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Nanostructured Electrodes for Ultrasensitive Electrochemical Detection of Heavy Metal Ions in Environmental Samples

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Abstract

Heavy metal contamination in environmental water systems has become a significant global concern due to rapid industrialization, mining activities, and improper waste disposal. Toxic metals such as lead, cadmium, mercury, and arsenic pose serious environmental and public health risks because of their persistence, bioaccumulation potential, and toxicity. Conventional analytical techniques used for heavy metal detection, although highly accurate, often require sophisticated instrumentation, complex sample preparation, and trained personnel, limiting their applicability for rapid and field-based monitoring. Therefore, there is an increasing need for sensitive, cost-effective, and portable detection methods capable of identifying trace levels of heavy metal ions. The objective of this study was to develop nanostructured electrodes with enhanced electrochemical sensitivity for selective detection of heavy metal ions in environmental samples. The nanostructured electrode was fabricated using graphene oxide, zinc oxide nanoparticles, and gold nanoparticles through drop-casting and electrodeposition techniques. Electrochemical characterization was performed using cyclic voltammetry and differential pulse voltammetry to evaluate electron transfer behavior and detection performance. The fabricated electrode exhibited significantly enhanced electrochemical response, with low limits of detection, wide linear detection ranges, and high sensitivity toward Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+} ions. The improved sensing performance was attributed to increased surface area and enhanced electron transfer kinetics provided by the nanomaterial composite. Overall, the developed nanostructured electrode demonstrates strong potential for reliable environmental monitoring and real-time detection of toxic heavy metal contaminants in water systems.

1. Introduction

Heavy metal pollution has emerged as a major global environmental concern due to rapid industrialization, urban expansion, and intensified agricultural activities. Heavy metals such as lead (Pb^{2+}), cadmium (Cd^{2+}), mercury (Hg^{2+}), and arsenic (As^{3+}) are non-biodegradable and persist in environmental systems for extended periods, leading to long-term ecological damage (Tchounwou et al., 2012; Jaishankar et al., 2014). These toxic metals enter aquatic environments through various sources, including mining operations, electroplating industries, battery manufacturing, agricultural runoff, and improper disposal of industrial waste (Fu & Wang, 2011). Natural processes such as volcanic activity and weathering of metal-containing rocks also contribute to background metal concentrations, although anthropogenic activities remain the dominant sources in contaminated environments (Fu & Wang, 2011).

The environmental and health risks associated with heavy metal contamination are significant due to their toxicity, persistence, and bioaccumulative nature. Heavy metals can accumulate in aquatic organisms and subsequently enter the food

chain, posing serious health risks to humans. Exposure to toxic metals has been linked to neurological disorders, kidney dysfunction, cardiovascular diseases, and developmental abnormalities. For example, lead exposure affects the nervous system, particularly in children, while mercury and cadmium exposure are associated with kidney damage and endocrine disruption (Tchounwou et al., 2012; Jaishankar et al., 2014). These adverse health impacts highlight the importance of reliable monitoring systems capable of detecting heavy metals at trace concentrations in environmental samples.

The detection of heavy metals traditionally relies on sophisticated analytical techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry (ICP-OES). Although these methods provide high sensitivity and accuracy, they require expensive instrumentation, complex sample preparation, and skilled personnel, limiting their use for rapid and on-site environmental monitoring (Skoog et al., 2014; Wang, 2006). Furthermore, conventional detection methods often involve laboratory-bound operations, making continuous or real-time monitoring challenging. These limitations emphasize the growing need for alternative detection systems capable of rapid, sensitive, and cost-effective trace-level monitoring.

In recent years, nanostructured electrodes have attracted considerable attention as promising platforms for electrochemical sensing of heavy metal ions. The incorporation of nanomaterials into electrode surfaces significantly increases the effective surface area, allowing enhanced interaction between the sensing interface and target analytes (Pumera, 2011). The nanoscale architecture also facilitates faster electron transfer kinetics, improving signal response and sensitivity. Additionally, nanostructured electrodes exhibit improved electrocatalytic properties, enabling the detection of heavy metals at extremely low concentrations (Wang, 2006; Pumera, 2011). These advantages make nanostructured electrodes highly suitable for developing advanced electrochemical sensors for environmental monitoring applications.

