sc. in Physics from University of Kalyani, India. His research interest lies in the field of materials science, nanotechnology, and sustainable energy harvesting by piezoelectric nanogenerator and triboelectric nanogenerator.



Dr. Prosenjit Biswas, Assistant professor. He is an Assistant Professor in the Department of Physics, Kalimpong College, Kalimpong, India. He has completed his Ph.D. from the Department of Physics, Jadavpur University, India in the year 2022. He completed his M.Sc. and B.Sc. in Physics in 2016 and 2014 respectively from the same university. His field of research interest includes synthesis of various nanoparticle, polymer composites, piezoelectric nanogenerator and development of multifunctional polymeric power cell.



Prof. Sukhen Das, Professor. Prof. Das is a Professor in Department of Physics, Jadavpur University, India. He attained his Bachelor's degree, Master's degree and Ph.D. in Physics from the same university in 1987, 1990 and 1995 respectively. Before joining Jadavpur University, he had been working as a Scientist-B and Scientist-C in CSIR-Central Glass & Ceramic Research Institute, India. He has guided several doctoral and post-doctoral researchers and has numerous research publications in various prestigious journals. The area of his research work focuses on material science, nanoscience, development of ceramics, polymeric material, antimicrobial bio-ceramics, nanomaterials and their application in various sectors.



Dr. Nur Amin Hoque, Postdoctoral research fellow He is a postdoctoral fellow at IISER, Mohali, India, working on "development of PVDF and its copolymer (PVDF TRFE) nanocomposite-based ultrasound transducer for detecting and generating of different high frequencies sound wave. ". He worked as Postdoctoral research fellow at Zhejiang University, Zhejiang, PR China from 2019 to 2020. He has completed his undergraduate and postgraduate degree in 2011 and 2013 and earned his Ph.D in Physics from Jadavpur University, India in 2018. His research interests lie in development of piezoelectric and high dielectric polymeric materials for designing effective energy harvester, wearable electronics, piezo-catalyst, Li/ Na ion cell, solar cell, ferroelectric perovskite materials development for photovoltaic application and self-charged photo-power-cell.



Ms. Namrata Das, Ph.D research scholar. She is currently pursuing her Ph.D from Department of Physics, Jadavpur University, India. She completed her Bachelor's degree and Master's degree in 2016 and 2018 respectively, in Physics from Jadavpur University as well. Her current research focuses on the fabrication of electroactive polymer composites, their various characterization techniques and their application in green energy harvesting domain such as piezoelectric nanogenerators and self-powered sensors.



Prof. Partha Pratim Ray, Professor. Prof. P P Ray is a Professor in Department of Physics, Jadavpur University, India. He obtained his Bachelor's degree, Master's degree in Physics from Calcutta University, India in the year 1994 and 1996 respectively and received his Ph.D degree in Physics from Jadavpur University in 2002. He worked as a visiting Scientist at Institute of Energy Conversion, University of Delaware, USA and at Ecole Polytechnique and Laboratoire de Génie Electrique de Paris, France. His research interests are on amorphous silicon, microcrystalline silicon, silicon-germanium based thin film solar cell, polymer-inorganic nanoparticle based solar cell, thin film Schottky diode.



Development of a lead-free, high-frequency ultrasound transducer with broad bandwidth and enhanced pulse-echo response, employing β -Ni(OH)₂/PVDF-TrFE piezoelectric composite

Namrata Das^a, Debmalya Sarkar^a, Nitin Yadav^b, Asfak Ali^c, Sukhen Das^{a,1,*}, Partha Pratim Ray^{a,2,*}, Nur Amin Hoque^{d,3,*}

^a Department of Physics, Jadavpur University, Kolkata 700032, West Bengal, India

^b Department of Physics, IISER Mohali, Sahibzada Ajit Singh Nagar, Punjab 140306, India

^c Department of Electronics and Telecommunication Engineering, Jadavpur University, Kolkata, West Bengal 700032, India

^d SAIS Department, Indian Association for the Cultivation of Science, Kolkata 700032, India

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ABSTRACT

Piezoelectric composite-based high-frequency ultrasound transducers (USTs) have gained significant prominence as a leading and effective tool in non-invasive medical diagnosis, non-destructive testing and diverse industrial applications. In this study, we present the fabrication of a lead-free, high-frequency ultrasound transducer (P-UST), having a very simple and unique assembly procedure. To achieve this, we employed PVDF-TrFE based piezoelectric composite thin film (NTr5) integrated with a transition metal hydroxide (β -Ni(OH)₂ nanoplates) and demonstrated its outstanding performance, thereby showcasing its potential in various applications. The composite exhibited exceptional β -phase crystallization, reaching impressive maximum value of 90.04%, owing to the favorable interaction between electrostatic ions and dipoles, along with the presence of strong surface polarization. Upon analysis, remarkable piezoelectric (d_{33} ~50.22 pm/V) and ferroelectric properties were observed in the composite material, accompanied by significant enhancement in surface roughness. Here, the piezoelectric property's impact on UST output is well-explained using Maxwell's equation. P-UST, being a versatile system, is capable of generating and receiving pulse signals. By conducting a pulse-echo test on an aluminium block with ultrasound gel, we achieved a peak-to-peak output voltage of 5.19 V, surpassing the output voltage magnitude of any previously reported UST in this field. The Fast Fourier transformed data of the voltage output revealed an impressive -6 dB bandwidth of 51.22 MHz (102.4%) with a high central frequency of 50.01 MHz. Hence, our P-UST's exceptionally high central frequency promises significantly enhanced ultrasound image resolution, which expands the potential for highly accurate medical assessments for advanced healthcare outcomes and improving patient well-being.

1. Introduction

Ultrasound, which lies in the frequency range of 20 kHz up to a few GHz has proved itself extremely useful and necessary in a broad range of fields. It has got numerous prominent applications in fields like medical science, material science, nanotechnology, testing, mixing, cleaning, navigation, communication etc [1,2]. In today's world, the ultrasound imaging technique is the most common medical diagnostic imaging

practice due to its non-invasive [3–5,6a,b], innocuous, pocket-friendly nature, and for its quality to suppress background interferences. The most widely used ultrasound probes [6b] or ultrasound transducers (USTs) work on the principle of piezoelectricity. The piezoelectric material present in the UST converts mechanical energy into electrical energy, making the transducer an effective diagnostic tool with broad bandwidth and high sensitivity [7]. Customarily, conventional USTs employ single crystals or piezoceramics like lead zirconate titanate (Pb

* Corresponding authors.

E-mail addresses: sdasphysics@gmail.com (S. Das), parthapray@yahoo.com (P. Pratim Ray), nuramin03@gmail.com (N. Amin Hoque).

¹ orcid.org/0000-0001-8372-3076.

² orcid.org/0000-0003-4616-2577.

³ orcid.org/0000-0003-1133-018X.

($Zr_xTi_{1-x}O_3$, PZT) [8,9], which possess a high electromechanical coupling coefficient. Although the aforesaid materials showcase good piezoelectric response, they have high acoustic impedance mismatch, narrow bandwidth, low electroacoustic energy-conversion efficiency, unsatisfactory heat-dissipation efficiency of metal, and much trouble is faced in the conformation of the aperture. In addition to this, these aforementioned piezoelectric materials utilized in the transducers have a considerable thickness, posing challenges when attempting to incorporate larger-sized crystals into compact and portable transducers.

While designing ultrasound transducers employing piezoelectric polymer thin films, it is important to have detailed knowledge about the characteristics and behavior of the polymer material for the effective implementation of it [10,11]. Properties like dielectric constant, the capability of working at a high frequency of more than 20 MHz and mechanical stability of the film have a noteworthy impact on the performance of the transducer. Thin film-based ultrasound transducers have proved themselves potentially useful in several biomedical imaging modalities [12–18] where an ultrasound pulse is transmitted into the body from the transducer and consequently the pulse gets reflected back from the interfaces between the body tissues, exhibiting excellent impulse receiving property. This reflected pulse having various acoustic impedances, is carried back to the transducer and eventually, we obtain physiological information about the tissues. Apart from biomedical applications, thin film-based ultrasound transducers have potential applications in the field of ultrasound nondestructive testing, abbreviated as NDT [19]. This is a characterization method where the thickness or the internal structure of a test sample is investigated with the help of ultrasound waves. For various concrete structures, tracking the structural integrity of the interior or the surface of the material and thereby evaluating the type of damage is done by NDT. In comparison to various conventional detection techniques, thin film-based USTs prove themselves more advantageous since the ultrasounds emitted from them can easily penetrate through several layers and can accurately detect flaws [20–22]. The field of polymer film-based USTs is still relatively unexplored, with only a limited number of studies reported so far. Among the recent advancements in this area, Du et al. demonstrated the use of polymer-based optoacoustic transducers for ultrasound imaging by employing a lead halide perovskite material [9]. Petritz et al. worked on ferroelectric transducers employing spin-coated PVDF-TrFE polymer [23a].

In the recent past, Poly(vinylidene fluoride) (PVDF) and its copolymers are being extensively used to fabricate thin films for transducers due to their excellent properties like yielding broad bandwidth, noteworthy mechanical flexibility, low acoustic impedance and can be used to fabricate very thin films. Poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), which is a copolymer of PVDF is also one of the most explored piezopolymers since it has high polarization, good solvent compatibility, high electromechanical coefficient, high thermal stability, very low mechanical and electrical loss in comparison to normal PVDF [7,23a,24]. Furthermore, various acoustic impedances of the reflected pulse from PVDF-TrFE based UST almost match with that of the living cells or tissues and with water, producing high-resolution images. Hence, PVDF-TrFE works in our concerned frequency range and the above-mentioned suitable characteristics of PVDF-TrFE make it a potential option to be used in designing an ultrasound transducer. PVDF and its copolymers are mainly comprised of the five main crystalline polymorphs, α , β , γ , δ , and ϵ [23b], categorized based on the bond orientation of the $-CH_2$ and $-CF_2$ dipoles. α -phase is the non-polar phase, normally formed by the melting of the polymer and having the trans-gauche chain formation which leads to the self-cancellation of the dipoles. Among the polar phases (β , γ and δ), β polymorph is the most important one with the conformation of TTTT due to its superior piezoelectric, ferroelectric, pyroelectric and dielectric properties [25]. Moreover, amidst the various copolymers of PVDF, PVDF-TrFE comprises of 20–50 mol% of TrFE which helps in easy polarization and crystallization of the polymer into piezoelectric β polymorph, owing to

the steric effects and the interaction between the dipoles [26].

There have been scarce reports on the development of UST utilizing polymer nanocomposites incorporated with transition metal hydroxide nanoparticles. Nickel hydroxide (a transition metal hydroxide) ($Ni(OH)_2$) has improved physiochemical properties and is a popular semiconducting metal hydroxide [27,28]. $Ni(OH)_2$ possesses good power density, colossal dielectric constant, enhanced specific energy and high cycle ability which leads to its immense utilization in the fields of supercapacitors, energy harvesters and storage devices [29,30]. It has also been experimentally proven that a very less mass% of $Ni(OH)_2$ when incorporated into the polymer matrix not only improves the polarization property, but also increases the ultrahigh breakdown strength of the composite [31a]. There are primarily two polymorphic states of nickel hydroxide, α - $Ni(OH)_2$ and β - $Ni(OH)_2$, which get transformed into γ - $NiOOH$ and β - $NiOOH$ respectively, when the formers get charged up. Among these two polymorphs, β - $Ni(OH)_2$ possesses greater stability in comparison to the α -polymorph [31b]. This is because, β - $Ni(OH)_2$ possesses a layered structure that enables easy ion movement. On the other hand, α - $Ni(OH)_2$ exhibits a more compact arrangement with stronger bonding, which leads to increased energy requirement for ion mobility and high internal strain within the crystal lattice. Here, in this work, we have synthesized ultrafine β -nickel hydroxide nanoplates from nickel acetate tetrahydrate by simple hydrothermal method. The nanocomposite composed of this synthesized β - $Ni(OH)_2$ nanoplates and the piezoelectric polymer PVDF-TrFE (30–70%) was prepared by a simple spin coating method. This technique has been used for film deposition due to its low cost, simplicity and comparatively easy process. Thin, homogeneous and uniform films can be obtained by employing this technique [32].

Our present work mainly demonstrates the designing of a lead-free ultrasound transducer utilizing β - $Ni(OH)_2$ nanoplates incorporated piezoelectric composite thin film, demonstrating exceptional performance. Upon characterization of the composite thin film, we observed a significant crystallization and an extremely high β phase content of 90.04%, which indicates that the nanoplates possess favorable piezoelectric characteristics. Further investigation into the piezoelectric and ferroelectric response of the composite thin film revealed an impressive and high piezoelectric coefficient (d_{33}) of 50.22 pm/V. Moreover, our transducer, capable of both generating and receiving pulse signals, exhibited exceptional performance showcasing a remarkable peak-to-peak output voltage of 5.19 V. Notably, the transducer demonstrated an exceptionally broad -6 dB bandwidth of 51.22 MHz (102.4%) having a central frequency of 50.01 MHz, which shall lead to significantly high-resolution ultrasound images. Considering the superior output voltage, ultra-broad bandwidth, and remarkably high central frequency, our designed transducer shows immense potential for successful implementation on an industrial scale. This lead-free transducer design holds promise for applications in the photoacoustic field, enabling the acquisition of high-resolution ultrasound images in various industrial and medical domains which enables the precise detection of abnormal tissues in living bodies, offering a significant, nontoxic advancement in medical imaging. Our polymer composite film-based ultrasound transducers have also effectively overcome the challenges encountered with piezoelectric crystal-based transducers. This is attributed to the significantly reduced thickness and smaller size of the composite. These exceptional characteristics, combined with the innovative design of the ultrasound transducer, contribute to its robustness, compactness and portability.

2. Experimental section

2.1. Materials

PVDF-TrFE powder (M.W. g/mol, Sigma-Aldrich, USA), N, N dimethylformamide (DMF), (Merck, India), nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$) (Merck, India) and lithium hydroxide (LiOH) (Merck,

India).

2.2. Synthesis of nickel hydroxide nanoplates

A simple hydrothermal process was employed for the synthesis of β -nickel hydroxide nanoplates with the help of nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and lithium hydroxide (LiOH). These chemicals were AR grade and were used without any further purification. 0.3 M nickel acetate tetrahydrate salt was dissolved in 60 mL of double distilled water and the prepared salt solution was kept under vigorous stirring on a magnetic stirrer. After thorough mixing for about 30 min, the pH of the solution was brought to 12 by gradual addition of 1 M lithium hydroxide to the salt solution. This prepared solution was then transferred to a Teflon-lined stainless steel autoclave setup (80 mL in volume), filling it up to 80 % of its capacity. The setup was then kept in a clean, dry hot air oven at 150 °C for 12 h. The light green coloured precipitate obtained was then centrifuged and washed with double distilled water quite a number of times to bring the pH of the precipitate to 7. Eventually, the precipitate was collected, dried at 80 °C for 12 h and ground into a fine powder with the help of a mortar pestle to obtain β -nickel hydroxide nanoplates [33]. We have prepared the β -form of $\text{Ni}(\text{OH})_2$ as it is the most stable form [31a].

2.3. Composite thin film fabrication

Nickel hydroxide based thin film was prepared by a simple spin coating method. To fabricate the polymer composite NTr5, we employed the widely used solution blending method [34,35]. This method is a classical and straightforward approach for preparing polymer

composites, involving the uniform dispersion of nanoparticles in a solvent that is compatible with both the polymer and the nanoparticles. This method is particularly effective in producing composite films with stable and homogeneous dispersions. A few more details about this method have been inserted in the [supporting data](#) file. First, 0.15 g of PVDF-TrFE powder was added to 3 mL of dimethylformamide (DMF) and kept under constant stirring at 60 °C. Then 5 mass% of β -nickel hydroxide nanoplates were added to the already prepared clear polymer solution and stirred continuously for 12 h. To achieve a uniform blend, the solution underwent additional ultrasonication for a duration of 30 min. Subsequently, 200 μL of this well-mixed solution was casted onto an aluminium substrate, which had a gold coating on it. The coating process involved spinning the substrate at 300 revolutions per minute (r.p.m.) for a period of 60 s, utilizing a Programmable Spin Coater SpinNXG-P1 from Apex Instruments. As a subsequent step, another 200 μL of the solution was applied onto the previously deposited film. This spin coating process was carried out at 700 r.p.m. for a duration of 120 s which allowed for the uniform distribution of the solution. Finally, it was dried in a clean dry hot air oven at 60 °C for 15 min, to form a uniform $\text{Ni}(\text{OH})_2$ incorporated (named NTr5). For the comparison of β -phase nucleation content in the composite thin film, a pure PVDF-TrFE thin film (PTr) was also synthesized as a control setup. The schematic diagram illustrating the fabrication process of NTr5 composite film with the help of the above-described simple spin coating method is shown in Fig. 1(a).

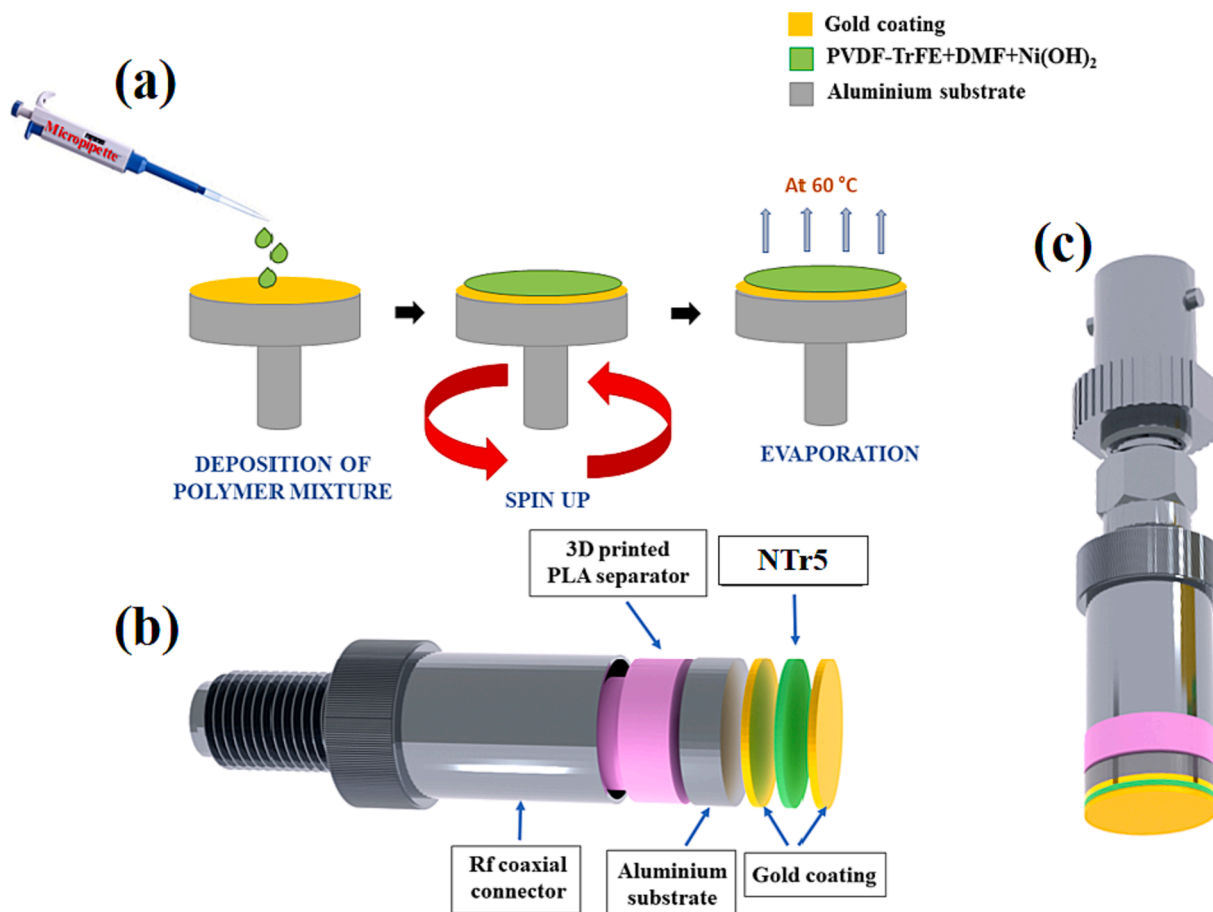


Fig. 1. (a) Schematic diagram illustrating the fabrication process of NTr5 composite thin film using simple spin coating method, (b) The assembly concept of the ultrasound transducer, exhibiting all the layers separately, (c) Complete schematic diagram of P-UST after assembly.

