

User User

Ph.D. Thesis of Hemant for Plagiarism

 Praveen Kumar

Document Details

Submission ID

trn:oid:::27535:136018720

Submission Date

Apr 21, 2026, 5:11 PM GMT+5:30

Download Date

Apr 23, 2026, 8:10 AM GMT+5:30

File Name

Ph.D. Thesis of Hemant for Plagiarism.pdf

File Size

7.0 MB

152 Pages

41,360 Words

249,996 Characters

6% Overall Similarity

The combined total of all matches, including overlapping sources, for each database.

Filtered from the Report

- Small Matches (less than 14 words)

Exclusions

- 98 Excluded Matches

Match Groups

-  **106 Not Cited or Quoted 6%**
Matches with neither in-text citation nor quotation marks
-  **1 Missing Quotations 0%**
Matches that are still very similar to source material
-  **0 Missing Citation 0%**
Matches that have quotation marks, but no in-text citation
-  **0 Cited and Quoted 0%**
Matches with in-text citation present, but no quotation marks

Top Sources

- 3%  Internet sources
- 2%  Publications
- 4%  Submitted works (Student Papers)

Integrity Flags

0 Integrity Flags for Review

Our system's algorithms look deeply at a document for any inconsistencies that would set it apart from a normal submission. If we notice something strange, we flag it for you to review.

A Flag is not necessarily an indicator of a problem. However, we'd recommend you focus your attention there for further review.

Match Groups

- 106** Not Cited or Quoted 6%
Matches with neither in-text citation nor quotation marks
- 1** Missing Quotations 0%
Matches that are still very similar to source material
- 0** Missing Citation 0%
Matches that have quotation marks, but no in-text citation
- 0** Cited and Quoted 0%
Matches with in-text citation present, but no quotation marks

Top Sources

- 3% Internet sources
- 2% Publications
- 4% Submitted works (Student Papers)

Top Sources

The sources with the highest number of matches within the submission. Overlapping sources will not be displayed.

- 1 **Student papers**
Shri Jagdishprasad Jhabarmal Tibrewala University on 2014-03-22 1%
- 2 **Student papers**
The Northcap University on 2026-04-01 <1%
- 3 **Publication**
Hemant K. Arora, Jyoti Shah, R.K. Kotnala, A.S. Rao, Nitin K. Puri. "Strategically en... <1%
- 4 **Internet**
link.springer.com <1%
- 5 **Internet**
dypatilunikop.org <1%
- 6 **Internet**
www.ncbi.nlm.nih.gov <1%
- 7 **Student papers**
Higher Education Commission Pakistan on 2025-06-24 <1%
- 8 **Publication**
Anjali Bankura, Anurag Gaur, Maneesha Garg. "Optimizing rGO concentration in ... <1%
- 9 **Internet**
dspace.dtu.ac.in:8080 <1%
- 10 **Publication**
Nikita Jain, Nitin K. Puri. "Zinc Oxide incorporated Molybdenum Diselenide Nanos... <1%

11	Publication	Hemant K Arora, Nikita Jain, Sunil Kumar, Nitin K Puri. "Vertically aligned 2D tin s...	<1%
12	Internet	fdocument.org	<1%
13	Internet	www.mdpi.com	<1%
14	Student papers	University College London on 2024-08-21	<1%
15	Student papers	IIT Delhi on 2026-01-01	<1%
16	Student papers	Delhi Technological University on 2026-04-13	<1%
17	Student papers	IIT Delhi on 2026-04-10	<1%
18	Student papers	British University in Egypt on 2020-06-19	<1%
19	Publication	Nikita Jain, Hemant K. Arora, Sunil Kumar, Nitin K. Puri. "First report on hydroelec...	<1%
20	Student papers	Anna University on 2026-04-18	<1%
21	Student papers	Delhi Technological University on 2026-04-09	<1%
22	Publication	Gonçalves, Filipa Nunes. "Plano Individual de Cuidados, Com Enfoque na Relação ...	<1%
23	Student papers	Savitribai Phule Pune University on 2016-07-21	<1%
24	Student papers	University of College Cork on 2022-10-21	<1%

25	Internet	afmdsrmist2024.in	<1%
26	Student papers	Clemson University on 2015-04-20	<1%
27	Student papers	University of Massachusetts - Amherst on 2026-03-08	<1%
28	Student papers	SASTRA University on 2019-10-08	<1%
29	Student papers	University of Glasgow on 2026-03-15	<1%
30	Internet	iopscience.iop.org	<1%
31	Internet	vtechworks.lib.vt.edu	<1%
32	Internet	www.coursehero.com	<1%
33	Publication	Anjali Bankura, Anurag Gaur, Maneesha Garg, R.K. Kotnala. "Tailoring of rGO in F...	<1%
34	Student papers	IIT Delhi on 2025-02-07	<1%
35	Student papers	Michigan State University on 2025-10-14	<1%
36	Student papers	Savitribai Phule Pune University on 2015-08-31	<1%
37	Publication	Sugiyama, Mutsumi, Yoshitsuna Murata, Tsubasa Shimizu, Kottadi Ramya, Chinn...	<1%
38	Student papers	Amity University on 2019-12-31	<1%

39	Publication	Avadhesh Kumar Yadav, Raghvendra Pandey, Prabhakar Singh. "Impedance spec...	<1%
40	Student papers	Higher Education Commission Pakistan on 2026-03-10	<1%
41	Publication	Kurugundla Gopi Krishna, Saidireddy Parne, Nagaraju Pothukanuri, Velavan Kath...	<1%
42	Student papers	Technological University Dublin on 2025-01-20	<1%
43	Student papers	University of Sheffield on 2013-08-19	<1%
44	Internet	docplayer.net	<1%
45	Internet	www.spectroanalysis.com	<1%
46	Student papers	Changjun High School International School on 2026-04-05	<1%
47	Publication	Ying Qiu, Yi Xie, Xinye Lin, Qinshu Zhang, Chongrong Ke, Daliang Li. "Research Pr...	<1%
48	Internet	diversedaily.com	<1%
49	Internet	igmlnet.uohyd.ac.in	<1%
50	Student papers	Nanyang Technological University on 2026-03-31	<1%
51	Student papers	Panimalar Engineering College on 2025-10-04	<1%
52	Publication	Sesan Abiodun Aransiola, Yakubu Adekunle Alli, Kondakindi Venkateswar Reddy, ...	<1%

53	Publication	Tao Gong, Longqing Chen, Xiaoyi Wang, Yang Qiu, Huiyun Liu, Zixing Yang, Thom...	<1%
54	Student papers	University of New South Wales on 2025-07-27	<1%
55	Student papers	University of Western Australia on 2026-04-03	<1%
56	Publication	Wu, T.M.. "Doped polyaniline/multi-walled carbon nanotube composites: Prepara...	<1%
57	Internet	accessapps.amdi.usm.my	<1%
58	Internet	ethesis.nitrkl.ac.in	<1%
59	Student papers	Anil Neerukonda Institute of Technology & Sciences on 2026-04-21	<1%
60	Student papers	Bilkent University on 2009-12-21	<1%
61	Student papers	Bradford College, West Yorkshire on 2025-05-25	<1%
62	Student papers	Brunel University on 2012-11-05	<1%
63	Publication	Kim, Hyesung. "Reactive DC Magnetron Sputtering for the Deposition of Semicon...	<1%
64	Publication	Nikita Jain, Savita Sharma, Nitin K. Puri. "Investigation of charge transport mecha...	<1%
65	Student papers	Universiti Teknologi Malaysia on 2012-07-24	<1%
66	Student papers	University College London on 2019-01-24	<1%

67	Student papers	University of Leeds on 2007-12-07	<1%
68	Publication	Zelong Ma, Danni Wang, Yu Wang, Baoan Bian, Bin Liao. "Effect of different conta...	<1%
69	Internet	coek.info	<1%
70	Internet	core.ac.uk	<1%
71	Internet	erepo.uef.fi	<1%
72	Internet	onlinelibrary.wiley.com	<1%
73	Internet	pubs.rsc.org	<1%
74	Internet	www.av5-ased.org	<1%
75	Internet	www.fmns.swu.bg	<1%

Synthesis, Characterization, and Engineering of 2D-Nanomaterials for Gas Sensor and Energy- Harvesting Hydroelectric Cell Devices

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By

HEMANT KUMAR ARORA
(2K20/PHDEP/01)

Under the Supervision of

PROF. VINOD SINGH
Professor
Department of Applied Physics
Delhi Technological University

PROF. NITIN K. PURI
Professor
Department of Applied Physics
Delhi Technological University



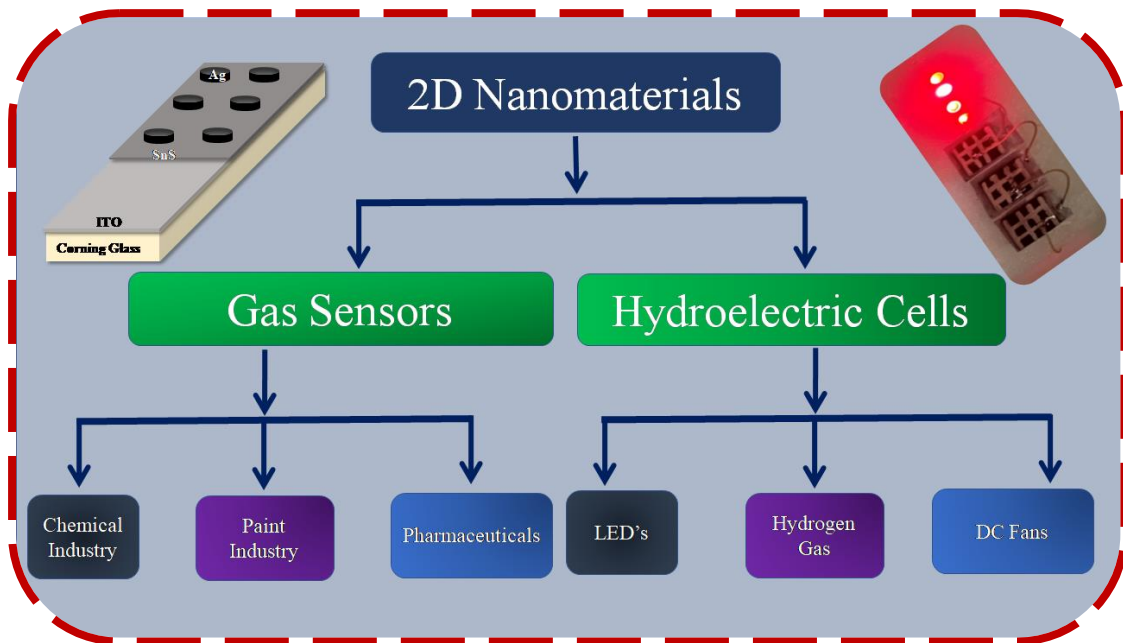
Department of Applied Physics
DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)

Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India

March, 2026

CHAPTER 1

Introduction and Scientific Motivation



This chapter begins by establishing the scientific foundation of the thesis through an in-depth discussion of nanoscience and nanotechnology, emphasizing their transformative influence on modern materials engineering and device innovation. The chapter then systematically categorizes nanomaterials based on their dimensionality zero-dimensional, one-dimensional, two-dimensional, and three-dimensional systems—highlighting how dimensional confinement directly influences electronic structure, charge transport, adsorption kinetics, and catalytic activity. Among these classes, special emphasis is placed on two-dimensional (2D) nanomaterials due to their atomically thin layered structure, exceptional surface-to-volume ratio, tunable band structure, and strong sensitivity to surface perturbations.

The chapter highlights the urgent requirement for ethanol sensors that exhibit high sensitivity, excellent selectivity, rapid response-recovery characteristics, long-term stability, and the capability to detect a broad range of concentrations at room temperature. In parallel, the chapter introduces the concept of sustainable energy generation through hydroelectric cell (HEC) device. It elaborates on the fundamental

mechanism of spontaneous water dissociation on defect-rich material surfaces, leading to ionic transport and electricity generation under at room temperature.

Through a critical evaluation of current literature, technological challenges, and performance limitations such as high operating temperatures, sluggish recovery kinetics, material instability, and limited integration between sensing and energy systems-the chapter identifies key research gaps that motivate the present investigation. Finally, it clearly articulates the objectives and scope of the thesis, outlining the systematic approach adopted to synthesize, characterize, and evaluate two-dimensional nanomaterials for room-temperature gas sensing and hydroelectric cell applications. By doing so, the chapter establishes a coherent scientific framework that underpins the research presented in the subsequent chapters.

1.1 Nanoscience and Nanotechnology

The field of nanoscience and nanotechnology has witnessed rapid and transformative growth owing to its immense potential to revolutionize industrial and commercial sectors. Nanostructured materials form the fundamental building blocks of this expanding domain. These materials are characterized by having at least one dimension below 100 nm and exhibit properties that lie between those of bulk materials and individual atoms [1,2]. As material dimensions shrink to the nanoscale, a significant increase in surface-to-volume ratio occurs, accompanied by the emergence of quantum confinement effects. These two factors collectively give rise to physicochemical properties that are markedly different from their bulk counterparts. The enhanced surface-to-volume ratio increases chemical reactivity, as a larger fraction of atoms resides at or near the surface, making them more accessible for interaction and adsorption [1,3]. Fig. 1.1 schematically illustrates the progressive increase in surface area-to-volume ratio as the material dimension decreases from a larger scale (i) to the nanoscale (ii).

At nanoscale dimensions, where the size of the material becomes comparable to characteristic physical lengths such as the electron mean free path or exciton Bohr radius, surface phenomena dominate overall material behavior. Simultaneously, quantum effects arise due to spatial confinement of charge carriers within reduced

dimensions, leading to modifications in electronic, optical, and transport properties. These size-dependent effects distinguish nanomaterials from both bulk materials and isolated atomic systems, making them uniquely suited for advanced technological applications.

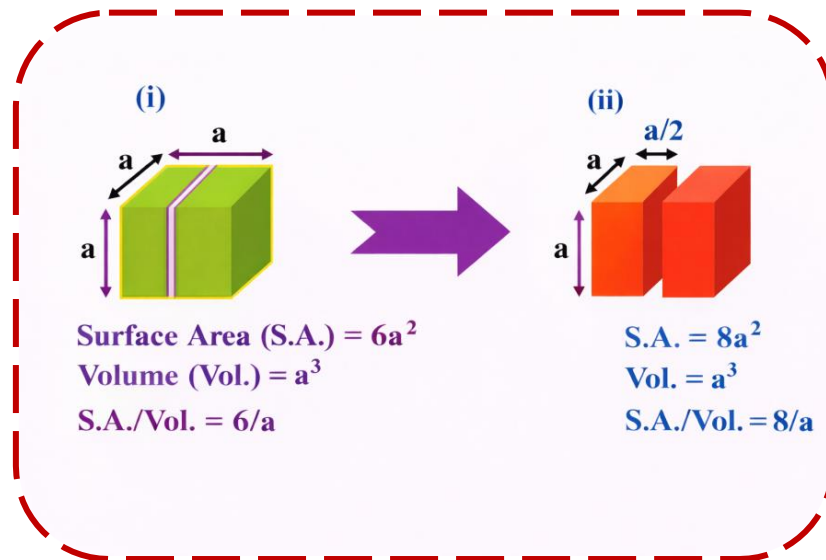


Fig. 1.1: Schematic illustrating the increase in surface area to volume ratio on going from a (i) larger dimension to a (ii) smaller dimension

1.2 Classification of Nanostructured Materials based upon Dimensionality

Nanostructured materials are commonly classified according to their dimensional confinement into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) categories.

In zero-dimensional (0D) nanomaterials, all three spatial dimensions are confined within the nanoscale range (typically < 100 nm). Representative examples include quantum dots and nanoparticles, where charge carriers are confined in all directions, leading to pronounced quantum effects. For instance, Houx *et al.* [4] reported the solvothermal synthesis of spherical WO_3 nanoparticles with diameters ranging from 5 to 30 nm. Although such nanoparticles exhibit enhanced surface activity due to their small size, they often suffer from agglomeration, which can significantly reduce their effective specific surface area. Achieving well-controlled size and morphology in 0D nanomaterials generally requires complex synthesis routes, stringent process parameters, and, in many cases, high-cost precursors. Moreover, their inherent tendency

to aggregate poses challenges in maintaining uniform dispersion, which may adversely affect device performance. Consequently, in the context of gas or vapor sensing applications, researchers frequently encounter limitations in obtaining consistent and reproducible outcomes when employing 0D nanomaterials [5].

In one-dimensional (1D) nanomaterials, two dimensions remain within the nanoscale while the third extends beyond it. Typical examples include nanorods, nanowires, and nanotubes. These structures facilitate directional charge transport along their extended axis while maintaining nanoscale cross-sectional dimensions. The formation of 1D nanostructures generally arises from anisotropic or preferential growth along a specific crystallographic direction, resulting in elongated morphologies. Compared to other nanostructured forms, 1D materials have attracted considerable attention due to their distinctive properties, particularly their ability to facilitate directional or axis-dependent charge transport. The confinement of charge carriers in the radial direction, combined with extended longitudinal dimensions, enables efficient electron flow along a single axis. This directional transport characteristic enhances their suitability for applications in electronics, sensing, and energy devices. [6-8].

Two-dimensional (2D) nanostructures are materials possessing nanoscale thickness—typically in the range of a few nanometers (1-10 nm) while their lateral dimensions extend from tens to several hundreds of nanometers [9]. Examples of 2D nanomaterials include nanosheets and nanoplates, which exhibit a large exposed surface area due to their ultrathin geometry. The high surface free energy associated with these structures enhances their chemical reactivity and facilitates adsorption-driven processes. As a result, the activation energy required for the dissociation of target species is often reduced, thereby minimizing the need for external energy input [10]. Although research on 2D nanostructures initially progressed at a modest pace, significant momentum was gained following the discovery of graphene. Owing to its exceptional electrical, mechanical, and thermal properties, graphene sparked widespread interest and accelerated the exploration of other layered two-dimensional materials. This breakthrough marked a turning point in nanomaterials research, positioning 2D systems at the forefront of advanced functional material development.

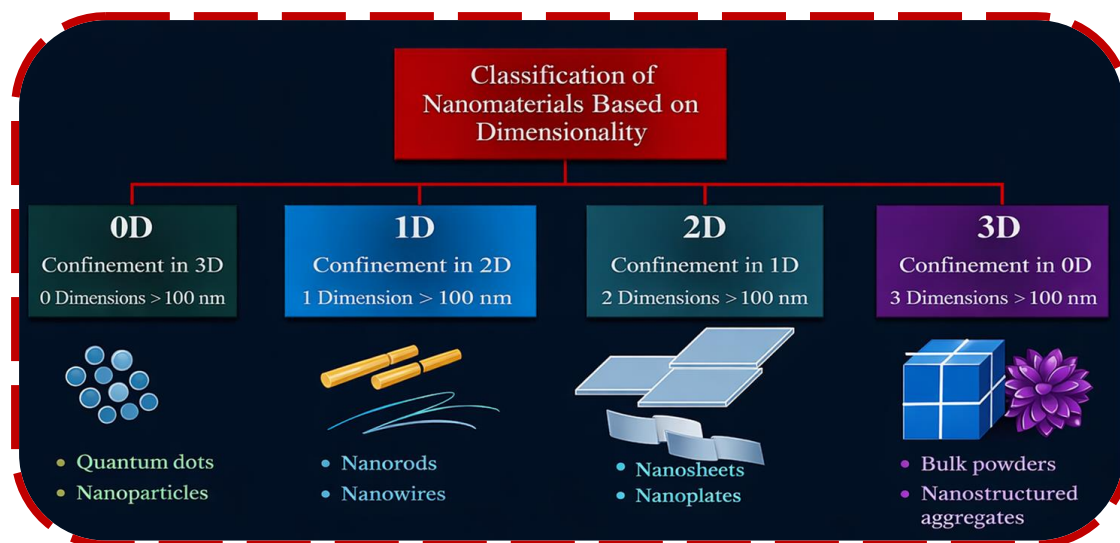


Fig. 1.2: Classification of nanostructured materials based on dimensions.

Among the various nanomaterial dimensionalities, research on two-dimensional (2D) nanomaterials has experienced remarkable growth, particularly following the discovery of graphene and its extraordinary properties in 2004 [2]. This breakthrough revealed the immense potential of atomically thin materials and initiated extensive exploration into other layered systems. The broad spectrum of structural, electronic, optical, and chemical properties exhibited by 2D nanomaterials is fundamentally governed by their reduced dimensionality. Their ultrathin architecture, combined with an exceptionally high surface-to-volume ratio, enhances interfacial interactions and enables their application across diverse technological fields.

Graphene remains the most extensively investigated 2D nanomaterial due to its exceptional properties, including its single-atom thickness, zero band gap, outstanding electrical conductivity, remarkable mechanical strength, and extremely large specific surface area. These attributes have made graphene highly attractive for applications in electronics, energy storage, catalysis, and sensing. However, despite its superior intrinsic properties, the large-scale production of high-quality graphene with high yield and low cost remains a significant challenge for industrial implementation. Consequently, graphene is often synthesized through the chemical or thermal reduction of graphene oxide (GO), as this approach is relatively inexpensive and scalable [11]. Reduced graphene oxide (rGO), although less conductive than pristine graphene due to residual defects and oxygen-containing functional groups, offers distinct advantages for

sensing applications. The presence of functional groups on rGO surfaces facilitates covalent bonding and surface functionalization, which enhances interaction with target analytes and improves sensing performance [2,12,13].

Beyond graphene and its derivatives, several other 2D nanomaterials have gained prominence, including transition metal chalcogenides (TMCs), graphitic carbon nitride (g-C₃N₄), and MXenes [14]. These materials exhibit tunable band structures, strong light–matter interactions, and rich surface chemistry, further expanding the application scope of 2D systems. The exceptional electronic and optical properties of 2D nanomaterials, along with the ability to tailor their behavior through defect engineering and surface functionalization, significantly enhance their technological appeal [1]. Moreover, the large fraction of exposed surface atoms in 2D materials allows facile functionalization and efficient interaction with surrounding media [15]. In addition to their electronic advantages, 2D nanomaterials demonstrate impressive mechanical characteristics such as flexibility, lightweight nature, and structural robustness, making them highly suitable for flexible, wearable, and portable sensing platforms [2].

Transition metal chalcogenides (TMCs) constitute an important subgroup of 2D materials characterized by tunable optical, electrical, and catalytic properties. Structurally, TMCs can be categorized into three principal subclasses [16]. The first subclass comprises **Transition Metal Dichalcogenides (TMDs)** with the **general formula MX₂**, where **M** represents a **transition metal** from **groups 4-10** and **X** denotes a **chalcogen** element such as sulfur, selenium, or tellurium. The second subclass includes Metal Monochalcogenides (MCs), represented by the formula MX, where M may include elements such as Al, Ga, In, Tl, Ge, Sn, Pb, or Sb, and X corresponds to S, Se, or Te. The third category consists of Transition Metal Trichalcogenides (TMTs), described by the formula MX₃, where M includes metals such as Ti, Zr, Hf, V, Nb, Cr, and related elements, while X represents S, Se, or Te.

Metal monochalcogenides (MCs) have recently emerged as an important class of two-dimensional (2D) layered materials for gas sensing applications due to their earth-abundant composition, environmental compatibility, tunable electronic properties, and strong surface reactivity toward adsorbed species [17-20]. Structurally, MCs consist of

covalently bonded metal and chalcogen atoms arranged in layered planes, with adjacent layers held together by weak van der Waals interactions [21,22]. This anisotropic bonding nature enables facile mechanical or chemical exfoliation into few-layer or monolayer sheets, thereby exposing a high density of active surface sites that are favorable for gas adsorption and charge transfer processes. Owing to their layered structures, adjustable band gaps, and amenability to surface modification, TMCs offer versatile opportunities for heterostructure fabrication and interfacial engineering. These characteristics make them highly promising candidates for next-generation gas sensing devices and multifunctional systems that require efficient charge transfer and strong surface interactions.

Among the MC family, tin sulfide (SnS) has attracted considerable attention as a promising semiconductor for gas sensing applications. SnS belongs to the IV–VI group of semiconductors and crystallizes in an orthorhombic layered structure with a moderate band gap of approximately 1.1–1.3 eV [23]. Its high optical absorption coefficient in the visible spectrum, chemical stability, non-toxicity, and cost-effectiveness make it an attractive material not only for sensing but also for optoelectronic and energy-related applications [24,25]. Additionally, SnS can be synthesized through relatively simple, scalable, and economically viable methods such as solvothermal routes, chemical vapor deposition, and mechanical exfoliation, enabling practical large-scale fabrication.

The layered morphology of SnS provides abundant exposed active sites and short charge transport pathways, both of which are beneficial for sensing performance. Various nanostructured forms of SnS including nanorods, nanowires, nanosheets, and nanoplates have been investigated for enhanced gas sensing. In particular, one-dimensional (1D) SnS nanostructures demonstrate improved sensing behavior owing to their high aspect ratio, efficient axial charge transport, and increased surface-to-volume ratio [26,27]. These morphological advantages contribute to enhanced adsorption kinetics and improved electrical conductivity compared to bulk or spherical structures [28].

SnS is intrinsically a p-type semiconductor, primarily due to native defects such as tin vacancies (V_{Sn}) and sulfur interstitials, which act as acceptor states and contribute to hole conduction. Its moderate band gap, relatively high intrinsic carrier concentration, and appreciable Hall mobility make it suitable for room-temperature gas sensing. However, the

electronic behavior of SnS is highly defect-sensitive. The formation of sulfur vacancies (V_S) can introduce donor levels near the conduction band, potentially inducing partial or dominant n-type conductivity depending on synthesis conditions and stoichiometric control. This defect-driven tunability enables modulation of carrier type and concentration, offering an additional degree of control over gas sensing characteristics [29].

The possibility of achieving n-type SnS behavior is particularly advantageous for gas sensing applications. n-type SnS can enhance sensitivity toward oxidizing gases by promoting electron depletion mechanisms at the surface, while p-type SnS typically exhibits strong responses toward reducing gases through hole modulation. This dual-conductivity nature broadens the range of detectable analytes and allows the design of heterojunction-based sensors with improved selectivity and response dynamics. Furthermore, controlled tuning between p-type and n-type conduction can facilitate the formation of p–n junctions, enhancing charge separation efficiency and expanding applications in photovoltaics, photodetectors, and catalytic systems [30].

Both experimental investigations and theoretical modeling studies have confirmed that the gas-sensing performance of SnS is strongly governed by its defect landscape, particularly the type and density of cationic (V_{Sn}) and anionic (V_S) vacancies [31]. These defects influence adsorption energetics, surface charge distribution, and carrier transport during gas–solid interactions. Consequently, defect engineering—through controlled synthesis parameters, post-annealing treatments, heteroatom doping, or surface functionalization plays a pivotal role in tailoring the electronic structure and enhancing low-temperature sensing performance of SnS-based devices.

Metal monochalcogenides, including SnS, can be synthesized through diverse physical and chemical approaches such as chemical vapor deposition, solvothermal synthesis, and mechanical exfoliation. These techniques allow precise control over stoichiometry, crystallinity, morphology, and defect concentration. Their layer-dependent electrical, optical, and mechanical properties can be further tuned via doping, defect modulation, or surface modification strategies [32–34]. Such versatility positions MCs, and SnS in particular, as highly adaptable materials for next-generation gas sensors and multifunctional energy-related applications.

In electronics and optoelectronics, nanomaterials are widely employed in field-effect transistors, photodetectors, light-emitting devices, and flexible circuits owing to their superior charge transport and bandgap engineering capabilities. In energy-related applications, they play a pivotal role in lithium-ion batteries, supercapacitors, hydroelectric cell device, solar cells, hydrogen evolution reactions, and photocatalysis, where enhanced surface activity and shortened diffusion pathways significantly improve performance. Nanomaterials are also extensively utilized in biomedical applications, including drug delivery, biosensing, imaging, and antimicrobial coatings, benefiting from their high reactivity and biocompatibility. In environmental remediation, they contribute to pollutant degradation, water purification, and catalytic conversion of hazardous gases. Furthermore, their mechanical robustness and lightweight nature support applications in structural composites, coatings, and flexible wearable technologies.

1.3 Requirement for Gas Sensor

Large-scale industrialization has significantly intensified environmental pollution across the globe. Environmental pollution refers to the introduction of harmful substances into natural systems, resulting in detrimental physical, chemical, and biological changes. Its consequences extend beyond localized contamination and include global challenges such as climate change, ecosystem imbalance, and biodiversity loss. Despite increasing awareness, the magnitude and long-term implications of environmental degradation have not been adequately addressed, leading to both natural and anthropogenic crises [17]. Among the various forms of environmental degradation, air pollution has emerged as one of the most critical threats to ecological stability and public health. Industrial operations are major contributors, releasing substantial quantities of toxic and hazardous gaseous pollutants into the atmosphere. In addition to industrial emissions, domestic and urban activities including vehicular exhaust, residential heating systems, cooking stoves, and open burning of waste significantly degrade air quality. Rapid urbanization, modern lifestyle patterns, and the widespread use of agricultural chemicals further exacerbate atmospheric contamination. Nevertheless, the primary driver of harmful gaseous emissions remains the combustion of fossil fuels across industrial, transportation, and energy-generation sectors [12].

A wide range of hazardous gases are released into the atmosphere through these activities, including carbon dioxide (CO₂), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), chlorine (Cl₂), ethanol (C₂H₅OH), ammonia (NH₃), and various volatile organic compounds (VOCs). These emissions originate from diverse sources such as industrial manufacturing units, chemical processing plants, thermal power stations, agricultural practices, and motor vehicles. VOCs are organic chemicals characterized by low boiling points and high vapor pressures, enabling them to readily evaporate and disperse into the air even under room-temperature (RT) conditions [15]. Due to these physicochemical properties, VOCs are widely distributed in both outdoor and indoor environments [35]. Numerous routine human activities contribute to VOC emissions such as transportation, application of paints and coatings, fuel combustion, industrial processing, and even respiration release measurable amounts of organic vapors into the atmosphere. In addition, personal care products, cleaning agents, adhesives, and various consumer goods represent significant sources of VOC exposure [36]. Exposure to such pollutants poses severe risks to human health, contributing to respiratory disorders, cardiovascular diseases, lung cancer, and other chronic health conditions. Consequently, the development of reliable, real-time, and highly sensitive detection systems for monitoring hazardous gases has become an urgent and essential requirement for environmental protection and public safety [37]. Some selected VOCs and their harmful effects and allowable exposure limits on human health are presented in Table 1.1.

Table 1.1: Lists the names, chemical formulas, health effects, and threshold values of VOCs.

VOC Name	Chemical Formula	Effect on Human Health	Threshold Value
Ethanol	C ₂ H ₅ OH	Headaches, nausea, vomiting, kidney failure, inflammation of the nose and throat, harm to the central nervous system, and even cancer.	1000 ppm
Formaldehyde	HCHO	Chest tightness or pain, shortness of breath, or irritation of the eyes	0.75 ppm
Acetone	CH ₃ COCH ₃	Headache, exhaustion, dry mouth, nausea, and lightheadedness	750 ppm
Methanol	CH ₃ OH	Vertigo, headache, bronchial tightness, nausea, and narrowing of the airways	200 ppm

Environmental pollution has emerged as a critical global challenge, largely driven by rapid industrialization and accelerated urban expansion [38,39]. Continuous economic growth and industrial activities have led to a substantial rise in the emission of volatile organic compounds (VOCs) into the atmosphere [3]. Consequently, nearly all daily activities contribute, directly or indirectly, to the accumulation of VOCs in the surrounding environment. Notably, indoor environments often exhibit VOC concentrations significantly higher than those observed outdoors, in some cases reaching levels up to ten times greater [40].

1.4 Sensors

A sensor is an electronic device or instrument designed to detect physical, chemical, or biological stimuli and convert them into measurable electrical signals that can be processed by electronic circuits. The concept of a sensor originates from the idea of replicating or extending human sensory capabilities, enabling machines to perceive and respond to environmental changes. The terms “sensor” and “transducer” are often used interchangeably, as both refer to devices that convert one form of energy or signal into another suitable output form. In essence, a sensor receives an input signal-such as temperature, pressure, light intensity, gas concentration, or biochemical activity and transforms it into a corresponding electrical response.

Sensors are indispensable components in modern technological systems, playing a crucial role in monitoring, control, automation, and safety. They enable real-time data acquisition and feedback regulation in complex systems across multiple sectors. Their applications span a broad range of industries, including automotive systems, aerospace engineering, telecommunications, consumer electronics, industrial process control, and structural health monitoring of machinery and infrastructure. In addition, sensors are widely employed in environmental monitoring to detect hazardous gases, toxic chemicals, explosive vapors, and other pollutants. Their ability to provide continuous, accurate, and rapid detection makes them essential tools for ensuring operational efficiency, environmental protection, and public safety [41].

1.4.1 Classification of Sensors

Sensors can be designed and classified in numerous ways depending on their intended application, transduction mechanism, fabrication methodology, operational mode, and type of output signal. One of the most fundamental classifications is based on the principle of operation, which broadly divides sensors into physical sensors and chemical sensors. This distinction is illustrated in Fig. 1.3.

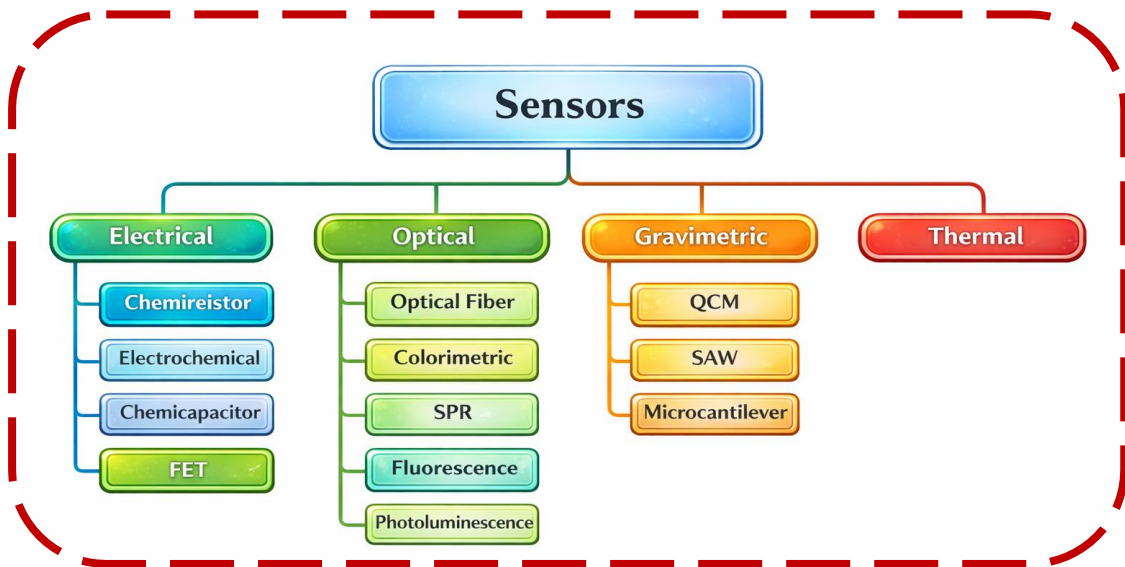


Fig. 1.3: Various types of sensors and sub-categories

Physical sensors are devices that detect and measure changes in physical parameters of a system. They operate by exploiting various physical phenomena such as photoelectric, piezoelectric, magnetostrictive, ionization, thermoelectric, and magnetoelectric effects. Through these mechanisms, physical sensors can monitor quantities including temperature, pressure, displacement, magnetic field, light intensity, and mechanical strain. Owing to their reliability and precision, physical sensors are widely employed in industrial automation, aerospace systems, structural health monitoring, automotive technologies, and consumer electronics.

In contrast, chemical sensors are specifically designed to convert chemical information into a measurable analytical signal. This information may correspond to the concentration of a particular analyte or to the overall composition of a chemical environment. Chemical sensors function through interactions between the target species and the sensing surface, typically involving adsorption, catalytic reactions, redox

processes, or charge transfer phenomena. The resulting chemical interaction is translated into an electrical, optical, thermal, or mass-based output. Various types of chemical sensors include chemiresistive gas sensors, humidity sensors, ionic sensors, biosensors, and electrochemical sensors. These devices are indispensable in environmental monitoring, medical diagnostics, industrial process control, food safety assessment, and homeland security applications.

The present research primarily focuses on the development and fabrication of chemiresistive gas sensors based on two-dimensional (2D) nanomaterials for the detection of volatile organic compounds (VOCs) and other hazardous gases. Chemiresistive sensors belong to a class of chemical sensors that operate by exhibiting measurable changes in electrical resistance upon exposure to gaseous analytes, particularly VOCs [42,43]. The magnitude of the resistance variation is directly correlated with the concentration of the target gas, enabling both qualitative detection and quantitative analysis. Since their introduction in the 1960s, chemiresistive sensors have gained widespread attention due to their simple device architecture, cost-effective fabrication, low power consumption, and compatibility with conventional electronic systems [44,45]. In addition, these sensors offer high sensitivity, good thermal and chemical stability, and the potential for miniaturization. Such advantages have facilitated their deployment across diverse fields, including environmental pollution monitoring, industrial safety and process control, food quality assessment, automotive exhaust analysis, defense and security systems, and medical diagnostics [46-49]. The integration of 2D nanomaterials into chemiresistive platforms further enhances performance by improving surface adsorption, charge transfer efficiency, and room-temperature sensing capabilities.

1.4.2 Chemiresistive Gas Sensor

A typical chemiresistive gas sensor consists of an active sensing layer deposited onto a suitable substrate, such as glass, indium tin oxide (ITO)-coated glass, or fluorine-doped tin oxide (FTO)-coated glass. The sensing material forms the functional component responsible for interacting with target gas molecules. To establish electrical connectivity, metallic electrodes commonly aluminum (Al), silver (Ag), or gold (Au) are deposited

onto the surface of the sensing film, forming reliable ohmic contacts. The electrical resistance of the sensor is then monitored using a multimeter or a dedicated electrical characterization system connected through these electrodes. Fig. 1.4 presents a schematic illustration of the typical architecture of a chemiresistive gas sensor.

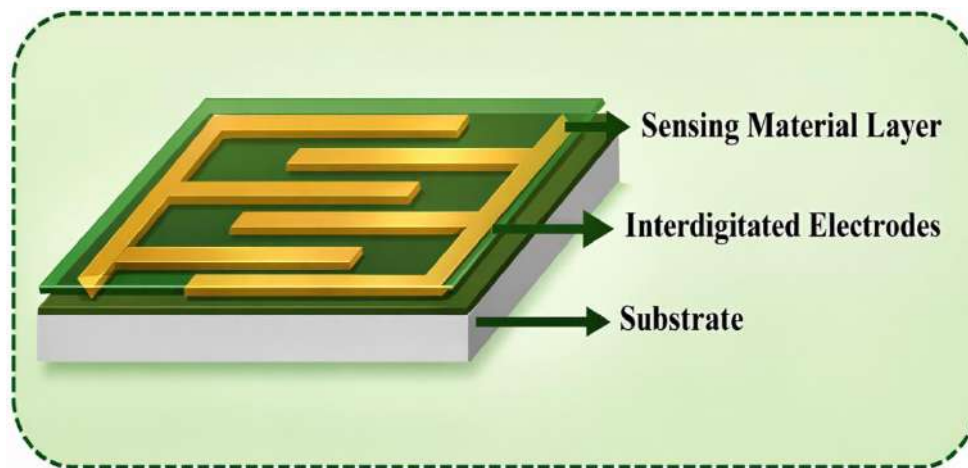


Fig. 1.4: Schematic diagram of a simple chemiresistor sensor

Over the past several decades, a wide range of nanostructured materials have been extensively investigated as active sensing layers in chemiresistive configurations for volatile organic compound (VOC) detection. These materials include two-dimensional (2D) nanomaterials, metal oxides, metal nanoparticles, conducting polymers, and various nanocomposites [50-52]. Their high surface area, tunable electronic properties, and enhanced adsorption capabilities make them particularly suitable for improving sensitivity, selectivity, and response dynamics in gas sensing applications. Advancements in sensor technology have further enabled the development of intelligent, interconnected systems collectively referred to as the Internet of Things (IoT). In such networks, data acquired from multiple sensors are integrated, processed, and analyzed to facilitate informed decision-making, improve operational efficiency, and enhance situational awareness. The integration of sensor platforms with wireless communication and data analytics has significantly expanded their functionality and real-time monitoring capabilities.

In recent years, growing global concern regarding atmospheric pollution and environmental degradation has intensified the demand for advanced sensing technologies.

The detection of toxic, hazardous, and flammable gases has become critically important in both domestic and industrial settings. Accidental gas leaks, industrial emissions, and indoor air contamination pose serious threats to human health and safety. Consequently, the development of highly sensitive, selective, and reliable gas sensors has attracted considerable research attention. Scientists and engineers worldwide are actively working to improve gas sensing materials, device architectures, and detection mechanisms to enable accurate real-time monitoring of hazardous gases and to address pressing environmental and safety challenges.

1.4.3 Key Gas Sensing Performance Parameters

The operation of a gas sensor is typically evaluated with some basic parameters as explained below:

- 1. Response:** The sensor response indicates the change in resistance or current when exposed to target gas molecules. The response may be described differently based on the type of gas:

$$\text{Response} = \frac{R_g}{R_a} \text{ (for reducing gases)} \quad (1.1)$$

$$\text{Response} = \frac{R_a}{R_g} \text{ (for oxidizing gases)} \quad (1.2)$$

where R_g and R_a represent the sensor resistance in the presence of gas and in air, respectively.

The relative response (%) can be calculated as:

$$\text{Relative response (\%)} = \frac{R_g - R_a}{R_a} \times 100 \text{ (for reducing gases)} \quad (1.3)$$

$$\text{Relative response (\%)} = \frac{R_a - R_g}{R_g} \times 100 \text{ (for oxidizing gases)} \quad (1.4)$$

The sensitivity is defined as the change in response per unit concentration of the analyte:

$$\text{Sensitivity} = \frac{\text{Response}}{\text{Gas concentration}} \quad (1.5)$$

2. **Response Time:** The response time is the time taken by the sensor to reach 90% of its maximum response when it is exposed to the target gas. A shorter response time is desirable in practical sensing.
3. **Recovery Time:** Recovery time is the time taken by the sensor to come back to 10% of the original value when the gas is removed. Rapid recovery guarantees enhanced sensor reusability and reliability.
4. **Selectivity:** Selectivity describes the ability of the sensor to detect a particular gas preferentially over other interfering gases under the same conditions.
5. **Reproducibility:** Reproducibility describes the capacity of a sensor to produce uniform responses under the same operating conditions in repeated measurement cycles.
6. **Stability:** Stability is the sensor's consistency in terms of its performance over a long time under stable experimental conditions.

1.5 Gas Sensing Mechanism

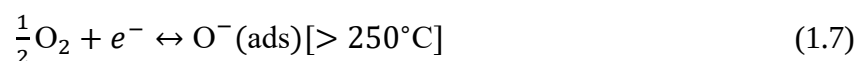
The gas-sensing behavior of two-dimensional (2D) materials is primarily governed by surface-mediated charge transfer processes arising from the interaction between target gas molecules and the active sites of the sensing layer. Owing to their ultrathin structure and high surface-to-volume ratio, 2D materials are highly sensitive to surface perturbations. When exposed to gaseous analytes, adsorption occurs either through weak van der Waals interactions (physisorption) or through stronger chemical bonding (chemisorption). This adsorption event facilitates electron exchange between the adsorbed gas species and the 2D semiconductor, thereby modulating the carrier concentration within the material. The resulting variation in majority carrier density leads to measurable changes in electrical resistance or conductance, forming the basis of chemiresistive sensing.

For p-type 2D semiconductors, including certain transition metal chalcogenides (TMCs), the sensing response depends on the nature of the interacting gas. Exposure to reducing gases such as NH_3 , H_2S , or ethanol results in electron donation to the sensing material. The injected electrons recombine with holes, reducing the hole concentration

and consequently increasing the electrical resistance. In contrast, oxidizing gases such as NO₂ or O₃ withdraw electrons from the semiconductor surface, effectively increasing hole concentration and leading to a decrease in resistance [17,53]. Upon removal of the target gas and re-exposure to ambient air, desorption of the adsorbed molecules restores the initial carrier equilibrium, allowing the sensor to recover its baseline resistance. The response time, recovery time, and reversibility of this adsorption–desorption cycle are critical parameters that determine overall sensor performance.

In many semiconductor-based 2D materials, especially metal oxides and defect-rich chalcogenides, oxygen adsorption plays a crucial role in the sensing mechanism. When the material is exposed to air, oxygen molecules adsorb onto the surface and capture electrons from the conduction band, forming ionized oxygen species such as O₂⁻, O⁻, or O²⁻, depending on temperature and surface conditions. This electron withdrawal creates a surface depletion region and induces band bending near the interface, significantly influencing the electrical conductivity of the material. Subsequent interaction between these adsorbed oxygen ions and incoming gas molecules alters the charge distribution and modifies the depletion layer width, thereby producing a detectable resistance change.

In the case of ultrathin 2D nanomaterials, where the thickness is comparable to or smaller than the Debye length, the entire channel can be affected by surface charge modulation. This complete carrier modulation enhances sensitivity and enables effective gas detection even at room temperature. The chemistry of the adsorbed oxygen species is highly dependent on temperature, represented by the following equilibria:



Additionally, defect sites, edge states, and vacancy centers further contribute to enhanced adsorption energetics and faster charge transfer kinetics, making 2D materials particularly attractive for low-power, high-performance gas sensing applications.

1.6 Requirement for Energy Harvesting

The extensive reliance on conventional energy resources has led to the rapid depletion of natural reserves such as crude oil, coal, and biomass-derived fuels. The rate at which these fossil fuel resources are being consumed is a matter of serious global concern. The escalating demand for energy worldwide is largely driven by population growth, rapid industrialization, urban expansion, and rising standards of living [54,55]. As a consequence, the sustainability of traditional energy systems has come under significant pressure.

In response to these challenges, the adoption of renewable energy technologies has steadily increased across the globe, as illustrated in Fig. 1.5 [56]. Presently, major renewable energy sources include geothermal energy, hydropower, wind energy, biomass, solar energy, photovoltaic systems, and tidal power [57]. Although substantial progress has been achieved, meeting the ever-growing global energy demand requires a significant expansion of clean energy generation capacity without exacerbating environmental pollution [58]. This transition necessitates a fundamental transformation in the global energy landscape, with renewable energy systems playing a central role in future energy production and consumption.

