ELECTROCHEMICAL ENERGY STORAGE AND GLUCOSE SENSING APPLICATIONS OF TRANSITION METAL OXIDE NANOMATERIALS

Ph.D. Thesis

By LICHCHHAVI



DISCIPLINE OF METALLURGY ENGINEERING & MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE August 2020

ELECTROCHEMICAL ENERGY STORAGE AND GLUCOSE SENSING APPLICATIONS OF TRANSITION METAL OXIDE NANOMATERIALS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by LICHCHHAVI



DISCIPLINE OF METALLURGY ENGINEERING & MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE August 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled ELECTROCHEMICAL ENERGY STORAGE AND GLUCOSE SENSING APPLICATIONS OF TRANSITION METAL OXIDE NANOMATERIALS in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, INDIAN INSTITUTE OF TECHNOLOGY INDORE, is an authentic record of my own work carried out during the time period from December 2015 to August 2020 under the supervision of Dr. Parasharam M. Shirage, Associate Professor, Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, and Dr. Amrendra Kumar Singh, Assistant Professor, Discipline of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute. December 05, 2020

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M.D onvener, DPGC Date: 05 01 2021

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere and deepest sense of gratitude to **Dr. Parasharam M. Shirage**, (Associate Professor, Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology (IIT) Indore) for his guidance during my Ph.D. tenure. I sincerely acknowledge him for introducing the present research topic, his inspiring guidance, constructive criticism, lab facility for conducting experimental research, and valuable suggestion throughout this research work. It would not have been possible for me to bring out this work without his help and constant encouragement. I acknowledge his assistance in helping me attend conferences, which has broadened my research horizon

I express my gratitude and thankfulness to my supervisor **Dr. Amrendra Kumar Singh** (Assistant Professor, Discipline of Chemistry, IIT Indore) for his continuous motivation and generous guidance throughout the project and also for helpful suggestions and comments during my progress report presentations. Without his endless support, this work would never be possible.

I express my deepest gratefulness to my PSPC members **Dr. Sanjay Kumar Singh** (Associate Professor, Discipline of Chemistry, IIT Indore), and **Dr. Abhirup Datta** (Associate Professor, Center of Astronomy, IIT Indore) for their valuable questions, insightful comments, and motivation.

I would like to thank former director Professor Pradeep Mathur and **Dr. N.K. Jain**, Director, IIT Indore for encouraging research and providing the essential experimental facilities. I acknowledge the support provided by **Sophisticated Instrumentation Center (SIC)** at IIT Indore, for performing XRD, SEM, EDX, UV-Vis, FTIR, measurements. I express my sincere gratitude and thankfulness for their help, support, and cooperation in performing and planning various experiments.

I acknowledge **IIT Indore** for providing me **fellowship under Teaching Assistant (TA) category,** providing expenses towards attending the international conference during my Ph.D. tenure, and for providing all the necessary characterization facilities for pursuing this research work.

I would like to express my sincere thanks to **Dr. Sawanta S. Mali, Dr. Chang Kook Hong** (Department of Advanced Chemical Engineering, Chonnam National University, Gwangju, South Korea), **Dr. Hyunju Lee**, **Dr. Yoshio Ohshita** (Toyota Technological Institute, Nagoya, Japan) for conducting XPS, HRTEM and PL characterization. I acknowledge **Dr. Srimanta Pakhira** (Discipline of Metallurgy Engineering and Materials Science, IIT Indore) for theoretical calculation help.

I would like to thank all of my Ph.D. lab-mates **Dr. Amit Kumar Rana**, **Dr. Yogendra Kumar**, **Dr. Prateek Bhojane**, **Dr. Kushal Mazumder**, **Dr. Manojit Pusty**, **Dr. Rukshana Pervin**, **Mr. Alfa Sharma** and **Mr. Subhash Chand Yadav** for being kind, helpful and wonderful individuals in every aspect of my research life. I sincerely express gratitude to my senior lab members **Dr. Darshna Potphode**, **Dr. Mahesh Verma**, **Dr. Bhuvaneshwari Sakthivel** for their kindness in performing research.

I am indebted to **Dr. Nivedita Jaiswal** my roommate and a very nice companion for always undoubtedly being there for me during my stay at IIT Indore. Her characteristic quiet charm facilitated a comfortable space for me in our hostel room and I am extremely grateful for her hospitality and friendship.

My hostel-mates Shweta Jindal, Sujata Pandey, Kalyani Avinash, Anjali Chaudhary, and Komal Mulchandani, all deserve a round of applause for making my hostel days memorable.

I would also like to thank all my friends, peers and my well-wishers especially Ashish Kumar, Sonal Mittal, Piyush Sinha, Pranav Tiwari, Divya, Dipika, Komal, Nabanita Saha and Dr. Amitesh Kumar for their effective suggestion, discussion, and contribution which helped me to finish my work successfully on time.

I would like to thank my brother **Mr. Abhinav Siddharth** who has been supportive, encouraging, and inspirational in every step that I have taken in my life, so far.

I express my deepest gratitude to **my parents** for their valuable sacrifice and love that helped me to complete this thesis. Their advice of being honest and meticulous in life has proven to be the most effective.

Last but not least, I would like to thank Almighty for giving me the strength, courage, knowledge, and ability to undertake this research study.

Date: 05 January 2021

Lichchhavi

Dedicated to My Beloved Parents, Teachers & All Well Wishers

V

LIST OF PUBLICATIONS (From the thesis work)

Journal Publications:

[1] **Lichchhavi Sinha**, Srimanta Pakhira, Prateek Bhojane, Sawanta Mali, Chang Kook Hong, Parasharam M. Shirage, "Hybridization of Co_3O_4 and α -MnO₂ Nanostructures for High-Performance Nonenzymatic Glucose Sensing", *ACS Sustainable Chem. Eng.*, 6,10, (2018) 13248-13261. (**Impact Factor: 7.632**) DOI: 10.1021/acssuschemeng.8b02835.

[2] Lichchhavi Sinha, Parasharam M. Shirage, "Surface Oxygen Vacancy Formulated Energy Storage Application: Pseudocapacitor-Battery Trait of W₁₈O₄₉ Nanorods", *Journal of The Electrochemical Society*, 166(14),
(2019) A3496-A3503. (Impact Factor: 3.721) DOI: 10.1149/2.1251914jes.

[3] Lichchhavi Sinha, Hyunju Lee, Yoshio Ohshita, Parasharam M.
Shirage, "Defect Mediated W₁₈O₄₉ Nanorods Bundle for Nonenzymatic Amperometric Glucose Sensing Application", *ACS Biomater. Sci. Eng.*, 6,4, (2020) 1909–1919. (Impact Factor: 4.490) DOI: 10.1021/acsbiomaterials.9b01791.

[4] **Lichchhavi**, Hyunju Lee, Yoshio Ohshita, Amrendra K. Singh, Parasharam M. Shirage, "Transformation of Battery to High Performance Pseudocapacitor by the Hybridization of $W_{18}O_{49}$ with RuO₂ nanostructures". (Accepted in Langmuir, Impact Factor: 3.557).

LIST OF CONFERENCES

[1] Poster presentation at "International Conference on Nanoscience and Nanotechnology (ICONSAT)-2016)" at Indian Institute of Science Education and Research Pune, India from 29 Feb-02 March 2016.

[2] Poster presentation in **"Innovative Technologies for Rural Development and their Commercialization (ITRDC-2017)"** at "Centre for Research Technology Developments", Sinhgad Institute, Solapur, India during 18- 21 February 2017.

[3] Poster presentation in **"International Conference on Advanced Rechargeable Batteries allied Materials (ICARBM-2017)"** at Centre for Materials for Electronics Technology (C-MET), Pune, India during 8 - 10 March 2017.

[4] Poster presentation in "Material Research Society of India (MRSI-AGM-2020)" at CSIR - Central Glass and Ceramic Research Institute, Kolkata, India during 11-14 February 2020.

<u>Courses</u>

[1] Completed a Global Initiative of Academic Network (GIAN) course on "Chemical Sensors: Principle, Technologies and Applications" by Prof. Dr. Giovanni Neri, University of Messina, Italy and Associate Prof. Dr. Parasharam M. Shirage, IIT Indore, India during 01-09 July 2016.

[2] Completed a GIAN course on "High-Pressure Synthesized Materials: A Chest of Treasure and Hints" by Prof. Dr. Akira Ayo, Tsukuba, AIST, Japan and Associate Prof. Dr. Parasharam M. Shirage, IIT Indore, India during 11-19 July 2016. [3] Completed an "**International Workshop on Advanced Nanoscience and Engineering**" organized by Discipline of Metallurgy Engineering and Materials Science, IIT Indore, India on 1 Dec 2017.

[4] Completed a TEQUIP Sponsored Short Course on "Advanced Surface Science and Engineering" organized by Discipline of Metallurgy Engineering and Materials Science, IIT Indore, India during 26-28 March 2018.

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ABBREVIATIONS

ESD	Energy Storage Device
SC	Supercapacitor
LIB	Li-ion battery
EDLC	Electrochemical Double-Layer
	Capacitor
PC	Pseudocapacitor
PANI	Polyaniline
PPY	Polypyrrole
AC	Activated Carbon
BDD	Boron Doped Diamond
CNF	Cellulose Nanofibers
CNT	Carbon Nanotubes
SWCNT	Single wall Carbon Nanotubes
MWCNT	Multi-Walled Carbon Nanotubes
ТМО	Transition metal oxide
МО	Metal Oxide
MC	Metal Carbide
TEABF4	Tetraethyl Ammonium
	Tetrafluoroborate
IL	Ionic Liquid
EMIMAc	1-ethyl-3-methylimidazolium
	acetate
PTFE,	Polytetrafluroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
GOx	Glucose oxidase
α-G	α- glucose
β-G	β-glucose

γ-G	γ-glucose
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance
	Spectroscopy
GCD	Galvanostatic Charging -
	Discharging
PVD	Physical Vapor Deposition
CVD	Chemical Vapor Deposition
ALD	Atomic Layer Deposition
PLD	Pulsed Layer Deposition
PHT-TiO ₂	poly (3-hexylthiophene)-Titanium
	dioxide
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron
	Microscope
BE	Binding Energy
HRTEM	High Resolution-Transmission
	Microscopy
SE	Secondary Electron
BSE	Backscattered electrons
EBSD	Electron Backscatter Diffraction
ET detectors	Everhart Thornley Detector
HRTEM	High Resolution-Transmission
	Electron Microscope
EDS	Energy dispersive detector
XPS	X-Ray Photoelectron
	Spectroscopy
ESCA	Electron Spectroscopy For
	Chemical Analysis
IR	Infrared
BET	Brunauer-Emmett -Teller

BJH	Barrett-Joyner-Halenda
WE	Working Electrode
RE	Reference Electrode
SCE	Standard Calomel Electrode
SHE	Standard Hydrogen Electrode
CE	Counter Electrode
ESR	Equivalent Series Resistance
CA	Chronoamperometry
JCPDS	Joint Committee for Powder
	Diffraction System
SAED	Selected Area Electron
	Diffraction
AA	Ascorbic acid
UA	Uric Acid
BiOI	Bismuth Iodide Oxide
SOV	Surface Oxygen Vacancy
PL	Photoluminescence
UV-Vis	Ultra Violet -Visible
SE	Scattered Electrons
STP	Standard Temperature and
	Pressure

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NOMENCLATURE

C _{dl}	Capacitance of an EDLC
C _H	Stern layer capacitance
C_{diff}	Diffusive layer capacitance
С	Capacitance
ε _r	Dielectric constant of the electrolyte
ε _o	Dielectric constant of vacuum
	permittivity
А	Surface area exposed
d	Diffusive layer thickness
Δq	Charge acceptance
ΔV	Change in Potential
ΔV	Change in Time
°C	Degree Celsius
W	Watt
Eo	Standard electrode potential
R	Gas constant
Т	Absolute Temperature
F	Faraday's Constant
Zi	Number of moles of electron
	involved
a _i	Activity of species i
Ζ	Impedance
R	Resistance
MnO_2/Co_3O_4	Hybridization between MnO ₂ and
	Co_3O_4

MnO _{2-x}	Oxygen deficient MnO ₂
n	Number of planes
E _b	Binding Energy
E _k	Kinetic Energy
Φ	Work Function
E _f	Fermi level Energy
hv	X-ray photon Energy
ħ	Planck's Constant
Р	Partial Pressure of adsorbates gas
Ро	Saturated pressure of adsorbates gas
Va	Volume of gas adsorbed
V _m	Volume of surface being covered by
	Monolayer
∫I∆t	Mathematical area
Ι	Current
m	Mass of active material
Ω	ohms
ν	Scan Rate
C_{sp}	Specific Capacitance
ΔV	V ₂ -V ₁ (potential Window)
Ι	Current
Z'	Real part of impedance in complex
	value
Ζ''	Imaginary part of impedance in complex value
ŕ	Frequency
% °	Percentage
A	Angstron
ν	Speed of mobile carriers
Vas	Asymmetric FTIR vibrational band
λ	Wavelength
----------	--------------------
E_{pa}	Anodic Potential
E_{pc}	Cathodic Potential
I_{pa}	Anodic Current
I_{pc}	Cathodic Current

CHAPTER 1

Introduction

1.1 Introduction of Supercapacitors

The rapid growth in the global economy, commercial markets in electric vehicles, portable electronic products, and fossil fuels have created an apparent voracious demand for high-performance energy storage devices (ESDs). However, it seems difficult to meet the increasingly higher standards of demands by using the current energy conversation or storage devices alone, such as lithium-ion batteries or fuel cells [1]. Supercapacitors (SCs) are the emerging devices that are capable of managing high power rates compared to batteries. Though supercapacitors have many-fold higher power density it has 3-30 times lower energy density as compared to batteries. The high power density advantage factor makes supercapacitors suitable for the applications in power busts which do not require high charge storage. Supercapacitors along with the battery can serve well for the devices which require both energy as well as power density. Fuel cells, batteries, and supercapacitors are the unconventional energy storage devices that work on the principle of electrochemical conversions. Supercapacitors store charges as conventional capacitors but in the absence of dielectric material. The capacitors consist of dielectric plates for electrostatic storage of charges whereas supercapacitors consist of two electrodes dipped in an electrolyte separated by a separator allowing the diffusion of electrolytic ions but restricting the establishment of direct contact between the electrodes. Supercapacitors overpass the vent between batteries and conventional

dielectric capacitors in order of maintaining cell voltage, specific power, and operating cost. The prime objective of a dielectric capacitor is to deliver the capacity of rapid storage and release of power which is called power density with the uptake of 196 kW/kg in a very short time (fractions of a second). This value is 10-100 times higher than the energy density of electrolytic capacitors. This property of fast energy delivery is undoubtedly favorable for systems designed for energy recovery, *i.e.*, powerful braking in a transport system. However, the characteristics which make supercapacitors an attention derivable system as compared to dielectric capacitors is its higher charge storage *i.e.*, energy density (0.5-0.6 kJ/L) capacity. Some of the features which make supercapacitors in demand are its higher power densities, quick charge, and discharge processes with proper and reliable power throughputs. The comparisons of supercapacitors along with other energy storage systems are explained graphically between energy (X-axis) and power density (Y-axis) in the Ragone plot as shown in Figure 1.1. Energy storage devices (ESDs) such as batteries, capacitors, flywheels, supercapacitors, and magnetic ESDs are located in the characteristic regions in the power energy plane in the Ragone plot [2]. Both axes are usually shown on a logarithmic scale which allows comparing performances of very different devices. Amongst ESDs like Lead acetate batteries, Nickel-Metal hydride batteries, Li-ion batteries (LIBs) with high energy density, and supercapacitors with high power densities are currently considered as excellent environmental friendly, low cost and high-performance ESDs to fulfill the increasing demands. The LIBs commonly can store a large amount of energy as high as 150-200W h/kg but less utilized due to their less power density (below 1000 W/kg) and poor cycle life (<1000 cycles). In contrast, supercapacitors provide much higher power density (10 kW/kg), long cycle life (exceeding 1×10^5 cycles) and fast chargedischarge processes (within seconds), but suffer from much lower energy density (only 5–10W h/kg) [3].



Figure 1.1 Ragone plot for energy storage devices.

1.2 Types of Supercapacitor

The mechanism for the charge storage phenomenon in electrochemical supercapacitors can be discussed according to its three types:

1.2.1 Electrochemical double-layer capacitor (EDLC)

EDLC exhibits higher energy density than the conventional capacitors, due to its maximum surface area and less charge separation distance. The schematics of the construction and working of EDLC is given in Figure 1.2. In EDLCs, an electrolyte (such as KOH, H₂SO₄, or Na₂CO₃) is placed between the two electrodes whereas in conventional capacitors dielectric mediums are found. The concept of EDLC is followed from the Helmholtz model which is further amended by Gouy and Chapman into the diffused layer model. The Helmholtz concept was given in the 19th Century and it proposed that the opposite charges are layered at the electrode/electrolyte interface and separated by some distances as it happens in conventional capacitors. Gouy and Chapman reformed it as the capacitance of two separated arrays of charges should increase reciprocally with their distance. Later, Stern proposed a combined

model of Helmholtz and Gouy and divided the model into two layers: inner region called as Stern layer (Compact layer) and a diffusive layer [4]. EDLC generally follows the same configuration as a parallel plate capacitor. The capacitance of an EDLC (C_{dl}) is a combination of the stern layer capacitance (C_{H}) and the diffusive layer capacitance (C_{diff}). Mathematically it is represented as equation no. (1.1):

$$\frac{1}{c_{dl}} = \frac{1}{c_H} + \frac{1}{c_{diff}} \tag{1.1}$$

The electrical conduction of an EDLC at the electrode surfaces is controlled by the electrical field generated across the electrode, electrolyte, and the chemical interaction between the electrode ions and electrolyte ions. Porosity plays a great role in enhancing the surface area of an electrode. The specific capacitances "C" for EDLCs are calculated by using equation no. (1.2):

$$C = \frac{\varepsilon_r \, \varepsilon_o \, X \, A}{d} \tag{1.2}$$

Where, " ε_r ", " ε_o " represent the dielectric constant in the electrolyte, and vacuum permittivity, "A" and "d" is the electrode surface exposed in the electrolyte (area) and diffusive layer thickness, respectively.

In EDLC, electrostatic storage of charge occurs due to the reversible reactions between the adsorbed ions of the electrolyte and the electrochemically stable active material of the electrode. The formation of double-layer capacitance in EDLCs is the consequence of charge segregation occurring at the electrode-electrolyte interface due to the polarization phenomenon. The charges get accumulated across the double-layer without a direct physical transfer across the interface. Henceforth, the double amount of charge gets stored across the double-layer capacitor. Currently, a large number of electrode materials show EDLC behaviors by depositing a double-layer of charge over the electrode. Among various materials, carbon has been widely explored due to its low cost,

availability, and abundance [4]. Besides carbon material, other attractive materials are metal oxides. These electrodes yield very high specific capacitance and low resistance.



Figure 1.2 Schematic diagram of the electrochemical double-layer capacitor (EDLC).

1.2.2 Pseudocapacitor (PC)

Pseudocapacitor stores charges owing to redox reactions occurring on the electrode surface with the help of faradaic ion transfer. This phenomenon is entirely non-electrostatic and arises by the result of electrochemical charge transfer between the electrode's active material and electrolyte. Since the whole capacitance process is based on redox reactions, PCs are similar in behavior with batteries but kinetically electroanalytical experiments offer a way discussed in chapter 2 that distinguishes between battery and pseudocapacitor. Pseudocapacitors can yield approximately (10-100) folds larger specific capacitances as compared to EDLCs but it lacks in terms of power performances [5]. The pseudocapacitance (*C*) is given by the derivative of charge acceptance (Δq) and changing potential (ΔV) as given in equation (1.3):

$$C = \frac{d(\Delta q)}{d(\Delta t)} \tag{1.3}$$

Pseudocapacitor possesses quick and reversible faradaic reactions at the interface between electrode and electrolyte which differentiates it from the EDLC supercapacitor. The schematic diagram of the typical pseudocapacitor is drawn in Figure 1.3. The capacitance generated by this mechanism is due to the development of a faradaic current from the redox reactions of the redox-active electrode materials like RuO₂, Co₃O₄, by applying a potential. The electron donor ions like Cl⁻, B⁻ get chemisorbed on the surface of the electrode causing electrosorption. Generally, an electrochemical capacitor consists of both the EDLC and Pseudocapacitor mechanism together, however, based on the dominant contribution of active material, one storage mechanism rules over the other which contributes less [4,5]. Generally, metal oxides like ruthenium oxides (RuO₂) [6], vanadium nitride (VN) [7], manganese oxide(MnO₂) [8], conducting polymers like polyaniline (PANI) [9], carbon-based hetero atoms[10], other transition metal oxides [11], and nanoporous carbon [12], shows pseudocapacitance. The drawbacks of pseudocapacitor electrodes that hinder its potential applications are the redox nature which allows the insertion and de-insertion of electrolyte molecules inside the electrode exhibiting the shrinking and swelling of the nanomaterial during charging and discharging. It also suffers from low conductivity which makes it perform poorly during a long life cycle while analyzing the stability of electrodes.



Redox active molecule
Figure 1.3 Schematic diagram of Pseudocapacitor(PC).

1.2.3 Hybrid capacitor

Electrochemical supercapacitors act as a bridge between batteries and capacitors, which is divided into two parts EDLC and discussed The deciding factors pseudocapacitors as above. of supercapacitors are electrode capacitance and cell voltage. So the effective way for enhancing the capacitances is to either modify the nanostructure in terms of porosity or morphology or to develop an asymmetric/hybrid supercapacitor. Here, supercapacitor (SC) utilizes the gap between the two electrodes and its potential difference for increasing the overall voltage of the cell. The SC maintains the asymmetry either by capacitor/capacitor type electrode (redox/redox type, EDLCs/redox type) or capacitor type/battery type SCs. The storage principles of hybrid supercapacitors are governed by the EDLC and PC storage principles. PCs do not fulfill the limitations of EDLC and vice versa, the combination of both the mechanisms conceals the limitations of the combining components with the advantage of providing high capacitances. With the development of the electronics market, there has been a huge demand for devices that store electricity with all the characteristics of extremely high storage and delivery capacity called energy/power densities and good firmness for long-running. The combined properties of Li-ion batteries with high energy density and Supercapacitors with a fast-charging rate have led to

the evolution of (battery-like) hybrid supercapacitors. Schematic of a battery-like hybrid supercapacitor composed of one Li ion-based electrode and another carbon-based electrode is given in Figure 1.4. It is well reported that asymmetric supercapacitors with two different electrodes made of different active materials perform higher as compared to symmetric supercapacitors. The commercially available symmetric hybrid SC comprises two products of activated carbon (AC) inside organic electrolyte with the operating potential up to 2.7 V [13]. The Assembly of two different electrodes forming an asymmetric SC is the AC and MnO₂ along with AC-Ni(OH)₂[14]. Recently, Yu et al. fabricated a boron-doped diamond (BDD) film with carbon nanofibers (CNFs). The BDD/CNF EDLC developed capacitance in $1M H_2SO_4$ electrolyte whereas BDD/CNF PC was prepared using $Fe(CN)_6$ aqueous solution. The overall performance of the system stayed up to 10,000 charging/discharging cycles without any degradation. The power density of EDLC and PC are 27.3 and 25.3 kW/kg. The obtained results confirmed the application of the BDD/CNF species in the field of batteries like supercapacitor [15]. The conducting polymers provide an extra advantage in hybrid SC. Conducting polymers store and release ions *i.e.*, during oxidation reaction the ions are transferred to the electrode, and while reducing the ions moves back to the electrolyte [13]. For the advancement in the field of the hybrid supercapacitor, there are various factors which led to the high yielding specific capacitance of a system.

- Nanomaterial used for electrode fabrication should have a high surface area.
- High Conductivity of the electrode.
- Development of 3-dimensional (3D) materials to accelerate the mobility of ions (porous structure).
- Minimization of diffusion activation energy by the use of carbonbased materials on different hybridization and allotropes.

• A suitable electrolyte should be used. For example, EDLCs use inert electrolyte whereas PC prefers redox-active electrolytes.



Figure 1.4 Schematic diagram of battery-like hybrid supercapacitor.

1.3 Construction of Supercapacitor

The electrochemical supercapacitor has a similar construction as of battery. It is also a combination of two electrodes immersed in an electrolyte separated by some distances and has a separator between the two electrodes. The comprising parts of a supercapacitor are the two electrodes, electrolyte, current collector, and separator as shown in Figure 1.5. The high energy storage characteristics of supercapacitors are very much dependent on these components.



Figure 1.5 Composition of a supercapacitor.

1.3.1 Electrodes

The charge storage capacity of an ES strongly depends upon the electrode materials used. The electroactive surface area of the electrode greatly influences the performance and participation of electrodes in the electrochemical reaction. Another important feature in the electrode which renders its properties in electrochemical reactions is porosity. The pore size of electrode materials that yielded maximum capacitances was very close to the electrolyte's ion size. The electrode materials of ES are divided into three types: (1) carbon-based material (2) conducting Polymers (3) metal oxides like manganese oxide (MnO₂), cobalt oxide (Co₃O₄), nickel oxide (NiO), ruthenium oxide (RuO₂), tungsten oxide (WO₃)

• **Carbon materials:** Carbon materials have advantages of high surface area, low cost, easy processing, high chemical stability, good electronic conductivity, non-toxicity, and wider operating range. Carbon-based ES shows a close mechanism as of EDLC. The electrochemical characterization curve of carbon materials confirms the EDLC mechanism of SC. High surface area carbon materials generally include activated carbon, carbon aerogels, carbon nanotubes, template porous carbon. Carbon-based electrodes show high resistivity which is generated due to the high internal resistances and which also decreases the specific capacitances of the system to a limited value. Another factor that affects the capacitances is pore sizes, surface area which is not accessible for the electrolyte ions, pore distribution, and moderate surface modification.

• **Conducting polymers (CPs)**: CPs are suitable for ES due to its low cost, less environmental impact, high conductivity, high potential window, high porosity, and flexible redox participation through chemical alteration. CPs store charges through the redox mechanism by the insertion–reinsertion mechanism of electrolyte ions. The whole process is a bulk phenomenon, Some of the conducting polymers are polyaniline (PANI), polypyrrole (PPY), Poly(3,4-ethylene-dioxythiophene) (PEDOT).

