

# High Performance Piezoelectric Energy Harvesting Based on PVDF-SnS<sub>2</sub> Nanocomposite

DISSERTATION THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE  
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We Gaurang Gautam and Mohit Kumar, Roll No(s). 2K20/MSCPHY/08 and 2K20/MSCPHY/14 student(s) of M.Sc. (Physics), hereby declare that the project Dissertation titled “High Performance Piezoelectric Energy Harvesting Based on PVDF-SnS<sub>2</sub> Nanocomposite” which is submitted by us to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment 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 the award of 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 following details:

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## **ABSTRACT**

This study focuses on fabricating flexible piezoelectric nanogenerators (PENGs) based on polyvinyl fluoride (PVDF) – tin diselenide (SnS<sub>2</sub>) composite. 2D-SnS<sub>2</sub> was synthesized via simple hydrothermal method and was mixed with PVDF to form the nanocomposite solution, which was then drop casted to form flexible thin films. The prepared SnS<sub>2</sub> was confirmed and characterized using X-ray diffractometry (XRD) and Raman spectroscopy. Different weight percentages of SnS<sub>2</sub> were added to bare PVDF to study the role of weight percentage on the output performance of the PENGs. The enhanced beta ( $\beta$ ) phase of PVDF-SnS<sub>2</sub> based PENGs was studied using XRD analysis, where a steep rise in the intensity of  $\beta$ -phase peak is observed, as the SnS<sub>2</sub> concentration (by wt. %) is increased. In order to analyse the piezoelectric outputs, the generation of piezo voltage (open circuit,  $V_{oc}$ ) and piezo current (short circuit,  $I_{sc}$ ) were recorded and compared. The  $V_{oc}$  and  $I_{sc}$  of fabricated PENGs composing different weight percentages of SnS<sub>2</sub> in PVDF, were reported to have higher  $V_{oc}$  and  $I_{sc}$  as compared to bare PVDF based PENGs. The trends of increasing  $\beta$ -phase and hence, increasing piezoelectric output on increasing the wt. % of SnS<sub>2</sub> were observed. Thus, the PENG fabricated from PVDF thin film with maximum SnS<sub>2</sub> concentration, i.e., 7 wt.% shows maximum beta phase enhancement and hence, maximum piezoelectricity.

## GRAPHICAL ABSTRACT

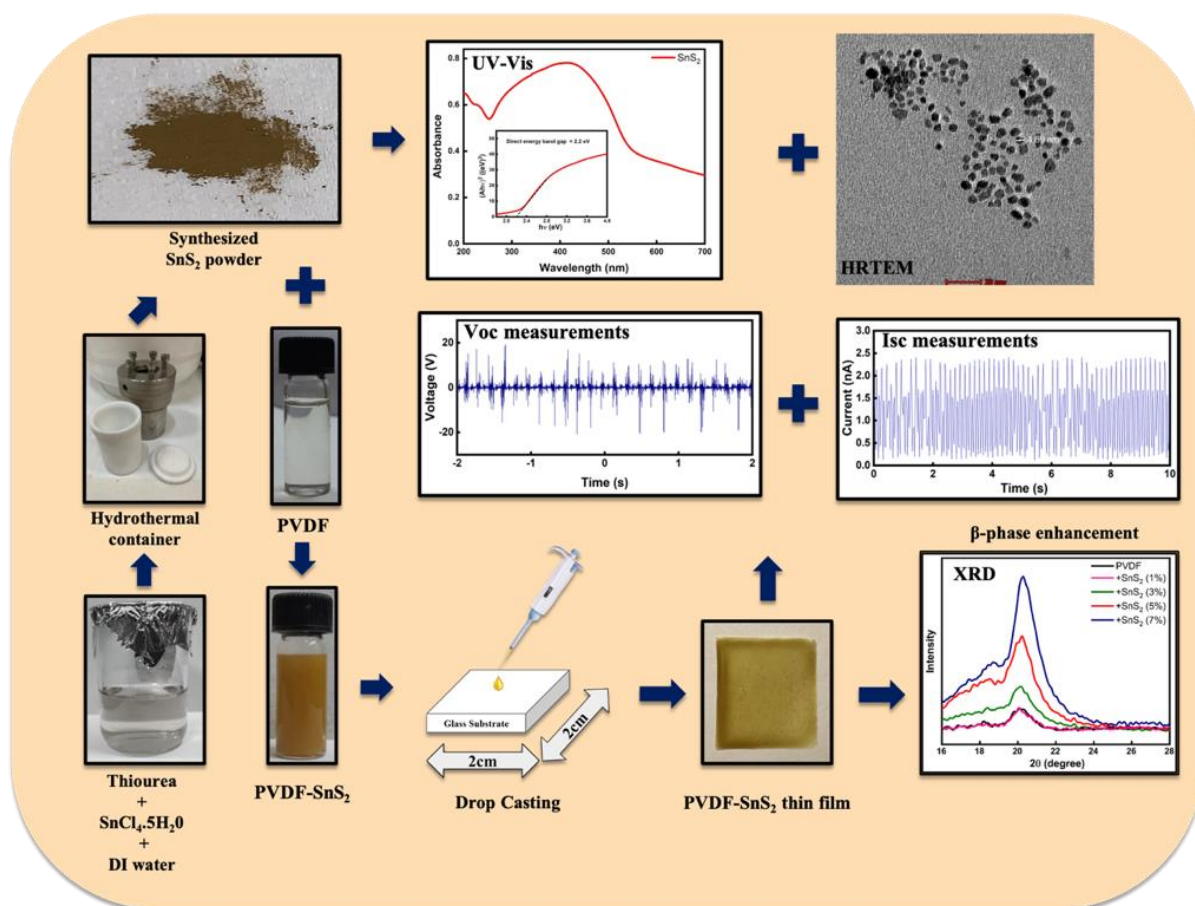


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## **LIST OF SYMBOLES AND ABBREVIATIONS**

NMs	Nano-materials
NPs	Nano-particles
2D	2 Dimensional
PVDF	Polyvinyl fluoride
DMF	N,N-Dimethylformamide
DI water	Deionised Water
SnS <sub>2</sub>	Tin Disulfide
2D SnS <sub>2</sub>	Two-dimensional Tin (IV) Sulphide
WHO	World Health Organisation
UV-Vis	Ultraviolet-Visible
SA: V	Surface area to volume ratio
XRD	X-Ray Diffractometer
PENGs	Piezoelectric Nanogenerators
β - Phase	Beta Phase
TEM	Transmission Electron Microscopy

# **CHAPTER 1**

## **1. INTRODUCTION AND OBJECTIVES**

### **1.1 INTRODUCTION**

In materials science, Nanotechnology is the most growing and active research area. The idea of modern nanotechnology originated from Richard Feynman, a Nobel Laureate in Physics in 1959. This concept was initially introduced during a lecture titled “There’s Plenty of Room at the Bottom” presented by Richard Feynman introducing the matter at atomic level. The following idea originates new ways of thinking and exploring the matter at atomic level. That’s why he is considered as the father of modern Technology [1]. Nanomaterials have been long used by Indian medicine System even before term “nano” introduced [2].

Nano is most fascinating area of research with incredible applications in different parts of science and medicine [3]. The development in altering and exploring properties of nanomaterials by changing their shape and morphology. In recent years impressive development in fabrication, synthesis and methodologies of nanomaterials. This field is emerging day by day rapidly. Nanoparticles plays a very vital role in nanotechnology [4]. Nanoscience has successfully created nanomaterials (NMs) with size less than or equal to 100 nm [5]. They exhibit novel and improved mechanical, optical and electronic properties because of its very small size [6], [7]. Many inert metals like silver also distinctive properties when it is downsized to the nanoscale [8].