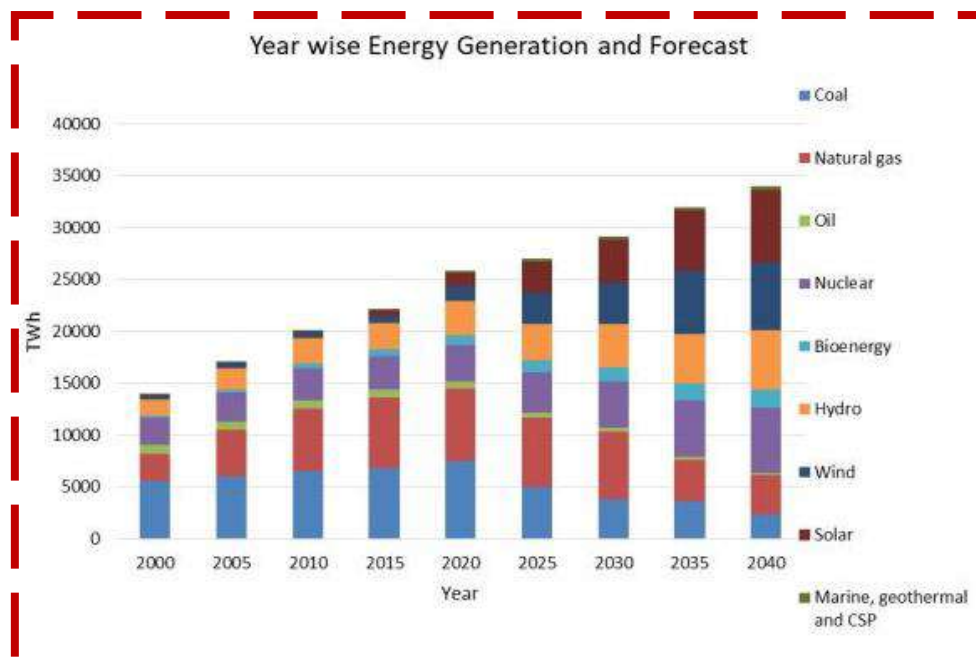


Fig. 1.5: World electricity generation by category of energy sources

The urgent need to reduce greenhouse gas emissions, particularly CO₂, and to minimize hazardous byproducts associated with fossil fuel combustion has intensified research efforts toward sustainable and environmentally benign energy technologies [59]. International frameworks and agreements on sustainable development have emphasized climate change mitigation, improved air quality, and universal access to reliable energy as key priorities. Under sustainable development scenarios (SDS), projections of global electricity generation highlight a progressive shift toward low-carbon and renewable technologies, as depicted in Fig. 1.5. Such a transition is essential to ensure long-term energy security, environmental protection, and socioeconomic stability.

The above graph indicates that global electricity demand is projected to reach nearly 35,000 TWh by the year 2040. It also reflects a gradual decline, beginning around 2020, in the contribution of conventional energy sources such as natural gas, coal, oil, and nuclear power to total electricity generation. In contrast, electricity production from renewable and sustainable sources—including solar, wind, and hydropower—exhibits a consistent upward trajectory. Projections suggest that renewable energy could account for more than 50% of total electricity generation by 2040 [60], underscoring a significant structural shift in the global energy mix.

Meeting this substantial rise in energy demand will require not only large-scale deployment of renewable technologies but also a strong emphasis on energy conservation, improved energy efficiency, and the development of innovative solutions for optimized utilization of sustainable resources. Advancements in materials science, storage technologies, and distributed generation systems will play a crucial role in enabling this transition. Fig. 1.6 further illustrates the year-wise comparison of annual growth in total final energy consumption across different energy carriers, including coal, oil, gas, electricity, biomass, and renewables, highlighting the evolving dynamics of global energy consumption patterns.

The current global energy landscape strongly highlights the transition toward renewable energy sources, with particular emphasis on solar power, as illustrated in Fig. 1.6. Solar energy is widely regarded as an abundant and virtually inexhaustible resource, making it one of the most promising alternatives to fossil fuels. Considerable research efforts have therefore been directed toward the development of advanced solar energy

conversion technologies using diverse material systems, including organic solar cells, thermoelectric materials, silicon-based photovoltaics, and perovskite solar cells [61,62].

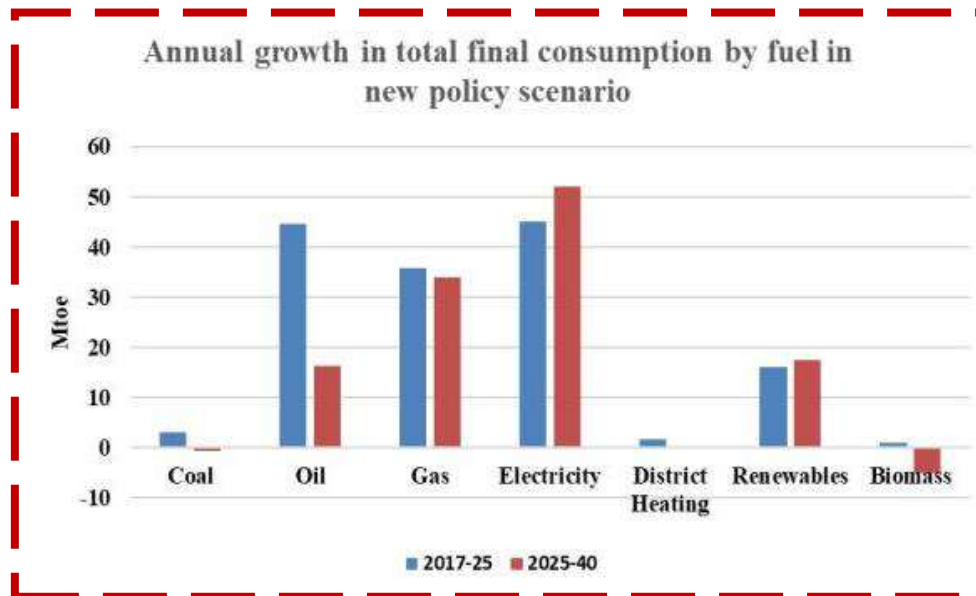


Fig. 1.6: Annual growth in total consumption by fuel

Despite its vast potential, solar energy faces inherent limitations. Its availability is restricted to daylight hours and varies significantly with geographic location, seasonal changes, and atmospheric conditions. Similarly, wind energy, though renewable and clean, is highly dependent on meteorological patterns and is often unpredictable, particularly in inland regions [63]. As a result, electricity generated from solar and wind sources are inherently intermittent in nature [62], posing challenges for maintaining a stable and reliable power supply.

1.7 Present Scenario on Green Energy

To address these intermittency issues, significant advancements have been made in energy storage technologies over the past few decades. Various energy storage systems such as capacitor banks, electrochemical batteries, pumped hydro storage, mechanical energy storage (MES), and thermal energy storage (TES) have been developed to store surplus energy during peak generation periods and supply it during demand fluctuations [64]. Among these, batteries have emerged as the most practical and widely adopted portable electrical energy storage systems across numerous applications [65]. These

systems, commonly referred to as Electrical Energy Storage (EES) technologies, function by converting electrical energy into stored chemical, mechanical, or thermal forms, which can be reconverted into electricity when required.

Looking ahead, next-generation energy technologies must achieve high energy conversion efficiency, reduced processing and deployment costs, and minimal or zero CO₂ emissions. The development of sustainable, efficient, and environmentally benign energy systems remains essential for ensuring long-term energy security and mitigating climate change impacts.

1.8 Types of Renewable Energy

The utilization of renewable energy sources offers significant advantages, including long-term economic benefits and enhanced environmental sustainability. Unlike fossil fuels, renewable resources are replenishable and contribute substantially to reducing greenhouse gas emissions and environmental degradation. To date, major renewable energy technologies have included solar, wind, hydroelectric cell, biomass, hydropower, and geothermal systems. Among these, wind energy and solar photovoltaic (PV) technologies have witnessed particularly rapid growth over the past few decades, emerging as key contributors to the global clean energy transition [66,67].

The present research shifts attention toward an alternative and emerging approach to sustainable energy generation-defect-engineered hydroelectric cells based on spontaneous water splitting. This approach explores the use of defect-rich materials capable of inducing water dissociation under ambient conditions, thereby generating electrical energy without relying on conventional photovoltaic or mechanical energy conversion processes. By leveraging surface defects and nanoscale material engineering, hydroelectric cell technology represents a promising pathway for environmentally benign and potentially low-cost energy generation.

1.9 Water splitting

Photosynthesis is a naturally occurring biological process through which green plants convert solar energy into chemical energy. In this process, carbon dioxide and water are

transformed into carbohydrates and oxygen in the presence of sunlight. A crucial step in photosynthesis involves the light-driven splitting of water molecules, a phenomenon known as photolysis, which takes place within the chloroplasts. During photolysis, water molecules absorb light energy, resulting in the release of electrons, protons (hydrogen ions), and oxygen. The extracted electrons are transferred to the reaction center chlorophyll, where they participate in the photosynthetic electron transport chain. Simultaneously, hydrogen ions are liberated into the surrounding medium, contributing to the formation of a proton gradient essential for energy conversion. When two water molecules undergo splitting, the oxygen atoms combine to form molecular oxygen (O₂), which is released as a byproduct. The overall reaction representing this process is expressed in equation 1.9



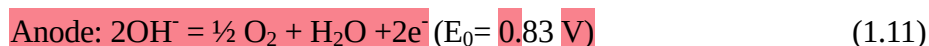
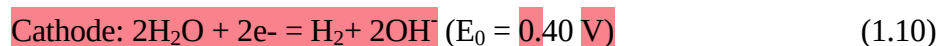
Inspired by the natural process of photosynthesis, researchers have developed and explored various approaches to achieve artificial photosynthesis for sustainable energy production. Artificial photosynthesis aims to mimic the light-driven water-splitting mechanism observed in plants to generate hydrogen and oxygen as clean energy carriers. Over the years, scientists have proposed and implemented multiple water-splitting techniques based on different physical, chemical, and electrochemical principles. Some of the prominent water-splitting methods are discussed below.

1.9.1 Electrolysis

Electrolysis of water is a widely known technique in which an external electric current is applied to drive the decomposition of water (H₂O) into its constituent gases, hydrogen (H₂) and oxygen (O₂). When an electric potential is applied across two electrodes immersed in water, the water molecules dissociate into hydrogen ions (H⁺) and hydroxide ions (OH⁻). These ions migrate toward oppositely charged electrodes under the influence of the electric field, resulting in hydrogen evolution at one electrode and oxygen evolution at the other.

Pure water, however, is a weak ionic conductor due to its low intrinsic ion concentration. To enhance electrical conductivity and facilitate efficient electrolysis, an electrolyte such as an acid or alkali is typically added. The presence of these ionic

species significantly improves charge transport within the solution, thereby promoting the water-splitting reaction. The phenomenon of electrolytic water splitting was first reported by Nicholson and Carlisle in 1800 [68], marking a foundational milestone in electrochemistry. In alkaline media, the electrochemical reactions occurring at the cathode and anode can be represented by the following equations:



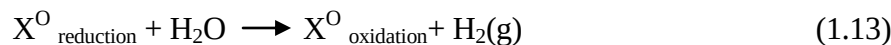
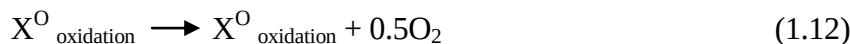
Water electrolysis typically operates at a minimum thermodynamic potential of approximately 1.23 V; however, in practical systems, an applied voltage of around 1.6 V or higher is required to overcome kinetic and overpotential losses. To achieve efficient hydrogen production with high purity ($\approx 99.8\%$), the process is generally carried out at elevated current densities, often in the range of 2 A cm^{-2} [69]. These operating conditions ensure sufficient reaction rates and gas evolution efficiency for large-scale hydrogen generation.

1.9.2 Photocatalytic Water Splitting

Another approach to water splitting involves high-temperature thermochemical redox cycles using metal oxides (generally represented as MO_2 , where M denotes a metal). In this method, water dissociation is driven by reversible oxidation–reduction reactions of the metal oxide at elevated temperatures. The catalytic material plays a crucial role in facilitating both the reduction and oxidation steps, particularly through its ability to accommodate and release oxygen via the formation of oxygen vacancies within its crystal lattice [70].

In a typical two-step thermochemical cycle, a metal oxide redox pair ($\text{X}_{\text{OX}}^{\text{O}}/\text{X}_{\text{red}}^{\text{O}}$) is employed for water splitting. In the first stage, the high-valence metal oxide is thermally reduced at high temperatures, resulting in the release of oxygen (O_2) and the formation of an oxygen-deficient, lower-valence oxide. In the subsequent stage, this reduced metal oxide reacts with water vapor at a comparatively lower temperature. During this reaction, the oxide is re-oxidized, and hydrogen gas (H_2) is liberated as a

product. The sequence of these reactions can be expressed through the following reaction steps.



Thermochemical water splitting using metal oxides such as Fe_2O_3 , ZnO , MnO_2 , and various spinel ferrites has been widely investigated through redox-based thermocycle processes [71-73]. Among oxide materials, spinel ferrites are particularly notable for their structural stability and robustness at elevated temperatures. The spinel crystal structure provides a flexible lattice framework that can accommodate non-stoichiometry under reductive atmospheres, especially at high temperatures [74].

During the reduction step of the thermochemical cycle, oxygen vacancies are generated within the spinel lattice, resulting in oxygen-deficient phases. These vacancies play a crucial role in the subsequent oxidation step, where the reduced ferrite reacts with water vapor. The lattice oxygen deficiency drives the splitting of H_2O molecules, leading to hydrogen evolution while replenishing the oxygen vacancies. The ability of ferrites to reversibly exchange oxygen with the surrounding gaseous environment makes them promising candidates for redox-driven water splitting processes [75]. Notably, doped zinc ferrites have demonstrated high water-splitting efficiency, with hydrogen conversion rates reported to reach approximately 62.5% under optimized conditions. Furthermore, several studies have shown that spinel ferrites can facilitate H_2O splitting at relatively moderate and practically achievable high temperatures, enhancing their feasibility for scalable thermochemical hydrogen production [76].

1.9.3 Photoelectrochemical Water Splitting

A photoelectrochemical cell (PEC) typically consists of a photoactive anode and/or cathode fabricated from semiconductor materials capable of absorbing light. When illuminated, the photoelectrode absorbs incident photons with energies equal to or greater than its band gap, resulting in the generation of electron-hole pairs. These photogenerated charge carriers participate in redox reactions at the electrode-electrolyte

interface, driving the oxidation and reduction of water molecules to produce oxygen and hydrogen, respectively.

Compared to conventional photocatalysis or separate photovoltaic (PV) electrolysis systems, PECs offer improved efficiency by integrating light absorption and electrochemical water splitting within a single device architecture. This direct coupling reduces energy losses associated with external power supplies and enables more compact system designs. One of the major advantages of PEC systems is their ability to operate without the need for an additional external electrical bias, provided sufficient photovoltage is generated. Among the various semiconductor materials investigated for PEC applications, titanium dioxide (TiO_2) has emerged as one of the most extensively studied due to its chemical stability, suitable band alignment, and resistance to photocorrosion. In addition to TiO_2 , other semiconductors such as ZnO , Fe_2O_3 (hematite), BiVO_4 , and WO_3 have also been explored as photoelectrode materials owing to their favorable band structures and light absorption properties.

1.10 Grotthuss Chain Reaction

In 1806, Theodor von Grotthuss proposed a fundamental mechanism to explain proton conduction in water, which was later validated during studies on water electrolysis. This mechanism, now known as the Grotthuss mechanism, describes the rapid transport of protons through a hydrogen-bonded network of water molecules. Instead of physical migration of individual protons over long distances, proton conduction occurs through successive proton hopping from one water molecule to another via transient hydrogen bonds, as illustrated in Fig. 1.7.

In defect-engineered materials such as metal ferrites, water dissociation predominantly occurs at unsaturated surface cations and oxygen vacancy sites. Oxygen vacancies act as electron-rich centers or dangling bonds, creating localized charge imbalance on the surface. These sites electrostatically attract the positively polarized hydrogen end of water molecules. Simultaneously, unsaturated surface cations interact strongly with the hydroxyl (OH^-) portion of the polar water molecule, facilitating its separation. This initial interaction leads to the formation of a chemisorbed hydroxyl layer distributed across the ferrite surface. The adsorption of water molecules onto these active sites is

referred to as chemisorption, while their dissociation into H^+ and OH^- species is termed chemidissociation [77].

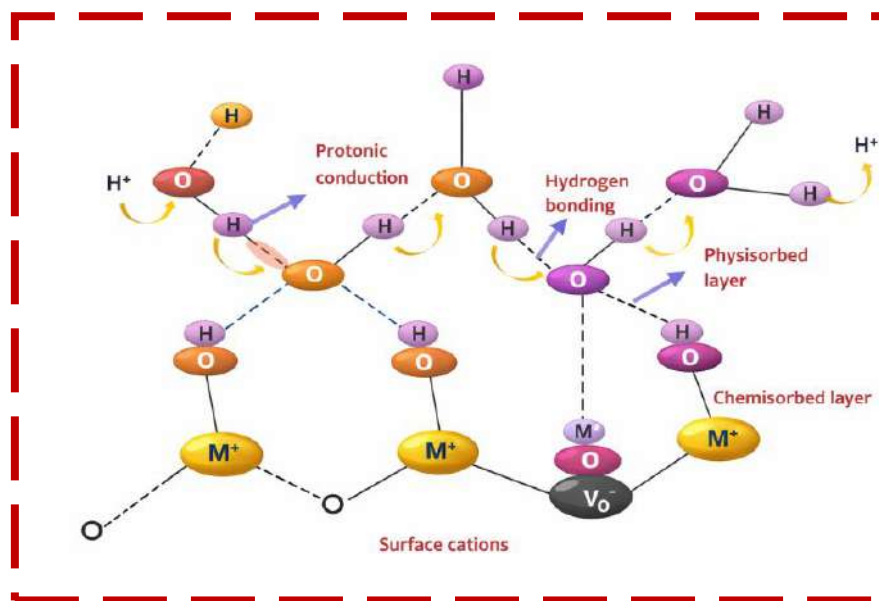


Fig. 1.7: Mechanism depicting the protonic conduction of water.

Subsequent water molecules are attracted to the chemisorbed hydroxyl layer and become physisorbed through hydrogen bonding interactions. These hydrogen-bonded networks provide pathways for proton transfer. As hydroxyl groups bind to surface cations, hydronium ions (H_3O^+) remain and can become confined within nanoporous structures. The accumulation of hydronium ions inside nanopores generates a substantial localized electric field. Using Gauss's law, this internal electric field has been estimated to be on the order of 2×10^4 V/m, which is sufficiently strong to promote further water dissociation in adjacent molecules. This cascading dissociation process, sustained by proton hopping along hydrogen-bonded chains, constitutes the Grotthuss chain reaction.

Ceramic-based nanomaterials are particularly suitable for such processes due to their inherent porosity and structural stability. Highly porous microstructures enhance water adsorption and facilitate both chemisorption and subsequent physisorption. The efficiency of water dissociation and proton conduction strongly depends on parameters such as pore radius, pore volume, pore size distribution, and average pore diameter. Oxygen vacancies and nanoscale porosity collectively enhance humidity sensitivity and

interfacial reactivity. To further improve these properties, controlled doping or substitution with monovalent, divalent, or trivalent ions has been widely explored, as such modifications can tailor defect density, surface activity, and charge transport behavior for optimized performance in sensing and energy-generation applications.

1.11 Hydroelectric Cell

Thermal water splitting generally requires very high temperatures to decompose H_2O into hydrogen and oxygen. In thermochemical redox cycles involving ferrites, the metal oxide is typically reduced at temperatures exceeding $1200\text{ }^\circ\text{C}$, followed by re-oxidation with water vapor to produce hydrogen. Such elevated temperature requirements impose significant material and energy constraints. Efforts to combine photo-driven processes with electrochemical water splitting have enabled a reduction in operational temperatures, in some cases lowering the effective dissociation temperature to around $850\text{ }^\circ\text{C}$ [77]. At ambient conditions, the thermodynamic minimum potential required for water splitting is 1.23 V . However, due to the inherently low ionic conductivity of pure water (approximately $0.055\text{ }\mu\text{S cm}^{-1}$), the reaction proceeds at a very slow rate unless an external electrolyte or catalyst is introduced to enhance charge transport and reaction kinetics.

Advancements in materials science have led to the development of various composites and functional materials aimed at improving water dissociation efficiency. Semiconductor materials such as sulfides, nitrides, oxides, and phosphates have been extensively investigated as photocatalysts for water splitting [78-80]. The underlying mechanism involves photon absorption by these semiconductors, resulting in the generation of electron-hole pairs. These charge carriers migrate to surface-active sites, where they drive redox reactions leading to hydrogen and oxygen evolution. Although substantial research has been devoted to green hydrogen production through practical and scalable technologies, achieving high efficiency, stability, and cost-effectiveness simultaneously remains a major challenge. Continued innovation in defect engineering, nanostructuring, and catalytic surface design is therefore essential to realize the full potential of sustainable water-splitting technologies.

To address the challenges associated with water dissociation at ambient conditions for electricity generation, the concept of the hydroelectric cell (HEC) was introduced in 2016 [81]. The hydroelectric cell represents an innovative approach toward green energy generation by enabling spontaneous water splitting under room-temperature conditions without the need for external electrical bias, corrosive electrolytes, or high thermal input. The power output achieved from HEC systems has been reported to be comparable, in certain configurations, to that of small-scale solar cells.

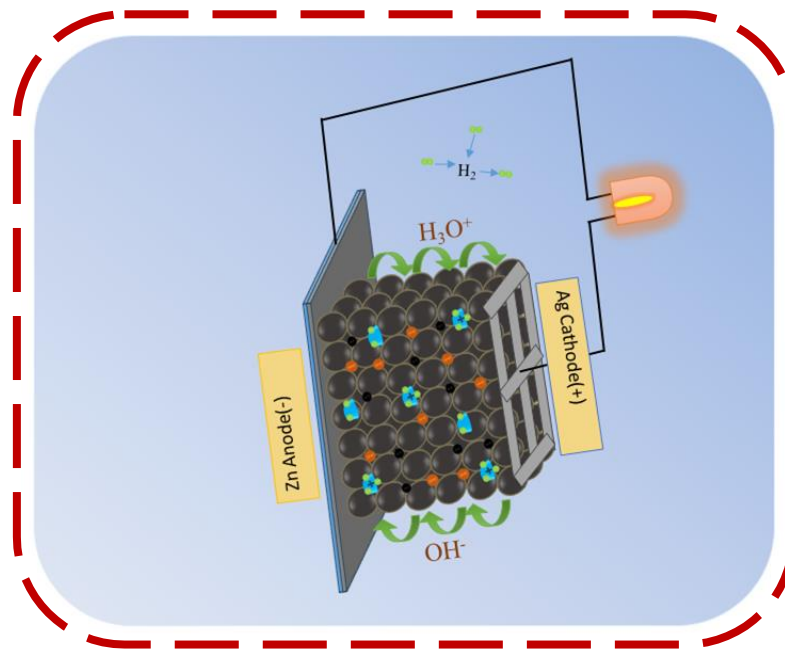


Fig. 1.8: Schematic diagram of HEC showing the conduction of electricity by dropping few water droplets.

The operating principle of a hydroelectric cell is rooted in the synergistic integration of nanoscience, electrochemistry, and materials engineering. The technology primarily relies on defect-rich, oxygen-deficient, and nanoporous materials that facilitate water molecule adsorption, dissociation, and subsequent ionic conduction. In particular, oxygen-deficient nanoporous spinel ferrites such as $\text{LiMgFe}_2\text{O}_4$ have been investigated as active materials for HEC devices. The presence of nanopores and unsaturated surface cations enhances water adsorption and promotes chemisorption processes. Increased porosity not only provides a larger surface area but also improves the availability of active sites for water molecule interaction, thereby facilitating efficient charge transfer and electrochemical reactions [82]. Porosity and oxygen defects increase in magnesium

ferrite by Li substitution at Mg site. LiMgFe pellet of 1inch² size HEC showed 8 mA and 0.98 V as reported in 2016 but now with rigorous research and development and optimization of process condition we reached to multifold increase in current as reported in 2016 [83].

1.12 Mechanism of Hydroelectric Cell

The operation of hydroelectric cells is fundamentally governed by surface-driven electrochemical phenomena that occur at the solid-liquid interface under ambient conditions. The defect-engineered nanoporous matrix of the HEC provides a highly active surface environment that promotes both adsorption and dissociation of water molecules without the need for external thermal or electrical energy. This distinguishes hydroelectric cells from conventional electrochemical systems, where water splitting typically requires high overpotentials or elevated temperatures.

The nanoporous architecture of the HEC pellet significantly increases the effective surface area available for water interaction. Nanoscale pores act as confined reaction chambers where water molecules experience strong electrostatic interactions with unsaturated surface cations and oxygen/sulphur vacancies. These defect sites serve as catalytic centers that lower the activation energy required for water dissociation, enabling spontaneous splitting at room temperature. The high density of oxygen vacancies enhances electron localization near the surface, further strengthening the interaction between the material and polar water molecules [84-85].

At the initial stage, chemisorption dominates the water-surface interaction. Water molecules are strongly anchored to coordinatively unsaturated metal cations, forming metal-oxygen bonds that destabilize the O-H bonds within the water molecule. This leads to the generation of hydroxide ions firmly bound to the surface and free protons that subsequently form hydronium ions [86]. The accumulation of chemisorbed hydroxide species induces a strong negative surface charge, which alters the local electrostatic environment and facilitates further water adsorption. Following chemisorption, physisorption becomes the dominant process, particularly within the nanopores. Physisorbed water molecules form an extended hydrogen-bonded network, enabling continuous proton transport through the confined pore channels. The presence

of trapped hydronium ions within these nanopores generates intense local electric fields, which further sustain water dissociation and stabilize ionic species. This coupling between surface chemistry and electrostatic confinement is central to the sustained operation of hydroelectric cells [87].

1.13 Electrochemical Reactions and Energy Generation

The electrochemical output of a hydroelectric cell arises from coupled oxidation and reduction reactions occurring at the respective electrodes. At the zinc anode, hydroxide ions migrating from the electrolyte region react with zinc metal, leading to the formation of zinc hydroxide and the release of electrons. This anodic oxidation reaction serves as the primary source of electrons for the external circuit.

The released electrons travel through the external load and are collected at the silver cathode. At the cathode, hydronium ions arriving from the nanoporous matrix undergo reduction by accepting electrons, resulting in the evolution of hydrogen gas and regeneration of water molecules. The separation of oxidation and reduction reactions across spatially distinct electrodes establishes a potential difference, driving continuous electron flow through the circuit and sustaining electrical power generation. Importantly, the electrochemical reactions in hydroelectric cells occur without the emission of harmful pollutants or greenhouse gases. Hydrogen evolution at the cathode represents a clean by-product, further reinforcing the environmentally benign nature of this energy harvesting technology [86,87].

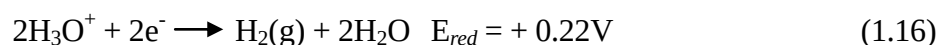
At the surface of HEC



At the anode (At the zinc electrode)



At the cathode (At the silver electrode)



1.14 Advantages of Hydroelectric Cell

Hydroelectric cells (HECs) based on water dissociation over solid oxide or ferrite pellets represent a promising alternative to conventional primary energy generation systems such as solar cells, fuel cells, and batteries. These devices employ compact, lightweight pellets fabricated through relatively simple and scalable processing routes. The precursor materials are typically low-cost and earth-abundant, and the operational mechanism does not involve greenhouse gas emissions. Notably, water dissociation in HECs occurs without the use of external electrolytes, acids, or alkalis; instead, a few drops of deionized water are sufficient to initiate the electrochemical process. This enables clean and sustainable electricity generation at room temperature, making the system potentially suitable for small-scale and domestic applications.

An additional advantage of HEC technology lies in its environmentally benign by-products, such as metal hydroxides and hydrogen gas. The hydrogen produced is of high purity and can itself serve as a clean, high-energy fuel. Furthermore, the solid-state configuration of HECs minimizes concerns related to end-of-life disposal, as the materials involved are generally non-toxic and stable. In contrast, many conventional battery systems rely on hazardous chemicals and heavy metals, leading to significant environmental challenges upon disposal. Spent dry cells, lead–acid batteries, and certain photovoltaic components are often discarded in landfills, contributing to soil and groundwater contamination. The large-scale disposal of such systems presents long-term ecological and public health risks.

Table 1.2: Comparison of hydroelectric cells with other sources of energy in terms of cost, output voltage generated current density, and their disposal environment.

Battery Type	Voltage Produced (V)	Output Current Generated	Cost (Rs.)	Disposal	References
Lead acid	2	3000 mAh	Rs. 800	Landfills with improper cycling	88
Solar cell	10	25 mA/cm ²	Rs. 70 per watt	Landfills	89
Li-ion	3.6 V–4.0 V	3000 mAh	Rs. 450–500	Landfills	90
HEC (Hydroelectric cell)	0.98 V–1 V	200–300 mA (maximum)	Rs. 17 (prepared in lab)	Biodegradable and non-toxic	91

Similarly, although solar energy is renewable and widely adopted, the manufacturing process of photovoltaic cells can be resource-intensive and environmentally burdensome. The production of solar panels involves the use of high-purity silicon, polymers, and, in some cases, heavy metals. Processing steps generate silica dust, silicon tetrachloride, and kerf losses during wafer slicing, while gases such as silane are used in coating processes each associated with environmental and occupational hazards. It has been projected that solar panel waste could reach tens of millions of metric tonnes by mid-century. Additionally, solar energy systems require high initial energy input during fabrication, are weather-dependent, demand substantial installation area, and often necessitate costly energy storage solutions to address intermittency. These limitations highlight the need for complementary or alternative green energy technologies, such as hydroelectric cells, that operate under ambient conditions with minimal environmental impact.

1.15 Primary Challenges and Strategies

The central challenge addressed in this thesis is the development of multifunctional nanomaterial systems capable of delivering high-performance gas sensing and efficient room-temperature energy harvesting within a single materials framework. Achieving this objective requires overcoming critical limitations associated with conventional materials, including insufficient surface reactivity, limited charge-transfer efficiency, instability under ambient conditions, and inadequate control over defect chemistry. Advances in nanotechnology provide the foundation for addressing these challenges through precise manipulation of composition, morphology, and defect states at the nanoscale. By engineering nanomaterials structure, the effective surface area is significantly increased, thereby maximizing the density of accessible active sites for adsorption-driven interactions. This enhancement is particularly crucial for chemiresistive gas sensors, where surface adsorption and interfacial charge transfer directly govern sensitivity and selectivity. Simultaneously, controlled tuning of the electronic band structure and defect distribution enables modulation of carrier concentration and transport pathways, resulting in improved response-recovery kinetics, and enhanced operational stability.

Simultaneously, the steadily increasing global energy demand necessitates the development of reliable and environmentally sustainable energy technologies, particularly for decentralized and remote locations where conventional grid connectivity is limited. In this context, hydroelectric cell technology has emerged as a promising green energy approach capable of generating electricity through water-mediated processes under ambient conditions. Efficient water dissociation at room temperature without the use of liquid electrolytes, acids, or high-temperature activation requires materials with abundant surface defects and optimized ionic transport pathways. However, creating and stabilizing such defect structures without compromising mechanical integrity or electrical conductivity at lower temperature remains difficult. This thesis strategically employs defect-rich nanomaterials, along with engineered interfaces, to enhance water adsorption, facilitate proton migration, and promote redox-driven electricity generation. Controlled defect introduction serves as a unifying principle, as these same surface imperfections provides active sites for water splitting in HEC device.

1.16 Thesis Problem

The present research focuses on the controlled synthesis and engineering of two-dimensional (2D) nanomaterials for dual applications in chemiresistive gas sensors and energy-harvesting hydroelectric cell (HEC) devices. A major objective is the development of ethanol gas sensors capable of stable and efficient operation at room temperature (RT). The motivation arises from the growing demand for low-power, highly sensitive, and durable sensing systems that can be seamlessly integrated into portable, flexible, and miniaturized electronic platforms.

Although significant advancements have been made in nanomaterial design and their incorporation into gas sensing and hydroelectric cell technologies, several critical challenges remain unresolved. In gas sensing applications, achieving rapid response and recovery, high selectivity, and long-term operational stability under ambient conditions continues to be demanding. Similarly, in hydroelectric cell systems, ensuring efficient and sustained water dissociation at room temperature, stable defect structures, and reproducible electrical output without external electrolytes presents substantial material

and device-level complexities. Therefore, the core challenge addressed in this thesis lies in tailoring 2D nanomaterials and their nanocomposites to achieve reliable performance, enhanced surface reactivity, controlled defect chemistry, and consistent functionality in both sensing and green energy harvesting applications under real-world conditions.

This thesis primarily addresses the following research objectives:

1. **Synthesis of 2D Nanomaterials:** Development of low-temperature synthesis strategies for the controlled fabrication of two-dimensional nanomaterials, with deliberate engineering of structural defects to tailor their electronic, surface, and functional properties.
2. **Room Temperature (RT) Operation:** To design and fabricate ethanol gas sensors and hydroelectric cell devices capable of stable, efficient, and sustained performance under ambient conditions. Emphasis is placed on minimizing power consumption, enhancing operational reliability, and ensuring seamless integration with modern low-power and complementary integrated circuit technologies.
3. **Enhanced Performance of Sensor:** To improve the sensitivity, selectivity, and dynamic response characteristics (response and recovery times) of ethanol sensors using the strategic application of two-dimensional (2D) nanomaterials.
4. **Stable HEC for powering LED's:** To fabricate hydroelectric cell devices for sustainable green energy generation capable of powering LED systems, utilizing strategically engineered two-dimensional (2D) nanomaterials to ensure enhanced performance and long-term operational stability.

1.17 Objectives of the Thesis

The comprehensive aim of this thesis is to design, synthesize, and integrate advanced nanocomposite systems based on two-dimensional (2D) nanomaterials for multifunctional technological applications, with particular focus on chemiresistive ethanol gas sensing and sustainable energy generation through hydroelectric cell (HEC) devices. The research is structured around the concept that deliberate nanoscale

engineering of material composition, morphology, and defect chemistry can directly influence and enhance macroscopic device performance.

A key objective of this work is to establish a systematic and scientifically grounded correlation between material-level modifications and device-level functionality. This involves detailed investigation of how structural parameters such as defect density, porosity, and surface functional groups govern adsorption behavior, carrier concentration modulation, interfacial charge transfer, and transport dynamics. By developing a comprehensive understanding of these structure-property-function relationships, the thesis aims to rationally optimize critical chemiresistive gas sensing parameters including sensitivity, selectivity, dynamic response, baseline stability, and reproducibility under ambient operating conditions.

Beyond sensing applications, this research also emphasizes the development of a green and sustainable energy harvesting platform based on hydroelectric cell device. The thesis seeks to fabricate room-temperature HEC device utilizing strategically defect-engineered 2D nanomaterials capable of facilitating water adsorption, ionic migration, and redox-driven charge generation without the need for external electrolytes or elevated temperatures. Demonstrating the capability of these devices to power LED systems serves as a practical validation of their energy conversion efficiency, stability, and real-world applicability.

The specific objectives of the thesis are as follows:

1. To conduct a comprehensive review of existing literature on two-dimensional (2D) nanomaterials and their nanocomposites, with particular emphasis on their roles in gas sensing and sustainable energy harvesting applications.
2. To synthesize 2D nanomaterials and their nanocomposite through diverse and controlled synthesis methodologies, enabling precise tuning of structural and functional properties.
3. To systematically characterize the synthesized materials in terms of their structural, morphological, electronic, and surface properties using advanced analytical techniques, including X-ray diffraction (XRD), field emission scanning

electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) surface area analysis.

4. To fabricate uniform and adherent thin films of the synthesized nanomaterials using suitable deposition techniques such as spin coating, electrophoretic deposition (EPD), and drop casting, for the development of chemiresistive gas sensor device.
5. To evaluate and optimize the gas sensing performance of 2D nanomaterial for the detection of environmentally relevant hazardous gases, with focus on sensitivity, selectivity, response-recovery dynamics, and operational stability.
6. To design and fabricate hydroelectric cell devices employing defect-engineered 2D nanomaterials and their nanocomposites for green energy harvesting through water dissociation under ambient conditions.

By systematically optimizing synthesis parameters, implementing precise microstructural engineering, and conducting comprehensive functional characterization, the findings of this study are organized and presented across six chapters. Each chapter details the key experimental procedures, major observations, analytical results, and their corresponding scientific interpretations.

1.18 Organization of the Thesis

The present thesis is systematically organized into six chapters, each dedicated to a distinct aspect of the research, as summarized below:

Chapter 1: Introduction and Scientific Motivation

This chapter begins with a comprehensive introduction to nanomaterials, outlining their fundamental concepts, dimensional classifications, and the distinctive physicochemical properties that arise at the nanoscale. It highlights how reduced dimensionality, enhanced surface-to-volume ratio, and tunable electronic structure make nanomaterials particularly attractive for advanced technological applications. Building upon this foundation, the chapter transitions to the application of nanomaterials in gas sensing, with special emphasis on chemiresistive sensing mechanisms. The growing demand for

high-performance gas sensors-particularly those capable of room-temperature (RT) ethanol detection for low-power is discussed in detail. The basic working principles of chemiresistive sensors are introduced, followed by a critical review of recent advancements in ethanol sensing technologies. Special attention is given to the role of two-dimensional (2D) nanomaterials and their nanocomposites, in enhancing adsorption dynamics, charge transfer efficiency, sensitivity, selectivity, and long-term operational stability.

The chapter further extends the discussion to the emerging application of nanomaterials in hydroelectric cell (HEC) devices for green energy harvesting. It outlines how defect-engineered nanostructures facilitate water adsorption, ionic transport, and redox reactions at room temperature, thereby enabling sustainable electricity generation. The chapter concludes by clearly defining the research gap, articulating the scientific motivation, and outlining the specific objectives of the present thesis, thereby establishing the conceptual and technological framework for the subsequent chapters.

Chapter 2: Experimental Methodologies - Synthesis, Characterization, Sensor and Hydroelectric Cell Fabrication, and Measurements

This chapter presents a detailed account of the experimental methodologies employed for the synthesis of two-dimensional (2D) nanomaterials. A hydrothermal synthesis approach is primarily adopted to achieve precise control over morphology, crystallinity, defect distribution, and phase purity of the prepared materials. Comprehensive structural, morphological, and surface characterizations are performed using advanced analytical techniques. X-ray diffraction (XRD) is utilized to determine crystal structure and phase composition; field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) provide detailed insights into surface morphology, microstructure, and lattice features; Raman spectroscopy and Fourier-transform infrared (FTIR) spectroscopy are employed to probe vibrational modes and chemical bonding; and Brunauer-Emmett-Teller (BET) analysis is conducted to evaluate specific surface area and porosity.

For sensor fabrication, thin films of the synthesized materials are prepared and electrodes are deposited via thermal evaporation to ensure stable electrical contacts and

reproducible performance. Gas sensing characteristics are systematically investigated using a custom-designed chemiresistive measurement setup under controlled environmental conditions. In addition, this chapter elaborates on the fabrication and electrochemical evaluation of hydroelectric cell device. Key performance parameters are assessed through current-voltage (I-V) measurements, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS), enabling detailed analysis of charge transport, interfacial processes, and overall electrochemical behavior of the HEC device.

Chapter 3: Vertically Aligned 2D Tin Sulfide (SnS) Nanoplates for Selective Detection of Ethanol Gas at Room Temperature

This chapter outlines the fabrication of a room-temperature (RT) ethanol gas sensor using SnS nanoplates obtained by a solvothermal route. The SnS sensor has demonstrated a significant response of 17.4 and a quick response/recovery time of 12.4/20.2 s when exposed to 400 ppm ethanol gas at room temperature. The sensor exhibits commendable sensing attributes including remarkable repeatability of three consecutive cycles and long term stability of 15 min to 400 ppm ethanol gas. The sensor showcases an impressive selectivity, particularly discerning ethanol amidst a diverse array of VOCs. These findings especially at room temperature, may pave the way for its potential deployment in innovative applications. Its integration into smart, compact, and Internet of Things (IoT)-based systems holds promise for advancements in gas sensing technology. These ground-breaking results emphasize the practicality and versatility of the developed SnS gas sensor in various real-world scenarios.

Chapter 4: Strategically Engineered Defects in 2D-SnS for Water Splitting: Green Energy Solution for Powering LEDs with Hydroelectric Cells

This chapter outlines the fabrication of hydroelectric cell prepared by low temperature solvothermal synthesis of 2D SnS. The nanostructure having orthorhombic phase which was confirmed by X-ray Diffraction pattern. The specific surface area obtained by BET analysis for SnS is $6.45 \text{ m}^2 \text{ g}^{-1}$ with pore diameter being approximately 17.07 nm. Nyquist curve for SnS based HEC in wet state exhibit ionic diffusion in the cell and also shows the high reduction in the impedance of the cell under the wet conditions.

The fabricated HEC of cross section area 4 cm^2 exhibited an off-load power output of 11.1 mW. The HEC showcases an impressive electric current output of 15 mA, demonstrating its capability to sustain stable performance with just a few drops of water. Furthermore, its remarkable persists consistently for 30 days, affirming its reliability and durability in various operational conditions. These findings may pave the way for its potential deployment in innovative applications. Electricity generation by HEC device does not emit any toxic gases therefore it can be the best strategy to save the environment and to achieve mission of net carbon zero.

Chapter 5: Vertically Aligned Tin Sulfide (SnS) - Decorated Reduced Graphene Oxide (rGO) Based Hydroelectric Cell Device to Generate Green Electricity by Water Splitting

Chapter 5 extends the investigations presented in Chapter 4 devoted to the synthesis of a SnS-rGO nanocomposite system with the objective of achieving enhanced electrical output under room-temperature (RT) conditions. The synthesis of SnS-rGO nanocomposite was successfully confirmed by X-ray diffraction (XRD) and Raman spectroscopy. BET analysis shows that the surface area, poresize, and pore volume increased to $47.09 \text{ m}^2 \text{ g}^{-1}$, 12.13 nm, and $1.66 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$. Nyquist curve for SnS based HEC in wet state exhibit ionic diffusion in the cell and also shows the high reduction in the impedance of the cell under the wet conditions. The fabricated HEC of cross section area 4 cm^2 exhibited an off-load power output of 31.96 mW. The HEC showcases an impressive electric current output of 34 mA, demonstrating its capability to sustain stable performance with just a few drops of water. Beyond electrical power generation, the evolution of hydrogen gas at the cathode presents an additional opportunity for clean hydrogen production, offering prospects for scalable hydrogen energy applications. Moreover, the simple design and water-driven operation of hydroelectric cells make them promising candidates for emergency power and lighting solutions in flood-affected or remote regions lacking access to conventional electricity.

Chapter 6: Conclusions, Future Scope, and Social Impact

This chapter presents a comprehensive synthesis of the principal findings and scientific insights derived from the entire research work, highlighting the significant advantages

of two-dimensional (2D) nanomaterials and their nanocomposites in room-temperature ethanol gas sensing and hydroelectric cell (HEC) applications. It consolidates the experimental observations and establishes a clear linkage between nanoscale material design and device-level performance. Chapter 6 emphasizes the critical role of interfacial engineering and defect modulation in achieving enhanced sensing characteristics such as high sensitivity, improved selectivity, rapid response-recovery behavior, and long-term operational stability under ambient conditions. The discussion further demonstrates that the same defect-engineered 2D nanomaterial systems can be effectively extended to green energy harvesting applications through water-driven hydroelectric cell devices, thereby validating their multifunctional potential.

In addition to summarizing the key conclusions, the chapter outlines prospective research directions. These include further architectural optimization of nanocomposite systems for improved charge transport and adsorption dynamics, expansion of sensing studies toward a broader range of environmentally and industrially relevant gases, and integration of the developed materials into flexible, wearable, and self-powered platforms suitable for next-generation smart technologies. From a broader societal perspective, this work contributes toward environmental safety and sustainable technological development by enabling low-cost, energy-efficient ethanol sensors capable of room-temperature operation. The developed sensing systems hold promise for applications such as breath alcohol analysis, industrial workplace safety monitoring, and environmental surveillance. Meanwhile, water-driven hydroelectric cells present a viable solution for emergency power generation and lighting in flood-prone, disaster-affected, or remote regions lacking reliable access to conventional electricity. The use of non-toxic, earth-abundant materials throughout the study further reinforces the environmental compatibility and long-term sustainability of the proposed technologies.

A schematic representation of the overall thesis organization and research workflow is presented in Fig. 1.9 to facilitate a clearer visualization of the sequential progression of the study.

