

SYNTHESIS AND CHARACTERIZATION OF Au-NPs/Bi₂O₃/PVDF NANOCOMPOSITE FOR PIEZOELECTRIC NANOGENERATOR AND SELF-POWERED PHOTODETECTOR

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MASTER OF SCIENCE

in

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by

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DECLARATION

We, **Aaditya Bhardwaj**, Roll No.: 24/MSCPHY/52 and **Shakti**, Roll No.: 24/MSCPHY/08 hereby certify that the work which is being presented in the thesis entitled "**Synthesis and Characterization of Au-NPs/Bi₂O₃/PVDF Nanocomposite for Piezoelectric Nanogenerator and Photodetector**", " in partial fulfillment of the requirements for the award of the Degree of Master of Science, submitted in the Department of Applied Physics, Delhi Technological University is an authentic record of my own work carried out during the period from August 2025 to May 2026 under the supervision of **Dr. Bharti Singh** and in co-supervision of **Dr. Govind Gupta**.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

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Abstract

The development of decentralized self-powered electronics is a paradigm shift in the physics of modern devices by alleviating the bottleneck of dependence on batteries through harvesting ambient mechanical and optical energy. In this thesis, we explored a piezoelectric nanocomposite based on Bi_2O_3 and PVDF polymer, synthesized using a solution-mixing and drop-casting method, with exceptional output properties for nanogenerator applications. We also synthesized a self-powered photodetector of the same composite using Thermal Vapour Deposition. A comparative and novel study is performed to investigate the impact of Au-NPs (gold nanoparticles) on the performance of the nanogenerator as well as under external mechanical loading. The synthesized nanocomposite films have a thickness of 50–70 μm . The FT-IR confirms the significant boost in electroactive phase of nanocomposites because of the incorporation of nanofillers. The SEM, FE-SEM confirms the successful synthesis of the nanocomposite structure corresponding to the β phase of PVDF. Elemental mapping using EDX also confirms the presence of Bi, Au, C, and O. Dielectric and P-E measurements confirm the ternary composite has the best storage capacity and least dielectric loss. The nanogenerator with Au-NPs/ Bi_2O_3 /PVDF mixture having 5% Bi_2O_3 of total PVDF and with doping of 500 μL of Au-NPs exhibits an enhanced output performance achieving an open circuit voltage of 48.4 V and an output power of 400 μW at a load resistance of 1 $\text{M}\Omega$ using the electrodynamic shaker device at a frequency of 9 Hz. The piezoelectric device is successfully used as a sensor for Morse code generation. The zero biased time-dependent I-T measurement reveals the self-powered nature of our Nanocomposite upon illumination with 355 nm, 455 nm, and 532 nm lasers.

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List of Symbols

Symbol	Description
P	Polarization (C/m ²)
τ_d	Average diffusion time (s)
r	Grain radius (m)
D	Diffusion coefficient (m ² /s)
n	Ideality factor (dimensionless)
q	Elementary charge (C)
μ	Carrier mobility (cm ² /V·s)
E	Electric field (V/m)
J_{drift}	Drift current density (A/m ²)
ε'	Dielectric constant
$\tan \delta$	Dielectric loss tangent
Q	Quality factor
P_r	Remanent polarization ($\mu\text{C}/\text{cm}^2$)
E_g	Band gap energy (eV)
h	Planck's constant (J·s)
ν	Photon frequency (Hz)
V_{OC}	Open circuit voltage (V)
F_{EA}	Electroactive phase content (%)
A_{840}, A_{764}	Absorption intensities at 840 and 764 cm ⁻¹
K_{840}, K_{764}	Absorption coefficients at 840 and 764 cm ⁻¹

List of Abbreviations

Abbreviation	Description
PENG	Piezoelectric Nanogenerator
PNG	Piezoelectric Nanogenerator
PVDF	Poly(vinylidene fluoride)
IoT	Internet of Things
Au-NPs	Gold Nanoparticles
DMF	N,N-Dimethylformamide
DMSO	Dimethyl Sulfoxide
NMP	N-Methyl Pyrrolidone
DMAc	Dimethylacetamide
DI	Deionized (water)
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
FE-SEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
PL	Photoluminescence
TR-PL	Time-Resolved Photoluminescence
P-E Loop	Polarization–Electric Field Loop
MWS	Maxwell-Wagner-Sillars
LSPR	Localized Surface Plasmon Resonance
SPR	Surface Plasmon Resonance
TVD	Thermal Vapour Deposition
LED	Light Emitting Diode
SCL	Space Charge Limited
RIP	Respiratory Inductive Plethysmography
UV	Ultraviolet
VESTA	Visualization for Electronic and Structural Analysis
PDF	Powder Diffraction File

Chapter 1

Introduction

1.1 Overview

The recent growth of Artificial Intelligence and IoT based devices has also increased the demand for energy. Along with this, the concern for environmental sustainability makes green and ambient energy harvesting more important, but only limited practical routes are available for harvesting such renewable energy. In past decade, piezoelectric nanogenerators (PENGs) have been studied as a useful route to harness mechanical energy into electrical energy. The application of piezoelectric nanogenerators is not limited to energy harvesting, but also includes self-powered electronics, wearable devices, healthcare, biomedical applications, wireless sensor and the Internet of Things (IoT) [1-4].

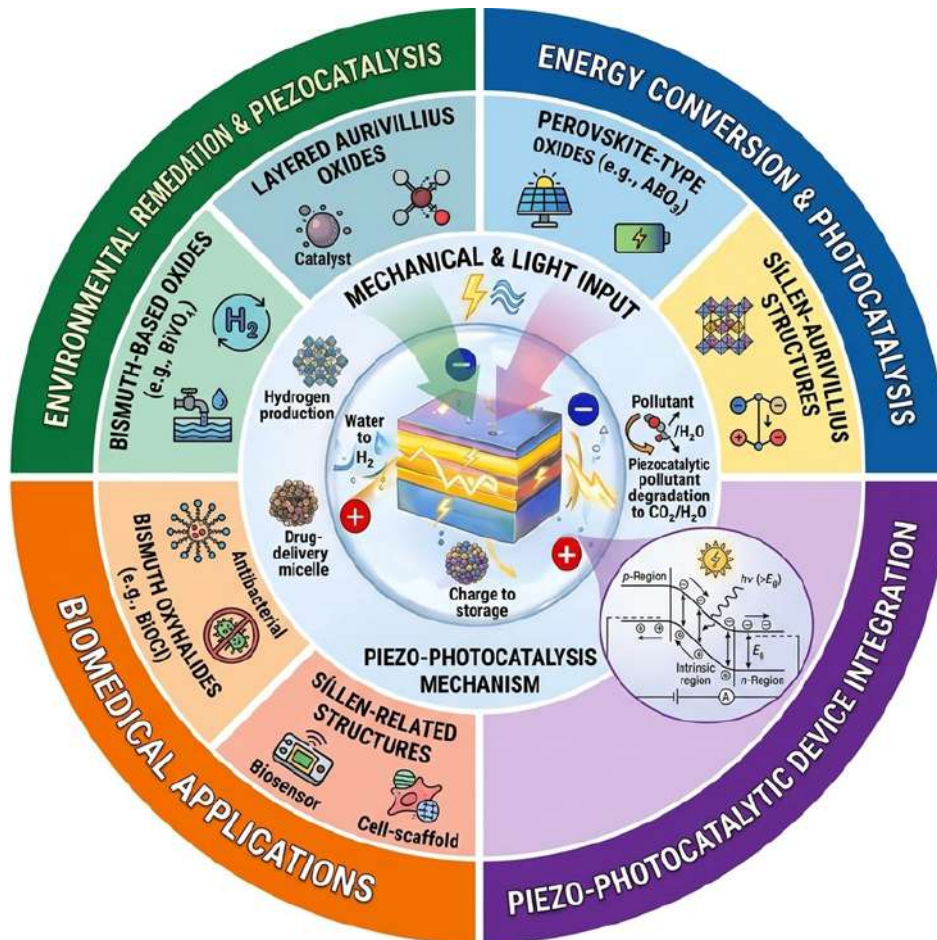


Figure 1.1: Comprehensive Application and Structural Landscape of Bismuth-Based Oxides.

1.2 Piezoelectricity

Piezoelectric materials are a class of smart materials because they can produce an electric charge upon the execution of mechanical stress, a phenomenon known as the direct piezoelectric effect. In the reverse case, if they are exposed to an external electric field, these materials show mechanical strain, which is called the inverse piezoelectric effect. Because of this two-way electromechanical coupling, these materials are useful for energy harvesting, sensing, and actuation applications where mechanical and electrical energy have to be converted into each other [5].

1.3 Principle of Piezoelectric Effect

The piezoelectric effect refers to an electromechanical coupling in which non-centrosymmetric crystalline materials can convert mechanical and electrical energy reversibly. This phenomenon is generally discussed in two forms: the direct piezoelectric effect, where surface charge is generated under applied mechanical stress (e.g., compression, tension, or bending), and the inverse piezoelectric effect, where an external electric field produces strain in the lattice.

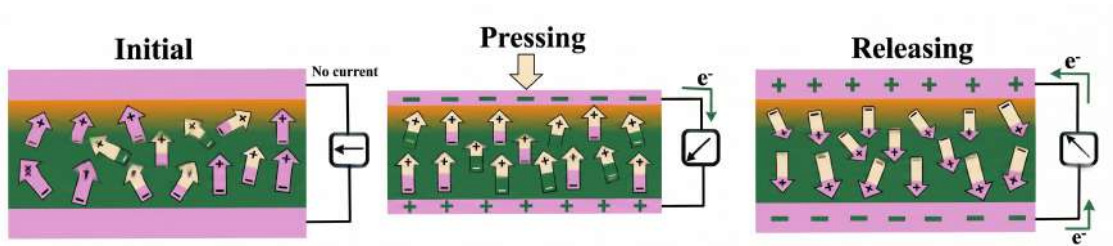


Figure 1.2: Schematic representation of PENG.

At the atomic level, the effect is controlled mainly by the symmetry of the crystal structure. In an unstressed crystal, the centres of positive and negative charge remain at the same position, and hence no net electrical polarization is produced. When an asymmetric mechanical load is applied, the ions are displaced slightly from their original positions. This displacement disturbs the charge balance inside the crystal and produces small electric dipoles, whose combined effect is observed as macroscopic electrical polarization [6].

A classic example of this is quartz (SiO_2). When no force is applied, the centers of positive (Si) and negative (O) charges coincide as a result material is electrically neutral. But under force, they shift apart and charges do not coincide, so electrical dipole moment arises. And the dipole moment is characterized by electrical polarization. Greater the distance between the charges higher the magnitude of the polarization (P). To compensate the electrical

polarization within the material which represents the electrical imbalance, charges are electrostatically induced on the electrodes. In context of the centre of charges, this effect is also known as displacement polarization. When the electrodes are subjected to electrical short-circuit, a charge flow will occur leading to the formation of an electric current. Also, measurement of an electric voltage is possible for the electrically unloaded electrodes. In inverse piezoelectric effect, the same processes take place within the piezoelectric material but their direction is reversed.

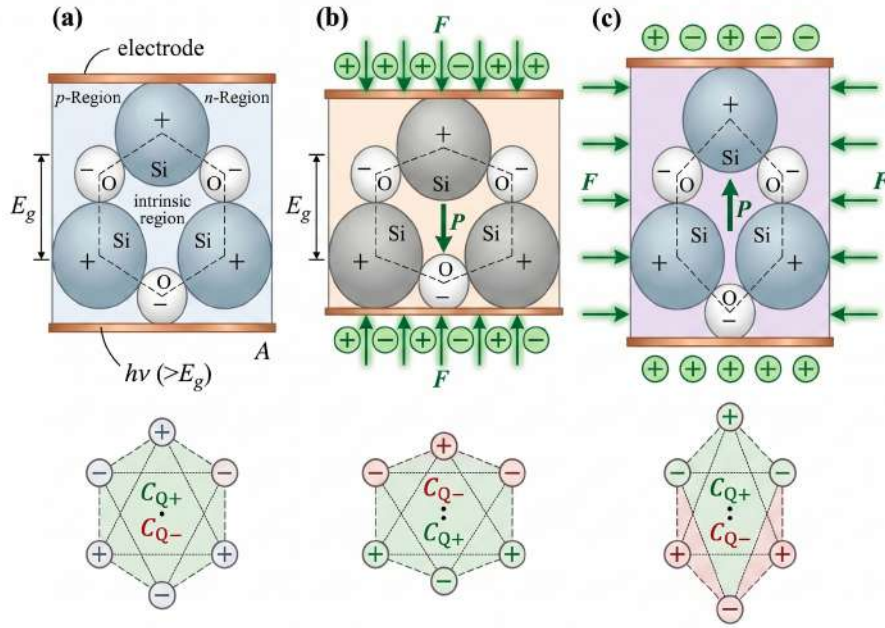
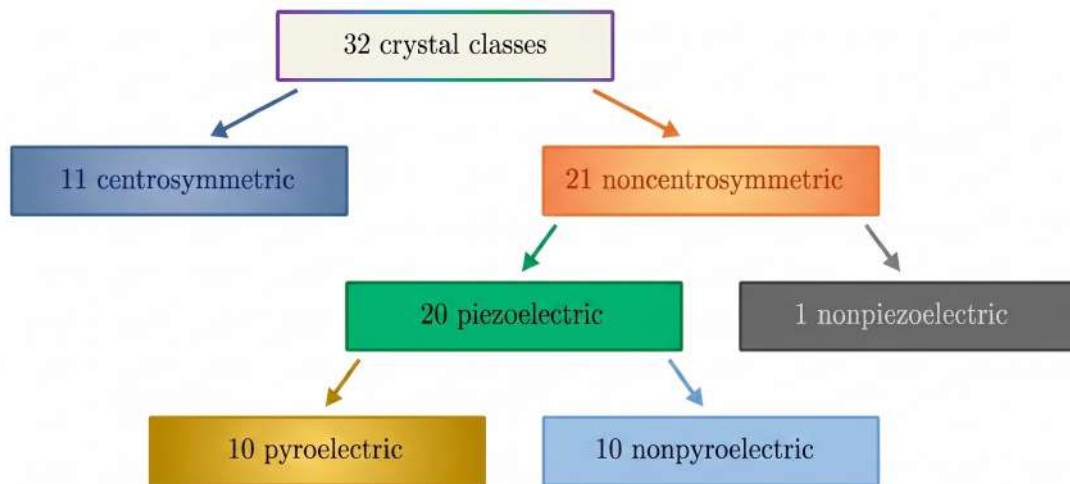


Fig (2)- (a) Original state of crystal without any mechanical force. (b) longitudinal and (c) transverse mode of direct piezoelectric effect due to mechanical forces F .

Figure 1.3: (a) Initial state of crystal under no mechanical force. (b) Longitudinal and (c) Transverse mode of direct piezoelectric effect under mechanical forces F .

1.4 Piezoelectric Material

In general, a crystal is characterized by a periodic arrangement of the atomic lattice structure in all directions of space. Unit cell is also described as the smallest but the repetitive arrangement within a crystal system. As per symmetry properties of the unit cell, we can distinguish between 32 crystal classes that are also termed crystallographic point groups. Piezoelectricity is only possible to those cells, which are asymmetric by nature. 21 out of the 32 crystal classes fulfill this property because they are non-centrosymmetric, which means that they do not have a center of symmetry. 20 out of these 21 crystal classes show piezoelectricity. While 10 crystal classes are pyroelectric, the remaining 10 crystal classes are non-pyroelectric. The 20 piezoelectric crystal classes can be grouped into the seven crystal systems [5].



Fig(6): Classification of the 32 crystal classes (crystallographic point groups).

Figure 1.4: Classification of the 32 crystal classes (crystallographic point groups).

1.5 Classification of Piezoelectric Materials

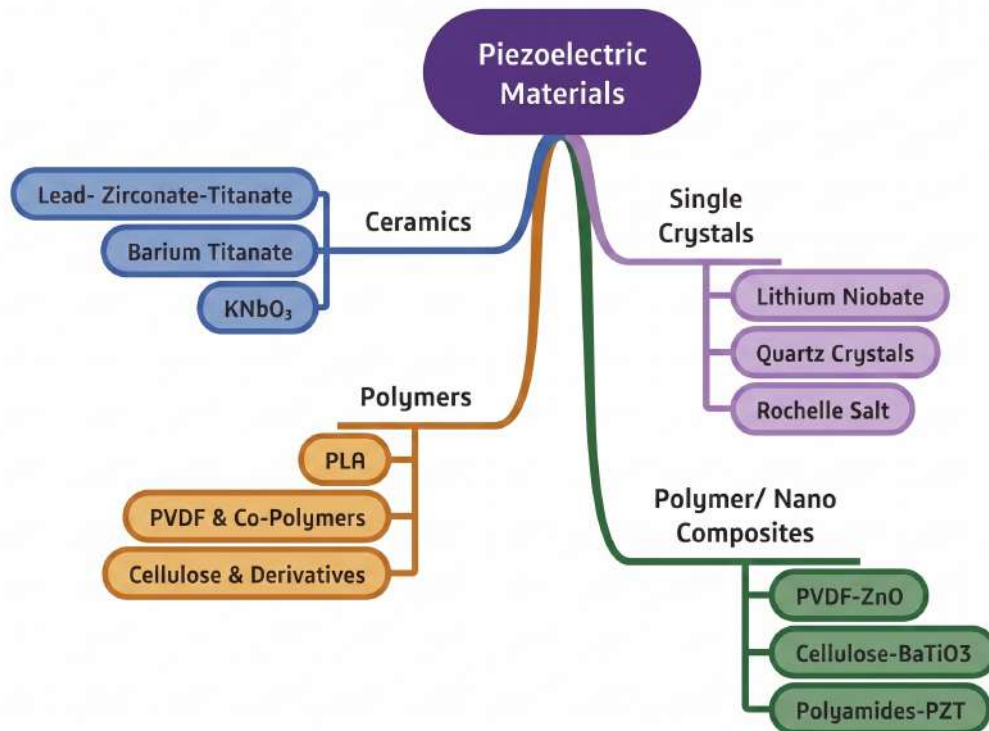


Figure 1.5: Classification of Piezoelectric materials.

1.6 Flexible Piezoelectric Material

Flexible piezoelectric materials have become important in the development of next-generation wearable electronics, self-powered sensors, and soft robotics. Unlike traditional rigid ceramic piezoelectrics, these flexible materials can undergo large mechanical deformations without fracturing, making them ideal for integration with soft surfaces such as human skin. This class of materials mainly uses ferroelectric polymers, such as polyvinylidene fluoride (PVDF) and its copolymers, because of their mechanical flexibility and biocompatibility [7].

Since, pure polymers usually give a lower piezoelectric coefficient, the usual approach is to add a ceramic phase to the flexible polymer rather than using the polymer alone. Electrospun fibres and sponge-like porous films are two examples of such designs; both are used to increase effective deformation and contact area under small pressure [8]. For this reason, flexible PENG films are suitable for body-motion signals such as walking, breathing, finger tapping and joint bending. The same pressure response can also be used in pulse or respiration monitoring. Recent studies are also moving toward lead-free and, where possible, biodegradable piezoelectric materials, since wearable and implantable devices raise environmental and biosafety concerns. However, cyclic durability, hysteresis loss and large-area fabrication still need further improvement.

1.7 Objective & Scope

This thesis is about the synthesis of a flexible lead-free nanocomposite for self-powered Piezoelectric nanogenerator for various Bio-mechanical motion sensing application and self-powered photodetector, primarily focused on **AuNPs/Bi₂O₃/PVDF**. This thesis is also focused on the study of synergistic enhancement in piezoelectric Voltage (V_{OC}) due to Schottky barrier effect as of incorporation of Au-NPs made for the enhancement of electroactive β -phase content of PVDF matrix.

To achieve this objective, our work mainly focused on the following steps:

- To synthesize and characterize PVDF, Bi₂O₃/PVDF, Au-NPs/PVDF, Au-Nps/Bi₂O₃/PVDF flexible nanocomposite.
- To fabricate the piezoelectric nanogenerator device and photodetector device.

1.8 Methodology

- Synthesis of PVDF, Bi₂O₃/PVDF, Au-NPs/PVDF, Au-Nps/Bi₂O₃/PVDF nanocomposite via Drop Casting method.

- Primary characterization of PVDF, $\text{Bi}_2\text{O}_3/\text{PVDF}$, Au-NPs/PVDF, Au-Nps/ $\text{Bi}_2\text{O}_3/\text{PVDF}$ nanocomposite for optimizing structural confirmation, including XRD, FT-IR, SEM and FE-SEM.
- Secondary characterization, like P-E loop, Dielectric Constant measurement, Photoluminescence, Time-resolved photoluminescence of PVDF, $\text{Bi}_2\text{O}_3/\text{PVDF}$, Au-NPs/PVDF, Au-Nps/ $\text{Bi}_2\text{O}_3/\text{PVDF}$ nanocomposite for the optimization of their electrical and optical properties.
- Device performance as well device stability testing for piezoelectric nanogenerator like testing of device output voltage for various frequency as well as various force and taking the current measurement for bigger number of cycles.
- Taking the I-V and I-T measurement of fabricated photodetector device.