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The unfortunate reason for the mechanical degradation of CP based electrodes is swelling and shrinking of the material during the chargingdischarging process. This leads to the corrosion of material and fading the stability performance of CP based electrode material.

• **Transition metal oxides (TMOs):** Transition metal oxides have high specific capacitances and conductivity, making them worthy for electrode material yielding high energy and power delivering SC. Ruthenium oxide shows a pseudocapacitive behavior, wide potential window, high conductivity, suitable in acidic medium but it is too expensive which renders its application in aerospace and military. Another transition metal oxide MnO₂ which is cheaper and less toxic, considered as an alternative to RuO₂. MnO₂ deficit by limited proton exchange in its crystal form with low electronic conductivity that sometimes affects its electrochemical performance of stability.

1.3.2 Electrolytes

The electrolyte used in the supercapacitor is the combination of salt and solvent. It is another important part of the ES, which generates ionic conductivity and charge compensation across the electrode in an electrochemical cell. The important parameters for the selection of an electrolyte are: (*a*) the ionic size and type, (*b*) electrode materials, (*c*) ion and solvent concentration, (*d*) ion and solvent interaction, and (*e*) potential window of the device, *etc.* Majorly there are three types of electrolyte:

• **Organic electrolyte:** Organic electrolytes have been commercially used to a large extent because of its high operating potential range from 2.5-2.8 V. It also works well with cheap current collectors and packaging. Generally, the organic electrolytes like conductive salts, *e.g.*, Tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in propylene carbonate are used for EDLCs, but the practical drawbacks of organic electrolytes are their specific capacitance, high cost, toxicity and dangerous as flammable. It also requires a tough assembling and lots of complex filtrations removing the impurities. It is also not flexible with

rising temperatures above 70° C because of the low ignition and detonation temperatures.

• **Ionic liquid electrolytes (ILs):** Both aqueous and organic electrolytes do not work well with high temperatures above 70 ° C and 80 ° C, respectively. IL electrolytes work well even at high temperatures due to their high thermal and chemical stabilities. It has a very high potential window, negligible vapor pressure, and inflammable properties. The commonly used IL electrolytes are 1-ethyl-3-methylimidazolium acetate (EMIMAc),1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMI-TFSI), *etc*.

• Gel and solid polymer electrolytes: In this electrolyte, polymer plays an important role in increasing the potential window with high stability and it also compensates the presence of electrolyte and separator together to make the device lightweight and less complex. A gel electrolyte incorporates a liquid electrolyte into a microporous polymer matrix that holds in the liquid electrolyte through capillary forces, creating a solid polymer film. The chosen separator must be insoluble in the desired electrolyte and provide adequate ionic conductivity. Non-polar rigid polymers such as PTFE, PVA, PVDF, and cellulose acetate offer good ion conductivity when used as gel electrolytes. This electrolyte supplies less conductivity as compared to liquid electrolytes but it improves the efficiency of ionic mobility inside the devices.

• Aqueous electrolyte: These electrolytes provide high capacitance and conductivity. The high charge storage is due to the lowering of ESR, which enhances the delivering power of the ES. However aqueous electrolyte is not the correct choice for commercial purposes because it only works in the small potential window due to constricted decomposition voltage. Some of the aqueous electrolytes which are commonly used are Na₂SO₄, H₂SO₄, KOH, Li₂SO₄, K₂SO₄, *etc*.

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1.3.3 Separator

A separator plays a role in preventing the physical contact between the two opposite electrodes. It should have a strong mechanical strength for providing sustainability and prevent the migration of carbon particles. The material should also allow the ionic conductivity and electronic insulating capability. It is thin, porous and chemically resistive towards corrosion from electrolytes. Batteries and ESs use cellulose paper, polymer, and glass wool as a separator in the devices to work well in ambient temperatures whereas organics utilizes glass, mica, and ceramic separators. Polyolefin is the most commonly used separator worldwide owing to its mechanical strength, low cost, flexibility, corrosion resistance, and porosity, *etc.*.

1.3.4 Current collector

It is used in ES devices to assemble and feed electric charges stored within the active capacitive material. Metal foils of aluminum, copper, and nickel with a thickness between 20 and 80 μ m are largely used as current collectors or electrode substrates due to high conductance properties and low costs as compared to gold and platinum. The current collector and electrode should have high adherence to avoid internal resistances.

1.4 Advantages of Electrochemical Supercapacitor (ES)

Electrochemical supercapacitors are preferred over batteries because of several attracting factors listed below:

• High power density

It is evident from the Ragone plot that ES displays a very high power density as compared to batteries and fuel cells. It occurs because it stores charges on both the electrode and also within the bulk part of the electrode's surface. Thus, the charging-discharging is not only limited to ionic conduction which enhances the rate of reaction. The high charging-discharge rate led to higher power density. ES approximately takes ~30 s in charging and discharging and it can deliver energy within ~0.1s. Batteries normally take a longer time (scale of hours) in charging as compared to ES [16,17].

• Long life expectancy

One of the drawbacks of batteries is the irreversible conversion of the chemical reagents and phase changes that occur due to the faradaic reactions involved. In ES, a negligible amount of chemical species gets converted and there is no phase change. ES specifies long cyclability (up to 1000000) and neither has it required maintenance during their lifetimes. The life expectancy for ES is estimated for 30 years which is far longer than Li-ion batteries [18,19].

• Long shelf life

Most of the batteries get degraded and become useless when left in a cell in an unused stage due to self-discharge and corrosion. Unlike batteries, it is reported that ES maintains its charge storage properties and remains intact after being unused over a while [18].

• High efficiency

The heat dissipated in the process of charging and discharging cycle in ES is relatively small. So its efficiency is high in comparison to batteries even when it is operated at a high power of < 1 kW/kg [20].

• Wide range of operating temperatures

ES can function in extreme environmental conditions like extremely high and low temperatures. The temperature ranges at which it is operational are 40° C to 70 °C. So, it is worthy of the defense applications where devices working under all temperature conditions during the war are needed.

Environmental friendliness and safety

ESs are less toxic, reliable, and easily disposable as compared to Li-ion batteries.

1.5 Challenges for Electrochemical Supercapacitor

Though ES have several advantages over batteries still, it also faces some challenges in the current era of technology which are summarized below:

• Low energy density

It is evident from the Ragone Plot that ES lacks in terms of energy density(~5Wh/kg) when compared with batteries (>50Wh/kg). For high energy density, a large size of ES is required which increases the cost of production. So, the effective protocol to overcome the less energy density challenge has become a major issue to meet the current requirement of the world.

• High cost

The costs of the raw materials used while the fabrication ES has become a major issue. The most important part which affects the cost of production of ES is electrodes. Thus for minimizing the cost of the electrode, a material is required which is cheap and abundant in nature. At present, Carbon and RuO₂ are the common material used for synthesizing electrodes commercially. Other factors also contribute to raising the cost of devices like separator, electrolyte, *etc*.

• High self-discharging rate

ES has a low duration and high self-discharging rate of 10-40% per day due to the instability of electrode in electrolyte [21].

• Industrialization of the supercapacitor

Due to varieties of applications and limited commercial products, researchers do not fulfill the available industrial standards. Some ES are commercially available but they lack performance, electrode structure, electrode layer thickness, porosity, and so on. Currently, carbon/carbon ES which is available commercially is providing typical energy of 4W h/kg.

1.6 Applications of Electrochemical Supercapacitor

The supremely advantageous ES has become the competitive choice for various practical applications like electric vehicles, electric hybrid vehicles, digital communication devices, digital cameras, mobile phones, electric tools, pulse laser techniques, uninterrupted power supplies, and solar cells [20, 22-25].

In memory back up devices, poor cycle life makes their frequent replacement expensive. Similarly, batteries for powered electric vehicles can't meet the peak load requirements which are mandatory during climbing by vehicles. ES has the advantage of overcoming these issues [26]. In the case of hybrid vehicles, batteries along with ES can improve the performance which comprises powerful acceleration, braking energy recovery, excellent cold-weather starting, and battery life. So, ES is a very strong candidate for the replacement of battery for energy storage and conversion applications.

1.7 Introduction of Glucose Sensor

Diabetes mellitus has become one of the primary concerns of the world and is highly responsible for many medical issues like heart disease, kidney failure, *etc.* About 200 million population in the world suffer from this chronic disease. Since diabetes has become a major issue in the world and till now there is no such cure of the disease, frequent monitoring of the blood glucose levels to avoid emergencies is required. Therefore, highly sensitive, low cost, and reliable glucose sensors with an excellent selectivity towards glucose have been the subject of concerns in medical science and food industries. The historical development of biosensors started in 1960 with the evolving enzymes based glucose sensor was designed by Updike and Hicks in 1967 [28]. Since then, vigorous research has been in progress on the biosensors that oxidize the glucose into gluconolactone for the effective blood glucose monitoring.

1.8 Electrochemical Principles of Glucose Biosensors

Since blood glucose monitoring has become the trending issue in the biosensor industry, numerous methodologies and ways have been developed manufacturing new biosensors like electrochemical glucose biosensor [29], colorimetry [30], conductometry [31], optical biosensor [32], and fluorescent biosensors [33].

1.8.1 Potentiometric glucose sensor

Potentiometry is commonly applied to measure glucose concentration greater than 10^{-5} M, which is the physiological range in most of the cases. At zero current flow, the potential between the reference electrode and the working electrode is measured. The reference electrode provides a constant potential, while the working electrode shows a potential depending on the concentration of an analyte. The potential difference measured between the electrode and electrolyte interfaces of species "*i*" is given by the Nernst equation (1.4):

$$E = E_o + \frac{RT}{ZiF} ln \frac{a_i^s}{a_i^\beta}$$
(1.4)

Where " E_o " is standard electrode potential, "R" is gas constant, "T" is absolute temperature, "F" is Faraday's constant, " a_i " is the activity of species i and " Z_i " is the no. of moles of electron involved, "s" is electrolyte phase, " β " is electrode phase.

The sensors do not show the accurate sensitivity for glucose, it is more sensitive towards fructose.

1.8.2 Impedimetric/Conductometric glucose sensor

The impedimetric biosensor is less demanding as compared to the potentiometric and the amperometric biosensor. In this sensor, electrochemical impedance spectroscopy (EIS) technique has been used to observe the electric double-layer structure of an electrode. Though this is an efficient technique, the impedance analysis in a wider frequency range is a complex and time-consuming task. The equation for the impedance in a simple RC circuit is given below:

$$Z^2 = R^2 + \frac{1}{(2fc)^2} \tag{1.5}$$

Where, "*Z*" = impedance, "*R*"=resistance, and "*C*"=capacitance.

1.8.3 Amperometric glucose sensor

Amperometry is an electrochemical technique that utilizes the linearly varying current to the target concentration at a fixed bias potential. Amperometric measurement utilizes three-electrode systems in which the glucose is oxidized at the working electrode composed of active material. Two electrode systems cannot be utilized in amperometric measurement because, at high current, there is a potential drop which is difficult to minimize. So, the addition of a third electrode "Auxiliary electrode" apart from working and the reference electrode is a must because the counter electrode provides a large surface area to make the counter and working electrode worthy for the flow of current despite having an applied voltage between working and a reference electrode.

1.9 Non-Enzymatic Glucose Sensor

There are two types of glucose biosensor based on mechanism has been widely accepted: (1) Enzymatic glucose biosensor and (2) Nonenzymatic glucose biosensor. Glucose oxidase (GOx) is the widely utilized enzyme for the oxidation of glucose because of its low cost and high selectivity and sensitivity. The most common drawbacks of enzymes based sensors are insufficient stability, low reproducibility, and the influence of oxygen limitation. It has a poor susceptibility towards low *pH* and high temperatures. So it is not suitable for the practical applications, whereas non-enzymatic glucose biosensors are free from the enzymatic demerits. This is probably the last generation of glucose sensors for analytical applications. This system was designed by Walther Loeb in which he categorized the glucose into three aqueous isomers α -glucose (α -G), β -glucose (β -G) and γ -glucose (γ -G) and at equilibrium, these isomers are stable [34,35]. Electroanalysis process comprises the adsorption of analyte on the electrode surface, resulting to form a suitable bond between the analyte and electrode due to *d*-electrons and *d*-orbital. Earlier a lot of metals (Au, Ag, Pt) and their composites were explored for the choice of the electrode in sensors. Three major problems still need to be resumed because of the choice of metal as an electrode:

(i) The selectivity of the sensor is limited because of the sluggish kinetics of the glucose electrooxidation.

(ii) Noble metals are always impaired by the irreversibly adsorbed chloride (Cl⁻) ions.

(iii) The selectivity of non-enzymatic glucose biosensors is poor in performance because some other interference species also get oxidized in the same potential window with better sensitivity.

1.10 Transition Metal Oxides for Glucose Sensor

Transition metal oxides based nanostructures such as nanowires, nanorods, nanotubes, nanoparticles electrode for glucose monitoring sensors are relatively more sensate, cheap, and swift. Here some of the literature based on the amperometric glucose sensing of transition metal oxides are discussed. ZnO nanomaterials have been well explored in the electronics field related to sensors and actuators owing to their semiconducting properties. It has several facilitating properties such as non-toxicity, fast electron transfer rate, and chemical stability which competes it for the oxide-based sensors [36]. ZnO works better in the presence of GO_x enzymes as it easily allows the enzymes to immobilize over its surface [37]. Nanoporous ZnO and 1-dimensional (1D) ZnO nanostructures have a larger surface to volume ratio and show high sensitivity toward glucose oxidation. Wei et al. reported a 1D nanorods structure of ZnO with high and reproducible sensitivity and short response time due to the presence of GO_x enzymes in phosphate buffer solution (pH-7.4). The ZnO nanostructure shows sensitivity but it lacks stability as it tends to dissolution in the electrolyte [38-40]. Similarly, Copper and Nickel oxide is an alternative choice for electrode fabrication. These metals tend to oxidize carbohydrates. Their natural abundance, the cheap

cost makes it one of the best choices for the sensors. Wang et al. synthesized the Pd (IV)-doped CuO nanofibers and CuO nanofibers electrodes and investigated the amperometric response on glucose. The electrode shows excellent selectivity, doped sensitivity, and reproducibility. Similarly, 3-dimensional (3D) CuO nanostructures were also investigated and concluded as an improved biosensors electrode [41,42]. TiO₂ represented as another promising material due to its environmentally friendly nature which has been frequently used for the immobilization of molecules. Bao et al. fabricated a layer of TiO₂ using hydrothermal synthesis on the MWCNT template. They found a porous nanostructure of TiO₂ which is a large scale enzyme used in the sensing reaction. Doong et al. developed a TiO₂ array for the biosensor for the detection of biomolecules like glucose, urea, and glutamate in blood and serum samples [43,44]. There are several other transition metal oxides like WO₃, MnO₂, NiO, PbO₂, Fe₃O₄, and RuO₂ which are reported for the amperometric sensing application and still a lot of modification is required for the desired glucose sensor device

1.11 Future Prospective and Challenges for Glucose Biosensor

For the accurate and specific monitoring of glucose in the blood, specific developments of biosensors devices are in progress. Nanotechnology is an emerging branch that tries to provide a device at a molecular level for the detection of glucose. Though the industrialization of glucose sensors has already produced an efficient biosensor, still a much more reliable, noninvasive glucose sensor is needed by diabetic patients. Transition metal oxide nanostructures have a favorable property of low price, less toxic, high surface to volume ratio, and a high rate of glucose oxidation to form gluconolactone by the immobilization of surface analyte. Much attention has been shifted towards the use of non-enzymatic glucose biosensors for the green detection of blood glucose levels. Additionally, transition metal oxides along with other composites and hybridization with other nanostructures, based electrodes are much more stable which gives an everlasting sensitivity during long cycles of measurement.

1.12 Objectives and Scope of the Thesis

The fundamental objectives of this thesis research work are to explore the electrochemical supercapacitor and glucose sensing application of transition metal oxide nanostructure. The main focus of this thesis is on the synthesis and characterization of transition metal oxides nanostructures and subsequently characterized for the electrochemical energy storage and glucose sensing applications. Transition metal oxides are the propitious candidate for the electrodes of electrochemical functions. The characteristics which make them worthy for electrochemical aspects are abundance, environmental favorability, diverse constituents, different morphologies based on dimensions of nanostructures, and large surface area. Though transition metal oxides have so many attracting features and also in the field of energy storage, their energy density is showing the enhancement to a large level as compared to other oxides, but some of its disadvantages like low conductivity, uncontrollable swelling and ion diffusion in the bulk state have restricted their practical applications at some extent. Hence an urge of modifications in transition metal oxides is needed for improving the electrochemical aspects of the oxides. Some of the modifications which improve the functionality of the oxides are, synthesis of novel nanostructure with high surface area morphology, rational designing of a metal oxide with another metal to form a hybrid nanostructure, formation of composite, creation of defects, etc. Herein in this thesis, the three unique and important approaches were used for enhancing the results of the transition metal oxide electrodes:

(1) Experimental synthesis of transition metal oxide nanostructures.

- (2) Hybridization of two different nanostructures.
- (3) Creation of defect, surface oxygen vacancy nanostructures.

The pointwise descriptions of the fundamental objectives of the work are as follows:

- To optimize the synthesis of Transition metal oxides (MnO₂, Co₃O₄, MnO₂/Co₃O₄, WO₃, W₁₈O₄₉, RuO₂, W₁₈O₄₉/RuO₂) using hydrothermal/solvothermal approach and subsequently characterized them for structural and morphological properties.
- To fabricate the electrodes of the synthesized transition metal oxides nanostructure as an active material for the electrochemical measurements with the proper selection of electrolytes.
- 3. To optimize the other electrochemical parameters and measurements for energy storage and glucose sensing applications
- 4. To study the effect of chemical modifications like the hybridization of 1-D nanorods of MnO_2 with Co_3O_4 and defect creation in WO_3 on the supercapacitor and non-enzymatic amperometric glucose sensor performances.
- To verify the practical and potential application of the electrode in the field of energy storage and glucose sensors

The hybrid approach allows for a reinforcing combination of properties of dissimilar components in a synergistic combination. In Chapter 3, the process of hybridization of Co_3O_4 nanoparticles with MnO_2 nanorods for evaluating the glucose-sensing activity is discussed. From the experiment, it is verified that MnO_2 is almost potentially silent in glucose sensing activity whereas incorporation of Co_3O_4 nanoparticles on MnO_2 nanorods enhances the sensitivity up to a large extent with wider linearity range. Again the work discussed in chapter 5 deals with the synergistic performance by hybridization of $W_{18}O_{49}$ nanorods with RuO_2 nanoparticles. There is a huge enhancement of specific capacitance and stability performance due to the transition from the battery mechanism to the pseudocapacitor mechanism.

Another important aspect for modulating the performance by creating the defects in the nanostructure is conducted in chapter 4 by an intentional creation of oxygen vacancy in WO₃ to yield $W_{18}O_{49}$. $W_{18}O_{49}$ nanorods have surpassed both the applications with better specific capacitance and sensitivity. Oxygen vacancy boosted the physical and chemical properties of metal oxides by increasing the electrical conductivity, surface area, electroactive sites, and chemical stability. Electrical conductivity has enhanced due to the participation of two or three cations in the electrochemical reaction. The oxygen vacant sites created more number of active sites for the full participation and interaction of electrolyte ions with electrode layers.

The final objective of this work is to contribute to an essential domain of power system by an assurance of continuous energy supply and improve the reliability without compromising the size, cost, and efficiency of the system. The thesis also contributes towards the continuous glucose monitoring of diabetes systems with better and efficient devices to produce accurate data for proper diagnosis and treatment.

1.13 Chapter Wise Organization of the Thesis

Chapter 1 Introduction:

In this chapter, a brief discussion over the introduction of different types of energy storage devices, their classifications, and the important construction of the devices has been done. It also discusses with the introduction of glucose sensors, important measuring ways, and material to fabricate the electrodes.

Chapter 2 Transition Metal Oxide Synthesis and Characterizations: In this chapter, the synthesis of transition metal oxides have been discussed. It describes the hydrothermal method used for the synthesis of transition metal oxides and the importance of 1-Dnanostructure in the electrochemical field. It also elaborated on the fabrication of electrodes using different techniques. Further, the basic and electrochemical characterization techniques are given in the end.

Chapter 3 Hybridization of Co₃O₄ and α-MnO₂ Nanostructures for High-Performance Non-enzymatic Glucose Sensing:

In this chapter, an elaborated synthesis and characterizations of α -MnO₂, Co₃O₄, and α -MnO₂/Co₃O₄ hybrid nanostructures have been discussed. It also discusses the effect of the hybridization of nanostructures over the non-enzymatic amperometric glucose sensing application.

Chapter 4 Defect Mediated bi-functional Application: Supercapacitor and Glucose Sensing of W₁₈O₄₉ Nanorods Bundle:

In this chapter, a discussion of the synthesis and characterization of the intentionally created oxygen vacant $W_{18}O_{49}$ nanostructure is done. It also mediates the effect of oxygen vacancies in both supercapacitor and non-enzymatic amperometric glucose sensing applications.

Chapter 5: Transformation of Battery to High-Performance Pseudocapacitor by the Hybridization of $W_{18}O_{49}$ with RuO_2 nanostructures:

In this chapter, the synthesis and characterization of oxygen vacant $W_{18}O_{49}$ and RuO_2 nanostructure are provided to form a hybrid $W_{18}O_{49}$ /RuO₂ nanostructure for energy storage application. It also discusses the important and noticeable changes in the mechanism of electrochemical characterization due to the hybridization effect.

Chapter 6: Conclusion and Future Scope: This chapter concluded the main results of the previous chapters and also explored the probable future scope of the research work which is still undone and can be completed.

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CHAPTER 2

Transition Metal Oxide Synthesis and Characterization Techniques

2.1 One Dimensional Nanostructure Synthesis

Nanostructures have been a center of attraction for the research community, particularly in the electronics industry due to the development of nanotechnology. The two globally hot topics *i.e.*, the demands of energy storage devices and demands of sensors have developed varieties of sustainable, efficient, and advanced methods for dealing with hot issues [1]. The present work is mainly focused on the 1-D nanostructure of transition metal oxides MnO_2 and $W_{18}O_{49}$ for the electrochemical applications. The research in this field suggested that the transition metal oxides are the most fascinating materials which have unique characteristics of reactive electronic transitions, wide band gap, high dielectric constants, and good electrical characteristics because of the filled s-shell of metallic ions and the unfilled d-shells. It also possesses semiconductive, ferromagnetic, and ferromagnetic states. Nanostructures are defined as the material with at least one dimension is in the 1-100 nm range and it is categorized into three different types of structural morphologies: zero dimensional (0-D), one dimensional (1-D) and two dimensional (2-D). Size and dimension mainly tune the electronic structure of the material which develops change in the chemical and physical properties. After the discovery of carbon nanotubes in the 1990s,

one dimensional (1-D) nanostructure has proven itself, a significant material having remarkable physical and chemical properties for electrochemical applications. The width and thickness of 1-D nanostructures are confined to the Nanoscale regime (1-100 nm) while the length can go beyond 100 nm. The 1-D nanostructure directly influences the current pathways, shorter ion diffusion length, enhancement in the electrode-electrolyte interfacial area, controlled mechanical degradation, and limitation in volume swelling and contractions. 1-D nanostructures mainly comprise nanorods, nanotubes, and nanobelts [2]. The synthetic methods of 1-D TMO include top-down approaches and bottom-up approaches. The integrated descriptions of some of the ways are given below:

2.1.1 Vapor-liquid-solid synthesis

Vapor-liquid-solid is a synthesis technique in which during the crystal growth, the material is directly absorbed via liquid catalysts. 1-D nanostructure is generally developed by the solid precipitation from the dispersed, supersaturated catalyst droplet. This way is useful in the situation of growing nanostructures with a controlled spatial location and range of the length and diameter. This method is generally favorable for growing TiO₂ nanowires using a control material flux process.

2.1.2 Physical/Chemical vapor deposition (PVD/CVD)

It is an approach in which a vacuum chamber a material reacts on the substrate or the precursor gets vaporized by inert gas and decomposes to form 1-D solid materials. The involvement of a chemical reaction during the vaporization process is called chemical vapor deposition and alternative for physical reaction called physical vapor deposition.

2.1.3 Atomic layer deposition (ALD)

Atomic layer deposition is a self-limited CVD process that is used to grow conformal thin films over a substrate with a film thickness in the range of nanometer level.

2.1.4 Pulsed laser deposition (PLD)

Pulsed laser deposition is a physical vapor deposition method that uses pulsed high laser power beams as a source of heating.

2.1.5 Carbothermal reduction

For the growth of one 1-D transition metal oxides (TMO) on a large scale, this process has been utilized due to its low cost. Various nanostructures like MnO_2 , ZnO, can be easily grown by Carbothermal reduction. The reaction mechanism for metal oxide (MO) reduction by gaseous metal carbides (MC₂) is given below in equation (2.1) and (2.2):

$$2MO(s) + MC_2(g) \to 3M(s) + 2CO(g)$$
 (2.1)

$$M(s) + 2C(s) \to MC_2(g) \tag{2.2}$$

2.1.6 Template methods

The template-based technique is employed for the synthesis of micro/nanostructures with controlled and desired properties. Different kinds of templates are favored like hard templates with the channel and porous structures such as anodized alumina membranes, mobil composition of matter (MCM-41) *i.e.*, hierarchical structure from a family of silicate and alumosilicate solids, Soft templates like block copolymers and surfactants. This technique offers some preference in terms of the growth of wire-like porous and spherical nanostructures.

2.1.7 Electrochemical synthesis

TMO can be synthesized using this technique by passing an electric current between two or more electrodes immersed in an electrolyte. The deposition of the structure takes place at the interfacial position of the electrode and electrolyte. It is favored because of easy process, low-temperature synthesis, readily available, and the size of the film that can be easily tuned by changing the electrochemical parameters still it is not accepted due to its incapability of growing the nanostructure on a large substrate and large scale for industrial applications.