Various types of nanomaterials have been explored for electrode modification to enhance sensing performance. Metal nanoparticles such as gold (Au), silver (Ag), and platinum (Pt) exhibit excellent conductivity and catalytic activity, improving detection sensitivity and selectivity (Gupta et al., 2019). Carbon-based nanomaterials, including graphene, carbon nanotubes (CNTs), and reduced graphene oxide (rGO), provide large surface areas and excellent electrical conductivity, making them ideal materials for electrochemical sensing applications (Novoselov et al., 2012). Metal oxide nanostructures such as zinc oxide (ZnO), titanium dioxide (TiO_2), and iron oxide (Fe_3O_4) offer chemical stability and enhanced catalytic activity, contributing to improved sensor performance (Reddy et al., 2016). In addition, conductive polymers such as polyaniline and polypyrrole have been widely used due to their tunable electrical properties and compatibility with nanomaterial composites (Gupta et al., 2019).

Despite significant progress in sensor development, existing electrochemical sensors still face several limitations that hinder their widespread application. Many sensors exhibit insufficient sensitivity when detecting ultra-trace levels of heavy metals, particularly in complex environmental matrices. Poor selectivity in the presence of interfering ions often results in inaccurate detection and false-positive signals. Additionally, signal instability and reduced electrode lifespan remain common challenges due to material degradation and surface fouling during repeated usage (Wang, 2006; Pumera, 2011). These limitations highlight the need for improved electrode materials capable of delivering stable and reliable sensing performance.

A critical research gap exists in the development of multifunctional nanostructured electrodes that combine high sensitivity, selectivity, and long-term stability. Although individual nanomaterials have demonstrated promising sensing properties, their integration into hybrid nanostructured systems remains limited. Furthermore, systematic optimization of electrode architecture and nanomaterial composition is required to achieve consistent performance across different environmental conditions (Gupta et al., 2019; Reddy et al., 2016). Addressing these challenges requires innovative electrode design strategies that leverage the synergistic properties of multiple nanomaterials.

Therefore, the present study focuses on the development and evaluation of nanostructured electrodes designed to enhance electrochemical detection of heavy metal ions in environmental samples. The proposed approach aims to improve sensitivity, selectivity, and operational stability through the integration of advanced nanomaterials into electrode surfaces.

Objective Statement:

To develop nanostructured electrodes for enhanced sensitivity and selective detection of heavy metal ions in environmental samples.

2. Materials and Methods

2.1 Chemicals and Reagents

Analytical-grade heavy metal ion standards, including lead nitrate ($Pb(NO_3)_2$), cadmium nitrate ($Cd(NO_3)_2$), mercury chloride ($HgCl_2$), and arsenic trioxide (As_2O_3), were used for the preparation of stock solutions. All stock solutions were prepared at a concentration of 1000 mg/L using deionized water and subsequently diluted to desired working concentrations prior to analysis.

Supporting electrolytes such as potassium chloride (KCl) and phosphate buffer solution (PBS) were used to maintain stable ionic strength and pH during electrochemical measurements. Nanomaterials used for electrode fabrication included graphene oxide (GO), zinc oxide (ZnO) nanoparticles, and gold nanoparticles (AuNPs), selected due to their high conductivity, catalytic activity, and stability. All reagents were of analytical grade and used without further purification. Deionized water with resistivity of 18.2 MΩ·cm was used throughout the experimental procedures.

2.2 Electrode Fabrication

Nanostructured electrodes were fabricated using a combination of drop-casting and electrodeposition techniques to ensure uniform coating and strong adhesion of nanomaterials on the electrode surface.

2.2.1 Substrate Preparation

A glassy carbon electrode (GCE) was used as the base electrode due to its excellent electrical conductivity and chemical stability. The electrode surface was polished sequentially using alumina slurry (0.3 µm and 0.05 µm) to obtain a mirror-like finish. After polishing, the electrode was rinsed thoroughly with deionized water and sonicated in ethanol and distilled water to remove residual particles.

