Enhanced Energy Conversion Efficiency of PVDF/WS_2 Hybrid based Piezoelectric Nanogenerator

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DECLARATION

We hereby certify that the work which is presented in the Research Work entitled **"Enhanced Energy Conversion Efficiency of PVDF/WS_2 Hybrid based Piezoelectric Nanogenerator"** in the fulfilment of the requirement for the award of the degree of Master of Science in Physics and submitted to the Department of Applied Physics, Delhi Technological University, Delhi is an authentic record of our own, carried out during a period from July 2024 to May 2025, under the supervision of Dr. Bharti Singh.

The matter presented in this thesis has not been submitted by us for the award of any other degree of this or any other Institute/University. The work has been communicated in Scopus indexed journal with the following details:

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ABSTRACT

Energy harvesting from ambient sources, particularly human motion is gaining considerable interest because of its potential to efficiently convert environmental mechanical energy into usable electrical power. Ongoing research is exploring piezoelectric nanogenerators (PENGs) as a means to convert vibrational mechanical energy into functional electrical output. Here in, we report the fabrication of PENG based on PVDF/WS_2 nanocomposite thin films. WS_2 nanosheets are synthesized by exfoliation method. Further, WS_2 with different weight percentages was incorporated in PVDF and the resulting thin films are analysed using XRD and FTIR. The output of nanogenerator is finally examined, determining the maximum output voltage (V_{OC}) without an external load and the maximum current (I_{SC}) when the output terminals were shorted. The results indicate that the incorporation of WS_2 nanosheets led to enhanced output of piezoelectric nanogenerator, exhibiting an elevated voltage of 19.6 V and a peak current of 11.03 μA corresponding to 2 wt% filler concentration of WS_2 and shows significant potential for renewable energy conversion and self-sustaining electronic devices.

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LIST OF SYMBOLS AND ABBREVIATIONS

2-D	**Two-dimensional**
PENGs	**Piezoelectric Nanogenerators**
PVDF	**polyvinylidene fluoride**
WS_2	**Tungsten disulphide**
DI water	**Deionised water**
DMF	**Dimethylformamide**
XRD	**X-ray diffraction**
SEM	**Scanning electron microscopy**
FTIR	**Fourier transform infrared**
V_{OC}	**Open -circuit voltage**
I_{SC}	**Short-circuit current**

CHAPTER 1

INTODUCTION AND OBJECTIVES

1.1. Introduction

The continuous evolution of autonomous sensor networks, portable devices and IoT (Internet of Things) platforms has emphasized the significance of developing self-sustaining energy solutions. Although batteries have traditionally met this demand, their limited lifespan and frequent need for replacement pose major drawbacks. To address these concerns, harnessing energy from surrounding environmental sources has emerged as an effective alternative[1,2,3]. There are several sources of energy present in our surrounding, such as, sunlight[4], wind[5], human motion, and water, to produce clean, renewable energy[6].

With growing interest in sustainable and portable power sources, piezoelectric nanogenerators have become one of the most viable technologies for harvesting energy from ambient mechanical stimuli and are beneficial in designing self-powered wearable and portable electronic device[7]. Zhong Lin Wang et. al. [8] first introduced piezoelectric nanogenerators (PENGs) in the year 2006. By exploiting the characteristics of piezoelectric materials, these devices generate electrical energy by harnessing mechanical inputs, useful for powering small scale electronics. Mechanical deformation in piezoelectric transducers polarizes the crystal lattice structure, separating positive and negative charge carriers and creating an electrical potential. Piezoelectric materials have attracted significant interest due to incredible potential to harness mechanical energy and generate useful electrical output [9,10,11]. Various materials such as lead zirconate titanate (PZT), barium titanate ($BaTiO_3$), lithium niobate ($LiNbO_3$) and sodium niobate ($NaNbO_3$) have been widely explored for piezoelectric applications, but these inorganic materials have a high energy conversion rate but because of its high toxicity, lack of durability and biocompatibility, they are less selected for use in the flexible nanogenerator.

On the contrary, polyvinylidene fluoride (PVDF) and other piezoelectric polymers and copolymers offer potential for mechanical-to-electrical energy conversion applications owing to their elevated piezoelectric coefficient, thermal and chemical durability, biocompatibility, and lightweight structure[12,13,14]. In its semicrystalline form, this polymer frequently exhibits in several structural forms, including α, β, γ, and δ. The β-phase, characterized by the

all-trans (TTTT) conformation, offers maximum piezoelectric response as a consequence of its higher dipole moment per unit volume, whereas the α-phase (TGTG conformation) is non-polar, whereas the γ-phase (T3GT3G conformation) has a weak piezoelectric coefficient. In comparison to PENGs constructed from inorganic piezoelectric materials, PENGs utilizing PVDF exhibit reduced electrical output efficiency[14,15,16,17,18]. The electrical output characteristics of piezoelectric nanogenerators utilizing PVDF has been significantly enhanced through the application of thermal, mechanical, and electrical treatments, which effectively increases β-phase crystallization and stabilization in PVDF. Moreover, the incorporation on nanofillers into the PVDF matrix can significantly promote the formation of β-phase, resulting in a flexible nanocomposite that exhibits improved piezoelectric output without sacrificing flexibility. The appropriate selection of fillers and their uniform integration into PVDF not only facilitates the nucleation of β-crystals but also augments the dielectric characteristics by increasing electric dipoles through significant interfacial polarization. To improve the ferroelectric characteristics of PVDF, nanofillers such as ZnO, RGO, BaTiO3 and various 2D materials like hBN, MXenes and TMDs are often introduced, as they facilitate β-phase crystallization by disrupting PVDF's symmetry [19,20].

Herein, chemically exfoliated WS_2 nanosheets were utilized to boost the piezoelectric output characteristics of PVDF films. To determine the optimum concentration of nanofillers, PVDF nanocomposite film with different content (1,2,3, and 5%) were synthesised using drop-casting technique and were used to fabricate PENG. Among all fabricated devices, the PENG with 2 % of WS_2 produce a maximum voltage 19.6 Volts and a maximum current of 11.09 μA at a tapping frequency of 7 Hz. Thus, the PENG is designed to extract mechanical energy from subtle human motions including finger tapping, foot tapping. These results demonstrate a practical approach for biomechanical energy harvesting from everyday human activities, highlighting the potential for sustainable applications in wearable electronics and portable systems.

1.2. Objectives

- To synthesise Tungsten disulphide using exfoliation method
- To optimize the nanofiller concentration of the polymer matrix.
- Fabrication of the nanofilms with tungsten disulphide as the nanofiller with varying weight percentage**.**

- Fabrication of the Piezo-nanogenerator (PENG).
- Measurement of the output performance of PENG.
- Utilization of the piezoelectric nanogenerator as an electronic device power source

1.3. LITERATURE REVIEW

1.3.1 Nanoparticles and nanotechnology

Nanotechnology involves the fabrication of nanostructures, the use of nanocomposites engineering physics, textile technology, and industrial processes. Like the impacts of mobile and molecular biology, semiconductor technology, and statistical methods in the previous century, it currently affects our environment and economy. Nanotechnology has significantly enhanced our lives by revolutionizing the management of commercial challenges in sectors such as sustainable materials, nanocomposite production, electronic devices, medical supply, energy and water, biotechnology, record-keeping systems, and national security. Nanotechnology represents a contemporary industrial revolution poised to significantly impact our economy and society. Consequently, the synthesis of 2D materials is a subject of heightened attention among scientists and researchers[21].

1.3.2. Nanoparticle Synthesis Techniques

Various strategies can be employed to produce nanoparticles. These techniques are applicable for producing nanoparticles, which can be dispersed in fluid or gaseous mediums. The synthesis of nanostructures can involve either atom-by-atom assembly or the size reduction of microparticles to nanoscale[22].