2.1.8 Hydrothermal/Solvothermal methods

This process has been widely used due to its large-scale production, simple, economical processing, size modulation capacity, and uniform dispersion for the growth of 1-D nanostructure. This method includes the synthesis of nanostructure under high and fixed pressure and temperature. It is mainly processed in an autoclave. A supercritical fluid is formed under a fixed temperature and pressure which increases the solubility of the solid precursors and leads to the precipitation of 1D nanostructure from the precursor. Ultimately, the growth and selfassembly of crystals will be achieved in the solution. Many nanomaterials find this technique suitable for the growth of their high-quality 1-D nanostructure like MnO₂, WO₃, VO₂, ZnO, NiO, etc. This method is also useful for the growth of a hybrid nanostructure, defect prone nanostructure, composites, and other desirable qualities in nanomaterials. The morphologies, structure, and properties can be easily tuned by just varying the optimized experimental parameters like temperature, time, concentration of precursor, medium, PH value, etc. Surfactants are sometimes employed for improving the hydrothermal processes and
making it effective. So, this technique has proven as a feasible and design guideline for the preparation of 1-D TMO [1,2].

2.2 Synthesis and Modification of Transition Metal Oxides (TMOs) in this Thesis

Transition metal oxides exhibiting different structures and multiple characteristics are one of the prominent choices for the electrochemical application. The astonishing and amazing behavior resembles the distinguished nature of outer *d*-electrons. These materials are considered for study in this thesis work due to its phenomenal and noteworthy properties. Transition metal oxides have narrow electronic bands because of the small overlap between the *d*- orbital of metal and *p*-orbital of oxygen. Following are the transition metal oxides synthesized using hydrothermal/solvothermal technique. The detailed experimental processes for growth are given in chapters 3, 4, and 5.

- 1. α -Manganese Dioxide (α -MnO₂)
- 2. Cobalt Oxide (Co_3O_4)
- 3. α -Manganese Dioxide and Cobalt Oxide hybrid (α -MnO₂/Co₃O₄)
- 4. Tungsten trioxide (WO₃)
- 5. Oxygen-vacant Tungsten oxide $(W_{18}O_{49})$ defect structure
- 5. Oxygen-vacant Tungsten oxide and Ruthenium dioxide hybrid

 $(W_{18}O_{49}/RuO_2)$

6. Ruthenium Oxide (RuO₂)

2.2.1 Modification of the electrode via hybridization process

Recently, a large amount of effort has been applied for integrating nanomaterials to construct more efficient devices in the field of energy storage and biosensors. Nanomaterials have several different, outstanding, and useful functionalities that distinguish it from their bulk structure. For electronics applications such as energy conversion, sensing performances, and photonics, parameters such as size, shape, and surface characteristics should be modulated for controlling the properties with distinct applications of interest. Amongst several other modulating ways, methods of hybridization where the synergistic properties are different from the properties of individual components are beneficial. The presence of two or more different components allows the flexibility of tuning the properties of the nanomaterials. Maximum TMOs have pursued a high surface area, good compatibility, high chemical stability, and good conductivity. Mott et al. combined Gold (Au) with Platinum (Pt) for evaluating the catalytic properties of the combined nanomaterial. It is observed that the low catalytic property of Au is strengthened by the action of Pt synergistically [3]. Zhao et al. have enlarged the surface area and increased the electrocatalytic performance of ZnO nanorods modifying with Au nanoparticles [4]. Yu et al. has developed a core-shell nanostructure of NiCo₂O₄ over the Polyaniline by hydrothermal treatment and yields a higher sensitive glucose biosensor by core-shell structure as working electrode [5]. Electrochemically redox materials like MnO₂, RuO₂, Ni(OH)₂ and Co(OH)₂ are suffering from poor mechanical strength in terms of brittleness and low conductivity which hinders its choice of becoming a device active material. Lima et al. and Choi et al. has effectively overcome the issues of brittleness and low electrical conductivity in their MnO₂ dispersed CNT based devices [6,7]. The augmented structure was engineered in such a way that the combined material retained excellent flexibility and mechanical sustainability. Another work conducted by Kadian et al. suggested a poly (3-hexylthiophene)-Titanium dioxide (PHT-TiO₂) based Nanohybrid structure which performed well for the highly sensitive and selective amperometric glucose detection in human saliva samples [8]. Chen et al., prepared a SWNT dispersed GO sheet core-shell nanostructure and explored its advantageous involvement in optoelectronics and energy storage applications [9]. Thus, there is precise research in the field of hybridization of multi-components where it is desirable to retain the properties of individual components during the synthesis. It is also shown and delivered that the rational design and controlled synthesis of the hybrid component are of great importance in enabling the fine-tuning of the properties and functions. In the present thesis, this hybridization method is well used in chapters 3 and 5 for the modification in a nanostructure to develop an electrochemical electrode suitable for glucose sensing and supercapacitor.

2.2.2 Modification of the electrode via defect creation

Transition metal oxides especially in the case of tungsten oxide, the electronic properties are completely dependent over the stoichiometric factors *i.e.*, creation of oxygen vacancy. The anticipated importance of oxygen vacancy in modulating the properties of a nanostructure is already being discussed in Chapter 1 (section-1.12). The higher degrees of oxygen vacancy create semiconductor-metallic properties [10]. The oxygen vacancy creation in tungsten oxide has an anisotropic nature in x- and ydirection which is beneficial for the anisotropic electronic properties [10]. W₁₈O₄₉ has been largely considered for the energy storage and electrochemical glucose sensing application as it carries the largest degree of oxygen deficiency in WO₃. The electrical conductivity and electrochemical performance of MnO₂ nanowires by increasing the kinetics of redox reaction were intrinsically improved by inducing oxygen vacancy [11-13]. Tong et al. has reported concerning to the synthesis of oxygen-deficient MnO₂ (MnO_{2-x}) by hydrogenation method and have realized the enhancement in the electrochemical performance by the action of increasing conductivity. Jain et al. has reported that the MgO nanostructure has a very wide band gap of 3.44 eV which restricts its electronics application. Further by the creation of oxygen vacancies in MgO shows a photoluminescence (PL) emission in the blue region which opens up its electronics applications by reducing the band gap [14]. It is noted that the introduction of defects in the nanomaterials enhances the

interaction with the foreign ions by introducing more active sites and enhances its interfacial properties. GuO et al. has established a defect oriented MXene/MoS₂-C nanostructures for the enhancement of the charge capacity of Lithium-Sulphur (Li-S) batteries. In this nanomaterial, a large number of Sulphur vacancies act as a positive charge generator. These sites act as active sites for accommodating the lithium polysulfide for the advancement of redox reactions and inhibition of the dissolution of polysulfide [15]. Additionally, the creation of defects can relatively increase the surface entropy of the system used as an active site for the electrochemical transformation. Chang et al. has studied that presence of oxygen vacancy incorporated the reduction in band gap and the shifting of Fermi energy level which is beneficial for the insertion and diffusion of Lithium-ion in Li-ion battery [16]. Another work in Li-Ion battery by Kim et al. has suggested that the oxygen vacancy in MoO_3 increases the interlayer distancing along the *b*-axis which promotes faster electrodynamics [17]. Therefore, the introduction of defects in crystal materials is found to alter and affect the electronic structure by modifying the physical and chemical characteristics.

Here, in this thesis (Chapter 4 and 5), we have discussed the experiment of the generation of oxygen deficiency in WO_3 by transforming to $W_{18}O_{49}$ for the enhanced electrochemical glucose sensing and supercapacitor applications.

2.3 Structural and Morphological Characterizations

2.3.1 X-Ray diffraction (XRD)

X-ray diffraction (XRD) is a powerful technique used to get the information about the phase purity, crystalline structure and nature, strain state, grain size, epitaxy, phases, orientation of the planes, and defect structure, *etc.* In 1912, Max Von Laue presented a concept that the crystalline materials behave as 3-D diffraction gratings for X-ray whose wavelengths are equivalent to the *d*-spacing between the two crystalline

planes. Later based on this concept, XRD has become a common technique for knowing the crystal structures and atomic spacing d. It also identifies the atomic arrangements in amorphous materials (including polymers). This is a non-destructive technique (without causing damage after characterization) which makes it worthy for the in-situ studies of the materials. Though XRD investigates the material with any composition but preferable material would be high atomic number (Z) elements because the diffraction intensity of lower-Z elements is low. Figure 2.1 shows the basic principle of the XRD experiment, where X-ray diffraction is based on the constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law as written in equation (2.3):

$$n\lambda = 2d\,\sin\theta \tag{2.3}$$

Where "*n*" is a positive integer, represents the order of the diffraction. *d* is the interplanar distance, and " λ " is the wavelength of the incident wave. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed, and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to *d*-spacing allows identification of the mineral because each mineral has a set of unique *d*-spacing. Typically, this is achieved by comparison of *d*-spacing with standard reference patterns.



Figure 2.1 Fundamental principles of X-ray diffraction (XRD).

2.3.2 Field emission-scanning electron microscope (FE-SEM)

FE-SEM is one of the most widely used tools in material research for surface morphology studies. In this technique, electrons are used instead of light waves to see the surface microstructure of the specimen. However, since electrons are excited to high energy (keV), so wavelengths of electron waves are quite small and resolution is quite high. The electromagnetic lenses used in it are not a part of the image formation system, but just help to focus the electron beam on the specimen surface. This provides two major advantages of SEM: range of magnification and depth of field in the image, giving three-dimensional information of an image. In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is commonly used as field emitter owing to its highest melting point and lowest vapor pressure, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot size 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample as shown in Figure 2.2 the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen, and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation which further produces an image. The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface.



Figure 2.2 Interaction of highly energetic electrons with matter.

Image processing in the FESEM occurs with the help of the digitization of the image. A digital image is viewed and saved of the 2-D intensity distributions which are rendered by a scintillator- photomultiplier

device that detects an electron. This process includes a raster-scanned primary beam. The detection of secondary electrons is responsible for the brightness of the image. The angle formed between the sample surface and the incident direction is responsible for the electron distribution. Like, if the angle formed between the incident ray and sample surface is 90°, then uniformity is maintained by the activated region resulting in an escape of electrons from the surface of a sample. Later, with the increase in angle, more than 90° the escape distance of one side of the beam gets decreased resulting in the eminence of the secondary electron. This produces a welldefined and 3-D image originating due to the shear and sharp surfaces and edges tend to be brighter than flat surfaces. FESEM can give the image up to 1nm range due to its high-resolution feature. Another type of electron detected in FESEM is Backscattered electrons (BSE) which consist of electrons with high energy causing due to the reflected or back-scattered electron from the interaction volume of the sample surface. It is mainly used for the mapping of better contrast between areas of different chemical compositions. The average atomic number of different regions is different because the brightness of the BSE is directly influenced by the atomic number and it increases. The backscattered electrons can also be used to form electron backscatter diffraction (EBSD) images for investigating the crystallographic nature of the sample surface. There are fewer backscattered electrons emitted from a sample than secondary electrons. The number of backscattered electrons leaving the sample surface upward might be significantly lower than those that follow trajectories toward the sides. Additionally, in contrast with the case with secondary electrons, the collection efficiency of backscattered electrons cannot be significantly improved by a positive bias common on Everhart-Thornley (ET) detectors. This detector positioned on one side of the sample has low collection efficiency for backscattered electrons due to small acceptance angles. The diagram of the construction of the FESEM is given in Figure 2.3.



Figure 2.3 Schematic of the different parts of FESEM.

2.3.3 High resolution-transmission electron microscope (HR-TEM)

HR-TEM has become a mainstay in the repertoire of characterization techniques for materials scientists. HR-TEM's strong cards are its high lateral spatial resolution (better than 0.2 nm "point-to-point" on some instruments) and its capability to provide both image and diffraction information from a single sample. In addition, the highly energetic beam of electrons used in TEM interacts with sample matter to produce characteristic radiation and particles; these signals often are measured to provide materials characterization using EDS, backscattered and secondary electron imaging, to name a few possible techniques. In TEM, a focused electron beam is incident on a thin (less than 200 nm) sample. The signal in TEM is obtained from both undeflected and deflected electrons that penetrate the sample thickness. The construction of a TEM is given in Figure 2.4. There are combinations of magnetic lenses below the sample which convey a signal to the detector via a

fluorescent screen, film plate, or a video camera. Accompanying this signal transmission is a magnification of the spatial information in the signal by as little as 50 times to as much as a factor of 10^6 . This remarkable magnification range is facilitated by the small wavelength of the incident electrons, and is the key to the unique capabilities associated with TEM analysis. There are two modes for the analysis of specimens: diffraction mode and image mode. A diffraction pattern is observed in diffraction mode on the screen which is obtained from the specimen after the interaction of the electron beam with the specimen surface. This diffraction phenomenon is similar to the X-ray diffraction pattern: a single crystalline nanomaterial will produce a spot pattern on the screen, a polycrystalline nanomaterial will produce diffraction spots or ring pattern (assuming the illuminated area includes a sufficient quantity of crystallites), and a glassy or amorphous material will produce a series of diffuse halos. The image mode produces an image of the illuminated sample area. The image can contain contrast brought about by several mechanisms: mass contrast, due to spatial separations between distinct atomic constituents; thickness contrast, due to non-uniformity in sample thickness; diffraction contrast, which in the case of crystalline materials results from scattering of the incident electron wave by structural defects; and phase contrast. The reasons for this simplicity are buried in the intricate electron optics technology that makes the practice of TEM possible. There are several drawbacks of the TEM technique. Many materials require extensive sample preparation to produce a sample thin enough to be electron transparent, which makes TEM analysis a relatively time-consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. Also, the field of view is relatively small, raising the possibility that the region analyzed may not be characteristic of the whole sample. There is potential that the sample may be damaged by the electron beam, particularly in the case of biological materials.



Figure 2.4 Schematic of the different parts of HRTEM.

2.3.4 X-ray photoelectron spectroscopy (XPS)

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. The sample is irradiated with mono-energetic X-rays causing photoelectrons to be emitted from the sample surface. An electron energy analyzer determines the binding energy of the photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of an element are determined. The information XPS provides about surface layers or thin-film structures is of value in many industrial applications including polymer surface modification, catalysis, corrosion, adhesion, semiconductor and dielectric materials, electronics packaging, magnetic media, and thin-film coatings used in many industries. XPS is based on the photoelectric effect as shown in Figure 2.5. The atom on the surface has a core electron which is in the interior of the shell and the binding energy of that core electron is somehow equal to the ionization energy (I.E) of that core electron. When an X-ray is incident on the surface of a conducting

sample, the photon energy of the X-ray adsorbed over its surface by the core electron of an atom. Again, if the energy of the photon (hv) is greater than the energy of the core electron, it knocks out the electron from the atom emitting out of the surface. The emitted electron having kinetic energy (E_k) is called the photoelectron. The binding energy (E_b) of the core electron is given by the Einstein relationship:

$$h\nu = E_b + E_k + \Phi$$
(2.4)
$$E_b = h\nu - E_k - \Phi$$
(2.5)

Where "*hv*" is the X-ray photon energy (for Al K_{α} , *hv* =1486.6 eV); " E_k " is the kinetic energy of photoelectron, which can be measured by the energy analyzer; and Φ is the work function induced by the analyzer, about 4~5 eV.

Since the work function Φ , can be compensated artificially, it is eliminated, giving the binding energy as follows:

$$E_b = h\nu - E_k \tag{2.6}$$

In the first approximation, the work function is the difference between the energy of the Fermi-level (E_f) and the energy of the vacuum level E_v which is the zero point of the electron energy scale.



Figure 2.5 XPS process.

This quantity is to be determined by the calibration of the spectrometer used. Binding energies lower than the excitation radiation (1486.6 eV for Al- $K\alpha$ and 1253.6 eV for Mg- $K\alpha$) are probed.

Each element has its characteristic electronic structure and thus a characteristic XPS spectrum. In the spectrum, the numbers of peaks appear in the background. The background originates from the photoelectrons which undergo energy changes between photoemission from the atom and the detection in the spectrometer.

2.3.5 Raman Spectroscopy

Raman spectroscopy technique used to study the frequency-based modes like vibrational, rotational, and other low-frequency modes in the field of condensed matter physics and chemistry. It is based on the inelastic scattering approaches, or also known as Raman scattering of monochromatic light from a laser in the visible, near-infrared, nearultraviolet range. The incident laser of different excitation wavelengths interacts with the phonons causing a shift in the energy of a laser photon either in an upward or downward direction. This shift in energy provides information on the modes of phonon of the synthesized material. It is a vibrational spectroscopy that works on the principle of infrared (IR) spectroscopy. In IR spectroscopy, IR bands develop due to a fluctuation in the dipole moment of a molecule whereas Raman bands originate due to a change in the polarization. These two techniques are often complementing each other because in some of the cases the transitions that can be done in Raman are restricted in IR. The working mechanism behind this process is that when a beam of laser light is invaded over a sample, photons are absorbed by the sample's surfaces and get scattered in different directions. The wavelength of the scattered photons is equivalent to the wavelength of the incident photon and this whole process is called Rayleigh scattering. A very little portion (almost 1 in 10^7) of the scattered radiation is shifted to a different wavelength called Raman scattering. The one where the shifting occurs on a higher or longer wavelength is termed as Stokes shift and if

for shorter wavelengths then called anti-Stokes shift. Figure 2.6 depicts the strokes and anti-stokes phenomenon during Raman scattering. In both the shifts, the electron decomposes on to another level in comparison to the level where it originated. According to Boltzmann distribution theory, the Stokes phenomenon is much more usual than the anti-stokes phenomenon because the common temperature range of an electron is usually found in its lowest energy states. Therefore, Stokes Raman scattering is generally studied for spectroscopy. According to the discussion conducted earlier about the similarity of Raman with vibrational spectroscopy, it is evolved that the transition in energy arises from the vibration occurring due to molecules. The molecular vibrations identify the functional groups and the molecule related to it when the energies are plotted in the form of a spectrum. Raman spectra plot is a plot where a relation of the intensity of Raman scattered radiation with frequency difference from the incident radiation (wavenumbers, cm⁻¹) is depicted. This difference in the frequency value is called the Raman shift and since it is a different value, Raman shift is independent of the frequency of the incident radiation.



Figure 2.6 Raman scattering phenomenon.

2.3.6 Brunauer Emmett Teller (BET) Surface area analyzer

The BET theory was named based on the initials of the three scientists Stephen Brunauer, Paul Emmett, and Edward Teller in 1938 which derived the concept for the surface area measurement [18]. It is an

extended concept of Langmuir's theory developed by Irving Langmuir in 1916. It is based on the multilayer adsorption of gaseous molecules over the surface as adsorbates to measure the surface. Langmuir theory is based on some of the assumptions:

- The whole surface and layers of the monolayer have the same adsorption energy for the adsorbates.
- There will not be any effect of adsorption at one site to its neighboring site.
- Adsorbate's activity is directly proportional to the concentration.
- Initially, the deposition will be a monolayer state.
- Each active site can be occupied only by one particle.

BET follows the multilayer adsorption theory with some additional assumptions as following:

- Gaseous molecules will be adsorbed layer by layer.
- There will not be any interactions between the multiple layers.
- All the above-mentioned theory is valid for all the layers.

Inert gases like Nitrogen (N_2) are generally preferred over other gases for the surface probing analysis on its standard boiling temperature 77 K. Nitrogen is used due to its availability in pure form and its strong bonding with most of the materials. For an obtrusive amount of adsorption, liquid N_2 is used for surface cooling since the interaction between gaseous and solid phases are usually weak. A fixed amount of Nitrogen gas is purged stepwise over the sample cell in various steps. The vacuum condition is compulsory for achieving relative pressure less than atmospheric pressure. As the pressure is reached to its maximum value, the adsorption of the gaseous molecules also reaches its saturation. A precise and accurate pressure monitor notifies the change in pressure within the adsorption process. The sample is removed from the nitrogen atmosphere and heated post the adsorption of the layer to produce the nitrogen-free sample and quantify the measurement. The collected data is presented in the form of BET isotherm. There are five possible types of adsorption isotherms based on the BET equation expressed as following:

$$\frac{1}{V_a\left(\frac{P}{P_o}-1\right)} = \frac{C-1}{V_m C} X^P / P_o + \frac{1}{V_m C}$$
(2.8)

Where "*P*" is the partial pressure of adsorbates gas in equilibrium, "*P*_o" is the saturated pressure of adsorbates gas, "*V*_a" is Volume of gas adsorbed at standard temperature and pressure (STP), "*V*_m" is the volume of the surface being covered by a monolayer of gases and "*C*" is the constant.

- **Type I isotherm:** In the BET equation, if P/P_o << 1 and C >> 1, then a type I isotherm forms which signifies monolayer adsorption.
- Type II isotherm: If C is very large to 1, type II isotherm forms which correspond to large deviations from the Langmuir model. A flat region is found in the curve verifying the monolayer formation.
- **Type III isotherm:** If C<<<1, type III isotherm obtained, which also shows a large deviation from the Langmuir model. It explains the formation of a multilayer. There is no fat portion in the curve which signifies the absence of monolayer.
- **Type IV isotherm:** This isotherm is quite similar to type III isotherm at low pressure; it signifies the formation of multilayer after monolayer. In this type, saturation level is attained at a pressure below the saturation vapor pressure which might have arisen due to condensed gases in the capillary pore of the adsorbent.
- **Type V isotherm** It shows the capillary condensation phenomenon and is similar to type IV isotherm.

2.4 Electrochemical Characterizations

Electrochemical characterization is a powerful technique to probe reactions involving electron transfers between electrodes and electrolytes. It makes the understanding of the mechanism behind the flow of electrons which leads to chemical changes. In this work, an electrochemical cell is used with a 3-electrode system and electrolyte for conducting the measurement in both supercapacitor and glucose sensing. The 3-electrode system comprises:

- Working electrode (WE): WE is made up of the redox-inert material of our interest in an optimized potential window. It is varied based on the experiment and the active material used. Since the electrochemical reaction occurs at the working electrode, it needs to be efficient in terms of adhesion, cleaning the well-defined surface area for its proper functioning.
- **Reference electrode (RE):** RE is used as a reference for measuring the potential of other electrodes in the electrochemical cell. This electrode has a well-defined and universal fixed potential. Some commonly and commercially used reference electrodes whose potential is independent of the electrolytes used are saturated calomel electrode (SCE), standard hydrogen electrode (SHE), and the AgCl/Ag electrodes. In this work, both the SCE and AgCl/Ag electrode are used in different experiments based on the nature of electrolyte.
- Counter electrode (CE): CE is used for completing the electrical circuit to measure the flow of current in between WE and CE. CE should be inert for avoiding the reaction taken place on CE for WE. Some of the common CEs are platinum wire, platinum sheet, and graphite rod. Here we have used a platinum sheet for experimenting.

2.4.1 Cyclic voltammetry (CV)

Cyclic voltammetry is an efficient technique for evaluating and understanding the mechanism of supercapacitor and electrochemical glucose sensor devices by measuring the current produced when an applied voltage is excess to that predicted by the Nernst equation (Equation 1.4). It is widely known for operating the electrical performance of energy storage devices and electrochemical biosensors. It works on the mechanism based on the positive voltage sweep charges to a definite voltage (potential window) and after reaching its maximum point, the sweep is immediately reversed back for discharging. The whole process follows the cyclic path of charging and discharging. The curve of CV signifies the reduction and oxidation process of a molecular species. It has advantages of determining the kinetic aspects of the degradation process and the measurement of specific capacitances. The curve can easily differentiate between the electrochemical double-layer capacitor (EDLC), pseudocapacitor (PC), and batteries-based mechanisms. A regular rectangular like curve during constant charging and discharging in CV shows the typical capacitive mechanism [19]. A PC is an intermediate stage between EDLC and batteries. EDLC stores charges on the doublelayer format on high surface area conductors whereas batteries are faradaic electron transfer reaction-based mechanisms to metal centers, it is possible only by the intercalations of charge compensating ions. Talking about the CV curve, EDLC usually exhibits potential independent capacitance and thus potential independent current. Batteries on the other side show defined peaks that are related to the oxidation and reduction to the metal centers involved in the storage of charges. The CV curve has been measured in a varied series of scan rate and corresponding specific capacitances are evaluated. The scan rate of the CV curve determines the speed of the reaction and the rate of scan of the applied potential. The

Faster scan rate reduces the size of the diffusion layer resulting in high current values [20].

The specific capacitances " C_{sp} " of supercapacitor are measured using equation (2.9) as given below:

$$C_{sp} = \frac{\int I \triangle t}{m \nu \triangle V} \tag{2.9}$$

Where " C_{sp} " is the specific capacitance of the electrode, " $\int I \triangle t$ " is the integrated area of the curve, "*m*" is the active mass of the electrode, "*v*" is the scan rate applied and " ΔV " is the potential window (V₂-V₁).

2.4.2 Galvanostatic charging and discharging (GCD)

GCD is an old and traditional electrochemical method for evaluating the important parameters in supercapacitors like specific capacitance, energy density, power density, stability, resistance. The GCD generally measures the response of potential with respect to time and derives the important characteristics of supercapacitors. The curve contains two stages where in the first stage, it involves the charging of a supercapacitor (SC) via a constant current and the next stage, it is discharged in a specific time or a voltage range. GCD is an exceptionally important technique for evaluating the difference between EDLC, pseudocapacitor, and battery. Nowadays it has been widely suggested both battery and EC are measured via chronopotentiometry measurements. According to the charge transfer mechanism, in an EC the voltage varies linearly with time during charging and discharging measurement because of the surface-controlled charge storage mechanism. In a typical battery, the voltage varies constantly during the charging and discharging process due to the phase transformation process. Now, for differentiating in between EDLC and PC, the GCD curve linear voltage variation with discharge time at a constant current, the difference lies as EDLC material shows a sharper slope due to its small charge storage capacity and shorter

discharging time[21]. The capacitance has been extracted from the constant value in an ideal capacitor showing a potential independent capacitance. The linear potential-time response can be explained by the following equation (2.10):

$$\triangle V = \triangle t X \frac{I}{C} \tag{2.10}$$

Where, " ΔV " is the final potential - initial potential (V₂-V₁), " Δt " is the discharging time, " Γ " is the constant current applied and "C" is the constant.

A discharging curve of a typical battery shows a noteworthy voltage plateau with different polarization zones. The plateau region originates from the phase transition and later it is followed by a voltage drop due to concentration polarization.

A Capacitor has a different curve feature; it should show a symmetric charging and discharging region which is a consequence of a small voltage hysteresis. The information analyzed from the GCD curves, energy density, power density, equivalent series resistance (ESR), capacitance is reliable in the context of all the energy storage devices. Sometimes a unique curve with mirror charge-discharge plot followed by a battery like discharge behavior is recognized as a mixed behavior of capacitive and battery. This type of mechanism is a general outcome from the nanostructured porous electrode having a large surface area. It produces a prominent EDLC [22]. So there is a potential drop due to its double-layer discharging mechanism followed by a plateau region signifying battery like behavior. As a result, nanostructure porous electrodes show a prominent capacitance by utilizing the discharging time besides the contribution of the battery discharge process. Thus, a linear discharge curve or triangle symmetrical charge-discharge curve is an essential criterion for a material to be EDLCs or PCs.