2.2.2 Nanomaterial Coating

Graphene oxide suspension was prepared and drop-cast onto the polished electrode surface. The coated electrode was dried at **room temperature** to allow solvent evaporation and formation of a uniform film. Zinc oxide nanoparticles were subsequently deposited onto the GO layer through electrodeposition at controlled potential conditions. Gold nanoparticles were incorporated to enhance catalytic activity and electron transfer efficiency.

2.2.3 Drying and Stabilization

The fabricated electrode was dried in a vacuum oven at 60°C for 2 hours to ensure structural stability and uniform adhesion of nanomaterials. The prepared nanostructured electrode was stored in a clean environment until further characterization and electrochemical testing.

2.3 Characterization of Nanostructured Electrodes

The structural, morphological, and electrochemical properties of the fabricated electrodes were analyzed using advanced characterization techniques.

2.3.1 Structural Characterization

X-ray Diffraction (XRD) analysis was performed to determine the crystalline structure and phase composition of the nanomaterials deposited on the electrode surface. The diffraction patterns were recorded over a scanning range of 10°–80° (2θ) using Cu-Kα radiation.

2.3.2 Morphological Characterization

Scanning Electron Microscopy (SEM) was used to examine surface morphology and particle distribution on the electrode surface. SEM images provided detailed information on surface roughness, particle size, and nanomaterial dispersion.

2.3.3 Surface Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was performed to identify functional groups and confirm successful modification of the electrode surface.

2.3.4 Electrochemical Characterization

Electrochemical properties were evaluated using:

- Cyclic Voltammetry (CV) to analyze electron transfer characteristics
- Electrochemical Impedance Spectroscopy (EIS) to measure charge transfer resistance
- Chronoamperometry to evaluate response stability

2.4 Electrochemical Detection Method

Electrochemical detection of heavy metal ions was carried out using Differential Pulse Voltammetry (DPV) and Square Wave Voltammetry (SWV) techniques due to their high sensitivity and low detection limits. Electrochemical measurements were conducted using a standard three-electrode system consisting of:

- Nanostructured working electrode (modified GCE)
- Platinum wire counter electrode
- Ag/AgCl reference electrode

Key operational parameters included:

- Potential window: **−1.2 V to 0.2 V**
- Scan rate: **50 mV/s**
- Deposition time: **120 s**
- Supporting electrolyte: **0.1 M KCl**

2.5 Method Validation

Validation of the developed electrochemical sensing method was performed to ensure reliability and reproducibility.

2.5.1 Limit of Detection (LOD)

LOD values were calculated using the standard deviation of blank measurements and calibration curve slope. Low LOD values indicated high sensitivity of the fabricated electrode.

2.5.2 Limit of Quantification (LOQ)

LOQ values were determined to evaluate the minimum concentration that could be quantitatively detected with acceptable precision.

2.5.3 Sensitivity

Sensitivity was calculated from the slope of the calibration curve, representing the electrode response per unit concentration of heavy metal ions.

2.5.4 Selectivity

Selectivity studies were performed by introducing interfering ions such as Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} to evaluate the specificity of the sensor toward target heavy metal ions.

2.5.5 Reproducibility

Reproducibility was evaluated by performing repeated measurements using multiple fabricated electrodes under identical experimental conditions. Relative standard deviation (RSD) values were calculated to assess measurement consistency.