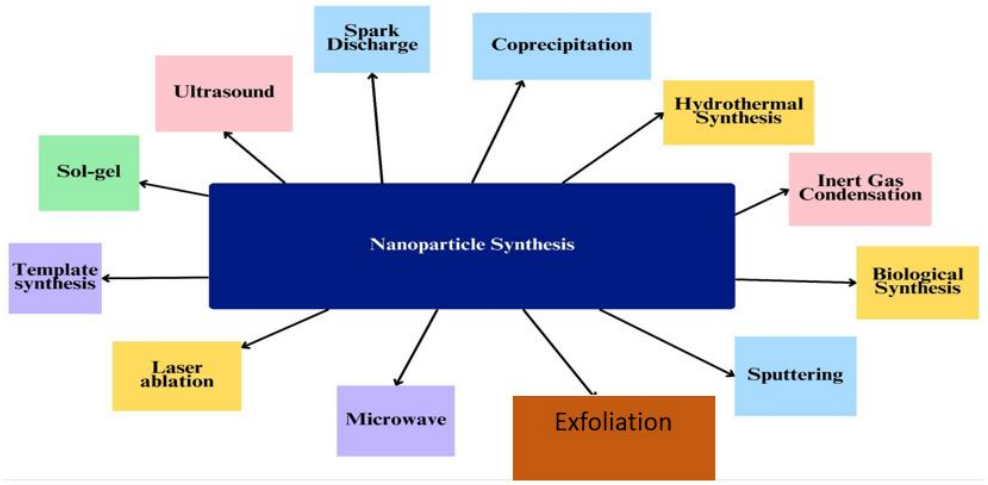

Figure 1.1.: Different types of Nanoparticle synthesis techniques.

1.3.2.1. Hydrothermal synthesis

Hydrothermal process is extensively employed to synthesize solids including fluorides, ceramics, complex oxides, microporous crystals, and superionic conducting materials. It is also utilized in the production of magnetic materials and luminescent phosphors. Novel condensed materials, including stacking sequence materials, are also available through it. Hydrothermal synthesis involves producing chemicals via reactions that take place inside a closed container with a heated solution, maintained at temperature and pressure higher than standard atmospheric conditions [23].

1.3.2.2. Sol-Gel method

The sol undergoes transformation throughout this chemical process, evolving into a biphasic structure that resembles a gel. This system has two phases: a liquid phase and a solid phase. The liquid phase may exhibit several morphologies, including individual particles or interconnected polymer networks. The sol-gel technique is extensively employed in material synthesis for synthesizing solid materials starting from molecular precursors, enabling the formation of ceramic powders in finely divided form through precipitation**.** These nanoscale single- and multi-component powders are manufactured for applications in dentistry and biology[24].

1.3.2.3. Exfoliation method

The exfoliation method is an extensively utilized in nanomaterial synthesis, particularly two-dimensional (2D) materials like graphene, MoS_2, and WS_2. The process involves separating layers of bulk materials into thin nanosheets, down to a single or few layers, using mechanical or chemical means[25,26].

1.3.3. Energy Harvesting

The increasing reliance on non-renewable fossil fuels and conventional chemical-based batteries to fulfil daily energy requirements has raised critical environmental and sustainability concerns. Consequently, extensive efforts have been directed in creating sustainable energy harvesting systems that make use of renewable sources including sunlight, wind, water flow, and mechanical motion. Among these, nanogenerators have gained prominence due to their capability to power autonomous systems. The swift expansion in IoT devices has further intensified the requirement for energy sources that are compact, lightweight, and flexible energy solutions. This has driven substantial progress in flexible and wearable electronic technologies, which are valued for their high sensitivity, mechanical resilience and biocompatibility. Nano-generators are essential in contemporary electronic devices due to their capacity to address the shortcomings of traditional power sources, such as substantial space requirements, limited durability, sensitivity to environmental fluctuations, and the production of harmful chemical waste[1,2,3].

1.3.4. Piezoelectric Nanogenerators (PENGs)

Recent advancements in piezoelectric materials have led to their widespread application in miniaturized devices for both energy harvesting and sensing purposes. Among these innovations, piezoelectric nanogenerators (PENGs) are emerging as a reliable energy solution which functions by utilizing ambient mechanical inputs- such as vibrations, pressure and motion- into electrical signals through intrinsic piezoelectric effect. These devices are gaining attention as sustainable alternatives to conventional energy storage systems, offering the advantage of clean energy generation PENGs are especially attractive for powering low-energy electronic systems, such as wearable technology, biomedical sensors, and remote environmental monitors. Compared to traditional batteries, they offer enhanced environmental

compatibility and long-term operability, making them ideal for integration into self-powered systems[7,10].

1.3.4.1. Working principle of PENGs

Piezoelectric nanogenerators (PENGs) generate electricity by utilizing the mechanical deformation of piezoelectric materials.

- Initially, in absence of mechanical input, the internal dipoles within the piezoelectric film remain randomly oriented, resulting in no electrical signal.
- When mechanical stress is introduced, the film undergoes deformation, aligning the dipoles and generating a polarization field. Due to the polarization effect, electrical charges are deposited on the electrode interfaces. As the charges accumulate, voltage is generated, prompting charge flow between the electrodes.
- After the external mechanical input is removed, the film restores its original structure integrity, causing the dipoles to relax and charges to flow in the opposite direction. This repetitive cycle of mechanical deformation and relaxation results in an alternating output voltage from the PENG.

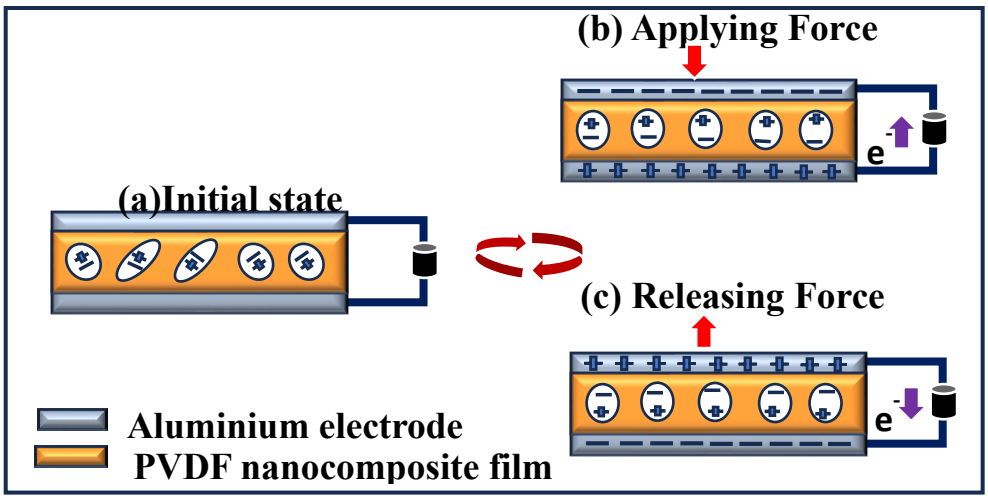

Figure 1.2.: Working mechanism of PENG.

1.3.4.2. Advantages of PENGs

PENGs serves as efficient transducers, converting mechanical movements-like pressure and movements, into electrical output.

- High energy harvesting efficiency: They enable reliable and continuous harvesting of ambient mechanical energy from the surrounding environment.
- Cost effective fabrication: PENGs can be produced using low-cost materials and simple fabrication processes, making them economically viable for large-scale deployment.
- Eco-friendly operation: Operating without external power sources, PENGs help reduce dependency on conventional batteries and minimize environmental impact.
- Suitability for self-powered systems: Their autonomous energy generation capability makes them ideal for use in portable, wearable, and remote sensing applications.

1.3.5. Material selection

Various inorganic materials such as lead zirconate titanate, barium titanate, lithium niobate have been extensively investigated for piezoelectric application due to their high piezoelectric coefficients and excellent energy conversion efficiencies. However, despite of their superior performance, these materials often suffer significant limitations, including brittleness, toxicity, poor flexibility, biocompatibility, which restrict their capability in emerging them as flexible and wearable energy harvesting devices. Thsese drawbacks have prompted a growing interest in alternative piezoelectric materials tahr are non-toxic, lightweight and flexible. In this context, polyvinylidene fluoride (PVDF), has garnered considerable attention as a promising candidate.