## **1.2 LITERATURE REVIEW**

### **1.2.1 Nanoparticles and Nanotechnology**

The field of science for the study of the phenomena at 1-100 nm particle size and nanomaterials ranging one dimension less than 100 nm [9], is termed as nano-science. Since the past decade a separate class of materials derived from nanomaterials as nanoparticles. Most fascinating are 2D materials. Due to their high conductivity, they have received a great scientific interest. In past two decades, nanoparticles exhibit many fascinating applications in variety fields like conductors, electronics, sensors, medicine, catalysis, optical and biological devices etc [11], [12] because of their unique properties, which vary from molecular or bulk materials. Researchers also have achieved decent awareness in nanomaterials due to their applications in medicine and unique properties [13]. So, Researchers and Scientists are more interested in targeting fabrication of 2D materials.

### **1.2.2 Methods for nanoparticle synthesis**

The top-down synthesis method of NMs initiates from a suitable starting material via sputtering, mechanical grinding etc. while second method synthesis smaller entities such as atoms and molecules are joined with each other and fabricated into NMs with processes like chemical methods and biological methods [15]. The small particles form a complex cluster by oxidation/reduction, nucleation and growth processes. Imperfections are introduced by a top-down so, bottom-up approach is most preferable approach for synthesis. NMs properties also depends on synthesis methods [16].

#### **1.2.2.1 Physical methods**

These methods include evaporation of the material followed by controlled condensation, pyrolysis and laser ablation. In this method nanoparticles are critically affected by parameters like time of drilling, medium and initial method [14]. It is typical representation of top-down

method [17]. This method is restricted to presence of chemical agents in the solution for 2D SnS<sub>2</sub>-NPs production. Its main limitations are expensive equipment and lower production rate compared to chemical methods. The additional handicap includes the high energy consumptions.

#### **1.2.2.2 Chemical methods**

The second route consists of sol-gel technique which is used to synthesis nanoparticles in liquid phase or colloidal solution. this method is a representation of bottom-up approach [18]. This process contains nanomaterials as subclass of colloids, which has dimensions in the nano range. The formed nanomaterials may be nanoparticles, fibres or nanoplates. The main advantage of this method are simple technique, low temperature synthesis, formation of variety particles in terms of shape and size, large quantities can be produced [19]. However, it has some disadvantages including toxic chemicals and hazardous reaction by-products.

#### **1.2.2.3 Biological synthesis**

Green synthesis is becoming an emerging route actively participating in the progress in the fields of science & industry [20]. Living cells are very complicated systems with hundreds of molecules containing various functional groups which easily helps in reduction of metal ions.

### **1.2.3 2D Materials**

2D Materials are often termed as “single-layered” crystalline materials because of the reason that they are made up of single-layer of atoms or are layered in structures. Applications of such single layered materials, are quite many, at the cost of further research to be done to make such applications more efficient. 2D materials are classed as 2D allotropes or composites of distinct elements, consisting of covalently bonded two or more elements).

#### **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.

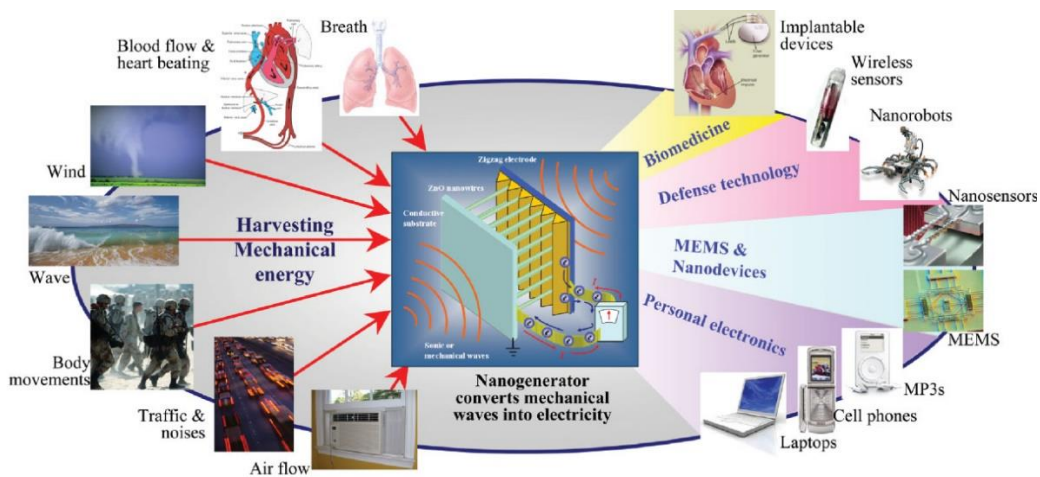
### **1.2.3.2 Applications of 2D materials**

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**

In recent times, the need of cleaner and sustainable energy sources has been rising due to ongoing energy crisis and environmental distress. Thus, the use of alternatives such as solar or mechanical energy which are comparatively better than coal or oil-based energy sources from an environmental point of view, must be explored. The common key concept behind translation of mechanical power into electrical power is piezoelectricity [1]. The mechanical energy in vibrations, biological movements or encompassing fluctuations in the environment can be harvested using PENGs [2].

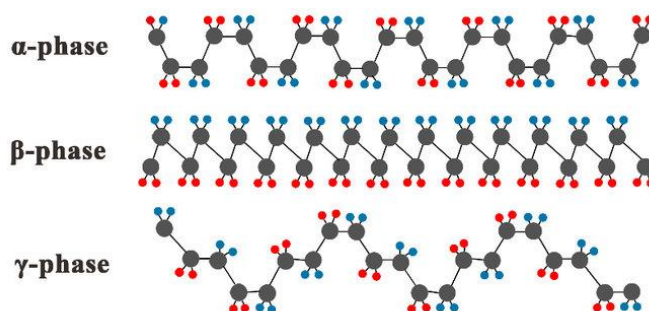
### **1.2.4.1 Piezoelectric nanogenerators (PENGs)**



**Figure 1.1.** Nanogenerator converts mechanical energy into electrical energy [5].

Since 2006, the piezoelectric materials are actively used by scientists in order to achieve efficient ways to harness external kinetic energy via various routes. A piezoelectric nanogenerators are energy harvesting devices which are highly capable of converting, usually wasted form of external kinetic energy into useful electrical energy through an action by a piezoelectric material of nano-structured.

### 1.2.5 PVDF



**Figure 1.2.** Structure of  $\alpha$ ,  $\beta$  and  $\gamma$  phases in PVDF

Polyvinyl fluoride (PVDF) is an eco-friendly, non-toxic, stable, flexible fluoropolymer that exists in various conformations like  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  [12]. Among all these structural phases, PVDF

in its  $\beta$ -phase shows excellent piezoelectricity [13], due to its all trans configuration. There are many ways for enhancing the  $\beta$ -phase of PVDF thermally [14], mechanically [15] and chemically [16]. Apart from these existing methods, use of additives such as ZnO [17,18] is also being recognised as an efficient technique of enhancing  $\beta$ -phase of PVDF. However, there are very few studies proposing MDs as effective additives for  $\beta$ -phase enhancement in PVDF [19]

### **1.2.6 SnS<sub>2</sub> NPs**

The SnS<sub>2</sub> crystal is n-type, composed of dense stacking of tin (Sn) layers between two sulphur (S) layers and has a band gap varying in the range 2.12 - 2.14 eV, according to the synthesis method used. It is ideal to be used for preparing thin films for various optoelectronic devices, due to its high charge carrier mobility (>200 cm<sup>2</sup>/Vs) and optical absorption coefficient (>10cm<sup>-1</sup>) [20]. Experimentally, the  $d_{33}$  and  $d_{31}$  for 2D SnS<sub>2</sub> have been reported as 2.2 and 1 pm/V respectively, using piezoelectric force microscopy (PFM) [21]. Moreover, the elements Sn and S, constituting SnS<sub>2</sub>, are abundantly available, cheap and non-toxic.