2.4. Designing of composite thin film-based ultrasound transducer (P-UST)

For fabricating the ultrasound transducer, firstly a cylindrical aluminium substrate was taken, having a diameter of 9 mm. The backing layer substrate of aluminium was tailor-made to specific requirements and the surface of the aluminium substrate was perfectly levelled to a smooth plane by the milling process with the help of a CNC machine, forming a T-like appearance. It was then properly washed several times with ethyl alcohol and was made free of any undesired impurities on the substrate. This layer acted as the backing layer of the ultrasound transducer. On this clean and smooth aluminium surface, gold was uniformly sputtered to form a thin uniform gold coating of approximately 20 nm in thickness with the help of Quorum Q150R Plus-Rotary Pumped Coater. This gold layer on the aluminium surface served as the bottom electrode of the ultrasound transducer. Thereafter, the composite thin film was spin coated onto the gold sputtered aluminium substrate according to the above-mentioned procedure in the Composite

thin film synthesis section, forming the matching layer of P-UST. PVDF-TrFE-based composites are particularly effective in this regard since their acoustic impedance closely align with that of living cells or tissues as well as water [36], resulting in the production of high-resolution images by the USTs, hence a separate matching layer was not required. Furthermore, these composite films exhibit a relatively low insertion loss, making it easier to match their acoustic impedance to that of human tissues [37,38]. The thickness of the composite NTr5 film was approximately 26 μm . Not only does the gold coating plays the role of an electrode (bottom electrode) in the transducer setup but also does it help in the proper binding of the polymer composite thin film to the aluminium substrate. Electrical poling of the composite thin film was done by first annealing NTr5 at 80 $^{\circ}\text{C}$ over the course of 1 h and then a slowly increasing DC voltage was applied from 0 kV to 32 kV, from a height of 13 mm. The detailed description and the various conditions maintained during the poling procedure has been added in the [supporting data](#) file. Subsequently, another layer of gold of about the same thickness as the former layer (~ 20 nm) was again sputtered over the

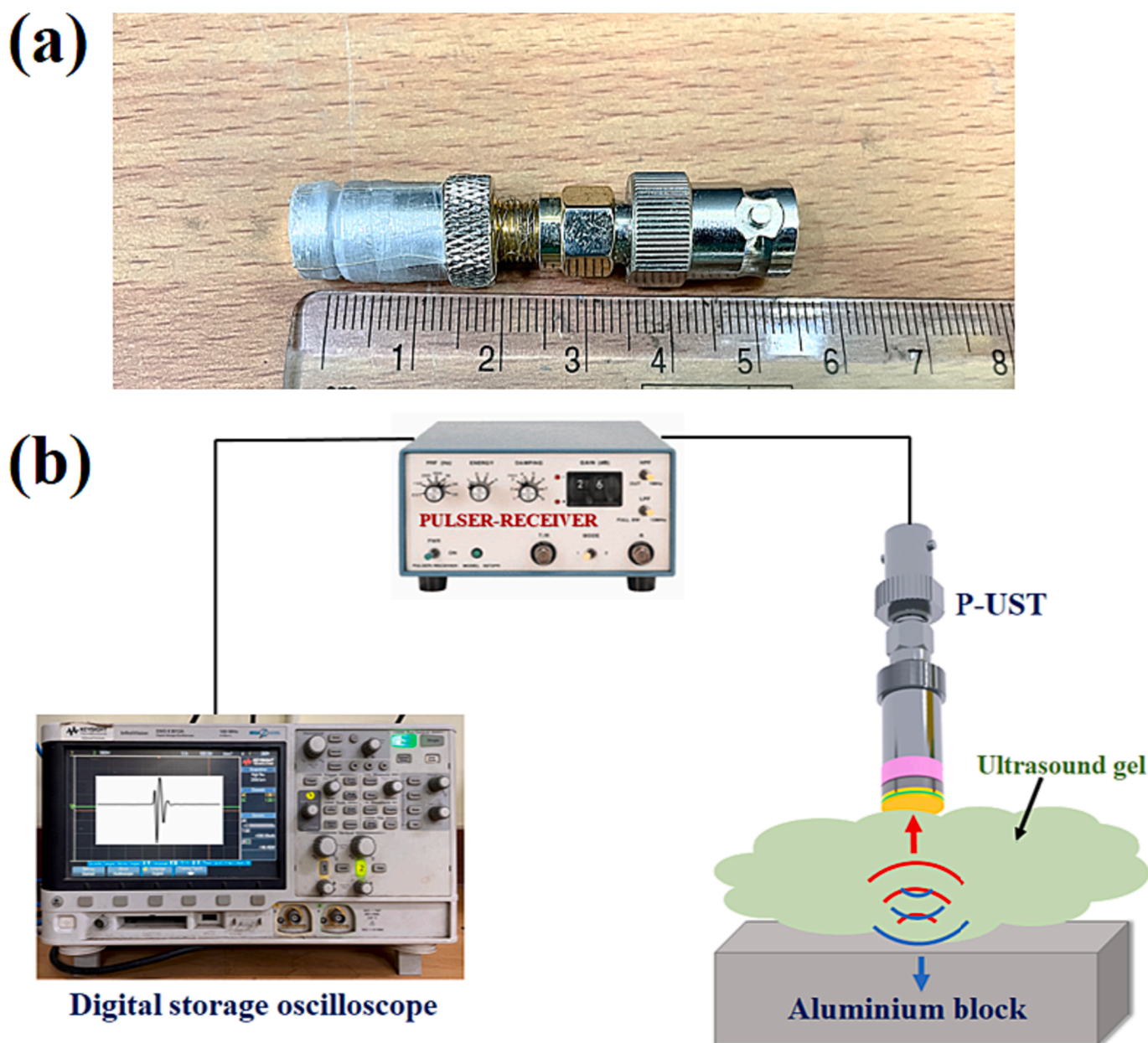


Fig. 2. (a) Digital image of the self-assembled ultrasound transducer P-UST, (b) Schematic diagram of the whole operating setup of our P-UST.

piezoelectric composite thin film, serving as the second electrode (top electrode) layer of the transducer. Thereafter, the daintily assembled four layers were securely attached to the central pin of an RF (radio frequency) coaxial connector. To prevent the T-shaped substrate from coming into contact with the outer conducting part of the RF coaxial connector, a 3D-printed PLA (polylactic acid) separator was added. This separator served as a protective barrier, ensuring that there was no direct contact between the T-shaped substrate and the outer conducting component of the RF coaxial connector, as can be seen from the schematic diagram of P-UST in Fig. 1(c). When all the aforementioned components were combined, the UST acquired a tubular shape with an approximate length of 6 cm. The assembly concept of the UST, exhibiting all the layers separately has been shown in Fig. 1(b). To establish the complete circuitry, a copper wire was utilized to connect the RF connector and the top electrode. This connection ensured the completion of the circuit when the transducer (P-UST) was connected to a pulser-receiver setup. The digital image of the self-assemble ultrasound transducer P-UST is illustrated in Fig. 2(a). This exclusive idea of using $\text{Ni}(\text{OH})_2$ stands out as there has been limited research on utilizing transition metal hydroxides in transducer designing. Herein, the assembly procedure for the UST is very unique and innovative, that sets it apart from conventional designs of ultrasound transducers. This new approach ensures that the transducer is exceptionally compact, portable and user-friendly, making it highly convenient and easy to use in practical life.

2.5. Experimental setup for the operation of P-UST

Our designed ultrasound transducer (P-UST) was attached to a pulser-receiver (OLYMPUS-5073PR) setup with 75 MHz and -3 dB of ultrasonic bandwidth. The receiver is characterized by a maximum bandwidth (-3 dB, $R_L = 50 \Omega$) ranging from 1 kHz to 75 MHz. The -3 dB bandwidth of the receiver stage is an inbuilt specification of this particular model. It offers an ultrasonic bandwidth of 75 MHz (-3 dB) and is equipped with a fast rise time spike pulser. This design extends its performance capabilities, especially when working with 50 MHz transducers. Subsequently, the output of the ultrasound transducer was captured and monitored by connecting it to a digital storage oscilloscope (Keysight Oscilloscope DSO-X 3012A). The pulse echo output data was acquired by operating P-UST over an aluminium block with a generous layer of ultrasound gel on it. The application of the gel enhanced the ultrasound's velocity, leading to an improved transmission. To analyze the pulsing and echo responses, the transducer was positioned 5 mm away from the aluminium target block. During operation, great care was taken to ensure optimal contact between the transducer and the gel, with the objective of eliminating any air gaps between the contacting surface of the transducer and the aluminium block. This meticulous approach aimed in enhancing the efficiency and accuracy of the transducer's performance for the transmission of pulses and the reception of echoes. Since, our fabricated P-UST not only generated an ultrasound signal but also acted as a receiver itself, therefore no separate pulse receiver was further required. The schematic diagram of the whole operating setup of our P-UST is demonstrated in Fig. 2(b) and this setup facilitated the detection and recording of the ultrasound signals, enabling further analysis and observation of the transducer's output.

3. Characterization techniques

3.1. Characterization of $\text{Ni}(\text{OH})_2$ nanoplates and composite thin film

A detailed study of the characteristics and the various properties of $\text{Ni}(\text{OH})_2$ powder and the piezoelectric composite thin film NTr5 was carried out. Structural morphologies like shape, size and pattern of the samples were examined using field emission scanning microscopy (FESEM; INSPECT F50, Netherlands) functioning at a bias voltage of 10 kV to 30 kV. EDS mapping was also performed for the analysis of the

elemental mapping of the sample with the help of Bruker Quantax EDS analyzer, equipped with the FESEM machine. The β -phase nucleation of NTr5 film has been studied with the help of Fourier transform infrared (FTIR) spectroscopy (FTIR-8400S, Shimadzu) in the wavenumber range of 450 cm^{-1} to 1350 cm^{-1} . The crystallographic structures of $\text{Ni}(\text{OH})_2$ powder and NTr5 were also inspected by X-ray diffraction analysis (XRD; Model-D8, Bruker AXS Inc., Madison, WI) with the help of monochromatic $\text{Cu-K}\alpha$ radiation, under 40 kV and 40 mA. Data was taken at a scan speed of 0.2 s/step for 2θ value of 10° to 80° . To confirm the enhancement of the piezoelectric and the ferroelectric properties of NTr5, Piezo force microscopy analysis was performed using the Piezo force module of the Piezoresponse Force Microscopy (PFM), Oxford Instruments, Asylum Research. For PFM analysis, NTr5 was subjected to a dual signal with a DC bias voltage ranging from -7 V to +7 V, applied across its thickness. The surface roughness of the composite was examined from the AFM image, obtained from the same instrument as well.

4. Results and discussion

4.1. Morphological and microstructural analysis

The morphologies of the synthesized $\text{Ni}(\text{OH})_2$ nanoparticles and the composite thin film NTr5 were analysed using Field Emission Electron Microscopy (FESEM). Fig. 3(a) shows the formation of distinct, uniform nanoplates of $\text{Ni}(\text{OH})_2$ with an average size of 70–170 nm. It can also be seen that the nanoplates have a flaky pattern with a flat and smooth surface. These morphological characteristics can increase the breakdown strength of the composite thin film [31]. Furthermore, the very small size of the nanoplates also increased the overall surface area of $\text{Ni}(\text{OH})_2$ nanoparticles, which in turn has increased the β -phase nucleation in the composite thin film due to enhanced polarization and high surface charge density [25]. The FESEM images of pure PVDF-TrFE thin film (PTr) and the composite thin film (NTr5) are represented in Fig. 3(b) and Fig. 3(c) respectively. Both the micrographs displayed roughened and non-uniform surfaces, composed of tiny grains which are randomly ordered [39]. The surface of the pure and the composite thin films showcases a crystalline laminar pattern over the entire area [40]. Fig. 3(c) clearly shows the homogeneous distribution and dispersion of $\text{Ni}(\text{OH})_2$ nanoplates over the entire surface of the polymer. To experimentally confirm the uniform dispersion of β - $\text{Ni}(\text{OH})_2$ nanoplates within the PVDF-TrFE matrix, we conducted elemental mapping for NTr5, as illustrated in the Figure S1 in the supporting data file. This elemental mapping visually represented the homogeneous distribution of the various key elements within the NTr5 composite. The results clearly indicated that the $\text{Ni}(\text{OH})_2$ nanoplates have been evenly distributed throughout the polymer matrix, demonstrating a random dispersion pattern. The EDS spectroscopy was employed to analyse the distribution of the various elements in $\text{Ni}(\text{OH})_2$, showcasing the various proportions of nickel (Ni), oxygen (O) and hydrogen (H) within the compound, as shown in Fig. 3(d). The inset of this figure exhibits the atomic weight% of the various elements in the nanoparticles. Thus, this characterisation technique also confirms the successful synthesis of $\text{Ni}(\text{OH})_2$ nanoplates.

4.2. Structural study of nanoparticles and electroactive β -phase analysis of composite (X-ray diffractogram)

The X-ray diffractogram pattern of β - $\text{Ni}(\text{OH})_2$ nanoplates, provides an overview about the purity and the well crystalline structure formation. The characteristic peaks in the diffraction pattern of $\text{Ni}(\text{OH})_2$ shows the reflection at the 2θ values of 19.52° (001), 33.01° (100), 38.57° (101), 52.12° (102), 58.98° (110), 62.69° (111), 70.48° (103), 72.71° (201). These peaks correspond to the hexagonal phase of β - $\text{Ni}(\text{OH})_2$, [41,42] confirming the formation of nickel hydroxide nanocrystals (JCPDS, file No. 14-0117) [33,43] and [44]. For detailed information about the crystal parameters and microstructure, Rietveld refinement

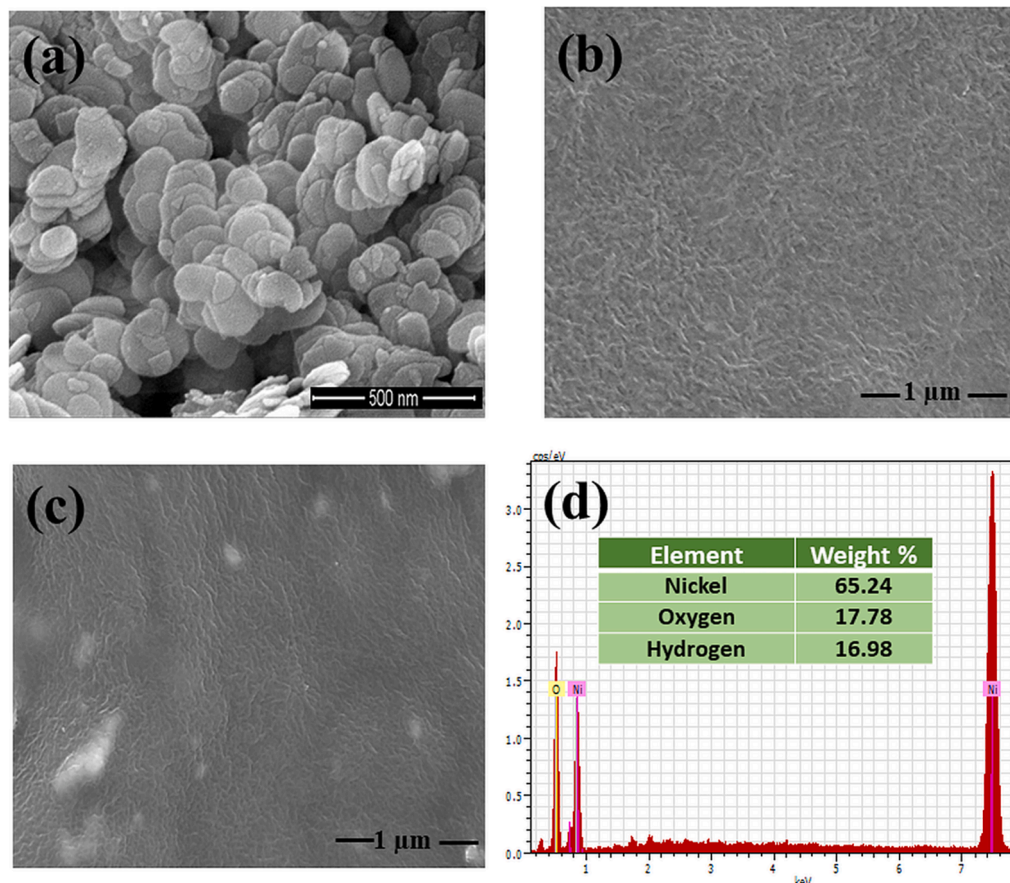


Fig. 3. (a) FESEM image of pure $\text{Ni}(\text{OH})_2$ nanoplates, FESEM images of (b) pure PVDF-TrFE thin film (PTr) and (c) the composite thin film (NTr5), (d) EDS spectrum of the various elements in $\text{Ni}(\text{OH})_2$ and the inset shows the weight percentage of the various elements present in the $\text{Ni}(\text{OH})_2$ nanoplates.