1.3.5.1. Polyvinylidene fluoride (PVDF)

Polyvinylidene fluoride (PVDF) and other piezoelectric polymers and copolymers offer potential for mechanical-to-electrical energy conversion applications owing to their elevated

piezoelectric coefficient, thermal and chemical durability, biocompatibility, and lightweight structure. In its semicrystalline form, this polymer frequently exhibits in several structural forms, including α, β, γ, and δ. The β-phase, characterized by the all-trans (TTTT) conformation, offers maximum piezoelectric response as a consequence of its higher dipole moment per unit volume, whereas the α-phase (TGTG conformation) is non-polar, while the γ-phase (T3GT3G conformation) has a weak piezoelectric coefficient. In comparison to PENGs constructed from inorganic piezoelectric materials, PENGs utilizing PVDF exhibit reduced electrical output efficiency. The electrical output characteristics of piezoelectric nanogenerators utilizing PVDF has been significantly enhanced through the application of thermal, mechanical, and electrical treatments, which effectively increases β-phase crystallization and stabilization in PVDF. Moreover, the β-phase of PVDF may be enhanced through the incorporation nanofillers into the PVDF matrix, resulting in a flexible nanocomposite that exhibits improved piezoelectric output without sacrificing flexibility. The appropriate selection of fillers and their uniform integration into PVDF not only facilitates the nucleation of β-crystals but also augments the dielectric characteristics by increasing electric dipoles through significant interfacial polarization. To improve the ferroelectric characteristics of PVDF, nanofillers such as ZnO, RGO, BaTiO3 and various 2D materials like hBN, MXenes and TMDs are often introduced, as they facilitate β-phase crystallization by disrupting PVDF's symmetry [14,15,16,17,27,28,29].

1.3.5.2 Two-dimensional materials

Two-dimensional (2D) layered non-centrosymmetric materials hold significant potential for electronic devices and nanoscale electromechanical systems. Recent research has increasingly focused on atomically thin two-dimensional materials due to their extraordinary and unconventional mechanical, optical, magnetic, and electrical capabilities. In 2D transition metal dichalcogenides (TMDs), the interlayer MX bonds are pivotal, unlike the sandwiched layers that are maintained by weak van der walls forces, allowing for facile cleavage at the layer surface. These TMDs are predominantly covalent compounds, commonly represented by formula MX_2, where M represents a transition meatal and X corresponds to a chalcogen atom. This has enabled the production of crystals with very tiny dimensions. Owing to their distinctive features- such as flexibility, optical transparency, mechanical stability, and biocompatibility- two dimensional materials are well suited for a wide range of advanced application. 2D materials are optimal for constructing energy harvesters such as PENGs. These

materials include graphene, TMDs (WS_2, MoS_2), h-BN, MXenes. 2D materials have properties like high surface area, tunable bandgap, flexibility, optical transparency, high thermal conductivity. 2D materials can be used in electronics, energy storage, optoelectronics, sensors, and in biomedical applications[30,31].

1.3.5.3. Tungsten disulphide (WS_2)

Tungsten disulphide (WS_2), a layered transition metal dichalcogenide (TMDC), has emerged as a multifunctional material due to its outstanding optical, electrical, and mechanical characteristics, which have enabled its integration into diverse fields such as optoelectronics, energy storage, and sensing. Its unique combination of a thickness-dependent bandgap, superior electron mobility, high surface area, flexibility, and transparency makes it particularly ideal for incorporation in flexible and wearable devices. Notably, WS_2 exhibits a high piezoelectric coefficient, which further strengthens its candidacy for use in energy harvesting systems and next-generation piezoelectric nanogenerators. WS_2 is also recognized for its potential in solar energy harvesting, attributed to its narrow bandgap, strong W-S bonding, and favourable electronic configuration, including a valence band with low electronegativity and a cationic conduction band capable of high reduction activity. The environmental stability and non-toxic of WS_2 further underscore its value in sustainable technologies. Additionally, its non-centrosymmetric crystal structure enhances its electrochemical performance and broadens its applicability in next-generation electronic systems. [32,33,34,35].

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

Tungsten disulphide, Lithium bromide, Hexane and PVDF powder were acquired from Sigma Aldrich, whereas N,N-Dimethylformamide (DMF) was obtained from Fisher. All the reagents were directly used without additional refinement or purification.

2.2. Exfoliation of WS_2 nanosheets:

To synthesize WS_2 nanosheets, 1 gram of tungsten (IV) sulphide was incorporated into a combination of lithium bromide and hexane, maintaining a molar ratio of 1:2. The mixture was exposed to ultrasonic agitation for 5 hours. Following sonication, the solution darkened, ensuring exfoliation. To facilitate separation, the solution was processed via centrifugation at 6000 rpm for 45 minutes. The resulting sample was then washed many times with DMF to eliminate any residual lithium bromide or hexane. After processing, the sample underwent oven drying at 90°C to yield WS_2 nanosheets powder. The synthesis process of WS_2 nanosheets is shown in figure 2.1.

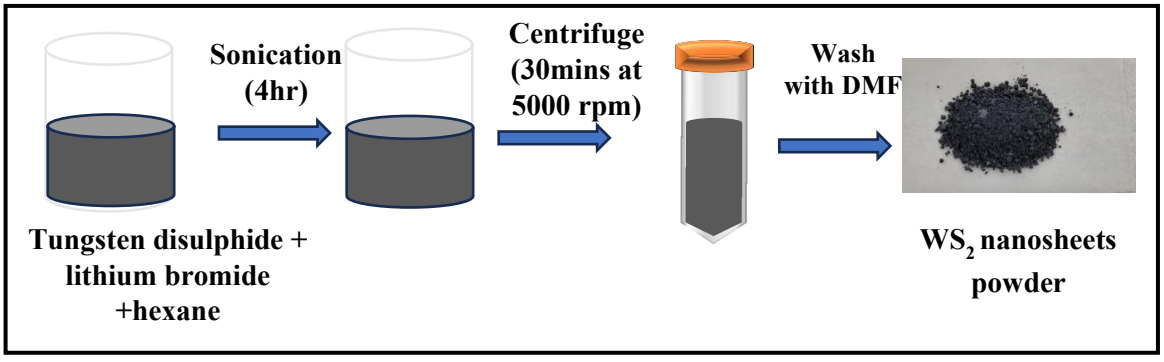

Figure 2.1.: Schematic illustration of synthesis of WS_2 nanosheets.

2.3. Synthesis pf PVDF/WS_2 nanocomposite thin films:

The process of nanocomposite films fabrication includes mixing of 1g of PVDF powder with 10 ml of DMF and agitated until a homogenous mixture was achieved. Subsequently, exfoliated WS_2 nanosheets were added into the PVDF solution at different weight percentages (1%, 2%, 3% and 5%). The solutions were sonicated for about an hour to ensure uniform distribution of nanosheets. Subsequently, each solution was drop-casted onto pristine glass slides and subsequently exposed to thermal treatment at 80°C in an oven for a duration of 2 hours to facilitate drying. Upon cooling, the thin films were carefully peeled off from the substrate using deionised water. Pure PVDF films were fabricated using the same method, except the addition of WS_2 nanosheets. The synthesis process is illustrated in figure 2.2. These were subsequently used for the fabrication of piezoelectric nanogenerators.

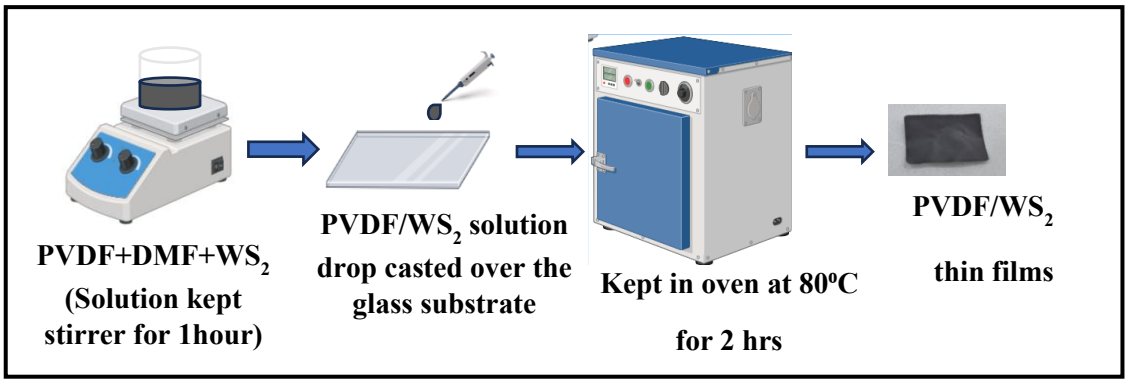

Figure 2.2.: Diagrammatic representation of the synthesis process for PVDF and PVDF/WS_2 films.

