Systematic Investigation of the Effect of SnS_2 nanofiller content on the piezoelectric performance of the PVDF-TrFE-based Nanogenerator

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE

OF

MASTER OF SCIENCE

IN

PHYSICS

Submitted by:

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MAY,2023

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We Harshvardhan and Palkin Yadav, Roll No(s). 2K21/MSCPHY/20 and 2K21/MSCPHY/36 student(s) of M.Sc. (Physics), hereby declare that the project Dissertation titled "Systematic Investigation of the effect of SnS_2 nanofiller content on the piezoelectric performance of the PVDF-TrFE-based nanogenerator" which is submitted by us to the Department of Applied Physics. Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master's in Physics is original and not copied from any source without proper citation. This work has not previously formed the basis for awarding any Degree, Diploma Associateship, Fellowship, or other similar title or recognition. This work has been published in SCI/SCI expanded/SSCI/Scopus journal OR peer-reviewed Scopus indexed journal with the following details:

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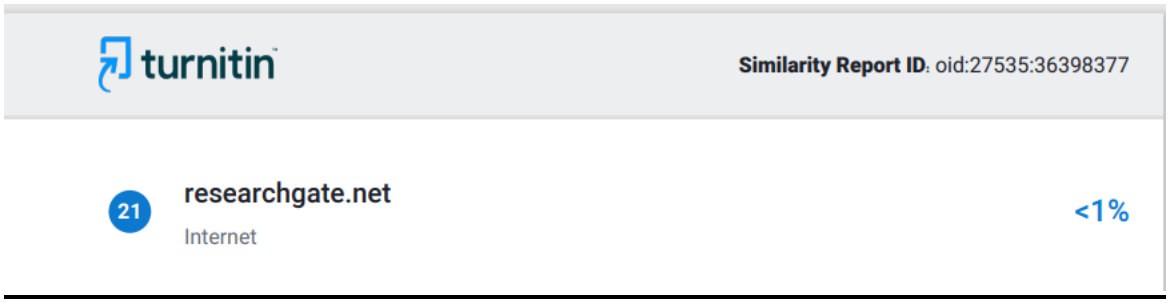
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ABSTRACT

In this work, SnS_2 is used as a nanofiller material to improve the response of the polymer-based piezoelectric nanogenerator because of its better inherent piezoelectric properties in comparison to other 2D materials. For this, first, nanoflakes of tin sulfide (SnS_2) were synthesized via the hydrothermal method, where the high purity of SnS_2 powder is confirmed by Raman spectroscopy and X-ray diffraction studies. The obtained powder of SnS_2 was then mixed with PVDF-TrFE in different weight percentages (0%, 1%, 3%, 5%, and 7%) of SnS_2 to synthesize polymer composite film via the drop-casting method. These films are then characterized with XRD and FTIR spectrometers, which show enhancement in the electroactive beta phase of the nanocomposite films after doping with SnS_2 powder, from 58.30% to 93.07%, which is in agreement with the polarization versus electric field (P-E) measurements that show increased remnant polarization after doping. These films are then used to fabricate a piezoelectric nanogenerator by adhering aluminum tape to both sides of the films. The piezoelectric nanogenerator's (PENG) output performance is analyzed by measuring the open-circuit voltage (V_{oc}) and short-circuits (I_{sc}) by tapping the nanogenerator with the help of a dynamic shaker, which shows that the output performance of Trifluoroethylene (PVDF-TrFE) based PENGs gets enhanced after the introduction of SnS_2 powder. The maximum piezoelectric voltage corresponding to the PENG made with 5% SnS_2 was 14.4 V, which was almost 1.5 times that of the PENG made with bare PVDF-TrFE. The output piezoelectric current followed a similar trend, with the 5% SnS_2 PENG producing 3.9μA of current, which was roughly 1.62 times more than the output of the bare PVDF-TrFE thin film. As a result, the present study demonstrates that adding SnS_2 to the PVDF matrix can significantly improve energy harvesting technologies based on PVDF's piezoelectric properties.

GRAPHICAL ABSTRACT

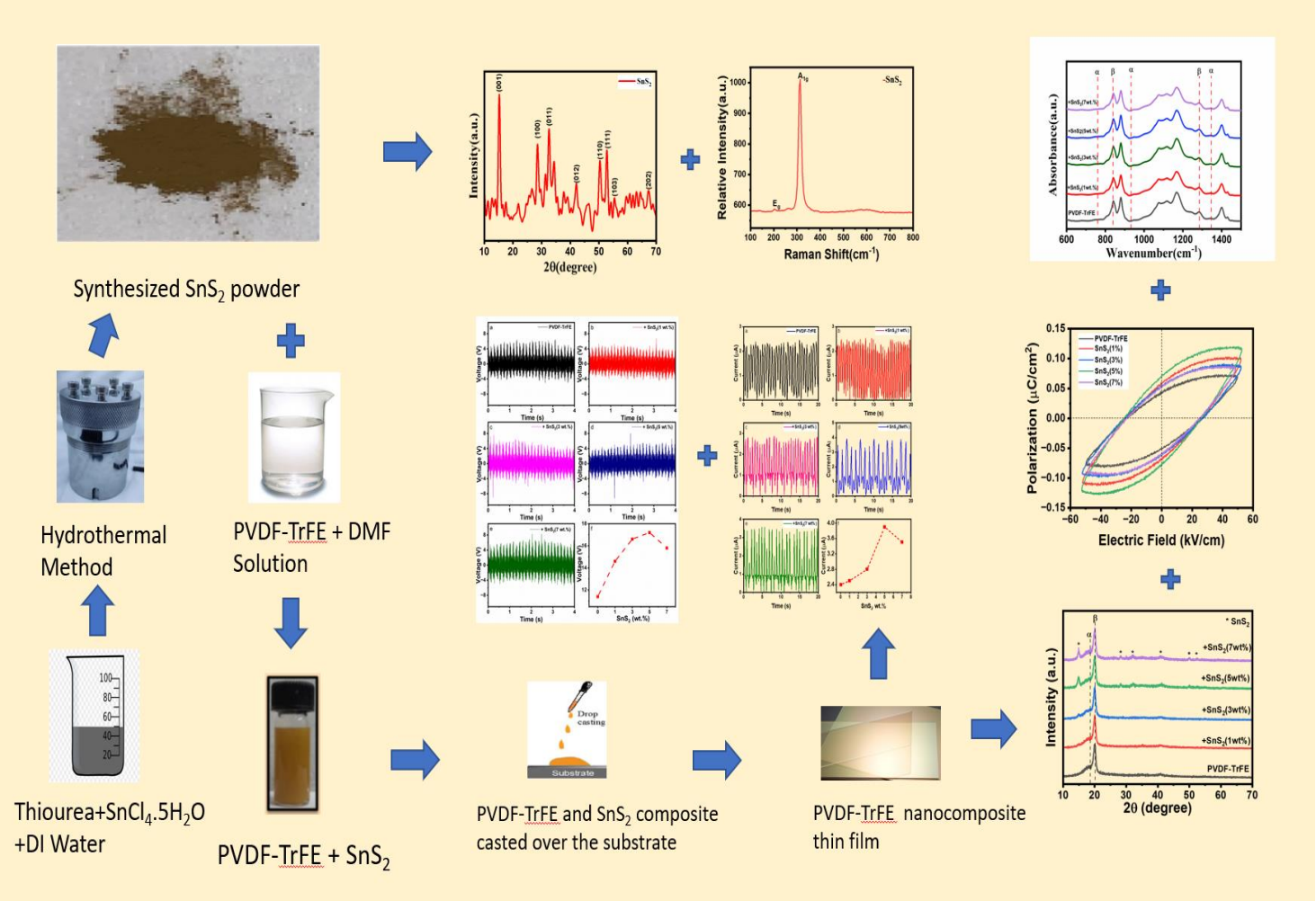

FIGURE 1.A Graphical Abstract

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LIST OF SYMBOLS AND ABBREVIATIONS

NMs	Nano-materials
NPs	Nano-particles
2D	2 Dimensional
PVDF	Polyvinyl fluoride
DI Water	Deionised Water
SnS_2	Tin Disulphide
2D SnS_2	Two-dimensional Tin(IV) Sulphide
XRD	X-ray Diffractometer
PENGs	Piezoelectric Nanogenerators
TMDs	Transition Metal Dichalcogenides

CHAPTER 1

1. INTRODUCTION AND OBJECTIVES

1.1 INTRODUCTION

The growing tempo of technological know-how and generation is often the result of human improvements and creativity. Those improvements added us to the concept of nanotechnology. Knowledge and reading substances at dimensions between 1 and a hundred nm is known as nanotechnology. Modern-day nanotechnology is credited to Richard Feynman, a physics Nobel Prize winner in 1965. He delivered a talk titled "There's Plenty of Room at the Bottom" during the 1959 American Physical Society meeting held at Caltech when he first discussed the idea of influencing matter at the atomic level [1]. Norio Taniguchi, a researcher at the University of Tokyo, coined the word "nanotechnology" in 1974 to describe the capacity to accurately manufacture materials at the nanoscale scale [2].