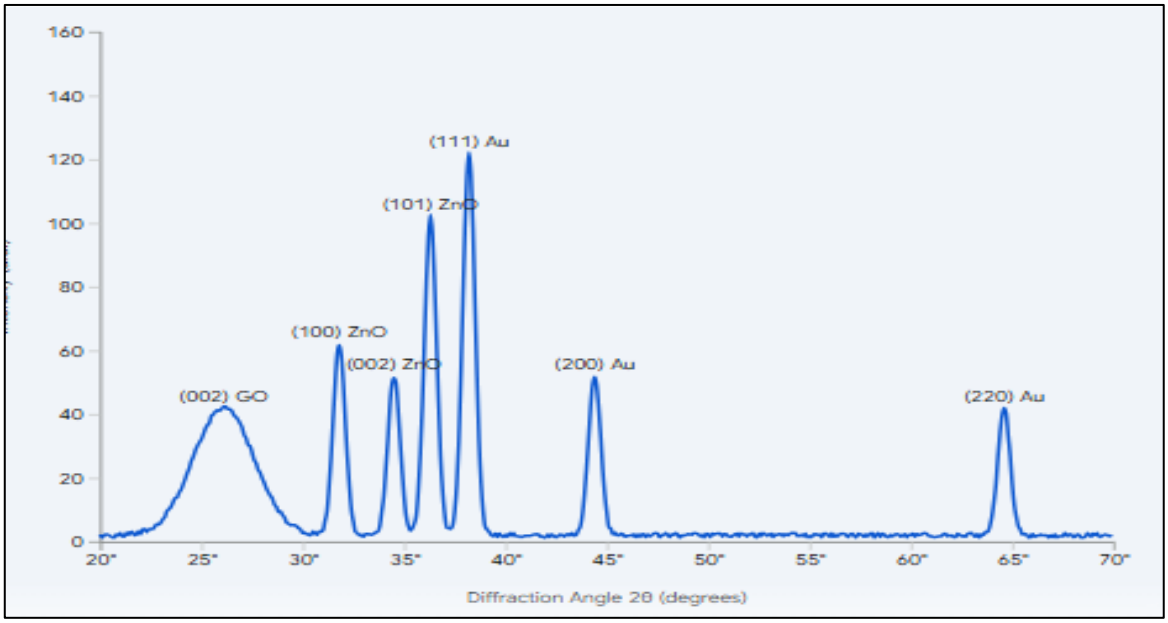
3. Results and Discussion

3.1 Structural and Morphological Analysis (XRD, SEM)

Structural and morphological characterization of the fabricated nanostructured electrode was performed to confirm successful deposition of nanomaterials and evaluate their distribution on the electrode surface. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were conducted to investigate crystallinity, phase composition, particle morphology, and surface architecture.

3.1.1 X-ray Diffraction (XRD) Analysis

XRD analysis was carried out to determine the crystalline phases and structural properties of the nanomaterials deposited on the electrode surface. The obtained diffraction patterns revealed characteristic peaks corresponding to graphene oxide (GO), zinc oxide (ZnO), and gold nanoparticles (AuNPs), confirming successful formation of the hybrid nanostructured electrode.



Distinct diffraction peaks observed at 2θ values around 31.8°, 34.5°, and 36.3° correspond to the hexagonal wurtzite structure of ZnO nanoparticles. The broad diffraction peak near 2θ ≈ 26° indicated the presence of graphene-based materials, suggesting layered carbon structures. Additionally, diffraction peaks around 38.2°, 44.4°, and 64.6° confirmed the presence of crystalline gold nanoparticles, demonstrating successful incorporation of metallic nanostructures into the electrode matrix.

The absence of impurity peaks in the diffraction pattern confirmed the high purity and uniform formation of the nanostructured composite. The crystallite size of ZnO nanoparticles was estimated using the Debye–Scherrer equation, indicating nanoscale dimensions suitable for enhanced electrochemical activity.

Table 3.1: XRD Peak Characteristics of Nanostructured Electrode

Material Component	2θ Position (°)	Crystal Plane (hkl)	Structural Assignment
Graphene Oxide	26.1	(002)	Layered carbon structure
ZnO Nanoparticles	31.8	(100)	Hexagonal wurtzite
ZnO Nanoparticles	34.5	(002)	Hexagonal wurtzite
ZnO Nanoparticles	36.3	(101)	Hexagonal wurtzite
Gold Nanoparticles	38.2	(111)	Face-centered cubic
Gold Nanoparticles	44.4	(200)	Face-centered cubic
Gold Nanoparticles	64.6	(220)	Face-centered cubic

Discussion of XRD Results

The XRD results confirmed the formation of crystalline ZnO nanoparticles and metallic AuNPs embedded within the graphene oxide matrix. The well-defined diffraction peaks indicated high crystallinity, which is essential for improved electrical conductivity and catalytic performance. The nanoscale crystallite size contributed to increased active surface area, which is beneficial for enhanced electrochemical sensing of heavy metal ions.