The specific capacitance C_{sp} calculated from the discharge curve by an electrode with total mass deposited "*m*" is given by using equation (2.11):

$$C_{sp} = \frac{I \bigtriangleup t}{m \bigtriangleup V} \tag{2.11}$$

2.4.3 Electrochemical impedance spectroscopy (EIS)

EIS is a salient and nondestructive tool for analyzing the capacitive and resistive performance of the material and defining the contribution of electrode and electrolyte interaction in the electrical and sensing performances of energy storage devices and electrochemical glucose sensors. It separately evaluates the various resistances found in the electrochemical cell, also it helps in the calculation of capacitances. It is a relation between the real part of the impedance (Z') and the imaginary part of the impedance (Z") called the Nyquist plot. The Nyquist plot derives the charge transfer resistances using the semicircular region of the curve. The pseudo charge transfer resistance which is directly related to the porosity of the material is well preserved in between high to low frequencies $(10^4 \text{ to } 1 \text{ Hz})$, whereas at low frequencies (<1 Hz), pure capacitive behavior arises. So, a pure capacitor mechanism should build a parallel graph with respect to the imaginary axis of the Nyquist plot [23]. Therefore, normally there is an inclination between the extended curve to the real axis which corresponds to the Warburg and ideal capacitive ionic diffusion. The impedance data is collected on an open circuit potential additionally by applying an alternating potential at a small amplitude over a wide range of frequencies ranging from 0.01 to 100 KHz. The graph obtained in between the impedance and frequency, bode plot signifies that with an increase in frequency, capacitances decrease. So, at higher frequencies, SC has become pure resistive, resisting the electrolyte ion to insert inside the pores of the electrode. The capacitance (C) has been obtained using the equation (2.12):

$$C = \frac{1}{2\pi f|Z|} \tag{2.12}$$

Where, "f" is the frequency and "|Z|" is the \pm impedance.

This method can also be sometimes helpful in differentiating the different types of charge storage mechanisms, EDLC, PC, and battery. The three different regions in the Nyquist plot are: intercept at the real impedance axis, semicircle in the high-frequency region, and a linear part within lowfrequency domain. EDLC shows almost a right-angle straight line to the real impedance axis with no semicircle and ion diffusion since there is no direct participation of the faradaic process. But in some of the EDLC materials like active carbon the semicircular region is prominent which might have arisen because it contains a redox functional molecule or doped redox atoms. In case of a PC, a very small semicircle in response to a surface controlled redox reaction is later followed by a 90° straight line to the Z'-axis. A typical battery should have a larger semicircle in comparison to PC which is followed by a 45° incline line to Z'- axis [24]. This technique has an advantage of showing the degradation behavior of the electrode and the only limitations are its small voltage range, discreteness in behavior after 10^6 Hz frequency.

2.4.4 Chronoamperometry (CA) technique

Chronoamperometry is an important technique for evaluating the sensing performance of the electrode in an electrochemical glucose sensor. It is a time-dependent process where a square wave external potential is applied in the potentiostatic format to the working electrode in a 3-electrode system. The current of the electrode which is plotted against time fluctuates after the injection of an analyte in response to the diffusion of an analyte from the bulk electrolyte over the sensors 'electrode surfaces. In summary, it is used for evaluating the current time relation of the diffusion-controlled sensing process occurring on an electrode's surface [25]. The value of current usually changes in comparison to change in the analyte's concentration. The active component's concentration in the electrochemical cell near the electrode's surface decays with the distance from the ion diffusion. Thus, Faradaic current near

the electrode surface decays over time as the mass transport limit is reached.

2.5 Summary

In this chapter, the varieties of nanomaterial growth techniques and characterization techniques like XRD, FESEM, HRTEM, Raman XPS, etc are discussed. Also, the electrochemical measurement techniques like CV, GDC, EIS, CA, etc. important for the supercapacitor, batteries, and glucose sensor applications are discussed.

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CHAPTER 3

Effect of Hybridization of α-MnO₂ and Co₃O₄ Nanostructures on Non-enzymatic Glucose Sensing

Publication:

1. Lichchhavi Sinha, Srimanta Pakhira, Prateek Bhojane, Sawanta Mali, Chang Kook Hong, Parasharam M. Shirage, "Hybridization of Co_3O_4 and α -MnO₂ nanostructures for high performance non enzymatic Glucose Sensing", *ACS Sustainable Chem. Eng.*, 6(10), (2018) 13248-13261. (Impact Factor: 7.632) DOI: 10.1021/acssuschemeng.8b02835

CHAPTER 3

Effect of Hybridization of α-MnO₂ and Co₃O₄ Nanostructures on Non-enzymatic Glucose Sensing

3.1 Overview

In the previous chapter, different strategies for the synthesis of TMO and its modification for the application of supercapacitor and glucose sensing were mentioned. Methods for enhancing the electrochemical applications of TMO nanostructure, followed by the structural, morphological, and electrochemical characterization techniques were also discussed. In the current chapter, the experimental work of the sensitive and selective non-enzymatic detection of glucose is achieved by the effects of 1D α -MnO₂ nanorods modified with the surface decoration of Co₃O₄ nanoparticles over the nanorods.

As discussed in Chapter 1, glucose biosensors have achieved considerable attention in the field of research owing to simplicity, excellent selectivity, high sensitivity, and potential ability for real-time and on-site analysis in various fields [1]. It is classified into two categories:

(i) Glucose oxidase (GOx) based enzymatic sensing,

(ii) Non-enzymatic glucose sensing [2].

Enzymes based sensors have a disadvantage of not working well in critical conditions, *e.g.*, ecological, food monitoring and bioprocess controller, *etc* [3]. The electrode material is considered as an important and crucial parameter for influencing the analytical skills of enzyme less

sensors. Carbon, platinum, gold, and palladium have been widely investigated as candidates for improving the sensing performance of nonenzymatic sensors [4]. Numerous electrodes are synthesized by metal oxides-based nanostructures but they display a poor limit of detection, low sensitivity, weak reproducibility, narrow linear range, and complex electrode fabrication process. However, some problems include poor selectivity, high cost and low sensitivity due to the surface poisoning by the adsorbed intermediates or chloride ions remain challenging [5]. Some strategies have developed for minimizing the cost and facilitating the kinetics of glucose electro-oxidation. The strategies are developing different variations of shapes and sizes in nanostructures, increasing active surfaces, alloying, and formation of nanocomposites [6-9].

TMO nanostructures like Zn based oxides [10-12], graphene oxide [13-15], and several composites like Ni-Co based oxides [16], Co-Fe based oxides [17] have attracted much interest in the scientific community owing to their wide-ranging applications. These materials are sensitive, relatively inexpensive, and have the advantage of rapid response associated with specific nanostructures (high surface to volume ratio) such as nanowires, nanorods, nanotubes, nanoparticles, nanofibers, etc. It can also be considered as immobilizing matrices for biosensor [18,19]. These materials enhance electron transfer kinetics and strong adsorption capability which provide suitable environments for the immobilization of biomolecules. This results in the enhancement of electron transfer characteristics which further enhances the bio-sensing performances [20]. Previously, a lot of literature has been reported on non-enzymatic glucose sensors based on transition metal oxides such as NiO [21,22], CuO[23,24], Co_3O_4 [25]. However, very limited literature is available on MnO₂ based glucose sensing. MnO₂ is an interesting transition metal oxide, having different structural forms (α , β , γ , δ) based on its tunnel structure. The high surface area and high redox activity of MnO₂ could deliver high capacity and good catalytic performance. It is assumed that this material can be

applied for biosensors research due to its remarkable properties like economical and chemical stability [26]. However, MnO_2 has a very strong demerit of poor conductivity (10^{-5} to 10^{-6} S/cm) which hinders its electronic applications. The major strategy for improving the performance is to search for a conducting material which will be integrated with MnO_2 to obtain a synergistic effect [27].

Cobalt oxides have acquired substantial research interest due to its diversity of oxidation states for charge transfer kinetics, high energy density, and high power density [27]. It is categorized as transition metal oxide with intriguing electronic, optical, electrochemical, and electrocatalytic properties [9]. Co_3O_4 based nanocomposites have demonstrated great potential in several applications up to now. The combined structure of MnO_2 with Co_3O_4 contains high electron conductivity. Co_3O_4 can provide a conducting network, high surface area (surface to volume ratio), chemical stability, and high electrical conductivity to MnO_2 and offer high redox features that enhance direct electron communication through the target analysis. To the best of our knowledge, the application.

In this work, α -MnO₂/Co₃O₄ hybrid nanostructures have been synthesized on carbon paper as an electrode material for non-enzymatic amperometric glucose detection by a simple hydrothermal process. The Co₃O₄ nanoparticles are homogeneously coated on the α -MnO₂ nanorods which are considered as favorable for the glucose oxidation by providing active sites to the glucose, to get oxidized. The synergistic and interfacial effects between the α -MnO₂ nanorods and Co₃O₄ nanoparticles lead to enhancement in its physical as well as chemical characteristics. The heterostructures of α -MnO₂ and Co₃O₄ possess huge structural importance by demonstrating its tendency to be oxidized and by offering augmentation or the process of strengthening each other. For comparison, α -MnO₂ and Co₃O₄ have also been synthesized separately and characterized subsequently. Thus, the α -MnO₂/Co₃O₄ heterostructure reveals its potential application for the non-enzymatic biosensor with high sensitivity and affordable cost.

3.2 Experimental Synthesis

3.2.1 Synthesis of 1D α-MnO₂ nanorods

 α -MnO₂ nanorods were synthesized using a simple hydrothermal method as reported earlier with some slight modifications[28]. 0.263 g of KMnO₄ was stirred into 30 ml of double deionized water (18.2 MΩ/cm) stirring. After 5 minutes of stirring, 1ml of conc. HCl (37%) was added. Again, it was left for 5 minutes in stirring mode to get a complete homogenous solution. The solution was transferred to a Teflon lined stainless steel autoclave of capacity 100 ml and placed at 140° C with raising temperature rate of 3° C/min for 16 hours in a muffle furnace. After completion of the reaction, it was allowed to cool down naturally to room temperature, the brown product was collected by filtration(using Whatman filter paper) and washed with deionized water (4-5 times), ethanol (3 times) to remove impurities. The resulting sample was obtained after final drying at 80°C for 24 hours in an aerobic environment.

3.2.2 Synthesis of Co₃O₄ nanomaterial

 Co_3O_4 nanostructures were also been synthesized by taking 1mM $Co(NO_3)_2 \cdot 6H_2O$ in 35 ml deionized water followed by the same procedure as in Section 3.2.3.

3.2.3 Synthesis of α-MnO₂ Co₃O₄ nanostructures

For the growth of the hybrid nanostructure of α -MnO₂/Co₃O₄, 50 mg of as-synthesized α -MnO₂ nanorods were dispersed in 35 ml of water (deionized water) and followed by 30 minutes sonication and 15 minutes stirring to prepare a homogenous suspension. 1mM Co(NO₃)₂·6H₂O was added while stirring to the above suspension and stirred for an additional 30 minutes. Then dropwise ammonia

solution was added for maintaining the pH~11 of the suspension. Subsequently, the solution was transferred to a Teflon lined stainless steel autoclave of capacity 100 ml and placed at 150°C temperature for 12 hours in a muffle furnace. The dark brownish product was collected by filtration (using Whatman filter paper) and washed with deionized water (5 times), ethanol (3 times) to remove impurities possibly remaining in the final products. The sample was obtained after drying at 80°C for 12 hours in an aerobic environment. The whole synthesis process of hybrid products is given in Figure 3.1(a).

3.2.4 Details of characterizations instruments

The phase purity and structural identification of α -MnO₂/Co₃O₄ were carried out by X-ray diffraction (XRD), D2-phaser Bruker, 30 kV/10 mA, Å), CuK_α irradiation (λ=1.54 Fourier transformation infrared spectroscopy(FTIR), X-ray photoelectron spectroscopy (XPS), Field emission scanning electron microscopy (FESEM, Karl Zeiss JEOL Scanning Electron Microscopy), high resolution-transmission electron microscopy (HRTEM, JEOL-2100), N2 adsorption-desorption study for Brauner-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size distribution was performed by automated gas adsorption analyzer (Quantachrome Autosorb iQ2). Electrochemical experiments were performed using the electrochemical analyzer (PGSTAT 302N) with a conventional three-electrode system. The auxiliary electrode was platinum and the reference electrode is saturated calomel (SCE) Ag/AgCl electrode.



Figure 3.1(*a*) Schematics of α -MnO₂/Co₃O₄ synthesis, (b) electrode fabrication for glucose sensing.

3.2.5 Electrode fabrication for amperometric glucose sensing:

1 mg each of synthesized α -MnO₂ and α -MnO₂/Co₃O₄ and Co₃O₄ powders were taken in three different tubes. They were sonicated in ethanol for about 20 minutes to make slurry at room temperature. A drop of Teflon suspension (5% Teflon in ammonia) was added as a binding agent. The suspension was drop cast over a 0.8 x 0.8 cm² carbon paper and left for drying for 2 hours at 80° C in a furnace. The ultimate masses were determined using a weighing balance. The measured mass is the mass difference between before and after dropcasting over carbon paper. The estimated loaded mass was ~1mg. The schematics for the electrode fabrication are given in Figure 3.1(*b*).

3.3 Results and Discussion

3.3.1 Morphology evolution and growth mechanism of the nanomaterial

Figure 3.2(a) shows the growth schematics of the hybrid nanostructure of α -MnO₂/Co₃O₄ and its morphological evolution. To grow 1D α -MnO₂ nanorods, initially, the precursor in double deionized water in the presence of strong hydrochloric acid was kept in an autoclave at a temperature 180°C, oxidized it into manganese oxide with some water molecules [Reaction (3.1)][29]. Initially, after the formation of MnO₂ nuclei from KMnO₄ precursor, the crystal phase of MnO₂ nuclei was mainly determined by the K⁺ ion concentration. The concentration of K⁺ ions strongly influences the structures/phases of MnO₂. KMnO₄ was optimized in solution up to a level to stabilize the formation of (2 x 2) tunnel structure α -MnO₂ [30]. The synthesized MnO₂ was dispersed into deionized water followed by the addition of cobalt nitrate (1mM) as a precursor. The reaction medium was made alkaline by adding an ammonium hydroxide (NH₄OH) solution in the final mixture of α -MnO₂ and Co_3O_4 . The NH₄OH reduced to form NH₄⁺ and OH⁻ [Reaction (3.2)]. Further dissociation led to the formation of NH_3^+ [Reaction (3.3)]. Ammonium hydroxide was used for keeping the medium alkaline with pH 9~10. Precipitation occurred and the nucleation was initiated on the same pH condition. Further addition of ammonia solution reduced the Co²⁺ ion concentration by producing the complex ion $Co(NH_3)_x^{2+}$. So, at pH~11, the divalent metal ions of Co^{2+} were fully coordinated with $\mathrm{NH_4^+}$ ions that come from $\mathrm{NH_4OH}$ to form $Co(NH_3)_x^{2+}$ ions [Reaction (3.4)][31,32]. Therefore, during the precipitation process, the numbers of nucleation sites were created and the number of nucleation centers was limited, the growth rate of the Co(OH)2 was slowed down due to the existence of $Co(NH_3)_x^{2+}$ ions forming Co_3O_4 particles [Reaction(3.5)]. The cobalt

hydroxide upon reaction with the MnO_2 formed $MnO_2.Co_3O_4$ as a final product. The plausible chemical reactions are shown below:

$$\begin{array}{rcl} 2\text{KMnO}_{4} + 2\text{H}_{2}\text{O} + 8\text{HCl} \\ & \rightarrow & 2\text{MnO}_{2}\text{H}_{2}\text{O}_{(aq)} + 3\text{Cl}_{2} + 2\text{KCl} + 6\text{H}_{2}\text{O}_{(aq)} & [3.1] \\ \\ NH_{4}OH \rightarrow NH_{4}^{+} + & OH^{-} & [3.2] \\ NH_{4}^{+} + & OH^{-} \leftrightarrow NH_{3}^{+} + H_{2}O & [3.3] \\ \\ Co^{2+} + 4NH_{3}^{+} \rightarrow [Co(NH_{3}^{+})_{4}]^{2+} & [3.4] \end{array}$$

$$Co^{2+} + 20H^- + H_20 \to Co(0H)_2 + H_20$$
 [3.5]

3.3.2 Material characterizations

Crystallinity and crystal phases of the prepared samples were investigated by X-ray diffraction (XRD) as shown in Figure 3.2 (a,b&c). The XRD patterns represent the phase of pure materials without any impurities. All the peaks in Figure 3.2(a) can be indexed to a pure tetragonal phase of the α -MnO₂ [space group-*I*4/*m*(87)] [JCPDS 44-0141]. The image in the inset shows the geometrical structure of α -MnO₂ having arrangements of double chains of [MnO₆] octahedral forming (2x2) tunnel structure. This structure is anticipated to be the most favorable structure for electrochemical studies; it provides an efficient electrochemical surface by maintaining tunnels size and interlayer separation between the $[MnO_6]$ octahedron [33]. The estimated lattice parameters for the α -MnO₂ are $a=b=9.787\pm0.006$ Å, $c=2.860\pm0.005$ Å. The peaks of Co₃O₄ showed obvious low intensity, indicating that decorated Co₃O₄ has a very small crystallite size compared to α -MnO₂ as shown in Figure 3.2(b) [34]. It shows the phase purity of the Co₃O₄ nanoparticles without any impurity. For hybrid α -MnO₂/Co₃O₄, the diffraction peaks at 36.85°, 38.54°, 65.2° can be indexed to (311), (222) and (440) planes of Co₃O₄ [JCPDS 42-1467, space group Fd-3m (227)], respectively and is well depicted in Figure 3.2(c).


Figure 3.2 XRD patterns of (a) α -MnO₂ nanorods (inset) 2x2-tunnel structure of α -MnO₂ nanorods, (b) Co₃O₄ nanoparticles, (c) α -MnO₂/Co₃O₄ nanorods.

The compositional and oxidation state validation of the prepared hybrid structures was done by using X-ray photoelectron spectroscopy (XPS). The full survey spectrum of MnO₂ is given in Figure 3.3(*a*) which shows distinctive XPS peaks of manganese, oxygen, and carbon as their auger peaks whereas the survey spectrum of MnO₂/Co₃O₄ in Figure 3.3(*b*) shows distinctive peaks of cobalt, manganese, oxygen, and carbon. Figure 3.3(*c*) shows the Mn2p spectra of MnO₂/Co₃O₄. Two distinctive peaks having spin-orbital splitting of 11.5 eV at binding energies 642.1 and 653.5 eV in the Mn2p spectrum signifies Mn2p_{3/2} and Mn2p_{1/2} in α - MnO₂/Co₃O₄, respectively. The deconvolution of the complex Co2p spectrum in Figure 3.3(*d*) shows the presence of two distinctive peaks *i.e.*, Co²⁺ and Co³⁺, respectively. Particularly two peaks at 779.9 eV and 795.1 eV, signified as $2p_{3/2}$ and $2p_{1/2}$ of Co³⁺. Peaks at 803.5 eV and 788.9 eV correspond to $2p_{3/2}$ and $2p_{1/2}$ of Co²⁺, respectively [72]. Two small peaks at 786.3 eV and 804.8 eV are Co²⁺ shake-up or satellite peaks of Co₃O₄. The energy difference between the peak of Co2p_{3/2} and the peak of Co2p_{1/2} is approximately ~15 eV. This data provides direct evidence for the presence of the Co₃O₄ phase in the synthesized α -MnO₂/Co₃O₄ hybrid structure. The XPS O1s spectra shown in Figure 3.3(e) consist of three components. The peak at about 529.6 eV is due to oxygen in the Co₃O₄ and α -MnO₂ crystal lattice, a typical value for cobalt oxide networks, while the peaks at about 531.4 eV and 532.6 eV are due to chemisorbed oxygen caused by surface hydroxyl [35].



Figure 3.3 Survey scan spectrum of XPS of (a) α -MnO₂ and (b) α -MnO₂/Co₃O₄ hybrid. The deconvoluted peak of (c) Mn2p,(d) Co2p, and (e) O1s of α -MnO₂/Co₃O₄ hybrid.

The detailed morphological and structural investigation of α -MnO₂ and α -MnO₂/Co₃O₄ were carried by the Transmission electron microscopy (TEM) and the images are presented in Figure 3.4(*a*) which confirms the uniform formation of nanorods and Figure 3.4(*b*) measures the diameter 45nm with several micrometers length. HRTEM analysis was carried out to confirm the crystallinity and morphology of the nanorods. Figure 3.4(*c*) shows the lattice fringes of α -MnO₂ nanorods, from where the inter-planar spacing of the nanorods is found to be 0.50 nm, corresponds to the (200) plane of α -MnO₂ which was also confirmed by the XRD data (Figure. 3.2). The selected area electron diffraction pattern (SAED) taken from the α -MnO₂ nanorods in Figure 3.4(*d*) confirms the single-crystalline nature of the prepared sample.



Figure 3.4 (a) TEM image, (b) HR-TEM image, (c) Lattice fringes, and (d) SAED pattern of α -MnO₂ nanorods.

Similarly, the TEM images are shown in Figure 3.5(*a*) & (b) demonstrate the formation of Co₃O₄ nanoparticles uniformly distributed over the α -MnO₂ nanorods. The lumpy surfaces besides the well-defined 1-D morphology reveal the decoration of isolated Co₃O₄ nanoparticles on 1-D α -MnO₂ and partly exposure of the MnO₂ surface. The interplanar spacing of the lumpy spots fringe is 0.25 nm corresponding to the (200) plane of Co₃O₄ nanoparticles over the 0.50 nm (200) plane of α -MnO₂ nanorods clearly shown in Figure 3.5(*c*). Thus, the SAED pattern having diffraction spots of the plane (200), (400) and (600) of α -MnO₂ and (311), (222) of Co₃O₄ confirms the combination of both the species in figure 3.5(*d*).



Figure 3.5 (a) TEM image, (b) HR-TEM image, (c) Lattice fringes, and (d) SAED pattern of α -MnO₂/Co₃O₄ nanorods.

3.3.3 Electrochemical studies for amperometric glucose sensing

The electrochemical properties of the electrodes, α -MnO₂, Co₃O₄, α -MnO₂/Co₃O₄ on carbon paper, and bare carbon paper were studied in 50 mM of NaOH solution in an electrochemical cell. Cyclic voltammetry

(CV) experiments were performed in the potential range of -0.1 to 0.6 V at 10 mV/s scan rate to observe the electrocatalytic activity of the nanorods. The electro-oxidation of glucose on α -MnO₂, Co₃O₄, and α -MnO₂/Co₃O₄ are displayed in Figure 3.6(α). The α -MnO₂ reveals the absence of redox peaks, showing typical rectangular shapes, revealing the surface faradaic reaction of the synthesized samples; *i.e.*, the surface electrosorption of Na⁺ cations and the fast-reversible successive surface redox reactions of the electrode utilizing interaction/extraction processes of the proton. The quasi-rectangular CV curves indicate the presence of adsorption and desorption processes at the interface of electrode/electrolyte. Moreover, no characteristic redox peaks are observed in the electrodes; indicating that the electrode is displaying a pseudo-constant rate over the complete voltammetric cycle [36].

To ascertain the effect of scan rate in CV, measurements were also carried out at different scan rates (10, 20, 30, 40 mV/s), and shown in Figure 3.6(b), no redox peaks appeared. The addition of glucose in the electrolyte, showing a negligible peak further demonstrated as very less response of glucose towards α -MnO₂. The CV curve of Co₃O₄ (curve 3) depicts a set of redox peaks at 0.37 V (oxidation). The CV (curve 4) of α -MnO₂/Co₃O₄ nanomaterial is also investigated in an alkaline solution (50mM NaOH) in the range of -0.1 V to 0.6 V vs. Ag/AgCl. A single well defined and high-intensity redox peak (oxidation) at 0.25 V is observed in an alkaline solution depicted in Figure 3.6(a) which can be assigned to the reversible transition between Co_3O_4 with CoOOH [Equation (3.7) & (3.8)]. This phenomenon indicates the involvement of OH⁻ in the electrochemical redox reaction of Co₃O₄. The oxidation potential of the hybrid α -MnO₂/Co₃O₄ electrode is changed concerning α -MnO₂ and Co_3O_4 . So, this shift in a negative direction is beneficial because it might have arisen from the enhanced contact area and large electron transport channels in the modified α -MnO₂/Co₃O₄ electrode material. This can assist the molecules and ions involved in the glucose oxidation of the system to

approach the active sites. As a result, this effect decreases the energy required for the reaction and accelerates the reaction dynamics [39]. The synergistic effects of both the Co_3O_4 and α -MnO₂ owned the higher catalytic activity. MnO₂ has a unique rod-like architecture that provides a high specific area as shown by BET result in Figure 3.8. It also improves the conductivity by decreasing the electron transfer resistance depicted through a typical rectangular curve behavior. The CV curve behavior of the hybrid nanostructure suggests that Co_3O_4 supplies a large amount of double-layer electron transport mechanism whereas MnO₂ (curve-2) acquires a large pseudo electron movement mechanism. This effect causes fast electron transport from the electrolyte to the electrodes. Stability of the well-dispersed Co₃O₄ nanoparticles over MnO₂ and the high active surface area provides channels to enhance the mass transportation in electrochemical reactions [36,37-40]. The CV curve of the bare carbon paper substrate is also measured for comparison (to know the effect of carbon paper); a much smaller area under the curve and current value observed (curve-1) in Figure 3.6(a).



Figure 3.6 (a)Comparison of cyclic voltammograms of (1) carbon paper(background) (black) (2) α -MnO₂, (Red) (3) Co₃O₄ (blue), and (4) α -MnO₂/Co₃O₄,(magenta)(b) Cyclic voltammogram of α -MnO₂/Co₃O₄ hybrid nanorods at different scan rates in 50mM NaOH.