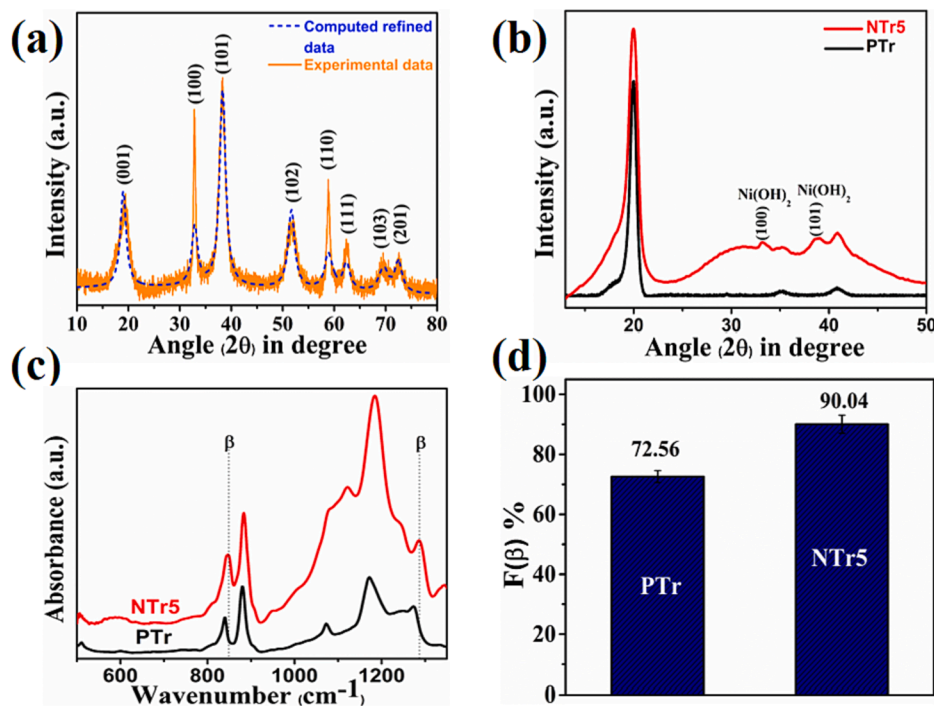


Fig. 4. (a) Experimental and computed refined X-ray diffractogram of $\text{Ni}(\text{OH})_2$ nanoplates, (b) X-ray diffractogram of pure PVDF-TrFE thin film (PTr) and the composite thin film (NTr5), (c) Fourier transform infrared spectroscopy analysis of PTr and NTr5 thin films, (d) Comparison of β -phase content of PTr and NTr5 thin films.

was performed for curve better fitting. Refinement of the experimental X-ray diffractogram was executed with the help of Maud v2.94 software. Fig. 4(a) illustrates the experimental and the computed refined X-ray diffractogram of Ni(OH)₂. The parameters for the refined computed XRD data at the end of the final cycle are represented in Table 1. Herein, the X-ray analysis conducted on the β-Ni(OH)₂ nanoplates determined their average crystalline size to be approximately 7.66 nm, thus providing valuable insights into the structural characteristics of the nanoplates.

The values of these salient parameters can also be obtained by calculations, using some renowned formulas as mentioned below. Using the Debye-Scherrer equation, the average crystalline size of β-Ni(OH)₂ can be predicted from the characteristic diffraction peaks with high intensities. According to this equation [45]:

$$D = \frac{K \lambda}{\beta_{1/2} \cos \theta} \quad (1)$$

where, D represents the crystalline size of the nanoparticles, K represents the Scherrer constant (0.98), λ represents the wavelength of the incident monochromatic Cu-Kα beam (1.54 Å), β denotes the full width at half maximum (FWHM) and θ represents the respective Bragg's angle. With the help of Bragg's equation, we can easily find the distance between the atomic layers or interplanar spacing (d) of the crystal. The equation is represented as:

$$2d \sin \theta = n \lambda \quad (2)$$

where, n represents the order of diffraction in the form of an integer. Since the β-Ni(OH)₂ has a hexagonal structure, the lattice parameters (a, b, c) of the nanoparticles can be easily calculated using the formula:

$$\frac{1}{d^2} = \frac{4}{3a^2} (h^2 + hk + k^2) + \frac{l^2}{c^2} \quad (3)$$

where, h, k and l represent the Miller indices and for hexagonal structure, we know that a = b ≠ c. The calculated average values of the lattice parameters are a = 3.13 Å, b = 3.13 Å, and c = 4.63 Å. These values are well matched with the theoretical value of lattice parameters from literature review [31a,46]. Subsequently, using these calculated values of a, b and c, we calculated the volume of a unit cell with the help of the equation:

$$V = a \times b \times c \quad (4)$$

The volume of a unit cell of the nanoparticle, denoted as V, was determined to be 45.35 Å³. The value of the dislocation density can be obtained using the formula:

$$\rho = \frac{1}{D^2} \quad (5)$$

where, ρ is the dislocation density. This parameter indicates the number of defects present in the nanoparticle, determined by the length of the

dislocation lines present in each unit volume of the sample crystal. The dislocation density value of nanoparticles is influenced by the presence of defects, and hence it exhibits variation depending on the number of defects present in the nanoparticles [45]. The calculated values of all the above-mentioned parameters have been represented in a tabular form in Table 2 for all the sharp distinct peaks. To analyze the thermal properties of β-Ni(OH)₂ nanoplates we conducted TGA (Thermogravimetric Analysis), where the thermographs revealed a three-step degradation process for the nanoparticles. The TGA graph and the description about the three step degradation process have been included in the supporting data file in Figure S4(a).

Fig. 4(b) shows the diffractogram of pure PVDF-TrFE thin film (PTr) and the composite thin film (NTr5). As seen from the XRD pattern, a prominent diffraction peak at 18.5° corresponding to the plane (020) is present in the case of PTr [47]. This peak is indicative of the presence of α-phase in pure PVDF-TrFE. For NTr5, the diffractogram displays a prominent peak at 19.9° corresponding to ((1 1 0), (2 0 0)) lattice planes [26,40,48] and [49]. This sharp peak clearly indicates the presence of crystalline β-phase in the composite due to the nucleation of the electroactive polar phase. The polar β-crystals in the composite are formed due to the addition of the Ni(OH)₂ nanoplates to the pure polymer and furthermore it waived off any α or γ crystallinity from NTr5. To verify the mass% loading of the nanoparticles in the composite film NTr5, the thermal analysis (TGA) of the composite was done, which almost matches with the actual mass% loading done. The data regarding this has been included in Figure S4.

Moreover, the β-nucleation in NTr5 is further explained experimentally from the FTIR analysis of the films.

4.3. Investigation of electroactive β-phase nucleation (FTIR spectroscopy analysis)

For proper knowledge about the dynamics of the samples and for further confirmation of the nucleation of the electroactive β-crystals in the composite, Fourier transform infrared spectroscopy analysis of PTr and NTr5 was carried out in the range of 500 cm⁻¹ to 1350 cm⁻¹, as displayed in Fig. 4(c). The spin coated composite film, with β-Ni(OH)₂ nanoplates incorporated in PVDF-TrFE, exhibited well packed characteristic absorbance bands at 840 cm⁻¹ and 1275 cm⁻¹, which is indicative of the formation of well-defined polar crystalline β-crystals [50]. No significant band at 1234 cm⁻¹ was observed for NTr5, concluding the transformation into TTTT form and no γ crystallization took place. A small band at 840 cm⁻¹ has been observed in pure PVDF-TrFE, which infers that there must be a trivial number of β-crystals in PTr. The absorption peaks at 763 cm⁻¹ and 978 cm⁻¹ can be attributed to in-plane bending motions, specifically indicative of the TGTG conformation characteristic of the alpha-phase [51]. The peak at 840 cm⁻¹ corresponds to the β-phase of PVDF-TrFE, which is due to CH₂ rocking, CF₂ stretching and skeletal C-C stretching, with this band being highly responsive to dipole orientation under electric field [52]. Moreover, the

Table 1

Crystallographic parameters for the refined XRD data of Ni(OH)₂ nanoparticles.

Parameters	Value for Ni(OH) ₂ nanoparticles
a (Å)	3.13
b (Å)	3.13
c (Å)	4.63
α (°)	90.00
β (°)	90.00
γ (°)	120.00
V (Å ³)	45.36
Crystallite size (nm)	7.665058
R _p (%)	8.09
R _{wp} (%)	11.13
χ ²	1.37
Microstrain	5.2135977 × 10 ⁻⁷

Table 2

Assessment of salient parameters like FWHM (β), Interplanar spacing (d), Crystallite size (D) and Dislocation density (ρ) from XRD analysis of Ni(OH)₂ nanoplates.

2θ (in degree)	Miller indices (h k l)	FWHM (β)	Interplanar spacing (d) (in Å)	Crystallite size of Ni (OH) ₂ (D) (in nm)	Dislocation density (ρ) (in nm ⁻²)
19.52	(001)	2.434	4.54	3.310	0.0912
33.01	(100)	0.574	2.71	14.422	0.0048
38.57	(101)	1.736	2.33	4.844	0.0426
52.12	(102)	2.242	1.75	3.938	0.0644
58.98	(110)	0.770	1.56	11.840	0.0071
62.69	(111)	1.121	1.48	8.289	0.0145
70.48	(103)	1.189	1.33	8.147	0.0150
72.71	(201)	1.357	1.29	7.263	0.0189

1275 cm^{-1} peak represented C–C symmetric stretching, CCC scissoring vibration, and CF_2 asymmetric stretching vibration in the beta-phase [50]. Notably, the ferroelectric crystallinity was greatly influenced by the C–F asymmetric stretch [53]. Therefore, we can confirm the fact that the addition of $\text{Ni}(\text{OH})_2$ nanoplates to the pure polymer has led to the huge enhancement of the electroactive β -crystals in NTr5, primarily due to the nucleation of the nanoplates with the PVDF-TrFE matrix and effective ion–dipole interaction in the composite. Hence, the spectroscopy analysis of the electroactive β -phase nucleation is in agreement with the diffractogram analysis of the films. More details about the FTIR spectra of PTr and NTr5 have been included in the supporting data file and in Figure S2. To measure the amount of electroactive β -polymorph present in the films, we also carried out a quantitative analysis of the FTIR spectra. The fraction of electroactive β -phase content $\{F(\beta)\}$ was calculated from the FTIR spectra using the Lambert – Beer law. This law was stated as [50]:

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right)A_\alpha + A_\beta} \times 100\% \quad (6)$$

where A_α is the absorbance at the band 764 cm^{-1} (for CF_2 and skeletal bending), A_β is the absorbance at the band 840 cm^{-1} (for CH_2 rocking, CF_2 stretching and skeletal C–C stretching). The value of K_β is $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and the value of K_α is $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, which are the absorption coefficients at the bands 840 cm^{-1} and 764 cm^{-1} respectively. From Fig. 4(d) we see that PTr has a $F(\beta)$ value of 72.56 % and NTr5 has a highly enhanced $F(\beta)$ value of 90.04 %. To show the effect of

poling on the composite, FTIR analysis of an unpoled composite has been done which demonstrated a $F(\beta)$ value of 82.8 %, which is much lower than $F(\beta)$ value of poled NTr5. The data regarding this and the FTIR spectra of poled and unpoled composites have been provided in the supporting data file in Figure S3.

4.4. Surface investigation, piezoelectric and ferroelectric study of NTr5

4.4.1. Surface roughness analysis by atomic force microscopy (AFM analysis)

AFM analysis was done to analyze the surface roughness and topography of the composite thin film NTr5, the image of which is shown in Fig. 5(a). As can be seen from the image, the high surface roughness is due to the incorporation of $\text{Ni}(\text{OH})_2$ nanoplates in the PVDF-TrFE matrix. Furthermore, the composite thin film exhibited nanoparticles that were evenly dispersed throughout its surface, indicating a well-distributed arrangement. Additionally, the film demonstrated a smaller spherulite size, suggesting the potential nucleation of an electroactive phase. Upon closer examination of the AFM topography, the presence of crystalline ellipsoidal lamellas[54] was clearly observed in the NTr5 film, which indicated the formation of an electroactive phase. Gwyddion 2.63 software was utilized to obtain three-dimensional AFM image of the film surface as illustrated in Fig. 5(b). The average height deviation from the mean plane (R_a) and the root mean square of the average height deviation from the mean plane (R_q) for the composite thin film were also obtained. The analysis revealed that the value of R_a for NTr5 was approximately 31.28 nm, while the R_q

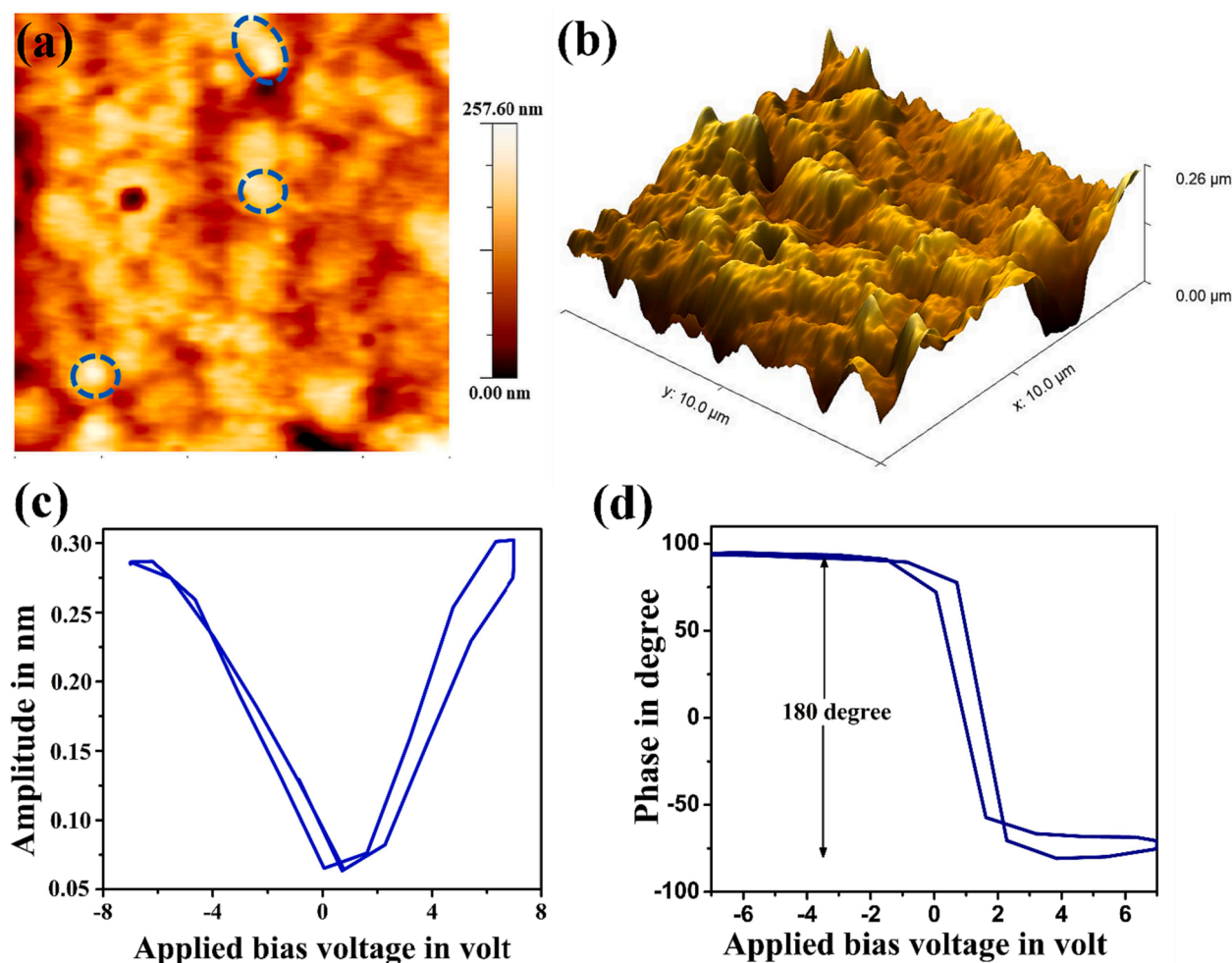


Fig. 5. (a) AFM topography image of NTr5 composite thin film, (b) 3D AFM image of NTr5 to analyze the surface roughness, (c) Piezoelectric displacement response of NTr5 on the application from -7 V to $+7 \text{ V}$ bias voltage with the help of PFM analysis, (d) PFM phase change hysteresis of NTr5 showing 180° of phase reversal.

value was approximately 38.47 nm. Using the aforementioned software, the average roughness of the NTr5 film was estimated to be approximately 158.117 nm and the overall thickness of the polymer composite was approximately 260 nm. The thickness of the composite has also been visually depicted on the scale of Fig. 5(a) and also corresponds to the z-axis of Fig. 5(b). These observations served as a strong indication of the formation of an electroactive phase within the film. As the surface roughness increased, the effective area available for charge accumulation within the composite matrix also increased. Consequently, this resulted in a higher surface charge density of the NTr5 film when it came into contact with other materials. Therefore, it is evident that the Ni(OH)₂/PVDF-TrFE nanocomposite film, with its higher surface roughness, exhibited greater piezo electrification compared to the bare PVDF-TrFE film. This is due to the larger contact area available for charge generation and accumulation on the composite film's surface.

4.4.2. Analysis of piezoelectric and ferroelectric properties (PFM analysis)

Piezo force microscopy analysis of the composite thin film NTr5 was performed for the confirmation of the enhancement of localized piezoelectric and ferroelectric properties when an external electric field was applied. The PFM technique allowed us to investigate and analyze the film's piezoelectric and ferroelectric response in terms of both amplitude and phase. In this switching spectroscopy analysis, an external voltage was applied to the composite, across its thickness with the help of a conducting tip. Thenceforth, the local deformation of the composite was measured, and the piezoelectric butterfly loop and the ferroelectric hysteresis response were recorded. A dual signal of DC bias voltage spanning from -7 V to +7 V was applied across the thickness of the composite. This applied bias voltage caused the film to undergo strain, which was then detected by a cantilever attached to the PFM tip. A detailed description about the DC bias voltage applied has been included in the supporting data file. In Fig. 5(c), the impact of applying the DC bias voltage on the strain amplitude can be observed. Increasing the positive DC bias voltage led to a crystal lattice expansion, resulting in a maximum deformation of 0.3 nm at approximately 7 V, as can be seen from the graph. Subsequently, as the applied bias voltage was reduced back to 0 V, the lattice started to contract and returned to its initial state. Likewise, when a negative DC bias was applied, the crystal lattice underwent expansion and contraction, forming a comprehensive piezoelectric butterfly loop during the entire process. This butterfly loop manifested the presence of the converse piezoelectric effect in the composite thin film NTr5 [54]. Since this plot represented the relationship between the amplitude of deformation formed in the composite and the applied bias voltage, by examining the slope of the linear region of the loop we could determine the piezoelectric coefficient d_{33} [55]. The obtained value of d_{33} from the graph was 50.22 pm/V. A comparative study for the maximum piezoelectric coefficient (d_{33}) our fabricated composite NTr5 with previously reported polymer composites has been included in the supporting data file in Table S1.