Nanotechnology has developed into the basis for amazing industrial applications and exponential growth in a period of about 50 years [2]. Nanoparticles can have unusually high surface areas due to their unique design. Exceptional magnetic, electrical, optical, mechanical, and catalytic properties can be achieved in nanostructures, which are very different from their bulk counterparts in these respects. By carefully regulating the size, shape, synthesis conditions, and appropriate functionalization, the properties of nanomaterials can be tailored to meet specific needs [3].

1.2 LITERATURE REVIEW

1.2.1 Nanoparticles and Nanotechnology

Nanotechnology consists of the fabrication of nanostructures, the usage of nanocomposites, and the utility of all of the experimental approaches at atomic to submicron scales in physical, chemical, and biological fields. This take a look at entails a vast spectrum of engineering physics, fabric technology, and production. It creates an impact on our surrounding and economy in this modern era and is comparable to that of semiconducting material technology, mobile and molecular biology, or statistics technology inside the previous century. Each detail of our lives has been stepped forward because of nanotechnology, which has revolutionized the way that commercial problems in fields like feasible materials, manufacturing of nanocomposite, electronics gadgets, drug supply, electricity and water, biotech, records techniques, and countrywide protection have been addressed. Our economy and society will be significantly impacted by nanotechnology; it is a modern industrial revolution [4]. So, researchers and scientists are more interested in targeting the fabrication of 2D materials.

1.2.2 Nanoparticle Synthesis Techniques

Numerous methods can be used to synthesize nanoparticles. Both dry particles and nanoparticles can be produced using these techniques, where they are dispersed either in a gaseous or liquid medium. By starting with atoms or by reducing the size of microparticles to nanoparticles, nanostructures can be created [5].

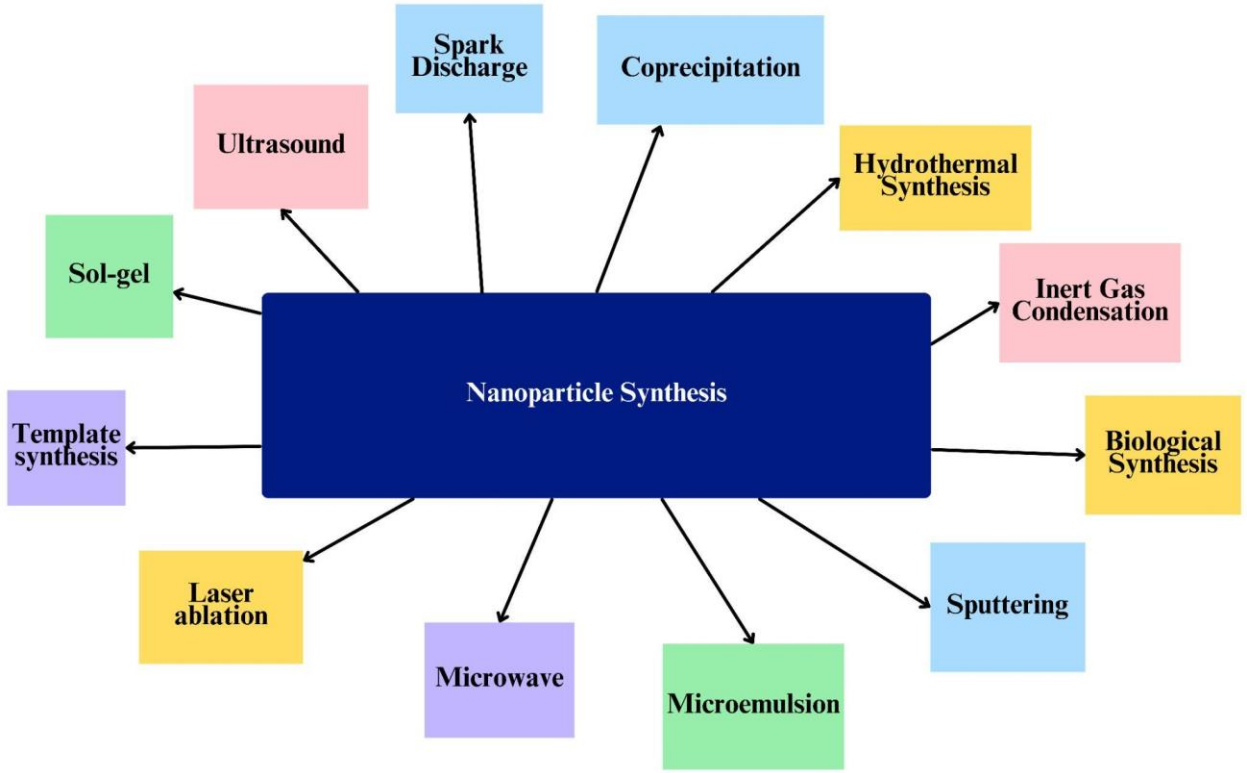


Figure 1.1. Nanoparticle Synthesis Techniques

1.2.2.1 Coprecipitation

Coprecipitation reactions occur when nucleation, growth, coarsening, and/or agglomeration activities take place at the same time [6].

1.2.2.2 Hydrothermal Synthesis

For the production of solids like microporous crystals, superionic conducting solids, complicated oxides, ceramics, and fluorides, the hydrothermal process is frequently used. It is also used for the preparation of magnetic materials and luminescence phosphors. Additionally, it provides access to novel condensed materials, including stacking sequence material. This also enables the production of nanoscale particles, thin films, and characteristic helical and chiral structures.

The term "hydrothermal synthesis" describes the process of creating chemicals by chemical reactions in a sealed, heated solution that is above the surrounding pressure and temperature [7].

1.2.2.3 Inert Gas Condensation (IGC)

IGC is a technique utilized to create a majority of metal nanoparticles.In IGC (Ion Gas Collisions), a high-pressure chamber filled with helium or argon in an ultrahigh vacuum environment is utilized to vaporize metals. When the metal atoms evaporate, they lose their kinetic energy and subsequently condense into smaller particles upon collision with the gas.. These particles then grow by Brownian coagulation and coalescence and finally form nanocrystals [8].

1.2.2.4 Sputtering

During the sputtering process, high-energy particles bombard the outermost layer of a material (the target), causing atoms to be emitted. Ions bombard the cathode or target, resulting in a momentum transfer process called sputtering. The sputtered atoms then impinge on a substrate, where they separate and form the desired layer [9].

1.2.2.5 Microemulsion

While microemulsions are employed in the synthesis of inorganic nanoparticles, the mechanism underlying nanoparticle formation within microemulsions remains incompletely comprehended. However, some scientists have proposed a mechanism for the creation of nanoparticles by the microemulsion technique.

The reactant-containing microemulsion fabric is mixed, causing the exchange of reactants to happen when water droplets collide within the microemulsion. The rapid exchange of reactants

leads to a precipitation reaction occurring inside the nanodroplets. This precipitation reaction is followed by the nucleation growth and coagulation of primary particles, which produces the final nanoparticles that are stabilized by surfactants and/or are surrounded by water [10].

