

**NANOFABRICATION OF COST EFFECTIVE
ELECTROCHEMICAL SENSOR USING NANOIMPRINTING
LITHOGRAPHY TECHNIQUE**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY**

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BY

NONGMAITHEM HEROJIT SINGH

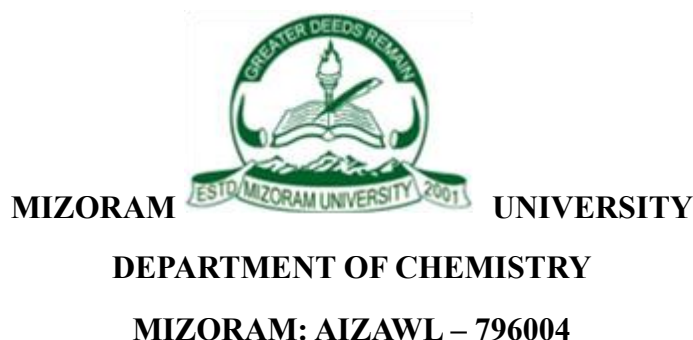
Department of Chemistry

Under the supervision of

Prof. N. MOHONDAS SINGH

Submitted

In partial fulfilment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl



Prof. N. Mohondas Singh, HoD

THESIS CERTIFICATE

This is to certify that the thesis entitled ***“Nanofabrication of cost effective electrochemical sensor using nanoimprinting lithography technique”*** submitted to Mizoram University, Aizawl for the award of the degree of Doctor of Philosophy by **Mr. Nongmaithem Herojit Singh (Regd. No.: MZU/Ph.D./1441 of 06.08.2019)**, research scholar in the Department of Chemistry, is the record of original research work carried out under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted elsewhere for any degree in any other Universities.

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I, **NONGMAITHEM HEROJIT SINGH**, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to do the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/ Institute.

This is being submitted to the Mizoram University for the Degree of Doctor of Philosophy in Chemistry.

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ABBREVIATIONS

3D	Three dimensional
Å/s	Armstrong per second
AFM	Atomic Force Microscopy
BPA	Bisphenol A
C ₂ H ₇ NO	monoethanolamine
C ₃ HO ₂	ethylene glycol monomethyl ether
CDs	Compact discs
cm	centimetre
CV	Cyclic voltammetry
DI	deionized
DPV	differential pulse voltammetry
e-beam	Electron beam
EDAX	Energy Dispersive X-ray Analysis
EIS	Electrochemical Impedance Spectroscopy
ErGO	Electrochemically reduced graphene oxide
eV	electrovolts
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared spectroscopy
GO	Graphene oxide
h	hour
H ₂ SO ₄	Sulfuric acid
HMTA	hexamethylenetetramine
HRTEM	High-Resolution Transmission Electron Microscope
IDEs	interdigitated electrodes
K ₃ [Fe (CN) ₆]	potassium ferricyanide
K ₄ [Fe (CN) ₆]	potassium ferrocyanide
KCl	Potassium chloride
kV	kilovolts

mA	milli ampere
min	minutes
mL	milli litter
NIL	Nanoimprinting lithography
nm	nano meter
PDMS	Polydimethylsiloxane
PL	Photoluminescence
rGO	Reduced graphene oxide
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	Zinc acetate dihydrate
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Zinc nitrate hexahydrate
ZnONRs	ZnO nanorod

CHAPTER 1. INTRODUCTION

1.1 Background of the study

A sensor is a crucial equipment that detects, quantifies, and reacts to physical or chemical impulses from its surroundings. These stimuli can include a wide array of influences like heat, light, sound, pressure, magnetism, or motion [Vig et al., (2000)]. The main role of a sensor is to transform these incoming signals into quantifiable electrical outputs, which enable the detection of variations in the intrinsic properties of materials or systems. The term "sensor" originates from the Latin verb sentire, which translates to "to feel," aptly highlighting the sensor's function in detecting environmental alterations and transmitting them via a transduction mechanism [Simoes et al., (2017)]. This coupling mechanism frequently entails the conversion of one energy form into another, usually electrical energy, which can be read and analyzed for monitoring, control, or diagnostic objectives.

Chemical sensors are a crucial subset of sensor technology, specifically engineered to identify and measure the presence or quantity of chemical compounds [Janata et al., (1992)], [Paolesse et al., (2017)]. These devices function by converting particular chemical interactions—such as adsorption, redox reactions, or complexation—into measurable signals, usually electrical or visual. Chemical sensors exist in the convergence of various scientific fields, amalgamating principles and techniques from chemistry, physics, biology, materials science, and electronics [Joo et al., (2008)]. Despite being a nascent discipline relative to conventional analytical instruments, chemical sensor technology has undergone significant expansion in recent decades. This expansion is primarily propelled by the growing demands across diverse industries for rapid, accurate, and inexpensive analytical instruments that can be utilized in the field or incorporated into automated systems [Kim et al., (2024)] [Hu et al., (2024)]. One of the most notable benefits of these sensors is their compact design, enabling portability and effortless integration into complex systems. Furthermore, these sensors usually have a high selectivity and sensitivity, which enables them to

reliably identify target analytes even at extremely minimal concentrations. They additionally allow for wide dynamic detection ranges, minimal fabrication and operation expenses, and the ability to execute real-time, in situ, and continuous monitoring without the need for complex sample preparation. These characteristics render sensors perfect for use in many different fields including environmental monitoring, industrial management, food and water safety, medical diagnostics, and national security.

Among the various types of sensors, such as optical, magnetic, mass-sensitive, and thermal-based devices, electrochemical sensors have achieved unique prominence [Baranwal et al., (2022)] [Kimmel et al., (2012)]. Electrochemical sensors are notable for their durability, accessibility, cost-effectiveness, and ability to be miniaturized and integrated into electronic systems [Karim et al., (2024)], [Yogeswaran et al., (2008)]. The universal appeal of electrochemical sensors is based on their established capacity to identify an extensive number of chemical and biological analytes, making them fundamental instruments in several sectors [Kajal et al., (2022)] [Munteanu et al., (2022)]. In agriculture, they serve to analyze soil and nutrients; in environmental science, they are utilized to identify pollutants and toxins; in the food industry, they ensure the safety and quality of products; and in healthcare, they assist in monitoring biomarkers and indicators of disease [Hernandez et al., (2020)], [Lobsey et al., (2012)], [Su et al., (2018)]. Table 1 highlights the application of electrochemical sensor in various fields. In contrast to standard analytical method like Enzyme-Linked Immunosorbent Assay (ELISA), Polymerase Chain Reaction (PCR), immunohistochemistry, and colorimetric assays, electrochemical sensors present significant advantages [Torrinha et al., (2022)], [Monzó et al., (2015)], [Karimi et al., (2020)]. These cover quicker response times, reduced sample needs, portability, and the possibility for point-of-care and on-site uses, all while providing reliable and stable outcomes. Table 1.2 highlights the advantage of electrochemical sensor over others techniques. The effectiveness of electrochemical sensors is heavily influenced by the characteristics of the electrode surface, which is vital for electron transfer processes and interactions with the target analytes [Sandhyarani et al., (2019)], [Sharma et al., (2018)]. Traditional electrodes composed of glassy carbon, platinum, and uncoated

gold frequently fall short in achieving the necessary sensitivity and selectivity for detecting trace levels [Wang et al., (1991)]. To solve this limitation, researchers have examined the enhancement of electrodes using a range of nanomaterials, including metals nanoparticles, carbon-derived nanostructures, and metal oxide nanostructures. Nanomaterials have transformed the domain of electrochemical sensing because of their distinctive physical and chemical characteristics [Kaur et al., (2020)], [Walcarius et al., (2013)]. Their elevated surface area relative to volume offers increased active sites for interaction with analytes, resulting in improved sensitivity [Zhuang et al., (2008)], [Okpoli et al., (2013)], [Gregg et al., (1985)]. Furthermore, nanomaterials like metal nanoparticles (Au, Pt), carbon-based nanostructures (graphene, carbon nanotubes), and metal oxide nanostructures (ZnO, TiO₂) demonstrate remarkable conductivity, catalytic properties, and stability in reactions [Do et al., (2023)], [An et al., (2019)], [Fazio et al., (2021)]. These properties result in faster electron transfer at the electrode surface and improve the detection abilities of the sensor.

Table 1 Application of electrochemical sensor in various fields.

Application areas	Examples/importance
Environmental monitoring	Detection of pollutant like NO ₂ , CO heavy metals, pesticides.
Healthcare & Medical	Blood glucose monitoring, lactate, cholesterol, neurotransmitters
Industrials safety	Gas leak detection, corrosion sensors
Food & Agriculture	Quality control, pesticide detection, spoilage sensors
Biotechnology	Biosensors for enzyme-substrate interaction studies.

In parallel with material advancements, the fabrication technique used to develop sensor electrodes provides a vital part in determining device performance, cost, and scalability. Development of advanced electrochemical sensors demands precise control of the electrode surface at both micro and nanoscale levels. A variety of nanofabrication techniques have been created for this purpose, such as

photolithography, electron beam lithography, soft lithography, and focused ion beam lithography [Tahir et al., (2021)], [Joshi et al., (2022)]. Although these techniques facilitate fine patterning and control, they tend to be expensive, time-consuming, and demand cleanroom facilities and highly qualified operators. This makes them less appropriate for large-scale manufacturing, especially for recyclable or adaptable sensors. Consequently, there is an increasing motivation for more straightforward, quicker, and budget-friendly manufacturing techniques that can achieve comparable results without complicated procedures and high costs. Nanoimprint lithography (NIL) is an arising nanofabrication technique that enables creating patterns at a low cost and with high throughput. NIL facilitates the transfer of nanoscale patterns onto a substrate through an elastic mold (like PDMS), and it can be effectively combined with additional fabrication processes such as thin film deposition and surface modification [Buhl et al., (2021)], [Nakagawa et al., (2022)], [Fialkova et al., (2024)].

Table 2. Advantage of electrochemical sensors over others techniques

Features	Electrochemical sensor	Others techniques
Cost	Low-cost and easy to fabricate	Often expensive
Miniaturization	Easy miniaturized	More complex to miniaturize
Selectivity	High, especially with functional coating	May required filter or complex algorithm
Energy consumption	Low power requirements	Some required high energy (e.g. laser based)
Respond times	Fast and real-time	Can be slower depending on technology
Portability	Ideal for field based, point-of-care devices	Often lab-based

The integration of NIL with thin film electrodes and modifications at the nanoscale presents an exciting approach for developing highly sensitive and economical electrochemical sensors. This nanofabricated electrode platform has the potential to boost analyte detection due to enhanced surface properties and optimized electron transfer routes. Because of the growing need for simplified, accessible, and highly

sensitive sensors, this study focuses on the nanofabrication of a cost-effective electrochemical sensor using the nanoimprinting lithography technique. The incorporation of NIL with electrochemical sensors seeks to tackle current issues in electrode production and enhance the development of effective sensing platforms for identifying environmental contaminants like heavy metals and toxic chemicals.

1.2 Electrochemical sensor

Electrochemical sensors utilize electrochemical transducers to transform chemical information, including analyte concentration and chemical identity, into quantifiable electrical signals, generally via redox reactions or ion-selective processes. Figure 1 shows the systematic diagram of an electrochemical sensor.

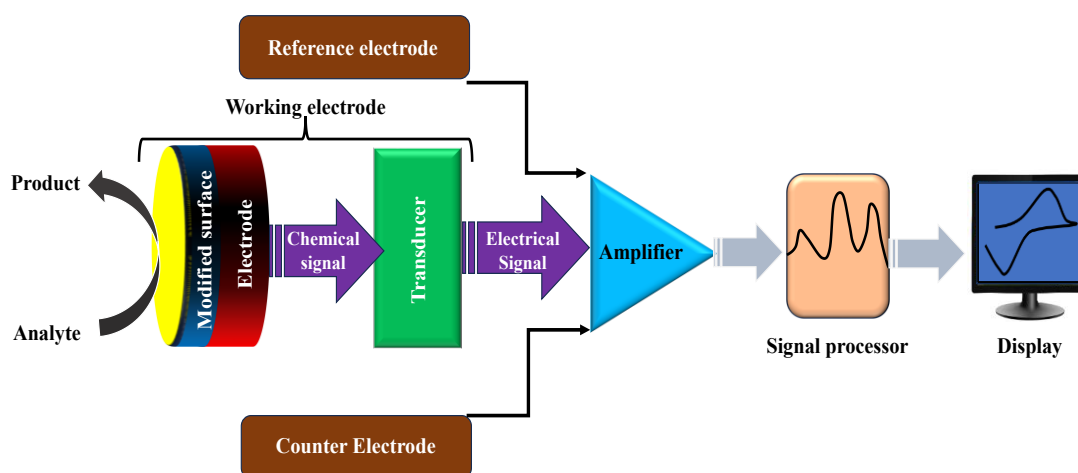


Figure 1. Schematic diagram of an electrochemical sensor

1.2.1 Principles:

Typically, the signal from an electrochemical sensor originates from an electrical response induced by the presence of an analyte. Table 3 presents several primary electrochemical methods along with their corresponding monitored electrical signals. Table 3 demonstrates that electrochemical responses, as monitored by various

methods, are fundamentally reliant on potential, resistance, and electrical current [Saputra et al., (2023)].

Electrochemical techniques employed as analytical methods can be classified into interfacial and noninterfacial categories, based on whether the signal originates from processes at the electrode-solution interface or from the bulk properties of the solution [Li et al., (2018)], [Simoes et al., (2017)].

Interfacial electrochemical methods involve analytical signals generated by processes occurring at the electrode-solution interface. These cover electron transfer reactions, ion adsorption or desorption, and various surface phenomena. The electrode directly facilitates and detects these reactions. Techniques including voltammetry, amperometry, potentiometry, and electrochemical impedance spectroscopy are classified within this category [Crow et al., (2017)].

Noninterfacial electrochemical methods, by contrast, obtain their signal from the bulk properties of the solution instead of from reactions at the electrode interface [Erkmen et al., (2022)]. These methods are based on alterations in parameters such as ionic conductivity, dielectric properties, or overall ion mobility within the solution, rather than on redox activity or surface phenomena. Conductometry serves as a notable instance of a noninterfacial method. The measurement of electrical conductivity in a solution is frequently utilized in titrations, particularly in the absence of redox reactions [Jaffrezic et al., (2008)], [Dzyadevych et al., (2014)].

Table 3. Summary of key electrochemical techniques, corresponding electrical parameters, and their measurement units.

Electrochemical Methods	Monitored Electrical Properties	Units
Potentiometry	Potential difference (volts)	V
Conductometry	Resistance (ohms)	Ω
Amperometry and Voltammetry	Current (amps) as a function of applied potential	I
Coulometry (Q)	Current as a function of time (coulombs)	C
Capacitance (C)	Potential load (farads)	F

1.2.2 Differences techniques of Electrochemical sensor

Electrochemical sensing techniques can be categorized based on the type of electrical signal measured, including potential, current, impedance, or charge.

1.2.3 Voltammetry technique

This technique encompasses the measurement of current in relation to an applied potential. Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV) are frequently employed voltammetric techniques. These techniques offer comprehensive details on diffusion behavior, reaction kinetics, and redox processes [Bond et al., (2005)], [Batchelor et al., 2015].

1.2.3.1 Cyclic Voltammetry

CV is an analytical method employed for investigating the redox nature of molecules (analytes) through the measurement of current as the electrode potential is altered [Kissinger et al., (1983)], [Mabbott et al., (1983)]. This method involves immersing electrodes in a solution containing the analyte, with a potentiostat employed to regulate the voltage between the electrodes while simultaneously recording the current response (as shown in figure 2). This configuration facilitates the establishment of a circuit enabling electron transfer between the analyte and the electrode surface. This technique exhibits high sensitivity and yields significant insights into the thermodynamics and kinetics of electron transfer processes. Linear sweep voltammetry refers to the experimental strategy in which the electrode voltage is systematically varied in a single direction. When the potential is reverted to its initial value after attaining a specific limit, the process is termed cyclic voltammetry (CV), and the corresponding graph is referred to as a cyclic voltammogram (as shown in figure 3). So, CV is an electrochemical method for studying or analysing the redox nature of chemical species. It needs the application of a varying voltage to an electrode while measuring the resulting current, allowing for the analysis of electron transfer processes and reaction kinetics [Marken et al., (2010)]. The range of voltages utilized during a scan is termed the potential window.

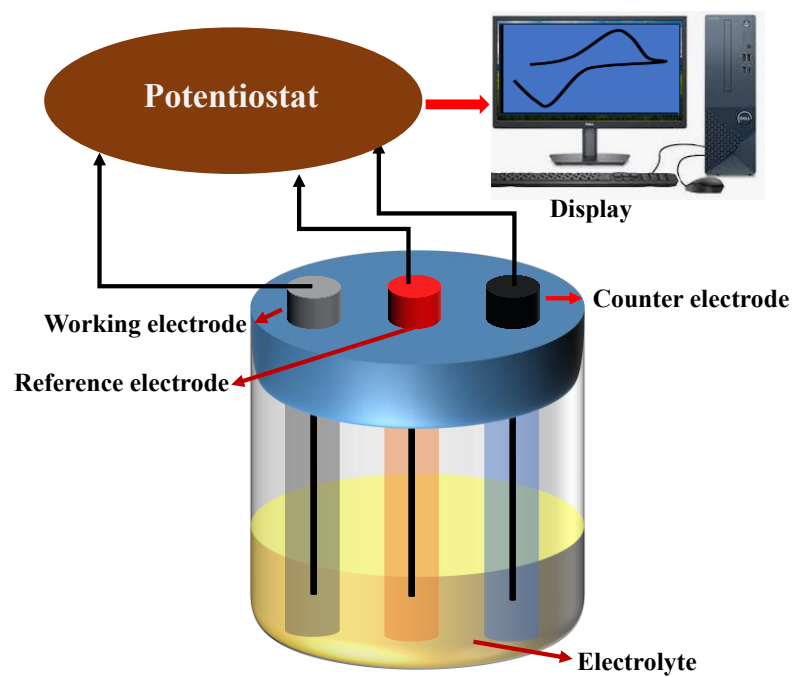


Figure 2. Systematic diagram of voltametric technique setup.

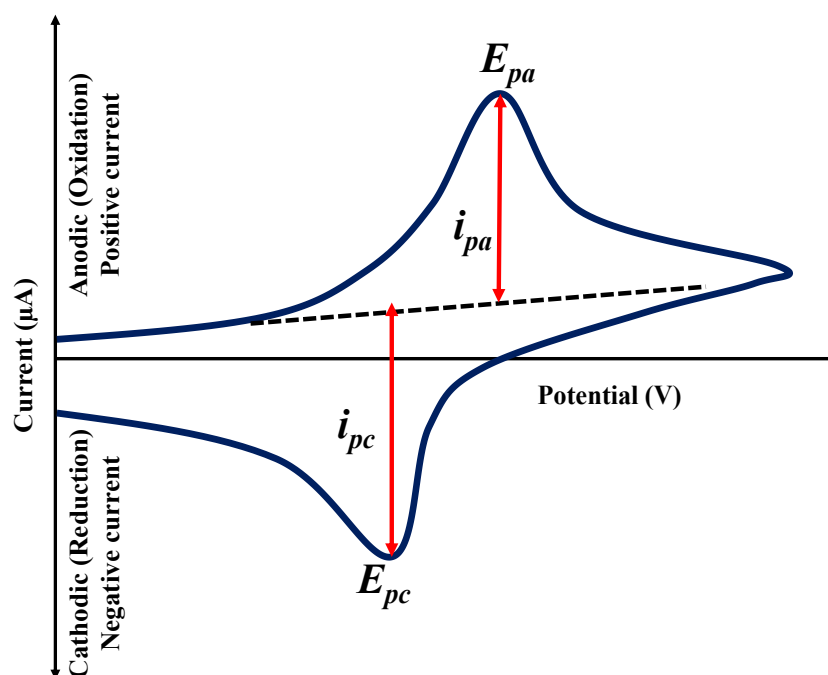


Figure 3. Diagram of a cyclic voltammogram

Electron transfer takes place when it is energetically favorable for electrons to migrate between the electrode and the analyte. Reduction occurs when the electrons at the electrode possess greater potential energy than the vacant molecular orbitals of the analyte, facilitating electron transfer to the analyte. Oxidation occurs when the electrons of the analyte possess greater energy than those in the electrode, including in the loss of electrons by the analyte [Heinze et al., (1984)], [Chevion et al., (2000)] (as shown in figure 4 The objective of these changes is to reduce the total energy of the system.

Voltammetry facilitates the understanding of redox characteristics and electronic structure of analytes by examining the relationship between current and varying electrode potential, thus serving as a significant tool in electrochemical research [Rafiee et al., (2024)] [Costentin et al., (2024)].

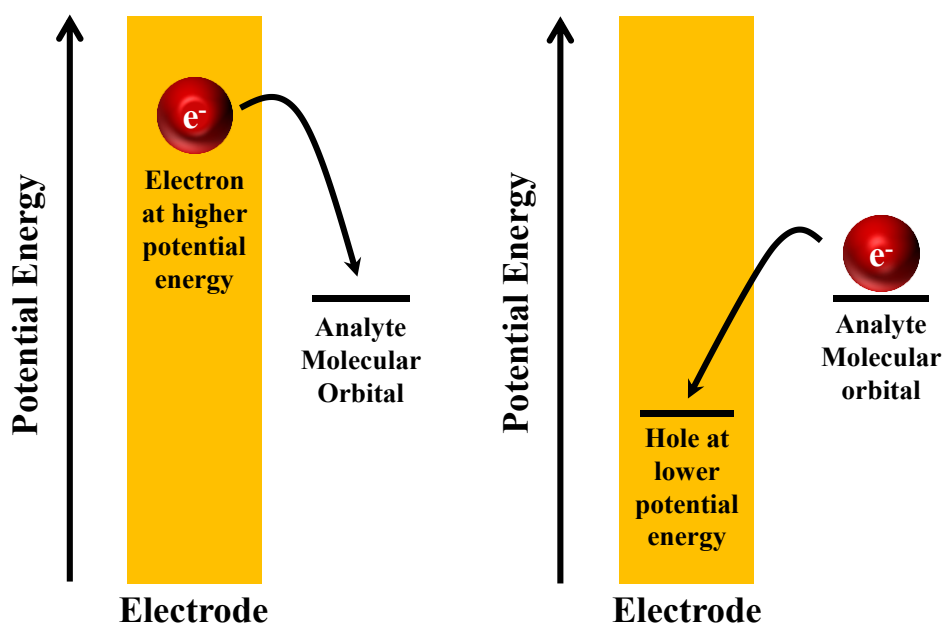


Figure 4. Schematic diagram of the electron transferring mechanism in between the electrode and the analyte.

Common Cell Components

The Potentiostat

An electronic device known as a potentiostat regulates the voltage between the working and reference electrodes while measuring the current flowing through the working electrode. This guarantees precise regulation of the applied potential and documents the current response, which is essential for cyclic voltammetry.

The Cell

An electrochemical cell is defined as the physical container that contains the electrolyte solution and the three electrodes: working, reference, and counter. The design aims:

- To establish a stable environment conducive to redox reactions. Ensure appropriate immersion and positioning of electrodes.
- Avoid contamination and external interference, such as that from air or light.
- Permit gas purging as necessary (e.g., utilizing nitrogen or argon to eliminate dissolved oxygen).
- Electrochemical cells exhibit diverse designs tailored to specific applications.
- With three-neck glass cells (equipped with lids) being commonly utilized for studies conducted in inert atmospheres.
- Custom-designed Teflon or glass cells for use with non-aqueous solvents.
- Miniature or on-chip electrochemical cells utilized for microelectrode investigations.
- Proper cleaning and conditioning of the cell is crucial to prevent contamination and ensure the reproducibility of measurements.

The Solvent

The solvent facilitates the dissolution of the supporting electrolyte and analyte. It must be inert, possess a broad electrochemical window, and not disrupt the electrochemical reactions. Common solvents comprise water, acetonitrile, and dimethylformamide (DMF).

The Electrolyte Salt

The supporting electrolyte improves the solution's conductivity and ensures a stable ionic strength. It must be chemically inert and completely dissociable in the solvent. Examples include KCl in aqueous solution, TBAP in organic media, and NaCl.

The Electrodes

Cyclic voltammetry (CV) relies on a three-electrode system to accurately control the potential and measure the resulting current. Each electrode plays a distinct role in the electrochemical process:

(I) Working Electrode (WE)

In an electrochemical setup, the working electrode acts as the primary site for oxidation and reduction processes involving the analyte.

Essential features of the working electrode:

- Must exhibit conductivity, inertness, and stability throughout the potential window of the experiment.
- Typical materials include Gold, Platinum, Glassy Carbon, Carbon Paste, Boron-Doped Diamond, Graphene-modified electrodes, ZnO-modified electrodes, and others.
- Size and Surface Area: Varies from microelectrodes at the micrometre scale to larger disk electrodes at the millimetre scale. The surface area has a direct impact on current response and sensitivity.

- **Surface Modification:** Frequently altered using nanomaterials (such as ZnO nanorods, reduced graphene oxide, metal nanoparticles, etc.) to improve sensitivity, selectivity, or catalytic properties.
- **Cleaning and Preparation:** Thorough cleaning is crucial for eliminating surface impurities and guaranteeing reproducibility. This process might include refining using alumina slurry, applying sonication, or conducting electrochemical cleaning.

(II) Reference Electrode (RE)

The reference electrode functions as a stable voltage standard and does not participate in current flow during electrochemical measurements.

Common reference electrodes:

- **Ag/AgCl (Silver/Silver Chloride):** Stable and widely used in aqueous systems.
- **Saturated Calomel Electrode (SCE):** Contains mercury and potassium chloride; good stability but toxic.
- **Non-aqueous reference electrodes:** For organic solvents, pseudo-reference electrodes like silver wire can be used with internal standards such as ferrocene.
- **Important characteristics:** The potential of the reference electrode should remain constant throughout the measurement. It should be placed close to the working electrode (often using a Luggin capillary) to minimize solution resistance (iR drop).

(III) Counter Electrode (CE)

The counter electrode, also referred to as the auxiliary electrode, completes the electrical circuit in an electrochemical cell. It serves as the site for a complementary redox reaction to balance the current generated at the working electrode.

Key points:

- Material: Should be conductive and inert. Commonly used materials include Platinum wire, Platinum mesh, or Carbon rods.
- Function: Provides current to the system and maintains charge balance during redox reactions at the working electrode.
- Size: Should have a larger surface area than the working electrode to ensure it does not limit the current.

Solvent Window

The solvent window is the range of potentials where the solvent and electrolyte remain electrochemically stable. Beyond this range, solvent decomposition occurs, which interferes with the electrochemical signal. A wider solvent window allows for the analysis of a broader range of analytes.

Peak Potential

Peak potential (E_p) refers to the potential at which the maximum current is observed for oxidation or reduction during the scan. It provides insight into the redox potential of the analyte and helps determine its redox mechanism.

Peak Current

In cyclic voltammetry, the peak current denotes the maximum current recorded during the oxidation or reduction of a redox-active species at the working electrode. when the applied voltage is swept linearly with time, the current rises until it attains a peak value when the potential approaches the formal redox potential of the analyte. At this stage, the rate of the electrochemical reaction is at its maximum due to the optimal driving force for electron transfer. Nevertheless, above this apex, the current starts to diminish despite a sustained rise in potential. This reduction is mainly due to the exhaustion of electroactive species at the electrode surface and the restricted rate of diffusion of fresh analyte molecules from the bulk solution to the electrode interface.

In systems regulated by diffusion-controlled processes, the correlation between peak current and scan rate is articulated by the Randles–Ševčík equation [Wu et al., (2022)]. The equation indicates that the peak current is directly proportional to the square root of the scan rate, the number of electrons participating in the redox reaction, the electrode surface area, the analyte concentration, and the square root of the diffusion coefficient. This relationship is mathematically represented as equation (1).

$$I_p = (2.69 \times 10^5).n^{3/2}.A.D^{1/2}.C.v^{1/2}$$

where I_p is the peak current in amperes, n is the number of electrons transferred, A is the electrode area in cm^2 , D is the diffusion coefficient in cm^2/s , C is the bulk concentration in mol/cm^3 , and v is the scan rate in V/s . This equation holds under the assumption of reversible, diffusion-limited electrochemical behaviour and room temperature conditions. The peak current is a crucial metric in defining the electrochemical behavior of a system. This technique is very effective for detecting analyte concentration in samples, assessing the efficacy of changed electrode surfaces, and investigating electron transfer kinetics. In reversible systems, the peak currents for oxidation and reduction are often comparable in the magnitude but opposite in direction. Departures from this symmetry may indicate quasi-reversible or irreversible processes, or potential complexities such as linked chemical reactions or adsorption phenomena. Moreover, the type of control mechanism whether diffusion-controlled or adsorption-controlled can be deduced by examining the correlation between peak current and scan rate. A linear correlation of peak current with the square root of the scan rate signifies a diffusion-controlled mechanism, whereas a straight linear link between peak current and scan rate suggests adsorption-controlled behavior [Yamada et al., (2022)], [Kinkelin et al., (2024)]. Consequently, peak current not only indicates the extent of electrochemical activity but also offers profound understanding of the essential transport and kinetic processes taking place at the electrode interface.

Scan rate effect

In cyclic voltammetry (CV), the scan rate typically expressed in millivolts per second (mV/s) refers to the speed at which the potential is swept during the

experiment. Investigating the influence of different scan rates is vital for gaining a deeper understanding of the electrochemical behaviour of a system. Varying the scan rate allows researchers to analyze the reaction mechanism, helping to distinguish whether a redox process is diffusion-controlled or adsorption-controlled [Yao et al., (2008)], [Nicholson et al., (1965)]. This insight is crucial for understanding the fundamental electrochemistry involved and for tailoring electrode materials and experimental setups to suit specific sensing applications [Bao et al., (2008)]. Additionally, scan rate studies enable the evaluation of key electrochemical parameters, such as the electron transfer rate constant, capacitance, and resistance of the electrode material [Izutsu et al., (2009)], [Elgrishi et al., (2018)]. These parameters are essential for assessing the performance of electrochemical sensors and for making comparative evaluations between different materials. Moreover, the scan rate plays a significant role in optimizing experimental conditions, as it can affect the stability and reproducibility of the CV response. Systematically analyzing the effect of scan rate helps in fine-tuning variables such as electrode surface area, electrolyte concentration, and temperature, ultimately leading to more reliable and accurate electrochemical measurements.

Electrochemical Reversibility

Electrochemical reversibility refers to the extent to which an electron transfer reaction at an electrode surface can proceed in both forward (oxidation) and reverse (reduction) directions under the applied potential. A system is said to be electrochemically reversible when the electron transfer between the analyte and the electrode occurs rapidly enough that the system maintains equilibrium at all stages of the potential scan. In such systems, the concentrations of oxidized and reduced species at the electrode surface adjust instantaneously in response to changes in potential, allowing the current response to accurately reflect the thermodynamics of the redox process. A key characteristic of a reversible redox reaction in cyclic voltammetry is the presence of well-defined and symmetric anodic and cathodic peaks. These peaks are usually of equal magnitude and opposite direction, and the separation between the peak potentials (ΔE_p) is close to the theoretical value. For a one-electron transfer at

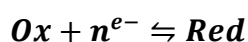
25°C, the theoretical ΔE_p is approximately 59 mV [Li et al., (2015)]. The ratio of anodic to cathodic peak current is ideally unity, and both are proportional to the square root of the scan rate, as predicted by the Randles–Ševčík equation.

In contrast, electrochemically irreversible systems are those where the rate of electron transfer is relatively slow, and the system does not reach equilibrium during the potential sweep [Espinoza et al., (2019)], [Klingler et al., (1980)]. As a result, the current response is influenced not only by the thermodynamic driving force but also by kinetic limitations. In such cases, the redox peaks become broader and less symmetrical, the peak separation increases significantly beyond the ideal 59 mV, and the peak current ratios may deviate from unity. Additionally, the peak potential shifts depending on the scan rate, indicating that the system is under kinetic control rather than diffusion control. There is also an intermediate condition known as quasi-reversibility, where the electron transfer rate is neither too fast to maintain equilibrium nor too slow to be completely limited by kinetics. In quasi-reversible systems, the electrochemical behaviour lies between the reversible and irreversible extremes [Diao et al., (1996)], [Pajkossy et al., (2019)]. The peak separation is larger than that of a reversible system but smaller than that seen in irreversible systems, and it also varies with scan rate. In such cases, the analysis of both peak current and peak potential can provide insight into the electron transfer kinetics and diffusion processes. Understanding the electrochemical reversibility of a system is crucial for interpreting cyclic voltammetry results accurately. It not only helps in identifying the nature of the redox process but also plays a vital role in designing and optimizing electrochemical sensors, especially those based on modified electrodes or nanomaterials, where the surface chemistry significantly influences the reversibility of electron transfer reactions.

Electrochemical Potential of the Analyte

The electrochemical potential of an analyte is a thermodynamic quantity that reflects the tendency of that species to gain or lose electrons during an electrochemical reaction.

In cyclic voltammetry, the electrochemical potential of the analyte is crucial in determining the **redox potential**, or **formal potential** (E^0), at which oxidation or reduction occurs. This redox potential is the electrode potential at which the oxidized and reduced forms of the analyte are present in equal concentrations at the electrode interface. It is closely related to the standard electrode potential E^0 , and can be described by the **Nernst equation** for a redox reaction of the form [Nernst et al., (2009)], [Parker et al., (1986)] equation (2):



$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{[Red]}{[Ox]} \right)$$

In this equation:

- E is the electrode potential,
- E^0 is the standard reduction potential,
- n is the number of electrons transferred,
- $[Ox]$ and $[Red]$ are the concentrations of the oxidized and reduced species, respectively.

The electrochemical potential thus not only governs the equilibrium state of the redox couple but also influences the observed peak positions in the voltammogram. A more positive electrochemical potential of the analyte indicates a greater tendency to accept electrons (be reduced), while a more negative potential suggests a tendency to donate electrons (be oxidized).

1.2.3.2 Differential Pulse Voltammetry

Differential Pulse Voltammetry (DPV) is an electroanalytical technique widely used for sensitive and selective detection of electroactive species. It is a type of pulse voltammetry that offers enhanced resolution and lower detection limits compared to traditional cyclic voltammetry (CV), making it especially useful in trace analysis and biosensing applications [Baluta et al., (2022)], [Romani et al., (2000)].

Principles:

The working principle of Differential Pulse Voltammetry (DPV) is based on the application of a series of voltage pulses superimposed on a slowly increasing base potential. Unlike cyclic voltammetry, where the potential is swept continuously, DPV introduces a staircase-like potential with superimposed pulses, allowing the measurement of current at two specific times during each pulse cycle [Lovric et al., (1982)], [Crespi et al., (2020)]. At each step, the current is sampled twice once just before the pulse (baseline) and again at the end of the pulse (peak response). The difference between these two current values is recorded and plotted against the applied base potential. This differential measurement significantly reduces the contribution of capacitive (non-Faradaic) current, which typically decays rapidly after a change in potential, and enhances the Faradaic (electron transfer) current associated with the analyte. As a result, DPV offers high sensitivity and sharp, well-defined peaks in the voltammogram [Ortuno et al., (2006)], [Melville et al., (2001)]. During the scan, as the potential approaches the redox potential of the analyte, an electron transfer reaction is triggered oxidation or reduction depending on the direction of the scan. The magnitude of the peak current is directly related to the concentration of the electroactive species, and the position of the peak on the potential axis corresponds to the formal potential of the redox couple. The precise control of the pulse height, duration, and interval between pulses allows fine-tuning of the measurement parameters, enabling researchers to resolve closely spaced redox peaks and detect analytes at very low concentrations [Osteryoung et al., (1988)].

1.2.4 Electrochemical Impedance Spectroscopy Technique

Electrochemical Impedance Spectroscopy is an advanced technique used to investigate the electrical properties of electrochemical systems by applying a small alternating current (AC) voltage over a wide range of frequencies [Macdonald et al., (2006)]. Unlike techniques like cyclic voltammetry or amperometry, which apply a sweeping or constant voltage to measure current, EIS focuses on how the system responds to small perturbations in potential, making it extremely sensitive to even minor changes at the electrode interface [Lazanas et al., (2023)], [Magar et al., (2021)].

In a typical EIS experiment, a small sinusoidal voltage usually just a few millivolts is applied to the working electrode, and the resulting current is measured. This voltage is not fixed but varies across a wide frequency range, often from a few megahertz down to millihertz. At each frequency, the system's impedance is calculated as the ratio of the voltage to the current. However, impedance is not just a single value like resistance; it includes both magnitude and phase, capturing resistive and capacitive (or sometimes inductive) properties of the system. This makes it uniquely capable of describing the dynamics of charge transfer, double-layer formation, diffusion, and other processes occurring at or near the electrode surface [Pajkossy et al., (2017)]. The results are usually presented as either a Nyquist plot or a Bode plot [Huang et al., (2016)]. In a Nyquist plot, the real and imaginary components of impedance are plotted against each other. Often, this results in a semicircle followed by a straight line, which visually represents different phenomena. The diameter of the semicircle, for instance, corresponds to the charge transfer resistance, a key parameter for sensing applications. When an analyte binds to a recognition element on the electrode surface such as a protein or DNA strand the interfacial properties change, typically leading to an increase in this resistance. This change can be quantified to determine the presence or concentration of the target analyte [Strong et al., (2021)], [Randviir et al., (2022)].

To interpret EIS data, researchers often use equivalent circuit models that mimic the behaviour of the electrochemical system using combinations of resistors, capacitors, and other elements. A common model is the Randles circuit, which includes components representing the solution resistance, double-layer capacitance, charge transfer resistance, and diffusion processes [Canales et al., (2022)], [Dhillon et al., (2017)]. Fitting the experimental data to such a model allows for the extraction of meaningful physical parameters, which can be used to understand reaction kinetics, surface modifications, or the effectiveness of a sensing platform.

One of the main advantages of EIS in electrochemical sensing is its ability to provide label-free detection. Because the technique is sensitive to any changes at the electrode surface, it can be used to monitor molecular interactions without the need for fluorescent or enzymatic labels. Additionally, EIS is non-destructive, meaning the

sample remains largely unchanged after analysis ideal for delicate biosensing applications [Lisdat et al., (2008)], [Bigdeli et al., (2021)].

1.2.5 Potentiometry Technique

Potentiometry is one of the earliest and simplest electrochemical techniques, widely used for chemical analysis, particularly in measuring ion concentrations in solutions. At its core, potentiometry involves the measurement of the electrical potential (voltage) between two electrodes immersed in a solution, without allowing a significant current to flow [Zdrachek et al., (2020)]. This makes it a non-invasive technique, where the system remains largely undisturbed during the measurement process. The heart of a potentiometric system lies in its electrochemical cell, which consists of two key components: the reference electrode and the indicator (or sensing) electrode. The reference electrode is designed to maintain a constant and known potential, regardless of the solution it's in. Common examples include the silver/ silver chloride (Ag/AgCl) and saturated calomel electrode (SCE).

These electrodes are stable and predictable, providing a solid baseline for comparison [Bobacka et al., (2008)]. The indicator electrode, on the other hand, is responsive to the activity (effective concentration) of a specific ion in the solution. When this electrode is placed in the analyte solution, it develops a potential that varies depending on the ion concentration it is sensitive to. A potential difference arises between the indicator and reference electrodes, and this is what the potentiometer measures. One of the best-known applications of potentiometry is the pH electrode [Huang et al., (2011)], where the indicator electrode is a glass membrane electrode sensitive to hydrogen ions. When immersed in a solution, the glass electrode generates a potential that changes with the concentration of hydrogen ions (i.e., the pH). This voltage is then read by a high-impedance voltmeter and interpreted as a pH value. The relationship between the ion concentration and electrode potential is described by the Nernst equation, which gives a direct, logarithmic relationship.

Beyond pH measurement, potentiometry has expanded through the development of ion-selective electrodes (ISEs). These are specialized electrodes with selective

membranes that respond to specific ions like sodium, potassium, calcium, fluoride, or nitrate. ISEs have become valuable tools in environmental monitoring, clinical diagnostics, and food quality testing. For example, potassium-selective electrodes are used in blood analysis to monitor electrolyte levels. Importantly, the sensitivity and specificity of potentiometric sensors are influenced by the nature of the ion-selective membrane. The membrane can be made from glass, crystalline solids, polymers, or even liquid ion exchangers, depending on the ion of interest. These membranes create a phase boundary potential when in contact with the analyte, and this potential changes as the ion activity changes. Since potentiometry does not rely on current flow, it is especially suitable for measuring systems that are sensitive or slow to respond. It is also advantageous for continuous and long-term monitoring, as it causes minimal disturbance to the sample [Isildak et al., (2021)]. However, it does have limitations, particularly when dealing with very low ion concentrations or in complex mixtures where interferences may arise.

1.2.6 Amperometry Technique

Amperometry is an electrochemical technique based on the measurement of current that flows in an electrochemical cell when a constant potential (voltage) is applied between two electrodes. Unlike potentiometry, which measures voltage without drawing current, amperometry actively drives an electrochemical reaction and measures the resulting current, which is directly related to the concentration of an electroactive species in the solution [Elbicki et al., (1984)], [Edmonds et al., (1988)].

