A potential high-capacity anode for Lithiumion battery: Carbonized SnO₂ Nanoparticles

M.Sc. Thesis

By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "A potential high capacity anode for Lithium-ion battery: Carbonized SnO_2 Np's. In the partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DEPARTMENT OF PHYSICS, Indian Institute of Technology, is an authentic record of my work carried out during the period from August 2022 to June 2023 under the supervision of Prof. Sudeshna Chattopadhyay, Department of Physics IIT INDORE. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Mar 07-06-2023

Signature of the student with the date

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This is to certify that the above statement made by the candidate is correct to the best of my /our knowledge.

Shut 2003

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Abstract

Nanomaterials have gained a lot of interest due to their application in various fields. Tin oxide (SnO_2) is an important n-type wide band gap semiconductor used as anode in Li-ion batteries due to its high theoretical capacity of 1494mAh/g. Small size of Carbonized SnO₂ Np's can mitigate the problems faced by SnO₂ as anode in Lithium-Ion batteries. So, in this work we synthesized SnO₂ Np's of crystallite size ~30 nm by Sol-gel technique and of crystallite size ~8 nm, and ~9 nm by varying pH using Co-precipitation technique and then we carbonized Commercial SnO₂, SnO₂ Co-precipitation pH8.7, and SnO₂ Co-precipitation pH10 using D (+) Glucose. The synthesized SnO₂ Np's and Carbonized SnO₂ Np's were then characterized using Raman Spectroscopy, X-Ray Diffraction, UV-Vis Spectroscopy and Scanning Electron Microscopy.

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ACRONYMS

XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
FWHM	Full Width Half Maximum
Sn1	Commercial SnO ₂ Nanoparticles
Sn2	SnO ₂ Nanoparticles synthesized by Sol-gel
Sn3	SnO ₂ Nanoparticles synthesized by Co-precipitation pH 10
Sn4	SnO ₂ Nanoparticles synthesized by Co-precipitation pH 8.7
Np's	Nanoparticles
Sn1@carbon	Commercial SnO ₂ carbon composite Nanoparticles
Sn3@carbon	SnO ₂ Co-precipitation pH 10 carbon composite Nanoparticles
Sn4@carbon	SnO ₂ Co-precipitation pH 8.7 carbon composite Nanoparticles

Chapter 1

Introduction

An n-type semiconductor with a 3.6 eV band gap, tetragonal tin oxide (SnO₂) is appropriate for a variety of uses. Its outstanding electrical, optical, and electrochemical properties of SnO₂ enable applications in solar cells, catalytic support materials, transparent electrodes, and solid-state chemical sensors. In this work, we explored its application as anode in lithium-ion batteries. Various methods, including sol-gel, molten-salt synthesis, microwave technique, Co-precipitation, hydrothermal method, etc. can be used to synthesize SnO₂ Np's. In this work, a simple sol-gel and co-precipitation method is used to synthesize SnO₂ Np's. SnO₂ occurs in various forms such as the rutile-type, CaCl₂-type, α -PbO₂-type, pyrite-type, ZrO₂-type, fluorite-type, and cotunnite-type [2]. The most important form of naturally occurring SnO₂ is cassiterite, a phase of SnO₂ with a tetragonal rutile structure. In this work, we synthesized SnO₂ of the tetragonal rutile phase. In stoichiometric SnO₂ (tetragonal rutile phase structure), the unit cell consists of six atoms, two six-coordinated tin, and four three-coordinated oxygen ions with oxidation states +4(Sn⁴⁺) and -2(O²⁻). The cations (Sn⁴⁺) are at the corners (0,0,0) and the center (1/2, 1/2, 1/2) of the unit cell, and the anions (O^{2-}) are at $\pm(x, x, 0)$ and $\pm(1/2+x, 1/2-x, 1/2)$ (x=0.307)[2]. The two apical Sn-O bond lengths are larger than the other four in the equatorial plane, which results in a distorted octahedral geometry of the SnO₂ crystal [3]. Rutile SnO₂ (a=4.737 A⁰, c= 3.186 A^0) belongs to the space group P4₂/mnm[2].



Fig 1.1 Stick-and-ball representation of SnO₂ crystal structures Rutile, CaCl₂.type, α-PbO₂-type, pyrite-type, fluorite-type, and cotunnite-type. Shaded grey and red spheres represent Sn and oxygen atoms respectively [2]

Lithium-ion batteries have been widely used as a power source for electronic devices due to their high design for high-capacity electrodes is essential for advancing Li-ion battery technology. Tin oxide (SnO₂) is considered the most promising alternative anode material for Li-ion batteries' energy density per unit volume and mass. However, the development of novel electrode materials or a new architecture is due to its theoretical reversible capacity of 1494 mAh g⁻¹, which is more than that of graphite (370 mAhg⁻¹)[4]. However, the performance of SnO₂-based electrodes is restricted by several issues. Extensive research has been conducted to enhance the performance of SnO₂-based electrodes by gaining a fundamental understanding of the lithiation/delithiation reactions, which are governed by two primary reactions in a Li-ion battery with SnO₂ as the working electrode [5].

 $SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O(i)$

 $Sn + 4.4 Li^+ + 4.4 e^- \rightarrow Li_{4.4}Sn$ (ii)

The first reaction involves the reduction of SnO_2 to Sn, which has long been considered irreversible and a primary driver of significant capacity loss and low Coulombic efficiency of SnO_2 and other oxide anodes. However, controlling the electrode's nanostructure and suppressing Sn coarsening through the high-density grain boundaries of SnO_2 nanocrystals can make the conversion from Li₂O to SnO_2 highly reversible. Therefore, small-sized SnO_2 particles can alleviate this issue.

The second reaction, which involves the formation of alloys Li_{4.4}Sn during insertion and dealloying Sn during extraction, can be reversed. However, the SnO₂-based anodes suffer greatly from this process, which has a significant impact on the lithium capacity. When dealloyed, Sn changes to the completely lithiated state of Li_{4.4}Sn, causing a volume change of over 200% [6] and producing enormous internal stress. As a result, the electrode material breaks down, and electrode contact is lost [7], resulting in rapid capacity fading. Various strategies have been employed to mitigate this issue, including the use of materials with unique nanostructures such as nanoneedles, core-shell structures [8], nanorods[9], and hollow structures[10]. However, the scalability of the synthesis process may limit the practical use of such nanostructures. One practical method to address this issue is to use small-sized SnO₂ Np's, which undergo less volume development during lithiation than large-sized SnO₂ particles.