The schematics of the glucose-sensing mechanism is represented in Figure 3.7 and the plausible reactions involved for the electrode α -MnO₂/Co₃O₄ at each oxidation and reduction point are as follows:

In curve 3 and 4 *i.e.*, for Co_3O_4 and α -MnO₂/Co₃O₄, there are two peaks:

$$Co_3O_4 + 4H_2O + 2e^- \leftrightarrow 3Co(OH)_2 + 2OH^-$$
 [3.6]

$$3Co(OH)_2 + 2OH^- \leftrightarrow 3CoOOH + 2H_2O + e^-$$
 [3.7]

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^-$$

$$[3.8]$$



Figure 3.7 Mechanism of electrolytic oxidation on glucose α -MnO₂/Co₃O₄ hybrid nanostructure in the presence of NaOH.

The peaks corresponding to each redox couple are not evidently distinguishable, and some are elusive, which might be due to surface modification of the Co_3O_4 nanostructure [41].

$$2CoO_2 + C_6H_{12}O_6(glucose) \\ \leftrightarrow 2CoOOH + C_6H_{10}O_6(gluconolactone)$$
[3.9]

 $2MnO_2 + C_6H_{12}O_6$ (glucose)

$\leftrightarrow 2MnOOH + C_6H_{10}O_6(\text{gluconolactone}) \quad [3.10]$

The surface area and pore size distribution results from N₂adsorption-desorption measurement (BET) which confirmed the mesoporosity, are displayed in Figure 3.8 (*a* & *b*). TEM images in figure 3.5 demonstrate the well interconnected and uniform nanorods of α -MnO₂/Co₃O₄ hybrid nanostructure which enhances the mobility of electrons in the whole body of nanorods. The specific surface area of α -MnO₂ is calculated to be $11\text{m}^2/\text{g}$ whereas, for α -MnO₂/Co₃O₄, it is three times higher than MnO₂ calculated as 33 m²/g, The high specific surface area has an advantage of high electrochemical performance.



Figure 3.8 Nitrogen adsorption-desorption isotherms of (a) α -MnO₂ and (b) α -MnO₂/Co₃O₄ hybrid.

The average pore diameter is almost the same for both the material which was calculated by BJH pore size distribution as 3 nm approximately and confirmed the mesoporous nature of the material. The average BJH pore size distribution curve of α -MnO₂ and α -MnO₂/Co₃O₄ hybrid is given in figure 3.9 (*a* & *b*) and the mesoporous nature is suitable for the mass transport and electrochemical activity [42]. So, the larger BET surface area of α -MnO₂/Co₃O₄ compared to α -MnO₂ and mesoporous nature can provide a shortened diffusion path for electrons and ions which enhance

the electrochemical sensing performance. The augmented amount of electron movement through tunnels of α -MnO₂ enhances the delocalization of electrons higher resulting in electrochemical performance of prepared α -MnO₂/Co₃O₄ hybrid nanorods [9]. The glucose which is adsorbed on the surface of the electrode accelerates further access of analyte on its catalytic active sites for the electrochemical reaction to occur and enhances familiar contact of the electrode and electrolyte with a shorter diffusion resistance.



Figure 3.9 BJH pore size distribution of (a) α -MnO₂ and (b) α -MnO₂/Co₃O₄ hybrid.

The high-rate diffusion of analyte (glucose) into the electrode surface oxidizes it into gluconolactone because of the role of Mn and Co ions from α -MnO₂/Co₃O₄, leading to increase in anodic peak current (I_{pa}) in an alkaline solution. The increased electrooxidation of glucose which is observed at α -MnO₂/Co₃O₄ is ascribed as the synergistic effect of α -MnO₂ and Co₃O₄ that prompted the electrical conductivity and number of active sites. Figure 3.10 (*a*) depicts the CV of α -MnO₂/Co₃O₄ at various increasing concentrations of glucose in 50 mM NaOH, measured at a fixed scan rate of 20 mV/s. The electrocatalysis of analyte in the favorable (positive) sweep is justified from the noticeable increment in I_{pa} with a very slight shift in the potential by the action of successive addition of glucose from 480 µM to 7 mM. **Figure 3.10** (a) Cyclic voltammograms of α -MnO₂/Co₃O₄ in 50 mM NaOH at 20 mV/s scan rate, (b) Calibration plot of peak current vs. glucose concentration

Figure 3.11 XPS spectra (a) Survey scan, (b) Mn2p, (c) Co2p, (d) O1s of the modified α - MnO_2/Co_3O_4 before and after the electrochemical amperometric glucose measurement.

The XPS measurement of the modified electrode, before and after the addition of glucose was performed and displayed in Figure 3.11 which depicts no prominent shift in the binding energy peak's of Mn2p, Co2p, and O1s. It demonstrates the diffusion-controlled reaction and the reversible nature of the mechanism. This enhancement in anodic peak current with the addition of glucose in the glucose-sensing cell demonstrates the electrocatalysis of glucose by α -MnO₂/Co₃O₄ nanostructure. Additionally, the calibration curve was plotted using the data set of Figures 3.10(*a*) and represented in Figure 3.10(*b*).

The curve shows the linear increase in the I_{pa} with an increase in glucose concentration, which reveals the excellent capability of the electrocatalytic mechanism of α -MnO₂/Co₃O₄ in glucose oxidation. Figure 3.12(a) represents the CV of α -MnO₂/Co₃O₄ at different scan rates (10 mV/s-40 mV/s) measured in 7 mM glucose in 50 mM NaOH. The anodic potential (E_{pa}) and cathodic potential (E_{pc}) (anodic potential and cathodic potential as shown in (inset) Figure 3.12(a) are slightly shifted towards negative and positive values as a function of an increase in scan rates. The calibration curve shows the linear relation between the I_{pa} and scan rate in Figure 3.12(b), which implies the typical diffusion-controlled electrochemical process.

Electrochemical impedance spectroscopy (EIS) was performed to analyze the catalytic action of glucose on the electrode of α -MnO₂/Co₃O₄ and shown in Figure 3.12(*c*). The Nyquist plot of the electrode consists of depressed overlapping capacitive semicircles in the high frequency and a linear region in low-frequency sides. Nyquist plot for the electrode was obtained in a bare 50 mM NaOH solution, 5 mM and 7 mM glucose in the parent NaOH solution. The diameter of the semicircle in the highfrequency region is related to the charge transfer resistance (*R_{ct}*) of the redox couple in the existence of glucose, the linear portion is attributed to the diffusion-limited process [23]. Modification in the electrolyte after the addition of 5 mM and 7mM glucose led to a smaller semicircle and decreased R_{ct} which is due to the efficient mass and charge transfer. This is explained through a uniform and high mass loading distribution of α -MnO₂/Co₃O₄ on carbon paper creating a necessary conducting path of electrons.



Figure 3.12 (a) Cyclic voltammograms of α -MnO₂/Co₃O₄,(b) Calibration plot of peak current with respect to scan rate,(c) EIS plot of α -MnO₂/Co₃O₄ electrode.

Amperometric glucose sensing is the simplest and economic technique for estimating sensitivity. The rapid oxidation of glucose in amperometric measurement makes this technique most suitable for the glucose-sensing application with high sensitivity, detection limit, and fast response time. In the current experiment, the glucose addition in 50 mM NaOH solution was measured at a fixed applied potential of 0.55V *vs* Ag/AgCl and the obtained curve is represented in Figure 3.13(*a* & *b*). The amperometric study was carried out using α -MnO₂/Co₃O₄ nanostructure with a successive increase in glucose amount in the cell. The resultant

current enhances monotonically, indicating excellent behavior for glucose sensors. The precise steady-state current response towards glucose is found in the ranges of 60 μ M to 7 mM with a fast response time of fewer than 5 seconds. The advantage of a hybrid network of α -MnO₂/Co₃O₄ nanorods causes an enhancement in the number of favorable sites and electron conductivity in the electrode which further ensures an excellent electrocatalytic feature of glucose. This signifies the excellent electrocatalytic behavior of glucose as a function of favorable sites corresponding to the electronic conductivity of related hybrid networks of α -MnO₂/Co₃O₄ nanorods.

Figure 3.13 (*c* & *d*) shows long-range linearity from 60 μ M to 7 mM glucose measured in 50 mm NaOH. The calibration plot measured in the range of 60 μ M to 7 mM fits the equation of linearity:

$$I(mA) = 0.13087 + 0.08138 C (mM)$$
 [3.11]

Where 0.13087 is the intercept, 0.08138 the slope, 'C' symbolizes concentration of the glucose and 'I' the resultant current. Sensitivity is calculated using the equation [43]:

$$Sensitivity = \frac{slope \ of caliberation \ plot, m \ (\mu A/mM)}{Active \ surface \ area(cm^2)}$$
[3.12]

The calculated sensitivity of biosensor is 127 μ A/mM/cm² (S/N=3) using an area of 0.64 cm², which is 3-4 times higher than MnO₂ based biosensor reported so far. The lowest limit of detection from the calculated sensitivity value is 0.03 μ M.



Figure 3.13(*a*) Amperometric current, I(mA) vs time T(s) response of α - $MnO_2/Co_3O_4,(b)2$ mM to 7 mM in 50mM NaOH at a constant applied potential of 0.55V, (vs Ag/AgCl), (c) Current vs. glucose concentration,(d) calibration plot of α -MnO₂/Co₃O₄ upto 7mM.

For comparing the performance, the amperometric measurement of the bare Co_3O_4 electrode was done. The obtained value of sensitivity calculated from the above-mentioned Equation (3.12) is 0.136 μ A/mM/cm². The steady-state current is found up to 700 μ M. It is found that the current response reaches saturation gradually in the Co_3O_4 nanoparticles electrode, indicating that all active sites of the electrode are covered with reaction intermediates at a high concentration of glucose in Co_3O_4 [43]. Figure 3.14 (a) & (b) represent the amperometric current response of the Co_3O_4 electrode after the successive injection of glucose and its calibration curves, respectively. From the above comparatives studies, the results reflect that the obtained value of the electrodes clearly shows the presence of a synergistic effect in the hybrid structure electrode α -MnO₂/Co₃O₄. α -MnO₂/Co₃O₄ has a major attribute of a glucose sensor, having long-range linearity, good response time, high sensitivity, and a lower detection limit in comparison to α -MnO₂ and Co₃O₄. The comparison for the performance of some other materials based on α -MnO₂, its composite, and Co₃O₄ are listed in Table 3.1. This table shows that the current biosensor has 3-4 times higher sensitivity with an excellent limit of detection and comparatively longer linearity range order.



Figure 3.14(a) Amperometric current response, I(mA) vs time T (s) response of $Co_3O_{4,}(b)$ Current vs. glucose concentration calibration plot of $Co_3O_{4,}$.

In Table 3.1, the performance comparison of the electrochemical glucose biosensors of MnO_2 and Co_3O_4 based composites are listed. Guo *et al.* has developed a 3-dimensional porous CNT/MnO₂ electrode by a dip and dry method followed by a potentiostatic deposition technology. They have achieved a sensitivity of 33.19 μ A/mM/cm²[19]. This electrode material lacks in its performance because of the low conductivity and high solubility in NaOH electrolyte. Another work carried by Meng *et al.* based on Cu/MnO₂ electrode [44] exhibits a glucose sensitivity of 26.96 μ A/mM/cm² with the help of a glassy carbon electrode (GCE) which is costly and is not suitable for practical applications of device fabrications.

Electrode	Linear	Sensitivity		References
materials	range	(µA/mM/cm ²	Detection	(Publishing
	(in mM))	limit	Year)
MnO ₂ /MWNT	0.01-28	33.19	0.03µM	[19], 2015
Cu/MnO ₂	2.5×10^{-4} -	26.96	0.02µM	[44], 2014
	1.02			
Pt/Au-MnO ₂	0.1-3.0	58.54	0.02µM	[8], 2013
GOx/MnO ₂	upto 3.15	31.6	-	[45], 2013
Co ₃ O ₄	upto 2.04	36.25	0.97µM	[46], 2010
Nanofibers				
MnO ₂	upto 2	-	1.8µM	[47], 2016
nanowires				
(enzymes				
based)				
MnO ₂ /CNT-air	0.1-3.2	24.2	3.0mM	[48], 2016
plasma				
MnO ₂ /Co ₃ O ₄	upto 7	127	0.03µM	Our Work

Table 3.1: Comparison	of other reported $MnO_{2,}$	Co_3O_4 based material,
and derivatives.		

In a similar work, glucose oxidase (GO_x) enzyme has been applied for the enhancement of sensitivity and found that it has risen to 31.6 μ A/mM/cm² with the help of enzyme [45].1-dimensional MnO₂ nanowires have been investigated for electrochemical biosensor applications by Han *et al.* and it is documented in the literature that the material is providing linearity up to 2mM which is an important drawback for practical glucose sensor. Also, the template method used for the growth of nanowires in this work is complex as compared to other chemical routes [47]. It is very important to compare the performance of the hybrid MnO_2/Co_3O_4 electrode with a Co_3O_4 based glucose sensors to investigate the synergistic effect of the hybrid nanomaterial. A two-step synthesis method consisting of electrospinning and calcination is used for the development of Co_3O_4 nanofibers by Ding *et al*. The material is exhibiting a very low glucose sensitivity of 36.25μ A/mM/cm². The low performance might have arisen due to the extreme temperature used in the calcination process which usually reduces the stability of the material in the electrolyte [46]. In our work, the controlled synthesis and rational design of the hybrid nanomaterial and electrode are of great importance in enabling the highperformance of glucose sensor which favors its potential application in diabetes.

3.3.4 Interference, stability, and reproducibility test

One of the major challenges in non-enzymatic glucose analysis is to eliminate the interference responses generated by some endogenous species such as Ascorbic acid (AA), Uric acid (UA), etc. In the psychological condition the level of glucose (3-8 mM) is much higher than that of these species (<0.5mM). To evaluate the selectivity of the sensor, two possible interfering biomolecules, ascorbic acid, uric acid which normally coexists with glucose in real samples (*e.g.* in human blood) were examined along with glucose. The blood glucose level of a normal human body is between 4 mM and 7 mM while the concentration of endogenous AA and UA is about 0.125 mM and 0.33 mM in blood samples respectively [46]. As demonstrated in Figure 3.15 (a), the ascorbic acid (0.125 mM) and uric acid (0.33 mM) in 50 mM NaOH can only result in 13 % and 16 % enhancement in current as compared to glucose (4 mM) which is insignificant and negligible to be considered as compared to glucose response. The long-term stability of the electrode is also a very important parameter for glucose sensing. After exposing the electrode to air for 7 days, its performance was re-evaluated in 50 mM NaOH with a 5

mM glucose solution and shown in Figure 3.15(*c*). The result displays good long-term stability of the electrode by retracing the current path on day 1. The stability performance of the material was also confirmed by the XPS measurement of the electrode before and after the glucose analysis as shown in Figure 3.11. The reproducibility was also investigated by 2 consecutive measurements of a single electrode made by α -MnO₂/Co₃O₄ from a range of 60 μ M to 600 μ M glucose in 50 mM NaOH. It shows a standard deviation of 8.3 % for (Reproducibility 1) and 8.4 % (Reproducibility 2) which is very close to the original data having a standard deviation of 8.3% as shown in Figure 3.15(*b*)



Figure 3.15(*a*) Response of α -MnO₂/Co₃O₄ in NaOH after the addition of interfering species. (inset) Bar graph for the responses generated, (b) Amperometric glucose sensing of two different electrodes of α -MnO₂/Co₃O₄ of the same batch, (c) Stability test of electrode after 7 days.

3.3.5 Real blood and serum sample analysis

For verifying the accuracy of α -MnO₂/Co₃O₄ samples in practical applications, the amperometric response of the modified electrode in 20 mL of 50 mM NaOH solution after injecting 200µL whole blood sample and 250 µL serum from human blood was evaluated. Measurement was done at an applied potential of 0.55 V shown in Figure 3.16. The same blood samples were also analyzed in the local medical pathology center and further compared. A whole human blood sample showed 92 mg/dL glucose (~4.16% less concentration) and serum sample showed 97.5 mg/dL glucose (~1.5% more concentration) as compared to clinically diagnosed (96 mg/dL) due to the presence of different types of molecules (cells, protein fragments, *etc.*). The α -MnO₂/Co₃O₄ modified electrode shows suitability for the practical detection of glucose in real samples.



Figure 3.16 Amperometric current responses, I(mA) vs time T(s) response of α -MnO₂/Co₃O₄ in blood and serum sample.

Thus, the real blood sample analysis showed that the hybrid nanomaterial, formed by MnO_2 and Co_3O_4 nanomaterial connected at the nanometer scale combines the intrinsic characteristics of its constituents to yield additional enhanced properties due to the synergistic effects between

the components. The binding strength between these two transition metal oxides MnO_2 and Co_3O_4 could ensure the effective interaction between the nanomaterials to produce additionally active catalytic sites in the MnO_2 . Co_3O_4 on the other hand is a low-cost material bundled with excellent electrochemical stability and conductivity. It is demonstrated that the synergistic effect between two metal oxides to attract electrolyte ions in a large range of potentials increases the rate of the oxidation reaction. The hybrid nanostructures and configuration of heterojunction offer an improved conductivity and enhanced charge transfer capability to promote the glucose sensing

3.4 Summary

In summary, we have successfully demonstrated the synthesis of α -MnO₂/Co₃O₄ hybrid nanostructure by decorating 1D α -MnO₂ with Co₃O₄ nanoparticles for glucose sensing and properties were investigated. The original rod-like structure of α -MnO₂ as a supporting base for Co₃O₄ nanoparticles has a great effect on the degree of synergistic effect. The analytical parameters for the α -MnO₂/Co₃O₄ nanostructures based glucose sensor were evaluated and it is found that the sensor is highly selective, reproducible, repeatable, reversible, and stable. The synthesized α -MnO₂/Co₃O₄ electrode exhibited a high sensitivity of 127 μ A/ μ M/cm² (S/N=3), which is 3-4 times higher in comparison with the other reported literature so far, a detection limit of 0.03 μ M, the wide linear range of 60 µM to 7 mM of glucose and a short response time of fewer than 5 seconds. This work provides a simple and versatile technique to design new kinds of highly active material for glucose sensing by simply modifying the structure to a hybrid nanostructure.

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CHAPTER 4

Defect Mediated Bi-Functional Application: Supercapacitor and Glucose Sensing of W₁₈O₄₉ Nanorods Bundle

Publication:

 Lichchhavi Sinha, Parasharam M. Shirage, "Surface Oxygen Vacancy Formulated Energy Storage Application: Pseudocapacitor-Battery Trait of W₁₈O₄₉ Nanorods", *Journal of The Electrochemical Society*, 166(14), (2019) A3496-A3503. (Impact Factor: 3.721) DOI: 10.1149/2.1251914jes.

2. Lichchhavi Sinha, Hyunju Lee, Yoshio Ohshita, Parasharam M. Shirage, "Defect Mediated $W_{18}O_{49}$ Nanorods Bundle for Nonenzymatic Amperometric Glucose Sensing Application", *ACS Biomater. Sci. Eng.*, 6,4, (2020) 1909–1919. (Impact Factor: 4.490) DOI: 10.1021/acsbiomaterials.9b01791

CHAPTER 4

Defect Mediated Bi-Functional Application: Supercapacitor and Glucose Sensing of W₁₈O₄₉ Nanorods Bundle

4.1 Overview

In chapter 3, the electrochemical glucose sensing application of α -MnO₂/Co₃O₄ hybrid nanostructure was studied. The highlights of the earlier work are the importance of the hybridization process in enhancing the electrochemical actions of α -MnO₂. The drawbacks of MnO₂ nanostructures are its low conductivity and easy dissolution in the electrolyte causing poor stability. Now our attention has been shifted towards selecting another nanomaterial, tungsten oxide, and increasing its intrinsic conductivity and stability performance by the action of defect engineering. In this chapter, the bi-functional electrochemical application of energy storage and amperometric glucose sensing has been successfully proclaimed the importance of defect prone nanostructure over the electrode fabrication.

The most effective strategy for tuning the properties of functional metal oxides is defect engineering. This process has been widely accepted to harmonize the physicochemical characteristics in the field of catalysis, energy storage, and sensors [1]. In some reported work, it is concluded that the incorporation of oxygen vacancies into metal oxides could improve the catalytic performances of the material [2,3]. Generally, oxygen vacancies are the most sensitive sites on the surfaces of metal oxides. These sites are contributing towards the enhancement of surface redox reactions which intensify electrochemical activities [4,5]. Earlier, some of the works like Huang *et al.* reported that tailoring of the oxygen deficient bismuth iodide oxide (BiOI) nanosheets exhibited higher photocatalytic activity in the order of 10 as compared to untreated BiOI [6]. Another reported work conducted by Zhai *et al.* on MnO_2 showed that due to the oxygen vacancy generated in the crystal structure, tremendous improvement has been made in the supercapacitor performance [7]. Xu et al. has developed a technique for incorporating oxygen vacancy inside the porous copper oxide for the enhanced electrocatalysis performance [8]. Eventually, all these reported works are trying to convey the importance of oxygen vacancies but the exact mechanism behind the effective utilization of oxygen vacancies is still unexplored and unidentified precisely. These works have also highlighted the electrochemical aspect of defect prone nanostructure which generated an urge of finding the suitability of the nanostructure in the field of electrochemical glucose sensing and supercapacitor.

Tungsten based suboxides nanostructures have been identified as promising semiconductor materials for various applications like sensing, electrochromic, photovoltaic, photocatalytic, field emission performance, etc, owing to its optimum band gap of 3.47 eV, and environmental friendliness [9-11]. Amongst other non-stoichiometric tungsten oxides, $W_{18}O_{49}$ has been broadly examined due to its favorable defect structure and the novel properties of mixed valency giving rise to an unusual physical and chemical property in the nanometer regime. It is used in trapping energy by heat-insulating film because of its mixed-valence tungsten ions. It is also stable and has the highest oxygen deficiency which makes it worthy of various prospects. The stable nature and highperformance of an electrochemical activity are determined by the diffusion-controlled redox processes occurring at material surfaces [12]. The relevant surface defects, *i.e.*, the surface oxygen vacancy (SOV) in metal oxides are the most remarkable ones and are anticipated to be actively presented in numerous reactions. High dispersion and strong anchoring of metal nanoparticles on the metal oxide surface occurs because of surface oxygen vacancy. Intentional creation of oxygen vacancies has been explored to improve the intrinsic conductivity and electrochemical activity of transition metal oxides by altering the geometric and electronic structures [13-15]. It serves as shallow donors in the electronic structure of metal oxides which improve the electrical conductivity and donor density.

Herein, we study a surface oxygen-deficient tungsten-based $W_{18}O_{49}$ nanostructure in a monoclinic phase grown by a solvothermal method. Further, the non-stoichiometric oxygen vacant tungsten oxide was applied as an electrode material for energy storage application which exhibited the high capacitive performance and long cycle life. The remarkable activity occurred because of high surface area morphology and porous nanostructure. The electrochemical electrode fabrication using $W_{18}O_{49}$ has shown an impressive glucose-sensing material by displaying a high sensitivity and good anti-interference stability with impressive response time and detection limit. More details are discussed in the next sections of this chapter.

4.2 Experimental Section:

4.2.1 Synthesis of WO₃ nanomaterial

1.9 g of Sodium tungstate (Na₂WO₄.2H₂O) was dissolved in 50 ml deionized water and stirred till it completely gets dissolved. Later, 1.5 g of oxalic acid (H₂C₂O₄.2H₂O) was added to the solution. The solution was acidified by adding a dropwise 3M/L HCl solution to reach a pH <1. Finally, a transparent solution was obtained in which 3 g K₂SO₄ was added. The final obtained solution was transferred in a 100 ml Teflon lined stainless steel autoclave and put into a muffle furnace at 100 °C for 24 hours. When the reaction was finished, the yellow product was

collected by the process of centrifugation and washed repeatedly with deionized water and ethanol. Finally, the product was dried at 60 °C overnight and used for further studies.

4.2.2 Synthesis of W₁₈O₄₉ nanomaterial

A solvothermal approach was used for the synthesis of $W_{18}O_{49}$ nanomaterials. In this procedure, 0.1 g WCl₆ was well dissolved in a 60 ml ethanol solvent to form a clear yellow translucent solution under magnetic stirring. The mixture was magnetically stirred for about 30 minutes, loaded into a 100 ml Teflon lined stainless autoclave, and heated at 180 ° C for 16 hours. After cooling to room temperature, the resultant solid blue color product was collected by centrifugation, washed repeatedly with water and ethanol and dried for 12 hours at 80° C. The schematic for the synthesis procedure is given in Figure 4.1(*a*).

4.2.3 Details of characterizations instruments

The phase purity, structural and morphological identification of the synthesized nanomaterials were carried out by D2-Phaser Bruker, 30KV/10 mA, X-Ray Diffractometer (XRD) instrument, Cu K α source (λ =1.5406 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS spectrometer with Al K α source (hv = 1486.6 eV). Field emission scanning electron microscopy images were taken from Supra55 Zeiss, FESEM microscope. High resolution-transmission electron microscopy images from HRTEM, JEOL-2100. N₂ adsorption-desorption study for Brauner-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size distribution were performed by automated gas adsorption analyzer Quantachrome Autosorb iQ2. Electrochemical experiments were performed using the electrochemical analyzer Autolab PGSTAT302N with a conventional three-electrode system. The auxiliary electrode was platinum and the reference electrode was saturated calomel electrode (SCE) Hg/HgCl

electrode. The working electrode was the carbon paper loaded with the synthesized nanomaterials.

4.2.4 Fabrication of working electrode:

The synthesized $W_{18}O_{49}$ and WO_3 powders (1 mg) were dispersed in ethanol (1 ml) in two different tubes. The obtained suspensions were sonicated for 10 minutes followed by the addition of 10 % carbon black and 1 drop Teflon suspension (in liquid ammonia). Again they were sonicated for 5 minutes to form a homogenous suspension. Further, it was drop cast over the carbon paper maintaining uniformity and dried at 80 °C for 12 hours. Deposited mass on the electrodes was ~0. 8 mg. The schematics for the fabrication of the electrode is provided in Figure 4.1(*b*)



Figure 4.1 (a) Synthesis of $W_{18}O_{49}$, (b) Fabrication of electrode.