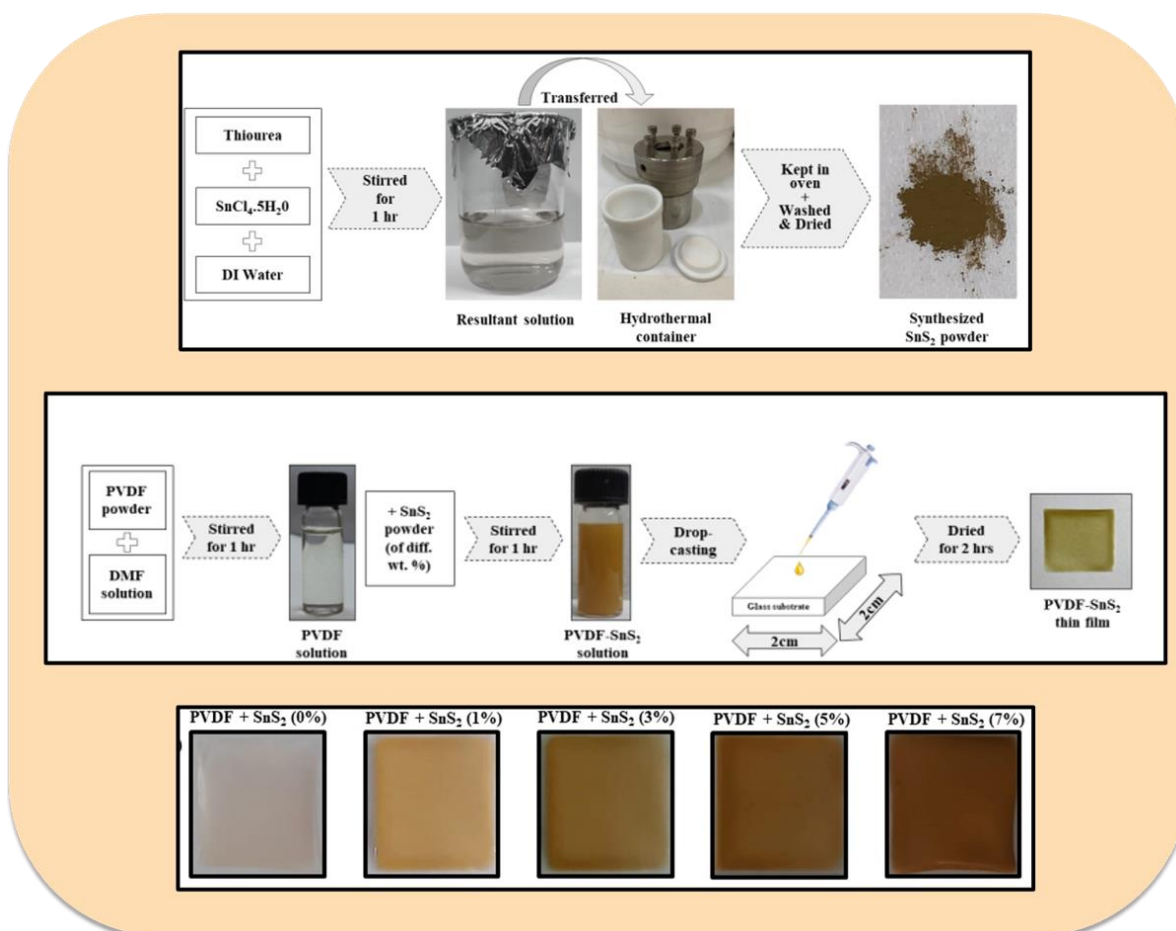
### **1.3 Aim and scope of study**

- Effect of augmentation of synthesized SnS<sub>2</sub> into matrix of PVDF.
- $\beta$ -phase enhancement of PVDF due to addition of synthesized SnS<sub>2</sub>.
- Flexible energy harvesting devices have been fabricated from PVDF-SnS<sub>2</sub> novel nanocomposite.
- The synthesized PENG thin films will possess great wearability because of the flexibility attributed due to PVDF.



## CHAPTER - 2

### 2. MATERIALS AND METHODS



**Figure 2.A** Chemicals and Methods used for synthesis

#### 2.1 Chemicals

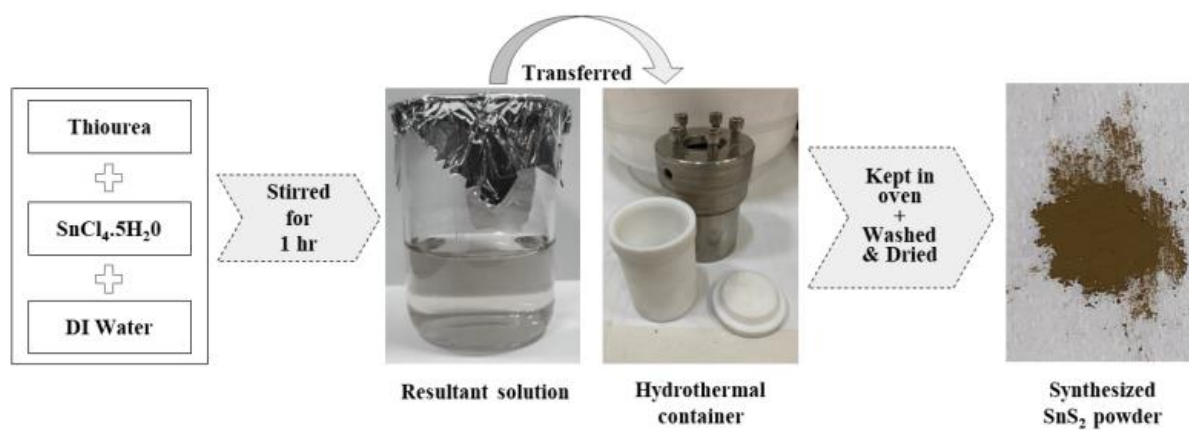
Thiourea, N,N-Dimethylformamide, PVDF powder and tin(IV) chloride pentahydrate were procured from Sisco Research Lab (SRL), Fisher, Alfa Aesar and Sigma Aldrich, respectively.

#### 2.2 SYNTHESIS METHODS

##### 2.2.1 Synthesis of SnS<sub>2</sub> powder

For synthesis of SnS<sub>2</sub>, a simple hydrothermal method was used. A schematic representation for the same has been given in Fig. 2.1. The reagents used as precursors, thiourea (CH<sub>4</sub>N<sub>2</sub>S) and

tin (IV) chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) were taken in a 50 mL beaker to make the required stoichiometric conglomeration. This mixture was stirred for 1 hour with 40 mL of distilled water. After stirring, the resultant solution was poured in a Teflon container and kept in an oven for 24 hours at 200 °C inside a stainless-steel autoclave. The resulting mixture was centrifuged after allowing it to cool down, followed by washing it twice with ethanol and distilled water and then dried in oven for 12 hours at 50 °C. The resultant product is grinded to form a fine yellowish-brown powder of  $\text{SnS}_2$ .