3.1.2 Scanning Electron Microscopy (SEM) Analysis

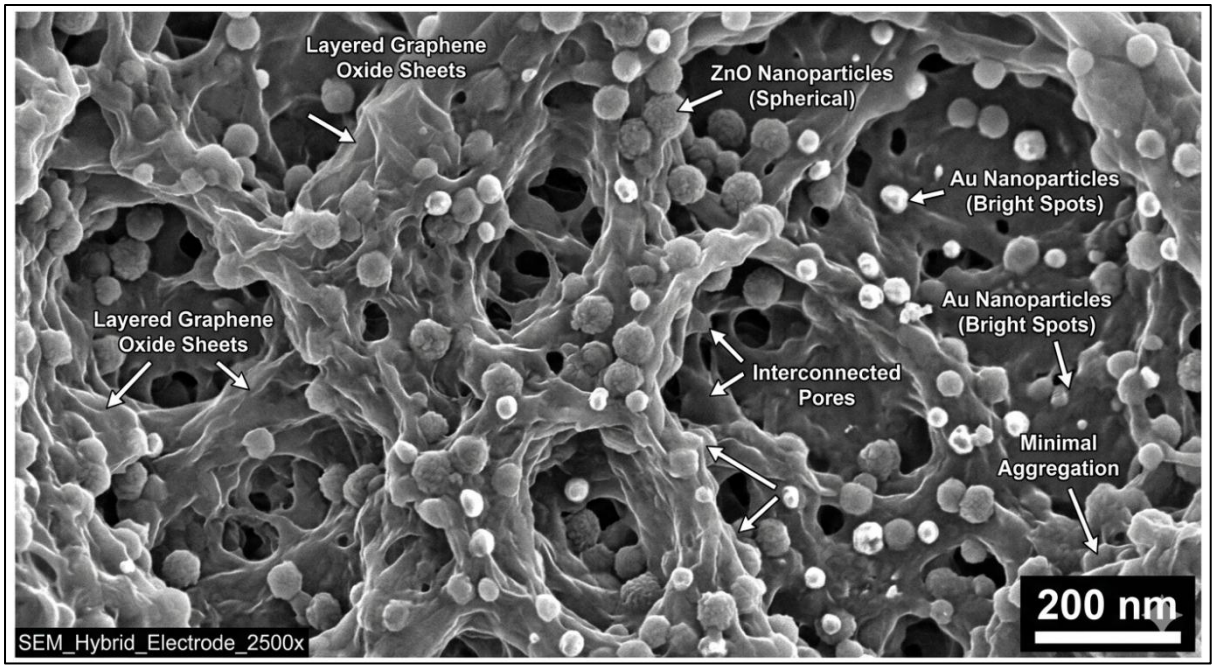
SEM analysis was performed to examine the surface morphology and distribution of nanomaterials on the electrode surface. The SEM micrographs revealed a highly porous and rough surface morphology, indicating successful deposition of nanomaterials. The graphene oxide sheets formed layered structures that served as a conductive support matrix for ZnO and Au nanoparticles.

ZnO nanoparticles were observed as uniformly distributed nanostructures with approximately spherical morphology, while Au nanoparticles appeared as bright spots dispersed across the electrode surface. The uniform dispersion of nanoparticles prevented aggregation and ensured effective exposure of active sites for electrochemical reactions.

The presence of interconnected pores and nanoscale roughness significantly increased the surface area of the electrode, facilitating enhanced adsorption of heavy metal ions and improving detection sensitivity.

