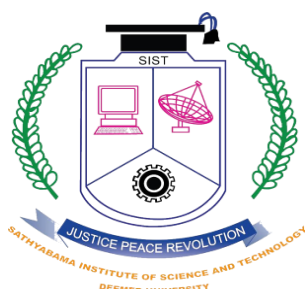


HIGH PERFORMANCE SUPERCAPACITOR OF TIN SULFIDE DECORATED MULTI-WALL CARBON NANOTUBE

Submitted in partial fulfillment of the requirements for the award of
Master of Science degree in Physics

By

**A.
B. JESSICA
(41590008)**



**DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCE AND HUMANITIES**

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

Accredited with "A" grade by NAAC I 12B Status by

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JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119.

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of A. Jessica (41590008) who carried out the project entitled "HIGH PERFORMANCE SUPERCAPACITOR OF TIN SULFIDE DECORATED MUTIWALL CARBON NANOTUBE" under my supervision from November 2022 to May 2023.

Internal Guide
(Dr. M. Dakshana)

Head of the Department
(Dr. S. Ravichandran)

Submitted for Viva voce Examination held on 9.5.2023 2023

INTERNAL EXAMINER

EXTERNAL EXAMINER
Dr. D. DINESH KUMAR
Associate Professor (Research)

DECLARATION

I A. JESSICA hereby declare that the Project Report entitled “HIGH PERFORMANCE SUPERCAPACITOR OF TIN SULFIDE DECORATED MUTIWALL CARBON NANOTUBE” done by me under the guidance of Dr. M. Dakshana (Internal), Department of Physics, Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics.

DATE: 09-05-2023

PLACE: CHENNAI



SIGNATURE OF THE CANDIDATE

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Abstract

There is huge research attention on electrical energy generation and storage systems is increasing global population and energy crisis. The supercapacitor is a clean energy storage system providing high energy and power density with long-lasting cycle life compared to other well-known electrical energy storage systems like batteries. Among, assorted electrode materials like metal oxides, conducting polymers etc., metal sulfides possess potential characteristics for energy storage applications. In this present work, we have used SnS as an electrode material due to its nontoxicity, cheapness, abundance in nature, and high theoretical capacitance, yet it still suffers from its poor intrinsic conductivity, a high-volume transition, and low coulombic efficiency resulting in a short life cycle. In order to overcome the drawbacks, SnS decorated multi-wall carbon nanotube (MWCNT) was prepared for electrode application. These prepared SnS-MWCNT nanocomposite has been analyzed using various characterization techniques to study its crystal structure, morphology and optical property. The developed SnS- MWCNT nanocomposite electrode material showed high specific surface area, high specific capacitance and high reversible redox reactions. Furthermore, SnS- MWCNT nanocomposite is regarded as a promising material for constructing efficient electrodes for high energy and power storage systems due its remarkable specific capacitance.

Keywords: Nanocomposite, supercapacitor, anchor, MWCNT, CV, TEM

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CHAPTER-1

Chapte-1 starts with a brief introduction of the metal sulfide nanostructures and their various synthesis methods. In addition to this, a short review of the supercapacitor applications was also discussed in this chapter. Finally, the chapter describes the importance of the project.

CHAPTER 1

1. INTRODUCTION

1.1 NANOMATERIALS

Nanomaterials have attracted many researchers in recent days due to their unique properties and successive application in science and industry. The word nano originates from the Greek through the Latin “nanus” which means small or dwarf miniature [1]. Nanomaterials (NMs) are made up of nanoparticles which are having diameters in the order of 1-100 nm [2]. Based on their size and shape these materials are classified into 0D, 1D, 2D, and 3D [3]. Fig1.1 represents the classification of nanoparticles [4]. Based on the electron movement along with the dimensions in the NMs it is classified into 0D, 1D, 2D. For example, In 0D NMs electrons are entrapped in a dimensionless space whereas in the 1D NMs electrons move along the x-axis, which is less than 100 nm. As well as in 2D and 3D NMs electrons move along the x–y-axis, and the x, y, and z-axis correspondingly [2]. The nanosized is commonly measured in 10^{-9} m [1]. The researchers have identified the influence of nanoparticles on physiochemical properties such as optical properties [3], thermal and electrical conductivity, catalytic activity, melting point, wettability, etc. [2]. In the 0D at a single point the length, breadth, and height are constant Eg. Nanodots. In 1D it carries only one parameter Eg. Graphene. In 2D it has both length and breadth Eg. Carbon nanotubes. In the 3D it has 3 parameters as in the 0D Eg. Gold nanoparticles. The nanoparticles are of various sizes, shapes, and structures. Based on the surface difference it can be uniform or irregular. Some of the nanoparticles are amorphous or crystalline with multi or single-crystal solids [5].

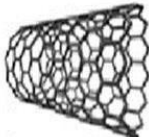
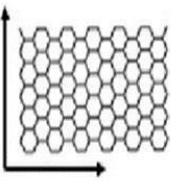
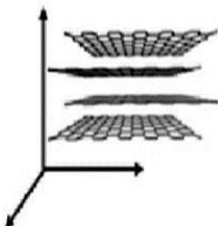
0D	1D	2D	3D
			
Fullerene	Carbon Nanotube	Graphene	Graphite

Fig 1.1 shows the Classification of nanoparticles

Based on the materials Nanoparticles are classified into four types:

- i) Carbon-based nanomaterials
- ii) Inorganic-based nanomaterials
- iii) Organic-based nanomaterials
- iv) composite-based nanomaterials

i) Carbon-based nanomaterials: Commonly the NM contains carbon and these are identified in dissection such as ellipsoids, spheres, and hollow tubes. Carbon nanofibers, graphene, and carbon nanotubes come under the carbon-based nanomaterials. In carbon-based nanomaterials important fabrication methods are arc discharge, chemical vapor deposition, and laser ablation.

ii) Inorganic-based nanomaterials: Metal and metal oxide are coming under the inorganic-based nanomaterials. The nanomaterials can be fabricated into metals such as Ag, Au NPs. Metal oxides are synthesized into ZnO, TiO₂ NPs. Semiconductors such as ceramics and silicon [2].

iii) Organic-based nanomaterials: organic-based nanomaterials are also called polymers [5]. Organic NM contains Carbon Nanotubes (CNT), Single Wall Carbon Nanotubes (SWCNT), Multi-Wall Carbon Nanotubes (MWCNT), graphite, and nanofibers [6]. The usage of non-covalent interactions for the design of molecules and self-assembly helps to convert the organic NM into convenient structures such as micelles, liposomes, and polymer NPs [2]. liposomes have a hollow core known as nanocapsules which are sensitive to electromagnetic radiation and thermal energy such as light and heat [5].

iv) Composite-based nanomaterials: Multiphase Nanomaterials and Nanostructured materials with one phase on the nanoscale dimension can be made by combining multiple nanoparticles together, or by combining nanoparticles with larger or bulk materials. The composites may be a combination of metal-based, carbon-based, or organic-based [2].

Materials can be enhanced by adding nanomaterials as additives. The addition of nanomaterials to fluids is referred to as nanofluids; when added to PCM, it's called nanocomposites. Eventually, they will be called nanofluids or nanocomposites [6].

Numerous techniques can be employed for the synthesis of NPs. They are mainly divided into two categories i.e.

(1) Top-down approach

(2) Bottom-up approach

1)Top-down approach:

Top-down is a destructive method. origin from the bigger molecule, it is decomposed into lower units, and at last these units are transformed into correct NPs. Some of the methods in this top-down approach are grinding/milling, physical vapor deposition (PVD), CVD, and decomposition techniques [3].

2)Bottom-up approach:

Bottom-up is a constructive method. It is the build-up of material from atoms to bunch nanoparticles or the production of nanoparticles, the most generally used methods are Sol-gel, spinning, pyrolysis, chemical vapor deposition (CVD), and biosynthesis [5].

1.2 METAL SULFIDES

In recent years metal Sulfides has been developed as one of the major potential applicants for energy storage applications [7]. Metal sulfides are the leading materials for electrochemical supercapacitors due to their excellent properties, high specific capacity, good electrical conductivity, high redox activity, unique crystal structure and low electronegativity [8]. As a result, metal sulfides, are commonly used in pseudo capacitors due to their simplicity, cost effectiveness, semiconducting behaviour and high specific capacitance. Several metal sulfides have been studied for supercapacitor applications, including SnS, CuS, ZnS, NiS, NiS₂, and CuS₂ [9]. Metal sulfides are divided into two main categories. They are Layered metal sulfides and non-layered metal sulfides. Layered metal sulfides consist of three atom layers (S-M-S) which are bound by covalent bonds, the individual layers are bound through the van der Waals forces. The example of Layered metal sulfides is SnS₂, VS₂, WS₂, and MoS₂. As, in

nonlayered Metal, sulfides are bound through chemical covalent bonds in all the three dimensions. Non-layered metal sulfides are FeS₂, NiS, CoS₂, MnS₂, and so on. Due to abundance, and eco-friendliness researchers have been attracted to metal sulfides [10]. Researchers have focused on one of the important factors on examining the interlayer spacing for capable of ion transport. The chance has led to the improvement of battery type supercapacitor metal sulfide electrode with enough interlayer spacing at lower potential and available to faster and active ion transport (Liu, Hong, et al., 2020; Zhan et al., 2018). When we use sulfide-based material as electrode material in the proper condition of size, structure and composition it can give good conductivity by reducing the diffusion paths. This metal Sulfide can be prepared by various methods such as Hydrothermal, Chemical layer deposition, Atomic layer deposition, Electrochemical synthesis and Electrodeposition etc. The metal sulfide morphologies have been derived to get the desired performance [11]. Comparing to metal oxides, metal sulfides play a major role in the supercapacitor because metal oxides are more expensive and exhibit poor conductivity and metal sulfides are considered as a promising active material because of their very good redox reversibility, relatively high capacity [12] For supercapacitor applications the metal sulfides have shown greater potential [10]. Based on the redox states metal sulfide are more suitable for pseudo capacitor. In compare to metal sulfides, nitrides and metal oxides shows poor electrochemical behavior and poor electrical conductivity. Even though conducting polymers have high electrical conductivity but they are not stable in thermal state. Metal oxide are expensive and their synthesis is ambiguous [13]. Metal sulfide can be easily synthesized and elaborated towards energy storage devices and made encouraging electrodes with enormous potential [11].

1.3 TIN SULFIDE (SnS)

In recent years, the construction and synthesis of Tin sulfide nanostructured electrodes have been conscious of increasing the electrochemical behaviour in supercapacitors [14]. Nano SnS electrode has good cycling stability and the capacitance is impressively higher in both alkali and neutral solutions [15]. The potential energy storage applications based on SnS electrode material has grasped huge research attention due to their excellent physical and chemical properties. SnS is a n-type semiconductors whose bandgap is about 2.2 to 2.5 eV. SnS are also called as herzenbergite. In SnS each unit cell is separated by a large distance which is of

two layers. These two neighbouring layers consists of an S atom. This layered structure helps in intercalation in Sodium-ion batteries and lithium-ion. Various methods have been employed for the improvement of electrochemical performance of tin sulfides, such as using carbonaceous matrices, doping with the metal ions etc[14]. Like a germanium sulfide (GeS), germanium selenide (GeSe) and Tin Selenide (SnSe), SnS is a layered-structure like compound. Due to their layered structure SnS reveals strong anisotropic vibrational properties. When analyses are taken along with their crystallographic axes these structure shows important differences in their physical properties even though the SnS layer compound are coupled with weak vander- waals forces. These weak forces in SnS provides intrinsically a chemical inert surface without hanging bonds and surface density states. Correspondingly the SnS surface becomes free from Fermi-level spinning. This truth makes them environmentally and chemically passive. The SnS compound carry orthorhombic disorder crystal-structure with a space group of lattice parameters $a = 0.432$, $b = 1.12$ and $c = 0.398$ nm. In acidic solution SnS exhibit good chemical stability, high melting and boiling point of about $880\text{ }^{\circ}\text{C}$ and $1230\text{ }^{\circ}\text{C}$. At room temperature the dissociation and work function of SnS are approximately equal to 4.2 to 4.5 eV respectively [16]. SnS has supportive properties such as direct optical band gap (~ 1.3 eV) high absorption coefficient in the visible region ($>10^4\text{ cm}^{-1}$), carrier mobility of $30\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, p-type electrical conductivity). The Sn and S are toxic less, inexpensive, and earth abundant materials. By the experimental studies the SnS material possess direct bandgap of ~ 1.3 eV and the indirect optical bandgap of about 1.049 eV –1.076 eV. As this bandgap is suitable for application devices the SnS properties of orthorhombic structure have been explored by preparing thin films using deposition techniques [17]. Himani et al.[18] Using a solvothermal method improved surfactant-free SnS nanorods for the supercapacitor application. They have reached the highly specific capacitance of ($\sim 70\text{ Fg}^{-1}$), energy density (149 Wh kg^{-1}), and power density (248 W kg^{-1}) [14]. Pujari et al. [19] Using a chemical bath deposition method cubic MnS thin films is fabricated and tested the supercapacitor performance. It reached the maximum specific capacitance of about 747 Fg^{-1} and the thin films exhibit an excellent capacitance maintaining of 85% after 2,000 CV cycles at 100 mVs^{-1} [14]. Rasmita et al. [19] followed using a hydrothermal method to fabricate the SnS nanoparticles. when SnS is mixed with carbon black in a ratio 1:4, the specific capacitance of nanoparticle was increased to 201 g^{-1} [14]. The growth method of SnS is pollution free[16].