Nanocoating the active material with carbon is another promising strategy to improve the performance of Li-ion batteries. Carbon has been extensively researched as a potential anode material [11], and its nanocoating is thought to perform various functions during cycling. It serves as a buffer layer, absorbing the stress brought on by volume change, and enhances the electronic conductivity of the nanocomposite electrode, preventing SnO_2 Np's agglomeration. However, carbon has very little storage capacity and is barely active [12], making systematic research into how carbon coating affects Li-ion battery performance desirable [13].

Co-existence between Li-Sn alloy phases of different compositions leads to capacity loss because these phases have different volumes per tin atom, and as such, the grains will most likely crack and fragment during cycling[14]. Therefore, keeping the grains that make up the particle of material as small as possible can prevent two-phase coexistence regions between bulk Li-Sn alloys of different compositions and increase SnO₂'s capacity as an anode in Li-ion batteries. Nanosizing reduces internal stresses during volume change and improves capacity and lifetime. Particle size reduction reduces the diffusion/transport length of ions and electrons and increases conductivity and capacity. Carbonized SnO_2 Np's can be produced in just two steps using a sol-gel and co-precipitation technique. Pure SnO_2 Np's of various sizes are synthesized first, followed by depositing a thick layer of D-(+)-Glucose over the Np's to create carbonized SnO_2 Np's.

Objective and Scope of Work

This work is focused on improving the performance of SnO_2 as anode in Lithium-ion batteries. Given the above discussion, the size of SnO_2 and glucose concentration are the two key parameters to maneuver the performance of SnO_2 as an anode.

Broadly objective is divided into the following categories:

- 1. To study the effect of pH on the crystallite size of SnO₂.
- 2. To study SnO₂ synthesized from sol-gel and co-precipitation.
- 3. To study carbonized SnO₂ Np's.



Figure 1.2 Schematic showing the ideal anode of Lithium-ion battery having SnO₂ Np's immersed in the carbon matrix

Chapter 2

Battery

Why there is a need for energy storage?

Enabling electrification of transportation:

- Need energy storage systems with higher energy and power densities.
- Improvements in costs, cycle life, and reliability.
- Faster recharge times.

Transformation of the electricity infrastructure:

- Aging infrastructure and energy storage can improve grid reliability and resiliency.
- The growth of renewables and distributed energy needs energy storage.
- Need lower costs, systems scalable from kWh to hundreds of MWh.
- Long life-cycle and low operating costs.



Figure 2.1 The characteristics of the electrode material are strongly related to battery performance parameters. The underlying chemical and structural characteristics of the active material can then be used to rationalize the attributes of the material. The feedback from device performance directs design and synthesis decisions that result in next-generation batteries [15].

Different components of the battery

Important components of a battery

- Anode
- Cathode
- Electrolyte
- Separator

A battery is made up of an anode (at which oxidation takes place), a cathode (at which reduction takes place), and an electrolyte that permits ionic conductivity [16]. Rigid separators (made of polymeric materials, such as PE, PP, Polyamides, Glass fiber, etc.) are used to keep the anode and cathode apart to prevent short circuits while facilitating ion transport in the cell. An electrolyte, an ionically conducting, electrically insulating medium, and two electrochemically active couples make up a battery. Ion transit through the electrolyte ensures electroneutrality while forcing electrons to go from one electrode to another through the external circuit.

A general set of requirements for choosing acceptable electrode materials

- Low cost
- Eco-friendly nature for processing
- Usage and recycle
- small, irreversible first-cycle loss
- a significant Coulombic efficiency
- The rapid diffusion of lithium/aluminum/ sodium ions into and out of the anode
- strong electrical and ionic conductivity
- When charged and discharged, minimal structural changes
- High mAh/g specific capacity
- The capability to create and keep a solid electrolyte interface (SEI) layer after cycling.

Separator requisites:

- Optimum thickness
- Optimum porosity
- Wettability
- Ionic conductivity
- Chemical and Electrochemical stability
- Thermal stability
- Mechanical properties

Electrolyte requisites:

- Good ionic conductivity and very low if any, electronic conductivity
- Chemical stability
- Low flammability and toxicity
- Low cost



Fig 2.2 Diagram illustrating how rechargeable Li-ion batteries are set up [17]

Li ions are taken from the cathode and injected into the anode during the charging process of a Li-ion battery, as shown in the figure, generating a flow of electrons in the outer circuit from one side to another. The opposite reaction takes place during the discharge process. The electrolyte carries lithium ions from one electrode to another electrode. This is how Lithium-ion battery works [17].

The Theoretical capacity of a material

The chemistry of the battery mostly determines its capacity. The theoretical capacity of electrode materials corresponds to the number of reactive electrons and the molar weight of the designed materials as expressed by Faraday's law [18]

 $C_{\text{Theoretical}} (\text{mAh g}^{-1}) = \frac{nF}{3.6 \times M} \qquad 2.1$

The number of metal ions (e.g., Li^+ , Mg^{2+} , Al^{3+}) ions accommodated in the host lattice correlates with the number of electrons. The equation suggests that, in theory, a higher capacity can be produced by a decreased molecular weight and the accommodation of more electrons per formula unit.

Working of Lithium-ion battery

SnO₂ as an electrode in Lithium-ion battery

Molar weight of $SnO_2 = 150$ g/mol

The two-step lithiation mechanism of SnO_2 contains a reduction of SnO_2 to Sn accompanied by the formation of a Li₂O matrix (equation 1) and subsequent formation of a Li_{4.4}Sn alloy (equation 2)[5]

 $SnO_2 + 4Li^+ + 4e^- \iff Sn + 2Li_2O$ (1)

 $\operatorname{Sn} + 4.4 \operatorname{Li}^{+} + 4.4 \operatorname{e}^{-} \Leftrightarrow \operatorname{Li}_{4.4}\operatorname{Sn}$ (2)

8.4 Li^+ ions are involved in these reactions, so n=8.4

So using equation 2.1, the theoretical capacity of the SnO₂ Li-ion battery is 1494 mAh/g

Sample Preparation and Characterization Techniques

This chapter deals with the details of the experimental methodology used for the experimental work carried out in the thesis and procedures for the synthesis and carbonization of SnO_2 Np's. It also summarizes various equipment used for various measurements carried out during research work.