**Figure 2.1.** A Schematic representation to synthesize 2D  $\text{SnS}_2$  nanoparticles

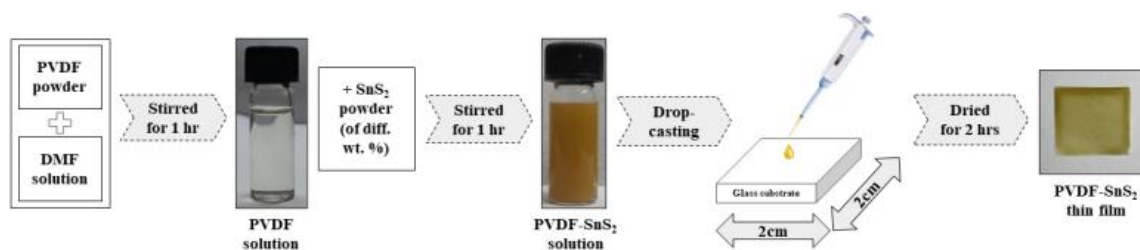
### 2.2.2 Synthesis of PVDF- $\text{SnS}_2$ solution

1g powder of PVDF and 10 mL of N, N-dimethylformamide (DMF) were taken in a beaker for stirring for 1 hour. To prepare a solution for the bare PVDF, the above mixture is continued to stir for another hour without any addition of  $\text{SnS}_2$ . To prepare solutions for different weight percentages, subsequent amounts (1%, 3%, 5% and 7% by wt.) of prepared  $\text{SnS}_2$  powder was added into the above mixture and then continued to stir for an hour to form PVDF- $\text{SnS}_2$  nanocomposite solutions of different weight percentages.

### 2.2.3 Fabrication of PVDF- $\text{SnS}_2$ thin films of different weight percentages

400  $\mu\text{L}$  of this PVDF- $\text{SnS}_2$  solution were then transferred onto an ultrasonically cleaned 2 cm  $\times$  2 cm glass substrate, via drop casting method using a micropipette (0-1000  $\mu\text{L}$ ). These glass

substrates were put in a glass petri dish and placed in the oven for annealing (80 °C, 2 hrs). After letting them cool off, the glass substrates were sprinkled with DI water. Since PVDF is highly hydrophobic in nature, the fabricated thin films immediately leave the substrate surface and thin films are obtained. Fig. 2.2 shows a schematic representation for synthesis of PVDF-SnS<sub>2</sub> thin film.



**Figure 2.2.** A pictorial representation for the synthesis of thin films of PVDF+SnS<sub>2</sub>

# CHAPTER - 3

## 3. RESULTS AND CHARACTERISATIONS

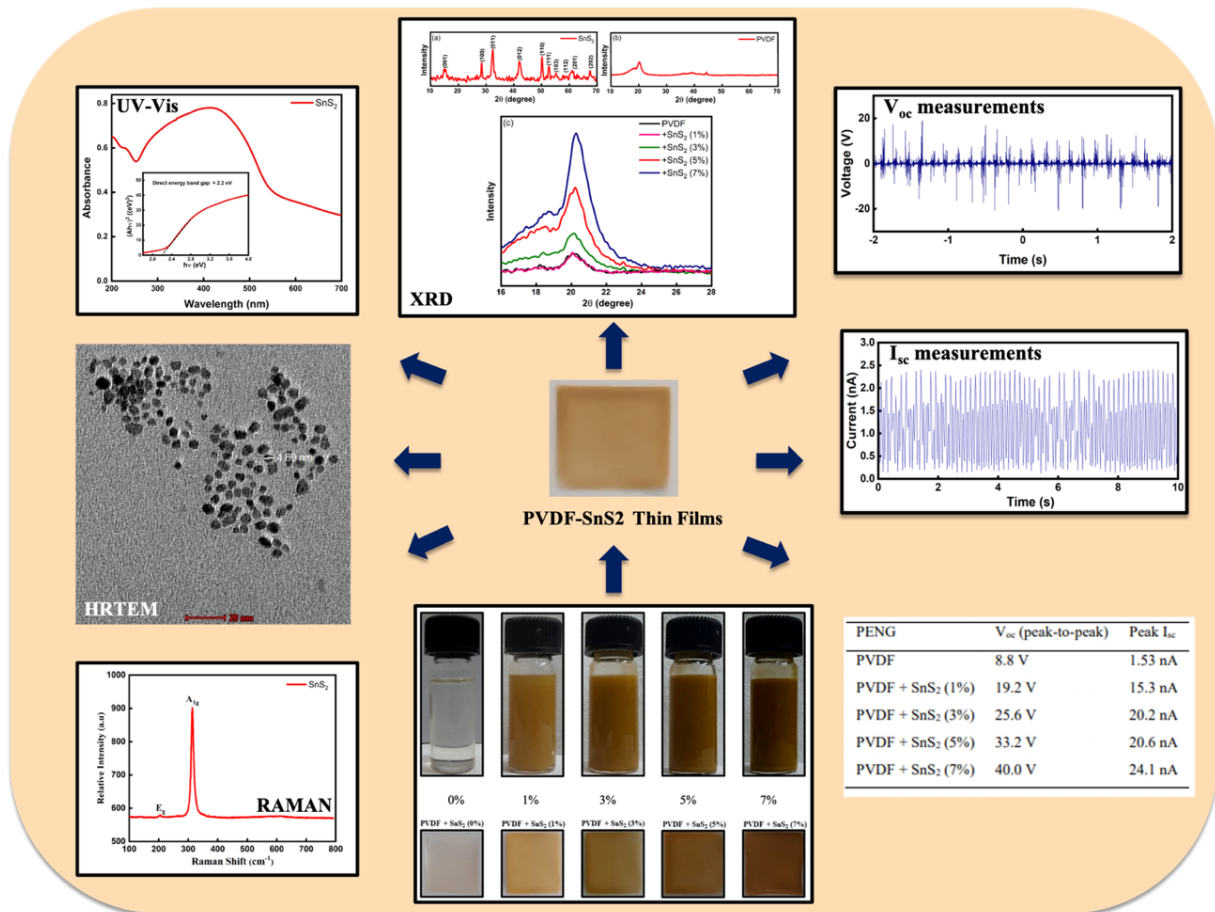
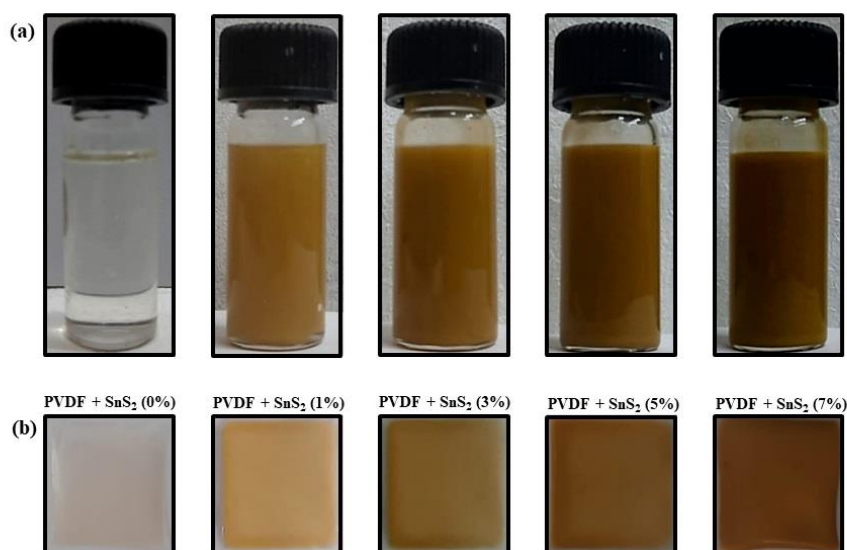


Figure 3.A Results and Characterizations.