Chapter 2

Literature Review and Theoretical Background

2.1 Overview: Polyvinylidene Fluoride (PVDF)

PVDF is a highly non-reactive thermoplastic from the fluoropolymer family. The term PVDF stands for poly(vinylidene fluoride), also called poly(1,1-difluoroethylene), and its repeating unit is represented as $(\text{CH}_2\text{-CF}_2)$. One useful feature of PVDF is that it can generate an electrical signal when it is subjected to sound, force, pressure, heat, or acceleration. It is also valued for its chemical and thermal resistance, but its piezoelectric response is the reason it is widely used in sensing and energy-harvesting studies. Although piezoelectricity was discovered by the Curie brothers in 1880, the piezoelectric behaviour of PVDF became known only in the late 1960s. Since then, PVDF has been used in traffic sensors, vehicle weighing systems, light-up shoes, and medical respiratory monitoring. For example, PVDF-based RIP belts can monitor breathing without requiring continuous external power [7–8].

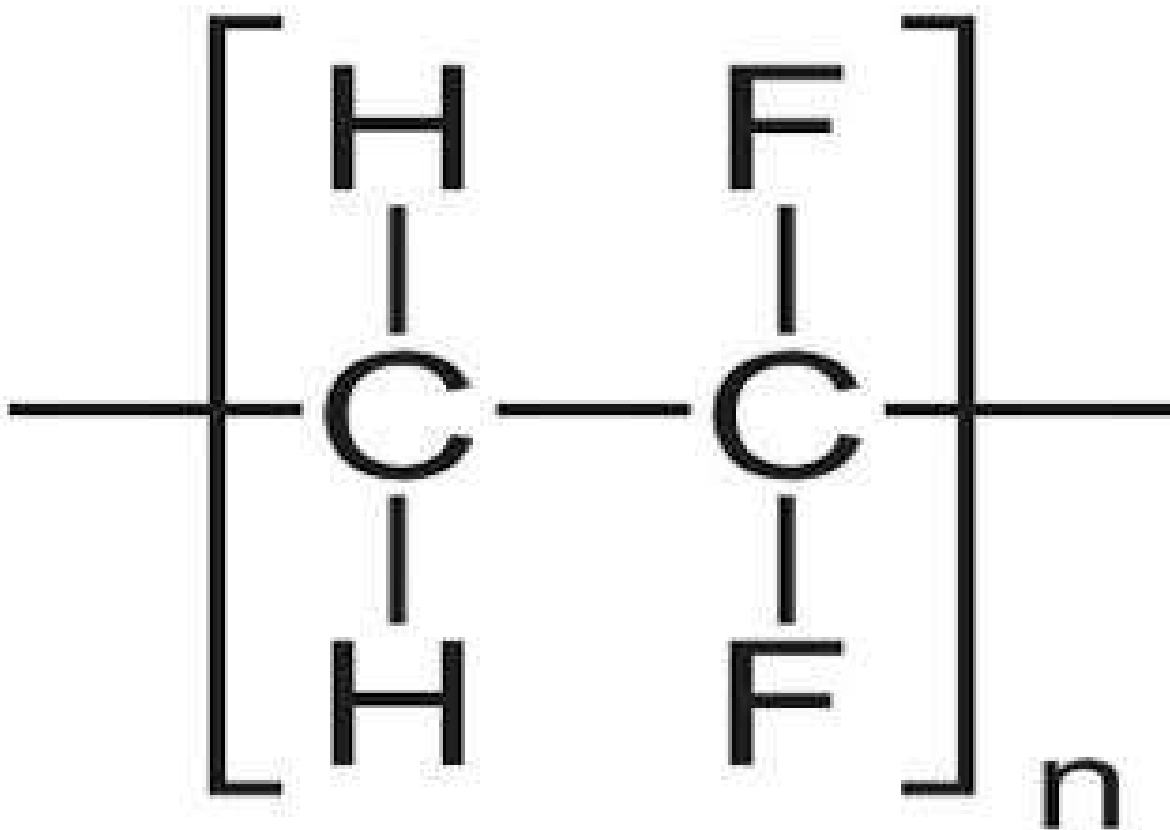


Figure 2.1: Structure of PVDF.

2.2 Physical and Mechanical Properties of PVDF

PVDF is a strong and flexible fluoropolymer, generally written as $-(\text{CH}_2-\text{CF}_2)_n-$. Although the repeat unit is simple, the polymer gives a useful combination of chemical resistance, thermal stability, mechanical strength, UV resistance and radiation tolerance. It is semi-crystalline; in other words, crystalline regions are present along with amorphous regions, and its melting point is about 177°C . Compared with many other fluoropolymers, PVDF is also easier to process and relatively economical, so it can be made into films, membranes, tubes and fibres. For piezoelectric studies, its polymorphism is especially important. PVDF may appear in alpha, beta, gamma and delta phases, but the beta phase is normally preferred because the chain dipoles are more effectively aligned in that structure. Processing route, stretching and electric-field treatment can shift the phase balance, and this is the reason PVDF properties can be tuned for sensors, batteries, electronic components, medical devices, chemical equipment, wire coating and weather-resistant coatings.

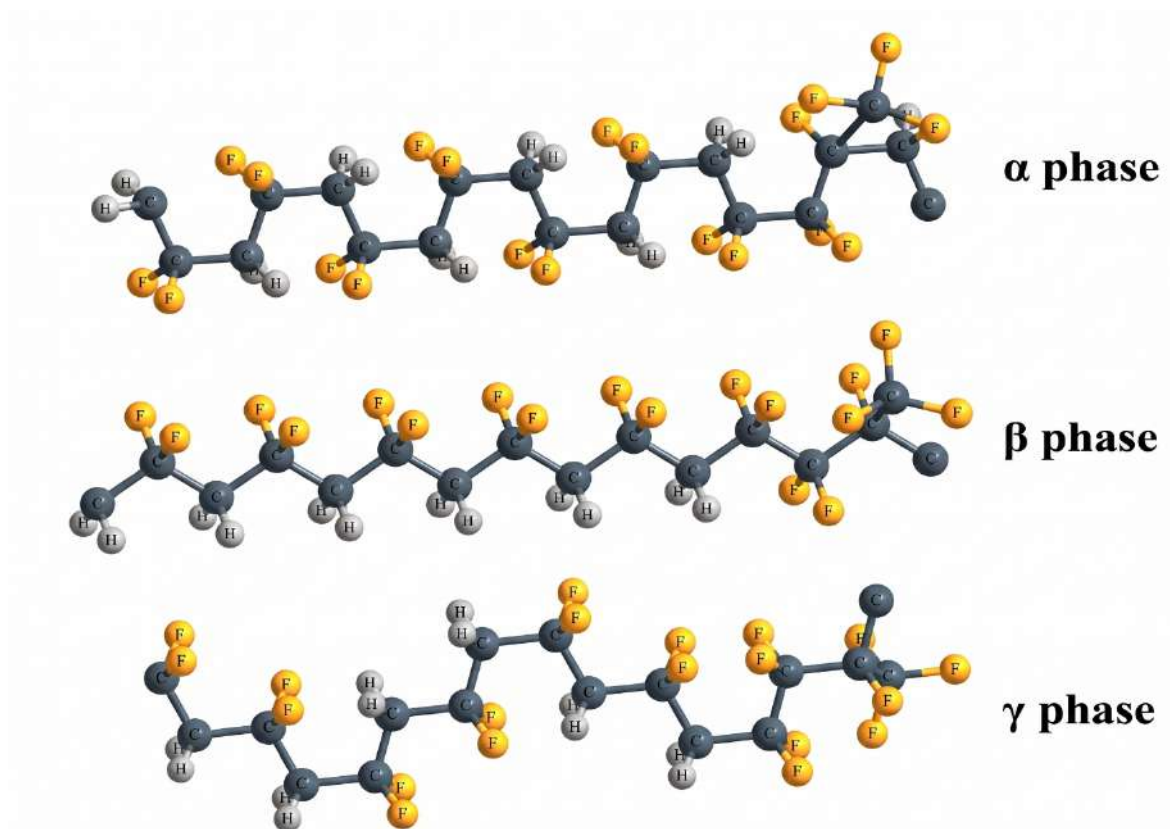


Figure 2.2: Different phases of PVDF.

Polyvinylidene fluoride (PVDF) exhibits excellent chemical stability and specific solubility behaviour because of its strong carbon-fluorine (C–F) bonds and low surface energy. Since it is hydrophobic, the polymer shows strong resistance to water absorption, which improves its stability in humid and corrosive environments. PVDF shows good resistance

to oxidative degradation, as well as a tolerance against several aggressive chemical media, including inorganic acids (e.g., hydrochloric and sulfuric acids), bases (e.g., sodium hydroxide and ammonia), halogens such as chlorine, and conventional organic solvents like alcohols, ketones, and hydrocarbons. Conversely, it is completely insoluble in aliphatic or aromatic compounds. Due to its semi-crystalline, polar nature, PVDF exhibits limited chemical resistance to high-temperature fuming acids and is selectively soluble in strong, highly polar aprotic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl pyrrolidone (NMP), and dimethylacetamide (DMAc); which are commonly used for solution-based processing and membrane fabrication.

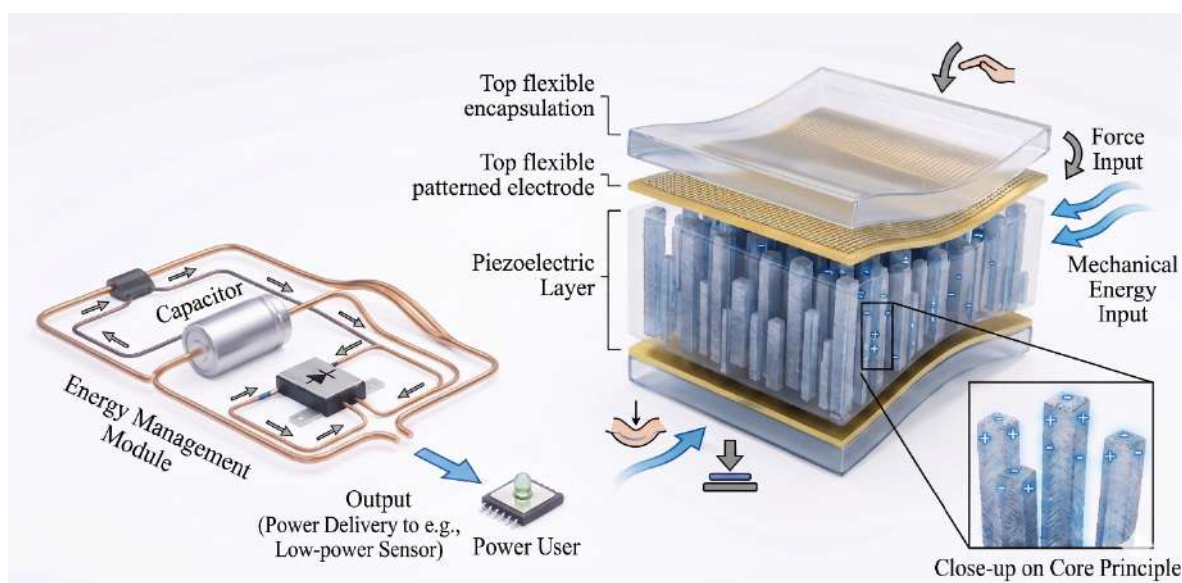


Figure 2.3: Schematic representation of Piezoelectric Nanogenerator mechanism.

2.3 Why We Choose Bismuth Oxide (Bi_2O_3)

Some metal Oxides have shown promising results in enhancing the mechanical and electrical properties of piezoelectric nanogenerators when embedded in semi-crystalline fluropolymers like polyvinylidene fluoride (PVDF), resulting in an efficient, flexible PENG device [5]. Bismuth Oxide (Bi_2O_3), among various post-transition metal oxides, has a narrow bandgap, high density, and an intrinsically high dielectric permittivity, which makes it excellent choice for an alternative to toxic lead-based piezoelectric ceramics and composites.

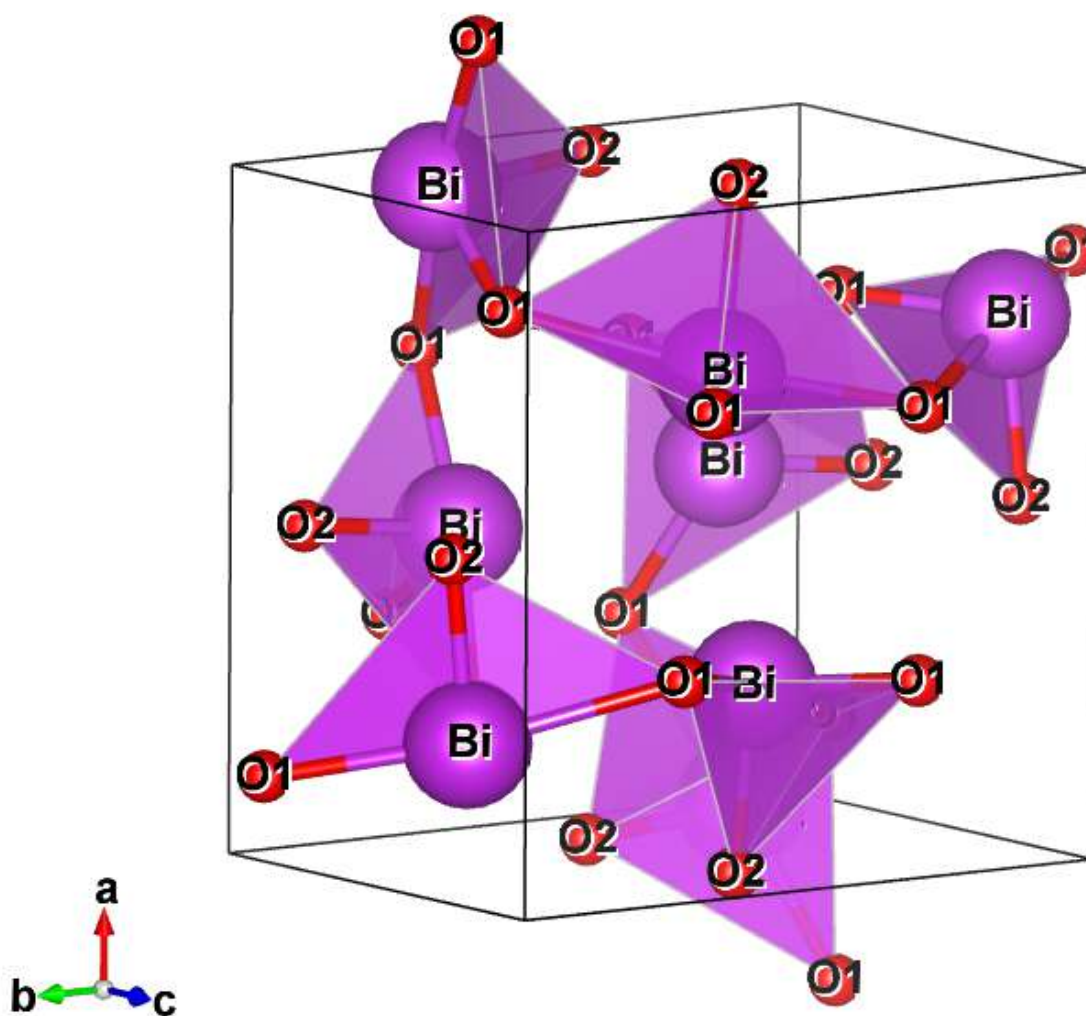


Figure 2.4: Crystal Structure of Bi_2O_3 .

In the work reported by Anirban al., Bi_2O_3 exhibits piezoelectric behaviour with maximum open-circuit voltage of 3.6 V [6]. Bi_2O_3 not only acts as a nucleating agent but also serves as a dispersed micro-capacitor network, which enhances localised charge storage because of the difference in dielectric constant with PVDF, making the nanocomposite films exhibit the Maxwell-Wagner-Sillars (MWS) effect [7].

Photodetectors are used in many areas, ranging from environmental monitoring to medical diagnostics. In this context, bismuth oxide (Bi_2O_3) is useful because it offers high photoconductivity, good air stability, a tunable band gap, UV sensitivity, comparatively low toxicity, and low material cost [8]. These properties are relevant because many conventional UV photodetectors are based on wide-bandgap semiconductors that have limited spectral response [9]. At the same time, much of the earlier photodetector work has been carried out on rigid substrates, which restricts applications in wearable electronics, flexible displays, and con-

formal optical sensors [10]. Therefore, preparing Bi_2O_3 -based photodetectors on flexible substrates is an important route for combining optical detection with mechanical flexibility.

Flexible substrates make Bi_2O_3 photodetectors more useful in practical devices, although they also make processing and stability more difficult. Glass and silicon substrates are mechanically rigid, so they are not suitable where bending or conformal contact is required. A flexible Bi_2O_3 device, on the other hand, can be considered for wearable optical sensors, rollable displays, biomedical devices and distributed environmental monitoring [10]. The comparatively low toxicity of Bi_2O_3 is another reason for interest in such close-contact applications [11]. Earlier reports on self-powered UV photodetectors, including Bi_2O_3 - SnO_2 quantum dot devices on PDMS with Schottky heterojunction behaviour, show that Bi_2O_3 can be integrated into deformable optoelectronic structures for UV sensing and protection [10–11]. Bi_2O_3 is a semiconducting oxide, and its reported optical band gap usually lies around 2–3.9 eV, depending on the phase and preparation route [14–15]. It can crystallize in alpha, beta, gamma, delta and epsilon forms. Among these, monoclinic alpha- Bi_2O_3 is the stable room-temperature phase and is commonly found in thin-film and nanoparticle samples [14–15]. Compared with many heavy-metal oxides, Bi_2O_3 is treated as a relatively safer material, which is why it is often discussed as an environmentally friendlier option. Some high-temperature phases, especially delta Bi_2O_3 , are also known for high oxide-ion conductivity and are therefore relevant to solid electrolyte and electrochemical systems [17–18]. For photodetectors, the important point is that Bi_2O_3 can show p-type behaviour and can form junctions with n-type oxides such as ZnO. These junctions help separate photogenerated charge carriers under UV illumination, which is why Bi_2O_3 -based composites are studied for improving responsivity and detectivity [9, 12–13, 19–20].

2.3 Physics of Photodetector

Photodetection begins with photon absorption in the semiconductor. When the incoming photon has energy larger than the band gap, an electron ejected from valence band and moves to the conduction band and a hole is left behind [27]. The separated carriers then give an electrical signal, usually measured as current or voltage under illumination [28]. Since Bi_2O_3 has a band gap reported in the broad range of about 2–3.9 eV, depending on phase and synthesis route, it can respond to UV light and in some cases to the visible region as well [29]. In simple terms, electron-hole pairs are produced when the photon energy, $E = h\nu$, exceeds the band gap energy E_g [27].

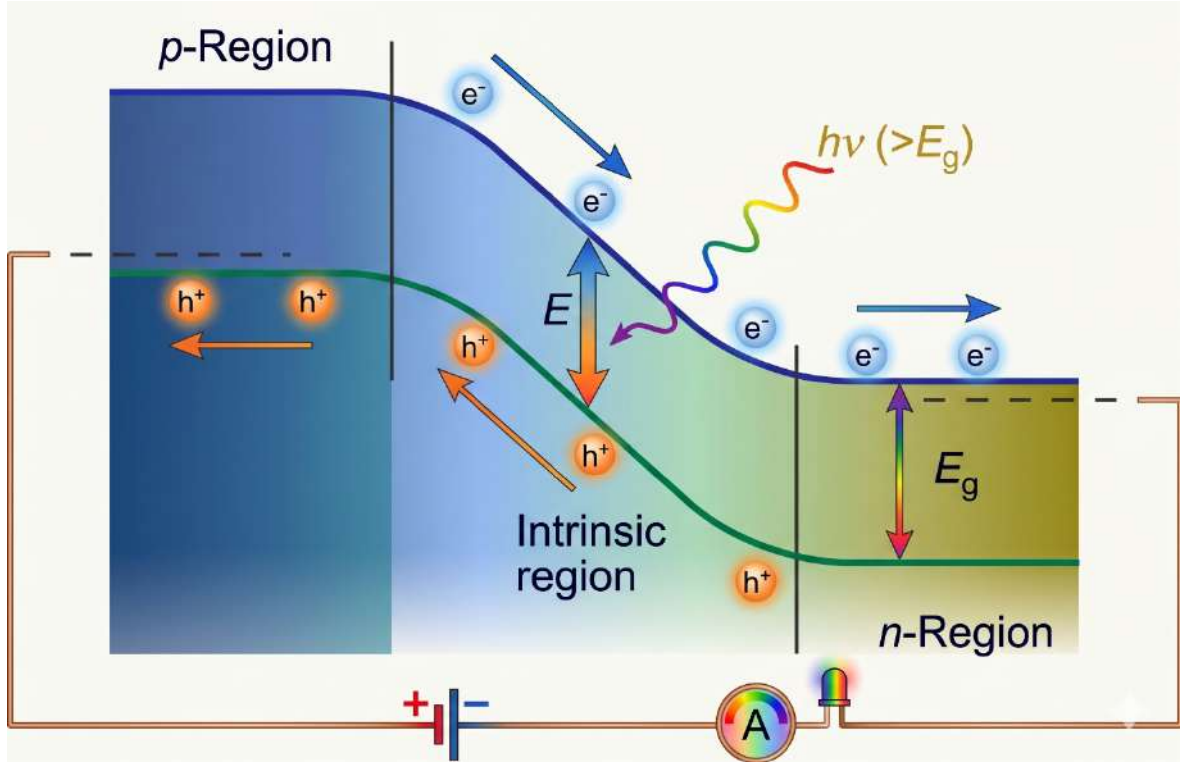


Figure 2.5: Schematic representation of a working photodetector.