3.1 Sample Preparation

3.1.1 Synthesis of SnO₂ Np's using Sol-gel

The sol-gel process is the synthesis of metal oxides from a liquid solution of precursor in which submicron solid phase particles (Sol) are suspended in liquid, which is then condensed to form a gel solution surrounded by a 3D network polymerized macromolecules.

Applications of a sol-gel process

- 1. Thermal insulation
- 2. Acoustic insulation
- 3. Protective optical coatings

Steps in the sol-gel process

- 1. Hydrolysis of precursor(sol formation)
- 2. Polycondensation
- 3. Aging
- 4. Drying
- 5. Calcination

Hydrolysis of precursor:

The precursor is an aqueous solution of the metal chloride. Metal chloride reacts with ethanol or water and forms the colloidal suspension (sol) of the metal hydroxide.

Polycondensation

Polycondensation stage results in the formation of the Gel- a rigid 3D network built of polymeric molecules and surrounded with solvent.

Aging

In the aging phase, polycondensation reactions continue to complete gel formation. The gel structure is reinforced by additional cross-links, which cause the gel matrix to contract and pull the solution out of the shrinking pores.

Drying: In this step, water and other liquids trapped in the pores of the gel structure are removed. Drying takes place at a temperature of about 100 Degree Celsius.

Calcination: Calcination takes place at an elevated temperature between 400 and 800 Degrees Celsius. During the calcination step, the dry gel structure is dehydrated according to the reaction



Figure 3.1: Schematic showing the synthesis of SnO₂ Np's by Sol-gel process

Sample Preparation

8g hydrated Tin chloride dihydrate (SnCl₂.2H₂O) dissolved in pure ethanol (C₂H₅OH) for hydrolysis of precursor. The solution was then subjected to magnetic stirring for 30 minutes in a beaker. Then 5 ml of acetylacetone was added dropwise to stabilize the sol. The solution is again subjected to stirring for 30 minutes. Then the solution was continuously refluxed at 80° C for 5 hr to form SnO₂ sol solution. Polyethylene glycol was added to control the size of SnO₂ by adding 1 ml in SnO₂ solution and then aged for 72 hr at 30° C. The sol was then dried at 100° C for 1 hr and gel is formed. Then to promote crystallization gel is then put in an alumina crucible and calcinated at 450° C for 1 hr, obtaining SnO₂ Np's synthesized by Sol-gel process.

3.1.2 Co-precipitation

A Co-precipitate is the simultaneous precipitation of more than one compound from a solution. It is the most convenient and cheapest technique to make Np's. In this method, the metal is precipitated as a hydroxide from a salt precursor in the presence of a base in a solvent.

Uses of Co-precipitation

- 1. To make a large quantity of magnetic nanomaterials.
- 2. To synthesize powder samples of various mixed oxides.
- 3. To synthesize nanomaterials in a variety of sizes.

Steps involved in co-precipitate Preparation of solution

- 1. Precipitate formation
- 2. Filtering and washing
- 3. Drying
- 4. Calcination
- 1. **Preparation of solution**: in this first, the precursor is dissolved in some solvent to form a clear solution of it.
- 2. **Precipitate formation**: In this precipitating agent is added to the precursor solution until the desired pH is reached and the precipitate starts forming.
- 3. **Filtering and washing**: In this precipitate is filtered and washed with ethanol and DI water to remove impurities coming with the precipitate.
- 4. **Drying**: This process involves drying the precipitate in the oven at about 100^{0} Celsius to remove water molecules.
- 5. Calcination: Calcination is then done at higher temperatures at about 400[°] to 800[°] Celsius.



Figure 3.2: Schematic showing the synthesis of SnO₂ Np's by a Co-precipitation process

Sample Preparation

0.27 M Tin Chloride dihydrate is dissolved in 164.14ml solution in a ratio 2:1 (DI water (112.8527 ml):Ethanol(51.29668 ml) and then subjected to constant stirring using a magnetic stirrer at room temperature. 8.207 ml HCl was added dropwise using a glass dropper. Stirring is continued for another half an hour. During the process, the solution becomes transparent. Then Ammonium Hydroxide has added to the solution till the pH reaches 8.7 while the solution is stirred. Stirring is continued for another 2 hours. The transparent solution turns to a gelatinous white precipitate. The stirring is stopped and the white gelatinous precipitate is allowed at night to settle down. The precipitate was filtered using Whatman filter paper. Precipitate remained on the filter paper. Then precipitate is washed with ethanol and DI water 4-5 times so that impurities get removed. This ensures the complete removal of impurities from the precipitate. Then the filter paper containing the precipitate is put in a petri dish and put inside the oven at 100° C without a lid then the yellow powder is formed. Then this powder is ground for 1 hr with mortar pastel. The powder then was put in an alumina crucible and calcinated at 400° C in an air atmosphere inside the box furnace. The box furnace was switched off and was allowed to reach room temperature on its own then finally obtained SnO₂ Np's. To obtain SnO₂ Np's of different sizes, we repeated the same procedure but changed the pH from 8.7 to 10.

3.1.3 Carbonization of the SnO₂ Nanomaterials

It is heating at high temperatures in the absence of oxygen to increase the carbon content in the Organic material like glucose. It is done in the presence of inert gas like argon or nitrogen. Purpose of the inert gas this that prevents the unwanted reaction such as oxidation of carbon to form CO_2 as here we are trying to increase the carbon content.



Figure 3.3 Schematic showing the Carbonization of SnO₂ Np's

Sample Preparation

- A 0.2 g quantity of Commercial SnO₂ (Sn1) powder was added to 40 ml glucose solution (360 mg D-(+)-Glucose in 40 ml DI water) to reach a concentration of 0.05M. After complete dispersion, the reaction solution was placed in a tube furnace at 180° C. for 4 hours. A dark brown precipitate was collected and dried at 60° C overnight. For carbonization, the dark brown powder thus produced was kept in a tube furnace at 500°C for 4 hours under N₂ with a heating rate of 5°C/min.
- A 1.5g quantity of SnO₂ Co-precipitation pH 8.7 (Sn4) powder was added to 40 ml Glucose solution (4.248 g D-(+)-Glucose in 40 ml DI water) to reach a concentration of 0.59 M then process is continued as in case of Sn1@carbon.
- 1.5 g SnO₂ Co-precipitation pH 10 (Sn3) powder was added to 300 ml Glucose solution (31 g D-(+)-Glucose in 300 ml DI water) to reach concentration of 0.59 M then process is continued as in case of Sn1@carbon.