1.2.2.6 Microwave

Popular applications of microwave-aided synthesis include nanotechnology and biological processes. Chemical reactions frequently occur more quickly than conventional convection heating techniques, with higher growth and minimum byproducts. Microwave reactors provide precise control over reactions, maintaining stable temperatures, pressures, and reproducibility across numerous reactions. These reactors utilize efficient engineering to separate the nucleation and growth stages during the synthesis of nanomaterials, even when the reaction commences at room temperature. The application of microwave-assisted heating enables the potential for selective activation of precursor materials for nanomaterials, thus aiding in scaling processes. For the creation of nanomaterials, microwave synthesis has the ability to selectively heat either the solvent or the precursor molecules [11].

1.2.2.7 Laser Ablation

When a laser beam interacts with a solid or liquid surface, it can result in the expulsion of materials from the surface. When a laser beam interacts with a surface, it generates heat, leading to the sublimation or evaporation of the surface material, especially at lower laser flux levels. In contrast, at higher laser flux levels, the material typically undergoes a transformation into plasma. The term "laser ablation" typically refers to the removal of material using a pulsed laser, although if the laser intensity is strong enough, it is also possible to ablate material using a continuous wave laser beam [12].

1.2.2.8 Sol-Gel

The sol-gel process is a technique employed for fabricating solid materials through the utilization of small molecules. During this chemical reaction, the sol (or solution) undergoes a transformation, transitioning into a biphasic system that resembles a gel. This system consists of a liquid phase and a solid phase, which can display diverse morphologies, ranging from individual particles to interconnected polymer networks. Precipitation can provide homogeneous and finely grounded ceramic powders. These nanoscale-sized powders with single- and multi-component compositions are manufactured for dental and biomedical purposes [13].

1.2.2.9 Ultrasound

The use of ultrasound as a technique for nanoparticle production has grown. Ultrasonic cavitation will develop when liquids are exposed to ultrasonic radiation. Ultrasonic cavitation creates a range of chemical and physical effects, including high temperatures, pressures, and cooling rates, which creates a special surrounding for chemical reactions in harsh circumstances. An excellent technique for creating nanoparticles with adjustable morphologies is ultrasound [14].

1.2.2.10 Spark Discharge

It is a low-cost industrial technique used for nanofabrication of innovative materials. It is also used for synthesis processes. A sufficiently strong electric field can produce an ionized, electrically conductive channel through a normally insulating medium, usually air or other gases or gas mixtures, resulting in a sudden electrical discharge known as an electric spark [15].

1.2.2.11 Template Synthesis

It is becoming more crucial to create an easy, environmentally acceptable approach for synthesizing nanoparticles as green chemistry gains more attention. According to reports, template synthesis, the synthesized nanoparticle as guests are confined into void spaces of porous substance that are being used as a host, is one of the most convenient ways for the manufacture of inorganic nanocomposites. The template serves two purposes. It serves as a base to sort out the various operations of a device, the active components, and the various association. First, it enables the reproduction of the structure with the highest degree of repeatability [5].

1.2.2.12 Biological Synthesis

The green chemistry method of biologically synthesizing nanoparticles links nanotechnology and biotechnology [16].

1.2.3 2D Materials

Non-centrosymmetric two-dimensional (2D) layered materials hold great potential for nanoscale electromechanical systems and electronic devices. Due to their exceptional and distinctive electric, optical, magnetic, and mechanical properties, two-dimensional (2D) materials that are atomically thin have drawn a lot of attention recently [17]. In contrast to sandwiched layers that are held together by weak van der Waals forces, facilitating easy cleavage along the layer surface, the intralayer MX bonds in 2D transition metal dichalcogenides (TMDs) play a crucial role. The chemical formula of these TMDs is typically MX_2, where M represents a metal and X denotes a chalcogen element, are mostly covalent in nature. As a result, it is now possible to create crystals with extremely thin thicknesses [18]. 2D materials are the best materials for the construction of

energy harvesters like PENGs because of their unique qualities like flexibility, transparency, mechanical stability, and nontoxicity [19].

1.2.3.1 Types of 2D materials

Various types of 2D materials are, TMDs or "Transition metal dichalcogenides", TMOs or Transition Metal Oxides, Graphene, Black phosphorus. LDH or "Layered Double Hydroxides", Laponite clay, hBN or "Hexagonal Boron Nitride" and gC_3N_4 or "Graphitic Carbon Nitride".

1.2.3.2 Properties of 2D Materials

2D materials possess many interesting properties such as large surface-to-volume ratio, Stackable layers, Ultra-thin, Transparency, and Flexibility.

1.2.3.2 Applications of 2D materials

2D materials have many applications in the fields of Energy production, Energy storage devices, Opto-electronic devices, Sensors, Detectors, and Catalysis.

1.2.4 Energy Harvesting

Today's lack of energy availability restricts both economic and human development. One of the primary responses to this issue should be to investigate clean and sustainable energy sources. Additionally, environmentally friendly energy sources like mechanical or solar power produce no emissions of carbon that could harm the environment or cause global warming, and they pose only a very small risk of doing so. There is always a surplus of energy in the environment that could be used by us, but it is instead "wasted." [20]. In this regard, recently, piezoelectric nanogenerators have gathered considerable attention by converting ambient mechanical energy to feasible

electrical energy with the help of piezoelectric nanogenerators. Various piezoelectric materials, including $BaTiO_3$, ZnO, PZT, etc., have been investigated so far [21].

1.2.4.1 Piezoelectric Nanogenerators (PENGs)

Devices based on functional piezoelectric materials such as piezoelectric and sensing devices have been advanced in the last ten years in which piezoelectric plays a significant role. Nanometer-scale piezoelectric materials are being developed into new products called piezoelectric nanogenerators. PENGs are capable enough to convert the available mechanical energy into useful electrical energy. They are eco-friendlier and more capable of producing feasible electrical energy as compared to chemical batteries. As a result, they are viewed as promising candidates for uses in renewable energy [22].

1.2.5 Polyvinylidene Fluoride (PVDF) and its copolymer

Piezoelectric polymers, such as polyvinylidene fluoride (PVDF) and its other copolymers such as hexafluoropropylene (HFP), trifluoro ethylene (TrFE), bromotrifluoroethylene (BTFE), and chlorotrifluoroethylene (CTFE), TrFE has received a lot of attention recently [23]. Even though the unit cells of the copolymers are less polar than those of pure PVDF, they often have a significantly higher level of crystallinity, which causes a greater piezoelectric response. As a result, copolymers are chosen in piezoelectric applications [24]. Polyvinylidene fluoride (PVDF) is a non-toxic, flexible, and cost-effective polymer that shows a piezoelectric effect when pressure or mechanical stress is applied. The crystalline phase of PVDF polymer appears in four distinct forms, which are α, β, γ and δ, these phases can be interconverted by applying heat, electrical field,

and pressure. From a thermodynamic perspective, the most stable and non-polar is the α-phase, whereas polar phases include β and γ phases. Electronics, sensors, actuators, and other applications use polar PVDF for energy harvesting. Out of all the crystalline phases, the β phase is important due to its enhanced polarization and piezoelectric sensitivity [25]. Due to this property, great effort has been made to enhance the thermal, mechanical, and chemical properties of the β phase of PVDF [26]. TrFE adds important characteristics to the PVDF homopolymer. First, unlike in the case of PVDF, the nonpolar α-phase can be changed to the polar β-phase, without the requirement of mechanical stretching, which makes materials more likely to crystallize in the polar β-phase. Different types of doping are also used to achieve the beta phase [27]. The good film-forming properties of PVDF make it comparable to nanogenerator applications. However, in practical applications, the electrical energy produced by pure PVDF is quite small. As a result, they need special processes like poling, adding filler materials, etc. We mainly consider adding nanofiller materials due to their various advantages, which include cost savings, the convenience of production, and improved electrical output. Some of the most popular nanofillers that are used to alter the symmetry of PVDF and improve its piezoelectric capabilities are ZnO and its various nanostructures, $NaNbO_3$, reduced graphene oxide 2D layered transition metal dichalcogenides MoS_2, $MoSe_2$, SnS_2 [20][28] [29] [30].