2.4 Photogeneration and Charge Carrier Dynamics

After photogeneration, electron-hole pairs may recombine, where electrons return to the valence band, releasing energy as heat or light and therefore do not contribute to photocurrent [1]. The recombination rate depends on the carrier lifetime, defect density, and the spatial separation of electrons and holes. For randomly generated charge carriers, the average diffusion time (τ_d) is given by:

$$\tau_d = \frac{r^2}{D\pi^2} \quad (2.1)$$

Where r is the grain radius and D is the diffusion coefficient of the carriers [8]. With decreasing crystallite size, the chances of recombination can be reduced, improving overall photocurrent generation. Recombination current is an important loss mechanism in photodetectors, occurring at low applied voltages when each electron excited from the valence band returns toward equilibrium by recombining with a hole [12]. The ideality factor (n) of a photodetector junction indicates the deviation from ideal thermionic behaviour and can indicate the dominant recombination mechanism. For a $\text{Bi}_2\text{O}_3/\text{n-Si}$ heterojunction, an ideality factor of approximately 2.44 has been reported, indicating that recombination currents are not distributed uniformly in the structure at local sites rather than uniformly across the junction [12].

2.5 Charge Transport and Conduction Mechanisms

At thermal equilibrium, charge carrier transport in semiconductors occurs through band conduction, where electrons and holes move through electronic states in the conduction and valence bands, respectively [15]. Under applied bias voltage, the electric field drives the motion of charge carriers. Where r is the grain radius and D is the diffusion coefficient of the carriers [8]. With decreasing crystallite size, the chances of recombination can be reduced, improving overall photocurrent generation. Recombination current is an important loss mechanism in photodetectors, occurring at low applied voltages when each electron excited from the valence band returns toward equilibrium by recombining with a hole [12]. The ideality factor (n) of a photodetector junction indicates the deviation from ideal thermionic behaviour and can indicate the dominant recombination mechanism. For a $\text{Bi}_2\text{O}_3/\text{n-Si}$ heterojunction, an ideality factor of approximately 2.44 has been reported, indicating that recombination currents are not distributed uniformly in the structure at local sites rather than uniformly across the junction [12]:

$$J_{\text{drift}} = q \cdot n \cdot \mu \cdot E \quad (2.2)$$

Here, q denotes the elementary charge, n is the carrier concentration, μ is the carrier mobility, and E is the electric field [12]. At higher bias, particularly when the semiconductor contains many defects, space-charge-limited (SCL) current may start to dominate. In that case, the injected carriers themselves build up space charge and control the current flow, instead of the contact injection alone [16]. The trap-filled-limit region appears after shallow traps near the band edge begin to fill; the conduction is then controlled by the filling of these traps. On a double-logarithmic I-V plot, this region is generally recognised from a slope close to 3 [16].

2.6 Plasmonic Enhancement of Optical Absorption

For Bi_2O_3 photodetectors, Au or Ag nanoparticles are commonly introduced to make better use of the incident light. Around these metal particles, surface plasmon resonance can concentrate the local optical field. This local field can increase absorption near the oxide surface and assist the formation of additional electron-hole pairs. Au nanospheres and nanorods of about 30 nm are often suitable because their localized surface plasmon resonance lies in a useful wavelength region. For nanorods, changing the aspect ratio, commonly around 2:1 to 3:1, shifts the SPR position and gives wavelength-selective enhancement. Reported Bi_2O_3 -based systems show that Au nanospheres on $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ can improve activity by nearly four times, while Au nanorods of 20–35 nm can give about 5–11 fold enhancement depending on size [17].

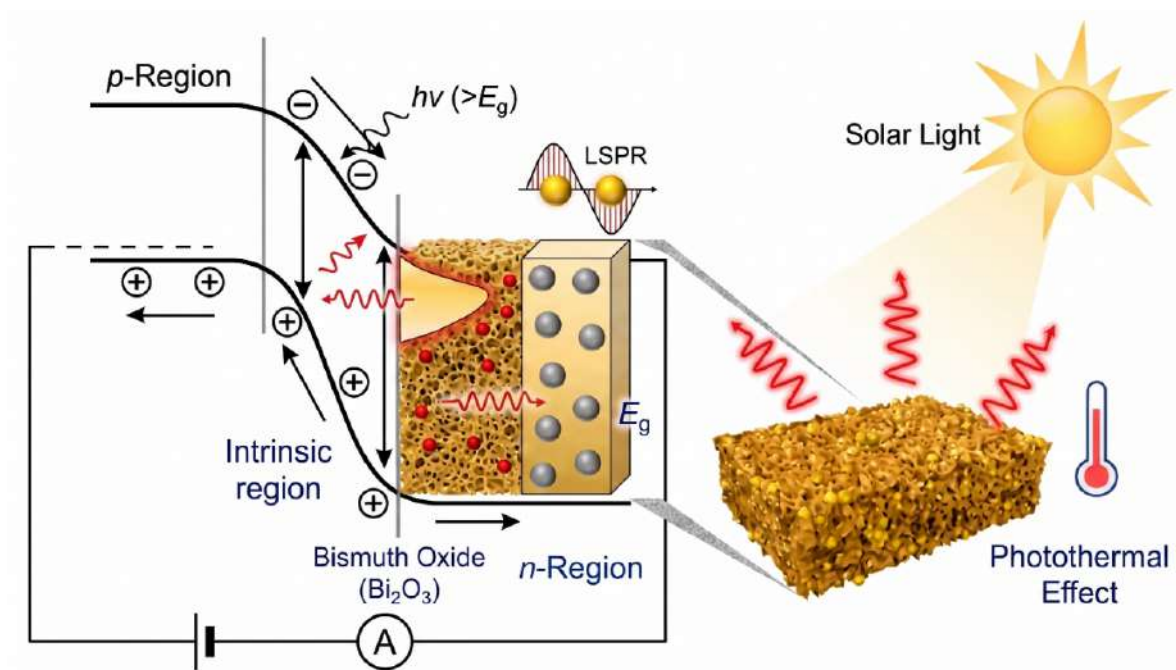


Figure 2.6: Schematic representation of LSPR.

Chapter 3

Synthesis and Device Fabrication

3.1 Materials and Reagents

PVDF powder (molecular weight-300,000 g/mol, in powder form) were acquired from Sigma Aldrich, whereas N, N-Dimethylformamide (DMF) was obtained from Fisher. Bismuth Oxide were purchased from Molychem having purity of 99%. Gold nanoparticles (741949) suspension in citrate buffer of 5 nm in diameter were purchased from Sigma Aldrich. The chemicals were directly used as provided, without any further processing.

3.2 Synthesis of Bi_2O_3 Nanocomposite without Au-NPs

PVDF nanocomposites films were synthesised by dissolving 1g of PVDF powder in 10 ml of DMF. The solution was then stirred for 4 hours using a magnetic stirrer, after which the processed solution was drop-cast onto a glass substrate using a micro-pipette. The amount of solution loaded for drop casting was kept constant for each glass plate to ensure uniform film thickness across all films. The casted glass plate was then kept in an oven at 343K for 2 hours. Finally the glass plate was dispersed in DI water, and due to the hydrophobic nature of PVDF, the processed films detached from the glass surface, yielding a PVDF nanocomposite film. Nanocomposite films of Bi_2O_3 were also synthesised by the drop-casting method. However, initially to reduce the particle size of Bi_2O_3 powder, it was first grind using agate mortar and pestle for 2 hours followed by ultrasonication for 30 minutes. Then the fine powder was dissolved with 1g PVDF in 10 ml of DMF and kept stirred on a magnetic stirrer for 4 hours. The latter processes were similar to those used for synthesis of PVDF nanocomposite films.

3.3 Synthesis of Bi_2O_3 Nanocomposite with Au-NPs

Au-NPs/PVDF nanocomposite films were synthesized by mixing 500 μL of Au-NPs slowly in a 1g PVDF dissolved in 10 ml of DMF while stirring on a magnetic stirrer to avoid any chances of agglomeration. A similar process was repeated afterwards, followed by the preparation of PVDF nanocomposite films. Au-NPs/ Bi_2O_3 /PVDF nanocomposites were synthesized with a similar procedure. The Bi_2O_3 powder was first grind in an agate mortar and pestle for 1 hour to reduce its particle size, after which it was transferred and dissolved with 1g of PVDF in 10 ml of DMF and 500 μL of Au-NPs. The resulting solution was then kept

stirred on a magnetic stirrer 4 hours, after which the same steps were followed as for the synthesis of PVDF nanocomposite films.

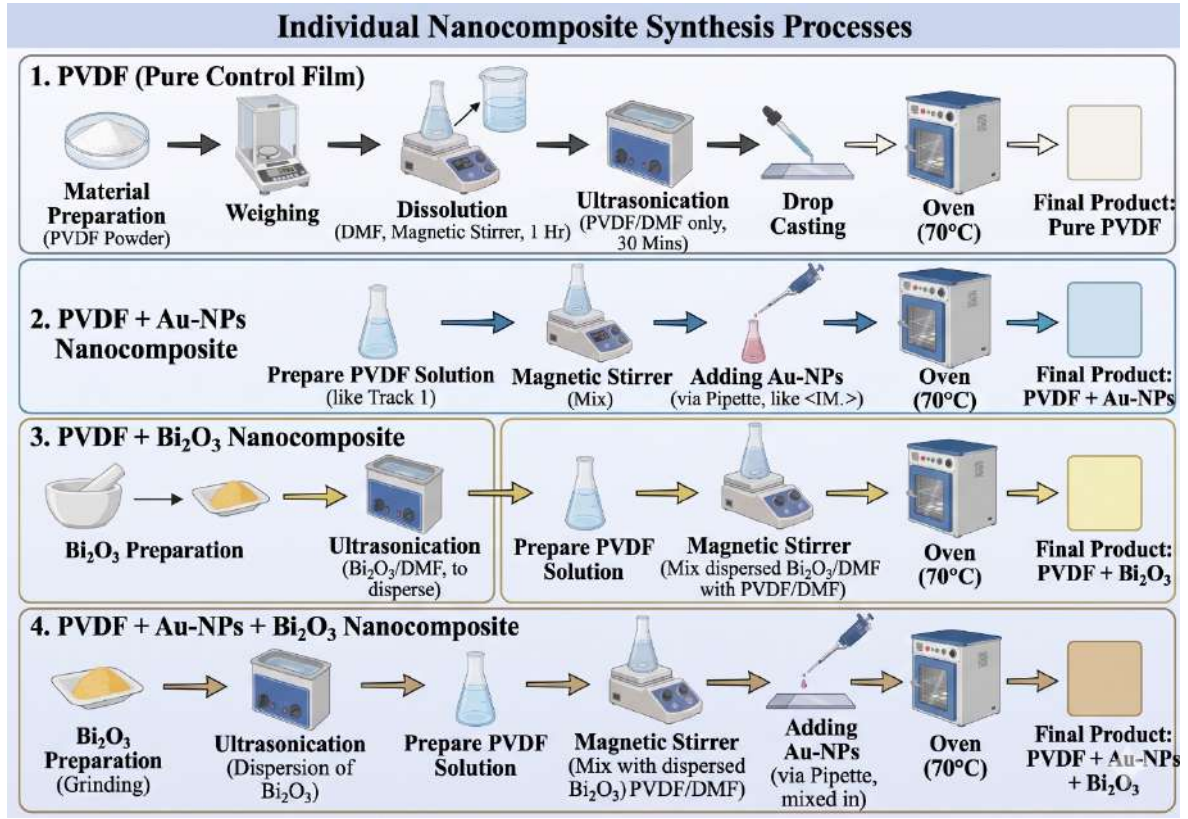


Figure 3.1: Synthesis process of Nanocomposite films with drop casting.



Figure 3.2: Photograph of synthesized nanocomposite films (a) PVDF. (b) Bi₂O₃/PVDF. (c) Au-NPs/PVDF. (d) Au-NPs/Bi₂O₃/PVDF.

3.4 Device Fabrication of PENG and Photodetector

The synthesised nanocomposite films (pure PVDF, Bi₂O₃/PVDF, Au-NPs/PVDF, Au-NPs/Bi₂O₃/PVDF) had a thickness of around 50–70 μm measured with a digital Vernier-Calliper. The PENG device was fabricated by cutting the nanocomposites films into 1 cm $\times$ 1 cm pieces. The aluminium tape was placed at the top and bottom, forming a sandwich structure and serving as the top and bottom electrodes. To measure the open-circuit voltage and current, two copper wires were attached to the upper and lower electrodes.

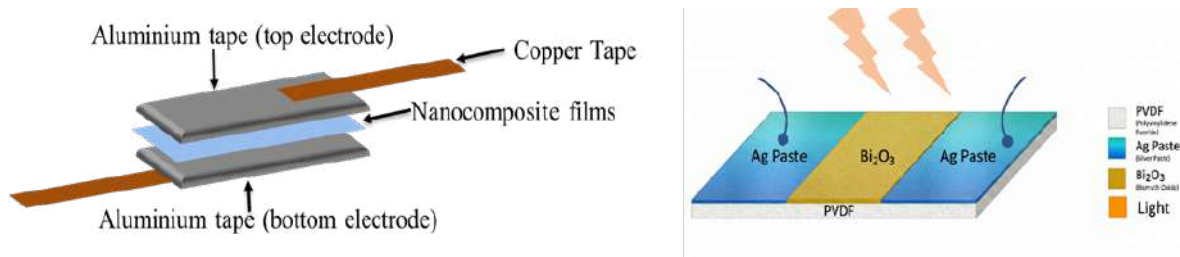


Figure 3.3: Schematic diagram of fabricated (a) PENG and (b) Photodetector.

For the Photodetector fabrication, the 20 mg Bi₂O₃ powder is taken into a boat of thermal vapour deposition, and taken PVDF as the substrate. The vacuum was fixed at 5.5×10^{-6} mbar. High current, which is about 235A was given to the electrode connected with the boat. The powder then evaporated and deposited on the PVDF substrate which were fixed at the top. The deposited film were taken out from the vacuum after some time and an electrode were made using a silver paste, keeping the distance between the two electrode fixed.

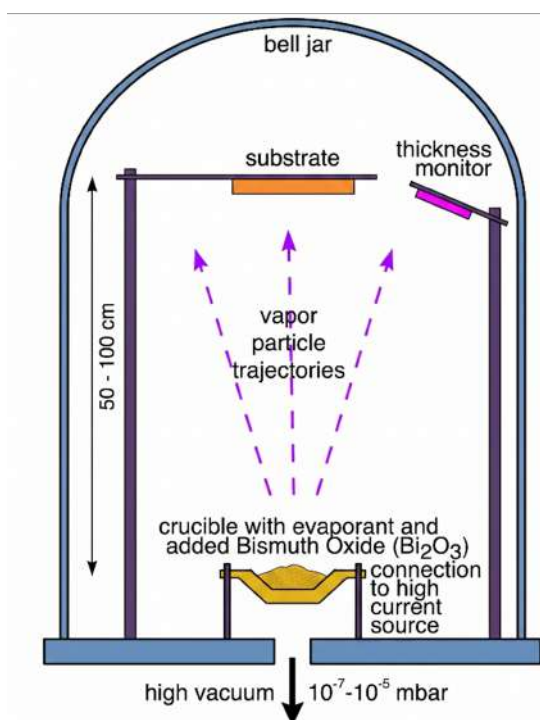


Figure 3.4: (a) Schematic representation of TVD (b) Picture of TVD.

Chapter 4

Results and Discussion

4.1 X-Ray Diffraction Analysis

The XRD profile of Bismuth Oxide (Bi_2O_3) Powder is shown in Fig. 5. The diffraction peaks at $2\theta = 27.1^\circ$, 31.0° , and 32.2° correspond to the plane (201), (002), and (220), respectively, and matches with earlier reports [8–9]. The crystallite size of the Bismuth Oxide powder was calculated using the Scherrer Equation and found to be approximately 29.47 nm. Rietveld refinement of XRD data was performed using the fullprof software. The estimated values of lattice parameter were found as $a = b = 7.86 \text{ \AA}$, $c = 5.59 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, which corresponds to the space group p-421c. Fig. 4 represents the crystal structure of Bismuth Oxide (Bi_2O_3), which is rendered using VESTA software.

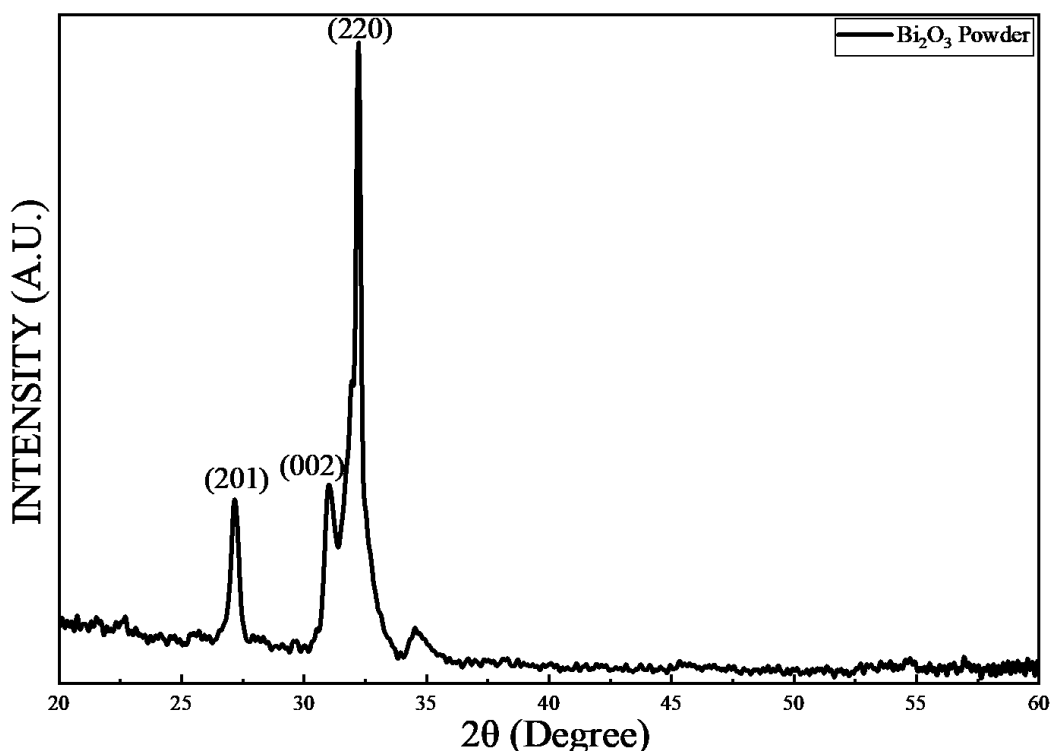


Figure 4.1: X-Ray Diffraction pattern of Bismuth Oxide Powder.

The XRD profiles of PVDF and all nanocomposite (PVDF with Bi_2O_3 and Au-NPs) are shown in Fig. 6. The presence of peaks that correspond to the Bi_2O_3 and Au-NPs confirms

the stability of the Bi_2O_3 and Au-NPs structural phases within the PVDF matrix. In Fig. 6, the peak at $2\theta = 20.3^\circ$ correspond to the semi-polar phase in PVDF [31–33]. Peaks appearing at $2\theta = 27.3^\circ$, 33.1° and 39.2° corresponds to the β -phase of Bi_2O_3 and to the presence of Au-NPs respectively [30, 32].

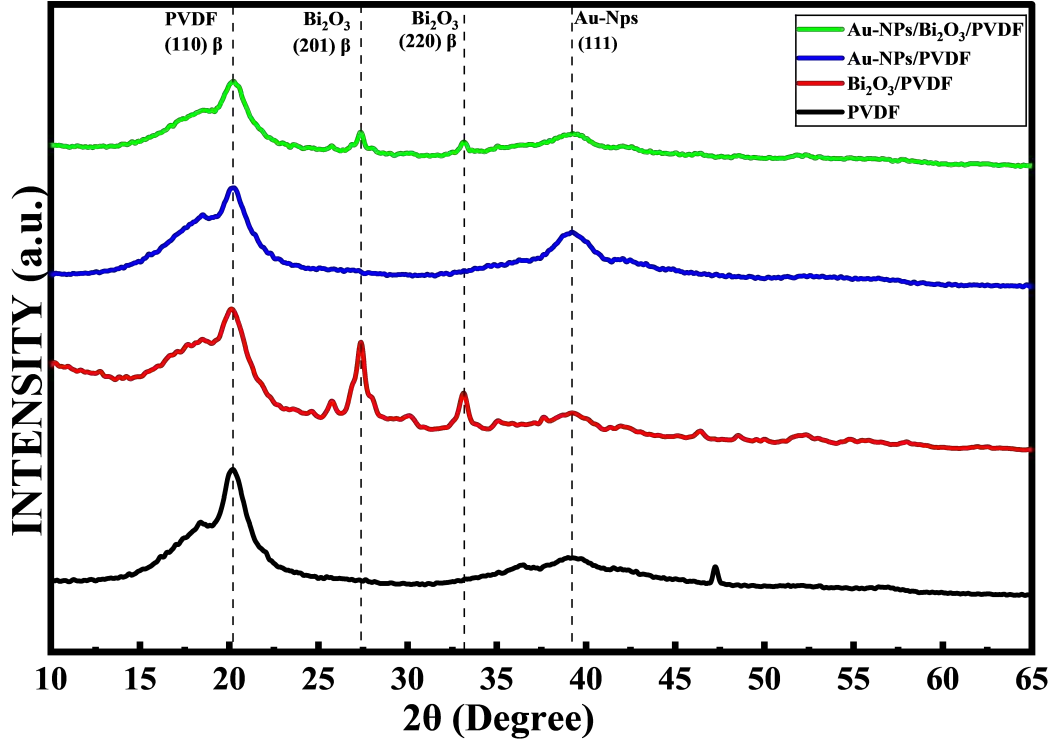


Figure 4.2: X-Ray Diffraction pattern of nanocomposite.