It should be noted that Sn1 is Commercial SnO_2 Nanoparticles, Sn2 is SnO_2 Nanoparticles synthesized by Sol-gel, Sn3 is SnO_2 Nanoparticles synthesized by Coprecipitation pH10, and Sn4 is SnO_2 Nanoparticles synthesized by Coprecipitation pH 8.7.

3.1.4 Hot air oven:

It is based on the principle of forced convection, which uses a motorized fan to force hot air evenly distributed throughout the interior of the room. This allows the sample to absorb heat and dry faster because they are always exposed to hot air.



Figure 3.4 Hot air oven

3.1.5 Magnetic stirrer

Magnetic stirring is a widely used mixing and stirring method in liquid media. It can be used in a wide temperature range. The main system consists of two parts: a moving magnet placed inside the liquid and a magnetic drive located outside the container. The magnetic drive has a wide range of different speeds for the smooth mixing of liquids of different viscosities. A moving magnet is a bar magnet that is encapsulated in a material that protects the magnet and prevents contamination of the liquid medium. The shape of the container and the viscosity of the stirring agent are the factors that determine the effective magnetic stirrer for a particular application.



Figure 3.5 Magnetic Stirrer

3.1.6 Argon-filled Glove box

The glove box is an insulated enclosure designed to maintain an inert atmosphere. Items can be moved in and out of the box using the front chamber, which acts as an airlock between the box and the outside air. The glove box system is a device that filters and removes active substances (both water and oxygen can reach below 1 ppm) through a purification system to maintain high purity in an inert gas environment. The box is mainly made of stainless steel and has a polycarbonate window and rubber gloves. It is used to protect the processed sample inside the box from the outside, especially against unwanted reactions with oxygen and water vapour.



Figure 3.6 Glove box

3.2 Characterization Techniques

3.2.1 UV -Visible Spectroscopy:

The amount of distinct wavelengths of UV or Visible light that are absorbed or transmitted by a sample about a reference or blank sample is measured by an analytical technique known as UV-Vis spectroscopy. The amount of energy needed to promote electrons to higher energy states depends on the type of bonding environment in which they are found, Because of this, various substances absorb light at various wavelengths. Identifying the specific wavelengths that correspond to maximal absorbance, is used in UV-Vis spectroscopy to examine or identify different substances.

Experimental setup

The basic parts of the spectrophotometer are a light source, a diffraction grating in a monochromator, and a detector (Figure 3.7). The light source consists of two lamps: a deuterium arc lamp (or D_2 lamp), which is in the range of 190 nm to 370 nm, used for the UV region: and a tungsten lamp (320-1100 nm) used for the visible region. The scanning monochromator allows the diffraction grating to step through each wavelength so that its intensity may be measured as a function of wavelength. This spectrophotometer is a double-beam instrument. The light is split into two beams before it reaches the sample. One beam is used as a reference, the other beam passes through the sample. The reference beam intensity is taken as 100% transmission (or 0 absorbances), and the measurement displayed is the ratio of two beam intensities. The output of the detector is a plot of Intensity Versus Wavelength which contains information about the sample. The detectors employed are typically a photomultiplier tube, a photodiode or charged coupled devices. In this work, UV-Vis absorption spectra of SnO_2 Np's were measured using a UV-Vis spectrophotometer in absorption mode in the wavelength range of 190-800 nm.



Figure 3.7: Schematic showing UV-Vis spectrophotometer

Theory:

UV-Vis spectroscopy is a technique that involves passing a beam of radiation (UV or visible light) with an energy equivalent to the electronic transition within a molecule, through a substance or solution. When the radiation passes through the sample, some of the light is absorbed by the electrons in the molecule, promoting them to a higher energy level. UV-Vis spectroscopy is based on the Beer-Lambert law, which states that the light absorbance of a given material is directly related to the sample concentration and path length. The law can be expressed using the equation:

 $A = \epsilon l c$

Where A is the absorbance at a given wavelength, ε is the molar absorption coefficient, l is the path length, and c is the concentration of the solution [19].

A UV-Vis spectrophotometer records the degree of absorption (i.e., intensity) and the absorption peak for each wavelength. The resulting spectrum is a graph of Absorbance Versus Wavelength. UV-Vis spectroscopy is useful in calculating the bandgap and the size of Np's. The absorption coefficient ε can be calculated from the Beer-Lambert law, as shown above. The band gap can be easily determined from the absorption spectra using the following equation:

$$\alpha$$
 (v)hv= B(hv - E g)ⁿ

Where E_g is the Bandgap Energy, B is a constant, hv is the incident photon energy, and α (v) is the absorption coefficient [20]. Since rutile phase SnO₂ is a direct bandgap semiconductor, the optical bandgap energy for the direct transition (n=1/2) can be estimated from the plot of (α (v)hv)² vs hv[1]. The intercept between the linear part of the fit and the x-axis gives the value of the bandgap energy of the material. When (α (v) hv)² is zero, the photon energy is equal to the Bandgap Energy, E_g .

3.2.2 Raman Spectroscopy

A Raman spectrum is like a chemical fingerprint that identifies a molecule, and just like a human fingerprint, it can be compared to reference libraries to very quickly identify and distinguish a molecule from others. It provides an overview of the sample: 1) chemical composition and properties 2) crystallinity 3) impurities and defects.