1.4 MULTI-WALL CARBON NANOTUBE (MWCNT)

Carbon materials are used in different forms as electrode material in supercapacitor application. The reason why the carbon materials are used as electrodes are because of the high surface area, availability, low cost and electrode production technologies have been established. Some of the examples for electrode in carbon materials are carbon nanotubes (CNT), carbon aerogels, graphene etc. CNT can be divided into Single-walled carbon nanotube (SWCNTs) or Multi-walled carbon nanotube (MWCNTs) generally both are used as electrode materials for supercapacitor. Carbon - based electrode materials are considered as auspicious candidate for supercapacitor applications due to their freely available surface area and good electrical conductivity. In addition to that they give a good balance for active materials due to their mechanical flexibility and open tubular network. As compared to activated carbon, CNT has low energy density because it has specific surface area about $<500 \text{ m}^2/\text{g}$. In order to improve specific capacitance CNT can be activated chemically with potassium hydroxide. The above method can be resulting in increasing the surface area of CNT and maintain its nanotubular morphology. The overall resistance components decide the power density in supercapacitor. A large attention is given to CNT as electrode material for supercapacitor due to its different pore size, good thermal and mechanical stability followed by greater electrical properties. CNT are produced by catalytic decomposition of hydrocarbons. By tuning its unique parameters, we can be able to achieve novel nanostructures and even control their crystalline structure. One of the important factors which determines the electrochemical achievement, pore size distribution, specific surface area, electrical conductivity and surface functionality. The carbon materials with high surface area results in high charge accumulation at the interface of electrode and electrolyte. Apart from that when increasing specific capacitance or carbon materials apart from pore size and high specific surface area, surface functionalization must be studied [21]. For Instance, when we focus into MWCNT (Multi Walled Carbon Nano Tube) due to its very high electrical conductivity and mechanical strength [22] It plays a major role in the electrochemical field providing large potential window [23]. Other than that CNT has different morphological properties which depending on surface and size they are used in semiconductors. CNT has special attract towards the electrochemical materials. By performing unique parameter variations SWCNT's and MWCNT's are

formed. The CNT with graphene sheet in a nanoscale tube like structure it forms SCNT. In addition to that another graphene is surrounded to form MWCNT [24]. MWCNT are nanoparticles that are notable for size and shape. MWCNT can be considered as graphite sheet rolled into a cylinder. MWCNT having maximum electron storage capability and conductivity related to that of copper. MWCNTs perform as electron reservoirs in the composites. In general, MWCNTs are good supporting materials due to the surface properties and resistance towards acid and base [25]. The pureness and morphology of the material plays vital role in determining the specific capacitance of CNT's. The MWCNT/Hg electrode shows 93% capacitance holding of its original value even after 4000 cycles because of the involvement of greatly balanced MWCNTs. The shape of the CV curve remains unbroken even after 4000 cycles which represent the high-rate capability sustainability. From the MWCNT/Hg composite has a stable conductive and porous network which is helpful for the pathway of improving conductivity and aid the charge transfer inside the electrode materials

Metal sulfide has some defects to be solved such as low electric conductivity, volume expansion and inactive kinetic reaction [10]. In order to overcome the inadequacy carbon- based materials are used as composites along with metal sulfides. For Instance, Li.et.al reported SnS / carbon composite has a specific capacitance of 36F/g which was synthesized by chemical precipitation method. The MWCNT shows good mechanical properties and fantastic stability which effective for the expansion of volume during charging and discharging process and in maintain good cycling stability of the electrode materials [26].

1.5 COMPOSITE

When carbon-based materials combined either with metal sulfides or conducting polymers to form a single electrode, this single electrode will have both physical and chemical charge storage mechanism hence its known as composite electrode. Carbon based materials provides high specific surface area and double layer of charge capacitive which strengthens the contact between electrolyte and pseudocapacitive materials. In composite electrode the pseudocapacitive material increases the capacitance through faradaic reaction. Till now, there are two types of composites: They are Binary and Ternary composite. Two different electrode materials are used in

Binary composite whereas, in the Ternary composite three unique electrodes are needed to form a single electrode [21].

1.6 SnS-MWCNT NANOCOMPOSITE

Using pure and hybrid metal sulfides in combination with carbonaceous materials reported a very good performance in supercapacitor application [8]. To overcome the stand alone materials disadvantages such as low conductivity, MWCNT is added to enhance the better conductivity and cyclic stability. Combining reduced graphene oxide (rGo) with molybdenum sulfide via a simple one pot hydrothermal approach, obtained a specific capacitance of about 253F/g at a current density of about 1 A/g [21]. Li et al. showed the maximum specific capacitance of about 36F/g for SnS/carbon nanostructured composite which is synthesized by Chemical precipitation method [26]. Chaopeng fu et. al. made a PTH/MWCNT composite which shows the specific capacitance of about 110F/g at 1 A/g current density [27]

In this present work, we have used SnS as an electrode material due its nontoxicity, cheapness, abundance in nature and high theoretical capacitance, yet it still suffers from its poor intrinsic conductivity, a high-volume transition and low coulombic efficiency resulting in a short life cycle. In order to overcome the drawbacks, SnS decorated multi-wall carbon nano tube (MWCNT) was prepared for electrode application. The as prepared SnS-MWCNT nanocomposite has been analyzed using various characterization techniques to study its crystal structure, morphology and optical property. The developed SnS- MWCNT nanocomposite electrode material showed high specific surface area, high reversible redox reactions and high specific capacitance about 306F/g for a current density of 1 A/g. Furthermore, SnS- MWCNT nanocomposite is regarded as a promising material for constructing efficient electrodes for high energy and power storage systems due its remarkable specific capacitance.

1.7 SUPERCAPACITOR

Among scientists and engineers there is a huge passion for the growth of pollution free energy storage devices for recent years, due to the fast deficiency of fossil fuels.[8]. Mean time for the energy production and consumption of fossil fuels leads to larger greenhouse gas emission, mainly carbon dioxide which leads to global warming. So, the aim is to increase the living standards in a country by giving larger approach

to renewable energy sources so that global environment can be protected [28]. Supercapacitors have large number of charging-discharging cycles, booming thermal operating range and high-power capability. Comparing to rechargeable batteries supercapacitor stores a large amount of charge [29] which influence a higher power and energy density along with smaller weight and volume. In addition, it has longer life cycle compared to the batteries above 500000 times. Supercapacitor and battery are reciprocal to each other because batteries are powerless and they can support high energy-to-weight ratios whereas supercapacitors have different power levels but have lower energy-to-weight ratios. Capacitors suffer from low energy density and higher self-discharge whereas supercapacitor it shows excellent power performance and energy [30]. Compared to supercapacitor batteries are less efficient, lower life cycles, less power density, and high charging time. whereas, Supercapacitor has long-lasting lifecycle of very less charging time and it can be charged and discharged like a regular battery and the heat range is about -40°C to 70°C provided with good electrical conductivity. Far-reaching uses of supercapacitors are in cell vehicles, electric vehicles, and load cranes [31]. The supercapacitor function is based on the distribution of ions and energy storage which comes from the electrolyte to the surface of the electrodes. Based on the charge storage supercapacitors are differentiated into three main categories they are: Electrochemical double-layer capacitors (EDLC), Pseudocapacitors, and hybrid supercapacitors [21]. Fig.1.2 shows the classification of supercapacitor [32]

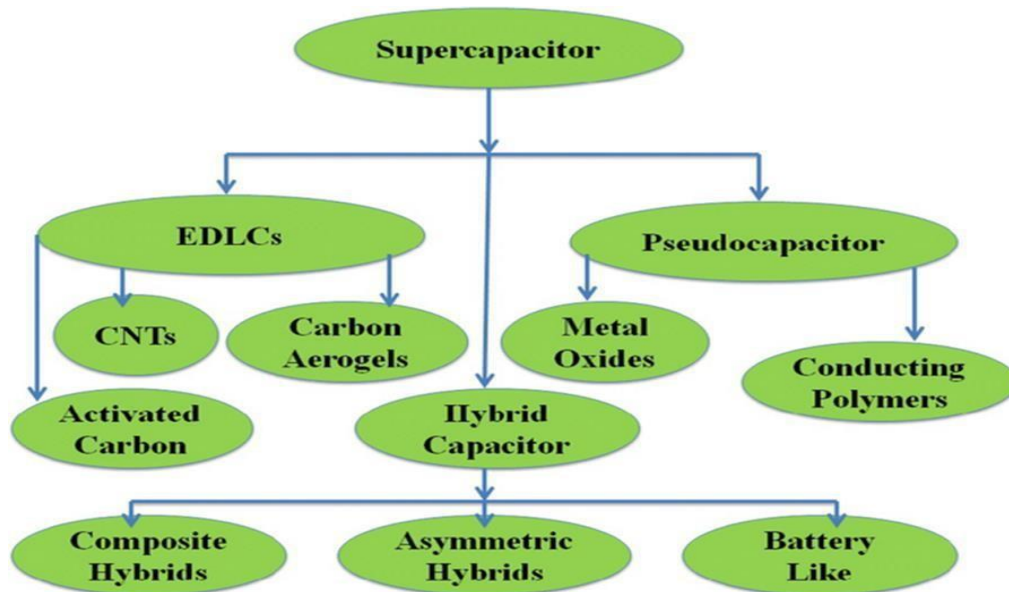


Fig. 1.2 shows the Classification of supercapacitor

1.7.1 Electric double layer capacitor (EDLC)

Electrochemical double layer capacitors (EDLCs) are created by using two carbon-based materials as an electrode, an electrolyte and a separator. It can store charge either by non-faradic process or electrostatically movement of ions which associate no transmission of charge between electrode and electrolyte. Fig 1.3 shows the working mechanism of Electric double layer capacitor [33]. The basis of energy storage is because of the (EDLC). When a required amount is provided, there is an aggregation of charges on the surface of the electrode because of difference in potential and the attraction of opposite charges, resulting in diffusion of electrolyte ions from the separator and these ions moves to the pores of the oppositely charged electrode. To eliminate the recombining of ions at electrodes a double layer of charge is formed. The EDLCs storage mechanism it allows fast energy comeback, delivery, and better power performance. There is no chemical reaction due to the non-faradic process. EDLC eradicates inflammation which is observed in the active material where batteries swell during charging and discharging [21]. The storage of charge in EDLCs is highly reversible. This allows EDLC to get higher cyclic stability. Commonly, the EDLCs' performance is constantly associated with the electrochemical behaviour for a large number of charge-discharge cycles likely 10⁶ cycles. Because of the cyclic stability EDLCs are not applicable for deep sea environments and mountains. By altering the nature of electrolytes the electrochemical performance of EDLC can be changed. Electrolytes of organic or aqueous can be used in EDLC. Commonly the

aqueous electrolytes H_2SO_4 , KOH , NaOH , and Na_2SO_4 , etc. have low minimum pore size, and low Equivalent Series Resistance compared to organic electrolytes Eg. Acetonitrile. To store charge in EDLC various types of carbon materials are used. Such as activated carbons, carbon nanotubes and carbon aerogels. Compared to carbon-based materials activated carbon is high specific surface area and high porous structure for the chemical reaction. A complicated porous structure consisting of various sized mesopores, macropores, and micropores is used in activated charcoal resulting in the high specific area. Carbon aerogels are made up of conducting carbon materials for a continuous network with the spread mesopores which consists of nanoparticles. Between the nanoparticles, covalent bonds are formed which can provide high porosity. Due to the chemical bonding and continuous structure of the current collector, it need not require any holding binding agents. Accordingly, binder-less electrodes like carbon aerogels lower the equivalent series resistance compared to the activated carbon. In recent years carbon nanotubes are attracted as important electrode material for EDLC. When we look into carbon nanotube-based electrodes it has a higher capacitance value compared to the activated carbon electrode carbon nanotubes have a balanced surface area compared to activated carbon-based electrodes [32].

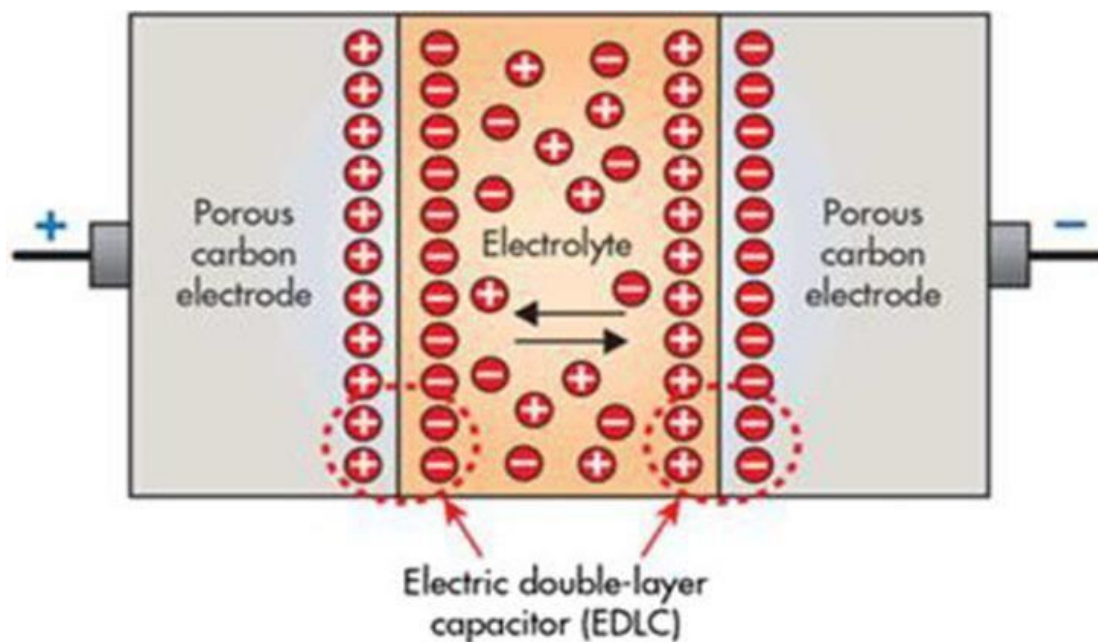


Fig. 1.3: Working mechanism of Electric double layer capacitor

1.7.2 Pseudocapacitor

The charge storage is electrostatic when compared to EDLCs. They store charge through a faradic process which associates the transmission of charge between electrode and electrolyte. Reduction and oxidation take place on the electrode material when the potential is applied to the pseudocapacitor this involves the section of charge beyond the double layer which results in the faradic current passing through the supercapacitor cell. Compared to EDLC, pseudo capacitors are involved in the faradic process and grant them to attain energy density and higher specific capacitance. Examples of pseudo-capacitors are metal oxides and conducting polymers. Like a battery, it involves reduction and oxidation takes place due to its faradic nature [21]. By the process of oxidation, reduction, electro-sorption, and intercalation redox process in pseudo capacitors are achieved. For the improvement of pseudo capacitors, three different types of electrochemical processes are applied such as redox reactions involving the ions from the electrolyte, absorption of surface ions from the electrolytes, doping, and undoing of operating ions into electrode materials. For the doping and undoing system, it is called as intercalation or deintercalation for the layered structure materials. Intercalation and deintercalation take place in the conducting polymer material and it is a bulk process. The first two processes are probably surface area dependent. Because of the micropores present in the electrode materials gives a higher surface area. It allows the delivery of ions from and to the electrodes in a cell. The faradic process allows the pseudo capacitors to attain high energy density and capacitance compared to the EDLCs. In pseudo-capacitors, the electrode material is used to store the charge. Generally, in the pseudo capacitors the electrode materials are conducting polymers and transition metal oxides and sulfides. Intrinsically conducting polymers arrange high capacitance and high conductivity. Because of the high conductivity, they give low equivalent series resistance values. These compounds may have metallic conductivity or semiconductors-like conductivity. Due to theoretically high conductivity transition metal oxide is also used as electrode material in pseudocapacitor. The devices which are based on conducting polymers and metal oxides apply faradic reactions, and the electrostatic charge separation at the electrode and the electrolyte interjunction. RuO_2 based pseudo capacitors reach high power and energy density. In this work, we have

attained perfect pseudo-capacitance for the composite material [32]. Fig 1.4 shows the working mechanism of Pseudocapacitor [34].