2.4. Characterization and electrical measurements:

To analyse the exfoliated WS_2 nanosheets, XRD (Bruker D8 Advance with Cu Kα X-ray source, 3.0 KW) was utilized for structural identification and SEM (JEOL Japan Model: JSM 6610LV) for evaluating surface morphology. PVDF/WS_2 thin films were characterized using XRD for phase determination, while Fourier Transform Infrared (Nicolet iS50 FTIR Tri-detector) spectrometer for investigating chemical bond structures and functional group distributions. An electrodynamic shaker (Micron MEV-0025) was employed to induce mechanical deformations in the piezoelectric devices, where parameters such as tapping frequency were varied to test the device performance. The electrical response was assessed by

measuring open-circuit voltage with an oscilloscope (Tektronix MD034) and short-circuit current using an electrometer (Keysight B2985B).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Crystallographic analysis of WS_2 nanosheets

XRD analysis of exfoliated WS_2 nanosheets is illustrated in figure 3.1. In the XRD spectra peaks at 2θ 14.86°, 29.43°, 44.58°, and 60.46°, are attributed to the (002), (004), (100) and (006) planes, respectively indicative of a hexagonal crystalline phase consistent with JCPDS card no. 08-0237. The (002) peak exhibits significantly greater intensity than the others, indicating a strong preferred orientation along its crystallographic plane during exfoliation. This strong peak suggests the well-defined crystalline nature of the WS_2 nanosheets[21].

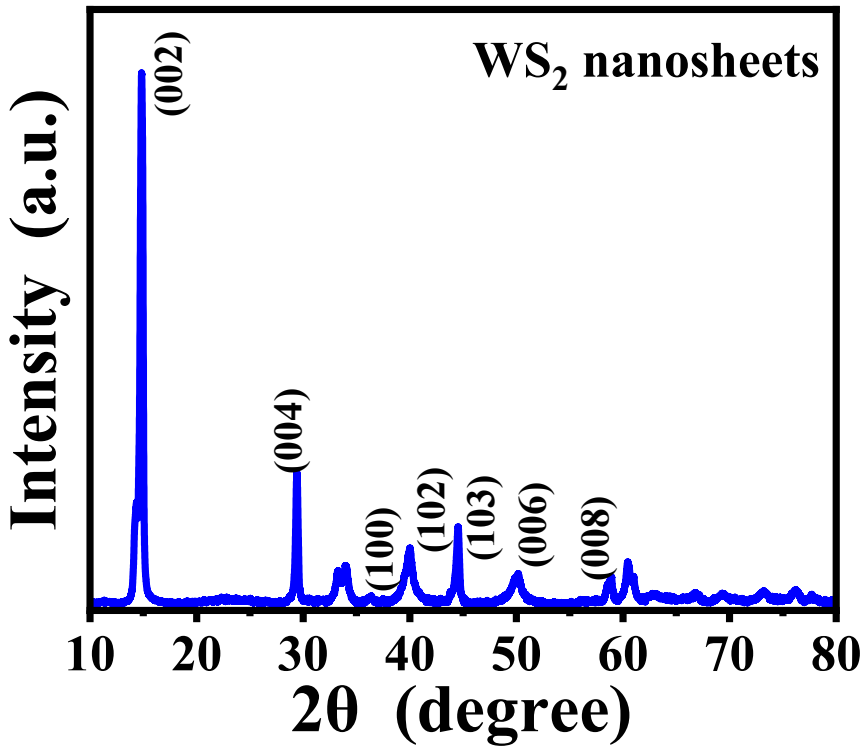

Figure 3.1: Crystallographic analysis of WS_2 nanosheets via XRD.

3.2. Morphological configuration of WS_2

The surface morphology of WS_2 samples was characterized using SEM. The SEM micrograph of WS_2 is illustrated in figure 3.2 demonstrated that the sample exhibits thin sheet structure which are well dispersed without any aggregation.

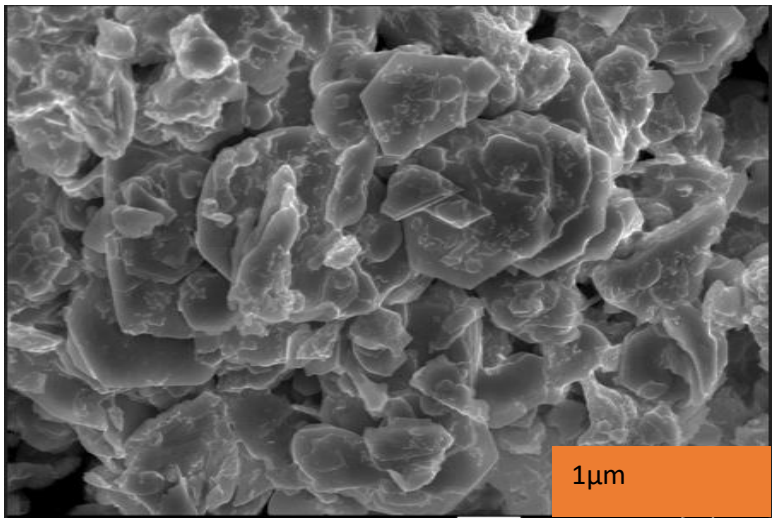

Figure 3.2.: SEM image of WS_2 nanosheets.

3.3. XRD of thin films

The crystallinity and phase evolution of PVDF and PVDF/WS_2 nanocomposite films were characterized through XRD analysis. Figure 3.3 displays the XRD pattern of PVDF and its nanocomposite films, where the peak associated with PVDF are indicated by * in the XRD pattern, while WS_2 -associated peaks are marked by #. The XRD spectra of pure PVDF film exhibits two characteristic peaks, the peak at 18.66° corresponding to (020) plane is attributed to non-polar α-phase, while the second peak at 20.32° corresponding to (110) plane is associated with polar β-phase of PVDF. While, PVDF/WS_2 nanocomposite films exhibits additional peak at 14.86°, which is identical to bare WS_2, which demonstrates that PVDF/WS_2 nanocomposite films were successfully synthesized without affecting the crystallinity of WS_2.

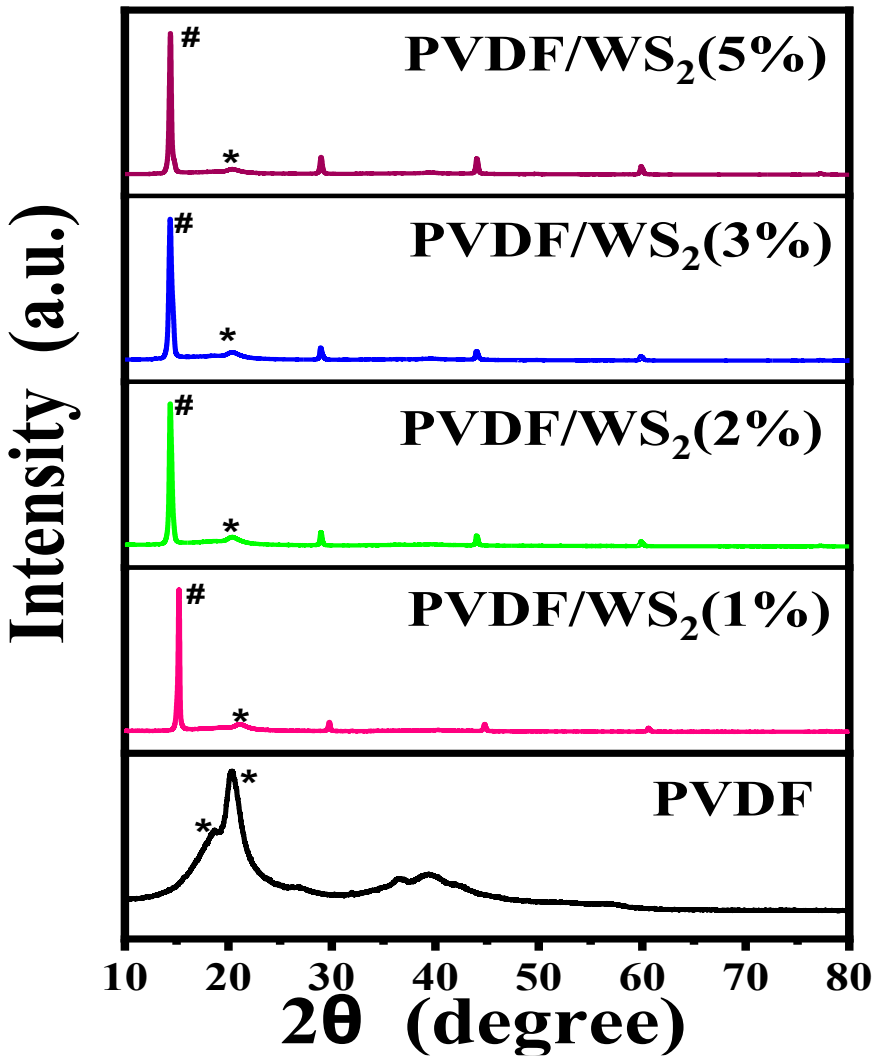

Figure 3.3.: *XRD analysis for PVDF and PVDF/WS_2 nanocomposite films.*

3.4. FTIR of thin films

Further, figure 3.4 presents the FTIR spectra of PVDF and PVDF/WS_2 nanocomposite films, revealing characteristics absorption peaks corresponding to α and β phases of PVDF [38,39]. The β-phase fraction can be calculated using Lambert-Beer law-based equation, which is related to characteristic IR absorbance peaks to phase content, given by the following mathematical expression:

$$F(\beta) = \frac{A\beta}{\left(\frac{K\beta}{K\alpha}\right)A\alpha + A\beta} \times 100\% \qquad [39]$$

In this equation, the absorption coefficients K_α and K_β corresponds to 6.1×10^4 cm^2/mol and 7.7×10^4 cm^2/mol at wavenumbers 762 cm^{-1} and 840 cm^{-1} respectively. The absorbance values at these wavenumbers are represented by A_α and A_β respectively [40]**.** Analysis indicates that the pure PVDF exhibits approximately 64% β-phase, whereas the fraction of electroactive β phase increases to 86% for PVDF/WS_2 nanocomposite films. The results show that, incorporation of 2 wt % WS_2 results in highest β-phase content of 86%, suggesting that WS_2 nanosheets effectively enhance development of β-phase crystallization in PVDF.

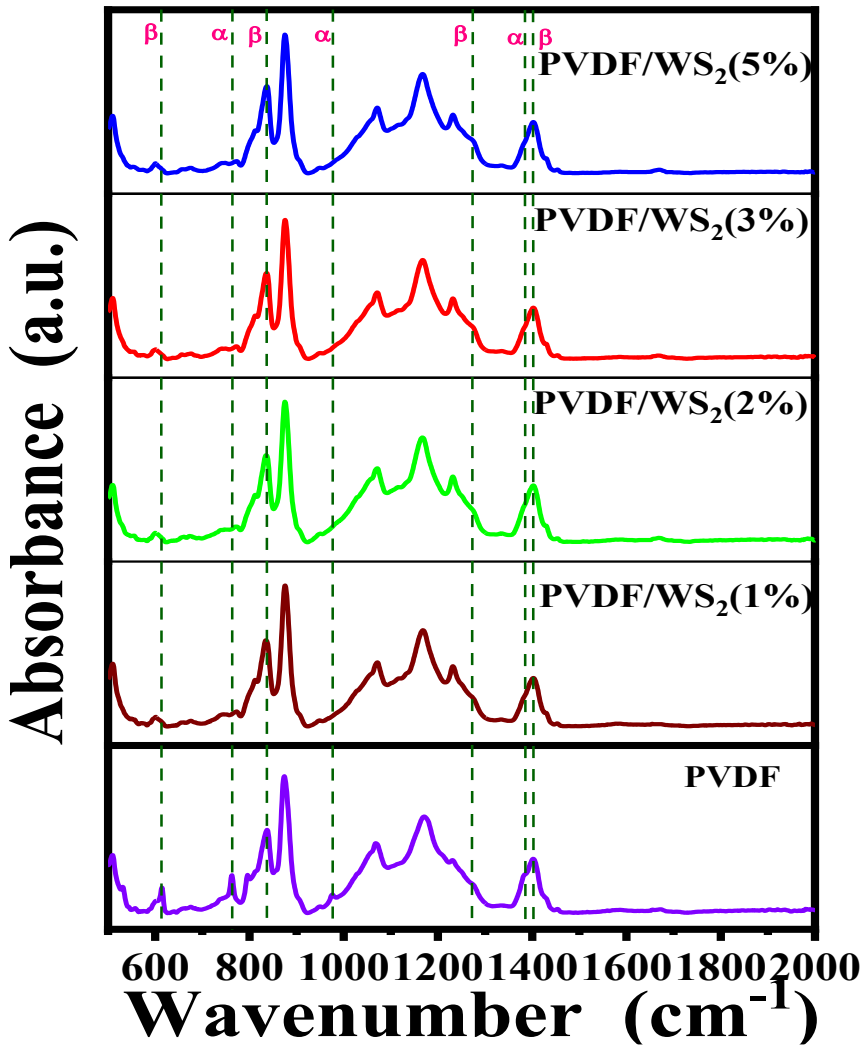

Figure 3.4.: FTIR analysis for PVDF and PVDF/WS_2 nanocomposite films.

3.5. Electrical performance of fabricated Piezoelectric Nanogenerator

For the evaluation of the piezoelectric behaviour of nanocomposite films, a nanogenerator device was constructed by making electrodes onto both surfaces of the films. Each film was initially trimmed into dimensions of 2x1 cm^2 and thereafter, aluminium tape is attached on both sides of the films for the fabrication of PENG devices. Finally, the copper wires were drawn from the electrodes for making necessary electrical connections, and the entire device was encapsulated using Kapton tape for insulation. Thereafter, the piezo response of the fabricated PENGs, was assessed by continuously tapping the device using an electrodynamic shaker unit. Figure 3.5 and 3.6 displays the electrical output characteristics, specifically the generated open-circuit voltage and short-circuit current for nanogenerators based on PVDF and PVDF/WS_2 nanocomposite films. The results indicate that the incorporation of WS_2 significantly produces higher voltage than pure PVDF-based nanogenerators. PVDF film generates only 8 V whereas, the nanocomposites films with filler concentration of 1%, 2%, 3% and 5% executed the output voltage of 11.8V, 19.6V, 14.8V and 8.6V respectively. The output voltage from PVDF/WS_2 device initially increases with increase in WS_2 filler concentration, but its value start decreasing after 2% of filler concentration. The device with 2wt% filler concentration yields the maximum open-circuit output voltage of 19.6 V. The results demonstrate that the device with a 2% filler concentration exhibits optimal performance, as confirmed by the XRD and FTIR analysis. Similar results have been obtained for the current measurements as well, PVDF/WS_2 film with 2% filler concentration can generate highest peak-to-peak short circuit current of 11.03 μA, while bare PVDF film-based PENG can generate only 3μA current. Table 1 presents a concise summary of the β-phase content and the corresponding electrical output values for each composition.