1.2.6 SnS_2 NPs

Tin disulfide (SnS_2), which is an n-type semiconductor with a large optical bandgap in the region of 2.12–2.14 eV, is made up of tin sheets atoms compressed between two closely packed sheets of sulfur atoms. Piezoelectric force microscopy (PFM) investigations have shown that the d_{33} and d_{31} for 2D SnS_2 are, respectively, 2.2 and 1 pm/V. To be used at this time in any real-world applications, the reported piezoelectricity in these 2D stacked materials has to be stronger [31].

1.3 Aim and scope of study

- Synthesis of SnS_2 nanoflakes by Hydrothermal method.
- To investigate the effect of different weight percentage of SnS_2 on the piezoelectric properties of PVDF-TrFE.
- Fabrication of a piezoelectric nanogenerator using Pristine PVDF-TrFE and PVDF-TrFE/SnS_2 nanocomposite films to harvest the mechanical energy.
- Analysis of the device performance by measuring the open-circuit voltage and short-circuit current.
- The output performance of the PVDF-TrFE/SnS_2 based PENG reveal that it is a potential candidate for driving low power electronic devices.

CHAPTER - 2

2. MATERIALS AND METHODS

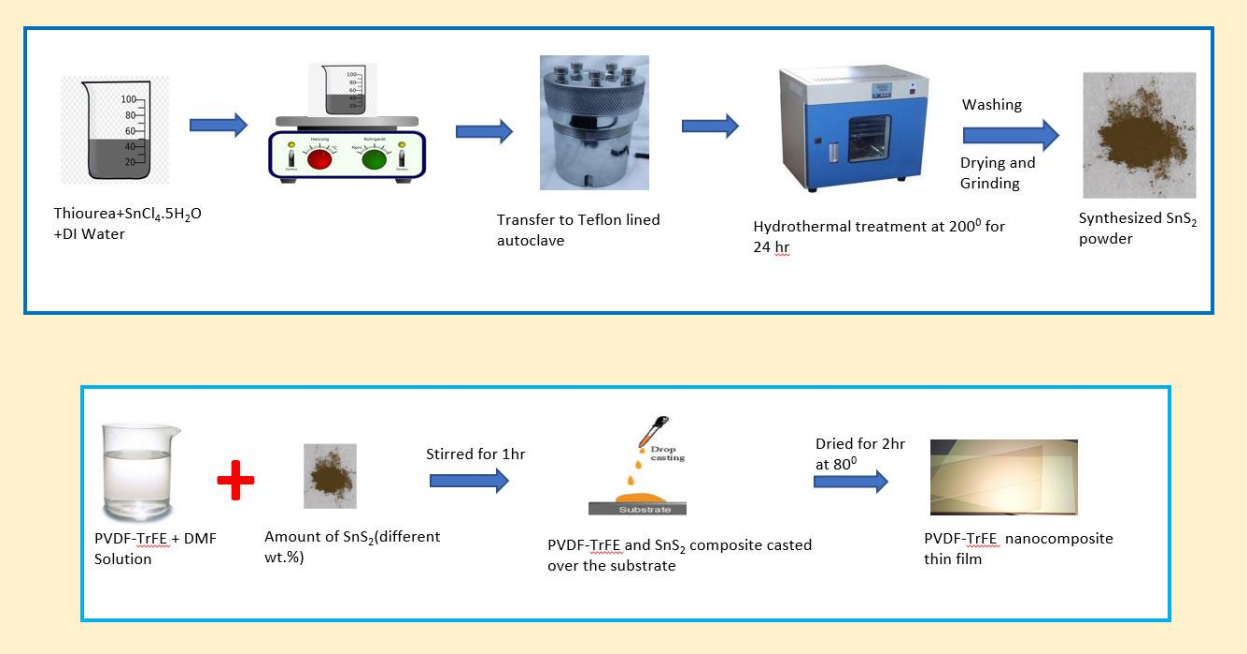


Figure 2.A Chemicals and methods used for synthesis

2.1 Chemicals

Thiourea (CH_4N_2S), N, N-Dimethylformamide, PVDF-TrFE powder and tin(IV) chloride pentahydrate ($SnCl_4.5H_2O$) were acquired from Sisco Research Lab (SRL), Fisher, Alfa Aesar and Sigma Aldrich, respectively.

2.2 SYNTHESIS METHODS

2.2.1 Synthesis of SnS_2 powder

A conventional hydrothermal process was employed for the synthesis of SnS_2. In Fig. 2.1., a schematic illustration of the same is provided. To synthesize the SnS_2 sample, the stoichiometric ratio of the precursor reagents, i.e., 0.3793g of thiourea (CH_4N_2S) and 1.2126g of tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$), was mixed with 40 mL of distilled water and shake for one hour for uniform dispersion. The resulting mixture was then transferred into a Teflon container, sealed in a stainless-steel autoclave, and kept in the oven for 24 hours at 200°C. After allowing the mixture to cool down, it was centrifuged. Following two ethanol and distilled water rinses, it was kept at 50°C in an oven for 12 hours to dry. The product obtained was a fine, yellowish-brown SnS_2 powder.

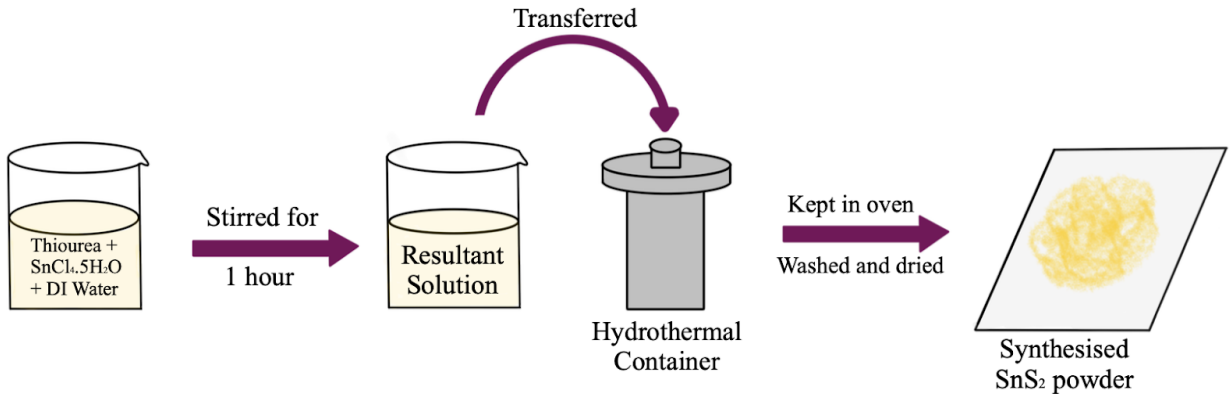


Figure 2.1. Schematic diagram for the hydrothermal method synthesis of SnS_2.

2.2.2 Synthesis of (PVDF-TrFE)/SnS_2 solution

N, N-dimethylformamide (DMF), 10 mL, and 1 g of PVDF-TrFE powder were added to a beaker and stirred for 1 hour. Without adding any SnS_2, the abovementioned mixture is stirred for an additional hour to create a solution for the bare PVDF-TrFE. After adding successive amounts of synthesized SnS_2 powder (1%, 3%, 5%, and 7% by wt%) to the abovementioned mixture and stirring for an hour, varied weight percentages of PVDF-TrFE/SnS_2 nanocomposite solutions were prepared.

Following that, 400 µL of this PVDF-TrFE/SnS_2 solution was dropped using a micropipette (0–1000 µL) onto a 2 cm x 2 cm glass substrate that had been cleaned ultrasonically. After that, the glass substrate with the solution drop casted on it is kept in the oven for two hours at 80 °C. The glass substrates were cooled, and then DI water was sprayed on them. Due to the natural hydrophobic nature of PVDF, thin films synthesized during fabrication instantly peel off from the substrate surface. PVDF-TrFE/SnS_2 thin film synthesis is schematically depicted in Fig. 2.