### 3.1 Optical profiles of PVDF-SnS<sub>2</sub> thin films

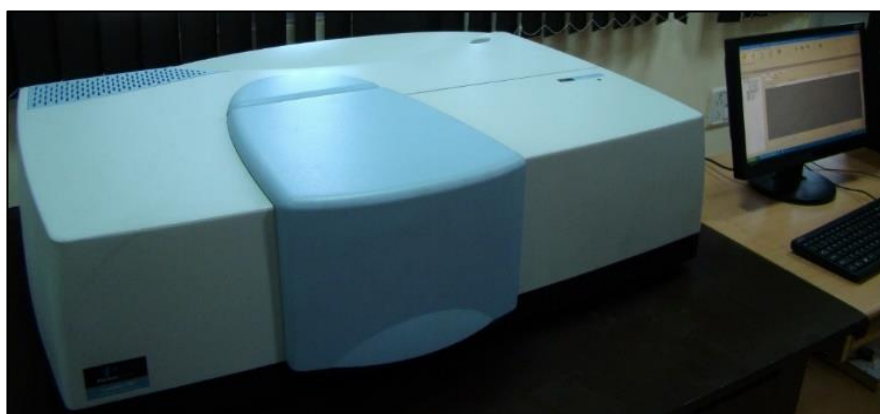


**Figure 3.1.** (a)PVDF-SnS<sub>2</sub> solutions and (b)thin films of different weight percentages

The optical profiles of PVDF-SnS<sub>2</sub> thin films(Figure 3.1), shows how the thin films become darker on addition of increased amounts of SnS<sub>2</sub> powder. The increased darkness, in turn makes the thin films opaque. The increased dark saturation of the thin films, however, doesn't translate into lowered flexibility, which is an advantageous point to note about PVDF-SnS<sub>2</sub> thin films.

### 3.2 UV- Vis Analysis

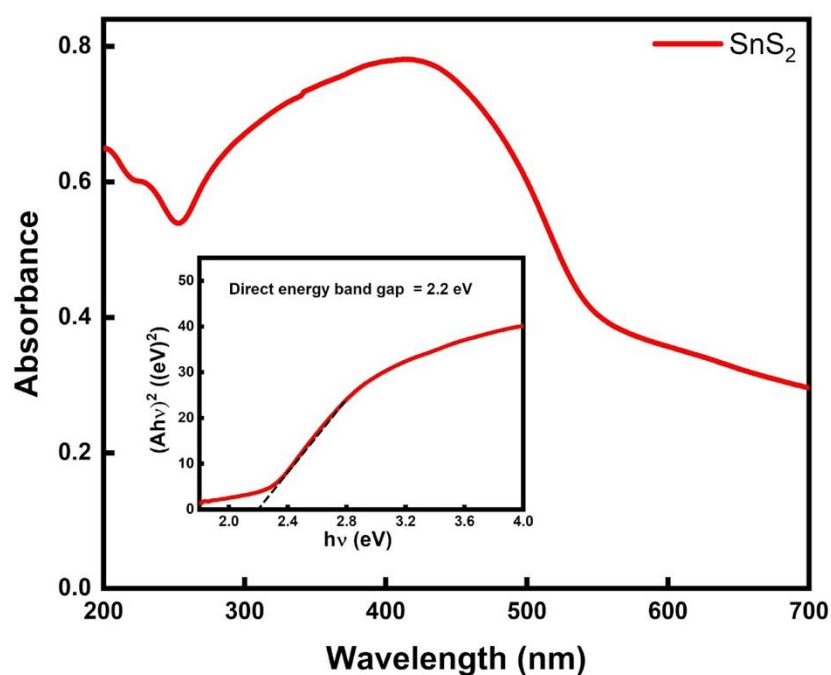
The absorption spectra for 2D SnS<sub>2</sub> powder was recorded using Perkin Elmer Lambda 750 spectrometer shown in Fig. 3.2. The observations were taken in the range 200 nm to 700 nm.



**Figure 3.2.** The “Perkin Elmer Lambda 750” spectrometer.

The absorption spectrum of prepared SnS<sub>2</sub> powder was recorded (Fig. 02) in UV and visible range to study the optical properties and to obtain the optical band gap of SnS<sub>2</sub>. Subsequently using the absorption spectra, a tauc plot, i.e., between  $(Ah\nu)^2$  and  $h\nu$  was drawn (where,  $A \rightarrow$  “absorption coefficient”;  $h \rightarrow$  “planck’s constant”;  $\nu \rightarrow$  “frequency”).

The linear portion in the tauc plot was extrapolated to form an intercept on the abscissa (energy), which gives direct band gap,  $E_g$ . Subsequently, the optical band gap of SnS<sub>2</sub> came out to be 2.2 eV which is in total agreement to previously reported values in literature [22].



**Figure 3.3.** UV-VIS analysis of synthesized SnS<sub>2</sub> powder

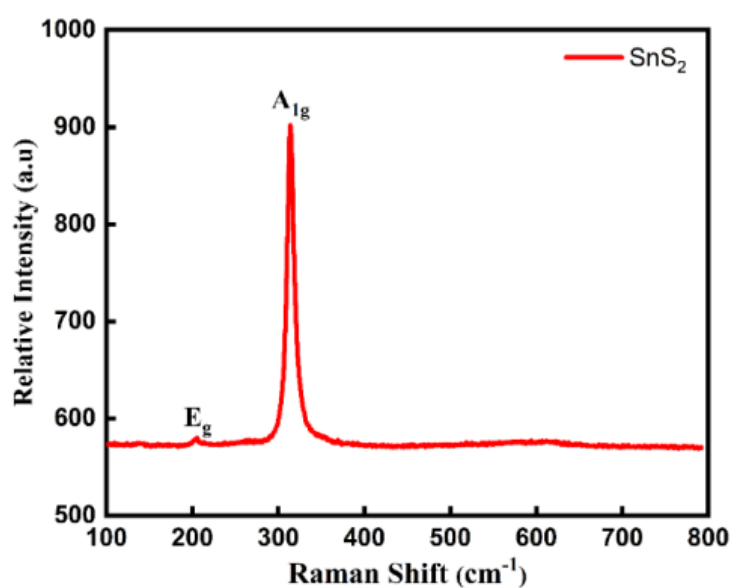
### 3.3 Raman analysis

Raman spectroscopy was performed on synthesized  $\text{SnS}_2$  by a Micro Raman Spectrometer by Renishaw plc. Which is shown in Fig. 3.4.



**Figure 3.4.** Micro Raman Spectrometer

For confirming composition of the phase of obtained sample, Raman spectroscopy was performed, the resulting spectrum is given in Fig. 3.5. The chemical composition of the samples is found to be homogeneous. In the Raman spectra, an evident peak of  $A_{1g}$  mode is observed at  $311 \text{ cm}^{-1}$  which is a characteristic peak of  $\text{SnS}_2$  [22]. These  $A_{1g}$  mode vibrations are totally symmetric under all symmetry operations, other than which there are  $E_g$  vibrations which are symmetric only under inversion.