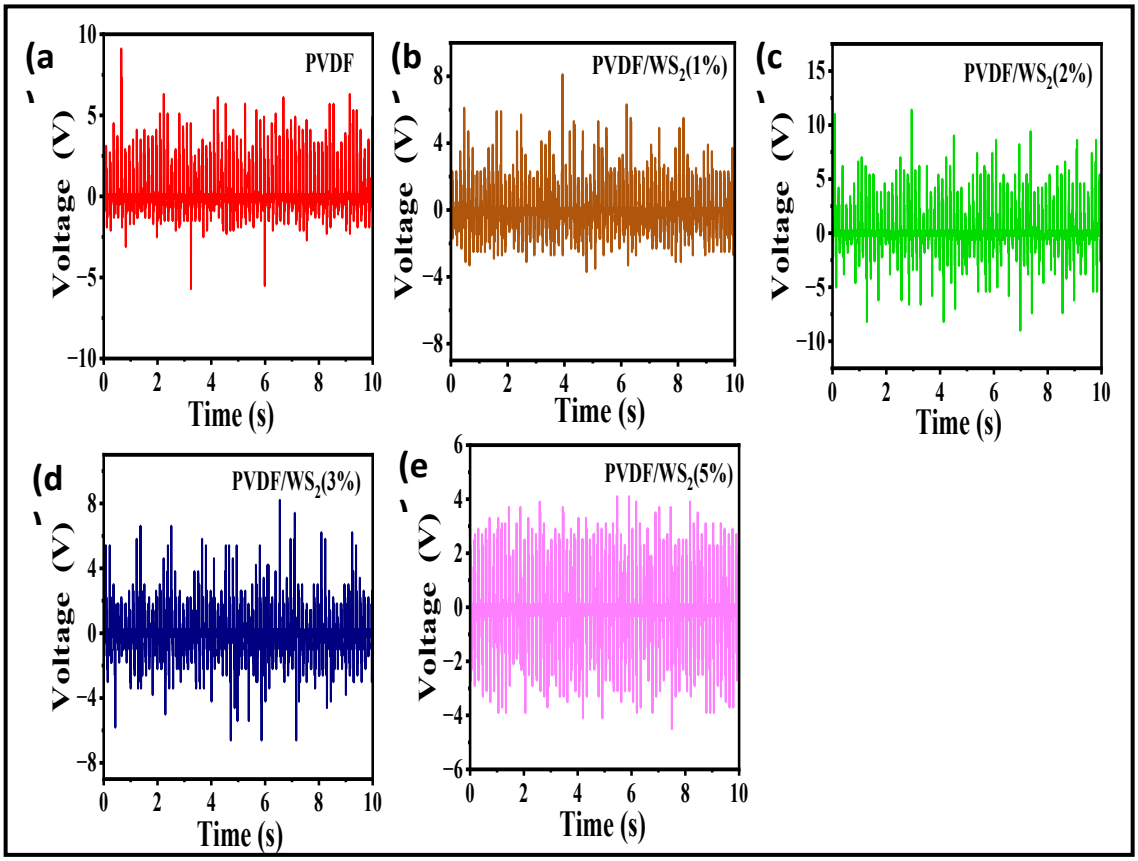

Figure 3.5.: Voltage measurement outputs (a) PVDF, (b-e) PVDF/WS_2 nanocomposites containing 1%, 2%, 3% and 5% of WS_2 respectively.

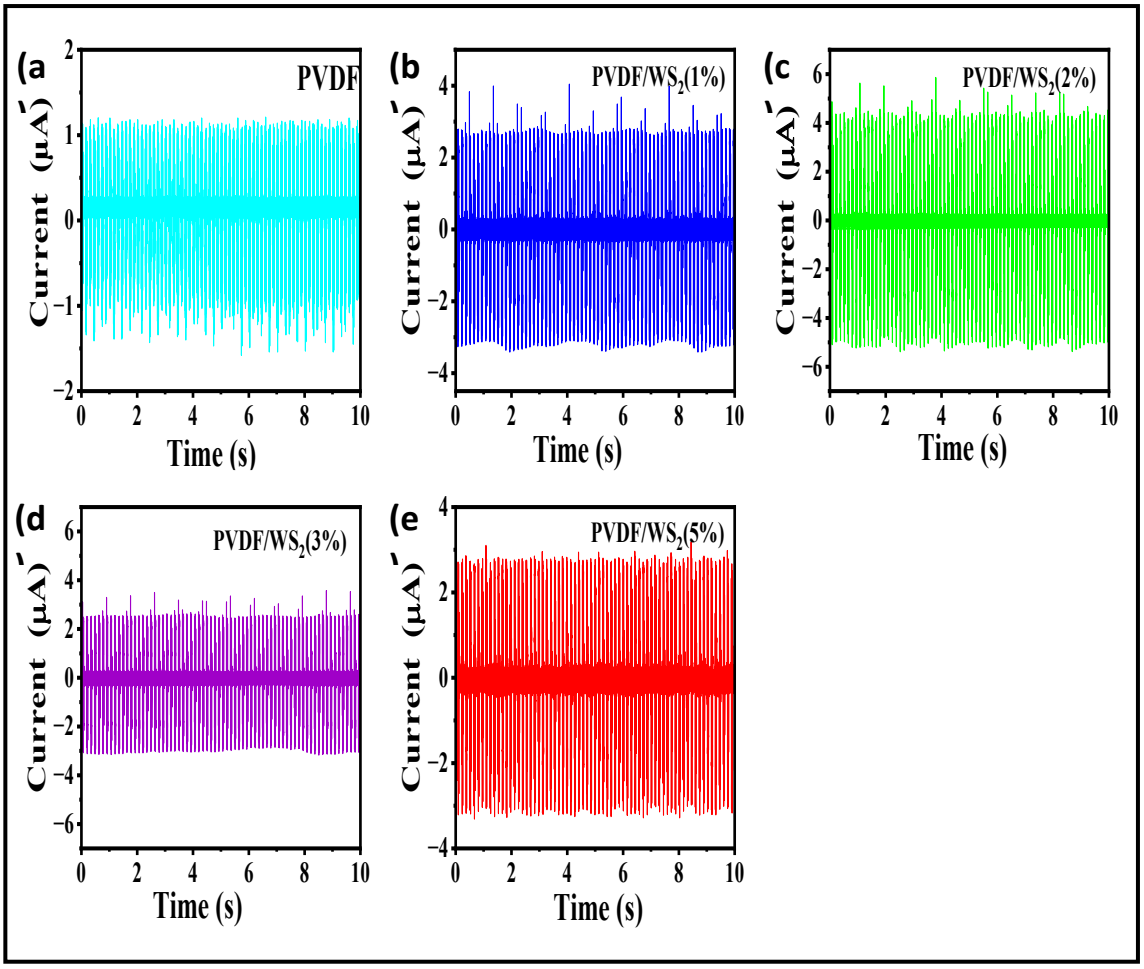

Figure 3.6.: Current measurement outputs (a) PVDF, (b-e) PVDF/WS_2 nanocomposites containing 1%, 2%, 3% and 5% of WS_2 respectively.

Table 1: **Calculated β-phase content, open circuit voltage (V_{OC}) and short circuit current (I_{SC}) for fabricated nanogenerators at a tapping frequency of 7 Hz.**

S No.	Sample	β-phase (in %)	V_{OC} (in V)	I_{SC} (in μA)
1.	PVDF	64	8	3
2.	1 wt%	82	11.8	7.28
3.	**2 wt%**	**86**	**19.6**	**11.03**
4.	3 wt %	84	14.8	6.52
5.	5 wt%	81.9	8.6	6.1

3.6. Applications

Furthermore, to validate the real-world applicability of the fabricated PENG devices, the capability to harvest mechanical energy was examined through various human motions. These

tests aim to demonstrate the functional performance of the nanogenerator under low-frequency, low-force stimuli that are typically encountered in daily activities. In the present study, controlled tapping motions, including finger tapping and thumb tapping, were performed manually to stimulate realistic inputs. As shown in figure 8, the electrical response of the PVDF/WS_2 (2 wt%) nanocomposite-based device under these stimuli indicates promising energy harvesting characteristics.

An open-circuit voltage 2.54V was observed from the PENG device when subjected to single-finger tapping as shown in figure 8(a). A more forceful thumb motion yielded a higher voltage output of 3.78 V, as illustrated in figure 8(b). These results demonstrate the device's high sensitivity and its effective conversion of mechanical deformations into electrical. The enhanced output is primarily due to the optimal dispersions of WS_2 within the PVDF matrix at 2 wt% concentration, which stimulates the formation of β-phase and facilitating efficient mechanical-to-electrical energy conversion.

Along with, voltage generation, the practical utility of the device was further demonstrated through a visual experiment involving the illumination of commercial light-emitting diodes (LEDs). The circuit configuration used for this demonstration is shown in figure 8(c). Upon mechanical actuation using an electrodynamic shaker, the stored energy from the PENG was successfully utilized to power LEDs, as illustrated in figure 8(d). This validates the device's potential to serve as a practical energy source for low-power electronic devices.

These findings reinforce the potential of PVDF/WS_2 nanocomposite-based PENGs for integration into self-powered electronic systems. The ability to harvest and convert mechanical energy, such as simple human motions, into useful electrical energy highlights their suitability for wearable electronics, portable sensors, and next generation energy-autonomous devices. Moreover, the simplicity of the device architecture and cost-effective fabrication process makes it a viable candidate for scalable energy harvesting solutions.