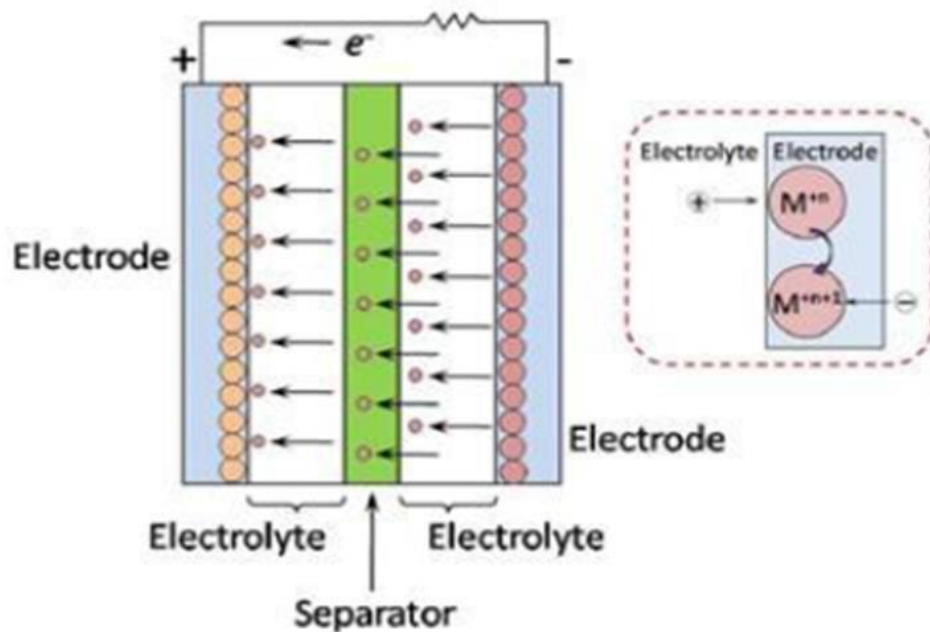


Fig. 1.4: Working mechanism of Pseudocapacitor

1.7.3 Hybrid supercapacitor

The combination of both EDLC and Pseudocapacitors are hybrid supercapacitors. In EDLC it offers good cyclic stability and good power performance. While the pseudocapacitor shows greater specific capacitance. Hybrid supercapacitor has energy source of battery type electrode and power source of capacitor type electrode in one cell, which increase the cell's voltage and leads to the improvement in the power and energy densities. Numerous combinations have been done with both the positive and negative electrodes in the aqueous and inorganic electrolytes [21]. compared to EDLC hybrid have high energy and power density without any effects on the cyclic stability and they cost-effectiveness. For the majority of hybrid supercapacitors, pseudo capacitance material such as NiO is used as a positive electrode [32]. Fig 1.5 shows the working mechanism of Hybrid supercapacitor [35].

Hybrid supercapacitor

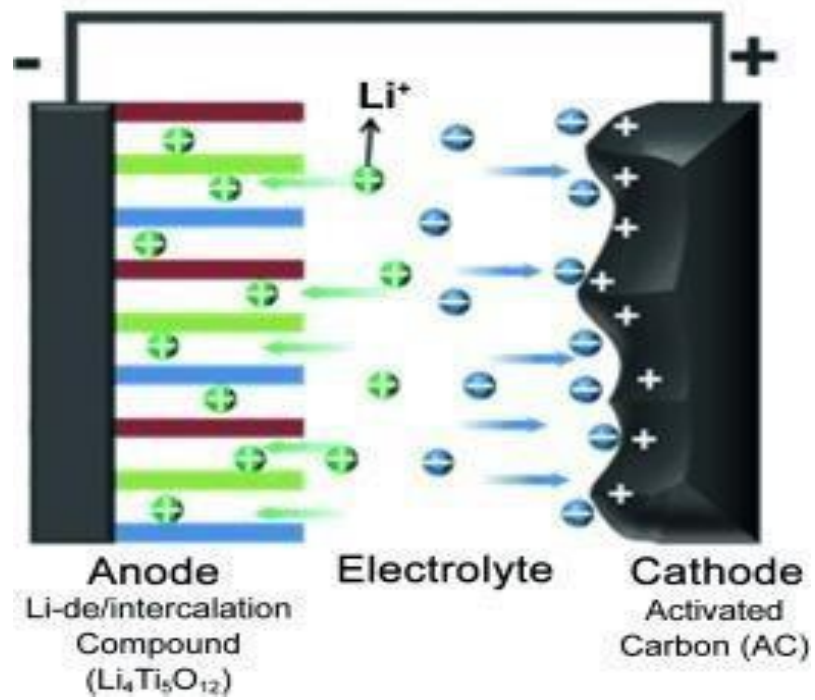


Fig. 1.5: Working mechanism of Hybrid supercapacitor

CHAPTER-2

Literature survey

Nanoscience has been a fascinating area of study for the past twenty years, both from a basic and an application standpoint.

1. Ravuri, S., Pandey, C. A., Ramachandran, R., Jeon, S. K., & Grace, A. N. (2018) A series of SnS/Graphene (SnS/G) nanocomposites at various concentrations of graphene were synthesized by a wet chemical route and the prepared composites were analysed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), High-Resolution Transmission Electron Microscopy (HRTEM) for its structural and morphological investigation. Results show that the prepared SnS nanoparticles in the composite are 30 nm sized and uniformly dispersed on graphene sheets 17(01n02), 1760022.
2. Zhao, M., Zhao, Q., Qiu, J., Xue, H., & Pang, H. (2016) This review is focused on the recent progress in nanostructured Sn-based electrode materials, including Sn, Sn alloys, Sn oxides dichalcogenides and oxysalts for lithium/sodium-ion batteries and supercapacitors. They are very attractive candidates for efficient electrochemical energy storage systems because of their unique physicochemical properties, such as conductivity, mechanical and thermal stability, and cyclability. This review sheds light on the sustainable development of advanced rechargeable batteries and supercapacitors, with a focus on Sn-based nanomaterials 6(98), 95449–95468.
3. Kumar, A., Kumar, N., Sharma, Y., Leu, J., & Tseng, T. Y. (2019) The effects of MWCNT addition on the electrochemical performance of rGO/MWCNT nanocomposite films are investigated. The structural and morphological studies of the films are performed by X-ray diffractometer, Raman spectrometer, surface area analyzer, thermogravimetric analysis, field emission scanning electron microscope, and transmission electron microscope. 14(1)
4. Subagio, A. (2019) Manganese dioxide and multi-walled carbon nanotubes (MWCNT) have received considerable recent interest for their potential application in supercapacitors, MnO₂ as a pseudocapacitor material and MWCNT as an electrochemical double layer capacitance (EDLC) material. . In this study, MnO₂ was mixed with MWCNT during the hydrothermal process.

KMnO₄ and MWCNT were mixed with 20 mL distilled water and stirred using a magnetic stirrer for 2 minutes, then placed into an autoclave. 9936–9947.

5. Barik, R., Devi, N., Perla, V. K., Ghosh, S. K., & Mallick, K. (2018): A facile hydrothermal method has been employed for the synthesis of stannous sulphide nanoparticles. . The electrochemical performance of the synthesized material was reinforced by introducing carbon black. The electro-capacitive properties of the hybrid material were investigated by cyclic-voltammetry and galvanostatic charge-discharge methods.
6. Wang, X., Yang, N., Li, Q., He, F., Yang, Y., Wu, B., ... Xiong, S. (2019). the carboxylated multi-wall carbon nanotubes (MWCNT) are utilized as a substrate for the in-situ growth of bimetallic NiCo-based MOFs (NiCo-MOF). . Due to the unique hierarchical structure and good synergistic effect, the NiCo-MOF/MWCNT composites exhibit excellent capacitance performances. the as-synthesized NiCo-MOF/MWCNT composites are a promising high-performance electrode material for supercapacitors.
7. Reddy, B. P., Sekhar, M. C., Vattikuti, S. V. P., Suh, Y., & Park, S.-H. (2018). Tin Sulfide (SnS_x) thin films were prepared using a solution-based spin-coating method. The applications of SnS in supercapacitors, electrochemical measurements were performed in a 0.2 M NaOH solution. *103*, 13–18.
8. Dubey, R., & Guruviah, V. (2019) Supercapacitor exhibiting high power density has emerged out as the most promising potential for facilitating the major developments in energy storage. The advent of different organic and inorganic nanostructured materials like nano carbons, metal oxides, nanosheets of graphene, and conducting polymers has enabled high-performance-fabricated devices.
9. Zhao, J., & Burke, A. F. (2021) Electrochemical capacitors (ECs) are particularly attractive for transportation and renewable energy generation applications, taking advantage of their superior power capability and outstanding cycle life. Testing of advanced ECs using materials more complex than activated carbons to testing electric double-layer capacitors (EDLCs) using carbon in both electrodes. *59*, 276–291.
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prepared by a simple hydrothermal route. The SnS₂/g-C₃N₄ composite shows a good specific capacitance.

11. Li, Y., Xie, H., & Wang, J. (2010) Carbon-coated SnS as electrode materials for supercapacitors were synthesized by high-energy ball milling and following co-heating with polyvinyl alcohol. The morphology and structure of prepared carbon-coated SnS were studied by high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). Electrochemical investigation indicated that carbon-coated SnS presented preferable electrochemical performances than pristine SnS. *15*(6), 1115–1119
12. Huang, K.-J., Wang, L., Zhang, J.-Z., Wang, L.-L., & Mo, Y.-P. (2014). The MoS₂/MWCNT composites exhibit superior electrochemical performance to pure MWCNT and MoS₂. The enhancement in the supercapacitor is believed to be due to the layered MoS₂/MWCNT conductive network which promotes not only efficient charge transport and facilitates the electrolyte diffusion, but also prevents effectively the volume expansion/contraction and aggregation of electroactive materials during the charge-discharge process. *67*, 234–240.
13. Li, Y., Xie, H., & Tu, J. (2009) Net-like nanostructured SnS/carbon composite was prepared by heating a mixture of SnS nanoparticles and resorcinol–formaldehyde sol at 650 °C. The morphology and structure of prepared SnS and SnS/carbon composite were studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Electrochemical investigation indicated that SnS/carbon composite presented superior electrochemical performances than pristine SnS. *63*(21), 1785–1787.
14. KIAMAHALLEH, M. V., ZEIN, S. H. S., NAJAFPOUR, G., SATA, S. A., & BUNIRAN, S. (2012). Electrode materials are the most important factors to verify the properties of the electrochemical supercapacitor. Recently, several works are conducted on the application of multiwalled carbon nanotubes (MWCNTs) and MWCNTs-based electrode materials for supercapacitors. The nanocomposites of MWCNTs and pseudocapacitive materials are the most promising electrode materials for supercapacitors because of their good electrical conductivity, low cost, and high mass density. *07*(02), 1230002

CHAPTER-3

Aim and Scope

Tin sulfide-based metal sulfides are attracted much attention due to their remarkable application in supercapacitors.

- Heterostructures of SnS and SnS/ MWCNT nanocomposite materials will be synthesized using a Hydrothermal method.
- SnS and SnS/ MWCNT nanocomposite on the size, morphology, and structural constitution will be studied.
- Studies on crystallite structure will be calculated using XRD.
- Studies on structure, size, and morphology will be characterized using Scanning Electron Microscope [SEM], and Transmission Electron Microscope [HR-TEM].
- Studies on chemical composition and oxidation state will be characterized using X-ray Photoelectron Spectroscopy [XPS].
- Electrochemical characterization techniques will be carried out using Cyclic voltametric [CV] and Galvanostatic charge, discharge studies [GCD].

CHAPTER- 4

EXPERIMENTAL DETAILS

Chapter 4 deals with the details of the synthesis and characterization techniques used for the prepared metal sulfide nanomaterials targeted in this project. Techniques used in this project, Hydrothermal method has been used for the synthesis of various nanomaterials explored in this project. The synthesized nanomaterials were examined by a variety of techniques in terms of the morphological, structural, optical, compositional and electrical properties. Moreover, the prepared nanomaterials were used for various applications such as Supercapacitor applications. In a word, this chapter provides all the detailed procedures for the synthesis, characterizations, and applications of targeted nanomaterials in this project.

CHAPTER-4

METHODS AND MATERIALS

4.1 INTRODUCTION

In this project SnS and SnS-MWCNT nanomaterials are prepared and analyzed. The metal sulfide nanomaterials were prepared by a facile Hydrothermal technique. The synthesized SnS and SnS-MWCNT nanomaterials were extensively characterized in terms of their morphological, structure, and electrochemical properties. Study the crystallite structure and structural properties of the nanomaterials and nanocomposites were characterized using an XRD pattern. The particle size and surface morphology can be studied using the characterization of Scanning Electron Microscope [SEM] and High Resolution-Transmission Electron Microscope [HR-TEM]. The chemical composition and oxidation state of the synthesized nanomaterials nanocomposite can be characterized using XPS. The Electrochemical studies were investigated by using Cyclic Voltametric [CV], Galvanostatic Charge, and Discharge analysis [GCD].

4.2 PREPARATION OF NANOMATERIALS

A remarkable research interest in nanotechnology has recently centered on the development of steadfast methods of synthesizing nanoparticles by controlling the sizes, shapes, and chemical compositions [36].

Numerous techniques can be employed for the synthesis of NPs. They are mainly divided into two categories. which is shown in the figure 4.1 Top-down bottom-up approach [37].

(1) Top-down approach

(2) Bottom-up approach [3]

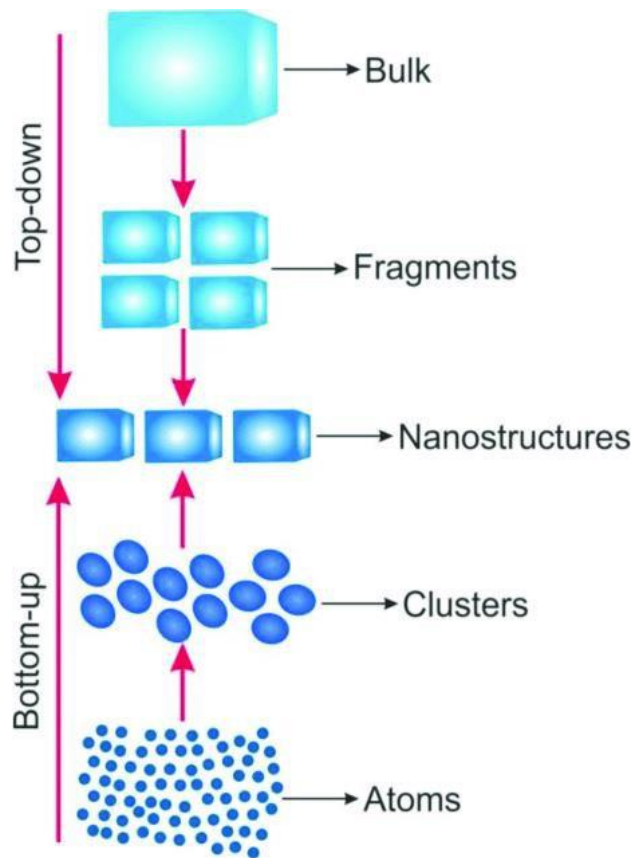


Fig. 4.1: Top-Down Bottom -UP approach

1) Top-down approach:

The Top-down approach comes under the physical process such as crushing and milling etc [36]. Top-down is a destructive method. origin from the bigger molecule, it is decomposed into lower units, and at last these units are transformed into correct NPs [3]. During the construction of the nanostructure, this Top-down approach has negative shock on the surface of the structure because of the crystallographic injury [36]. Some of the methods in this top-down approach are grinding/milling, physical vapor deposition (PVD), CVD, and decomposition techniques [3].