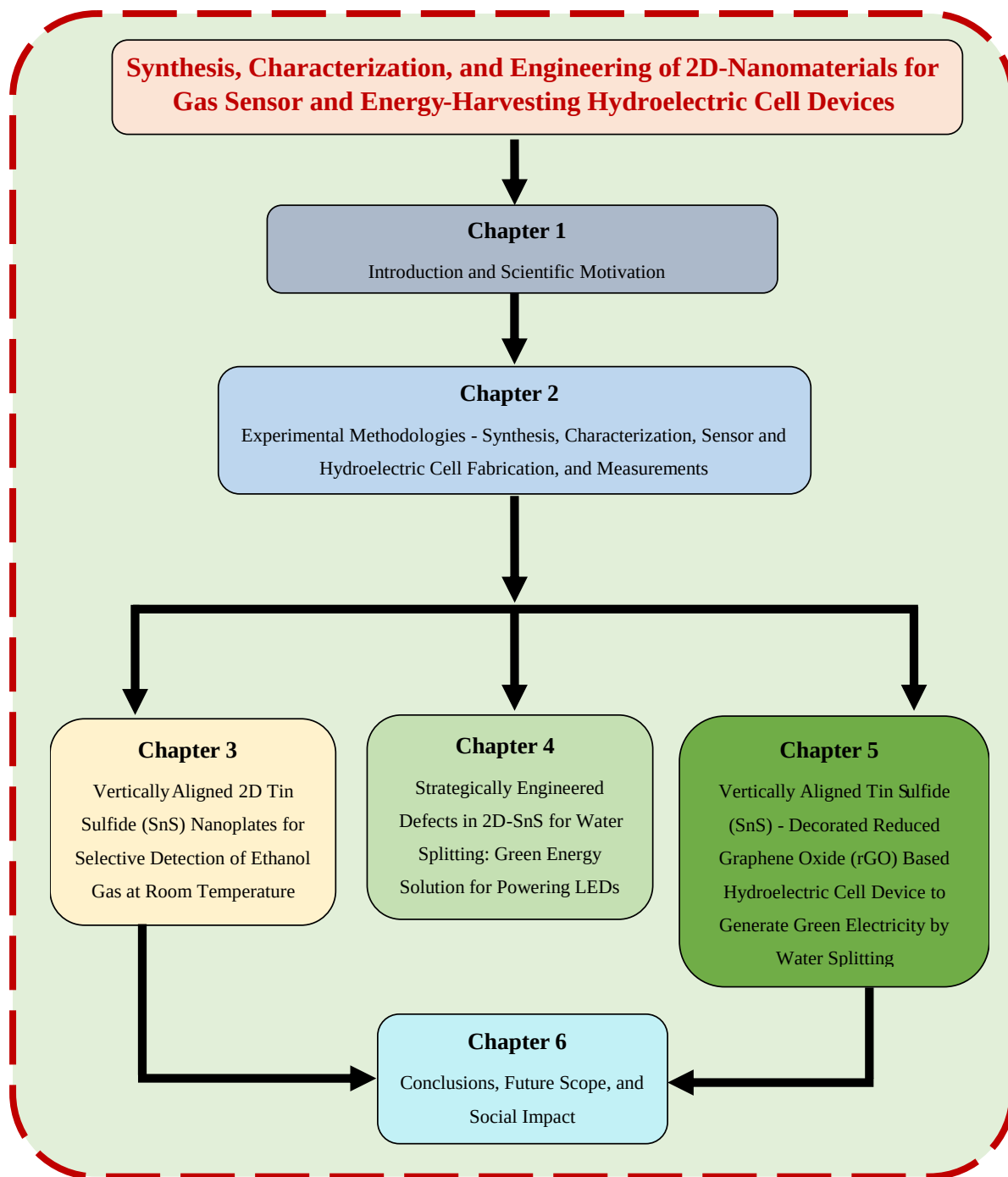
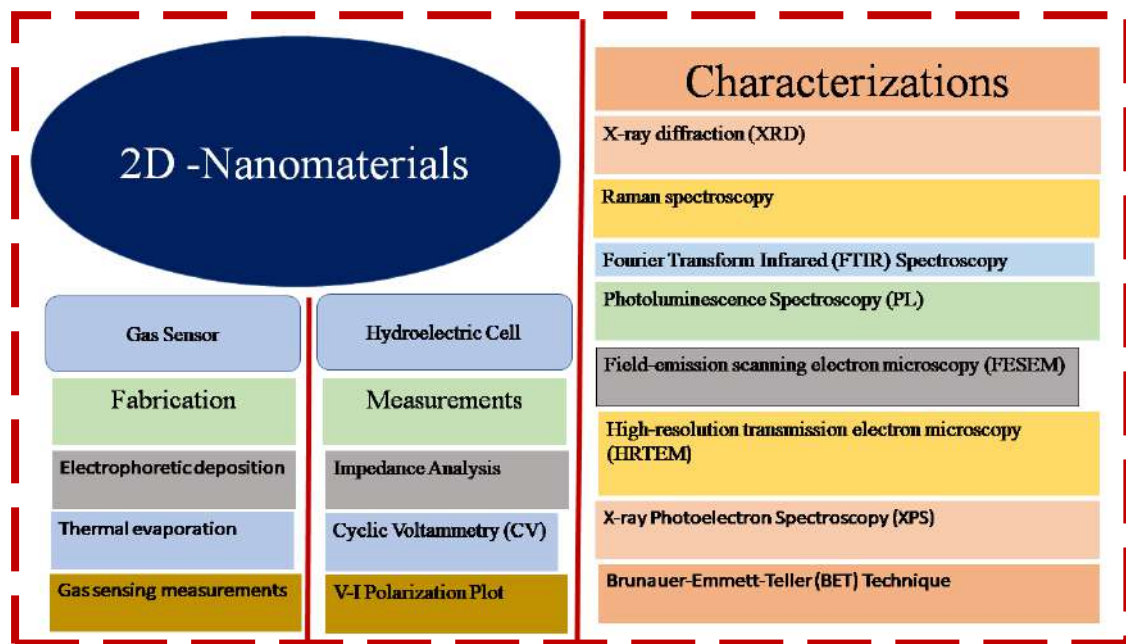


Fig. 1.9: Flowchart for the organisation of the thesis.

CHAPTER 2

Experimental Methodologies: Synthesis, Characterization Techniques, Sensor and Hydroelectric Cell Fabrication, and their Measurements



This chapter presents a comprehensive description of the experimental procedures adopted for the synthesis of two-dimensional (2D) nanomaterials and their nanocomposites, the fabrication of thin-film gas sensors, and the development of hydroelectric cell (HEC) devices for green energy generation. It also outlines the various characterization techniques employed to evaluate the structural, morphological, surface, and electrical properties of the synthesized materials. The nanocomposites were primarily synthesized using the solvothermal method, which offers controlled crystallization, uniform particle growth, and tunable defect engineering. Structural phase identification and crystallinity were examined using X-ray diffraction (XRD). Surface morphology and microstructural features were analyzed through field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). Raman spectroscopy was utilized to investigate vibrational characteristics and assess structural disorder and defect states. The Brunauer–Emmett–Teller (BET) technique was employed to determine the specific surface area and

porosity of the nanocomposites, which are critical parameters influencing adsorption-driven processes.

Electrical characterization was carried out using current–voltage (I–V) measurements with a precision source meter to evaluate conductivity and charge transport behavior. Electrochemical impedance spectroscopy (EIS) was performed using an impedance analyzer to differentiate grain and grain boundary resistances and to gain insight into the charge transport mechanism. The gas sensing performance of the fabricated devices was evaluated using a customized chemiresistive gas sensing setup under controlled environmental conditions. In addition to gas sensing applications, hydroelectric cell pellets were prepared using the synthesized materials to demonstrate room-temperature green electricity generation through spontaneous water splitting. The fabricated HEC devices were tested for their ability to generate sufficient power to illuminate LED lights, highlighting their potential for sustainable energy harvesting applications.

A brief summary of all the above experimental procedures is given in this chapter.

2.1 Synthesis of Nanocomposites of 2D Nanomaterials

A wide range of synthesis techniques has been developed to fabricate nanocomposites based on two-dimensional (2D) nanomaterials with precisely tailored structural and functional characteristics for diverse technological applications. Broadly, these synthesis strategies can be categorized into two principal approaches: (i) top-down and (ii) bottom-up methods.

In the top-down approach, nanostructures are derived from bulk materials through physical or physicochemical processes that reduce the material dimensions to the nanoscale. Techniques such as mechanical grinding, milling, exfoliation, or thermal and chemical decomposition are commonly employed to achieve size reduction. While this method can be straightforward, controlling uniformity and defect distribution at the nanoscale can be challenging.

Conversely, the bottom-up approach involves the controlled assembly of atoms, ions, or molecules into nanostructures via chemical reactions, nucleation, and growth mechanisms. This strategy allows better regulation of composition, morphology,

crystallinity, and defect density, making it highly suitable for fabricating nanomaterials with application-specific properties. The choice of synthesis route plays a pivotal role in determining the final material characteristics and directly influences performance in targeted applications. Furthermore, for large-scale implementation and industrial deployment, it is essential to develop synthesis processes that yield high-quality materials in substantial quantities with excellent reproducibility and cost-effectiveness.

In the present study, a simple, cost-effective, and environmentally benign solvothermal method was employed to synthesize nanocomposites based on 2D nanomaterials. Using this approach, SnS and reduced graphene oxide (rGO) nanocomposites were successfully prepared with controlled morphology and defect characteristics. A concise overview of the adopted synthesis procedures is provided in the following sections, while detailed experimental protocols and optimization parameters are described comprehensively in Chapters 3, 4, and 5.

2.1.1 Solvothermal Synthesis Route

Fig. 2.1 illustrates a representative schematic of the solvothermal synthesis process used for the preparation of nanostructured materials. The solvothermal technique is a widely adopted bottom-up approach that enables controlled growth of nanomaterials in a sealed reaction environment. This method can be performed using either aqueous or non-aqueous solvents, depending on the solubility of precursors and the desired physicochemical properties of the final product.

In a typical solvothermal procedure, suitable precursor compounds are dissolved or dispersed in a selected solvent to form a homogeneous solution or suspension. The reaction mixture is then transferred into a sealed autoclave, usually lined with Teflon to prevent corrosion and contamination. Upon sealing, the autoclave is heated to a temperature often exceeding the boiling point of the solvent under atmospheric conditions. Due to the confined environment, elevated temperature and autogenous pressure are simultaneously generated inside the vessel. This high-temperature–high-pressure environment promotes nucleation and crystal growth, facilitating the formation of well-defined nanostructures.

The closed reaction system plays a crucial role in enhancing solubility, accelerating reaction kinetics, and enabling controlled crystallization. As a result, highly crystalline, phase-pure, and uniformly dispersed nanoparticles can be obtained when appropriate precursors, solvents, reaction temperatures, and durations are selected. The solvothermal process offers excellent control over particle size, morphology, and defect formation, which are critical parameters for tuning material properties. This versatile method has been successfully employed to synthesize a wide range of nanomaterials, including TiO₂ nanoparticles, ZnO nanostructures, carbon spheres, transition metal chalcogenides, ferrites, and various composite systems. One of the major advantages of the solvothermal approach is its ability to tailor crystalline phase, particle dispersion, and morphological characteristics by adjusting reaction parameters such as temperature, pressure, precursor concentration, solvent polarity, pH, reaction time, and the use of surfactants or structure-directing agents. Even minor variations in these parameters can significantly influence particle growth mechanisms, defect density, and surface chemistry, ultimately affecting the functional performance of the synthesized materials [1-3].

The key components involved in a typical solvothermal reaction are outlined below:

- 1. Reactant Precursors:** These are the primary chemical species that act as the starting materials for the solvothermal process. The selection of appropriate precursors is critical, as they determine the composition and phase of the final product. When dissolved or dispersed in a suitable solvent under controlled temperature and pressure conditions, these precursors undergo nucleation and crystal growth, ultimately forming the desired nanomaterial. The chemical purity, concentration, and reactivity of the precursors significantly influence particle size, crystallinity, and defect formation.
- 2. Mineralizers and Auxiliary Additives:** To regulate the reaction environment, mineralizing agents-typically acids or bases are often introduced to adjust the pH of the solution. These mineralizers play a crucial role in enhancing precursor solubility, promoting controlled dissolution, and facilitating recrystallization during crystal growth. In addition to mineralizers, various auxiliary additives may be incorporated into the reaction mixture. These include reducing agents,

complexing agents, capping agents, surfactants, and stabilizers. Such additives help control nucleation rates, particle growth dynamics, morphology, agglomeration behavior, and long-term stability of the synthesized nanostructures. By carefully tuning these parameters, it becomes possible to tailor the structural and functional properties of the resulting nanomaterials for specific applications.

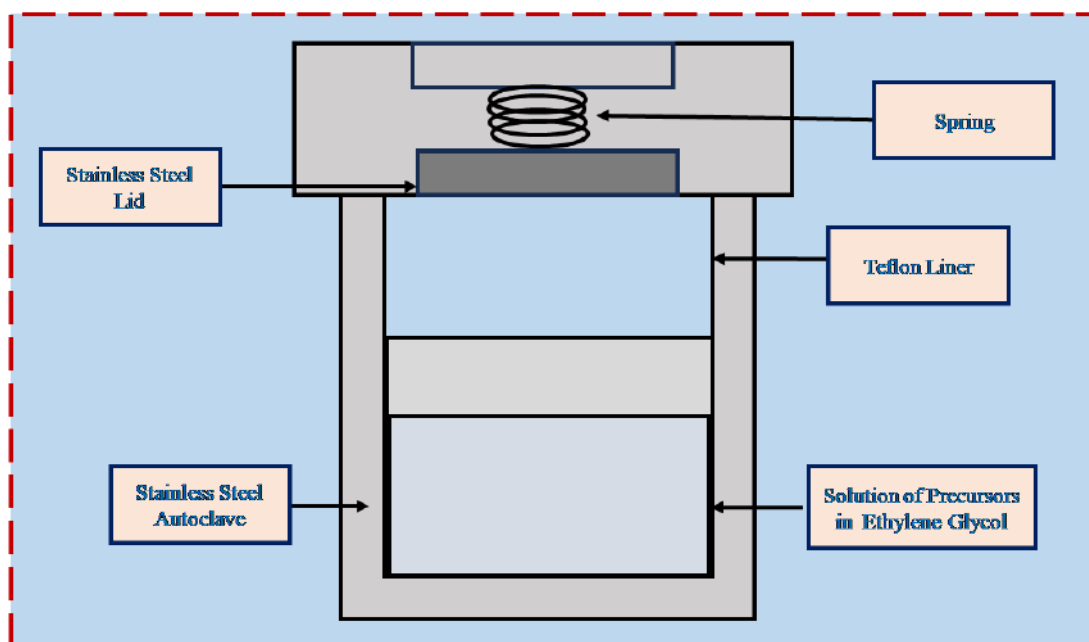


Fig. 2.1: Set-up of the hydrothermal autoclave used in the solvothermal synthesis.

The solvothermal technique presents several striking advantages that make it a desirable procedure for the synthesis of nanomaterials:

1. **Economic Feasibility and Scalability:** The hydrothermal process is cost-effective and adaptable for both laboratory-scale research and large-scale industrial production. Its relatively low equipment and operational requirements make it an economically sustainable synthesis route, while its reproducibility supports scalable manufacturing of nanomaterials.
2. **Precise Control Over Size and Morphology:** One of the major advantages of the hydrothermal method is its ability to finely tune particle size, shape, and structural features by adjusting reaction parameters such as temperature, time, precursor concentration, and pH. This level of control enables the fabrication of

nanomaterials with tailored structural, electronic, and functional properties suited for specific applications.

3. **Compatibility with Hybrid Synthesis Techniques:** The hydrothermal approach can be effectively integrated with complementary methods such as sonochemical, electrochemical, and microwave-assisted techniques. Such hybridization broadens the scope of material design and facilitates the development of advanced nanostructures and multifunctional composites.
4. **Simple and Reusable Experimental Setup:** The hydrothermal system typically involves a straightforward autoclave-based setup that is easy to operate and maintain. The apparatus can be reused for multiple synthesis cycles, enhancing its practicality, efficiency, and overall sustainability in experimental research and material development.

2.2 Characterization Techniques

Various characterization techniques have been employed to verify the successful formation of nanocomposites of 2D nanomaterial and its nanocomposite. The structural study begins with X-ray diffraction (XRD), followed by morphological analysis using field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). Raman spectroscopy has been utilised for the analysis of vibrational modes. Fourier transform infrared spectroscopy (FTIR) has been employed for examining the functional groups. The defect characteristics of the material were systematically investigated using photoluminescence (PL) spectroscopy. This section provides a concise overview of the operating principles of each characterization approach used in our research.

2.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is one of the most powerful and widely utilized characterization techniques for investigating crystalline materials. It provides comprehensive information regarding crystal structure, phase composition, lattice parameters, crystallite size, microstrain, dislocation density, texture, thermal expansion coefficients, density estimation, and overall crystallinity of a sample [4]. Owing to its versatility and non-

destructive nature, XRD has become an indispensable tool in materials science, solid-state physics, chemistry, and engineering research.

The foundations of powder X-ray diffraction were established in the early twentieth century, particularly through the pioneering work of Debye, Scherrer, and Hull between 1916 and 1917, which laid the groundwork for modern powder diffraction analysis [5,6]. Over subsequent decades, the technique underwent significant advancements, especially with the emergence of computational tools. A major breakthrough occurred when Hugo Rietveld introduced a computer-based refinement method for analyzing entire powder diffraction patterns, now known as Rietveld refinement. This approach enabled precise modeling of complex crystal structures and marked a transformative step in crystallographic analysis, facilitated by the rapid growth in computational capabilities during the latter half of the twentieth century.

Modern XRD techniques employ sophisticated algorithms capable of resolving intricate crystal structures from powder samples. The evolution from early transmission experiments on simple cubic systems to contemporary analyses involving structures with thousands of atoms per unit cell demonstrates the remarkable progress achieved in X-ray diffraction technology. X-rays used for diffraction studies are electromagnetic radiations with wavelengths typically ranging from 0.1 Å to 100 Å. For crystallographic investigations, wavelengths between 0.5 Å and 2.5 Å are commonly employed, as they are comparable to interatomic spacings in solids, allowing effective diffraction to occur.

X-rays are generated using an X-ray tube housed within a vacuum chamber containing a cathode and an anode assembly. The cathode typically consists of a tungsten filament, while the anode (target) is commonly made of copper. Upon heating, the tungsten filament emits high-energy electrons via thermionic emission. When a high potential difference typically between 30 and 60 kV is applied, these electrons are accelerated toward the copper target. The collision of high-energy electrons with copper atoms results in the ejection of inner-shell (K-shell) electrons. Electrons from higher energy levels (L and M shells) subsequently transition to fill these vacancies, emitting characteristic X-ray radiation in the process. The most commonly used characteristic lines are $\text{CuK}\alpha$ ($\lambda \approx 1.54 \text{ Å}$) and $\text{CuK}\beta$ ($\lambda \approx 1.39 \text{ Å}$). To obtain monochromatic

radiation suitable for precise diffraction measurements, a nickel filter is employed to absorb the $\text{CuK}\beta$ component, allowing only the $\text{CuK}\alpha$ radiation to pass through for analysis [7].

The fundamental principle underlying XRD was elucidated in 1913 by William Henry Bragg and William Lawrence Bragg, who demonstrated that X-rays incident on a crystalline material are diffracted at specific angles depending on the atomic arrangement within the lattice. They proposed that a crystal can be considered as a series of parallel atomic planes separated by an interplanar spacing, denoted as (d) . When incident X-rays interact with these planes, constructive interference occurs if the path difference between waves reflected from successive planes equals an integer multiple of the X-ray wavelength.

This condition for constructive interference is expressed by Bragg's Law:

$$2d\sin\theta = n\lambda \quad (2.1)$$

where (d) is the interplanar spacing, θ is the angle of incidence (Bragg angle), (λ) is the wavelength of the incident X-rays, and (n) represents the order of diffraction. Bragg's Law forms the theoretical basis for interpreting diffraction patterns and extracting crystallographic information from XRD measurements.

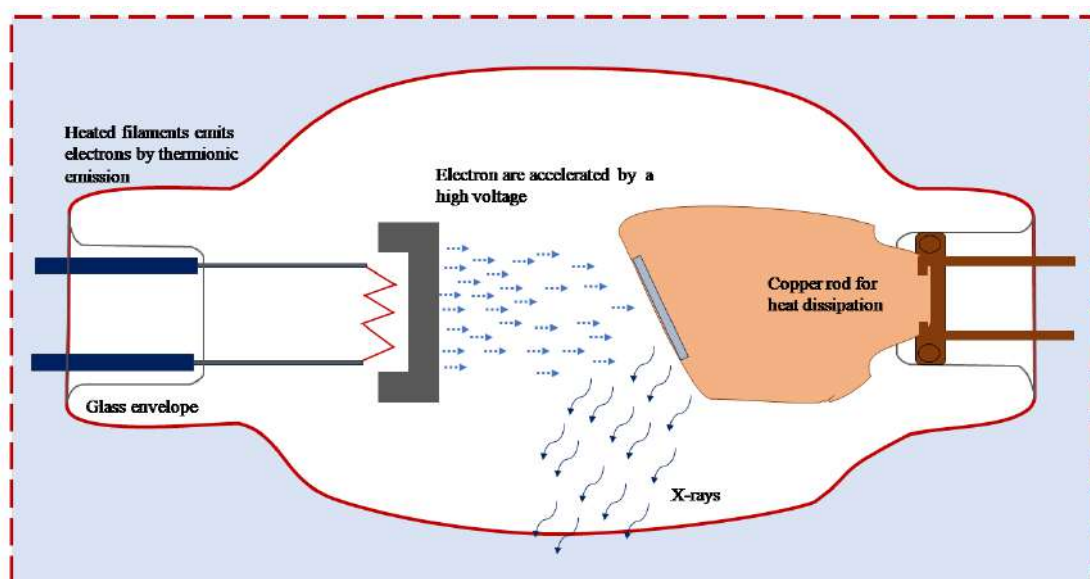


Fig. 2.2: Schematic showing the generation of X-rays in an X-ray tube.

Bragg reflection occurs for those wavelengths of the incident X-rays, λ , which satisfy the condition $\lambda \leq 2d$ and embraces the range in which diffraction from crystalline structures can be observed. The resulting diffraction peaks occur at specific angular positions dependent on various crystallographic parameters, which include the unit cell dimensions, space group symmetry, and overall symmetry of the crystal lattice. These structural attributes collectively influence both the position and intensity of the diffraction peaks. The relationship governing the intensity distribution of the diffracted X-rays can be expressed mathematically as follows:

$$F_{hkl} = \sum f_n e^{2\pi(hu_n + kv_n + lw_n)} \quad (2.2)$$

The atomic coordinates within the crystal lattice are given by (uvw), the Miller indices of the crystal planes are represented by hkl, and f_n is the electron scattering factor of each atom. Such an analytical expression is particularly applicable for powdered samples where there are several crystallites oriented in all directions within the sample, enabling the incident X-ray beam to encounter all the possible lattice planes which satisfy Bragg's condition. This leads to a diffraction pattern comprising peaks corresponding to specific sets of parallel planes, whose angular positions are determined by constructive interference [8]. By X-ray diffraction, it is also possible to estimate the average crystallite size of the material using the relation:

$$D = k\lambda\beta\cos\theta \quad (2.3)$$

The X-ray diffraction (XRD) measurements in this study were carried out using a D8 Advance Bruker diffractometer (Germany) available at the Advanced Instrumentation Centre (AIC), Department of Applied Physics, Delhi Technological University, Delhi, India. The diffraction data were recorded at room temperature (RT) employing $\text{CuK}\alpha$ radiation with a wavelength of 1.54 Å as the incident X-ray source. Data acquisition was performed in step-scan mode with a step size of 0.02° and a scanning rate of 2° per minute. The recorded diffraction patterns were analyzed and indexed by comparing them with standard reference files from the Joint Committee on Powder Diffraction Standards (JCPDS) database, as well as with previously reported literature to confirm phase purity and structural characteristics.

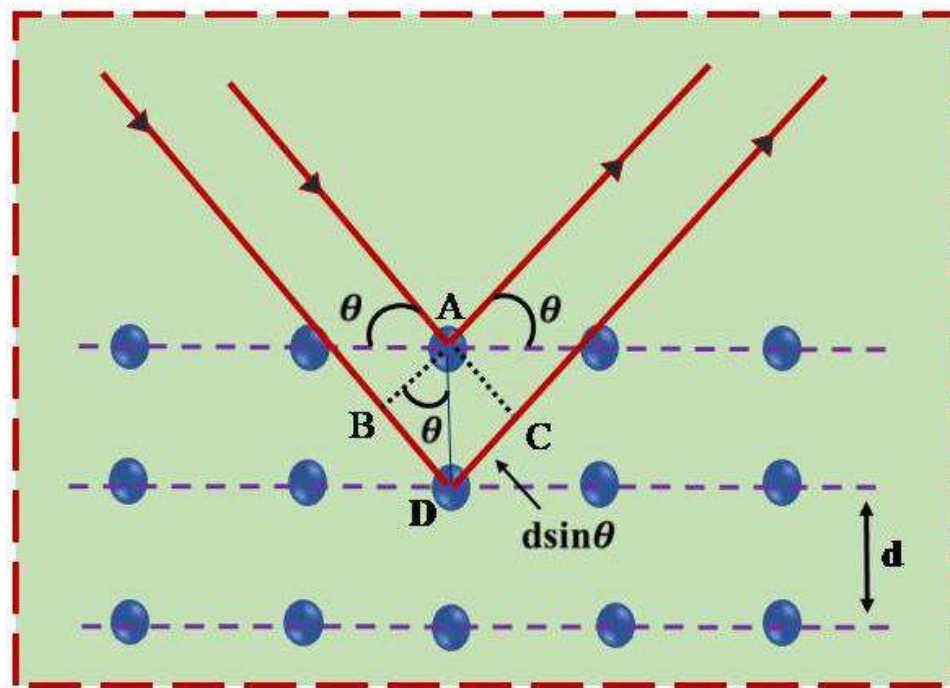


Fig. 2.3: Schematic showing the diffraction of X-rays obeying Bragg's law.

2.2.2 Raman spectroscopy

Raman spectroscopy is a powerful and non-destructive analytical technique widely employed to investigate the chemical composition and structural characteristics of materials through the identification of their vibrational and rotational modes. It provides a unique molecular “fingerprint” that enables precise identification of different compounds based on their characteristic bond vibrations. The phenomenon underlying this technique was first discovered in 1928 by the Indian physicist Sir C. V. Raman, for which he was later awarded the Nobel Prize. Since then, Raman spectroscopy has evolved into an indispensable tool in materials science, chemistry, physics, and nanotechnology [9].

The technique is based on the inelastic scattering of monochromatic light, typically from a laser source, when it interacts with matter. When incident photons strike a sample, most of the light approximately 99.99% is elastically scattered without any change in energy, a process known as Rayleigh scattering. However, a very small fraction of photons (roughly one in ten million) undergoes inelastic scattering, resulting in a shift in photon energy. This inelastic scattering constitutes the Raman effect and

provides valuable information about molecular vibrations, lattice dynamics, and bonding characteristics.

Importantly, Raman scattering does not involve excitation to a real electronic energy level. Instead, the incident photon temporarily perturbs the electron cloud of the molecule, creating a non-existent “virtual” energy state. As the molecule relaxes from this transient state, it re-emits a photon with either lower or higher energy depending on the energy exchange with vibrational modes of the molecule. If the molecule absorbs energy from the incident photon and transitions to a higher vibrational (ro-vibronic) state, the scattered photon has lower energy, giving rise to the Stokes line. Conversely, if the molecule is already in an excited vibrational state (due to thermal population) and transfers energy to the scattered photon, the emitted photon possesses higher energy, resulting in the Anti-Stokes line [10,11].

The intensity difference between Stokes and Anti-Stokes lines is explained by Boltzmann distribution statistics. Since most molecules reside in their ground vibrational state at room temperature, Stokes scattering is significantly more intense than Anti-Stokes scattering. For this reason, modern Raman spectrometers primarily rely on Stokes lines for analysis. To ensure accurate measurement, highly intense Rayleigh scattered light must be filtered out using optical components such as notch filters or edge filters, which selectively suppress the elastic scattering component while allowing Raman-shifted photons to pass through for detection.

The fundamental principle of Raman spectroscopy can be understood in terms of molecular polarizability. When electromagnetic radiation interacts with a molecule, it induces a temporary electric dipole moment proportional to the electric field of the incident light. This induced dipole moment (P) can be expressed as:

$$P = \alpha \cdot E \quad (2.4)$$

where α represents the molecular polarizability and E denotes the electric field of the incident radiation. Raman-active vibrational modes arise when there is a change in molecular polarizability during vibration. Therefore, only those vibrational modes that involve a variation in polarizability contribute to the Raman spectrum. This

distinguishes Raman spectroscopy from infrared (IR) spectroscopy, which depends on changes in dipole moment rather than polarizability [12].

One of the major advantages of Raman spectroscopy is its minimal requirement for sample preparation. Samples can be analyzed in solid, liquid, or gaseous states without complex treatment. Moreover, due to the highly focused laser beam with a very small spot size, only a tiny quantity of material is required for analysis. Raman spectroscopy is also particularly advantageous for studying aqueous systems because water produces relatively weak Raman signals compared to its strong absorption in IR spectroscopy.

In nanomaterials research, Raman spectroscopy plays a critical role in determining crystal structure, phase purity, defect density, strain effects, and interfacial interactions. In two-dimensional (2D) materials, Raman analysis is especially valuable because vibrational modes are highly sensitive to layer thickness, structural disorder, doping, and surface functionalization. Peak shifts, changes in intensity, and peak broadening can indicate lattice distortions, defect incorporation, or composite formation. Thus, Raman spectroscopy not only confirms phase formation but also provides insight into nanoscale structural modifications that directly influence electronic, sensing, and catalytic properties [13].

Modern Raman spectrometers typically consist of three primary components: a monochromatic laser source, an optical system for directing and collecting scattered light, and a spectrometer coupled with a detector such as a charge-coupled device (CCD). Advanced systems may incorporate confocal microscopy, enabling spatially resolved mapping of materials to assess compositional uniformity and defect distribution. Such capabilities are particularly important for thin films and nanocomposite materials used in gas sensing and energy harvesting applications.

Overall, Raman spectroscopy serves as an essential structural and chemical characterization tool. By probing vibrational transitions arising from molecular polarizability changes, it provides deep insight into bonding, crystallinity, defect states, and phase interactions. Its non-destructive nature, minimal sample preparation, and high sensitivity make it especially suitable for investigating advanced nanomaterials designed for gas sensing and hydroelectric cell devices.

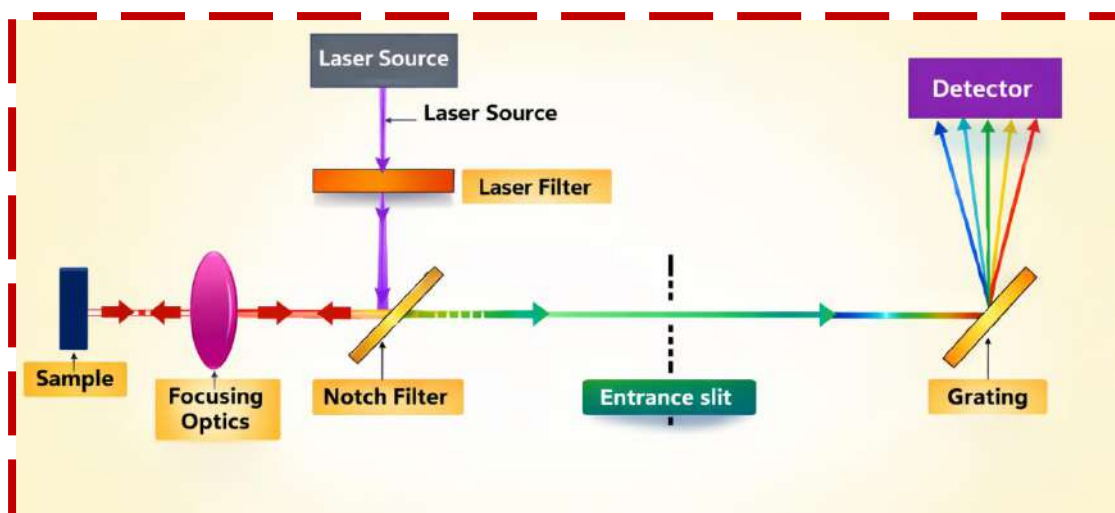


Fig. 2.4: Schematic representation of Raman spectrometer.

In the present study, Raman analysis of the nanocomposites of 2D nanomaterials and metal oxides was done with the help of the WITec alpha 300 RA (Germany) spectrometer available at the Advanced Instrumentation Research Facility (AIRF), Jawaharlal Nehru University (JNU), Delhi, India.

2.2.3 Fourier Transform Infrared (FTIR) Spectroscopy for Functional Group Identification

Fourier Transform Infrared (FTIR) spectroscopy is a powerful analytical technique employed for the identification of functional groups and chemical bonding characteristics in materials. It operates in the infrared region of the electromagnetic spectrum, typically covering the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. Within this spectral window, most organic and inorganic compounds exhibit characteristic vibrational absorptions, enabling precise molecular fingerprinting. Owing to its simplicity, rapid data acquisition, and minimal sample preparation requirements, FTIR has become an indispensable tool in research laboratories for the structural analysis of solids, liquids, thin films, coatings, and even gaseous samples.

The fundamental principle of FTIR spectroscopy is based on the interaction of infrared radiation with molecular vibrations. When a material is exposed to IR radiation, specific wavelengths are absorbed if their energy matches the vibrational energy levels of chemical bonds within the molecule. Upon absorption, molecules transition to higher

vibrational energy states. As they relax back to their ground state, energy differences corresponding to bond vibrations are reflected in the absorption spectrum. Since each chemical bond such as C-H, O-H, C=O, M-O, or S-S possesses a distinct vibrational frequency depending on atomic mass and bond strength, every compound exhibits a unique IR absorption pattern. This characteristic absorption profile acts as a molecular fingerprint, enabling qualitative identification of functional groups present in the sample [14].

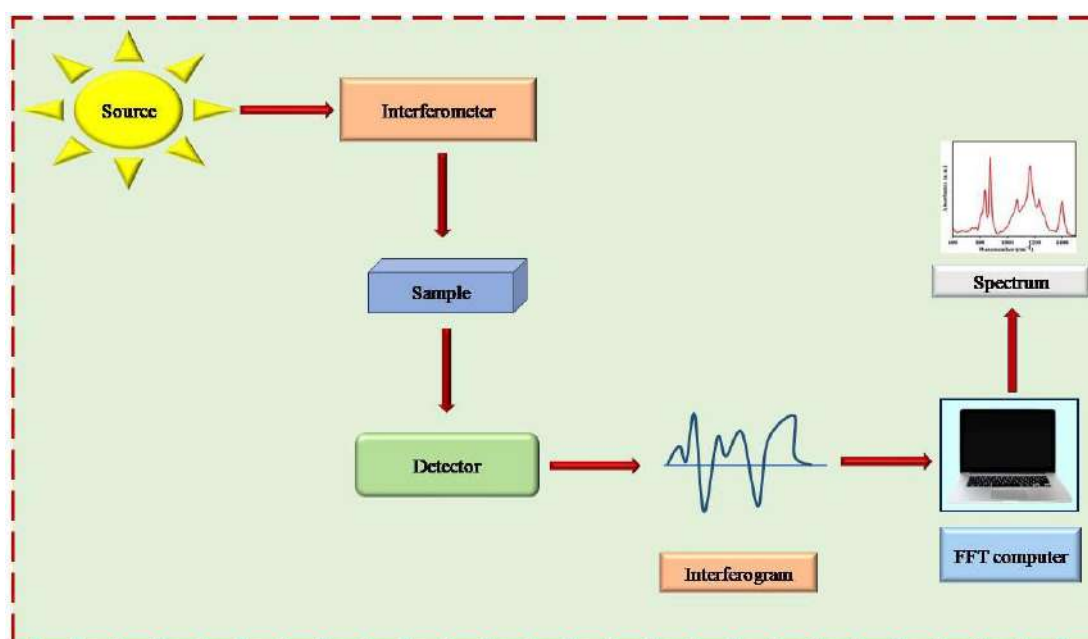


Fig. 2.5: Block diagram of FTIR spectroscopy.

In FTIR analysis, the resulting spectrum is typically represented as either transmittance or absorbance plotted against wavenumber (cm^{-1}). The spectrum contains a series of peaks corresponding to stretching, bending, twisting, or wagging vibrational modes. The region above 1500 cm^{-1} is commonly referred to as the functional group region, where characteristic bond vibrations appear, while the region below 1500 cm^{-1} is known as the fingerprint region, which provides highly specific structural information. By comparing the observed peaks with standard reference data, the chemical composition and bonding environment within the material can be systematically interpreted.

Unlike conventional dispersive IR spectrometers, FTIR employs a Michelson interferometer to collect spectral information. In this configuration, IR radiation from a

broadband source passes through a collimator and reaches a beam splitter, which divides the beam into two paths. One beam reflects from a fixed mirror, while the other reflects from a moving mirror. The difference in optical path length between the two beams generates an interference pattern known as an interferogram. After recombination, the modulated beam interacts with the sample, where selective absorption occurs depending on the molecular structure. The transmitted or reflected signal is detected and mathematically transformed using a Fourier Transform algorithm to convert the interferogram into a conventional frequency-domain spectrum [15]. The use of the Michelson interferometer offers several advantages, including high spectral resolution, rapid data acquisition, improved signal-to-noise ratio, and enhanced sensitivity. Additionally, FTIR spectroscopy enables averaging of multiple scans to reduce noise and improve spectral clarity. The technique is also compatible with various sampling modes such as transmission, reflection, and attenuated total reflectance (ATR), which further enhances its versatility for thin films and nanomaterial characterization [16].

In the context of nanomaterials and nanocomposites, FTIR plays a crucial role in confirming surface functionalization, identifying bonding interactions, and verifying the presence of chemical groups introduced during synthesis. For example, in 2D nanomaterials and their composites, FTIR can detect oxygen-containing groups ($-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$), metal–oxygen bonds, sulfide linkages, and other surface modifications that influence sensing performance and interfacial charge transfer. The technique is particularly valuable in evaluating graphene oxide (GO), reduced graphene oxide (rGO), metal chalcogenides, and hybrid nanocomposites, where surface chemistry significantly governs electronic and adsorption properties. Thus, FTIR spectroscopy serves as a rapid, non-destructive, and highly informative characterization method for understanding chemical structure, surface chemistry, and functional group interactions in advanced nanomaterials, making it an essential component of comprehensive material analysis.

2.2.4 Photoluminescence Spectroscopy

Luminescence refers to the emission of light from a material following the absorption of external energy. Among its various forms, photoluminescence (PL) is a widely used

optical characterization technique in which light (photons) serves as the excitation source. When a material is irradiated with electromagnetic radiation of suitable energy, it absorbs photons and subsequently re-emits light as a result of electronic transitions within the material. PL spectroscopy is a non-destructive, highly sensitive analytical method that provides valuable insights into the electronic structure, band gap, defect states, and recombination mechanisms of semiconductors and nanomaterials [17].

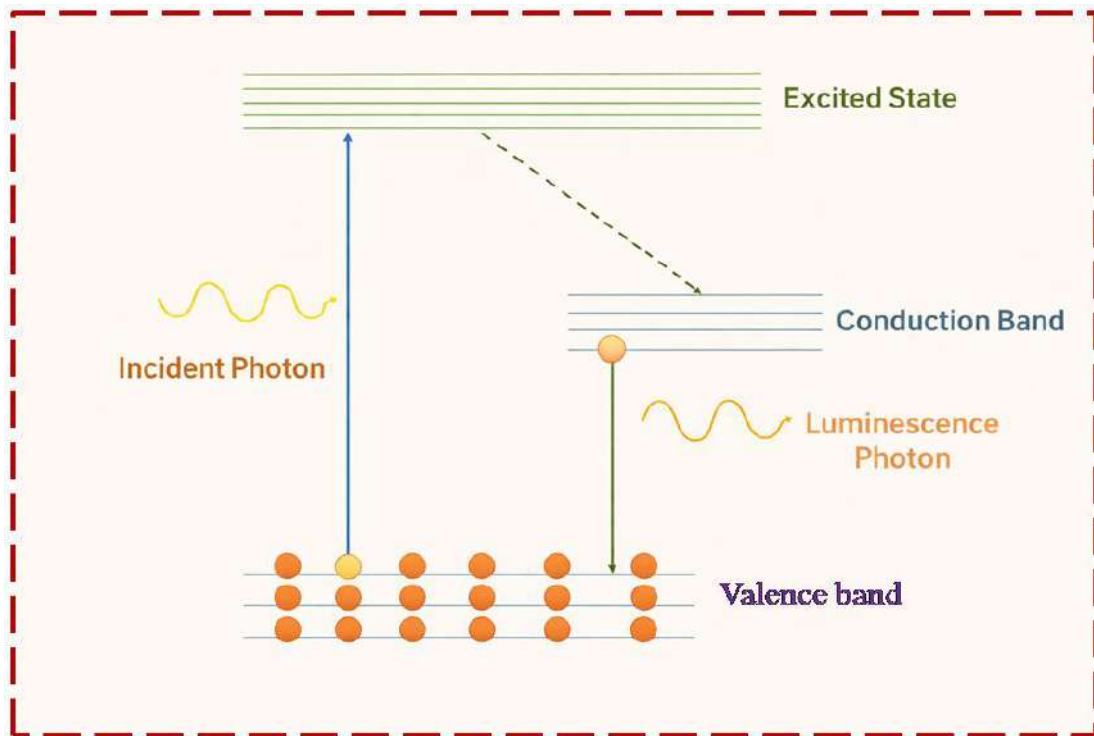


Fig. 2.6: Working principle of photoluminescence measurement.

In a typical PL experiment, the surface of the sample is illuminated using a monochromatic light source, often a laser of fixed wavelength and energy. The incident photons excite electrons from the valence band to higher energy states, typically into the conduction band, thereby generating electron–hole pairs. These excited charge carriers are not stable and eventually return to lower energy states through recombination processes. During radiative recombination, the energy difference between the excited and ground states is released in the form of emitted photons. The emitted photon energy is generally lower than the excitation energy due to energy losses associated with relaxation processes, and it corresponds to the difference between the electronic states involved in the transition.

The photoluminescence process can be broadly divided into three fundamental stages: excitation, relaxation (thermalization), and recombination. Upon excitation, electrons absorb photon energy and are promoted to higher energy levels. These excited carriers then undergo rapid non-radiative relaxation toward the lowest energy states within the conduction band or defect levels. Finally, recombination occurs, which may be either radiative or non-radiative. In radiative recombination, photon emission takes place, producing the PL signal, whereas non-radiative pathways dissipate energy as heat without photon emission.

PL emission spectra are typically recorded as intensity versus wavelength or photon energy. The intensity of the emitted light reflects the efficiency of radiative recombination processes within the material. Strong PL intensity indicates a high probability of radiative transitions, while reduced intensity may suggest enhanced non-radiative recombination due to defects or surface states. To minimize interference from scattered excitation light, the emitted signal is collected using a monochromator positioned at approximately 90° relative to the incident beam. This configuration improves measurement accuracy and reduces background noise.

Various types of electronic transitions contribute to photoluminescence, including band-to-band recombination, free excitonic transitions, free-to-bound transitions, and donor–acceptor pair recombination. In semiconductors and nanostructured materials, intrinsic defects and impurities often introduce discrete energy levels within the forbidden band gap. These defect states can act as shallow donors (located slightly below the conduction band) or shallow acceptors (situated slightly above the valence band). Recombination through these localized states results in characteristic emission peaks that typically appear at longer wavelengths (lower energies) compared to the band-edge emission. Therefore, PL spectroscopy serves as a powerful tool for probing defect-related transitions and understanding the influence of structural imperfections on material performance [18-19].

Due to its high sensitivity to electronic and structural variations, PL spectroscopy is extensively applied in the characterization of nanomaterials, thin films, and semiconductor devices. It provides crucial information regarding band gap energy, defect density, surface states, and recombination dynamics, all of which play a

significant role in determining the performance of materials in applications such as gas sensing, optoelectronics, photocatalysis, and energy harvesting systems.

2.2.5 Field-Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) is an advanced surface characterization technique that provides high-resolution imaging by employing a field emission electron source to generate a highly focused electron beam. In FESEM, the electron beam is scanned across the specimen surface in a raster pattern, producing detailed morphological and microstructural information. Unlike conventional scanning electron microscopy (SEM), which typically uses a thermionic tungsten filament as the electron source, FESEM utilizes a field emission gun (FEG). The FEG produces an electron beam with significantly higher brightness and coherence often up to three orders of magnitude greater emission intensity resulting in superior spatial resolution, enhanced image contrast, and improved signal-to-noise ratio.

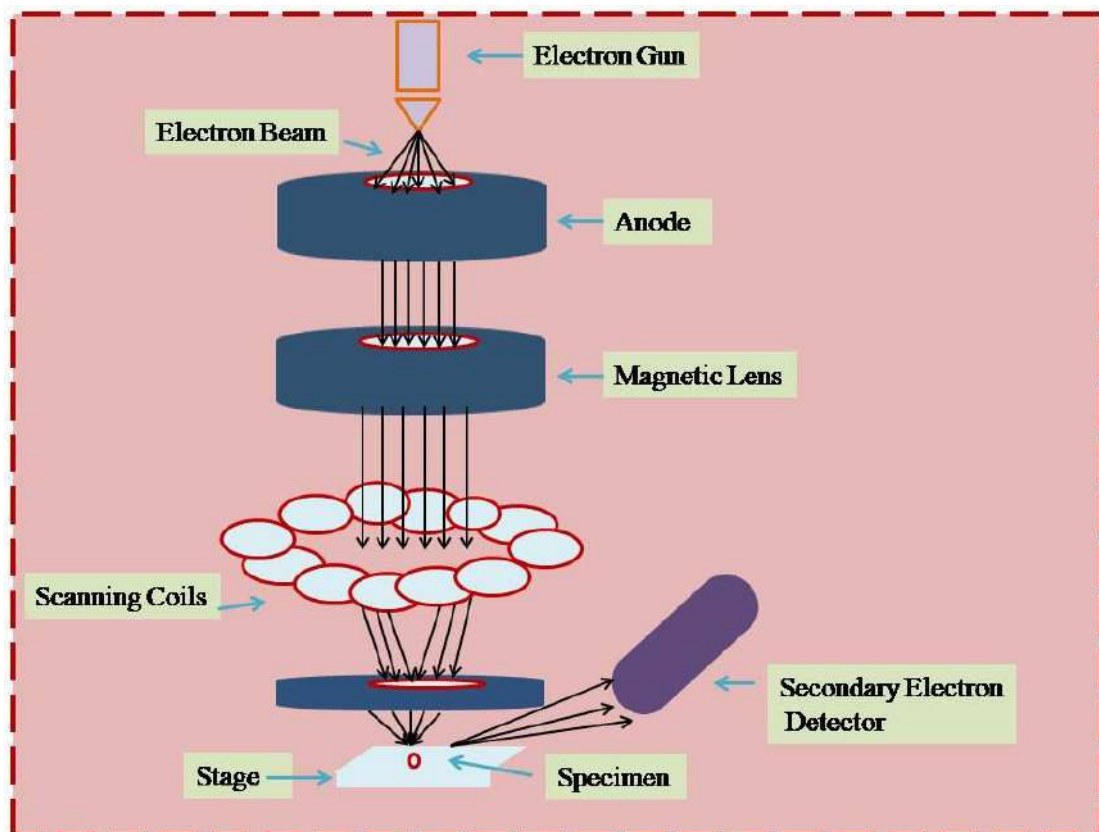


Fig. 2.7: Schematic showing the components of an FESEM.

The instrument operates under ultra-high vacuum conditions to ensure stable electron emission and minimize beam scattering. The emitted electrons are accelerated by a high potential difference and focused into a narrow, monochromatic beam using a series of electromagnetic lenses and metallic apertures. The finely controlled beam diameter enables nanoscale imaging, making FESEM particularly suitable for studying nanostructured materials, thin films, and composite systems [20].

When the focused electron beam interacts with the specimen surface, a complex range of signals is generated due to elastic and inelastic scattering processes. These emitted signals provide complementary information regarding surface morphology, composition, and crystallographic features. The most commonly detected signals include secondary electrons (SE), backscattered electrons (BSE), characteristic X-rays, and Auger electrons. Secondary electrons are produced when the incident primary electrons transfer sufficient energy to loosely bound outer-shell electrons of the specimen atoms, causing their ejection. Due to their low kinetic energy and limited escape depth, secondary electrons originate predominantly from the near-surface region of the sample. This surface sensitivity makes them ideal for high-resolution topographical imaging, enabling detailed visualization of grain boundaries, porosity, surface roughness, and nanostructure morphology. Backscattered electrons, in contrast, arise from elastic collisions between the incident electrons and atomic nuclei in the specimen. The probability of backscattering increases with the atomic number (Z) of the constituent elements. Consequently, regions containing heavier elements appear brighter in BSE images, whereas lighter elements appear darker. This atomic number contrast makes BSE imaging highly valuable for compositional mapping and phase differentiation in heterogeneous or multi-component materials [21].