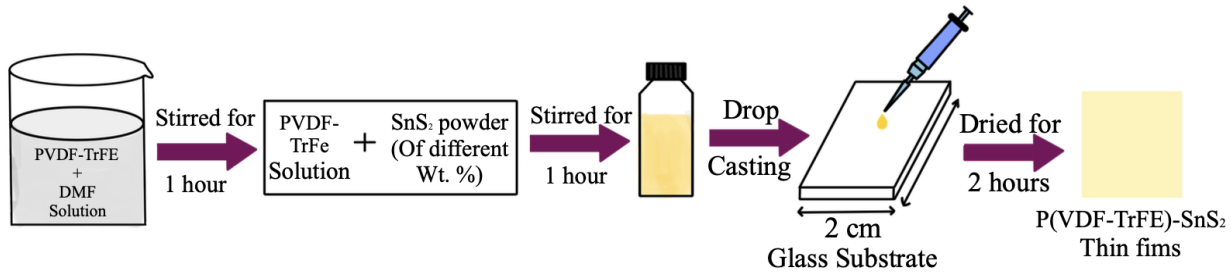
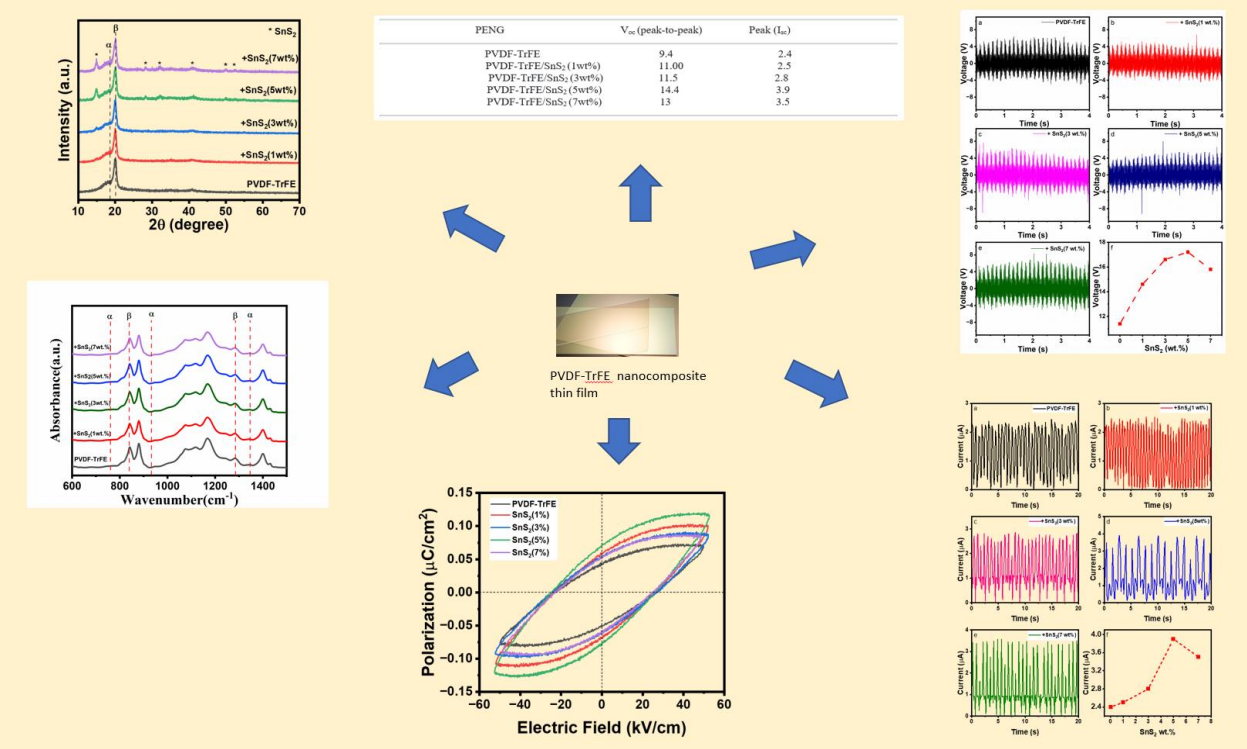


Figure 2.2. Schematic diagram demonstrating the synthesis of PVDF-TrFE+SnS_2 thin film.

CHAPTER - 3



PENG	V_{oc} (peak-to-peak)	Peak (I_{sc})
PVDF-TrFE	9.4	2.4
PVDF-TrFE/SnS_2 (1wt%)	11.00	2.5
PVDF-TrFE/SnS_2 (3wt%)	11.5	2.8
PVDF-TrFE/SnS_2 (5wt%)	14.4	3.9
PVDF-TrFE/SnS_2 (7wt%)	13	3.5

Figure 3.A Results and Characterization

3.1 Characterization Techniques

Raman spectroscopy was performed on synthesized SnS_2 powder samples using a Renishaw plc Micro Raman Spectrometer with a 514 nm laser. The crystalline structure of the SnS_2 samples was analyzed using a Rigaku Ultima-IV X-Ray diffractometer equipped with a Cu-Kα source (wavelength of 1.54 Å). Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Spectrum II instrument. The presence of the electroactive β-phase in the synthesized thin films was confirmed using X-ray diffraction (XRD) analysis. To investigate the enhancement of the β-phase and its impact on the piezoelectric performance, polarization-electric field

measurements were conducted on PVDF-TrFE and PVDF-TrFE/SnS_2 films using a Marine India PE loop tracer. The open circuit voltage output (Voc) and short circuit current (Isc) from the fabricated PVDF-TrFE/SnS_2 films were measured using an oscilloscope (Tektronix MDO500) and a digital multimeter (Keithley DMM7510), respectively.

3.2 Results

3.2.1 XRD analysis

The phase purity and crystallite size of SnS_2 were investigated using the XRD technique. Figure 3.1. shows the XRD patterns of the synthesized SnS_2 powder by the hydrothermal method. The JCPDS card for SnS_2 matches all of the peaks accurately (card number:23-0677). The peaks at $2\theta = 15.26, 28.68, 32.59, 42.24, 50.41, 52.83$ correspond to the (001), (100), (011), (012), (110), (111), (103), (112), (201), and (202) lattice planes respectively which confirm the formation of the hexagonal phase of SnS_2. No extra peaks of SnS, SnSnO, or SnO_2 were detected in the spectra. Further, the Debye-Scherrer relation was used to calculate the average crystallite size [32].

$$D = \frac{0.9\lambda}{(\beta cos\theta)}$$

Where λ is the wavelength of the X-ray beam used (1.54Å), β is the Full width at half maximum (FWHM) of the peak, and θ is the Bragg angle.

The average crystallite size for SnS_2 powder obtained from the above formula is 10 nm.

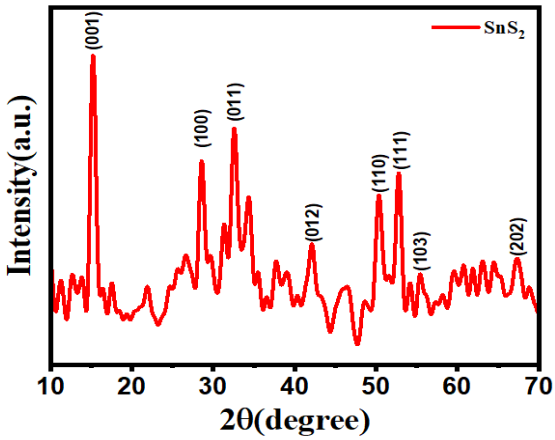


Figure 3.1. XRD analysis for synthesized(powder) SnS_2 nanoflakes

3.2.2 Raman analysis of SnS_2

The phase composition of the synthesized sample was examined using Raman spectroscopy, which is shown in Figure 3.2. In Figure 3.2, It displays two major peaks at 203 cm^{-1} and 311 cm^{-1} corresponding to the E_g and A_{1g} modes of vibration, respectively. The A_{1g} mode of vibration is symmetric under all symmetric operations, whereas E_g is symmetric under inversion. The large surface-to-volume ratio at the nanoscale typically results in quantum confinement followed by a nano-size effect. The Raman spectra's first-order E_g mode peak is diminished as a result of these nano-size effects [31].