In a typical amperometric setup, you have a working electrode, a reference electrode, and often a counter electrode (making it a three-electrode system). The reference electrode maintains a stable potential, the working electrode is where the redox reaction occurs, and the counter electrode completes the circuit by allowing current to flow. The potential applied to the working electrode is carefully chosen to selectively oxidize or reduce the analyte of interest. For example, consider a glucose sensor [Gorton et al., (1991)]. Glucose oxidase enzyme is immobilized on the working electrode surface. When glucose from a sample diffuses to the electrode surface, it reacts with the enzyme, producing hydrogen peroxide as a by-product. If a potential is

applied that allows the oxidation of hydrogen peroxide, a current is generated. This current is proportional to the amount of hydrogen peroxide present, and thus, to the concentration of glucose in the solution. This is the fundamental principle of many biosensors.

The key relationship in amperometry is that the current is proportional to the concentration of the analyte this makes it ideal for quantitative analysis. The current arises from electron transfer reactions at the electrode surface, and it can be limited by either the kinetics of the electron transfer or the rate at which the analyte reaches the electrode by diffusion (mass transport). There are different modes of applying the potential in amperometric measurements. In single-potential amperometry, the potential is held constant and the current is monitored over time. This is the most basic form, and is widely used for continuous monitoring of an analyte. Another variant is chronoamperometry, where the potential is suddenly stepped from one value to another, and the resulting current-time profile is analyzed. This helps to understand diffusion-controlled behavior and kinetics [Amine et al., (2018)].

Amperometry is extremely sensitive, capable of detecting analytes in very low concentrations often in the nanomolar or even picomolar range. It is also fast, providing real-time responses, which makes it ideal for applications like medical diagnostics, environmental monitoring, food safety testing, and industrial process control [Parellada et al., (1998)], [Curulli et al., (2021)], [Stetter et al., (2008)]. However, it has its limitations too. Since the technique relies on redox activity, the analyte must be electroactive or be converted into an electroactive species. Also, interfering species present in the sample that can be oxidized or reduced at the same potential can affect the accuracy. To address this, electrode surface modifications (like incorporating nanomaterials, polymers, or enzymes) are often used to improve selectivity and sensitivity.

1.3 Nanoimprint Lithography Technique

Nanoimprint Lithography (NIL) is an emerging nanofabrication method that enables the creation of highly ordered nanoscale patterns with high precision and

reproducibility. Unlike traditional lithographic techniques such as photolithography or electron beam lithography that rely on complex optics or charged particle beams, NIL is a purely mechanical process. It involves the physical deformation of a resist or a soft material layer using a patterned mold or stamp under controlled conditions of temperature and pressure [Traub et al., (2016)] (as shown in figure 5). This technique offers a straightforward and cost-effective means of replicating nanostructures over large areas and is particularly attractive for applications that require high throughput and low production cost [Schift et al., (2015)], [Wu et al., (2016)]. The process typically begins with the fabrication of a mold containing the desired nanoscale features. In many applications, including the present study, a polydimethylsiloxane (PDMS) mold is used due to its flexibility, ease of fabrication, and compatibility with a variety of substrates. The mold is then pressed against a substrate that has been coated with a deformable layer.

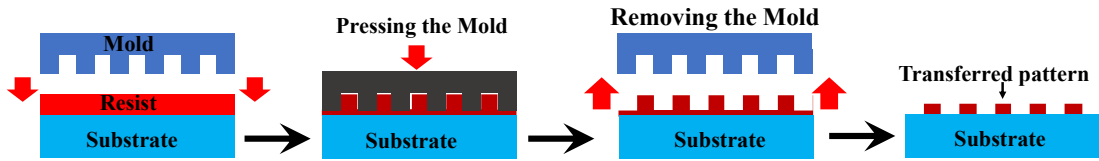


Figure 5. Schematic diagram of NIL process.

In this work, a ZnO seed solution was spin-coated onto a thin film gold electrode, serving both as a functional layer and as a surface suitable for imprinting. The imprinting is performed thermally, typically at moderate temperatures (in this case, around 70°C), allowing the ZnO seed layer to conform to the nanoscale patterns on the PDMS mold. Upon cooling and removal of the mold, the pattern is retained on the ZnO-coated gold substrate. This patterned substrate serves as a template for subsequent nanostructure growth. In the current study, the imprinted ZnO layer provides a guided platform for the hydrothermal growth of ZnO nanorods. The nanoimprinted surface influences the alignment and density of the nanorods, which is crucial for applications in electrochemical sensing. The patterned features promote

enhanced surface area and improved electron transport properties, which are vital for increasing sensor sensitivity.

NIL stands out as a promising technique for the fabrication of nanostructured materials not only because of its simplicity and scalability but also due to its capability to generate uniform and reproducible nanostructures without the need for expensive infrastructure [Guo et al., (2007)]. Its application in the development of electrochemical sensors, as demonstrated in this work, highlights its potential in producing cost-effective and high-performance sensing platforms for environmental monitoring and biomedical diagnostics.

1.4 Motivation of the present study

The increasing levels of environmental pollution caused by heavy metals and organic pollutants such as endocrine-disrupting chemicals (EDCs) [Chang et al., (2009)] pose a significant threat to public health and ecological systems. Traditional analytical techniques for detecting these contaminants such as atomic absorption spectroscopy (AAS) [Radu et al., (2009)], inductively coupled plasma mass spectrometry (ICP-MS) [Balaram et al., (2023)], and high-performance liquid chromatography (HPLC) although highly accurate, are often expensive, time-consuming, require skilled personnel, and are not suitable for portable or on-site analysis [Tripathi et al., (2020)]. These limitations highlight the urgent need for low-cost, simple, sensitive, and selective sensor systems that can be deployed for real-time monitoring of pollutants in the environment. Electrochemical sensors have emerged as promising alternatives due to their high sensitivity, rapid response time, low power consumption, and ease of miniaturization. However, their performance is highly dependent on the surface characteristics and materials used in electrode fabrication. Conventional planar electrodes often suffer from limited active surface area, poor selectivity, and low signal-to-noise ratio, which restrict their practical application in detecting trace levels of environmental toxins [Cogan et al., (2014)].

In this context, nanomaterials such as zinc oxide (ZnO) nanorods have shown great potential to improve sensor performance due to their high surface area, unique

electronic properties, and excellent chemical stability. ZnO nanorods provide abundant active sites for analyte interaction and enhance electron transfer between the electrode surface and the analyte, resulting in higher sensitivity and lower detection limits. Similarly, gold thin films are known for their superior conductivity, electrochemical stability, and biocompatibility, making them ideal substrates for sensor applications.

The challenge, however, lies in the fabrication of such nanostructured electrodes in a scalable, reproducible, and cost-effective manner. Many nanofabrication techniques like electron beam lithography and focused ion beam lithography offer excellent precision but are limited by their high cost, complexity, and limited scalability. Nanoimprint lithography (NIL) offers a compelling solution to this problem. It is a low-cost, high-throughput technique that can replicate nanoscale patterns onto a substrate using a physical mold. Unlike photolithography, NIL does not require expensive optics or cleanroom environments, making it suitable for large-area patterning and commercial sensor production. The rationale of this study, therefore, stems from the integration of these advantages: the use of NIL for patterning electrodes, the deposition of gold thin films to serve as a stable conductive base, and the growth of ZnO nanorods to enhance sensitivity and selectivity. This study aims to develop a cost-effective nanofabrication strategy that enables the scalable production of high-performance electrochemical sensors capable of detecting environmental pollutants such as heavy metal ions and endocrine disruptors.

By bridging the gap between advanced nanofabrication and practical sensing applications, this research not only provides a new methodology for electrode development but also contributes to the broader goal of environmental protection through accessible and effective monitoring tools. The successful implementation of this work could lead to the development of portable sensing platforms for in-field testing, offering a valuable tool for both environmental agencies and public health initiatives.

1.5 Scope of the study

The scope of this study encompasses the design, fabrication, surface modification, characterization, and electrochemical evaluation of nanostructured electrodes for the development of a cost-effective electrochemical sensor. The work is rooted in the integration of nanotechnology and sensor engineering, with a particular focus on applying nanoimprint lithography (NIL) for electrode nanofabrication and zinc oxide (ZnO) nanorods for enhancing sensor sensitivity.

This study begins with the fabrication of thin film gold electrodes on microscope glass slides using electron beam (e-beam) deposition, where a thin adhesion layer of chromium (Cr) is also deposited. These gold electrodes serve as the base platform for further nano-patterning and surface modification. The NIL technique is employed to imprint nanoscale patterns onto the gold electrode using a Polydimethylsiloxane (PDMS) mold replicated from compact disc (CD) grating structures. Prior to imprinting, a ZnO seed layer is spin-coated on the substrate to facilitate the vertical growth of ZnO nanorods during the subsequent hydrothermal synthesis process. The scope of this study also includes the systematic characterization of the fabricated electrodes at each step. Various advanced tools are used to analyze surface morphology, composition, crystal structure, and optical properties. These include Field Emission Scanning Electron Microscopy (FESEM), High-Resolution Transmission Electron Microscopy (HRTEM), X-ray Diffraction (XRD), Energy-Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), Photoluminescence (PL), Atomic Force Microscopy (AFM), Raman, and Fourier Transform Infrared Spectroscopy (FTIR).

The fabricated electrodes are evaluated for their electrochemical performance using cyclic voltammetry (CV) and related techniques. The electrochemical sensing ability is tested specifically for environmental pollutants, such as heavy metals (e.g., cadmium and copper ions) and endocrine-disrupting chemicals (e.g., bisphenol A). The sensing mechanism is based on monitoring changes in redox current during the interaction between the analyte and the nanostructured electrode surface. Factors such as

sensitivity, linear detection range, limit of detection (LOD), reproducibility, and selectivity are studied in detail.

The study also includes optimization of parameters such as imprinting pressure and temperature, seed layer deposition time, ZnO nanorod growth duration, and electrode incubation time with analytes to achieve maximum sensor performance. The sensor system is evaluated under laboratory conditions, with a focus on developing a reproducible, low-cost, and scalable fabrication method that can be translated into practical environmental sensing applications.

1.6 Objectives of the study

The objectives of the current study will be:

- 1. Fabrication of electrochemical sensors using the novel electrodes nanoimprinting lithography technique.**
- 2. Characterization of the fabricated electrode using the analytical techniques, viz., electrochemical sensor using FESEM (Field emission scanning electron microscope), DPV (differential pulse voltammetry), etc.**
- 3. The electrochemical response of the electrodes are to be studied using CV (Cyclic voltammetry), EIS (Electrochemical impedance spectroscopy).**
- 4. The sensing ability of the fabricated electrodes is to be studied for toxic chemicals.**

1.7 Organisation of Thesis

This thesis is structured into six chapters, each of which builds upon the previous one to present a comprehensive view of the research work carried out on the development of a cost-effective electrochemical sensor using nanoimprinting lithography. The organization is designed to move from general concepts to specific experimental findings, providing the necessary theoretical background, methodology, results, and conclusions.

Chapter 1: Introduction

This chapter introduces the study by providing the background and motivation for developing nanostructured electrochemical sensors. It outlines the importance of detecting environmental pollutants such as heavy metals and endocrine disruptors and explains how nanomaterials and nanofabrication techniques can address the limitations of conventional sensors. It also defines the objectives, scope, rationale, and organization of the thesis.

Chapter 2: Literature Review

This chapter reviews the relevant literature on electrochemical sensing technologies, the role of nanomaterials like ZnO nanorods and gold thin films in sensor applications, and various nanofabrication methods. Special emphasis is placed on nanoimprint lithography (NIL) and its advantages in producing scalable and low-cost nanostructures.

Chapter 3: Materials, Methods, and Characterization Techniques

This chapter describes the materials used and the detailed methodology followed for the fabrication of the sensor electrodes. It also outlines the electrochemical sensing set up procedures and the analytical techniques used for characterizing the materials and structures, including XRD, FESEM, HRTEM, EDS, AFM, XPS, FTIR, Raman, PL, and cyclic voltammetry.

Chapter 4: Results and Discussion

This chapter presents the experimental results obtained at each stage of the fabrication and characterization process. It discusses the morphology, structure, and composition of the fabricated electrodes and the electrochemical performance of the sensors. The chapter also analyses how different fabrication parameters affect the sensor's sensitivity and selectivity toward target analytes such as cadmium, copper ions, and bisphenol A. Results are compared with existing literature to highlight improvements and innovations.

Chapter 5: Conclusions and references

This chapter summarizes the key findings of the research and highlights the significance of using nanoimprint lithography for cost-effective electrochemical sensing. It also reflects on the limitations encountered during the study and proposes future research directions, such as integration into portable devices, testing in real environmental samples, and extension to other analytes.

CHAPTER 2. LITERATURE REVIEW

2.1 Advancements in the field of electrochemical sensors

Nagy et al., (2007) conducted an extensive review exploring the development and progression of microelectrode research, offering valuable insights into recent advancements in this area. Their review, which has been cited over 100 times, emphasizes the increasing sophistication of microelectrodes and includes brief yet informative discussions on the fabrication techniques and applications of both potentiometric and voltametric microsensors. This work underscores how miniaturization has enhanced analytical precision and expanded the utility of electrochemical sensors in various fields. In another significant contribution, Riu et al., (2006) focused on electrochemical sensors built from nanostructured materials, specifically those with at least one dimension under 100 nanometres. Their widely cited review provided a detailed overview of multiple classes of nanostructures, including nanoparticles, nanorods, and nanowires, highlighting their fabrication methods, physicochemical properties, and unique advantages in sensor applications. Special attention was given to their use in environmental analysis, where such nanostructures have proven essential for detecting trace pollutants due to their high surface area and improved electron transfer characteristics. In a broad and structured review, Eric et al examined key aspects of electrochemical sensor development, dividing their discussion into five sections: potentiometric sensors, voltammetric sensors, electrochemical biosensors, sensors in fluidic systems, and electrochemical gas sensors [Eric et al., (2002)]. Their review serves as a foundational reference, covering both theoretical principles and emerging applications across various sensing platforms. Privett et al offered a focused summary of electrochemical sensor research published during 2006 and 2007. Their review included topics such as potentiometric and chronopotentiometric sensors, reference electrodes, and biosensors, presenting a snapshot of the rapid developments occurring during that period [Privett et al., (2008)]. Their work captures the transition from traditional systems to more sophisticated and specialized sensor technologies. Further developments in the field were reviewed by

Renedo et al., who focused on screen-printed electrodes (SPEs). Their work covered a wide range of SPE configurations, including unmodified electrodes, film-coated surfaces, and electrodes modified with enzymes or antibodies [Renedo et al., (2012)]. The authors discussed how the affordability and ease of production associated with printable materials have accelerated the adoption of SPEs, especially in portable and disposable sensing systems. The surge in related publications reflects the growing relevance of this technology in both laboratory and field-based analyses.

2.2 Nanomaterials based Electrochemical sensors and its application in medical/ environmental monitoring fields.

Luo et al. contributed a comprehensive review on the role of nanoparticles in electrochemical sensing, particularly emphasizing their functions in catalysis, electron transfer enhancement, biomolecule immobilization, labelling, and their use as reactive agents. The authors presented numerous examples to illustrate how different types of nanoparticles contribute to the advancement of sensor technologies. Their findings reinforced the idea that nanoparticles significantly boost the performance of electrochemical sensors, expanding their applicability across diverse analytical domains. Rassaei et al reviewed the application of nanoparticles in environmental monitoring through electrochemical sensing. They emphasized the strong potential of nanoparticles to elevate the competitiveness of these sensors, particularly due to their high sensitivity and adaptability. However, they also pointed out that while most research has concentrated on novel sensor fabrication, fewer studies have been dedicated to optimizing performance in real sample analysis. This highlights the ongoing need for translating laboratory innovation into real-world environmental applications [Rassaei et al., (2011)]. Wang et al have provided a comprehensive overview of the recent advancements in the field of electrochemical sensors, particularly those leveraging the unique properties of metal and semiconductor nanoparticles. Their review spans a wide array of sensor types, including genosensors, protein and enzyme-based biosensors, gas sensors, and sensors designed for the detection of various organic and inorganic compounds. Importantly, they delve into the diverse assay strategies employed in biosensor and bioelectronic applications,

showcasing how metal and semiconductor nanoparticles are integrated into systems that utilize electrochemical, electrical, and magnetic signal transduction techniques. These strategies not only enhance sensitivity and selectivity but also broaden the application scope of such sensors across biomedical and environmental monitoring domains [Wang et al., (2009)]. Luo and Smyth delved into the functional roles of nanoparticles in electrochemical sensors and biosensors, outlining how different types of nanoparticles metallic, oxide, and semiconducting, have been employed in a variety of sensing systems. Their review clarified how nanoparticles contribute distinct functionalities depending on the context, whether as catalysts, enhancers of conductivity, or as platforms for biological molecule attachment, thus broadening the versatility and effectiveness of sensor systems [Luo et al., (2006)].

Recent literature highlights significant strides in the development of nanomaterial-enhanced electrochemical sensors, showcasing their growing relevance in biomedical, environmental, and analytical applications. Liu et al. (2021) provided a comprehensive overview of various electrochemical sensor types, placing particular focus on the role of nanomaterials in electrode surface modification. Their review delved into preparation techniques, underlying mechanisms, and the current limitations, while also outlining future research directions in this evolving field. In a similar vein, Zhu et al. (2014) reviewed progress made between 2013 and 2014 in nanomaterial-based electrochemical sensors and biosensors. They explored innovations in electrode design, signal amplification strategies, and cutting-edge electroanalytical techniques, particularly emphasizing the trends in sensor miniaturization and system integration. Rajendrachari et al. (2022) shifted the focus toward functionalized nanomaterials used in the fabrication of electrochemical sensors aimed at detecting a range of bioactive compounds, including DNA, glucose, thrombin, and various pharmaceutical agents. Their work underscored the robustness and versatility of these materials as foundational elements for advanced sensor platforms. Earlier, Chen et al. (2013) also emphasized the importance of nanomaterials in enhancing the capabilities of electrochemical sensors for biomedical use. Their review illustrated how this interdisciplinary domain, bridging chemistry, nanotechnology, and life sciences, can support innovations in nanomaterial synthesis, targeted drug delivery, supramolecular

chemistry, and theranostics. Furthering this discussion, Malode et al. (2024) highlighted the growing application of nanomaterial-based sensors in drug detection and bioanalysis. They pointed out how these sensors contribute significantly to human health monitoring and environmental safety through their repeatability, specificity, and high sensitivity.

Malik et al. (2023) presented a broad overview of biosensors developed using a variety of nanostructures such as metal and metal oxide nanoparticles, nanowires, nanorods, carbon nanotubes, quantum dots, and dendrimers. Their work captured recent advancements in biosensor technology, fuelled by progress in nanotechnology and material science. A significant advancement in multifunctional sensor design was presented by Rustomji et al. They reported on the fabrication and characterization of a novel thin-film electrochemical sensor that integrates multiple sensing modalities into a single low-cost platform. This sensor is capable of performing electrolytic conductivity and cyclic voltammetry measurements, while simultaneously monitoring temperature using an on-chip resistance temperature detector (RTD). This integration of thermal and electrochemical sensing functionalities into one compact device marks a significant step forward in sensor miniaturization and multifunctionality. The innovative design enables real-time analysis of complex systems with high precision, making it highly applicable in both laboratory research and industrial process monitoring [Rustomji et al., (2015)]. Building upon the theme of nanomaterial-enabled sensing, George et al., (2018) have focused their review on the recent progress in the design and synthesis of morphologically distinct metal oxide nanoparticles. Their discussion includes a wide spectrum of metal oxides derived from elements such as iron, manganese, titanium, copper, zinc, zirconium, cobalt, nickel, tungsten, silver, and vanadium. They have further emphasized how these nanoparticles, both as individual components and as part of composite materials, have been employed in electrochemical and photoelectrochemical sensing. The unique surface morphologies and chemical properties of these nanostructures enable selective interaction with target analytes, thereby improving the detection capabilities of sensors in the field of chemical and biochemical analysis. Yusoff et al., (2015) have contributed a focused review on the application of gold nanoparticles (AuNPs) in the detection of dopamine

(DA), a vital neurotransmitter with significant clinical relevance. Their work provides an overview of the synthesis and functionalization of AuNPs and their hybrid composites with other organic and inorganic materials, including other noble metals. After highlighting the importance of dopamine monitoring in medical diagnostics, they examined a range of analytical techniques that exploit the optical and electrochemical properties of AuNPs. These techniques include electrochemiluminescence (ECL), surface-enhanced Raman scattering (SERS), colorimetric assays for visual detection, and a broad spectrum of electrochemical sensor designs. This review underscores the versatility of AuNPs and their capacity to be tailored for sensitive and specific detection strategies in clinical diagnostics. In a distinct approach, Bialas et al., (2021) have explored the catalytic performance of sensors based on metal nanoparticles, emphasizing how their activity varies depending on environmental conditions. Their review is notable for categorizing sensors according to the type of metal used such as gold, silver, platinum, and others to systematically investigate how these metals influence sensor performance. This categorization enables a clearer understanding of the intrinsic properties of metal nanoparticles and how factors such as temperature, pH, and surrounding matrix affect their electrochemical behaviour. By identifying both similarities and differences in sensor performance across various studies, the authors provide valuable insights into the rational design of metal nanoparticle-based sensors for specific applications. Singh et al., (2023) have presented an extensive overview of electrochemical biosensors that utilize transition metal and transition metal oxide nanoparticles. Their work emphasizes the role of these nanoparticles as electrode modifiers in enhancing sensor response for a wide range of analytes including glucose, ascorbic acid, uric acid, and several other organic and inorganic species. The review highlights the electrocatalytic properties, high surface area, and excellent conductivity of transition metal nanoparticles, which collectively contribute to improved sensitivity, faster response times, and lower detection limits. Such advancements are particularly significant in the development of point-of-care diagnostic tools and environmental monitoring systems. In a more application-specific study, Li et al., (2024) developed a highly stable and selective electrochemical sensor platform using molecularly imprinted polymers (MIPs) coated onto gold nanoparticle/black phosphorus nanocomposites (BPNS-AuNPs). The incorporation of

gold nanoparticles into black phosphorus sheets not only enhances the electrochemical activity of the composite but also improves the material's stability, a known limitation of pristine black phosphorus. The resulting MIP/BPNS-AuNP composite exhibited an exceptional linear detection range from 0.005 to 10 μM and a remarkably low detection limit of 0.80 nM for the target analyte, PEF (presumably pentafluorophenol or a related compound). The high sensitivity ($3.199 \mu\text{A } \mu\text{M}^{-1}$) observed in this system demonstrates the potential of such hybrid nanomaterials for developing advanced electrochemical sensors with high selectivity and durability. Furthering the scope of gas sensing technologies, Medvedeva et al., (2016) and co-authors focused on the design and development of electrochemical sensors for the selective and continuous monitoring of toxic gases, specifically carbon monoxide (CO) and hydrogen sulfide (H_2S). Their study introduced thin film nanocomposite electrodes that exhibit enhanced sensitivity and selectivity, paving the way for the fabrication of compact and highly responsive gas sensors. The materials used in these electrodes not only facilitate efficient gas adsorption but also provide robust electrochemical interfaces for real-time monitoring in industrial and environmental settings. Maiorano et al., (2023) and colleagues introduced an innovative, straightforward, and sustainable approach for large-scale fabrication of gold electrodes with controllable gold loadings and customizable pattern designs. Their method leverages the deposition of a gold precursor ink followed by immediate ultraviolet (UV) light exposure, which enables simultaneous printing and photodeposition of solid gold patterns. This strategy significantly streamlines the microfabrication process, making it more adaptable and scalable for sensor development. In a separate study, Jindal et al., (2024) and her team explored the electrochemical sensing capabilities of tungsten oxide thin film electrodes doped with various elements including chromium, cobalt, silver, mercury, and lead. Their research was motivated by the increasing demand for advanced sensing technologies capable of detecting hazardous environmental and biological species. The doped tungsten oxide layers were thoroughly analyzed for their sensitivity and selectivity toward targeted analytes, highlighting their promise as versatile electrochemical sensing platforms. Kokulnathan et al., (2024) developed a novel electrochemical sensing platform based on a ZnO nanorods (ZnO-NRs) and chitosan nanofibers (CTS-NFs) composite. This hybrid nanostructure was employed for the

detection of 4-nitrochlorobenzene (4-NCB), demonstrating significantly enhanced performance compared to individual components or unmodified glassy carbon electrodes (GCE). The ZnO-NRs@CTS-NFs/GCE composite electrode exhibited exceptional analytical capabilities, including superior sensitivity, low limit of detection (LOD), broad detection range, high selectivity, and excellent reproducibility. Its applicability was successfully demonstrated through the detection of 4-NCB in various real-world water samples including river, pond, and industrial wastewater. Bhan et al., (2024) reported the chemical synthesis of one-dimensional vertically aligned nanorods (VANRs) of ZnO on fluorine-doped tin oxide (FTO) substrates. These nanostructured electrodes were employed for the electrochemical detection of aniline using square wave voltammetry (SWV). Their study represents a significant advancement in sensor technology, being the first to utilize surface-grown 1D ZnO VANRs for highly sensitive and accurate aniline detection, thereby opening new avenues for environmental monitoring applications. Zhang et al., (2024) and co-researchers focused on the development of an electrochemical biosensor for lactate detection using lactate oxidase (LOx) and glutaraldehyde (GA) modified indium-doped ZnO nanorods. The biosensor exhibited a wide linear detection range (0.1–36 mM), a sensitivity of 0.73301 $\mu\text{A}/\text{mM}$, and low quantification and detection limits of 2.7 μM and 0.8 μM , respectively. The utilization of doped ZnO nanostructures enhanced the enzymatic electrochemical performance, enabling precise detection of lactate, a critical metabolite in human physiology. Kallakkattil et al., (2024) fabricated a high-performance electrochemical sensor for chloramphenicol (CAP) detection using a ZnO/multi-walled carbon nanotube (MWCNT) nanocomposite. ZnO nanoparticles were synthesized via a green route using an aqueous leaf extract of *Rhoeo discolor*, and subsequently combined with MWCNTs through a sonochemical process. The resulting ZnO/MWCNT/graphite electrode demonstrated a wide linear range (1–250 μM), high sensitivity (11.15 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$), and low limits of detection (0.35 μM) and quantification (1.16 μM). Detailed studies on the influence of loading mass, pH, and scan rate validated the optimized electrode response. Juang et al., (2024) and co-workers developed a highly efficient electrochemical sensor based on three-dimensional flower-like ZnO nanorods supported by graphene oxide and decorated with platinum nanoparticles. This composite exhibited excellent sensing performance

for p-methoxyphenyl tetrazolium (PMTZ), achieving an ultra-low detection limit ($1.85 \times 10^{-2} \mu\text{M}$), broad linear range (0.2 to 116.2 μM), and remarkable sensitivity (1.59 $\mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$), showcasing the synergistic effect of ZnO, GO, and Pt in enhancing electrochemical activity. Pitiphattharabun et al., (2024) and colleagues fabricated a reduced graphene oxide (rGO)/ZnO composite electrode for acetylcholine (ACh) detection. GO was synthesized via a modified Hummers' method and further converted to rGO/ZnO nanocomposite using hydrothermal treatment. The composite's electrocatalytic behavior toward ACh was evaluated using cyclic voltammetry (CV) and chronoamperometry, demonstrating the material's potential as a biosensor for neurotransmitter detection. Dutt et al., (2024) and collaborators synthesized an rGO/MnO₂ nanocomposite for the fabrication of a 4-nitrophenol electrochemical sensor through electrodeposition on carbon fiber (CF). The sensor showed excellent selectivity, sensitivity, and stability, making it a promising tool for environmental pollutant detection using a cost-effective and efficient nanocomposite platform. Gaidukevic et al., (2022) and team developed graphene-based electrochemical platforms for dopamine detection. They thermally reduced graphene oxide to improve its electrocatalytic properties, achieving high sensitivity and stability for dopamine sensing, thus underscoring the potential of graphene materials in neurotransmitter detection applications. Verma et al., (2021) and collaborators proposed a sensitive electrochemical sensing platform for bisphenol A (BPA) using a reduced graphene oxide-molybdenum trioxide nanoparticle (rGO_MoO₃Nps) nanocomposite. The electrode, fabricated via electrophoretic deposition on indium tin oxide (ITO) glass, displayed a wide detection range (0.76 nM to 0.82 μM), high sensitivity (13.96 μA per log nM cm^2), and extremely low detection limit (0.12 nM), making it highly effective for endocrine-disrupting chemical detection. Rashid et al., (2021) developed an electrochemical sensor for the direct detection of pyocyanin, a biomarker for *Pseudomonas aeruginosa* infections. Their design incorporated gold nanoparticle-functionalized reduced graphene oxide (AuNPs/rGO) onto screen-printed electrodes. The sensor exhibited a clinically relevant detection range (1–100 μM) in biological fluids such as PBS, saliva, and urine, with detection limits as low as 0.27 μM , 1.34 μM , and 2.3 μM , respectively.

2.3 Advancement in the field of Nanoimprinting Lithography

Chang et al., (2011) and co-researchers explored nano-electrode fabrication through the growth of MWCNTs on silicon wafers patterned using nanoimprint lithography (NIL) with an iron catalyst. This work demonstrates the integration of nanomaterials with lithographic techniques to create high-performance electrode structures for nanoelectronics and sensors. Barcelo et al., (2016) provided an extensive overview of NIL's applications across various fields including electronics, optics, and plasmonics. Their review highlights NIL as a transformative tool in the nanofabrication landscape, capable of achieving high-resolution patterning for the advancement of nanodevices and sensing platforms. Lastly, Kim et al., (2010) and collaborators demonstrated a novel NIL approach using silver nanoink for direct metal patterning. Their study presented both direct nanoimprinting using PDMS stamps to create silver features several hundred nanometers wide, and indirect imprinting for sub-100 nm structures. The swelling characteristics of PDMS were harnessed to control pattern formation, revealing the method's potential for flexible and high-resolution nanopatterning.

2.4 Electrochemical sensors for heavy metal ions detection

The electrochemical detection of heavy metal ions has garnered significant attention, with recent reviews highlighting advancements in sensor design and performance. Cui et al., (2015) highlighted the unique properties of inorganic nanomaterials, organic small molecules and polymers, enzymes, and nucleic acids used in modifying electrodes to enhance the sensitivity and selectivity of electrochemical sensing. Their review emphasized the design strategies and detection mechanisms through representative examples. Gumpu et al. (2015) provided insights into the toxicity mechanisms of various heavy metal ions, particularly their role in inducing oxidative stress. They also discussed electrochemical biosensors developed with different types of interfaces for detecting these toxic metal ions. Liu et al. (2019) reviewed the recent progress in nanomaterial-enabled screen-printed electrochemical sensors for heavy metal ion detection. Their work systematically summarized the fabrication methods and analytical performance of disposable sensors based on carbon nanomaterials (such as carbon nanotubes and graphene), metal nanomaterials (such as gold and silver

nanoparticles), and metal oxide nanomaterials (such as Fe_3O_4 and Bi_2O_3 nanoparticles). He et al. (2020) developed a nanocomposite consisting of bismuth nanoparticles integrated with MXenes ($\text{Ti}_3\text{C}_2\text{T}_x$, where $\text{T}_x = -\text{O}, -\text{OH}, -\text{F}$), referred to as $\text{BiNPs}/\text{Ti}_3\text{C}_2\text{T}_x$. This composite was used to modify a glassy carbon electrode (GCE), forming an electrochemical sensor capable of detecting Pb^{2+} and Cd^{2+} ions in various water samples. The study assessed the sensor's sensitivity, selectivity, and repeatability, confirming its reliable performance. Mourya et al. (2019) introduced a sensor modified with blast furnace slag (BFS), which enhanced the electrocatalytic activity toward Pb^{2+} detection. The electrochemical response was analyzed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV). The sensor demonstrated a linear detection range from 1 to 5 μM with a high correlation coefficient ($R^2 = 0.99$), and the calculated transfer coefficient (α) and rate constant (K_s) were 0.664 and 1.08 s^{-1} , respectively. Key experimental parameters, including pulse height, step height, and pH, were also optimized to improve performance. Zhang et al. (2024) proposed a versatile detection platform based on a composite of horseradish peroxidase encapsulated in zeolitic imidazolate frameworks-8 ($\text{HRP}@ZIF-8$), combined with thionine, gold nanoparticles, and ionic liquid-reduced graphene oxide (IL-rGO). This system demonstrated the ability to detect a range of metal ions, including those lacking typical electrochemical signatures, showcasing its broad applicability and innovative sensing capabilities. Song et al. (2024) presented a review summarizing recent advancements in carbon nanomaterial-based electrochemical sensors for heavy metal detection. Their overview highlighted the promising potential of these sensors in various applications, including food safety and environmental monitoring. The authors emphasized that ongoing developments in carbon nanomaterial-modified platforms will continue to improve detection technologies, ultimately contributing to public health and environmental protection.

CHAPTER 3. METHODOLOGY

3.1 Materials and Chemicals.

In this study, microscope glass slides (dimensions: $76.1 \times 25.4 \times 1.4$ mm) were obtained from Recombigen Laboratories Pvt. Ltd. Polydimethylsiloxane (PDMS) was sourced from Dow Chemical Company, and commercial compact discs (CDs) were procured from a local stationery shop for patterning purposes. Bisphenol A (BPA) was purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 98%) was acquired from Sigma-Aldrich. Hydrogen peroxide (H_2O_2 , 30%) was obtained from Merck, respectively. Ethanol and acetone were supplied by Sigma-Aldrich. Potassium chloride (KCl, 99.5%) was obtained from Sisco Research Laboratories, while potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$) and potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$) were sourced from Merck. Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$), ethylene glycol monomethyl ether (C_3HO_2) and monoethanolamine ($\text{C}_2\text{H}_7\text{NO}$) were purchased from Merck. Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was obtained from Sigma-Aldrich. Additional reagents such as potassium permanganate (KMnO_4) were procured from Alfa Aesar, sodium nitrate (NaNO_3) from Merck, and hydrochloric acid (HCl) from Merck.

Laboratory equipment used in this study included glass beakers (Bello Naturals Care), nitrile gloves (Kashi Surgical), Whatman double filter paper, and Petri dishes. A muffle furnace (LABGO) was used for annealing processes, and a hot air oven (LABPRO) was used for drying. Spin coating was carried out using a programmable spin coater (SpinNXG-P1, Apex Instruments). A centrifuge (manufacturer not specified) and an ultrasonicator (manufacturer not specified) were employed for centrifugation and sonication processes, respectively. Weighing procedures were performed using a digital balance (manufacturer not specified). Centrifuge tubes were procured from a commercial supplier (not specified). A 3D printer (WOL3D Ender, Model 2022) and 1.75 mm PLA filament (Shenzhen Creality 3D Technology Co., Ltd., China) were used for printing components; additional PLA filaments were sourced from GS Automation.

Thin film deposition of chromium and gold was carried out using an electron beam deposition unit (Hind High Vacuum, Model: BC-300). Gold (25 karat, 99.99% purity) was purchased from Tanishq, and chromium (99% purity) from Sigma-Aldrich. All synthesis and experimental procedures were conducted using Millipore-grade deionized (DI) water.

3.2 Fabrication of Electrode

In this work, the working electrode was fabricated on the clean thin film glass slide using e-beam evaporation technique. The material used for fabrication of working electrode is 24 karat Gold. The fabricated working electrode was then modified with nanomaterials and 2D material to increase its sensitivity. The stepwise fabrication process and its modification procedures are explained detailly bellow.

3.2.1 Fabrication of thin film Au-electrode using e-beam deposition.

In this work, an electron beam (e-beam) evaporation system was employed to fabricate a thin film gold (Au) electrode onto pre-cleaned microscope glass slides. The slides were precisely cut into square dimensions of 2.5 cm $\times$ 2.5 cm (Figure 7) and thoroughly cleaned to eliminate any surface contaminants. The cleaning process involved immersing the glass pieces in a piranha solution—comprising concentrated H₂SO₄ and 30% H₂O₂ in a 3:1 volume ratio for 2 hours using ultrasonicator. This was followed by sequential ultrasonicing cleaning with deionized (DI) water, ethanol, and acetone for an additional 2 hours. The cleaned substrates were allowed to dry in a hot air oven at 60–70°C for 1 hour to ensure complete removal of moisture.

The thin film deposition was carried out using an electron beam evaporation system (Model BC-300) manufactured by Hind High Vacuum Co. Pvt. Ltd. (Figure 6). The deposition process took place under high vacuum to maintain a contaminant-free environment inside the chamber. The system was evacuated to a vacuum base pressure of 1.6×10^{-6} mbar to eliminate residual gases. Separate crucibles containing small pellets of chromium (Cr) and gold (Au) were placed in the deposition chamber as the source materials. Cr and Au were deposited at rates of 0.8 Å/s and 1 Å/s, respectively, using beam currents of 11 mA for Cr and 260 mA for Au, under the maintained vacuum

conditions. A digital thickness monitor was used to control the deposition thickness of each layer. The glass substrates were firmly fixed within the deposition area to ensure uniform coating. Upon activating the e-beam source, the metal sources were evaporated and deposited onto the glass surface. Due to gold's poor adhesion to glass, a 10 nm layer of Cr was first deposited as an adhesion promoter. This was followed by the deposition of a 50 nm Au layer to form the electrode. The Cr interlayer enhanced the mechanical stability and adhesion of the Au film during subsequent handling and applications (Figure 8). Once the desired thickness was achieved, the coated glass slides were removed from the chamber, resulting in clean and uniform thin-film Au electrodes (Figure 9).



Figure 6. E-beam deposition machine used for fabrication of thin film Au electrode.



Figure 7. Microscope glass slide cutting process for fabrication Au thin film electrode.

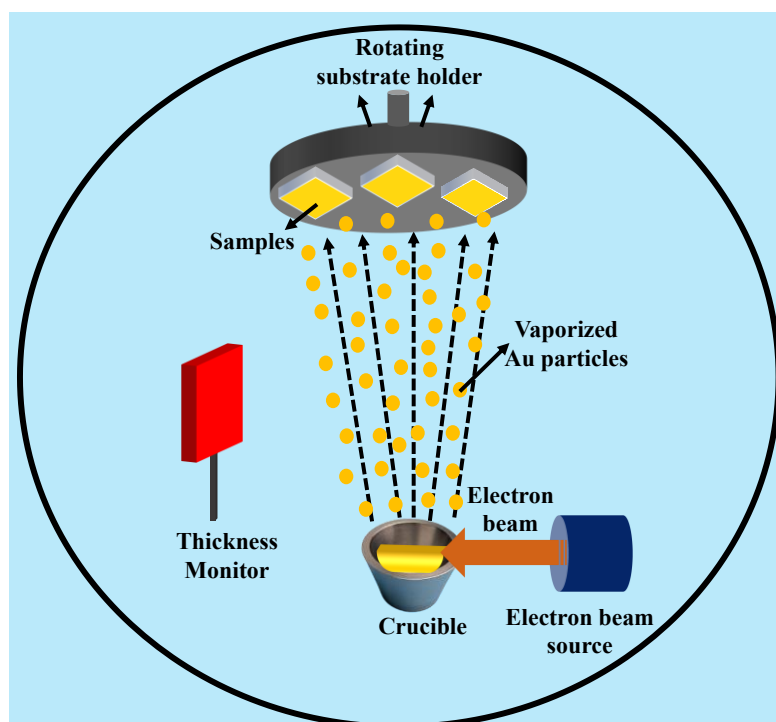


Figure 8. Schematic diagram for the fabrication of thin film Au electrode

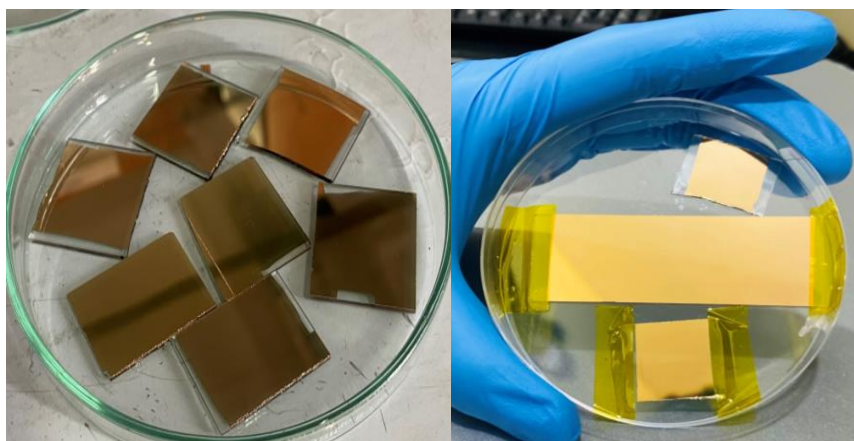


Figure 9. The fabricated clean thin film Au electrodes.

3.2.2 Fabrication of ZnO nanorod (ZnONRs) modified Au-thin film electrode via NIL.

The fabrication process initiates with the development of a PDMS (polydimethylsiloxane) mold imprinted with a grating pattern sourced from a compact disc (CD). To obtain this pattern, the reflective top layer of a CD is carefully stripped using adhesive tape, exposing the underlying grating structure. The CD is then cut into manageable segments and cleaned in isopropanol via ultrasonic treatment. Post-cleaning, the CD fragments are dried at 60 °C.