In addition to electron signals, characteristic X-rays are generated when primary electrons displace inner-shell electrons from atoms within the specimen. As higher-energy electrons transition to fill these vacancies, energy is released in the form of X-ray photons with element-specific energies. These X-rays are detected and analyzed using Energy Dispersive X-ray Spectroscopy (EDX or EDS), which enables qualitative and quantitative elemental analysis. EDX mapping can further reveal spatial

distribution of elements across the sample surface, providing insight into compositional uniformity and phase formation.

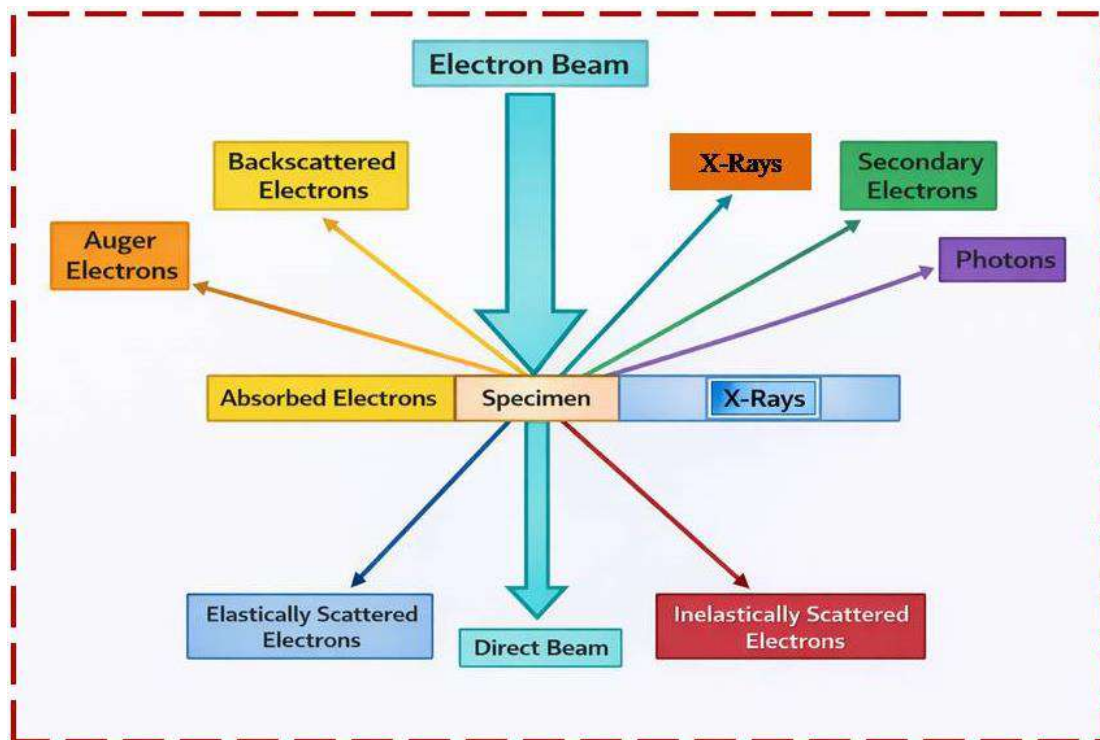


Fig. 2.8: Interaction of electrons with the specimen.

Another important signal generated during electron–matter interaction is the Auger electron. Instead of emitting X-ray radiation, the energy released during electronic transitions may be transferred to another electron, which is subsequently emitted from the atom. Auger electrons are highly surface-sensitive due to their low energy and short escape depth. When combined with X-ray analysis, Auger spectroscopy enhances the precision of elemental characterization, particularly for surface-modified or defect-engineered nanomaterials. Because FESEM requires conductive pathways for proper imaging, non-conductive samples are typically coated with an ultrathin conductive layer commonly gold (Au), palladium (Pd), or a gold–palladium alloy to prevent surface charging and improve image clarity. In certain cases, low accelerating voltages may also be employed to minimize charging effects without coating. Overall, FESEM serves as a powerful tool for investigating the surface morphology, particle size distribution, porosity, microstructural evolution, and compositional variations of nanomaterials.

Field Emission Scanning Electron Microscopy (FESEM) provides highly detailed information regarding surface morphology and elemental composition at extremely high magnifications, combined with an exceptionally large depth of field. Compared to conventional SEM systems that rely on thermionic emission sources, FESEM employs a field emission gun capable of producing a highly coherent and intense electron beam. This results in significantly enhanced image clarity, reduced electrostatic distortions, and spatial resolutions reaching up to ~ 0.5 nm under optimal operating conditions [22]. The superior beam stability and reduced energy spread contribute to sharper contrast and improved surface sensitivity, making FESEM particularly suitable for nanoscale investigations.

One of the major strengths of FESEM lies in its ability to generate crisp, high-precision images with minimal charging artifacts, especially when imaging nanostructured and thin-film materials. The improved resolution enables detailed visualization of fine morphological features such as grain boundaries, layered architectures, nanopores, defect sites, and interfacial junctions parameters that are critically important in correlating structural characteristics with functional performance. Owing to these advantages, FESEM has become an indispensable characterization tool across multiple scientific and technological domains. In physics, it is employed for advanced structural and crystallographic investigations. In chemistry, it aids in analyzing surface reactions, catalytic interfaces, and reaction-induced morphological changes. In biological sciences, FESEM enables high-resolution imaging of cellular and sub-cellular structures. Material scientists extensively utilize it for microstructural evaluation of advanced functional materials, while electronic engineers rely on it for microchip inspection, defect analysis, and failure diagnostics in semiconductor devices.

In the present research work, the surface morphology of nanocomposites based on two-dimensional nanomaterials was investigated using a Zeiss GeminiSEM 500 (Germany), available at the University Science Instrumentation Centre (USIC), University of Delhi, Delhi, India. The detailed morphological insights obtained through FESEM analysis play a crucial role in understanding structure–property relationships in gas sensing and hydroelectric cell applications.

2.2.6 High-Resolution Transmission Electron Microscopy (HRTEM)

Transmission Electron Microscopy (TEM) is one of the most powerful characterization techniques available for nanoscale and atomic-scale analysis of materials. By transmitting a highly energetic and finely focused electron beam through an ultrathin specimen, TEM enables direct observation of internal structure, crystallography, and microstructural features with exceptional spatial resolution. The extremely short wavelength of high-energy electrons—several orders of magnitude smaller than that of visible light allows TEM to achieve resolutions down to fractions of a nanometer, making it possible to visualize lattice planes and even atomic columns in crystalline materials [23].

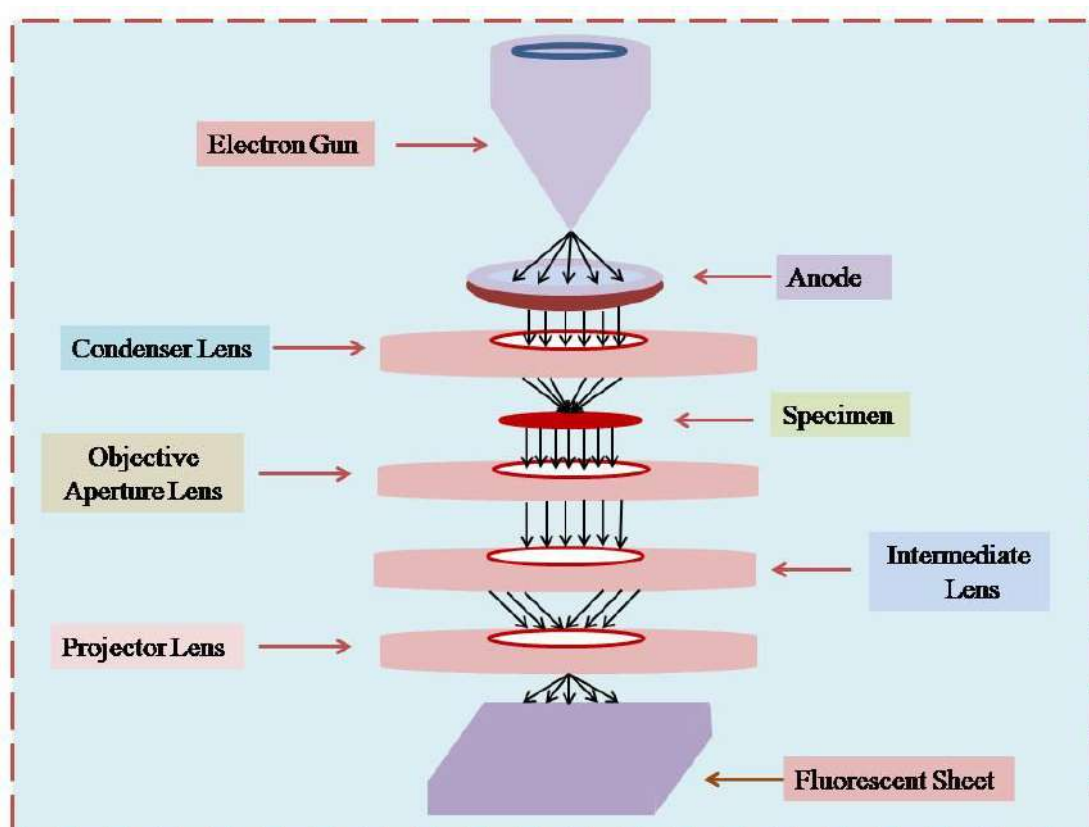


Fig. 2.9: Schematic showing the setup of HRTEM.

In a typical TEM system, electrons are generated by an electron source (thermionic or field emission) and accelerated by a high voltage, typically ranging from 100 kV to 300 kV. The accelerated electrons pass through condenser lenses that focus and control beam convergence before interacting with the specimen. The sample is mounted on a

thin copper grid and must be sufficiently electron-transparent, generally below ~ 100 – 200 nm in thickness, to minimize excessive scattering and absorption. The transmitted and scattered electrons are then collected by the objective lens, which forms either an image or a diffraction pattern. Additional intermediate and projector lenses further magnify the signal before it reaches the imaging system, such as a fluorescent screen or a high-sensitivity CCD/CMOS camera [24].

One of the key advantages of TEM is its ability to operate in multiple analytical modes, each providing complementary structural information. In conventional bright-field TEM, contrast arises primarily from differences in mass-thickness and diffraction effects. Regions that scatter electrons strongly appear darker, while thinner or less dense areas appear brighter. Dark-field imaging, on the other hand, selectively collects diffracted electrons from specific crystallographic planes using an aperture, producing images in which selected domains appear bright against a dark background. This technique is particularly useful for identifying phase distributions and crystallographic orientations.

High-Resolution TEM (HRTEM) represents a more advanced imaging mode that allows direct visualization of lattice fringes corresponding to specific crystallographic planes. By analyzing interplanar spacing (d -spacing) from HRTEM images, one can confirm phase formation, determine crystallinity, and evaluate defect structures such as dislocations, stacking faults, and grain boundaries. For nanocomposite systems, HRTEM is invaluable for observing interfacial contact between different phases and verifying the formation of heterostructures. Selected Area Electron Diffraction (SAED) is another important capability of TEM. In this mode, diffraction patterns are obtained from a selected microscopic region of the sample. The resulting diffraction spots or rings provide information about crystal symmetry, orientation, and phase identity. Single-crystalline materials produce distinct spot patterns, while polycrystalline or nanocrystalline materials yield ring patterns. By indexing these patterns, lattice parameters and crystal structure can be determined with high accuracy [25].

The interaction between the incident electron beam and the specimen involves complex scattering phenomena. Elastic scattering, which does not involve energy loss, is

primarily responsible for diffraction and coherent imaging. Inelastic scattering, involving energy transfer to the specimen, can provide additional chemical and electronic information. Advanced TEM systems may incorporate analytical techniques such as Energy Dispersive X-ray Spectroscopy (EDS) for elemental analysis and Electron Energy Loss Spectroscopy (EELS) for probing chemical bonding and valence states. Modern TEM instruments operate under ultra-high vacuum conditions to ensure minimal beam scattering and maintain beam stability. They are equipped with computerized control systems for precise alignment, focus correction, aberration compensation, and automated data acquisition. Aberration-corrected TEM systems can further enhance spatial resolution and image clarity by correcting lens imperfections.

In the context of nanomaterials research, TEM plays a critical role in establishing structure property relationships. For two-dimensional (2D) nanomaterials, TEM enables determination of layer thickness, sheet morphology, edge structure, and defect distribution. It also helps confirm successful synthesis of nanocomposites by visualizing dispersion of secondary phases, interfacial bonding, and structural integration. In gas sensing applications, TEM analysis assists in correlating particle size, porosity, and crystallinity with adsorption behavior and charge transport properties. Similarly, for hydroelectric cell devices, TEM helps identify defect structures, oxygen vacancies, and nanoscale porosity that influence water dissociation and ionic conduction.

Overall, TEM provides comprehensive morphological, crystallographic, and microstructural insight at the atomic scale. Its ability to directly observe lattice arrangements, defects, and interfaces makes it indispensable for advanced materials characterization, particularly in the development of high-performance 2D nanomaterials for sensing and sustainable energy applications. The wavelength of electrons decreases significantly with increasing accelerating voltage, thereby enhancing spatial resolution in transmission electron microscopy. By employing a high accelerating voltage typically up to 300 kV particularly in field emission gun (FEG) systems, electrons attain shorter wavelengths and higher beam coherence. This improvement directly enhances point resolution and enables the acquisition of high-resolution TEM (HRTEM) images capable of resolving atomic-scale lattice fringes and crystallographic features with exceptional clarity [26].

In the present study, advanced structural and morphological investigations were carried out using state-of-the-art TEM facilities. High-resolution imaging and diffraction analyses were performed using a JEOL JEM-2100F (Japan) at the Advanced Instrumentation Research Facility (AIRF), Jawaharlal Nehru University (JNU), New Delhi. Complementary TEM studies were conducted on an FEI Tecnai 200 (USA) available at the Sophisticated Analytical Instrument Facility (SAIF), All India Institute of Medical Sciences (AIIMS), New Delhi.

2.2.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a powerful, surface-sensitive, and non-destructive analytical technique widely used for determining the elemental composition, chemical states, and electronic structure of materials. The method is fundamentally based on the photoelectric effect, first explained by Albert Einstein in 1905, for which he was awarded the Nobel Prize in Physics in 1921. By measuring the energies of electrons emitted from a material upon X-ray irradiation, XPS provides detailed insights into both the elemental identity and oxidation states of atoms present on the surface of a sample [27].

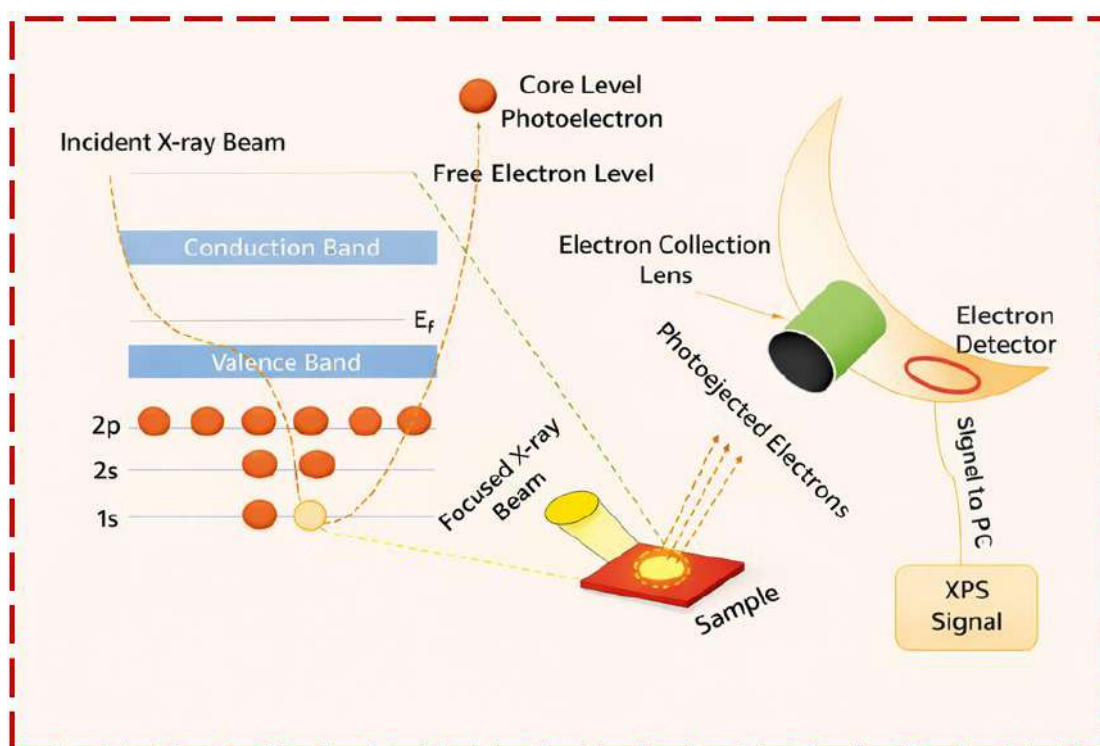


Fig. 2.10: Typical working mechanism of X-ray photoelectron spectroscopy.

XPS analysis is performed under ultra-high vacuum (UHV) conditions to prevent interference from atmospheric gases and to ensure accurate detection of emitted electrons. In a typical XPS setup, the sample surface is irradiated with monochromatic, high-energy X-rays, commonly Mg K α (1253.6 eV) or Al K α (1486.6 eV) radiation. When these incident photons interact with the atoms in the sample, they transfer sufficient energy to eject core-level (inner-shell) electrons if the photon energy exceeds the electron's binding energy.

The incident photon energy ($h\nu$) is distributed in three primary ways. First, part of the energy is consumed in overcoming the binding energy (E_b) that holds the electron within the atom. Second, a portion accounts for the work function (ϕ) of the spectrometer, which represents the energy required to remove the electron to the vacuum level. The remaining energy appears as the kinetic energy (KE) of the emitted photoelectron. According to the principle of energy conservation, the relationship among these quantities can be expressed as:

$$E = h\nu - h\nu' - \phi \quad (2.5)$$

By accurately measuring the kinetic energy of the emitted electrons using an electron energy analyzer, the binding energy can be calculated. Since each element has characteristic binding energy values for its core electrons, XPS spectra serve as elemental fingerprints. Moreover, slight shifts in binding energy commonly referred to as chemical shifts provide crucial information about the oxidation state, bonding configuration, and local chemical environment of the element.

In addition to qualitative identification, XPS enables quantitative surface analysis. The intensity (or integrated area) of a specific photoelectron peak is proportional to the concentration of the corresponding element within the sampling depth. Typically, the X-ray beam penetrates only about 1-10 nanometers into the material, making XPS an extremely surface-sensitive technique. This shallow probing depth is particularly advantageous for studying thin films, nanostructures, surface functionalization, oxidation behavior, and interface chemistry [28]. Furthermore, XPS can detect multiple oxidation states of a single element by analyzing peak splitting and satellite features in the spectrum. Deconvolution of high-resolution spectra allows differentiation between

various chemical environments, such as metal-oxygen, metal-sulfur, or carbon-oxygen bonds. Consequently, XPS plays a critical role in investigating defect states, surface vacancies, doping effects, and interfacial charge transfer phenomena in advanced nanomaterials.

In the context of nanomaterials and nanocomposites, XPS is extensively employed to confirm elemental composition, verify successful reduction or functionalization (for example, in graphene oxide to reduced graphene oxide transformation), and assess the presence of oxygen vacancies or surface defects in metal chalcogenides and oxide systems. Its ability to correlate electronic structure with chemical composition makes XPS an indispensable tool for understanding surface-driven processes in gas sensing and energy harvesting applications.

2.2.8 Brunauer-Emmett-Teller (BET) Technique

The porous characteristics of materials are commonly evaluated using nitrogen adsorption-desorption isotherm analysis, which remains one of the most widely adopted techniques for determining surface area and pore structure. The effective surface area and pore volume are key parameters governing the functional performance of porous materials, particularly in applications such as gas sensing, catalysis, adsorption, and energy storage. These parameters are derived from the adsorption behavior of nitrogen molecules on the surface of the material under controlled conditions.

Nitrogen gas is typically used as the adsorbate because of its chemical inertness, availability in high purity, and well-defined physical properties. Measurements are generally conducted at the boiling point of liquid nitrogen (77 K), where adsorption processes are highly reproducible. Nitrogen is also economically favorable compared to other probe gases such as argon (Ar), krypton (Kr), or carbon dioxide (CO₂), although these alternatives may be employed in specific cases depending on pore size and material characteristics.

The adsorption-desorption data are interpreted using the Brunauer-Emmett-Teller (BET) theory, developed to describe multilayer adsorption of gas molecules on solid

surfaces. According to BET theory, gas molecules initially form a monolayer on energetically favorable adsorption sites of the material surface. Once this monolayer is complete, additional layers of gas molecules can adsorb on top of the first layer, leading to multilayer formation. The outermost layers behave similarly to a liquid phase in equilibrium with the vapor phase. The BET equation, applied within a specific relative pressure range (typically 0.05-0.30), enables calculation of the monolayer adsorption capacity, from which the specific surface area of the material is determined [29].

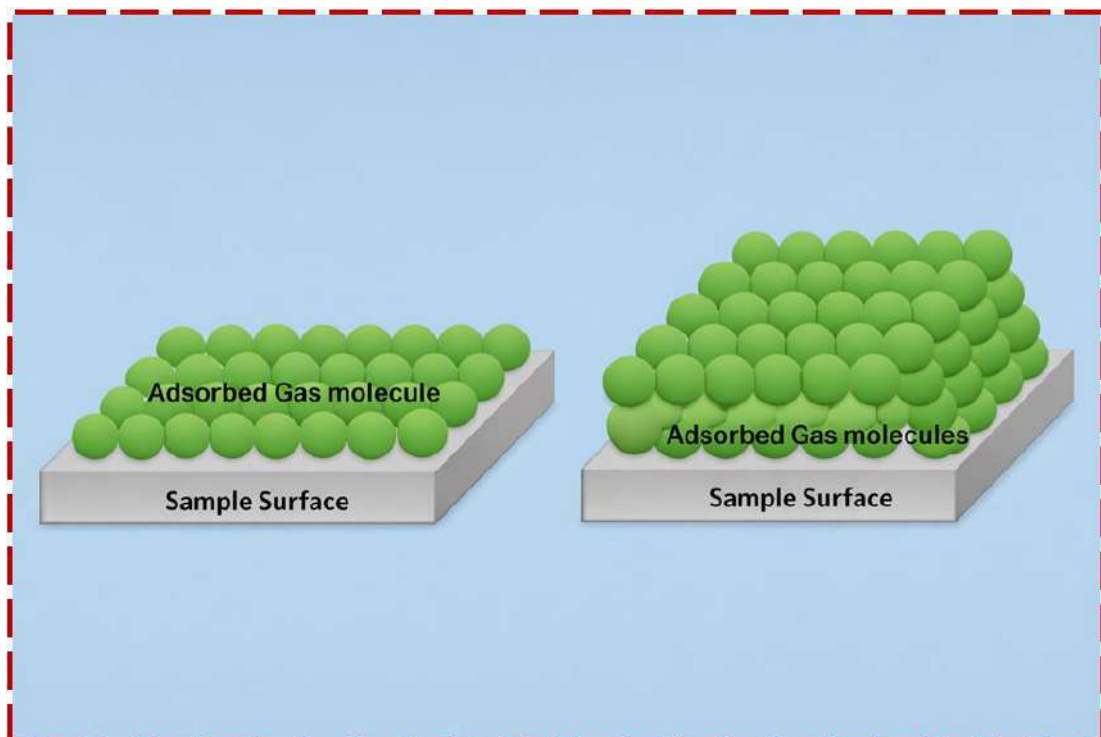


Fig. 2.11: Gas adsorption on the sample surface (a) following monolayer coverage by Langmuir Theory (b) following multilayer coverage by BET Theory

During the measurement, the quantity of nitrogen adsorbed is recorded over a relative pressure (P/P_0) range of approximately 0.05 to 0.995 at 77 K. The resulting adsorption–desorption isotherm provides valuable insight into the surface and pore characteristics of the material. At low relative pressures, monolayer and multilayer adsorption dominate, often indicated by a distinct “knee” in the isotherm corresponding to monolayer completion. At higher relative pressures, capillary condensation occurs within mesopores, leading to a steep increase in adsorption volume. This phenomenon is particularly significant for mesoporous materials and contributes to pore size and

volume estimation. The International Union of Pure and Applied Chemistry (IUPAC) classifies adsorption isotherms into six primary types and identifies four characteristic hysteresis loop patterns, which help determine pore geometry and connectivity. The presence and shape of hysteresis loops between adsorption and desorption branches provide information about mesoporous structures such as cylindrical, ink-bottle, or slit-shaped pores.

While BET theory is suitable for non-porous, macroporous, and mesoporous materials, it has limitations for strictly microporous systems where pore filling mechanisms differ from multilayer adsorption assumptions. For detailed pore size distribution analysis in mesoporous materials, the Barrett–Joyner–Halenda (BJH) method is commonly applied. The BJH model assumes cylindrical, non-interconnected pores and utilizes the Kelvin equation to correlate condensation pressure with pore radius. Through this approach, pore volume, average pore diameter, and pore size distribution can be quantitatively determined.

Overall porosity of a material can further be estimated by comparing the pore volume to the total volume of the solid. In practical terms, bulk density obtained from X-ray crystallographic data (d_{bulk}) and experimentally measured density (d_{exp}), often calculated using the Archimedes principle, are used to estimate the fraction of void space within the material. Thus, nitrogen adsorption–desorption analysis combined with BET and BJH models provides a comprehensive understanding of surface area, pore structure, and porosity, which are critical factors influencing adsorption efficiency, surface reactivity, and charge transport behavior in nanostructured materials [30].

$$\% \text{ Porosity} = (1 - d_{\text{bulk}}/d_{\text{exp}}) \times 100 \quad (2.6)$$

Where d_{bulk} is the X-ray density of the bulk crystallite, and d_{exp} is the experimental density measured using Archimedes' water displacement principle. The present research focuses on the measurement of specific surface area, using a Quantachrome NOVA 2200e (U.S.) instrument housed at the Department of Physics & Astrophysics, University of Delhi, Delhi, India, from the synthesized nanocomposites of 2D nanomaterials discussed in Chapter 3,4, and 5.

2.3 Gas Sensor Fabrication

The nanocomposite films comprising 2D nanomaterials and metal oxides were prepared using the electrophoretic deposition technique for sensor fabrication. Thereafter, metal electrodes were deposited onto the synthesized films using the thermal evaporation method.

2.3.1 Electrophoretic Deposition (EPD) Technique

Electrophoretic deposition (EPD) is a simple, cost-effective, and highly adaptable technique for producing uniform, compact, and well-adhered thin films. In this process, an external electric field is applied to a stable suspension of charged particles dispersed in a suitable liquid medium such as deionized water, ethanol, isopropanol, acetonitrile, or other organic solvents. Under the influence of the electric field, the charged particles migrate toward the oppositely charged electrode and deposit onto the substrate surface, forming a coherent film.

A typical EPD setup consists of a two-electrode configuration immersed in a suspension contained within a glass beaker. The electrodes are positioned at a fixed distance to ensure controlled electric field distribution. Generally, a platinum (Pt) rod serves as the reference or counter electrode, while a conductive substrate often attached to a copper (Cu) rod acts as the working electrode where deposition occurs. For achieving homogeneous coatings, it is essential that the particles are uniformly dispersed in the solvent using appropriate dispersion techniques. The choice of solvent plays a critical role in controlling particle mobility, suspension stability, and deposition quality.

Key operational parameters such as applied voltage, electrode spacing, particle concentration, and deposition time must be carefully optimized to obtain films with the desired thickness, microstructure, and mechanical integrity. The use of suitable dispersing agents or stabilizers may be necessary to prevent particle agglomeration; however, their concentration must be precisely controlled to avoid contamination or residual impurities in the deposited film. Since EPD requires electrically conductive substrates, materials such as metal foils, ITO-coated glass, or FTO-coated glass are commonly employed [31-33].

Post-deposition heat treatment or annealing is often carried out to enhance film adhesion, remove residual solvents or organics, and improve crystallinity and structural stability. Overall, EPD offers excellent control over film thickness and morphology, making it a promising technique for fabricating coatings in applications such as sensors, energy devices, catalysts, and advanced functional materials.

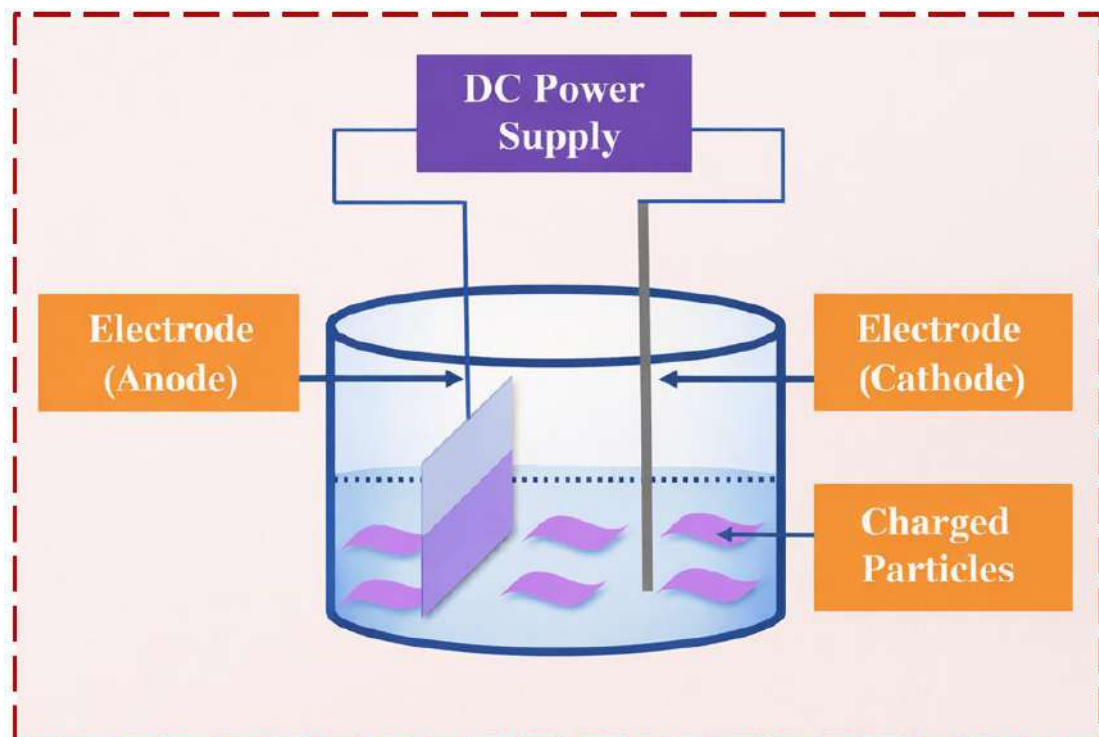


Fig. 2.12: Schematic showing the fabrication of film via EPD technique.

2.3.2 Thermal Evaporation Technique for Electrode Deposition

The thermal evaporation technique is a well-established thin film deposition method extensively employed for electrode fabrication owing to its high precision, operational simplicity, and capability to produce uniform and adherent coatings. In this process, a source material is thermally heated under high-vacuum conditions until it undergoes evaporation or sublimation. The generated vapor species travel through the evacuated chamber with minimal collision and subsequently condense onto the substrate surface, forming a continuous thin film that largely retains the intrinsic properties of the parent material. The vacuum environment plays a critical role in minimizing contamination, suppressing unwanted chemical reactions, and enabling controlled film growth with

high purity and reproducibility. Owing to these advantages, thermal evaporation has been widely utilized in the fabrication of electronic, optoelectronic, sensing, and energy-related devices.

The deposition process is typically carried out through a sequence of carefully controlled steps. Initially, the vacuum chamber is prepared by placing the substrate and the evaporation source inside the system. The chamber is then evacuated to achieve high-vacuum conditions, which ensure long mean free paths for the vapor species and enhance the quality of the deposited film. Maintaining a stable vacuum also improves film adhesion and uniformity by preventing oxidation or impurity incorporation during deposition.

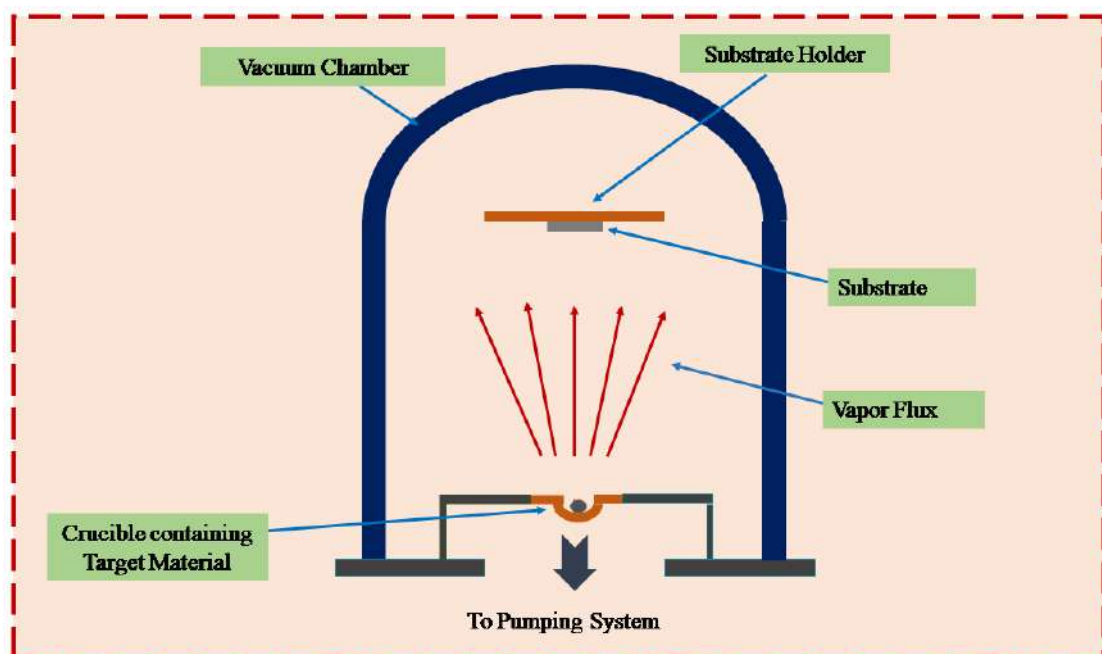


Fig. 2.13: Schematic representation of thermal evaporation system.

Subsequently, the source material—commonly available in the form of pellets, wires, or granule is heated using either resistive heating elements or an electron beam. Upon reaching a sufficiently high temperature, the material transitions into the vapor phase. The vaporized atoms or molecules then travel toward the substrate in a line-of-sight trajectory due to the low-pressure environment within the chamber. During the deposition stage, these vapor species condense upon reaching the relatively cooler substrate surface. The condensation process leads to nucleation and growth of a thin film layer. The deposition rate is governed

by several parameters, including the source temperature, the distance between the source and substrate, and the chamber pressure. Precise control over these parameters allows for accurate thickness tuning and consistent film quality [34,35].

Finally, film growth characteristics such as thickness, morphology, crystallinity, and surface roughness are influenced by deposition duration, substrate temperature, vacuum level, and evaporation rate. By optimizing these variables, highly uniform, smooth, and electrically conductive films suitable for electrode fabrication can be achieved. This level of control makes thermal evaporation particularly advantageous for fabricating metal contacts in gas sensors, hydroelectric cells, and other thin-film-based device architectures.

In the present work, metal electrodes were deposited on the films synthesized using the EPD technique by employing the thermal evaporation method for facilitating gas sensor fabrication, as presented in Fig. 2.13. The deposition of electrodes was carried out with the help of the Smart Coat 3.0 system (Hind High Vacuum) available at the Computational Functional Materials Research Laboratory (CFMRL), Department of Applied Physics, Delhi Technological University, Delhi, India. The electrical characterization of the fabricated sensors was carried out afterward using the Keithley Source Measuring Unit (SMU) 2450, located in the Nanomaterials Research Laboratory (NRL), Department of Applied Physics, Delhi Technological University, Delhi, India.

2.4 Gas Sensing Measurements

The sensing characteristics of the fabricated device were measured using an indigenously developed chemiresistive gas sensing setup available at the Nanomaterials Research Laboratory (NRL), Department of Applied Physics, Delhi Technological University (DTU), as shown in Fig. 2.14. A stainless steel (SS) chamber with an inlet and outlet is used, along with two mass flow controllers (MFCs) for accurate control of gas flow. A source measuring unit (SMU) supplies a constant current to the sensing device during the measurement process.

A rough vacuum is created inside the SS chamber using a rotary pump to remove residual gases at the very beginning of the sensing experiment. Then, dry air is introduced, which establishes the base resistance of the sensor. After that, a controlled

mixture of ethanol vapor and dry nitrogen gas introduced into the chamber. The ethanol gas concentration in ppm was calculated by using equation (2.7):

$$C = \frac{22.4 \times \Psi \times \rho \times V_1}{M \times V_2} \times 1000 \quad (2.7)$$

In the above formula (equation 2.7), C stands for ethanol concentration (in ppm), Ψ is the gas volume fraction, ρ is the density of ethanol in $\text{kg} \cdot \text{m}^{-3}$, V_1 is the volume of ethanol in L, M is the molecular weight of ethanol in $\text{kg} \cdot \text{mol}^{-1}$, and V_2 is the volume of the SS chamber in m^3 [36]. Inside the chamber, the relative humidity (RH) is measured using a digital hygrometer. The resistance change of the sensing films upon gas exposure can be recorded using the LabVIEW-based data acquisition software interfaced with the SMU or independently with a Keithley digital multimeter (DMM7510). All sensor experiments are performed at room temperature, 27 °C, in a controlled atmosphere.

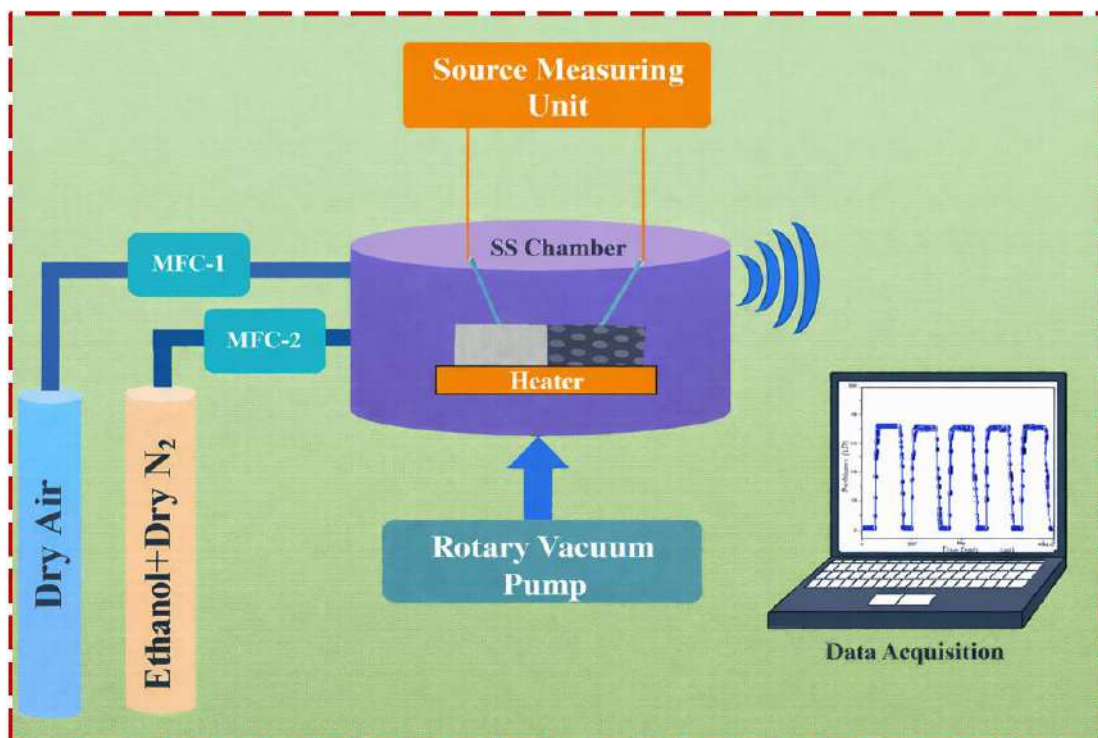


Fig. 2.14: Chemiresistive gas sensing setup.

2.5 HEC Analysis using V-I Polarization Plot

The performance evaluation of electrochemical cell and battery systems is commonly conducted through steady-state voltage-current (V-I) characterization. The V-I curve

serves as a fundamental diagnostic tool for assessing the electrical behavior and operational stability of energy generation devices. In this measurement, either the voltage or the current is controlled, while the corresponding response parameter is recorded. By systematically varying the load conditions, the relationship between output voltage and operating current can be determined, providing insight into the discharge characteristics of the system.

For primary energy generation devices, the discharge profile is a critical parameter that reflects the internal electrochemical processes and resistive losses within the cell. The V-I curve reveals the polarization behavior of the system, which describes the deviation of the cell potential from its equilibrium value as a function of operating current. Polarization arises due to various factors, including activation overpotentials, ohmic resistance, and mass transport limitations. By drawing a controlled current from the cell and measuring the corresponding voltage response, these polarization effects can be quantitatively analyzed [37]. In practical measurements, the external load applied to the cell is adjusted to vary the current output, resulting in a corresponding change in voltage. This method allows determination of key performance parameters such as open-circuit voltage (OCV), short-circuit current (I_{sc}), internal resistance, and maximum power output. The slope of the V-I curve in different current regions provides valuable information about ohmic losses and electrochemical kinetics within the system.

For hydroelectric cells (HECs), which represent a sustainable and environmentally benign energy generation platform, V-I characterization plays a crucial role in understanding their operational mechanism. The measured V-I response integrates the cumulative electrochemical behavior occurring at the working electrode–pellet interfaces, electrical contact resistance, ionic conduction pathways, water dissociation kinetics, and other resistive contributions within the device. Thus, the V-I curve offers a comprehensive overview of the energy conversion efficiency and polarization losses in HEC systems. By identifying and quantifying these losses, strategies can be developed to optimize material composition, defect density, porosity, and electrode design to improve overall device performance.

Temperature is another important variable that influences electrochemical performance. Changes in temperature can significantly alter reaction kinetics, ionic mobility, and internal resistance, thereby modifying the V-I characteristics of the cell. Consequently, V-I analysis can also be employed to compare the performance of different HEC configurations under varying environmental or operational conditions [38].

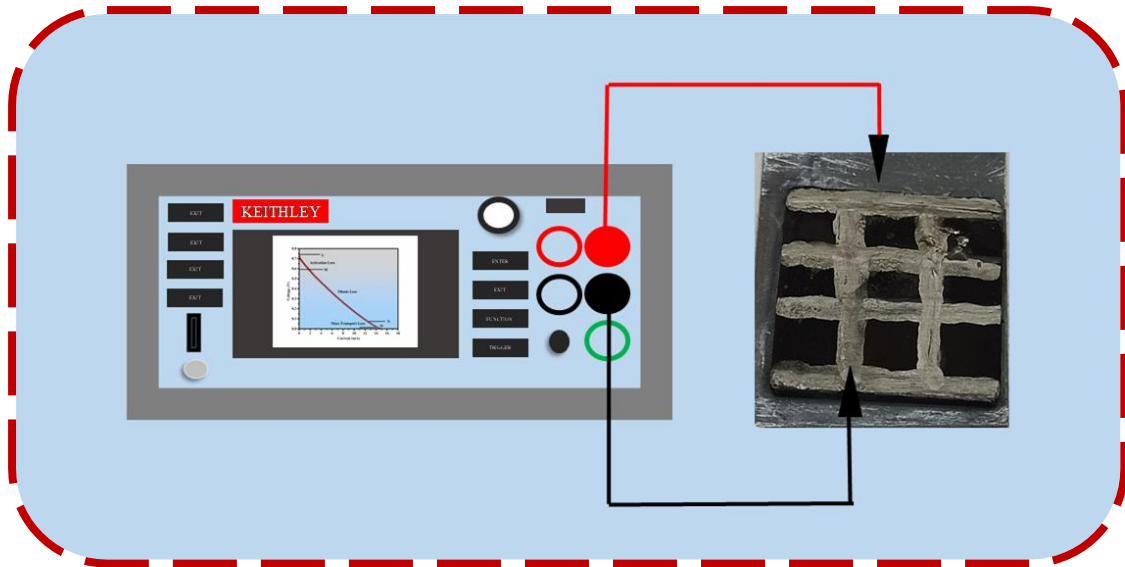


Fig. 2.15: Keithley sourcemeter for I-V measurements.

In the present study, V-I measurements of the hydroelectric cell fabricated using magnesium ferrite-based materials were carried out using a Keithley 2430 1 kW pulse source meter. During the experiment, the source meter functioned as a load (current sink) rather than a charging source. The source voltage was maintained at 0 V, and the current compliance was adjusted to control the discharge rate. Initially, the open-circuit voltage was recorded under zero-current conditions. Thereafter, the current was gradually increased in a stepwise manner while monitoring the corresponding voltage drop until short-circuit conditions were reached. Under short-circuit conditions, the maximum deliverable current of the HEC was determined.

2.5.1 Impedance Analysis

Electrochemical impedance spectroscopy (EIS) is a powerful and indispensable technique for probing the internal electrical and electrochemical processes occurring

within hydroelectric cells (HECs). This method provides detailed insight into charge transport, interfacial polarization, ionic conduction, and defect-related phenomena that govern device performance. By analyzing the response of a material to a small alternating current (AC) perturbation, impedance analysis enables a deeper understanding of the mechanisms responsible for water dissociation, ion migration, and charge transfer within the cell.

In an impedance measurement, a small sinusoidal AC voltage (V_{ex}) is applied across the electrodes of the semiconducting or electrochemical system. This excitation generates an alternating current response whose amplitude and phase shift relative to the applied voltage are carefully recorded. The phase difference between voltage and current reveals the contributions of resistive (conduction) and reactive (capacitive or inductive) components within the material. From this response, both the resistance and capacitance of the system can be determined.