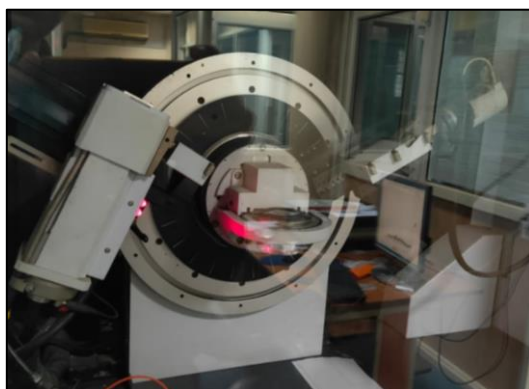
**Figure 3.5.** Raman analysis of synthesized  $\text{SnS}_2$  powder



As we move towards nanoscale, the large SA: V often causes quantum confinement and resulting nano size effects. Due to these nano size effects, first order  $E_g$  mode peak is diminished in the Raman spectra [23].

### 3.4 XRD Analysis

XRD pattern for the  $\text{SnS}_2$  powder and thin films obtained on addition of various wt. percentage of  $\text{SnS}_2$  to PVDF solution was obtained from “BRUKER-D8 advanced”. The average crystallite size is estimated using Scherer’s relation. The machine is shown in Fig. 3.6.

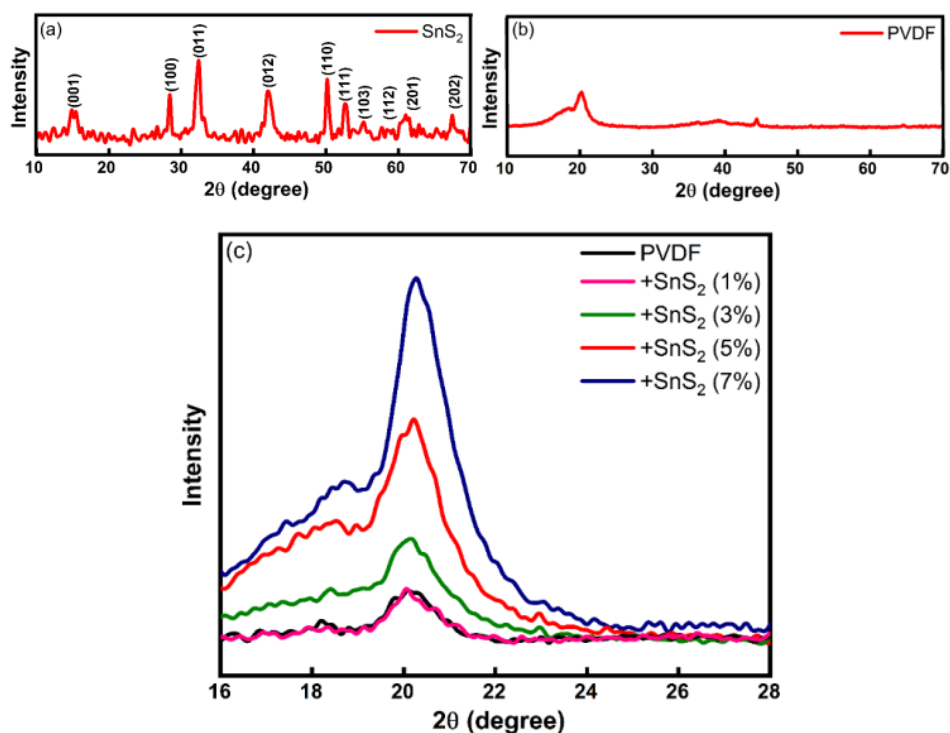


**Figure 3.6** The “BRUKER-D8 advanced” to obtain XRD pattern

The XRD of synthesized  $\text{SnS}_2$  powder, shown in Fig. 3.7 (a) contained Bragg’s reflection intensity peaks which were identified as lattice planes (001), (100), (011), (012), (110), (111), (103), (112), (201) and (202) from JCPDS card for  $\text{SnS}_2$  (card number: 23-0677), confirming the formation of hexagonal phased  $\text{SnS}_2$ .

The crystal structure of the thin films prepared from bare PVDF powder were also characterized by XRD analysis, which is demonstrated in Fig. 3.7 (b). A reflection peak observed at  $18.5^\circ$ , corresponds to the  $\alpha$ -phase of PVDF which is non-polar in nature and hence, doesn’t contribute

to the overall piezoelectricity of the material. The reflection intensity peak occurring at  $20.2^\circ$  is of the  $\beta$ -phase of the material.



**Figure 3.7.** XRD analysis for (a) synthesized (powder) 2D SnS<sub>2</sub> (b) bare PVDF (thin film) (c) PVDF+SnS<sub>2</sub> (thin films, at different wt.%)

The XRD pattern of prepared thin films of different weight percentages (1%, 3%, 5%, 7%) of SnS<sub>2</sub> added to PVDF is demonstrated in Fig. 3.7 (c). The reflection peak of  $\beta$ -phase of PVDF shows a significant rise in intensity with an increase in the amount of SnS<sub>2</sub> added, which in turn leads to enhancement of overall piezoelectricity of the nanocomposite.

The “Debye-Scherrer relation” [24],

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$
, was used to calculate the average crystallite size which came out to be 11 nm (for SnS<sub>2</sub> powder) and 22 nm (for PVDF-SnS<sub>2</sub> (7%) thin film).

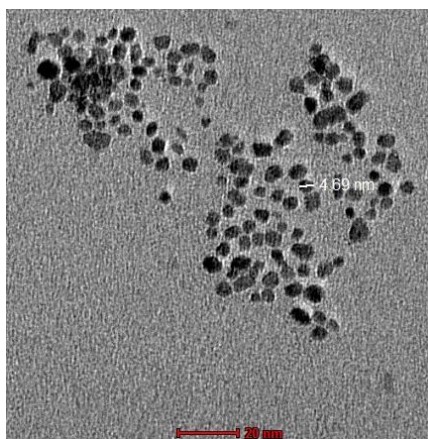
### 3.5 SnS<sub>2</sub> Morphology

Shape and size of the prepared 2D SnS<sub>2</sub> was calculated using HRTEM. HRTEM was done using TALOS (at 200 kV). Image of the instrument is shown in the Figure 3.8.



**Figure 3.8.** HRTEM using TALOS

To determine the morphological characteristics of SnS<sub>2</sub>, TEM analysis was done. The powder sample of SnS<sub>2</sub> was dispersed in DMF solvent and coated on a mesh grid made of copper after ultrasonication. From resulting TEM image (Figure 3.9), we can observe spherical nanoparticles with particle size about 4.69 nm are formed.