4.2 Fourier Transform Infrared Spectroscopy Analysis

FTIR spectra of all the fabricated nanocomposite films are shown in Fig. 7. The bare PVDF shows the dominant non-polar α -phase as evident from the vibrational bands at 1214, 1150, 976, 856, 795, 766, and 763 cm^{-1} . The bands related to the semi-polar γ -phase appeared at 1234 and 812 cm^{-1} , and the polar β -phase appeared at 1275 cm^{-1} [12–14]. PVDF contains a low β -phase content (about 71%), which limits its piezoelectric energy-harvesting properties. The incorporation of Bi_2O_3 and Au-NPs increases the β -phase content at the expense of α -phase in the PVDF matrix. The bands at 764 cm^{-1} and 840 cm^{-1} are used to determine the electroactive phase content using the formula [10]:

$$F_{EA} = \frac{A_{840}}{\frac{K_{840}}{K_{764}} A_{764} + A_{840}} \times 100 \quad (4.1)$$

Here, A_{840} and A_{764} are the absorption intensities at 840 and 764 cm^{-1} , respectively. K_{840}

and K_{764} are the absorption coefficients corresponding to the bands 840 and 764 cm^{-1} with values of $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively. The electroactive phase content increases as Bi_2O_3 and Au-NPs are loaded into the PVDF matrix, reaching 84% for Au-NPs/ Bi_2O_3 /PVDF, 83% for Au-NPs/PVDF, 81% for Bi_2O_3 /PVDF, and 71% for the bare PVDF composite film.

Table 4.1: Electroactive content of β -Phase in nanocomposite.

Material	β-Phase
PVDF	71%
Bi_2O_3 /PVDF	81%
AuNPs/PVDF	83%
AuNPs/ Bi_2O_3 /PVDF	84%

4.3 SEM, FE-SEM & EDX Analysis

The surface morphology of the nanocomposite film taken by SEM is shown in Fig. (18) exhibits a homogeneous mixing of nanofillers in PVDF matrix with uniformly oriented fibrils and spherulitic chain like structure of the composite, which is a typical feature of β -Phase in PVDF.

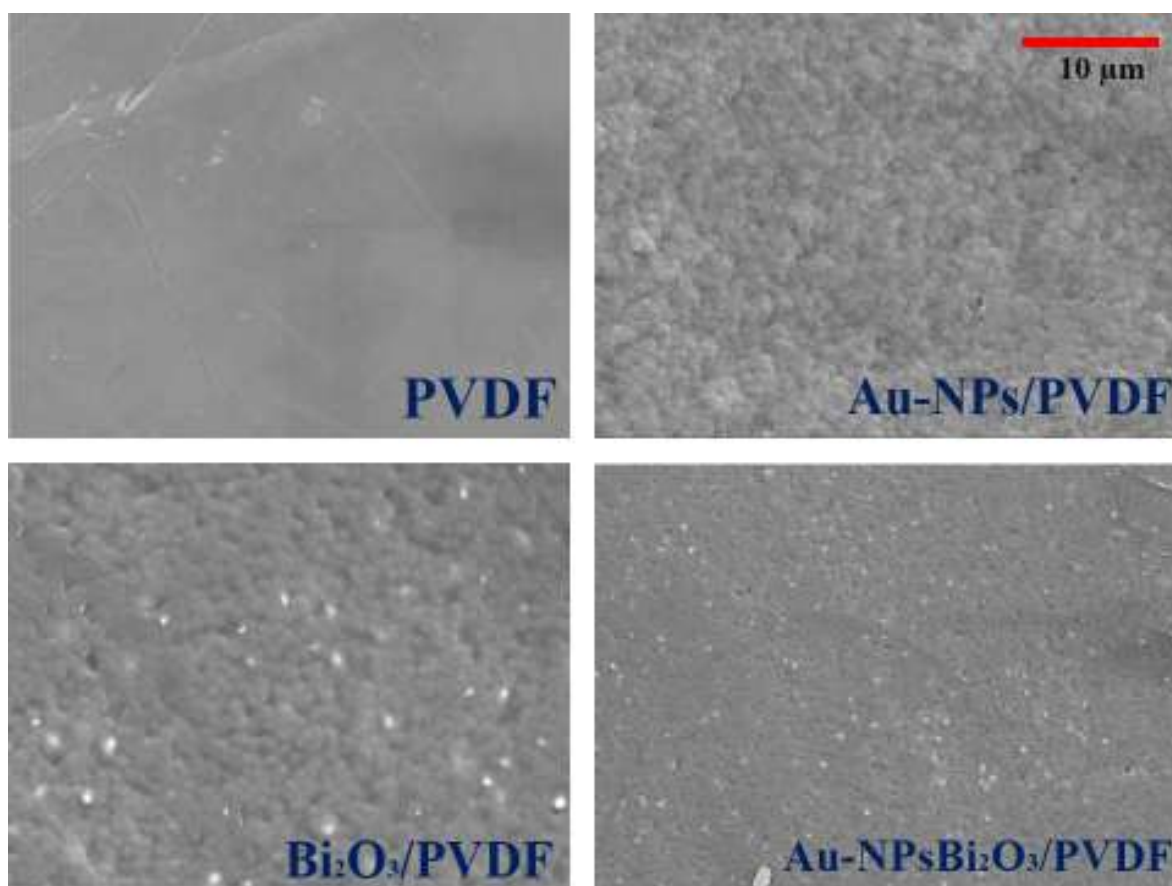


Figure 4.3: SEM images of Nanocomposite.

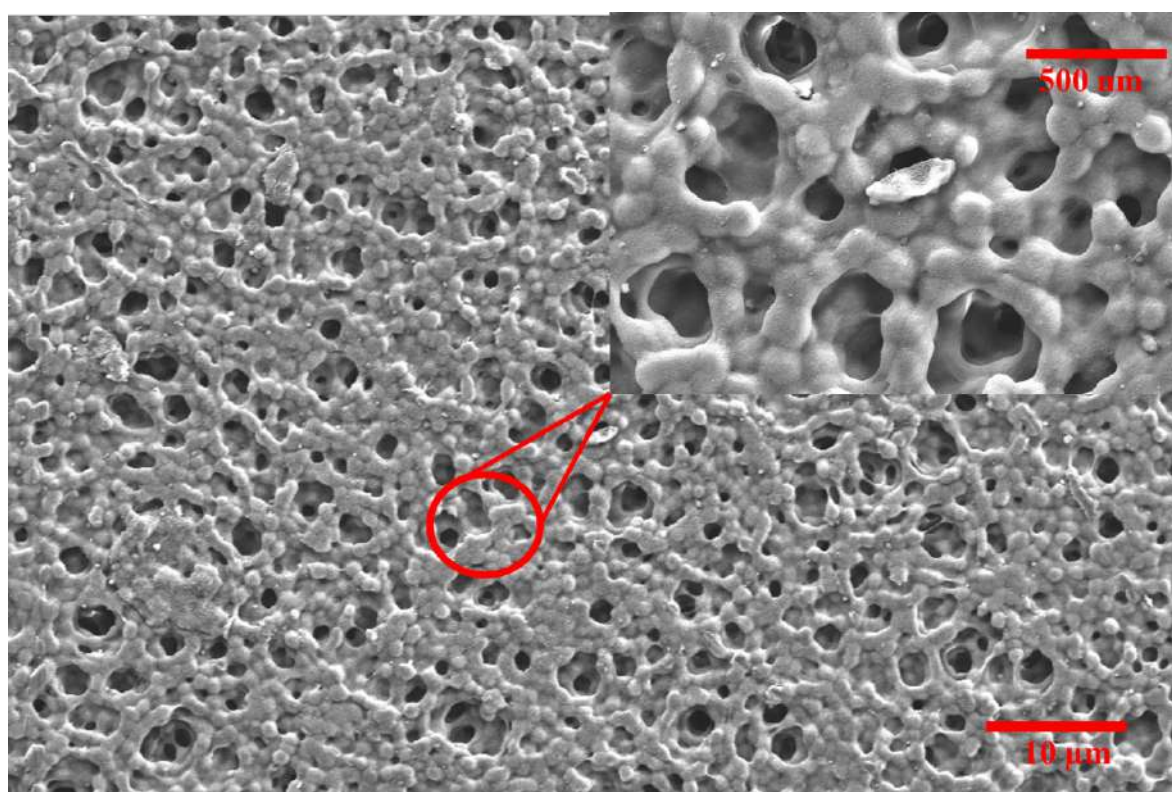


Figure 4.4: FE-SEM image of AuNPs/Bi₂O₃/PVDF.

The Fe-SEM micrograph of the AuNPs/Bi₂O₃/PVDF film shows that the surface is not compact, but sponge-like and porous. The main image at the 10 μm scale and the magnified inset together show connected pores across the observed region. Most pores are rounded or slightly irregular instead of sharply faceted, so the morphology is more consistent with phase separation during casting. From the image, the pores are roughly in the 1–5 μm range, with smaller openings surrounding some larger pores. This kind of porosity should help diffusion of analyte or electrolyte species and also expose more active surface. The bright small spots on the pore walls are assigned to AuNPs, since gold gives stronger contrast in Fe-SEM because of its higher atomic number. The visible particles are around 20–25 nm. The rough and nodular pore walls also point to Bi₂O₃ domains distributed within or on the PVDF scaffold, unlike the smoother surface expected for neat PVDF. The combined oxide-polymer-nanoparticle morphology therefore increases interfacial area. No clear cracks, gaps or debonding are seen at the filler-polymer boundary, suggesting acceptable adhesion within the composite. Overall, the observed morphology supports mechanical continuity while providing a porous surface suitable for device applications.

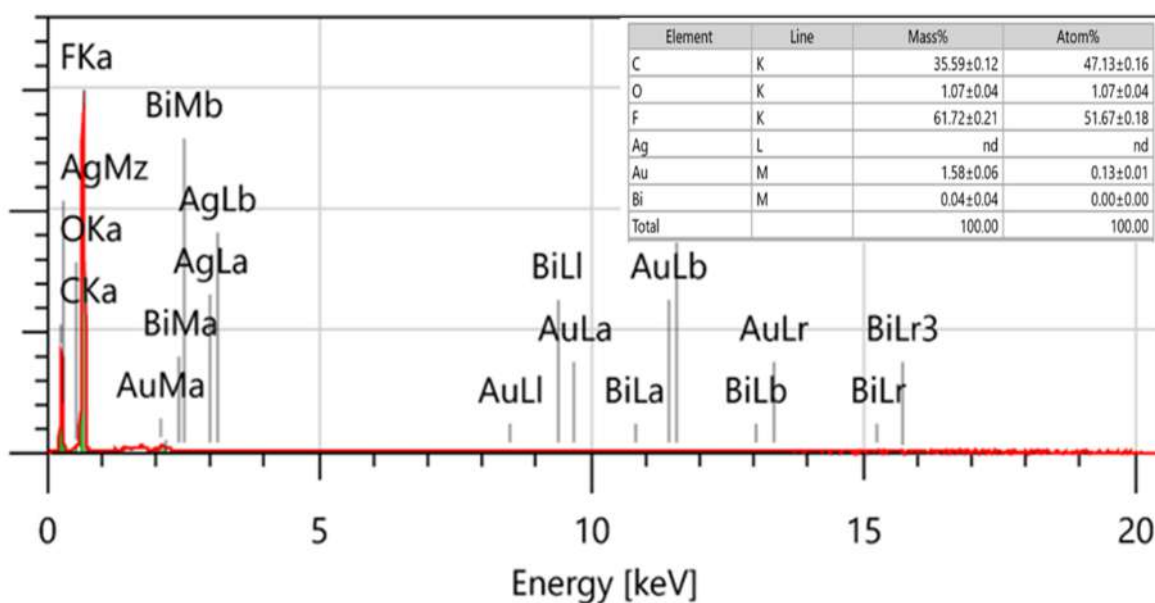


Figure 4.5: EDX profile of AuNPs/Bi₂O₃/PVDF nanocomposite.

The EDX elemental mapping of the nanocomposite film of AuNPs/Bi₂O₃/PVDF is shown in Fig. (20), confirming the presences of Bi, C, F, O, and Au, which unambiguously confirms the formation of AuNPs/Bi₂O₃/PVDF nanocomposite.

4.4 Dielectric Measurement Analysis

The dielectric constant (ϵ') was recorded for pristine PVDF, Bi₂O₃/PVDF, Au-NPs/PVDF and Au-NPs/Bi₂O₃/PVDF in the frequency range of about 1×10^6 to 1×10^7 Hz. In all

four samples, ϵ' decreases as frequency increases. This is reasonable because dipoles and interfacial charges cannot follow a fast alternating field as effectively as they follow a slower one. The trend is also consistent with Maxwell-Wagner-Sillars (MWS) polarization, where charge build-up at filler-polymer boundaries is stronger at lower frequency.

From Fig. (21), pristine PVDF remains the lowest-dielectric sample over the whole frequency range, falling from about 2.3 at the lower-frequency side to about 1.8 near 1×10^7 Hz. This lower response is expected because the main contribution in neat PVDF comes from reorientation of the $-\text{CH}_2-\text{CF}_2-$ dipoles. After adding Bi_2O_3 , the dielectric constant increases at every measured frequency, which can be linked to the higher permittivity of the oxide phase and to extra charge accumulation at the oxide-polymer interface. Au-NPs/PVDF also performs better than neat PVDF, most likely because AuNPs create local field concentration around the particles. The ternary Au-NPs/ Bi_2O_3 /PVDF film gives the highest ϵ' value. Here the two fillers work together: Bi_2O_3 supplies a high-permittivity phase, while AuNPs contribute localized field enhancement. The additional internal interfaces also support MWS polarization, so the ternary film retains a higher dielectric response even toward the upper end of the measured frequency range.

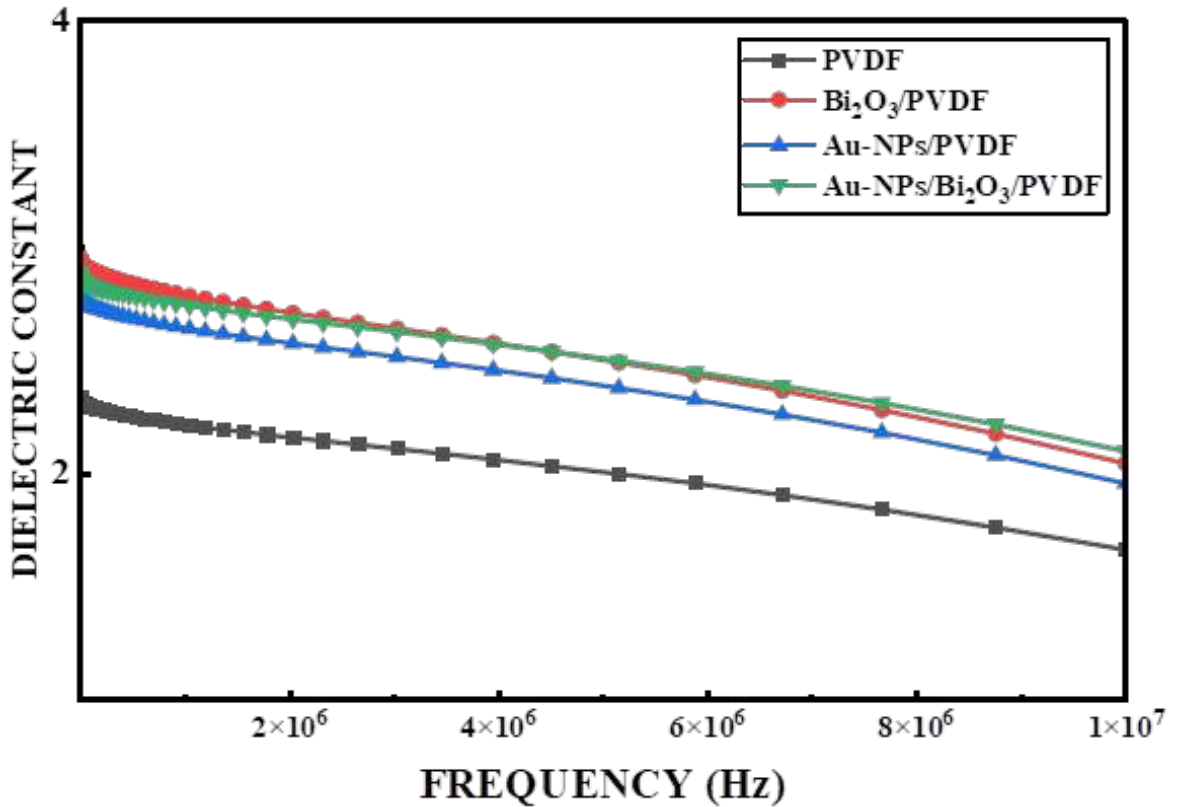


Figure 4.6: Dielectric Constant graph of Nanocomposites.

4.4.2 Dielectric Loss ($\tan \delta$) vs. Frequency

The dielectric loss tangent ($\tan \delta$) curves in Fig. (22) show how much energy is dissipated in each sample during the same frequency sweep. Since $\tan \delta$ is the ratio of dissipated energy to stored energy, a lower value is preferred for high-frequency sensing, electronic, and energy-storage applications. Pristine PVDF gives the highest $\tan \delta$ over most of the frequency range, increasing from near zero to about 0.030 at 1×10^7 Hz. This behaviour suggests that conduction loss and free-charge contribution become more pronounced at higher frequency in the unfilled polymer. The $\text{Bi}_2\text{O}_3/\text{PVDF}$ sample shows a lower loss profile, with a peak of about 0.020 in the mid-frequency range, which may be related to interfacial relaxation at the oxide-polymer boundary. $\text{Au-NPs}/\text{PVDF}$ also shows lower loss than pristine PVDF, although its loss remains slightly higher than $\text{Bi}_2\text{O}_3/\text{PVDF}$ over much of the range. This may occur because AuNPs improve the dielectric response but can also introduce limited electron hopping between particles.

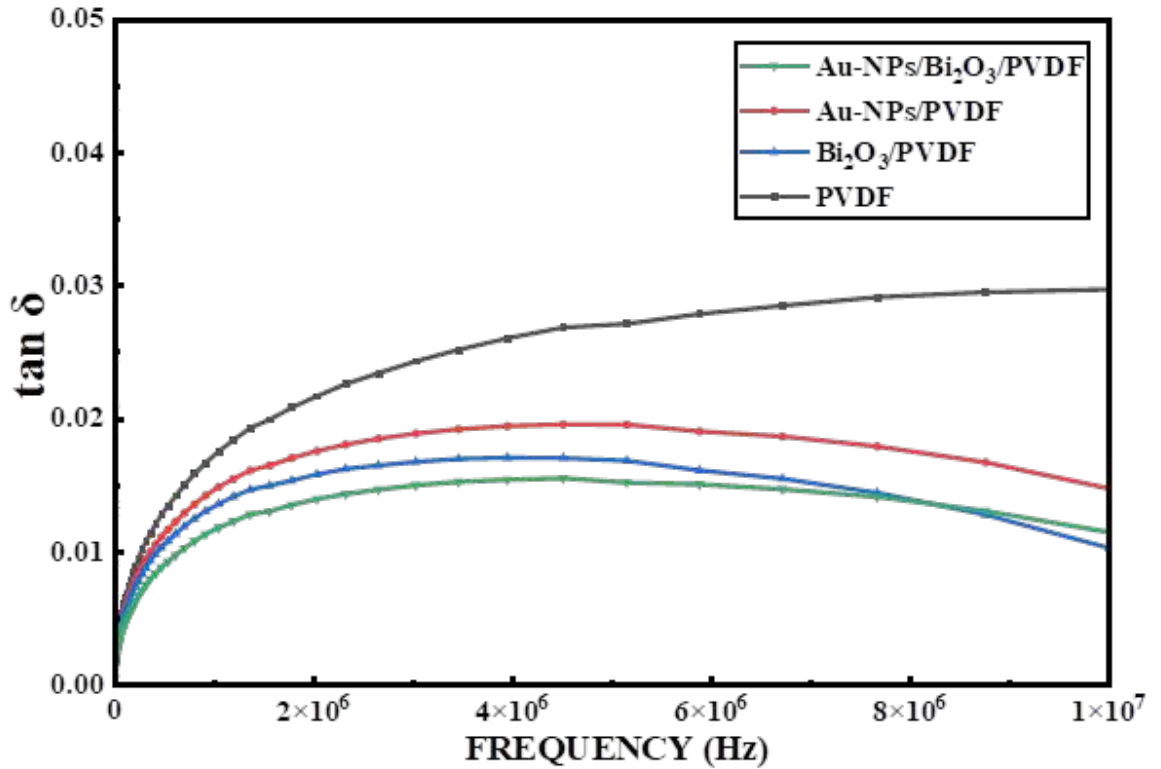


Figure 4.7: Dielectric loss graph of Nanocomposites.