Every Raman spectrometer has three main components: an excitation source, a sampling device, and a detector. Raman spectroscopy is the study of matter using the inelastic scattering of monochromatic light. It has become a ubiquitous tool in modern spectroscopy, biophysics, microscopy, geochemistry, and analytical chemistry. Monochromatic light striking a transparent substance is emitted with almost no attenuation. Matter scatters a small fraction of light in all directions (although mostly forward). Weakly scattered radiation contains photons with incident frequency v_o (elastic or Rayleigh scattering) but also contains other frequencies such as v_o - v_i and v_o + v_i where v_i is the molecular transition frequency of the material (usually rotational or vibrational). This inelastic scattering of light is known as Raman scattering. [21]



Figure 3.8 Schematic showing Raman Spectrometer

Inelastic scattering of light from a sample is the foundation of Raman spectroscopy. The molecules of a sample are temporarily transported to a virtual energy state when a photon with the frequency v_o and energy hv_o strikes them. After that, a photon with the frequency v and energy hv is released. The Raman spectrum, which is a plot of scattering intensity versus frequency shift, is a function of the rovibronic states of the molecules. As a result of the sample's electron cloud interacting with the electric field of the monochromatic light, the molecules become excited to a new rovibronic state and undergo a variation in their electric dipole polarizability. The following equation governs the Raman shift v in wavenumber units (cm⁻¹):

$$\mathbf{v} = (1/\boldsymbol{\lambda}_0) - (1 / \boldsymbol{\lambda})$$

Rayleigh scattering (also known as elastic scattering) occurs when the majority of excited molecules in the sample produce scattered radiation with a frequency that is the same as the frequency of the incident radiation.

However, a small amount of the scattered light also experiences Raman scattering (also known as inelastic scattering) because its frequency is different from the incident frequency. The Stokes-shift is the downshift of the scattered photon to a lower energy (lower wavenumber) state that occurs when the molecule's final state is higher than its initial energy state. On the other hand, the Raman scattered photon shifts to higher energy (higher wavenumber) when the final molecular state is lower in energy than the initial state; the relating upshift is alluded to as the Antistokes-shift. The Raman spectra are thus made out of both Stoke lines and Antistokes lines.

3.2.3 X-ray Diffraction

X-ray diffraction is a valuable technique that is regularly used to determine the crystalline phases present in materials and to analyse their structural properties [22]. One standard method for producing X-rays for research is by accelerating electrons with high voltage and allowing them to collide with a metal target. The collision knocks an electron out of the inner shell of the target metal atom, and electrons from higher states drop down to fill the void, releasing X-ray photons with precise energies that correspond to the energy levels of the electrons. Copper, molybdenum, and cobalt are commonly used as target materials for crystal diffraction, with characteristic radiation at 1.5418 Å.

The emitted X-rays are then collimated and directed at the target sample. Constructive interference between the scattered X-rays from constituent planes of atoms give rise to diffraction phenomena according to Bragg's equation: $2d \sin \theta = n\lambda$, where d is the spacing between equidistant parallel planes, λ is the wavelength of the incident X-ray, n is an integer and θ represents the angle between the incident X-ray beam and the normal to the sample surface. The peak positions are determined by the diffracting planes of atoms, and the atoms in the diffracting plane determine the peak intensity.

The XRD system consists of three primary components: (1) an X-ray source (tube), (2) the goniometer (which contains the sample holder and provides movement to the sample), and (3) the X-ray detector. In our work, we used powder X-ray diffraction. In powder X-ray diffraction, the sample revolves around the collimated X-ray beam at an incidence angle θ , while the detector is mounted on the

diffracted arm at an angle of 2θ to gather the distributed X-rays. A goniometer is used to keep the incident sample and rotate the sample accordingly.

In a random polycrystalline sample with thousands of crystallites, all possible diffraction peaks should be observed. There will be a small number of crystallites that are properly oriented to diffract for each set of planes. Powder diffraction is based on the fundamental assumption that there are statistically significant numbers of crystallites, not just one or two, for each set of planes.



Fig 3.9: Schematic showing XRD

3.2.4 SEM

The scanning electron microscope (SEM) is a powerful tool for producing detailed, magnified images of objects by scanning their surfaces to create high-resolution images. SEMs can also be utilized for elemental mapping or spot chemical analysis using energy-dispersive X-ray spectroscopy (EDS) and distinguishing phases based on the mean atomic number using backscattered electrons. Backscattered Electron images can be particularly useful for distinguishing between phases in multiphase samples.

All SEMs have essential components, including a source of electrons ("gun"), three electron lenses, a stage, and detectors for each signal of interest. Devices for data and display output are also necessary, as well as infrastructure requirements such as a power supply, a vacuum system, a cooling system, and a vibration-free floor in a room free from surrounding electric and magnetic fields.[23,24]

In SEM, electron beams are fired from the electron gun and pass through lenses and apertures to focus them onto the sample surface. Imaging occurs under vacuum conditions to prevent interactions between atoms or molecules present in the microscope column and the electron beam. The electron beams scan the sample in a raster pattern, scanning the surface area in lines from side to side, top to bottom. Interactions between the electron beam and atoms on the surface of the sample create signals in the form of secondary electrons and rays, which are characteristic of the sample. Detectors in the microscope pick up these signals to create high-resolution images displayed on a computer screen.

In an SEM, the accelerated electrons possess a significant amount of kinetic energy. As the electrons are decelerated in the solid sample, the energy is lost through various signals resulting from interactions between the electrons and the sample. Signals such as Secondary electrons, Backscattered electrons, and Diffracted Backscattered electrons can be used for various applications, such as mineral orientation and crystal structure analysis. Backscattered electrons are particularly useful for showing compositional contrasts in multiphase samples, while secondary electrons are best for showing morphology and topography on samples. SEM analysis is generally considered to be non-destructive.



Figure 3.10 Schematic showing SEM

Chapter 4

Results and discussion

4.1 Characterization of SnO₂ Np's

4.1.1 Raman Spectroscopy

Raman Spectroscopy is considered a versatile and sensitive technique to examine modifications in vibrational phonon modes crystallinity, disorder, and size effects in nanometric crystallites. The present research focuses on vibrational modes of rutile Sn1, Sn2, Sn3, and Sn4.

 $I = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + 2B_{1u} + 4E_u$

Of these 18 modes, four are Raman active $(A_{1g}, B_{1g}, B_{2g}, and E_g)$, two are IR active $(A_{2u} and E_u)$, and two are silent. Due to the necessary dipole change, one A_{2u} mode and two E_u modes are only active in the IR. The oxygen atoms vibrate in all Raman active modes, while the Sn atoms remain stationary. The A_{1g} mode vibrates in the plane perpendicular to the z-axis, whereas the E_g mode vibrates along the direction of the z-axis.