2) Bottom-up approach:

The bottom-up approach comes under the chemical and physical processes [36]. Bottom-up is a constructive method. It is the build-up of

material from atoms to bunch to nanoparticles [5]. Compared to the Top-down, Bottom-up approach has an excellent construction of nanostructure material with proper structure and spreading [36]. For the production of nanoparticles, the most generally used methods are Sol-gel, spinning, pyrolysis, chemical vapor deposition (CVD), and biosynthesis [5]. Fig. 4.2 shows the synthesis techniques of nanoparticles [38].

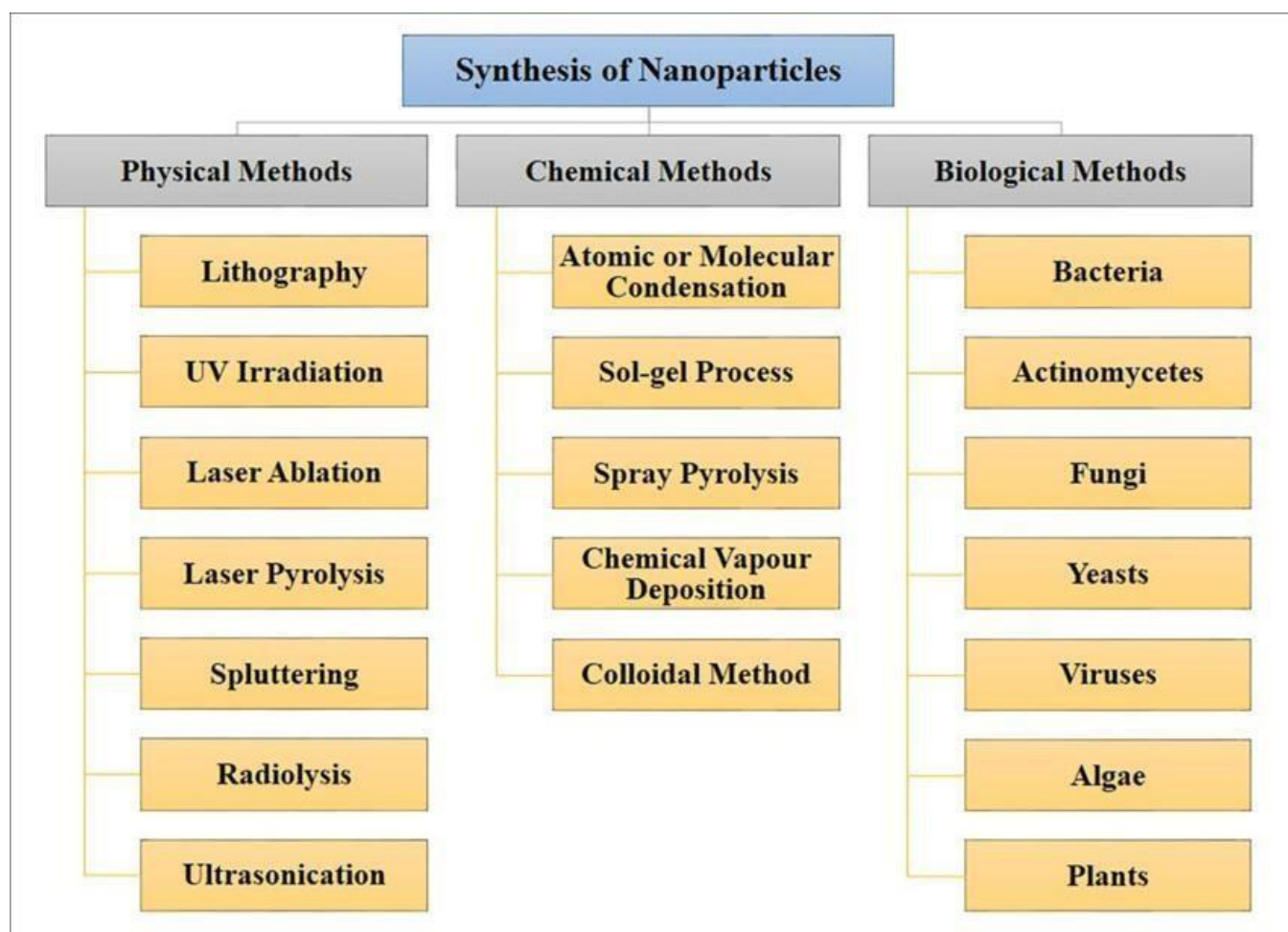


Fig.4.2: Synthesis techniques of nanoparticles

4.2.1 Sol-gel Technique

A colloidal suspension of particles in a liquid phase is known as a sol. The gel is a solid macromolecule dissolved in a liquid. sol-gel is the most used bottom-up approach. Precursors utilized most frequently in the sol-gel method are metal oxides and chlorides. The precursor is subsequently mixed with the host liquid by sonication, shaking, or stirring, resulting in a system with a liquid and solid phase. The nanoparticles are recovered through phase separation using a variety of techniques, including centrifugation, filtration, and moisture removal [5]. The general method of synthesizing sol-gel technique is shown in the Fig.4.3 [39].

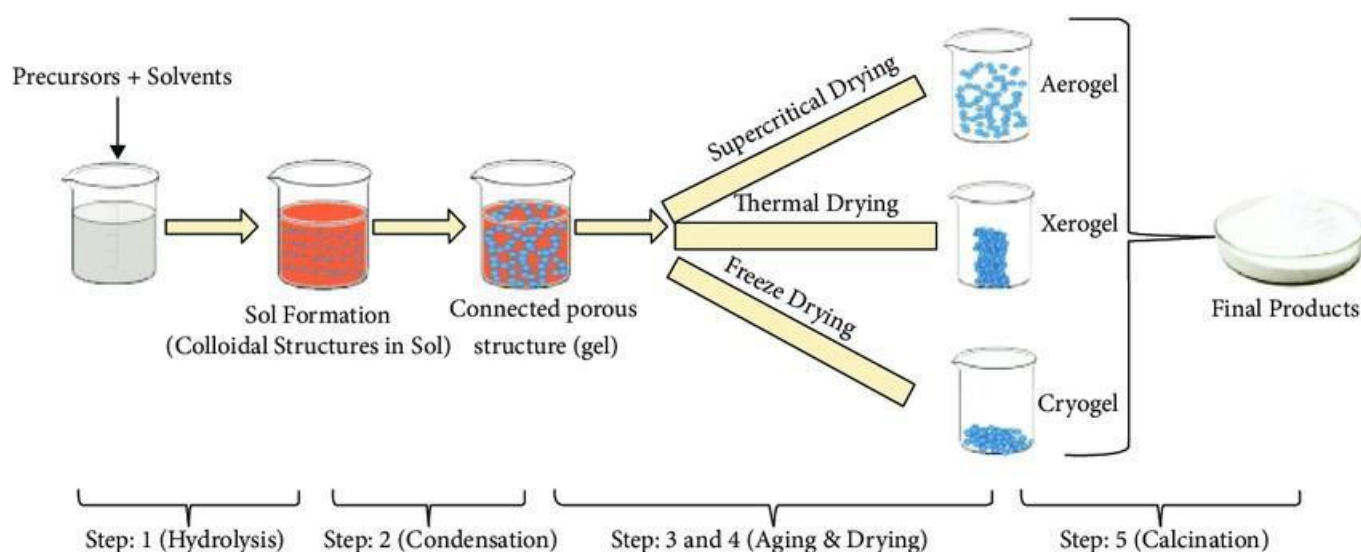


Fig.4.3 shows the Process of sol-gel technique

4.2.2 Hydrothermal synthesis

The general method used for the fabrication of chemical reactions is the Hydrothermal method. In this hydrothermal method, a sealed autoclave reactor is used as an aqueous solvent or mineralizer under high temperature and pressure [40]. It is a liquid-based reaction approach [41]. The Fig. 4.4 clearly shows the hydrothermal synthesis technique and set up [42]. The hydrothermal synthesis method has the advantage of producing massive, high-quality crystals as well as the capacity to crystallize compounds that are unstable close to their melting points. Disadvantages

are the high-cost equipment and the inability to monitor the crystal growth [43]. Additionally, it is a well-known method for creating nanostructures.

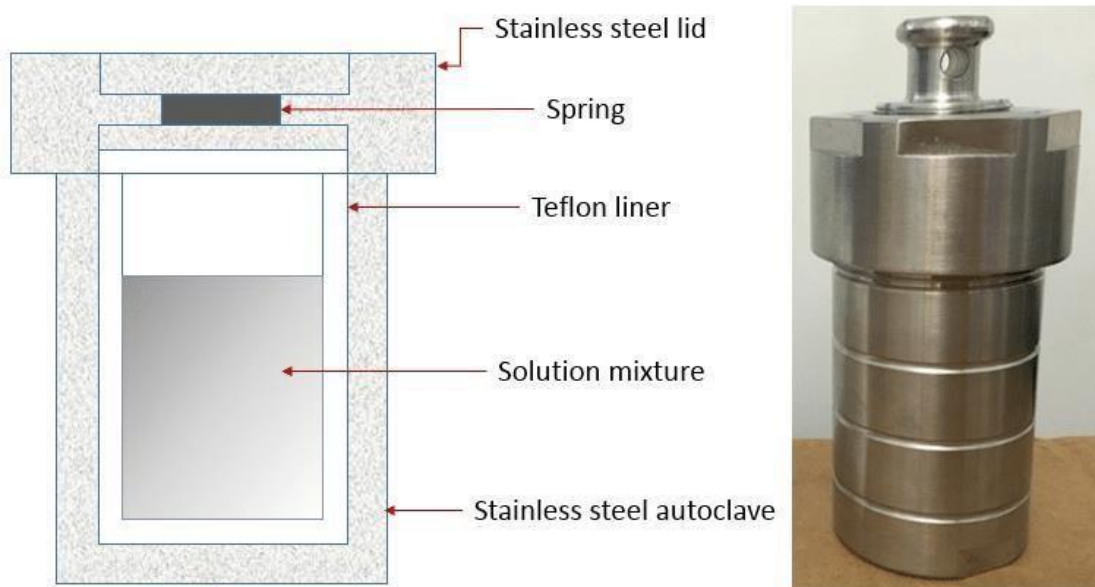


Fig.4.4: Process of Hydrothermal technique

4.3 MATERIALS

All chemicals were purchased in analytical grade and used without further purification. Tin chloride (SnCl_2) and sodium Sulfide (Nas) were purchased from Sigma Aldrich. polyvinylpyrrolidone (PVP) was obtained from Nice Chemical Company and was used as a precursor. Ethanol and Acetone were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL). All the glassware used in this work was acid washed. Ultrapure water was used for dilution and sample preparation.

4.4 Experimental procedure

SnS and SnS-MWCNT composite was synthesized by Hydrothermal Method.

4.4.1 Synthesis of SnS

In this work, SnS was synthesized by a facile Hydrothermal Method. To begin with 0.2 Mole of Tin chloride (SnCl_2) is dissolved in 50 ml of distilled water. The reaction was stirred for 5 minutes. To reduce agglomeration, 1g of Polyvinyl pyrrolidone is added to the above-prepared solution and allowed to stirred for 5 minutes. In the above solution, 0.2 Mole of Sodium Sulfide (NaS) is dissolved, in 50

ml of distilled water is added in drop wise manner. After 2 hours of stirring, it is transferred to the autoclave and it is maintained at 160°C for 24 hours. The resultant product was washed thoroughly with deionized water for removal of residuals followed by washing with acetone. This washed solution is dried in an air oven for 5 hours at 120°C. Finally, the SnS nanomaterial is grinded and packed.

4.4.2 Synthesis of SnS-MWCNT nanocomposite

To prepare SnS-MWCNT a facile One step Hydrothermal Method is adopted. For which 250 mg of MWCNT is dissolved in 50 ml of distilled water. The above solution is sonicated for 15 minutes for better dispersion. The reaction was stirred for 30 minutes. To the above solution, 0.2 Mole of Tin chloride (SnCl_2) dissolved in 50 ml of distilled water is added in drop wise manner. To reduce agglomeration, 1g of Polyvinyl pyrrolidone is added and allowed to stirred for 5 minutes. Later, 0.2 Mole of Sodium Sulfide (Na_2S) dissolved, in 50 ml of distilled water is added in drop wise manner to the above solution. After 2 hours of stirring, the resultant solution is transferred to the autoclave and it is maintained at 160°C for 24 hours. The final product was washed thoroughly with deionized water for removal of residuals followed by washing with acetone. This washed solution is dried in an air oven for 5 hours at 120°C. Finally, the SnS-MWCNT nanocomposite is grinded and packed.



0.2 M of SnCl_2 was dissolved in 50 ml of D.I And stirrer for 15 minutes.



PVP 1g was added to the above solution



0.2 M of NaS was dissolved in 50 ml of D.I and added to the above solution



Transferred in an autoclave and maintained at 160°C for 24 hours.



Grinded and packed sample

Fig 4.5 shows the fabrication method of SnS

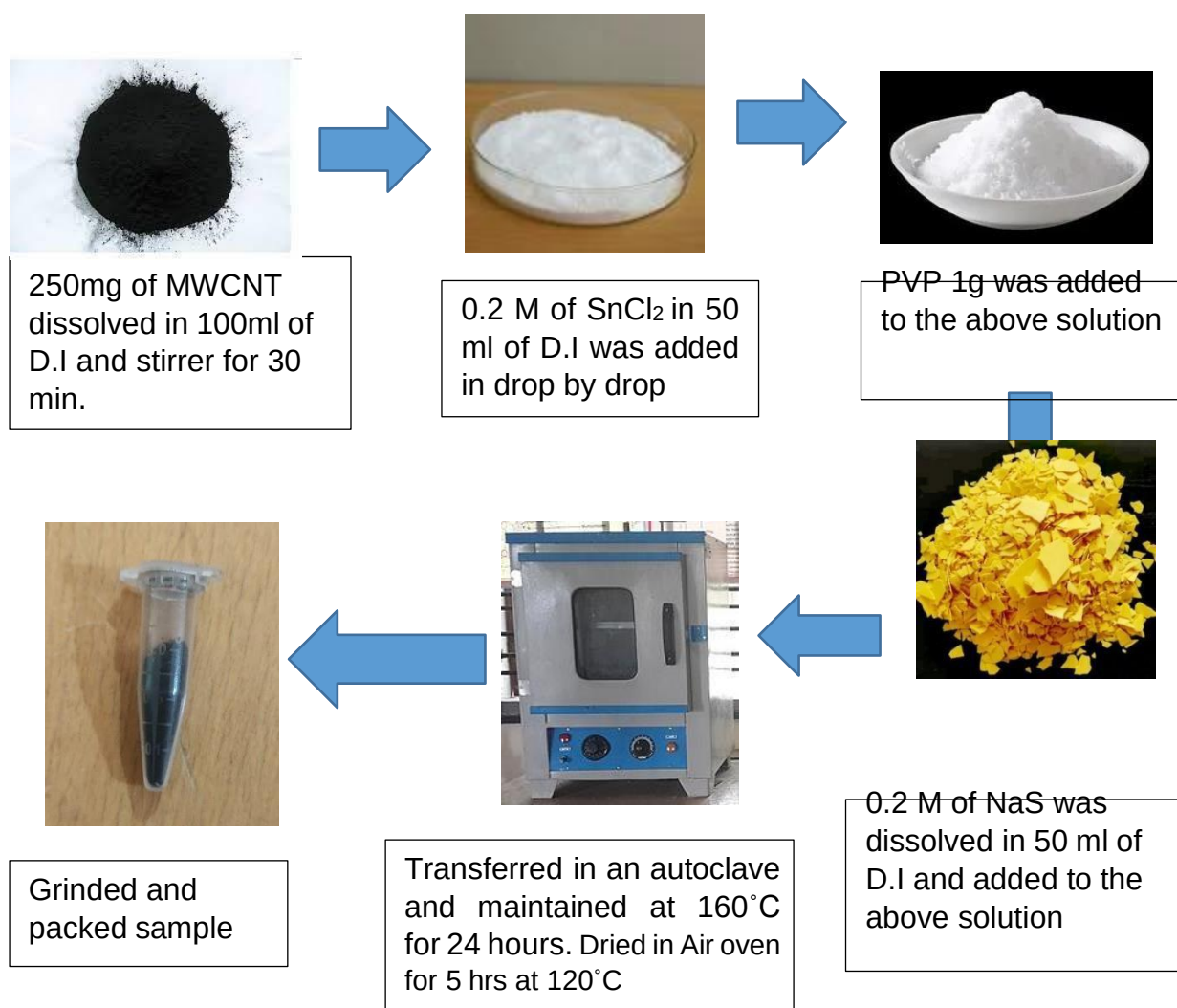


Fig.4.6 shows the fabrication method of SnS-MWCNT nanocomposite

4.5 FABRICATION OF ELECTRODE

The electrochemical behaviour of the prepared samples was carried out using SP-300 electrochemical workstation in three cell electrode system. The electrochemical performances were exhibited using cyclic voltammetry (CV), Galvanostatic Charging Discharging (GCD), and Electrochemical Impedance Spectroscopy (EIS) analysis with 3 M KOH electrolyte. Platinum wires and saturated calomel electrode (SCE) were taken as a counter and reference electrode, respectively and a desired concentration