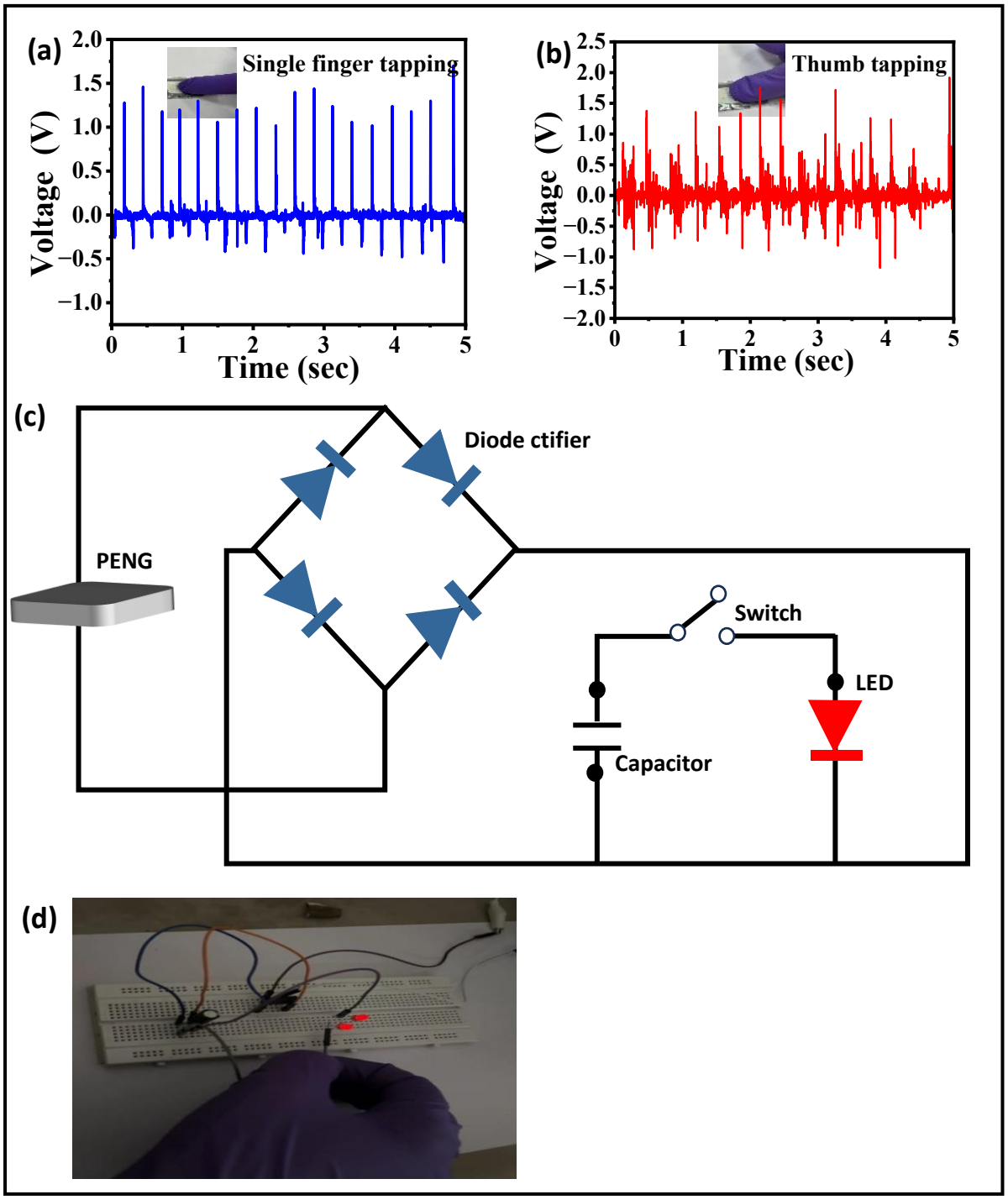

Figure 3.7.: Voltage measurements (a)single finger tapping, (b) thumb tapping; and (c) schematic circuit diagram, (d) image of lightning LED using PENG.

CHAPTER 4

CONCLUSIONS AND FUTURE SCOPE

4.1. Conclusions

PVDF, PVDF/WS_2 flexible thin films with varying filler contents (0%, 1%, 2%, 3% and 5%) have been synthesised, and their piezoelectric responses have been examined. The PENG device incorporating 2 wt% WS_2 exhibited superior performance, producing a voltage output of 19.6 V and a corresponding current of 11.03 μA. The enhanced piezoelectric output performance is ascribed to WS_2 influence in the alignment of β-phase dipoles in PVDF. The incorporation of WS_2 provides a conductive pathway that facilitate charge transport within the films, hence enabling the alignment PVDF dipoles and enhancing the overall piezo response. Finally, the potential application of the PVDF/WS_2 film (with 2% filler concentration) based PENG device was demonstrated by harvesting energy from human actions like single finger tapping and thumb tapping. The PENG device with 2 wt% WS_2 content exhibited superior performance, characterized by measured voltage of 19.6 V and a corresponding current of 11.03 μA. The generated voltage was also used to power LED, thereby demonstrating the real time application of fabricated nanogenerator.

4.2. Future scope

Although PVDF and its copolymers are widely regarded as viable materials for the development of flexible piezoelectric nanogenerators, further optimization is essential to bridge the gap between laboratory-scale performance and real-world application. This research seeks to enhance the operational capabilities of PVDF-based PENGs through a deeper understanding of their structural and material properties. Key design parameters -including output power. Operational reliability, cost efficiency, and fabrication simplicity- must be met to enable widespread adoption. Ongoing advancements in material selection, architectural innovation, and processing methods are likely to yield high performance flexible PENGs, thereby facilitating the commercial realization of technologies in areas such as mechanical energy conversion and autonomous, self- powered devices.

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APPENDIX

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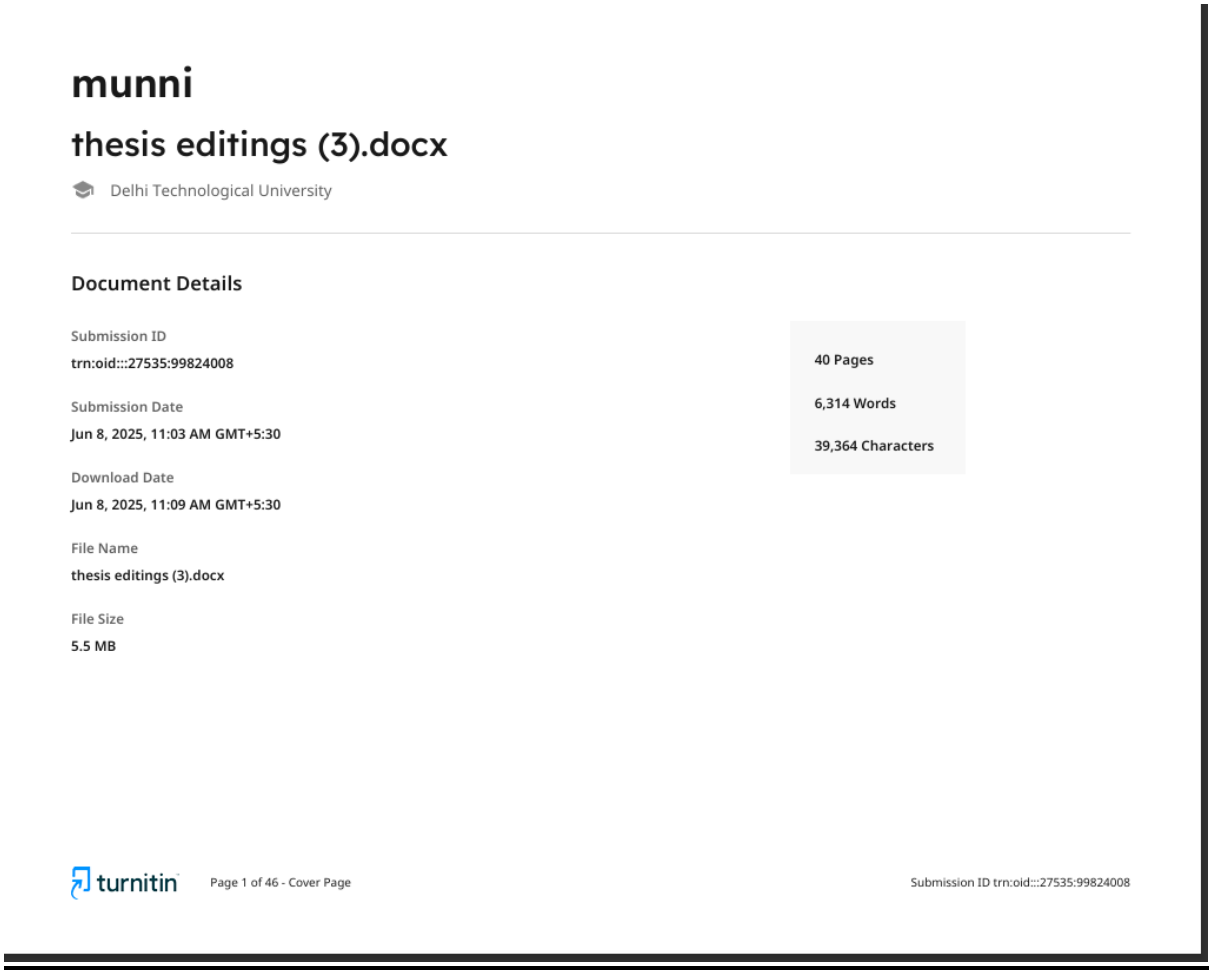