A PDMS mixture is prepared by blending PDMS base with a curing agent in a 10:1 weight ratio, followed by thorough stirring. To remove entrapped air bubbles, the mixture undergoes vacuum degassing for several minutes. The degassed PDMS is poured onto the clean CD surface and cured in an oven at 80 °C for 3 hours. This step results in the transfer of the CD's surface relief pattern onto the cured PDMS mold. For seed layer deposition, a 0.5 M ZnO seed solution is prepared using zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$, ethanolamine, and 2-methoxyethanol as solvents. The structured PDMS mold is then coated with this seed solution through spin coating. The coating is performed at varying spin rates and durations—1000, 3000, and 6000 rpm for 5, 10, and 15 minutes respectively—under a temperature setting of 40 °C to ensure uniform film formation. Following the coating process, the PDMS mold

carrying the ZnO seed layer is brought into contact with a clean gold-coated glass substrate (gold thickness ~ 50 nm). This assembly is subjected to thermal nanoimprinting at 80°C for 20 minutes using a thermal imprinting machine (see Figure 10). After imprinting, the setup is allowed to cool to room temperature, and the PDMS mold is gently peeled away, thereby transferring both the grating structure and the ZnO seed layer onto the gold surface. The patterned and ZnO-seeded Au thin-film electrode is then annealed at 300°C for 1 hour to enhance the adhesion and crystallinity of the seed layer. Subsequent growth of ZnO nanorods (ZnONRs) is achieved via a hydrothermal process, following a method adapted from Singh et al., (2024) and Sing et al., (2025). The modified electrode is immersed in a growth solution composed of 0.005 M zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and 0.005 M hexamethylenetetramine (HMTA) in deionized water. This reaction takes place in a 100 mL Teflon-lined autoclave at 70°C for 8 hours. Upon completion of the growth phase, the sample is removed, rinsed, and subjected to a final annealing treatment at 300°C for 1 hour to further improve the crystallinity of the ZnO nanorods (see Figure 11).

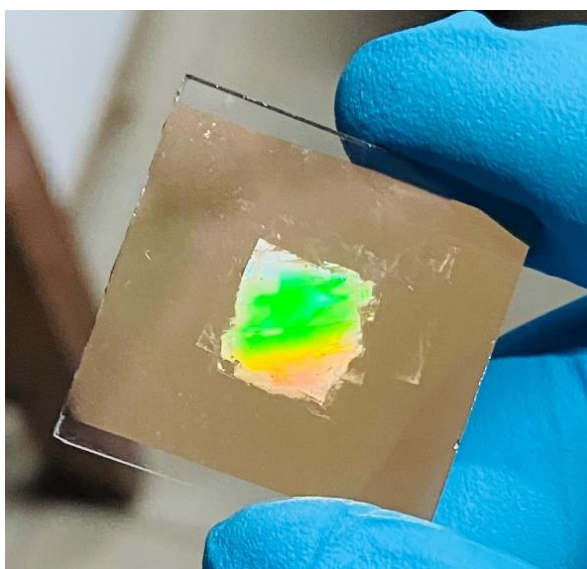


Figure 10. Thin film Au electrode after transferring the CD grating pattern of ZnO seeds layer.

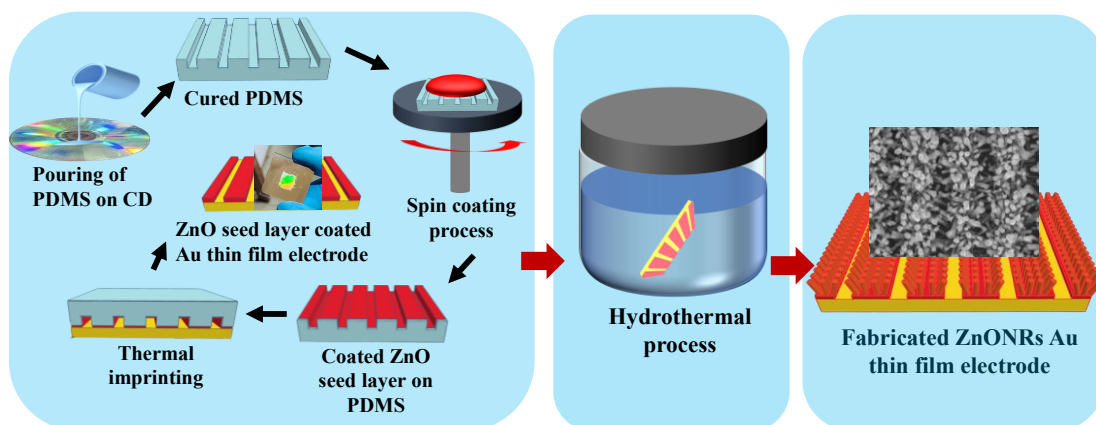


Figure 11. Schematic diagram for the fabrication of ZnONRs-Au thin film electrode.

3.2.3 Fabrication of reduced graphene Oxide-Modified thin film Au electrode.

In this study, a thin film gold (Au) electrode was utilized as the primary electrode material. The fabrication of the gold thin film was performed using an electron beam evaporation system, wherein a clean microscope glass slide ($2.5\text{ cm} \times 2.5\text{ cm}$) served as the substrate. Initially, a chromium (Cr) adhesion layer approximately 10 nm thick was deposited, followed by a 50 nm layer of gold.

To modify the electrode surface, graphene oxide (GO) was synthesized using a modified approach based on Hummer's method [Paulchamy et al., (2015)]. In this procedure, 4 grams of graphite powder were thoroughly combined with 92 millilitres of concentrated sulfuric acid (98%) in a 500 mL flask. The reaction mixture was maintained in an ice bath to regulate the temperature and minimize heat generation. Gradual addition of 2 grams of sodium nitrate (NaNO_3) and 15 grams of potassium permanganate (KMnO_4) enabled controlled oxidation of the graphite. Due to the highly exothermic nature of the reaction, the KMnO_4 was introduced slowly, preventing the temperature from exceeding 100°C with the help of the ice bath. The mixture was continuously stirred at the controlled low temperature for 2 hours. Afterward, the ice bath was removed, and the mixture temperature was raised and maintained at 35°C for an additional hour. Subsequently, 184 mL of deionized water was cautiously added while stirring, which caused the temperature to rapidly increase to 98°C . This elevated

temperature was sustained for 1 hour. After another 30 minutes of heating at 98°C, an additional 184 mL of DI water and 40 mL of 30% hydrogen peroxide (H₂O₂) were added to the solution under vigorous agitation, and the stirring was continued for 30 minutes as in figure 12 (a). To purify the product, the mixture was filtered and washed with a 5% hydrochloric acid solution to eliminate residual metal ions. This was followed by repeated rinsing with DI water until the pH of the filtrate became neutral. The final product was then dried at ambient temperature, yielding graphene oxide (GO) as a dry material figure 12 (b). the schematic diagram for the synthesis of GO is shown in figure 13.



Figure 12. (a) Synthesis of GO solution (b) synthesised GO after drying

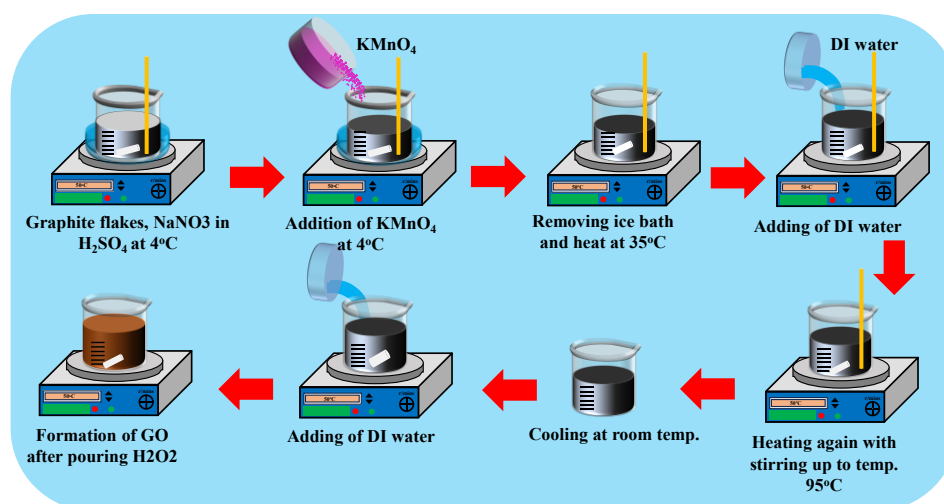


Figure 13. Schematic diagram for the synthesis of GO.

A 1 mg/mL GO dispersion was prepared in distilled water and sonicated for 5 hours at room temperature to ensure uniform distribution. Then, 100 μL of this GO solution was drop-cast onto the surface of the gold-coated glass slide and allowed to dry naturally at room temperature. For electrochemical reduction process, a three-electrode setup was used, comprising the GO-modified Au thin film as the working electrode, a platinum sheet as the counter electrode, and an Ag/AgCl reference electrode. The electrolyte solution consisted of 0.1 M potassium chloride (KCl). Cyclic voltammetry (CV) was conducted within a potential window of 0.5 V to -1.5 V over 12 cycles to monitor the electrochemical reduction of GO. The CV results, illustrated in Figure 14, show a decreasing trend in the reduction peak current with successive cycles. After 12 cycles, the reduction peak disappeared, indicating complete reduction of GO to reduced graphene oxide (rGO) on the electrode surface. Thus, we got our final ErGO-Au electrode (the whole fabrication process is shown in figure 15).

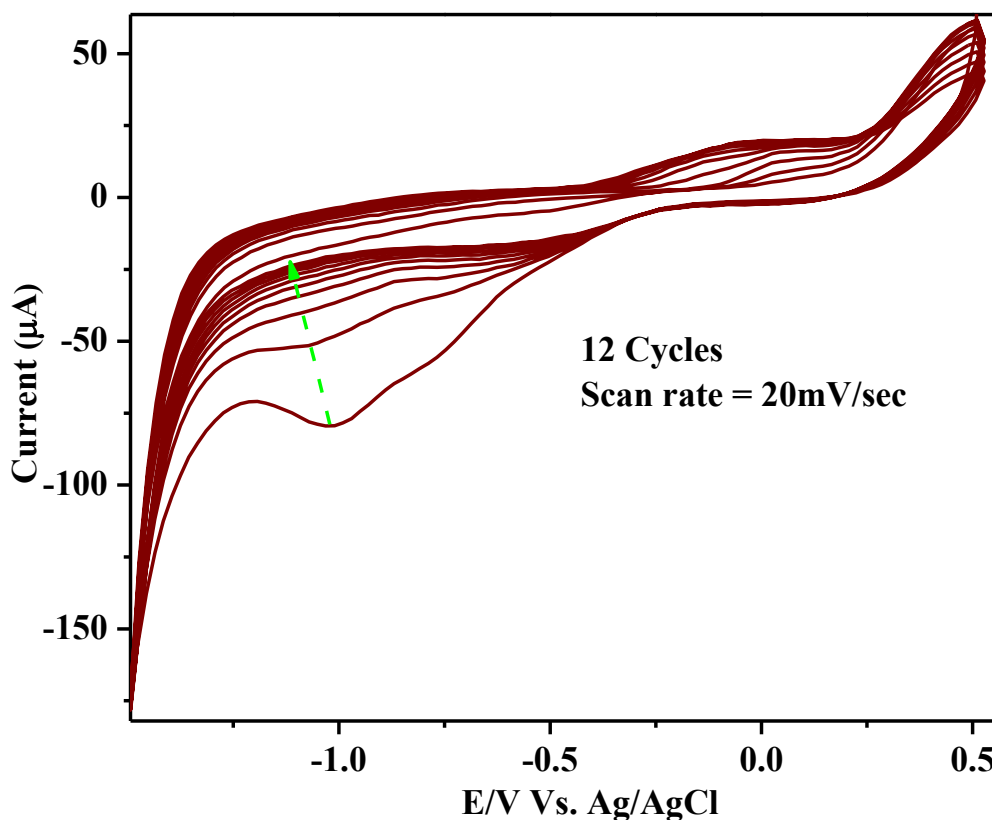


Figure 14. Cyclic voltammogram for electrochemical reduction of GO to ErGO

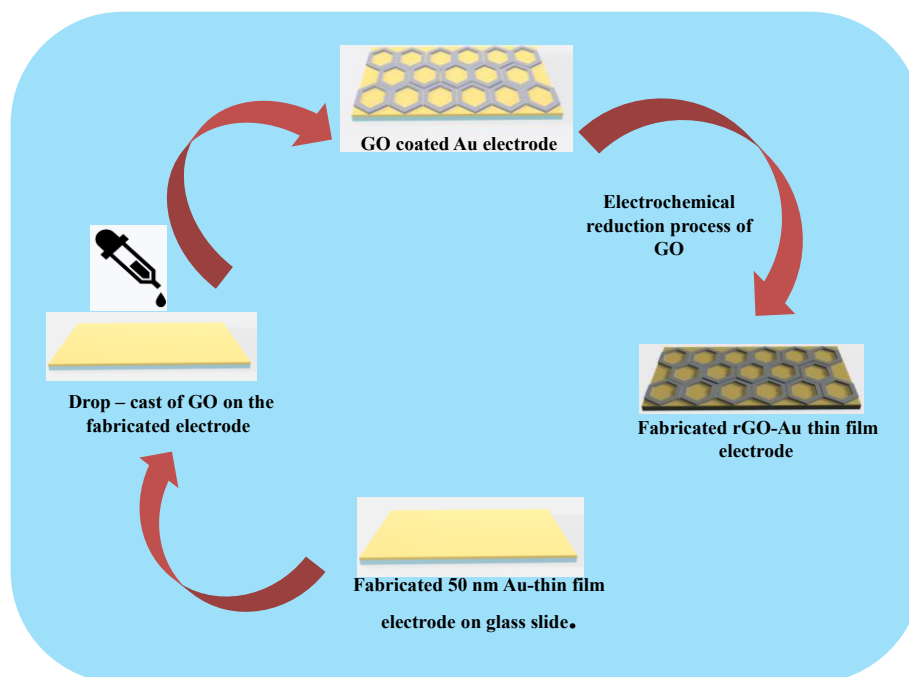


Figure 15. Schematic diagram for fabrication of ErGO-Au thin film electrode.

3.2.4 Fabrication of Gold- Interdigitated electrodes.

The fabrication of gold interdigitated electrodes (Au-IDEs) on microscope glass slides followed a multi-step process. Initially, standard glass slides were sectioned into $2\text{ cm} \times 2\text{ cm}$ squares using a precision diamond cutter. These smaller glass substrates underwent a rigorous cleaning protocol, beginning with ultrasonication in Piranha solution to eliminate organic residues. They were subsequently rinsed thoroughly with deionized water and ethanol to ensure complete removal of contaminants and were then left to dry completely. After drying, a pre-fabricated stainless steel IDE mask was affixed onto the clean glass pieces using thermal adhesive tape. The masked substrates were then placed inside an electron beam (e-beam) deposition system, where the chamber vacuum was stabilized at approximately 6.7×10^{-6} mbar, as outlined in Singh et al., (2024). Separate crucibles containing chromium and gold were prepared for sequential metal deposition. Inside the deposition chamber, a thin chromium adhesion layer (10 nm) was first deposited at a rate of 1.01 Å/s to promote strong bonding between the glass surface and the gold layer. This was immediately followed by the deposition of gold at a rate of 1.8 Å/s , forming a conductive layer with a thickness of

50 nm. Upon completion of the metal deposition, the system was allowed to cool gradually before the glass substrates were carefully extracted. The stainless-steel IDE mask was then gently removed, revealing precisely patterned Au-IDEs (as shown in Figure 17 and figure 18 (a)). Field Emission Scanning Electron Microscopy (FESEM) analysis confirmed that each fabricated Au-IDE comprises 18 pairs of electrodes, with individual electrode widths measuring approximately $439.3\ \mu\text{m}$ and an inter-electrode spacing of roughly $513\ \mu\text{m}$ (shown in figure 18 (b)). the schematic diagram for the fabrication of Au IDE is shown in figure 16.

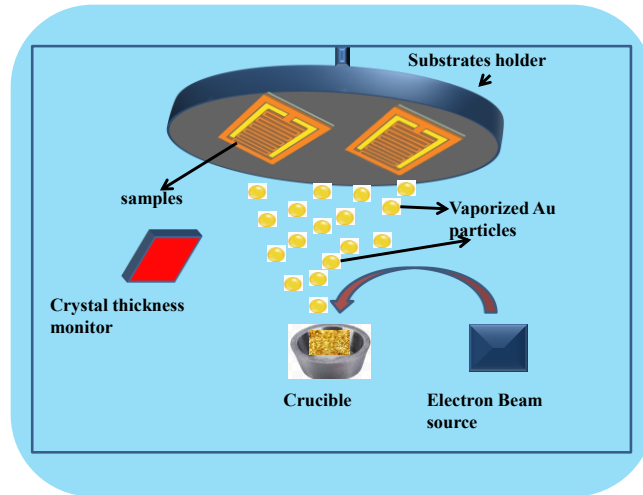


Figure 16. schematic diagram for the fabrication of Au IDE.

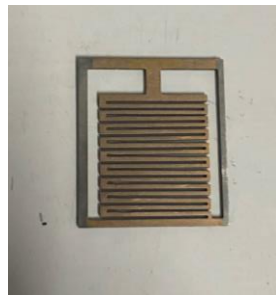


Figure 17. IDE mask

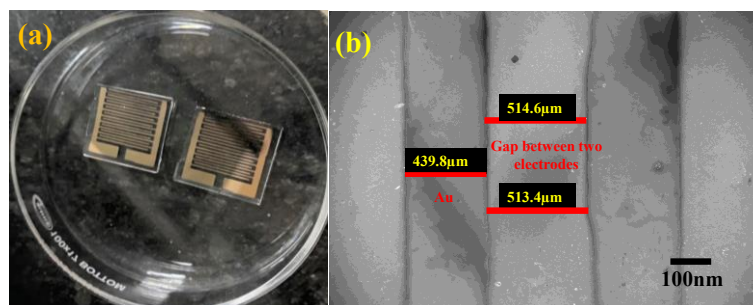


Figure 18. (a) fabricated Au IDE (b) FESEM image of Au IDE

3.2.5 Fabrication of ZnONRs modified Au-IDE.

The fabrication process began with the growth of ZnO nanorods on the surface of pre-constructed Au interdigitated electrodes (Au-IDEs) using a hydrothermal method, as previously reported. Initially, a ZnO seed solution was formulated by dissolving 0.1 M zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] in 10 mL of propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$). To stabilize the solution, 0.1 M monoethanolamine ($\text{C}_2\text{H}_7\text{NO}$) was gradually introduced under continuous stirring. This seed solution was then applied to the Au-IDEs using a two-step spin-coating process first at 2000 rpm and then at 1000 rpm. After coating, the substrates were annealed at 300°C for 2 hours in a furnace to enhance the adhesion and improve the crystallinity of the ZnO seed layer.

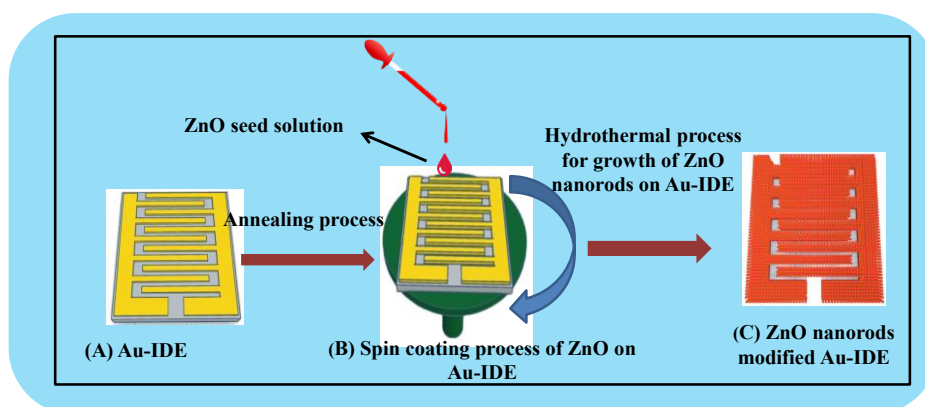


Figure 19. schematic diagram for fabrication of ZnONRs-Au IDE

For the subsequent hydrothermal growth, an aqueous solution containing 0.01 M zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and 0.01 M hexamethylenetetramine (HMTA) was prepared. The Au-IDEs, now coated with the ZnO seed layer, were submerged in this growth solution inside a 100 mL autoclave. The sealed autoclave was heated in a furnace at 80°C for 6 hours to promote nanorod formation. After completion of the reaction, the substrates were carefully removed, rinsed with deionized water, and subjected to a post-growth annealing treatment at 200°C for 1 hour to further enhance the crystalline quality of the ZnO nanorods (schematic fabrication process diagram shown in Figure 19). This method successfully yielded ZnO nanorods on Au-IDEs, rendering them highly suitable for advanced sensing technologies.

3.4 Electrochemical Measurement set up.

Electrochemical measurements in this work were conducted using both three-electrode and two-electrode configurations, depending on the type of sensor being evaluated.

3.4.1 Three-Electrode System set up

For the majority of the electrochemical sensing studies, a three-electrode system was employed. In this configuration, the working electrode was the fabricated thin-film modified Au electrode, the reference electrode was an Ag/AgCl (saturated KCl) electrode, and the counter electrode was a platinum sheet.

A custom-designed electrochemical cell was developed to perform the measurements. The design was first conceptualized using Tinkercad, which allowed precise estimation of the cell volume and exposed working electrode area. Based on this design, the final cell was fabricated using a 3D printer with PLA (Polylactic Acid) polymer. PLA was chosen for its excellent chemical stability and compatibility with electrochemical applications. In addition to the cell container, a supporting structure resembling a table with four legs was designed. This structure included a hole at the top designed to fit an Allen key, which served to securely hold the thin-film working electrode and align it with the electrochemical cell (all the 3D printed electrochemical cell design is shown in figure 20). The electrochemical cell was fabricated with four corresponding holes to accommodate the legs of the table-like structure. A central circular aperture was also

created in the container, over which the thin-film working electrode was placed and sealed with an O-ring to prevent leakage and define the effective electrode area exposed to the electrolyte. Once the assembly was complete, the table-like structure was inserted into the cell container by fitting its legs into the designated holes. The setup was secured by tightening two Allen keys into the side holes in the legs of the structure, ensuring mechanical stability and proper alignment. The system was then tested for any potential leakage. Upon successful validation, the electrolyte solution was introduced into the cell for electrochemical analysis. A schematic representation of the setup is provided in Figure 21.

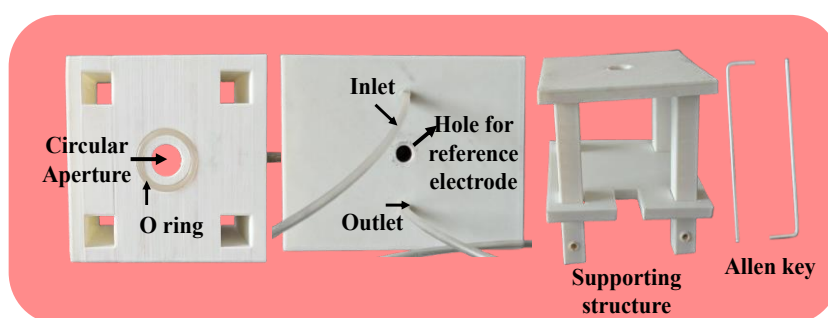


Figure 20. different structures of electrochemical cell.

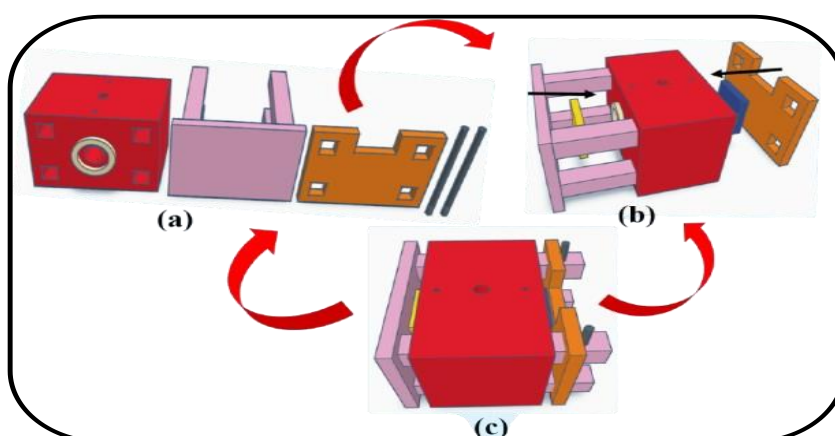


Figure 21. (a) schematic diagram of different structures of electrochemical cell (b) assembling all the structures for the electrochemical cell setup (c) completed setup of electrochemical cell by assembling all the structures.

3.4.2 Two-Electrode System

For the fabricated Au thin film IDE modified with ZnONRs, a two-electrode system was utilized. In this configuration, no separate reference electrode was required. The IDE consists of two comb-like electrodes arranged alternately. One comb was designated as the working electrode, while the other served as the counter electrode. A custom 3D-printed electrochemical cell container, specifically tailored for the IDE, was also developed (as shown in Figure 22).

For electrical connection, copper tape was used to establish contact between the working electrode and the electrochemical workstation (as shown in figure 23). This setup allowed for stable and reproducible electrochemical measurements, facilitating the evaluation of the sensor performance in both three- and two-electrode configurations.

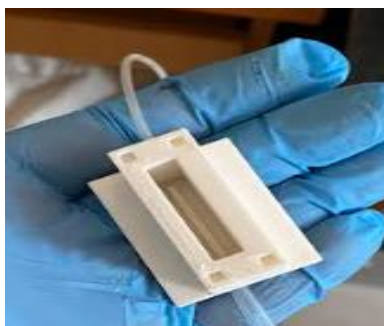


Figure 22. Electrochemical cell for two electrode systems.

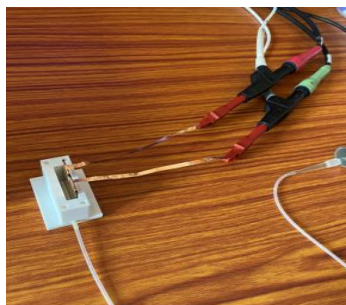


Figure 23. CV measurement setups for two electrode configurations.

3.5 Characterisation tools/ techniques

3.5.1 XRD

In materials research, the scientist has many analytical questions related to the chemical composition and crystalline constitution of materials. X-ray Diffraction (XRD) is a widely used analytical technique for investigating the crystallographic structure, phase composition, and other structural properties of materials. It is based on the principle that when a beam of monochromatic X-rays interacts with a crystalline solid, it is scattered in specific directions, producing a diffraction pattern. This diffraction pattern provides valuable information about the atomic arrangement within the crystal lattice. Materials researchers therefore use XRD to analyze a wide range of materials, from powders to solids, thin films and nanomaterials. The phenomenon of X-ray diffraction was first observed in 1912 by Max von Laue, who demonstrated that X-rays could be diffracted by crystals, confirming the wave nature of X-rays. This discovery laid the foundation for crystallography. Shortly after, in 1913, William Lawrence Bragg and his father, William Henry Bragg, formulated Bragg's Law, which mathematically describes the diffraction of X-rays by crystal planes. Their work enabled the determination of atomic structures of materials, for which they were awarded the Nobel Prize in Physics in 1915. Over the years, XRD has played a crucial role in various scientific breakthroughs, including the determination of DNA's double-helix structure in 1953 by Watson and Crick. Today, XRD remains an indispensable technique in materials science, physics, chemistry, and biology.

X-ray diffraction occurs when a beam of X-rays interacts with the periodic atomic planes of a crystalline material. The atoms in the crystal act as scattering centers for the X-rays, causing them to interfere constructively or destructively. When constructive interference occurs, a diffraction peak is observed at a specific angle. This interaction follows Bragg's Law, which provides a fundamental relationship between the wavelength of X-rays, the diffraction angle, and the spacing between crystal planes.

Bragg's Law

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Bragg's Law

Bragg's Law is mathematically expressed as equation (3):

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

Where

n is the order of diffraction (an integer).

λ is the wavelength of the incident X-ray.

d is the interplanar spacing of the crystal.

θ is the Bragg angle at which constructive interference occurs.

Derivation of Bragg's law.

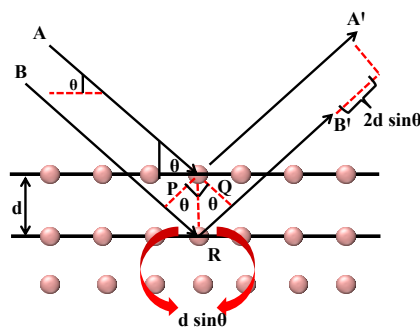


Figure 24. Schematic diagram of Bragg's diffraction

Bragg's law can be derived by considering two incident beams (A and B) striking adjacent atomic planes at an angle θ , with the planes separated by a distance d . Upon reflection, these beams (A' and B') will produce maximum intensity only when their waves remain in phase. Since beam B travels a greater distance than beam A, a path difference is introduced. This extra path length, represented by PQR, must correspond to an integer multiple of the wavelength (λ) to satisfy the condition for constructive interference. The interplanar spacing (d) and the angle of incidence, also known as the Bragg angle (θ), are related to the distances BC and CD in the following manner:

$$PR = QR = d \sin \theta$$

Since the total path difference (PQR) is the sum of PR and QR, we get:

$$PQR = PR + QR = 2d \sin \theta$$

For constructive interference to occur, this path difference must be an integer multiple (n) of the X-ray wavelength (λ), leading to the well-known Bragg's equation:

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

This equation explains why diffraction peaks appear at certain angles and is used to determine the crystal structure of a material. By measuring the diffraction angles and knowing the X-ray wavelength, the interplanar spacing can be calculated, structural analysis and allowing for phase identification comparing with the database available at Joint Committee on Powder Diffraction Standards (JCPDS) or International Centre for Diffraction Database (ICDD).

Interplanar Spacing Formulas for Different Crystal Systems

The interplanar spacing d for a given set of Miller indices (hkl) varies based on the crystal system. The general formula is:

$$\frac{1}{d^2} = \text{Function of } (h, k, l, a, b, c, \beta)$$

Where a , b , c are the lattice parameters and β is the monoclinic angle.

i) Cubic system, $\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$

ii) Tetragonal system, $\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$

iii) Hexagonal system, $\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2+k^2+hk}{a^2} \right) + \frac{l^2}{c^2}$

iv) Monoclinic system, $\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2h \cos \beta}{ac} \right)$

Where a , b , c are the lattice parameters, h , k , l are the Miller indices and β is the monoclinic angle.

Scherrer Equation for Crystallite Size Estimation.

The Scherrer equation is used to estimate the crystallite size from the broadening of diffraction peaks equation (4):

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where,

D = crystallite size

K = shape factor (typically 0.9)

λ = X-ray wavelength

β = full width at half maximum (FWHM) in radians

θ = Bragg angle

Instrumentation

A typical X-ray diffractometer consists of: (i) X-ray Source (ii) Sample Holder (iii) Monochromator (iv) Goniometer (v) Detector (vi) Data Processing System.

(i) X- ray Source

The X-ray source is a crucial component in X-ray diffraction (XRD) instrumentation, as it generates the X-rays required for probing the atomic structure of materials [Ermrich et al., (2013)]. The most commonly used X-ray sources in laboratory-based XRD systems are X-ray tubes, while synchrotron radiation sources are used for high-resolution studies in specialized research facilities. An X-ray source in X-ray diffraction (XRD) generates X-rays that are used to probe the crystal structure of materials. The X-rays produced by an X-ray tube contain multiple wavelengths, but for accurate diffraction studies, a monochromatic X-ray beam (single wavelength) is required. For XRD applications, characteristic X-rays are used. They occur when an electron from the K-shell (inner shell) is ejected by an incoming electron. Electrons from higher energy levels (L-shell) then fill the vacancy, emitting X-rays of precise energy. The most common targets include:

- Copper (Cu, $K\alpha = 1.5406 \text{ \AA}$) – widely used due to its high intensity and moderate penetration.
- Molybdenum (Mo, $K\alpha = 0.7107 \text{ \AA}$) – used for small unit cells or thicker samples.
- Cobalt (Co, $K\alpha = 1.7903 \text{ \AA}$) – preferred for samples containing iron to reduce fluorescence effects.

(ii) Sample Holder.

A sample holder in XRD is a critical component used to position the sample in the X-ray beam path accurately. It ensures proper alignment, minimizes background noise, and prevents sample displacement during measurement. The design of the sample holder varies depending on the type of sample (solid, powder, thin film, or liquid) and the XRD instrument geometry (θ - θ or θ - 2θ configurations).

(iii) Monochromator.

A monochromator is a device used in XRD to filter out unwanted radiation and ensure that only X-rays of a specific wavelength (monochromatic X-rays) reach the sample.

Purpose of a Monochromator

- X-ray tubes generate both characteristic radiation and bremsstrahlung (white) radiation. The monochromator removes unwanted wavelengths, improving peak resolution and reducing background noise.
- It enhances signal-to-noise ratio and minimizes errors caused by fluorescence from the sample.

Types of Monochromators

Crystal Monochromators:

- Utilize a perfect crystal (e.g., graphite, Ge, Si) to selectively reflect only a specific X-ray wavelength according to Bragg's Law.
- Graphite monochromators are commonly used due to their high efficiency in filtering Cu K α radiation.
- Filter Monochromators
- Thin metal foils (e.g., nickel filter for Cu radiation) absorb unwanted wavelengths while allowing the characteristic radiation to pass.
- Less precise than crystal monochromators but effective for routine diffraction measurements.

(iv) Goniometer.

The **goniometer** is one of the most essential components in an XRD instrument. It is the mechanical system that precisely controls the **angular positions** of the X-ray source, the sample, and the detector during the diffraction experiment. This allows the instrument to scan through different **2 θ angles** to capture diffraction peaks from the sample. There are several types of goniometer geometries based on the nature of the measurement:

Bragg-Brentano Geometry (θ –2 θ Configuration)

- Most commonly used in powder XRD.
- The sample is stationary or rotates at angle θ , and the detector moves at 2θ .

Parallel Beam Geometry

- Used for thin films or irregular samples.
- Provides better control over sample displacement errors and surface irregularities.

Debye-Scherrer Geometry (Capillary method)

- Used for small amounts of powders in capillaries.
- The sample rotates while the X-ray beam and detector remain fixed or move minimally.

(v) Detector

The **detector** is a key component of the XRD system. Its main function is to **measure the intensity of X-rays** that are diffracted from the sample at various angles. By recording the intensity of these diffracted beams as a function of angle, the detector helps produce the XRD pattern, which is used to identify the material's crystal structure.

Functions of the Detector

- Detects Diffracted X-rays at specific angles.
- Measures Intensity of the X-ray signal.
- **Converts X-ray Photons into Electrical Signals** for digital recording.
- **Works in Synchronization** with the goniometer to scan across the required angular range

(vi) Data Processing System

The data processing system is the computational and software-based component of the XRD instrument. After the detector collects diffraction data (intensity vs. angle), the data processing system analyzes, interprets, and visualizes this information to extract meaningful structural details about the sample.

3.5.2 Transmission Electron Microscope (TEM)

TEM is a high-resolution characterization technique capable of imaging individual atoms within crystalline materials, achieving spatial resolutions as fine as 0.1 nm smaller than typical interatomic distances [Poppa et al., (1993)]. This makes TEM an indispensable tool for analyzing materials at the atomic to nanometer scale. It provides detailed insights into particle size, shape, crystallinity, and interparticle interactions.

In TEM, a high-energy electron beam generated by an electron gun is transmitted through an ultra-thin specimen, typically less than 100 nm in thickness. As the electrons interact with the specimen, they generate a highly magnified image, which can be captured on various imaging devices such as photographic film, a fluorescent screen, or electronic detectors like a scintillator coupled with a charge-coupled device (CCD). TEM was first demonstrated in 1931 by Max Knoll and Ernst Ruska. The first commercial TEM was introduced in 1939. In recognition of his pivotal contributions to the development of this technique, Ruska was awarded the Nobel Prize in Physics in 1986. The fundamental principle of TEM is based on the wave nature of electrons, described by the de Broglie equation:

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2mv}} = \frac{h}{\sqrt{2mV}}$$

- λ is the electron wavelength
- h is Planck's constant,
- m is the mass of the electron,
- v is the velocity of the electron,
- E is the kinetic energy of the electron, and
- V is the applied accelerating voltage.

As the accelerating voltage increases, the electron wavelength decreases, enhancing the beam's ability to penetrate deeper into the specimen often several microns thus enabling imaging at atomic resolution.

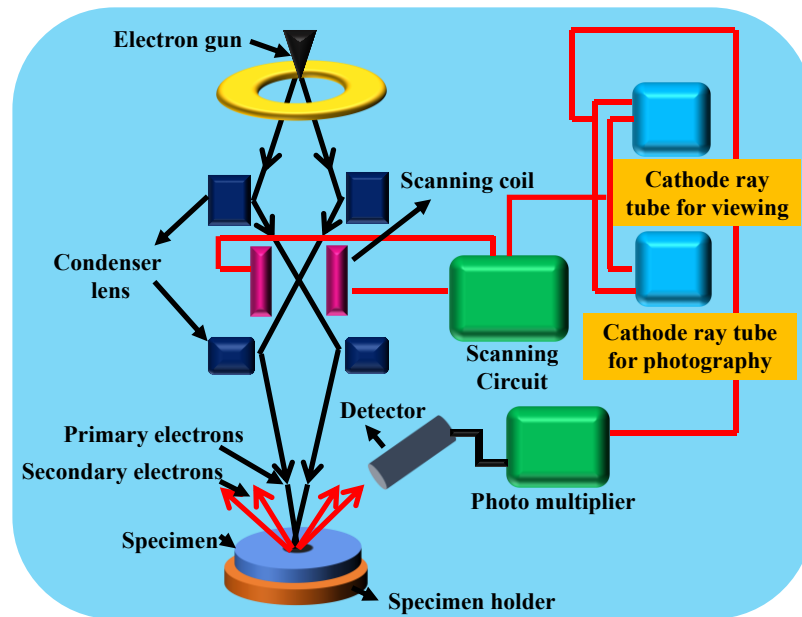


Figure 25. Schematic diagram of TEM

Image resolution is a fundamental parameter in microscopy that defines the minimum distance between two distinguishable points in a specimen. It is important to differentiate resolution from magnification, as increasing magnification alone does not guarantee improved image clarity. Without sufficient resolving power, a magnified image may remain blurred and difficult to interpret. Figure 25 show the schematic diagram of TEM.

The resolving power of a microscope is governed by the following equation (5):

$$d = \frac{\lambda}{2NA}$$

where:

- d is the minimum resolvable distance,
- λ is the wavelength of the incident beam, and
- NA is the numerical aperture of the objective lens system.

The de Broglie wavelength of electrons is substantially shorter than that of visible light. For instance, at an accelerating voltage of 160 kV, the electron wavelength is approximately 2.85×10^{-3} nm—about one million times shorter than the average wavelength of visible light. This extremely short wavelength is what enables Transmission Electron Microscopy (TEM) to achieve ultra-high resolution and magnification levels up to one million times greater than those attainable with conventional optical microscopes. A Transmission Electron Microscope (TEM) generally comprises several key components: an electron source, a vacuum system, a specimen stage, a series of electromagnetic lenses, and detectors. Electrons are emitted from a pointed cathode (typically tungsten or LaB₆) when it is thermionically heated. These electrons are then accelerated towards the anode under high voltage, typically ranging from 100 to 300 kV. The high accelerating voltage reduces the electron wavelength, thereby enhancing the resolution of the microscope due to the wave nature of electrons.

Once accelerated, the electron beam passes through a small aperture in the anode and enters the lens system. Electromagnetic coils within the condenser lenses generate magnetic fields that focus the electron beam onto the specimen. As the beam interacts with the ultra-thin specimen, some electrons are transmitted while others are scattered, depending on the sample's atomic structure and thickness. The transmitted and scattered electrons are subsequently collected and focused by the objective lens, forming an image of the sample. This image can then be further magnified by intermediate and projector lenses, and visualized on a fluorescent screen or captured using a CCD camera or other digital detectors. High-Resolution TEM (HRTEM) enables direct imaging of atomic arrangements within a material, providing critical insights into crystal structure and defects at the atomic scale. Additionally, Selected

Area Electron Diffraction (SAED) is often used in TEM to analyze the crystalline structure of materials. In this technique, diffracted high-energy electrons form distinct diffraction patterns—spots or rings—based on the crystal lattice. These patterns can be analyzed to determine interplanar spacings using the following relationship equation (6):

$$d_{h,k,l} = \frac{L\lambda}{R}$$

where:

- $d_{h,k,l}$ is the interplanar spacing of the crystal,
- L is the camera length (a constant for a given TEM configuration),
- λ is the electron wavelength, and
- R is the radius of the diffraction ring.

This diffraction-based analysis is fundamental in identifying crystal phases, orientations, and lattice parameters of materials at the nanoscale

3.5.3 SEM and EDAX

The Scanning Electron Microscope (SEM) comprises several key components: an illumination system, specimen stage, objective lens, magnification system, data recording system, and a chemical analysis system [Topa et al., (2010)]. Typically, tungsten filaments are used as the source of illumination, while magnetic lenses serve to magnify the image. Similar to Transmission Electron Microscopy (TEM), SEM uses two or three lenses positioned above the specimen these acts as condensers and the final lens, known as the objective lens, focuses the electron beam into a narrow probe approximately 10 nm in diameter.