of the prepared SnS and SnS-MWCNT nanocomposite were used as active materials for working electrodes. The sample is mixed with polyvinylidene fluoride (PVDF) which is used as a binder and carbon black (super P) which used as conducting materials in 80:10:10 wt percentage. The electrode fabrication method has followed two steps: In the first step, a piece of Nickel Foam (NF) was immersed into diluted HCL solution for 10 mins after that, it is cleaned with deionized (DI) water followed by sonication using ethanol solution for 5 min to remove the outer layer of NiO from the NF surface. Subsequently, the cleaned NF was dried in an oven at 60 °C and then measured the weight of the bare NF. The next step was to make a slurry, an N-methyl-2-pyrrolidone (NMP) was used as a solvent for the samples separately and grounded well and coated on NF. Next, the coated NF was dried at 100 °C for 4 h to confiscate any solvent present on the surface of coated NF. Then the modified electrode was again weighed to measure the weight difference between the empty NF and coated NF. The calculated mass loading of the sample coated on nickel foam was 2 mg. The specific capacitance (Sc) of the fabricated electrode was evaluated from CV data using the following

$$C_s = I \Delta t / m \Delta V$$

Where Sc represents the specific capacitance (F/g). I denote the current density (A), A is the discharge time (s), ΔV represents the potential window (V) and m denotes the mass (g) of the active materials. Finally, the specific capacitance of the modified electrode was calculated using CV and GCD data from the electrochemical workstation [44].

4.6 CHARACTERIZATION OF PREPARED METAL SULFIDE NANOMATERIALS

By using XRD the structural qualities of the prepared samples were evaluated. The prepared nanoparticles size and the surface can be studied using SEM. To further confirm the surface morphology and structural properties of the nanomaterial, with high magnification sample is analyzed by using HR-TEM. XPS can be used to characterize the chemical makeup and oxidation state of the synthesized nanomaterial and nanocomposite. Galvanostatic Charge and Discharge analysis (GCD), as well as Cyclic Voltametric (CV), were used to investigate the electrochemical properties.

4.6.1 X-ray diffraction

A non-destructive method for figuring out a material's crystal structure is X-ray diffraction. A crystal lattice is a parallel plane-shaped three-dimensional arrangement of atoms in space separated from one another by a distance (d). The sample's XRD pattern is influenced by the dimensions and shapes of the crystal's fundamental unit cell [45-49]. XRD is the major technique to determine the crystal structure of a material. The JCPDS database, which is the industry standard for XRD patterns, is used to identify the phase of a wide range of crystalline phases in solid specimens. XRD has the main advantage of characterizing both the products and precursor with a brief nanoparticle [50]. XRD is used for inorganic materials for the estimate of phase pristine and crystallinity [51]. X-Ray diffraction is based on the principle of Braggs law.

$$n\lambda = 2d \sin\theta$$

where d is the distance between the atomic layers in a crystal, λ is the wavelength of the incident X-ray beam, and n is an integer which is the order of the reflection and the path difference in the condition of wavelength between waves scattered by the adjacent planes of atoms, θ is the Bragg angle or angle of incidence [52]. A monochromatic beam of X-rays is allowed to fall on a sample and the reflected X-rays are detected by a detector [53]. The Fig 4.5 shows the working principle of X-Ray diffraction [54]. The synthesized material XRD pattern was calculated by the Debye-Scherrer equation

$$D = K\lambda / \beta \cos\theta$$

Where D is the average crystalline size, λ is the wavelength of the incident light, (1.5405 Å), β is the full width half maximum (FWHM) of the peak, θ is the diffraction angle, K is the particle shape coefficient (0.9) for the spheres.

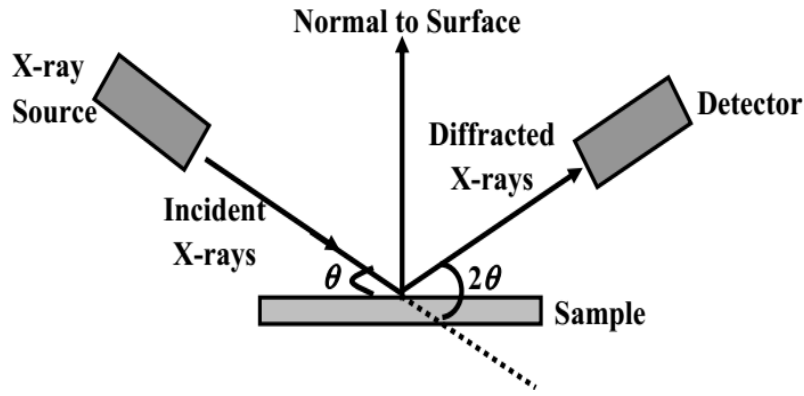


Fig. 4.7: Working mechanism of X-Ray Diffraction

4.6.2 Field Emission Scanning Electron Microscope (FE-SEM)

A scanning electron microscope is a type of electron microscope which shows the working principle of Field Emission Scanning Electron Microscope in the Fig. 4.6 [55]. that creates images of materials by sweeping a concentrated beam of a high-energy electron across the surface of solid specimens to produce a range of signals. Scanning Electron Microscope (SEM) is a largely used conductive method for diagnosing and investigating nano and micro range particles of solid objects. The main advantage of a Scanning Electron Microscope [SEM] is it can diagnose the particle size in the resolution range of about 10nm which is $100 \text{ \AA}$. For the analysis of the location of each separate crystal and composition, SEM is associated with other techniques such as Energy Dispersive X-Ray Analysis [EDAX] [56]. From the EDAX we can find the elemental composition.

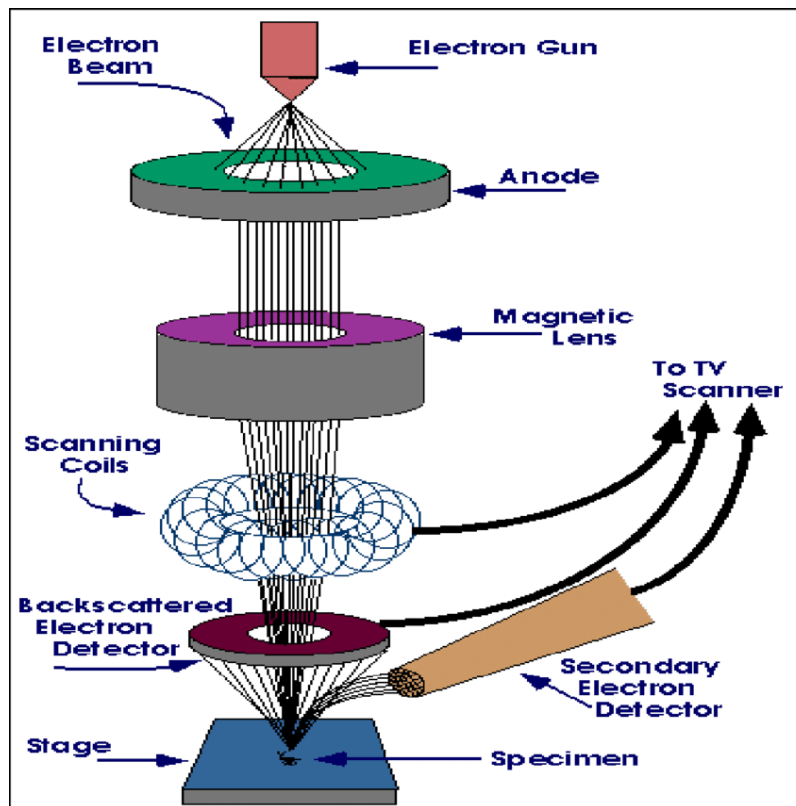


Fig.4.8 Working mechanism of Field Emission-Scanning Electron Microscope

4.6.3 High Resolution-Transmission Electron Microscope [HR-TEM]

By using a High-Resolution Transmission Electron Microscope, a fine crystallographic arrangement of samples can be studied even at an atomic scale. The Fig. 4.7. shows the working principle of FE-HR-TEM [57]. The LaB6 and tungsten are largely used in electron guns, thus far field emission is in more usage. Compared to Scanning Electron Microscope the HR- TEM is found at a higher growing voltage which is constructed at the high voltage range of 1 MV and above. The improvement in the application of high voltage increases the image resolution, this is accomplished by the decrease in the electron wavelength and also higher penetration. Which can even study the thicker sample.

The basic principle of HRTEM is the same as the deflection of light by a glass lens is the same as the electromagnetic fields, being deflected by the beam of electrons. To focus the electron beam on an area the condenser is used as a first lens, most of the

electrons come in contact with this area and pursue their way, while others transmit the sample without any contact. Where most of the electrons are reached at the objective lens, which results in forming the improved image which is shown in the other magnifying lens. The image obtained in the HR-TEM is usually black and white because of the adjustment done between the electrons that hit the fluorescent screen and the electrons are restricted in the microscope tube.

The micrograph consists of a light area called electron-dense and a dark area called electron illuminated. The sample is kept in the pole pieces of the objective lens where the thickness of the sample should be less than 100 nanometers. The series of projector lenses and objective lenses gives a magnification of about 10^6 or above is achieved. In the HR-TEM diagnosis lattice image can be obtained at atomic range resolution chemical things at a structural resolution of about 1 nm or even the best resolution. The Transmission Electron Microscope images were obtained by Energy Dispersive Spectra (EDS) and their following Selected Area Electron Diffraction (SAED) [58].

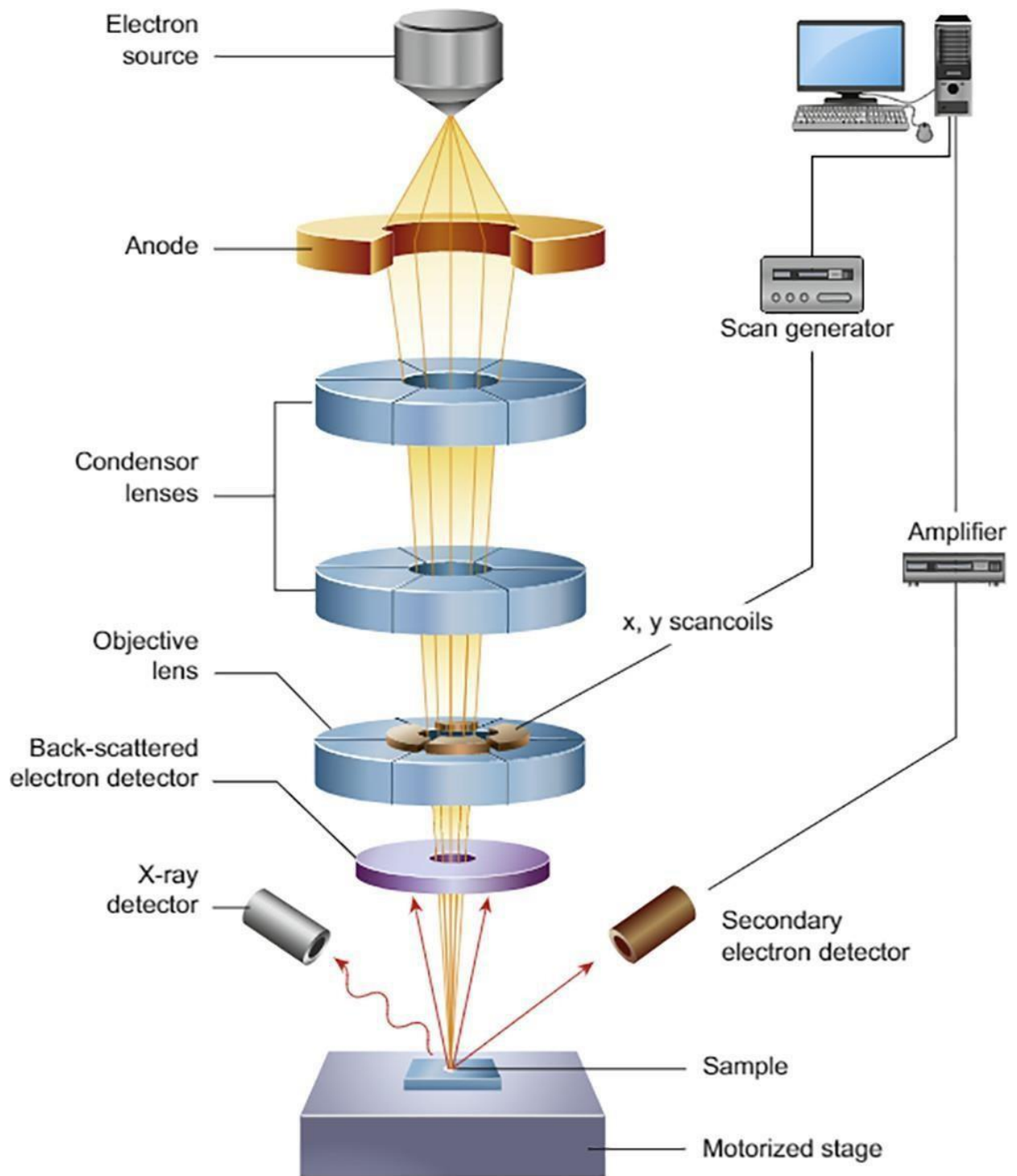


Fig.4.9 Working mechanism of High Resolution-Transmission Electron Microscope

(a) Selected Area Electron Diffraction (SAED)

Inside a TEM instrument, a diffraction technique is used in the Selected Area Electron Diffraction which helps to study the crystal defects and crystal structure of the sample, this is known as the crystallographic technique. X-Ray diffraction and Selected Area Electron Diffraction both are the same but in Selected Area Electron Diffraction it examines the sample in the hundred nanometer in size whereas in the X-Ray diffraction, it examines an area of numerous centimeters in size. From the Selected Area Electron Diffraction, one can be able to see the desirable particular area of the diffraction pattern of the sample.