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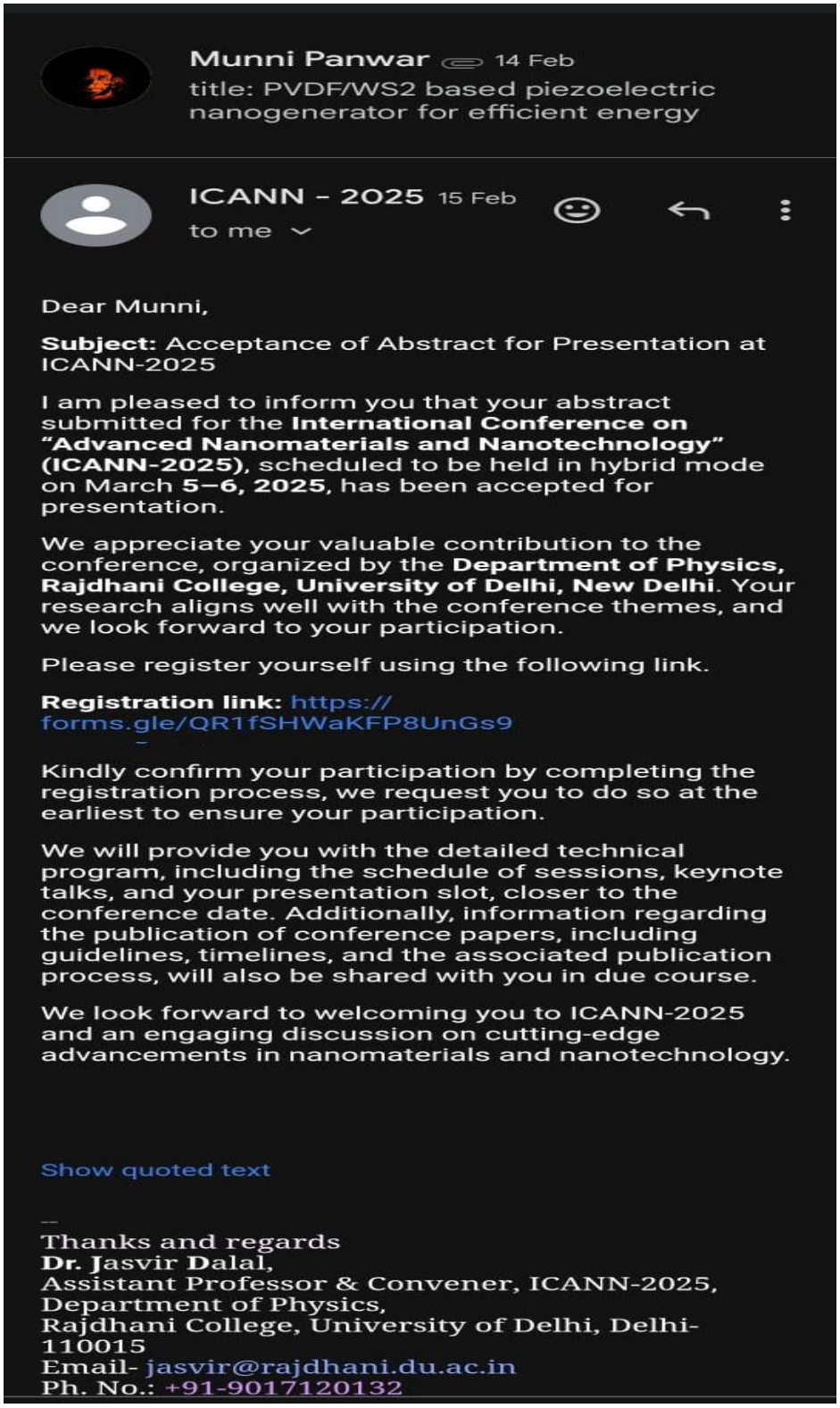

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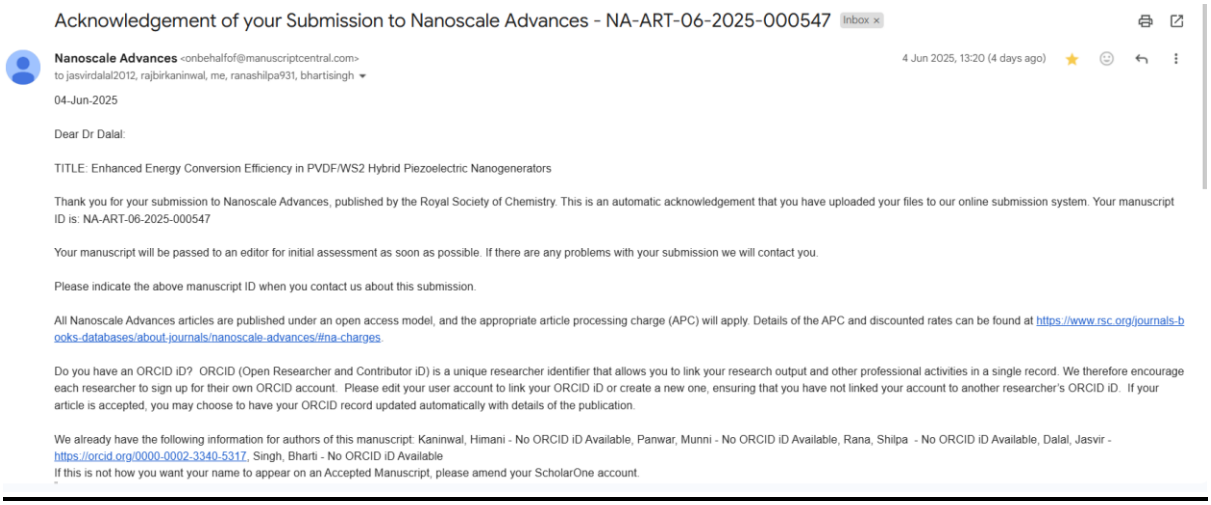

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SUBMITTED PAPER

Enhanced Energy Conversion Efficiency in PVDF/WS_2 Hybrid Piezoelectric Nanogenerators

Munni[a], Himani[a], Shilpa Rana[a], Jasvir Dalal [b,1], Bharti Singh [a,*]

[a] *Department of Applied Physics, Delhi Technological University, Main Bawana Road, Delhi, 110042, India*

[b] *Department of Physics, Rajdhani College, Delhi University, Delhi-110015, India*

Abstract:

Energy harvesting from ambient sources, particularly human motion is gaining considerable interest because of its potential to efficiently convert environmental mechanical energy into usable electrical power. Ongoing research is exploring piezoelectric nanogenerators (PENGs) as a means to convert vibrational mechanical energy into functional electrical output. Here in, we report the fabrication of PENG based on PVDF/WS_2 nanocomposite thin films. WS_2 nanosheets are synthesized by exfoliation method. Further, WS_2 with different weight percentages was incorporated in PVDF and the resulting thin films are analysed using XRD and FTIR. The output of nanogenerator is finally examined, determining the maximum output voltage (V_{OC}) without an external load and the maximum current (I_{SC}) when the output terminals were shorted. The results indicate that the incorporation of WS_2 nanosheets led to enhanced output of piezoelectric nanogenerator, exhibiting an elevated voltage of 19.6 V and a peak current of 11.03 μA corresponding to 2 wt% filler concentration of WS_2 and shows significant potential for renewable energy conversion and self-sustaining electronic devices.

[1] Corresponding Authors Email: jasvirdalal2012@gmail.com (J. Dalal), and bhartisingh@dtu.ac.in (B. Singh)