The rutile-type SnO_2 has four Raman active modes: A_{1g} (634cm⁻¹), B_{1g} (123cm⁻¹), B_{2g} (773cm⁻¹), and E_g (473cm⁻¹). E_g refers to in-plane oxygen vibration, A_{1g} corresponds to the asymmetric stretching vibration of oxygen octahedral and B_{1g} corresponds to the symmetric stretching vibration of oxygen octahedral [25]



Figure 4.1 Stick and ball representation showing A_{1g} , B_{2g} , and E_g mode of vibration. Red represents oxygen and grey represents tin. [25]



Figure 4.2 Raman Spectra of (a) Sn1, (b) Sn4, and (c) Sn3



Figure 4.3 Shift in A_{1g} position towards lower wavenumber with decrease in size of Np's

Raman Spectra of Sn2 does not have any characteristic peak of SnO₂. We suggest that this might be because of organic ligands during synthesis decorating the nanoparticle surface. Raman groups of Sn4 are 625.79 cm⁻¹, 496 cm⁻¹, and 758.75 cm⁻¹ (in Figure 4.2 (b)), for Sn3 are 627 cm⁻¹, 476 cm⁻¹, and 760.70 cm⁻¹(in Figure 4.2(c)) and for Sn1 are 632 cm⁻¹, 504 cm⁻¹, and 770 cm⁻¹ (in Figure 4.2(a)) which compare to A_{1g} , E_g , and B_{2g} vibrational modes respectively. As the size of the Np's decreases, the mode A_{1g} shifts to a lower wavenumber [26]. As can be seen in Figure4.3, A_{1g} is at 632 cm⁻¹ in Sn1 having crystallite size ~40 nm (confirmed by XRD data), It shifts to 625.79 cm⁻¹ in Sn4 having crystallite size ~8 nm (confirmed by XRD data) and to 627cm⁻¹ in Sn3 having crystallite size ~9nm(confirmed by XRD data) . Simultaneously modes B_{2g} and E_g approach A_{1g} in nanomaterials for example they shift towards lower and higher wavenumber individually [26] as it can be seen in Figure 4.3(a), 4.3(c) and 4.3(d). A_{1g} and B_{2g} shifts towards lower wavenumber due to the participation of low-frequency phonons. This phenomenon occurs due to phonon confinement, whereas the size of the material is reduced, the rule that only zone center phonons participate is relaxed, allowing phonons away from the centre of the Brillouin zone to participate. This effect is more pronounced for optical phonons, as their frequency decreases as they move away from the zone center [27].

4.1.2 X-ray Diffraction

To identify the crystalline structure and crystallite size of the synthesized SnO_2 Np's, XRD studies were carried out. Figure 4.4(a) gives the XRD pattern of Sn1, Sn2, Sn3, and Sn4. The obtained XRD pattern corresponds to the tetragonal rutile phase of the SnO₂ crystal structure as confirmed by JCPDF data (card no 00-041-1445) and the samples are polycrystalline.



Figure 4.4 (a) XRD of Sn1, Sn2, Sn3 and Sn4 (b) Broadening of peak corresponding to (110) plane from Sn1 to Sn4

It can be seen in Figure 4.4(b) that the FWHM increases from Sn1 to Sn4. The narrowing of peaks is directly related to the increase in the average crystallite size of Np's [29]. The crystalline size of the SnO_2 NPs can be estimated by using Debye Scherrer Formula as shown

$$D = (k * \lambda) / \beta \cos \Theta$$

Where 'D' represents average crystallite size, 'k' is the shape factor having value 0.9, ' λ ' is the wavelength of Cu-ka radiation (1.54059 Ű), ' β ' indicates FWHM of peak, and ' Θ ' is the Bragg's angle in degrees[30]. The calculated average crystalline size of SnO₂ NPs is ~40 nm (Sn1), ~30 nm (Sn2), ~9 nm (Sn3), and ~8 nm (Sn4) respectively. The crystallite size is assumed to be the size of a coherently diffracting domain and it is not necessarily same as particle size. [45]



Figure 4.5: Comparison of XRD pattern of Sn4 and Sn3

As it can be seen from inset of Figure 4.5 that highly intense peak corresponding to (110) plane in Sn4 has more broadening in comparison to Sn3 as FWHM increases from 0.9 in Sn3 to 1.01 in Sn4 indicating smaller crystallite size of Sn4 as compared to Sn3. So with increase in pH, crystallite size of SnO₂ Np's synthesized by Co-precipitation process decreases. There is shift in position of peak towards higher angles corresponding to (110), (200), (310), and (321) plane by 0.11, 0.12, 0.4, and 0.25 degrees and towards lower angles corresponding to (202) plane by 0.21 degrees with increase in pH. This might be because of lattice strain [45]. As lattice strain leads to change in d spacing (distance between parallel planes) which in turn leads to change in peak position towards lower or higher angles according to Bragg Diffraction formula(2d sin $\Theta=n\lambda$). The characteristic peaks corresponding to (110)

and (101) plane of Sn4 are slightly higher in intensity than of Sn3 but all other peaks of Sn3 and Sn4 are nearly same in intensity. There is only one extra peak observed in Sn4 at position 29.7 degree and of relative intensity 15 but all other peaks confirm to tetragonal rutile phase structure of SnO_2 .

4.1.3 UV- Vis Spectroscopy

5 milligrams of the nanopowder were dissolved in 5 ml of isopropyl alcohol to investigate the optical properties of the particles. The solution is then subjected to ultrasonication for 15 minutes to achieve uniform suspension of the SnO₂ Np's in the isopropyl alcohol. The nanopowder solution and isopropyl alcohol are then subjected to absorption spectrometry. The obtained absorption spectra of Sn1, Sn2, Sn3 and Sn4 are shown in Figure 4.6. The first absorption maxima (λ_{max}) of Sn1, Sn2, Sn3, Sn4 is observed at 289 nm, 288 nm, 295 nm, and 280 nm respectively. A secondary absorption peak can be seen at 223 nm, 246 nm, 221 nm, and 249 nm respectively. The samples show a consistent rise from 800 nm to ~400 nm after which change in slope is observed. It is to be noted that, to have more accurate results, We will do UV-Vis spectroscopy in reflection mode by making pellet of SnO₂.