The measured capacitance corresponds to the dielectric behavior of the sample for a given electrode area and inter-electrode spacing. The loss tangent ($\tan \delta$) represents the ratio of energy dissipated to energy stored in the material and reflects the presence of structural defects, impurities, grain boundaries, and lattice imperfections. These structural irregularities cause a delay between polarization and the applied electric field, leading to energy dissipation in the system [39]. The electrical behavior of polycrystalline or nanostructured materials is typically influenced by multiple regions, including grains (bulk), grain boundaries, and electrode–material interfaces. Each of these regions can be represented by an equivalent parallel resistor–capacitor (RC) circuit. The overall impedance response of the material arises from the series combination of these individual parallel RC elements [40]. The relaxation time constant (τ) for each region is given by:

$$\tau = RC \quad (2.8)$$

where R and C represent the resistance and capacitance of the corresponding region. Each region exhibits dominance in different frequency ranges, often appearing as distinct semicircular arcs in impedance plots at low, intermediate, and high frequencies.

The complex impedance $Z^*(\omega)$ is expressed as:

$$Z^*(\omega) = Z'(\omega) + Z''(\omega) \quad (2.9)$$

where (Z') is the real (resistive) component and (Z'') is the imaginary (reactive) component of impedance. A Nyquist plot, also known as a Cole–Cole plot, is obtained by plotting $-\text{Im}(Z)$ versus $\text{Re}(Z)$. In such a plot, the intercept of the semicircular arc on the real axis corresponds to the resistance of the respective region, while the peak of the semicircle provides information related to capacitance and relaxation behaviour.

If the bulk (grain) resistance dominates over the grain boundary resistance, a single broadened semicircle is typically observed. Conversely, when grain boundary resistance is significant, two distinct semicircles may appear, corresponding to bulk and grain boundary contributions. Deviations from ideal semicircular behavior often indicate non-Debye relaxation processes, commonly observed in nanomaterials with inhomogeneous microstructures or high defect densities. In such cases, constant phase elements (CPEs) are introduced into the equivalent circuit model to account for distributed relaxation phenomena [41].

In the present study, dielectric and impedance spectroscopic analyses were performed to investigate the electrical transport properties of iron oxide-based pellets and their corresponding hydroelectric cell devices. Measurements were carried out using a Wayne Kerr 6500B impedance analyzer. Silver contacts were applied on both sides of the pellet to ensure good electrical contact, and a small AC perturbation voltage of 50 mV was applied. The frequency range was varied from 100 Hz to 10^7 Hz to capture contributions from bulk conduction, grain boundaries, and electrode interfaces. Furthermore, impedance measurements were conducted on both dry and water-activated (wet) hydroelectric cells to evaluate ion migration kinetics and defect-mediated conduction behavior. Comparison of impedance responses under different hydration conditions enabled estimation of ionic conductivity, polarization resistance, and the role of water-assisted proton transport mechanisms in HEC operation.

Thus, impedance analysis serves as a comprehensive diagnostic tool for understanding charge transfer, defect dynamics, interfacial polarization, and ionic conduction

processes in hydroelectric cell systems, thereby guiding material optimization for enhanced energy generation performance.

2.5.2 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a highly effective and widely used electrochemical technique for investigating oxidation–reduction (redox) mechanisms in molecular and material systems. It serves as an essential tool for qualitatively analyzing electron transfer processes, reaction kinetics, and the thermodynamic characteristics of electrochemical reactions occurring within a system. The earliest experimental observations of cyclic voltammetry date back to 1938, and the theoretical interpretation of the technique was later developed by Randles. In a CV experiment, the potential applied to the working electrode is varied linearly with time within a defined potential window. Upon reaching a predetermined potential limit, the scan direction is reversed, returning to the initial potential. This forward and reverse scanning generates a cyclic voltammogram that reflects the redox behavior of the electroactive species.

The experimental setup required to obtain a cyclic voltammogram includes an electrochemical cell, a potentiostat, a current–voltage converter, and a data acquisition system. The electrochemical cell typically consists of three electrodes such as working, reference, and counter electrodes immersed in a suitable electrolyte and solvent. The working electrode is the site where the redox reaction occurs within the applied potential range. Electrical neutrality in the cell is maintained by ion migration through the electrolyte solution. The reference electrode provides a stable and well-defined potential against which the working electrode potential is measured. Common reference electrodes include the standard calomel electrode (SCE), standard hydrogen electrode (SHE), and Ag/AgCl electrode. The counter electrode completes the circuit and facilitates current flow resulting from electron transfer between the working and counter electrodes [42,43].

The potentiostat is an electronic instrument that controls and maintains a constant or variable DC potential at the working electrode while measuring the resulting current. During cathodic polarization (negative sweep), the electroactive species undergoes reduction, whereas oxidation occurs during the reverse (anodic) sweep. These processes

generate characteristic cathodic and anodic peaks in the voltammogram. According to IUPAC convention, the applied potential is plotted along the x-axis (from lower to higher potential), and the resulting current response is plotted along the y-axis.

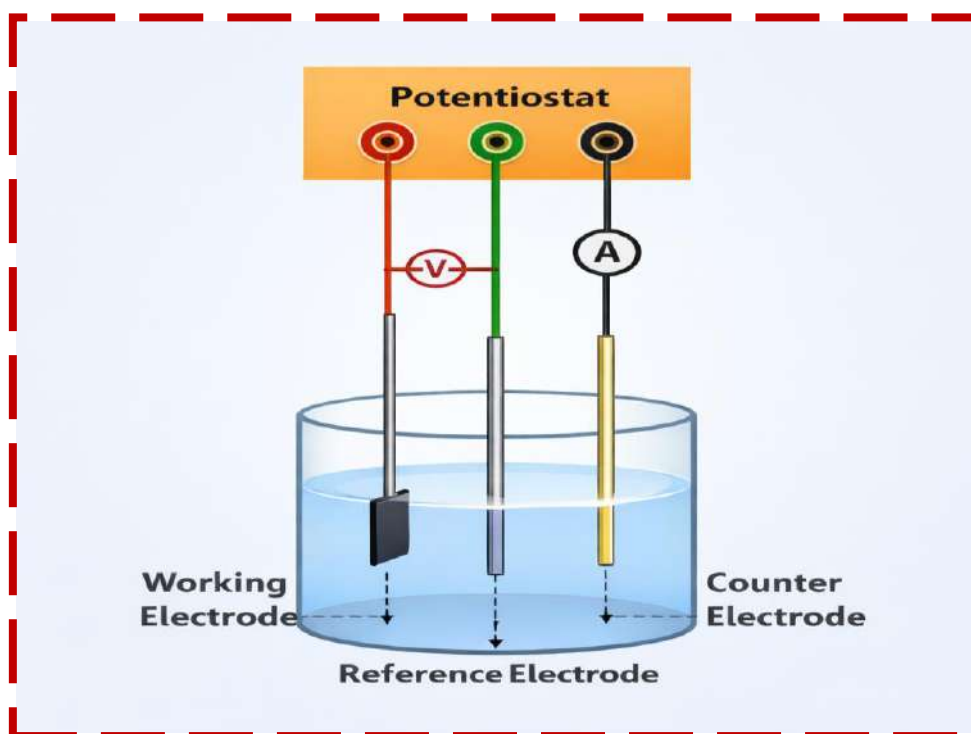
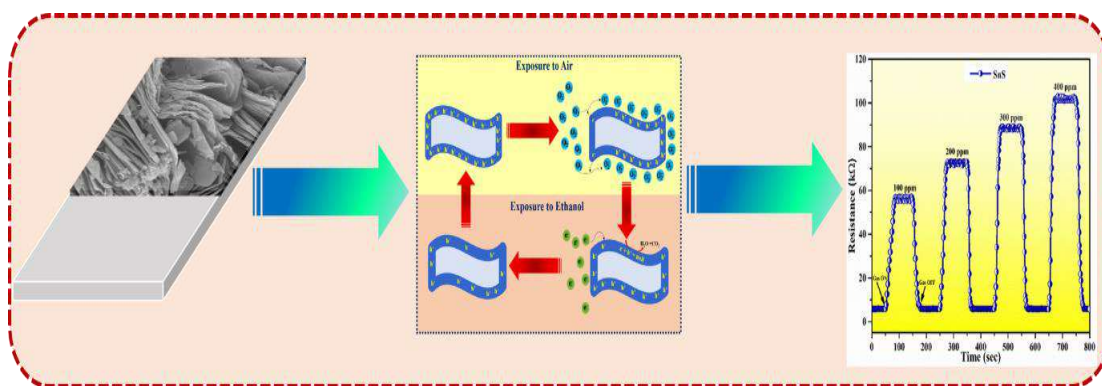


Fig. 2.16: A set up to obtain CV from SnS pellet based working electrodes.

Cyclic voltammetry is applicable to a broad range of materials, including organic compounds, inorganic systems, polymers, oxides, semiconductors, and thin films that involve electron transfer processes. Depending on the kinetics of electron transfer and mass transport, the redox system may exhibit reversible, quasi-reversible, or irreversible behavior. For a reversible one-electron transfer process, the peak-to-peak separation between anodic and cathodic peaks should ideally be close to 59 mV at room temperature. The peak positions can be used to estimate the half-cell potential of the redox reaction. When the rate of electron transfer at the electrode surface is slower than the rate of mass transport, the system exhibits electrochemical irreversibility.

CHAPTER 3

Vertically Aligned 2D Tin Sulfide (SnS) Nanoplates for Selective Detection of Ethanol Gas at Room Temperature



In this chapter, we have demonstrated a chemiresistive room temperature ethanol gas sensor based on vertically aligned tin sulfide (SnS) nanoplates. The sensor has been fabricated by depositing the SnS powder sample on ITO sheets using electrophoretic deposition (EPD), followed by the deposition of silver (Ag) electrodes using the thermal evaporation technique. The sensor obtained has exhibited a response value (R_g/R_a) of 17.4 to 400 ppm ethanol gas concentration, a quick response, and a recovery time of 12.4 s and 20.2 s at room temperature. The sensor has demonstrated long-term stability of 15 minutes, impressive selectivity, and remarkable repeatability across three successive test cycles of ethanol gas at 400 ppm. Based on the experimental sensing results, a plausible mechanism has been proposed for the sensor. The sensing response of SnS-based sensor at room temperature expands its potential for innovative applications across industries, marking a significant advancement in sensing technology.

3.1 Introduction

Ethanol, a typical volatile organic compound (VOC) has deeply penetrated our daily lives, however, it is crucial to recognize that its prolonged exposure strongly affects human health by causing nose and throat irritation, vomiting, kidney failure, nausea, headaches, central nervous system damage, and can even cause cancer[1-3]. It is a

flammable gas with an explosion range of 3.3 – 19%, which can lead to many traffic accidents[4]. Ethanol in its vapor form combines with other gases which creates an explosive mixture[5-7]. Addressing the immediate and potential risks linked to the exposure of ethanol to both human health and the environment has emerged as a top priority. Researchers have shown significant interest in chemiresistive sensors for detecting VOCs, among various sensor types[3]. This enthusiasm stems from the sensor's affordability, straight forward monitoring methods, simple design, and high chemical stability as well as thermal stability [3, 4, 8].

In the realm of gas sensing materials, researchers confront numerous challenges in terms of sensitivity, selectivity, stability, and several other aspects to satisfy the rising demand for highly efficient sensing devices[9]. Therefore, the growing emphasis on developing newer sensing materials capable of detecting volatile, toxic, and flammable gases is becoming important to overcome crucial environmental challenges such as pollution, health risks, climate instability, and many more [10, 11]. In recent years, there has been a surge in attention towards tin sulfide (SnS) among researchers involved in sensor technology, photodetectors, solid-state batteries, photovoltaic cells, and holographic recording media[10, 12]. It is a metal chalcogenide semiconductor that is non-toxic, cheap, highly stable, widely available, and has a distinctive layered structure [13-15]. It has an indirect bandgap of ~ 1.3 eV, a high concentration of majority charge carriers ($10^{15} - 10^{18} \text{ cm}^{-3}$), and a high Hall mobility of $\sim 100 \text{ cm}^2/\text{V.s}$ [16, 17]. These properties collectively position SnS as a promising prospect for investigation in ethanol gas sensing applications. Few research studies based on SnS for ethanol gas sensing applications have been reported. For example, Afsar et al. synthesized SnS nanoflakes for the detection of ethanol at different temperatures ranging from 25 °C to 200 °C. The response of SnS nanoflakes was improved as the temperature was increased to 200 °C [12]. In another study, Ma et al. hydrothermally synthesized flower-like n-type SnS bonded by PVDF (vinylidene fluoride) for ethanol sensing application. The sensor displayed a response at an optimum temperature of 240 °C [18]. All of the aforementioned studies demonstrate that SnS-based gas sensors operate at high temperatures. Elevated operating temperatures pose challenges to sensor durability, device fabrication, and sustained sensitivity and stability of various applications [19]. Additionally, factors

such as flexibility, low power consumption, and miniaturization become difficult to achieve at high-temperature conditions [20-23]. Therefore, in this paper, we have solvothermally synthesized SnS for the detection of ethanol at room temperature (27 °C).

To the best of our knowledge, no reports are focussing on room-temperature chemiresistive sensing of ethanol based on solvothermal synthesized SnS nanoplates. Solvothermal synthesis is highly favored among various synthesis techniques due to its cost-effectiveness, high yield of the material, utilization of mild synthesis conditions, minimal energy requirements, and simple equipment, along with the benefit of control over the morphology of the synthesized structures. Tin sulfide (SnS) is a promising material for gas sensing applications due to its unique properties and ability such as high surface-to-volume ratio, durability, abundance, synergistic effect, and selectivity to form nanocomposites [10]. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and Brauer-emmett-teller (BET) have revealed the successful formation of vertically aligned SnS nanoplates. The sensor has been fabricated using the electrophoretic deposition (EPD) technique and it has been tested for various ethanol gas concentrations. The EPD technique of film deposition has been chosen for film formation due to its numerous advantages, including the achievement of smooth, homogeneous, and uniform films. Moreover, the economic viability of this method makes it a preferred choice for depositing films. Various sensing tests including response, response time and recovery time, repeatability, and selectivity suggest that the sensor operates at room temperature with a high response value. A sensing mechanism has been proposed to explain the room temperature ethanol sensing of the as-fabricated SnS sensor.

3.2 Experimental Section

3.2.1 Chemicals Used in the Synthesis

The chemicals essential for the synthesis included stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99%), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%), and thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99%). All the chemicals belong to AR grade with the highest purity of 99%.

3.2.2 Synthesis of SnS

A single-step solvothermal process was employed to synthesize SnS nanoplates. Briefly, 0.5 M stannous chloride dihydrate was dissolved in 40 ml of ethylene glycol and stirred for 30 minutes. Simultaneously, 1.2 M citric acid and 1.5 M thiourea were dissolved separately in 40 ml of ethylene glycol, with continuous stirring for 30 minutes. The solution of citric acid and thiourea was then mixed with the solution of stannous chloride dihydrate for another hour. The resulting mixture solution was then transferred to a 100 ml stainless steel autoclave which was kept inside a hot air oven at a temperature of 180 °C for 24 h. Finally, the precipitate was washed with DI water and ethanol and dried overnight at 80 °C.

3.2.3 Fabrication of the SnS Sensor

To fabricate the SnS sensor for the detection of ethanol gas, a series of steps were executed. The SnS powder obtained from the above-mentioned procedure was deposited onto the indium-tin-oxide (ITO) sheets using electrophoretic deposition (EPD)[24,25]. In this process, the SnS powder was thoroughly dispersed in acetonitrile at a concentration of 0.5 mg/mL. The solution was placed in an EPD cell equipped with a copper (Cu) wire and a platinum counter electrode. The ITO was attached to the Cu and an optimized constant potential (18 V) was applied for 60 s. This resulted in the formation of the SnS film having active area of deposition $1 \times 1 \text{ cm}^2$, which was then left to air-dry overnight at room temperature. Finally, the thermal evaporation technique (Smart Coat 3.0, Hind High Vacuum) was utilized to deposit silver (Ag) electrodes onto the prepared film. The stainless steel (SS) mask design employed in the silver electrode deposition on the sensing device. During the evaporation, the chamber was maintained at a pressure of 4×10^{-6} mbar. The resulting silver electrodes had a thickness of 100 nm. This film was employed to conduct sensing measurements.

3.2.4 Characterizations

The XRD characterization was performed using a Bruker D8 instrument with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and a scan rate of 0.02° per increment. The morphological

features of the 2D nanostructure were confirmed through field emission scanning electron microscopy (FESEM) analysis. The FESEM images were obtained using a ZEISS Gemini instrument conducted at an accelerating voltage (EHT) of 15 kV. The surface area measurements were determined using the Brunauer-Emmett-Teller (BET) method with a Quantachrome Nova 2200e surface area analyzer, operating at a temperature of 77.4 K. The film of SnS was deposited onto pre-hydrolyzed ITO using the electrophoretic deposition (EPD) technique at a low potential of 18 V for 2 min. Electrochemical impedance spectroscopy (EIS) was conducted to obtain Nyquist plots of wet cells, utilizing a Wayne-kerr 6500B instrument within a frequency range of 20 Hz-120 MHz.

3.2.5 Gas Sensing Measurements

The gas sensing device was probed inside a specialized custom-built closed chamber crafted from stainless steel[26]. The SnS sensor receives a constant current from the source measuring unit (SMU). To initiate the ethanol detection process, an initial rough vacuum pressure was generated within the gas sensing chamber using a rotary pump. Subsequently, dry air was introduced for 50 s to establish the baseline resistance. Following this, a mixture of 1% ethanol gas balanced with dry nitrogen gas was introduced into the gas sensing chamber. Within the gas sensing chamber, the ethanol gas concentration was determined in parts per million (ppm) using the following equation:

$$C = \frac{22.4 \times \Psi \times \rho \times V_1}{M \times V_2} \times 1000 \quad (3.1)$$

In this formula (Eq. 3.1), the concentration of ethanol gas (C) in ppm was calculated based on the volume fraction (Ψ), the density of ethanol (ρ in kg.m^{-3}), volume of ethanol gas (V_1 in L), molecular weight of ethanol (M in kg.mol^{-1}), and volume of the gas sensing chamber (V_2 in m^3)[27, 28]. To measure the temperature, the SnS sensor was positioned on the substrate holder with a surface temperature controlled through a thermocouple-based feedback mechanism. A LabView data acquisition software,

connected to the source measuring unit, was employed to monitor and record the fluctuations in resistance exhibited by the SnS sensor.

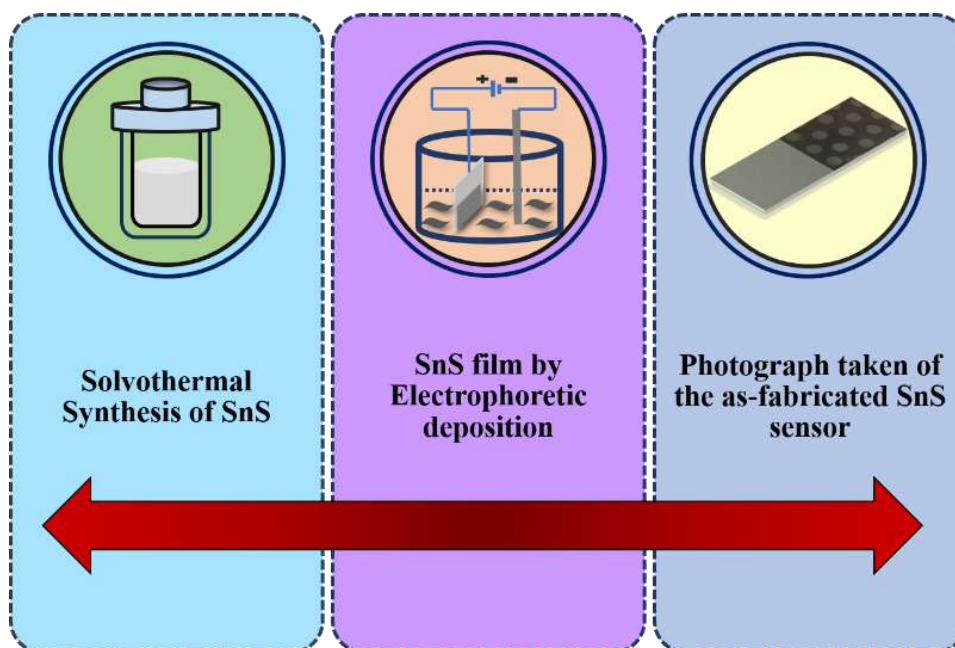


Fig. 3.1: Schematic representation of fabrication of the SnS sensor.

3.3 Results and Discussion

3.3.1 Structural Elucidation Using XRD

X-ray diffraction pattern (in the range of $20^\circ - 80^\circ$) of SnS nanoplatesis displayed in Fig. 3.2. From the XRD pattern crystallinity studies (which includes interplanar spacing and phase formation) of the as-synthesized sample is analysed [29]. The diffraction peaks of as-synthesized SnS nanoplates (Fig. 3.2) are attributed to (101), (201), (210), (011), (111), (311), (102), (020), (112), (511), (221), (601), (420), (512), and (711) planes of pure orthorhombic phase of SnS with the space group Pbnm (62) (JCPDS card no. 390-354) characterized by lattice parameters $a = 4.313 \text{ \AA}$, $b = 11.258 \text{ \AA}$, and $c = 3.995 \text{ \AA}$. [30]. The interplanar spacing of the six highest intensity peaks is calculated using Bragg's relation: $n\lambda = 2d \sin\theta$. Where 'n' denotes an integer, and 'd' represents the spacing between crystal lattice planes [31]. Table 3.1 presents the d-spacing values calculated for various high-intensity planes of SnS nanoplates.

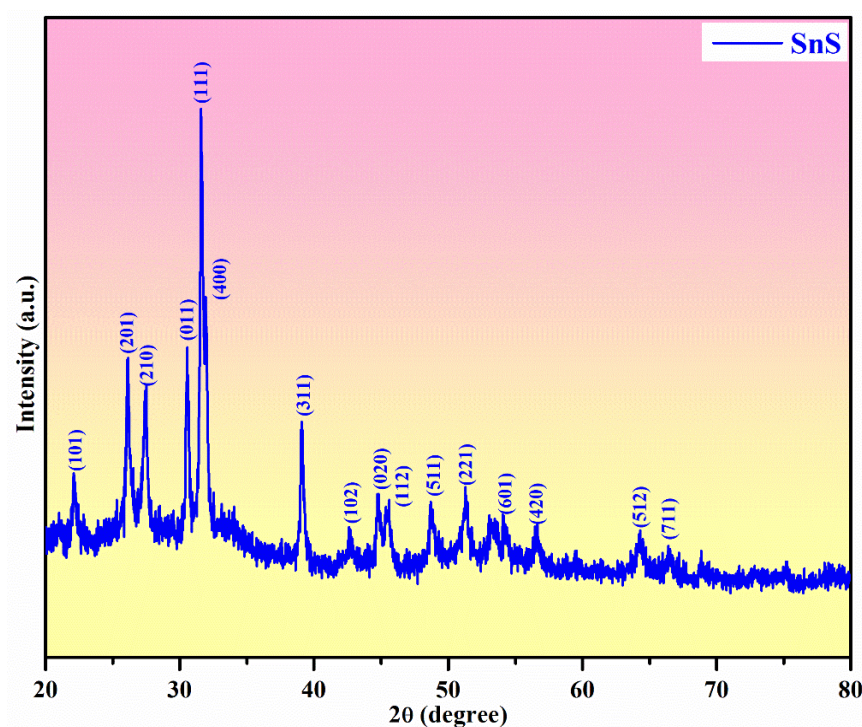


Fig. 3.2: XRD spectrum of SnS nanoplates.

Table 3.1: d-spacing values calculated for various planes of SnS nanoplates.

Sample	2θ (degree)	hkl planes	d spacing (nm)
SnS	26.02	(201)	0.342
	27.40	(210)	0.325
	30.6	(011)	0.291
	31.5	(111)	0.283
	31.9	(400)	0.280
	39.08	(311)	0.230

A prominent peak observed at $2\theta = 31.5^\circ$, corresponding to the (111) reflection plane of as-synthesized SnS. In this structure, Sn and S atoms are tightly bonded in layers with weak Van der Waals forces. This indicates that the nanoplates are polycrystalline SnS with a strong (111) reflection plane [30,31]. The preferred orientation of the nanoplates is likely due to the growth process being controlled by nucleation. Additionally, mechanical processing such as grinding can introduce strain, which may alter the preferential orientation. These factors collectively contribute to the observed (111) orientation in as-synthesized sample. Our findings are consistent with previous studies on SnS nanostructures.

3.3.2 Surface Morphology and Surface Area Analysis by FESEM, BET Isotherm

FESEM analysis is done to study the morphology of the as-synthesized SnS. As displayed in Fig. 3.3 (a and b) for different magnifications of FESEM, the sample so formed shows vertically aligned SnS nanoplates. The nanoplates are stacked over one another and are found to be interconnected compactly. Such type of morphology provides a high surface area for the adsorption of gases in the field of gas sensing [32]. To investigate the specific surface of the SnS nanoplates, the Bruanauer-Emmett-Teller (BET) technique is utilized as shown in Fig. 3.4.

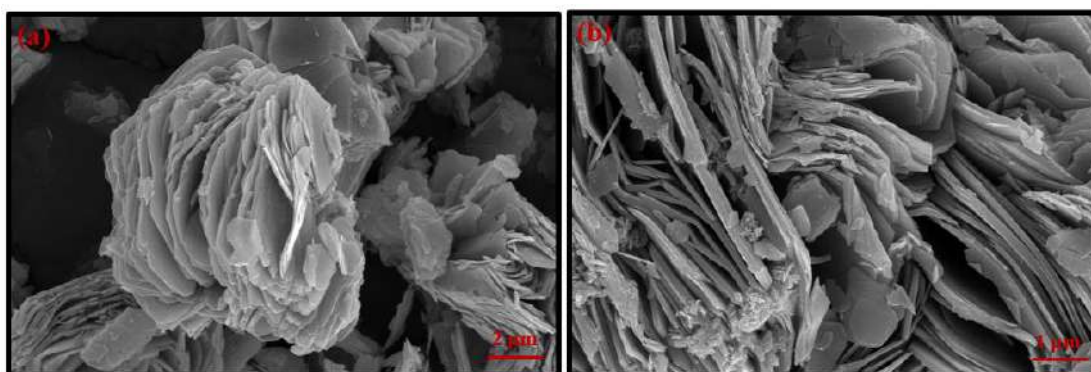


Fig. 3.3 (a and b): FESEM images of as-synthesized SnS nanoplates.

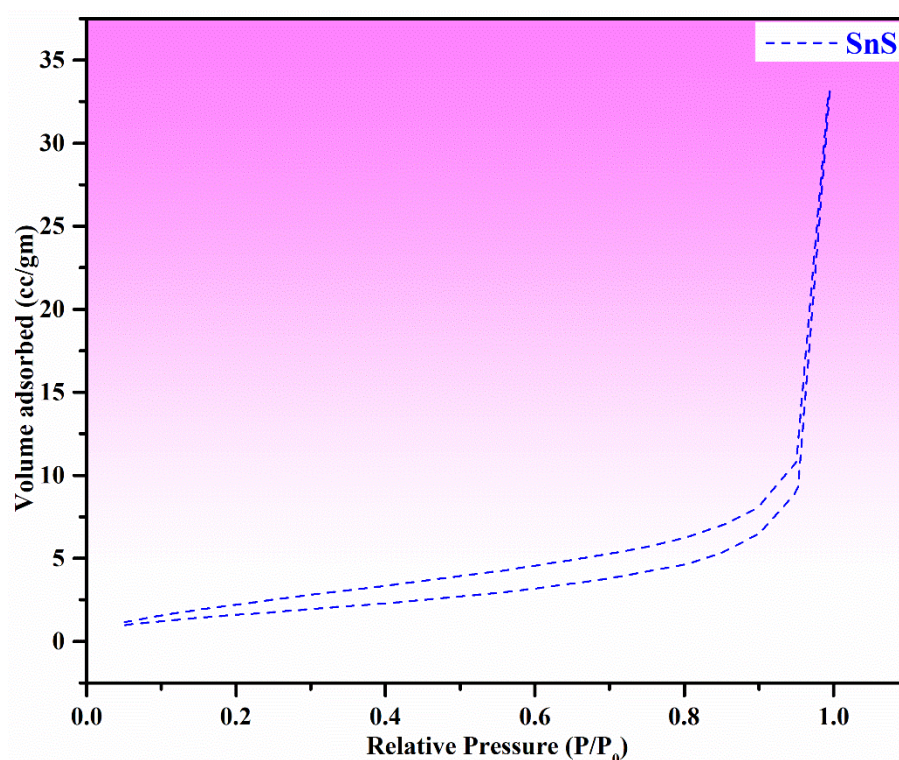


Fig. 3.4: BET analysis: N_2 adsorption-desorption isotherm of SnS nanoplates.

Nitrogen gas is selected as the probing gas to generate adsorption-desorption isotherms. The SnS nanoplates exhibit type-IV behavior with hysteresis which is consistent with the IUPAC classification[33]. The specific surface area of the SnS nanoplates is calculated using the multipoint BET method, yielding a value of $6.45 \text{ m}^2 \text{ g}^{-1}$.

3.3.3 Ethanol Gas Sensing Performance Test at Room Temperature

3.3.3.1 Response of the Sensor toward Various Concentrations of Ethanol Gas

The ethanol gas sensing measurements are performed for the three different concentrations of ethanol i.e. 100 ppm, 200 ppm, 300 ppm, and 400 ppm at room temperature. Fig. 3.5 displays the performance of the sensor in terms of resistance vs time profile for the ethanol gas at room temperature. The sensing response of the device is computed by the following expression:

$$R = R_g/R_a \quad (3.2)$$

where R_g is the resistance of the sensor in the ethanol environment and R_a is the initial resistance of the sensor in air. Using the above expression, the response of the sensor is calculated to be 6.7, 9.6, 12.4, and 17.4 at ethanol gas concentrations of 100 ppm, 200 ppm, 300 ppm, and 400 ppm respectively.

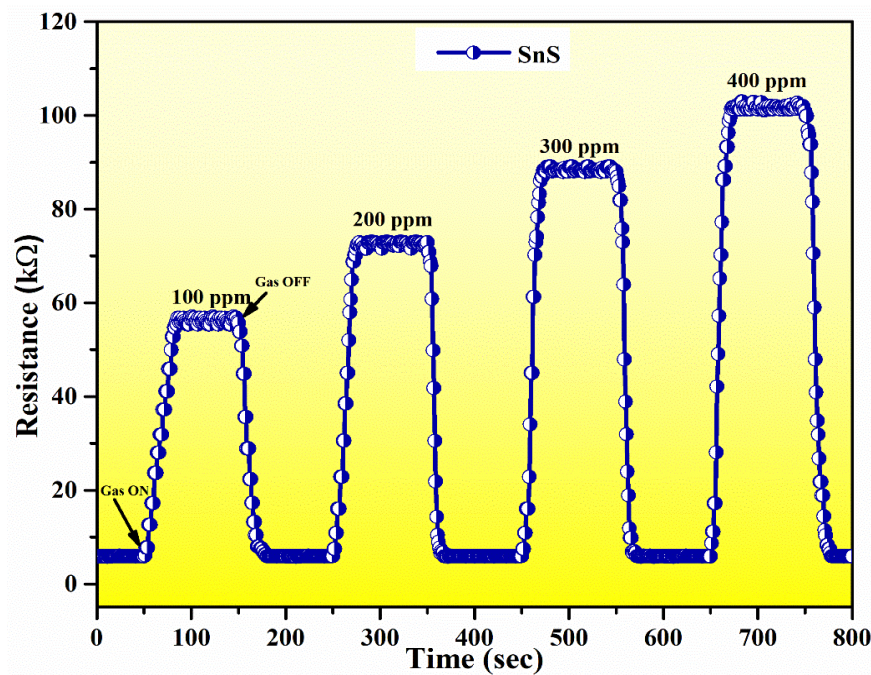


Fig. 3.5: Real-time change in resistance of the SnS sensor with various concentrations of ethanol gas at room temperature

Importantly, it is observed that with an increase in ethanol concentration, the response increased significantly. As the ethanol gas is turned off in the chamber the resistance of the sensor recovers to its initial state quickly. These findings prove that the SnS sensor exhibits a good response to ethanol gas at room temperature despite prior studies showing that the ethanol sensor based on SnS works at high temperatures.

3.3.3.2 Response and Recovery Time of the Sensor

The sensor's response time (t_{resp}) is determined to be 25.3 s, 19.6 s, 15.2 s, and 12.4 s for ethanol gas concentrations of 100 ppm, 200 ppm, 300 ppm, and 400 ppm, respectively as displayed in Fig. 3.6. The recovery time (t_{rec}) is calculated to be 7.4 s, 13.8 s, 16.9 s, and 20.3 s for corresponding gas concentrations as displayed in Fig. 3.6. The response time of a sensor is the time required to reach 90% of its maximum response from the baseline, while the recovery time is the time needed to return to 10% of the baseline after reaching the maximum response.

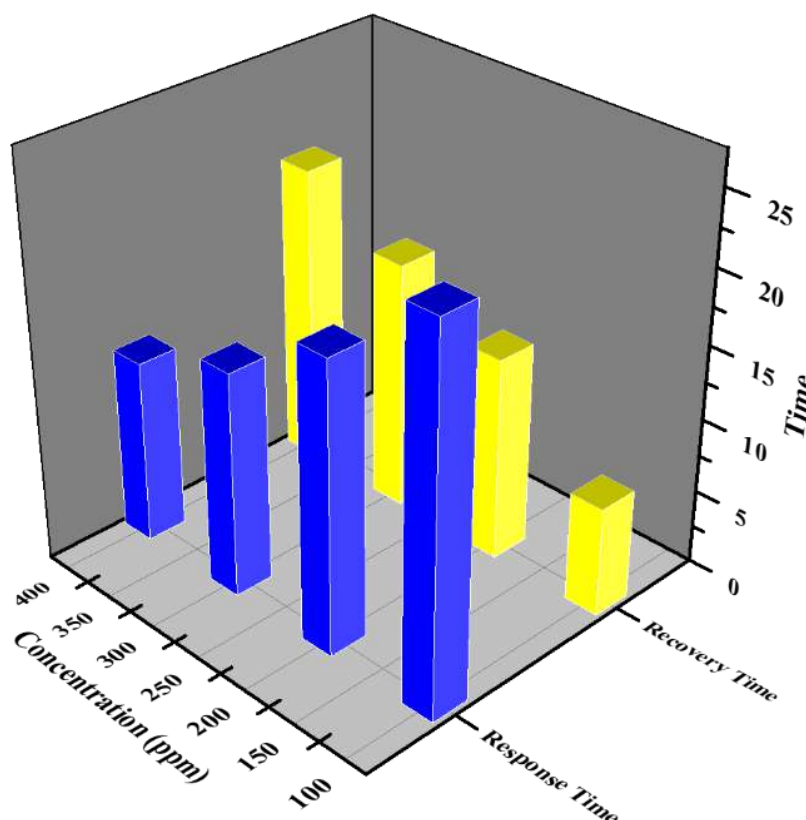


Fig. 3.6: Bar chart showing a variation of Response time and Recovery time wrt. concentration of ethanol gas at room temperature.

Notably, an observable trend emerges: as the concentration of the ethanol gas increases, the response time exhibits a decrease while the recovery time demonstrates an increase. A reduction in response time could be attributed to the presence of ample sites on the sensor's surface, facilitating efficient gas adsorption. Conversely, the prolonged recovery time may arise from the chemisorption of the ethanol molecules and the subsequent desorption of their reaction products from the sensor's surface, which necessitates additional time.

3.3.3.3 Repeatability of the Sensor

In assessing the real-time application of the SnS sensor, we observed remarkable repeatability across three successive test cycles of ethanol gas. The corresponding repeatability results for the SnS sensor are depicted in Fig. 3.7 highlighting its consistency. The repeatability test involved maintaining a constant concentration of 400 ppm of ethanol gas within a sequence of dry air-ethanol gas-dry-air at room temperature. Notably, the sensor resistance exhibits a nearly identical pattern for 400 ppm ethanol gas, showcasing the exceptional reversibility of the SnS sensor in its responsiveness to ethanol gas.

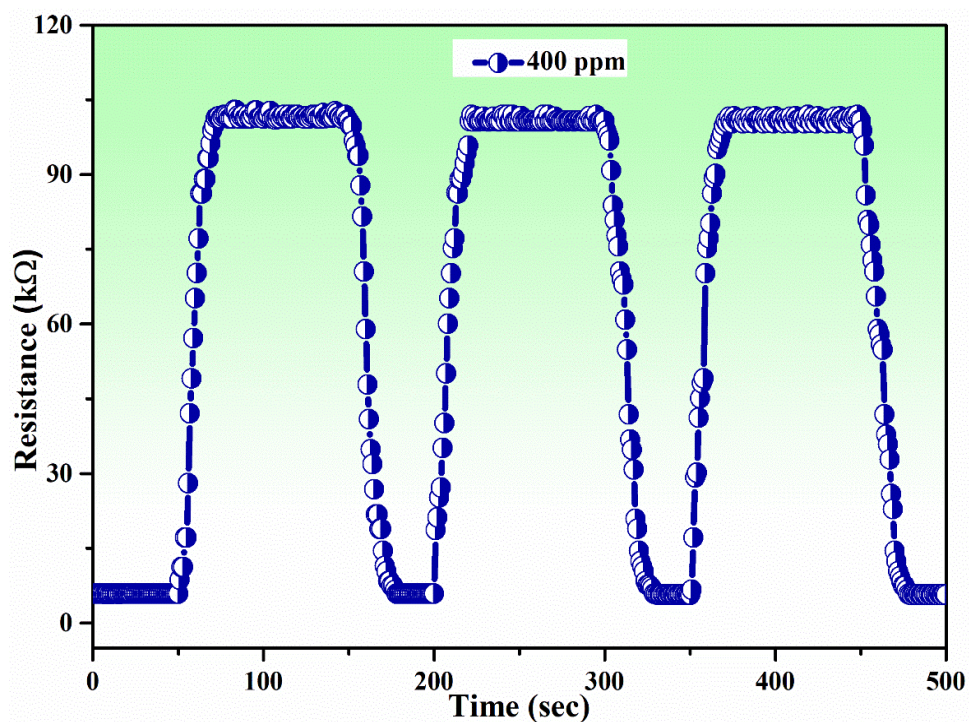


Fig. 3.7: Repeatability test SnS sensor towards 500 ppm of ethanol gas at room temperature.

3.3.3.4 Stability and Selectivity of the Sensor

In addition to the above-mentioned sensing parameters (i.e. response, response time, recovery time, repeatability) a reliable sensor should demonstrate prolonged stability and selectivity. The long-term stability of the SnS sensor is illustrated in Fig. 3.8 when it is exposed to 400 ppm ethanol gas for a continuous 15 mins. Remarkably, the sensor exhibits outstanding stability throughout the duration, showing no signs of degradation.

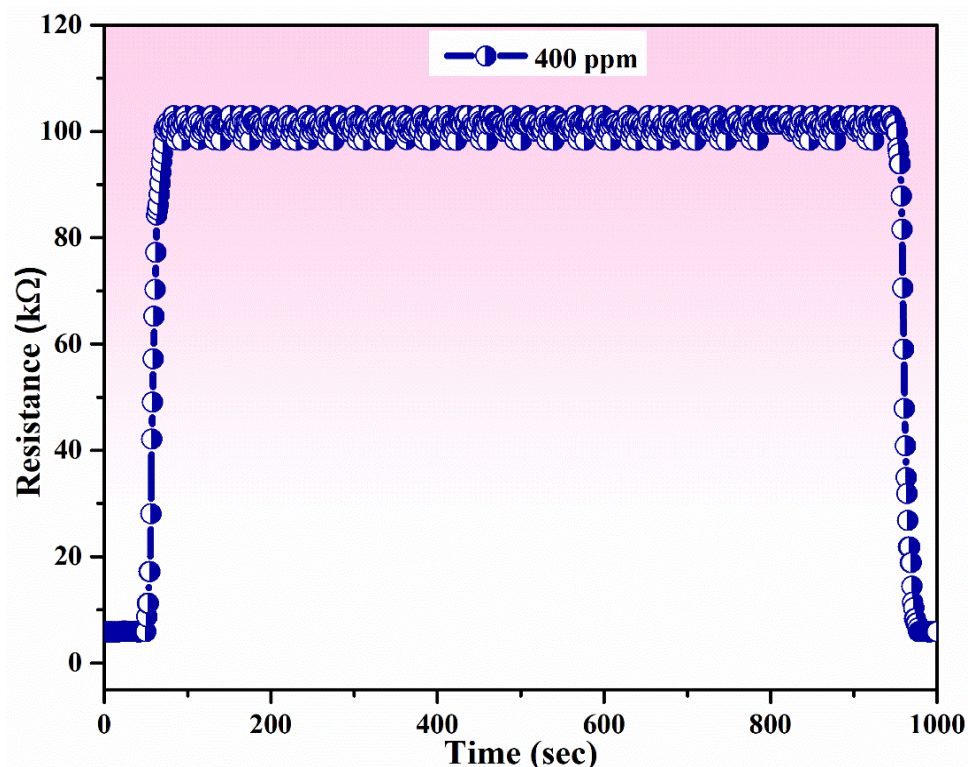


Fig. 3.8: Long-term stability of SnS sensor exposed to 400 ppm ethanol gas for 15 mins at room temperature.

The sensor's ability to selectively detect specific gases in diverse environments is investigated by analysing its cross-response. This involves testing the SnS sensor with various volatile organic compounds (VOCs), including methanol, acetone, benzene, formaldehyde, and isopropyl alcohol (IPA). The obtained results as illustrated in Fig. 3.9 highlight the sensor's remarkable selectivity. Notably, at a concentration of 400 ppm ethanol, the SnS sensor demonstrated a substantial response of approximately 17.4. in

comparison, its response to other VOCs, such as methanol, acetone, benzene, formaldehyde, and IPA was found to be 9.2, 10.8, 5.4, 2.9, and 3.7 respectively.

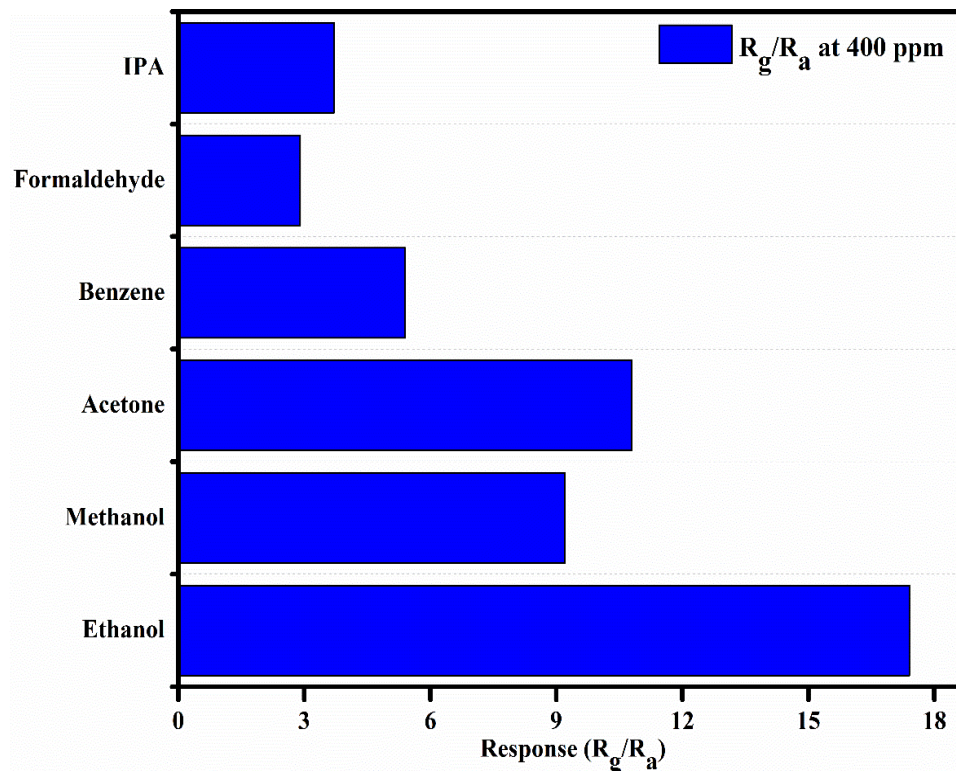


Fig. 3.9: The cross-responses of the SnS sensor towards 400 ppm ethanol and other VOCs.

3.3.3.5 Effect of Humidity on the Sensor

Fig. 3.10 illustrates the effect of humidity on the SnS sensor. As anticipated, the gas sensor's response decreases as the relative humidity (RH) increases. At relative humidity levels of 52%, 61%, and 73%, the corresponding responses were 17.5, 16.2, and 15.1, respectively. The reduction in response caused by humidity is due to a decrease in available adsorption sites, which become occupied by water vapor. As a result, fewer target gas molecules are adsorbed onto the sensing layer, leading to a lower response.

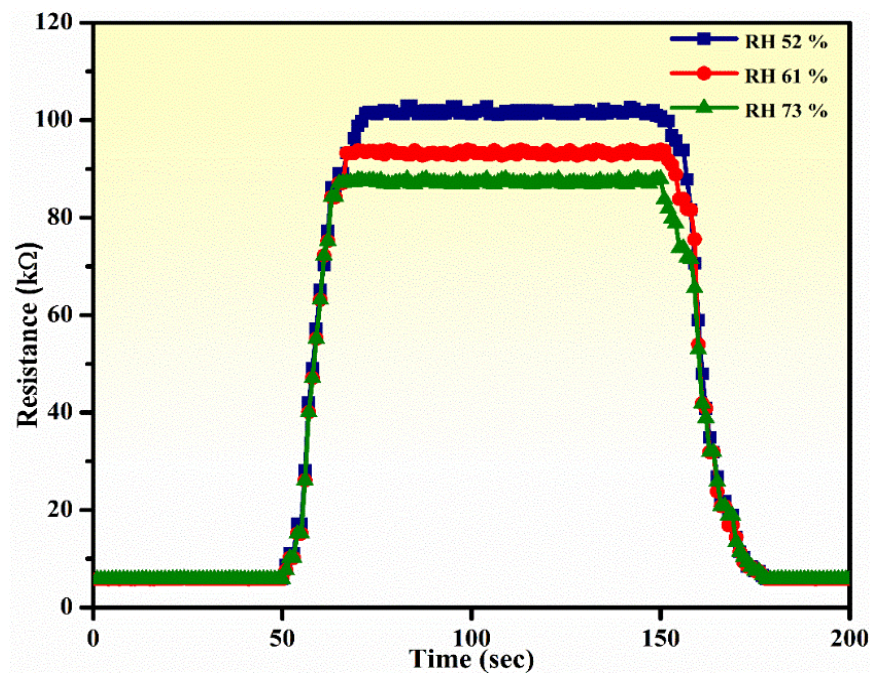


Fig. 3.10: Effect of RH on the response of the SnS sensor to 400 ppm of ethanol gas at room temperature.