By analyzing the hysteresis loop [56,57] in Fig. 5(d), we can ascertain that NTr5 exhibited a complete ferroelectric hysteresis loop in terms of phase, with approximately 180° of phase reversal. This behavior can be attributed to the orientation of dipoles induced by the application of the DC bias voltage. This phase transition arose from the polarization reversal in the composite due to swapping of the local electric domains from an antiparallel configuration to a parallel one, or vice versa. This swapping is well consistent with the electrical domain of the tip of PFM, when the bias voltage was applied. Importantly, the incorporation of Ni(OH)₂ into the PVDF-TrFE matrix led to a nanoscale enhancement of piezoelectric and ferroelectric properties.

4.5. Theoretical analysis of the working of P-UST

From the knowledge of electrodynamics, we can analyze the working principle of the composite thin film NTr5, which is dielectric in nature. We know that the displacement electric field D for any dielectric me-

dium that participates in the dipole formation can be expressed as:

$$D(r, t) = \epsilon_0 E(r, t) + P(r, t) \quad (7)$$

where, ϵ_0 is permittivity of free space, E is the electric field and P is the polarization. Considering only the free charges in the composite thin film, Maxwell's equation in matter can be expressed as [58]:

$$\nabla \times \vec{H} = \vec{J}_f + \frac{\partial \vec{D}}{\partial t} \quad (8)$$

(Ampere's circuital law with Maxwell's addition)

where, $\vec{H}$ is the magnetic field, and $\vec{J}_f$ represents the current density due to the flow of free electron. For the case of a linear isotropic medium, $\frac{\partial \vec{D}}{\partial t}$ can be represented as:

$$\frac{\partial \vec{D}}{\partial t} = \epsilon_0 \frac{\partial \vec{E}}{\partial t} + \frac{\partial \vec{P}}{\partial t} \quad (9)$$

Herein, $\frac{\partial \vec{P}}{\partial t}$ is associated with the enhancement of the piezoelectric effect by effectively increasing the value of P . On the application of no external electric field E , the increment of surface charge leads to better polarization. When the polarization works in the z direction, we can write [25,59,60]:

$$\frac{\partial P_z}{\partial t} = \frac{\partial \sigma_p(z)}{\partial t} \quad (10)$$

where, $\sigma_p(z)$ represents surface charge density of the piezoelectric material. From the above equation, we can articulate that the surface charge density is directly proportional to the change of piezoelectric polarization of the piezoelectric material. Therefore, the noteworthy small size of Ni(OH)₂ nanoplates has led to the increment of the polarization and surface charge density. Now to understand the relation between the increase in surface charge or polarization and the performance of ultrasound transducer, we need to analyse electromechanical coupling coefficient k , which indicates the effectiveness with which a piezoelectric material converts electrical energy into mechanical vibrations and vice versa. Electromechanical coupling coefficient k can be represented as [13]:

$$k^2 = \frac{\text{stored mechanical energy}}{\text{input mechanical energy}} = \frac{e_{33}^2}{\epsilon_{33}^D \epsilon_{33}^S} \quad (11)$$

where, e_{33} is the piezoelectric stress constant, ϵ_{33}^D is the elastic constant, ϵ_{33}^S is the clamped dielectric permittivity. Now, the polarization term is related to the piezoelectric stress constant e_{33} by the relation [61,62]:

$$P = \sum e_{ij} \epsilon_j \quad (12)$$

where, ϵ represents the strain tensor [63]. Now, the resonant frequency and the acoustic impedance of a material are primarily determined by the inherent property of the material, namely the speed of sound within it. An appropriate match in acoustic impedance between the ultrasound transducer and the medium through which the ultrasound waves propagate is of paramount importance for optimizing transducer performance. The relevant parameters for achieving this impedance match are outlined below [13]:

$$\omega_o = 2\pi c_p \quad (13)$$

$$Z_a = \rho c_p \quad (14)$$

where, ω_o represents the resonant frequency, c_p represents the speed of sound inside the piezoelectric material, Z_a represents the acoustic impedance and ρ represents the density. In order to optimize power transmission, it is crucial that the input electrical impedance of the ultrasound transducer, specifically at the designated frequency is real and

that its input resistance aligns with the electrical impedance of the power source. The electromechanical coupling coefficient 'k' serves as a crucial metric for evaluating how efficiently a piezoelectric material can convert electrical energy into mechanical energy and vice versa. In the context of transducer design, a higher k value is much desirable as it signifies superior energy conversion capabilities and results in a broader bandwidth, thereby enhancing overall performance of the ultrasound transducer.

The efficiency of a transducer represents the effectiveness of the device to convert the mechanical energy into electrical signals. The efficiency η can be mathematically represented as:

$$\eta = P_{out}/P_{in} \quad (15)$$

where, P_{out} represents the electrical output power and the mechanical input power is represented by P_{in} .

From this equation we can infer that a material with a superior piezoelectric effect (high piezoelectric coefficient) leads to a higher output electrical power, yielding superior transducer efficiency. This in turn increases the sensitivity of the ultrasound transducer as well, since the higher piezoelectric effect, which is characterized by a high value of piezoelectric coefficient, increases the change in electric polarization for a particular change in mechanical strain.

The signal-to-noise ratio (SNR) measures the fraction of the strength of the anticipated signal to the unwanted background noise. On the increment of the output voltage, the desired signal turns out to be more prominent in comparison to the noise. This leads to an enhancement of the SNR, allowing better detection and analysis of the preferred signals from the ultrasound transducer. The presence of $\text{Ni}(\text{OH})_2$ nanoparticles help in mitigating the electrical and thermal noises, which results in an improved SNR ratio. This feature is very noteworthy in ultrasound imaging applications where there is a demand for high-quality and low-noise signals, crucial for accurate medical diagnosis.

4.6. Output performance of P-UST (Pulse-echo test)

Herein, we demonstrate the intrinsic bidirectional ultrasound signal transmission performance by utilizing a single transducer, to both generate and receive ultrasound pulse signals. The received pulse signals provide evidence of the successful transmission process and validate the transducer's capability to effectively capture back the ultrasound signals. Using the setup depicted in Fig. 2(b), where the transducer P-UST was operated over an aluminium block with a liberal layer of ultrasound

gel on the block, we conducted a pulse-echo test to assess the output performance of the transducer. Fig. 6(a) demonstrates the pulse-echo signal which was obtained by our designed transducer P-UST. The amplitude of the voltage signal of our fabricated transducer surpasses that of any commercial ultrasound transducer available in the market, showcasing exceptional performance. Notably, it achieved an impressive peak-to-peak output voltage of 5.19 V. To verify the effect of nanoparticles in the polymer matrix, output data was also acquired from a UST employing pure polymeric film. The data regarding this have been included in the supporting data file in Figure S5. The output voltage magnitude of our P-UST exceeds that of any previously reported ultrasound transducer in the field. To optimize the echo amplitude, the tilt angle between the transducer and the aluminium target block was

Table 3

Comparative table showing the output performances our fabricated P-UST, with previously reported piezoelectric composite based ultrasound transducers.

Title of the article	Piezoelectric composite used	Maximum output voltage for the ultrasound transducer
3D printing of piezoelectric element for energy focusing and ultrasonic sensing [64]	Piezoelectric-composite slurry with BaTiO_3 nanoparticles	0.301 V
A KNN composite-based piezoelectric helix for ultrasonic transcutaneous energy harvesting [65]	KNN composite-based piezoelectric helix	1.70 V
KNNS-BNZH Lead-Free 1–3 Piezoelectric Composite for Ultrasonic and Photoacoustic Imaging [66]	(KNNS-BNZH)/epoxy 1–3 composite	0.78 V
Flexible piezoelectric micro ultrasonic transducer array integrated on various flexible substrates [67]	PVDF based composite	75 mVpp
High-performance potassium sodium niobate piezoceramics for ultrasonic transduce [68]	KNN-BNZ-AS-Fe/epoxy 1–3 composite	0.80 V
Our present work	$\beta\text{-Ni}(\text{OH})_2/\text{PVDF-TrFE}$ composite based piezoelectric ultrasound transducer	5.19 V

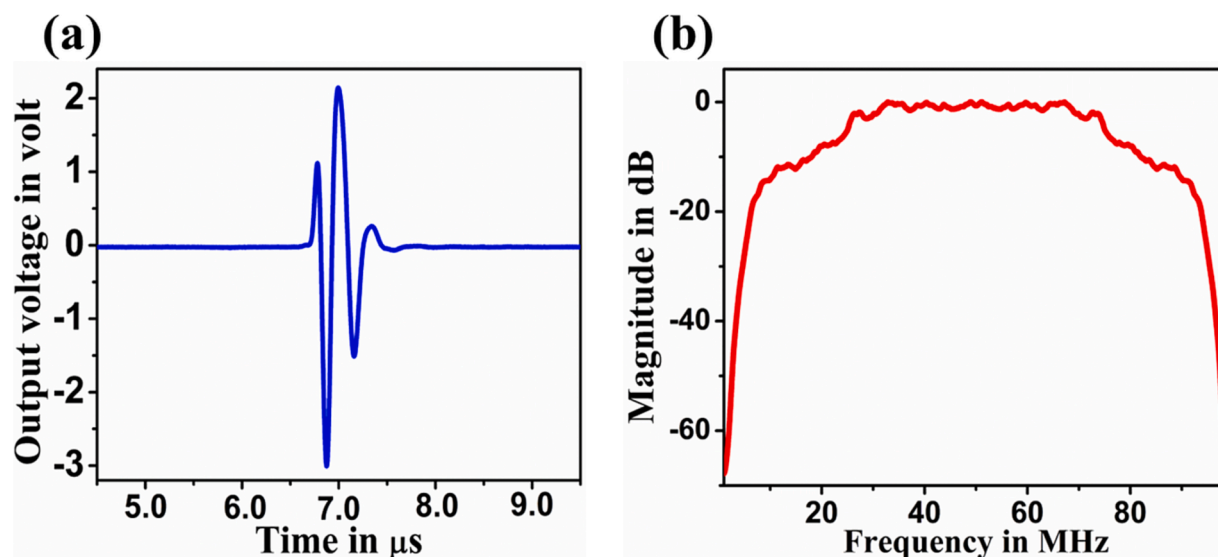


Fig. 6. (a) Experimental pulse echo signal received by our designed transducer P-UST, (b) Fast Fourier Transformed output of the voltage pulse echo signal.

adjusted accordingly. A comparative study has been done in Table 3, showing the output performances our fabricated P-UST, with previously reported piezoelectric composite based ultrasound transducers.

Subsequently, we conducted a comparison between the time-domain waveform of the output voltage and its corresponding spectrum in the frequency domain. By subjecting the voltage versus time output signal to a Fast Fourier Transform (FFT)[69,70], we transformed the acquired voltage data into the frequency domain, obtaining the amplitude in decibels, plotted against frequency in MHz as shown in Fig. 6(b). To obtain the output signal in amplitude vs frequency format, we utilized the Fourier Transform formula:

$$\text{Amplitude(dB)} = 20 \times \log_{10}(|X(f)|) \quad (16)$$

where $|X(f)|$ represents the Fourier Transform of the magnitude of the signal in the frequency domain. When we take the absolute value of the Fourier Transform and apply the logarithmic transformation, the amplitude in decibels can be expressed relative to the reference level.

Our fabricated transducer, incorporated with β -nickel hydroxide and PVDF-TrFE, consistently demonstrated robust and prominent signal strength within the frequency range of 24.41 MHz to 75.63 MHz. The detection performance of our transducer exhibited an ultra-broad bandwidth with a central frequency of 50.01 MHz. Upon analysis of the magnitude vs frequency graph, it was determined that the ultrasound wave exhibited a -6 dB bandwidth of 51.22 MHz. Remarkably, the measured -6 dB percentage bandwidth was significantly wider, approximately of 102.4 %. This value of wide bandwidth suggested that the output signal could cover a broader frequency range, along with its noteworthy high central frequency emphasizes the transducer's competence to capture a widespread spectrum of ultrasound frequencies efficiently. The exceptionally high central frequency achieved by our P-UST is expected to result in significantly enhanced resolution of ultrasound images compared to those obtained from commercially available ultrasound transducers.

Upon implementation, our P-UST has the potential to detect abnormalities in living tissues on the basis of the density disparities between normal and abnormal tissues. By exploiting this distinction, the transducer can generate high-resolution images that facilitate accurate identification and diagnosis of abnormalities in tissues. Thus, the improved resolution resulting from the ultra-high central frequency, opens up new possibilities for precise and reliable diagnosis, monitoring, and treatment of medical conditions using the transducer's high-quality imaging capabilities. Furthermore, the output voltage data obtained from our novel P-UST significantly surpasses the voltage values achieved by any other piezoelectric film-based ultrasound transducer in previous studies within this field. This remarkable distinction sets our P-UST apart as a groundbreaking advancement in the realm of ultrasound transducers in terms of voltage generation too.

5. Conclusion

In summary, our main focus was to investigate how β -Ni(OH)₂ nanoplates affected the enhancement of the electroactive β -phase in poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) within the fabricated nanocomposite thin film. Additionally, this work introduces a novel approach by integrating highly piezo-active transition metal hydroxide into the polymer matrix for the development of transducer that demonstrates exceptional performance. Upon examination of the FESEM micrograph, it was evident that flaky Ni(OH)₂ nanoplates of uniform shape and distinct nature were formed with smooth, flat surfaces, exhibiting an average size ranging from 70 to 170 nm. The X-ray diffractogram revealed an average crystalline size of the β -Ni(OH)₂ nanoplates to be approximately 7.66 nm. The fabrication process of the β -Ni(OH)₂ nanoplates-modified composite (NTr5) involved the spin coating method. Notably, the achieved maximum crystallization of the β -phase in the composite was 90.04 %, which is exceptionally high. The

significant increase in crystallization, rising from a $F(\beta)$ value of 72.56 % in pure PVDF-TrFE to the aforementioned value for the composite, can be attributed to the favorable electrostatic ion-dipole interaction and strong surface polarization within the polymer composite structure. To investigate and analyze the piezoelectric and ferroelectric response of the composite thin film NTr5, Piezo Force Microscopy analysis was also conducted. Application of a positive DC bias voltage caused a crystal lattice expansion, resulting in a maximum deformation of approximately 0.3 nm at 7 V. Conversely, a negative DC bias voltage on the composite induced expansion and contraction of the lattice, which led to the formation of a comprehensive piezoelectric butterfly loop, confirming the presence of converse piezoelectric effect in NTr5. The slope of the graph yielded a d_{33} value of 50.22 pm/V. Utilizing NTr5, we proceeded to design a compact and portable ultrasound transducer (P-UST). The effect of piezoelectric property on the output of UST has been well explained theoretically with the help of Maxwell's equations, which is in accordance with our experimental data. To assess its performance, we had conducted a pulse echo test on an aluminium block using ultrasound gel on it. Herein, the bidirectional transmission of ultrasound signals was evaluated by utilizing our single transducer P-UST, which was capable of both generating and receiving pulse signals. We achieved a remarkable peak-to-peak output voltage of 5.19 V. Additionally, the fast Fourier transformed graph revealed a noteworthy range of frequency signal strength, spanning from 24.41 MHz to 75.63 MHz. P-UST demonstrates an exceptionally wide -6 dB bandwidth of 51.22 MHz (102.4 %), with a central frequency of 50.01 MHz. Herein, we can affirm that this wide bandwidth obtained in our case makes it advantageous for our designed transducer to be effectively utilized in high-frequency applications. Hence, it can be concluded that our designed ultrasound transducer, which is lead-free, non-toxic, and cost-effective, holds great potential for the utilization across a range of construction and biomedical applications. Considering the superior output voltage obtained, the ultra-broad bandwidth, and the remarkably high central frequency, our designed transducer emerges as a promising candidate for the successful implementation on an industrial scale since P-UST can lead to a significant enhancement in the resolution of ultrasound images. This noteworthy feature paves the way for new opportunities in accurate diagnosis, monitoring and treatment of serious medical conditions.

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CRediT authorship contribution statement

Namrata Das: Conceptualization, Data curation, Methodology, Writing – original draft. **Debmalya Sarkar:** Conceptualization, Data curation. **Nitin Yadav:** Data curation, Methodology. **Asfak Ali:** Software. **Sukhen Das:** Supervision, Writing – review & editing. **Partha Pratim Ray:** Supervision, Writing – review & editing. **Nur Amin Hoque:** Supervision, Data curation, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.146322>.

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Wenzel model motivated, superwetable micro-motified membrane for droplet-driven, real-time acid rain sensor via sequential contact electrification strategy

Namrata Das^a, Debmalya Sarkar^a, Souvik Sau^{a,b}, Asfak Ali^c, Sayoni Mandal^c, Sukhen Das^{a,**}, Partha Pratim Ray^{a,***}, Nur Amin Hoque^{d,*}

^a Department of Physics, Jadavpur University, Kolkata, 700032, West Bengal, India

^b Department of Physics, Bangabasi College, Kolkata, 700009, West Bengal, India

^c Department of Electronics and Telecommunication Engineering, Jadavpur University, Kolkata, West Bengal, 700032, India

^d SAIS Department, Indian Association for the Cultivation of Science, Kolkata, 700032, India

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ABSTRACT

Fabrication of a bio-inspired, raindrop energy-powered, acid rain sensor is presented, working under solid-to-liquid interface contact electrification. Inspired by micro-motifs of petunia flower petal surface, an innovative 'replication' method utilizing template-sacrifice technique is applied to develop the triboelectric membrane. PTFE and synthesized Ag₂S nanoparticles are incorporated into PDMS to create hydrophobic, single electrode triboelectric nanogenerator (b-STNG) with noteworthy output performance and durability. COMSOL Multiphysics software is used to model the potential distributions at varying distances through finite-element analysis. Microstructures exhibit synergistic enhancement of charge transfer, hydrophobicity and contact-separation between triboelectric layer and water drop, with enhanced sensitivity of 34.4 V/kPa and high contact angle of 135.8°. Hydrophobicity of b-STNG due to introduction of rough surface topography is theoretically described using Wenzel model of wetting. When exposed to rainwater, b-STNG responds remarkably, displaying high degree of sensitivity to liquid's pH and ion concentration, due to screening effect of H⁺ ions. Utilizing this feature in conjunction with Arduino, a real-time rainwater pH sensor system with coloured LED indicator is designed to detect acid precipitation. Thus, in addition to harvesting energy from randomly falling raindrops, b-STNG is able to monitor pH of rainwater in real-time, enabling timely precaution from potential environmental harm.

1. Introduction

In light to the growing global energy crisis, there has been a world-wide interest in utilizing renewable resources such as solar, tidal, water wave, waterfall, rainwater and various biological movements [1,2], in order to reduce carbon emissions and achieve carbon neutrality. Among the most extensively utilized renewable energy sources, distributed mechanical energy produced by liquid flow [3] has a promising future. This approach has broadened the range of applications for solid-liquid nanogenerators and demonstrate their prospective in the realms of sensing and micro-nano energy harvesting. Rainfall is a significant supply of fresh water and it is a highly advantageous concept to convert

the kinetic energy of randomly falling raindrops [4,5] into electrical energy before they contact the ground.