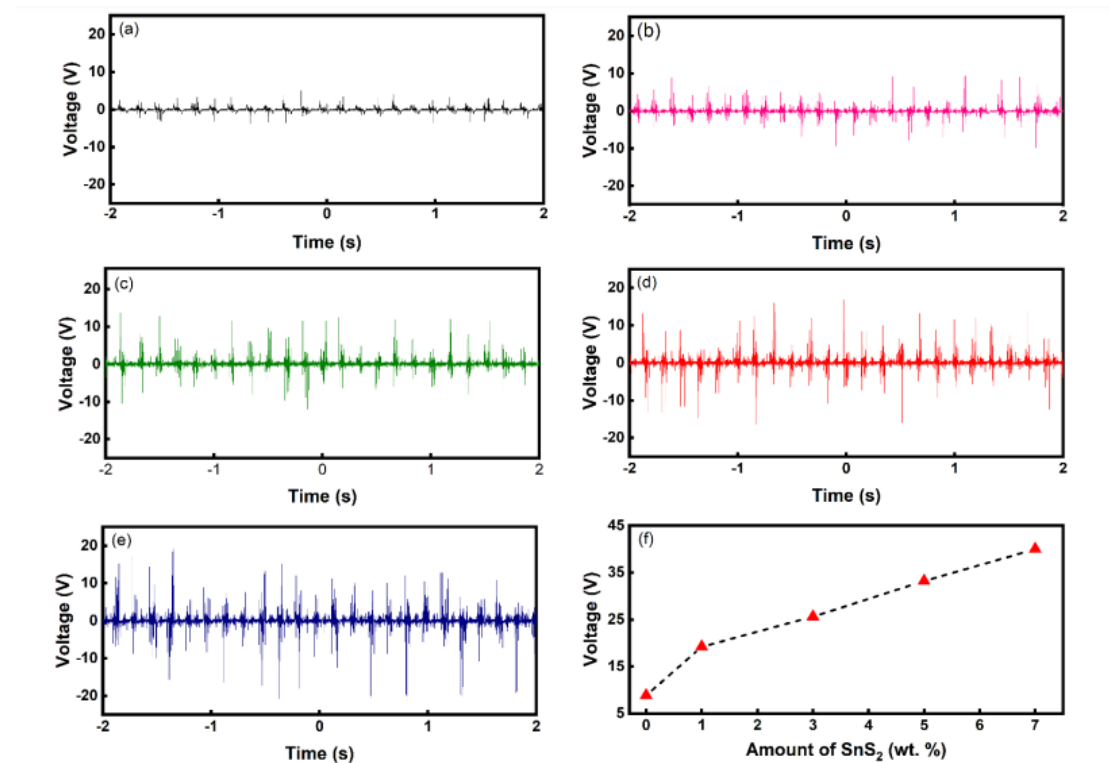
**Figure 3.9.** HRTEM images of 2D SnS<sub>2</sub>-nanoparticles

### 3.6 $V_{oc}$ and $I_{sc}$ Measurements for the PVDF-SnS<sub>2</sub> based PENGs

For studying the piezoelectric response of the prepared PENGs, thermal deposition of aluminium electrodes was done on both sides of the thin films. A tapping motion was created on the PENGs by using an electrodynamic shaker at a constant frequency of 6 Hz.

#### 3.6.1 $V_{oc}$ Measurements

The resulting output of open circuit voltage generated from PENGs (of different wt. %), due to the tapping was recorded for 4 s, given in Fig. 4.6 (a-e). Fig. 4.6 (f) shows the variation of obtained piezo voltage (“peak-to-peak”) generated as a function of weight percentage of SnS<sub>2</sub> added to PVDF for fabrication of PENGs.



**Figure 3.10.**  $V_{oc}$  generation in thin film of (a) Bare PVDF (b) PVDF+SnS<sub>2</sub> (1%) (c) PVDF+SnS<sub>2</sub> (3%) (d) PVDF+SnS<sub>2</sub> (5%) (e) PVDF+SnS<sub>2</sub> (7%) (f) Variation in  $V_{oc}$  (peak-to-peak) as a function of amount of SnS<sub>2</sub> (wt.%) added to PVDF

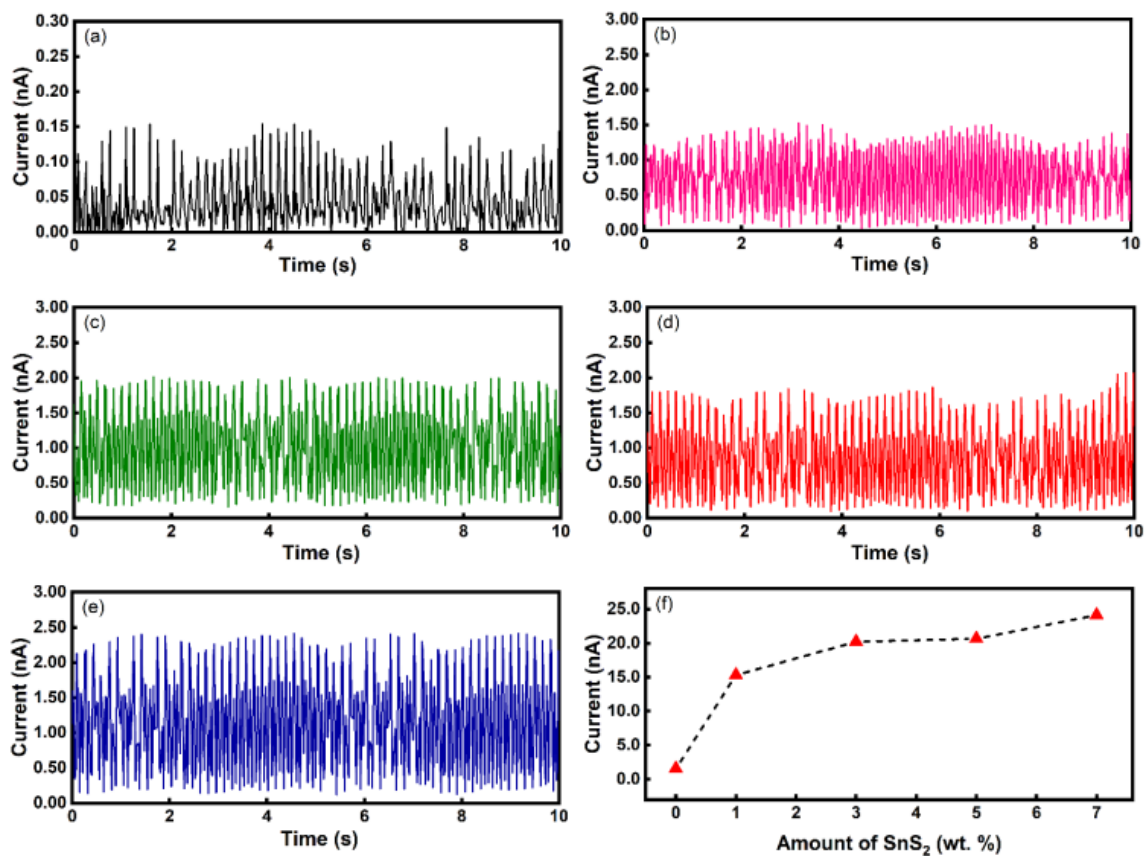
As can be observed from Table I, the output of PENGs is found to increase with the amount of SnS<sub>2</sub> added to PVDF, thus the synthesized SnS<sub>2</sub> enhances the piezoelectricity of PVDF based PENGs. We noted that the maximum output of peak-to-peak voltage (8.8 V) generated by bare PVDF based PENG was amplified to nearly 4.5 times (40 V) by addition of SnS<sub>2</sub> (7 wt. %).

**Table I. Obtained  $V_{oc}$  and  $I_{sc}$  values (tapping frequency: 6 Hz)**

PENG	$V_{oc}$ (peak-to-peak)	Peak $I_{sc}$
PVDF	8.8 V	1.53 nA
PVDF + SnS <sub>2</sub> (1%)	19.2 V	15.3 nA
PVDF + SnS <sub>2</sub> (3%)	25.6 V	20.2 nA
PVDF + SnS <sub>2</sub> (5%)	33.2 V	20.6 nA
PVDF + SnS <sub>2</sub> (7%)	40.0 V	24.1 nA

### 3.6.2 I<sub>sc</sub> Measurements

For measuring short circuit current for all PENGs, same tapping frequency, i.e., 6 Hz and load resistance of 4.7  $\Omega$  was applied. Fig. 6 shows the resulting peak values of short circuit current for the PENGs of bare PVDF, PVDF + SnS<sub>2</sub> (at 1%, 3%, 5% and 7% by wt), which were found to be 1.53, 15.3, 20.2, 20.6 and 24.1, respectively (in nA). It is observed that addition of SnS<sub>2</sub> leads to appreciable increase in the current output which increases with wt.% of SnS<sub>2</sub>, given in Fig. 6 (f).