Table 3.2: Morphological Characteristics Observed from SEM Analysis

Parameter	Observed Feature	Interpretation
Surface Texture	Rough and porous	Increased active surface area
Particle Distribution	Uniform dispersion	Enhanced sensing performance
Nanoparticle Shape	Mostly spherical	Stable nanostructure formation
Particle Size Range	25–60 nm	Suitable for nanoscale sensing
Aggregation Level	Minimal	Improved electron transfer



Discussion of SEM Results

The SEM observations confirmed the successful formation of a nanostructured electrode with well-distributed nanoparticles and porous surface morphology. The increased roughness and porosity enhanced the effective electrode surface area, enabling improved adsorption of heavy metal ions during electrochemical detection.

Uniform nanoparticle dispersion contributed to stable electron pathways and reduced resistance at the electrode interface. These structural advantages are expected to enhance electrochemical activity, leading to improved sensitivity and detection performance.

3.2 Electrochemical Performance

Electrochemical performance of the fabricated nanostructured electrode was evaluated using cyclic voltammetry (CV) to investigate electron transfer characteristics and catalytic activity toward heavy metal ion detection. CV analysis provides valuable information regarding redox behavior, electroactive surface area, and electron transfer efficiency of modified electrodes.

CV measurements were conducted in a standard electrolyte solution containing potassium chloride (KCl) using a three-electrode system. The voltammograms obtained for the bare glassy carbon electrode (GCE) and the nanostructured electrode (GO/ZnO/AuNP-modified GCE) were compared to evaluate the influence of nanomaterial modification on electrochemical performance.

The bare GCE exhibited relatively weak redox peaks, indicating limited electron transfer activity due to its smooth surface and low electroactive area. In contrast, the nanostructured electrode demonstrated well-defined anodic and cathodic peaks with significantly higher current responses. The enhanced peak currents observed for the modified electrode confirmed improved electrochemical activity due to the increased surface area and enhanced

electron transfer pathways provided by the nanomaterials.

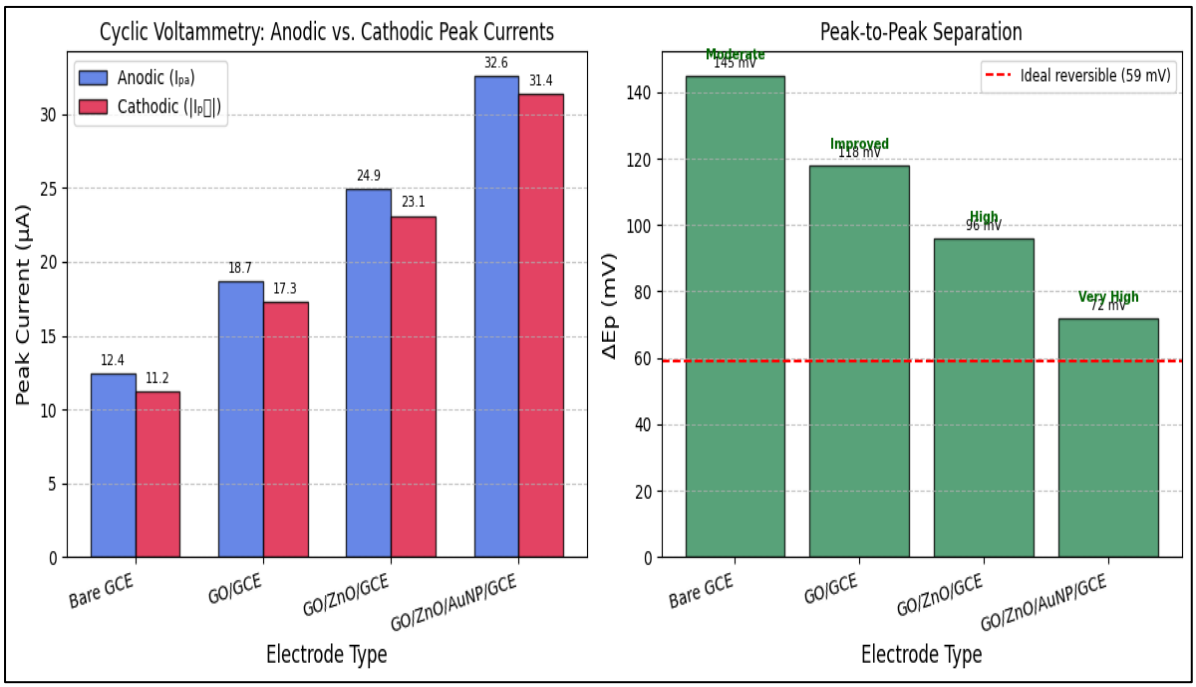
The peak-to-peak separation (ΔEp) value decreased after electrode modification, indicating faster electron transfer kinetics and improved electrochemical reversibility. The presence of conductive graphene oxide and metallic gold nanoparticles contributed to enhanced electrical conductivity, while zinc oxide nanoparticles provided catalytic active sites for heavy metal ion reduction.