The sample of the phase and the crystal structure are comprehensible depending on the diffraction obtained from the scattered electrons by the lattice. Already it is operated in a diffraction pattern it can be easily understood whether it is a single crystal, amorphous or polycrystalline. Selected Area Electron Diffraction pattern consists of atoms each atom dependable with the planes of the lattice of a specific miller index in a single crystal. Selected Area Electron Diffraction pattern has all chances to indicate the atom. If the sample is an polycrystalline in essence each ring in the Selected Area Electron Diffraction matches with the some group of lattice planes.

(b) Energy Dispersive X-Ray Analysis (EDX)

EDX has been taken to investigate the elemental composition of the sample. The Fig 4.8. shows the working principle of Energy Dispersive X-Ray Analysis [59]. It is associated with the SEM and TEM to analyze the surface of the sample. When the bombarding electrons come in contact with the sample electrons some of the electrons are hit off. The elemental composition can be analyzed by the change of electrons on the sample which results in the X-Ray through this it can study the characteristics of the material.

It gives information about the elementary composition of each separate point or plots the lateral circulation of elements from the image of the area. Depending upon the X-Rays received EDX spectrum relates to the energy levels of the majority of X-Rays captured. The obtained original peak to an atom is constant with a single element. In the EDX spectrum, the intensity peak is directly proportional to the chemical

composition of the specimen, if the peak is higher in the spectrum the concentration will be more [60].

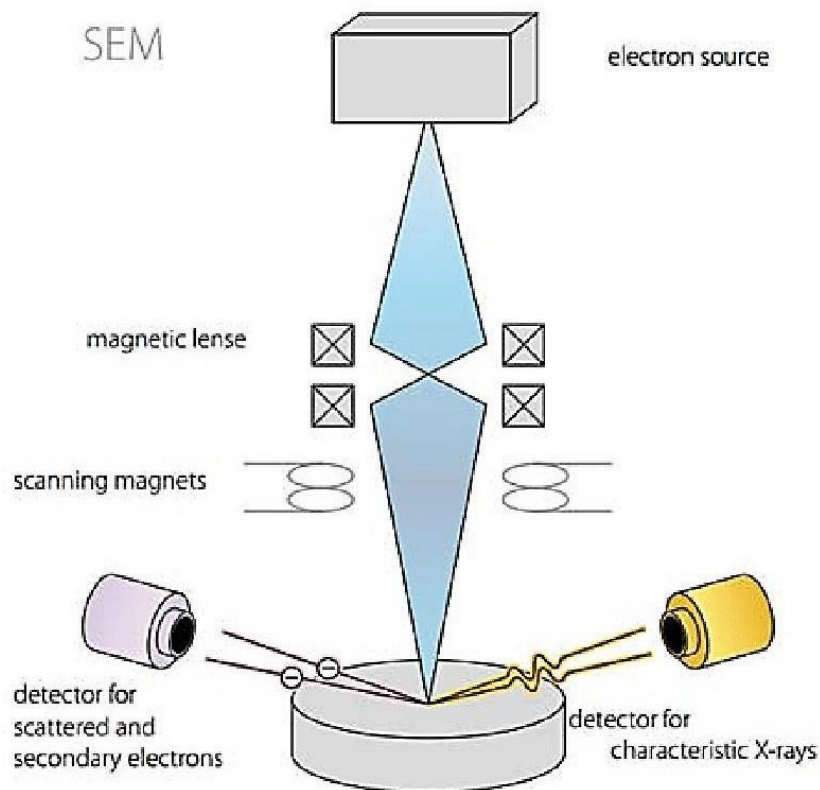


Fig. 4.10 Working mechanism of Energy Dispersive X-Ray Analysis

4.6.4. X-ray Photoelectron Spectroscopy

The X-Ray Photoelectron technique is widely used in the area of chemical engineering and material science for the analysis of the composition of surfaces and interfaces. The Fig. 4.9 shows the working principle of XPS [61]. The main strength of the XPS technique is the chemical shift which refers to the change in the binding energies of the core-level electrons because of the reaction caused by the atom. This helps in examining the bonding structure.

The monochromatic X-Rays sample is irradiated as a result of the emission of photoelectrons where its energies are investigated by the elements within the volume of the sample. XPS graph is plotted against a number of electrons against the binding energy.

The electrons which are emitted from the specimen are analyzed in the range of 1-10 nm. When the X-Ray beam is irradiated from the sample, the electrons which are on the upper surface of the material will break. The material can be predicted based on the work function and binding energy. From the material, the comparable kinetic energy of the emitted electrons will be marked using an energy electron diagnosis and this results in the transformed XPS signals.

Every element has its different binding energy values which are associated with every atomic core orbital, in the photoelectron spectrum each element has its own different peaks in the photoelectron spectrum which coincide with the kinetic energy solved by the energy of the photon and their related binding energies. The arrival of peaks at the correct energies ensures the presence of a particular present in the sample. The absorption of the specimen was related to the peak intensity, quantitative analysis of surface composition is also possible.

The powdered samples are absorbed into a steel holder using double tape. Using the electron gun the property of the charge is reduced [62].

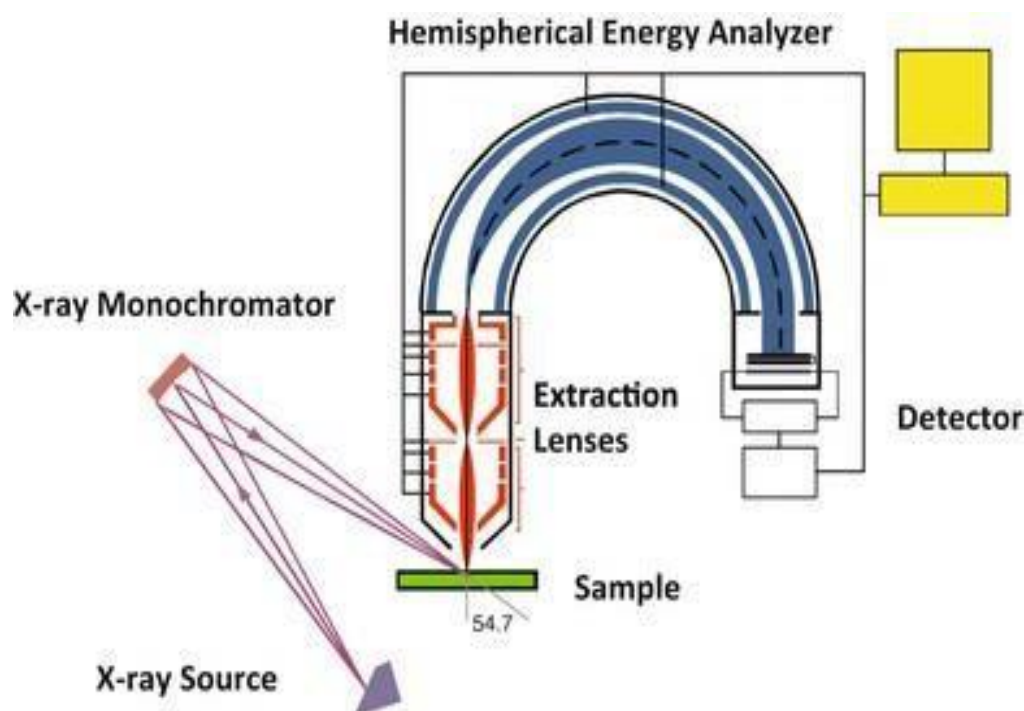


Fig. 4.11: Working mechanism of X-Ray Photoelectron Spectroscopy

4.6.5 Electrochemical characterization

The electrochemical characterization is used to analyze the electrochemical characterization of the materials and its performance. In a three-electrode system, the electrode material is taken as the active material which is tested by the half cell. There is a three-electrode system that consists of

- The working electrode
- The counter electrode and
- The reference electrode

The voltage of the potential is sustained at a constant narrow potential range in order to submit the working electrode of the potential. Platinum is taken as the counter electrode generally because it can pass the current through the working electrode, this blocks the reference electrode from current carrying which results in a change in the potential of the reference electrode. The active material of the practical performance is found in a 2 full-cell electrode system, compared to a half-cell the practical supercapacitor has positive and negative electrodes. All the electrodes are kept with active materials in a full-cell system. Commonly for the practical application of capacitor, two electrode is enough but to study the electrode materials three electrode system is needed.

a) Cyclic Voltammetry (CV)

It is achieved to observe the electrochemical reactions of the electrode material in an approximate way. When the potential applied to the working electrode slope is continuous corresponds to the time initiating from the open circuit potential to the set potential. In the same way, the potential revives to the alternative set potential. In this diagnosis, the parameters cycle and scan rate are kept constant. The rules to examine the electrochemical specification of the electrode material is maintaining the redox potential without improving the CV of the potential window.

This technique gives an idea of accelerate atoms of redox potentials of the following electroactive materials, combined it give a available diagnosis on the media at the redox process time. In order to gather the element to make a touch to the related electrode surface, the solution element is being electrolyzed. To carry out the electron transfer the surface is made with the positive or negative voltage.

In simple cases, the electrode surface is initially charged to a specific voltage relative to the reference half-cell, such as calomel or Ag/AgCl. The electrode's voltage is then changed to a higher (or lower) voltage at a set rate, and it is then returned to its initial value at the same slow rate. When the surface of the electrodes is touched, a sizable quantity of current is seen in the electrode circuits, when the electrode is sufficiently positive or negative, the solution species is prompted to either take the electrons away from the surface or give the electrons back.

The results of the cyclic voltammetry are shown graphically as a curve, with the current represented by the X-axis and the voltage by the Y-axis. The analysis is done at numerous different scan rates. The analysis is done on CHI 660E electrochemical workstation.

The charge current also seems to be independent of potential. Therefore, when the applied potential is negative, the sign of the linked current changes. However, it has been found that in a resistive system, the current is dependent on the potential. When the system's resistance is discovered to be at its highest, the tilted plot's slope increases. As a result, the shape transforms from rectangular to parallelogram. When a faradaic system is involved, the CV results deviate from a rectangular form due to oxidation and reduction peaks, which can be used to establish the presence of redox species in the system.

b) Galvanostatic Charge Discharge Analysis (GCD)

To ascertain the active materials' specific capacity and capacitance. The most reliable technique is galvanostatic charge-discharge analysis. When doing an analysis, the cell's linked current flow value is immediately changed from zero to a specific finite value. The working electrode is charged and discharged at a predetermined voltage range while the operation is time-lapse recorded. During this process, a continuous positive and negative current alternately flows over the working electrode. The GCD is predicted to show a triangle charge-discharge curve if the working electrode exhibits optimal capacitive behavior. GCD analysis is done in this work at a variety of current densities.

c) Electrochemical Impedance Spectroscopy (EIS)

EIS can be used to determine an electrochemical system's impedance. By adding an alternating potential that modifies the sinusoidal wave's frequency, one may measure the ratio of the corresponding current signal to the alternating potential in an electrochemical system. The impedance that is produced when the potential quotient is divided by the current is seen as a complex number. The Nyquist plot is used to analyze electrochemical impedance, with the actual component being the X-Axis and the imaginary part being the Y-Axis. With an amplitude of 5 mV, electrochemical impedance is measured in this work between 0.01 Hz and 100 kHz [63].

CHAPTER-5

RESULTS AND DISCUSSION

Chapter 5 describes the main results and discussion of the project. This chapter is divided into several sections and each section describes the synthesis, detailed characterizations, and particular application of metal sulfide nanomaterial.

Section 5.1 describes the X-Ray diffraction of the SnS and SnS-MWCNT nanocomposite crystalline structure, characterization, and applications of nanoparticles grown via the Hydrothermal method using commonly used laboratory chemicals.

Section 5.2 demonstrates the FE-SEM images and their characterization based on SnS and SnS-MWCNT nanocomposite

Section 5.3. demonstrates the HR-TEM images and their characterization based on SnS-MWCNT nanocomposite.

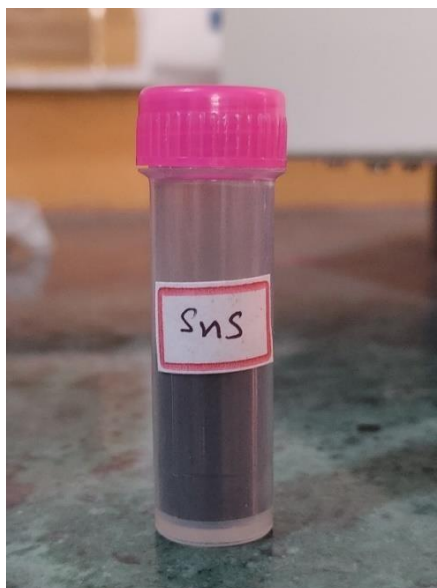
Section 5.4. demonstrates the XPS activity of SnS-MWCNT nanocomposite.

Section 5.5. determine the Electrochemical characterization of SnS-MWCNT nanocomposite.