4.3 Results and Discussion

4.3.1 Material characterizations

Figure 4.2 (a) shows the X-ray diffraction (XRD) pattern of $W_{18}O_{49}$ All the obtained peaks match well with the monoclinic phase of $W_{18}O_{49}$ having space group P2/m(10) [JCPDS-05-0392]. Full Prof Software was utilized for calculating the lattice parameters using Rietveld refinement (with Bragg R-Factor- 6.325, RF factor-3.06, and $\chi^{2=1.76}$) process as shown in Figure 4.2(a) (inset). The obtained lattice parameters are $a = 19.072 \pm 0.003$ Å, $b = 3.785 \pm 0.003$ Å and $c = 14.574 \pm 0.007$ Å. The two sharp peaks at the position of 2θ = 23.4° and 47.7 ° correspond to the reflections from (010) and (020) planes of W₁₈O₄₉, respectively. The other diffraction peaks are comparatively lacking in intensity and sharpness which emphasizes the preferential growth along (010) direction. The basic unit for the $W_{18}O_{49}$ nanostructure is WO_6 octahedrons which share their corners and edges to make a nanostructure [16,17]. The XRD pattern of WO_3 nanostructure is given in figure 4.2 (b) which shows the purity of synthesized nanomaterial. All the obtained peaks match well with the hexagonal phase [JCPDS file: 33-1387] of WO₃. No peaks are obtained for other phases of WO₃.



Figure 4.2 X-ray diffraction pattern of (a) $W_{18}O_{49}$ nanomaterial (inset) Rietveld refined X-ray diffraction pattern, (b) synthesized WO_3 nanomaterial.

Raman spectroscopy measurement was conducted for verifying the phase and chemical structure of $W_{18}O_{49}$ as given in figure 4.3. The bands at lower wavenumber 137 cm⁻¹ and 259 cm⁻¹ correspond to the W-O-W and O-W-O bending modes present in $W_{18}O_{49}$. The bands at higher wavenumber present at 702 and 803 cm⁻¹ correspond to the W-O stretching modes. These bending and stretching modes confirm the formation of defect prone tungsten oxide, $W_{18}O_{49}$ [18].



Figure 4.3 Raman spectra of $W_{18}O_{49}$.

The X-ray photoelectron spectroscopy (XPS) was carried out to determine the possible defects, surface composition, and elemental valence of the oxygen-deficient nanostructure. The survey XPS spectra of $W_{18}O_{49}$ nanostructure is shown in Figure 4.4(*a*). The survey spectrum indicates the presence of Tungsten and oxygen. The W4f core level spectrum in Figure 4.4 (*b*) can be deconvoluted into (i) with spins W4f_{5/2} at 37.8 eV and W4f_{7/2} at 35.7 eV. This peak corresponds to W atoms having chemical valence +6, (ii) another peak with lower binding energy at 34.6 eV, and 36.7 eV resulting from the emission of W4f_{5/2} and W4f_{7/2} core levels from the chemical valence of +5 of W atoms[10,15,19]. It indicates the nonstoichiometric *i.e.* oxygen-deficient (WO_{3-x}) synthesis of tungsten oxides. The O1s spectra can be deconvoluted into three peaks as

given in Figure 4.4(*c*). The peak at 530 eV is configured to lattice oxygen, i.e., bond of W-O-W. The peak at 531.9 eV is indexed to O atoms which are in the proximity of vacancy created by oxygen and the peak at 532.6 eV which arises as to the adsorption of oxygen from hydroxyl groups on the surface of the nanomaterials [11]. These results suggest the presence of vacancies of oxygen atoms corresponds to the surface defects rather than forming WO₃ forming W₁₈O₄₉.



Figure 4.4 (a) X-ray photoelectron spectra (survey scan) of $W_{18}O_{49}$, Deconvoluted peak of (b) W4f, (c) O1s spectra.

Later, the XPS analysis of WO₃ nanomaterial was conducted and given in Figure 4.5 (*a*) and (*b*) shows the comparison of C1s spectra from both carbon tape and WO₃ with carbon tape. The C1s spectrum of WO₃ at 288 eV shows a clear upward shift (~2.2 eV) in binding energy as compared to that of a pure carbon tape at 285.8 eV, which might have arisen due to sample charging effect. Considering the upward shift in
binding energy (2.2eV) the calibrated W4f of WO₃ is positioned at 35.7 and 37.7 eV of W⁶⁺ oxidation states [20] as shown in Figure 4.5(*c*). Likewise, figure 4.5(*d*) shows the calibrated O1s peak positioned at 530.8 eV which is for the lattice oxygen present in WO₃ crystal. The O1s peak in between 534 to 538 eV might have occurred from a carbon tape and adsorbed water also. These values match well with the reported WO₃ samples [20,21].



Figure 4.5 XPS spectra (a) C1s of only carbon tape, (b) C1s from carbon tape with WO_3 nanomaterial,(c) W4f from WO_3 , (d) O1s of WO_3 nanomaterial.

Figure 4.6 shows the comparison of photoluminescence (PL) spectra of $W_{18}O_{49}$ and WO_3 nanomaterial at room temperature in the wavelength range of 400-800 nm with an excitation wavelength of 375 nm. It was used to analyze the surface defect present in the nanomaterial. The PL spectra for $W_{18}O_{49}$ correspond to the domination of broad emission bands in the blue region as shown in Figure 4.6(inset). The band

centered at 435 nm emission is related to the presence of oxygen vacancies [22]. In the case of WO₃, very low-intensity emission is observed, since it is an indirect band gap semiconductor which should have very low emission efficiency [23]. The strong blue emission in $W_{18}O_{49}$ is strong evidence of the presence of large amounts of oxygen vacancies as compared to WO₃.



Figure 4.6 Photoluminescence (PL) spectra of WO_3 (Red) and $W_{18}O_{49}$ (Black), (inset) magnified image from 400-500nm wavelength.

The morphology and structure of the materials were examined by Field emission scanning electron microscope (FESEM) and High resolution-transmission electron microscope (HRTEM), respectively. Figure 4.7(*a*) and (*b*) represents the FESEM images indicating that the $W_{18}O_{49}$ consists of bundles of 1D nanorods of length ~600 nm and diameter 10-20 nm. The uniform distribution of the bundle can be seen in Figure 4.7(*a*). To obtain information regarding crystallinity and morphology, the $W_{18}O_{49}$ nanorod bundles are further characterized by HR-TEM. Figure 4.7(*c*) confirms the formation of bundles of the nanorods as depicted by the FESEM data. The Selected area electron diffraction (SAED) pattern obtained in Figure 4.7(*d*) is of the area highlighted in Figure 4.7 (*c*) which shows (010) and (020) planes of $W_{18}O_{49}$. The ring formation along with the diffraction spots suggests the formation of the polycrystalline material. Since $W_{18}O_{49}$ has an oxygen substoichiometry, it summarizes an extended planar defect. The streaking pattern of the diffraction spots perpendicular to the nanorods axis indicates the presence of the unequally spaced planar defects parallel to the growth direction [24]. Figure 4.6 (*d*), (inset) shows the lattice fringes of a single $W_{18}O_{49}$ nanorod. The calculated *d*-spacing is 0.39 nm, corresponding to the (010) plane of $W_{18}O_{49}$ which agrees well with the XRD data represented in Figure 4.2(*a*).



Figure 4.7(*a*) Low and (*b*) high magnification FESEM image, (*c*) HR-TEM image, (*d*) Selected Area Electron Diffraction (SAED) pattern of $W_{18}O_{49}$ nanostructure), (inset) lattice fringes of the highlighted part of HRTEM image.

Amongst other tungsten based oxides, W18O49 usually exhibit the anisotropic growth along (010) direction tending to form 1D nanostructure. So by the above analysis of the HRTEM result, it is observed that the growth is along the (010) direction. The inner architecture *i.e.*, surface area and pore size of nanomaterials play a vital role in the electrochemical application. Nitrogen adsorption-desorption studies of the nanomaterials were carried out and displayed in Figure 4.8(a) and 4.9(a). The calculated specific surface areas of $W_{18}O_{49}$ and WO_3 nanostructures are 82.309 m^2/g and 8.29 $m^2\!/g,$ respectively. $W_{18}O_{49}$ shows 10 times higher surface area compared to WO3. So, this huge difference might arise due to the agglomeration of nanorods towards the nanorods bundle, as it is a wellknown fact that 3D nanostructure has a high surface area compared to 1D nanostructure [25,20]. The average pore sizes of both the nanomaterial have also been calculated as 2.4 nm for W₁₈O₄₉ and 1.8 nm for WO₃ using Barrett Joyner Halenda (BJH) pore size distribution as shown in Figure 4.8(b) and 4.9(b), respectively. The mesoporous nature of $W_{18}O_{49}$ nanostructure makes it worthy for the proper mass transport and appropriate electrochemical activity by having a shortened diffusion path for electrons and ions [22, 26].



Figure 4.8(*a*) N_2 adsorption-desorption isotherm, (b) Average BJH pore size distribution for $W_{18}O_{49}$.



Figure 4.9 (a) N_2 adsorption-desorption isotherm, (b) BJH pore size distribution for WO₃.

4.3.2 Electrochemical characterizations

Figure 4.10 shows the electrochemical energy storage performance of the W₁₈O₄₉ nanomaterials in 1M H₂SO₄ aqueous electrolyte using three-electrode systems. The results of the cyclic voltammetry (CV) curve investigating (Figure 4.10(a)was initially evaluated for the electrochemical behavior of W₁₈O₄₉ nanostructure in a positive potential window of 0 to 0.80 V (vs V_{SCE}) at different scan rates. It can be observed from Figure 4.10(a) that when applied voltage reduced the mobility of electrons through the $W_{18}O_{49}$ nanorods, the current switched to a more negative side. This phenomenon can be best described in the charge injection model which suggests that, at the time of the hydration process, electrons present in the electrode along with the H^+ ion of the H₂SO₄ electrolyte are reinstalled together in the electrode. During the scan, the non-rectangular behavior shows a controlled faradaic mechanism taking place by the bulk of the electrode material *i.e.*, Pseudocapacitor-battery type behavior. It is because of the reversible redox reaction, oxidation, and reduction process that occurs at the interface for different valence states of W in the electrode [27,28]. The Reaction (4.1) for the redox pair is represented as:

$$WO_{3-x} + yH^+ + ye^- \leftrightarrow H_yWO_{3-x} \tag{4.1}$$

The anodic peak is being compatible with the oxidation of WO_{3-x} converted to H_yWO_{3-x} , *i.e.*, the hydration process takes part in the process. The high current value is maintained in such a large potential window. The specific capacity *i. e.*, charge storage performance has been evaluated using Equation (4.2) [29]:

$$C = \frac{1}{mv \bigtriangleup V} \int I dV \tag{4.2}$$

Where "*C*" is the specific capacity in "mA h /g", "*fIdV*" is the integrated area of the curve, "*m*" is the mass in "g", "*v*" is the scan rate in "mV/s" and " ΔV " is the potential window in "V".

The highest specific capacity of 470 mA h/g has been achieved at the minimum scan rate 1mV/s and the lowest specific capacity of 191 mA h/g has been achieved at a scan rate of 90 mV/s, the values of the specific capacity at different scan rates are provided in Figure 4.10(b). Figure 4.10(b) suggests that at a lower scan rate the specific capacity is higher and shiting towards a higher scan rate the specific capacity decreased. It can be analyzed that at a lower scan rate the complete interaction of electrolytic ions takes place with the electrode but at a higher scan rate, the number of ions is more than the available electrode surface area. The proper utilization of the active surfaces on the electrode is difficult because of the diffusion of ions into the pores. More importantly, the cyclic voltammetry (CV) results revealed good capacity retention of the $W_{18}O_{49}$ nanorods suggesting that the rate of the faradaic reaction of the electrodes is sufficient for maintaining the response of current at a very high scan rate [30]. Another feature that can be revealed from Figure 4.10(a) CV curve, *i.e.*, a distinguishable shift in the peak potential with respect to scan rate arisen as the generation of ohmic resistance and the polarization effect occurred due to the fast rate of electron transfer or

diffusion kinetics. Galvanostatic charging-discharging (GCD) measurement has also been performed at different applied values of currents in the potential window of 0 to 0.85 V (vs V_{SCE}) and represented in Figure 4.10(c). The curve shows the significant deviation from the ideal triangular nature reported for ideal electrochemical double-layer capacitors. It shows a non- linear discharging curve (*i.e.*, slopes) significant for the redox mechanism possessed by electrode material. The discharge curve also shows a potential (IR) drop till 0.4 V(vs V_{SCE}) followed by the slope which is an epitomic feature of an intermediate state between Pseudocapacitor-battery type behavior [31-34,29]. The steep increase in the potential above 0.4 V in GCD is also justified while the abrupt decrease of current in the CV. The voltage drop in the GCD curve is due to the equivalent series resistance (ESR) generated because of the combination of all types of resistance generated by electrode and electrolyte [28,30,35]. The specific capacity evaluated by the GCD curve using the following equation (4.3)[29]:

$$C = \frac{2X I X \triangle t_{dis}}{m X \triangle V} \tag{4.3}$$

Where "*C*" is the specific capacity in "mA h /g", "*I*" is the constant current density in "mA/g", "*m*" is the total active mass in "g", " Δt_{dis} " is the discharging time and " ΔV " is the potential window in "V". The charging-discharging curves are shown in Figure 4.10(*c*) at a different current density of 1.25, 2.5, 3.75, 5, 6.25, 8, 10,12.5 A/g, and corresponding specific capacities are calculated and displayed in figure 4.10(*d*). Figure 4.10(*d*) depicts that as the current density increased, the value of specific capacity decreased, which is because of the pores available in the active exposed surface are utilized for the storage of charges and further with an increase in current density the ions neither get the accessible pore sites nor proper time for the migration of electrolytic ions. It results in the degradation of the performance of the electrode. The highest specific capacity of 452 mA h /g is achieved at the lowest current

density of 1.25 A/g. As it is visible from the cyclic voltammetry (CV) and galvanostatic charging-discharging (GCD) plot, a very slight difference in the values of specific capacity takes place. The reason can be explained as these two measurements are completely different from each other in terms of mechanism, the ions move rapidly over the surface in CV whereas in GCD the electrode gets charged with respect to (w.r.t.) potential applied and discharges slowly in the electrolyte. It is noted that the specific capacity obtained from GCD is lower than calculated from CV, which renders an inadequate surface redox reaction due to the reduced surface for electrolyte ions at huge current densities [29,31].



Figure 4.10 (a) Cyclic voltammograms of $W_{18}O_{49}$ at different scan rate, (b) Specific capacity vs scan rate plot from cyclic voltammetry,(c) Galvanostatic charging-discharging at different current density,(d) Specific capacity vs current density plot from GCD.

Electrochemical impedance spectroscopy (EIS) measurements within a range of frequency 0.01 Hz-100 kHz are done by applying an AC voltage. Figure 4.11(a) shows a Nyquist plot of the electrode before and after the cyclic voltammetry. There are two regions formed in the Nyquist plots based on the range of frequency, *i.e.*, at high frequency, a compressed semicircular arc, and at low-frequency, an inclined line having an intercept on the X-axis. The high-frequency region, and the point of intersection *i.e.*, solution resistance (Rs) with the impedance axis comprises the internal resistance of the working electrode, the resistance of the electrolyte, and the contact resistance between the electrode and electrolyte. The calculated value of Rs obtained after fitting the parameter is 1.13 Ω . The other semicircular arc corresponds to the charge transfer resistance (Rct), i.e., the resistance generated due to the charge transfer occurs while the faradaic reaction or the double-layer deposition of charge on the electrode surface. The calculated value is 1.40 Ω , it infers a very low Rct in the electrode. The low-frequency impedance is also known as Warburg impedance which generates resistance because of the diffused proton into the pores of the electrode and the electrolyte. Similarly in the same frequency region, the vertical line shows the capacitive information of the electrode and also some diffusion resistance. The obtained EIS result can be overall analyzed as depicting a low combination of resistance which generates a favorable environment for the electrolyte ions to acquire the electrode surface.

The life cycle test was performed at a current density of 12.5 A/g for 2000 cycles, which is shown in Figure 4.11(*b*). It retained 100 % capacity retention up to 1500 cycles with constant stability throughout the measurement. After 1500 cycles, a slight decrease in specific capacity is observed due to the irreversibility in the reactions as well as the disappearance of the surface oxygenated functionalities [36]. After 2000 cycles, 87.5 % capacity retention is attained.



Figure 4.11(*a*) *Electrochemical impedance spectroscopy before and after cyclic voltammetry, (b) Stability test upto 2000 cycles of* $W_{18}O_{49}$ *electrode.*

4.3.3 Proposed mechanism for high energy storage performance in $W_{18}O_{49}$ nanorods bundle

Oxygen vacancy plays a very important role in the introduction of impurity energy levels inside the existing band gap of the transition metal oxides. So, it is an effective way to increase the conductivity and finally the performance of electrodes in the electrochemical reactions by lowering the coordination number of the compound [37-39]. Theoretically, it is shown by Li *et al.* that oxygen vacancy in $W_{18}O_{49}$ endorses a metal like property. It is well reported that compared with stoichiometric tungsten oxide, the band gap of non-stoichiometric tungsten oxide is less as shown in Figure 4.12 [40]. The calculated band using the Tauc plot of Ultraviolet-Visible (UV-Visible) spectra is 3.2 eV and shown in Figure 4.12(inset). The large number of free electrons observed from the metallic character dominates in the case of $W_{18}O_{49}$, suggesting that it should have a stronger ability to absorb light with a wider absorbance range. The detailed mechanism about the importance of the morphology and structure of W₁₈O₄₉ nanostructure is provided in Figure 4.13. CV curves recorded on W₁₈O₄₉ nanostructured material in the present study show more current per unit area than other reported tungsten-based oxide, supporting that this

defect structure has more active surface sites. The difference in the performance of the defect structure to other tungsten-based material is because of the hydration processes involved in the synthesized nanostructure. The oxygen deficiency enhances the hydration processes by increasing the valence states W^{6+} or W^{5+} . It also plays a crucial role in the formation of hydrogen tungsten bonds by the co-injection of electrons and positively charged ions in an outer circuit [41]. The high current, quasi linear proportionality between the current and the scan rate in cyclic voltammetry revealed that the high power characteristics of the electrode suggest the fast charge transfer and ion diffusion. The improved electrochemical performance evolves a fact, about bearing a channel to the electrolyte access and enhanced surface area may enhance ion and electron rapid transport. The excellent electrocatalytic performances of the $W_{18}O_{49}$ nanostructure electrode may be linked to the oxygen vacancies which can increase the rate that electrons reach the surface to increase reaction probability as trapping centers.



Figure 4.12 UV-Vis spectra of $W_{18}O_{49}$ nanomaterials (inset) Tauc plot for the band gap calculation





Such superior capability of the defect nanostructure might belong to its superior structure which can provide:

- (i) Good conductivity
- (ii) Highly reactive sites and reduced diffusion path for ions.

As a key role, oxygen vacancies are ordinarily the most reactive sites on its surface. As trapping centers, oxygen vacancies can increase reaction probability which can improve the catalytic performance of the nanomaterial. So the electron transport may directly influence the electrochemical storage performance. Some comparative studies based on the other reported literature are given in Table 4.1 for supercapacitor application

Material	Electrolyte	Capacitive	Potential	References
(electrode)		performance	Window	
			(V vs	
			SCE)	
WO ₃ /PANI	$1 \text{ M H}_2 \text{SO}_4$	168 at 1.28	05 to 0.7	[42]
		mA/cm ²		
Ordered	$2 \text{ M H}_2 \text{SO}_4$	103F/g	-0.2 to	[43]
mesoporous			0.8	
tungsten				
oxide/carbon				
Ti/IrO ₂ /WO ₃	0.5 M	46 F/g at 50	0.2 to 1.2	[44]
film	H_2SO_4	mV/s		
Ordered	$1 \text{ M H}_2 \text{SO}_4$	175 F/g at 2	-0.2 to	[24]
mesoporous		mV/s	0.7	
carbon/WO3-				
x				
nanocompos				
ites				
WO.H ₂ O	0.05 M	25.2 mF/cm^2	0.3 to	[45]
	H_2SO_4	at 0.3	0.15	
		mA/cm ²		
Graphene/na	$1 \text{ M H}_2 \text{SO}_4$	143.6 F/g at	0 to 1.0	[46]
nosheets/W		01 A/g		
O ₃				
composite				
W ₁₈ O ₄₉	1 M H ₂ SO ₄	452 mA h /g	0 to 0.8	Our work
nanorods		at 1.25 A/g		
bundle		and 470 mA		
		h /g at 2		
		mV/s		

Table	4.1	Comparison	of	energy	storage	performance	of	other	tungsten
based	elec	trodes.							

The results achieved in current work displays that the defects mediated $W_{18}O_{49}$ exhibits an excellent energy storage application. From Table 4.1, it is concluded that the $W_{18}O_{49}$ shows the highest charge storage capacity, in comparison to earlier reported literature. Zou et al. synthesized WO₃ nanostructure via electrodeposition method and later was combined with PANI, a conducting polymer. Thereby the electrochemical energy storage performance was measured of the composite electrode. Due to the incorporation of conducting polymer, the material enhanced its charge storage capacity but the stability was compromised [42]. Another work conducted by Jo et al. obtained nanocomposites of non-stoichiometric tungsten oxide with carbon and measured the pseudocapacitor behavior of the nanostructure. The synthesis process was quite complex and the use of carbon limited its conductivity and stability [43]. Farsi et al. developed an agglomerated hydrated tungsten trioxide and calculated a very low area capacitance of 25.3 mF/cm² [45]. The present work where the superior electrochemical performance of the tungsten oxide is achieved due to the oxygen vacancies, porous nanoarchitecture, and an optimum surface area of the nanorods bundle stimulated to intrinsically improve the conductivity, active sites, reversibility, faster charge transfer kinetics, etc..

4.3.4 Non-enzymatic amperometric glucose sensing characterization

The suitability of $W_{18}O_{49}$ and WO_3 electrode for electrochemical sensing performance was analyzed by an important technique cyclic voltammetry (CV) in potential window -0.1 to 0.6 V (vs V_{SCE}) in 50 mM of NaOH solution at a scan rate of 30 mV/s. CV plot of $W_{18}O_{49}$ represented in Figure 4.14(*a*) displays the absence of redox peak which illuminates the pseudo-constant behavior of $W_{18}O_{49}$ over the studied cycles. The experiment was carried out at different scan rates (10 mV/s, 20 mV/s, and 30 mV/s) using cyclic voltammetry to check the effect on the $W_{18}O_{49}$ electrode in absence of glucose. No trace of redox peaks was spotted as shown in Figure 4.14(*b*). A 60 µM glucose injected in the electrolyte (50 mM NaOH medium) shows an evidently detectable shift in the shape of the cyclic voltammetry curve. The alteration in the CV pattern is because of the occurrence of a pair of well-defined and intensified redox peaks (oxidation peak at 0.1 V and reduction peak at 0.35 V). These peaks are developed due to the reversible transition between WO_{3-x} and H_xWO_{3-x} [equation 4.7]. After every 50 seconds, 60 μ M of glucose was added successively in the electrolyte and it can be seen that with the increase in the concentration of glucose, the corresponding intensity of anodic current peak intensifies and increased. The enhancement in anodic current may be due to the electrocatalysis of glucose by defect prone tungsten oxide nanostructure due to availability of more number of adsorption sites and surface area. These parameters are crucial for the enhancement in the electrochemical interaction between the analyte and electrode significantly [25], which is reflected in Figure 4.14 (b). Figure 4.14(c) shows the cyclic voltammetry of the electrode in the presence of 60 µM glucose at different scan rates (10-30 mV/s). A slight positive shift can be observed in the oxidation potential of the $W_{18}O_{49}$ electrode which may be due to the enhanced contact area and large electron transport passage. The enhancement in the approachable area accommodates the molecules or ions to address the active sites at the span of the glucose oxidation process [26].

The $W_{18}O_{49}$ electrode was examined by the electrochemical impedance spectroscopy (EIS) to study the changes of electrode surface states and charge transfer properties of the electrode. There are mainly two noticeable regions observed in the Nyquist plot as shown in Figure 4.14(*d*):

(ii) Depressed semicircle in the high-frequency range

(ii) The Linear region with an intercept on the real axis of impedance within the low-frequency region.

The semicircle diameter of the Nyquist plot indicates the charge transfer resistance (R_{ct}) which controls the electron transfer kinetics of the redox probe at the electrode surface. The linear region in the curve signifies the diffusion-controlled process of the ions inside the electrode [47]. The electrode in the pure NaOH electrolyte exhibits the largest semicircle and the highest charge transfer resistance. The addition of 60 µM and 120 µM glucose in electrolyte reduces the diameter of the semicircle. It suggests the reduction in R_{ct} with respect to the addition of 60 and 120 µM glucose. It further sums up the effective mass and charge transfer kinetics of the electrode surface [51].



Figure 4.14 (a) Comparison of cyclic voltammetry (CV) with and without glucose, (b) CV without glucose at different scan rate, (c) CV with 60 μ M glucose at different scan rates, (d) EIS performance with and without glucose of $W_{18}O_{49}$ electrode.

Amperometric measurements were conducted to understand the response of electrodes towards the successive addition of glucose concentration into 50 mM NaOH. The measurements were carried out at an optimized potential of 0.55 V (vs V_{SCE}). Figure 4.15(*a*) shows the amperometric response of the $W_{18}O_{49}$ electrode by successive injection of an analyte, *i.e.*, glucose leads to the enhancement in the current. Wide glucose concentrations *i.e.*, 60 µM to 1.6 mM were added in NaOH and a specific undeviating current response was found within a minimum response time of 5 seconds. With the addition of glucose into NaOH solution, the current increases monotonically, which indicates that $W_{18}O_{49}$ electrode material is highly sensitive to glucose.

Figure 4.15(*b*) displays the calibration curve, which is plotted using the obtained values of current with respect to concentration from Figure 4.15(*a*). The calibration curve infers the linearity of current by the action of different concentrations of glucose. The derived linear fit equation is expressed as I(mA) = 1.07114E - 4C + 0.00541, where *I* is the current in mA and *C* is the concentration of glucose in μ M with the correlation coefficient of (R)=0.98401 and fast response of <5 sec up to 1.6 mM glucose. The typical linear behavior suggested that the redox reaction is a surface-confined process and the glucose molecules are directly oxidized on the surface of the W₁₈O₄₉ electrode [48-50]. The measured detection of limit has obtained a value of 0.02 μ M (S/N=3). The oxygen vacant sites present in the electrode can infer the electronic interaction between the analyte glucose and the equation – (4.4) is 167 μ A/mM/cm² [51].

$$Sensitivity = \frac{slope \ of caliberation \ plot, m \ (\mu A/mM)}{Active \ surface \ area(cm^2)}$$
(4.4)



Figure 4.15(*a*) Amperometric response at different glucose concentration, (*b*) Calibration plots of the amperometric response of W₁₈O₄₉ electrode.