Figure 26 illustrates the schematic layout of the SEM. During operation, the finely focused electron probe scans the specimen surface in two perpendicular directions horizontally (x-axis) and vertically (y-axis). The x-axis scanning is controlled by a fast

sawtooth-wave generator, which supplies current to scanning coils aligned along the optical axis. These coils generate a magnetic field in the y-direction, deflecting the electron beam along the x-direction. The slower y-axis scanning is controlled by a second sawtooth-wave generator.

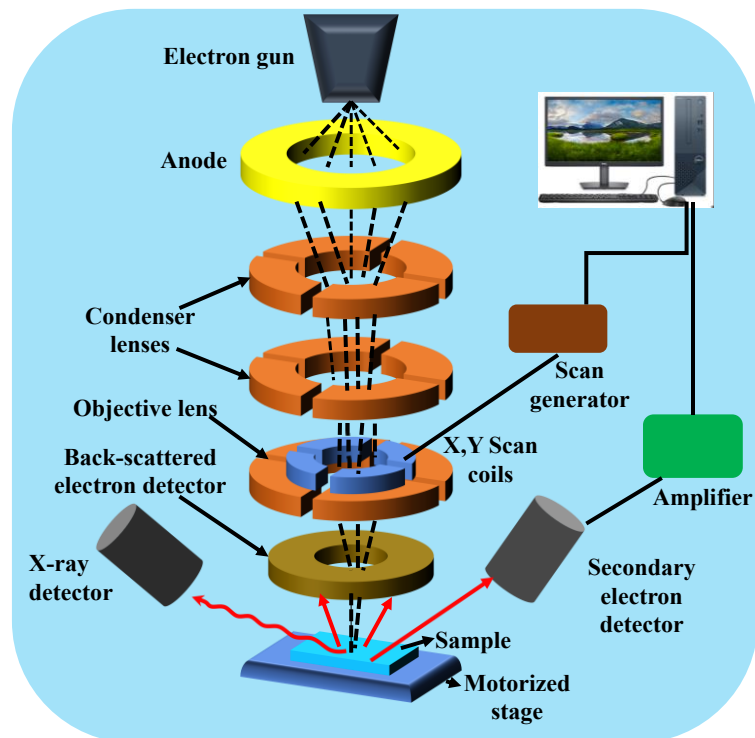


Figure 26. Schematic diagram of SEM

As the electron beam interacts with the specimen, it loses energy through repeated scattering and absorption within the material. These interactions cause the emission of various signals: elastically scattered electrons (reflected), electromagnetic radiation, and secondary electrons (from inelastic scattering). These emissions are captured by detectors. The resulting signals are amplified and displayed on a cathode ray tube (CRT), allowing high-resolution image capture via connected cameras.

Additionally, the x-rays emitted during electron-specimen interactions can be analyzed to determine the elemental composition of the sample using techniques such as Energy

Dispersive X-ray Analysis (EDAX), which requires appropriate accelerating voltages. Importantly, the specimen must be electrically conductive; non-conductive samples are usually coated with a conductive material to enable accurate imaging.

Energy Dispersive X-ray Analysis (EDAX) is a vital technique used to identify the elemental composition of a sample. It is based on the principle that each element has a unique atomic structure, which results in characteristic peaks in the X-ray spectrum [Goldstein, 2003]. The X-rays responsible for this analysis are emitted by electrons transitioning from inner atomic shells, and the energy or frequency of these X-rays is directly related to the atomic number of the element, as described by the equation:

$$E = C_1 (Z - C_2)^2$$

In this formula, C_1 and C_2 are constants that vary depending on the specific electron transitions (such as K, L, or M lines). By knowing the energy values of these characteristic lines, the atomic number of the element—and thus its identity—can be determined [Goldstein, 2003]. Figure 2.5 presents a schematic diagram illustrating electron transitions within an atom.

To prepare a sample for elemental analysis and surface morphology studies, the material is first finely ground and dispersed in a suitable solvent. The resulting suspension is then deposited onto a carbon-coated film and placed into the SEM chamber. The chamber is evacuated to create a low-pressure environment, and the sample is scanned using a high-voltage electron beam. This process allows for both the visualization of surface features and the determination of elemental composition through the images and spectra generated.

3.5.4 FTIR Spectrometer

Fourier Transform Infrared (FTIR) spectroscopy is a cost-effective, fast, straightforward, and non-destructive analytical technique that holds great potential for broader application in material analysis [Berthomieu et al., (2009)]. This method utilizes infrared (IR) spectroscopy to obtain spectra based on emission, absorption, and Raman scattering properties of solids, liquids, or gases. When infrared radiation passes

through a sample, part of the radiation is absorbed while the rest is transmitted. The resulting FTIR spectrum reflects both molecular absorption and transmission characteristics.

FTIR analysis provides valuable insights into the vibrational and rotational behaviors of chemical bonds and the molecular structure of materials. The peaks observed in an FTIR spectrum correspond to the vibrational frequencies of atomic bonds within the sample. Since each material has a unique FTIR spectrum—akin to a molecular fingerprint—this technique is highly effective for identifying unknown substances. No two different materials share the same FTIR signature, making it a reliable tool for substance identification [Banwell and McCash, 1994; Colthup et al., 1964]. Additionally, the intensity of the peaks in the spectrum can be used to estimate the quantity of a substance present in a sample. The IR region used in FTIR spectroscopy is generally divided into three parts based on wavelength: near-infrared, mid-infrared, and far-infrared.

In a traditional FTIR instrument, a prism or diffraction grating is used to disperse the infrared radiation from the source into individual frequencies, much like a prism disperses white light into its component colors. However, this method was time-consuming because it required scanning each frequency individually. To overcome this limitation, FTIR instruments use an optical device called an interferometer, which allows simultaneous measurement of all IR frequencies. The interferometer encodes the full IR spectrum into a unique signal. This encoded signal, which cannot be directly interpreted, must be decoded into individual frequency components using a mathematical process known as Fourier transformation. This approach significantly reduces the time needed for analysis and enhances the efficiency of the technique.

A typical FT-IR (Fourier Transform Infrared) spectrometer comprises three main components: the IR source, the interferometer, and the detector. The infrared source is usually a glowing blackbody that emits broad-spectrum IR radiation. This emitted IR energy first passes through an aperture, which regulates the amount of energy directed toward the sample to ensure appropriate intensity for analysis. The regulated IR beam then enters the **interferometer**, the core component of FT-IR instruments. The

Michelson interferometer is the most commonly used design. It consists of a beam splitter, a fixed mirror, and a movable mirror. The beam splitter divides the incoming IR radiation into two separate beams. One beam reflects off the fixed mirror and travels a constant path length, while the other beam reflects off the movable mirror, resulting in a varying path length due to its motion. As the two beams are reflected back to the beam splitter, they recombine and interfere with each other. This interference creates a complex signal pattern known as an interferogram, which contains encoded information about all the IR frequencies present in the original beam.

The interferogram then passes through the sample chamber, where interaction with the sample generates IR absorption signals based on the material's molecular structure. Finally, these signals reach the detector, which captures the data for further analysis. Using Fourier transformation, the complex interferogram is mathematically converted into a conventional IR spectrum, revealing detailed information about the sample's molecular composition.

3.5.5 Photoluminescence spectrometer

Photoluminescence (PL) is a phenomenon where a material spontaneously emits light as a result of optical excitation. This emission occurs when a material absorbs photons and subsequently re-emits them as it returns to a lower energy state. PL studies serve as a powerful, non-destructive tool for characterizing a wide range of material properties [Gfroerer et al., (2000)]. They provide valuable insights into the electronic structure of a material, and are particularly effective in detecting and analyzing electronic states due to their high sensitivity.

PL spectroscopy allows for the identification and analysis of various features within a material, including surface states, interface characteristics, and impurity levels. By analyzing the emission spectra generated during a PL measurement, researchers can distinguish these features with precision. Furthermore, the transient PL intensity resulting from pulsed excitation can be used to determine the lifetime of bulk states or non-equilibrium interfaces, providing dynamic information about carrier recombination processes. Temperature changes can significantly affect PL emission

intensity, making PL spectroscopy an effective method for studying temperature-dependent behaviors in materials. Time-resolved photoluminescence (TRPL) is particularly important for investigating ultrafast processes within materials, as it can capture rapid changes in emission over short time scales. However, materials with inherently low radiative efficiency may not yield significant results with conventional PL techniques, requiring more specialized methods for analysis. The optical activity of a material—its ability to absorb and emit light—plays a critical role in determining impurity levels and other electronic properties. PL excitation and emission spectra are typically recorded using a fluorometer, an instrument specifically designed for fluorescence analysis. There are two primary types of fluorometers: the filter fluorometer and the spectrofluorometer.

In a filter fluorometer, optical filters are employed to isolate specific wavelengths of incident and emitted light. In contrast, a spectrofluorometer uses a monochromator, usually incorporating a diffraction grating, to perform this wavelength selection with higher precision. Although spectrofluorometers are generally more expensive than filter fluorometers, they offer significant advantages. The primary benefit is their ability to scan across a broad wavelength range, enabling more detailed spectral analysis of the sample.

Despite the differences in wavelength selection mechanisms, the fundamental working principle of both types of fluorometers remains the same. Light from a source—typically within the excitation range of the target material—passes through an excitation filter or monochromator. This component ensures that only light of the desired energy reaches the sample. Upon exposure to this light, the sample becomes excited, absorbing energy and subsequently emitting fluorescence as it relaxes back to its ground state.

The emitted fluorescence is radiated in all directions, but only a portion of it is collected for detection. Before reaching the detector, this emission passes through a second monochromator or emission filter, which serves to block unwanted light such as Rayleigh and Raman scattered photons. To minimize interference from the excitation light, the emission filter is commonly placed at a 90-degree angle relative

to the incident light path. This orthogonal configuration significantly enhances the signal-to-noise ratio, thereby improving detection sensitivity and lowering the detection limit, especially compared to a 180-degree geometry [Rendell, 1987]. Fluorometers rely on various light sources to excite fluorescent molecules, and several types of lamps and light-emitting devices are commonly utilized for this purpose. Traditional light sources used in fluorometric analysis include xenon arc lamps, xenon-mercury arc lamps, high-pressure mercury vapor lamps, and more recently, light-emitting diodes (LEDs), as noted by Lakowicz (1983). Among these, xenon arc lamps are one of the most widely used sources due to their ability to emit a continuous and broad spectrum of light, typically covering a wavelength range from approximately 190 nanometers (nm) to 1200 nm. This broad spectral output makes xenon lamps highly suitable for exciting a wide range of fluorophores, as they can emit both ultraviolet and visible light. Furthermore, their consistent and intense light output enhances the sensitivity of the fluorometric measurements. However, while xenon-mercury arc lamps and mercury vapor lamps are also used in certain contexts, their application in fluorometry is somewhat limited. Mercury vapor lamps, in particular, are less suitable for general-purpose fluorometric applications because they emit light at specific, narrow wavelengths corresponding to the mercury emission lines. This concentrated spectral output does not provide the flexibility required for exciting different fluorophores, especially those needing wavelengths outside the mercury spectrum.

On the other hand, laser light sources, while highly monochromatic and intense, present certain limitations in fluorometric setups. The main advantage of lasers is their extremely narrow emission bandwidth, which eliminates the need for additional optical components such as excitation filters or monochromators. However, this same characteristic becomes a drawback in practice. Since lasers emit at a fixed wavelength, they lack the tunability required to adapt to different excitation requirements. This makes them less versatile and somewhat inconvenient for applications that demand flexibility in the excitation wavelength.

In recent years, LEDs have emerged as a highly promising alternative light source for fluorometers. LEDs offer numerous benefits that make them attractive for both current and future fluorometric technologies. Their low power consumption and long operational lifespan reduce maintenance costs and energy usage, making them economically and environmentally favorable. Moreover, LEDs are now available in a wide array of emission wavelengths, which allows for better matching with specific fluorophores and enhances the efficiency of fluorescence excitation. With ongoing technological advancements, the spectral range and brightness of LEDs continue to improve, positioning them as a leading choice for future fluorometric instrumentation.

Aside from light sources, the detection system in a fluorometer plays a crucial role in determining sensitivity and signal quality. Photomultiplier tubes (PMTs) are commonly employed for detecting fluorescence signals due to their ability to amplify weak light signals effectively. A typical PMT contains multiple dynodes—usually between 6 to 12—which work in succession to amplify the photoelectron signal generated by incoming photons. The output from the PMT is an anodic current that correlates with the intensity of the detected light.

However, the performance of a PMT is highly sensitive to the supplied voltage. While increasing the voltage can boost the signal gain and improve detection sensitivity, it also significantly amplifies the background noise. Excessively high voltages may lead to a poor signal-to-noise ratio, compromising the accuracy and reliability of the measurements. Therefore, it is essential to optimize the operating voltage to strike a balance between maximizing signal strength and minimizing noise. This trade-off is critical in ensuring high-quality fluorescence measurements and underscores the importance of careful calibration and system tuning in fluorometric analysis.

In conclusion, the choice of light source and detection system in fluorometry has a profound impact on the performance of the instrument. While traditional lamps like xenon arc sources offer broad-spectrum output, newer technologies such as LEDs provide significant advantages in terms of energy efficiency, wavelength specificity, and operational longevity. At the same time, the effectiveness of detection components like PMTs is contingent upon proper voltage regulation to maintain an optimal balance

between sensitivity and noise. Collectively, these considerations shape the ongoing development of more efficient, versatile, and precise fluorometric systems.

3.5.6 Ultraviolet (UV) Spectrometer

The Ultraviolet (UV) Spectrometer is a type of spectrophotometer that measures light absorption in the ultraviolet and visible regions (typically from 200–800 nm). UV spectroscopy began in the early 19th century when Johann Wilhelm Ritter discovered ultraviolet light in 1801, noticing that invisible rays beyond violet could cause chemical reactions [Perkampus et al., (2013)]. This set the stage for later discoveries about how light interacts with matter. By the early 20th century, the development of quantum theory helped scientists understand that molecules absorb UV light due to electronic transitions. This led to the creation of instruments that could measure this absorption. A major breakthrough came in the 1940s with the invention of the Beckman DU spectrophotometer, the first widely used commercial UV-vis spectrometer. It made UV spectroscopy more accessible and reliable for scientific analysis. Since then, UV spectroscopy has become a core technique in chemistry, biology, and environmental science, evolving with advances in optics and electronics.

A UV spectrometer operates by analyzing how a substance absorbs light in the ultraviolet and visible regions of the electromagnetic spectrum—typically between 200 and 800 nanometers. The key principle behind this is that molecules can absorb energy from UV or visible light, which causes electrons within the molecules to become “excited”—they jump from a lower energy level to a higher one. This absorption is specific to each compound, depending on its molecular structure, especially its electronic configuration and the presence of conjugated double bonds or aromatic rings. The process begins with a light source, which is usually a deuterium lamp for the UV region and sometimes a tungsten-halogen lamp for the visible region. This light is directed through a monochromator, which uses a prism or diffraction grating to separate the light into individual wavelengths. The instrument then selects a specific wavelength to pass through the sample. The sample is placed in a cuvette, usually made of quartz (since regular glass absorbs UV light and would interfere with the results). As the light passes through the sample, some of it is absorbed depending

on the substance's chemical makeup, and the rest is transmitted through. After the light passes through the sample, a detector measures the intensity of the transmitted light. A common type of detector is a photodiode or a photomultiplier tube, which converts the light into an electrical signal. This signal is then processed and displayed as an absorbance value, typically plotted on a graph showing absorbance versus wavelength—called an absorption spectrum. The amount of light absorbed at each wavelength can be related to the concentration of the absorbing species in the sample using Beer-Lambert's law, which states that absorbance is directly proportional to the concentration of the substance and the path length of the light through the sample.

Beer-Lambert's law equation (7):

$$A = \text{Log}_{10} \left(\frac{I_0}{I} \right) = \epsilon \cdot c \cdot l$$

Where

I_0 : intensity of the incident light,

I : intensity of the transmitted light,

ϵ : molar absorptivity,

c : concentration

l : path length.

This makes UV spectroscopy not only useful for identifying compounds based on their unique spectra but also for quantifying how much of a compound is present in a solution.

3.5.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a powerful technique used to analyze the surface composition and chemical states of materials. It emerged in the mid-20th century as scientists sought better ways to understand the composition and electronic structure of material surfaces [Seah et al., (1980)]. The technique was developed

primarily by Swedish physicist Kai Siegbahn and his research team during the 1950s and 1960s. They built upon earlier work on the photoelectric effect, applying it to X-rays to eject electrons from materials and analyze their energy. This led to the creation of XPS as a surface-sensitive analytical method capable of detecting not just elements but also their chemical states. Siegbahn's pioneering work was recognized globally, and in 1981, he was awarded the Nobel Prize in Physics for his development of high-resolution electron spectroscopy, which included XPS. Since then, the technique has evolved significantly, with advances in vacuum technology, detectors, and data processing making modern XPS systems more powerful, precise, and accessible for a wide range of scientific and industrial applications.

XPS is based on the photoelectric effect, a fundamental physical process first explained by Albert Einstein, where photons (light particles) strike a material and cause electrons to be ejected. In XPS, instead of using visible or ultraviolet light, the technique uses X-rays to excite the atoms in a solid material. When X-rays with a known energy strike the surface of a sample, they interact with the atoms in the material and can knock electrons out of their inner (core) shells. These ejected electrons are called photoelectrons. The energy required to remove an electron from an atom is known as the binding energy, which is unique to each element and sensitive to its chemical environment. The core idea of XPS is to measure the kinetic energy of these photoelectrons as they escape from the surface of the sample. Because the energy of the incoming X-rays is precisely known, and we can measure the kinetic energy of the outgoing electrons, we can calculate the binding energy of each electron using the equation:

$$E_b = h\nu = E_k - \phi$$

Here:

- E_b is the binding energy of the electron,
- $h\nu$ is the energy of the X-ray photon (typically Al K α or Mg K α radiation),
- E_k is the measured kinetic energy of the photoelectron,

- ϕ is the work function of the spectrometer (a correction factor).

Once the binding energies are calculated, they can be matched to known values in XPS databases to determine what elements are present. But XPS doesn't stop there—it can also detect chemical shifts, which are slight changes in binding energy due to differences in the chemical state or bonding of the atom. For example, iron in Fe^{2+} will show a different peak position than iron in Fe^{3+} . Because photoelectrons can only escape from the uppermost layers of a material (due to their short inelastic mean free path), XPS is inherently a surface-sensitive technique. It typically probes a depth of about 1 to 10 nanometers.

The entire process takes place in an ultra-high vacuum (UHV) chamber to ensure that the electrons travel freely to the detector without colliding with air molecules. The sample is placed inside this chamber, exposed to the X-ray beam, and a spectrometer measures the energies of the emitted electrons. Advanced XPS systems may also include tools for depth profiling (e.g., by sputtering away surface layers) or mapping, which allows for the spatial distribution of elements across the surface to be visualized.

In summary, XPS works by using X-rays to eject electrons from a material's surface and measuring their energies to identify the elements present, their amounts, and their chemical states—all within just a few nanometers of the surface. This makes it an incredibly valuable tool for analyzing coatings, corrosion, thin films, and surface treatments across a wide range of materials.

3.5.8 Raman Spectroscopy

Raman Spectroscopy is a non-destructive analytical technique used to study the vibrational, rotational, and other low-frequency modes in a system (usually molecules). Raman spectroscopy traces its origins back to 1928, when the Indian physicist Chandrasekhara Venkata Raman discovered the phenomenon now known as the Raman Effect [Keresztury et al., (2002)]. Raman, while studying the scattering of light, observed that when light passes through a material, most of it is scattered without any change in wavelength, a process known as Rayleigh scattering. However, a small fraction of the light was scattered at different wavelengths, which was a clue that the

scattered light had interacted with the molecular vibrations of the material. This discovery was revolutionary because it provided a way to study the vibrational energy states of molecules, offering insights into their structure and composition. Raman spectroscopy remained challenging for many years, primarily due to the weak intensity of the Raman scattered light, which made it difficult to detect and measure.

The true potential of Raman spectroscopy began to be realized in the 1960s with the invention of the laser. The laser provided a monochromatic, intense light source that was perfect for exciting Raman scattering, greatly enhancing the sensitivity and effectiveness of Raman spectroscopy. This marked the beginning of its widespread adoption in laboratories and industry. The development of more sophisticated detectors, computational tools, and optical components over time made Raman spectroscopy increasingly accessible and versatile, allowing it to be used across a wide variety of fields, from chemistry and material science to medicine and art restoration.

Raman spectroscopy is based on a phenomenon called the Raman Effect, which occurs when light interacts with molecules. It all starts with a laser (usually a monochromatic light source, often in the visible or infrared spectrum) being directed at a sample. The laser light strikes the sample, and most of the light is scattered by the sample in the same direction and with the same energy, a process known as Rayleigh scattering. This scattered light doesn't give any new information about the sample—it's essentially just a reflection of the incoming laser. However, a small fraction of the light undergoes a different kind of scattering, known as Raman scattering, where the energy of the scattered light changes. This energy shift is crucial because it contains information about the vibrational modes of the molecules within the sample. When a photon (light particle) interacts with the sample, it can transfer some of its energy to the molecules (if the photon loses energy) or absorb some of the molecule's energy (if the photon gains energy). In Stokes scattering (the more common type), the photon loses energy to the molecule and thus has a longer wavelength than the incident light. On the other hand, in Anti-Stokes scattering, the photon gains energy from the molecule, resulting in a shorter wavelength than the incident light. These shifts in wavelength correspond to the specific vibrational modes of the molecules in the

sample. The amount of energy lost or gained depends on the nature of the vibrations in the sample, such as how the atoms are bonded, their masses, and how the atoms move within the molecule. These vibrational modes are unique to each molecule, and because of this, the shifts in light can act like a "fingerprint" for the substance being analyzed. Once the scattered light is collected, it passes through a filter to remove the Rayleigh scattered light (which is the intense light at the same wavelength as the laser) and is then directed to a detector. The detector measures the intensity of the scattered light as a function of its wavelength shift from the incident light. This data is then plotted as a Raman spectrum, which shows peaks at different wavelengths. Each peak corresponds to a particular vibrational mode of the sample's molecules, providing insight into the chemical composition and structural characteristics of the material.

In this way, Raman spectroscopy enables scientists to study the molecular and atomic structure of materials without needing to modify or destroy the sample, making it a non-destructive technique. It is also incredibly powerful because the Raman spectrum can reveal a lot of information about a substance, including bond types, functional groups, crystallinity, and even the stress or strain in materials. Thus, Raman spectroscopy works by analyzing how light interacts with the vibrations of molecules, providing a detailed molecular fingerprint that can be used to identify and characterize materials in a variety of fields like chemistry, biology, medicine, and materials science.

3.5.9 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a type of scanning probe microscopy that provides incredibly detailed images of surfaces at the nanometer scale. Rather than using light or electrons (as in optical or electron microscopes), AFM uses a mechanical probe to feel the surface of a sample. The AFM was invented in 1986 by Gerd Binnig, Calvin Quate, and Christoph Gerber. It was developed as a complementary technique to the Scanning Tunneling Microscope (STM), which Binnig had co-invented a few years earlier in 1981 at IBM Zurich. At the heart of an AFM system is a tiny, sharp tip mounted on the end of a flexible cantilever [Magonov et al., (2008)]. This tip is extremely fine—just a few nanometers in diameter—allowing it to interact with the sample surface at the atomic or molecular level. The cantilever acts like a spring. When

the tip comes close to the surface of the sample, various forces between the tip and the sample (such as van der Waals forces, electrostatic forces, or chemical bonding forces) cause the cantilever to deflect. Now, this deflection is the key to imaging. A laser beam is focused onto the back of the cantilever, and as the cantilever bends, the reflected laser beam changes its angle. This reflected beam is detected by a photodiode or a position-sensitive detector, which measures even the tiniest changes in the cantilever's position. By monitoring this deflection, the system can detect how the tip is interacting with the surface at any given point. As the tip scans across the surface (usually in a raster pattern), the system keeps the interaction force between the tip and the sample constant. This is typically done using a feedback loop that adjusts the height of the cantilever up or down as needed. The amount of vertical movement required to keep the force constant is recorded and used to construct a topographic map of the surface.

There are several modes of operation in AFM. The most common are contact mode, tapping (or intermittent contact) mode, and non-contact mode. In contact mode, the tip stays in continuous contact with the surface. This can provide high-resolution images but might damage soft samples. In tapping mode, the cantilever is oscillated near its resonant frequency and only briefly touches the surface during each oscillation—this reduces damage and is useful for delicate samples. In non-contact mode, the tip doesn't touch the surface at all; instead, it senses van der Waals forces from a short distance away.

AFM can do more than just imaging. It can also measure mechanical properties (like stiffness or adhesion), magnetic and electric forces, and even manipulate atoms and molecules. Because it doesn't require any special sample preparation (like coating with metal), and it can work in air, liquid, or vacuum, AFM is extremely versatile and widely used in materials science, biology, and nanotechnology.

CHAPTER 4. RESULTS AND DISCUSSIONS

4.1 Nanoimprint Lithography-Fabricated Zinc Oxide Nanorod-gold Electrode for detection of Cadmium Ions and thiram.

4.1.2 Introduction.

A rapidly emerging interdisciplinary field is evolving at the intersection of electrochemistry and nanotechnology, offering groundbreaking opportunities to revolutionize how we design and utilize materials for a wide range of applications [Chen et al., (2013)], [Rohilla et al., (2021)]. Central to this field is the integration of nanotechnology into electrode surfaces, which has unlocked new avenues for enhancing the performance, efficiency, and specificity of devices used in sensing, energy storage, and electronics [Broza et al., (2013)], [Dong et al., (2012)]. By manipulating material characteristics at the nanoscale level, researchers can impart unique properties to electrodes—features that are often not achievable with conventional, bulk materials [Martínez-Otero et al., (2011)]. Electrodes modified with nanostructured materials exhibit a host of advantageous properties due to their significantly increased surface area, the ability to tailor their chemical reactivity, and their capacity to modulate electrochemical behavior [Yumak et al., (2011)]. These traits are especially crucial for improving the kinetics of electron transfer, which is a key mechanism in many electrochemical processes. Enhanced surface area allows for more active sites where chemical reactions can take place, while customizable reactivity enables selective interaction with specific analytes or compounds. Additionally, fine-tuning the electrochemical characteristics at the nanoscale can lead to improved signal-to-noise ratios and greater sensitivity in sensor devices, or better charge-discharge performance in energy storage systems like batteries and supercapacitors. One of the most compelling examples of nanomaterial-enhanced electrodes is the incorporation of zinc oxide (ZnO) nanorods [Marie et al., (2015)]. ZnO has emerged as a highly promising material due to its wide bandgap (~3.37 eV), excellent electrical conductivity, and superior optical transparency, which make it ideal for use in optoelectronic devices, solar cells, chemical sensors, and biosensors [Mehmandoust et

al., (2022)]. The one-dimensional (1D) nanostructure of ZnO nanorods confers several benefits. First, the rod-like shape inherently increases the surface-to-volume ratio, thereby maximizing the contact area with analytes or electrolytes. Second, the 1D structure provides directional pathways for electron transport, which significantly enhances charge carrier mobility and reduces resistance in electrochemical systems [Rovina et al., (2016)]. These characteristics contribute to faster and more efficient charge transfer processes, which are essential for high-performance electrochemical sensors and energy devices.

In parallel with advancements in material selection and synthesis, nanoimprinting lithography (NIL) has gained traction as a cutting-edge technique for fabricating nanostructures with precise geometrical control [Mohapatra et al., (2018)]. This technique involves the use of a mold or stamp containing nanometer-scale patterns, which is then pressed into a pliable polymer or resist layer coated onto a substrate [Wouters et al., (2004)]. After curing or solidifying the resist, the mold is removed, leaving behind a faithful replica of the nano-patterned design. Nanoimprinting lithography stands out due to its cost-effectiveness, scalability, and high throughput, making it particularly attractive for industrial-scale applications.

NIL enables the creation of customized electrode morphologies with meticulously engineered nanoscale features, which can directly influence and enhance the electrochemical performance of the devices [Pimpin et al., (2012)]. By combining NIL with nanomaterials like ZnO nanorods, researchers can produce highly ordered, reproducible, and application-specific electrode architectures that cater to the demands of next-generation technologies [Liao et al., (2020)]. These technologies include everything from ultra-sensitive medical diagnostic tools to advanced energy harvesting systems and high-resolution electronic displays [Mohapatra et al., (2016)].

Several recent studies have explored various nanomaterial-based electrochemical sensors for the detection of cadmium ions (Cd), each utilizing different strategies for sensor fabrication and material design. For instance, one study reported the successful synthesis of a conductive electrochemical sensor based on a UiO-66-NH₂@PANI composite, where polyaniline (PANI) was polymerized around the amine-

functionalized metal–organic framework (MOF) UiO-66-NH₂. This composite demonstrated high sensitivity toward Cd²⁺ due to the chelation between metal ions and amine groups, achieving a linear detection range from 0.5 to 600 µg·L⁻¹ with a detection limit of 0.3 µg·L⁻¹ [Wang et al., (2017)].

Another related work employed a composite of UiO-66-NH₂ and multi-walled carbon nanotubes (MWCNTs), synthesized via a one-pot hydrothermal method, to construct a voltammetric sensor for Cd²⁺ detection. This sensor exhibited a linear range from 0.5 to 170 µg·L⁻¹ and a detection limit of 0.2 µg·L⁻¹, benefiting from the enhanced conductivity and surface area provided by MWCNTs [Wang et al., (2021)].

Additionally, a separate approach used graphene/graphene oxide (GR/GO) composites—prepared with a high-speed dispersive homogenizer from graphite oxide—as a metal-free alternative for electrochemical sensing. The GR/GO composite electrode offered superior performance over individual GR or GO electrodes, delivering a wide linear range (0–10 µM), high sensitivity, low detection limit (0.087 µM), and excellent stability and selectivity in water samples [Shan et al., (2022)].

In contrast to these studies, the present research introduces a novel and cost-effective methodology for Cd²⁺ ion detection by employing NIL-modified zinc oxide nanorods (ZnONRs) deposited on microscope glass slide substrates. This fabrication approach has not been previously reported for Cd²⁺ detection. The use of readily available and inexpensive microscope slides as the electrode platform significantly reduces production costs, making the technique more accessible and practical for broader applications. Furthermore, the study focuses on optimizing the arrangement and distribution of ZnONRs on the electrode surface and investigating their electrochemical performance in detecting heavy metal ions. This distinct fabrication method, coupled with the use of NIL modification and ZnONRs, sets this research apart from earlier works and underscores its potential for developing affordable and efficient sensing technologies.

4.1.3 Results and Discussion

4.1.3.1 XRD analysis

X-ray diffraction (XRD) examination was systematically conducted for evaluating the crystalline structure of the synthesized zinc oxide (ZnO) nanostructures. The examination was performed employing a X-ray diffractometer (Rigaku Oxford Diffraction SuperNova), which is known for its high accuracy and performance in materials characterization. This instrument utilized a copper (Cu) $K\alpha$ radiation source having wavelength of 1.5406 Å, a standard choice for XRD studies due to its effectiveness in probing crystal structures. The diffractometer operated in a parallel beam mode configuration, which minimizes specimen displacement errors and enhances peak resolution.

All the patterns were recorded within 2θ range from 10° to 80° , allowing for the detailed observation of all significant diffraction peaks associated with the material under investigation. A step size of 0.02° was used during the scan, ensuring high-resolution data, while the scan rate was maintained at 20 degrees per minute to optimize the balance between speed and data quality. The operating conditions were consistently maintained at 40 kV and 40 mA throughout the measurement process to ensure stable X-ray output and reproducible results.

In Figure 27, the XRD pattern of the ZnO nanostructures, synthesized via a hydrothermal method and deposited onto a thin film gold electrode, is exhibited. The pattern reveals a series of sharp and intense peaks, signifying the high crystallinity of the ZnO material. Prominent diffraction peaks were noted at 2θ values of 31.91° , 34.39° , 36.31° , 47.43° , 56.80° , and 77.73° , which are associated with the (100), (002), (101), (102), (110), and (202) planes characteristic of the hexagonal wurtzite phase of ZnO. [Li et al., (2008)]. These values are in excellent concurrence with the standard reference data from JCPDS card No. 36-1459 [Kathalingam et al., (2012)], confirming the successful formation of the desired ZnO phase.

In addition to the ZnO peaks, characteristic diffraction peaks of gold (Au) originating from the underlying electrode substrate were also identified. These peaks were observed at 2θ positions of 38.35° , 44.69° , and 64.76° , which correspond to the (111),

(200), and (220) planes of face-centered cubic (FCC) gold, in agreement with the standard JCPDS reference data for Au (Card No. 04-0784).

The Scherrer equation was employed to estimate the average crystallite size of the ZnO nanostructures [Tankhiwale et al., (2012)], which relates the broadening of XRD peaks to the size of coherent diffraction domains. The analysis yielded an average crystallite size of approximately 16.12 nm, consistent with the expected nanorod morphology. This nanoscale dimension further supports the successful synthesis of ZnO nanostructures with controlled dimensions.

The Scherrer equation is given by:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where:

- D = average crystallite size (in nanometers)
- K = shape factor (typically around **0.9**, depending on crystallite shape)
- λ = X-ray wavelength (for Cu $K\alpha$, **1.5406 Å**)
- β = full width at half maximum (FWHM) of the diffraction peak (in **radians**)
- θ = Bragg angle (i.e., half of the 2θ value)

The observed slight shift in the ZnO diffraction peak positions, when compared to standard reference data, can be attributed to **lattice strain** introduced by the gold thin film electrode used as the growth substrate. This strain likely arises from differences in **lattice constants** or **thermal expansion coefficients** between the ZnO and the gold substrate, resulting in either compressive or tensile stress within the ZnO crystal lattice. Such stress can cause minor distortions in the crystal structure, which manifest as peak shifts in the XRD pattern. This observation highlights the significant role of the substrate in dictating the **crystallographic orientation, lattice parameters, and overall structural integrity** of ZnO nanorods (ZnONRs), especially in thin film systems.

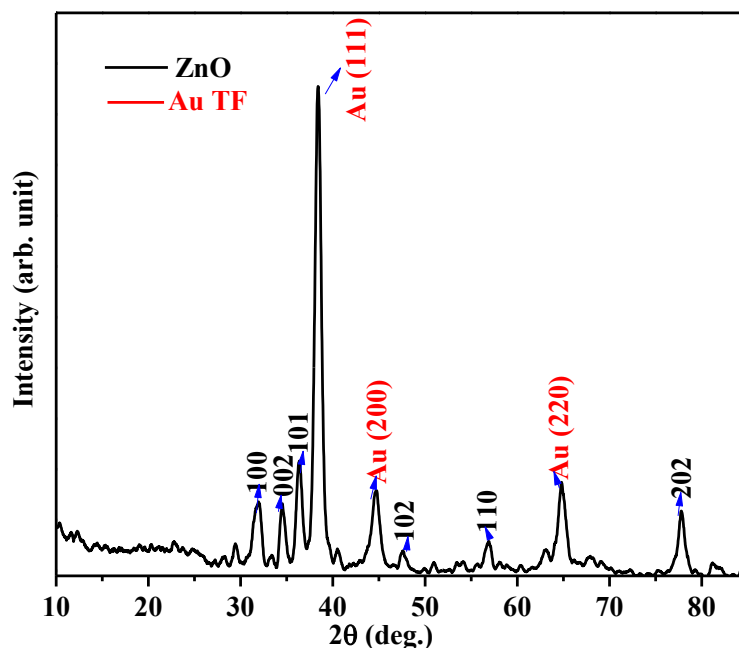


Figure 27. XRD pattern of thin film Au electrode modified with ZnO.

4.1.3.2 FESEM images and TEM analysis

Field Emission Scanning Electron Microscopy (FE-SEM) examination was performed using a Zeiss Supra 55 to investigate the morphology and microstructure of the samples. The system operated at an accelerating voltage of 5 kV, which enabled the acquisition of high-resolution surface images. Constituent elements were evaluated through EDS using an Oxford X-Max detector under the same 5 kV operating voltage, with a working distance sated to 10 mm and a data acquiring period of 60 seconds. High-Resolution Transmission Electron Microscopy (HR-TEM) was performed with a Thermo Scientific Talos F200X G2 instrument at 200 kV accelerating voltage. A minimal quantity of ZnO was dispersed in 1 mL of ethanol and ultrasonicated for 10 minutes for HRTEM analysis. This suspension was then drop-cast onto a copper grid and allowed to dry overnight at room temperature in a contamination-free environment. Figure 28 (a) shows the FE-SEM surface morphology of the ZnO seed layer deposited onto a Au thin film electrode. The image confirms that the PDMS spin-coated ZnO seed layer successfully replicated the distinct CD grating structure. Figures 28 (b–c) depict the hydrothermally synthesized ZnO nanorods (ZnONRs) formed on

the thermally treated seed layer. The corresponding EDS spectrum, shown in Figure 28 (d), reveals prominent peaks for Zn, O, Au, Si, and C. The peaks for Zn and O are attributed to the ZnO nanorods, while the Au signal arises from the underlying gold electrode. The Si peak originates from the microscope glass slide used as a substrate, and the C peak is attributed to both the carbon tape used during sample mounting and the presence of minor organic impurities.

Further morphological details of ZnONRs were obtained using TEM and HR-TEM. Figure 29 (a) displays a representative TEM image of the ZnONRs, while Figure 29 (b) shows their HR-TEM structure. The HR-TEM image analysis indicates d-spacing of 0.24 nm, corresponding to the [101] crystal planes, suggesting preferential growth in the [101] direction with a hexagonal wurtzite structure [Wahab et al., (2009)], [Wang et al., (2006)]. Additionally, the inset of Figure 29 (a) features a Small Angle Electron Diffraction (SAED) pattern exhibiting concentric bright rings, indicating the single-crystalline nature of the ZnONRs [Agnihotri et al., (2015)].

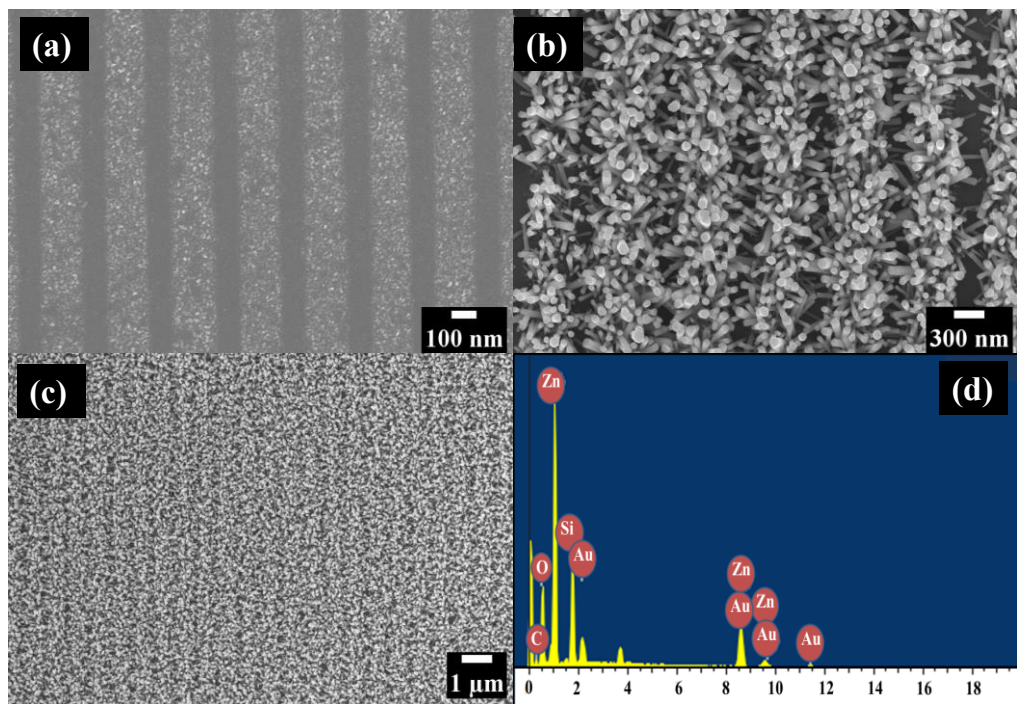


Figure 28. (a) FESEM image of the ZnO seed layer coated on the surface of the Au electrode, where the coating process preserved the CD grating pattern. (b) And (c)

FESEM images depicting the ZnONRs growing on the CD grating-patterned ZnO seed layer. (d) EDS spectra of Au electrode surface modified with ZnONRs.

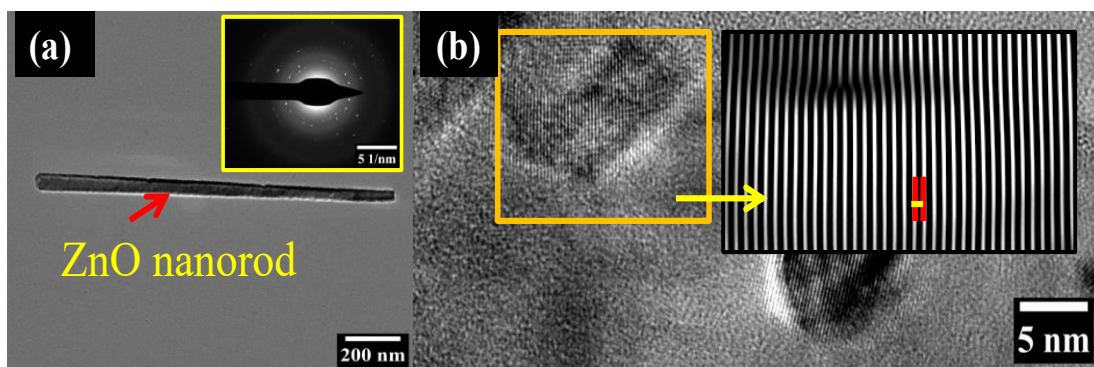


Figure 29. (a) TEM image shown by modified ZnONRs as well as its SAED pattern (inset) (b) HR-TEM image of ZnONRs.