CHAPTER – 5

5. RESULT AND DISCUSSION

The as prepared pristine SnS and SnS-MWCNT nanocomposite via a facile hydrothermal method is analyzed in various parameters like crystallite structure, surface morphology, chemical composition and chemical redox reactions using various characterization techniques like X-Ray diffraction, FE-SEM, HR-TEM, XPS, and Electrochemical analysis for studying the supercapacitor application. Fig 5.1 and Fig 5.2 displays the photographic image of our prepared SnS and SnS-MWCNT nanocomposite



**Fig.5.1 Prepared sample
Of SnS**



Fig.5.2 Prepared sample of SnS-MWCNT

5.1 X-RAY DIFFRACTION ANALYSIS

Fig.5.3 displays the XRD patterns of Pure SnS and SnS / MWCNT nanocomposite. The X-ray diffraction (XRD) approach was used to read the phase purity of the as-synthesized SnS [7]. The obtained diffraction peaks reflect the orthorhombic structure of Single phase SnS [64] with an absence of impurity peaks. The diffraction peaks of MWCNT / SnS are broad and highly intense compared to pure SnS nanoparticles. The XRD pattern exhibits a very high intense peak at $2\theta = 32.04^\circ$ the other noticed peak positions are at 26.48° , 32.04° , 38.31° , 44.73° , 52.18° [17]. The corresponding planes are (1 0 2), (0 1 3), (1 0 4), (0 2 2), and (1 1 5) which exactly match with JCPDS card no.00-001-0984 [65]. The XRD pattern of MWCNT shows a sharp peak at $2\theta=26.57^\circ$ analogous to the (0 0 2) planes which is a very common diffraction plane of graphite with hexagonal structure and explains the presence of carbon in the sample [66,67]. Relying on the sheerer formula [68] as displayed in equation (1) the crystal size of both samples was calculated and found to be 27.12 nm for SnS nanoparticle and 32.43 nm for SnS / MWCNTs nanocomposite. The surface morphology and particle size of the prepared samples are further studied in detail via Scanning Electron Microscopic techniques.

$$D_{hkl} = \frac{K\lambda}{\cos\theta} \quad \text{----- (1)}$$

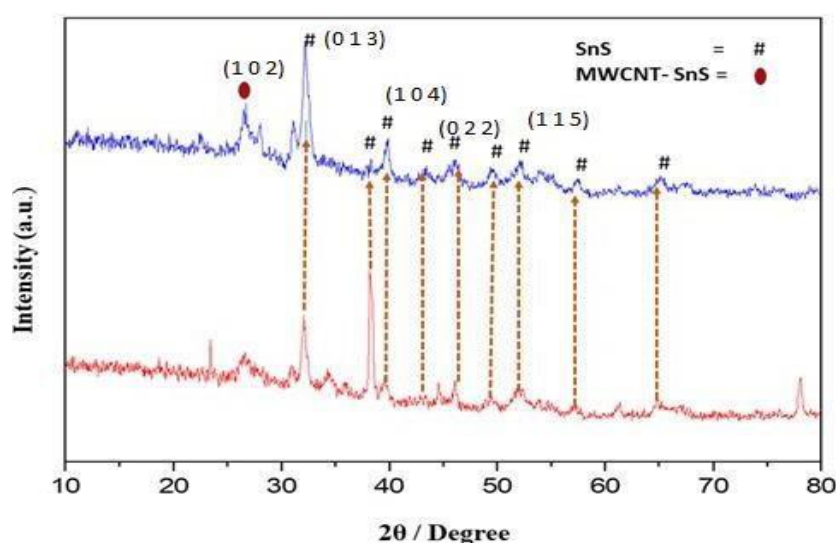


Fig. 5.3. Displays the X- Ray Diffraction pattern of SnS and SnS-MWCNT nanocomposite

5.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPE

The surface morphology of the prepared SnS and MWCNT – SnS nanocomposite were characterized using Field Emission Scanning Electron Microscope. Fig. 5.4 reflects the FESEM image of SnS as seen in Fig.5.4(a) the sample exhibits a 2-D layer-like structure in different orientations overlapped or coalesced by a spherical particle-like surface morphology. In Fig.5.4 (c, d) the Spherical particle like subunits aids in the development of the 2- D layer-like structure (Fig.5.4 (b) As a result the pure SnS has formed heterostructure surface morphology which plays as a pathway for the fast diffusion of ions between electrode and electrolyte. Fig.5.5 displays the elemental mapping of SnS nanoparticles confirming the presence of Sn and S. Fig. 5.6(a). displays the FESEM image of SnS – MWCNTs nanocomposite. The sample results in the formation of 3-D tube (Fig. 5.6(b) like structure which originates from 2-D layer like morphology of SnS. Fig. 5.6(b) clearly displays the Hetrostructure formation of SnS – MWCNTs nanocomposite accompanying both 2-D layer and 3-D nanotube like surface morphology. The addition of MWCNT along with SnS has made the sample to provide a novel and stable surface morphology which attributes for a high surface area, the 3- D tube like structure (Fig. 5.6 (c, d)) aids in fast faradaic redox process by providing more Electrochemical redox active sites.

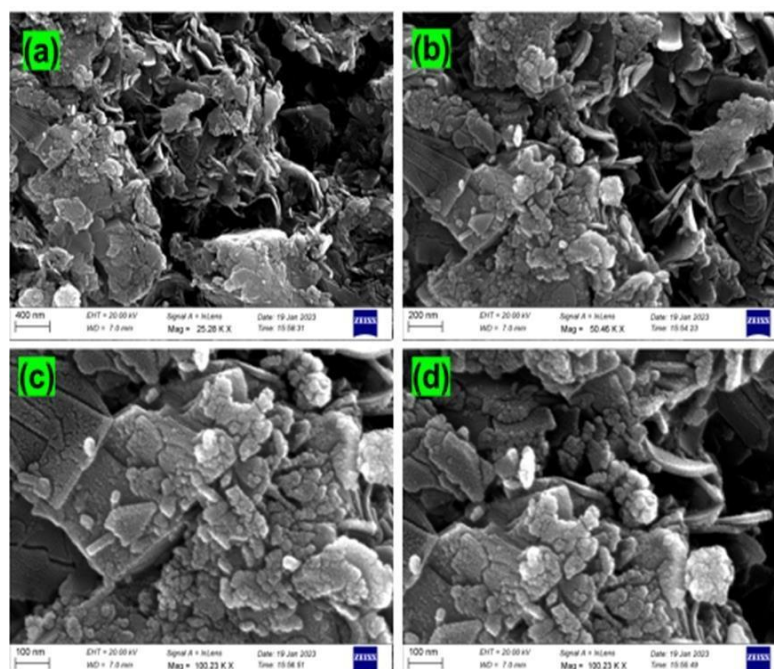


Fig.5.4 displays the FE-SEM images of SnS

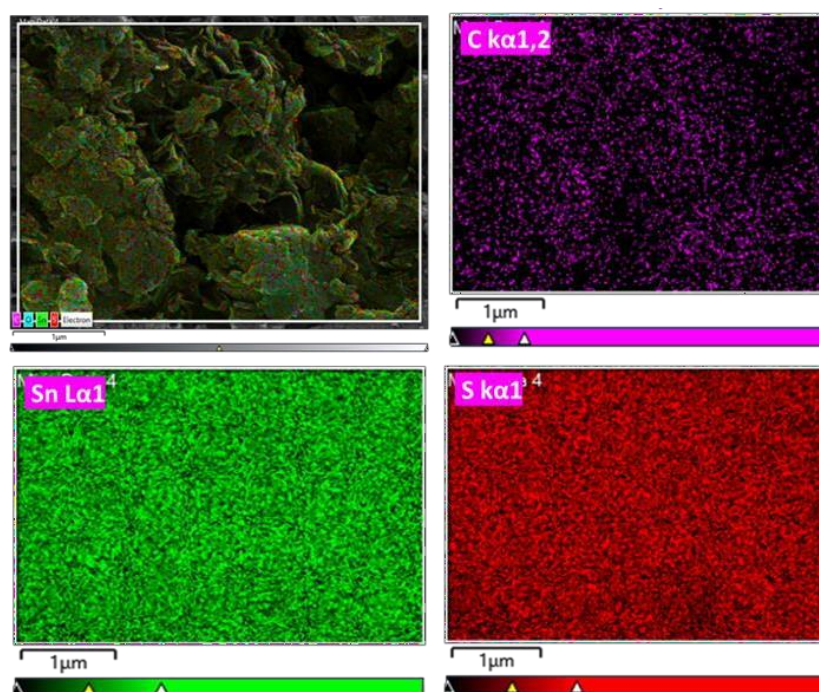


Fig.5.5 displays the Elemental mapping of SnS

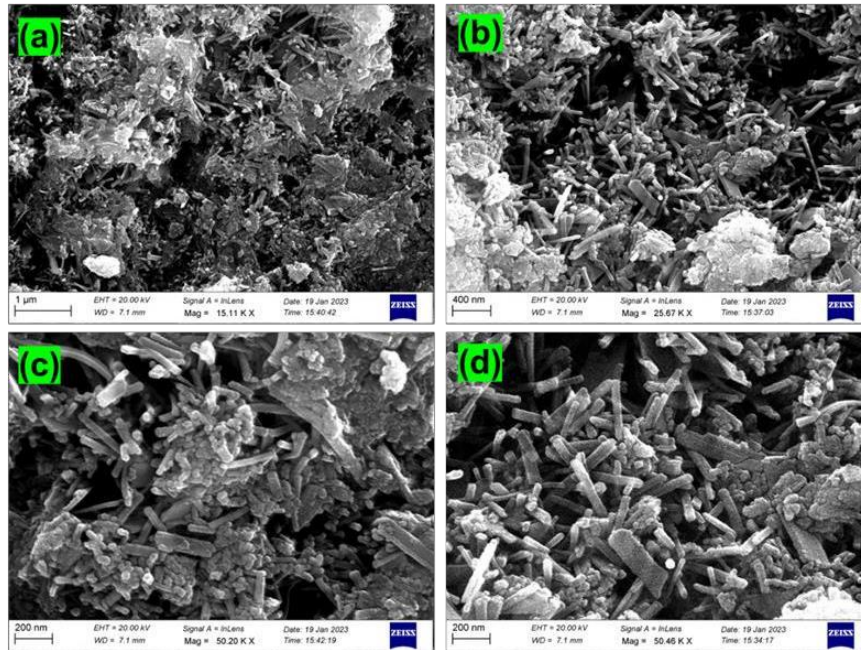


Fig.5.6 displays the FE-SEM images of SnS-MWCNT

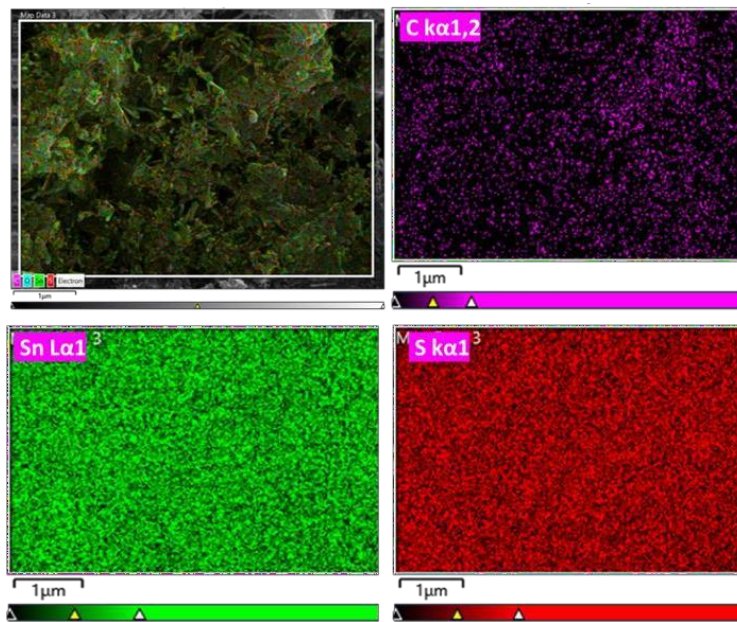


Fig.5.7 displays the Elemental mapping of SnS-MWCNT

5.3 HIGH- RESOLUTION TRANSMISSION ELECTRON MICROSCOPE ANALYSIS

The morphology of the as-prepared SnS / MWCNT nanocomposite Hetero – Structure was examined by a High-resolution Transmission electron microscope as displayed in Fig. 5.8 at different magnifications. Fig.5.8(a) shows lower magnification HR-TEM images of SnS / MWCNT nanocomposite, which dispose the 2- D sheet like surface morphology of SnS and has a negligible presence nano tube like structure of MWCNT's attached to it. The high magnification of HR-TEM images in Fig. 5.8(c - h) shows the fine resolution of nano-tube like surface morphology originating from 2-D layer like structure. Their corresponding Selected area diffraction pattern (SAED) is presented in the inset of Fig. 5.8(i), which revealed the polycrystalline nature of the prepared SnS / MWCNT nanocomposite. The unique heterostructure of the prepared SnS / MWCNT nanocomposite make it as a suitable candidate for energy storage applications by providing high surface area to under sustainable faradaic redox reactions for long cycles with noticeable specific capacitance value and appreciable retention of specific capacitance even after large number of charge discharge cycles.

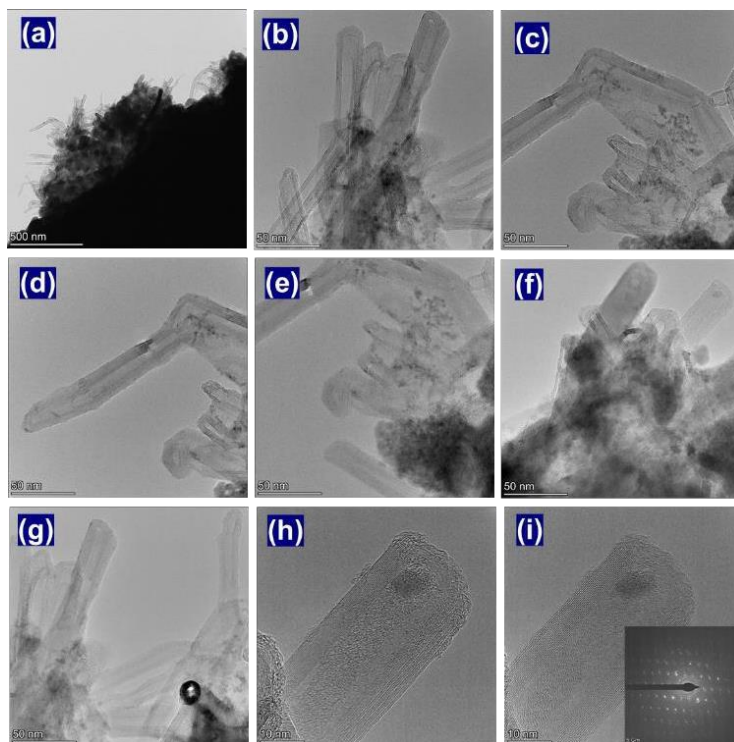


Fig.5.8 displays the HR-TEM images of SnS-MWCNT nanocomposite

5.4 X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS

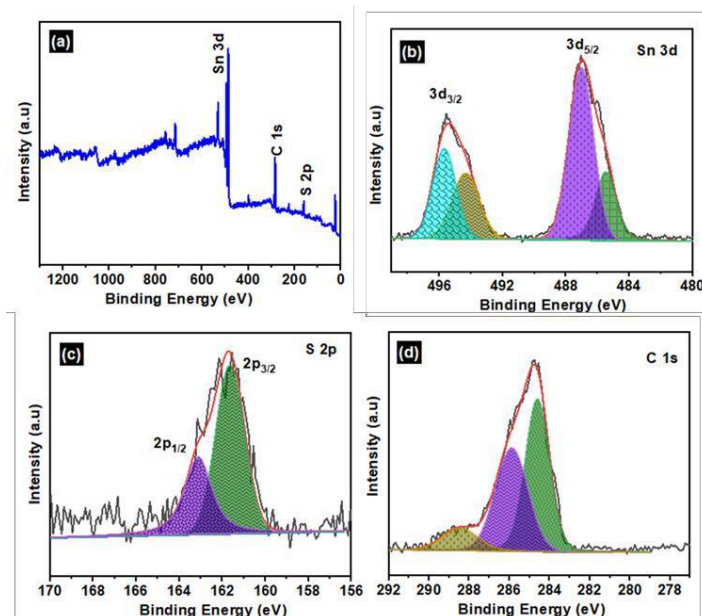


Fig.5.9. shows the XPS characterization

In this study, XPS (Fig.5.9(a)) was used to investigate the constituent elements, binding energies, and oxidation states of the SnS- MWCNT system. There is no peak associated with metallic sulphur ($164.1 \text{ eV} \pm 0.2$), which indicates the absence of metallic sulphur in the system [69]. There are two peaks observed (Fig.5.9(c)) for S 2p peaks at 163.1 eV and 161.7 eV from the SnS system that is lower than the metallic sulphur binding energy, confirming the bonding between Sn atoms [70]. Sulphur is bonded with Sn^{2+} and Sn^{4+} and has a binding energy difference of 1.5 eV, yielding a broad sulphur peak for S^{2-} [71]. Sn3d high-resolution spectra (Fig.5.9(b)) show binding energy positions at 485 eV and 494 eV which correspond to $\text{Sn}3d_{5/2}$ and $\text{Sn}3d_{3/2}$, respectively. $\text{Sn} 3d_{5/2}$ shows a broad peak due to the presence of mixed oxidation states of Sn^{2+} and Sn^{4+} . A small peak observed at 485.5 eV of $\text{Sn} 3d_{5/2}$ and 161.7 eV of $\text{S} 2p_{3/2}$ can be attributed to Sn^{2+} and S^{2-} in SnS [72]. The observed value for $\text{Sn} 3d_{5/2}$ has a chemical shift of 0.9 eV less than that of pure metallic Sn (484.6 eV) [70]. These chemical shifts are due to the electron transfer from Sn to S, which forms a chemical bond between

Sn and S. The binding energy of 487.0 eV is assigned to Sn^{4+} for the SnS system. High-resolution C1 spectra reveal three distinct peaks as well as a main peak at 284.7 eV, which is typically a graphitic carbon peak. The other two peaks at 285.9 eV and 288.5 eV are due to the presence of hydroxyl (C-O and C-OH) and carboxyl functional groups. A broader C 1s peak at 285 eV and 289 eV is a characteristic peak for MWCNTs [73].