Triboelectric nanogenerators (TENGs) have proved to be a viable energy technology for harvesting erratic, randomly dispersed and low-frequency water drop energies. Droplet based TENGs [6–9] emerge as highly effective technology for renewable energy conversion since it can function in situations involving a limited water supply. TENG operates on the principles of triboelectric effect [10] and electrostatic induction to transform mechanical energy into electrical energy. When two materials with different triboelectric polarities come into periodic contact and separation [11], they create electric potential differences. This drives the flow of electrons through an external load, enabling the

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: sdasphysics@gmail.com (S. Das), parthapray@yahoo.com (P.P. Ray), nuramin03@gmail.com (N.A. Hoque).

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generation of continuous electrical output. In the context of TENG, output performance is significantly influenced by the surface roughness of the dielectric layer [12]. The most practical method to enhance the sensitivity of the TENG is by optimizing the effective contact area between the triboelectric layers. A textured or rough triboelectric surface containing micro or nanostructures exhibits a greater specific surface area, leading to a substantial enhancement in charge transfer density. Diverse micro or nano structure designing technologies [13,14] including lithographic technology, self-assembled layers, chemical deposition and template dissolution method have been employed in numerous studies to enhance surface roughness. However, these conventional fabrication methods are intricate and expensive. This suggests a need for a simple structural design that employs a versatile and cost-effective fabrication method. Furthermore, it is essential to increase the intrinsic charge density for the triboelectric layer for achieving even greater improvements of the energy conversion efficiency of the nanogenerator [19].

By taking inspiration from various architectures in nature, bio-inspired TENG [15–17] designs that mimic biological structures have been widely applicable since they are more efficient and easily tunable depending on the intended output results. Drawing inspiration from the petal surface structure of petunia flower (*Petunia x atkinsiana*), we have developed a flexible triboelectric PDMS composite membrane (tribo-negative layer) with well-defined microstructures by imitating petunia petal surface. This replication process was achieved through a unique template sacrifice method. Poly(dimethylsiloxane) (PDMS) [16] has been used in this work, since it is one of the most effective negative friction layer among other triboelectric materials because of its high electronegativity, superior transparency and flexibility. Among the recent works on bio inspired templates used, Zhu et al. developed a triboelectric electronic skin for sensitive tactile sensing which was inspired by the microstructures of a rose petal [16]. Wang et al. fabricated a low cost bionic triboelectric nanogenerator for health monitoring inspired by the microstructures on lotus leaf [17]. A few more research works have been done on bio inspired template based triboelectric nanogenerators but a very few works have been done using metal chalcogenide nanoparticles. Silver sulfide (Ag_2S), a metal chalcogenide, exhibits intriguing characteristics including a monoclinic crystal structure, a relatively narrow band gap [18] ranging from 0.9 eV to 1.05 eV, a considerable absorption coefficient, good optical properties and commendable chemical stability [19,20]. Since, Ag_2S has a high chemical stability and comparatively narrow band gap [21], it facilitates effective charge transfer and charge separation during triboelectric operations.

The liquid-solid interacting triboelectric nanogenerators (L-S TENGs) [22] are gaining significant attention due to their practical applications, particularly in the field of self-powered sensors. These sensors utilize the contact between liquid droplets and solid surfaces [7], having enormous potential in various fields [6]. In order to further increase the hydrophobicity of the polymeric composite membrane, we added PTFE to it due to its extremely hydrophobic nature. Moreover, its remarkable resistance to both acid and alkali solutions [23] and its extensive usage as a dielectric material in TENGs suggested that it would be non-reactive to the acid solutions that were further employed in our experiments. In this study, we designed a highly hydrophobic, compact single electrode triboelectric nanogenerator (b-STNG) comprised of the triboelectric layer (b-APC) with bio-mimetic boat shaped micro motifs that can harvest mechanical energy from water droplets as well as from basic finger touch. Upon application of force by fingers, b-STNG could generate an open circuit voltage of 374 V and a short circuit current of 11.44 μA . The b-STNG was found to have a maximum power density of 3.25 W/m^2 at $10^7 \Omega$ and a sensitivity of 34.4 V/kPa up to an external pressure of 0.185 kPa. To verify that b-STNG can harness electrical energy from raindrops, we examined the water drop energy harvesting capabilities of this hydrophobic device with varying parameters, also showing noteworthy sensitivity to both the pH and ion concentration of

liquid. Owing to this, we could implement this raindrop-powered TENG as a pH sensor to detect acid rain. Since the low pH of acid rain can lead to inflammatory skin conditions and a number of respiratory illnesses, early detection of acid rain can be very much beneficial for the general well-being of people. Numerous famous architectural structures made of calcareous materials like limestone and marbles are also greatly affected by acid precipitation. Plants are also directly impacted by acid rain to a large extent. Their growth and productivity gets lowered since the acid rain affects the soil composition greatly. Hence, the bio-mimetic b-STNG was able to accurately detect the pH value of rainwater in real-time with the help of coloured LED indicator system and it can minimize possible ecological impact by enabling prompt protection against acid rain in the environment.

2. Experimental section

2.1. Materials

Silver nitrate (AgNO_3) (99.9 % Sigma–Aldrich), sodium sulfide (Na_2S) (98 % Sigma Aldrich), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (99 % SRL chemical), ammonia solution (NH_3) (25 % indiaMART), polydimethylsiloxane (PDMS) gel (Sylgard 184, Dow Corning), Polyvinyl alcohol (PVA) (Loba Chemie), polytetrafluoroethylene (PTFE) (Sigma–Aldrich) and de-ionized (DI) water were used. The reagents utilized in the experiments were of analytical grade and of highest purity and the chemicals were employed in their as-received state without undergoing additional purification.

2.2. Synthesis of silver sulfide nanoplates

The synthesis of silver sulfide nanoplates was carried out using a simple hydrothermal method, utilizing silver nitrate (AgNO_3), sodium sulfide (Na_2S), ammonia (NH_3) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$). In the first solution, 2.5 mmol of AgNO_3 was combined with 50 mL of DI water and was subjected to vigorous stirring on a magnetic stirrer for 2 h. Simultaneously, in the second solution, 10 mL of ethylene glycol was added to 1.25 mmol of Na_2S and stirred for 1 h. The second solution was then combined with the first solution, undergoing continuous stirring and heating at 70 °C for 2 h. 10 mL of ammonia solution was gradually added to it drop-wise while maintaining constant stirring and heating. The prepared solution was carefully poured into 80 mL teflon-lined stainless steel autoclave setup, filling it up to 80 % of its volume. This setup was placed in a clean, dry hot air oven and was heated at 160 °C for 12 h. The resulting precipitate exhibited a blackish colour. After the precipitate cooled to room temperature, it was subjected to centrifugation and thorough washing with double-distilled water multiple times to adjust the pH to 7. The collected precipitate was then dried in a Petri dish at 60 °C in an oven for 48 h and subsequently ground into a fine black-coloured powder using a mortar and pestle, yielding silver sulfide nanoplates.

2.3. Fabrication of micro-structured PVA mould based on petunia petal (negative replica)

The initial step involved cleaning a fresh petunia flower with deionized water for a few times, followed by cutting the petal into rectangular shape. To ensure uniform surface microstructures, the edges of the petal were carefully removed. Subsequently, rectangular section of the petal was dried using air blow and securely fixed onto a glass slide. A 15 wt% polyvinyl alcohol (PVA) solution was prepared by dissolving PVA in deionized (DI) water at 80 °C, by continuously stirring it for a duration of 5 h. Then, the PVA polymer solution underwent a 20-min ultrasonic treatment to effectively eliminate any bubbles present. The prepared PVA solution was then carefully poured on the flat rectangular flower petal mould using coating method. The mould with the PVA solution underwent a 2 h heating process at a temperature of 70 °C.

Following this, the petunia petal was detached from the dried PVA using adhesive tape, providing the micro-patterned negative PVA template.

2.4. Fabrication of Ag_2S incorporated, micro-structured PDMS composite (positive replica)

1 g of PDMS (Sylgard 184, Dow Corning, ratio of 10:1) was thoroughly mixed and was made bubble-free by keeping the mixture under

vacuum for 10 min. To the mixture, 0.5 mass% of silver sulfide nanoparticles were added and mixed thoroughly for 15 min, to obtain a homogeneous mixture. The micro patterned negative PVA template was then coated with this mixture and pre-cured for 35 min at 30 °C. Next, PTFE particles with an amount of 1 mg/cm² were coated onto the mixture by mechanical sieving and the composite was cured at room temperature for 12 h. Subsequently, it underwent a 3 h heating process in a 80 °C water bath, leading to the complete dissolution of the PVA

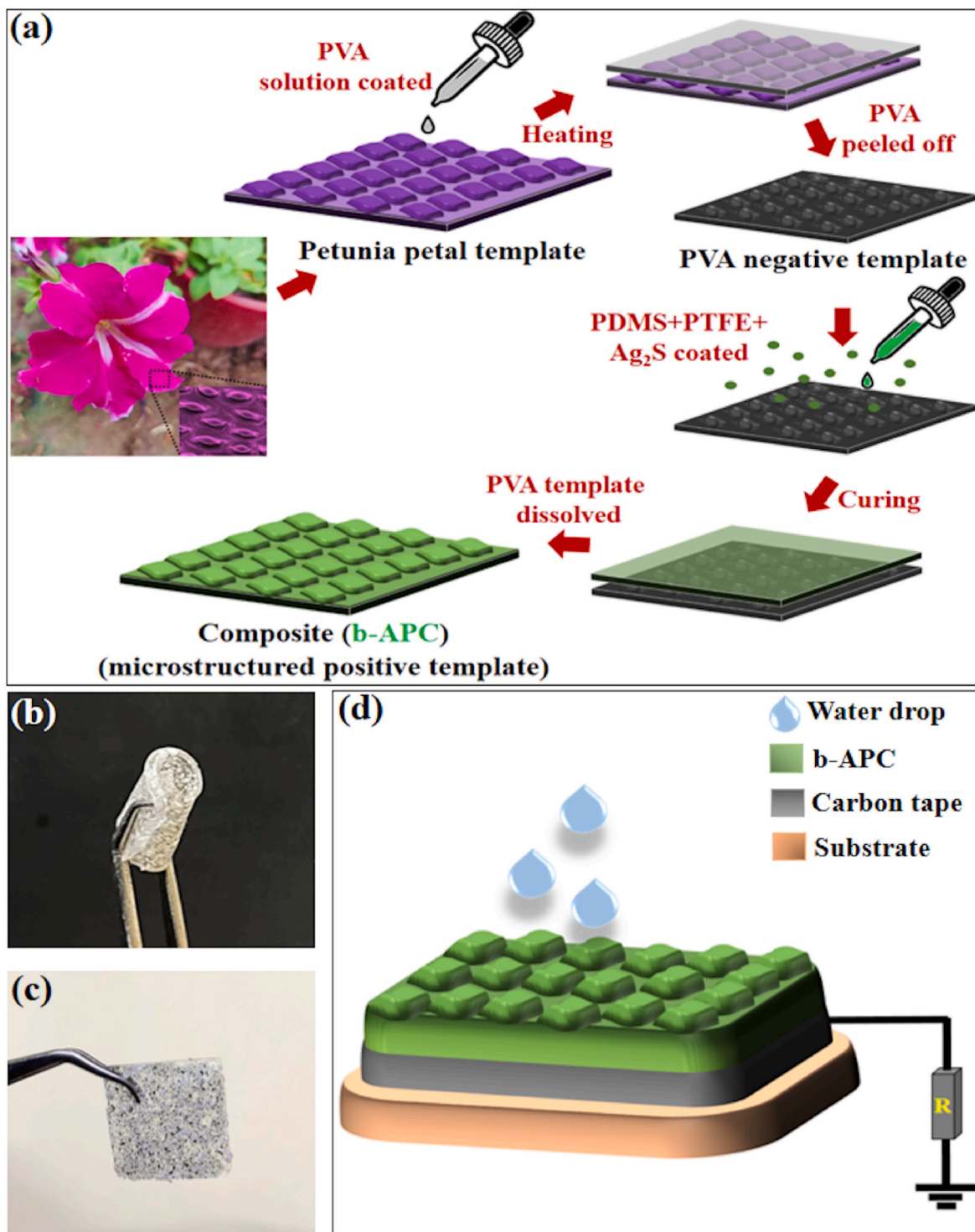


Fig. 1. Micro-structured composite membrane and triboelectric device. (a) Schematic diagram illustrating the fabrication process of b-APC by replication method via template sacrifice technique, (b) Digital photograph demonstrating the flexibility of b-APC, (c) Digital photograph of the triboelectric layer b-APC, (d) Assembled b-STNG showing all its layers and components.

template. This resulted in the formation of a bio-mimetic PDMS composite membrane incorporated with Ag_2S nanoplates and PTFE (named b-APC), exhibiting micro motifs identical to those of the petunia flower petal surface, as can be seen in Fig. 1(a). The embedded PTFE particles bonded on to the triboelectric layer resulted in a stretchable and highly hydrophobic triboelectric layer of the TENG. Fig. 1(c) represents the digital photograph of the triboelectric layer b-APC and Fig. 1(b) demonstrates how highly flexible the composite is.

2.5. Designing of the bio-inspired, single electrode triboelectric nanogenerator (b-STNG)

Firstly, for the preparation of a stretchable substrate, we began by thoroughly mixing two components of Ecoflex 00–30, namely 0.5 g each of Ecoflex A and Ecoflex B in a Petri dish. Then this mixture was uniformly spread onto a rectangular plate and allowed to cure at room temperature for a period of 10 h. After the curing process the substrate was carefully peeled off, yielding a thin and flexible substrate. A rectangular piece of carbon tape was affixed to the substrate, which acted as the electrode. Along with this, a small rectangular portion with the dimension of $3.6 \text{ cm} \times 2.6 \text{ cm} \times 0.08 \text{ cm}$ was cut from b-APC and was affixed on the Ecoflex substrate. A connecting wire was attached between b-APC and the electrode for obtaining electrical measurements. Finally the highly flexible and hydrophobic bio-inspired, single electrode triboelectric nanogenerator named b-STNG was designed successfully. The surface modification and the incorporation of PTFE not only boosted the electrical performance but also provided b-STNG with excellent mechanical and chemical stability. Raindrops normally possess kinetic energy during their descent and electrostatic energy is produced when they come into contact with air. Herein, we have investigated the water drop energy harvesting capability of our hydrophobic b-STNG to confirm that our device can harness electrical energy from randomly falling raindrops. The assembled nanogenerator showing all its components have been demonstrated in Fig. 1(d).

3. Result and discussion

3.1. Morphological analysis

The structural analysis of the synthesized Ag_2S nanoparticles and the microstructured composite membrane b-APC was done using Field Emission Electron Microscopy (FESEM). Fig. 2(a) clearly shows distinct and uniformly shaped plate-like structures of the Ag_2S nanoparticles. The Ag_2S particles range in size from 85 to 170 nm and exhibit a smooth, flat polyhedral structure. This nano-polyhedron structure of Ag_2S was chosen for synthesis via the hydrothermal process due to its ease of operation, high yield and good reproducibility [24].

A full bloom magenta coloured petunia flower, as displayed in Fig. 1(a), was chosen carefully for examination. The FESEM image of a petal section from this flower was taken to study the microstructures on it. Fig. 2(b) represents the FESEM images of the microstructure of the petunia petal, which is composed of extremely organized and aligned boat like patterns. These 3D micro motifs, termed ‘micro-boats’ measured approximately $15\text{--}21 \mu\text{m}$ in length and $7\text{--}13 \mu\text{m}$ in width. In Fig. 2(d), the FESEM image of b-APC also clearly showed ‘micro-boats’ that exhibit a prominent similarity in shape, pattern and arrangement to those found in the petunia petal. This similarity highlights a remarkable resemblance between the petal micro motifs and that of the fabricated bio-mimetic positive replica (b-APC), indicating successful bio-mimicking of the petunia petal surface structures. To further examine the size and shape of the micro-boats, Fig. 2(e) displays an enlarged FESEM image of the b-APC surface. This configuration forms a nano-in-micro structure within the composite, significantly enhancing the sensitivity of the triboelectric nanogenerator [16]. As shown in Fig. 2(c), we carried out elemental mapping for b-APC in order to experimentally verify the distribution of Ag_2S nanoplates and PTFE particles within the PDMS matrix. According to the results, there was a random dispersion pattern and an even distribution of Ag_2S nanoplates and PTFE particles throughout the polymer matrix. Structural analysis of PDMS film and PTFE particles has been included in the supporting data file in Fig. S1 (a) and (b). We employed EDS spectroscopy to analyze the distribution of the various elements of Ag_2S , PTFE and PDMS in b-APC composite. This study revealed the various proportions of silver (Ag), sulfur (S), silicon

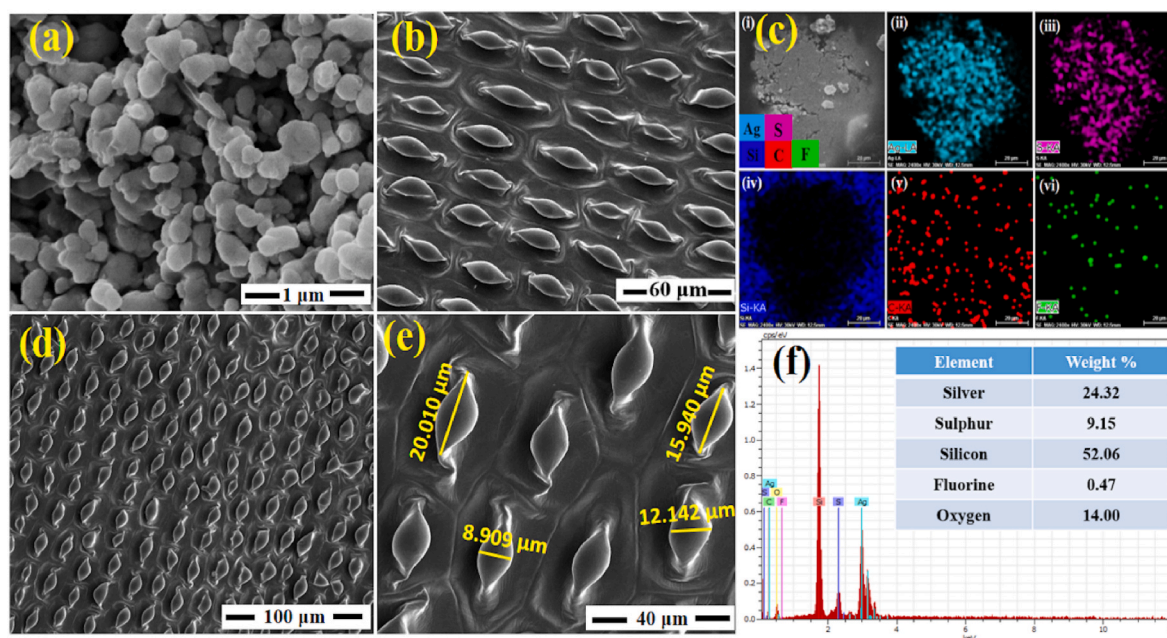


Fig. 2. Morphological analysis of Ag_2S and b-APC surface. (a) FESEM image of pure Ag_2S nanoplates, (b) FESEM image of the microstructures of petunia flower petal surface, (c) Elemental mapping for b-APC verifying distribution of Ag_2S and PTFE within PDMS matrix (d) FESEM image of b-APC showing micro-boat structures, (e) Enlarged FESEM image of b-APC surface, (f) EDS spectrum of various elements present in b-APC and inset showing the corresponding weight percentages.