4.1.4 Electrochemical analysis

4.1.4.1 Active surface area of the working electrode

The sensitivity of an electrochemical sensing platform is highly influenced by the working electrode's active surface area. A larger active surface area generally leads to increased sensitivity, making this parameter critical for accurate electrochemical measurements [Sawkar et al., (2022)]. In this study, the active surface areas of a bare gold (Au) electrode and a gold electrode modified with zinc oxide nanorods (ZnONRs-Au) were evaluated using cyclic voltammetry (CV). The measurements were carried out in an aqueous solution of 0.1 M KCl containing 0.001 M of the redox couple $\text{K}_3[\text{Fe}(\text{CN})_3]/\text{K}_4[\text{Fe}(\text{CN})_6]$.

Figure 30 presents the cyclic voltammograms obtained from both electrodes under identical conditions. The ZnONRs-Au electrode exhibited a significantly higher peak current, both in oxidation and reduction, within the potential sweep of -0.2 V to 0.8 V, when differentiate to the bare Au electrode. This indicates enhanced electrochemical activity due to the modification with ZnONRs. The inset of Figure 30 clearly illustrates the difference in oxidation peak currents between the two electrodes. To quantify the

active surface area of the electrodes, the Randles-Sevcik equation was applied [Sawkar et al., (2021)]:

$$I_p = (2.69 \times 10^5).n^{3/2}.A.D_o^{1/2}.v^{1/2}.C$$

In this equation:

- I_p is the peak current (in amperes),
- n is the number of electrons involved in the redox reaction,
- A is the active surface area of the electrode (in cm^2),
- D_o is the diffusion coefficient of the redox species ($7.6 \times 10^{-6} \text{ cm}^2/\text{s}$) [Bukkitgar et al., (2018)],
- v is the scan rate of the voltammetry experiment (in V/s),
- C is the concentration of the redox species (1 mM).

Based on this equation, the active surface area was estimated to be 0.29 mm^2 for the bare Au electrode and 0.40 mm^2 for the ZnONRs-Au electrode. This substantial increase in surface area with ZnONRs modification is attributed to the nanostructured morphology of the ZnO nanorods, which provides a highly textured and porous surface. Such a surface architecture allows for more electroactive sites to be available for redox reactions and enhances the interface between the electrode and the electrolyte. As a result, the ZnONRs-Au electrode facilitates more efficient charge transfer processes, which is manifested as higher current responses in the cyclic voltammograms. This improved electron transfer capability directly contributes to better performance in electrochemical sensing applications, making ZnONRs-Au a superior choice over a flat, bare gold electrode. Figure 31 (a) displays the cyclic voltammetry (CV) response of the ZnONRs-Au electrode at varying scan rates in an electrolyte solution composed of 0.1 M potassium chloride (KCl) and 1mM potassium ferricyanide/ferrocyanide ($\text{K}_4 [\text{Fe} (\text{CN})_6]/\text{K}_3 [\text{Fe} (\text{CN})_6]$). As illustrate in the voltammograms, the peak current increases as the scan rate increases. This behaviour

is characteristic of electrochemical systems where the redox mechanism is influenced by both electrons transfer kinetic and the diffusion of electroactive species. At higher scan rates, the redox species have less time to diffuse to the electrode surface before the potential changes, which typically leads to sharper and higher peak currents. However, the limited diffusion time can also reduce the total charge passed, affecting the shape of the voltammogram. Despite this, a consistent trend of increasing current with increasing scan rate is observed, reflecting enhanced current response due to faster potential sweeping. Figure 31 (b) illustrates a graph showing the relationship between anodic peak current and the square root of the scan rate. The data reveals a strong linear relationship, defined by the equation $y = 18.508x + 122.2$, with a correlation coefficient $r^2 = 0.996$. This strong linear correlation suggests that the redox process is primarily controlled by diffusion kinetics, rather than surface adsorption or other rate-limiting factors. In electrochemical systems, a linear relationship between peak current and the square root of the scan rate, as described by the Randles–Ševčík model, indicates the rate at which the redox species reach the electrode surface is controlled by diffusion through the solution. This implies that the ZnONRs-Au electrode enables efficient electron transfer under diffusion-limited conditions, further supporting its suitability for use in sensitive electrochemical sensing applications.

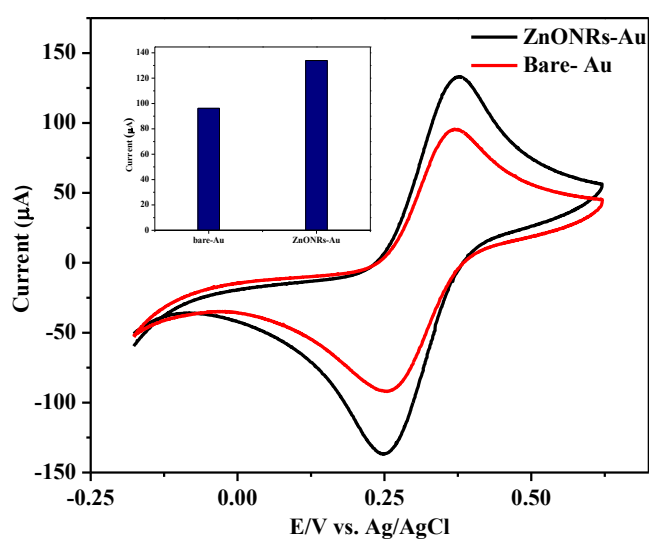


Figure 30. Cyclic voltammograms recorded using a two-electrode setup with ZnO nanorods on Au (black curve) and bare Au (red curve) were obtained in an electrolyte

solution of 0.1 M KCl containing 0.001 M $\text{K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$ (scan rate = 20 mV/s). The corresponding bar graph is shown in the inset.

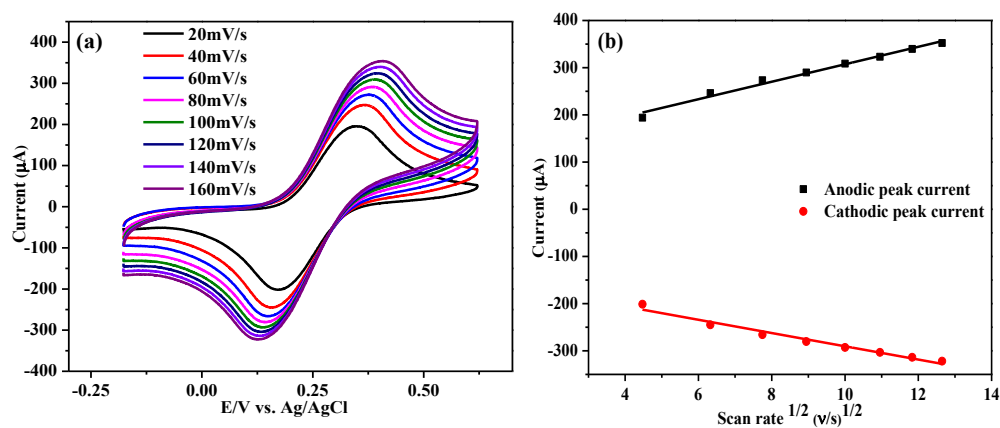


Figure 31 (a) Cyclic voltammograms obtained using the ZnONRs-Au electrode at varying scan rates and (b) the corresponding plot of peak current (I_p) versus the square root of the scan rate.

4.1.4.2 Performance Evaluation of ZnONRs-Au for Cd^{2+} Ion Detection

A comparative study was carried out to assess the electrochemical performance of a bare gold (Au) electrode versus a ZnO nanorod-modified gold electrode (ZnONRs-Au) in the detection of Cd^{2+} ions using cyclic voltammetry (CV). For this purpose, a 0.001 M Cd^{2+} solution prepared in 0.1 M KCl served as the electrolyte. As illustrated in Figure 32, the ZnONRs-Au electrode consistently exhibited higher oxidation peak currents compared to the unmodified Au electrode, highlighting its superior sensitivity and enhanced electron transfer capabilities.

The bare Au electrode, however, demonstrated several limitations. During repeated CV measurements, typically after two to three cycles, the gold layer began to deteriorate, likely due to corrosion under the test conditions. This degradation compromised the structural integrity and electrochemical stability of the electrode, resulting in inconsistent and unreliable readings. In contrast, the ZnONRs-modified electrode displayed significantly improved durability, suggesting that the nanorod coating provides a protective and stable interface for metal ion detection.

To further evaluate its sensing performance, the ZnONRs-Au electrode was employed for the detection of Cd^{2+} ions at varying concentrations. A stock solution of 1 mM Cd^{2+} in 0.1 M KCl was serially diluted to prepare a range of lower concentrations. These were then tested using CV measurements to determine the electrode's sensitivity across different Cd^{2+} ion levels. The CV responses for each concentration are presented in Figure 33 (a). As expected, the oxidation peak current increased proportionally with rising Cd^{2+} ion concentrations, confirming a direct and measurable electrochemical response. The corresponding calibration curve, shown in Figure 33 (b), plots the oxidation peak current against the Cd^{2+} ion concentration. Based on this calibration, the limit of detection (LOD) for the ZnONRs-Au electrode was calculated to be $20.88 \pm 0.9 \mu\text{M}$, demonstrating the electrode's effectiveness in cadmium detection.

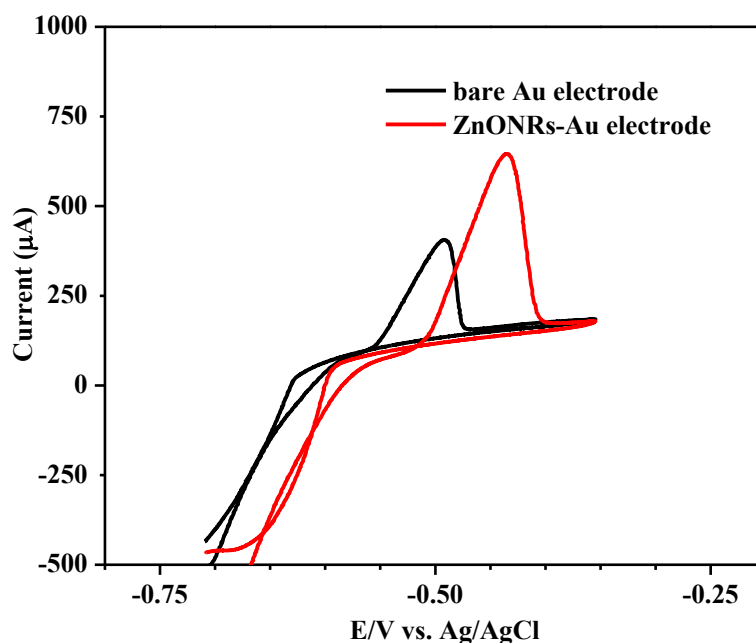


Figure 32. The cyclic voltammogram shown by the ZnONRs-Au electrode in detecting 0.001 M Cd^{2+} ions dissolved in an aqueous solution of 0.1 M KCl in comparison with bare Au electrode (scan rate of 20 mV/s).

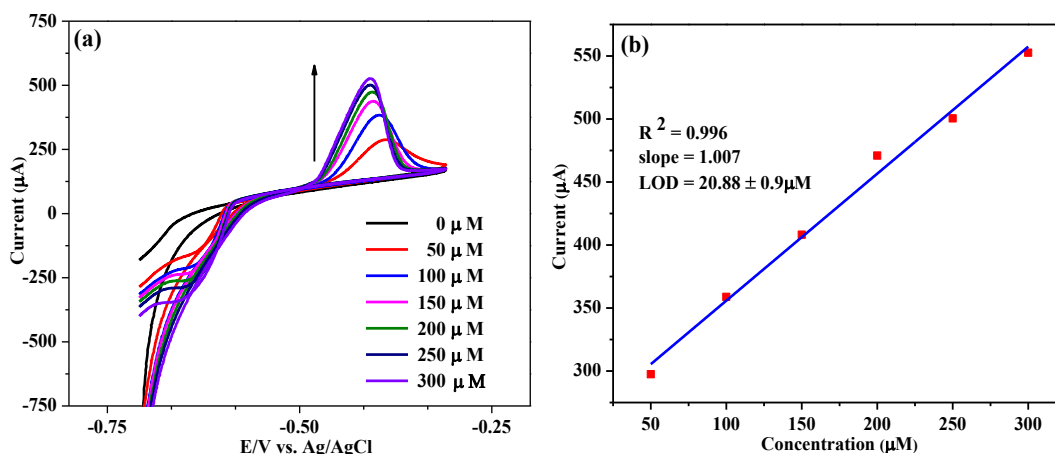


Figure 33. (a) Cyclic voltammograms shown by ZnONRs-Au electrode at varying concentrations of Cd^{2+} containing in an electrolyte solution of 0.1 M KCl at pH 7, and (b) the corresponding calibration curve illustrating the relationship between peak current and Cd^{2+} concentrations.

4.1.4.3 Detection of Thiram Using ZnONRs-Modified Electrode via DPV.

The fabricated zinc oxide nanorod (ZnONRs)-modified electrode was employed for the electrochemical detection of thiram. ZnONRs possess a high surface area and abundant surface defects, which provide numerous active sites for the adsorption of analyte molecules. These characteristics enable the ZnONRs to interact directly with thiram molecules without the need for any additional linking agents. To evaluate the detection capability of the fabricated electrode, a number of thiram solutions with varying levels of concentration were prepared applying the dilution method from a standard stock solution. The ZnONRs-modified electrode was immersed in each solution for 30 minutes at 4 °C to ensure adequate adsorption of thiram onto the electrode surface. After adsorption, the electrochemical response of the electrode was assessed through DPV. The measurements were carried out in an electrolyte solution comprising 0.001 M $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ dissolved in an aqueous solution of 0.1 M KCl (at 20 mV/s scan rate). The peak current (I_p) was measured for each concentration of thiram under consistent conditions.

It was observed that **the current response decreased progressively with increasing concentrations of thiram**. This decrease is attributed to the blocking effect of thiram

molecules adsorbed onto the ZnONRs surface, which block process of electron transfer between the redox species and reactive site of the electrode. A calibration curve plotting peak current (I_p) against thiram concentration exhibited a linear trend, with a correlation coefficient (R^2) of 0.98, as illustrated in Figure 34. Based on this calibration curve, the following analytical parameters were calculated:

- **Limit of Detection (LOD):** 0.74 μM
- **Limit of Quantification (LOQ):** 2.46 μM
- **Sensitivity:** 6.33 $\mu\text{A}/\mu\text{M}$

Table 4. shows the comparison of our developed electrode with other electrode for the detection thiram, and revealing that our result show good and lower LOD.

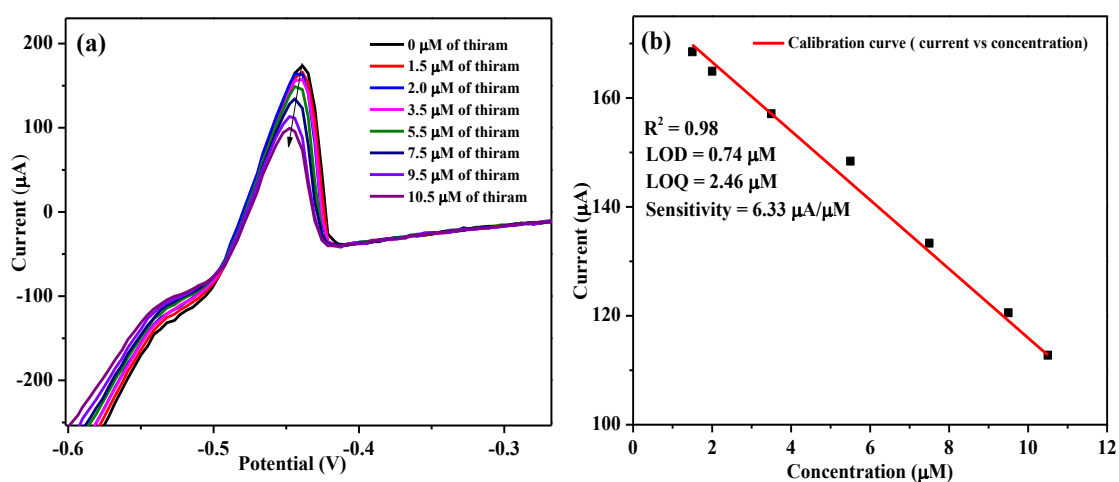


Figure 34 (a) DPV curves of the fabricated ZnONRs-Au recorded at varying concentration of thiram containing in an electrolyte solution of 0.1M KCl (pH of 7) at 20 mV/s scan rate. (b) Calibration curve showing the relationship between current and concentration thiram.

Table 4. Comparison with Previously Reported Electrodes for Thiram Detection

Electrode	Detection technique	LOD	References
PLL@AuNPs/ITO	DPV	2.23 μ M	Wai et al., (2022)
2D-GO@WS2/SPCE	LSV, DPV	0.02 μ M	Abid et al., (2024)
CPE	DPV	2.07 μ M	Ubada et al., (1990)
SPE-MWCNT	SWV	1.60 μ M	Wong et al., (2013)
Pt/AgNPs	DPV and CV	0.731M	Pedro et al., (2025)
ZnONRs-Au	DPV	0.7 μ M	This work
PLL: Poly-L-Lysin, AuNPs: Gold nanoparticles, ITO: Indium tin oxide, 2D: Two dimension, CPE: Carbon paste electrode, SPE-MWCNT: Screen printed electrode-multi-walled carbon nanotubes, Pt: Platinum, AgNPs: Silver nanoparticles, LSV: Linear Sweep Voltammetry, SWV: Square-Wave Voltammetry			

4.1.4.4 Repeatability and reproducibility nature

Figure 35 demonstrates the repeatability of the developed electrode, indicating its ability to produce highly consistent results under identical experimental conditions. To assess repeatability, two cyclic voltammetry (CV) measurements were conducted using the same sensor under a fixed set of parameters. As shown in Figure 35, the current responses from both measurements closely overlap, suggesting minimal variation between successive scans. The calculated relative standard deviation (RSD) of the peak current between the two measurements is only 0.15%, which reflects excellent repeatability. This low RSD value confirms that the developed sensor can reliably reproduce its electrochemical response, an essential characteristic for analytical applications where precision and consistency are critical. These results highlight the potential of the sensor for use in real-time or routine monitoring where repeatable and dependable measurements are required.

Figure 36 illustrates the current response of the developed sensor over a two-week period, highlighting its reproducibility following a preservation process. The sensor's performance was assessed by comparing the post-preservation responses to the initial measurement obtained prior to preservation. After the preservation, two separate measurements were taken at different time points within the two-week duration to evaluate the consistency of the sensor's response. The comparison reveals that the sensor is capable of maintaining a high degree of functional reproducibility over time. Specifically, it was able to recover 95% and 94% of the original peak current during the first and second post-preservation measurements, respectively. These results demonstrate that the developed sensor not only maintains its structural integrity but also retain its electrochemical activity to a significant extent. The findings confirm that the sensor exhibits excellent reproducibility and reliability for potential long-term applications.

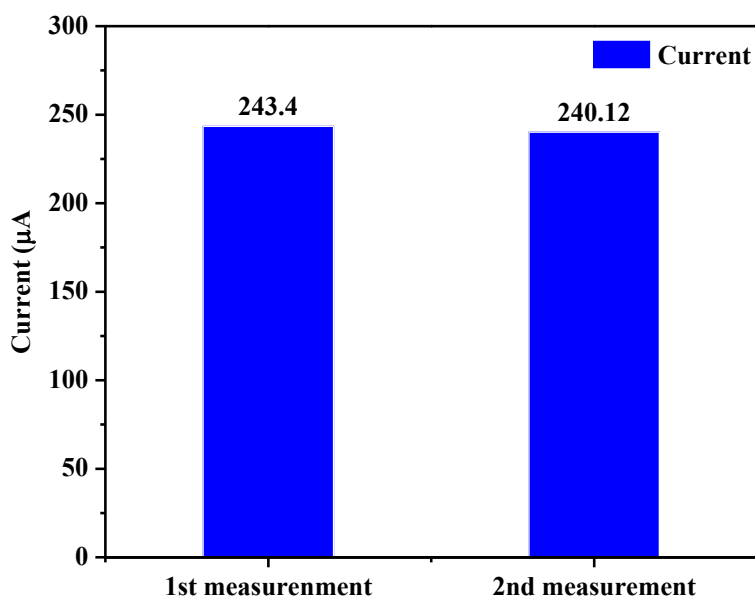


Figure 35. Bar chart illustrating the repeatability of the ZnO nanorod Au-IDE electrode based on two consecutive CV measurements.

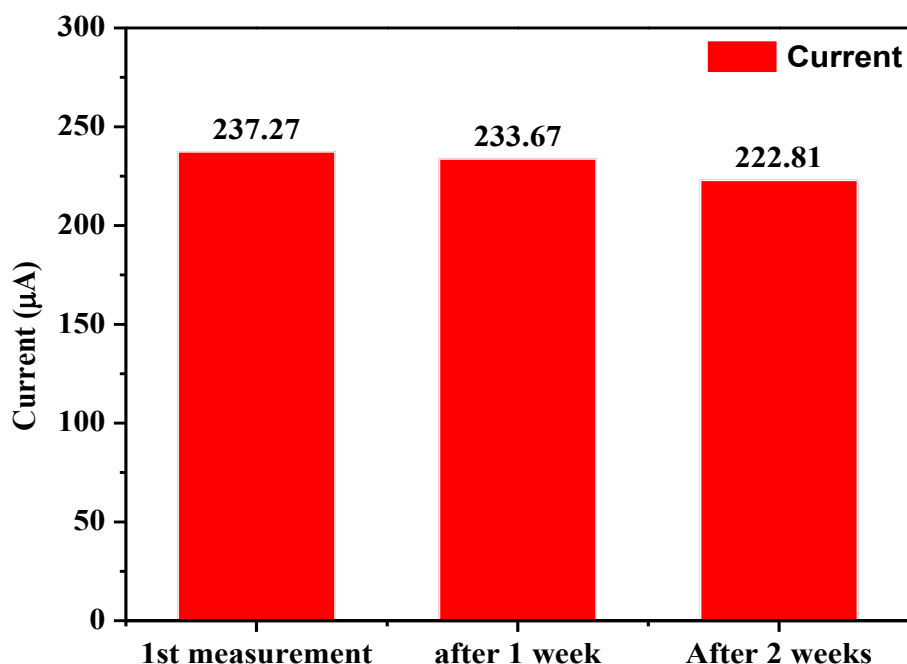


Figure 36. Bar chart illustrating the reproducibility of the ZnO nanorod Au electrode over a two-week period.

4.1.4.3 Real sample analysis of Cd^{2+} and thiram.

For real sample analysis, underground water was collected from Dhanbad and used to evaluate the practical performance of the fabricated electrode. Three water samples were spiked with known concentrations of Cd^{2+} ions. Cyclic voltammetry (CV) measurements were conducted under the same experimental conditions optimized during the standard tests. As shown in Table 5, the results demonstrate that the ZnONRs-Au electrode is highly effective in detecting Cd^{2+} ions in underground water, confirming its suitability for real-world environmental monitoring.

Table 5. Cd^{2+} ions analysis in underground water

Samples	Added spiked (μM)	Found (μM)	Recovery %
1.	4	2.7	90.6%
2.	8	7.34	95.86%
3.	10	9.4	97.27%

To assess the practical reliability of the fabricated electrode for thiram, we conducted tests using real environmental samples. Drain water was collected from a paddy field located in Kakching, which serves as a representative source of potentially contaminated agricultural water. Three separate samples were prepared by adding known concentrations of thiram (a commonly used pesticide) to the collected drain water. These spiked samples were then analyzed using the same differential pulse voltammetry (DPV) procedure applied in the standardized detection experiments. By comparing the measured current responses to the expected values based on the known thiram concentrations, we were able to calculate the recovery percentages. The results, summarized in the table, show that the electrode maintains good accuracy and sensitivity in complex real-world samples, indicating its reliability for practical applications in environmental monitoring.

Table 6. Comparison with Previously Reported Electrodes for Thiram Detection

Sample No.	Spiked amount (μM)	Found amount (μM)	Recovery%
1	6	5.98	99%
2	8	7.97	99.6%
3	10.6	10.36	97.7%

4.1.5 Conclusion

This study demonstrated the effectiveness of fabricating a ZnO nanorod (ZnONRs)-modified thin film gold (Au) electrode using nanoimprint lithography (NIL). NIL proved to be a precise and reliable technique for controlling the surface morphology of the electrode at the nanoscale. The resulting nanostructured surface significantly increased the surface area, thereby enhancing electrochemical interactions and facilitating the efficient immobilization of ZnO nanoparticles. These features contributed to improved sensitivity and a low limit of detection (LOD), achieving values as low as $20.88 \pm 0.9 \mu\text{M}$ for cadmium ion (Cd^{2+}) and $0.76 \mu\text{M}$ for thiram detection. The developed electrode was also effective in detecting Cd^{2+} ions and thiram in underground water samples and drain water collected from paddy field, demonstrating good recovery %.

4.2 Simultaneous electrochemical detection of two heavy metal ions using a zinc oxide nanorod-modified gold electrode fabricated via nanoimprint lithography.

4.2.1 Introduction

Heavy metal contamination continues to be a significant global issue due to its long-lasting toxicity, inability to degrade naturally, and tendency to accumulate in ecosystems and living organisms [Mitra et al., (2022)], [Schwartz et al., (2003)]. Detecting multiple heavy metal ions such as copper (Cu^{2+}), cadmium (Cd^{2+}), and mercury (Hg^{2+}) simultaneously in environmental samples like water and soil is crucial for early warning systems and ensuring regulatory compliance [Zhang et al., (2023)], [Chen et al., (2021)]. While conventional methods such as atomic absorption spectroscopy and inductively coupled plasma mass spectrometry offer high accuracy and sensitivity, they often involve complex equipment, require trained personnel, and can be time-intensive [Baranwal et al., (2022)], [Simões et al., (2017)]. Electrochemical sensing technologies present a promising alternative, offering advantages such as ease of use, portability, affordability, and quick response times [Bakker et al., (2002)], [Zhu et al., (2015)]. Nevertheless, the effectiveness of these sensors is closely tied to the surface characteristics and design of the working electrode. In this regard, nanostructured electrodes have gained attention for their ability to significantly improve the sensitivity and selectivity of electrochemical detection.

Recently, significant advancements have been made in the development of electrochemical sensing techniques for the detection of heavy metal ions in aqueous media. This review highlights recent innovations in electrochemical methods—particularly potentiometric, voltammetric, and amperometric techniques—and the modification of electrode interface materials to enhance detection performance [Sulthana et al., (2024)]. One notable development is an ultra-sensitive electrochemical sensor constructed using ZIF-67@antimonene (AMNFs) nanocomposites. Based on first-principles density functional theory, this work demonstrated the strong adsorption properties of antimonene toward Cu^{2+} , Pb^{2+} , and Hg^{2+} , enabling their simultaneous determination with high sensitivity [Zhang et al.,

(2023)]. Another study proposed a ratiometric electrochemical sensing approach for detecting Cd^{2+} , Pb^{2+} , and Cu^{2+} , utilizing a composite of ferrocene carboxylic acid-functionalized metal-organic framework ($\text{Fc-NH}_2\text{-UiO-66}$) and thermally reduced graphene oxide (trGNO), forming an efficient sensing platform denoted as trGNO/ $\text{Fc-NH}_2\text{-UiO-66}$ [Wang et al., (2020)]. In a separate study, an iron oxide/graphene ($\text{Fe}_2\text{O}_3/\text{G}$) nanocomposite electrode combined with in situ plated bismuth (Bi) was evaluated for the trace detection of Zn^{2+} , Cd^{2+} , and Pb^{2+} , demonstrating notable electroanalytical performance [Lee et al., (2016)].

Similarly, a hybrid sensor based on graphene aerogel (GA) and metal–organic framework (MOF) composites was designed for the simultaneous detection of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} . This sensor achieved excellent sensitivity and selectivity in aqueous solutions [Alshawhi et al., (2022)]. Further work introduced a novel electrochemical sensor utilizing square wave voltammetry (SWV) and a platinum electrode modified with poly(3,4-ethylenedioxythiophene) and $\text{Na}\alpha$, $\text{Na}\alpha$ -bis(carboxymethyl)-L-lysine hydrate (PEDOT/NTA), which successfully detected Hg^{2+} , Pb^{2+} , and Zn^{2+} in water samples [Lu et al., (2018)].

Additionally, a polyglycine-modified graphene paste electrode (PGMGPE) was developed for the detection of Hg^{2+} and Pb^{2+} in both water and biological matrices, showing strong applicability in real-world scenarios [Raril et al., (2020)].

In this study, nanoimprint lithography (NIL) is employed to design and fabricate a gold (Au) thin film electrode enhanced with nanostructured zinc oxide (ZnO) features to improve its electrochemical performance. ZnO is a well-known semiconductor valued for its high surface reactivity, biocompatibility, and strong interaction with metal ions, making it an ideal material for enhancing heavy metal ion sensing. The fabricated ZnO-modified Au thin film electrode is then tested for its capability to simultaneously detect two different heavy metal ions using electrochemical methods.

4.2.2 Results and Discussions

4.2.2.1 XRD characterization

X-ray diffraction (XRD) analysis was performed to examine the crystal structure of the synthesized zinc oxide (ZnO) nanorods (NRs). This analysis utilized a Rigaku Oxford Diffraction SuperNova X-ray diffractometer, equipped with a $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$), enabling accurate detection of the sample's diffraction pattern.

The resulting XRD spectrum, presented in Figure 37, was measured across a 2θ range of 10° to 80° , providing detailed insight into the phase composition and crystallographic orientation of the material. Several distinct diffraction peaks were observed at 2θ angles of 31.80° , 34.58° , 36.40° , 47.69° , 57.01° , 63.10° , and 67.67° , which correspond to the (100), (002), (101), (102), (110), (103), and (112) planes of the hexagonal wurtzite ZnO crystal structure. These peaks match the standard diffraction data reported in JCPDS card no. 36-1451 [Basnet et al., (2019)]. Notably, the strong intensity of the (002) reflection indicates a preferred orientation of the ZnO nanorods along the c-axis, suggesting vertical alignment of the rods on the substrate. Additional peaks detected at 2θ values of 38.35° , 44.49° , 64.79° , and 77.54° are assigned to the (111), (200), (220), and (311) planes of gold (Au), which is consistent with the underlying Au thin film and confirmed by reference to JCPDS card no. 04-0784 [Ren et al., (2015)].

The crystallite size of the ZnO nanorods was estimated using the Scherrer equation, which relates peak broadening in the XRD pattern to the size of coherent scattering domains. Based on this calculation, the average crystallite size was determined to be approximately 15.63 nm, indicating the formation of highly crystalline nanoscale ZnO structures on the Au-coated substrate.

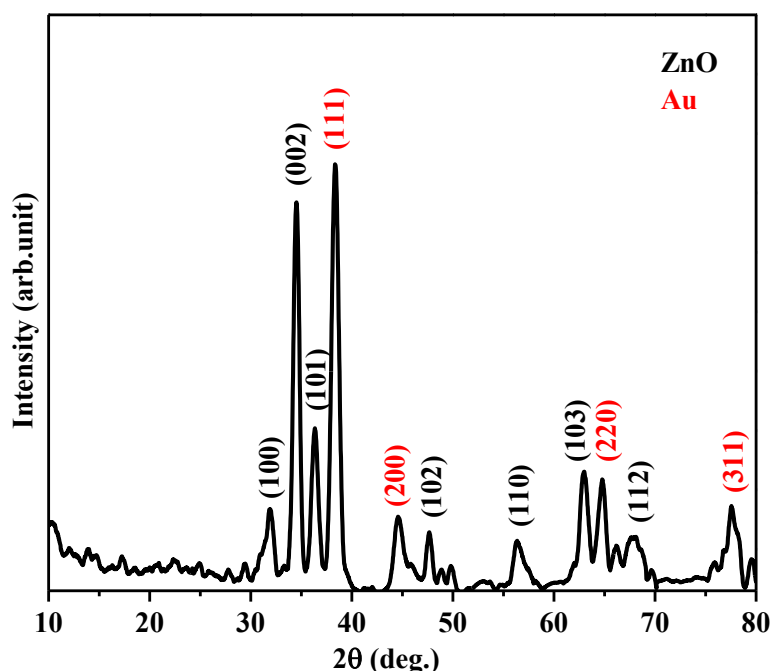


Figure 37. XRD pattern of ZnO and Au deposited on a glass substrate

4.2.2.2 XPS analysis

X-ray Photoelectron Spectroscopy (XPS) analysis, conducted using a PHI 5000 Versa Probe III instrument, was employed to examine the elemental composition and chemical states of the sample. The survey spectrum displayed distinct peaks for carbon (C), zinc (Zn), and oxygen (O), confirming their presence in the material in Figure 38. A prominent C 1s peak was observed at a binding energy of 284.4 eV as in Figure 39 (c). This peak is typically attributed to adventitious carbon, which is commonly present on the surface of samples exposed to air. Importantly, this C 1s peak is also used as an internal reference for calibrating the binding energy scale, thereby minimizing the effects of sample charging during measurement [Wagner et al., (1979)]. The high-resolution Zn 2p spectrum displayed two characteristic peaks at binding energies of 1022.8 eV and 1044.3 eV, corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2} spin-orbit components, respectively, as shown in Figure 39 (a). The energy separation (ΔE) between these two peaks is approximately 21.5 eV, which is consistent with the presence of Zn in the Zn²⁺ oxidation state. This observation confirms that zinc exists in the +2-oxidation state, typical of ZnO.

The O 1s core-level spectrum showed a strong peak centered around 530.0 eV, which is characteristic of lattice oxygen (O^{2-}) ions in the wurtzite ZnO structure, as shown in Figure 39 (b) [Ahmad et al., (2016)]. This peak indicates that oxygen is chemically bonded in the Zn–O lattice. The shape and position of the O 1s peak can also provide insight into different oxygen species, including lattice oxygen and oxygen associated with surface hydroxyl groups or adsorbed species. In this case, the dominant peak suggests a well-formed ZnO phase with oxygen atoms fully incorporated into the crystal lattice, surrounded by Zn^{2+} ions.

The presence of strong and well-defined Zn 2p and O 1s peaks confirms the successful synthesis of high-purity ZnO nanomaterial. The absence of significant satellite peaks or peak shifts further supports the formation of stoichiometric ZnO with minimal defects or secondary phases.

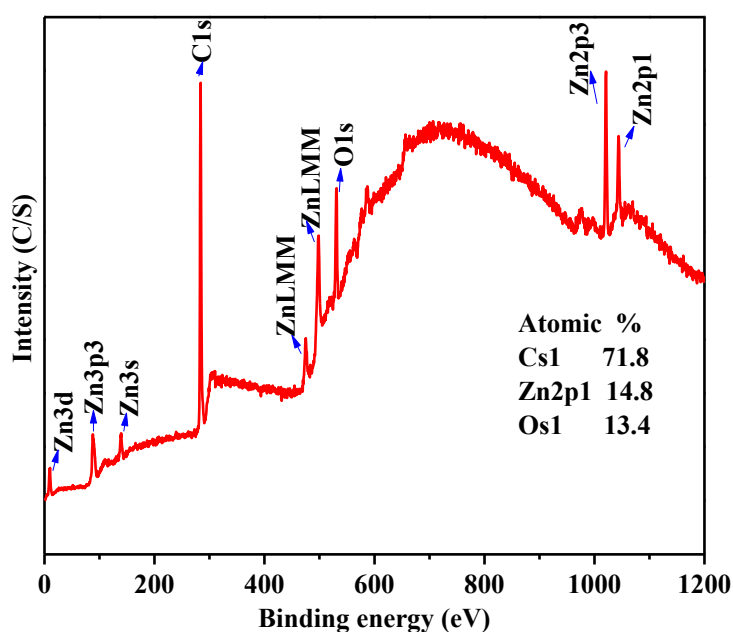


Figure 38. XPS survey spectra of ZnO nanorods.

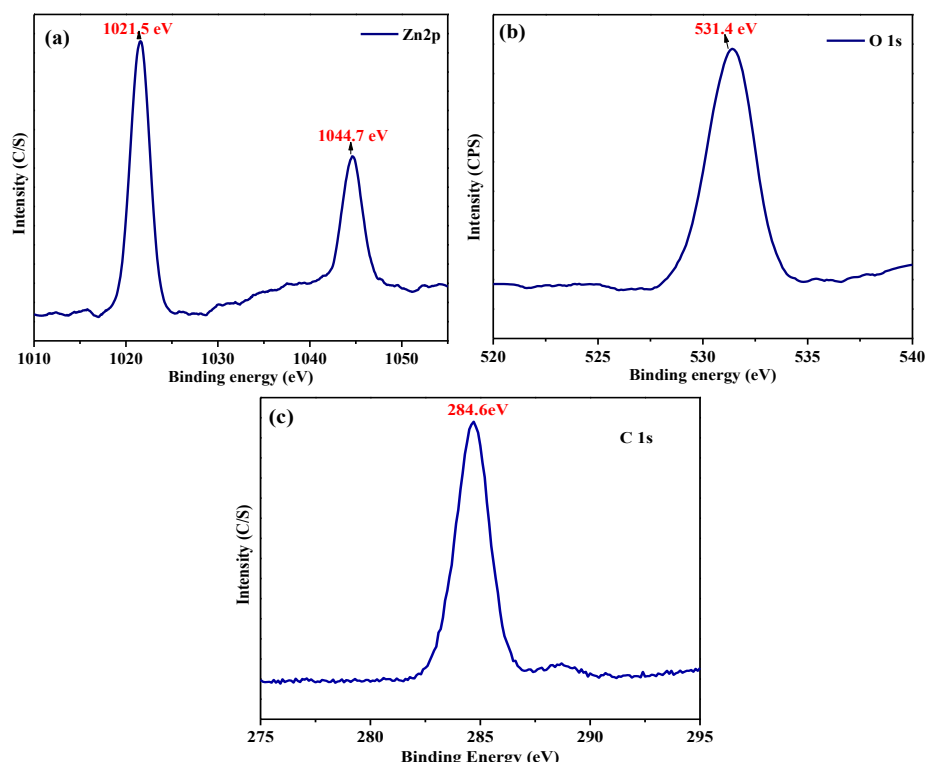


Figure 39. XPS spectra of (a) Cs1 (b) Zn2p (c) Os1

4.2.2.3 FESEM characterization

Field Emission Scanning Electron Microscopy (FESEM) analysis was performed utilizing a Zeiss Supra 55 system to investigate the surface morphology and structural arrangement of the synthesized material. As illustrated in Figure 40 (a), the FESEM micrograph clearly demonstrates that the hexagonal zinc oxide nanorods (ZnO NRs) exhibit a predominantly horizontal orientation along the seed layer. These nanorods are uniformly distributed and exhibit a well-organized grating-like alignment, indicating a controlled and consistent growth process. Furthermore, a detailed examination of the particle size distribution, derived from the histogram presented in Figure 40 (b), reveals that the average diameter of the ZnO NRs is approximately 47.34 nanometers. This measurement suggests a high degree of uniformity in the nanorod dimensions, which is essential for applications requiring consistent nanoscale features.

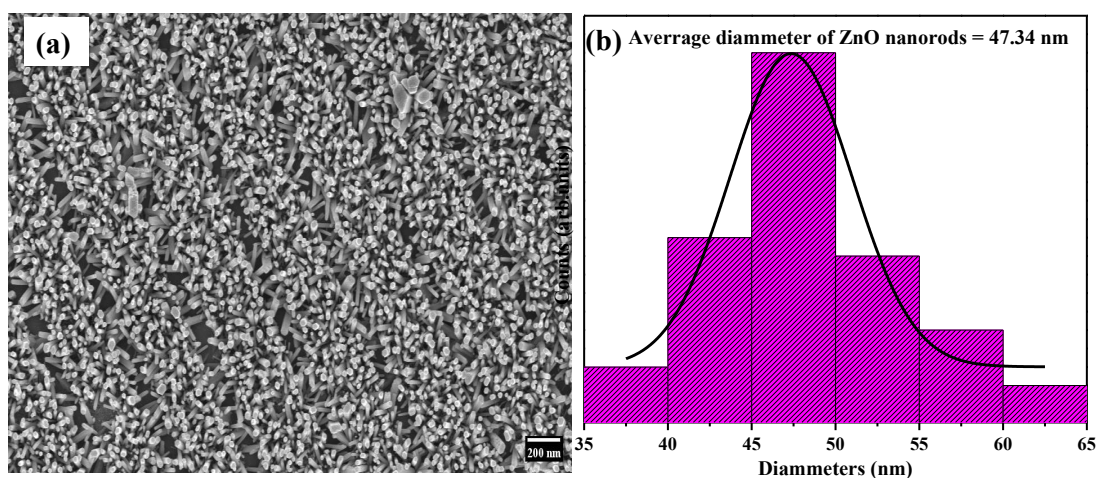


Figure 40 (a) FESEM image showing ZnONRs arranged in a CD grating pattern. (b) Histogram illustrating the distribution of average diameters of the ZnONRs.