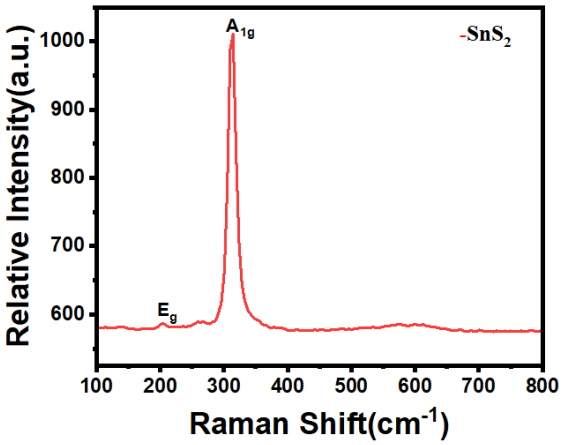


Figure 3.2. Raman spectra of synthesized SnS_2 powder.

3.2.3 XRD analysis of thin films

Figure 3.3. shows the XRD pattern of thin films made of synthetic polymer nanocomposite materials with various weight percentages of SnS_2 (1%, 3%, 5%, and 7 wt%) in a PVDF-TrFE matrix. All the films exhibit two characteristic peaks, peak at 18.5° is attributed to the non-polar nature in PVDF-TrFE and does not enhance the substance piezoelectricity, whereas the peak at 20.2 degree corresponds to the polar phase, which is responsible for the piezoelectric property. The peaks of SnS_2 are marked with "*". Also, it has been observed from the figure that with an increase in the concentration of SnS_2, there is a significant rise in the intensity of the peaks corresponding to SnS_2, which further shows the successful synthesis of polymer nanocomposite films with varying concentrations.

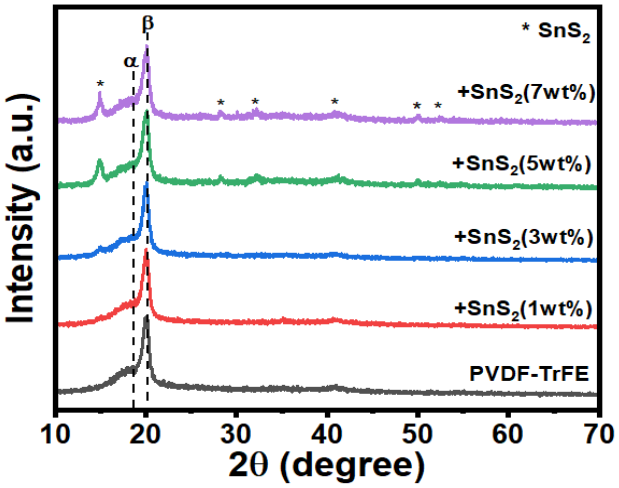


Figure 3.3. XRD analysis for PVDF-TrFE thin film at different wt% of SnS_2 added

3.2.4 FTIR analysis of thin films

Fourier transform infrared spectroscopy of synthesized flexible polymer nanocomposite thin films is depicted in Figure 3.4. The figure shows the α and β phase peak positions. Since the β phase has the highest dipole moment, it is essential for the piezoelectric properties of PVDF-TrFE. The content of the β phase is calculated by the formula

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

Where K(β)= 7.7 X 10^4 cm^2/mol and K(α)=6.1 X 10^4 cm^2/mol are the absorption coefficients at 840 cm^{-1} and 762 cm^{-1} respectively [33]. The content of the β phase was calculated to be 58.30%, 83.48%, 86.42%, 93.07%, and 88.70% for PVDF-TrFE at 0%, 1%, 3%, 5%, and 7% weight percentages of SnS_2. It shows that the β-phase of PVDF-TrFE shows significant enhancement by doping of SnS_2, and it has also been observed that after doping, the first β phase increases up to 5 wt% of SnS_2 and then decreases due to agglomeration of particles [34].

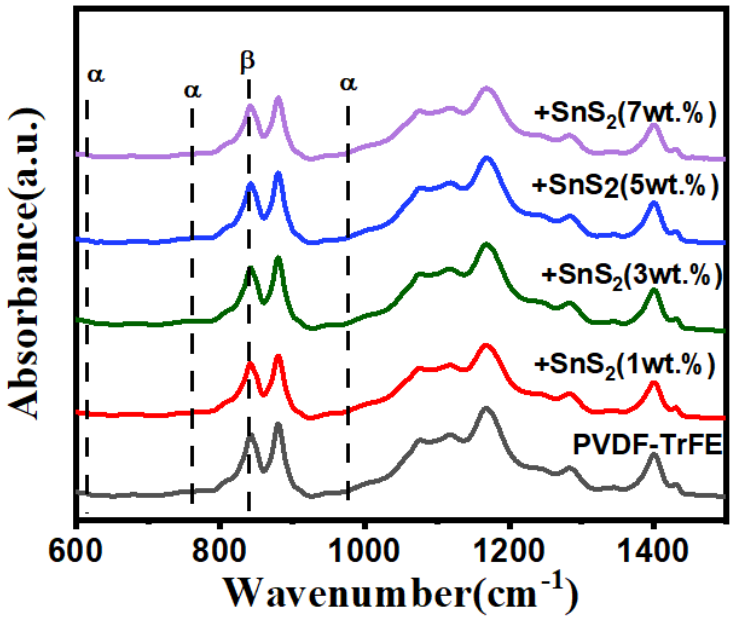


Figure 3.4. FTIR spectra of PVDF-TrFE flexible thin films produced at various SnS_2 weight percentages

3.2.5 PE Measurement

For the thin films, PE loops have been measured using a Marine India-made PE loop tracer. PE loops of PVDF-TrFE with various weight percentages of SnS_2 in PVDF-TrFE are shown in figure 3.5. The loop shows that in comparison to bare PVDF-TrFE film, remnant polarization is increased after the inclusion of SnS_2 in PVDF-TrFE, reaching its maximum value for 5 wt% (weight percentage) of SnS_2 in PVDF-TrFE. The PVDF-TrFE remnant polarisation value that was obtained at various weight percentages of SnS_2 are 0.043, 0.05, 0.054, 0.70, 0.050 $\mu C cm^{-2}$ at 0%, 1%, 3% ,5%, 7% weight percentage of SnS_2 respectively. When used as piezoelectric nanogenerators, a greater output voltage will be produced by the film whose remnant polarization is higher.

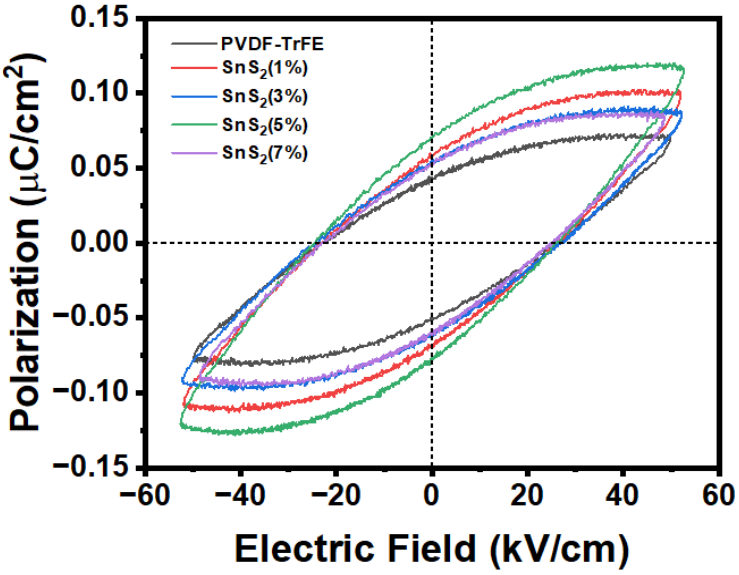


Figure 3.5. PVDF-TrFE polarisation electric field hysteresis loop at different SnS_2 addition weight percentages.

3.2.6 V_{oc} and I_{sc} measurement of PVDF-TrFE at various weight percentages of SnS_2

Further, to fabricate the piezoelectric nanogenerator, aluminum tapes were applied on both sides of the PVDF-TrFE and PVDF-TrFE nanocomposite films as an electrode, followed by connecting copper wire to the electrode. Subsequently, the piezoelectric response of the polymer nanocomposite film was evaluated by tapping it using an electrodynamic shaker at a frequency of 6Hz.The output open-circuit voltage produced by PENGs (of different weight %) as a result of the tapping was measured for 4 s and is shown in Fig. 8. The variation of the resulting piezo voltage as a function of varying concentrations of SnS_2 is shown in Figure 3.6. The obtained peak-to-peak open circuit voltage of different films are shown in Table 1.