Table 3.2: A comparison of performance parameters of this work with previous work for ethanol gas sensing.

Sensor Materials	Concentration (ppm)	Sensor Response	Operating Temperature (°C)	Response/ Recovery Time (sec)	Refs.
SnS	300	13 %	300	29 / 21	[34]
SnS	10	130 %	200	2 / 9	[12]
SnS/PVDF	100	92.96 %	240	1.8 / 90	[18]
SnS/SnS ₂	100	30.12	200	18/14	[35]
PbS/SnS ₂	60	45.64%	RT	104 / 84	[36]
MoSe ₂	500	4.5	RT	11/18	[8]
SnS	400	17.4	RT	12.4 / 20.2	This work

$$\text{Sensor Response } S (\%) = (R_g - R_a / R_a) \times 100 \quad (3.2)$$

3.3.3.6 Limit of Detection of the Sensor

The calibration plot of the sensor response is shown in Fig. 3.11. It illustrates a linear increase in response to an increase in the concentration of ethanol gas, ranging from 100

to 400 ppm. This linear relationship indicates that the sensor's response is directly proportional to the ethanol concentration within this range. The limit of detection (LOD) is calculated using an advanced scientific method. Typically, the LOD is defined as the gas concentration at which the material's response value equals 1. However, when calculating the LOD, it is essential to consider the actual mechanical noise of the equipment. According to the IUPAC definition, a response signal is considered valid when the signal-to-noise ratio is equal to 3. The noise can be calculated as the root-mean-square deviation ($\text{rms}_{\text{noise}}$). The LOD of the sensor is calculated using the formula $(\text{LOD}) = 3 (\text{rms}_{\text{noise}}/\text{slope})$, where the slope is obtained from the fitted calibration curve [37]. The LOD for the fabricated SnS sensor is estimated to be 71 ppm of ethanol. The fitting was done using the linear regression equation ($y = 2.8 + 0.0349x$), where x represents ethanol gas concentration and y represents the response ($\text{K}\Omega$), respectively [38].

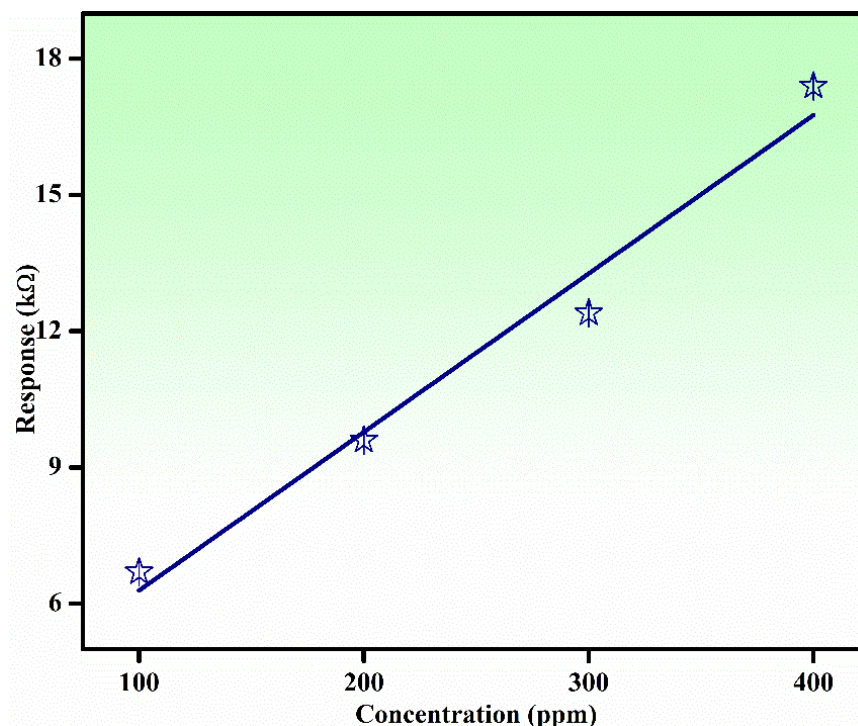


Fig. 3.11: Calibration plot of response ($\text{K}\Omega$) vs ethanol concentration (ppm).

3.3.3.7 Ethanol Gas Sensing Mechanism

To elucidate the gas sensing results, a proposed gas-sensing mechanism of the SnS sensor is illustrated in the schematic diagram (Fig. 3.12). The sensing behavior of the

SnS sensor showed a typical p-type characteristic response during ethanol gas exposure (Fig. 5). When exposed to air, SnS nanoplates adsorb oxygen molecules. The adsorbed neutral oxygen molecules undergo partial ionization transforming into O_2^- ions at room temperature by acquiring electrons from the valence band of the SnS nanoplates as shown in Eq. 3.3 and 3.4:



The reduction of these electrons from the valence band induces a modification in the charge status of the surface of the sensor, creating a positive accumulation layer of holes. Simultaneously, it establishes a negative charge layer of O_2^- ions that extend across the entire surface of the SnS sensor. Consequently, the overall resistance of the sensor decreases, reaching a constant value after saturation. Subsequently, when the SnS sensor is exposed to ethanol gas, molecules of ethanol gas react with the oxygen ions present on the surface of the sensor. This results in the release of electrons which further causes electron-hole annihilation (The reaction is shown in Eq. 3.5.). The overall concentration of the hole is decreased which increases the resistance of the SnS sensor. The overall negative charge on the surface of the sensor is decreased.



The results obtained affirm the superior performance of the developed SnS-based sensor for ethanol detection. Specifically, the sensor exhibits rapid ethanol detection with a high response of 17.4, along with complete recovery at room temperature. The enhanced sensing response to ethanol gas at room temperature can be credited to the distinctive vertically aligned SnS nanoplates. This specific morphology results in a high surface-to-volume ratio which facilitates ample adsorption sites for ethanol gas molecules [39]. Consequently, this reduces response and recovery times while amplifying the overall sensing response. These noteworthy capabilities surpass the achievements of various prior studies focussed on ethanol gas sensing.

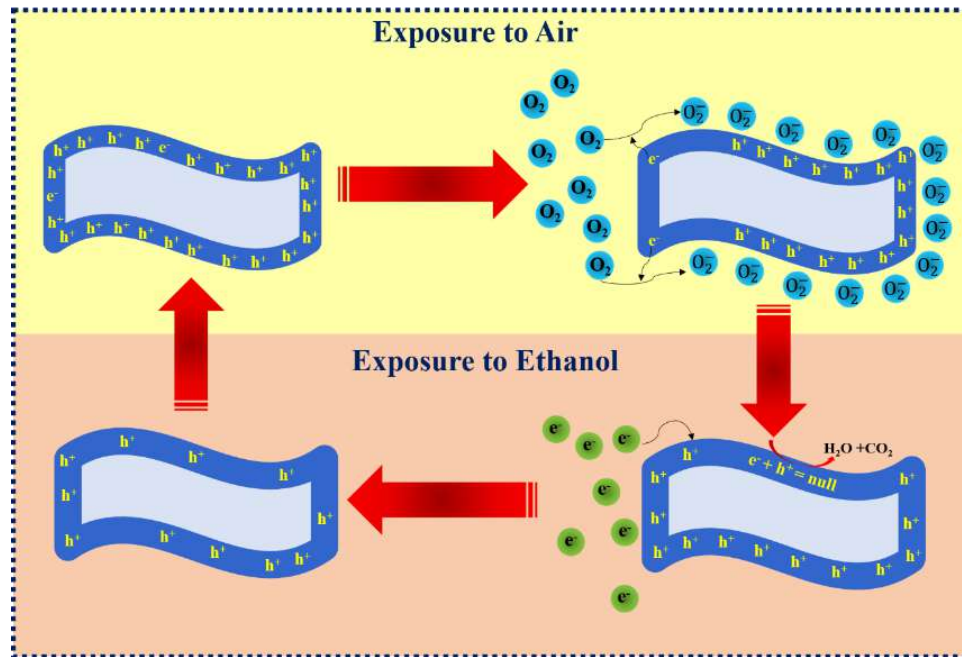


Fig. 3.12: Schematic representation of the interaction mechanism between the SnS sensor and ethanol gas at room temperature.

3.3.3.8 Hall Effect and EIS Measurements

The electrical properties of the prepared SnS thin film with silver contacts at all the 4 edges were measured using the Van der Pauw Hall effect method at room temperature. The resistivity of the prepared SnS film is calculated using following equations:

The carrier concentration (n) was measured by the formula:

$$n = \frac{1}{qR_H} \quad (3.6)$$

where R_H is the Hall coefficient and q is the elementary charge approximately 1.6×10^{-19} C.

$$R_H = \frac{V_H \times T}{I \times B} \quad (3.7)$$

Where, V_H is the Hall voltage (V), T is the Thickness of the sample (cm), I is the Current through the sample, and B is the Magnetic field.

$$\text{Mobility } (\mu) = \frac{R_H}{\rho} \quad (3.8)$$

Where, ρ is the resistivity of the material. [40,41]

The carrier concentration (n), resistivity (ρ), and mobility (μ) was calculated to be $14.20 \times 10^{15} \text{ cm}^{-3}$, $5.2 \text{ } \Omega\text{cm}$, and $84.61 \text{ cm}^2/\text{V.s}$ respectively for the SnS nanoplates.

The complex impedance Z^* (Z'' versus Z') plot for SnS nanoplates was obtained by plotting the imaginary part (Z'') against the real part (Z') at room temperature. The spectra consist of a small semicircle at high frequencies and a larger second semicircle at lower frequencies. The regions of interest for evaluating the grain and grain boundary resistance correspond to the first and second semicircles of the spectra, respectively. In this context, the equivalent circuit used to describe the EIS spectra of the SnS thin film is composed of two RC elements, each consisting of a resistor in parallel with a capacitor, related to the grain and grain boundary contributions [42,43]. The resistance values of the grain and grain boundaries are obtained from the intercepts of the corresponding semicircles with the real axis (Z'), which gives (R_g) and (R_{gb}). The grain resistance (R_g) exhibited by the Nyquist curve is nearly $40 \text{ } \Omega$, and the grain boundary resistance (R_{gb}) is $(3.2 \times 10^2) \text{ } \Omega$.

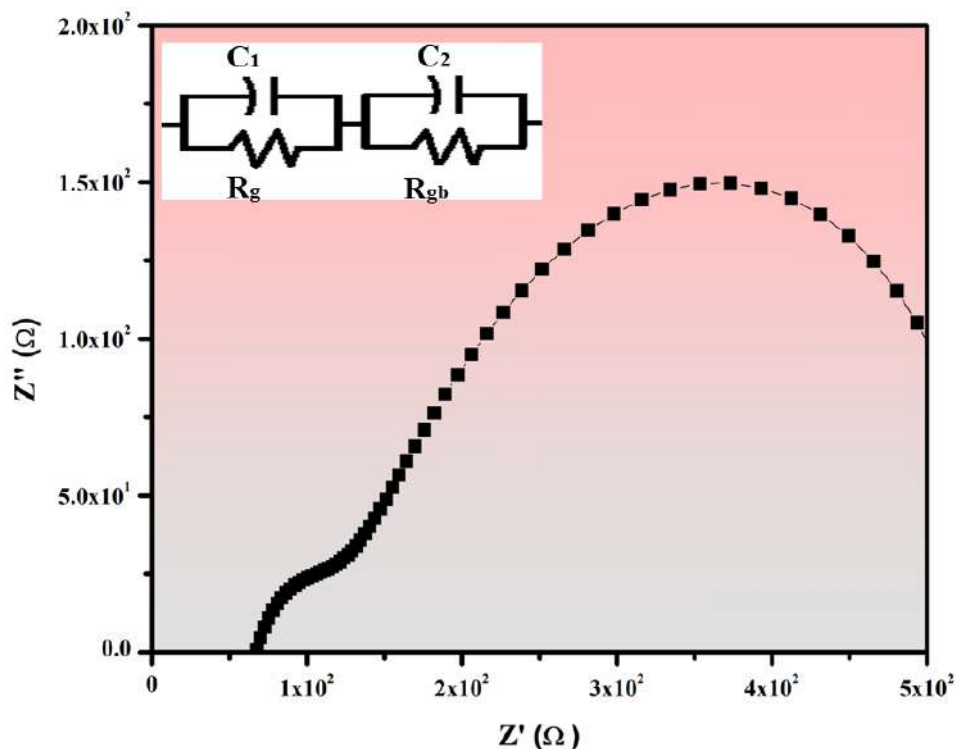


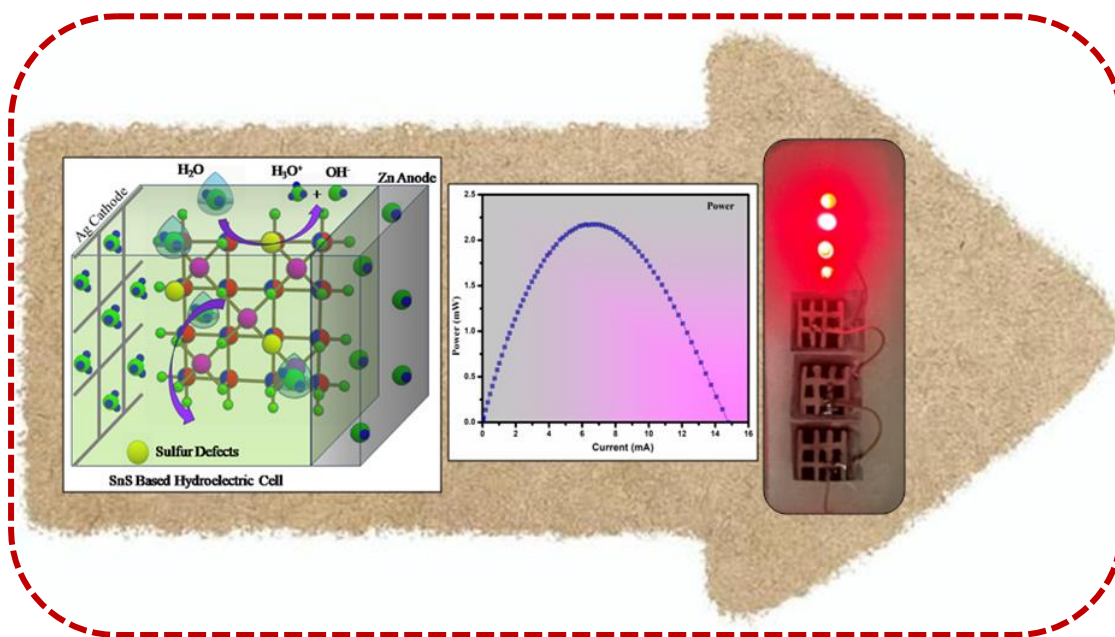
Fig. 3.13: Impedance spectrum and equivalent circuit diagram of SnS nanomaterial.

3.4 Conclusion

In summary, a highly sensitive ethanol gas sensor based on vertically aligned SnS nanoplates has been developed successfully. The SnS sensor has demonstrated a significant response of 17.4 and a quick response/recovery time of 12.4/20.2 sec when exposed to 400 ppm ethanol gas at room temperature. The sensor exhibits commendable sensing attributes including remarkable repeatability of three consecutive cycles and long-term stability of 15 mins to 400 ppm ethanol gas. The sensor showcases an impressive selectivity, particularly discerning ethanol amidst a diverse array of VOCs. The improved ability to detect ethanol gas at room temperature is due to the distinctive vertically aligned SnS nanoplates which offer a notable surface-to-volume ratio, thereby creating abundant sites for the adsorption of ethanol gas molecules, enhancing the sensing response. These findings especially at room temperature, may pave the way for its potential deployment in innovative applications. Its integration into smart, compact, and Internet of Things (IoT)-based systems holds promise for advancements in gas sensing technology. These ground-breaking results emphasize the practicality and versatility of the developed SnS gas sensor in various real-world scenarios.

CHAPTER 4

Strategically Engineered Defects in 2D-SnS for Water Splitting: Green Energy Solution for Powering LEDs with Hydroelectric Cells



In the previous chapter, a two-dimensional (2D) SnS-based chemiresistive sensor was successfully designed and evaluated for ethanol detection under room-temperature (RT) conditions. The developed sensor exhibited a markedly improved sensing performance, including higher response magnitude, faster response and recovery times, and enhanced reproducibility compared to several previously reported ethanol sensing systems. Encouraged by the superior sensing characteristics of 2D-SnS, the investigation was further expanded to explore its multifunctional potential beyond gas sensing. Recognizing that surface defects play a critical role in adsorption-driven processes, controlled defect engineering was strategically introduced into the 2D-SnS nanomaterial. The purpose of defect induction was to enhance surface reactivity, increase sulphur vacancy, and promote improved interaction with water molecules. The defect-engineered 2D-SnS was subsequently employed for the fabrication of a hydroelectric cell (HEC) device aimed at sustainable energy harvesting. The fabricated SnS-based HEC, with an area of 4 cm², delivers a short circuit current of 15 mA, an

open circuit voltage of 0.74 V, and an offload output power of 11.1 mW. The practical feasibility of the developed HEC was demonstrated by successfully powering light-emitting diodes (LEDs), highlighting its potential as a low-cost, eco-friendly, and portable energy source. Thus, the research establishes a coherent progression from room-temperature ethanol sensing to green energy generation using a unified 2D material platform. This transition underscores the multifunctional capability of 2D nanomaterials, bridging environmental monitoring and sustainable energy technologies within a single material framework.

4.1 Introduction

The development of green energy system has become essential for solving the issues posed by electricity demand and deterioration of the environment [1]. As the depletion of fossil fuels looms and the global population burgeons, there is a pressing need to meet rising energy demands while mitigating environmental pollution [2,3]. Also, the global warming and climate change have been compounded by rising greenhouse gas emission, which are driven by the need to meet the energy demands of a growing technology like gadgets, sensors, and etc. [4]. The scientific community has been making continuous efforts to obtain green energy through photocatalytic water splitting from available renewable energy sources, thus contributing to meet the world's energy needs [5,6]. Recently, hydroelectric cells (HEC) have garnered significant attention owing to their cost-effectiveness, environmentally friendly nature, and production of nontoxic by-products [7]. HEC is also an incredibly efficient method for generating hydrogen gas as a byproduct, which serves as a green fuel and can be utilized in fuel cells [8]. In this way, HEC because of its green energy source of electricity production by water splitting can be considered as an excellent substitute for the other energy sources such as solar system and hydropower [9,10]. Extensive research efforts have been directed towards exploring various ferrites, metal oxides, and their nanocomposites, with the aim of facilitating green energy generation through hydroelectric cells, eliminating the need for acids, electrolytes, light, or specific temperature conditions [10-11]. Key factors like porosity, lattice strain, and defects (including oxygen vacancies) are crucial in facilitating water dissociation on the material's surface. Electric current is generated through a redox reaction occurring at

zinc and silver electrodes, which are affixed to opposite faces of the pellet fabricated as HEC [12-13]. Various materials, including $\text{Mg}_{0.8}\text{Li}_{0.2}\text{Fe}_2\text{O}_4$, Al_2O_3 , TiO_2 , and MgO , have been explored for hydroelectric cell (HEC) applications. In 2016, it was reported that $\text{Mg}_{0.8}\text{Li}_{0.2}\text{Fe}_2\text{O}_4$ -based HECs produced a short-circuit current of 8 mA, marking a significant milestone [7]. Additionally, several other metal oxides have been investigated, with SnO_2 yielding a short-circuit current of 22.2 mA, Al_2O_3 producing 6.5 mA, TiO_2 generating 2.3 mA, and MgO yielding 1.5 mA [14]. Gupta et al. elaborated on the impact of doping on ZnO-based HEC output, demonstrating an enhancement of short-circuit current from 9 mA in pure ZnO to 25 mA for K-doped ZnO [15]. Furthermore, a Mg-doped Al_2O_3 -based HEC exhibited a short-circuit current of approximately 16 mA [12].

Extensive exploration of various oxides, along with dopants and composites, has motivated further investigation into new materials with enhanced properties. The Metal oxide semiconductors (MOS) prepared for hydroelectric cell have certain limitation such that the defects can be induced at high temperature only [16-17]. Therefore, development of new material for HEC is required that can be synthesized at lower temperature and has more active sites for water splitting [18]. In recent years, 2D nanomaterials have garnered significant research interest due to their potential as foundational building blocks for the next generation of electronic devices [19]. These 2D semiconductor nanomaterials exhibit appealing electrical properties, including higher intrinsic mobilities compared to those found in organic electronics [20]. These materials exhibit enhanced electronic mobility, a high surface-to-volume ratio, and rapid response to surrounding environmental changes [21]. 2D nanomaterials, characterized by their layered structure, naturally form 2D nanomaterials due to stronger in-plane bonding relative to their out-of-plane van-der Waals interactions between layers [22,23].

Recently, transition metal chalcogenides (TMCs) have drawn significant attention for their promising applications in hydroelectric cells. Notably, layered SnS has garnered significant attention for its unique properties, finding applications in gas sensors, supercapacitors, photodetectors, resistive switching, hydrogen evolution reaction photocatalysis, solar cells, and more [24-28]. Significant efforts have been directed

towards engineering layered SnS structures to increase the number of exposed sites [29]. SnS is a material that naturally exhibits p-type properties due to excess of sulphur (S) atoms. However, some authors have reported that the presence of sulphur (S) vacancies can impart n-type properties to SnS [30,31]. An alternative explanation for the n-type behavior observed in SnS is intrinsic doping, particularly through a disproportionally Sn-rich stoichiometry. Non-stoichiometry has been acknowledged as an effective strategy for altering majority carriers from holes to electrons in chalcogenides. This is achieved through the formation of anion vacancies and an excess of cations. Specially, an excess of Sn or a deficiency of S has been shown previously to induce n-type behavior in SnS nanostructures [32,33].

In the present investigation, we have synthesized 2D SnS nanosheets by one step solvothermal method for the fabrication of HEC. According to available research, no work has been carried out on SnS nanosheets for the green electricity generation by hydroelectric cell (HEC). The analysis of structure, morphology were done using XRD and FESEM. To explain the presence of sulphur vacancies and defects in the lattice of SnS nanosheets, the spectroscopic techniques such as Raman and PL are used. SnS based HEC demonstrates the remarkable output voltage and short circuit current values of 0.74 V and 15 mA, respectively. The as fabricated HEC produces the maximum power of 11.1 mW. The findings of this investigation are encouraging, indicating that power generation via hydroelectric cell has developed as a viable alternative to other renewable energy sources. Moreover, the utilization of SnS based HEC for water splitting opens avenues for meeting future hydrogen needs.

4.2 Material Structural Characterization

The X-ray diffraction (XRD) pattern was collected using a Bruker D-8 advanced instrument with $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) over a 2θ range of 20–80 degrees to determine the phase and crystallite size of the as-prepared SnS nanosheets. Raman spectra were obtained using a Raman spectrometer (α -Witek 300 RA) with a laser excitation wavelength of 532 nm. Photoluminescence (PL) spectroscopy was conducted to explore the defects of the samples at room temperature. PL spectra were acquired using a photoluminescence spectrometer (Perkin Elmer, LS 55) with a Xenon lamp as

the excitation source, spanning the range of 200–800 nm with an excitation wavelength of 234 nm. Fourier-transform infrared (FTIR) spectroscopy was performed using a Perkin Elmer Spectrum II instrument across the wavenumber range of 400–4000 cm^{-1} to acquire FTIR spectra. The surface morphology of the as-prepared samples was examined using a ZEISS Gemini field emission scanning electron microscope (FE-SEM), and energy-dispersive X-ray spectroscopy (EDX) was performed to confirm the elemental composition. High-resolution transmission electron microscopy (HRTEM) was done using FEI Technai 200. XPS spectra were recorded on a Physical Electronics make PHI 5000 Versa Probe III spectrometer. Additionally, the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) technique was employed to analyze specific surface area, and pore volume, pore size. The voltage and current of the developed hydroelectric cells (HECs) of SnS were measured using a Keithley-2400 source meter. The Cyclic Voltammetry was done using Metrohm Autolab Potentiostat. Electrochemical impedance spectroscopy (EIS) was conducted to obtain Nyquist plots of wet cells, utilizing a Wayne-kerr 6500B instrument within a frequency range of 20 Hz-120 MHz.

4.3 Experimental Section

4.3.1 Materials Required

Stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99%), and Ethylene Glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%). All the chemicals were purchased from Fisher chemicals. The Thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99%) used in this study was purchased from Sigma Aldrich. All the chemicals belong to AR grade with highest purity of (99%).

4.3.2 Synthesis of SnS Nanosheets

The synthesis of 2D SnS nanosheets was conducted via the solvothermal method. The procedure commenced by dissolving 0.1 M of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml of ethylene glycol, followed by continuous stirring for 30 minutes. Subsequently, an appropriate quantity of citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was introduced into the solution. Next, 3.33 grams of thiourea ($\text{CH}_4\text{N}_2\text{S}$) was added, and the mixture was stirred continuously for 1 hour. The resultant solution was then transferred to a 200 ml stainless steel autoclave, sealed, and

maintained at 180 °C for 24 hours before being allowed to cool to room temperature. The resultant black sample was washed several times with deionized (DI) water and anhydrous ethanol through centrifugation, followed by drying at 80 °C for 24 hours. Fig. 4.1 shows the synthesized prepared SnS nanosheets using the solvothermal method.

4.3.3 Fabrication of Hydroelectric Cell

The as synthesized SnS nanosheets were processed into a square pellet (area = 4 cm²), as illustrated in Fig. 4.1, using a hydraulic press by applying pressure of 5.5 tons. The pellet underwent annealing at 300°C for 2hrs to induce sulphur defects. A zinc sheet was attached to one of its faces of the pellet whereas the silver paste was applied over the other face in a comb pattern. Zinc acts as the anode whereas the silver paste acts as the inert cathode. Low-resistance wires were soldered to both electrodes to fabricate a SnS based Hydroelectric cell. Fig. 4.1 shows the fabricated hydroelectric cell based on SnS nanosheets used for electricity generation.

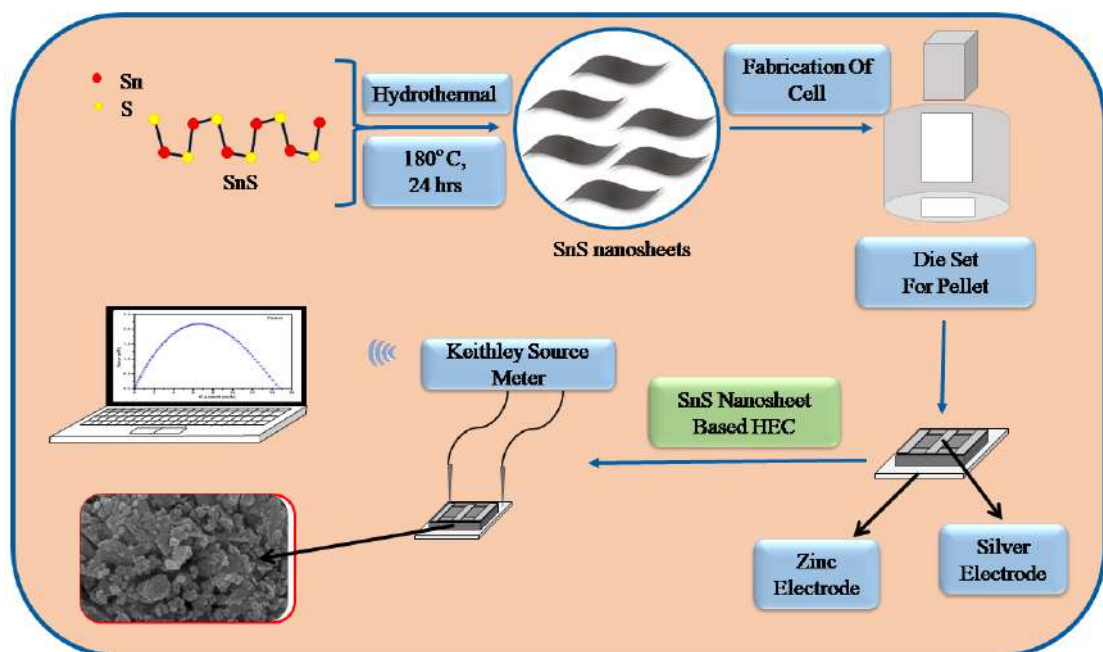


Fig. 4.1: Schematic diagram illustrating the preparation of SnS Nanosheets and fabrication of HEC.

4.4 Results and Discussion

4.4.1 X-ray Diffraction (XRD)

Fig. 4.2 (a) displays the XRD analysis of the as-prepared SnS nanosheets, providing insight into the crystal structure of the synthesized sample through XRD technique. The XRD spectra exhibits distinct peaks corresponding to various crystalline planes of SnS including (101), (201), (210), (011), (111), (400), (311), (102), (411), (020), (112), (511), (221), (601), (420), (512) and (711) at angles of 21.9°, 26.1°, 27.4°, 30.5°, 31.6°, 32.1°, 39.1°, 42.7°, 44.8°, 45.4°, 48.7°, 51.2°, 52.9°, 54.2°, 56.6°, 64.29°, 66.48°, respectively. The diffraction patterns of SnS matches with the standard JCPDS card of orthorhombic SnS (JCPDS 39-0354) [34]. Remarkably, the peaks corresponding to the SnS phase exhibit exceptional sharp and strong intensity, suggesting a high level of crystallinity. Significantly, there were no impurity peaks, such as those attributed to SnS₂ and SnO₂, were detected in the XRD patterns. This suggests that the solvothermal process yielded highly phase-pure and crystalline SnS nanosheets. The interplanar spacing of the four highest intensity peaks was calculated using Bragg's relation:

$$n\lambda = 2d \sin\theta \quad (4.1)$$

Where 'd' denotes the d-spacing values calculated for various high intensity planes of SnS nanosheets. The d-spacing values in Table 4.1 from the XRD analysis of 2D SnS nanosheets provide key insights into the crystalline structure and orientation. These values indicate the distance between atomic planes, confirming the layered structure characteristic of 2D materials and highlighting the nanosheets' preferential orientation, which is essential for applications such as water splitting or optoelectronics where orientation impacts performance.

Table 4.1: d-spacing values calculated for various planes of SnS nanoflakes

Sample	2θ (degree)	hkl planes	d spacing (nm)
SnS	26.01	(201)	0.34
	30.5	(011)	0.29
	31.6	(111)	0.28
	39.1	(311)	0.23

4.4.2 Raman Spectroscopy

Raman spectroscopy is a robust characterization tool for detecting diverse material phases based on discrete vibrational modes that indicate the nature of the chemical bond order of the atomic arrangement. SnS possesses 21 optical active modes, comprising 12 are Raman active modes, 7 infrared active modes, and 2 inactive modes [8]. As per the literature, the reported Raman active modes for SnS include A_g , B_{2g} , B_{3g} , while B_{2u} is identified as the infrared active mode for the SnS nanostructure [35]. Fig. 4.2(b) shows the Raman spectrum of the as prepared sample of SnS for HEC. The spectra exhibit two distinct peaks located at 99, 224. The peaks at 99 cm^{-1} and 224 cm^{-1} corresponded to the characteristic A_g mode of SnS originating from the interatomic vibration between the metal (Sn) and chalcogen S atoms [36-38]. Based on XRD and Raman spectra, It indicates that the as-prepared SnS nanosheets formed orthorhombic phase.

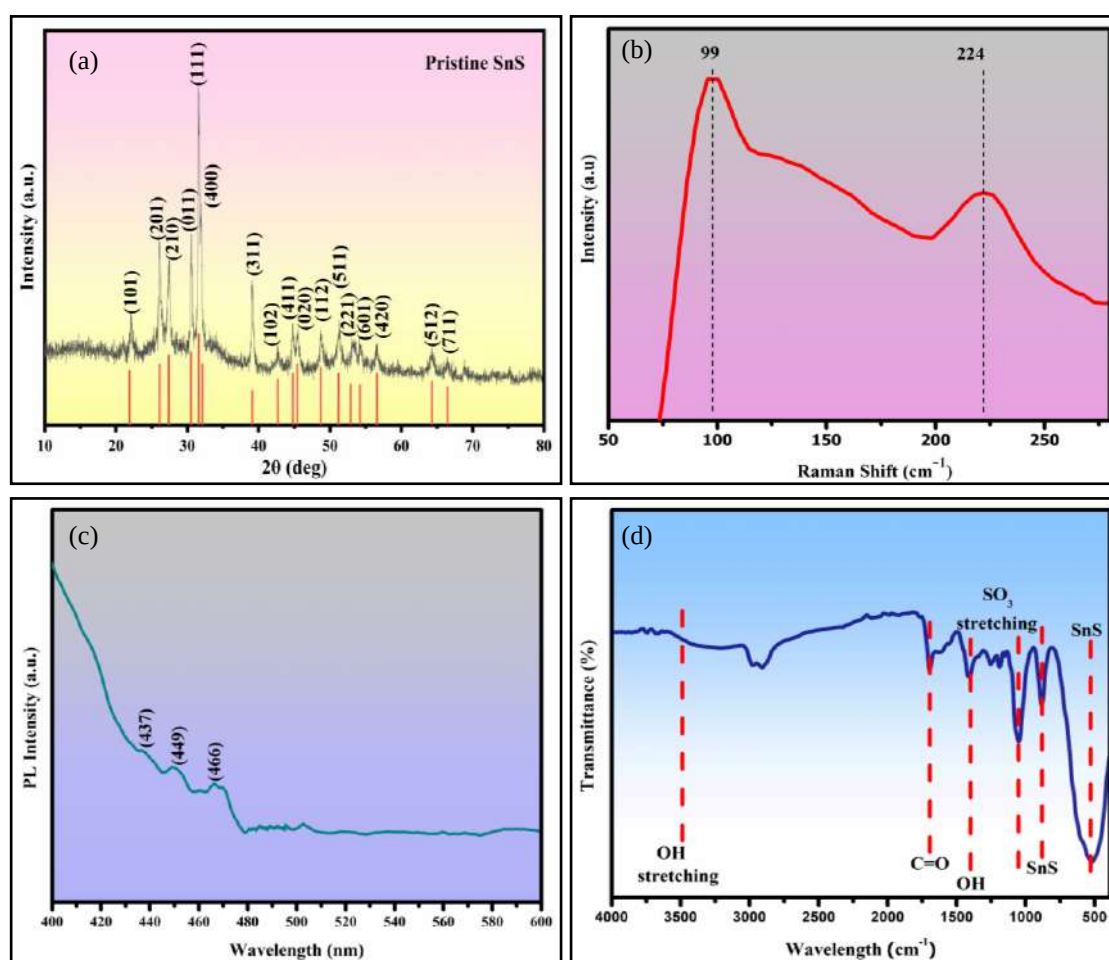


Fig. 4.2: (a) X-ray diffraction pattern, (b) Raman spectra, (c) Photoluminescence (PL) spectra and (d) FTIR spectra of the as synthesized SnS nanosheets.

4.4.3 Defects Study in SnS Nanosheets

PL spectra are a very efficient, non-destructive contactless approach for characterizing and evaluating the quality of surfaces and interfaces, as well as to probing defect levels inside material. The Fig. 4.2(c) shows the PL spectra of SnS recorded at an excitation wavelength of 234 nm in the range of 400-600 nm. It mainly consist of three peaks at 437 (UV emission), 449, 466 (blue emission) nm [39]. The broad emission spectra of the SnS may arise from various defects such as high density of Sn, Sulphur vacancies introduced during the process. Besides sulphur and Tin vacancies, various kinds of defects such as interstitial, stacking faults have also been induced in the nanosheets [18]. The emission peak observed at 437 nm corresponds to Sn interstitial (I_{Sn}) and dangling bonds present at the surface of the SnS pellet [40]. The emission at 466 nm is ascribed to indirect band to band transition and the peak at 449 nm corresponds to Sulphur vacancy (V_S) which plays crucial role for water splitting by HEC at room temperature [41].

4.4.4 Fourier Transform Infrared (FTIR)

Fig. 4.2(d) shows the Fourier Transform Infrared (FTIR) spectrum of the synthesized SnS sample. The sample shows a peak forming at approximately 536 cm^{-1} and 873 cm^{-1} which can be ascribed to SnS bonding [42,43]. There is also a band at 1047 cm^{-1} that is due to SO_3 stretching [44]. The band occurring at 3480 cm^{-1} and 1400 cm^{-1} is typically attributed to the bending vibrations of water molecules (OH) [45]. The weak signal may instead result from surface-adsorbed moisture during sample preparation. The peak near 1750 cm^{-1} could correspond to the C=O stretching vibration, potentially pointing to the presence of carbonyl groups or other oxygen-containing functional groups on the surface. The characteristic peaks of SnS in the FTIR study and XRD result ($2\theta = 31.6^\circ$), confirms the existence of SnS nanostructure. Fig. 4.3(a) shows the structure of the 2D SnS nanostructure and Fig. 4.3(b) shows the induced sulphur vacancies in the SnS nanostructure.

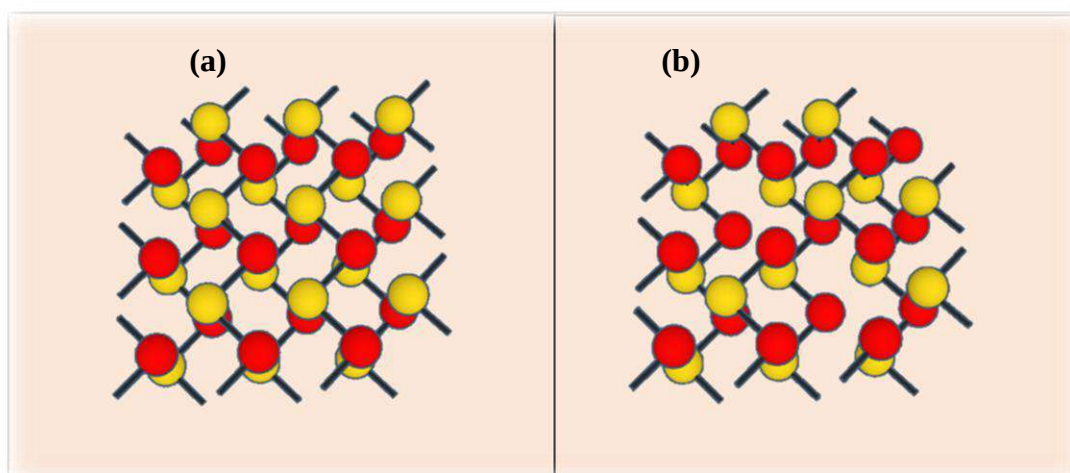


Fig. 4.3: Structure of SnS and S defective SnS ($\text{SnS} + V_S$) where S and Sn atoms are shown as yellow and red balls, respectively.

4.4.5 Surface Morphology and Porosity Analysis

4.4.5.1 Field Emission Scanning Microscopy (FESEM) and Electron Dispersive X-ray Spectroscopy (EDX)

Recognizing the critical role of material microstructure in hydroelectric cell applications, Field Emission Scanning Microscopy (FESEM) serves as a vital tool for investigating the surface morphology of the synthesized sample. The morphology and structures of the SnS sample intended for HEC applications have been examined through Field Emission Scanning Microscopy (FESEM) images, showcased in Fig. 4.4(a). These images highlight the lamellar sheets of different thickness (100-150 nm). The sheets are stacked over one another, demonstrating the occurrence of agglomeration, which may be interpreted as a result of nanosheets attempting to minimize surface energy. The emergence of sheets showcases anisotropic growth and shaped by the unique surface energies inherent to distinct planes. The formation of nanostructures in sheet-like morphology reflects a competitive growth along different crystalline directions. Furthermore, the morphology reveals the presence of a porous network within the sample. Subsequent analysis of this porous network has been conducted using the BET technique. The sample's elemental composition was determined utilizing Energy Dispersive X-ray Spectroscopy (EDX), as shown in Fig. 4(e). The EDX spectra of sample indicated the presence of Sn and S without the presence of any other elements. Elemental mapping images of as prepared-sample further confirmed the uniform distribution of Sn and S in SnS. The Sn/S ratio of SnS nanosheets was determined to be 1.14.

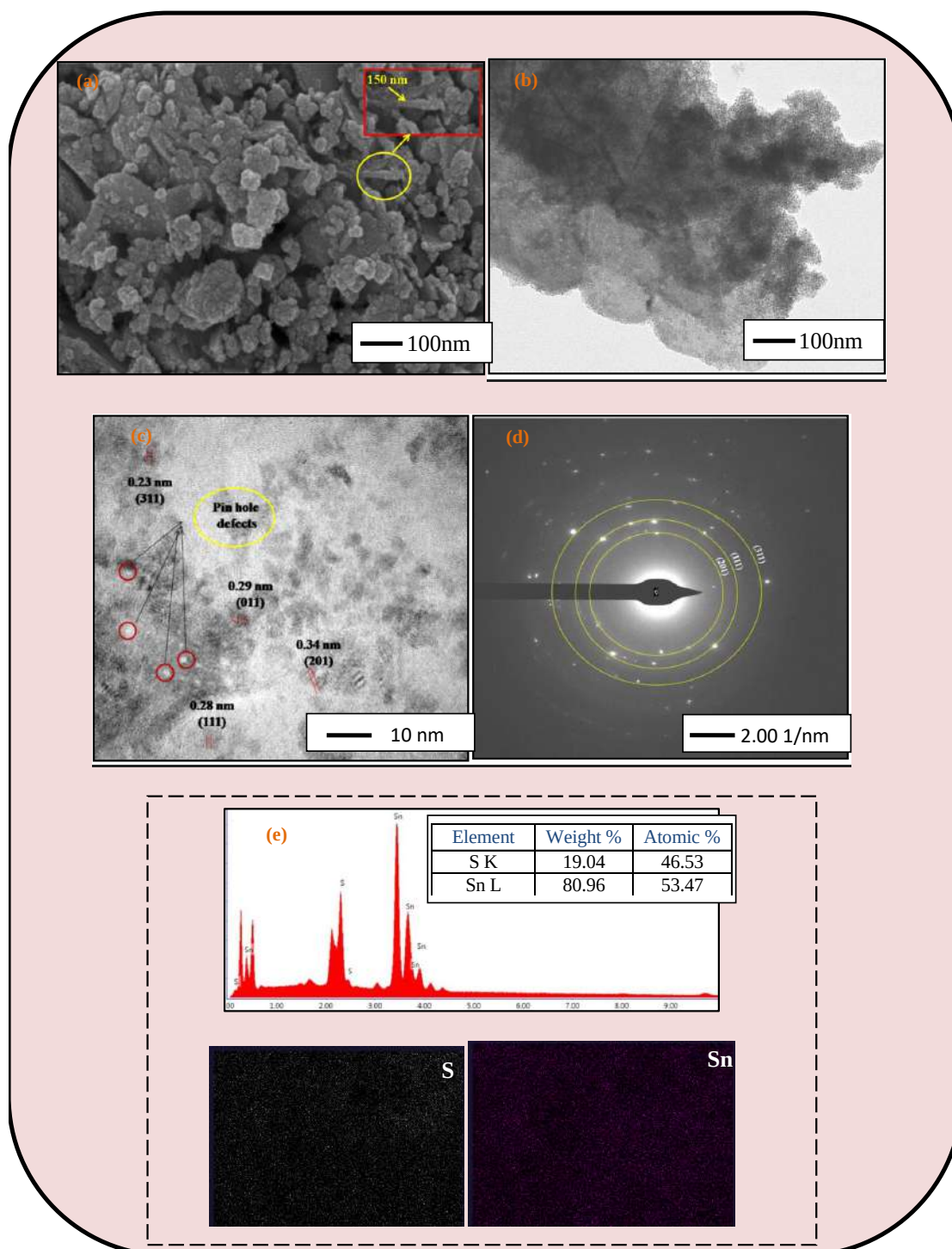


Fig. 4.4: (a) FESEM, (b) HRTEM images, (c) HRTEM with defects and d-spacing, (d) SAED pattern, and (e) EDX spectra and elemental mapping of SnS nanosheets

4.4.6 High Resolution Transmission Electron Microscopy (HR-TEM)

High Resolution Transmission Electron Microscopy (HR-TEM) is conducted by first sonicating a dispersion of SnS sample in ethanol and then loading a single drop of this

dispersion onto a TEM copper grid. Sample's HR-TEM image was acquired to determine the nanostructures shape and size. Fig. 4.4(b) is the bright-field TEM micrograph of as prepared sample for HEC. The HR-TEM image reveals the sheet like morphology of the nanostructures. As shown in Fig. 4.4(c) these sheets are in contact with each other and also show some pin hall defects on its surface that promotes the flow of ions through hydroelectric cell. The SnS sheets produced here have small lateral length, grow randomly and contribute to an overall increase in the stacking length of layers. From Fig. 4.4(c), the measured inter planer distances are 0.28 nm, 0.34 nm, 0.29 nm, and 0.23 nm, corresponding to the (111), (201), (011), and (311) crystallographic planes of the orthorhombic SnS phase (PDF No. 39-0354). These nanosheets form a continuous network that facilitates ion flow in the HEC. In Fig. 4.4(d), the selected area electron diffraction (SAED) pattern further confirms that the measured inter planer distances correspond to the (201), (111), and (311) diffraction planes of the orthorhombic SnS phase (PDF No. 39-0354). The HR-TEM and FESEM results are in fair agreement with each other.

4.4.7 X-ray Photoelectron Spectroscopy (XPS)

XPS, a surface sensitive and non-destructive spectroscopic technique, has been used to explore the oxygen states and surface elements present in SnS nanosheets annealed at 300°C. The XPS profile was recorded, and the findings are illustrated in Fig. 4.5. The survey spectra for SnS sample exhibited characteristic binding energy levels corresponding to Sn and S elements. Importantly, no peaks indicative of contaminants were detected, as shown in Fig. 4.5 (a). The high-resolution Sn 3d spectrum displayed two prominent peaks at 494.9 eV and 486.8 eV, corresponding to the Sn 3d_{3/2} and Sn 3d_{5/2} energy states, respectively, which are characteristic of Sn²⁺ in SnS [57,58]. Additionally, the S 2p spectrum showed peaks at 168.96 eV (S 2p_{1/2}) and 161.8 eV (S 2p_{3/2}), confirming the presence of S²⁻ in SnS [57,58]. It is noteworthy that the detection of Sn²⁺ signals conclusively confirms that the Sn²⁺ oxidation state is the dominant and exclusive oxidation state present in SnS nanosheets annealed at 300°C, indicating the stability and purity of the material under these conditions.