The $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$ ternary composite gives the lowest dielectric loss among the four samples. Its $\tan \delta$ increases only up to about 0.015 in the mid-frequency region and then decreases toward about 0.011 near 1×10^7 Hz. This controlled loss may be due to the close contact among AuNPs, Bi_2O_3 , and PVDF, which restricts long-range movement of free carriers while still allowing interfacial polarization. The triple-phase interfaces can trap

or pin some charges, reducing their movement under the alternating electric field. As a result, resistive loss is reduced in the ternary composite.

4.4.3 Quality Factor vs. Frequency

The quality factor (Q) shown in Fig. (23) is calculated as the inverse of $\tan \delta$, that is $Q = 1/\tan \delta$. A higher Q value generally indicates lower dielectric loss and better energy storage efficiency. At lower frequencies, all samples show relatively high Q values because their $\tan \delta$ values are low in that region. As the frequency approaches the mid-range, 3×10^6 to 5×10^6 Hz, the Q value decreases for all compositions, corresponding to the peak region in the $\tan \delta$ curves. At still higher frequencies, Q rises again as $\tan \delta$ decreases. Pristine PVDF has the lowest Q values throughout the frequency range, confirming its higher loss as a dielectric material. The $\text{Bi}_2\text{O}_3/\text{PVDF}$ and $\text{Au-NPs}/\text{PVDF}$ composites show intermediate Q values, with $\text{Bi}_2\text{O}_3/\text{PVDF}$ slightly better in most of the range. The $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$ ternary composite gives the highest Q response, reaching nearly 90–100 near 1×10^7 Hz, whereas pristine PVDF remains around 40–45 at the same frequency. The higher Q value is mainly a result of the reduced $\tan \delta$ in the ternary composite.

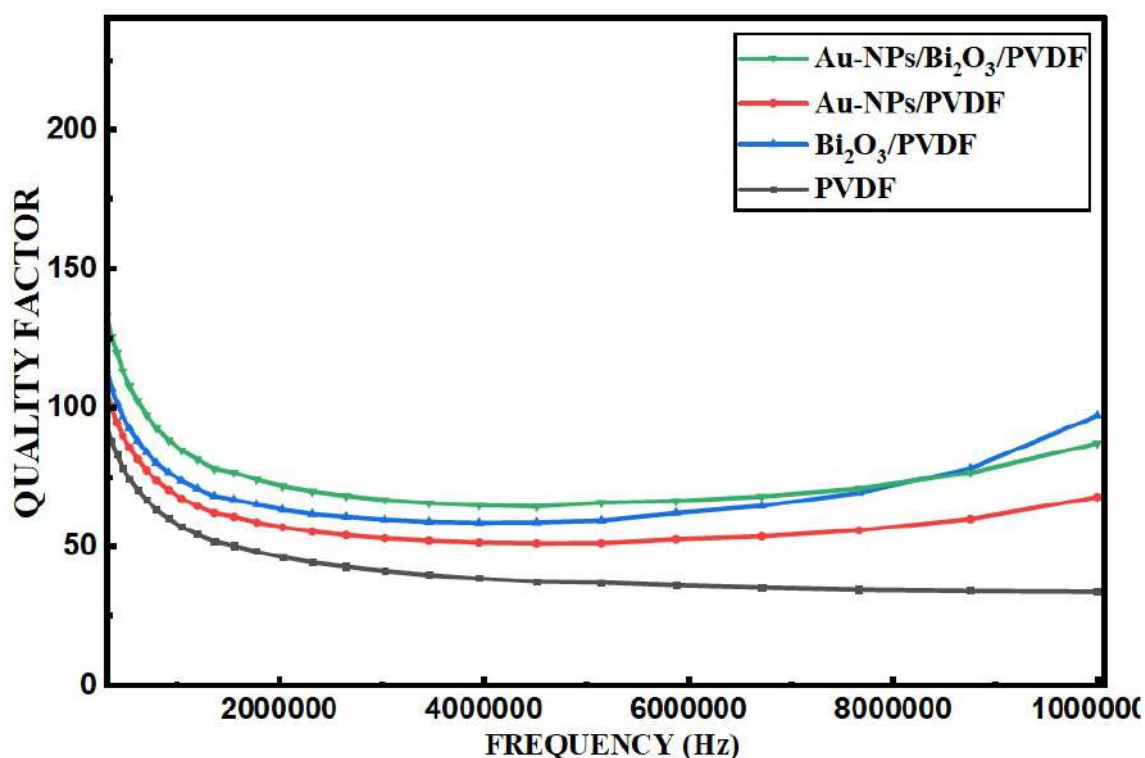


Figure 4.8: Quality Factor graph of Nanocomposites.

The Q response is consistent with the loss behaviour discussed above. Since the ternary film has the lowest $\tan \delta$, it also gives the best quality factor. This means that adding AuNPs

together with Bi_2O_3 improves the dielectric response without introducing the same level of energy dissipation. The Au-NPs/ Bi_2O_3 /PVDF composite therefore offers a useful combination of higher dielectric constant, lower loss and higher Q , which is favourable for flexible electronic devices, self-powered sensing and high-frequency piezoelectric conversion.

4.4 P-E Loop Morphology

The polarization-electric field (P-E) loops of pristine PVDF, Bi_2O_3 /PVDF, Au-NPs/PVDF and Au-NPs/ Bi_2O_3 /PVDF were measured using two capacitance settings, 47 nF and 100 nF, at 80, 100 and 120 kV. These six measurements are shown as panels (a-f). The loops are elliptical and only moderately saturated, which is expected for PVDF-based composite films where full ferroelectric saturation is not reached within the applied field range. The loop area gives an indication of energy loss in one cycle, while the remanent polarization (P_r) at zero field indicates how much polarization is retained. As the applied voltage is increased from 80 to 120 kV, the loop span also increases. In several panels, the Au-NPs/ Bi_2O_3 /PVDF loop is wider than the others, suggesting a stronger ferroelectric-like contribution in the ternary composite.

4.4.1 Remanent Polarization Analysis: Capacitance and Voltage Dependence

At 100 nF and 80 kV (panel b), the highest P_r is obtained for Au-NPs/ Bi_2O_3 /PVDF, with a value of $0.04342 \mu\text{C}/\text{cm}^2$. The corresponding values for Bi_2O_3 /PVDF, Au-NPs/PVDF and PVDF are 0.03342 , 0.02561 and $0.00230 \mu\text{C}/\text{cm}^2$, respectively. At 100 nF and 100 kV (panel d), Bi_2O_3 /PVDF gives the highest P_r value, $0.03603 \mu\text{C}/\text{cm}^2$, followed by Au-NPs/PVDF, PVDF and Au-NPs/ Bi_2O_3 /PVDF. At 120 kV under the same capacitance (panel f), Au-NPs/PVDF reaches $0.08160 \mu\text{C}/\text{cm}^2$, while PVDF, Au-NPs/ Bi_2O_3 /PVDF and Bi_2O_3 /PVDF

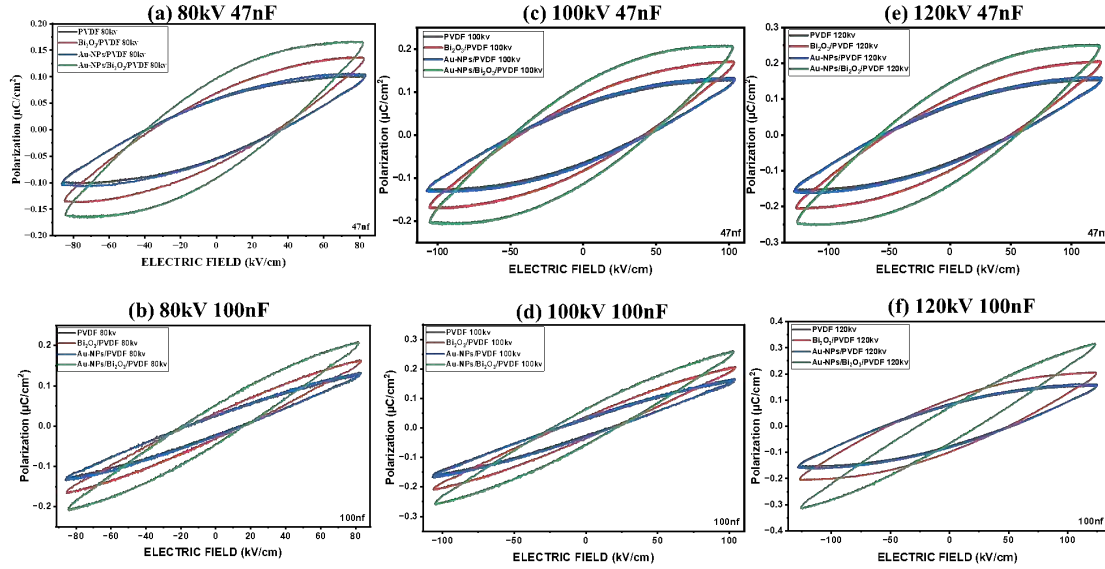


Figure 4.9: P-E loop of Nanocomposites at different range with 47nF and 100nF capacitance.

give 0.07671, 0.06800 and 0.03874 $\mu\text{C}/\text{cm}^2$. Under 47 nF, the order changes again. $\text{Bi}_2\text{O}_3/\text{PVDF}$ is highest at 80 kV, whereas pristine PVDF gives the largest P_r at 100 and 120 kV. Therefore, the P_r value is not controlled by composition alone; the circuit capacitance and the applied voltage also affect the measured response/PVDF is highest at 80 kV, whereas pristine PVDF gives the largest P_r at 100 and 120 kV. Therefore, the P_r value is not controlled by composition alone; the circuit capacitance and the applied voltage also affect the measured response. $\text{Bi}_2\text{O}_3/\text{PVDF}$ is highest at 80 kV, whereas pristine PVDF gives the largest P_r at 100 and 120 kV. Therefore, the P_r value is not controlled by composition alone; the circuit capacitance and the applied voltage also affect the measured response.

The changes in P_r ranking should therefore be read carefully. Even when one sample gives a higher numerical P_r under a particular 47 nF condition, the overall behaviour still has to be compared with loop shape and dielectric loss. From this broader view, the Au-NPs/ $\text{Bi}_2\text{O}_3/\text{PVDF}$ film remains important because the 100 nF data show a strong P_r at lower voltage and several of its loops are wider than those of the binary or neat films. The improvement is likely due to the combined effect of AuNPs and Bi_2O_3 : AuNPs provide local field enhancement, while Bi_2O_3 adds high-permittivity interfaces inside PVDF. These interfaces help dipole switching, although some high P_r values in PVDF or $\text{Bi}_2\text{O}_3/\text{PVDF}$ at 47nF may include leakage-related charge as well as true ferroelectric switching.

4.5 Steady-State Photoluminescence (PL) Analysis

Fig. (25) shows that the $\text{Bi}_2\text{O}_3/\text{PVDF}$ binary film has two partially separated emission bands, around 381 and 410 nm. In bismuth oxide, such near-UV/violet emissions are normally associated with intrinsic defect centres, including oxygen vacancies and Bi^{3+} lone-pair related

states. The $\text{Bi}^{3+} 6s^2$ lone pair may contribute to the near-UV transition, so the two peaks suggest that more than one emitting centre is present in the Bi_2O_3 phase inside PVDF. Beyond about 430 nm, the binary film gives only weak visible emission. The Au-NPs/ Bi_2O_3 /PVDF sample behaves differently. Its Bi_2O_3 -related near-UV emission becomes weaker, while a broad visible band appears near 500 nm and extends into the green-orange region. This band is consistent with localized surface plasmon resonance of AuNPs in a dielectric environment. The higher visible intensity therefore indicates that AuNPs change the emission pathway under the given excitation condition. The reduction of the Bi_2O_3 -related near-UV peaks in the ternary composite is also useful for understanding the interaction between Bi_2O_3 and AuNPs. It suggests that part of the excitation energy from Bi_2O_3 defect states may be transferred to the AuNP plasmon channel through near-field coupling. In this process, photogenerated carriers or excitations associated with Bi_2O_3 defect states are partly redirected toward plasmonic emission rather than recombining only through the original near-UV pathway. This shifts the emission weight from the near-UV region toward the visible green region and increases the overall radiative output. The result also supports the Fe-SEM observation that AuNPs are in close contact with the Bi_2O_3 /PVDF matrix. From an application point of view, this visible-emission enhancement is useful for photocatalytic and photodetection applications where visible-light harvesting is desirable.

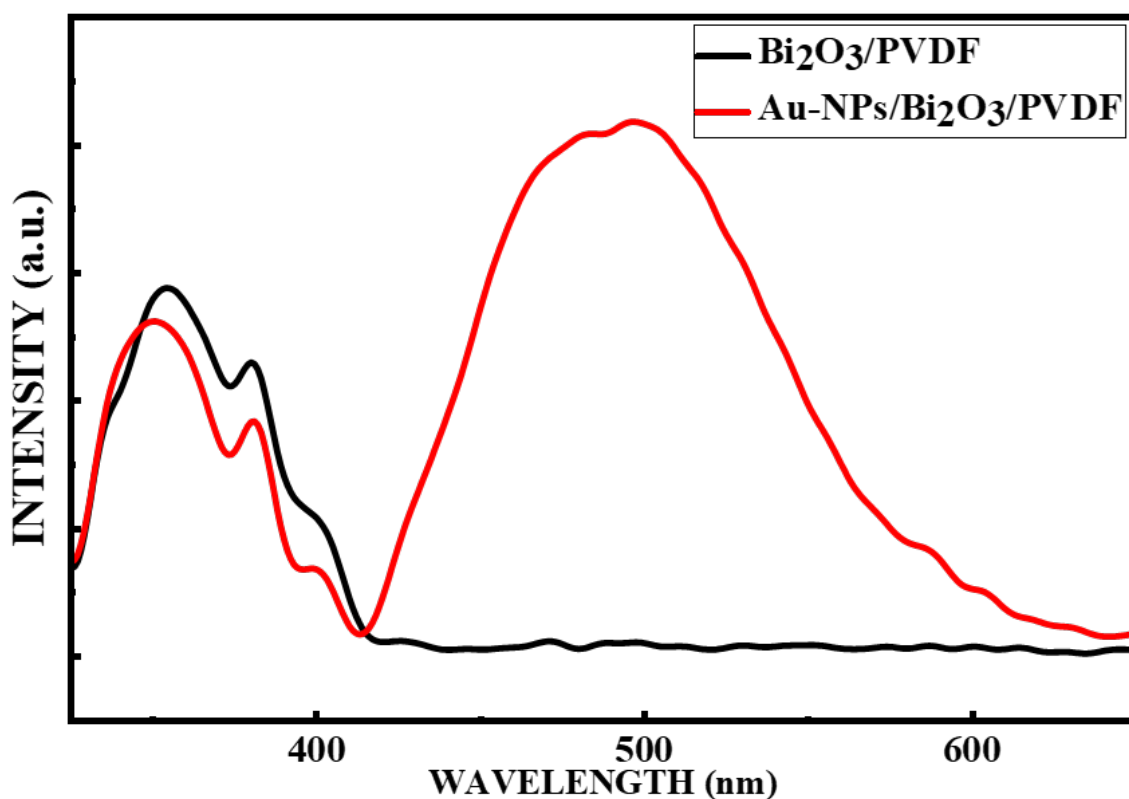


Figure 4.10: Steady-State graph of Secondary (Bi_2O_3) and tertiary nanocomposite.

4.5 Time-Resolved Photoluminescence (TR-PL) Analysis

The time-resolved photoluminescence (TR-PL) decay curves of $\text{Bi}_2\text{O}_3/\text{PVDF}$ and $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$ were recorded on a semi-logarithmic scale from 20 ns to 200 ns. The average lifetime obtained from multiexponential fitting is 2.29 ns for $\text{Bi}_2\text{O}_3/\text{PVDF}$ and 4.04 ns for $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$. The $\text{Bi}_2\text{O}_3/\text{PVDF}$ curve, shown as the black curve in Fig. (26), decays slowly over the measured time window. Since the decay does not follow a simple monoexponential form, bi-exponential fitting was used, suggesting that more than one recombination pathway is present. The measurable photon counts persisting beyond 150–200 ns indicate that some photoexcited carriers are trapped in long-lived defect states, such as oxygen vacancies or surface traps in Bi_2O_3 , before recombining radiatively.

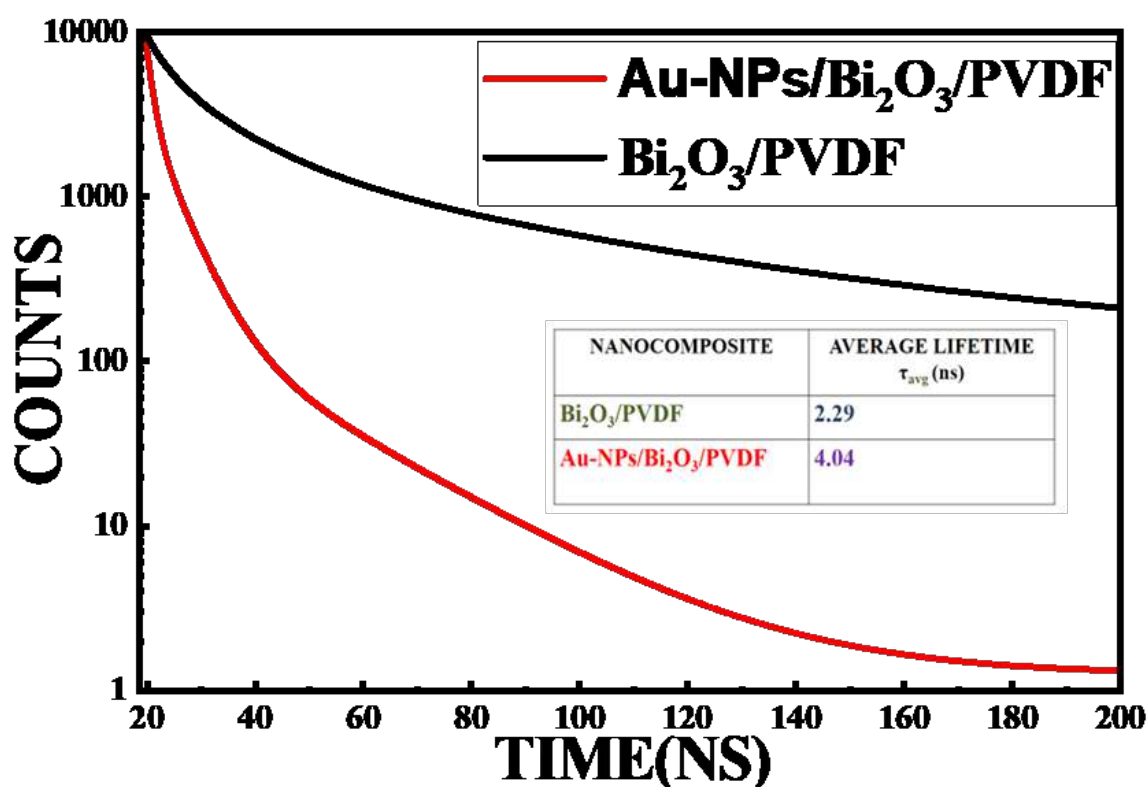


Figure 4.11: TR-PL decay curve of Secondary (Bi_2O_3) and ternary nanocomposite.

Thus, the 2.29 ns average lifetime represents the combined contribution of different trap-assisted decay components. The slow tail of the curve also suggests that some deeply trapped carriers may have lifetimes extending beyond the recorded window. The $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$ curve, shown as the red curve, has a different decay behaviour. The photon count drops faster from about 10,000 counts at 20 ns to near-background values before 150 ns, showing faster depopulation of the excited state in the ternary composite. This faster visual decay after AuNP incorporation can be related to plasmon-enhanced spontaneous emission. In this pro-

cess, the local optical field around the AuNPs increases the radiative decay rate of nearby Bi_2O_3 emitters, similar to the Purcell effect. The average lifetime of 4.04 ns for the ternary sample is therefore not contradictory, even though the curve falls faster at early times. It has to be interpreted with the multiexponential nature of the decay and the new plasmon-coupled emission pathway. The fitted average lifetime should not be read as one single physical decay time. It is a weighted value obtained from several decay components. In the ternary film, carriers located close to AuNPs may recombine quickly through plasmon-assisted radiative routes, while carriers in Bi_2O_3 regions farther from AuNPs can remain trapped for a longer time. Thus, the AuNPs introduce a fast decay path for part of the excited population, but the remaining slower components still affect the average lifetime. The value of 4.04 ns should therefore be interpreted as a mixed lifetime. The broad 500 nm emission may also contribute to the fitted value because the plasmon-coupled emission has its own radiative dynamics.