(Si), fluorine (F) and oxygen (O) within the composite, as can be seen from Fig. 2(f). The inset of Fig. 2(f) displays the atomic weight percentages of the various elements in b-APC. This characterization technique confirmed the successful fabrication of Ag₂S and PTFE-incorporated PDMS composite membrane. The crystallographic and structural analysis of Ag₂S powder and b-APC composite membrane was also performed using X-ray diffraction, which has been included in Figs. S2(a) and (c) in the supporting data file. These characterization results therefore confirm the fruitful synthesis of Ag₂S nanoparticles. To obtain comprehensive information about the crystal parameters like crystallite size, interplanar spacing, macrostrain and dislocation density of Ag₂S and its microstructure, some mathematical calculations [50] were done which have been included in Table S1 in the supporting data file.

Moreover, the EDS spectroscopy of Ag₂S was also employed to analyze the distribution of the various elements in the nanoparticles, showcasing the various proportions of silver (Ag) and sulfur (S), as shown in Fig. S2(b). To analyze the dynamics of our fabricated polymeric composite and confirm the incorporation of PDMS, PTFE and Ag₂S in the b-APC composite, we utilized Fourier Transform Infrared (FTIR) spectroscopy in absorbance mode. Additionally, we prepared a pure PDMS film and subjected it to FTIR spectroscopy as well. This analysis study has been included in Fig. S2(d) in the supporting data file.

3.2. Surface wettability analysis of the composites

The water contact angle (WCA) of the microstructured triboelectric layer b-APC was studied, along with the WCA of three other polymer films: (i) pure PDMS film, (ii) film composed of PDMS and PTFE and (iii)

film containing PDMS, PTFE and Ag₂S, all of which had smooth and non-structured surfaces. The physical properties of a liquid droplet are primarily determined by the surface tension of the solid surface it interacts with. The shape a droplet takes upon contacting a solid surface is directly influenced by the surface tensions of the three interfaces [25]: (i) liquid/gas interface (γ^{LG}), (ii) liquid/solid interface (γ^{LS}) and (iii) solid/gas interface (γ^{SG}). All of these interfaces significantly contribute to this interface-induced surface tension, as can be seen from Fig. 3(a). All of the three interfaces are extremely necessary to determine the equilibrium shape of the droplet. The contact angle that a liquid droplet forms on a solid surface depends upon the three interface induced surface tension terms, influencing the overall shape of the droplet. As illustrated in Fig. 3(a), at the 'triple line point' where all the three forces converge, the net force is zero. This signifies an equilibrium state and can be represented by the Young's law [25,26]:

$$\gamma^{LG} \cos \theta = \gamma^{SG} - \gamma^{LS} \quad (1)$$

This equation is used for characterizing the behaviour of the solid surface based on the angle θ , where θ represents the Young's contact angle. Young's equation is based on the assumption that the surface is homogeneous and has a smooth topography. When (i) the contact angle θ is less than 90°, the solid surface exhibits hydrophilic characteristics and when (ii) θ is greater than 90°, the solid surface exhibits hydrophobic characteristics.

Herein, we have taken a water droplet of 15 μ L for the water contact angle (WCA) measurements. The water contact angle (WCA) of the pristine, smooth PDMS film surface was found to be 94.6°. This indicates that pure PDMS film exhibits low hydrophobic characteristics [27] as can be seen from Fig. 3(b). We fabricated a smooth surfaced film

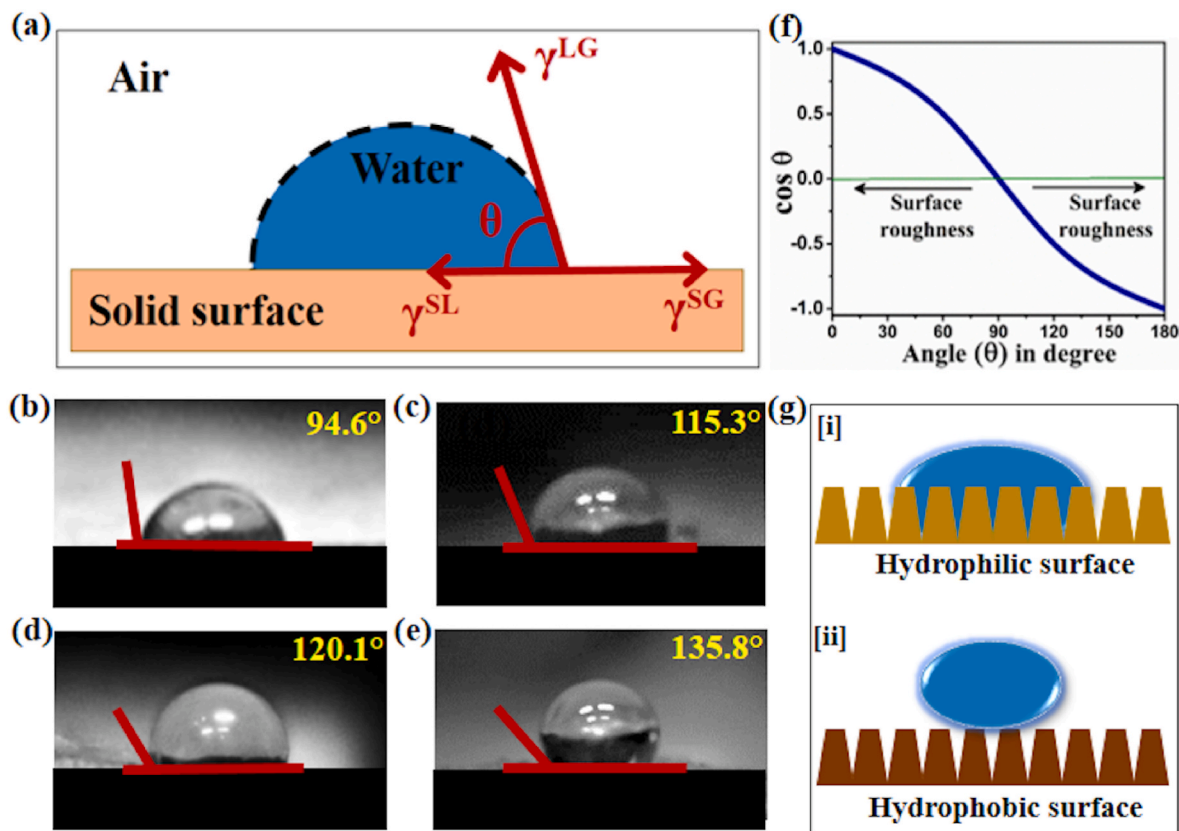


Fig. 3. Surface wettability analysis of fabricated membranes. (a) Schematic diagram showing the surface tension forces at the solid-liquid-gas interface, determining hydrophilic or hydrophobic property of the solid surface and equilibrium shape of liquid drop, (b) WCA of pristine, smooth PDMS film surface, (c) WCA of smooth surfaced film composed of PDMS and PTFE, (d) WCA of smooth surfaced composite with PDMS, PTFE and Ag₂S, (e) WCA of microstructured b-APC, (f) Graphical plot representing equation (2), demonstrating the role of surface roughness on surface wettability, (g)[i] Impact of roughness on water drop for hydrophilic surface, [ii] Impact of roughness on water drop for hydrophobic surface.

composed of PDMS and PTFE, which had a WCA of 115.3° , as shown in Fig. 3(c). Upon adding PTFE, there has been a notable improvement in the WCA compared to that of pure PDMS polymer. This is because PTFE is highly hydrophobic in nature [6] and thus it adds to the hydrophobicity of this composite membrane. To fabricate the third polymeric composite, we incorporated 0.5 % Ag_2S nanoparticles into the mixture of PDMS and PTFE. This composite membrane resembled b-APC in composition but differed by having a smooth surface. The WCA of this composite was 120.1° , as can be seen in Fig. 3(d). Incorporation of Ag_2S nanoplates enhanced the surface roughness of the polymeric composite membrane to some extent and this led to the increment of the WCA of polymeric composite. According to Cassie-Baxter effect, the micro and nanoscale roughness of Ag_2S surfaces increased the hydrophobicity [28]. Ag_2S induced rough surfaces, causing some air pockets to develop between the water drop and the composite surface, which decreased the area of contact and thus increased the hydrophobicity of the surface. Finally for the bio-mimetic microstructured b-APC, the WCA was 135.8° , as shown in Fig. 3(e). This value was significantly higher compared to the other polymeric films, indicating a noteworthy increase in WCA due to the combined effect of the bio-inspired micro motifs and the presence of PTFE and Ag_2S in b-APC. This property consequently enhanced the efficiency of contact-separation between water droplets and the triboelectric layer, reducing the contact-separation time [15]. A bar graph representation of the WCA for the four fabricated films has been represented in the supporting data file in Fig. S4(a), for easier comparison and visual comprehension.

To analyze the impact of roughness over a particular surface qualitatively, we need to examine the surface wettability of both hydrophilic and hydrophobic surfaces. On a rough or structured hydrophilic surface, a droplet fills the gaps of the roughness and wets the entire solid surface area, as depicted in Fig. 3(g)[i]. In contrast, on a rough or structured hydrophobic surface, the droplet rests elevated on the irregularities. This results in the droplet contacting only a portion of the total solid surface area with air pockets remaining underneath, as depicted in Fig. 3(g)[ii].

When a liquid droplet reaches equilibrium on a solid surface (hydrophilic or hydrophobic), some external work is required to shift the contact line across the surface. Hence, the net force should be zero where the surface tensions of the three interfaces meet together. To qualitatively characterize a surface's hydrophilic and hydrophobic properties, we can use the following equation:

$$\cos \theta_r = r \cos \theta \quad (2)$$

where, θ_r is the measured contact angle and r is the roughness factor.

Equation (2) is referred to as the Wenzel model of wetting [29,30], proposed by Wenzel in 1936, which establishes the relationship between surface roughness and wettability. The roughness factor (r) can be represented as:

$$r = \frac{\text{actual wetted area of the rough surface}}{\text{projected area}} \quad (3)$$

According to this equation, it is evident that the roughness factor $r \geq 1$ always ($r = 1$ for perfectly smooth surface and $r > 1$ for rough surfaces). Therefore, it can be said that the roughness factor always exceeds unity in practical scenarios, as can be easily concluded from Fig. 3(g). For a hydrophilic surface $\theta < 90^\circ$ and thus $\cos \theta > 0$. Given that $r > 1$ for real life scenario, it follows that $\cos \theta_r > \cos \theta$, which means that θ_r is smaller than θ i.e., much less than 90° . Therefore, if any smooth surface is hydrophilic in nature, it will become more hydrophilic when roughened or structured. Conversely, for any hydrophobic surface, $\theta > 90^\circ$ by its inherent property. Further when this hydrophobic surface is roughened more, its hydrophobicity is increased significantly since $\theta_r > \theta$. This relation according to the Wenzel model of wetting has been well explained graphically in Fig. 3(f). This implies that roughening a smooth surface intensifies its inherent hydrophobicity or hydrophilicity, making

hydrophobic surfaces more hydrophobic and hydrophilic surfaces more hydrophilic in nature. For this reason, the composite surface was designed to have a rough topography by incorporating bio-inspired micro motifs on b-APC. PDMS is naturally hydrophobic in nature and the addition of PTFE and Ag_2S had further increased this property. Hence, the microstructured surface additionally enhanced the inherent hydrophobicity of b-APC, making b-STNG highly suitable for water drop-based energy harvesting and sensing applications.

3.3. Output performance of b-STNG (from finger tapping motion)

Our bio-inspired single-electrode triboelectric nanogenerator (b-STNG) harvested mechanical energy from finger tapping motions by utilizing the principles of contact electrification and electrostatic induction [31,32]. According to the triboelectric series [33], the tribo-electrification phenomenon resulted from negative charges on the surface of b-APC (due to the presence of PDMS and PTFE) and positive charges on the surface of human skin. Initially, at equilibrium, when the b-APC was in complete contact with human fingers, oppositely polarized triboelectric charges were induced and there was a charge transfer between these two layers. When b-APC and fingers were separated, the negative charges on the surface of b-APC induced positive charges on the carbon electrode, causing free electrons to flow from the electrode to the ground [34]. This generated an output voltage signal, which gradually decreased as the negative triboelectric charges on b-APC nearly cancelled out the induced positive charges on the electrode. As the human fingers gradually approached b-APC again, induced positive charges on the carbon electrode decreased, causing electrons to flow in the opposite direction. This continued until the human skin and b-APC became fully contacted, resulting in a reversed output signal.

To analyze the effect of microstructures on the tribonegative layer, we designed another TENG following the same procedure but with a smooth-surfaced tribonegative layer (without microstructures) and compared its results with those of b-STNG. The open circuit voltage (V_{oc}) was investigated by connecting the TENGs to a digital storage oscilloscope (Keysight, Oscilloscope DSO-X 3012A) and applying a constant periodic axial force of 12.3 N with fingers. The calculations for the imparting force [35,36] have been shown in the supporting data file. The TENG with a smooth-surfaced tribonegative layer exhibited a voltage of 267 V, while the b-STNG produced a significantly higher output voltage of 374 V, as shown in Fig. 4(a). Upon application of same amount of force, the short circuit current (I_{sc}) of the devices were measured using an electrometer (Keysight, Electrometer B2985). The TENG with the smooth-surfaced tribonegative layer showed a short circuit current of 8.84 μA , while our microstructured b-STNG showed a considerably higher current of 11.44 μA , as can be seen in Fig. 4(b). This demonstrated that the microstructured triboelectric layer which was fabricated, inspired by the petal surface structure of the petunia flower, enhanced the output performance significantly. The probable reason behind this is that for the TENG with microstructured triboelectric layer, the effective surface area coming into contact is higher in comparison to the one which has a smooth surface. It is evident that the output voltage of a TENG improves with increased effective surface area [31]. Thus we can infer that the V_{oc} of b-STNG was henceforth increased due to the micro motifs present on b-APC due to the increment of contact area. To illustrate the impact of surface roughness on the output performance of triboelectric nanogenerator, we designed two additional TENGs using the same fabrication process as that of b-STNG but with different surface-structure templates. Comparison of the output performances of these devices have been included in the supporting data file in Fig. S9. Additionally, to explore the impact of Ag_2S and PTFE concentration mixed with PDMS in the triboelectric layer, the output performance of various devices with varying concentrations have been analysed and has been included in the supporting data file in Fig. S10 (a) and (b). The amount of PTFE particles were varied as 0.5 mg/cm^2 , 0.75 mg/cm^2 , 1 mg/cm^2 and 1.25 mg/cm^2 and the weight percentage of Ag_2S

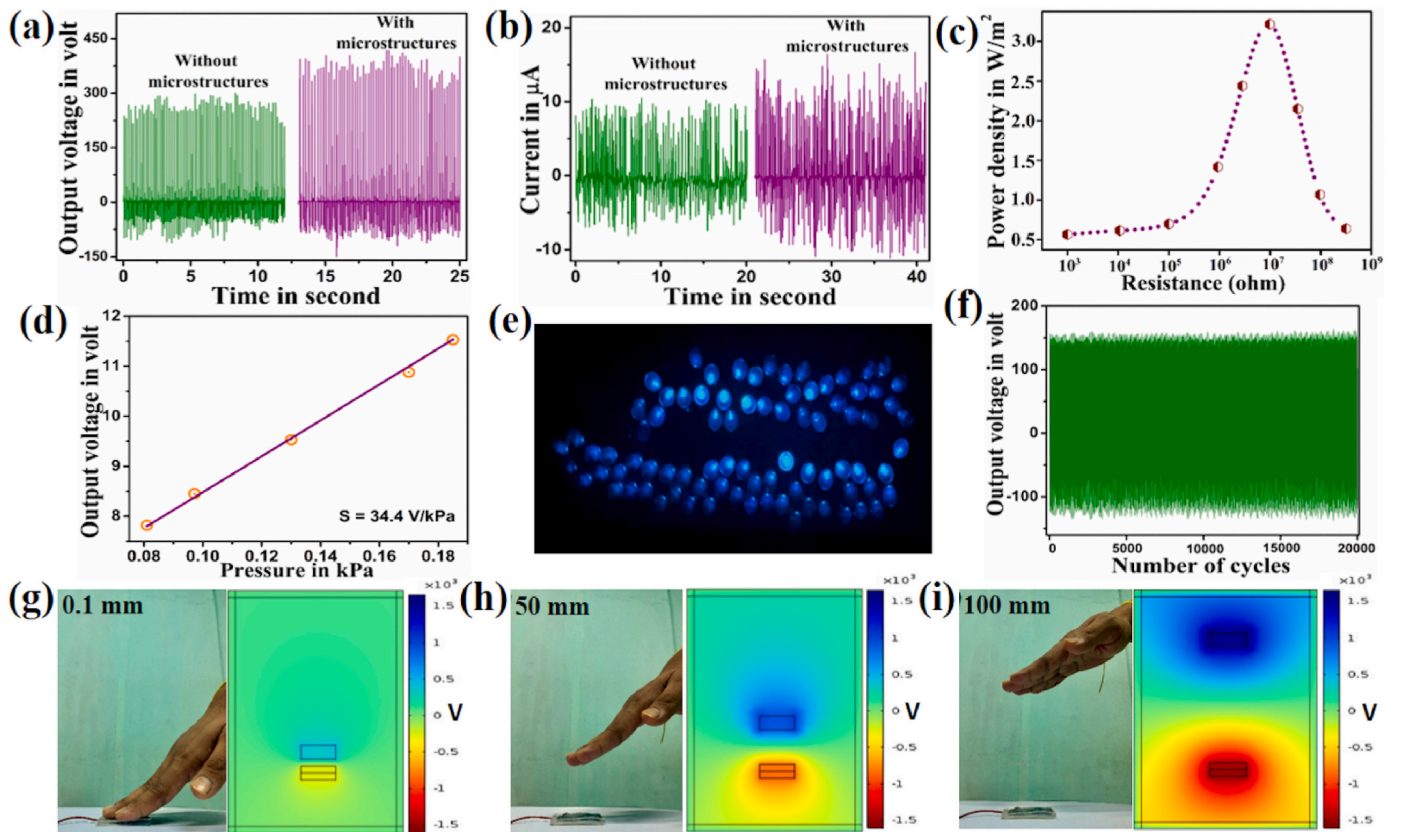


Fig. 4. Performance analysis of b-STNG corresponding to finger tapping motion. (a) Voc of TENG with smooth-surfaced triboelectric layer and that of microstructured b-STNG, (b) Isc of TENG with smooth-surfaced triboelectric layer and that of microstructured b-STNG, (c) Power density of b-STNG for varying load resistances, (d) Sensitivity plot for b-STNG, (e) Digital image of lighting up of blue LEDs on imparting force by fingers, (f) Long term stability test of b-STNG for 20,000 periodic cycles; Finite Element Analysis results of potential distribution of b-STNG based on COMSOL software: (g) when fingers completely touch b-STNG, (h) when fingers are at a distance of 50 mm from b-STNG and (i) when fingers are at a distance of 100 mm from b-STNG.

nanoparticles were varied as 0.25 %, 0.5 %, 0.75 % and 1.0 %.