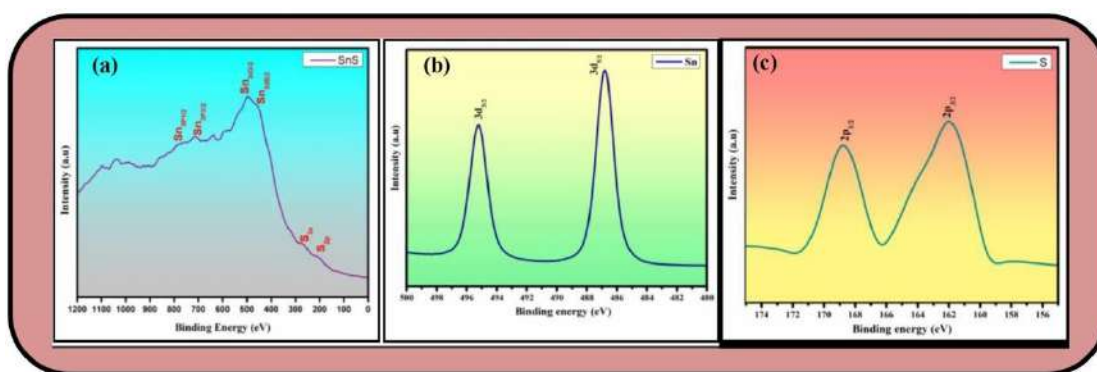


Fig. 4.5: Survey (a) and high-resolution ((b) Sn 3d and (c) S 2p) XPS profiles of SnS nanosheets

Neither technique detected any peaks characteristic of the SnS_2 phase, further corroborating the purity of the SnS phase and the absence of SnS_2 under the given annealing conditions. This comprehensive analysis underscores the stability of the SnS phase at annealing temperature at 300°C , validating the structural and chemical integrity of the sample for potential applications.

4.4.8 BET and BJH Analysis

Surface area and pore size are the important parameter have significant role in water splitting. To get the specific surface area distribution in the as-prepared sample Bruanauer-Emmett-Teller (BET) analysis was done. The nitrogen (N_2) adsorption-desorption isotherm and Barret-Joyner-Halenda (BJH) derived pore size distribution of SnS nanosheets presented in Fig. 4.6(a).

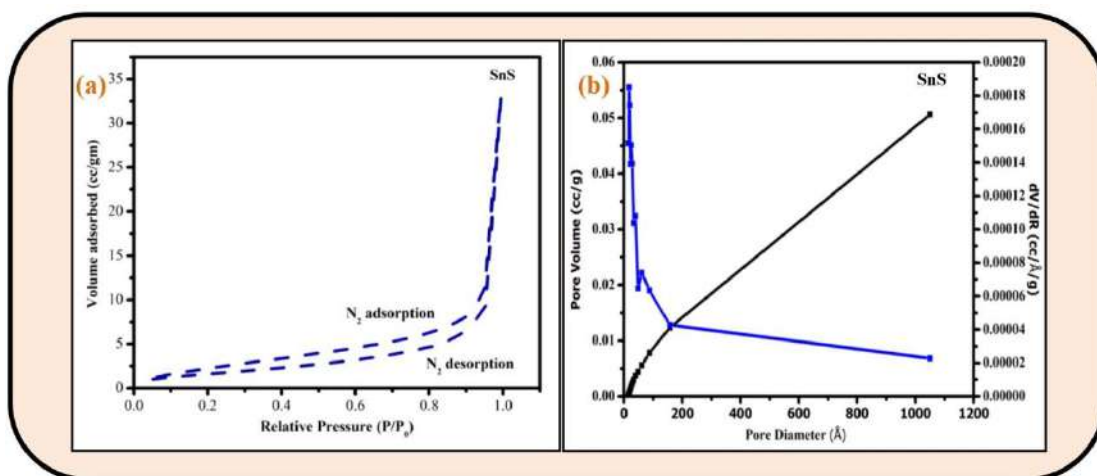


Fig. 4.6: (a) The N_2 adsorption and desorption isotherm and (b) pore size distribution of SnS.

The SnS nanosheets exhibited type IV isotherms with distinct hysteresis at P/P_0 values ranging from 0.1 to 0.9, indicating the presence of mesoporous structures [46]. As depicted in Fig. 6(b), a wide distribution of pore sizes in the range of 50-1050 Å was observed in the SnS nanosheets. Analyses revealed that SnS possesses a mesoporous structure with an average pore diameter 17.07 nm and pore volume $4.9 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$, along with a BET surface area $6.45 \text{ m}^2 \text{ g}^{-1}$. The high porosity observed in the SnS nanosheets is attributed to the removal of S at certain specific sites, providing more active sites for trapping the hydronium ions for further water splitting process.

4.5 Working Performance of SnS based HEC

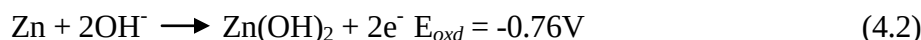
It is well known that metal oxides and metal sulfides have unsaturated or uncoordinated cations $M^{\delta+}$ and vacancies as $V^{\delta-}$ on their surfaces, which serve as active defect pair sites $M^{\delta+} - V^{\delta-}$ for the adsorption and chemidissociation of polar water molecules [47]. In the case of SnS, Sn^{2+} cations and vacancies on the surface attract the oxygen atoms of water molecule. These sulphur vacancies trap the electrons and strongly attract OH^- ions from the H_2O molecule. As water reaches the defect pairs of electronegative surface cations and sulphur vacancies, it chemidissociates into hydronium and hydroxide ions. Upon dissociation, OH^- ions water molecule gets physisorbed on the surface, while protons hop via hydrogen-bonded water molecules. The dissociated hydroxide and hydronium ions diffuse through SnS pellet and migrate towards their respective electrodes. Hydroxide ions react with Zinc electrode, forming zinc hydroxide and releasing electrons. These electrons migrate towards the silver electrode via external circuit. Meanwhile, hydronium ions diffuse towards the silver electrode and evolve hydrogen gas [48,49].

The occurrence of redox reactions on both electrodes is responsible for the generation of current and voltage in the cell. These are the electrochemical half-reactions that should occur on the cell's surface and its electrodes.

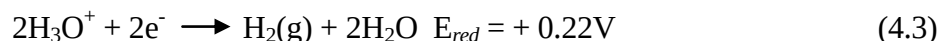
At the surface of SnS HEC



At the anode (At the zinc electrode)



At the cathode (At the silver electrode)



4.5.1 V-I Polarization Curve

The performance of SnS based HEC was assessed using the voltage-current polarization (V-I) curve. The three regions of V-I polarization curves of electrochemical cells (a) Low Current Density region (LCD) (b) Moderate Current Density Region (MCD) (c) High Current Density Region (HCD).

In the LCD region a rapid voltage drop is observed which is ascribed to as activation loss region. The cause of this loss is the potential required to overcome the energy barrier of the electrochemical reaction. In the MCD region the linear sweep is observed that represents the Ohmic losses in the HEC are also responsible for the cell's resistance to ionic flow. In the HCD region a sudden drop in voltage is observed due to abundant aggregation of ions on the surface of electrodes [50]. This type of loss is termed as mass transport loss or concentration loss. All the above mentioned losses occurring in HEC are shown in Fig. 4.7 (a) represented by LM, MN, NO [51]. The SnS HEC delivers a higher offload current of 15 mA and potential produced is 0.74 V as shown in Fig. 4.7 (b). The power is calculated by using formula $P = V \cdot I$, therefore the calculated power is 11.1 mW.

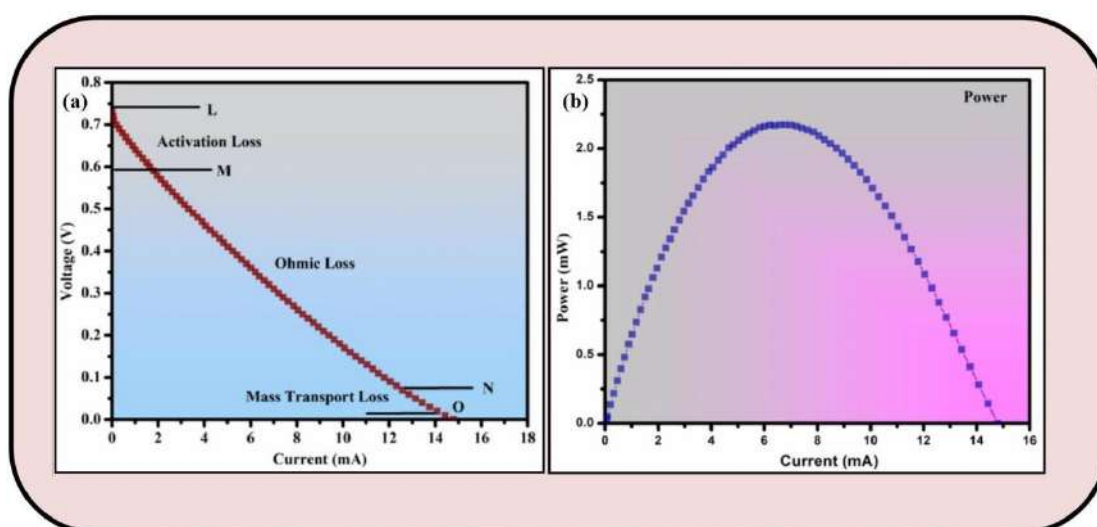


Fig. 4.7: (a) Room Temperature V-I polarization curve and (b) power of as fabricated SnS based HEC.

4.5.2 Stability, Repeatability and Application of SnS based HEC

In addition to the above mentioned parameters (i.e. current, voltage and power) a reliable HEC should demonstrate prolonged stability. The long term repeatability of SnS based HEC is illustrated in Fig. 4.8 (a). highlighting its consistency. In assessing the real time application of the SnS based HEC, we observed remarkable repeatability for 30 days with slightly drop in current with time. The HEC was employed to power 4 LED diodes by using few drops of water. This was achieved by configuring the 3 cells in series, while the LED diodes were arranged in parallel, as illustrated in Fig. 4.8 (b).

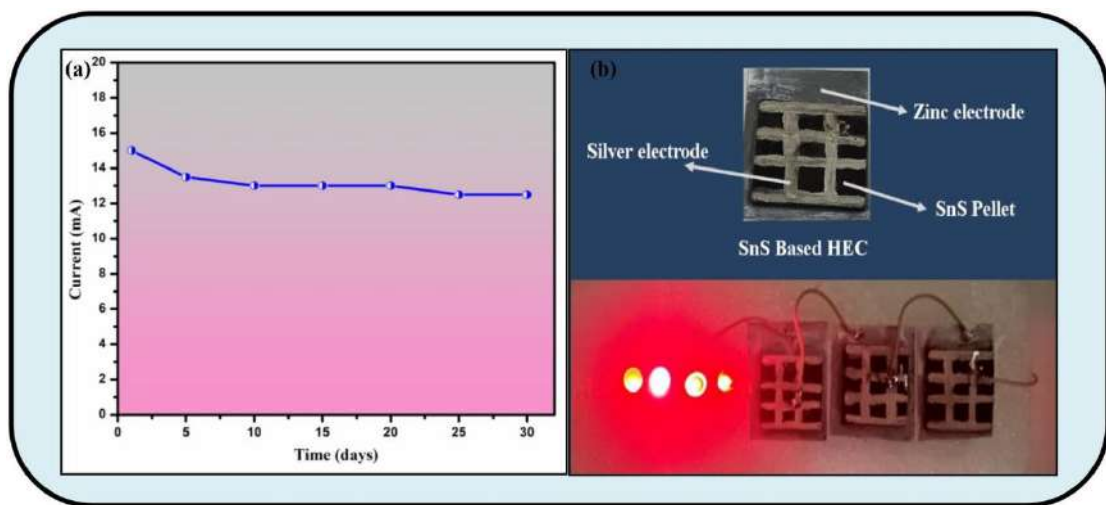


Fig. 4.8: (a) Represents repeatability and stability, and (b) shows the application of SnS based HEC device for powering LED lights.

Table 4.2: Comparison of voltage and current produced by various fabricated hydroelectric cells.

Hydroelectric Cell	Max. Current (mA)	Voltage (V)	Reference
MgGd _{0.02} Fe _{1.98} O ₄	6.8	0.85	54
NiO	12	1.03	55
C doped TiO ₂	7	0.74	56
SiO ₂	1.1	0.96	14
MgO	1.5	0.94	14
TiO ₂	2.3	0.90	14
ZnO	5.0	0.90	14
SnS	15	0.74	Present work

4.5.3 Cyclic Voltammetry (CV)

The electrochemical behavior of SnS was further elucidated through cyclic voltammetry (CV) analysis of the as-prepared sample conducted at room temperature as shown in Fig. 4.9 (a). This analytical technique delivers crucial insights into the electrochemical reactions occurring at the surface of electrode's. In this study, SnS was employed as the working electrode, while platinum served as the counter electrode, and Ag/AgCl was utilized as the reference electrode. The experiments were carried out in a 0.3M KOH electrolyte solution. During scanning, a potential window ranging from -0.6 to 1.5 V was applied to SnS, with a scan rate of 20 mV/s. The resulting CV curve exhibited a peak anodic current of 3.2 mA and a peak cathodic current of 5.3 mA. Notably, the peak anodic potential and peak cathodic potential of SnS were measured at 0.36 V and 0.29 V, respectively. The observed behavior of the CV curves indicates a faradic capacitive mechanism, characterized by reversible and rapid desorption/adsorption of ions at the electrode surface without inducing any phase change in the electrode material [52].

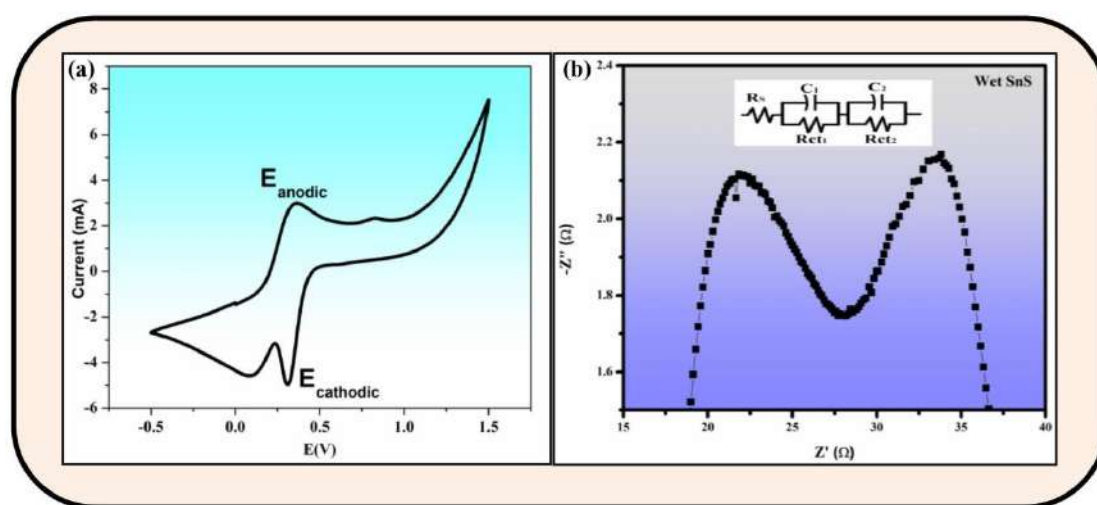


Fig. 4.9: (a) CV curve of SnS electrode in 0.3 M KOH solution and (b). Nyquist curve of wet SnS HEC.

4.5.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was adopted to investigate the resistance of the SnS nanosheets prepared for HEC. The charge transport mechanism within HEC has been investigated through the Nyquist impedance response of the fabricated HEC.

Fig. 4.9 (b). depicts the Nyquist plot of wet SnS HEC cell. The Nyquist plot of the SnS based HEC was obtained at an open circuit potential. As illustrated in the Nyquist plot, the diameter of the semicircle corresponds to the interfacial charge transfer resistance (R_{ct}), representing the resistance of the electrochemical reactions [53]. To identify the roles of the electrode, charge transfer, and ionic diffusion in SnS-based HEC, the experimental Nyquist data were fitted with an equivalent circuit, shown in the inset of Fig. 4.9 (b). The intercepts with the real axis at high frequencies represent the overall ohmic series resistance (R_s) of the cell. The R_s of SnS was 17.3Ω , indicating a lower series resistance of SnS nanomaterials that leads to higher J_{sc} of 15.9 mA cm^{-2} . There are two well defined semicircles in the middle in and low frequency ranges for the plot of SnS. The left arc represents the charge transfer occurring at the Zinc electrode and pellet interface. The R_{ct1} can be calculated by fitting the left arc, and found to be 5.27Ω indicating good electrochemical activity of SnS. The right arc indicates the finite layer Nernst mass diffusion impedance within the pellet. SnS demonstrates a higher R_{ct2} value (7.32Ω), suggesting deficient diffusion, thereby impeding ion transport and elevates electrode resistance.

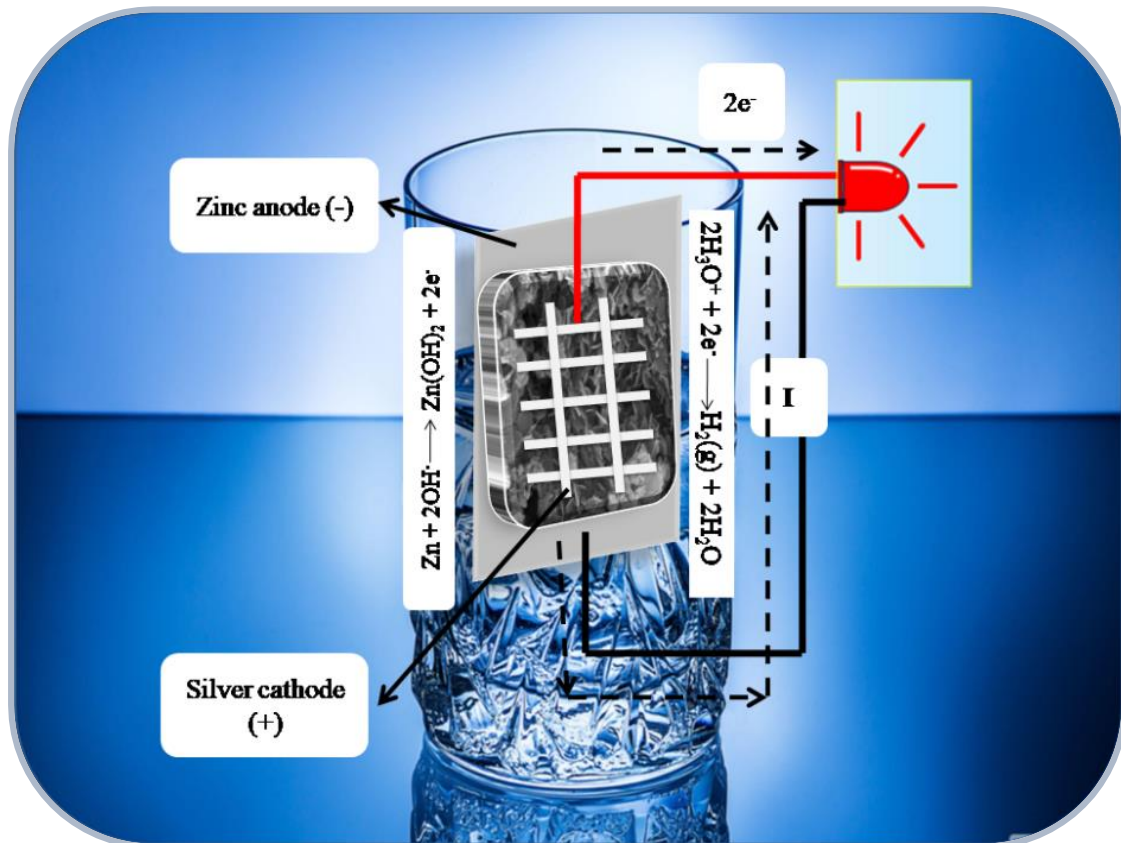
4.6 Conclusion

In summary, SnS based hydroelectric cell was prepared by low temperature solvothermal synthesis of 2D SnS. The nanostructure having orthorhombic phase which was confirmed by X-ray Diffraction pattern. The specific surface area obtained by BET analysis for SnS is $6.45 \text{ m}^2 \text{ g}^{-1}$ with pore diameter being approximately 17.07 nm . Nyquist curve for SnS based HEC in wet state exhibit ionic diffusion in the cell and also shows the high reduction in the impedance of the cell under the wet conditions. The fabricated HEC of cross section area 4 cm^2 exhibited an off-load power output of 11.1 mW . The HEC showcases an impressive electric current output of 15 mA , demonstrating its capability to sustain stable performance with just a few drops of water. Furthermore, its remarkable persists consistently for 30 days, affirming its reliability and durability in various operational conditions. The power output produced via water splitting by HEC is encouraging and proves to be green energy source at low cost. These findings may pave the way for its potential deployment in innovative

applications. Electricity generation by HEC device does not emit any toxic gases therefore it can be the best strategy to save the environment and to achieve mission of net carbon zero. These ground-breaking results emphasize the practicality of HEC device as alternative to solar cells and fuel cells.

CHAPTER 5

Vertically Aligned Tin Sulfide (SnS) Decorated Reduced Graphene Oxide (rGO) Based Hydroelectric Cell Device to Generate Green Electricity by Water Splitting



In the previous chapter, a two-dimensional (2D) SnS-based hydroelectric cell (HEC) was successfully developed and systematically evaluated for green energy generation through room-temperature water splitting. The fabricated device demonstrated significantly enhanced performance, characterized by higher current output, spontaneous water dissociation under ambient conditions, and improved reproducibility compared to several previously reported HEC systems. These results confirmed the strong potential of defect-engineered 2D-SnS as an efficient material platform for sustainable electricity generation. Motivated by the promising characteristics of 2D-SnS, the research was further extended to develop a SnS-rGO nanocomposite with the objective of achieving superior electrical output. Considering the critical role of surface

defects and interfacial charge transfer in water adsorption and redox-driven processes, controlled defect engineering was strategically implemented within the SnS-rGO hybrid structure. The incorporation of reduced graphene oxide (rGO) was aimed at enhancing electrical conductivity, facilitating rapid charge transport, and improving overall electrochemical performance.

The defect-engineered SnS-rGO nanocomposite was subsequently utilized to fabricate an advanced hydroelectric cell device for sustainable energy harvesting. The developed SnS-rGO based HEC, with an active area of 4 cm², delivered a short-circuit current of 34 mA and an open-circuit voltage of 0.94 V, resulting in an off-load output power of 31.96 mW. This represents more than a twofold enhancement in current output compared to the pristine SnS-based device, establishing a clear and coherent progression in performance through nanocomposite engineering. Importantly, the device maintained stable and consistent performance over a duration of 12 weeks, demonstrating excellent reliability and durability under various operational conditions. Furthermore, the simple architecture and water-driven operation of hydroelectric cells make them highly attractive for emergency power supply and lighting applications in flood-affected, disaster-prone, or remote regions where conventional electricity infrastructure is unavailable.

5.1 Introduction

The urgent need to mitigate climate change, global warming, and the rapid depletion of fossil fuel resources has driven intensive research toward sustainable and environmentally benign energy technologies [1]. Although renewable energy sources such as solar, wind, and conventional hydropower have achieved technological maturity, their widespread deployment is often constrained by intermittency, climatic dependence, and complex infrastructure requirements [2,3]. Consequently, there is growing interest in alternative energy-harvesting approaches that can operate continuously under ambient conditions while utilizing abundant natural resources [4].

In this context, hydroelectric cells (HECs) have recently emerged as a novel class of green energy devices capable of generating electrical power directly from water without the need for external bias, light irradiation, or chemical fuels [5]. Unlike conventional electrochemical or photoelectrochemical systems, HECs exploit defect-induced surface

electric fields in ceramic and semiconducting materials to dissociate water molecules into hydroxide (OH^-) and hydronium (H_3O^+) ions at room temperature. The directional migration of these ionic species, coupled with electron transport through the solid matrix and an external circuit, leads to spontaneous electricity generation [6,7]. This unconventional energy conversion mechanism has attracted significant attention due to its simplicity, environmental compatibility, and scalability.

Previous studies have demonstrated that the performance of HECs is critically governed by the surface chemistry and defect structure of the active material. Metal oxides and ferrites such as NiFe_2O_4 , ZnFe_2O_4 , CeO_2 , and doped spinel systems have been extensively investigated as HEC materials [8,9]. In these systems, intrinsic defects such as oxygen vacancies, unsaturated metal cations ($\text{M}^{\delta+}$), grain boundaries, and surface dipoles act as active sites for the adsorption and chemidissociation of polar water molecules [10]. Despite these advances, oxide-based HECs often suffer from limited electrical conductivity and interfacial charge recombination, which restrict current density and power output. To overcome these limitations, hybrid material strategies have been explored, particularly the incorporation of conductive carbonaceous materials such as reduced graphene oxide (rGO). rGO-based composites, including CeO_2 -rGO, SnO_2 -rGO, and ferrite-rGO systems, have demonstrated significantly enhanced hydroelectric performance due to improved electron mobility, reduced internal resistance, and increased effective surface area [11-13]. Furthermore, oxygen-containing functional groups on rGO enhance hydrophilicity, facilitating efficient water adsorption and ion transport—an essential requirement for sustained HEC operation.

In parallel with oxide systems, metal sulfides have emerged as promising alternatives due to their distinct electronic structures, higher polarizability, and defect chemistry. Sulfide materials typically possess chalcogen vacancies and unsaturated metal cations that can generate stronger surface dipoles compared to their oxide counterparts. Tin Sulfide (SnS), a layered group IV-VI metal chalcogenide, non-toxicity, earth abundance, and favorable electronic properties. SnS exhibits p-type semiconducting behavior and an orthorhombic layered structure that supports anisotropic charge transport and strong surface-water interactions. Several studies have reported that the introduction of sulfur (S) vacancies can induce n-type conductivity in SnS [14-16]. In this context, an

alternative and widely accepted explanation for the emergence of n-type behavior in SnS is intrinsic doping arising from a tin-rich (Sn-excess) stoichiometry. Controlled non-stoichiometry has been recognized as an effective approach for tuning the dominant charge carriers in chalcogenide semiconductors, enabling a transition from p-type to n-type conduction [17]. This carrier type modulation occurs through the generation of anion vacancies and a relative excess of metal cations, which act as donor-like defect states. In particular, sulfur deficiency or excess tin incorporation has been demonstrated to introduce shallow donor levels near the conduction band, thereby promoting electron-dominated transport and resulting in n-type behavior in SnS nanostructures [18]. The integration of SnS with reduced graphene oxide to form an SnS-rGO nanocomposite represents a rational materials design strategy for advanced hydroelectric cells device. In this hybrid architecture, SnS provides abundant defect-rich active sites for water dissociation, while rGO serves as a highly conductive electron transport network that facilitates rapid charge collection and minimizes recombination losses. The intimate interfacial contact between SnS nanosheets and rGO sheets induces interfacial charge redistribution and enhanced built-in electric fields, further promoting efficient ion-electron separation [19]. Additionally, the rGO framework improves mechanical stability and maintains electrical integrity during prolonged exposure to aqueous environments, a critical requirement for long-term HEC operation.

In the present investigation, we report the synthesis of an SnS-rGO nanocomposite and its application as an active material for green energy generation using hydroelectric cell device. According to available research, no work has been carried out on SnS-rGO nanocomposite for the green electricity generation by hydroelectric cell (HEC) device. Although rGO-based oxide HECs have been widely reported, systematic investigations on sulfide-carbon hybrid systems, particularly SnS-rGO nanocomposites, remain scarce. The analysis of structure, morphology were done using XRD and FESEM. To explain the presence of sulphur vacancies and defects in the lattice of SnS nanosheets, the spectroscopic techniques such as Raman and PL are used. SnS based HEC demonstrates the remarkable output voltage and short circuit current values of 0.94 V and 34 mA, respectively. The as fabricated HEC produces the maximum power of 31.96 mW. The findings of this investigation are encouraging, indicating that power generation via

hydroelectric cell has developed as a viable alternative to other renewable energy sources. Finally, a defect-assisted water dissociation and charge transport mechanism is proposed to elucidate the synergistic roles of sulfur vacancies, interfacial polarization, and rGO assisted electron conduction in enhancing hydroelectric energy conversion efficiency. Moreover, the utilization of SnS-rGO based HEC device for water splitting opens avenues for meeting future hydrogen needs.

5.2 Material Structure and Characterization

The X-ray diffraction (XRD) pattern was collected using a Bruker D-8 advanced instrument with $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) over a 2θ range of 20-80 degrees to determine the phase and crystallite size of the as-prepared SnS nanosheets. Raman spectra were obtained using a Raman spectrometer (α -Witek 300 RA) with a laser excitation wavelength of 532 nm. Photoluminescence (PL) spectroscopy was conducted to explore the defects of the samples at room temperature. PL spectra were acquired using a photoluminescence spectrometer (Perkin Elmer, LS 55) with a Xenon lamp as the excitation source, spanning the range of 200-800 nm with an excitation wavelength of 234 nm. The surface morphology of the as-prepared samples was examined using a ZEISS Gemini field emission scanning electron microscope (FE-SEM), and energy-dispersive X-ray spectroscopy (EDX) was performed to confirm the elemental composition. Additionally, the BET (Brunauer-Emmett-Teller) technique was employed to analyze pore characteristics such as pore volume, pore size, and specific surface area. The voltage and current of the developed hydroelectric cell device (HECD) of SnS-rGO nanocomposite was measured using a Keithley-2400 source meter. The Cyclic Voltammetry was done using Metrohm Autolab Potentiostat. Electrochemical impedance spectroscopy (EIS) was conducted to obtain Nyquist plots of wet cells, utilizing a Wayne-kerr 6500B instrument within a frequency range of 20 Hz-120 MHz.

5.3 Experimental Section

5.3.1 Materials Required

Stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99%), Ethylene Glycol and ($\text{C}_6\text{H}_6\text{O}_2$, 99%), Sulphuric acid (H_2SO_4), Phosphoric acid (H_3PO_4),

Potassium Permanganate (KMnO_4), Double Distilled water (H_2O), Hydrazine Hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$), Ethanol ($\text{C}_2\text{H}_5\text{OH}$), Hydrochloric acid (HCl).. All the chemicals were purchased from Fisher chemicals. The Thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99%) used in this study was purchased from Sigma Aldrich. All the chemicals belong to AR grade with highest purity of (99%).

5.3.2 Synthesis of GO

Graphene Oxide (GO) was prepared by Modified Hummers Method, using the expandable graphite powder as the starting material. 26.7 ml of concentrated H_3PO_4 was added to 240 ml of concentrated H_2SO_4 in a 9:1 ratio in a conical flask followed by the addition of 2 gm of graphite powder to the above solution and allowed to stir for 30 min. Then the KMnO_4 was added very slowly to the solution. The temperature was raised to 50 °C and maintained for the following 12 hrs. Then, 260 ml of H_2O in the form of ice was added to the solution. Then slow addition of H_2O_2 was done until the color became dark brown [20]. The resultant brown-coloured solution was left overnight and then filtered out using centrifugation followed by various washings until the pH reached 7. The sample was dried at 70 °C to obtain the GO powder which was brown.

5.3.3 Synthesis of Reduced Graphene Oxide (rGO)

Reduced graphene oxide (rGO) was synthesized via the chemical reduction of graphene oxide (GO) using hydrazine hydrate as a reducing agent. Initially, 500 mg of GO powder was dispersed in 500 mL of deionized water and ultrasonicated for 2 h to achieve complete exfoliation and uniform dispersion of GO sheets. The resulting stable suspension was then subjected to continuous magnetic stirring, after which 200 μL of hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) was added dropwise. The reaction mixture was subsequently heated and maintained at 85 °C for 24 h to promote effective reduction of oxygen-containing functional groups present on the GO surface. A gradual color change from brown to deep black was observed, signifying the successful formation of rGO nanosheets.

Upon completion of the reduction process, the black precipitate was collected by filtration and thoroughly washed several times with deionized water to remove residual hydrazine and reaction by-products. The purified rGO was then dried in a hot-air oven at 80 °C for 24 h, yielding dry rGO nanosheets suitable for subsequent composite synthesis.

5.3.4 Synthesis of SnS-rGO Nanocomposite

The SnS-rGO nanocomposite was synthesized via a hydrothermal route by incorporating 0.01g of reduced graphene oxide (rGO) into the SnS matrix. Initially, an appropriate amount of rGO (1 mg mL⁻¹) was dispersed in ethanol and subjected to ultrasonic treatment for 1 h to achieve a uniform and stable suspension. In parallel, a 0.1 M solution of SnCl₂·2H₂O was prepared in 100 mL of ethylene glycol and magnetically stirred for 30 min to ensure complete dissolution. Subsequently, a suitable amount of citric acid (C₆H₈O₇) was added to the solution to act as a complexing agent, followed by the addition of 3.33 g of thiourea (CH₄N₂S) as the sulfur source. The reaction mixture was continuously stirred for an additional 1 h to promote homogeneous mixing and precursor interaction.

The rGO dispersion was then gradually introduced into the Sn-S precursor solution under continuous stirring, and the resulting homogeneous suspension was further stirred for 1 h. The final reaction mixture was transferred into a 200 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 200 °C for 24 h. After naturally cooling to room temperature, the obtained black precipitate was collected by centrifugation and thoroughly washed several times with deionized water and anhydrous ethanol to remove residual impurities. The purified product was subsequently dried at 80 °C for 24 h to obtain the SnS-rGO nanocomposite powder. A schematic illustration of the stepwise synthesis procedure for the SnS-rGO nanocomposite is presented in Fig. 5.1.

5.4 Fabrication of Hydroelectric Cell Device (HECD)

The as-synthesized SnS-rGO nanocomposite were compacted into a square-shaped pellet with an effective surface area of 4 cm² using a hydraulic press under an applied

pressure of 5.5 tons, as schematically illustrated in Fig. 5.1. Pelletization was carried out to ensure good mechanical integrity and intimate interparticle contact, which is essential for efficient charge transport in the hydroelectric cell configuration. The obtained pellet was subsequently annealed at 300 °C for 2 h to induce sulfur-related defects and enhance surface defect density. Such defect engineering is plays a crucial role in promoting water adsorption and dissociation at the semiconductor surface, thereby improving hydroelectric energy generation. A zinc sheet was attached to one of its faces of the pellet whereas the silver paste was applied over the other face in a comb pattern. Zinc acts as the anode whereas the silver paste acts as the inert cathode. Low-resistance wires were soldered to both electrodes to fabricate a SnS-rGO nanocomposite based Hydroelectric cell device.

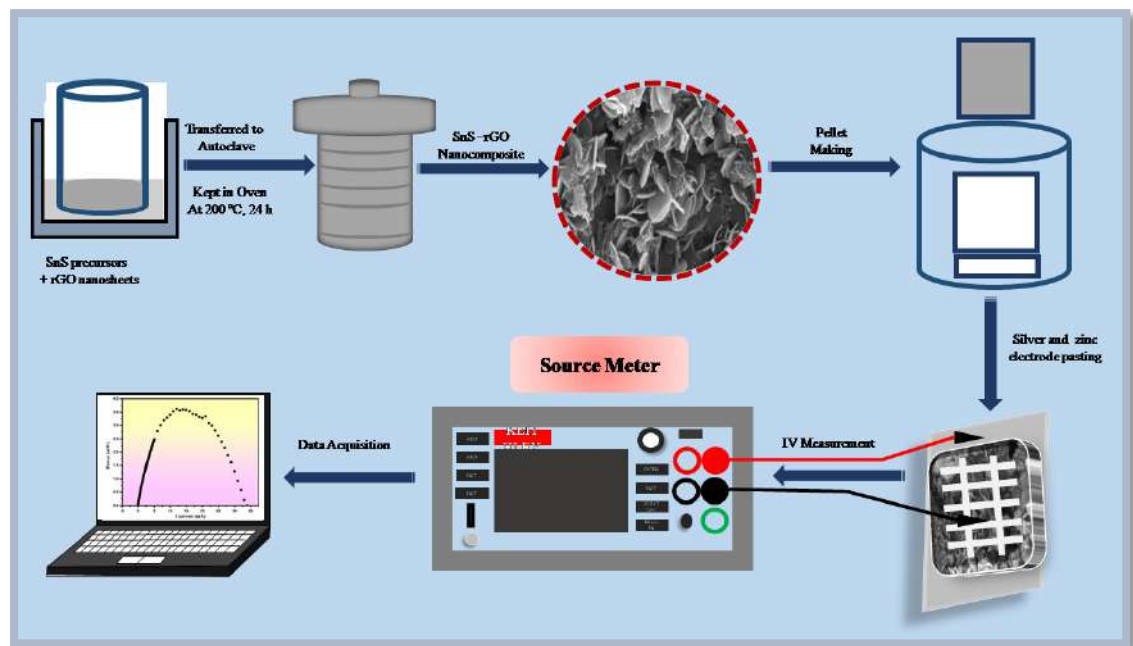


Fig. 5.1: Schematic diagram illustrating the preparation of SnS-rGO nanocomposite and fabrication of hydroelectric cell device.

5.5 Results and Discussion

5.5.1 X-ray Diffraction

Fig. 5.2(a-b) presents the X-ray diffraction (XRD) pattern of the as-prepared GO, rGO and SnS-rGO, providing detailed insight into the crystalline structure of the synthesized nanostructures. For graphene oxide (GO), a prominent diffraction peak observed at

11.01° and a weak peak at 23.78° are indexed to the (002) and (100) planes, respectively, consistent with previous reports [19]. Upon reduction, two broad diffraction features centered at 25.08° and 43.6° appear, corresponding to the (002) and (100) planes of rGO, confirming the successful reduction of GO [20].

The XRD pattern of the SnS–rGO nanocomposite exhibits a series of well-defined diffraction peaks corresponding to the orthorhombic SnS phase. The reflections indexed to the (101), (201), (210), (011), (111), (400), (311), (102), (411), (020), (112), (511), (221), (601), (420), (512), and (711) planes appear at 2θ values of 21.93°, 26.14°, 27.42°, 30.51°, 31.66°, 32.12°, 39.14°, 42.77°, 44.81°, 45.42°, 48.74°, 51.25°, 52.94°, 54.21°, 56.63°, 64.29°, and 66.48°, respectively. These diffraction peaks are in excellent agreement with the standard JCPDS card for orthorhombic SnS (JCPDS No. 39-0354) [21], confirming the successful formation of the SnS–rGO nanocomposite phase within the composite. As shown in Fig. 5.2(b), distinct characteristic diffraction peak corresponding exclusively to rGO is observed in the composite pattern around 21.4°. This can be attributed to the relatively low concentration of rGO nanosheets incorporated into the SnS matrix. Notably, the diffraction peaks associated with the SnS phase are sharp and intense, indicating a high degree of crystallinity. Furthermore, the absence of impurity-related peaks corresponding to secondary phases such as SnS₂ or SnO₂ confirms that the solvothermal synthesis route yields phase-pure and highly crystalline SnS–rGO nanocomposite.

The interplanar spacing of the four highest intensity peaks was calculated using Bragg's relation: $n\lambda = 2d \sin\theta$. Where 'n' denotes the d-spacing values calculated for various high intensity planes of SnS–rGO nanocomposite.

Table 5.1: d-spacing values calculated for various planes of SnS–rGO nanocomposite

Sample	2θ (degree)	hkl planes	d spacing (nm)
SnS–rGO	26.14	(201)	0.41
	30.51	(011)	0.36
	31.66	(111)	0.34
	39.14	(311)	0.30

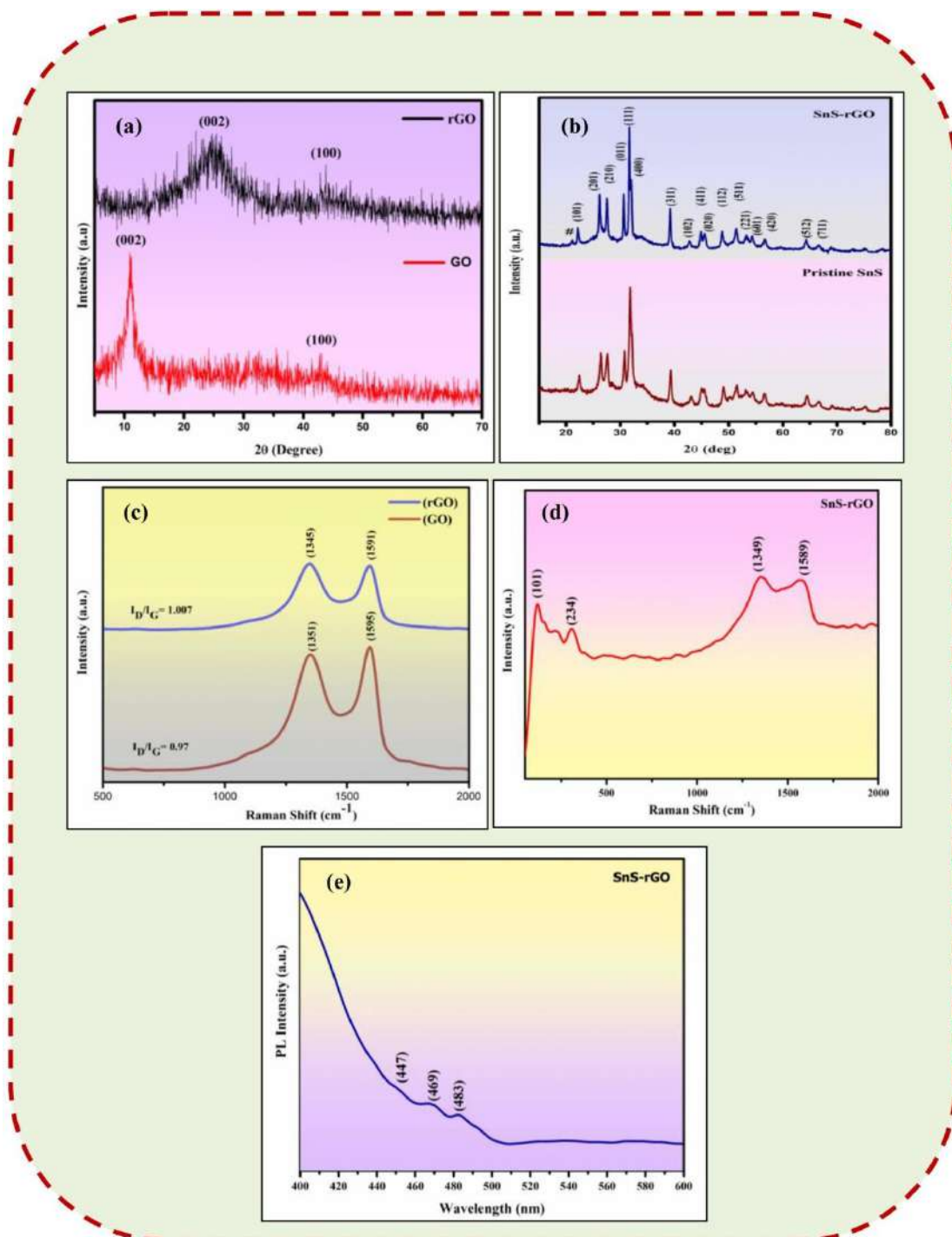


Fig. 5.2: (a-c) X-ray diffraction pattern of GO, rGO and SnS-rGO nanocomposite (d) Raman spectra of GO and rGO, (e) Raman spectra of SnS-rGO nanocomposite (f) Photoluminescence (PL) spectra of SnS-rGO nanocomposite.

5.5.2 Raman Spectroscopy

The Raman spectra of GO, rGO and SnS-rGO nanocomposite is shown in Fig. 5.2(c,d).

Two characteristic peaks of GO are observed at 1351 cm^{-1} and 1595 cm^{-1} which

corresponds to the D and G bands of graphene, respectively. The D band represents lattice disorders in the sp^2 -hybridized C atoms and the G band is related to the highly oriented sp^2 hexagonal graphitic lattice [22]. The D and G bands of rGO are located at 1345 cm^{-1} and 1591 cm^{-1} , respectively as shown in Fig. 5.2(c). The intensity ratio (I_D/I_G) increased from 0.97 to 1.007 when GO is chemically reduced to rGO indicating the partial modification of surface functional groups containing oxygen [19]. The results indicate that GO is successfully reduced to rGO after chemical reduction by hydrazine hydrate. Fig. 5.2(d) shows the Raman spectrum of the as prepared sample of SnS-rGO for HEC. The spectra exhibit two distinct peaks located at 101, 234. The peaks at 101 cm^{-1} and 234 cm^{-1} corresponded to the characteristic Ag mode of SnS originating from the interatomic vibration between the metal (Sn) and chalcogen S atoms [24-26]. Also, two typical carbon peaks are observed confirms the presence of G band at 1349 cm^{-1} and the D band at 1589 cm^{-1} confirms the presence of reduced graphene oxide in the SnS-rGO nanocomposite [27]. Based on XRD and Raman spectra, it indicates that the as-prepared SnS-rGO nanocomposite formed orthorhombic phase.

5.5.3 Defects Study in SnS-rGO Nanocomposite

PL spectra are a very efficient, non-destructive contactless approach for characterizing and evaluating the quality of surfaces and interfaces, as well as to probing defect levels inside material. The Fig. 5.2(e) shows the PL spectra of SnS-rGO recorded at an excitation wavelength of 234 nm in the range of 400-600 nm. It mainly consist of three peaks at 447 (UV emission), 469, 483 (blue emission) nm [28]. The broad emission spectra of the SnS-rGO may arise from various defects such as high density of Sn, Sulphur vacancies introduced during the process. Besides sulphur and Tin vacancies, various kinds of defects such as interstitial, stacking faults have also been induced in the nanosheets [14]. The emission peak observed at 447 nm corresponds to Sn interstitial (I_{Sn}) and dangling bonds present at the surface of the SnS-rGO pellet [19]. The emission at 469 nm is ascribed to indirect band to band transition and the peak at 483 nm corresponds to Sulphur vacancy (V_S) which plays crucial role for water splitting by HEC at room temperature [28].

5.5.4 Surface Morphology and Porosity Analysis

5.5.4.1 Field Emission Scanning Microscopy (FESEM) & Electron Dispersive X-ray Spectroscopy (EDX)

Considering the role of microstructural features in governing the electrokinetic performance of hydroelectric cell (HEC) devices, field-emission scanning electron microscopy (FESEM) was employed to examine the surface morphology and interfacial characteristics of the synthesized materials. Figs 3(a-b) show FESEM images of graphene oxide (GO) and reduced graphene oxide (rGO) revealing characteristic thin, wrinkled, and sheet-like morphologies. These features arise from the partial restacking of graphene layers after chemical reduction and provide a high specific surface area with abundant edge defects and functional groups, which are favorable for water adsorption in HEC systems. The FESEM micrographs of the SnS-rGO nanocomposite, presented in Fig. 5.3(c-d), reveal the formation of vertically aligned SnS nanoflakes with thicknesses ranging from approximately 120 to 200 nm. The nanoflakes are densely packed and uniformly distributed, forming interconnected clusters within which rGO sheets are intimately embedded. The rGO nanosheets appear as thin carbonaceous layers that interconnect adjacent SnS nanoflakes, creating a continuous and highly conductive network throughout the composite. This intimate SnS-rGO interfacial contact is critical for facilitating rapid electron transport and minimizing internal resistance during hydroelectric energy generation.