Overall, the TR-PL results show that adding AuNPs changes the carrier relaxation pathway in the Bi_2O_3 /PVDF matrix. The AuNPs reduce the dominance of non-radiative trap-assisted recombination by offering a competing plasmon-coupled radiative pathway, which is also supported by the stronger steady-state PL intensity. When the longer average lifetime is considered together with the faster initial decay and enhanced PL intensity, the ternary composite appears to harvest photoexcited carriers more efficiently through radiative channels. This behaviour is useful for photocatalysis, photodetection, and plasmon-enhanced energy conversion. Thus, the steady-state PL and TR-PL results indicate that Au-NPs/ Bi_2O_3 /PVDF has improved photophysical behaviour compared with Bi_2O_3 /PVDF.

Chapter 5

Applications

5.1 PENGs as Energy Harvesting Applications

To measure the piezoelectric response for energy harvesting applications, the PENGs device has been fabricated as shown in Fig. 14(a). The effective area of the device is $1 \times 1 \text{ cm}^2$, and the piezoelectric effect was measured by repeated hammering at a 1 Hz, 3 Hz, 5 Hz and 9 Hz frequency and with force dependent measurement at 1N, 5N and 10N without any external electrical poling. The open circuit voltage and current were recorded for all devices. The open circuit voltage is shown in Fig. (27) and short circuit current in Fig. 28 (d).

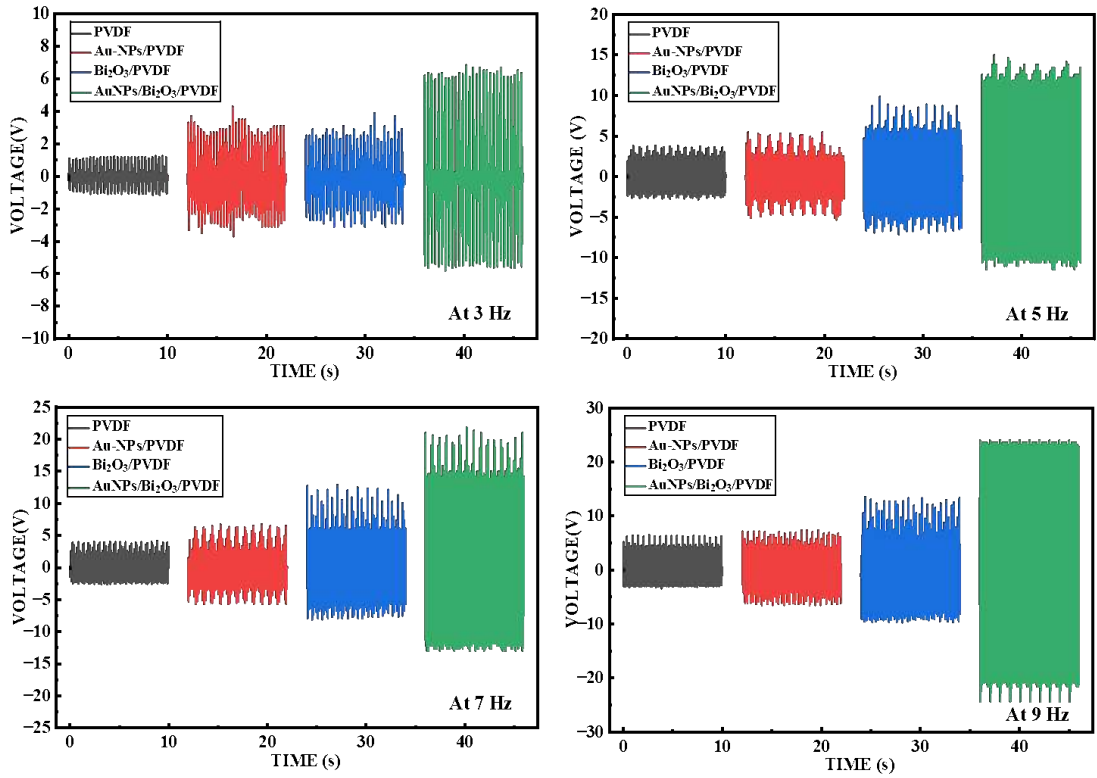


Figure 5.1: Open circuit voltage of all PENGs nanocomposites at different frequencies.

The bare PVDF device shows an open-circuit voltage of about 5.64 V and a short-circuit current of about $0.03 \mu\text{A}$. For the nanocomposite devices, both voltage and current increase, reaching about 48.4 V and $0.118 \mu\text{A}$ for Au-NPs/Bi₂O₃/PVDF. The increase is connected

with the presence of AuNPs in the $\text{Bi}_2\text{O}_3/\text{PVDF}$ film. Because AuNPs and the surrounding dielectric/oxide phases have different work functions, local band bending can occur at their interfaces and Schottky-type barriers may form. These barriers slow down charge leakage and recombination, so more of the mechanically generated charge is retained during repeated tapping. This gives a larger effective potential across the device and therefore a higher output voltage.

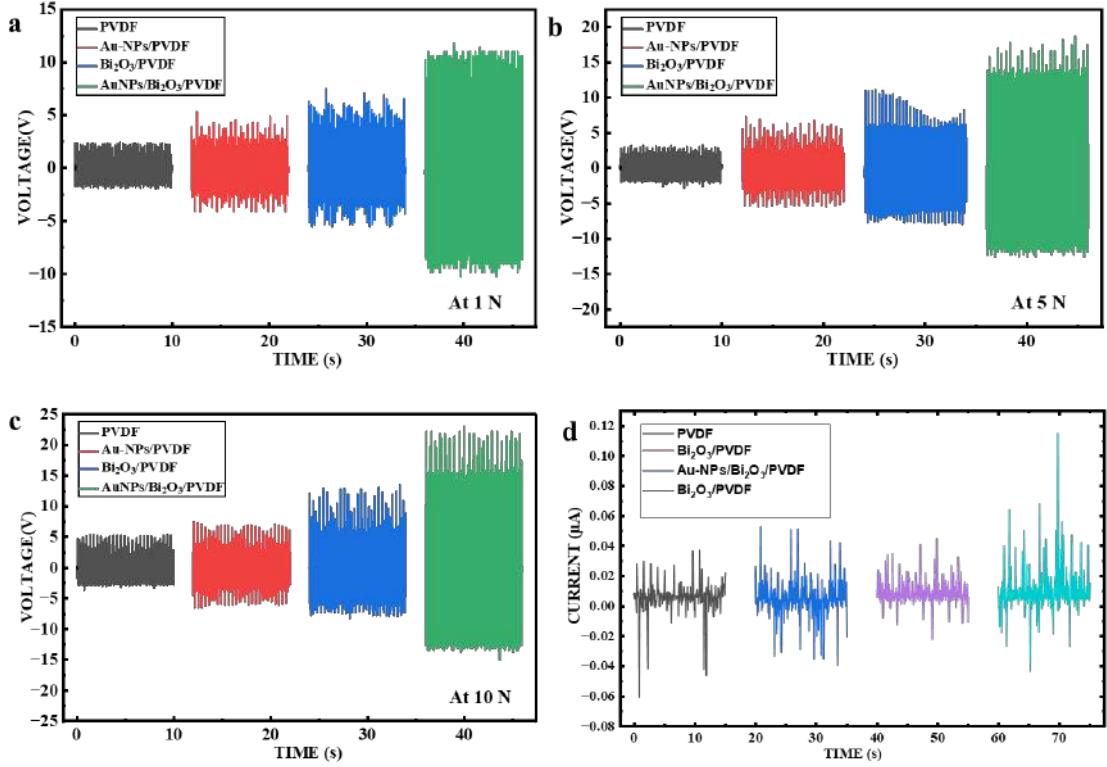


Figure 5.2: Open circuit voltage of all PENGs nanocomposites at different Force and 28(d) I_{sc} of PENG.

The addition of AuNPs into the $\text{Bi}_2\text{O}_3/\text{PVDF}$ matrix improves the piezoelectric output through structural nucleation and interfacial polarization. Even without light, AuNPs can act as nucleating centres that support the conversion of PVDF from the non-polar α phase to the electroactive β phase. This occurs because surface charges on AuNPs interact with the electronegative fluorine atoms in PVDF chains and help align local dipoles. The AuNPs at the $\text{Bi}_2\text{O}_3/\text{PVDF}$ interface also support Maxwell-Wagner-Sillars (MWS) polarization, which increases the dielectric response and helps charge transfer. In addition, LSPR associated with AuNPs may contribute to local field enhancement. However, for the stress-driven piezoelectric output in Au-NPs/ $\text{Bi}_2\text{O}_3/\text{PVDF}$, the major contribution is the Schottky barrier effect, where interfacial barriers help trap charges and reduce recombination [34–37].

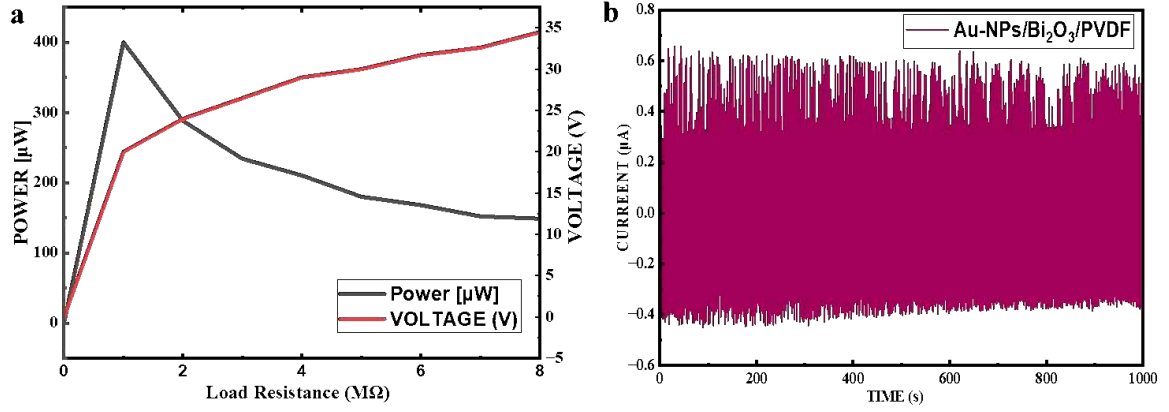


Figure 5.3: (a) Power output variation (b) Device stability test.

The output of all the PENG devices is better than that of bare PVDF. The variation of output power and voltage of the Au-NPs/Bi₂O₃/PVDF device as a function of load resistance is shown in Fig. 29(a), producing a maximum output power of 400 μW across a load resistance. Fig. 29(b) corresponds to the short-circuit current of the prepared piezoelectric nanogenerator of Au-NPs/Bi₂O₃/PVDF over 1000 cycles. The graph shows no significant changes in the output of short-circuit current, which exhibits the stability of the material over repeated cycles of stressing and de-stressing.

5.2 Bio-Mechanical Motion Sensing Application

To demonstrate the energy-harvesting capability of the Au-NPs/Bi₂O₃/PVDF nanocomposite

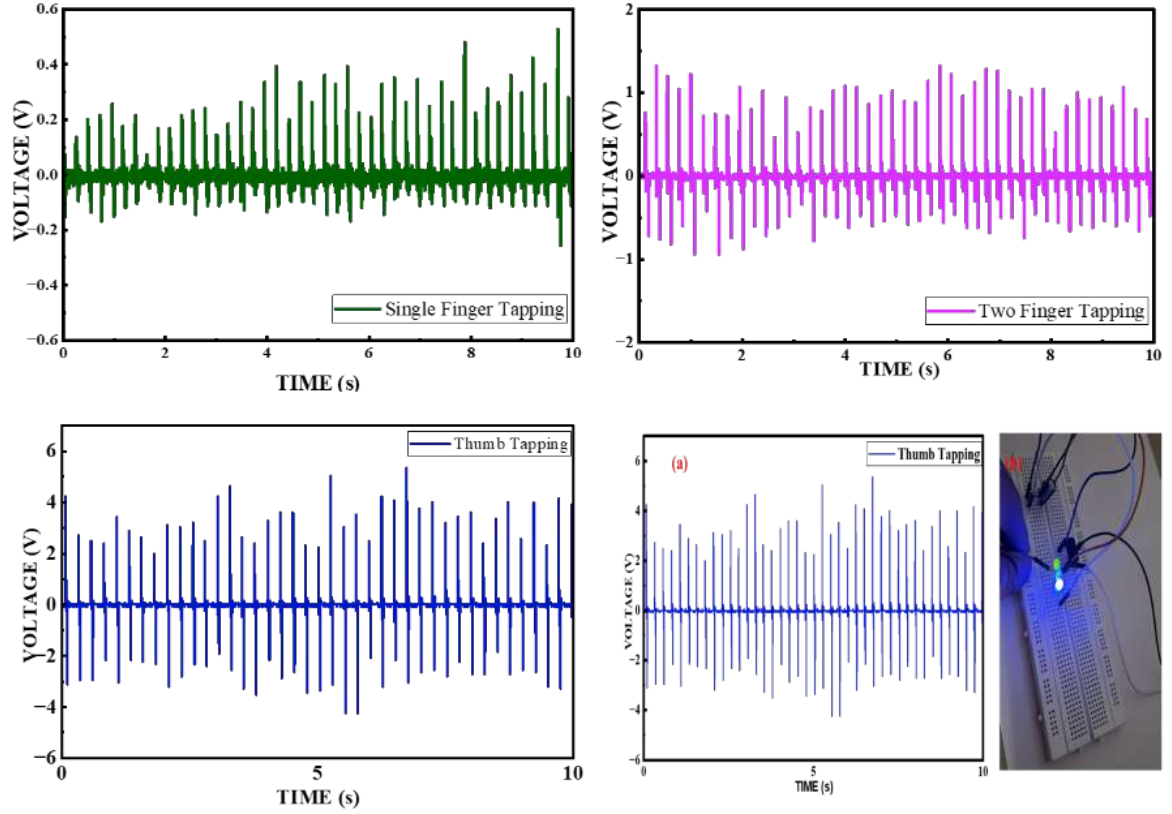


Figure 5.4: Different tapping as well as glowing of LED shown in 30(a).

device via biomechanical motions, we performed thumb tapping and recorded the resulting output voltage. The output voltage corresponding to thumb tapping (≈ 9.6 V) is shown in Fig. 14 (a). Also, using a hand-hammering motion, the same device successfully illuminated an array of commercially available LEDs, shown in Fig. 14 (b). These results show that Au-NPs/Bi₂O₃/PVDF nanocomposite films have significant potential for biomechanical motion-sensing applications, enabling sensitive detection of small mechanical movements.

5.3 Charging-Discharging of Capacitor

The graph presents the charging-discharging profiles of two capacitors (10 μ F and 20 μ F) driven by the AuNP/Bi₂O₃/PVDF nanocomposite piezoelectric nanogenerator (PNG) under periodic mechanical excitation.

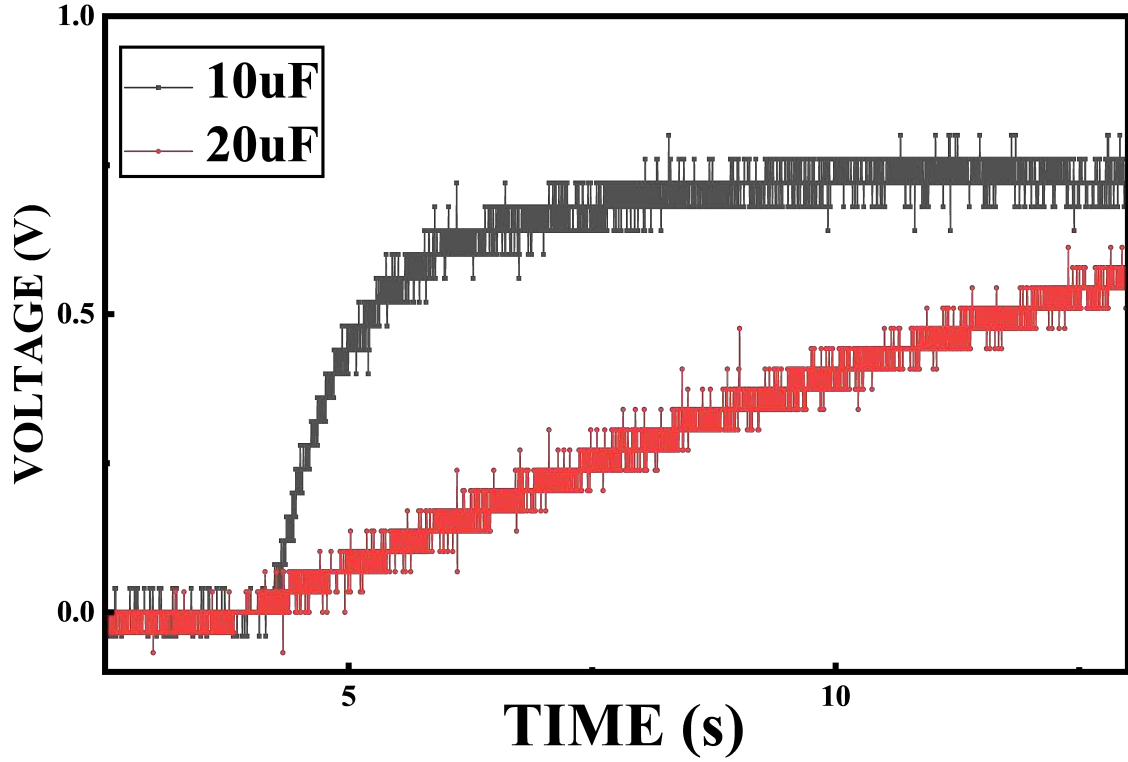


Figure 5.5: Charging-Discharging of two capacitor via AuNPs/Bi₂O₃/PVDF PENG.

The 10 μ F capacitor reaches about 0.75 V within nearly 4–5 seconds, showing faster charge accumulation because of its smaller capacitance. In comparison, the 20 μ F capacitor charges more slowly and reaches about 0.60 V after nearly 12 seconds, without complete saturation during the recorded time. This is expected because a larger capacitance needs more charge to reach the same voltage, and therefore the effective charging time constant is higher under the limited output current of the PENG.

5.4 Demonstration of Morse Code

We have successfully demonstrated the use of our fabricated PENG for transmitting emergency messages by integrating it with an Arduino microcontroller under Morse code. Morse code is an internationally recognized method in which text characters are assigned a unique sequential combination of dots and dashes, as shown in Fig. 32. Here, we have defined a short interval signal as a dot and a long interval signal as a dash. Thus, when we tap our PENG with our finger for a short duration of time, it shows a dot, and it shows a dash when tapped for a longer duration of time. For a clear demonstration of waveforms, we have defined one finger tap as a dot and four consecutive finger taps as a dash. As shown in Fig. 2 (a-g), waveforms of all the alphabets are obtained using an oscilloscope. We can clearly see in these graphs that there is a sharp peak signal on a single tap corresponding to a dot,

and also there are four consecutive sharp peak signals when tapped four times corresponding to a dash. We have also obtained waveforms of some words used in emergencies, like “SOS”, “SAVE”, “RUN”, etc., using the above-defined signal patterns shown in Fig. 3 (a-f). Similarly, we have displayed these different alphabets and emergency words using an Arduino microcontroller, and we also transmitted these emergency messages to a mobile using wireless Bluetooth communication, as shown in the Supplementary videos. Hence, we have successfully demonstrated the use of our fabricated PENG as an emergency communication device. This device can also be used by disabled persons for communication.