**Figure 3.11.** I<sub>sc</sub> generation in thin film of (a) Bare PVDF (b) PVDF+SnS<sub>2</sub> (1%) (c) PVDF+SnS<sub>2</sub> (3%) (d) PVDF+SnS<sub>2</sub> (5%) (e) PVDF+SnS<sub>2</sub> (7%) (f) Variation in peak I<sub>sc</sub> as a function of amount of SnS<sub>2</sub> (wt.%) added to PVDF

Table II summarizes and compares the piezoelectric response obtained here with previously reported results, from which we can conclude the validity and effectiveness of this study in present times.

**Table II. Comparison of previously reported performances of PENGs**

Device composition	Synthesis method	Output voltage	Output Current	Reference
MoS <sub>2</sub>	CVD	20 mV	30 pA	[25]
WSe <sub>2</sub>	CVD, turbostatic stacking	90 mV	100 pA	[26]
SnSe	Mechanical exfoliation	-760 mV	-1 nA	[2]
PVDF-RGO	Solution Casting	1.915 V	-	[27]
PVDF-TrfE/Graphene	CVD, spin coated	-3 V	-0.37 $\mu\text{Acm}^{-2}$	[28]
PVDF-TrfE	Spin coated	7 V	59 nA	[29]
PVDF-Graphene	Electrospinning	7.9 V	4.5 $\mu\text{A}$	[30]
PVDF-Graphene (Ce <sup>3+</sup> )	Electrospinning	11 V	6 nA/cm <sup>2</sup>	[31]
PVDF-MoS <sub>2</sub>	Salt intercalation, electrospinning	14 V	-	[32]
PVDF-RGO-Ag	Solution Casting	18 V	-	[33]
PVDF-MoSSe	Solution Casting	31.2 V	1.26 $\mu\text{A}$	[34]
PVDF-SnS <sub>2</sub>	Drop casting	40.0 V	24.1 nA	This work

## **CHAPTER - 4**

### **4. CONCLUSIONS AND FUTURE SCOPE**

#### **4.1 Conclusions**

A flexible piezoelectric energy harvesting device based on thin films of PVDF-SnS<sub>2</sub> nanocomposite was successfully fabricated and studied. After confirming and characterizing the synthesized SnS<sub>2</sub> using Raman scattering and XRD analysis, it was added to PVDF in different amount increments (by wt. %). The piezo response of PVDF-SnS<sub>2</sub> based PENGs was found to be highly dependent on the weight percentage of SnS<sub>2</sub> that has been added to PVDF. XRD analysis also revealed that the insertion of SnS<sub>2</sub> into PVDF lattice caused significant enhancement of its  $\beta$ -phase and hence, its overall piezoelectricity. For studying the efficiency of PENG devices in generating electrical power, the output voltages and currents were recorded for all devices of different wt. %. The peak piezo voltage output found for the PENG fabricated at 7% of SnS<sub>2</sub>, i.e., 40 V was about 4.5 times the piezo voltage output for bare PVDF based PENG. Similar trend was observed for output piezo current, where the 7% SnS<sub>2</sub> PENG showed generation of 24.1 nA current which was nearly 15 times the output for bare PVDF thin film. Hence, the current study establishes that the piezoelectric performances of PVDF based energy harvesting devices can be significantly amplified by augmenting SnS<sub>2</sub> into the PVDF matrix.

#### **4.2 Future Scope**

- SnS<sub>2</sub> can be used to further investigate the role of copolymers
- Similarly, the dependence of thickness can also be experimented and investigated.
- Also, SnS<sub>2</sub> containing a chalcogenide (i.e., S) can be further used to experimentally prove the increasing piezoelectricity while moving left-to-right in periodic table.



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## High performance piezoelectric energy harvesting based on PVDF-SnS<sub>2</sub> nanocomposite

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### ABSTRACT

This study focusses on fabricating flexile piezoelectric nanogenerators (PENGs) based on polyvinyl fluoride (PVDF) – tin diselenide (SnS<sub>2</sub>) composite. 2D-SnS<sub>2</sub> was synthesized via simple hydrothermal method and was mixed with PVDF to form the nanocomposite solution, which was then drop casted to form flexible thin films. The phase purity of prepared SnS<sub>2</sub> powder was confirmed and characterized using X-ray diffractometry (XRD) and Raman spectroscopy. Different weight percentages of SnS<sub>2</sub> were added to bare PVDF to study the role of weight percentage on the output performance of the PENGs. The enhanced beta ( $\beta$ ) phase of PVDF-SnS<sub>2</sub> based PENGs was studied using XRD analysis, where a rise in the intensity of  $\beta$ -phase peak is observed, as the SnS<sub>2</sub> concentration (by wt. %) is increased. In order to analyse the piezoelectric outputs, the generation of piezo voltage (open circuit,  $V_{oc}$ ) and piezo current (short circuit,  $I_{sc}$ ) were recorded and compared. The  $V_{oc}$  and  $I_{sc}$  of fabricated PENGs composing different weight percentages of SnS<sub>2</sub> in PVDF, were reported to have higher  $V_{oc}$  and  $I_{sc}$  as compared to bare PVDF based PENGs. The trends of increasing  $\beta$ -phase and hence, increasing piezoelectric output on increasing the wt. % of SnS<sub>2</sub> were observed. Thus, the PENG fabricated from PVDF thin film with maximum SnS<sub>2</sub> concentration, i.e., 7 wt% shows maximum beta phase enhancement and hence, maximum piezoelectricity.

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### 1. Introduction

In recent times, the need of cleaner and sustainable energy sources has been rising due to ongoing energy crisis and environmental distress. Thus, the use of alternatives such as solar or mechanical energy which are comparatively better than coal or oil-based energy sources from an environmental point of view, must be explored. The common key concept behind translation of mechanical power into electrical power is piezoelectricity [1]. The mechanical energy in vibrations, biological movements or encompassing fluctuations in environment can be harvested using piezoelectric nanogenerators (PENGs) [2].

The substantial interfacial expanse and small diffusion path length [3] of two-dimensional (2-D) nanostructure materials make them ideal prospects for manifold applications such as sensing [4], energy harvesting [5], photonics [6] and electronics [7,8]. Owing to appreciable chemical, optical and electrical attributes, the xuse of

2-D metal dichalcogenides (MDs) in nanoelectronics is being researched extensively [9,10]. The crystals of MDs are composed of 2-D layers stacked one over the other via van der Waals weak interaction forces whereas strong covalent bonds are responsible for intralayer interactions [11]. This enables the creation of stable crystals of very sparse thickness, of atomic scale. This property of MDs is being experimentally studied to investigate their potential use in energy harvesting, i.e., using PENGs [5].

Polyvinyl fluoride (PVDF) is an eco-friendly, non-toxic, stable, flexible fluoropolymer that exists in various conformations like  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  [12]. Among all these structural phases, PVDF in its  $\beta$ -phase shows excellent piezoelectricity [13], due to its all trans configuration. There are many ways for enhancing the  $\beta$ -phase of PVDF thermally [14], mechanically [15] and chemically [16]. Apart from these existing methods, use of additives such as ZnO [17,18] is also being recognised as an efficient technique of enhancing  $\beta$ -phase of PVDF. However, there are a very few studies proposing MDs as effective additives for  $\beta$ -phase enhancement in PVDF [19].

The SnS<sub>2</sub> crystal is n-type, composed of dense stacking of tin (Sn) layers between two sulfur (S) layers and has a band gap vary-

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