5.5 ELECTROCHEMICAL CHARACTERIZATION

The electrochemical performances were exhibited using cyclic voltammetry (CV), Galvanostatic Charging Discharging (GCD), and Electrochemical Impedance Spectroscopy (EIS) analysis with 3 M KOH electrolyte. Cyclic voltammogram (CV) curves of pristine SnS and SnS/MWCNT composite electrodes at room temperature are presented in Fig.5.10. We can see that two CV curves replicates the faradaic behaviour by its visible oxidation and reduction peaks which mean that prepared electrodes exhibit highly electrochemical reversibility between 0.0 to 0.6 V for different scan rates. The outline of SnS/MWCNT composite electrode presents change in pseudocapacitive structure for higher scan rates, indicating the SnS/MWCNT composite has both faradaic and capacitive response and is more suitable for working as an electrode for supercapacitor. The galvanostatical charge–discharge curves of pristine SnS and SnS/carbon composite electrodes are shown in Fig. 5.11. The potential–time relationships on charge–discharge profiles are all approximately linear, which further confirms that both electrodes have regular pseudocapacitive behaviors and good cycling stabilities. Like oxide electrode materials such as MnO_2 and RuO_2 etc., the capacitance of SnS is considered to be mainly originated from pseudo-capacitance, which is due to reversible redox reaction happened between electrode and electrolyte. With charge–discharge curves in Fig. 5.11,

The Specific capacitance value can be calculated [29] from

$$C_{\text{sp}} = \frac{I \Delta t}{m \Delta v} \quad \text{-----} \quad (2)$$

where C, I, Δt , ΔV and m are indicating the specific capacitance, galvanostatic current, charge–discharge time, potential cut-off window and mass of electro-active material. Electrochemical performances of SnS/carbon MWCNT electrode, calculated from Eq.

(2), have been obviously improved. The SC of SnS/MWCNT composite reaches 306 F/g, while pristine SnS delivers less SC of 85 F/g. The Galvanostatic charge / Discharge profile for various current density and corresponding specific capacitance values of both samples are given in the table.1 & table 2. Such results are superior to the performances of nano SnS prepared by Jayalakshmi M. et al. [8]. It is believed that Nano tube like nanostructure of SnS/MWCNT composite could provide larger contact areas between electrode and electrolyte, which facilitates the redox reactions and helps to obtain more pseudo-capacitances. In addition Fig 5.11(d) displays the cyclic stability of the prepared SnS/MWCNT composite where sample is made to undergo 10000 charge discharge cycles at a current density of 6 A/g. and its observed that the sample provides a noticeable specific capacitance retention value of 34 F/g even after successive charge/ discharge cycles, which is considered as a important attribute for practical energy storage applications. Evidently, SnS/ MWCNT composite has prominently good electronic conductivity than pure SnS. On the other hand, electrochemical impedance spectrums of SnS Fig.5.10(c). and Fig.5.11(c). SnS/ MWCNT composite samples also prove that SnS/MWCNT composite has lower charge transfer resistance of 5 Ohms while, pristine SnS shows charge transfer resistance of 100 ohms. So, excellent electronic conductivity and lower charge transfer resistance of SnS/MWCNT composite are beneficial to electronic exchange between electrode and electrolyte, leading to more pseudo-capacitance faradic reactions and generating larger capacitances than that of pure SnS electrode [15]. Table 1 display the comparison of specific capacitance value with the previous reported literature.

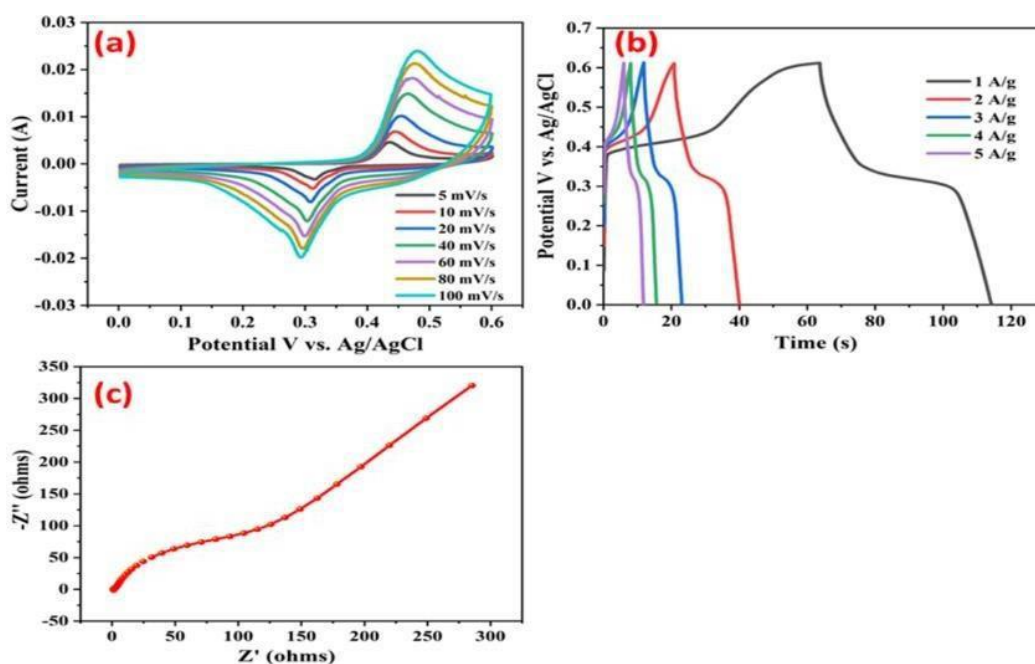


Fig.5.10 shows the Electrochemical Characterization Studies of SnS nanoparticles. Fig. 5.10 (a) discloses the Cyclic Voltammetry curves, Fig. 5.10 (b) shows the Galvanostatic Charge/ Discharge curves at various current density, Fig. 5.10 (c) represents the Electrochemical Impedance Spectroscopy measurements.

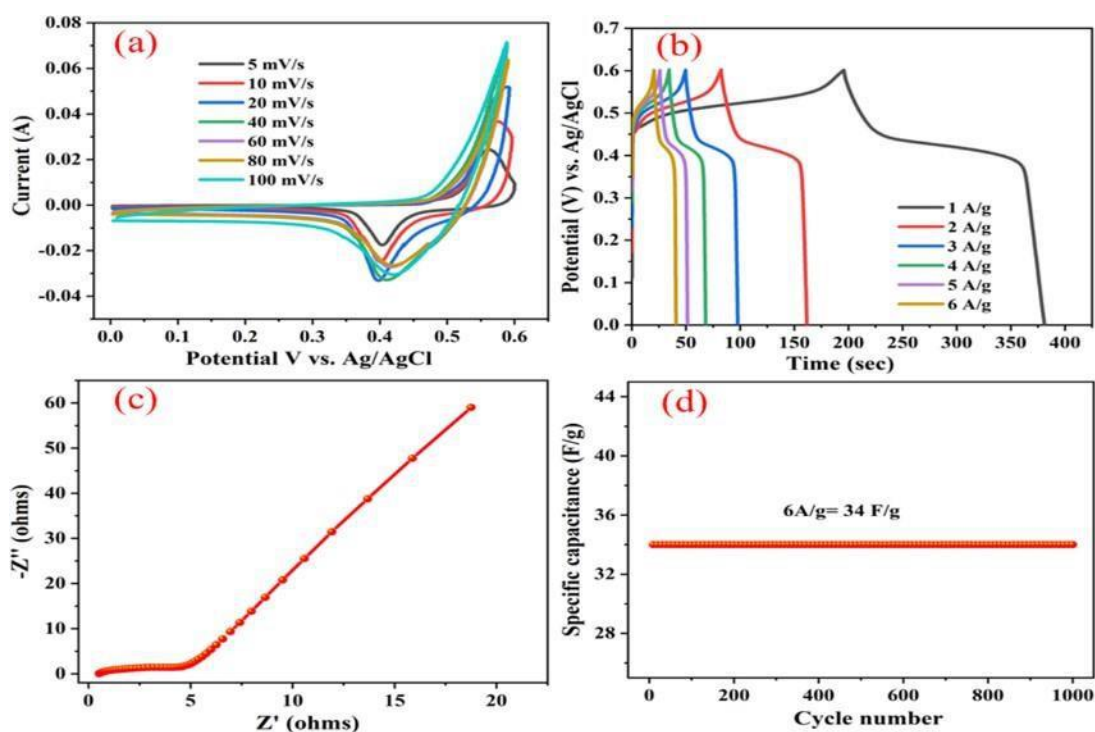


Fig. 5.11 shows the Electrochemical Characterization Studies of SnS-MWCNT nanocomposite. Fig. 5.11 (a) discloses the Cyclic Voltammetry curves, Fig. 5.11 (b) shows the Galvanostatic Charge/ Discharge curves at various current density, Fig. 5.11 (c) represents the Electrochemical Impedance

Spectroscopy measurements. The Cyclic Stability Test at a high current density of 10 A/ g is shown in Fig.5.11 (d)

1.SPECIFIC CAPACITANCE DATA OF PURE SnS

Pristine SnS	
Current Density	Specific Capacitance
1A/g	85 F/g
2A/g	32.5 F/g
3A/g	18.6 F/g
4A/g	12.8 F/g
5A/g	9.6 F/g
EIS=100 ohms	

Table 1. Current Density Vs Specific Capacitance for Pristine SnS sample

2.SPECIFIC CAPACITANCE DATA OF SnS-MWCNT NANOCOMPOSITE

SnS/ MWCNT composite	
Current Density	Specific Capacitance
1A/g	306 F/g
2A/g	131.6 F/g
3A/g	81.3 F/g
4A/g	56.16 F/g
5A/g	42.5 F/g
6A/g	34 F/g
EIS=5 ohms Stability; 6A/g=34 F/g	

Table 2. Current Density Vs Specific Capacitance forSnS/ MWCNT composite

COMPARISION TABLE

Electrode materials	Specific capacitance Fg-1	Current density Ag-1	Reference
SnS/carbon	36.1	5 mV s-1	[64]
SnO2@C	37.8	-	[14]
SnO2/graphene	34.6	-	
ZnS/G	197.1	-	[26]
CNT@CuS	114	-	
WS2/RGO	350	-	
nano SnS	14.98	1 A/g	[75]
MnO2/MWCNT 3:1	252	-	[22]
Activated MOFS	122	0.5 A/g	[76]
carbon/MWCNT			
PTH/MWCNT	110	1 A/g	[27]
rGo with Molybdenum	253	1 A/g	[21]
Pure SnS	85	1 A/g	Our work
SnS-MWCNT nanocomposite	306	1 A/g	Our work

CHAPTER- 6

CONCLUSION

Numerous intensive research projects in the field of nanotechnology have demonstrated great promise in recent years. Significant advancements have been made in the synthesis of desired inorganic nanomaterials, and researchers have reported on and presented a variety of these materials for potential uses in the literature. The advancement of nanomaterials facilitates our transition to a prosperous and comfortable future. These resources provide more precise solutions to the many unmet demands and problems faced by humanity. If an understanding of assembly at microscopic structures can be gained, there is countless potential for enhanced gadgets, structures, and materials.

With foundational and research opportunities in all fundamental cognitive sciences, nanotechnology has advanced to the level of a major science. A key function of nanotechnology is to close the communication gap between the atomic and molecular scales of fundamental sciences.

The overall findings of our research, which were reported in the preceding chapter, are summarized here,

In Chapter 1, a brief overview of metal sulfide nanostructures, their various techniques of synthesis for preparation of SnS and SnS-MWCNT nanocomposite have been provided.. Additionally, the supercapacitor applications is also demonstrated in this chapter.

In chapter 2 contains the literature survey to which I have been referring from the beginning of the project.

The objective of the project is discussed in Chapter 3

The prepared metal sulfide SnS and SnS-MWCNT nanocomposite materials were mainly synthesized by the Hydrothermal method is briefly explained in this chapter 4

The main results and discussion are demonstrated and discussed in Chapter 5

CHAPTER-6

6.1 SUMMARY AND CONCLUSION

- Metal sulfide-based materials are attracted as electrode materials for supercapacitor application.
- Polyvinylpyrrolidone was used as a surfactant to reduce particle size.
- Herein, the SnS and SnS-MWCNT nanocomposite was synthesized by the Hydrothermal method at 160°C for 24 hours.
- Crystallite structure and surface were confirmed by XRD. The crystallite size was calculated by the Debye Scherrer formula the size was found that nanoparticles respectively.
- The surface morphology and particle size of the material can be studied through FE-SEM. The SEM microscopy demonstrated the synthesized nanoparticles were in the nanoscale region with heterostructure of the sphere and sheet-like structure for pure SnS and for nanocomposite SnS-MWCNT it's a sphere and tube-like structure.
- From the HR-TEM analysis, we have further confirmed the surface morphology and confirmed the presence of SnS/ MWCNT nanocomposite from the obtained SAED diffraction.
- From, XPS characterization we have studied the oxidation states of the prepared SnS/ MWCNT nanocomposite.
- Using Cyclic Voltametric studies, we confirmed the presence of Pseudocapacitive behavior of our SnS and SnS/ MWCNT nanocomposite sample.
- Using, Galvanostatic charge/ discharge analysis we have calculated the specific capacitance of our SnS and SnS/ MWCNT nanocomposite samples.
- When compared to the stand-alone SnS material (85 F/g) the SnS-MWCNT nanocomposite, exhibits a high specific capacitance of 306 F/g which is attributed to its unique heterostructure surface morphology.

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