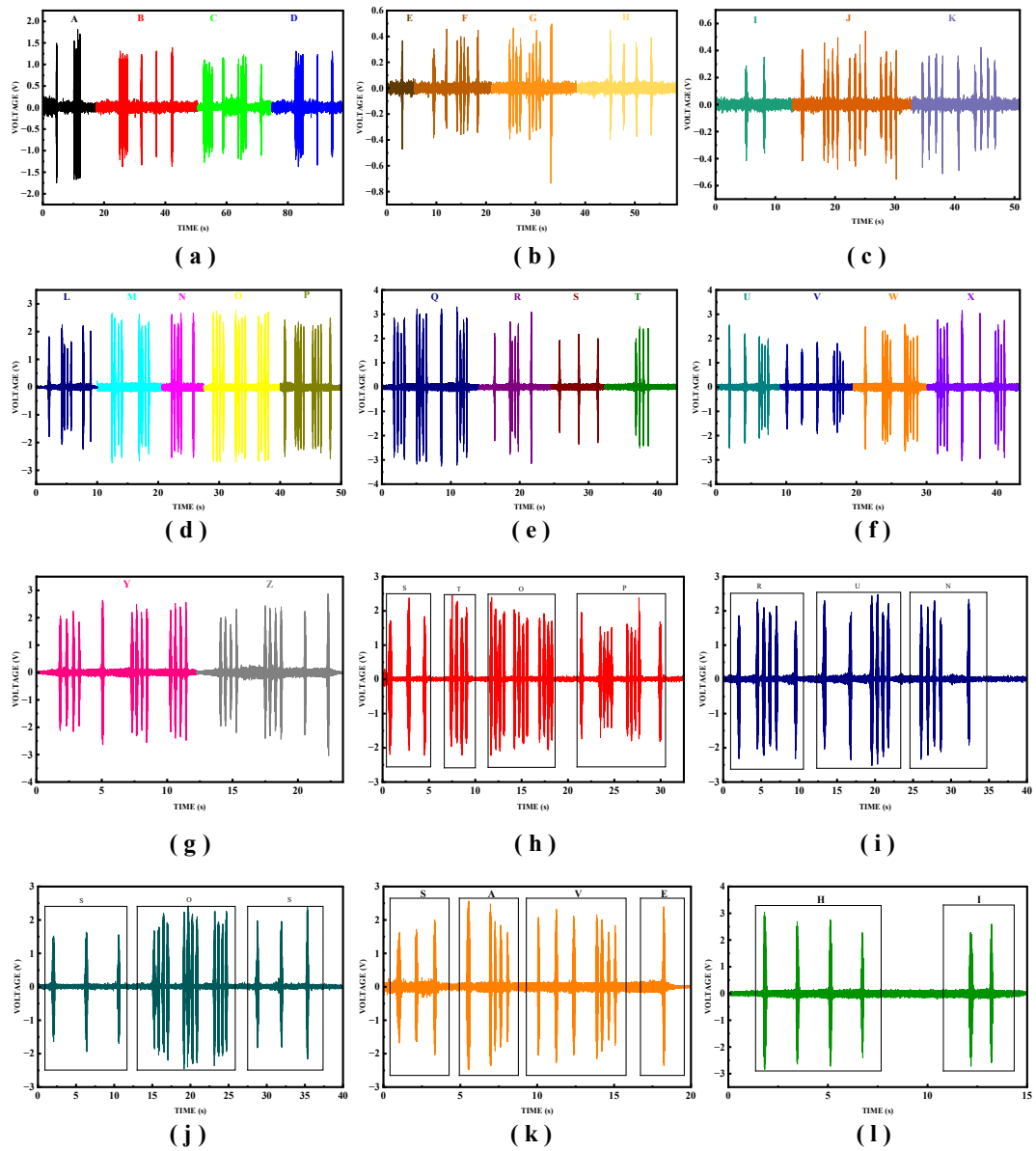


Figure 5.6: (a – f): Morse Code pattern of alphabets from A to Z.

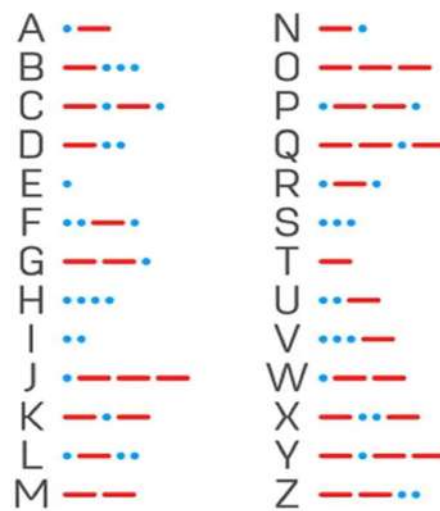


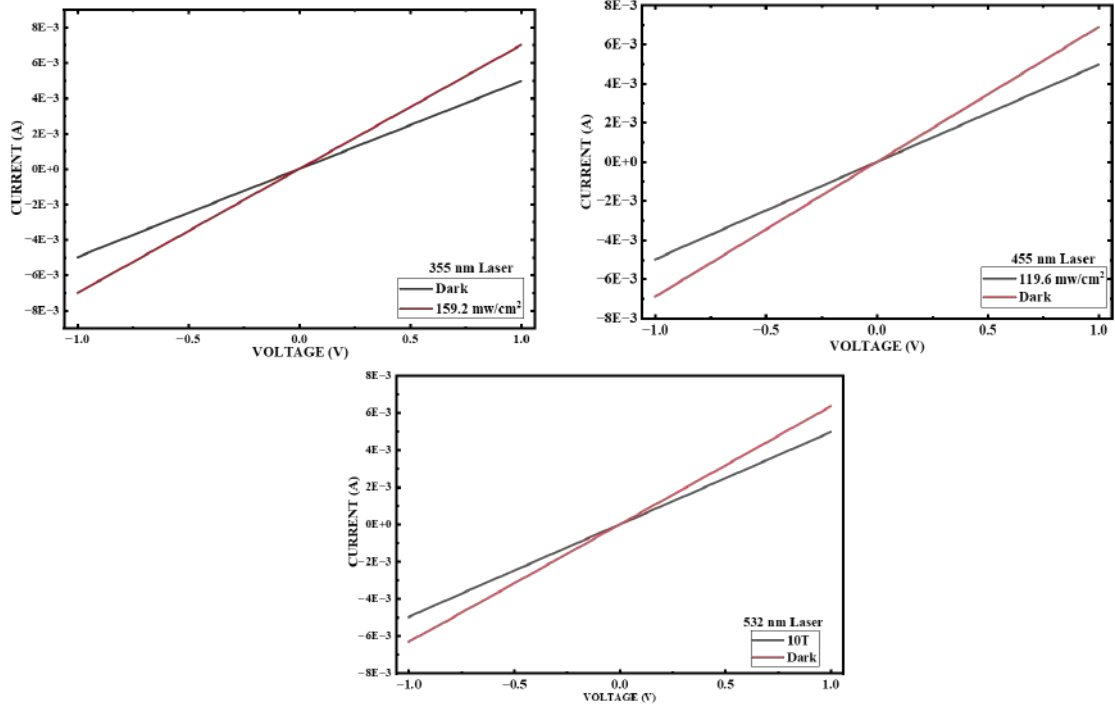
Fig. 1: International Morse Code

Figure 5.7: International Morse Code.

5.5 Self-Powered Photodetector

The current-voltage characteristics of the Bi_2O_3 nanocomposite photodetector were measured from -1 V to $+1$ V under 355 nm UV light (159.2 mW/cm²), 455 nm blue light

(119.6 mW/cm²), and 532 nm green light, together with the corresponding dark current. In all three cases, the I-V curves are nearly linear and approximately symmetric about the origin. This indicates that the metal-semiconductor contact behaves mainly as an ohmic contact. Therefore, the charge transport is largely drift controlled, and no strong rectifying Schottky contact is observed between the electrode and the Bi₂O₃ layer.



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Figure 5.8: I-V curve of Device at different Laser Light illumination.

Under 355 nm UV light at 159.2 mW/cm², the measured current remains above the dark current throughout the voltage sweep. At +1 V, the illuminated current is about +6.5 mA, compared with nearly +5 mA in the dark. This is understandable because 355 nm light has an energy close to 3.49 eV, which is higher than the approximate Bi₂O₃ band gap of 2.8 eV. The UV photons can therefore excite electrons across the band gap and increase the number of mobile carriers. The difference current, $\Delta I = I_{\text{light}} - I_{\text{dark}}$, becomes larger with bias, indicating that the applied field helps collect the generated carriers. The 455 nm response is less straightforward. At positive bias, the dark current is higher than the illuminated current, while at negative bias the illuminated current becomes larger. This crossover near 0 V may arise from photoconductive quenching, trap-assisted recombination, or a small photovoltaic contribution from the internal field of the nanocomposite. Since 455 nm photons have an energy of about 2.73 eV, close to the Bi₂O₃ band gap, oxygen-vacancy-related trap states may play an important role under this illumination.

For 532 nm green light, the photocurrent is smaller than the UV response but is still clearly measurable at positive bias. At +1 V, the illuminated current is about +6.5 mA, while the

dark current is about +4.5 mA. Since the photon energy at 532 nm is only about 2.33 eV, it is below the direct band gap of Bi_2O_3 . The response is therefore most likely related to sub-bandgap absorption through oxygen vacancies or other surface defect levels. This visible-light response suggests that defect states extend the working range of the Bi_2O_3 -based device beyond the UV region.

Zero-Bias Time-Resolved Photocurrent

Photocurrent transients were also measured at zero applied bias. In this condition no external field is present, so the current has to come from internal effects such as built-in potential at the electrode-semiconductor contact, band bending, or unequal diffusion of photogenerated carriers. A zero-bias current therefore cannot be explained by ordinary ohmic drift alone. It is

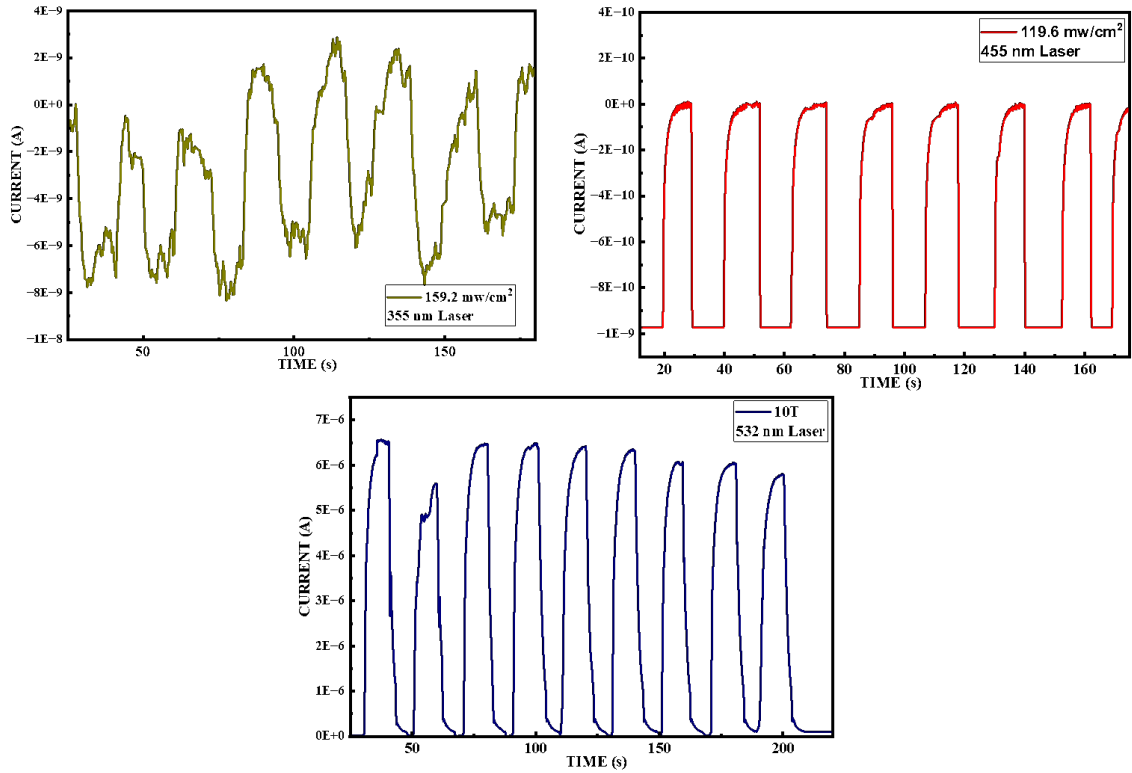


Figure 5.9: I-T curve of the device under three different Laser (Switch off–Switch On) condition.

useful because it reflects the intrinsic photoelectric response and the role of defects and junction asymmetry. The repeated response under all three wavelengths shows that the Bi_2O_3 nanocomposite can work in a self-driven photodetection mode, which is important for low-power devices.

355 nm UV Excitation (159.2 mW/cm²)

Under 355 nm UV illumination at zero bias, the photocurrent fluctuates between about -9 nA and $+3$ nA. The response does not show sharp on/off edges, and a noticeable amount of cycle-to-cycle noise is superimposed on the periodic signal. The change of current sign at zero bias is important. In a symmetric ohmic device, without an external field, a net DC photocurrent should appear only when generation, collection or recombination is not spatially balanced. The positive-to-negative variation may therefore come from two competing processes: an initial photovoltaic current due to band bending at the electrode interface and a later trap-filling process at defect centres. As traps become charged, the internal space-charge profile can change and the measured current can invert. Such behaviour is commonly associated with persistent photoconductivity and trap-induced space-charge build-up in oxide semiconductors. The UV response is only at the nanoampere level, which means that at zero bias carrier generation is strongly balanced by recombination. The comparable noise level also suggests that trap charging and discharging occur over a range of time scales rather than through one fixed trap level.

455 nm Blue Excitation (119.6 mW/cm²)

Among the three illumination conditions, the 455 nm zero-bias I-t trace is the most regular. When the laser is switched on, the current reproducibly moves to about -1 nA. After the laser is switched off, it returns almost immediately to the baseline. The same behaviour is repeated for more than eight cycles over about 160 seconds, and no obvious drift or loss of signal amplitude is seen.

The negative polarity of the zero-bias photocurrent is the defining and most significant feature of this dataset. At zero applied field, a negative photocurrent means that illumination drives a net conventional current in the direction opposite to what simple majority carrier photogeneration would predict. This is physically equivalent to a photovoltaic response where the internal junction field preferentially sweeps minority carriers, in an n-type Bi_2O_3 matrix, these would be photogenerated holes toward the collecting electrode in a direction that reduces the majority carrier current. In essence, the 455 nm photons, whose energy (≈ 2.73 eV) is near-resonant with the Bi_2O_3 bandgap, efficiently populate the valence band and generate well-separated electron-hole pairs that are subject to the built-in potential at the electrode interface. The holes, being minority carriers in n-type Bi_2O_3 , drift preferentially toward one electrode under the asymmetric band bending, generating a photovoltaic current that registers as a negative signal in the measurement convention used. The sharpness of both the rise and fall transients is equally notable. The rise time the transition from dark baseline to the illuminated, 1 nA plateau, appears to occur within a few seconds at most, and the fall time upon switching off is nearly instantaneous. This near-ideal step-function response confirms that carrier generation and recombination at 455 nm proceed through shallow or

band-edge states with short lifetimes, contrasting sharply with the trap-dominated sluggish dynamics at 355 nm.

532 nm Green Excitation (10T Condition)

Under 532 nm green illumination, the zero-bias I-t signal is the largest among the three measurements. The photocurrent reaches about 6.5–6.8 μA during illumination, which is several orders higher than the currents recorded under 355 and 455 nm. This is notable because 532 nm photons, with an energy of about 2.33 eV, are below the Bi_2O_3 optical band gap. Each light-on cycle shows a fast rise followed by a slower decrease toward a steadier value before the light is turned off. When the light is removed, the current drops quickly and then returns to the baseline after a short relaxation. This rise-and-decay shape is consistent with trap-state filling. At the start of illumination, available traps are filled and a large transient current appears. Once many traps are occupied, the current moves toward a lower steady level controlled by generation and trap-assisted recombination. The repeated peak height suggests that the traps are mostly emptied during the dark interval before the next cycle.

Chapter 6

Conclusion, Future Scope and Social Impact

In this dissertation, flexible polymer-nanocomposite-based photodetectors were successfully designed, fabricated, and characterized by systematically evaluating both a baseline $\text{Bi}_2\text{O}_3/\text{PVDF}$ matrix and $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$, for advanced plasmon-assisted nanocomposite. X-ray diffraction (XRD) patterns confirmed the successful synthesis of the nanocomposite thin films, FT-IR verifying the crucial crystallization of the enhancement of electroactive, polar β -phase of PVDF alongside the distinct structural phases of the embedded Bi_2O_3 and Au nanoparticles. Photoluminescence (PL) spectroscopy revealed distinct emission profiles corresponding to optical bandgaps of 3.21 eV and 3.06 eV, pointing to the coexistence of different crystalline phases within the Bismuth Oxide nanostructures that offer tunable absorption bands favorable for multi-wavelength photodetection. The synthesized nanocomposite of $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$ shows good dielectric constant better storage capacity among all, confirms from dielectric and P-E measurement. The fabricated nanogenerator of $\text{Au-NPs}/\text{Bi}_2\text{O}_3/\text{PVDF}$ shows synergistic enhancement of piezovoltage 48.4 V. The fabricated device also shows good stability upon tested upto 1000 cycles. The fabricated photodetector shows ohmic contact at the electrode and nanocomposite interface which shows good response for 355nm, 455nm and 532nm laser on dark to illumination. Upon zero bias implementation, this device shows exceptionally well response to all three laser having current in nA range which shows the self-powered nature of the fabricated photodetector. In future, this work can be extended to explore out the possibility of Schottky contact, which can lead the potential of this type of device to be a neuromorphic device and hence shows resistive switching. Furthermore, other metallic nanoparticles such as silver or platinum can be explored for the hybrid nanocomposite which may significantly boost the output voltage as well as photodetection capability, because of their specific barrier formation capability.

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Synergistic Enhancement of Piezoelectric Nanogenerator based on PVDF/Bi₂O₃/Au-NPs nanocomposite for Biomechanical motion sensing Applications

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Abstract— In this study, we report a piezoelectric nanocomposite based on Bi₂O₃ and PVDF polymer, synthesized using a solution-mixing and drop-casting method, with exceptional output properties for nanogenerator applications. A comparative and novel study is performed to investigate the impact of Au-NPs (gold nanoparticles) on the performance of nanogenerators under external mechanical loading. The synthesized nanocomposites films is having a thickness of 50-70 μm . The nanogenerator with Au-NPs/Bi₂O₃/PVDF mixture having 5% Bi₂O₃ of total PVDF and with doping of 500 μL of Au-NPs exhibits an enhanced output performance achieving an open circuit voltage of 48.4 V and an output power of 400 μW at a load resistance of 1M Ω using the electrodynamic shaker device at a frequency of 5 Hz.

Keywords—PENGs, Au-NPs, Bi₂O₃

I. INTRODUCTION

Recent advances in Artificial Intelligence and IoT have increased global energy demand. However, with a focus on environmental sustainability, the need for harvesting green and ambient energy increases exponentially, but there are a few methods through which renewable energy can be harvested. In the past decade, piezoelectric nanogenerators (PENGs) have emerged as a potential and effective tool to harness mechanical energy into electrical energy. The vibrant application of piezoelectric nanogenerators is not limited to energy harvesting; it extends to self-powered electronics, wearable devices, healthcare, biomedical applications, wireless sensors and the Internet of Things (IoT) [1-4]. Metal Oxides have shown promising results in enhancing the mechanical and electrical properties of piezoelectric nanogenerators when embedded in semi-crystalline fluropolymers like polyvinylidene fluoride (PVDF), resulting in an efficient, flexible PENG device [5]. Bismuth Oxide (Bi₂O₃), among various post-transition metal oxides, has a narrow bandgap, high density, and an intrinsically high dielectric permittivity, which makes it excellent choice for an alternative to toxic lead-based piezoelectric ceramics and composites. In the work reported by Anirban et al., Bi₂O₃ nanocomposite exhibits piezoelectric behaviour with

maximum open-circuit voltage of 3.6 V [6]. Bi₂O₃ not only acts as a nucleating agent but also serves as a dispersed micro-capacitor network, which enhances localised charge storage because of the difference in dielectric constant with PVDF, making the nanocomposite films exhibit the Maxwell-Wagner-Sillars (MWS) effect, which describes interfacial polarization in heterogeneous materials, arising from the accumulation of migrating charge carriers at the boundaries between phases with differing electrical conductivities and permittivities. This localized charge trapping at internal interfaces significantly governs the low-frequency dielectric response and macroscopic electrical properties of composite systems. [7]. In this work, a flexible piezoelectric nanogenerator (PENG) combining Bi₂O₃ powder with PVDF polymer has been fabricated. The performance characteristics of PENGs devices under different mechanical loads, using electrodynamic shaker as well as human body movements, has been tested. In recent times, gold nanoparticles have been used in many devices to enhance their output performance because of their pronounced localized surface plasmon resonance (LSPR) and robust Schottky barriers. Gold nanoparticles (Au-NPs) have a high electron density and higher work function (5.36 eV), which helps them act as isolated floating-gate or deep-level charge traps [18]. Therefore, to study the plasmonic and robust Schottky barrier effect in the nanocomposite films, pristine gold nanoparticles (Au-NPs) and Au-NPs doped Bi₂O₃ in PVDF matrix nanocomposite films were synthesized. Open-circuit voltage and short circuit current measurements of all PENG devices were obtained observed that the device with Au-NPs/Bi₂O₃/PVDF based nanogenerator exhibits the highest output voltage of 48.4 V, in comparison to pristine Au-NPs/PVDF and Bi₂O₃/PVDF based device.

II. MATERIALS AND ELABORATION

A. Materials

Polyvinylidene fluoride [PVDF] (99%) and dimethylformamide [DMF] (99%) were obtained from Thermo-Fisher Pvt. Bismuth Oxide [Bi₂O₃] (99%) was obtained from Molychem India LLP Pvt., whereas gold

nanoparticles (Au-NPs) of 5 nm diameter were obtained from Sigma-Aldrich Pvt. All the chemicals were utilized without any further extensive treatment in their original form.