4.2.2.4 HRTEM and SAED analysis

High-resolution transmission electron microscopy (HRTEM) analysis was performed using a Thermo Scientific Talos F200X G2 microscope. As shown in Figure 41 (a), the HRTEM image reveals the ZnONRs grown on the seed layer, clearly exhibiting the (100) crystallographic plane characteristic of the hexagonal wurtzite structure. The measured interplanar spacing (d-spacing) for this plane is approximately 0.28 nm. The image in Figure 41 (b) shows the Selected Area Electron Diffraction (SAED) pattern, which features distinct circular diffraction spots. These spots indicate that the ZnONRs are polycrystalline in nature, meaning they are composed of multiple crystalline domains with different orientations. The observed d-spacing values 0.280 nm, 0.248 nm, and 0.168 nm correspond to the (100), (101), and (110) planes of ZnO, respectively. These measurements align well with previously reported standard values [Li et al., (2001)], confirming the structural integrity and crystallographic orientation of the synthesized nanorods.

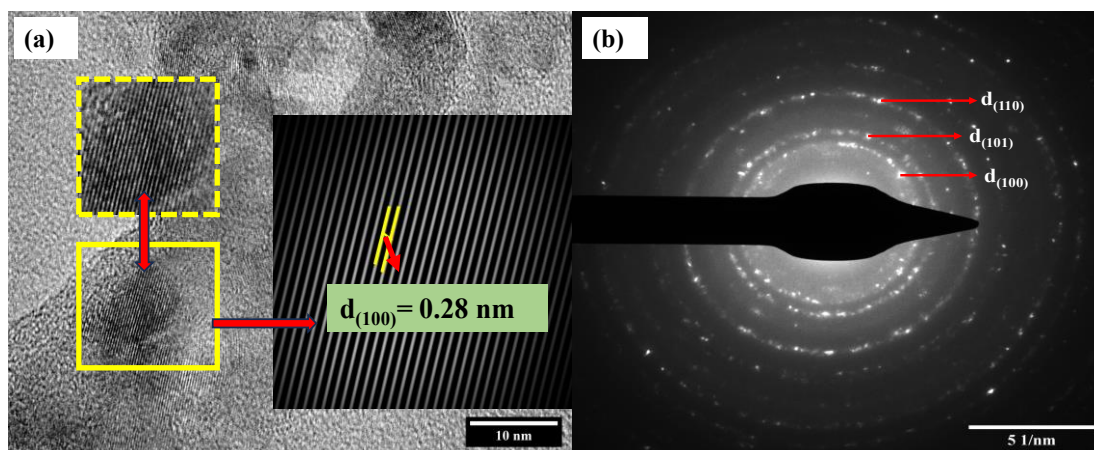


Figure 41. (a) HRTEM image of ZnO NRs showing lattice fringes for the (100) plane (~ 0.28 nm), typical of the hexagonal wurtzite structure. (b) shows SAED pattern confirming polycrystallinity, with d-spacings matching the (100), (101), and (110) planes.

4.2.3 Electrochemical Analysis

Electrochemical measurements were conducted using a standard three-electrode system, consisting of the synthesized ZnONRs-Au electrode as the working electrode, a silver/silver chloride (Ag/AgCl) electrode serving as the reference, and a platinum (Pt) sheet used as the counter electrode. As shown in Figure 42, CV was performed in a 0.1 M KCl electrolyte solution. The ZnONRs-Au electrode demonstrated significantly higher current responses compared to the unmodified (bare) gold electrode. This increase in current indicates enhanced electrochemical activity, which can be attributed to the unique properties of the ZnONRs. Specifically, the nanorod structure offers a larger electroactive surface area and promotes more efficient electron transfer between the electrode surface and the electrolyte. These characteristics make ZnONRs-Au a more effective platform for electrochemical reactions than bare Au.

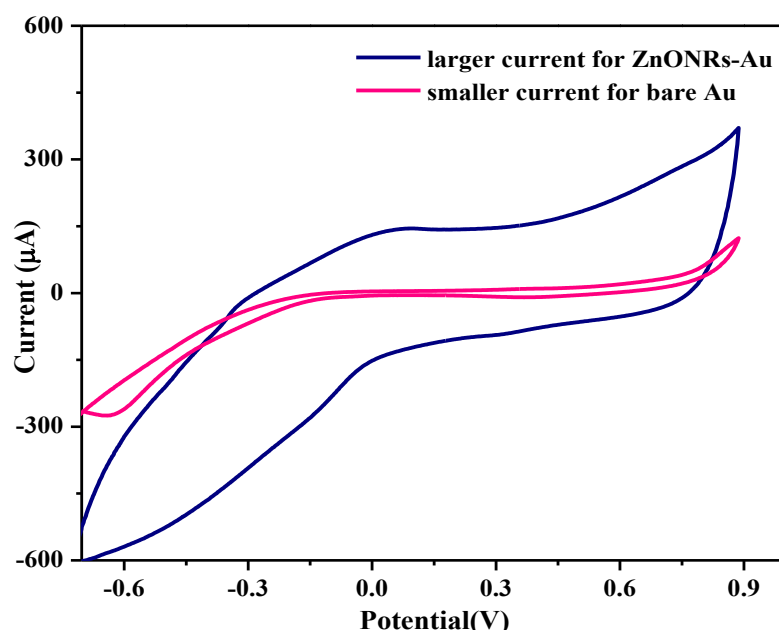


Figure 42. Cyclic voltammograms of ZnO nanorods on Au and bare Au electrodes recorded in an electrolyte solution of 0.1 M KCl at a scan rate of 20 mV/s, illustrating the comparative current responses.

4.2.3.1 Accumulation Time

To explore how accumulation time influences electrochemical performance, voltammetric analyses were conducted using a 1 mM solution of potassium ferricyanide/ferrocyanide on a ZnO-NRs/Au thin film electrode as shown in Figure 43. Accumulation durations ranged from 10 to 70 seconds. The peak current progressively increased up to 30 seconds, indicating more effective accumulation of analyte molecules on the electrode surface. At 30 seconds, the current reached its peak, and the voltammetric signal appeared sharp and distinct, suggesting optimal interaction between the electrode and analyte. However, when the accumulation time exceeded 30 seconds, a decrease in peak current was observed a typical trend in electrochemical sensors. This reduction is likely due to electrode surface saturation, which restricts further analyte adsorption. Moreover, the depletion of the concentration gradient near the electrode over time can hinder the transport of analyte molecules to the surface [Sawkar et al., (2022)]. These results highlight the importance of optimizing accumulation time, identifying 30 seconds as the ideal duration for achieving the highest current response and analyte uptake.

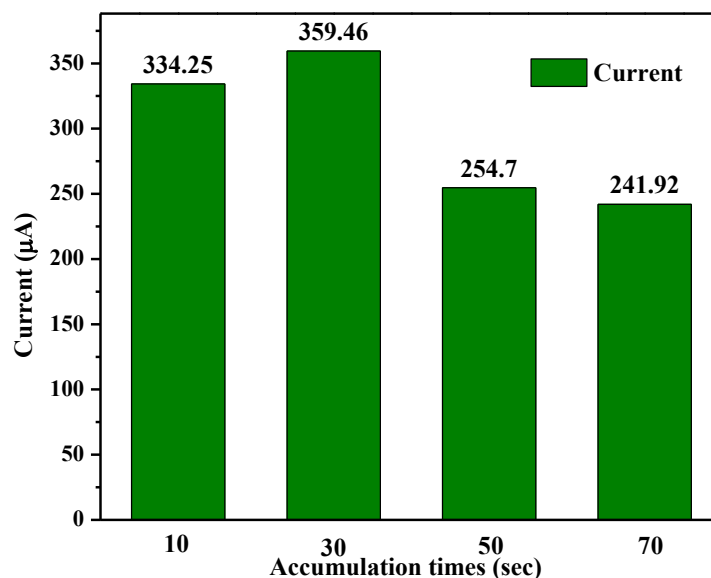


Figure 43. Graph showing the relationship between analyte accumulation time at the electrode surface and the resulting current response

4.2.3.2 Effect of Scan Rate

The impact of scan rate on the performance of the fabricated sensor was examined using an electrolyte aqueous solution of 0.1 M KCl containing 1 mM potassium ferricyanide/ferrocyanide, a widely used reversible redox system in electrochemical research. As depicted in Figure 44 (a), cyclic voltammograms recorded at scan rates ranging from 20 to 160 mV/s showed a proportional increase in both anodic and cathodic peak currents with increasing scan rate. This behavior suggests that the electrode possesses strong electrochemical responsiveness and stability. The linear correlation between peak currents and scan rate (as illustrated in Figure 44 (b)) implies a surface-confined redox mechanism. Additionally, the linear dependence of peak current on the square root of the scan rate, represented by the regression equation $I_{pc} = 28.53v + 90.97$ ($R^2 = 0.99$), indicates that the process is primarily governed by diffusion-controlled kinetics.

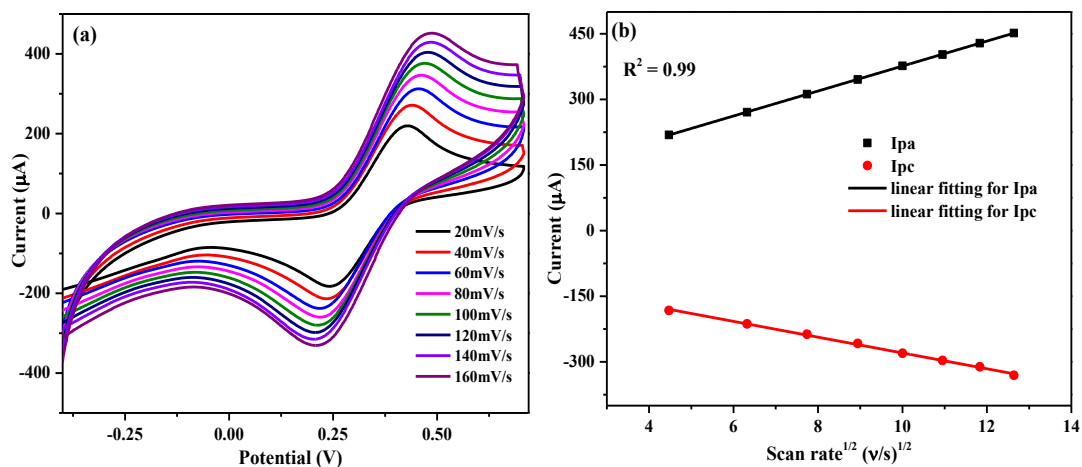


Figure 44. Cyclic voltammograms of ZnO nanorods on Au electrodes recorded in an electrolyte solution of 0.1 M KCl with 1 mM $K_4 [Fe(CN)_6]/K_3 [Fe(CN)_6]$ and in 1 M KCl at various scan rates; (d) shows the linear relationship between peak currents and the square root of scan rates.

4.2.3.3 Simultaneous Determination of Cd^{2+} and Cu^{2+} Ions

Cyclic voltammetry (CV) was utilized as the analytical method to quantitatively assess Cd^{2+} and Cu^{2+} ions using the developed sensor. The primary aim of the concentration variation study was to examine the sensor's performance across a spectrum of analyte concentrations, specifically to evaluate its sensitivity and limit of detection (LOD). Phosphate-buffered saline (PBS) at pH 7.0 served as the supporting electrolyte, while metal ion concentrations ranging from 5 μM to 65 μM were analyzed. As shown in Figure 45 (a), the peak current (I_p) observed in the CV curves increased consistently with higher ion concentrations, confirming a direct correlation between concentration and electrochemical response. This trend validates the sensor's capability to accurately detect and quantify Cd^{2+} and Cu^{2+} within the tested range. In figure 45 (b) Calibration curves for both metal ions displayed linear relationships between peak current and concentration, with regression equations of $I_p (\mu A) = 1.072 \times C + 14.32$ for Cd^{2+} and $I_p (\mu A) = 0.965 \times C + 8.55$ for Cu^{2+} , where C is the ion concentration in μM . The high R^2 values of 0.995 and 0.996 indicate excellent linearity and reproducibility. Based on these calibration plots, the detection limits were determined to be 2.45 μM for Cd^{2+}

and 1.5 μM for Cu^{2+} . These findings highlight the sensor's high sensitivity and effectiveness in simultaneously detecting Cd^{2+} and Cu^{2+} ions under neutral pH conditions.

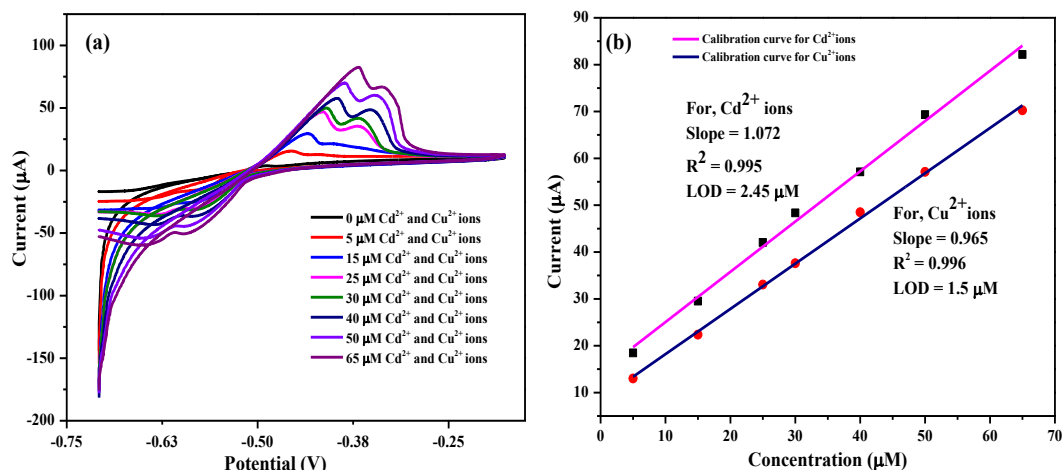


Figure 45. (a) Cyclic voltammograms of ZnO nanorods modified on Au electrode (ZnONRs/Au) recorded in phosphate-buffered saline (PBS, pH 7) with varying concentrations of Cd^{2+} and Cu^{2+} ions. (b) Calibration plot showing the relationship between ion concentration and peak current, used to determine the limit of detection.

4.2.3.4 Real Sample Analysis

The performance and reliability of the developed sensor were evaluated by analyzing a real tap water sample collected from Dhanbad. To assess its effectiveness, the sample was spiked with three known concentrations of Cd^{2+} and Pb^{2+} . The electrochemical responses of these spiked samples were then measured using CV. The results, summarized in **Table 7**, demonstrate that the proposed sensor is capable of accurately detecting Cd^{2+} and Pb^{2+} in real water samples.

Table 7. Real sample analysis of Cd²⁺ and Cu²⁺ ions in tap water sample

Samples	Amount of added spike (in μM)		Found				Recovery (%)	
	Cd ²⁺	Cu ²⁺	Cd ²⁺ (μM)	Cd ²⁺ (μA)	Cu ²⁺ (μM)	Cu ²⁺ (μA)	Cd ²⁺	Cu ²⁺
1	18	10	17.50	33.35	9.28	17.72	97.22 %	92.8%
2	24	24	23.48	39.81	23.76	31.707	97.8%	99%
3	31	31	30.74	47.52	30.46	37.74	99.1%	98.2%

4.2.4 Conclusion.

A ZnONRs/Au thin film electrode was effectively fabricated using nanoimprint lithography (NIL) for the simultaneous electrochemical detection of Cd²⁺ and Cu²⁺ ions. The sensor demonstrated high sensitivity, achieving limits of detection (LOD) of 2.45 μM for Cd²⁺ and 1.5 μM for Cu²⁺. Its practical performance was further validated through analysis of tap water samples, confirming the sensor's reliability and potential for real-world environmental monitoring of heavy metal pollutants.

4.3 Low-cost interdigitated Gold Electrode Modified with ZnO Nanorods for Enhanced Electrochemical Detection of Bisphenol A

4.3.1 Introduction

Interdigitated electrodes (IDEs) are a type of electrode structure characterized by two interlocking, comb-shaped conductive patterns. These patterns are typically fabricated from metals like gold, platinum, or other conductive materials due to their excellent electrical properties and stability [Sanderson et al., (1985)], [Bard et al., (1986)]. IDEs are widely applied in electrochemical and biosensing technologies because of several advantages: they have a high surface-area-to-volume ratio, are straightforward and cost-effective to manufacture, and offer enhanced sensitivity in detection processes [Barnes et al., (2012)], [Ding et al., (2017)]. The interdigitated design plays a key role in promoting **redox cycling** a process in which an analyte is oxidized at one electrode (often called the generator) and then diffuses to a neighbouring electrode (the collector) to be reduced. This back-and-forth movement of electrons between electrodes significantly boosts the overall detection signal [Liu et al., (2014)], [Sugime et al., (2018)]. The sensitivity of IDEs can be fine-tuned by altering the number of electrode “fingers” and adjusting the spacing between them. Tighter spacing and more fingers generally improve performance [Varshney et al., (2009)], [Postlethwaite et al., (1996)]. Unlike traditional three-electrode systems, IDEs can function with just two electrodes that simultaneously act as the **working and counter electrodes**, eliminating the need for a reference electrode [Liu et al., (2004)], [Khan et al., (2016)]. This not only simplifies the device architecture but also reduces the required sample volume, improves the signal-to-noise ratio, and enables faster measurement times [Tomčík et al., (2001)], [Bustin et al., (1996)].

Additionally, **zinc oxide (ZnO)** is often used in combination with IDEs. As a semiconductor metal oxide, ZnO has the unique capability of adsorbing a wide range of organic pollutants directly onto its surface without the need for chemical linkers. This makes it particularly suitable for sensing applications where detecting contaminants is crucial [Zhang et al., (2016)].

One such pollutant of growing concern is **bisphenol A (BPA)**, an endocrine-disrupting chemical commonly used in the production of plastics and resins. BPA can leach into water sources and accumulate in the environment, posing risks to both aquatic ecosystems and human health by mimicking hormonal activity. Due to its persistence and bioactivity, sensitive and rapid detection of BPA in environmental samples is essential. IDE-based sensors, particularly those modified with ZnO, have shown great potential for detecting trace levels of BPA, offering a practical solution for environmental monitoring and pollution control. In this study, a cost-effective method was developed to fabricate thin-film gold interdigitated electrodes (Au-IDEs) on microscope glass slides using a stainless-steel IDE mask in combination with an electron beam (e-beam) deposition system. This fabrication approach offers an affordable alternative to conventional microfabrication techniques such as photolithography and soft lithography, which are not only expensive but also require specialized equipment that may not be readily available in all research or industrial settings.

The key innovation of this work lies in the simplicity and low cost of the fabrication process for Au-IDEs used in bisphenol A (BPA) detection. Unlike previous studies that rely on high-cost materials and complex fabrication processes, this approach significantly reduces production costs and simplifies implementation. This makes it particularly advantageous for large-scale manufacturing and for use in settings with limited access to advanced microfabrication facilities. Additionally, the fabrication process is straightforward and avoids time-consuming or intricate steps, enhancing both reproducibility and operational efficiency. This simplicity ensures consistent electrode performance and minimizes experimental variability, supporting broader applicability of the method. After fabrication, the Au-IDEs were further modified with zinc oxide (ZnO) nanorods, which enhanced their sensitivity. These nanorods facilitated the adsorption of BPA at their defect sites without the need for linker molecules, enabling effective electrochemical detection. Detailed procedures for the fabrication process are provided in earlier section of the methodology.

4.3.2 Result and discussion.

4.3.2.1 XRD analysis

Figure 46 shows the XRD pattern of ZnO nanorods deposited on the surface of the IDE Au electrode. The pattern reveals prominent diffraction peaks at 2θ angles of 34.46° , 36.401° , 47.79° , 62.95° , and 77.71° . These peaks, upon further evaluation, are typically associated with the (002), (101), (001), (102), (103), and (202) crystallographic planes of hexagonal wurtzite-structured ZnO nanorods [Kalpana et al., (2018)]. The observed diffraction data align well with the standard reference pattern for ZnO (JCPDS card no. 36-1451) [Basnet et al., (2019)]. Additionally, diffraction peaks at 2θ values of 38.35° , 44.69° , and 64.76° correspond to the (111), (200), and (220) planes of gold, which are characteristic of the IDE Au electrode and match the JCPDS standard no. 04-0784 [Geng et al., (2017), [Jelen et al., (2023)]. The average crystallite size of the ZnO nanorods was calculated to be approximately 15.12 nm using the Scherrer equation [Meitei et al., (2019)], [Vinila et al., (2022)]. These results confirm the successful modification of the Au-IDE surface with ZnO nanorods, as indicated by the crystallite size and diffraction characteristics.

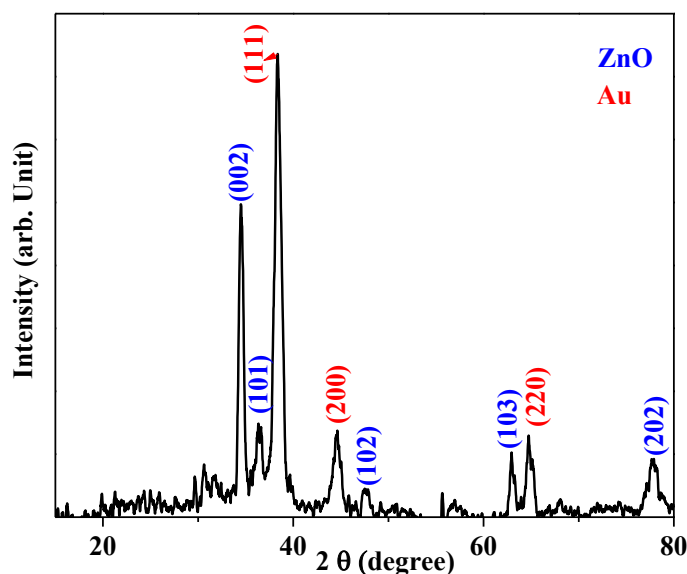


Figure 46 XRD pattern of ZnONRs hydrothermally deposited on the surface of Au interdigitated electrodes (Au-IDE).

4.3.2.2. FESEM and HRTEM Analysis

Figure 47 displays the surface morphology of ZnO nanorod arrays grown on the Au-interdigitated electrode (Au-IDE). Figures 47 (a) and (b) show FESEM images of the ZnO nanorods at different magnifications. At low magnification (Figure 46 (a)), the image demonstrates a uniform and vertically aligned growth of ZnO nanorods. The higher magnification image (Figure 47 (b)) clearly shows the nanorods' well-defined hexagonal structure [Meng et al., (2005)]. From these FESEM images, and based on the histogram shown in Figure 48, the average diameter of the nanorods is calculated to be approximately 50.8 nm [Kurda et al., (2015)].

Energy-dispersive X-ray spectroscopy (EDX) was performed to investigate the elemental composition of the ZnO nanorods. The EDX spectrum (Figure 49) shows prominent peaks for zinc and oxygen, confirming the presence of ZnO. Additionally, peaks for silicon and gold are observed, which are attributed to the glass substrate used in fabricating the Au-IDE and the Au-IDE itself, respectively.

For HRTEM analysis, ZnO nanorods were carefully scraped from the Au-IDE surface using a fine, sharp blade. The collected sample was dispersed in 1 mL of ethanol and ultrasonicated for 10 minutes. A small droplet of the resulting suspension was then drop-cast onto a copper TEM grid in a clean environment and left to dry. Figures 50 and 51 present the HRTEM image and the selected area electron diffraction (SAED) pattern of the ZnO nanorods. The HRTEM image (Figure 50) shows clear lattice fringes, confirming that the ZnO nanorods are single crystalline in nature with a wurtzite crystal structure [Li et al., (2001)]. Analysis of the lattice fringes reveals interplanar spacings of 0.246 nm and 0.263 nm, which correspond to the (002) and (101) planes, respectively. The SAED pattern further supports this, indicating d-spacings of 0.242 nm and 0.265 nm for the same planes, consistent with the HRTEM data [Sankara Reddy et al., (2013)].

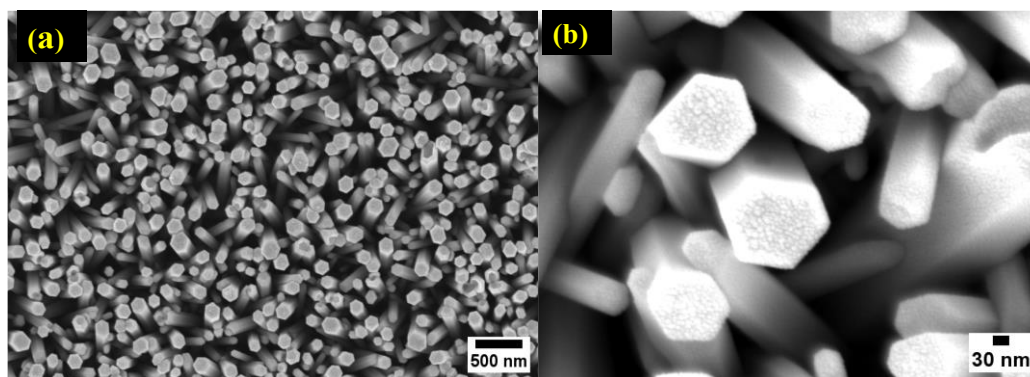


Figure 47 (a) and (b) present FESEM images of ZnONRs grown on Au-IDE at varying magnifications. The nanorods exhibit a hexagonal structure, protruding perpendicularly from the surface, and are uniformly distributed across the substrate.

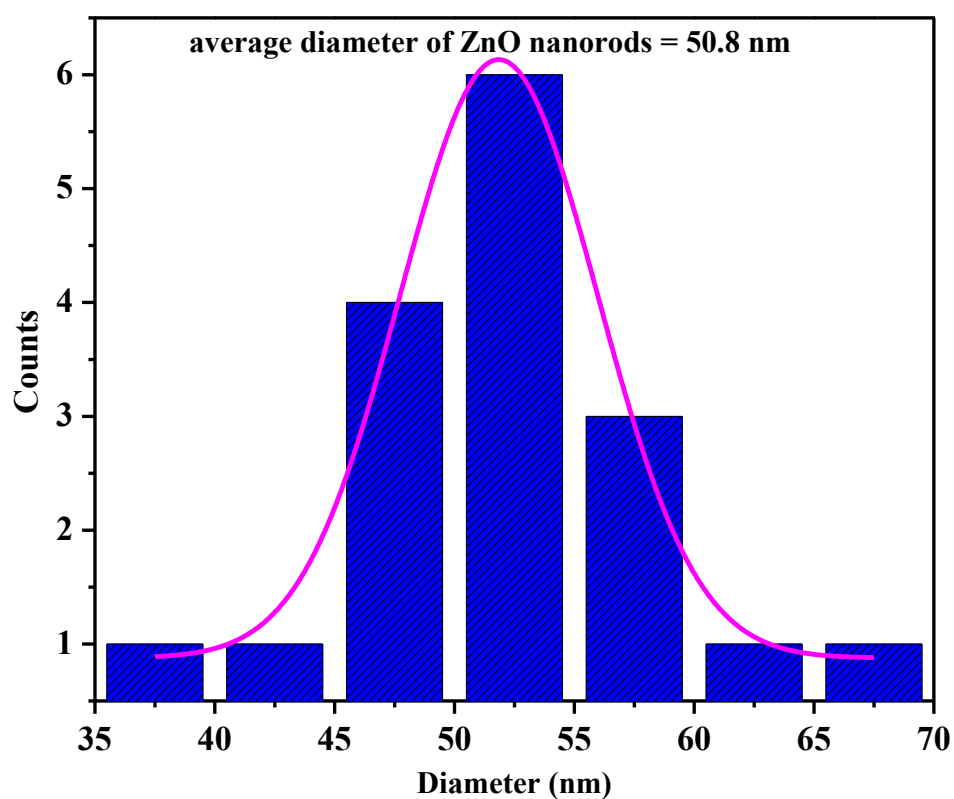


Figure 48 Histogram illustrating the distribution of average diameters of ZnO nanorods.

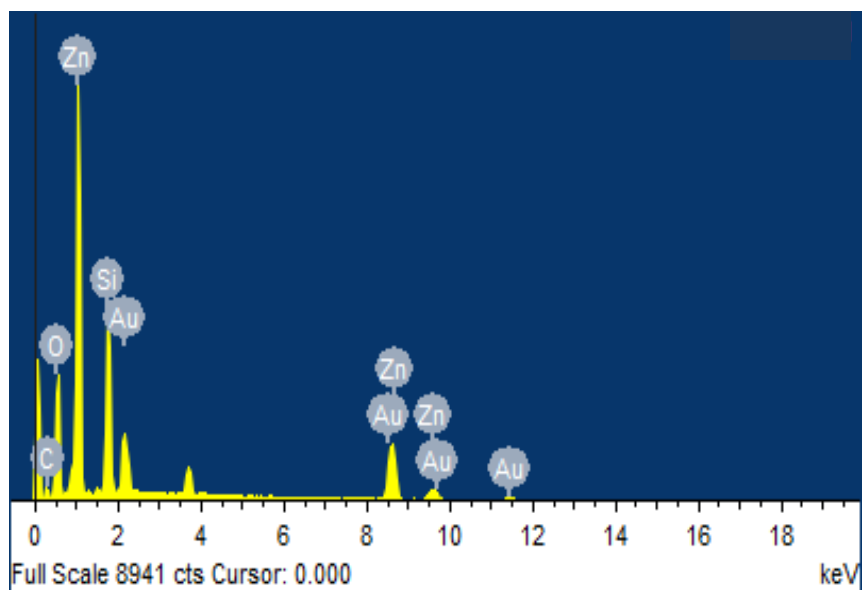


Figure 49. The EDS spectrum analysis of ZnO nanorods

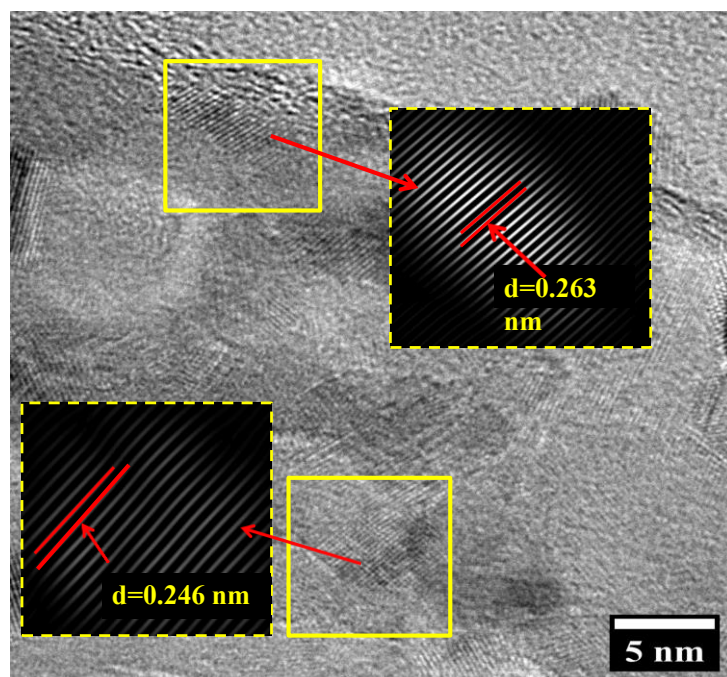


Figure 50. HRTEM image of ZnO nanorods on the Au-IDE electrode, showing lattice fringes for the (101) and (002) planes with d-spacings of 0.263 nm and 0.246 nm, respectively.

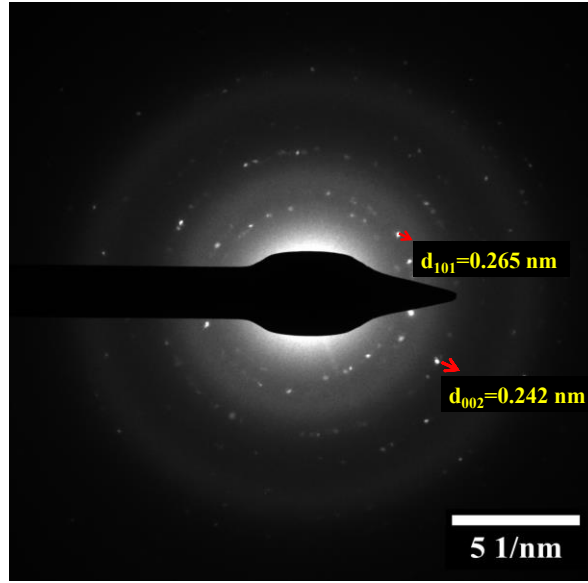


Figure 51. SAED image depicting the crystallographic pattern of ZnO nanorods.

4.3.3.5 UV-vis spectroscopy

A **Distinct** absorption peak is observed at 386 nm in the UV–vis spectrum of ZnO, as shown in Figure 52, aligning with the report by Lam et al. (2014). This peak corresponds to the near-band-edge (NBE) transition, which results from a direct electronic transition between the valence and conduction bands. This behavior is typical of ZnO, a direct bandgap semiconductor. The photon energy associated with this wavelength was determined using the Planck–Einstein equation.

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg/s}$), c is the speed of light ($3 \times 10^8 \text{ m/s}$) and λ is the wavelength. To estimate the optical band gap more precisely, **Tauc plot analysis** was employed. For direct bandgap semiconductors like ZnO, the Tauc relation is expressed as:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where α is the absorption coefficient (derived from absorbance), $h\nu$ is the photon energy, A is a proportionality constant, and E_g is the optical band gap. An estimated

optical band gap in the range of approximately 2.9 to 3.07 eV was obtained by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot, as shown in Figure 53."

The observed slight decrease in band gap compared to bulk ZnO can be linked to several factors, including intrinsic defects like oxygen vacancies and zinc interstitials, surface-related states, or internal strain within the crystal lattice of the nanorods. These elements can generate localized energy levels within the band gap, thereby reducing the apparent optical transition energy. Furthermore, the unique morphology and nanoscale dimensions of the ZnO nanorods can alter their optical properties due to quantum confinement and surface effects. UV-vis spectroscopy and Tauc plot analyses validate the direct band gap nature of the synthesized ZnO nanorods and indicate minor band gap narrowing, likely caused by defect states and size-related phenomena. These features enhance their suitability for electrochemical sensing applications, where modulation of the band gap can impact electron transfer rates and sensor performance.

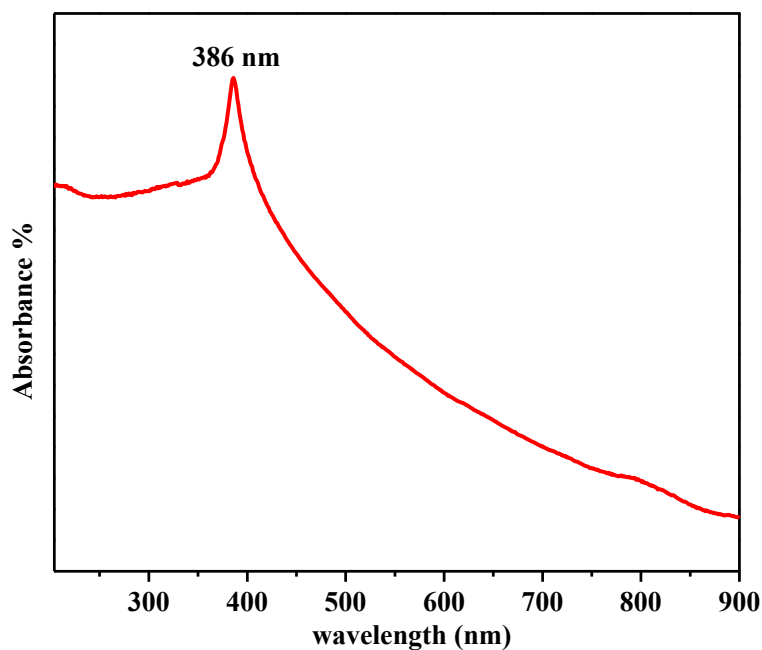


Figure 52. UV-vis spectrum of ZnONRs.

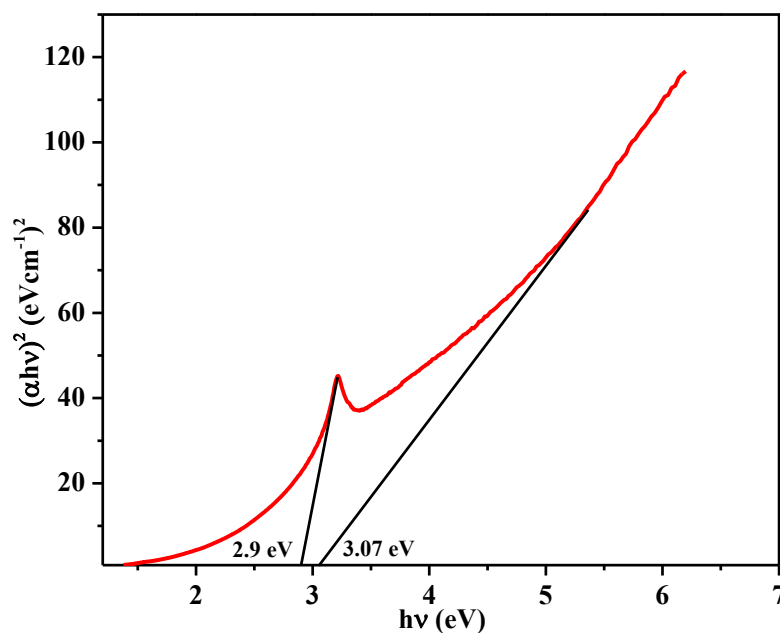


Figure 53. Curve of $(\alpha h\nu)^2$ Vs $h\nu$.

4.3.3.4 Photoluminescence and XPS Analysis

The existence of surface defect on ZnONRs were verified by the analysis of photoluminescence and XPS characterisation. Figure 54 presents the photoluminescence (PL) spectrum of ZnO nanorods grown on the surface of an Au interdigitated electrode (Au-IDE). The spectrum exhibits a near-band-edge (NBE) emission peak at approximately 393 nm in the ultraviolet region, attributed to the radiative recombination of photoexcited electrons in the conduction band with holes in the valence band, an intrinsic transition typical of ZnO [Wang et al., 2016; Zhang et al., 2014]. Additionally, a broad visible emission centered around 549 nm is responsible for the defect-related states, such as oxygen vacancies (O_v) and zinc interstitials (Zn_i), indicating the presence of surface defects in the ZnO nanorods. These defects are crucial as they serve as active sites for bisphenol A (BPA) adsorption. To further verify the existence of these surface imperfections, XPS was performed, focusing on the O1s region (Figure 55). The O1s spectrum was deconvoluted into three separate peaks located at 529.7 eV, 531.5 eV, and 532.1 eV, which are attributed to lattice oxygen (O_L), oxygen vacancies (O_v), and

chemisorbed oxygen species (O_c), respectively. These results corroborate the existence of surface defects in the ZnO nanorods.

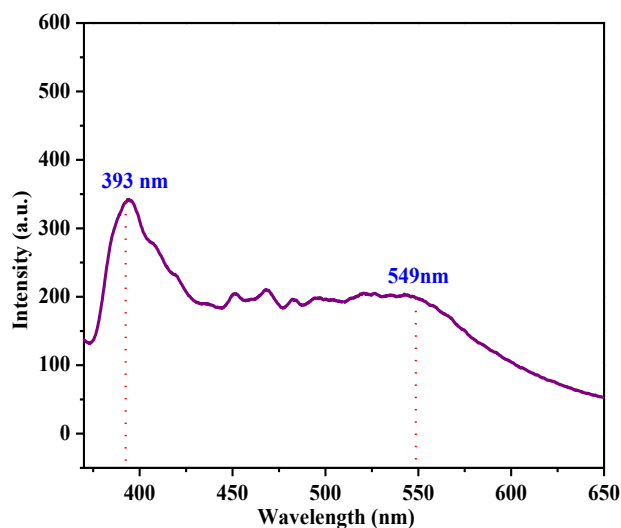


Figure 54. The PL spectra of ZnO nanorods taken with an excitation wavelength of 345.0 nm and an emission wavelength scan ranging from 355.0 nm to 650.0 nm.

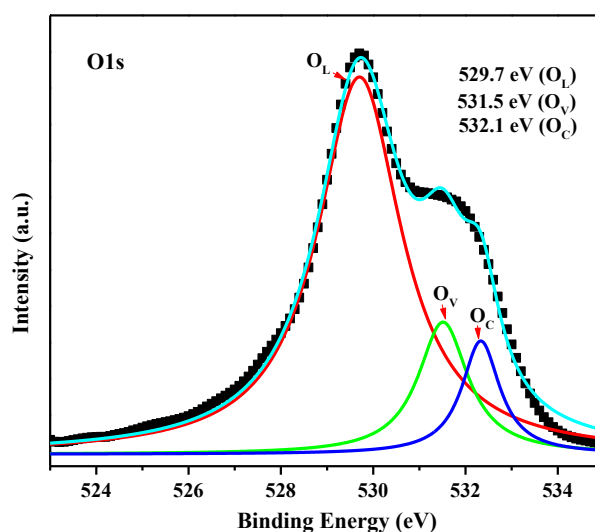


Figure 55. The spectrum of XPS of the O1s region for ZnO nanorods emphasizes the presence of surface defects.