Table 1

Values of Open circuit voltage(V_{oc}) and Short circuit current (I_{sc}) attained (Tapping frequency: 6 Hz)

PENG	V_{oc} (peak-to-peak)(V)	Peak (I_{sc}) (μA)
PVDF-TrFE	9.4	2.4
PVDF-TrFE/SnS_2 (1%)	11.00	2.5
PVDF-TrFE/SnS_2 (3%)	11.5	2.8
PVDF-TrFE/SnS_2 (5%)	14.4	3.9
PVDF-TrFE/SnS_2 (7%)	13	3.5

It was found that the peak-to-peak output voltage (9.4 V) generated by pure PVDF-TrFE based PENG increased by nearly 1.5 times with the addition of SnS_2 (5 wt%) (14.4 V).

Short circuit current measurements were also taken at the same frequency for all the fabricated piezoelectric nanogenerators. The PENGs of PVDF-TrFE in its purest form and PVDF-TrFE combined with SnS_2 (at 1%, 3%, 5%, and 7% by wt%) resulted in peak short circuit current values of 2.4, 2.5, 2.8, 3.9 and 3.5 μA, respectively, as shown in Figure 3.7. It is observed that the current measurements also show a significant rise with the incorporation of SnS_2 in the polymer matrix.

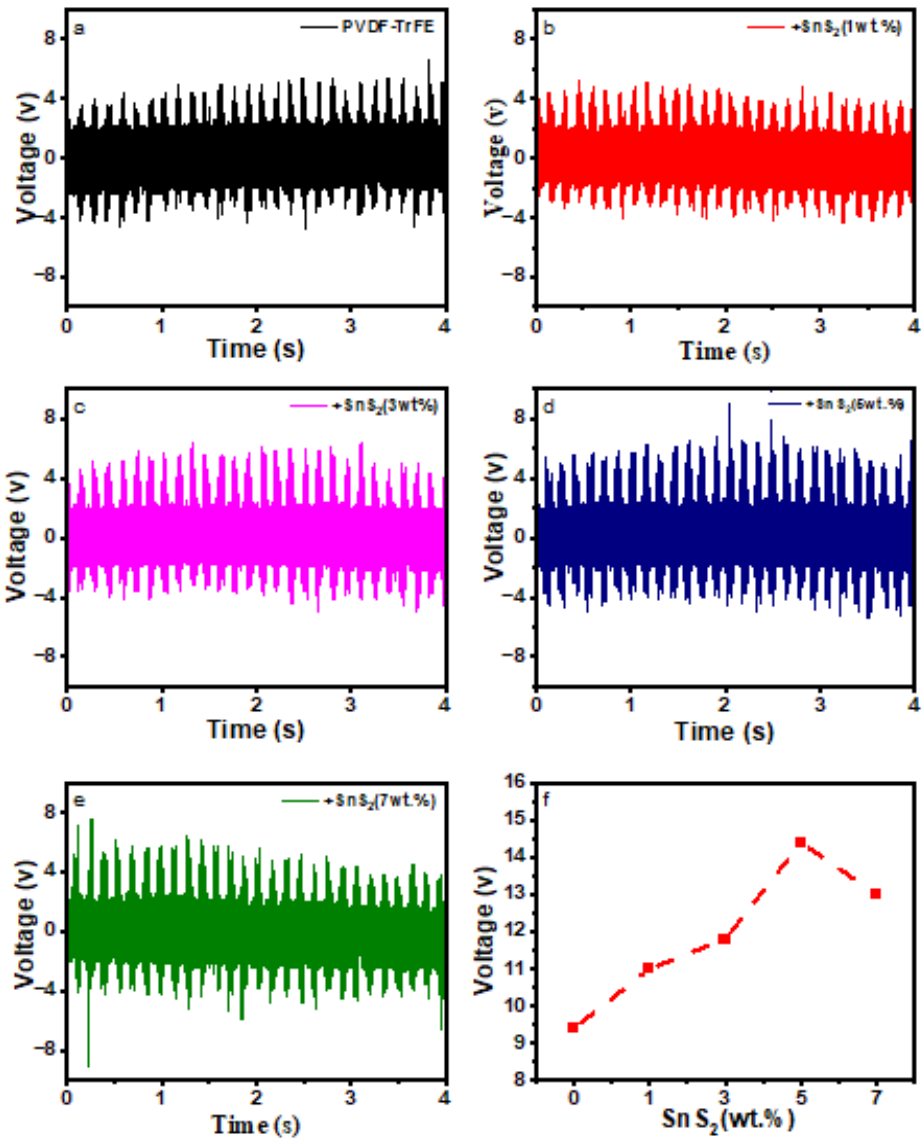


Figure 3.6. Open circuit voltage generation in the thin film PVDF-TrFE in its purest form and PVDF-TrFE combined with SnS_2 (at 1%, 3%, 5%, and 7% by wt%)

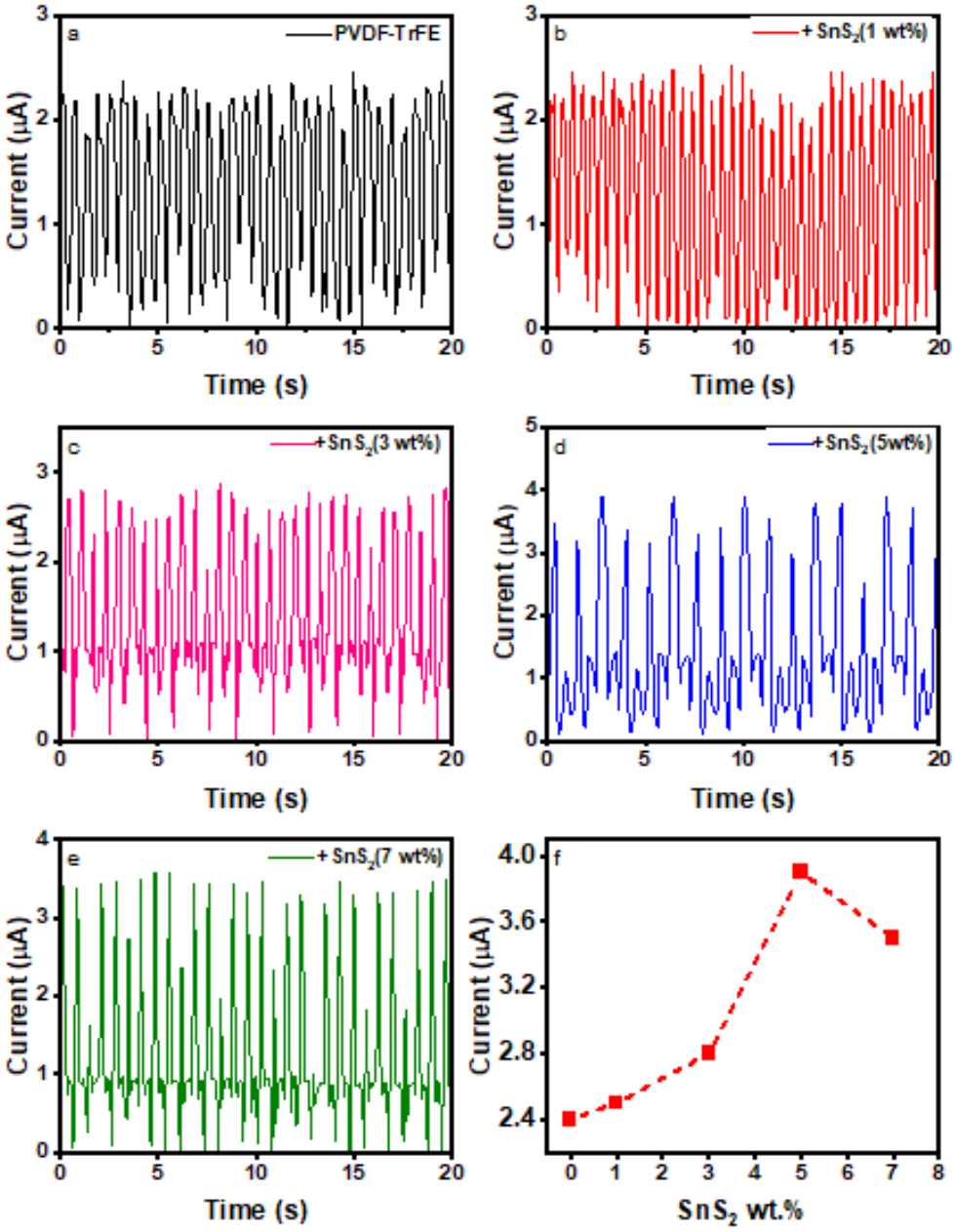


Figure 3.7. Short circuit current generation in the thin film PVDF-TrFE in its purest form and PVDF-TrFE combined with SnS_2 (at 1%, 3%, 5%, and 7% by wt%).