Importantly, the nanoflakes are interconnected in a neck-to-neck configuration, forming a three-dimensional porous network with open channels extending throughout the composite. This interconnected porous architecture plays a crucial role: it provides continuous pathways for electron transport across the SnS-rGO nanocomposite framework. Such structural connectivity is highly desirable for hydroelectric cell operation, as it enhances ionic mobility, promotes defect accessibility, and sustains long-term electrokinetic activity. The porosity and surface area of the composite were further quantified using Brunauer-Emmett-Teller (BET) analysis, confirming the presence of a mesoporous structure conducive to HEC performance. The elemental composition and spatial distribution of the SnS-rGO nanocomposite were investigated using energy-dispersive X-ray spectroscopy (EDX).

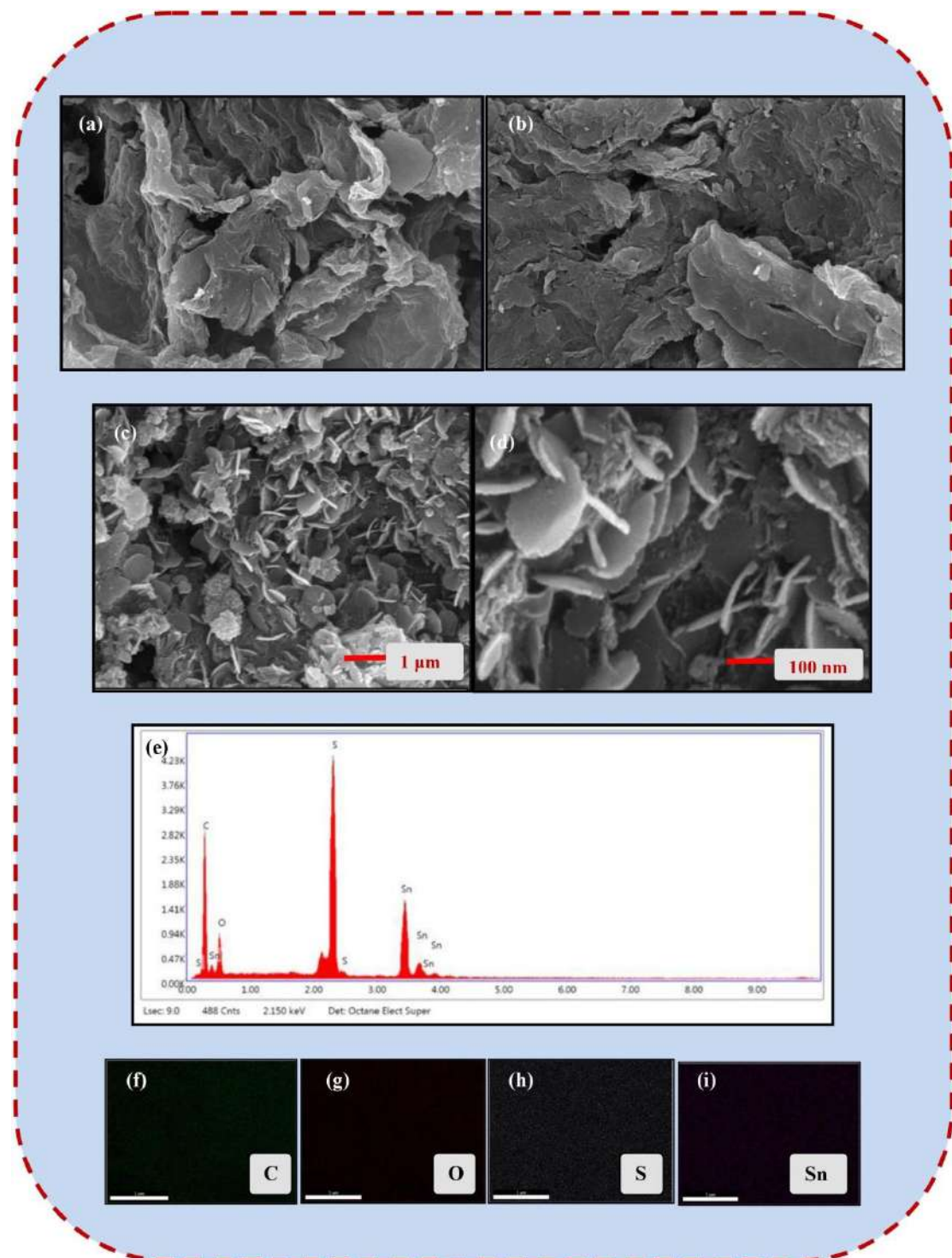


Fig. 5.3: (a-b) FESEM of GO and rGO, (c-d) FESEM of SnS-rGO nanocomposite at 1 μm and 100 nm, (e) EDX spectra and (f-i) elemental mapping of SnS-rGO nanocomposite.

As shown in Fig. 5.3(e), the EDX spectrum confirms the presence of carbon (C), oxygen (O), tin (Sn), and sulfur (S), with no detectable impurity elements, indicating high chemical purity of the synthesized composite. Furthermore, Fig. 5.3(f-i) shows the

elemental mapping images demonstrate a homogeneous distribution of C, O, Sn, and S throughout the composite, confirming uniform dispersion of rGO within the SnS matrix and consistent interfacial integration across the sample.

5.6 BET and BJH Analysis

The surface area and pore architecture of active materials are among the most critical parameters influencing water dissociation kinetics, ion transport, and overall energy conversion efficiency in hydroelectric cell (HEC) device. To quantitatively assess the characteristics of the as-synthesized SnS-rGO nanocomposite, Brunauer–Emmett–Teller (BET) surface area analysis was performed using nitrogen (N₂) adsorption–desorption measurements. The corresponding N₂ adsorption–desorption isotherm and Barrett–Joyner–Halenda (BJH) pore size distribution curves are presented in Fig. 5.4(a) and Fig. 5.4(b), respectively. The SnS-rGO nanocomposite exhibits a type IV adsorption–desorption isotherm accompanied by a well-defined hysteresis loop over a relative pressure (P/P₀) range of 0.1–1.0, which is characteristic of mesoporous materials [29–30]. The presence of this hysteresis loop arises from capillary condensation within mesopores and confirms the formation of an interconnected porous network throughout the composite. Such mesoporosity is particularly advantageous for hydroelectric cell applications, as it facilitates rapid infiltration of water molecules and provides continuous pathways for ionic diffusion.

The BJH pore size distribution reveals a broad and hierarchical distribution of pore diameters spanning approximately 40 to 1100 Å, indicating the coexistence of mesopores and larger macroporous channels. Quantitative analysis indicates that the SnS-rGO nanocomposite possesses an average pore diameter of 12.13 nm, a total pore volume of $1.66 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$, and a BET-specific surface area of $47.09 \text{ m}^2 \text{ g}^{-1}$. The relatively high surface area ensures a large density of exposed defect sites, which are essential for effective water adsorption and dissociation under ambient conditions. The enhanced porosity and surface area of the SnS-rGO nanocomposite can be attributed to the synergistic effects of rGO incorporation and defect engineering within the SnS lattice. The partial removal of sulfur atoms at specific lattice sites during synthesis and post-annealing treatment leads to the formation of sulfur vacancies, which act as both electronic defect states and structural voids. These vacancies generate localized electric

fields that promote the polarization and dissociation of water molecules, while the associated pores provide favorable sites for trapping hydronium (H_3O^+) ions and facilitating their migration toward the cathode.

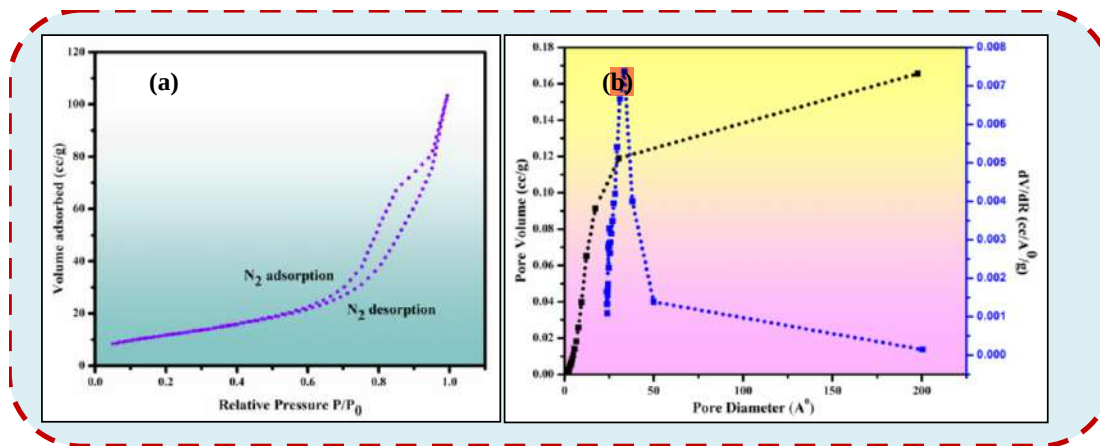


Fig. 5.4: (a) The N_2 adsorption and desorption isotherm and (b) pore size distribution of SnS-rGO nanocomposite.

5.7 Working Mechanism of Hydroelectric Cell Device

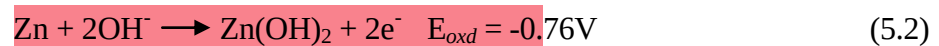
As illustrated in Fig. 5.5 (a), the performance of SnS-rGO based hydroelectric cell was assessed using voltage-current polarization (V-I) plots. With distinct working regions of HEC device, the voltage drop across the external variable load is given as a function of current. The short-circuit current (I_{sc}) and open-cell voltage V_{oc} of SnS-rGO nanocomposite based HEC device showed a 34 mA current and 0.94 V open-cell voltage, as shown in Table 5.2. It is observed that the metal oxide's and metal sulphide surface has unsaturated metal cations $\text{M}^{\delta+}$ and some vacancies such as oxygen or sulphur vacancies $\text{V}^{\delta-}$ on the surface. This $\text{M}^{\delta+} - \text{V}^{\delta-}$ pair is known as active defect pair sites for adsorption as well as for chemidissociation of water molecules. In SnS-rGO nanocomposite, the unsaturated metal cations and sulphur vacancies (BET, and Raman spectroscopy) attract oxygen from a water molecule. These oxygen vacancies trap the electrons and attract hydroxyl ions of water molecules. This water molecule dissociates into hydronium and hydroxide ions when it approaches the defect pairs of electronegative surface cations and sulphur vacancies. Hydroxide ions create chemical bonds with unsaturated cations on the surface, and a chemisorbed layer of OH^- ions physisorbed the water molecules with the help of hydrogen bonding. Hydronium ion

hopping occurs inside the open nanopores on the surface due to hydrogen bonding traps. The physisorbed water molecules in hydronium and hydroxide ions are further dissociated by the concentrated trapped ions, which provide enough electric potential. As a result of the Grotthuss chain reaction, hydronium ions migrate toward the cathode. The following are the electrochemical half-reactions that should occur on the electrode and the SnS-rGO nanocomposite surface.

At the surface of SnS-rGO nanocomposite HEC device



At the anode (At the zinc electrode)



At the cathode (At the silver electrode)



5.7.1 V-I Polarization Curve

SnS-rGO nanocomposite HEC device generates a higher offload current in comparison to our previous report of SnS based HEC. It is due to more surface energy generated by the unsaturated surface cations, oxygen and sulphur vacancies formation in SnS-rGO nanocomposite, which is validated by FESEM and BET results. Thus, SnS-rGO nanocomposite requires less activation energy for water molecule dissociation, which results in a higher current value. Typical polarization zones are shown in the V-I polarization curve SnS-rGO nanocomposite HEC at various load levels in Fig. 5.5. The breakdown of water (H_2O) molecules into H_3O^+ and OH^- ions, as well as redox processes at electrodes, generate current and voltage in HEC device. The V-I curves are divided into three portions, AB, BC, and CD (as shown in Fig. 5.5(a)), which explain the different types of polarization losses used to characterize the cell's operational zones. The open-circuit voltage of the cell at an infinite load was denoted by point A. The activation loss, which is prevalent in the lower current density regions, is given by the region AB. The activation loss is directly related to the rate of the electrochemical reaction. This loss is responsible for the delay in the initiation of the water dissociation process on the mesoporous surface and in the collection of ions by the respective

electrodes. The Ohmic region (BC) represented the internal resistance of the hydroelectric cell material to ion flow along with electron flow resistance offered by cell electrodes. It is observed that a large linear Ohmic region is useful for HEC operation observed in the SnS-rGO nanocomposite based cell, which signifies the low internal resistance of the cell material. This may be because of increased defect centers, which promote the ion transfer via H_3O^+ hopping and migration of OH^- via sulphur vacancies. The mass transport loss/concentration loss, which is present in the higher current density zones, is represented by CD. The concentration loss is observed for SnS-rGO nanocomposite, which accounts for a higher concentration of dissociated ions and a limited amount of charge transport at highly active electrodes. The active linear region and the high current value obtained for SnS-rGO HEC are beneficial for facile, portable, and lowcost electricity generation by dissociation of the water molecule. In the present study, the maximum power of 31.96 mW obtained for a SnS-rGO HEC device with an area of 4.0 cm^2 is higher among all reported HECs, as shown in Table 5.2. The addition of rGO to SnS enhances the current magnitude from 15 mA for SnS to 34 mA for SnS-rGO nanocomposite [23]. The improved sulphur vacancies and the surface area increase the water dissociation, resulting in an increase in the current. Because of the facile charge transfer between rGO and SnS, the barrier to OH^- diffusion via grain boundaries is reduced, resulting in a lower Ohmic loss. The current HEC's potential is higher than previously reported HEC cells, indicating that the redox reaction and the water dissociation rates are balanced.

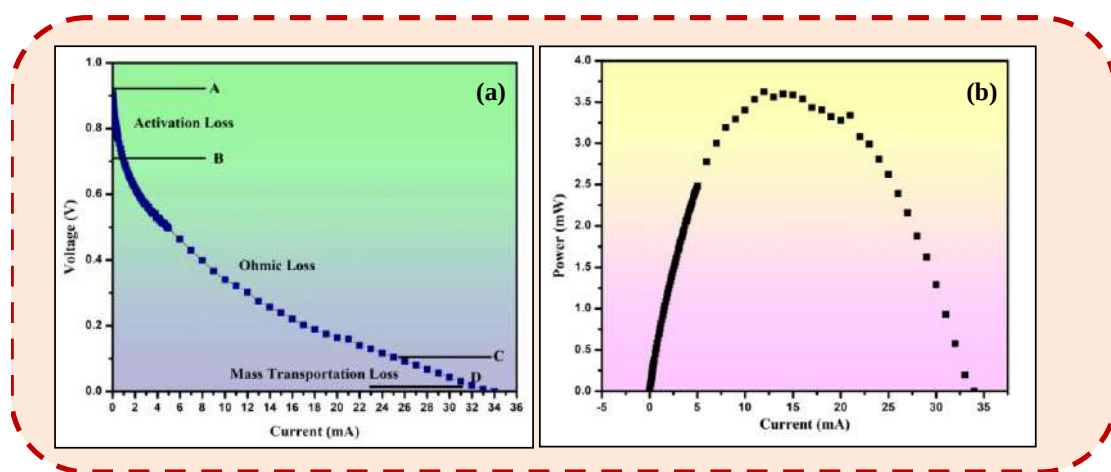


Fig. 5.5: (a) Room Temperature V-I polarization curve and (b) power of as fabricated SnS-rGO nanocomposite based HEC.

5.7.2 Stability, Repeatability and Application of SnS based HEC

In addition to the above mentioned parameters (i.e. current, voltage and power) a reliable HEC should demonstrate prolonged stability. The long term repeatability of SnS based HEC is illustrated in Fig. 5.6(a) highlighting its consistency. In assessing the real time application of the SnS-rGO nanocomposite based HEC device, we observed remarkable repeatability for 12 weeks with slightly drop in current with time.

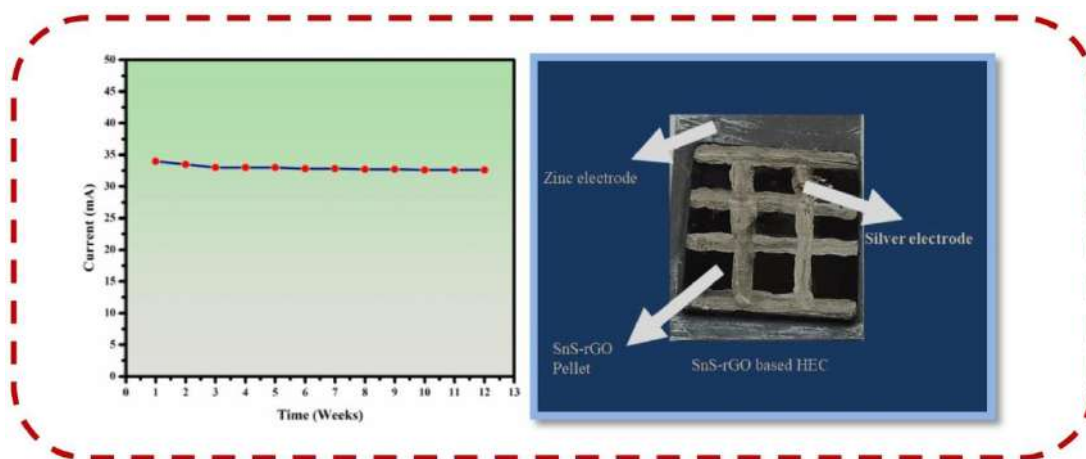


Fig. 5.6: (a) Represents repeatability and stability, and (b) shows as prepared HEC device.

Table 5.2: Comparison of voltage and current produced by various fabricated hydroelectric cells.

Hydroelectric Cell	Max. Current (mA)	Voltage (V)	Reference
MgGd _{0.02} Fe _{1.98} O ₄	6.8	0.85	14
NiO	12	1.03	14
C doped TiO ₂	7	0.74	14
SiO ₂	1.1	0.96	14
MgO	1.5	0.94	14
CeO ₂	13.6	0.85	11
CeO ₂ -rGO	21.3	0.82	11
SnS	15	0.74	23
SnS-rGO	34	0.94	This Work

5.7.3 Cyclic Voltammetry (CV)

The electrochemical behavior of SnS-rGO nanocomposite was further elucidated through cyclic voltammetry (CV) analysis of the as-prepared sample conducted at room

temperature as shown in fig. 5.7(a). This analytical technique delivers crucial insights into the electrochemical reactions occurring at the surface of electrode's. In this study, SnS-rGO nanocomposite was employed as the working electrode, while platinum served as the counter electrode, and Ag/AgCl was utilized as the reference electrode. The experiments were carried out in a 0.3M KOH electrolyte solution. During scanning, a potential window ranging from -0.4 to 1.6 V was applied to SnS-rGO nanocomposite, with a scan rate of 25 mV/s. The resulting CV curve exhibited a peak anodic current of 8.2 mA and a peak cathodic current of 7.9 mA. Notably, the peak anodic potential and peak cathodic potential of SnS-rGO nanocomposite were measured at 0.28 V and 0.17 V, respectively. The observed behavior of the CV curves indicates a faradic capacitive mechanism, characterized by reversible and rapid desorption/adsorption of ions at the electrode surface without inducing any phase change in the electrode material [31].

5.7.4 Electrochemical Impedance Spectroscopy (EIS)

The charge transport mechanism of the fabricated hydroelectric cell (HEC) was examined using Nyquist impedance spectroscopy. Fig. 5.7(b) presents the Nyquist plots of the wet SnS-based HEC. Across the investigated frequency range, the plots display a single semicircular arc, indicating a dominant charge-transfer process. The incorporation of rGO into SnS leads to an approximately one-order-of-magnitude reduction in series resistance, suggesting enhanced OH^- and H_3O^+ ion conduction and a corresponding increase in current output. For the SnS-rGO HEC, the high-frequency semicircle corresponds to an internal resistance of $\sim 12.5 \Omega$, as extracted from equivalent circuit fitting (Fig. 5.7(b)). Hydronium ions migrate toward the electrodes via a hopping mechanism, while hydroxyl ions are transported through defect sites, collectively contributing to the reduced internal resistance. Furthermore, water dissociation in the nanocomposite-based HECs significantly lowers the resistance and facilitates ionic transport. Owing to the high proton conductivity of rGO, the overall conductivity of the nanocomposite HEC increases upon wetting, as evidenced by the Nyquist response. Additionally, the presence of rGO reduces the grain boundary resistance of SnS, enabling efficient hydroxyl ion migration along grain boundaries.

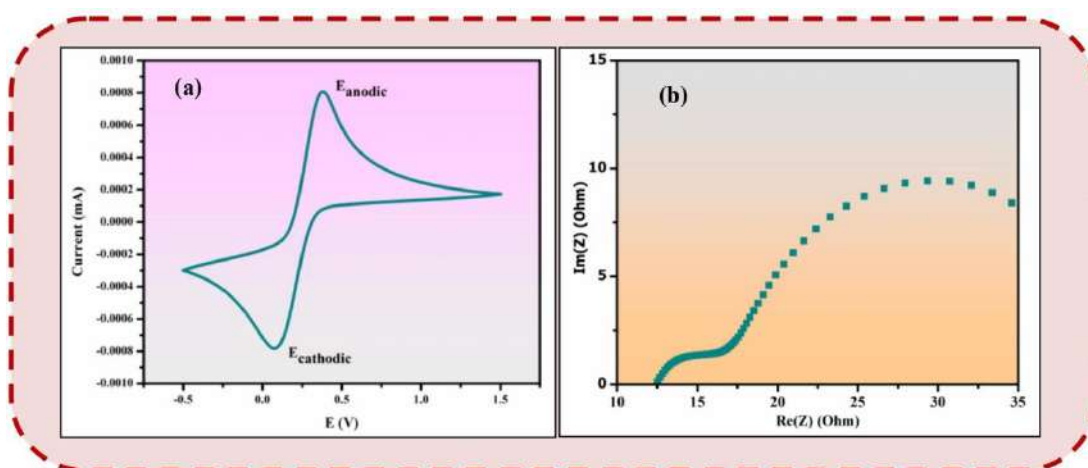


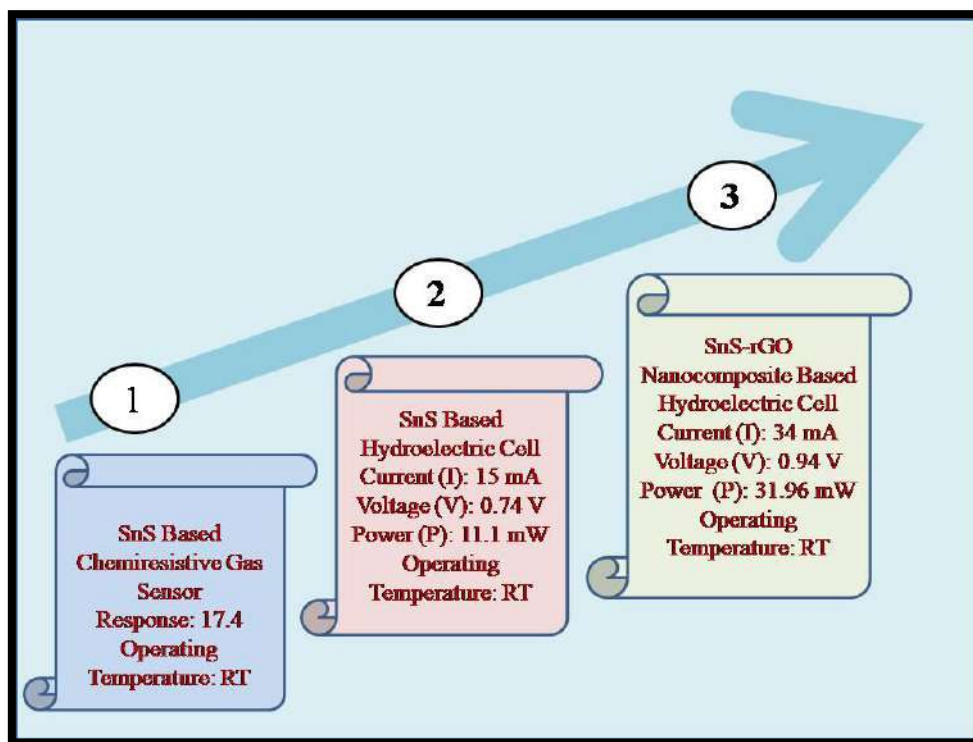
Fig. 5.7: (a) CV curve of SnS-rGO electrode in 0.3 M KOH solution and (b). Nyquist curve of wet SnS-rGO nanocomposite HEC.

5.8 Conclusion

The SnS-rGO nanocomposite was successfully synthesized using the solvothermal method, as confirmed by X-ray diffraction (XRD) and Raman spectroscopy. BET analysis shows that the surface area, poresize, and pore volume increased to $47.09 \text{ m}^2 \text{ g}^{-1}$, 12.13 nm , and $1.66 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$. Nyquist curve for SnS based HEC in wet state exhibit ionic diffusion in the cell and also shows the high reduction in the impedance of the cell under the wet conditions. The fabricated HEC of cross section area 4 cm^2 exhibited an off-load power output of 31.96 mW . The HEC showcases an impressive electric current output of 34 mA , demonstrating its capability to sustain stable performance with just a few drops of water. Furthermore, its remarkable persists consistently for 12 weeks, affirming its reliability and durability in various operational conditions, showcasing its potential as an alternative green energy source. These results highlight the strong potential of defect-engineered SnS-rGO nanocomposite as efficient and reliable materials for hydroelectric energy harvesting. Beyond electrical power generation, the evolution of hydrogen gas at the cathode presents an additional opportunity for clean hydrogen production, offering prospects for scalable hydrogen energy applications. Moreover, the simple design and water-driven operation of hydroelectric cells make them promising candidates for emergency power and lighting solutions in flood-affected or remote regions lacking access to conventional electricity.

CHAPTER 6

Conclusions, Future Scope and Social Impact



The primary objective of this chapter is to comprehensively summarize and critically interpret the major observations, experimental findings, and scientific conclusions derived from the present research on two-dimensional nanomaterials for gas sensing and hydroelectric cell applications. In this chapter conclusions are summarized in accordance with the preceding chapters, providing a coherent overview of the systematic progression from material synthesis to structural characterization and device-level performance evaluation. By consolidating the experimental insights obtained throughout the study, this section highlights the logical development and scientific consistency that underpin the overall research framework.

5.1 Summary of Research Work

In particular, this thesis takes advantage of the unusual physicochemical behaviour of 2D nanomaterials and their corresponding nanocomposites for two important

technological applications: environmental gas sensing, especially ethanol detection, and green electrical energy production via hydroelectric cells. The ultimate aim of this work was to develop and fabricate room-temperature gas sensors that exhibit low power consumption, high sensitivity, rapid response-recovery behavior, and long-term operational stability. Simultaneously, the study sought to explore the untapped potential of defect-engineered 2D nanomaterials in enabling spontaneous water-splitting for electricity generation at room temperature.

The scientific rationale, synthesis strategies, and experimental methodologies employed to achieve these objectives were systematically developed and presented across Chapters 1 to 6. These chapters describe the systematic synthesis of 2D SnS and its nanocomposite-based materials under controlled experimental conditions, comprehensive structural and spectroscopic characterization. Subsequently, the electrical and electrochemical properties of the synthesized materials were systematically evaluated, followed by the fabrication and performance assessment of chemiresistive gas sensor and hydroelectric cell (HEC) devices. The interrelationship between surface defect engineering, charge transport mechanisms, adsorption kinetics, and ionic conduction behavior was carefully examined to establish structure property performance correlations. The chapter further outlines prospective research directions and emerging opportunities, laying the foundation for future advancements in nanomaterials based gas sensors and hydroelectric cells. In this chapter, the significant outcomes of the research are consolidated, reflecting the underlying scientific reasoning, experimental methodology, and comprehensive investigations undertaken throughout the thesis, as follows:

Chapter 1 provides a comprehensive introduction to the fundamental concepts of nanotechnology and nanomaterials, emphasizing their transformative impact on modern sensing and energy technologies. It begins by outlining how **the unique physicochemical properties of nanomaterials such as high surface-to-volume ratio, tunable** electronic structure, **and** defect-engineered surface activity have enabled significant advancements in device performance. Particular attention is given to two-dimensional (2D) nanomaterials, whose layered structure and surface-dominated behavior make them

highly suitable for applications requiring enhanced interfacial interactions and efficient charge transport.

Building upon this foundation, the chapter discusses the growing global interest in developing advanced gas sensing technologies, especially ethanol gas sensors capable of operating efficiently at room temperature (RT) with low power consumption. The urgent need for highly sensitive, selective, and stable sensors under ambient conditions is highlighted, given the increasing environmental and industrial concerns associated with volatile organic compounds. The chapter reviews existing ethanol sensing technologies, with special emphasis on chemiresistive sensors due to their structural simplicity, scalability, cost-effectiveness, and compatibility with electronic integration. The role of nanotechnology and materials engineering in enhancing sensing performance through morphological control, defect modulation, and compositional optimization is critically examined.

Extending beyond gas sensing, the chapter introduces hydroelectric cells as an emerging green energy harvesting technology. It explains how defect-rich nanomaterials can facilitate spontaneous water dissociation and sustain ionic transport without external bias, thereby generating green electrical energy. The conceptual connection between gas sensing and hydroelectric cell operation is established through shared surface-driven mechanisms, including adsorption, defect-assisted charge modulation, and interfacial electrochemical processes. This integrated approach reveals the potential of 2D nanomaterials to function as multifunctional material platforms, effectively bridging room-temperature gas sensing and sustainable electricity generation through hydroelectric cell (HEC) devices.

Chapter 2 presents a comprehensive account of the experimental methodologies employed for the synthesis, fabrication, and characterization of two-dimensional (2D) nanomaterials and their nanocomposites. It elaborates on the electrophoretic deposition (EPD) technique adopted for the preparation of uniform sensing films, emphasizing its effectiveness in achieving controlled film thickness, homogeneous surface coverage, and strong adhesion to the substrate. The chapter provides a detailed discussion of the structural, morphological, and compositional characterization techniques used to establish

structure–property relationships. X-ray diffraction (XRD) analysis was performed to determine the crystalline structure, phase purity, and lattice parameters of the synthesized materials. Field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) were employed to investigate surface morphology, nanoscale architecture, and microstructural features such as layer thickness and porosity. Raman spectroscopy was utilized to analyze vibrational modes, crystallinity, and defect-induced structural variations. Fourier transform infrared (FTIR) spectroscopy was conducted to identify functional groups and bonding characteristics, while X-ray photoelectron spectroscopy (XPS) was performed to examine elemental composition, chemical states, and defect-related surface chemistry.

The chapter further describes the fabrication of chemiresistive gas sensor devices, wherein metallic electrodes were deposited onto the synthesized sensing films using thermal evaporation to ensure reliable electrical contact. The sensing performance of the fabricated devices was evaluated using a custom-designed chemiresistive gas sensing setup, which enabled precise control of gas concentration, exposure time, and environmental parameters for accurate assessment of response, recovery, and stability. For hydroelectric cell (HEC) investigations, electrical output characteristics, including current and voltage measurements, were recorded using a precision source-measure unit. To gain deeper insight into electrochemical behavior, cyclic voltammetry was performed to analyze redox activity and charge storage characteristics. Furthermore, electrochemical impedance spectroscopy (EIS) was conducted to elucidate the charge transport mechanisms, interfacial resistance, and ionic conduction pathways within the hydroelectric cell system.

Chapter 3 reports the solvothermal preparation of SnS nanostructures and investigates their performance as active materials in room-temperature chemiresistive ethanol gas sensing. The SnS sensor has demonstrated a significant response of 17.4 and a quick response/recovery time of 12.4/20.2 sec when exposed to 400 ppm ethanol gas at room temperature. The sensor exhibits commendable sensing attributes including remarkable repeatability of three consecutive cycles and long-term stability of 15 mins to 400 ppm ethanol gas. The sensor showcases an impressive selectivity, particularly discerning ethanol amidst a diverse array of VOCs. The improved ability to detect ethanol gas at room temperature is due to the distinctive vertically aligned SnS nanoplates which offer a

notable surface-to-volume ratio, thereby creating abundant sites for the adsorption of ethanol gas molecules, enhancing the sensing response. These findings especially at room temperature, may pave the way for its potential deployment in innovative applications. Its integration into smart, compact, and Internet of Things (IoT)-based systems holds promise for advancements in gas sensing technology.

Chapter 4 aims to synthesis and fabricate 2D SnS based hydroelectric cell by low temperature solvothermal method. The fabricated HEC of cross section area 4 cm^2 exhibited an off-load power output of 11.1 mW. The HEC showcases an impressive electric current output of 15 mA, demonstrating its capability to sustain stable performance with just a few drops of water. The specific surface area obtained by BET analysis for SnS is $6.45\text{ m}^2\text{ g}^{-1}$ with pore diameter being approximately 17.07 nm. Nyquist curve for SnS based HEC in wet state exhibit ionic diffusion in the cell and also shows the high reduction in the impedance of the cell under the wet conditions. Furthermore, its remarkable persists consistently for 30 days, affirming its reliability and durability in various operational conditions. The power output produced via water splitting by HEC is encouraging and proves to be green energy source at low cost. Electricity generation by HEC device does not emit any toxic gases therefore it can be the best strategy to save the environment and to achieve mission of net carbon zero.

Chapter 5 addresses the development of a SnS-rGO nanocomposite using a solvothermal approach optimized for improved interfacial bonding and electronic conductivity. The structural integrity and successful composite formation were validated through X-ray diffraction (XRD) analysis, while Raman spectroscopy was utilized to investigate vibrational modes, structural defects, and the synergistic interaction between SnS nanostructures and the rGO matrix. BET analysis shows that the surface area, pore size, and pore volume increased to $47.09\text{ m}^2\text{ g}^{-1}$, 12.13 nm, and $1.66 \times 10^{-2}\text{ cm}^3\text{ g}^{-1}$. Nyquist curve for SnS based HEC in wet state exhibit ionic diffusion in the cell and also shows the high reduction in the impedance of the cell under the wet conditions. The fabricated HEC of cross section area 4 cm^2 exhibited an off-load power output of 31.96 mW. The HEC showcases an impressive electric current output of 34 mA, demonstrating its capability to sustain stable performance with just a few drops of water. Furthermore, its remarkable persists consistently for 12 weeks, affirming its reliability and durability in various

operational conditions, showcasing its potential as an alternative green energy source. These results highlight the strong potential of defect-engineered SnS-rGO nanocomposite as efficient and reliable materials for hydroelectric energy harvesting. The simple design and water-driven operation of hydroelectric cells make them promising candidates for emergency power and lighting solutions in flood-affected or remote regions lacking access to conventional electricity.

5.2 Salient Outcomes of the Thesis

Main findings and contributions of this thesis are as follows:

- **A p-type chemiresistive gas sensor** was successfully fabricated using solvothermally synthesized **SnS nanoplates** as the sensing material. The vertically aligned nanoplate architecture provides a high density of active surface sites, which significantly enhances gas adsorption. This structural advantage leads to improved sensing performance, including higher sensitivity, faster response and recovery characteristics, and stable operation under ambient conditions.
- **Defect-engineered n-type SnS nanosheets and its nanocomposite** were employed to fabricate a **green energy-harvesting hydroelectric cell device (HECD)**, capable of dissociating water molecules at room temperature without the use of any acid, base, or external electrolyte.

5.3 Future Prospective

The present thesis explores the unique physicochemical properties and functional advantages of two-dimensional (2D) nanomaterials and their nanocomposites for applications in environmental monitoring and sustainable energy generation. Particular emphasis is placed on the development of chemiresistive gas sensors for detecting hazardous VOC gases and on hydroelectric cell (HEC) devices for green energy harvesting. Through a systematic investigation of material synthesis, structural characteristics, and functional performance in both sensing and energy generation, this study establishes a strong foundation for advancing next-generation sensing and energy technologies. The outcomes of this research open several promising avenues for future exploration and technological innovation, including:

- 1. Scalable Synthesis of Monolayer 2D Nanomaterials:** Monolayer two-dimensional (2D) nanomaterials exhibit exceptional physicochemical, electronic, and optical properties that are distinctly different from those of their bulk counterparts due to strong quantum confinement and surface-dominated phenomena. These unique characteristics make them highly promising candidates for next-generation sensing, optoelectronic, and energy-related applications. However, the practical realization of device miniaturization and large-scale integration of monolayer-based sensors requires precise, reproducible, and scalable synthesis techniques capable of producing high-quality materials with controlled thickness and minimal structural defects. To achieve this goal, the development of advanced synthesis approaches such as chemical vapor deposition (CVD), atomic layer deposition (ALD), molecular beam epitaxy (MBE), and liquid-phase exfoliation is of critical importance. These techniques can enable controlled growth of large-area monolayers with uniform crystallinity, optimized defect density, and high reproducibility. Another important direction involves the development of cost-effective and environmentally sustainable synthesis strategies that allow mass production without compromising material quality. Achieving wafer-scale fabrication and transfer techniques compatible with existing microelectronics manufacturing processes will significantly accelerate the commercialization of 2D nanomaterial-based devices. Therefore, continued progress in scalable synthesis technologies will be crucial for bridging the gap between fundamental laboratory research and practical industrial deployment. Such advancements will enable the widespread utilization of 2D nanomaterials in high-performance gas sensors, flexible electronics, and sustainable energy harvesting devices for real-world applications.
- 2. Performance Enhancement of Metal Chalcogenides via Advanced Material Engineering Strategies:** The functional performance of metal chalcogenides can be substantially enhanced through targeted material engineering approaches, including compositional modification, defect tuning, and hybridization with complementary nanomaterials. Incorporating materials such as reduced graphene oxide (rGO), metal oxides, conductive polymers, or other 2D nanostructures can create hybrid architectures that exhibit synergistic effects. These hybrid systems

improve charge transport pathways, increase surface reactivity, and enhance interfacial stability, which are essential factors for achieving superior sensing performance and improved energy harvesting capability. Furthermore, careful control over the electronic structure, defect density, and surface chemistry of metal chalcogenides through tunable compositional design can significantly enhance gas adsorption behavior, sensitivity, and selectivity toward target analytes. Such modifications can also promote efficient chemidissociation of water molecules, which is crucial for improving the performance of hydroelectric cell HEC devices. By optimizing these structural and electronic parameters, metal chalcogenide based systems can achieve stable and efficient operation under room-temperature conditions. These advancements open new opportunities for the development of next-generation multifunctional devices, including low-power or self-powered gas sensors and environmentally sustainable hydroelectric cell systems for green energy generation. Such technologies are particularly promising for continuous operation under ambient conditions, contributing to energy-efficient sensing platforms and sustainable energy harvesting solutions.

3. **Exploration of Emerging 2D Nanomaterials for Advanced Sensing and Energy Technologies:** The exploration of next-generation two-dimensional (2D) nanomaterials has opened new pathways for developing high-performance gas sensing and energy harvesting devices. In addition to widely studied materials such as graphene and transition metal chalcogenides, several emerging 2D materials including MXenes (e.g., $\text{Ti}_3\text{C}_2\text{T}_x$), borophene, phosphorene, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), hexagonal boron nitride (h-BN), and transition metal carbides and nitrides have attracted significant research interest. These materials exhibit exceptional physicochemical characteristics, such as high electrical conductivity, tunable band structures, large surface-to-volume ratios, and chemically active surfaces, making them highly promising candidates for sensing and energy-related applications. In addition, layered transition metal oxides and chalcogenides such as MoS_2 , WS_2 , SnS_2 , and TiS_2 provide abundant active sites and strong interaction with gas molecules, which are advantageous for achieving high sensing responses and efficient surface reactions. The integration of these materials into hybrid or heterostructured architectures can further amplify their functional capabilities.

Combining different 2D materials with conductive carbon frameworks, metal oxides, or polymer matrices can generate synergistic effects that enhance electron transport, increase active adsorption sites, and improve interfacial charge transfer processes. Such engineered heterostructures can lead to the development of highly sensitive and selective gas sensors with improved response and recovery dynamics. Moreover, these hybrid systems can be tailored to detect multiple gases simultaneously while maintaining stable operation under ambient conditions. Beyond gas sensing, these advanced materials also hold immense potential for energy harvesting technologies, particularly hydroelectric cell HEC devices that operate through water dissociation and ionic transport mechanisms. Their defect-rich structures and tunable surface chemistry can facilitate water adsorption, promote proton conduction, and enhance electrochemical reactions required for electricity generation. As a result, these materials can contribute to the development of self-powered sensing platforms where the energy generated from hydroelectric cells can be utilized to operate gas sensing devices.

4. **Developing Wearable Sensors and standalone Hydroelectric Cells:** The advancement of flexible gas sensors represents a significant step toward the realization of real-time, wearable, and portable electronic devices. These sensors can be seamlessly integrated into textiles, wearable accessories, or flexible substrates, enabling continuous and non-invasive monitoring of environmental conditions as well as physiological parameters. The incorporation of mechanically robust, bendable, and conformable nanocomposite materials ensures mechanical durability and operational stability while maintaining high sensing performance. Such flexible sensing platforms hold immense potential for next-generation wearable technologies capable of providing real-time health monitoring, fitness tracking, and personal safety alerts. In parallel, hydroelectric cell (HEC) technology offers a promising solution for sustainable energy generation, particularly in remote or resource limited regions. These devices are capable of producing electrical energy at room temperature through water dissociation without the use of harmful chemicals or external electrolytes, making them environmentally friendly and sustainable. The electricity generated from hydroelectric cells can be utilized to power low-energy electronic devices such as LED lights, small DC fans, and even

self-powered gas sensors. Therefore, integrating flexible sensing platforms with hydroelectric cell based energy harvesting systems may pave the way for autonomous, self-powered monitoring devices that can operate reliably in both urban and remote environments.

5. **Development of Lab-on-Chip (LoC) Technologies for Integrated Sensing Platforms:**

The advancement of Lab-on-Chip (LoC) technologies represents an important direction for integrating gas sensing, diagnostic, and analytical functionalities onto compact, multifunctional platforms. These miniaturized systems enable the simultaneous execution of multiple analytical processes within a single device, thereby reducing analysis time, sample volume, and operational complexity. Progress in micro- and nanofabrication techniques, along with improved material integration strategies and scalable manufacturing processes, will be essential for enhancing the efficiency, reliability, and cost-effectiveness of LoC devices. Successful large-scale deployment and commercialization of LoC systems have the potential to significantly transform various application domains, including environmental monitoring, healthcare diagnostics, and point-of-care medical testing. Such platforms can provide rapid, real-time, and highly accurate analytical capabilities, enabling timely decision-making and improved monitoring of environmental and biological conditions. These developments enhance device sensitivity, enable multiplexed detection, and facilitate seamless integration with electronic readout systems. As a result, LoC platforms are expected to become increasingly valuable tools for both research and industrial applications, contributing to the development of portable, efficient, and intelligent sensing systems.

6. **Alternative Approach For Sustainable Energy Generation With Valuable By-Products:**

Hydroelectric cell (HEC) technology has the potential to address the growing demand for sustainable and decentralized energy, particularly in remote or off-grid regions. These devices offer a promising alternative to conventional energy sources such as fossil fuels and, in certain applications, can complement renewable technologies like solar cells. The electricity generated through hydroelectric cells is environmentally benign and does not involve the emission of toxic gases or harmful

by-products. In addition to electricity generation, the process also produces green hydrogen as a by-product, which is considered a clean and high-energy fuel for next-generation transportation systems and industrial applications. Therefore, scalable development of hydroelectric cell technology could contribute significantly to sustainable energy infrastructure and support the transition toward low-carbon emission energy systems.

The present research focuses on the synthesis of advanced nanomaterials and the fabrication of functional devices, including chemiresistive gas sensors for the detection of ethanol at room temperature and hydroelectric cells for green energy harvesting. By employing advanced nanomaterial systems, surface engineering strategies, and innovative fabrication techniques, this work aims to significantly enhance the efficiency, reliability, and reproducibility of both gas sensing and hydroelectric cell technologies. The developed ethanol gas sensors demonstrate the capability for accurate and sensitive detection under ambient conditions, which is particularly important for applications in environmental monitoring, industrial safety, and process control systems. Ethanol vapors are widely present in industries such as pharmaceuticals, food processing, chemical manufacturing, and fuel production, and prolonged exposure to these vapors can pose serious health risks. Therefore, the development of highly sensitive and reliable room-temperature gas sensors is essential for ensuring safe working environments and preventing hazardous exposure to volatile organic compounds.

Beyond their technological advantages, the fabricated ethanol gas sensors offer significant social benefits by contributing to safer and healthier living environments. Due to their low power consumption and cost-effective fabrication, these sensors have strong potential for large-scale deployment in smart cities, environmental monitoring networks, and portable health monitoring devices. Such technologies can play an important role in enhancing community safety, workplace protection, and overall environmental well-being. In addition to sensing applications, the hydroelectric cells fabricated in this research demonstrate a promising approach toward sustainable and environmentally friendly energy generation. These devices generate electricity through water dissociation at room temperature without the need for harmful chemicals, acids, or electrolytes. The electricity produced by hydroelectric cells can be used to power low-energy electronic devices such

as LEDs, small DC fans, portable sensors, and communication modules. This capability makes hydroelectric cells particularly valuable for use in remote or off-grid regions where conventional electricity infrastructure is limited or unavailable.

From a societal perspective, fabricated gas sensor and hydroelectric cell devices offers several benefits. Ethanol gas sensors at room temperature contribute to meaningful social benefits, offering ways for safer and healthier environments. Their high sensitivity and real-time detection capability could prevent industrial accidents and exposure to injurious vapors, supporting air quality monitoring in public and residential areas. In parallel, hydroelectric cells provide a clean and sustainable source of energy without producing toxic emissions or environmental pollutants, thereby supporting global efforts toward carbon-neutral and environmentally responsible technologies. Hydroelectric cells can serve as an important energy solution in emergency situations such as natural disasters, floods, or remote field operations where reliable electricity is urgently required. Their simple design, low cost, and ability to operate using water make them suitable for portable energy generation systems that can support lighting, communication, and monitoring devices during emergencies. In addition, the production of green hydrogen as a by-product during the water dissociation process offers further opportunities for clean fuel generation, which is important for future hydrogen-based energy systems, transportation, and industrial applications.