4.3.4. Electrochemical Analysis

Cyclic voltammetry was performed utilizing the ZnO nanorods-modified Au-IDE electrode in an electrolyte aqueous solution of 0.1 M KCl that included 0.001 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ / $\text{K}_4[\text{Fe}(\text{CN})_6]$ and to evaluate its ability to generate oxidation and reduction currents for potential electrochemical sensing applications. As shown in Fig. 56, distinct oxidation and reduction peaks appear within the applied potential range of -0.2 to 0.7 V, indicating redox activity at the electrode surface. During the forward (positive) scan, ferricyanide ions are attracted to the positively polarized electrode and undergo reduction to ferrocyanide, resulting in an oxidation current. In the opposite direction, during the reverse (negative) scan, ferrocyanide ions move toward the surface of the electrode that is negatively charged. They are then oxidized back to ferricyanide, which results in the generation of a reduction current. Figure 56 presents a comparison between the redox behavior of the developed modified Au-IDE and that of the unmodified Au-IDE. The modified electrode (depicted in blue in Fig. 57) exhibits significantly enhanced oxidation and reduction currents approximately 1.5% greater than those of the bare Au-IDE (shown in green). This improved electrochemical performance is attributed to the ZnO nanorods, which increase the electrode's surface area, provide additional pathways for electron transfer, and promote greater adsorption of redox-active molecules [Beitollahi et al., (2020)].

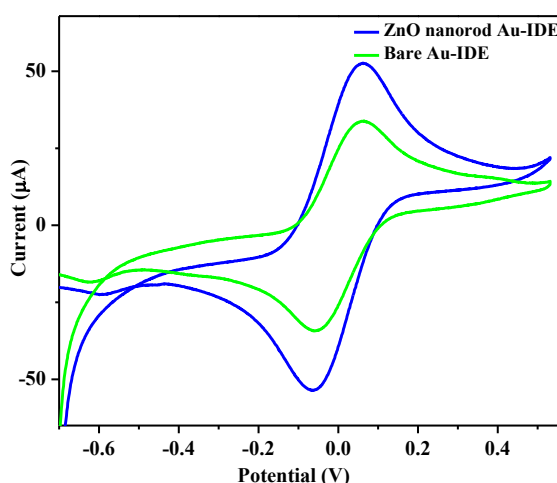


Figure 56. Cyclic voltammogram of ZnO nanorod-modified (blue) and bare (green) Au-IDE recorded in an electrochemical cell containing 0.1 M KCl electrolyte solution

and 0.001 M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$, showing enhanced redox currents for the modified electrode.

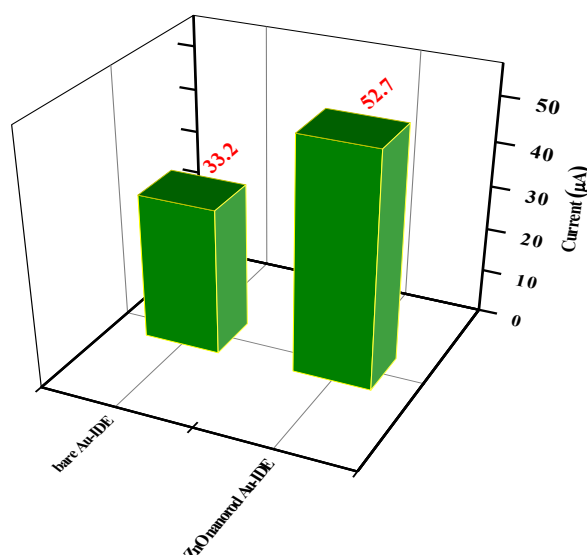


Figure 57. The difference in oxidation current between developed modified Au-IDE and bare Au-IDE. The developed modified Au-IDE exhibits a higher oxidation current of 1.5 % compared to the bare Au-IDE.

4.3.4.1 EIS Nyquist plot

Figure 58 presents the Nyquist plots derived from Electrochemical Impedance Spectroscopy (EIS) for both the ZnO-modified interdigitated electrode (IDE) and the bare IDE. In these plots, impedance is typically represented in which the x-axis commonly displays the real component of impedance (Z') and the y-axis the imaginary component (Z''). The shape and slope of the curve provide valuable insight into the electrochemical properties of the electrode surfaces, particularly their charge transfer resistance and capacitive behavior. In the case of the ZnO-modified IDE, the curve is noticeably steeper, indicating a greater slope approaching the vertical axis. This behavior is characteristic of enhanced capacitive behavior and faster charge transfer at the electrode–electrolyte interface. A steeper curve suggests lower charge transfer resistance and a more ideal capacitive response, which is often desirable in sensing and energy applications [He et al., (2009)]. This improvement can be attributed to the presence of the ZnO layer, which increases the effective surface area, provides more active sites for electron and ion exchange, and promotes better interfacial conductivity.

Conversely, the bare IDE exhibits a flatter curved line, indicating higher charge transfer resistance and reduced capacitive behavior. The flatter response reflects a less efficient interface for charge movement, likely due to the limited surface functionality and reduced interaction with the electrolyte.

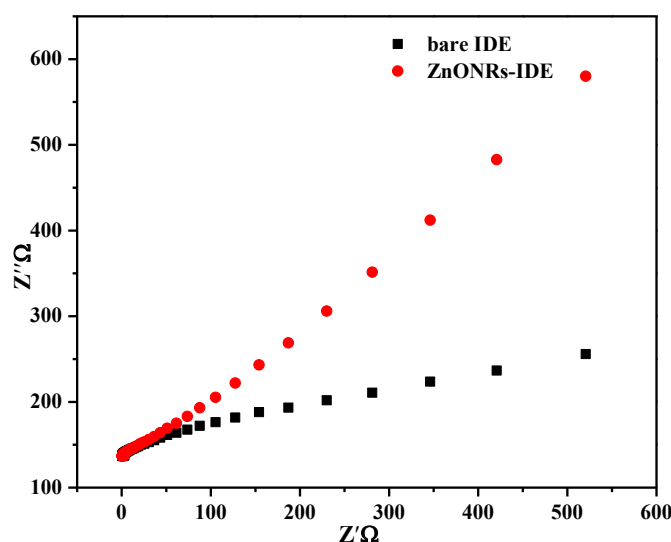


Figure 58. EIS Nyquist plot of bare IDE and ZnONRs-IDE

4.3.4.2 Effect of Scan rates

Figure 59 (a) depicts the impact that the scan rate has on the cyclic voltammogram of the ZnO nanorods-modified Au-IDE. This was accomplished by applying potentials from -0.2 V to 0.7 V at varying scan rates ranging from 20 to 120 mV/s in a solution that contained 0.1 M KCl as the supporting electrolyte and 0.001 M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$.

The reversible redox characteristics of the ferricyanide/ferrocyanide pair at the electrode interface yield well-define anodic and cathodic peaks, as illustrated in the figure. The peak-to-peak separation (ΔE_p) is measured at 58.4 mV, which corresponds to a typical reversible single-electron redox process [Alshaw et al., (2022)]. However, there is a slight rise in ΔE_p as the scan rate rises from 20 mV/s to 120 mV/s, suggesting a combined influence of diffusion and electron transfer kinetics.

Figure 59(b) shows that both anodic and cathodic peak currents increase proportionally with the square root of the scan rate. Moreover, the electron transfer process in the ferricyanide/ferrocyanide redox reaction is mainly controlled by diffusion at the electrode surface, as indicated by the high linear correlation ($r = 0.98$) between the peak currents and the scan rate's square root [Pei et al., (200)]. The electrochemically active surface areas of the developed modified Au-IDE and the unmodified Au-IDE were calculated to be 0.67 mm^2 and 0.25 mm^2 , respectively, using the Randles-Sevcik equation [Ghasemi et al., (2023)]. This indicates that the ZnO nanorod modification enhances the electrode's active surface area. Consequently, the modified electrode provides more interaction sites for the electrolyte and analyte, resulting in higher sensitivity and making it more suitable for electrochemical sensing applications compared to the bare Au-IDE.

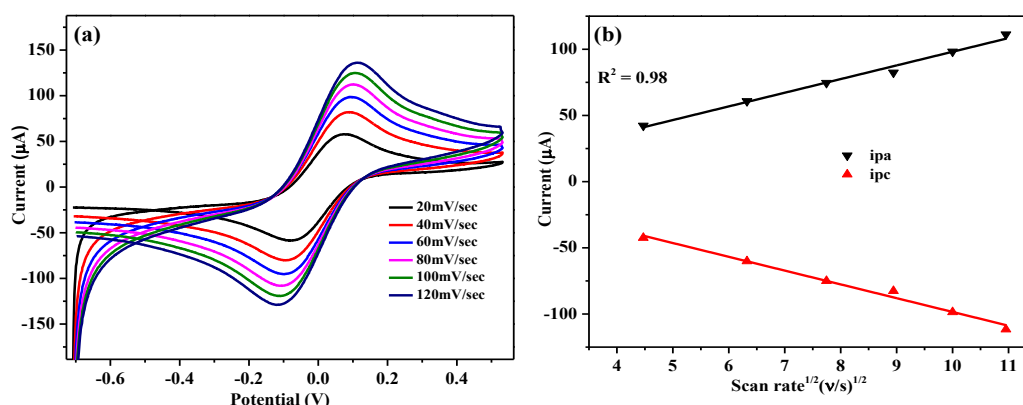


Figure 59 (a) Cyclic voltammogram of ZnONRs/Au-IDE recorded at various scan rates in a cell containing $0.001 \text{ M K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ dissolved in an electrolyte solution of 0.1 M KCl at pH 6 (scan rate = 0.02 V/s). **(b)** Linear plot of I_{pa}/I_{pc} vs. $\sqrt{\text{scan rate}}$ ($r^2 = 0.97$) indicates a diffusion-controlled electron transfer process.

4.3.4.2 Cyclic Voltammetry Detection of BPA

Abundant adsorption sites for BPA are provided by ZnO nanorods because of their large surface area and the number of surface defects. As a result, ZnO nanorods directly modified on an IDE-Au electrode can effectively bind BPA without requiring a linking agent. The strength of the interaction between BPA and the ZnO nanorods is influenced by the pH of the BPA solution. To evaluate this effect, a 1 mM BPA solution was prepared in a water-ethanol mixture, applying different pH levels of phosphate-buffered saline (PBS) solutions (6.0, 6.5, 7.0, 7.7, and 8.0). After being submerged in the pH 6 BPA solution, the ZnO nanorod-modified Au-IDE electrode was incubated for an hour at 4°C. The electrode was taken out and allowed to air dry at room temperature after incubation. Then, using an applied potential range of -0.2 V to 0.7 V, CV measurements were performed in a redox solution of 0.001 M $K_4 [Fe (CN)_6]/K_3 [Fe (CN)_6]$ in 0.1 M KCl. This process was carried out again using BPA solutions with varying pH values. The oxidation current dropped as the pH dropped, as shown in Fig. 60, indicating enhanced BPA binding affinity to the ZnO nanorods under more acidic conditions. Cyclic voltammetry was also used for detecting BPA at different concentrations using the modified electrode. A water-ethanol mixture was used to create a stock BPA solution (1 mM) and subsequently diluted with PBS (pH 6) to obtain a series of BPA solutions at different concentrations. The ZnO nanorods-modified Au-IDE electrode was incubated in each solution at 4°C for 1 hour to facilitate BPA adsorption. After incubation, the electrode was thoroughly dried and subjected to CV analysis in the same redox probe solution dissolved in an electrolyte solution of 0.1 M KCl applying over a potential range of -0.2 to 0.7 V. Figure 61 (a) shows a gradual decrease in both oxidation and reduction currents as BPA concentration increases. The variation is explained by the absorption of BPA molecules that occupy in the active sites of the electrode surface, which prevents electrons from moving from the electrode to the redox pair. Figure 61 (b) displays a calibration plot of oxidation current against BPA concentration, indicating a limit of detection (LOD) of 8.5 μM [Sawkar et al., (2022)].

Our fabricated electrode is compared to electrodes that have been reported in the past for the detection of BPA, and the results are presented in Table 8. The findings indicate

that although our electrode offers a lower detection limit than several other designs, some electrodes still demonstrate superior sensitivity. Nonetheless, it offers several key benefits, including lower cost, a simpler fabrication process, and broader applicability. These strengths make it a practical and scalable option for real-world BPA detection.

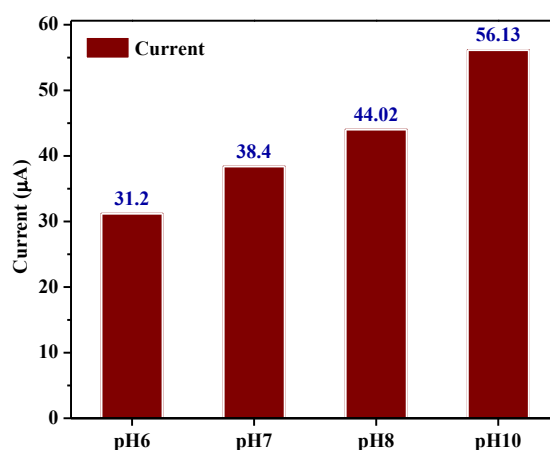


Figure 60. Oxidation current of the ZnO nanorod Au-IDE in BPA solutions at different pH levels, indicating that lower pH enhances the adsorption affinity of BPA.

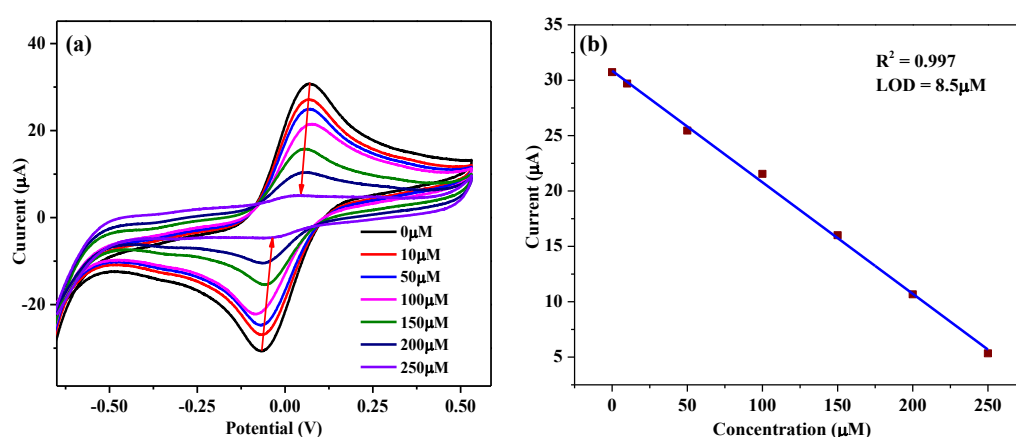


Figure 61. (a) Cyclic voltammograms of the ZnO nanorod-modified Au-IDE recorded at varying concentrations of BPA under an optimized pH of 6, using the redox probe (i.e. Ferric/ferrocyanide ions dissolved in 0.1 M KCl electrolyte solution). (b)

Corresponding calibration curve showing the relationship between BPA concentration and oxidation current, with the limit of detection (LOD) estimated at 8.5 μM .

Table 8. Comparison of the developed sensor with others reported sensors for Bisphenol A detection

Comparison of the Developed Electrochemical Sensor with Previously Reported Sensors for Bisphenol A Detection			
Electrochemical sensor	Detection method	Limit of detection	References
ZnO nanorods-Au-IDE	CV	8.5 μM	This work
GCE-PEDOT	CV	55 μM	[Mazzotta et al., (2013)]
GCE-PEDOT	Amperometry	22 μM	[Mazzotta et al., (2013)]
CS-Caped/ZnS QDTs	Fluorescence	8 μM	[Cao et al., (2014)]
CNHs-Nafion/GCE	Amperometry	1.8 μM	[Xu et al., (2013)]
Au-Pt@SiO ₂ /Au GN	SWV	1.8 $\mu\text{g L}^{-1}$	[Wu et al., 2019]
rGO-Ag/PLL/GCE	DPV	0.54 μM	[Li et al., (2017)]
MWCNT/AuNP/Paper	LSV	29.91 $\mu\text{g L}^{-1}$	[Li et al., (2016)]
Gr-AgCuNP/Au	LSV	299.07 $\mu\text{g L}^{-1}$	[Pogacean et al., (2016)]
Pt/PDDA-DMP/GCE	DPV	136.97 $\mu\text{g L}^{-1}$	[Zheng et al., (2016)]
GCE: Glassy Carbon Electrode; PEDOT: poly(3,4-ethylenedioxythiophene); CS: Chitosan; QDTs: Quantum dots; CNHs: Carbon nanohorns; GN: Graphene; SWV: Square Wave Voltammetry; rGO: Reduced graphene oxide; PLL: poly-L-lysine; MWCNT: Multi-walled carbon nanotube; AuNP: Gold nanoparticle; Gr-AgCu: Graphene-bimetallic nanoparticle composites; PDDA: poly (diallyl dimethyl ammonium chloride); DMP: diamond powder; DPV: Differential Pulse Voltammetry; LSV: Linear Sweep Voltammetry.			

4.3.4.3 Repeatability and Reproducibility Characteristics

The fabricated ZnO nanorod Au-IDE electrode was tested for repeatability and reproducibility using cyclic voltammetry (CV) in an optimized environment using redox probe i.e. 0.001 M ferricyanide/ferrocyanide ions dissolved in 0.1 M KCl electrolyte solution at pH 7. Repeatability was examined by performing four successive CV scans on the same electrode within a single day at regular time intervals as shown in figure 62. The results indicated excellent repeatability, with a relative standard deviation (RSD) of just 0.13%.

To assess reproducibility, the electrode was stored in an airtight Petri dish and tested weekly over a span of two weeks. The CV results showed that the electrode retained 92.4% and 90.2% of its initial peak current after two weeks, respectively as shown in figure 63. These findings confirm that the proposed electrode maintains strong repeatability and reproducibility over time.

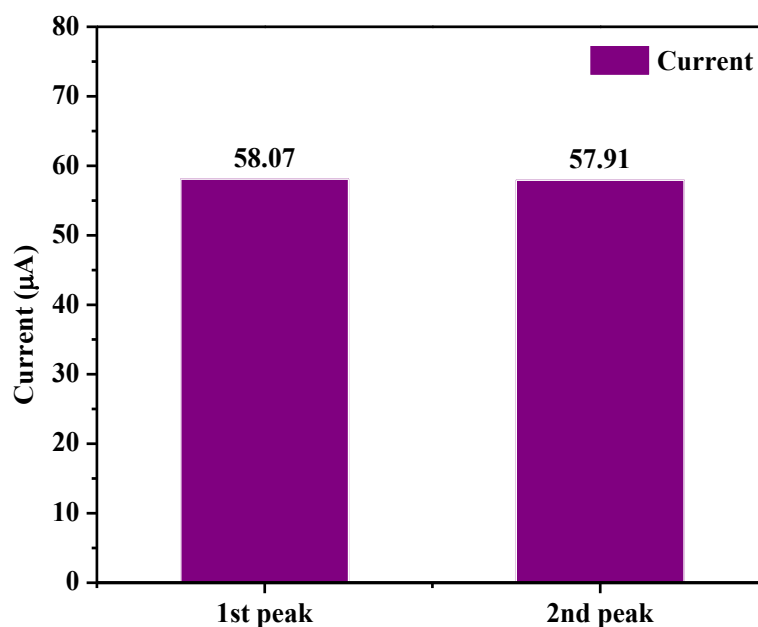


Figure 62. Bar chart illustrating the repeatability of the ZnO nanorod Au-IDE electrode.

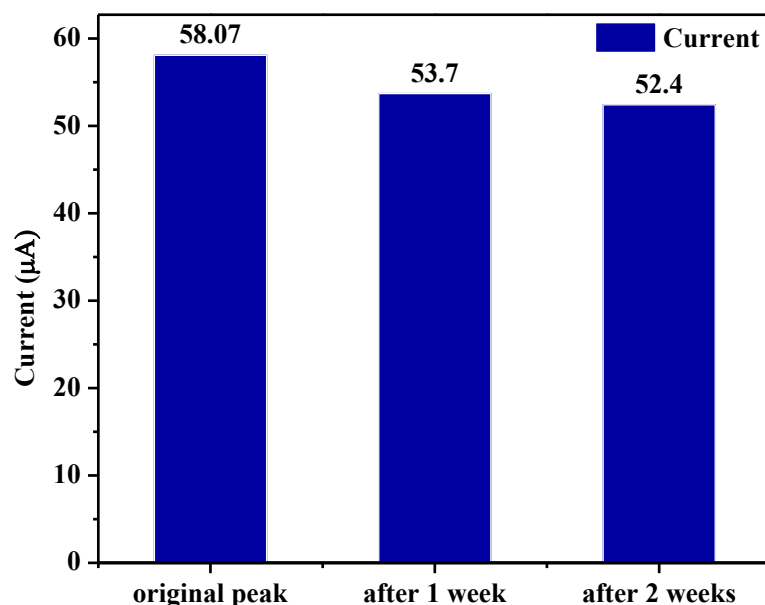


Figure 63. Bar chart illustrating the reproducibility of the ZnO nanorod Au-IDE electrode over a two-week period.

4.3.4.4 Real Sample Analysis

We conducted real-world tests using tin fish water samples taken from a local shop in Mizoram under ideal conditions to ensure the electrode's reliability. Three of these samples were spiked with known concentrations of BPA and analyzed using the cyclic voltammetry (CV) technique. The results, presented in **Table 9**, demonstrate the effectiveness of our electrode in detecting BPA in actual sample matrices.

Table 9 Real sample analysis of BPA in tin fish water sample.

Samples	Added spike (μM)	Found (μM)	Recovery %
1	10	9.84	95.4%
2	20	19.3	95%
3	30	28.18	93%

4.3.5 Conclusion

In summary, a cost-efficient approach was established for fabricating a thin-film gold interdigitated electrode on a glass slide, utilizing a stainless-steel IDE mask in combination with E-beam thin film deposition. The resulting Au-IDE consisted of 18

pairs of alternately arranged electrodes, each with a width of 439.8 μm and an inter-electrode spacing of approximately 514 μm . Surface modification with ZnO nanorods greatly improved the device's sensitivity. Using the ZnO-modified Au-IDE, electrochemical detection of bisphenol A (BPA) was successfully demonstrated, achieving a limit of detection (LOD) of 8.5 μM . These findings highlight the effectiveness and economic feasibility of the ZnO nanorod-modified Au-IDE as a promising platform for electrochemical sensing applications.

4.4 Thin film gold electrode modified with electrochemically reduced graphene oxide for sensing cadmium ions.

Gold (Au) nanoparticle-based electrodes are widely used in electrochemical sensors due to their excellent conductivity, chemical stability, and biocompatibility [Yi et al., (2022)], [Petrucchi et al., (2022)]. To enhance their performance for specific sensing tasks, innovative fabrication and surface modification methods are essential. Thin-film Au electrodes on glass substrates offer an attractive solution, combining gold's advantages with the ease of integration and fabrication typical of thin films [Toudeshkchoui et al., (2019)]. Glass is an affordable, readily available material that provides a smooth, durable surface ideal for uniform film deposition and easy surface modification, which is critical for tailoring electrode properties.

Recent advances in nanomaterials have significantly boosted sensor performance [Curulli et al., (2020)], [Zhu et al., (2015)]. Two-dimensional (2D) materials, in particular, have garnered a lot of attention due to the fact that they possess distinctive physical, chemical, and electrical properties. [Kumar et al., (2022)], [Devi et al., (2024)]. Their large surface-to-volume ratio, tunable band gaps, and mechanical flexibility make them ideal for enhancing sensor-analyte interactions. As a result, many 2D materials are being explored in electrochemical sensors for detecting environmental pollutants, biomolecules, and pharmaceuticals [Ab Latif et al., (2022)], [Li et al., (2022)]. Reduced graphene oxide (rGO) is one of the most promising 2D materials for electrochemical applications. Derived from partially reduced graphene oxide, rGO maintains some oxygen-containing groups while regaining conductivity, offering high porosity, large surface area, and excellent electron transport [Joshi et al., (2021)], [Zare-Dorabei et al., (2016)]. These features make it ideal for electrode surface modification. Recent work has shown that microwave-assisted synthesis is an efficient, scalable method for producing rGO-based nanocomposites. For example, rGO–MoS₂ decorated with Fe₃O₄ nanoparticles (rGO–MoS₂@Fe₃O₄) has been used to detect compounds like epinephrine and para-nitrophenol (p-NP) [Kalia et al., (2024)], [Kalia et al., (2022)].

In these hybrids, rGO enhances conductivity and surface area, supporting uniform dispersion of the active components and boosting sensor sensitivity. rGO composites have also been used for detecting toxic chemicals such as hydrazine. Modified gold electrodes with rGO–MoS₂ improved electron transfer and detection limits [Rana et al., (2023)]. Other studies have explored rGO combined with materials like WS₂ and TiO₂ nanowires for sensing and environmental cleanup. For instance, rGO@WS₂ and rGO–WS₂/Fe₃O₄ synthesized via microwave methods were used to detect p-NP and dopamine [Rana et al., (2022)], [et al., (2022)], while GO/rGO-coated TiO₂ nanowires achieved photoreduction of Cr (VI) under simulated sunlight [Rahmat et al., (2022)]. These rGO-based hybrids combine the advantages of rGO with other nanomaterials to improve sensitivity, selectivity, and stability. However, their complex synthesis processes can limit scalability and practical use. To overcome this, the current study introduces a simpler, scalable method: depositing a 50 nm gold (Au) thin film on glass using e-beam deposition, followed by electrochemical reduction of GO to form ErGO. This straightforward technique enables the low-cost, rapid fabrication of sensitive electrodes for detecting cadmium (Cd²⁺) ions, demonstrating efficient potential for real-world applications.

4.4.2 Results and discussion

4.4.2.1 XRD characterization

XRD analysis was utilized to look into the crystalline properties of graphite, synthesized graphene oxide (GO), and reduced graphene oxide–gold (rGO–Au) thin film electrodes. **Figure 64** displays the XRD patterns of these materials. For graphite, the XRD pattern reveals sharp diffraction peaks at $2\theta = 26.440^\circ$, which corresponds to the **(101) crystal plane** with an interlayer spacing (**d-spacing**) of **3.368 Å**. This value is characteristic of graphite's layered structure, as reported in standard reference data (JCPDS No: 75-2078) [Stobinski et al., (2014)], [Shalaby et al., (2015)]. In the case of synthesized GO, a strong peak appears at $2\theta = 10.60^\circ$, indicating a **(001) plane** with a d-spacing of **8.33 Å**. The oxidation of graphite results in the inclusion of oxygen-containing functional groups, which is the cause of this increase in d-spacing. [Hidayah et al., (2017)], [Jiao et al., (2017)]– [Paredes et al., (2018)]. For the ErGO coated on thin film Au electrode, the XRD pattern shows a shifted peak at $2\theta =$

24.170°, corresponding to the **(002) plane** with a d-spacing of 3.67 Å. This shift suggests the partial restoration of the graphene structure following the electrochemical reduction of GO. Additionally, the XRD pattern of the rGO–Au electrode includes a distinct peak at $2\theta = 49^\circ$, attributed to the **(001) crystallographic plane** of Au thin film coated on the glass substrate.

The interlayer spacing (d-spacing) was calculated using **Bragg's Law**, expressed as:

$$n\lambda = 2d \sin \theta \text{ or } d = \frac{n\lambda}{2 \sin \theta}$$

Where:

- $\lambda = 1.5406 \text{ Å}$ (wavelength of Cu K α radiation),
- θ is the diffraction angle (in radians),
- $n = 1$, the order of reflection,
- and d is the interplanar spacing.

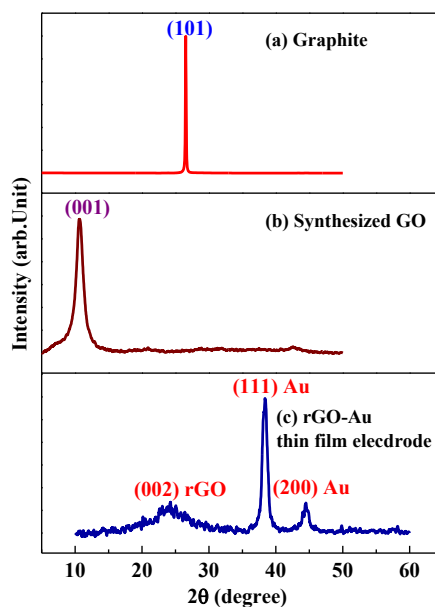


Figure 64. XRD patterns of (a) graphite powder, (b) synthesized GO, and (c) ErGO deposited on Au thin film electrode.

4.4.2.2 FT-IR analysis

Figure 65 presents the FTIR patterns of graphite, synthesized graphene oxide (GO), and electrochemically reduced graphene oxide (ErGO), highlighting the differences in their functional groups. In the spectrum of **graphite**, a single notable peak is observed around **1712.1 cm⁻¹**, corresponding to **C=C stretching vibrations** of the sp² carbon framework. Since there are no additional notable peaks, it can be concluded that oxygen-containing functional groups are not present.

For **synthesized GO**, the FTIR spectrum reveals the introduction of various oxygen functional groups as a result of the oxidation process. A strong and broad absorption band appears around **3348.42 cm⁻¹**, attributed to **O-H stretching vibrations** from hydroxyl groups. A pronounced peak near **1712.79 cm⁻¹** corresponds to **C=O stretching vibrations of carboxylic acid groups**. Additional significant peaks include a **C=C skeletal vibration** at **1620.21 cm⁻¹**, **C-OH stretching** (hydroxyl) at **1219.1 cm⁻¹**, and **C-O stretching** (from epoxy and alkoxy groups) around **1041.56 cm⁻¹**. Furthermore, a peak at **771 cm⁻¹** represents **C-C skeletal vibrations**, indicating the partially retained graphitic structure. In the case of **ErGO**, the FTIR spectrum shows peaks at **1720.5, 1558.48, 1219.01, and 771.53 cm⁻¹**. The peak about 1720.5 cm⁻¹ still pertains to C=O stretching, although with reduced intensity compared to GO, suggesting partial reduction of carboxylic groups. The band at **1558.48 cm⁻¹** likely indicates **C=C skeletal vibrations**, shifted from the GO spectrum due to restoration of conjugated π -systems. The persistence of the **1219.01 cm⁻¹** and **771.53 cm⁻¹** peaks suggests residual hydroxyl and C-C skeletal structures. Notably, the broad O-H stretching band around 3348 cm⁻¹ is absent, indicating successful removal of most hydroxyl groups during electrochemical reduction.

4.4.2.3 Raman Spectroscopy Analysis

Raman spectroscopy serves as a prominent and efficient method for differentiating between graphene oxide (GO) and reduced graphene oxide (rGO). In this study, Raman spectra were acquired using a micro-Raman spectrometer (Maker: Horiba Scientific, France, Model: LabRAM HR-UV-Open) with a laser excitation wavelength of 532 nm. The spectra for both GO-Au and rGO-Au thin film electrodes

are shown in **Figure 66**. Both electrodes display characteristic D and G bands in their Raman spectra. The D band arises due to structural defects within the graphene lattice, while the G band is associated with the in-plane vibrational modes of carbon atoms with sp^2 hybridization. For the GO-Au electrode, the D and G bands are detected at 1341.59 cm^{-1} and 1592.53 cm^{-1} , respectively. In comparison, the rGO-Au electrode shows these bands at 1350.58 cm^{-1} and 1586.53 cm^{-1} . Typically, the D band in GO-Au is broader and more intense than that in rGO-Au, whereas the G band in rGO-Au is narrower and more pronounced than in GO-Au.

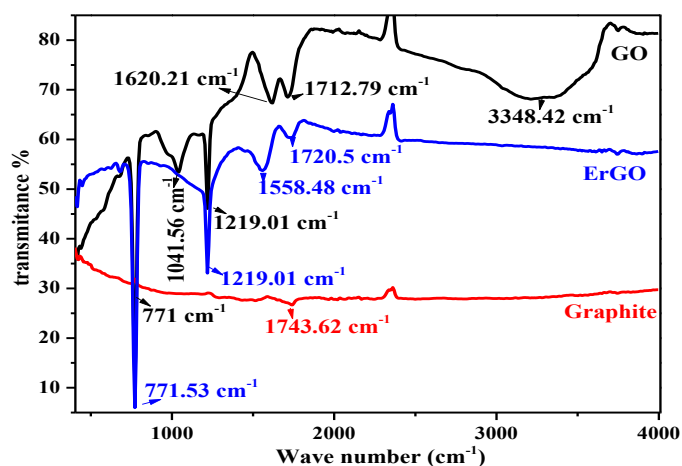


Figure 65. FTIR spectrums of graphite powder, synthesised GO and ErGO.

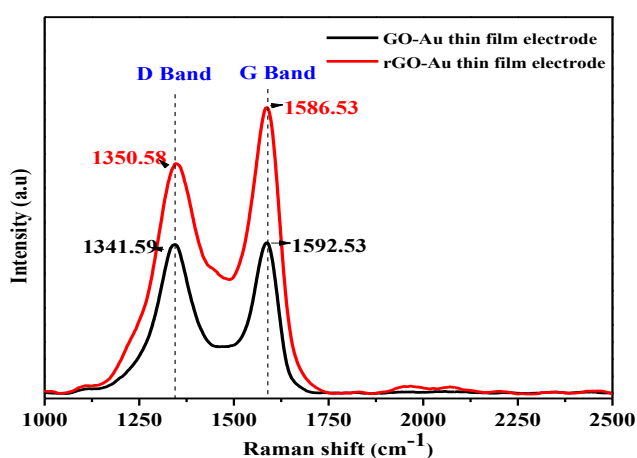


Figure 66. Raman spectra of (Black) GO - Au thin film electrode and (Red) rGO - Au thin film electrode.

4.4.2.4 FESEM and HRTEM Characterization

FESEM analysis was performed to observe the differences in surface morphology between graphene oxide (GO) and reduced graphene oxide (rGO), which result from their distinct chemical structures and synthesis methods.

In Figure 67 (a), the FESEM image of GO deposited on a gold thin film electrode shows a typical wrinkled and folded surface. This texture results from the incorporation of oxygen-containing functional groups such as hydroxyl, carboxyl, and epoxy which deform the orderly carbon lattice and cause surface irregularities. Figure 67 (b) shows that rGO has a more homogeneous and orderly surface compared to GO. This improvement is attributed to the elimination of most oxygen-containing groups at the time of the reduction process, which helps to restore the sp^2 -hybridized carbon framework. The FESEM image of GO (as shown in Figure 67 (a)) displays wrinkled and layered flakes on the surface, indicating that the graphene layers were successfully and fully oxidized to form GO. These flaky structures are characteristic of GO due to the introduction of oxygen-containing functional groups between the layers. Upon electrochemical reduction using CV, as shown in Figure 67 (b), the morphology changes noticeably. The FESEM image of rGO reveals crumpled, that are loosely stacked and exhibit a disordered, corrugated structure.

Figure 67 (C) displays the thin layer TEM image of the rGO. The high-resolution TEM (HRTEM) image in Figure 67 (d) displays visible fringe patterns, revealing a plane-to-plane distance of 0.351 nm corresponding to the (002) plane. Additionally, the SAED pattern in Figure 68 presents hexagonal diffraction spots, indicating a d-spacing of 0.363 nm for the (002) plane.

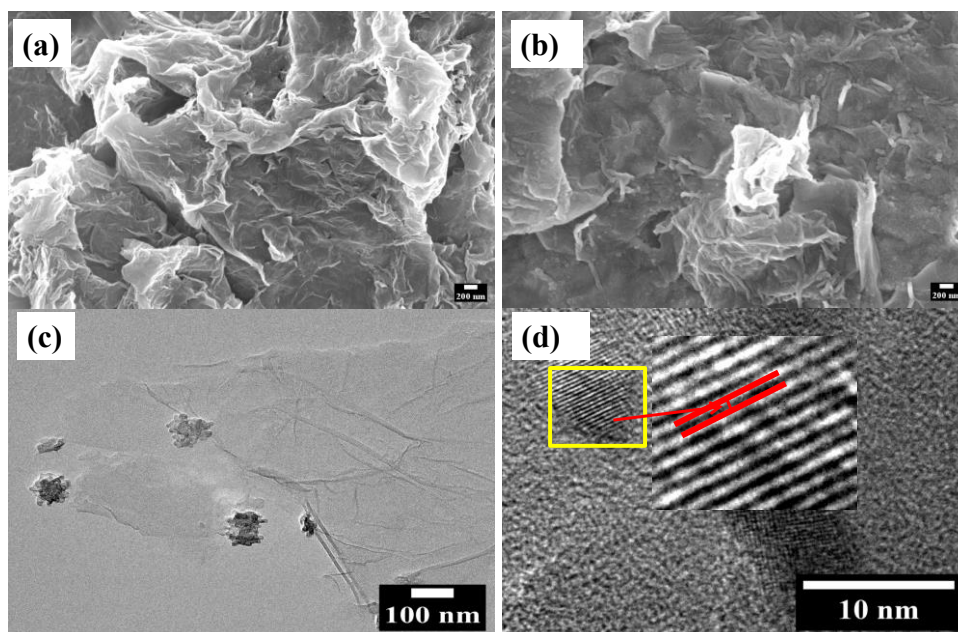


Figure 67. FESEM image of GO on Au thin film electrode (a), (b) rGO on Au thin film electrode, (c) TEM image of rGO and (d) HRTEM image of rGO.

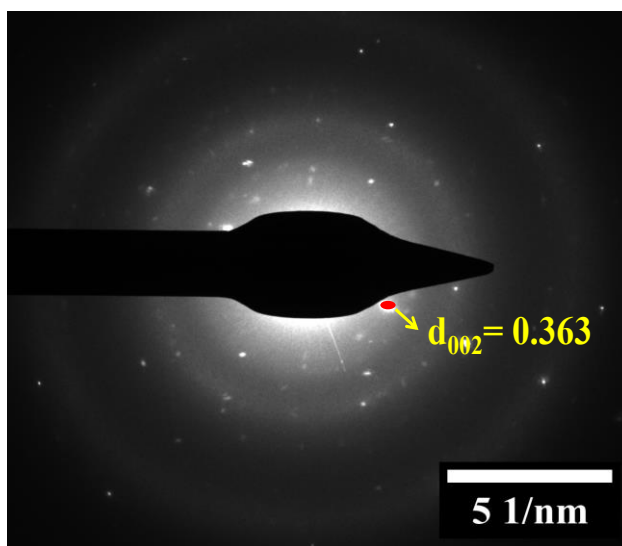


Figure 68. SAED image of ErGO, highlighting its crystalline structure with a d-spacing of 0.363 nm for the (002) plane, which closely matches the d-spacing observed in the HRTEM analysis.

4.4.2.5 AFM analysis

AFM analysis was carried out to examine the surface morphology and thickness profiles of the fabricated thin-film samples, which include a bare gold (Au) thin film, graphene oxide (GO), and reduced graphene oxide (rGO). The AFM measurements were carried out using Bruker's Dimension Icon and Multimode 8 instruments, which are well-suited for high-resolution topographical imaging and nanoscale surface characterization. As shown in figure 68, the AFM results revealed evident differences in the surface heights (thicknesses) of the samples. Specifically, the bare Au thin film exhibited the lowest height among the three, indicating a relatively smooth and uniform surface. In contrast, the GO layer displayed a greater height than the bare Au, which is consistent with the deposition of an additional material layer (graphene oxide) onto the gold substrate. GO tends to have a wrinkled or flake-like morphology due to the inclusion of oxygen-containing functional groups that arise its interlayer spacing and surface roughness. Interestingly, the reduced graphene oxide (rGO) sample showed an even greater height than the GO layer. This increase in thickness after the reduction process can be attributed to structural rearrangements and possible aggregation of graphene sheets during the chemical or thermal reduction of GO. Reduction removes some oxygen functionalities, partially restoring the conjugated carbon network and leading to changes in stacking behavior, flake overlap, and surface roughness. These morphological changes are reflected in the increased thickness measured by AFM.

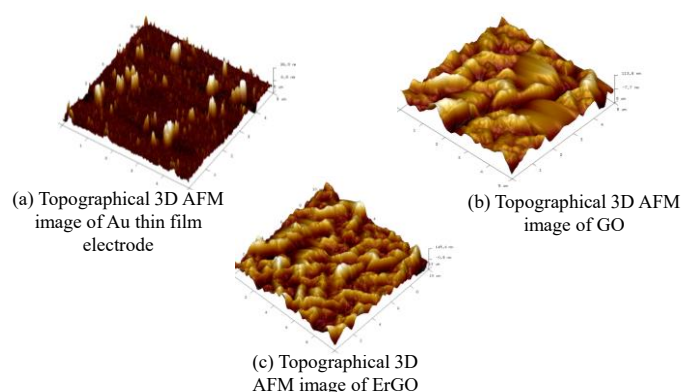


Figure 69. AFM image of (a) Au thin film electrode (b) GO and (c) ErGO

4.4.3 Electrochemical Performance Evaluation

Electrochemical characterization was carried out at room temperature using a potentiostat configured in a standard three-electrode system. In this setup, the working electrode consisted of a reduced graphene oxide gold (rGO-Au) thin film, with a platinum sheet serving as the counter electrode and an Ag/AgCl electrode as the reference. The electrolyte utilised for the measurements was a 0.1 M KCl solution. Figure 70 presents the cyclic voltammetry (CV) curves for three different electrodes tested in a cell containing 0.001 M $K_3[Fe(CN)_6]$ / $K_4[Fe(CN)_6]$ dissolved in an electrolyte solution of 0.1 M KCl. As shown in figure 70, the rGO-Au thin film electrode exhibited significantly higher oxidation and reduction peak currents compared to the GO-Au and Bare-Au thin film electrodes the applied the potential window of -0.2 V to 0.8 V. This enhanced sensitivity is attributed to the rGO-Au electrode's high surface area-to-volume ratio and impressive conductivity. The electroactive surface areas of the electrodes were estimated using the Randles–Sevcik equation, yielding values of 0.002357 mm^2 for rGO–Au, 0.001502 mm^2 for GO–Au, and 0.001082 mm^2 for Bare–Au electrodes. These results confirm that the rGO–Au electrode possesses a larger electrochemically active surface area than the other two.