Figure 4.6: Comparison of UV Vis Absorption Spectra of Sn1, Sn2, Sn3, and Sn4



Figure 4.7: Plot of $(\alpha hv)^2$ vs Energy for band gap determination of (a) Sn1 (b) Sn2 (c) Sn4 (d) Sn3

Energy(eV)

The optical bandgap energy (E_g) was calculated by using Tauc's relation [31] as given in the following equation:

$$(\alpha hv) = A (hv - E_g)^n$$

Energy(eV)

Where α is the optical absorption coefficient, h is Planck's constant, v is the frequency of the incident photon, hv is the energy of the incident photon, n =1/2 for direct bangap transition and E_g is the energy

of the optical bandgap. The plot $(\alpha hv)^2$ vs (hv) is obtained from it. Absorbance (A) is obtained from UV-Vis absorption. The absorption coefficient (α) is calculated from the Beer-Lambert law [32].

$$A = \alpha c l$$

Where A is the absorbance, c is the concentration in moles/litre (which is 0.0066M), and l is the length of the cuvette (which is 1 cm).

The value of the optical bandgap can be measured by extrapolating a straight line from the plot to intersect the horizontal photon energy axis (absorption equal to zero). From Figure 4.7(a), 4.7(b), 4.7(c) and 4.7(d), It is observed that the optical bandgap energy of Np's does not follow the usual pattern of increase in band gap with decrease in size of Np's. The band gap of Sn1, Sn2, Sn3 and Sn4 is found to be 3.724 eV, 3.62 eV, 3.02 eV, and (3.53 eV and 3.9 eV) respectively. In Sn4 as shown in figure 4.7 (c), 3.53 eV and 3.9 eV corresponds to direct band gap transitions [40]. In Sn2 as shown in figure 4.7 (b), 3.62 eV corresponds to dipole forbidden transition which is rather unusual occurrence [40]. Compared to the direct bulk band gap of SnO₂(~3.68 eV)[41], as decrease in size increase the band gap of Np's is found to increase as well as decrease . This might happen due to the fact that SnO₂ Np's do not follow quantum confinement effect [7] strictly owing to the presence of defect sites in the crystal lattice and oxygen vacancies. [42]

Urbach Energy

To know more about the degree of defects in SnO_2 , we calculated the Urbach Energy. In optical absorption, electrons near the band edges can be excited from the valence band to the conduction band across the energy band gap [30]. However, during this process, if these electrons encounter any disorder, it can cause the density of their states, denoted by ρ (hv) where hv is the photon energy, to extend into the energy gap. These extended states, known as localized defect states, create a tail in the absorption spectrum. The width of this tail is represented by the Urbach Energy E_u, which is often interpreted as the width of the tail of localized states in the band gap. Therefore, Urbach Energy is a measure of the degree of disorder in the material, and the presence of localized states can significantly affect the optical properties of the material. Urbach Energy is estimated from the exponential portion of the Urbach tail using the equation

$$\alpha = \alpha_0 \exp((E - E_g) / E_u)$$

Where α , α_o , E, E_g, and E_u are the absorption coefficient, arbitrary constant, incident energy, and Urbach Energy respectively [34]. Urbach energy is directly linked with the degree of electronic distordeness within the crystals. The graph drawn for ln(α) versus hv is shown in Figure 4.8 and Urbach energy is calculated from the inverse slope of it. The calculated Urbach Energy (E_u) of the Sn1, Sn2, Sn3, and Sn4 is found to be in higher within eV range. To have more accurate results for Urbach Energy, we will do UV-Vis Spectroscopy in reflection mode by making pellet of SnO₂.



Figure 4.8: ln (α) versus hv plot to determine Urbach Energy of (a) Sn1 (b) Sn2 (c) Sn3 (d) Sn4

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4.2 Characterization of Carbonized SnO₂ Np's

4.2.1 Raman Spectroscopy

Sn-C bond as linkage bridge displays stabilized reversibly conversion reaction that Sn and Li₂O could be converted to SnO₂ during the charging process. Sn-C bond could provide an ultrafast electron transfer path of SnO₂ material. The Sn-C bond facilitates the fixation of SnO₂ on the carbon matrix and effectively reduces the SnO₂ agglomeration [35]. As shown in Figure 4.9, A_{1g} vibration mode of Sn1 (630 cm⁻¹) in the Sn1@Carbon shifts to a lower frequency (619 cm⁻¹), it's the Sn-C interaction perturbing modes of SnO₂. Similarly A_{1g} vibration mode of Sn3 (627 cm⁻¹) in Sn3@carbon shifts to lower frequency (614.91 cm⁻¹) as shown in Figure 4.11 and A_{1g} vibration mode of Sn4(625.79 cm⁻¹) in the Sn4@carbon shifts to lower frequency(612.5cm⁻¹) as shown in Figure 4.10.



Figure 4.9 Comparison of Raman Spectra of Sn1@carbon and Sn1



Figure 4.10 Comparison of Raman Spectra of Sn4@carbon and Sn4



Figure 4.11 Comparison of Raman Spectra of Sn3@carbon and Sn3

Raman spectra can provide insights into the defects and disorders found in carbon-related Structures. Carbonized SnO_2 having D band, G band, and overlapping 2D and 2G band are shown in Figure 4.9. The Raman spectra of carbonized SnO_2 which is similar to the D and G band in graphene grown on SiC by graphitization.

 I_D/I_G ratio tells about the graphitization degree. Higher the graphitization, the better the degree of conductivity. I_D/I_G helps determine the structural disorder of the synthesized material. I_D/I_G for carbon with poor crystallinity lies in the range of 1 to 2.6 and for highly crystalline carbon its value is in the range of 0.1 to 0.3 [38]. I_D/I_G calculated by taking the ratio of area under D peak and G peak after doing curve fitting. It comes out to be 1.7 for Sn1@Carbon, 1.62 for Sn3@ carbon , 1.25 for Sn4@ carbon and 1.1 for graphene grown on SiC (from Figure 4.12).