To investigate the load capacity of b-STNG, we used multiple load resistances with varying values, ranging from 10^3 to 10^9 , as displayed in Fig. 4(c) b-STNG exhibited varying instantaneous power density values for varying load resistances and the power density (P) was calculated using the formula [31]:

$$P = \frac{V^2}{R_L \times A} \quad (4)$$

Here, V is the output voltage of b-STNG, R_L represents the load resistance value and A represents the effective surface area of b-STNG ($3.6 \text{ cm} \times 2.6 \text{ cm}$). The maximum power density for our b-STNG was obtained to be 3.25 W/m^2 at $10^7 \Omega$. The relationship between output current and power density of b-STNG with varying load resistances has been further analysed and has been included in the supporting data file in Fig. S8. For establishing the fact that our b-STNG can detect and can produce a considerable voltage from small mechanical vibrations, we calculated the sensitivity of our device. To obtain this, we utilized five types of Indian currency coins with varying masses (₹1, ₹2, ₹5, ₹10 and ₹20). These coins were dropped onto the device one at a time from a height of 8 cm, giving varying output voltages. Using the pressure values for each case, a linear graph of output voltage vs pressure was plotted, as shown in Fig. 4(d) and the sensitivity (S) of the device was finally obtained to be 34.4 V/kPa up to an external pressure of 0.185 kPa , using the formula [32]:

$$S = \frac{\Delta V}{\Delta P} \quad (5)$$

Here, ΔV and ΔP represent the change in output voltage and applied

external pressure respectively. As shown in Fig. 4(e), by making proper electrical circuit connection and using a full-wave rectifier, b-STNG was able to instantly light up 93 blue LEDs connected in series when a periodic force was applied by fingers as shown in video VS1. A frequency dependent study for output voltage of b-STNG has been included in the supporting data file in Fig. S3. Here the output voltage data has been taken for a varying frequency of force (applied force of 5 N), using a customised piezo-tribo impart testing machine. To evaluate the long term stability of b-STNG, its output performance was tested for over 20,000 periodic cycles on application of 5 N force using the piezo-tribo imparting machine. It was observed that the output voltage remained steady and continuous with minimal deviation, as shown in Fig. 4(f).

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To gain a more precise quantitative analysis of the operation and power generation mechanism of b-STNG from finger tapping motion, Finite Element Analysis (FEA) has been employed using COMSOL Multiphysics. This analysis simulates the potential distributions at varying separation distances between the triboelectric layer and human skin [37]. The constructed model was based on human skin, the triboelectric layer b-APC consisting of PDMS, PTFE and Ag_2S , along with a grounding carbon electrode, all layers with dimensions of $40 \times 40 \text{ mm}^2$. The thicknesses were assumed to be 1 mm for the human skin, 0.5 mm for the triboelectric layer and 0.5 mm for the carbon electrode. The skin surface was assumed to have a uniform charge density of $+5 \mu\text{C/cm}^2$ while the b-APC surface was assumed to have a charge density of $-5 \mu\text{C/cm}^2$. Fig. 4(g)–(i) represent the simulation outcomes of the potential distribution in b-STNG for varying separation distances of 0.1 mm, 50 mm and 100 mm between human skin and the triboelectric layer b-APC.

When the human skin was in full contact with b-APC surface, the electric potential value became nearly zero on both surfaces. As the separation distance increased, the electric potential difference between the two surfaces gradually increased. When the layers were separated by 100 mm, the electric potential on the skin surface reached 1.5 kV, while the triboelectric layer exhibited a negative electric potential of nearly -1.5 kV, as shown in Fig. 4(i). Thus, based on the Finite Element Analysis results of b-STNG, it is evident that the potential difference between human skin and the negative triboelectric layer increased gradually as the separation distance between them increased [38,39].

3.4. Output performance of b-STNG (for falling water drop)

In liquid-solid interacting triboelectric nanogenerators (L-S TENGs), when a liquid drop comes into contact with a solid surface, the phenomenon of sequential liquid-solid contact electrification occurs and results in the creation of an electric double layer (EDL). L-S TENG finds widespread use in droplet energy harvesting [40] where the hydrophobic property of the triboelectric layer plays a fundamental role in enhancing the output performance and its durability. The hydrophobic nature of PTFE particles also significantly improved the contact separation efficiency between water droplets and the triboelectric layer. Additionally, the strong electronegativity of PTFE particles enhanced the charge transfer between the water droplet and the tribonegative layer [6]. Thus, the electrical performance of b-STNG was greatly enhanced by the inclusion of PTFE particles and the microstructures, in contrast to TENG without these modifications. For the two designed triboelectric nanogenerators as stated above, a study on water repellence was also conducted to analyze the shape of the water drop on the TENGs' surfaces. The digital images depicting the surface wettability of the TENGs have been included in the supporting data file in Figs. S4(b) and (c).

The schematic representation of working principle of our designed b-STNG, based on liquid-solid interaction has been illustrated in Fig. S5, in the supporting data file. The underlying principle of b-STNG depending upon Maxwell's displacement current and its output voltage (V_{OC}) has also been well explained in the supporting data file. As shown in Fig. 5, the following parameters were considered to determine the impact of external conditions on the output voltage and short-circuit current of the b-STNG: angle of inclination (θ), height of descent (H), frequency of descent and volume of water drop. Additionally, the output of our device was also tested for water drops from various water sources along with salt solution and sugar solution. Fig. 5(a)–(c) illustrate the influence of inclination (the angle between the triboelectric layer and the horizontal base) on the output voltage and short-circuit current of b-STNG. The output voltage and current data were taken for 0° (5 V, 0.1 μ A), 15° (9 V, 0.6 μ A), 30° (10 V, 0.7 μ A), 45° (19 V, 1.3 μ A) and 60° (15 V, 1.1 μ A) as displayed in Fig. 5(b) and (c) and it can be seen that maximum output was obtained at an angle of 45° . As the inclined angle was progressively raised from 0° to 45° , the uneven distribution of the water drops along the slope was highlighted. The front end of the drop spread faster and the change of contact area improved, leading to a rise in the charge transfer speed. Consequently, the electrostatic induction was increased and the output performance was improved. When the inclination angle was increased above 45° , the water drops shrunk and the spreading over the inclined plane promptly reached its highest value. Hence, the output data deteriorated as a result of the restricted horizontal spreading and reduced spreading area of the water droplets [41]. For this experiment the water drop volume was 50 μ L and it was dropped from a height of 10 cm.

Fig. 5(d)–(f) represent the schematic representation and the output performances of b-STNG with the increase of the falling height (H) of water drop on b-STNG. The output voltage and current data were taken for 5 cm (15 V, 1.2 μ A), 10 cm (18 V, 1.3 μ A), 15 cm (21 V, 1.5 μ A), 20 cm (22 V, 1.6 μ A) and 25 cm (25 V, 1.7 μ A). The maximum output voltage and current were observed for 25 cm, keeping the drop volume

at 50 μ L and $\theta = 45^\circ$. Here, we observed that the output performance improved with an increase in falling height. This is because the friction between water drop and the air generates more free charges in the drop before it contacted the triboelectric film. Therefore greater falling height led to more duration of contact between water drop and air, leading to improved output results. Simultaneously, the spreading area on the triboelectric surface increased as height increased. This increment of the output performance with height can be explained with the help of the following equation [9]:

$$W_e = \frac{\rho v^2 d}{\sigma} \quad (6)$$

Here, W_e represents the Weber number, ρ represents the fluid density, v represents fluid velocity, d represents drop radius and σ represents the surface tension of the fluid. When the diameter and surface tension of water drop are fixed, the Weber number rises with the velocity. This means that greater the ratio of inertial force to surface tension, greater will be the spreading area and velocity under the influence of inertial force. Due to the microstructured and rough surface of triboelectric layer, the inertial force increases the interface pressure among the triboelectric film surface and the water drop, consequently expanding the effective contact area. As a result, the surface of b-APC becomes a larger diffusion region for water drops, leading to a greater amount of friction charge between the water drops and the film surface.

Fig. 5(g)–(i) display the schematic depiction and output performance of b-STNG on the basis of the frequency of individual droplet contact with b-APC. The output voltage and current data were taken for 2 Hz (13 V, 0.9 μ A), 3 Hz (17 V, 1.2 μ A), 4 Hz (21 V, 1.4 μ A) and 5 Hz (18 V, 1.2 μ A). The graphs show that the open circuit output voltage and short-circuit current of the b-STNG increase with frequency up to 4 Hz, after which there was a drop in both voltage and current at 5 Hz. This is due to the fact that a higher frequency caused a faster injection of surface charges into the saturated state, increasing the number of transferred charges [42]. However, when the frequency was raised over a certain point, the discrete water drops became a continuous flow of water. Because of the constant impact of water, the surface charges could not be transmitted over time and hence the output performance decreased.

The relationship between the water drop volume and the output performances of b-STNG is depicted in Fig. 5(j)–(l). The data for the output voltage and current were taken for 30 μ L (16 V, 1.1 μ A), 40 μ L (18 V, 1.2 μ A), 50 μ L (20 V, 1.3 μ A), 60 μ L (24 V, 1.7 μ A) and 70 μ L (22 V, 1.6 μ A). The results indicated that the output data of the b-STNG initially increased gradually, reaching a peak at 60 μ L, and then decreased as the water droplet volume continued to increase. This is because when the water drop volume was quite large, the induced charge between the water drop and the triboelectric layer was not transferred adequately [43].

Previous studies have demonstrated that electrolytes contained in water have an impact on the output performance of a nanogenerator [40]. On the basis of this fact, b-STNG was tested for various water samples and aqueous solutions as can be seen in Fig. 5(m)–(o). The output voltages and current of b-STNG were tested for DI water (16 V, 1.2 μ A), tap water (19 V, 1.4 μ A), rain water (31 V, 2.2 μ A), salt solution [solution of 0.90 % w/v of NaCl; 9 g/L saline] (10 V, 0.8 μ A) and sugar solution [5 % w/v glucose solution; (50 g/L)] (11 V, 0.7 μ A). In contrast to DI water, the output from the tap water was larger but the output from the sugar and salt solutions was much smaller, as illustrated in Fig. 5(n) and (o). This is due to the fact that at low ion concentrations, the output values increase with increasing ion concentration. On the other hand at higher concentration of ions in the solution, the output decreases with the increase in ion concentration [40]. This occurs because the ions in the solution neutralize the charges on the PTFE and b-APC collectively at larger concentrations. Since DI water contains no ions and tap water has a low ion concentration, the output performance of b-STNG for tap water was significantly better than that of DI water. When rainwater was used, the outputs were nearly twice that of DI water because the electrolyte

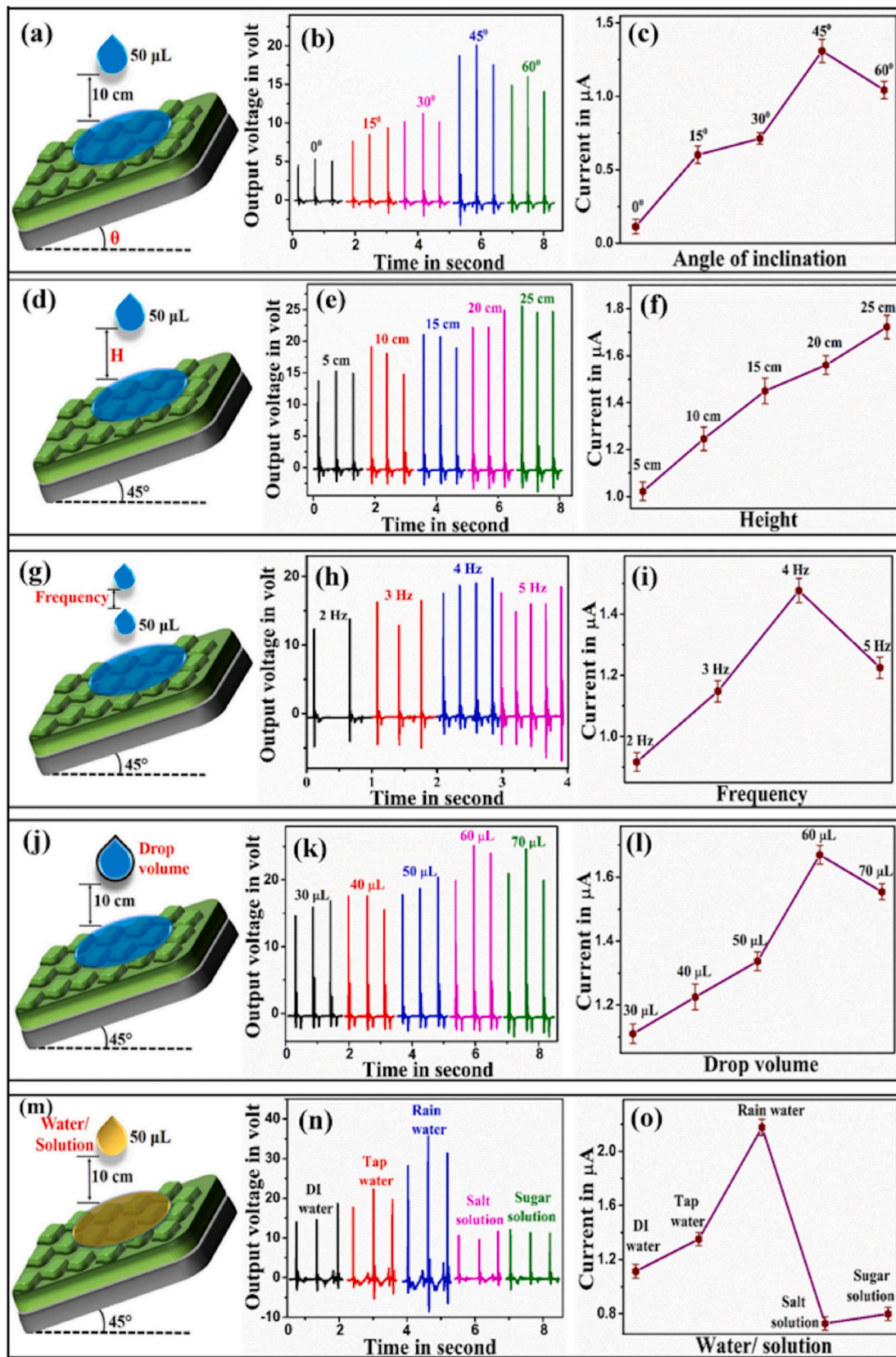


Fig. 5. Performance analysis of b-STNG for falling water drop illustrating the influence of varying parameters. (a)–(c) Schematic representation and influence of angle of inclination on V_{OC} and I_{SC} of b-STNG, (d)–(f) Schematic representation and V_{OC} , I_{SC} of b-STNG with the increase of the falling height (H) of water drop on b-STNG, (g)–(i) Schematic depiction and V_{OC} , I_{SC} of b-STNG with changing frequency of individual droplet contact with b-APC, (j)–(l) Schematic depiction and V_{OC} , I_{SC} of b-STNG with increase of water drop volume, (m)–(o) Schematic depiction and V_{OC} , I_{SC} of b-STNG with water samples from various sources and aqueous solutions.

concentration of rainwater closely matched the ion concentration at which triboelectric nanogenerators driven by electrolyte solutions achieve maximum outputs [40]. As can be seen in the first few seconds of video VS3, water was gathered from natural rainfall by placing a beaker in an open area, in order to conduct the experiment utilizing rainwater. It is known that triboelectric charges get created as raindrops fall from the sky because of contact electrification between the raindrops and the air or airborne particles. As raindrops travel long distances, friction between the water droplets and the air generates triboelectric charges during their descent from the clouds to the ground. These charges are then retained in the collected rainfall. This is the reason that collected rainwater naturally has positive charges in it. The collected rainwater was carefully stored by avoiding any kind of contamination, which allowed the positive charges to remain in the rainwater. Thus, the combined effect of triboelectric charges retained in the collected rainwater and the friction between the raindrop and the air during its 10 cm descent produced significantly higher output results. This observation in the output results inspired us to utilize b-STNG as a rainwater harvester and an acid rain sensor. Due to its high sensitivity to ion and electrolyte concentrations, b-STNG can effectively detect voltage and current fluctuations at different pH levels of acid solutions.

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The hydrophobicity and surface modifications of b-APC significantly improved the efficacy of contact-separation between the triboelectric layer and the water drops. The charge transmission between the drop and the triboelectric layer was also greatly improved by the exceptional electronegativity of PTFE particles and PDMS. Therefore, as compared to TENG without modification, the electrical performance of b-STNG was significantly improved by the bio-inspired surface modifications as well as the incorporation of PTFE particles.