CHAPTER - 4

4. CONCLUSIONS AND FUTURE SCOPE

4.1 Conclusion

In the present study, flexible thin films of pristine PVDF-TrFE+SnS_2 were synthesized successfully by drop casting method with different weight percentages of SnS_2.After conducting XRD and FTIR tests, it was observed that the electroactive β-phase of PVDF-TrFE was enhanced with increasing weight percent of SnS_2 in the polymer matrix. The output voltage and output current of all devices at different weight percentages were recorded to investigate the effectiveness of the PENG device in producing electrical power. The peak piezo voltage output for the PENG made with 5% SnS_2 was 14.4 V, which was almost 1.5 times that of the PENG made with bare PVDF-TrFE. The output piezo current followed a similar trend, with the 5% SnS_2 PENG producing 3.9μA of current, which was roughly 1.62 times more than the output of the thin film of bare PVDF-TrFE. Therefore, adding SnS_2 to the PVDF-TrFE matrix in the current study demonstrates that it can greatly improve the piezoelectric capabilities of energy-harvesting devices based on PVDF-TrFE.

4.2 Future Scope

- The effect of thickness of PVDF-TrFE/SnS_2 nanocomposite films on the output performance of the nanogenerator can be analyzed further.
- Also, the effect of different chalcogenide atoms on the piezoelectric performance of the PVDF-TrFE/TMDs nanocomposite-based PENG can be further analyzed by moving from Sulphur (S) to Selenium (Se) in the periodic table.

- Furthermore, the device performance of the as-synthesized PENG can be further enhanced by hybridizing it with different types of nanogenerators such as triboelectric nanogenerators, electromagnetic nanogenerators, etc.

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Research/Conference Paper

Materials Today: Proceedings

Systematic Investigation of the effect of SnS2 nanofiller content on the piezoelectric performance of the PVDF-TrFE-based nanogenerator

--Manuscript Draft--

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Keywords:	PVDF-TrFE; SnS2; PENG; Energy Harvesting; thin films
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	Palkin Yadav
	Bharti Singh, Ph.D
Abstract:	In this work, SnS2 is used as a nanofiller material to improve response of the polymer-based piezoelectric nanogenerator because of its better inherent piezoelectric properties in comparison to other 2D materials. For this, first, nanoflakes of tin sulfide (SnS2) were synthesized via the hydrothermal method, where the high purity of SnS2 powder is confirmed by Raman spectroscopy and X-ray diffraction studies. The obtained powder of SnS2 was then mixed with PVDF-TrFE in different weight percentages (0%, 1%, 3%, 5% and 7%) of SnS2 to synthesize polymer composite film via drop casting method. These films are then characterized with XRD and FTIR spectrometer which shows enhancement in the electroactive beta phase of the nanocomposite films after doping of SnS2 powder, from 58.30% to 93.07%, which is in agreement with the polarization versus electric field (P-E) measurements that show increased remnant polarization after doping. These films are then used to fabricate a piezoelectric nanogenerator by adhering aluminum tape on both sides of films. The piezoelectric nanogenerator's (PENG) output performance is analyzed by measuring the open-circuit voltage (Voc) and short-circuit (Isc) by tapping the nano-generator with the help of a dynamic shaker, which shows that the output performance of Trifluoroethylene(PVDF-TrFE) based PENGs gets enhanced after the introduction of SnS2 powder.The peak piezo voltage output for the PENG made with 5% SnS2 was 14.4V, which was almost 1.5 times that of the PENG made with bare PVDF-TrFE. The output piezo current followed a similar trend, with the 5% SnS2 PENG producing 3.9μA of current, which was roughly 1.62 times more than the output of the bare PVDF-TrFE thin film. Finally, the nanogenerator output is used to power the commercially available light-emitting diodes (LEDs). As a result, the present study demonstrates that adding SnS2 to the PVDF matrix can significantly improve the energy harvesting technologies based on PVDF's piezoelectric properties.
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Systematic Investigation of the effect of SnS_2 nanofiller content on the piezoelectric performance of the PVDF-TrFE-based nanogenerator

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Abstract

In this work, SnS_2 is used as a nanofiller material to improve the response of the polymer-based piezoelectric nanogenerator because of its better inherent piezoelectric properties in comparison to other 2D materials. For this, first, nanoflakes of tin sulfide (SnS_2) were synthesized via the hydrothermal method, where the high purity of SnS_2 powder is confirmed by Raman spectroscopy and X-ray diffraction studies. The obtained powder of SnS_2 was then mixed with PVDF-TrFE in different weight percentages (0%, 1%, 3%, 5%, and 7%) of SnS_2 to synthesize polymer composite films via drop-casting method. These films are then characterized with XRD and FTIR spectrometers which show enhancement in the electroactive beta phase of the nanocomposite films after doping of SnS_2 powder, from 58.30% to 93.07%, which is in agreement with the polarization versus electric field (P-E) measurements that show increased remnant polarization after doping. These films are then used to fabricate a piezoelectric nanogenerator by adhering aluminum tape on both sides of the films. The piezoelectric nanogenerator's (PENG) output performance is analyzed by measuring the open-circuit voltage (V_{oc}) and short-circuit (I_{sc}) by tapping the nanogenerator with the help of a dynamic shaker, which shows that the output performance of PVDF-TrFE based PENGs gets enhanced after the introduction of SnS_2 powder. The maximum output voltage of 14.4V is obtained corresponding to the PENG with 5 wt% SnS_2, which was almost 1.5 times that of the PENG made with bare PVDF-TrFE. The output piezoelectric current follows the similar trend, with the 5% SnS_2 PENG producing 3.9μA of current, which was roughly 1.62 times more than the output of the bare PVDF-TrFE thin film. As a result, the present study demonstrates that adding SnS_2 to the PVDF matrix can significantly improve energy harvesting technologies based on PVDF's piezoelectric properties.
Keywords: PVDF-TrFE; SnS_2; PENG; Energy Harvesting; Thin films

1. Introduction

Today's lack of energy availability restricts both economic and human development. One of the primary responses to this issue should be to look into clean and sustainable energy sources. Additionally, environmentally friendly energy sources like mechanical or solar power produce no emissions of carbon that could harm the environment or cause global warming, and they pose only a very small risk of doing so. There is always a surplus of energy in the environment that could be used by us, but it is instead "wasted" [1]. In this regard, recently, piezoelectric nanogenerators have gathered considerable attention by converting ambient mechanical energy to electrical energy with the help of piezoelectric materials. Various piezoelectric materials, including $BaTiO_3$, ZnO, PZT, etc., have been investigated in this context[2].

Among these piezoelectric polymers, such as polyvinylidene fluoride (PVDF) and its other copolymers such as hexafluoropropylene (HFP), trifluoroethylene (TrFE), bromotrifluoroethylene (BTFE), and chlorotrifluoroethylene (CTFE), TrFE has received a lot of attention recently [3]. Even though the unit cells of the copolymers are less polar than those of pure PVDF, they often have a significantly higher level of crystallinity, which causes a greater piezoelectric response. As a result, copolymers are chosen in piezoelectric applications [4]. Polyvinylidene fluoride (PVDF) is a non-toxic, flexible, and cost-effective polymer that shows a piezoelectric effect when pressure or mechanical stress is applied. The crystalline phase of PVDF polymer appears in four distinct forms, which are α, β, γ