Figure 4.12: Comparison of Sn1@carbon, Sn3@carbon and Sn4@carbon with graphene on SiC

D band arises from a translational breaking mode, which is related to the presence of defects, grain boundaries, functional groups, or structural disorder and indicates a defective or disordered form of graphite. G band is related to first-order phonon scattering, as expected in sp2 carbon, and represents the presence of crystallite graphite. [36]. As discussed, for example, by Wang and Allred [37] the formation of two characteristic bands D at ~ 1350 cm⁻¹ and G at ~ 1590 cm⁻¹ in the Raman spectra

show the presence of graphitic carbon. From Figure 4.12, Carbonised Sn1 having two bands, D at 1348 cm⁻¹ and G peak at 1582 cm⁻¹ and two weak peaks referred to as second order (2D and 2G) bands, were observed overlapping between 2D and 2 G bands 2700 cm⁻¹ and 2900 cm⁻¹. The 2 D and 2G peaks appear regardless of crystal defects, Carbonised Sn3 has two bands, D at 1340 cm⁻¹ and G at 1595 cm⁻¹, Carbonized Sn4 has two bands, D at 1331 cm⁻¹ and G at 1595 cm⁻¹, and graphene on SiC has D band at 1350 cm⁻¹ and G band at 1580 cm⁻¹.

Weight loss during Carbonization

From Figure 4.13, it can be seen that the weight loss of 34.11 mg happened during carbonization of Sn1. The minuscule weight loss that appears below 400° C is attributed to the removal of water and residual organic molecules absorbed on samples. The major weight loss above 400° C indicates the burn of carbon framework, and the residue product is SnO₂.[40]



Figure 4.13: Weight loss after Carbonization of Sn1

4.2.2 SEM

To know the morphology and size of Sn1@carbon, SEM was carried out. As it can be seen in Figure 4.14, spherical Np's formed.



Figure 4.14 SEM image of Sn1@carbon

Size of the Sn1@carbon is calculated from the SEM image in the following manner: 1.52 cm = 2 micron (from the bottom left of SEM image)

We chose three particles from the image and calculated the size of them

- 0.52 cm = 684 nm
- 0.5 cm = 657 nm
- 0.49 cm = 645 nm

Avg. size calculated of SnO₂@carbon nanoparticle is 662 nm

4.2.3 XRD

The crystal structure and phase purity of the as synthesized sample were determined by XRD. The XRD pattern of Sn3@carbon and Sn4@carbon are similar to Sn3 and Sn4 which confirms tetragonal rutile structure of the carbon composites. In the Sn3@carbon (Figure 4.16) and Sn4@carbon (Figure 4.17), the peak of carbon could not be identified, which reveals the amorphous carbon in the composites. The crystallite size of the composite is calculated using Debye Scherrer equation. It comes out to be ~12 nm for Sn3@carbon and ~11 nm for Sn4@carbon which shows that after carbonization crystallite size of Sn3 and Sn4 have increased. It can be observed from Figure 4.15 and 4.16 that intensity of peaks are high after carbonization of Sn3 and Sn4. Peak intensity is mainly increased due to the increment of crystallinity and crystal size. This indicates that Carbonization process helps the crystallization of SnO₂ Np's [46]. From Figure 4.15, it has been observed that there is shift in peaks position corresponding to Miller indices (110), (101), (111), (211), (202), (310), and (321) of Sn4@carbon. Sn4@carbon's peaks corresponding to Miller indices (110), (111), (310), and (321) shifts towards higher angles by 0.03, 0.07, 0.31, and 0.15 degrees and its peaks corresponding to Miller indices (101), (211), and (202) shifts towards lower angles by 0.09, 0.21, and 0.11 degrees. This shift in peak positions towards lower or higher angles might be because of lattice strain [45]. As lattice strain leads to change in d spacing then according to bragg's diffraction formula (2dSin (θ)) $=n\lambda$) peak is shifted towards lower or higher angles accordingly.



Figure 4.15: Comparison of XRD pattern of Sn4 and Sn4@carbon



Figure: 4.16 Comparison of XRD pattern of Sn3 and Sn3@carbon

4.2.4 UV Vis Spectroscopy

To know the change in bandgap after carbonization, UV-Vis absorption spectrometry was carried out. Figure 4.17 and Figure 4.18 shows the tauc's plot of $(\alpha hv)^2$ vs hv for the samples Sn3 and Sn3@carbon. For the direct allowed transition, extrapolating the linear portion of this pot to the zero absorption provides the value of band gap. The optical band gap is estimated to be 3.02 eV of Sn3 and 5.65 eV for Sn3@carbon. We believe that the Carbonization of SnO₂ Co-precipitation pH 10 improved the crystallinity of SnO₂ Np's, declines the fraction of grain boundaries as well as cause a decrease of defect states near the band gap, and consequently increases the band gap.[44]



Figure 4.17: Band gap plot of Sn3



Figure 4.18: Band gap plot of Sn3@carbon

7.1 Conclusions

We synthesized the SnO₂ Np's of crystallite size ~8 nm, ~9 nm, ~30 nm, and ~40 nm confirmed by XRD data. Raman spectra of synthesized SnO₂ by Co-precipitation process confirmed the formation of SnO₂ Np's. It showed A_{1g} peak shifts towards lower wavenumber with decrease in size of Np's. XRD data of Sn1, Sn2, Sn3, and Sn4 confirmed the formation of tetragonal rutile phase of SnO₂. Sn1, Sn2, Sn3, and Sn4 have absorbance maxima in the region between 270 nm and 300 nm. The optical band gap energy of Np's does not follow the usual pattern of increase in band gap with decrease in size of Np's. Carbonization of SnO₂ Np's was done using glucose solution. Raman spectra of Sn1@carbon, Sn3@carbon, and Sn4@carbon have D and G peak like Graphene on SiC. I_D /I_G ratio of all the synthesized carbon composite samples indicated that amorphous carbon is formed. It also confirmed the spherical SnO₂ Np's formed. XRD of the Sn3@carbon and Sn4@carbon showed that Carbonization helps the crystallization of SnO₂ Np's. After Carbonization, bandgap of Sn3 has increased.

7.2 Future Prospects

Integrating the benefits from different aspects of the present study, there is much scope to extend this work further in the future. Some possible studies are described below:

- It would be of great interest to make use of SnO₂ of different sizes and make SnO₂-ZrO₂ composite as an anode in lithium-ion batteries.
- To make SnO₂ carbon composite of different sizes as a cathode in an Aluminium ion battery.
- To study the photocatalytic property of SnO₂.
- To make SnO₂ thin film by magnetron sputtering and then studying its properties.
- To use SnO₂ Np's of different sizes by varying pH and annealing temperature for Supercapacitor application.
- To do SnO₂ coating on separator of Lithium-ion batteries to improves the capacity of it.

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