3.5. Output results of b-STNG for acidic solution

When moisture and other acidic compounds combine in the atmosphere, acid precipitation ($\text{pH} < 5.6$) with high hydrogen ion concentrations is created due to the presence of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). The potential of the L-S TENGs for pH measurement of aqueous solution drops has been demonstrated by a number of earlier research works [44–46]. Since our triboelectric device is highly sensitive to ions, as earlier stated in the previous section, we have used b-STNG as a self-powered pH sensor that can be effectively used as an acid rain sensor. Acid rain is mostly composed of H_2SO_4 and HNO_3 , thus in order to confirm the proof-of-concept, artificial acid rainwater was created by combining H_2SO_4 and HNO_3 separately to create two acid solutions. A water sprinkler was used to shower acid solutions on b-STNG to produce a simulated acid rainfall environment with raindrop flow rate of 100 mL/min. Fig. 6(a) and (b) display the open circuit output voltage and short circuit current obtained from b-STNG by sprinkling H_2SO_4 solution having different pH gradients. The output data for H_2SO_4 solution was obtained for pH 3 (4 V, 0.3 μA), pH 4 (12 V, 0.8 μA), pH 5 (20 V, 1.4 μA) and for pH 6 (25 V, 1.7 μA). Similarly, the output results were tested for HNO_3 solution with varying pH gradients, as can be seen from Fig. 6(c) and (d). The data for the output voltage and current for HNO_3 solutions were taken for pH 3 (6 V, 0.5 μA), pH 4 (15 V, 1.1 μA), pH 5 (19 V, 1.2 μA) and for pH 6 (31 V, 1.9 μA). It is evident from the graphs that lower the pH of both acid solutions, lesser are the output results. This is because the contact electrification process is hindered by the H^+ ions found in acidic solutions, which results in a charge screening effect. When the pH falls, the conductivity of the artificial acid rain solution rises and it becomes greater to that of the conductivity of a regular raindrop. An increase in conductivity of a solution indicates an increased concentration of ions in it, resulting in a screen effect and a reduction in electron transport at the liquid-solid interface. Therefore, the transfer of

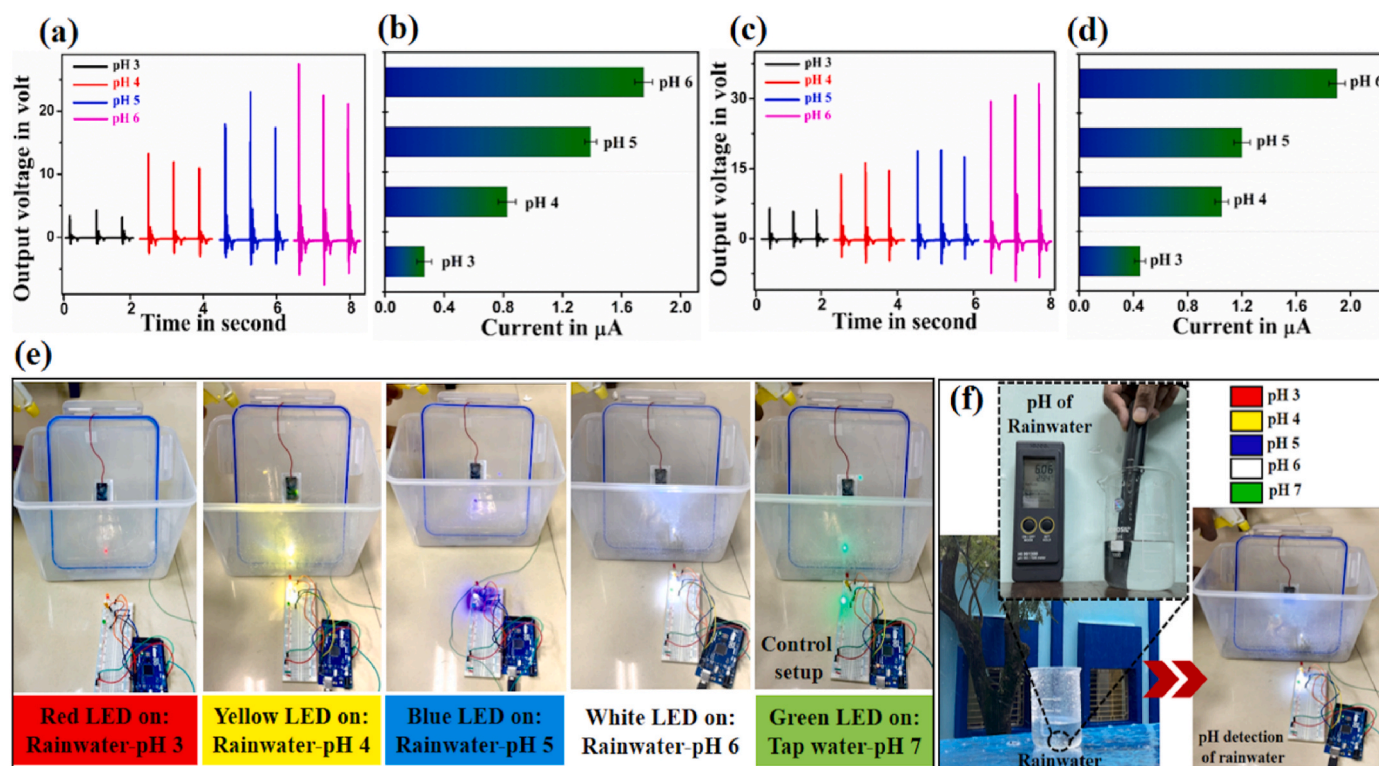


Fig. 6. Real-time acid rain sensing and pH detection via coloured LED indicators. (a)–(b) V_{OC} and I_{SC} obtained from b-STNG by sprinkling H_2SO_4 solution having different pH gradients, (c)–(d) V_{OC} and I_{SC} obtained from b-STNG by sprinkling HNO_3 solution having different pH gradients, (e) b-STNG as a self-powered pH sensor system with different coloured LED indicators corresponding to different pH values, (f) b-STNG working as acid rain sensor system for real time pH detection of collected rainwater.

negative charges decreases as the amount of absorbed hydrogen ions increases, and as a result we get lesser output outcomes [44,46]. Another observation made from Fig. 6(a)–(d) was that, for a given pH, the output data for H_2SO_4 solution was less than that for HNO_3 solution. This is because HNO_3 produces only one H^+ ion per molecule but H_2SO_4 molecule create two H^+ ions, indicating that H_2SO_4 is more acidic in nature. The influence of pH value and ion concentration of the solution on the performance of b-STNG, based on electron transfer, hydrogen ion adsorption and screening effect has been further elaborated on the basis of a schematic diagram in Fig. S7 in the supporting data file. The contact electrification mechanism of acidic solution and b-APC surface on the basis of ion concentration of the solution has also been elaborated in Fig. S7.

Furthermore, compared to the output results for actual rainwater, the output voltage and current for acid solutions were substantially lower. This is because rainwater naturally has positive charges in it. Research has demonstrated that triboelectric charges are produced as raindrops descend from the sky due to contact electrification between the raindrops and the air or airborne particles [44]. Based on these results, it can be inferred that our b-STNG may be used to successfully distinguish the acidity of water as the outputs for rainfall are quite high and the outputs drastically decrease when tested for drops of acid solution. A test was conducted to confirm the degree of stability of b-STNG even after prolonged contact with an acidic solution. The output voltage data of the device was obtained after every 2 h (up to 6 h), by applying force with fingers, which has been included in the supporting data file in Fig. S6. The output data displayed no noticeable degradation even after 6 h, thus inferring that b-STNG can function quite effectively in acidic conditions for a very long period.

3.6. Self-powered acid rain sensor for real time pH detection of rainwater

A self-powered acid rain sensor system was developed, utilizing the output data from b-STNG for a range of pH values to detect the pH of acid rain as displayed in Fig. 6(e). Firstly, an Arduino Mega system was used through a laptop to send the output signal produced by sprinkling the artificial acid rain (mixture of HNO_3 solution and H_2SO_4 solution in 1:1 ratio) on the triboelectric device. Next the data was collected, processed and analysed after the produced output data from b-STNG was passed through the microcontroller unit (MCU) module. The output voltage corresponding to each pH value were brought under 5 V using a voltage divider. A low-pass filter and rectifier module, which were connected to the processing circuit for rectifying the signal, were used to filter the produced output signal. LEDs with varying colours were connected to the circuit that indicated the pH value of the acidic solution in real time. The output signal obtained was rectified and delivered to the Arduino Mega system and was also sent to the LEDs for pH indication. Acid rain in real life has a pH range of 3–6, thus coloured LEDs were chosen to correspond with this range. In addition to detecting acid rain, a control setup was also taken indicating a pH of 7 which corresponds to normal water. The LEDs were colour coded according to the pH levels as follows - Red LED: pH 3, Yellow LED: pH 4, Blue LED: pH 5, White LED: pH 6, Green LED: pH 7 (Control setup for regular water). By adjusting the HNO_3 and H_2SO_4 acid concentration, acidic solutions with different pH values were made to simulate artificial rains of different pH values. Fig. 6(e) illustrates how upon sprinkling an acidic solution with a certain pH on b-STNG, LEDs matching that pH lighted up instantaneously as shown in video VS2. When a red or yellow LED lit up, it meant that the acidity of the rainwater was extremely high, which is dangerous and calls for caution. Significantly high level of acid rain was still indicated by the lighting up of blue LED, which represented a pH of 5. A white LED represented typical rainfall and signalled no threat to the environment. Additionally, when regular water was sprayed on the triboelectric device, our self-powered sensing system could react to it by promptly turning on the green LED, indicating a pH of 7.

Supplementary data related to this article can be found online at

<https://doi.org/10.1016/j.mtener.2025.101812>.

After detecting the pH of the lab prepared artificial rainwater by b-STNG, a real-life model was designed to determine the unknown pH of collected natural rainwater as demonstrated in video VS3. The primary motives for preparing this model were (i) real-time identification of the unknown pH of collected natural rainwater and (ii) displaying the value of matched pH with the help of coloured LED indicators. This proposed system could expand the practicality of the designed b-STNG in real-time self-powered acid rainwater monitoring applications. To easily understand the working steps of the designed model, we divided it into three stages. In the first stage, a beaker was placed in an open place to collect the natural rainwater. In the second stage, the actual pH of collected rainwater was measured with a pH meter and the result showed that it had a pH of 6.06 as shown in the inset of Fig. 6(f) and in video VS3. After that, the collected rainwater was poured into a water sprinkler and was showered on b-STNG to produce a simulated acid rainfall with raindrop flow rate of 100 mL/min. In the third stage, the device generated output voltage signals corresponding to the particular pH value and were passed to the laptop through the ARDUINO Mega system to prepare a data set, which was further analysed by a MCU module. After analysing the data, the white LED lit up immediately, as depicted in Fig. 6(f) and continued glowing until we stopped sprinkling the collected rainwater. According to the list of coloured LED indicators of pH, glowing of white LED indicated pH 6 of the collected rainwater, which also matched with the result of the pH measured with a pH meter, as shown in Fig. 6(f). Therefore, the prepared real-life model concluded that the fabricated b-STNG can successfully detect the unknown pH of rainwater in real-time. Real-time information on the pH properties of raindrops was crucial for determining the level of danger rainfall might cause to the environment. Thus, actual information of the pH properties of raindrops can be predicted to reduce possible harm by enabling prompt preparedness for acid rain in our daily lives. A comparative study has been done based on the performance of b-STNG and other acid rain sensors existing in the TENG field. The details regarding this have been included in the supporting data file.

Numerous health issues, including those related to the skin, heart, lungs and bones have been directly and indirectly linked to acid precipitation. Toxic metals such as aluminium and mercury can leach into collected rainwater and water bodies due to acid rain. These metals henceforth pollute drinking water and build up in the food chain leading to renal dysfunction, brain and blood disorders and various cancers [47]. Acid rain also affect plants to quite an extent. These damages mainly include decreased growth, productivity and harvest owing to damage to photosynthetic process and reproductive organs. Higher level of acid concentration in soil also modifies genes that are critical for their defence against abiotic stress. It can also causes soil acidification, modifies the microbial and enzymatic activity, and the equilibrium of carbon and nitrogen metabolism [48]. Therefore, it is crucial to promptly determine whether the rainfall is acidic in nature and to take appropriate safeguards for the safety of all living things. Since many renowned architectural buildings which are part of cultural heritage are constructed of calcareous materials, such as marble and limestone. Acid rain can seriously harm these materials, emphasizing the importance of conservation [49]. Taj Mahal, one of the new Seven Wonders of the World is an Indian marble mausoleum that reacts with sulfuric and nitric acids of acid rain. This has resulted in the monument developing pits, decolourization and becoming lustreless. Our self-powered b-STNG might be used to promptly determine the pH of rainwater and assist in the execution of preventive actions to save these historically significant buildings if implemented close to such architectural monuments.

4. Conclusion

In summary, we developed a bio-inspired, highly hydrophobic, single electrode triboelectric nanogenerator operating under liquid-solid interface contact electrification that could harvest mechanical energy

not only from simple finger contact but also from water droplets. To create the negative triboelectric layer (b-APC), a unique 'replication' approach employing template sacrifice methodology has been utilized. The triboelectric surface has micro motifs shaped like boats, inspired by the micro patterns on petunia flower petal surface. The negative triboelectric layer was fabricated using PDMS, PTFE particles and synthesized Ag₂S nanoplates. The hydrophobicity of the triboelectric membrane increased significantly with the addition of PTFE particles and mostly due to the introduction of rough topography on the surface of the layer, which has also been theoretically described by the Wenzel model of wetting. Our device b-STNG could generate an open circuit voltage of 374 V and a short circuit current of 11.44 μ A, upon application of force by fingers. In comparison to a TENG designed without microstructures, the output data for b-STNG demonstrated an increase of more than 1.4 times and 1.3 times, respectively, in terms of V_{OC} and I_{SC} . It was found that b-STNG has a maximum power density of 3.25 W/m² at 10⁷ Ω and a sensitivity of 34.4 V/kPa at 0.185 kPa of external pressure. With the use of finite-element analysis through COMSOL Multiphysics software, potential distributions at various stages of the b-STNG power production process were modelled. Our water drop driven, contact electrification based b-STNG responded to rainwater exceptionally well, showing great sensitivity to the pH of the liquid as well as to its ion concentration, due to the shielding effect of H⁺ ions. Our b-STNG was also evaluated for a range of changing parameters of water drop and the output was also tested for water drops from various water sources and different aqueous solutions to better investigate the influence of different factors. In order to detect acid rain, we designed a self-powered, real-time pH sensor system using b-STNG combined with a MCU module. Alongside this, a real-life model was designed to determine the unknown pH of collected natural rainwater. This model could identify the unknown pH of collected natural rainwater instantly and displayed the value of matched pH with the help of coloured LED indicators. Thus, in addition to harvesting energy from randomly falling raindrops, our b-STNG was able to predict the pH value of rainfall in real-time, reducing possible environmental impact and providing prompt precaution from acid rain in our everyday life.

CRediT authorship contribution statement

Namrata Das: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Debmalya Sarkar:** Investigation, Data curation, Conceptualization. **Souvik Sau:** Software. **Asfak Ali:** Investigation. **Sayoni Mandal:** Methodology. **Sukhen Das:** Writing – review & editing, Supervision, Conceptualization. **Partha Pratim Ray:** Writing – review & editing, Validation, Supervision. **Nur Amin Hoque:** Writing – review & editing, Supervision, Data curation.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtener.2025.101812>.

Data availability

Data will be made available on request.

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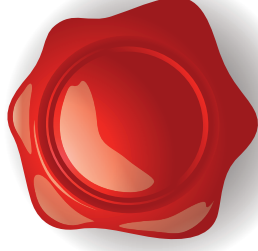
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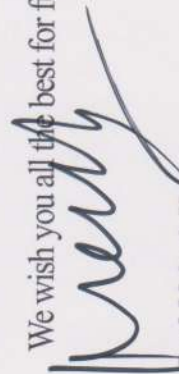
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We wish you all the best for future endeavors!



Prof. Mahesh Kumar
Chair IUMRS ICA 2022



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CERTIFICATE

of Participation

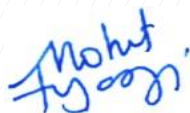
Namrata Das

Jadavpur University, Kolkata

has presented a paper and participated in this symposium
held at GITAM Deemed to be University, Visakhapatnam,
during 20- 24 December 2023



L. M. Pant
Convener
DAE SSPS 2023



Mohit Tyagi
Scientific secretary
DAE SSPS 2023



Jitendra Bahadur
Scientific secretary
DAE SSPS 2023



Dated: 24 Dec 2023



European Materials Research Society

2024 Spring Meeting

May 27 | May 31 - Strasbourg Convention Centre

CERTIFICATE OF PRESENTATION

We certify hereby that

Namrata DAS

Jadavpur University

Kolkata

India

has attended the E-MRS 2024 SPRING MEETING held at the Exhibition & Convention Center in Strasbourg (France) from May 27 to May 31 and presented the contribution entitled:

Water Drop-mediated Triboelectric Nanogenerator Employing Microporous Polymeric Film, Using Single-step Microwave Irradiation

During the session "P12_Nanogenerators" of Symposium P on 30/05/2024 at 13:45



European Materials Research Society
23, rue du Loess - B.P. 20
67037 STRASBOURG Cedex 2 (France)

E-MRS

BP 20 - 67037 Strasbourg Cedex 2 – France - Tel : + 33 3 88 10 63 72 - emrs@european-mrs.com

www.european-mrs.com



Materials Research Society of India (MRSI)

(Kolkata Chapter)

Certificate of Participation



This is to certify that *Namrata Das* of *Jadavpur University* has participated at the

“Young Scientists’ Colloquium 2024”

Organised by

Materials Research Society of India (MRSI), Kolkata Chapter

On Wednesday, December 11, 2024

at Ramakrishna Mission Vidyamandira, Belur Math, Howrah-711202

Swami Mahaprajnananda
Chairman, YSC 2024

Dr. Uttam Kumar Ghorai
Convenor, YSC 2024

Prof. N. R. Bandyopadhyay
Chairman, MRSI, Kolkata



7th Regional Science & Technology Congress, 2024-25

Comprising Districts of the Region: 6 (Kolkata Region)



PRESIDENCY
UNIVERSITY
KOLKATA

Certificate of Presentation

Certified that

Namrata Das

affiliated with

Jadavpur University, Kolkata, West Bengal, India.

has presented a Paper titled

Water Drop-mediated Triboelectric Nanogenerator Employing Microporous Polymeric Film, Using Single-step Microwave Irradiation

Namrata Das, Debmalya Sarkar, Sukhen Das, and Partha Pratim Ray

in Physical Sciences

Congress, 2024-25 held on 17th - 18th January, 2025 at Presidency University, Kolkata.

Dr. Sharmistha Paul
Nodal Officer of the DSTBT, GoWB
& Joint Organising Secretary

Prof. Soumendu Chatterjee
Joint Organising Secretary

Prof. Nirmalya Narayan Chakraborty
Vice-Chancellor

Jointly Organised by : Presidency University, Kolkata
And

Department of Science and Technology and Biotechnology, Government of West Bengal

International Conference on Energy Conversion & Storage (IECS-2025)

27-29 January 2025

IIT Madras, Chennai

Certificate of Participation

This is to certify that

Namrata Das

Dr./Mr./Mrs./Ms.....

participated in the **IECS 2025** held at IIT Madras, Chennai, Tamil Nadu,
India during **January 27-29, 2025**.

R. Juvani

Convener

Prof. Kothandaraman R.



Prof. P. Venkatakrishnan

Co-convenor

Prof. P. Venkatakrishnan



Certificates of awards





ASSOCIATION OF INDIAN UNIVERSITIES, NEW DELHI
&

JADAVPUR UNIVERSITY, KOLKATA

ANVESHAN 2019-20

STUDENTS' RESEARCH CONVENTION (EAST ZONE)



CERTIFICATE OF PARTICIPATION

This is to certify that Mr./Ms./Dr. NAMRATA DAS
Son/Daughter of Shri. ARINDAM DAS
enrolled in Ph.D
Department/Faculty of Basic science
of JADAVPUR UNIVERSITY University/Institute participated in
East Zone Student Research Convention held at Jadavpur University during February 12-13, 2020.

His/Her proposal/project entitled Cotton Pappus Based Piezoelectric Nanogenerator
..... and Touch-Sensor
under the category of BASIC SCIENCE and secured First position.

Dr. Amarendra Pani

Dr. Amarendra Pani
Jt. Director & Head, Research
Association of Indian Universities
New Delhi

Dr. Rajat Ray

Dr. Rajat Ray
Zonal Coordinator, Anveshan, 2019-20
&
Dean of Students, Jadavpur University

Prof. Suranjan Das
Vice-Chancellor
Jadavpur University

Best Poster Award

IECS2025

27-29 January 2025, IIT Madras, Chennai, India

Awarded to

Ms. Namrata Das

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