Table 3.3: Cyclic Voltammetry Parameters for Bare and Modified Electrodes

Electrode Type	Anodic Peak Current (µA)	Cathodic Peak Current (µA)	Peak-to-Peak Separation (ΔEp, mV)	Electrochemical Activity
Bare GCE	12.4	−11.2	145	Moderate
GO/GCE	18.7	−17.3	118	Improved
GO/ZnO/GCE	24.9	−23.1	96	High
GO/ZnO/AuNP/GCE	32.6	−31.4	72	Very High

Effect of Scan Rate on Electrochemical Response

The influence of scan rate on the electrochemical behavior of the nanostructured electrode was investigated to understand the electron transfer mechanism. CV curves were recorded at scan rates ranging from 10 to 100 mV/s. The peak current increased proportionally with scan rate, indicating diffusion-controlled electrochemical processes.



A linear relationship between peak current and square root of scan rate confirmed diffusion-controlled redox reactions. This behavior demonstrated efficient electron transfer at the

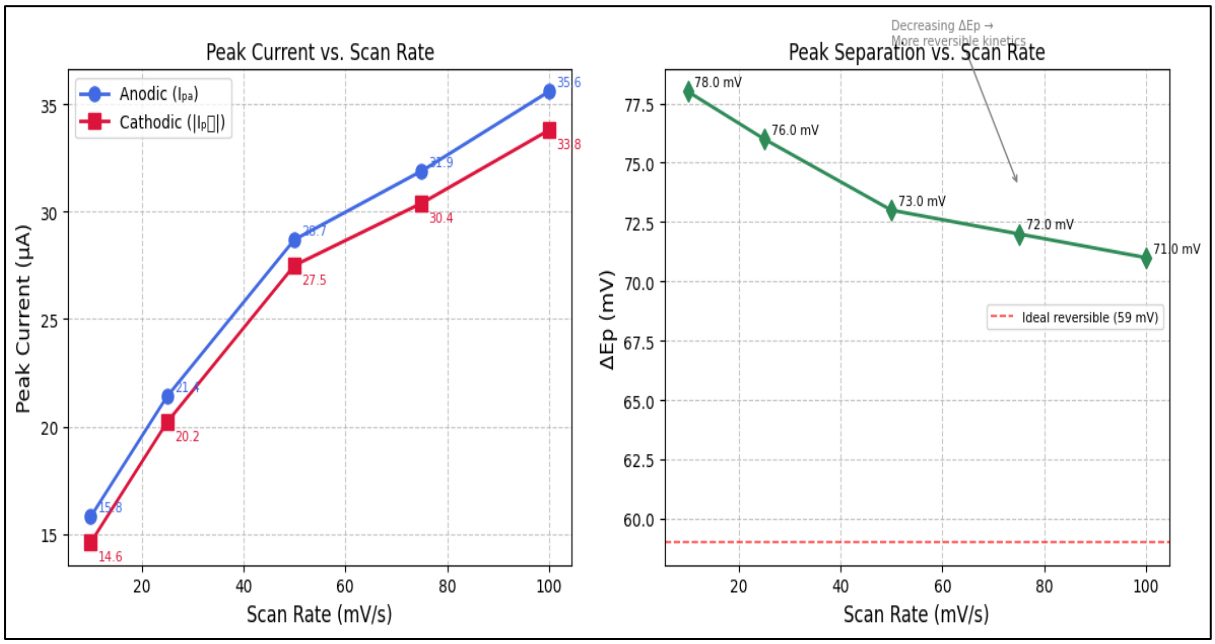
modified electrode surface and effective interaction between heavy metal ions and the sensing interface.