B. Synthesis of Bi_2O_3 nanocomposites without Au-NPs

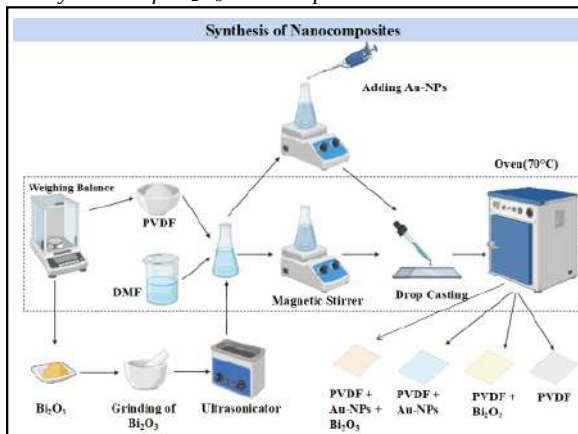


Fig 1. Synthesis process of Nanocomposites films with drop casting

PVDF nanocomposites films were synthesised by dissolving 1g of PVDF powder in 10 ml of DMF. The solution was then stirred for 4 hours using a magnetic stirrer, after which the processed solution was drop-cast onto a glass substrate using a micro-pipette. The amount of solution loaded for drop casting was kept constant for each glass plate to ensure uniform film thickness across all films. The casted glass plate was then kept in an oven at 343K for 2 hours. Finally the glass plate was dispersed in DI water, and due to the hydrophobic nature of PVDF, the processed films detached from the glass surface, yielding a PVDF nanocomposite film. Nanocomposite films of Bi_2O_3 were also synthesised by the drop-casting method. However, initially to reduce the particle size of Bi_2O_3 powder, it was first grind in an agate mortar and pestle for 2 hours and then ultrasonicated for 30 minutes. Then the fine powder was dissolved with 1g PVDF in 10 ml of DMF and kept stirred on a magnetic stirrer for 4 hours. The latter processes were similar to those used for synthesis of PVDF nanocomposite films.

C. Synthesis of Bi_2O_3 nanocomposites with Au-NPs

Au-NPs/PVDF nanocomposite films were synthesized by mixing 500 μL of Au-NPs slowly in a 1g PVDF dissolved in 10 ml of DMF while stirring on a magnetic stirrer to avoid any chances of agglomeration. A similar process was repeated afterwards, followed by the preparation of PVDF nanocomposite films. Au-NPs/ Bi_2O_3 /PVDF nanocomposites were synthesized with a similar procedure. The Bi_2O_3 powder was first grind in an agate mortar and pestle for 1 hour to reduce its particle size, after which it was transferred and dissolved with 1g of PVDF in 10 ml of DMF and 500 μL of Au-NPs.

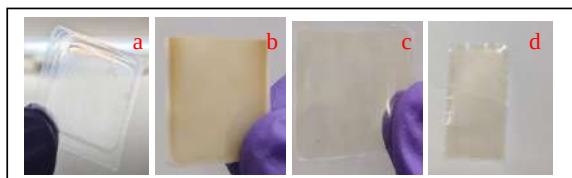


Fig 2. Photograph of synthesized nanocomposite films (a) PVDF. (b) Bi_2O_3 /PVDF. (c) Au-NPs/PVDF. (d) Au-NPs/ Bi_2O_3 /PVDF.

The resulting solution was then kept stirred on a magnetic stirrer 4 hours, after which the same steps were followed as for the synthesis of PVDF nanocomposite films.

D. Thickness measurement and Poling

The synthesised nanocomposite films (pure PVDF, Bi_2O_3 /PVDF, Au-NPs/PVDF, Au-NPs/ Bi_2O_3 /PVDF) had a thickness of around 50-70 μm measured with a digital vernier calliper.

E. Device structure of PENGs

The PENG device was fabricated by cutting the nanocomposites films into 1 cm $\times$ 1 cm pieces. The aluminium tape was placed at the top and bottom, forming a sandwich structure and serving as the top and bottom electrodes. To measure the open-circuit voltage and current, two copper wires were attached to the upper and lower electrodes.

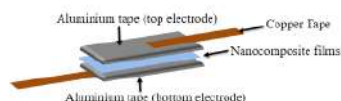


Fig 3. Schematic diagram of device structure

III. RESULTS AND DISCUSSION

A. Structural Phase of Bi_2O_3 Powder

The XRD profile of Bismuth Oxide (Bi_2O_3) Powder is shown in Fig. 5. The diffraction peaks at $2\theta = 27.1^\circ$, 31.0° , and 32.2° correspond to the plane (201), (002), and (220), respectively, and matches with earlier reports [8-9].

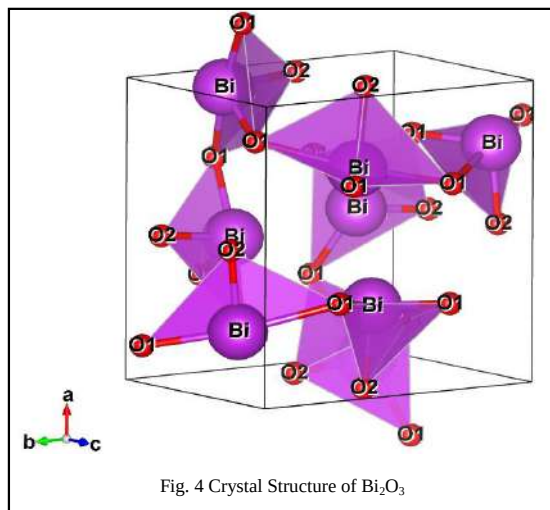


Fig. 4 Crystal Structure of Bi_2O_3

Bismuth Oxide exhibits (Bi_2O_3) a complex polymorphism consisting of five distinct crystallographic phases α , β , γ , δ and ω with the monoclinic α -phase being the most thermodynamically stable at room temperature. The β - Bi_2O_3 structure is characterized by a layered arrangement where bismuth atoms are coordinated by oxygen in a distorted

environment, creating an inherent structural asymmetry that facilitates electron-hole separation.

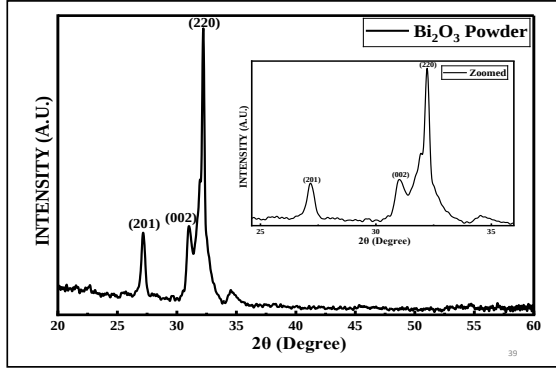


Fig. 5 The XRD profile of Bi_2O_3 powder

The crystallite size of the Bismuth Oxide powder was calculated using the Scherrer Equation and found to be approximately 29.47 nm. From Rietveld refinement of XRD data using the fullprof software, estimated the values of lattice parameter which corresponds as $a = b = 7.86 \text{ \AA}$, $c = 5.59 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, confirms the space group $p-421c$. Fig. 4 represents the crystal structure of Bismuth Oxide (Bi_2O_3), which is rendered using VESTA software.

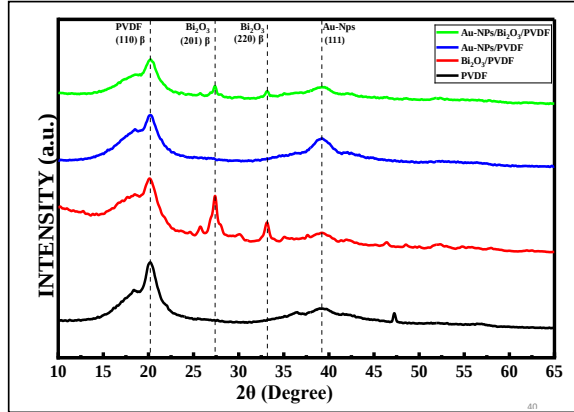


Fig. 6 The XRD profiles of all nanocomposites.

The XRD profiles of PVDF and all nanocomposites (PVDF with Bi_2O_3 and Au-NPs) are shown in Fig. 6. The presence of peaks that correspond to the Bi_2O_3 and Au-NPs confirms the stability of the Bi_2O_3 and Au-NPs structural phases within the PVDF matrix. In Fig. 6, the peak at $2\theta = 20.3^\circ$ correspond to the semi-polar phase in PVDF [10-12]. Peaks appearing at $2\theta = 27.3^\circ$, 33.1° and 39.2° corresponds to the β -phase of Bi_2O_3 and to the presence of Au-NPs respectively [9,11].

B. FTIR Spectroscopy analysis

FTIR graph of the fabricated nanocomposite films are shown in Fig. 7. The bands related to the semi-polar γ -phase appeared at 1234 and 812 cm^{-1} , and the polar β -phase appeared at 1275 cm^{-1} [12-14]. PVDF contains a low β -phase content (about 35%), which limits its piezoelectric energy-harvesting properties. The incorporation of Bi_2O_3 and Au-NPs increases the β -phase content at the expense of α -phase in the PVDF matrix. The bands at 766 cm^{-1} and 838 cm^{-1} are

used to determine the electroactive phase content using the formula 1[10].

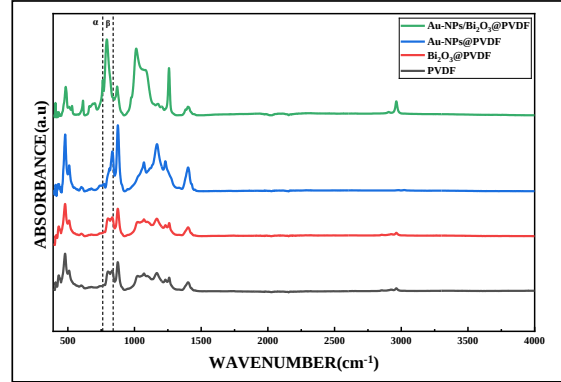


Fig. 7 FTIR profile of all nanocomposites.

$$F_{EA} = \frac{A_{838}}{K_{838} A_{766} + A_{838}} \times 100\% \quad (1)$$

Here, absorption intensities at A_{840} and A_{764} are 838 and 766 cm^{-1} , respectively. K_{838} and K_{766} are the absorption coefficients corresponding to the bands 838 and 766 cm^{-1} with values of $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively. The electroactive phase content increases as Bi_2O_3 and Au-NPs are loaded into the PVDF matrix, reaching 84% for Au-NPs/ Bi_2O_3 /PVDF, 83% for Au-NPs/PVDF, 81% for Bi_2O_3 /PVDF, and 71% for the bare PVDF composite film.

C. Morphological and Compositional properties of Au-NPs/ Bi_2O_3 /PVDF nanocomposite

The morphology and elemental composition of Au-NPs/ Bi_2O_3 /PVDF nanocomposite film was analyzed by SEM and EDX in Fig. (8) and (9). The surface morphology of the nanocomposite film is shown in Fig.(8) exhibits a homogeneous mixing of Au-NPs/ Bi_2O_3 in PVDF matrix with uniformly grown fibrils and spherulitic chain like structure of the composite, which is a typical feature of β -Phase in PVDF.

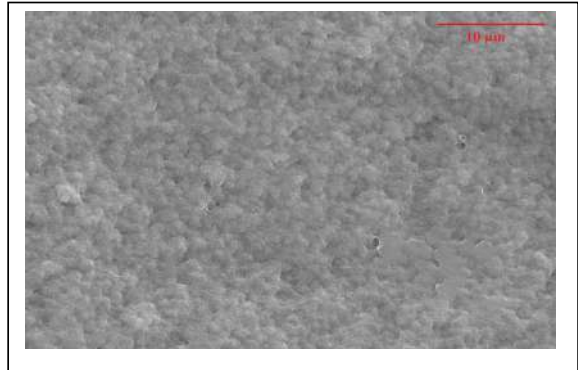


Fig. 8 SEM image of AuNPs/ Bi_2O_3 /PVDF nanocomposite

The elemental mapping using EDX, of the same film is shown in Fig. (9), confirming the presences of Bi, C, F, O, and Au.

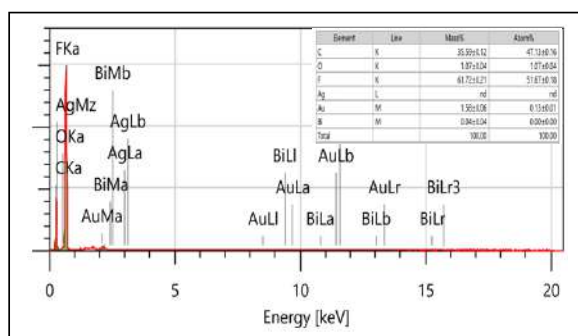


Fig. 9 EDX profile of AuNPs/Bi₂O₃/PVDF nanocomposite

D. Piezoelectric nanogenerator performance

The PENGs device has been fabricated as shown in Fig. (3), to measure the piezoelectric response for energy harvesting applications. The effective area of the device is $1 \times 1 \text{ cm}^2$, and the piezoelectric output was measured by repeated hammering at a 5 Hz frequency without any external electrical poling. The open circuit voltage and current were recorded for all devices. The open circuit voltage is shown in Fig. (10) and short circuit current in Fig. (11). The bare PVDF

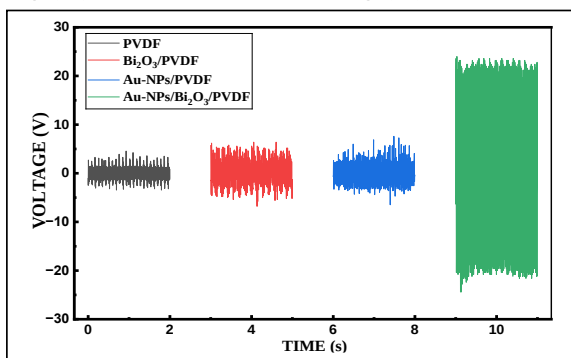


Fig. 10 Open circuit voltage of all PENGs nanocomposites.

device show open circuit Voltage of $\sim 5.64 \text{ V}$ and short circuit current of $\sim 0.03 \mu\text{A}$ with increase in trends for nanocomposite devices reaching maximum upto $\sim 48.4 \text{ V}$ and $\sim 0.118 \mu\text{A}$ for Au-NPs/Bi₂O₃/PVDF because of the incorporation of Au-NPs in the matrix of Bi₂O₃/PVDF which increases the voltage and current synergistically due to significant difference in work functions between the gold nanoparticles and the surrounding dielectric matrix, energy band bending occurs at the phase interfaces which establishing robust Schottky barriers. These barriers act as deep-level energy wells that efficiently capture and localise the generated electrons. As a result of physically trapping these charges, the gold nanoparticles severely restrict internal carrier recombination and suppress leakage currents. This sustained charge separation maintains a massive built-in potential difference across the film, yielding a giant voltage output. The incorporation of gold nanoparticles (Au-NPs) into the Bi₂O₃ matrix significantly enhances the piezoelectric output voltage of the nanogenerator through a synergistic combination of structural nucleation and interfacial polarization. Even in the absence of light, the Au-NPs act as high-surface-area nucleating agents that facilitate the transition of PVDF from the non-polar α -phase to the

electroactive ferroelectric β -phase. This transformation is driven by the strong electrostatic interaction between the surface charges of the Au-NPs and the highly electronegative fluorine atoms in the PVDF chains, which induces local dipole alignment. Subsequently, the presence of Au-NPs at the Bi₂O₃ and PVDF interface promotes Maxwell-Wagner-Sillars (MWS) polarization, increasing the dielectric constant and optimizing the charge transfer efficiency. Consequently, the localized surface plasmon resonance (LSPR) characteristic of the Au-NPs contributes to a more robust internal electric field and improved crystallinity, leading to a substantial increase in the harvested piezoelectric potential compared to the pristine composite. However, the dominant mechanism in the synergistic enhancement of the output voltage of Au-NPs/Bi₂O₃/PVDF nanocomposite is dominated by Schottky Barrier behavior as the generation of output voltage is focused on the stress mechanisms leading the Schottky barrier to trap the charges. [19-22]

The output of all the PENG devices is better than that of bare PVDF. The variation of output power and voltage of the Au-NPs/Bi₂O₃/PVDF device as a function of load resistance is shown in Fig. 13, yielding a maximum output power of $400 \mu\text{W}$ across a load resistance

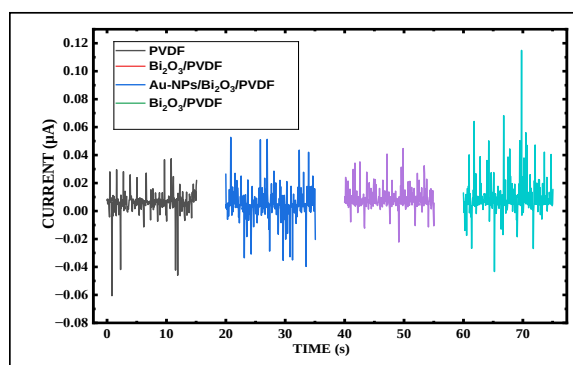


Fig. 11 Short-circuit current of all PENG devices.

of $1 \text{ M}\Omega$. Also, the output voltage gets saturated at higher resistance. Fig. 12 corresponds to the short-circuit current of the prepared piezoelectric nanogenerator of Au-NPs/Bi₂O₃/PVDF over 1000 cycles. The graph shows no significant changes in the output of short-circuit current, which exhibits the stability of the material over repeated cycles of stressing and de-stressing.

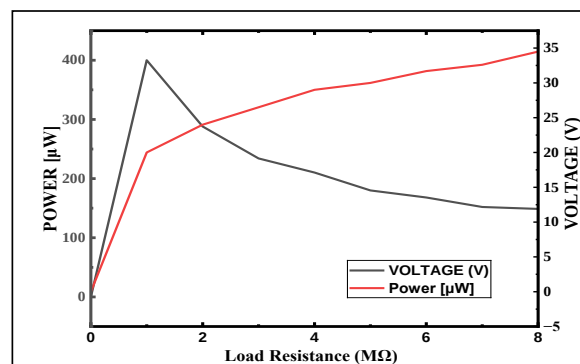


Fig. 12 Variation of power and voltage with load resistance

E. Biomechanical motion sensing and LED glowing

To demonstrate the energy-harvesting capability of the Au-NPs/Bi₂O₃/PVDF nanocomposite device via biomechanical motions, we performed thumb tapping and recorded the resulting output voltage. The output voltage corresponding to thumb tapping (~9.6 V) is shown in Fig. 14 (a). Also, using a hand-hammering motion, the device illuminated an array of commercially available LEDs successfully, shown in Fig. 14 (b).

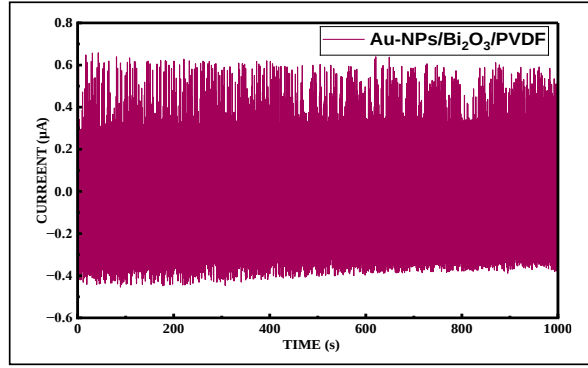


Fig. 13 Device stability over 1000 cycle

These results show that Au-NPs/Bi₂O₃/PVDF nanocomposite films have significant potential for biomechanical motion-sensing applications, enabling sensitive detection of small mechanical movements.

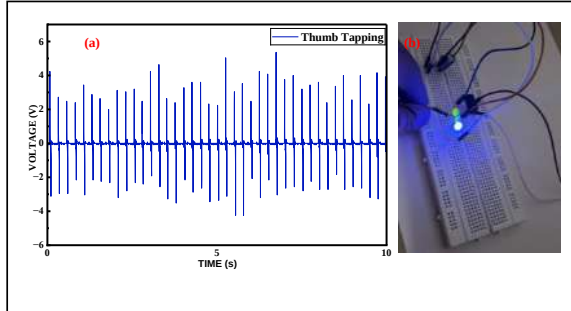


Fig. 14(a) Open circuit voltage corresponding to thumb pressing and (b) glowing of the LED with the output voltage generated from thumb pressing

F. Comparison with published literature

Detailed analysis was carried out of nanocomposites containing Bismuth Oxide, and the resulting comparison is presented in Table 1. It was observed that PENGs based on Bi₂O₃/PVDF have the highest piezoelectric voltage output and current, thus, shows synergistic contribution of conducting Au nanoparticles and semiconducting Bismuth oxide in the PVDF matrix.

Table 1 Comparison of our piezoelectric performance of Bismuth-based piezoelectric nanogenerator with previous reports in the literature.

Piezoelectric Material	Fabrication Method	Peak to Peak V_{os} (V)	References
Bi ₂ O ₃ /PVDF	Drop casting	3.6	[6]
PVDF/Bi ₂ Al ₄ O ₉ /RGO	Drop Casting	5.92	[15]
BiFeO ₃ :Sr	Sol-gel	6.35	[16]
BiT/PVDF	Spin Coating	0.8	[17]
Bi ₂ O ₃ /PVDF	Drop Casting	14.1	This work
Au-NPs/PVDF	Drop casting	13.2	This work
Au-NPs/Bi ₂ O ₃ /PVDF	Drop casting	48.4	This work

IV. CONCLUSION

In this work, we demonstrated the synthesis of flexible films of pure PVDF and Bi₂O₃/PVDF, Au-NPs/PVDF and Au-NPs/Bi₂O₃/PVDF nanocomposite films for the piezoelectric nanogenerator application. In this paper, we first report the synergistic behaviour of gold nanoparticles when embedded into a bismuth-oxide and PVDF matrix, which significantly increases the piezoelectric output performance. The fabricated device also demonstrated a physical motion sensing application along with the glowing of the LED. Overall, the incorporation of gold nanoparticles enhances the piezoelectric performance of the nanocomposites.

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