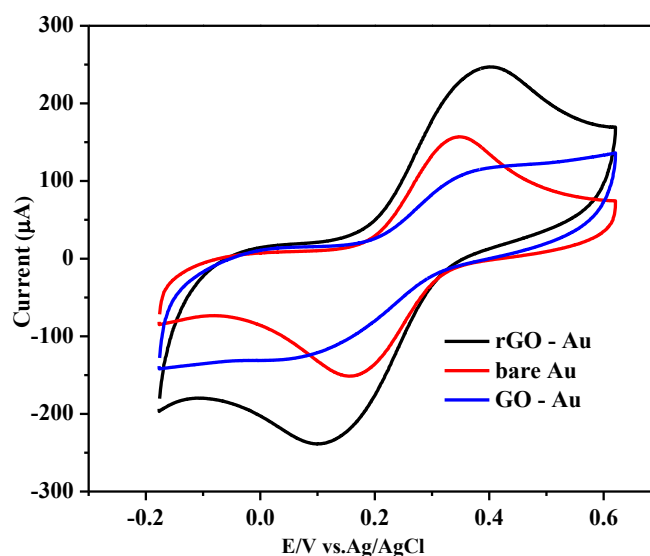


Figure 70. CV responses of the three different electrodes in solution of 1 mM $K_3[Fe(CN)_4]$ / $K_4[Fe(CN)_6]$ in an electrolyte solution of 0.1 M KCl at 20 mV/s scan rate

i.e., (black) rGO - Au thin film electrode, (red) Au thin film electrode and (blue) GO-Au thin film electrode.

The effect of scan rate on the cyclic voltammetry (CV) behavior of rGO-Au thin film electrodes was examined in a solution containing 0.1 M KCl and 0.001 M $K_4[Fe(CN)_6] / K_3[Fe(CN)_6]$ (shown in Fig. 71 (a)). We can observe the increase in the peak current with higher scan rates when the applied voltage was swept from -0.2 V to 0.7 V. However, at elevated scan rates, the peak current shows a slight decline due to reduced diffusion efficiency. Figure 71 (b) demonstrates a linear correlation between the peak current and the square root of the scan rate, confirming diffusion-controlled electrochemical behavior.

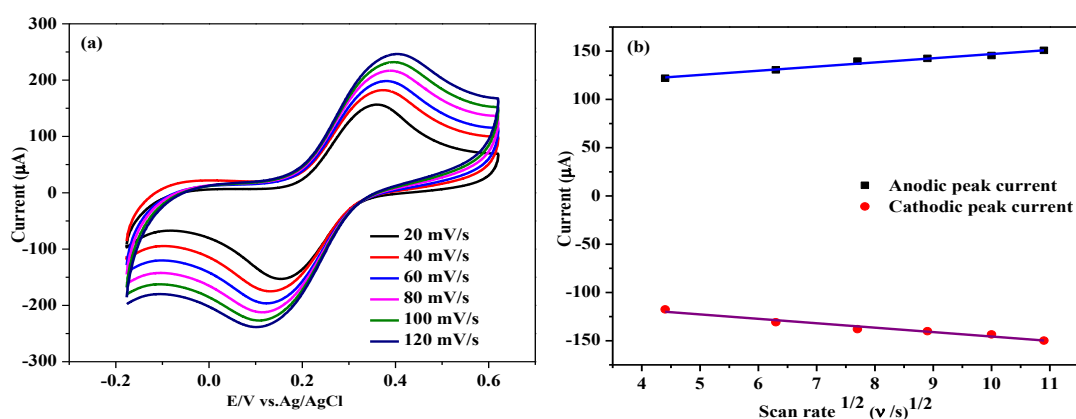


Figure 71. (a) CV curves of the rGO-Au thin film electrode recorded at various scan rates in a solution containing 1 mM $K_3[Fe(CN)_6] / K_4[Fe(CN)_6]$ in 0.1 M KCl. (b) A linear correlation between the peak current and the square root of the scan rate, indicating a diffusion-controlled process.

4.4.3.1 Electrochemical determination of Cd^{2+} ion.

The performance of the fabricated electrode for detecting Cd^{2+} ions was evaluated using cyclic voltammetry (CV) at varying Cd^{2+} concentrations in a 0.1 M KCl solution. Figure 72 (a) presents the cyclic voltammogram shown by the electrode between -0.6 to -0.3 V. As depicted, the I_{pa} increases with rising Cd^{2+} concentrations up to a certain

threshold, the detection limit. Beyond this point, further increases in concentration lead to a decline in peak current. This reduction is attributed to the saturation of active sites on the electrode surface, which hampers electron transferring process efficiency in the electrode junction and the electrolyte at higher ion concentrations. The LOD was determined by plotting the oxidation peak current against the Cd^{2+} concentrations, as illustrated in Figure 71 (inset), yielding a value of $1.34 \mu\text{M}$.

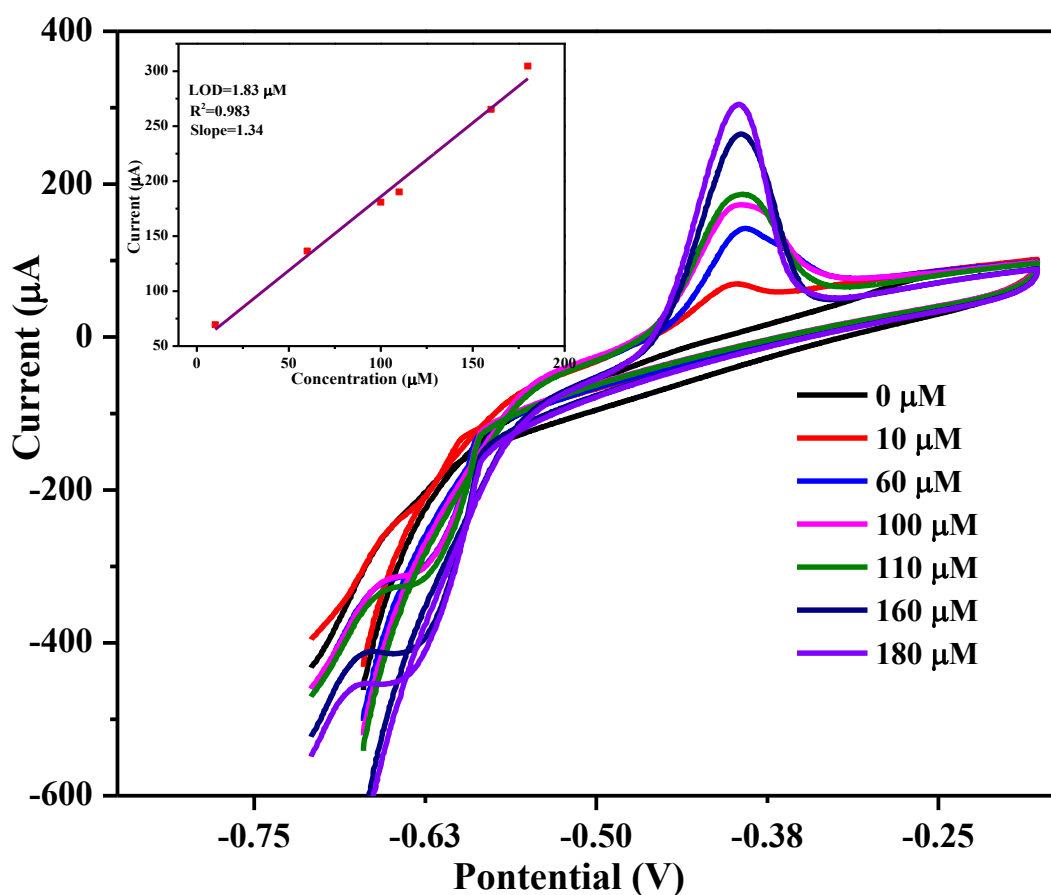


Figure 72. Cyclic voltammetry (CV) response of the rGO–Au thin film electrode at varying analyte concentrations (scan rate: 20 mV/s), with the inset showing the plot of current versus concentration used to estimate the LOD (inset).

4.4.3.2 Repeatability and Reproducibility of the Electrode

The fabricated electrode was tested for the repeatability and reproducibility nature using cyclic voltammetry (CV) in a cell containing 0.001 M ferricyanide/ferrocyanide

ions in an electrolyte solution of 0.1 M KCl at pH 7, following the optimized settings described earlier. To assess repeatability, two consecutive CV scans were performed on the same electrode within a single day, maintaining consistent time intervals between scans. As shown in Figure 73, the electrode exhibited impressive repeatability, with a relative standard deviation (RSD) of just 0.415%.

Reproducibility was assessed by storing the electrode in an airtight container or Petri dish and testing it weekly over a three-week period. The electrode retained 99.6%, 97.08%, and 97.11% of its initial peak current after one, two, and three weeks, respectively (Figure 73). These results indicate that the proposed electrode exhibits strong repeatability and long-term stability.

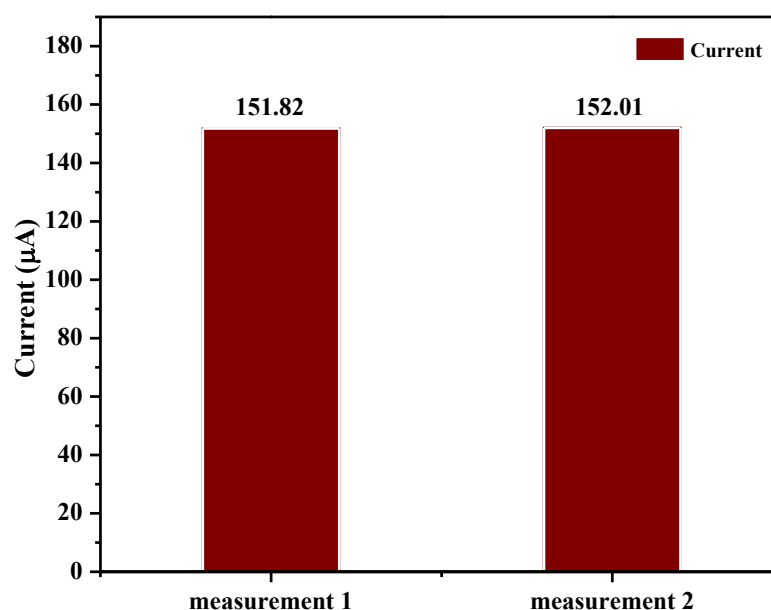


Figure 73. Oxidation current responds by rGO-Au thin film electrode in 2 consecutive CV measurements within a day at regular time interval. The result shows good repeatability of 0.415 RDS%.

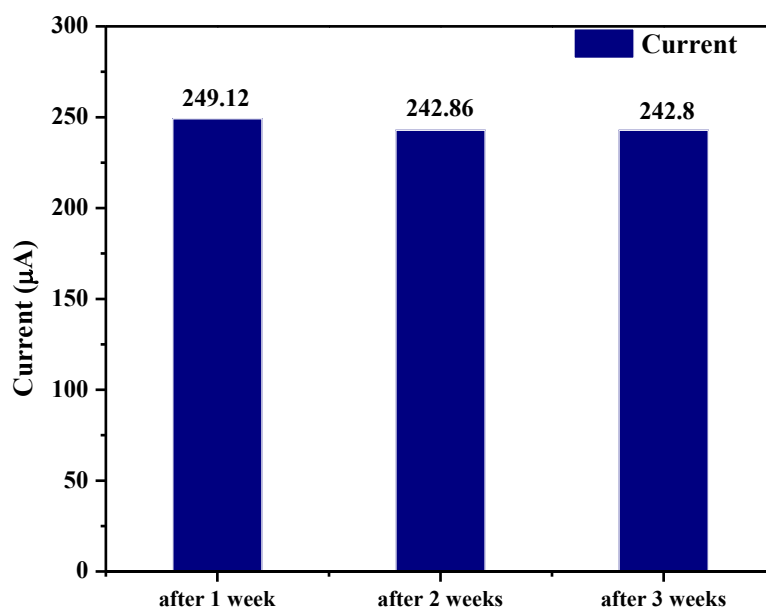


Figure 73. Oxidation current respond of rGO-Au thin film electrode in 3 measurements taken over 3 weeks.

4.4.4.4 Real Sample Analysis

The proposed electrode was tested to evaluate the reliability nature in actual samples. Tap water was collected from IIT (ISM) Dhanbad, and experiments were conducted under optimized conditions. To assess the electrode's capability in detecting Cd ions, known concentrations of Cd were added to three separate water samples (spiked samples), and the current responses were recorded using the cyclic voltammetry (CV) technique. The observations from these tests are summarized in Table 10. The results confirm that the proposed electrode is effective in detecting Cd ions in real-world water samples.

Table 10. Real sample analysis of Cd ions in tap water.

Samples	Added spike (μM)	Found (μM)	Recovery%
1	60	59.2	96.6%
2	90	90.19	98.8%
3	115	114.8	98.7%
4	125	124.8	98.8%

4.4.5 Conclusion.

The study developed a modified gold electrode by reducing graphene oxide (GO) on a thin film Au substrate, resulting in a highly conductive reduced graphene oxide (rGO) - modified Au electrode via electrochemical reduction. This process created a robust and conductive rGO layer, enabling sensitive detection of Cd^{2+} with a low LOD of 1.35 μM . The electrode demonstrated excellent repeatability (0.415 RDS%) and reproducibility. This work highlights the effectiveness of rGO in enhancing Au electrode performance for detecting heavy metal ions, offering promising advancements for electrochemical sensors in environmental monitoring and safety.

CHAPTER 5. CONCLUSION

5.1 Conclusion

The primary objective of this thesis was to explore and develop cost-effective, high-performance electrochemical sensors through the application of advanced nanofabrication techniques, with a particular focus on nanoimprint lithography (NIL). The motivation for this work stems from the growing global demand for rapid, reliable, and economical methods for detecting environmental contaminants, especially in the face of increasing industrialization and the associated rise in pollution. Heavy metal ions such as cadmium, as well as organic pollutants like bisphenol A and thiram, pose significant risks to human health and the ecosystem, necessitating the development of sensitive and selective detection platforms. Traditional sensing technologies, although effective, often involve high costs, complex fabrication steps, and limited scalability. To address these challenges, this research investigated the integration of NIL—a technique known for its low cost, high throughput, and ability to create nanoscale features—with a variety of nanomaterials to fabricate novel electrochemical sensing platforms. NIL's potential to produce reproducible and uniform nanostructures makes it an ideal candidate for the mass production of sensor devices. By leveraging the precision of NIL and the unique properties of nanomaterials like zinc oxide nanorods (ZnONRs) and reduced graphene oxide (rGO), the research aimed to engineer sensors that not only exhibit superior electrochemical performance but also remain economically feasible for widespread environmental monitoring applications. The work encompassed the full fabrication process—from substrate preparation to electrode deposition and modification—and systematically evaluated each sensor configuration for its sensitivity, selectivity, stability, and overall applicability in detecting hazardous analytes in environmental samples.

In the initial phase of the study, considerable emphasis was placed on the fabrication of reliable and reproducible thin-film gold (Au) electrodes using electron beam (e-beam) deposition. This technique was chosen for its high precision and ability to

produce uniform thin films with excellent electrical conductivity, which are essential characteristics for the base of high-performance electrochemical sensors. These Au thin films served as the foundational platform for further functionalization with nanostructured materials to enhance sensor performance. The next critical step involved the modification of these gold electrodes with zinc oxide nanorods (ZnONRs), which were synthesized and patterned using the nanoimprint lithography (NIL) technique. The NIL process enabled the formation of well-aligned, uniformly distributed ZnONRs on the electrode surface, significantly increasing the effective surface area and providing abundant active sites for analyte interaction. This structural advantage directly contributed to improved sensitivity and detection capability of the sensors. Furthermore, the incorporation of NIL not only ensured scalability and cost-effectiveness but also improved the reproducibility of the sensor fabrication process, which is a key requirement for commercial applications. Beyond ZnONRs, the study also explored the integration of reduced graphene oxide (rGO) as a functional nanomaterial due to its extraordinary electron transport properties and high specific surface area. The combination of these nanostructures with gold thin films resulted in synergistic enhancements in electrochemical response, particularly in terms of lowering detection limits and increasing signal-to-noise ratios. This comprehensive fabrication strategy, involving multiple electrode architectures and material combinations, provided a versatile framework for tailoring sensor properties to specific environmental detection needs.

Furthermore, this study expanded beyond conventional planar electrode configurations to investigate the fabrication and electrochemical behavior of gold interdigitated electrodes (IDEs), which offer distinct advantages in terms of miniaturization, signal amplification, and integration into portable sensing devices. The IDEs were fabricated using e-beam deposition techniques and subsequently modified with zinc oxide nanorods (ZnONRs), further enhancing their surface-to-volume ratio and electrochemical performance. The interdigitated design significantly reduced the diffusion distance for analytes and facilitated more efficient electron transfer between the electrode surface and target molecules. This architecture is particularly advantageous for the development of compact, low-power sensors suitable for field

applications and wearable technologies. When modified with ZnONRs, these IDEs demonstrated remarkable sensitivity and selectivity for detecting bisphenol A (BPA), a widely used industrial compound known to disrupt endocrine function. The enhanced detection capability is attributed to the synergistic effects of the high surface area provided by the nanorods and the efficient charge collection afforded by the IDE structure. Importantly, the use of ZnONRs in modifying IDEs further validated the scalability and reproducibility of the overall fabrication strategy, confirming its applicability to both traditional electrode platforms and advanced sensor designs. The successful demonstration of ZnONRs-modified Au-IDEs for detecting organic pollutants underscores the flexibility of the NIL-based fabrication approach and its potential for enabling the next generation of compact, affordable, and high-performance environmental sensors.

The electrochemical characterization was performed using both two-electrode and three-electrode systems. The sensor configurations were tested for their ability to detect environmentally significant analytes, including cadmium ions, thiram, bisphenol A, and the simultaneous detection of multiple heavy metals.

Key findings of the research include:

1. **High Sensitivity and Selectivity:** The NIL-fabricated ZnONRs/Au electrodes demonstrated excellent sensitivity and selectivity for cadmium ions and thiram. The high surface area and specific binding sites of ZnONRs contributed significantly to the sensor's performance.
2. **Simultaneous Detection Capability:** The sensor based on ZnONRs-modified gold electrodes effectively detected multiple heavy metal ions concurrently, highlighting the versatility and practical utility of the NIL-fabricated sensors in complex environmental samples.
3. **Low-Cost and Scalable Fabrication:** The use of NIL in fabricating nanostructures not only reduced production costs but also ensured uniformity and reproducibility, essential for commercial deployment of electrochemical sensors.

4. **Graphene-Enhanced Sensing:** Incorporating electrochemically reduced graphene oxide onto thin-film Au electrodes substantially improved the detection limits for cadmium ions, validating the synergistic effect of combining graphene nanostructures with metal electrodes.
5. **Advanced IDE Platforms:** The gold IDEs modified with ZnONRs offered a robust and miniaturized sensing platform for the detection of bisphenol A, a critical endocrine-disrupting compound. The integration of nanorods enhanced the electrochemical response due to improved analyte adsorption and charge transfer dynamics.

In conclusion, this research validates the application of nanoimprint lithography as a viable, scalable, and cost-effective method for fabricating high-performance electrochemical sensors. The study also provides a comparative analysis of different nanomaterial modifications, including ZnONRs and rGO, on various electrode platforms. By combining nanostructured materials with advanced lithography techniques, this work lays the foundation for future development of portable, sensitive, and selective sensors for real-time environmental monitoring and point-of-care diagnostics.

Moving forward, the strategies developed in this thesis could be further enhanced by integrating microfluidics, wireless communication modules, and machine learning algorithms for signal processing, ultimately contributing to the advancement of smart sensor systems and the Internet of Things (IoT) in environmental monitoring.

5.2 References

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Examination passed	Year of Passing	Board/ University	Class/ Division	% of Marks	Subjects
All India Secondary School Examination	2009	Central Board of Secondary Education	I	82%	Eng., Hindi, Maths, Science, Social Science
All India Senior School Certificate Examination	2011	Central Board of Secondary Education	I	84%	Eng., Maths., Physics, Chemistry, Biology
B. Sc.(H) Chemistry	2014	University of Delhi	I	66.8%	Chemistry, Physics, Maths.,
M.Sc. Chemistry	2016	University of Delhi	II	58..4	Chemistry

LIST OF PUBLICATION

A. Publication from thesis

1. **Singh, Nongmaithem Herojit**, Rakesh Singh Moirangthem, Shagolsem Romeo Meitei, and N. Mohondas Singh. "Fabrication and characterization of zinc oxide nanorods-modified electrodes using nanoimprint lithography for electrochemical sensing of heavy metal ions." *Thin Solid Films* 807 (2024): 140550. (IF 2)

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2. **Singh, Nongmaithem Herojit**, Rakesh Singh Moirangthem, Brojendro Singh Shagolsem, and N. Mohondas Singh. "Development of a low-cost gold IDE electrode modified with ZnO nanorods for enhanced electrochemical sensing of bisphenol A." *Inorganic Chemistry Communications* 178 (2025): 114416. (IF 4.4)

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B. Publication as Co-author

1. Shagolsem, Brojendro Singh, **Nongmaithem Herojit Singh**, Niveda Leishangthem, Naorem Ramananda Singh, Naorem Premjit Singh, and N. Mohondas Singh. "Plant-synthesis of co-doped tin dioxide nanocomposite with magnetic activity and its photocatalytic performance assessment on dyes and pesticides." *Ceramics International* 50, no. 24 (2024): 54420-54437. (IF 5.1)

<https://doi.org/10.1016/j.ceramint.2024.10.297>

2. Lianmawii, Lal, Brojendro Singh Shagolsem, Nongmaithem Herojit Singh, and N. Mohondas Singh. "A comparative study on the photocatalytic activity of MgNiS: Eu³⁺ and MgNiS: Sm³⁺ nanoparticles for the degradation of eriochrome black T dye." *Inorganic Chemistry Communications* 172 (2025): 113694. (IF 4.4)

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3. Meitei, Shagolsem Romeo, Nongmaithem Herojit Singh, Pheiroijam Nonglen Meitei, and Leimapokpam Sophia Devi. "Hexagonal ZnO nanorods synthesized via

hydrothermal method: a study of their structural and optical properties and photodetection potential." *Journal of Materials Science: Materials in Electronics* 35, no. 36 (2024): 1-7. (IF 2.8)

<https://doi.org/10.1007/s10854-024-14052-8>

4. Naorem, Ramananda Singh, Naorem Premjit Singh, Brojendro Singh Shagolsem, Nongmaithem Herojit Singh, Jogat Gogoi, and Nongmaithem Mohondas Singh. "Effect of annealing temperatures on the structural and photoluminescence properties of Tb³⁺ ions doped BiPO₄ nanophosphors." *Materials Technology* 37, no. 12 (2022): 2289-2299. (IF 2.9)

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C. Conferences/workshop

1. Attended international conference on “Nano science and Nanotechnology (ICONN)”, held during March 27-29, 2023 at SRM Institute of science and technology, Tamil Nadu.

2. Attended international conference on “Recent Advances in Energy Materials and its Applications (ICRAEMA-23)”, held during 30-31, May 2023 at Department of Physics , Pachhunga University College, Mizoram

3. Attended INUP-i2i, 6th User Awareness workshop on Fabrication and characterization Facility for Nanotechnology, held at IIT Delhi During 4-5 March, 2023.

4. Attended international conference on Science and Technology for Innovative and Sustainable Development (STISD-2023) jointly organized by Department of Chemistry and Department of Industrial Chemistry, Mizoram University, Aizawl during 28-30th June, 2023



Fabrication and characterization of zinc oxide nanorods-modified electrodes using nanoimprint lithography for electrochemical sensing of heavy metal ions

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ABSTRACT

This paper uses the nanoimprint lithography (NIL) technique to present the fabrication and characterization of Zinc oxide nanorods (ZnONRs)-modified electrodes. Characterization of the resulting electrode involved X-ray diffraction, Field Emission Scanning Electron Microscope and Transmission electron microscopy. The electrode surface was modified with ZnONRs using the NIL technique to increase the sensitivity of the electrochemical sensor for detecting small quantities of heavy metal ions, which remain a major concern due to their toxicity and environmental harm. Electrochemical measurements and sensing performance evaluations were conducted to analyze the electrochemical properties and sensitivity of the ZnONRs - modified electrodes. The results demonstrated increased sensitivity towards cadmium ions present in aqueous solutions, and the limit of detection is found to be $20.88 \pm 0.9 \mu\text{M}$.

1. Introduction

Electrochemistry and nanotechnology have formed an exciting area that improves sensors, energy storage systems, and electronics [1,2]. The electrode material should be conductive and Gold (Au) electrode is known for its high conductivity and chemical stability. Electrodes can enhance surface area, reactivity, and electrochemical behavior by modifying the electrode surface with nanoparticles [3,4]. This electrode could potentially modify applications that rely on effective electron transfer [5]. Zinc oxide nanorods (ZnONRs) have shown enormous potential for optoelectronic and energy applications because of their impressive properties as a wide-band gap semiconductor [6]. Its one-dimensional structure enhances surface area and charge transport, which proves advantageous for electrochemical reactions and sensing [7,9].

Using nanoimprint lithography (NIL), precise nanostructures can be created on substrates, allowing for the customization of electrode surfaces [8,10,11]. This technique can be used repeatedly and is perfect for making specific electrode shapes [12,13]. The application approach in

this work is different from previous research works. In this work, NIL modified ZnONRs-Au electrode was used for the electrochemical detection of Cadmium ions (Cd^{2+}). This method has not been explored in previous research for detecting Cd^{2+} ions. Unlike previous studies, the electrode fabrication process in this work is also particularly noteworthy for its cost-effectiveness. Microscope glass slides are used as a platform substrate for electrode fabrication due to their wide availability and cost-effectiveness. This option dramatically decreases the cost of preparing the electrode, making the process more affordable and adaptable than alternative methods that may necessitate pricier or more specialized materials. This study aims to make and study NIL- modified ZnONRs electrodes. The focus is on how the nanorods are arranged on the electrode surface and how well they work electrochemically in heavy metal ion sensing.

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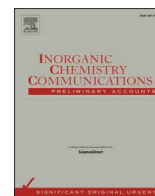
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Research Article

Development of a low-cost gold IDE electrode modified with ZnO nanorods for enhanced electrochemical sensing of bisphenol A

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ABSTRACT

This study introduces an economical technique for fabricating thin film Gold Interdigitated electrode (Au-IDE) on microscope glass slides utilizing a stainless steel IDE mask and electron beam deposition. The resultant Au-IDEs comprise of 18 electrode pairs, each measuring 439.8 μm in width and separated by a distance of $\sim 513 \mu\text{m}$. Zinc oxide (ZnO) nanorods were grown on the Au-IDEs' surface to increase sensitivity for sensing applications. The optimized ZnO nanorod-modified Au-IDEs were employed for the electrochemical detection of bisphenol A, attaining a detection limit of 8.5 μM .

1. Introduction

Interdigitated electrodes (IDEs) are a kind of electrode which design consisting of two interlocking comb-like metal structures, typically made from gold, platinum, and other similar conductive materials [1,2]. These electrodes are extensively utilized in electrochemical sensors and biosensors owing to extensive surface area to volume ratio, their simplicity, cost-efficiency, enhanced sensitivity and effortless fabrication process [3–7]. The Interdigitated arrangement enables effective redox cycling, where oxidized analytes at one electrode (the generator) diffuse to the adjacent electrode (the collector) for reduction, increasing sensitivity [4,5]. The sensitivity of the IDEs is influenced by the number of alternately arranged electrode and the distance between each electrode [6–8]. IDEs possess advantages over three-electrode systems as they serve dual roles as both working and counter electrodes, thereby avoiding the necessity for a reference electrode [9,10]. This optimizes their design, decreases sample volume necessities, and enhances the signal-to-noise ratio while facilitating quicker response times [11,12]. Zinc oxide (ZnO) is a metal oxide semiconductor which allows the adsorption of many organic pollutants without using any kind of linkers [13]. In this study, a cost-efficient method was utilized to fabricate a thin-film Au-IDE on the microscope glass slides employing a stainless steel IDE mask and an e-beam deposition system. This method of fabrication of IDEs provides an affordable substitute to standard microfabrication

techniques, including photolithography and soft lithography, which are not only expensive but also widely accessible. The main novelty of this research work lies in the cost-effectiveness and simplicity of the fabrication process for the Au-IDE electrode used in the detection of bisphenol A (BPA). In contrast to earlier studies that necessitate costly materials, sophisticated microfabrication methods, and specialized equipment not universally available in research or industrial environments, our approach presents a significantly more economical and logical alternative. This study's fabrication process avoids the necessity for expensive materials and complicated techniques, making it considerably more economical. This is especially beneficial for extensive production and applications in resource-constrained environments where access to advanced microfabrication facilities is limited. Furthermore, the employed methodology is simple and devoid of complex, time-intensive procedures, thereby improving both reproducibility and efficiency. The straightforward fabrication process guarantees uniformity in electrode performance, minimizing variability in experimental results and facilitating broad applicability. The customized Au-IDEs were then modified with ZnO nanorods, which improved their sensitivity and facilitated the adsorption of widely recognized organic pollutants such as BPA at defect sites of surface ZnO nanorods without requiring a linker. This modification enabled the electrochemical detection of BPA utilizing the ZnO-modified Au-IDE.

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DEPARTMENT : Chemistry

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EXTENSION : NIL

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ABSTRACT

**NANOFABRICATION OF COST EFFECTIVE
ELECTROCHEMICAL SENSOR USING
NANOIMPRINTING LITHOGRAPHY TECHNIQUE**

**AN ABSTRACT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY**

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DEPARTMENT OF CHEMISTRY

SCHOOL OF PHYSICAL SCIENCES

SEPTEMBER, 2025

**NANOFABRICATION OF COST EFFECTIVE ELECTROCHEMICAL
SENSOR USING NANOIMPRINTING LITHOGRAPHY TECHNIQUE**

BY

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Department of Chemistry

Under the supervision of

Prof. N. MOHONDAS SINGH

Submitted

In partial fulfilment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl.

Abstracts

Chapter 1. Introduction

Electrochemical sensors have emerged as indispensable tools in various fields, including environmental monitoring, medical diagnostics, food safety, and industrial process control, owing to their inherent advantages such as high sensitivity, fast response time, low power consumption, and the ability to perform real-time analysis. However, the widespread application of electrochemical sensors is often limited by challenges related to fabrication costs, reproducibility, and miniaturization. To overcome these challenges, the integration of nanotechnology into sensor design and fabrication has become a key area of research, with the aim of significantly improving sensor performance while reducing production costs. In this context, nanoimprinting lithography (NIL) has gained significant attention as a promising nanofabrication technique due to its cost-effectiveness, scalability, and capability to replicate well-defined nanostructures with high precision. Unlike conventional photolithography, NIL does not require expensive optical systems or high-energy radiation sources, making it a suitable candidate for large-area, low-cost sensor fabrication. By creating nanoscale features on the electrode surface, NIL can effectively enhance the active surface area, promote electron transfer kinetics, and improve the overall electrochemical response of the sensor. This thesis focuses on the development and optimization of a nanostructured electrochemical sensor fabricated using NIL, with an emphasis on achieving high sensitivity and reliability while maintaining affordability and scalability. The study explores various aspects of the NIL process, including mold design, imprinting conditions, and material compatibility, to fabricate reproducible and functional nanostructures on sensor substrates. Furthermore, the influence of these nanostructures on the electrochemical behavior of the sensor is systematically investigated to establish a clear correlation between surface morphology and sensing performance.

By leveraging the advantages of NIL, this work aims to demonstrate a practical pathway toward the mass production of highly efficient and low-cost electrochemical sensors. The fabricated sensor platforms are evaluated for their potential application in detecting specific target analytes, such as heavy metals or biomolecules, with a focus

on analytical performance metrics such as sensitivity, selectivity, limit of detection, stability, and reproducibility. Overall, this research contributes to the advancement of nanofabrication strategies for next-generation electrochemical sensors and provides insights into the practical implementation of NIL in sensor technology.

Chapter 2. Literature reviews

The development of electrochemical sensors has undergone significant transformation over recent decades, driven by the growing demand for reliable, sensitive, and economically viable sensing platforms. A substantial body of research has focused on enhancing sensor performance through nanostructuring techniques that increase surface area, promote electron transfer, and enable the selective detection of target analytes. This literature review critically examines the evolution of electrochemical sensor design, with an emphasis on the integration of nanotechnology, particularly nanofabrication methods, to improve sensor characteristics.

In addition, the review surveys recent advancements in NIL-assisted electrochemical sensor fabrication, where nanostructured electrodes have demonstrated significant improvements in sensitivity, selectivity, and detection limits. The influence of nanostructure geometry, pattern density, and material selection on electrochemical behavior is explored in depth. Studies focusing on the detection of heavy metals, biomolecules, and environmental contaminants using NIL-based sensors are examined, offering insights into application-specific design strategies.

Furthermore, the review identifies existing gaps in the literature, such as the need for improved reproducibility, integration with flexible substrates, and real-world testing under complex sample conditions. It also outlines future research directions, including the development of multifunctional sensors, hybrid fabrication methods, and the incorporation of machine learning for data analysis and sensor calibration.

By consolidating current knowledge on NIL and its role in electrochemical sensor fabrication, this literature review establishes a comprehensive foundation for the research presented in this thesis. It underscores the importance of NIL as a key enabler in the pursuit of low-cost, high-performance sensors that can meet the demands of next-generation analytical technologies.

Chapter 3. Materials, Methods, and Characterization Techniques

This chapter provides a detailed account of the materials, fabrication procedures, experimental setup, and characterization techniques used in the development of a cost-effective electrochemical sensor. The fabrication process was carefully designed to create uniform and reproducible nanostructures on the sensor surface, involving multiple steps such as substrate cleaning, mold preparation, imprinting, and post-treatment procedures. Special emphasis is placed on the NIL technique due to its ability to pattern large areas with nanoscale precision, offering a scalable route to fabricate high-performance electrodes at reduced cost.

In addition to the fabrication methodology, this chapter outlines the assembly and configuration of the electrochemical sensing setup, including the use of a three-electrode system comprising the developed working electrode, a reference electrode (Ag/AgCl), and a platinum counter electrode. The conditions for electrochemical measurements such as supporting electrolyte composition, scan rates, and potential windows are described to ensure reliable and repeatable sensor performance.

A suite of advanced material characterization techniques was employed to evaluate the physical, chemical, and electrochemical properties of the fabricated sensors. Structural analysis was performed using X-ray diffraction (XRD) to determine the crystallographic phases. Surface morphology and nanostructure uniformity were examined through field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM). Elemental composition and distribution were analyzed using energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), providing insights into surface chemistry and elemental states. Additionally, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and photoluminescence (PL) spectroscopy were employed to investigate molecular bonding, vibrational characteristics, and optical behavior of the materials, respectively. Electrochemical characterization was conducted using cyclic voltammetry (CV) to evaluate redox behavior, electron transfer efficiency, and sensor responsiveness.

Together, the materials, methods, and analytical techniques presented in this chapter form the foundation for understanding the structure function relationship in the fabricated sensor and assessing its potential for practical sensing applications.

Chapter 4. Results and discussions

This chapter presents an in-depth analysis and discussion of the experimental results obtained from four distinct yet interconnected research investigations focused on the fabrication and performance of nanostructured electrochemical sensors. All the sensors were developed using cost-effective fabrication strategies, and surface modification with nanomaterials such as zinc oxide nanorods (ZnONRs) and electrochemically reduced graphene oxide (ERGO). These works aim to address the growing need for sensitive, selective, and economical sensors capable of detecting environmental toxins including heavy metals and industrial organic pollutants.

The first study investigates a NIL-fabricated ZnONR-modified gold electrode for the dual detection of cadmium ions and thiram. The zinc oxide nanorods were grown onto a patterned gold electrode, significantly increasing the surface area and electron transfer capabilities. Electrochemical analysis using differential pulse voltammetry (DPV) revealed strong sensing performance, with detection limits of $20.88 \pm 0.9 \mu\text{M}$ for cadmium ions and $0.74 \mu\text{M}$ for thiram. These results demonstrate that the fabricated sensor is effective in simultaneously detecting both metallic and organic contaminants, making it suitable for environmental applications where multiple analytes coexist.

The second investigation focuses on the **simultaneous electrochemical detection of cadmium (Cd^{2+}) and copper (Cu^{2+}) ions** using a ZnONR-modified thin film gold electrode fabricated via NIL. The nanorods provide enhanced surface reactivity and improved binding sites for metal ions. Cyclic voltammetry (CV) was employed to evaluate the electrochemical response, achieving detection limits of $2.45 \mu\text{M}$ for Cd^{2+} and $1.5 \mu\text{M}$ for Cu^{2+} . The study confirmed the high selectivity, reproducibility, and stability of the fabricated electrode, emphasizing its potential for real-time monitoring of heavy metal ions in water bodies and industrial waste.

The third investigation explores the development of a **low-cost interdigitated electrode (IDE) platform**, fabricated by electron beam evaporation through a stainless steel shadow mask onto microscope glass slides. This method yielded gold IDEs comprising 18 finger-like electrode pairs, each $\sim 439.8\ \mu\text{m}$ wide and separated by $\sim 513\ \mu\text{m}$. These Au-IDEs were then modified with ZnO nanorods to boost sensitivity. The modified electrodes were tested for the detection of **bisphenol A (BPA)**, a widespread endocrine-disrupting compound. Electrochemical testing showed a detection limit of $8.5\ \mu\text{M}$ for BPA, validating the efficacy of the design. The simplicity and affordability of this fabrication approach make it highly suitable for large-scale, disposable sensor applications.

The fourth and final study introduces a **thin-film gold electrode modified with electrochemically reduced graphene oxide (ERGO)** for the detection of cadmium ions. The modification process enhanced the electroactive surface and introduced functional groups favorable for heavy metal ion adsorption. The electrode was extensively characterized using techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy to confirm successful material integration and surface morphology. Electrochemical characterization through CV demonstrated excellent sensitivity with a notably low detection limit of $1.34\ \mu\text{M}$ for Cd^{2+} , outperforming several conventional sensor configurations.

Collectively, these four research contributions demonstrate the critical role of nanostructuring, surface functionalization, and innovative lithographic methods in enhancing electrochemical sensor performance. The combination of NIL-based patterning, ZnONR and ERGO surface modifications, and accessible fabrication techniques such as shadow masking presents a powerful strategy for developing scalable, cost-effective, and highly responsive electrochemical sensors. These sensors show strong potential for deployment in environmental monitoring, industrial safety assessments, and public health applications, where real-time and accurate detection of harmful contaminants is of paramount importance. The comparative discussion across the studies also provides a valuable perspective on how electrode architecture and

material choice influence analytical performance, offering guidance for future research in the field of electrochemical sensing.

Chapter 5. Conclusion and references

This chapter presents a concise summary of the major findings obtained throughout the course of the research, emphasizing the successful application of nanoimprint lithography (NIL) as a powerful, scalable, and cost-effective fabrication technique for developing high-performance electrochemical sensors. Across multiple studies, the integration of zinc oxide nanorods, gold thin films, interdigitated electrodes, and electrochemically reduced graphene oxide demonstrated that nanostructured surfaces significantly enhance the sensitivity, selectivity, and reproducibility of sensors for detecting heavy metals (Cd^{2+} , Cu^{2+}), pesticides (thiram), and organic pollutants (bisphenol A).

The results confirmed that NIL not only enables the creation of highly ordered nanoscale patterns with excellent reproducibility but also provides a pathway toward low-cost sensor manufacturing suitable for large-scale deployment. Each sensor configuration explored in this work showed promising detection limits and consistent electrochemical performance, validating the feasibility of NIL-based sensors in real-world applications.

Despite these achievements, the study also encountered certain limitations. These include the need for more robust packaging for field use, challenges in maintaining long-term electrode stability, and limited testing in complex real-world environmental matrices. Furthermore, while the sensors demonstrated good selectivity, cross-sensitivity with structurally similar compounds warrants further investigation.

To address these limitations and move toward real-world application, future research directions are proposed. These include the integration of NIL-based sensors into miniaturized, portable sensing platforms; validation with real environmental and biological samples; and the extension of this fabrication approach to the detection of a broader range of analytes including other heavy metals, pharmaceutical residues, and pathogens. Such advancements could further establish NIL as a transformative tool in

the development of next-generation electrochemical sensors for environmental, biomedical, and industrial monitoring.

The chapter concludes with a comprehensive list of references that supported the theoretical framework, experimental procedures, and analysis throughout this thesis.