WO₃ electrode was also being examined by cyclic voltammetry in the same electrolyte 50mM NaOH for its suitability in glucose sensing as shown in figure 4.16(*a*). In the absence of glucose, the curve shows a similar behavior as in $W_{18}O_{49}$ and a set of redox peaks after injecting 60µM glucose which reveals the electroactive nature of WO₃ for glucose sensing. Further, it was measured amperometrically and the corresponding calibrated linear curve based on current and concentration is shown in figure 4.16(*b* & *c*). The nanomaterial (WO₃) shows a lesser response to increasing glucose concentration *i.e.*, less change in current compared to $W_{18}O_{49}$ electrode. The sensitivity of WO₃ has been calculated as 104 µAmM⁻¹cm⁻² using the same equation (4.4) The calibrated linear curve estimated the linearity of WO₃ which is maintained till 800 µM which is again lesser as compared to the oxygen vacant $W_{18}O_{49}$.



Figure 4.16 (a) Cyclic voltammetry (CV) of WO₃ with and without glucose at 20mV/s scan rate,(b) amperometric measurement of WO₃ electrode with successive addition of glucose till 900 μ M,(c) calibration curve of amperometric measurement with linear fitting.

4.3.5 Mechanism for the electrochemical glucose sensing

The chemical reaction (4.5 & 4.6) which allows the formation of $W_{18}O_{49}$ is given below:

$$WCl_6 + RCH_2OH \rightarrow (RCH_2O)_m - WCl_n + mHCl$$

$$(RCH_2O)_m - WCl_n + H_2O \rightarrow WO_{3-x} + RCH_2OH + HCl$$

$$(4.6)$$

Where R is the alkyl group

To explain the operating characteristics of a metal oxide glucose sensing, the profound influence of defects and surface reactions taking place in the metal oxide surface are important aspects. The proposed possible electrocatalytic mechanism is given in Figure 4.17. The $W_{18}O_{49}$ surface towards the oxidation of glucose can be expressed by the reaction (4.7):

$$WO_{3-x} + OH^{-} + gluocse(C_6 H_{12}O_6)$$

$$\rightleftharpoons H_x WO_{3-x} + gluconolactone(C_6 H_{10}O_6) + H_2O$$

$$+ e^{-}$$
(4.7)

The conversion between WO_{3-x} and H_xWO_{3-x} oxidizes glucose towards gluconolactone. This oxidation process of glucose leads to the enhancement in the current as given in the current vs. time plot in figure 4.14(a). The analyzed electrochemical amperometric data and the calculated sensitivity intended to know about the mechanism of the highperformance. The understanding of defect chemistry scrutinized the importance of oxygen vacancies which generally stays inside the oxide compounds and modulates the chemical and physical properties [53]. Apart from being an intrinsic defect, the oxygen deficiency plays a crucial role in controlling the functionalities of metal oxide compounds likewise strong electron correlation in quantum materials [54-56] and energy materials [57,58]. The oxygen vacant sites provide the electron trapping centers to the electrolytic ion which increases the reaction probability [59,60]. The researchers have identified different aspects of metal oxides growth with divergent morphologies like nanoflowers, nanorods, nanofibers, etc., proposing various advantages [61-63]. Since in the current work, the grown nanostructure is an agglomerated bundle of nanorods, these morphologies have multidimensional access. It offers more avenues for the electron to access the electrocatalyst within the high surface area of the electrode material [64,65]. In support, this tailored and designed vacancy prone nanostructure having a deficiency of oxygen supplying large electroactive sites which would benefit the electrocatalytic performance of the W₁₈O₄₉ electrode for the possible electrochemical application.

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Figure 4.17 Possible glucose reaction mechanisms on the surface of $W_{18}O_{49}$ electrode.

Another possible reason for the enhanced performance may be the support or carbon substrate which is chosen for the fabrication of electrodes. The carbon paper provides assistance that improves the mobility of the charge carrier resulting in enhancing the conductivity of the electrode [66]. The comparison of the sensitivity result of other reported nanostructures is provided in Table 4.2 which it is evident that the $W_{18}O_{49}$ nanorods bundle presented in current research work exhibited the best sensing characteristics with a wider linear range.

Electrodes	Linear	Lowest	Sensitivity	References,
	range	Detection		
		Limit		
MnO ₂ /Co ₂ O ₄	60uM- 7	0.03 µM	127	[/19]
101102/00304	mM	0.05 µm	127	
	111111			
WO ₃ –Pd	65-	4.2 μΜ	11.4	[67]
	375µM			
			μA/μM/cm ²	
rGO/CuS NFs	1.2000µM	0.19µM	53.5	[68]
	•	•	μ A/mM/cm ²	
			•	
Co ₃ O ₄	upto 2.04	0.97 µM	36.25	[69]
Nanofibers	mM		µA/mM/cm ²	
Dt/Au MnO	0130	0.02 mM	58 51	[70]
PUAu-MIIO ₂	0.1-5.0	0.0211111	36.34	[/0]
	IIIM		µA/mvi/cm	
WO ₃	60µM-	0.05 µM	104	This work
	800 µM		μA/mM/cm ²	
WieOre	60uM-	0.02 uM	167	This work
VV 18 V 49	1.6 mM	0.02 µ141	$\mu \Lambda/mM/cm^2$	
	1.0 1111/1		μΑ/πηνι/επ	

Table 4.2 Comparison of glucose sensing performance of other reportedtransition metal oxides.

4.3.6 Interference and stability test for glucose sensing

Elimination of the effect of the intervention of other species like Ascorbic acid (AA), Dopamine, Uric acid (UA), *etc.*, is a major worry for the non-enzymatic glucose sensors. So, for knowing the effect of the other species, a measurement was performed in presence of the molecule glucose (4 mM and 7 mM), AA(0.125 mM), UA(0.33 mM), dopamine (0.05mM) which generally are found in the real blood samples of human body. The concentration of the molecules was decided based on the concentration present in actual blood [49]. Figure 4.18(*a*) represents the response of $W_{18}O_{49}$ with some interference molecules, 0.125 mM AA, 0.33 mM UA, 0.05 mM dopamine, and 1.260 mM glucose. The obtained results after the amperometric measurement provide a negligible response of the interference molecules as compared to glucose in NaOH. Hence, we can safely conclude that $W_{18}O_{49}$ nanostructure material is highly selective to glucose. The stability performance of the electrode is also an important issue, so a stability test has been done after the exposure of the electrode with glucose for successive seven days. The performance has been recalculated after seventh day and shown in figure 4.18(*b*).



Figure 4.18(a) Response of $W_{18}O_{49}$ electrode with some interference molecules, 0.125 mM AA, 0.33 mM UA, 0.05 mM dopamine and 1.260 mM glucose, (b) Amperometric response of glucose for stability test in $W_{18}O_{49}$ electrode.

The FESEM image of the $W_{18}O_{49}$ electrode was also taken before and after seventh day as displayed in figure 4.19 (*a* & *b*). The FESEM images and the performance of the amperometric response of electrodes after seventh day, show no surface poisoning and decaying. The reproducibility and stability of the electrode show an advantage over the enzymatic sensors in terms of usage. This electrode sustained good long-term stability of the material indicating the merging of the two plots measured on day 1 and 7.



Figure 4.19(a) FE-SEM image of $W_{18}O_{49}$ electrode before electrochemical measurement, (b) FESEM of $W_{18}O_{49}$ electrode after seventh day of stability Test.

4.3.7 Real blood and serum sample analysis

A real blood sample test with the help of the oxygen-deficient tungsten oxide's ($W_{18}O_{49}$) electrode has been done. To understand the accuracy of the electrode for sensitivity and selectivity towards glucose in presence of other interfering species, blood serum has been extracted from the freshly drawn blood samples of humans and later has been diagnosed amperometrically via electrochemical route. The amperometric response has been measured by injecting 0.5 ml serum in 30 ml of 50 mM NaOH solution with the same potential 0.55V (vs V_{SCE}). The blood samples have also been diagnosed clinically in local pathology centers and compared further as shown in figure 4.20. The serum sample shows 84.5 mg/dL of glucose (~2.5% less glucose content) with respect to clinically obtained reports (87 mg/dL) which may be due to the presence of different molecules (cells, proteins, fragments, *etc.*). The plot for the amperometric experiment has been given in fig. 8, where it is visible that negligible response has occurred due to other interference species which suggests the

practical application of $W_{18}O_{49}$ defect mediated tungsten oxide electrode for non-enzymatic amperometric glucose sensing.



Figure 4.20 Response of $W_{18}O_{49}$ electrode with real serum sample of human (inset) images of serum extracted from freshly drawn blood sample.

4.4 Summary

In summary, a facile and simple solvothermal approach has been used for the synthesis of $W_{18}O_{49}$ nanorods bundles. The energy storage and glucose sensing applications have been investigated with different characterization techniques. In case of energy storage application, the CV and GCD data pattern shows the pseudocapacitive behavior *i.e.*, Faradaic charge transfer mechanism. Owing to a unique morphology that possesses good surface area and oxygen vacancies, resulted in enhancing the electron transfer which leads to high energy storage. The electrochemical energy storage characterization deduces a Pseudocapacitor-battery type behavior with a high specific capacity of 452 mAh /g and long durability up to 2000 cycles. The superior performances are due to the contribution of oxygen vacancies which can capture charge carriers, large contact area, and reduced diffusion path of ions. Electrochemical measurements illustrate that the defect structure, $W_{18}O_{49}$ can be successfully applied as a promising material for the energy storage application

In the case of non-enzymatic amperometric glucose sensing, the electrode performed well by functioning a very high sensitivity of 167 μ A/mM/cm². It has a very low detection limit of sensing, 0.02 μ M, and a response time of < 5 sec. The compared WO₃ electrode has poorly performed with a sensitivity of 104 μ A/mM/cm⁻². WO₃ also maintained linearity up to 800 μ M which is lower with respect to W₁₈O₄₉. The surpassing and comparative high-performance of W₁₈O₄₉ should be attributed to oxygen vacant sites for capturing electrons and also it enhances the surface area for the interaction between analyte and electrode. This work of sensors illustrates that the non-stoichiometric structure W₁₈O₄₉ performs well as compared to WO₃ and so it can be successfully used as a challenging electrode material for glucose biosensor.

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CHAPTER 5

Transformation of Battery to High-Performance Pseudocapacitor by the Hybridization of $W_{18}O_{49}$ with RuO_2 nanostructures

Publication:

1. Lichchhavi, Hyunju Lee, Yoshio Ohshita, Amrendra K. Singh, Parasharam M. Shirage, "Transformation of Battery to High Performance Pseudocapacitor by the Hybridization of $W_{18}O_{49}$ with RuO₂ nanostructures". (Accepted in Langmuir)
CHAPTER 5

Transformation of Battery to High-Performance Pseudocapacitor by the Hybridization of W₁₈O₄₉ with RuO₂ nanostructures

5.1 Overview

This chapter is the extended work of Chapter 4 in which a defect mediated electrochemical properties, energy storage and glucose sensing of $W_{18}O_{49}$ has been studied. The mechanism of the charge storage, specific capacity, sensitivity, and other important functional characteristics of a supercapacitor and sensors were explored in the previous chapter. Here the work is broadened by the effect of hybridization with RuO₂ on the $W_{18}O_{49}$ nanomaterial and analyzing the changes over the charge storage capacity along with the mechanism involved.

Electrochemical supercapacitors fabricated using nanostructures play a crucial role in overcoming the demand of energy consumption and its storage [1-3]. Considerable attention in the field of electrochemical supercapacitors has been drawn in recent years due to its high specific power, longer cycle life, and capability of forming a bridge between conventional capacitors and battery/fuel cells. The major fields where the supercapacitors can be utilized are textiles industry, electronics industry, hybrid vehicles and energy generators, *etc.* [4,5]. Along with supercapacitors, some other conventional energy storage devices are batteries that work on the mechanism of reversible oxidation and reduction of an electrolyte with the metallic electrode depending on the affinity of the metal. Due to the slow propagation of ions, it gives high energy density but deficit in terms of power density. The large specific capacitance of these devices on its electrode/electrolyte interfaces is due to the associated kinetics of two mechanisms: (i) EDLC (Electrochemical double-layer capacitance, which is a non-faradaic process. (ii) Pseudocapacitance, which is a faradaic process. EDLC stores charges by the action of electrostatic deposition of charges forming a double-layer on the electrode. It mostly depends on the exposed surface area of the electrode. Pseudocapacitors store charges by the action of reverse redox reaction which maintains the energy density of the electrode material comparable to the batteries without compromising the power density, but it lacks in terms of poor electronic conductivity and cycle life. The rapid growth taking place in the field of material science incorporates the development of hybrid nanomaterials [6,7] where the size and shape can be manipulated by varying the synthesis methods. These hybrid materials by the action of the synergistic activity of two or more distinct nanomaterials into one unit is an efficient way for the enhancement of the properties by altering the electrical [8,9] and chemical properties [10].

Tungsten oxides are very much explored as a pseudocapacitor material due to the high electrical conductivity and different phases. The materials having multiple phases are suitable for the ion movement which is essential for the electrochemical activities. The electrochemical features of the nanostructure favored electronic applications such as sensors, field emission, electrochromic devices, and photocatalysis. The monoclinic structure of tungsten oxide with multiple oxidation states has an oxygen deficiency which helps in reducing the resistivity and enhances the electrochemical features [11].

 RuO_2 nanostructures have some extraordinary features of high theoretical capacitance (1300-2200 F/g), conductivity (105 S/cm). The

most desirable properties are its high chemical stability in an acidic medium which makes it worthy for electrochemical applications [12,13]. Though it has several attractive properties, it is far away from industrial applications due to disadvantages like agglomeration, low intrinsic resistance, and weak conductivity in the nano regime [14]. Besides this, the material is also expensive because of its low abundance. So to minimize these unfavorable features, the focus has been shifted towards combining RuO₂ with some other nanomaterial which is expected to compensate for the undesirable properties. Earlier, it is reported the effect of a combination of RuO2 with carbon-based material, such as activated carbon [15], graphene [13], carbon nanotubes [16] and carbon aerogels [17], etc. The electrochemical result has also been reported where Deng et al. attained charge storage of 479 F/g by RuO₂/graphene hybrid material [18]. Again, Amir et al. have synthesized RuO₂/rGO by a sol-gel process and achieved a specific capacitance of 509 F/g [19]. Zheng et al. has obtained a specific capacitance of 768 F/g from the amorphous RuO₂. Literature-based on RuO₂, it is found that amorphous RuO₂ plays a significant role in supercapacitor electrodes with high energy and power density [20,21].

Here, we have synthesized $W_{18}O_{49}$ hybridized with RuO₂ nanostructures on carbon paper substrate and measured the electrochemical energy storage properties. The RuO₂ nanoparticles are homogeneously coated on the $W_{18}O_{49}$ nanorods which are considered as favorable for the electrochemical activity by changing the kinetics mechanism. The hybrid nanostructure exhibited the synergistic and interfacial effect between the $W_{18}O_{49}$ nanorods and RuO₂ nanoparticles. The combined effect of both the morphologies revealed huge structural importance by demonstrating its tendency to be oxidized as well as by offering augmentation or the process of strengthening one other that affects the energy storage capacity. The result is compared with $W_{18}O_{49}$ synthesized in chapter 4 and RuO₂ synthesized separately. The electrochemical data revealed that the battery type $W_{18}O_{49}$ material transformed to Pseudocapacitor by RuO₂ nanoparticles decoration. Thus, the hybrid heterostructure discloses its potential application in supercapacitors with high charge storage, low cost, high and long stability, *etc*.

5.2 Experimental Section

5.2.1 Synthesis of W₁₈O₄₉ nanomaterial

 $W_{18}O_{49}$ nanorods were synthesized using a solvothermal approach as already mentioned in section 4.2.1 (chapter 4). As a precursor 0.1 g of tungsten salt, Tungsten hexachloride (WCl₆) in 50 ml ethanol was taken and stirred for 15 minutes. A clear yellow color transparent solution was obtained. Later, it was transferred to a 100 ml Teflon lined contained stainless autoclave and kept it into a muffle furnace for 16 hours at 180 °C. After the reaction, the dark blue color precipitate was collected using centrifugation and washed 3-5 times using deionized water and ethanol. The obtained mass was dried at 80 °C for 5-6 hours and the final product was collected.

5.2.2 Synthesis of RuO₂ nanomaterial

RuO₂ nanomaterial was synthesized using the hydrothermal approach. First, 5 mM Ruthenium chloride (RuCl₃) as a precursor in 40 ml double deionized water (resistivity = 18.2 MΩ/cm) was stirred for 5 to 10 minutes at room temperature. While stirring, drop by drop ammonia solution was added and maintained pH at 11. Later the solution was transferred to a Teflon lined stainless steel autoclave and heated at 150 °C for 12 hours. A black color precipitate was obtained, which was filtered using deionized water and ethanol. The collected product was further dried at 80°C for 12 hours in a muffle furnace.

5.2.3 Synthesis of W₁₈O₄₉/RuO₂ hybrid nanomaterial:

The hybrid $W_{18}O_{49}/RuO_2$ nanorods were synthesized using a hydrothermal approach as shown in Figure 5.1. 87 mg of $W_{18}O_{49}$ powder was dispersed in 40 ml double deionized water by ultrasonication. Later, 5 mM Ruthenium chloride (RuCl₃) was added into the dispersed solution and stirred for 5-10 minutes. While stirring, drop by drop ammonia solution was added and maintained pH at 11. The solution was kept in a Teflon lined stainless steel autoclave for the reaction at 150 °C for 12 hours. The black color powder was collected by the centrifugation process and washed by deionized water and ethanol. Later it was dried at 80°C for 12 hours. The final obtained product was the hybrid nanostructure of $W_{18}O_{49}/RuO_2$.

5.2.4 Details of characterization instruments

The phase purity, structural and morphological identification of the synthesized nanomaterials was carried out by D2-Phaser Bruker, 30KV/10mA, X-Ray Diffractometer (XRD) instrument, CuKa source $(\lambda = 1.5406 \text{ Å})$. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS spectrometer with Al Ka source (hv = 1486.6 eV). Field emission scanning electron microscopy images were taken from Supra55 Zeiss, FESEM microscope. High resolutiontransmission electron microscopy images from HRTEM, JEOL-2100. N₂ adsorption-desorption study for Brauner-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size distribution was performed by automated gas adsorption analyzer Quantachrome Autosorb iQ2. Electrochemical experiments performed using were the electrochemical analyzer (PGSTAT 302N) with a conventional threeelectrode system. The platinum, saturated calomel (SCE) Hg/HgCl electrode and the carbon paper loaded with the synthesized nanomaterials were used as an auxiliary (anode), reference, and working electrodes, respectively. 1M H₂SO₄ was utilized as the electrolyte for the supercapacitor study.



Figure 5.1 Plausible mechanisms for $W_{18}O_{49}/RuO_2$ synthesis.

5.3 Results and Discussion

5.3.1 Material characterizations

The crystal phase and the structure information of the materials were analyzed by x-ray diffraction technique. Figure 5.2(*a*) shows the typical x-ray diffraction pattern of the W₁₈O₄₉ and W₁₈O₄₉/RuO₂ materials. All the peaks of W₁₈O₄₉ can be indexed to the monoclinic W₁₈O₄₉ phase. No impurity peak has been found, which reveals the formation of the pure phase W₁₈O₄₉. The highest intensity at 2 Θ =23.4° corresponds to (010) plane depicting the orientation of the crystal growth along (010) direction. The lattice parameters of W₁₈O₄₉ were calculated by Rietveld refinement using Full Prof software as given in the previous chapter, Figure 4.2 (*a*)(inset). The lattice parameters calculated for the monoclinic phase are $a\neq b\neq c$ (*a*=1.831±0.008), *b*=0.378±0.002) and *c*=1.402±0.008) nm and $a=\beta=90^\circ$, $\gamma=115.20^\circ$, (space group =*P*2/m(10)) (JCPDS-05-0392). Figure 5.2 (inset) shows the XRD pattern of RuO₂ which consists of a broad hump without well-defined diffraction peaks indicating its poor crystalline nature. Kim *et al.* has reported in their work that complete crystallinity in the case of RuO₂ was only achieved at very high synthesizing or annealing temperature (more than 300° C). So, here it is noteworthy that at 150°C reaction temperature, the amorphous phase of RuO₂ was obtained [21-23]. The XRD pattern of $W_{18}O_{49}/RuO_2$ given in Figure 5.2(*b*) similarly shows that except for the peak of $W_{18}O_{49}$ no discernible reflections corresponding to crystalline RuO₂ structure can be detected which again validates the amorphous nature of RuO₂ in hybrid nanomaterial. The peaks of $W_{18}O_{49}$ show the obvious low intensity indicating that the dispersed RuO₂ nanoparticle's crystallite size is very small as compared to $W_{18}O_{49}$ [24].



Figure 5.2 XRD pattern of the (a) $W_{18}O_{49}$ and (b) $W_{18}O_{49}/RuO_2$ (inset) XRD pattern of RuO_2 .

The morphological studies using HR-TEM were conducted for $W_{18}O_{49}/RuO_2$ to understand the development of nanostructure and represented in Figure 5.3. The images reveal the formation of two different nanostructures, $W_{18}O_{49}$, and $W_{18}O_{49}/RuO_2$ hybrids. $W_{18}O_{49}$ exhibits nanorods with an average diameter of 10 nm as shown in figure 5.3(*a*). The interplanar distances were calculated as 0.378 nm using

"image J software" in Figure 5.3(*b*), well coincide with the distance of (010) plane of $W_{18}O_{49}$, which is also validated by the XRD results. Selected area electron diffraction (SAED) pattern (inset) shown in Figure 2(*b*) shows the diffraction spots along with the rings confirm the polycrystalline nature of the $W_{18}O_{49}$ nanomaterial [25]. The SAED pattern was indexed using image J software, which confirms the presence of (010) and (020) planes of $W_{18}O_{49}$ which is already analyzed from the lattice fringes. The HRTEM analysis of the hybrid $W_{18}O_{49}$ /RuO₂ shown in Figure 5.3(*c*) depicts almost similar morphology of $W_{18}O_{49}$ in addition to the uniform dispersion of RuO₂ over $W_{18}O_{49}$ nanorods. Also, the amorphous nature of the RuO₂ nanoparticles seen in XRD images is perceptible from the SAED pattern (Figure 5.3(*d*)) showing the formation of rings.



Figure 5.3 High resolution-transmission electron microscope (HRTEM) images of (a) $W_{18}O_{49}$ nanorods, (b) Lattice fringes (inset) SAED pattern of $W_{18}O_{49}$, (c) $W_{18}O_{49}/RuO_2$ hybrid, (d) SAED pattern of $W_{18}O_{49}/RuO_2$ hybrid nanostructure.

5.3.2 Synthesis mechanism of W₁₈O₄₉/RuO₂ hybrid nanomaterial

The formation of $W_{18}O_{49}$ and the $W_{18}O_{49}/RuO_2$ hybrid can be expressed through the following reaction equations (5.1, to 5.4)

$$WCl_6 + RCH_2OH \rightarrow (RCH_2O)_m - WCl_n + mHCl$$
 (5.1)

$$(RCH_2O)_m - WCl_n + H_2O \rightarrow WO_{3-x} + RCH_2OH + HCl$$
 (5.2)
Where *R* symbolizes CH₃ (alkyl) group

The formation of RuO₂ could be expressed as follows:

$$Ru^{3+} + 3H_2O + NH_3 \to NH_3Ru(OH)_3 + 3H^+$$
(5.3)

$$2(NH_3)Ru(OH)_3 + OH^- \rightarrow 2RuO_2 H_2O + 2NH_4OH$$
(5.4)

The poor crystalline nature and growth along (010) direction of W₁₈O₄₉ was analyzed from the XRD and HR-TEM which might occur due to the defect structures present in the nanomaterial. The presence of oxygen defects has been demonstrated by XPS characterization. The predictable phenomenon of oxygen vacancies in tungsten oxide generally occurs due to the 3-fold equatorial coordinative O (O3f) atoms in the octahedrons of WO₃. Surface entropy will be high if the growth will be along a linear direction and thus the orientation will be along the *b*-axis. It is generally formed by the solvothermal approach in the presence of ethanol. Possibly the formation of an intermediate occurs $WCl_{6-x}(OC_2H_5)_x$, when tungsten chloride gets dissolved in ethanol [26-28]. Similarly, after the formation of $W_{18}O_{49}$ nanomaterials, it has been tried to disperse RuO₂ nanoparticles over the nanorods to form a hybrid nanostructure of $W_{18}O_{49}$ and RuO₂. The precursor used for the synthesis of the nanomaterials is ruthenium chloride, RuCl₃ as a source of Ru³⁺ cations. The Ru³⁺ ions form a complex molecule, $Ru(NH_3)_n^{3+}$ when drop by drop ammonia was added in the solution to reach the pH 11. When this solution is heated, at an optimized temperature of 150°C for 12 hours, the ionic product exceeds

the solubility limit which causes precipitation. The precipitate leads to the formation of RuO_2 nuclei followed by its growth to nanoparticles.

For the further understanding and investigation of the synthesized the XPS spectra of $W_{18}O_{49}$ and $W_{18}O_{49}/RuO_2$ nanomaterials, nanomaterials were obtained and are depicted in Figure 5.4 The chemical composition and chemical valence of the nanomaterials were determined by the XPS studies. Figure 5.4(a), a survey scan of $W_{18}O_{49}$ shows the presence of tungsten and oxygen at their binding energies. Figure 5.4(b), a survey scan of W₁₈O₄₉/RuO₂ depicts the presence peak of Ru3d and Ru3p along with W and O. No impurities peak other than carbon was found. The different oxidation states of W with a well resolved W4f doublet peaks at the spin-orbital splitting of 2.17 eV between $4f_{5/2}$ and $4f_{7/2}$ spin states have been assigned and shown in Figure 5.4(c) [29]. It is reported that the peaks corresponding to W^{6+} ion are centered at a binding energy of 35.4 and 37.6 eV [30,31] while the other two peaks at 34.8 and 36.7 eV corresponds to the W^{5+} oxidation valence of tungsten [32-35]. The occurrence of two oxidation states is one of the prominent features of $W_{18}O_{49}$ [36] Figure 5.4(d) shows the Ru3d+C1s spectra of $W_{18}O_{49}/RuO_2$ hybrid nanomaterials. Generally, the Ru3d_{5/2} spectrum is used for identifying the electronic states of Ru, since the Ru3d_{3/2} and C1s spectrum are merged due to the carbon contamination due to the exposure in the air. Ru3d_{5/2} peak of the synthesized hybrid $W_{18}O_{49}$ is centered at 281.1 eV corresponding to the binding energy of Ru⁴⁺, further which confirms the presence of RuO₂. The doublets Ru3d_{3/2} and Ru3d_{5/2} occurred with a spinorbital splitting of 4.1 eV which is consistent with the other reported literature [37]. The other major peak of O1s was found in the survey scan has been deconvoluted into three other major peaks as shown in Figure 5.4(e). The peak found at binding energy 530 eV symbolizes lattice oxygen W-O-W i.e., oxygen present in tungsten oxide and ruthenium oxide. The peak at 531.9 eV is due to the proximity of oxygen vacancy



present in $W_{18}O_{49}$ [32,38,39]. The XPS analysis confirms the presence of $W_{18}O_{49}$ with a high order oxygen vacancy.

Figure 5.4 X-ray photoelectron spectroscopy (XPS) spectra of synthesized nanomaterials (a) survey scan of $W_{18}O_{49}$, (b) Survey scan of $W_{18}O_{49}/RuO_2$ hybrid. Deconvoluted spectra of (c) W4f, (d) Ru3d+C1s and (e) O1s.

BET measurement was conducted to understand the architecture of the nanostructure. The nitrogen adsorption-desorption measurements of $W_{18}O_{49}$ and $W_{18}O_{49}/RuO_2$ were measured and shown in Figure 5.5 (a & b). The calculated surface area of $W_{18}O_{49}$ and $W_{18}O_{49}/RuO_2$ was found to be 82.309m²/g and 149.698 m²/g, respectively. It is worth to mention that the measured surface area for the hybrid $W_{18}O_{49}/RuO_2$ nanostructure is almost double than that of $W_{18}O_{49}$, which indicates that hybrid materials are promising for electrochemical energy storage applications. By employing the Barrett Joyner Halenda (BJH) technique the average pore size distribution was measured. The pore size of 3 nm and 3.8 nm were obtained for $W_{18}O_{49}$ and $W_{18}O_{49}/RuO_2$, respectively, indicating the mesoporous nature of the material. The mesoporous size is considered as the perfect size range for the electrochemical storage performance as it provides a narrow and smaller path for the mobility of electrons and ions [26].



Figure 5.5(a) N_2 adsorption-desorption isotherm of $W_{18}O_{49}$, (b) N_2 adsorption-desorption isotherm of hybrid $W_{18}O_{49}/RuO_2$.

5.3.3 Electrochemical energy storage characterization

The energy storage properties of the synthesized materials were electrochemically evaluated. Figure 5.6(a) represents the cyclic voltammetry (CV) curve of the hybrid W₁₈O₄₉, RuO₂, and W₁₈O₄₉/RuO₂ nanomaterials measured at 5 mV/s. From figure 5.6(a), it is very clear that hybrid W₁₈O₄₉/RuO₂ nanostructure has better electrochemical performance than intrinsic $W_{18}O_{49}$ and RuO_2 nanomaterials. $W_{18}O_{49}$ electrode signifies the battery behavior corresponding to the non-rectangular shape of the curve; RuO₂ is typical supercapacitor behavior while W₁₈O₄₉/RuO₂ shows pseudocapacitor properties. Figure 5.6(b) presents the typical cyclic voltammetry (CV) curve of the hybrid W₁₈O₄₉/RuO₂ nanomaterial. In the figure, cyclic voltammetry curves at different scan rates ranging from 1-100 mV/s were conducted in an optimized potential window on a scale of 0 to 0.80 V (vs V_{SCE}). The material exhibited an excellent combination of both pseudocapacitor behavior inherited from W₁₈O₄₉ and the typical rectangular nature, double-layer charge deposition from RuO₂ [40,41]. At a higher scan rate, a uniform set of redox peaks visible, oxidation and

reduction are reversible which indicates the different valences of $W_{18}O_{49.}$ The anodic and cathodic peaks are due to the reversible reaction between WO_{3-x} and H_yWO_{3-x} and are represented in equation (5.5):

$$WO_{3-x} + yH^+ + ye^- \leftrightarrow H_yWO_{3-x} \tag{5.5}$$

At a lower scan rate, the rectangular behavior is the capacitive contribution of RuO_2 indicating high rate capability. The specific capacitance measured from the CV curve has been evaluated from equation (5.6):

$$C = \frac{1}{m\nu\Delta V} \int IdV \tag{5.6}$$

Where "C" is Specific Capacitance, "m" is the mass of the active material, "v" is scan rate, " ΔV " is potential window and " $\int IdV$ " is integrated area of the CV curve. The highest specific capacitance of 1126 F/g was achieved at a 1mV/s scan rate. It is reduced up to 436 F/g at the highest scan rate of 90mV/s, which is the usual observation in electrochemical energy storage materials. The values of obtained specific capacitance at different scan rates are given in Figure 5.6(c). It is depicted from the relation between specific capacitance and scan rate that as the scan rate is increased specific capacitance gets reduced due to the non-availability of sufficient electrode surface for the electrolytic ion [42]. Also, the effective interactive surface area is reduced because of the diffusion of electrolyte ions inside the pores of the electrode which makes the electrode, less functional for the electrochemical reaction [43]. For comparison, the cyclic voltammetry at different scan rates of the other two electrodes W₁₈O₄₉ and RuO₂ was also performed. The electrochemical characterization graphs of W₁₈O₄₉ are given in the previous chapter 4 (Section 4.3.3) and RuO_2 is given in figure 5.8 which also agrees with the phenomenon of a decrease in specific capacitances with an increase in scan rate. In Figure 5.6(a), the $W_{18}O_{49}$ electrode signifies the pseudocapacitor-battery behavior corresponding to the non-rectangular shape of the curve. It may be due to a faradaic

reaction occurs at the interface of electrode and electrolyte [26]. Due to the battery nature, the charge storage performance in the unit of specific capacity is 470 mA h/g at a minimum scan rate of 1mV/s, however, it decreased to 191 mA h/g with increasing scan rate of 90mV/s as shown in Figure 4.10(*b*). From Figure 5.8(*a*) the CV curve of RuO₂ shows the rectangle-like shapes at various scan rates indicate the perfect electrochemical reversibility of the faradaic redox transitions on the electrode surface. The highest specific capacitances calculated are 812 F/g and it also decreases with increasing scan rate as shown in Figure 5.8(*b*).



Figure 5.6(a) Comparative Cyclic voltammetry (CV) curves for $W_{18}O_{49}$, RuO₂, and $W_{18}O_{49}/RuO_2$ hybrid at a scan rate of 5mV/s, (b) CV of $W_{18}O_{49}/RuO_2$ hybrid,(c) Plot of specific capacitance vs. scan rate of $W_{18}O_{49}/RuO_2$ hybrid material.

The charge storage capacitance performance of hybrid $W_{18}O_{49}/RuO_2$ was evaluated from the charge-discharge performance by applying a series of constant current as shown in Figure 5.7(*a*). The potential window

selected for the galvanostatic charging-discharging (GCD) measurement was kept the same as for CV. The GCD curves of a hybrid show an exact triangular behavior that can be contributed from RuO_2 implying good capacitive characteristics. The very small IR drop at the beginning of the discharging current is evident for a low equivalent series resistance in the electrochemical interactions [44]. Specific capacitance is calculated by using the equation (5.7) at different current densities [22]:

$$C = \frac{I \triangle t}{m \triangle V} \tag{5.7}$$

Where "C" = specific capacitance, " Γ " = constant current applied, " Δt " = discharging time, "m" = mass of the electrode, and ΔV = potential window. The highest specific capacitance achieved was 1050 F/g at a minimum current density of 1A/g. The specific capacitance decreases with the increasing current density as shown in Figure 5.7(b) due to insufficient response time for the diffusion of ions from the electrolyte to reach the material surfaces. The conducted GCD measurement of electrodes W₁₈O₄₉ and RuO_2 as shown in Figure 4.10(c) (chapter 4) and 5.8(c) confirms the mechanism portrayed from CV measurement. The GCD curve of W₁₈O₄₉ shows a slight deviation from the ideal triangular behavior and it depicts a sudden IR drop after 0.4 V. This is a characteristic feature of the intermediate state between pseudocapacitor and battery type electrodes [26,45-48]. The highest specific capacity achieved is 452 mAh/g at a minimum current of 1.25 A/g which is half the value obtained from the hybrid electrode. Similarly, the GCD curve of RuO₂ shows typical triangular characteristics implying good capacitive characteristics [49]. The very low IR drop shows the low intrinsic equivalent resistance of the electrode. The specific capacitance calculated from the GCD curve of RuO₂ is 582 F/g at a low current density of 1A/g. In both the electrodes (W₁₈O₄₉ and RuO₂) cases the specific capacitances decreased with increasing current density as shown in Figure 4.10 (d) (chapter 4) & 5.8(*d*).

The Electrochemical impedance spectroscopy (EIS) measurement is shown in Figure 5.7(c) was conducted to evaluate the capacitive behavior of the hybrid nanomaterial. Their curve comprises mainly two regions, the high-frequency region, and the low-frequency region. The high-frequency region corresponding to the intercept at the Z' axis demonstrated the equivalent series resistance. The overall sum of the resistances presents in the system is resistance due to the electrode, electrolyte, and the developed resistance because of the contact between electrode and electrolyte [50]. The Nyquist plot in Figure 5.7(c) shows the comparison of the equivalent series resistance of the hybrid W₁₈O₄₉/RuO₂ before cyclic voltammetry, after cyclic voltammetry, and after stability test. From the curve, it is implied that the equivalent series resistance of hybrid material in all three cases has approximately the same resistance which depicts a very slow degradation of electrodes in the electrochemical measurement. Moreover, an additional feature *i.e.*, the diameter of the semicircle at the highfrequency region symbolizes the resistance generated due to the transfer process of charge in between electrode and electrolyte, R_{ct} [51]. The R_{ct} value before and after cyclic voltammetry and after stability test shows the low charge transfer resistances which enables the electrode for long time stability of the electrode. Interestingly an important part of the curve is the vertical line (lower frequency region) which is called Warburg resistance, which occurs due to the diffusion of electrolyte ions in the core of the porous electrode which later becomes helpful for the decaying of electrodes [52]. The Nyquist plot after the stability test displays a nearly vertical line with the least slope towards the Z'' axis (imaginary part) displaying an ideal capacitive nature. The Nyquist measurement was conducted for $W_{18}O_{49}$ and RuO_2 as shown in Figure 4.11(*a*) and Figure 5.8(e). Both the electrode shows excellent capacitive behavior.

From these results, it strongly represents the eligibility and suitability of hybrid nanostructure $W_{18}O_{49}/RuO_2$ for better charge storage result. The real potential and the durability of the electrodes were analyzed

by the stability test. The hybrid $W_{18}O_{49}/RuO_2$ nanostructured material performed well till 3000 cycles of charging and discharging at a constant current density of 10A/s as compared to $W_{18}O_{49}$ which is shown in Figure 5.7(*d*). It shows a constant behavior (100 % capacitive retention) until 1300 cycles. A small degradation resulting in 92.7% capacitive retention after 1300 cycles, which arises due to the resistance generated and the irreversible reactions that have taken place on the surfaces. Again after a constant behavior, it decreases its performance up to 87.5 % after 2600 cycles.



Figure 5.7 (a) Galvanostatic charging-discharging (GCD), (b) Specific capacitance vs. current (in mA), (c) Electrochemical impedance spectroscopy (EIS), (d) Stability test upto 3000 cycles of $W_{18}O_{49}/RuO_2$.



Figure 5.8 (a) Cyclic voltammetry (CV), (b) Specific capacitance vs. scan rate,(c)Galvanostatic charging-discharging (GCD), (d)Specific capacitance vs. current (in mA), (e) Electrochemical impedance spectroscopy (EIS) of RuO₂.

5.3.4 Plausible mechanisms for the high energy storage performance:

The hybrid nanostructure provides a synergistic path to improve the electrochemical result. A Synergistic effect is simply assigned to the combination of properties of two different structures yielding a better outcome which should always be greater than the sum of the individual structure. The combination of $W_{18}O_{49}$ and RuO_2 plays a vital role in the hybrid nanostructure by simply enhancing the properties. To improve the electrochemical performance, conductivity is an important constituent. The oxygen vacant sites present in $W_{18}O_{49}$ introduce impurity energy level bands inside the preexisted bandgap of the transition metal oxides. Oxygen vacancy increases the conductivity of the material by lowering the coordination atom of the molecule [53,54]. Hence, the high mobility due to the free electrons significant for metallic character suggested the stronger ability of light absorption. The y-axis from the cyclic voltammetry curves measured for W₁₈O₄₉/RuO₂ hybrid nanostructure in the present work shows a high magnitude of the current value as compared to other oxides as reported earlier. RuO₂ is a pseudocapacitor material that is being validated from the CV curve obtained in figure 5.8 (a). Pseudocapacitance arises from fast and reversible electron-exchange reactions at or near the electrode surface [55]. Besides this, the factor responsible for the enhancement of the electrochemical feature is an enhanced surface area due to the hybridization process and the accessibility of path for the electrolytic ions transport. The combined effect from W₁₈O₄₉ providing vacant sites as a trapping center for the electrolytic ions and the RuO₂ which increases the active sites for the possible electrochemical reaction sums up the high energy storage performance. The overall mechanism has been shown in Figure 5.9. The elevated performance of the hybrid nanostructure is due to the contribution of (i) higher conductivity, (ii) more active sites, and (iii) unique morphology. In the present hybrid system of $W_{18}O_{49}/RuO_2$, the individual performance of both battery-like W₁₈O₄₉ provides high energy density while the pseudocapacitive RuO₂ enables high power capability in the system. Table 5.1 shows the comparison of obtained results in the present study with W₁₈O₄₉ and RuO₂ based nanostructure for supercapacitor applications.



Figure 5.9 Plausible mechanisms for high electrochemical performance.

From Table 5.1, it is evident that hybrid W₁₈O₄₉/RuO₂ materials exhibit better electrochemical performance in comparison with W₁₈O₄₉, RuO₂, and published earlier literature. In the previously reported literature, the work conducted by Jo et al. has shown the importance of the synergistic effect of WO₃ and mesoporous carbon for supercapacitor applications. But this material has specified a specific capacitance of 175 F/g but this material is not stable due to its low conductivity influenced by carbon [59]. Cai et al. have replaced carbon with graphene nanosheets to increase the conductivity of the composite nanomaterial but the specific capacitances achieved were lower due to the internal stacking that occurred because of graphene nanosheets [60]. Farsi et al. has developed a hydrated form of tungsten trioxide by acid precipitation method and achieved an aerial capacitance of 0.014 to 0.039 F/g [61]. This work lacks in terms of low charge storage as well as the methodology used for the synthesis was quite complex and dangerous. These high and superior performances of $W_{18}O_{49}/RuO_2$ in the present work may be due to the introduction of synergistic effect comprising oxygen vacant sites, high surface area, high conductivity, and active sites due to the RuO_2 nanoparticles and narrow path for electrolytic ions.

Sr.	Electrode	Solution	Charge	Voltage	References
No.			storage	range (V)	
			performance		
			(F /g)		
1.	WO ₃ /PANI	1M H ₂ SO ₄	168	0.5 - 0.7	[56]
2	Tungsten oxide	2M H ₂ SO ₄	103	-0.2 - 0.8	[57]
3	Ti/IrO ₂ /WO ₃ film	0.5 M H ₂ SO ₄	46	0.2 - 1.2	[58]
4	Carbon/WO ₃ nanocomposites	1M H ₂ SO ₄	175	-0.2 - 0.7	[59]
5	Graphene nanosheets	1M H ₂ SO ₄	143 at 0.1 A/g	0 - 1.0	[60]
6	WO.H ₂ O	0.05 M H ₂ SO ₄	25.2 mF/cm ²	0.3- 1.5	[61]
7	W ₁₈ O ₄₉ nanorods bundle	1M H ₂ SO ₄	470 mA h/g at 2mV/s	0 - 0.8	This Work
8	RuO ₂ nanoparticles	1M H ₂ SO ₄	812F/g at 1mV/s	0 - 0.8	This Work
9	W ₁₈ O ₄₉ /RuO ₂ hybrid electrode	1M H ₂ SO ₄	1126 F/g at a scan rate of 1mV/s	0 - 0.8	This Work

Table 5.1 Comparison of electrochemical Supercapacitor performance ofother TMO with $W_{18}O_{49}/RuO_2$.

5.4 Summary

A feasible and low-cost synthesis approach has been utilized for achieving W₁₈O₄₉/RuO₂ hybrid structures. The electrochemical results of W₁₈O₄₉/RuO₂ indicate that the charge storage capacitance of hybrid material is significantly better than $W_{18}O_{49}$ and RuO_2 nanomaterials. The hybrid material represents the prominent pseudocapacitive nature in the CV and GCD. *i.e.*, the Faradaic charge transfers mechanism. These hybrid nanostructures declare the transformation from the battery to pseudocapacitor mechanism resulting in enhancement of the energy storage performance. The hybrid nanostructures show a higher specific capacitance of 1126 F/g and long durability up to 3000 cycles which is two times higher as compared to $W_{18}O_{49}$ and RuO_2 . The high and superior performances may be due to the introduction of synergistic effects comprising oxygen vacant sites, high surface area, high conductivity, and active sites due to the RuO₂ nanoparticles and narrow path for the electrolytic ions. These results also depict the significance of energy efficiency as a metric of pseudocapacitive electrode performance.

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CHAPTER 6

Summary and Future Scope

6.1 Thesis Summary

In summary, the thesis has been comprehended by the electrochemical applications: supercapacitor and non-enzymatic amperometric glucose sensing of transition metal oxides (TMOs). It also focuses on the synthesis, basic structural, morphological, and electrochemical characterizations of TMOs, MnO₂, Co₃O₄, MnO₂/Co₃O₄ WO_3 , $W_{18}O_{49}/RuO_2$ hybrid hybrid W18O₄₉, synthesized by hydrothermal/solvothermal method. Above all, the work has been followed towards exploring the two important effects agreed for enhancing the electrochemical properties *i.e.*, creation of defects and hybridization in the synthesized TMO nanomaterials. A chapter-wise summary is as follows:

Chapter 1 provides the introduction of supercapacitor, types, and the basic mechanism behind the storage of charges. Similarly, it also introduces the introduction of electrochemical non-enzymatic glucose sensors, its basic mechanism, and the construction of devices. The electrode synthesis is an important and crucial task for device fabrication and this chapter deals with the importance of transition metal oxides (TMOs) in the electrochemical electrode.

Chapter 2 summarizes the fundamental techniques of synthesis of nanomaterial and the importance and benefit of hydrothermal techniques

as easy and environmentally friendly techniques towards developing a desirable structure and morphology. It also describes the basic characterization techniques like XRD, SEM, HR-TEM, XPS, Raman Spectroscopy, and electrochemical techniques like CV, GCD, EIS, and Chronoamperometry, *etc*.

Chapter 3 is initiated by putting an effort towards enhancing the transition metal oxide's intrinsic properties and its effect on the electrochemical application. Initially, 1D α -MnO₂, Co₃O₄, and α -MnO₂/Co₃O₄ hybrid were synthesized by a simple and economical hydrothermal technique. Further, highly sensitive and selective nonenzymatic detection of glucose has been achieved by the hybridization of 1D α -MnO₂ nanorods modified with the surface decoration of Co₃O₄ nanoparticles. The rational design and controlled synthesis of the hybrid nanostructures are of great importance in enabling the fine-tuning of their properties and functions. Compared with the performances of pure components MnO_2 nanorods and Co_3O_4 nanoparticles, these hybrid nanostructures demonstrate a maximum electrooxidation toward glucose. The glucose sensing performances of fabricated hybrid structures were measured by cyclic voltammetry (CV) and chronoamperometry. The synthesized α -MnO₂/Co₃O₄ electrode exhibits a high sensitivity of 127μ A/mM/cm² (S/N=3), with a detection limit of 0.03μ M, wide linear range of 60 μ M to 7 mM of glucose with a short response time of fewer than 5 seconds. The favorable properties of the nanostructure fortify its potential utilization in the clinical detection of diabetes.

Chapter 4 analyzed that this hybrid nanomaterial has a tendency of dissociating in electrolyte and ultimate weight loss of electrode in the electrolyte. It also has less current density justified from the CV curve. So, Tungsten based suboxides nanostructures have been identified as promising semiconductor materials for its fruitful role in electronics and its environmental friendliness properties. Amongst other non-

stoichiometric tungsten oxides, $W_{18}O_{49}$ has been broadly examined due to its favorable defect structure and the novel properties of mixed valency giving rise to an unusual physical and chemical property in the nanometer regime. These findings will have a profound effect on understanding and mechanism of the surface-induced vacancy to the process of electrochemical activity in terms of energy storage and glucose sensor.

Porous spherical bundles of W₁₈O₄₉ nanorods with rich oxygen vacancy are generated by a facile, low-cost solvothermal approach and further evaluated for the bi-functional applications: Supercapacitor and glucose sensing. The remarkable electrochemical activity of $W_{18}O_{49}$ nanostructure is referred to the development of oxygen vacancy and nanostructure network leading to maximize the active sites and surface for the electrolyte ions. Energy storage electrochemical area characterizations calculated the specific capacity of 470 mA h/g at a scan rate of 1mV/s and 452 mA h/g at a very high current density of 1.25 A/g was calculated in 1M H₂SO₄ electrolyte. The experimental results revealed that surface oxygen vacancy enhances the adsorption and reaction site for electrolyte ions indicating the good electrochemical activity of the W₁₈O₄₉ nanostructured materials. GCD summarizes an intermediate mechanism of pseudocapacitor–battery for $W_{18}O_{49}$ sensing nanorods. Glucose characterization deduces that in comparison with non-oxygen deficient WO_3 , this defect prone version of tungsten oxide ($W_{18}O_{49}$) possesses a doubled linearity range up to 1.6 mM maximum electrooxidation towards glucose by giving a 1.6 times higher sensitivity of 167 μ A/mM/cm², 0.5 times lower detection limit of 0.02 μ M (S/N=3) and swift response time of 5 seconds.

Chapter 5 investigated that further due to low stability and conductivity in $W_{18}O_{49}$ nanomaterial, $W_{18}O_{49}$ is additionally modified to $W_{18}O_{49}/RuO_2$ hybrid nanomaterial. This work uses a novel approach of hybridization of $W_{18}O_{49}$ nanostructure with RuO_2 for the alteration of the kinetics to control the electrochemical performance in energy storage applications. The result displays that the hybridization of the nanostructures plays an important role in yielding high specific capacitance of the electrode material. Due to the augmentation of $W_{18}O_{49}$ and RuO_2 nanostructures, the Galvanostatic Charging and discharging (GCD) mechanism exhibited the transformation from the battery type characteristics of $W_{18}O_{49}$ into the typical pseudocapacitor feature of hybrid architect nanostructure due to defect creations. The electrochemical measurement shows the doubling of specific capacitance of 1126 F/g and 1050 F/g in Cyclic Voltammetry (CV) and GCD, respectively, in comparison with $W_{18}O_{49}$ and RuO_2 and earlier reports. The enhancement in the stability performance up to 3000 cycles of hybrid is indebted to the stable nature of $W_{18}O_{49}$ and high conductivity of RuO_2 . These outcomes have an intense effect on the mechanism of hybrid nanostructure regarding the synergistic effect of both $W_{18}O_{49}$ and RuO_2 on its application in energy storage.

In summary, the aimed objectives in this thesis are achieved successfully, and work contributes to the novelty and literature for the development of the energy storage and glucose sensing materials and technologies.

6.2 Future Scope

This thesis is an effort of developing an electrode material from the TMO nanomaterials for supercapacitor and glucose sensing applications. In the future, this work is extended or modified by developing a flexible and working device of both the applications. In the electronic system, wearable electronics, medical implants, supercapacitors are coming up with solutions that could not be thought of earlier. Medical implants like pacemakers, knee implants, and others will be powered by them, and they will harvest energy from body heat and movements. This will obviate any replacement over a lifetime. In power for vehicles, already buses, trams, and trains have started running on ultracapacitors. Trains are also making use of Kinetic Energy Recovery Systems (KERS) and saving a huge

amount of energy. As energy density increases, cars may also start being powered by them. Presently many functions are being increasingly taken over by supercapacitors in vehicles, helping increase battery life also in the process. The researchers are working towards developing contact lenses that are based on a tear or seat-based glucose sensor. It is further possible to fabricate such a smart glucose sensor device that works on natural human behavior. The work can also be supported by exploring other suitable ways of enhancing the characteristics of nanomaterial. Some of the possible work is noted down below:

- Though the work deals with the 1-D transition metal oxides, it is possible to synthesize other-dimensional metal oxides nanomaterial (1,2,3 dimensions) and modify its morphologies for observing the effect of surface area over electrochemical properties.
- Here, for electrode fabrication, carbon paper is used, which acts as a current collector. This collector only works well in the H₂SO₄ electrolyte for supercapacitor application. There is a possibility of synthesizing electrodes with the help of Nickel foam or another flexible substrate as a collector for the porous and flexible nature.
- A drop cast method for electrode fabrication has been used in the research work, which lacks in terms of adhesion and resulting in a high mass loading and mass losses while electrochemical measurement. It can be replaced by some direct deposition technique for enhancing the adhesion and optimum mass loading. The specific capacitance and sensitivity of the electrodes are inversely dependent on the total mass of the active material present on the electrode.
- Electrolyte based study in the electrochemical applications is helpful for many practical purposes. So, different electrolytes

like organic, inorganic, acidic can be tried for the real and onsite uses.

• A proper supercapacitor or hybrid supercapacitor device can be fabricated to evaluate the energy and power density with the help of the different synthesized nanomaterial for the electrode.