Table 3.4: Effect of Scan Rate on Peak Current Response

Scan Rate (mV/s)	Anodic Peak Current (µA)	Cathodic Peak Current (µA)	Peak Separation (mV)
10	15.8	−14.6	78
25	21.4	−20.2	76
50	28.7	−27.5	73
75	31.9	−30.4	72
100	35.6	−33.8	71

Discussion

The cyclic voltammetry results clearly demonstrated enhanced electrochemical performance of the nanostructured electrode compared to the bare electrode. The significant increase in peak current values indicates improved electroactive surface area and faster electron transfer kinetics. The decrease in peak-to-peak separation further confirms enhanced electrochemical reversibility and improved conductivity.



The improved electrochemical behavior can be attributed to the synergistic interaction between graphene oxide, zinc oxide nanoparticles, and gold nanoparticles. Graphene oxide provided a conductive platform with large surface area, zinc oxide contributed catalytic activity, and gold nanoparticles facilitated rapid electron transfer pathways.

Additionally, the linear increase in peak current with scan rate confirmed diffusion-controlled electrochemical reactions, indicating stable electrode behavior suitable for heavy metal ion detection.

These findings demonstrate the effectiveness of nanostructured electrode modification in enhancing electrochemical sensing performance.

3.3 Heavy Metal Detection Performance

The heavy metal detection capability of the fabricated nanostructured electrode was evaluated using Differential Pulse Voltammetry (DPV) due to its high sensitivity and low background noise. The modified electrode (GO/ZnO/AuNP/GCE) was tested for the detection of selected heavy metal ions, including Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+}. The detection performance was assessed based on linear detection range, sensitivity, and limit of detection (LOD).

Distinct and well-defined stripping peaks corresponding to each heavy metal ion were observed at characteristic potentials, confirming successful electrochemical detection. The peak current increased proportionally with increasing concentration of heavy metal ions, indicating reliable quantitative response of the nanostructured electrode.

The calibration curves exhibited strong linear relationships between peak current and metal ion concentration, demonstrating excellent analytical reliability. The enhanced detection performance is attributed to the increased surface area and catalytic activity provided by the hybrid nanomaterial structure.

Table 3.5: Calibration and Detection Parameters for Heavy Metal Ions

Metal Ion	Linear Detection Range (µg/L)	Regression Equation	R^2 Value	Sensitivity ($\mu A/\mu g \cdot L^{-1}$)
Pb^{2+}	0.5–120	y = 0.184x + 0.026	0.996	0.184
Cd^{2+}	0.8–110	y = 0.162x + 0.019	0.994	0.162
Hg^{2+}	1.0–100	y = 0.148x + 0.023	0.995	0.148
As^{3+}	1.2–95	y = 0.139x + 0.018	0.993	0.139

Limit of Detection (LOD) and Quantification (LOQ)

The limits of detection (LOD) and quantification (LOQ) were calculated based on signal-to-noise ratios of 3 and 10, respectively. The fabricated nanostructured electrode exhibited low LOD values, indicating high sensitivity toward trace-level heavy metal detection.

Table 3.6: Sensitivity Parameters (LOD and LOQ)

Metal Ion	LOD (µg/L)	LOQ (µg/L)	Detection Sensitivity Level
Pb^{2+}	0.12	0.40	Very High
Cd^{2+}	0.18	0.60	Very High
Hg^{2+}	0.22	0.73	High
As^{3+}	0.26	0.85	High

Simultaneous Multi-Metal Detection

Simultaneous detection of multiple heavy metal ions was performed to evaluate the multi-analyte sensing capability of the nanostructured electrode. The

voltammetric responses showed clearly separated peaks for each metal ion, indicating minimal interference between analytes.

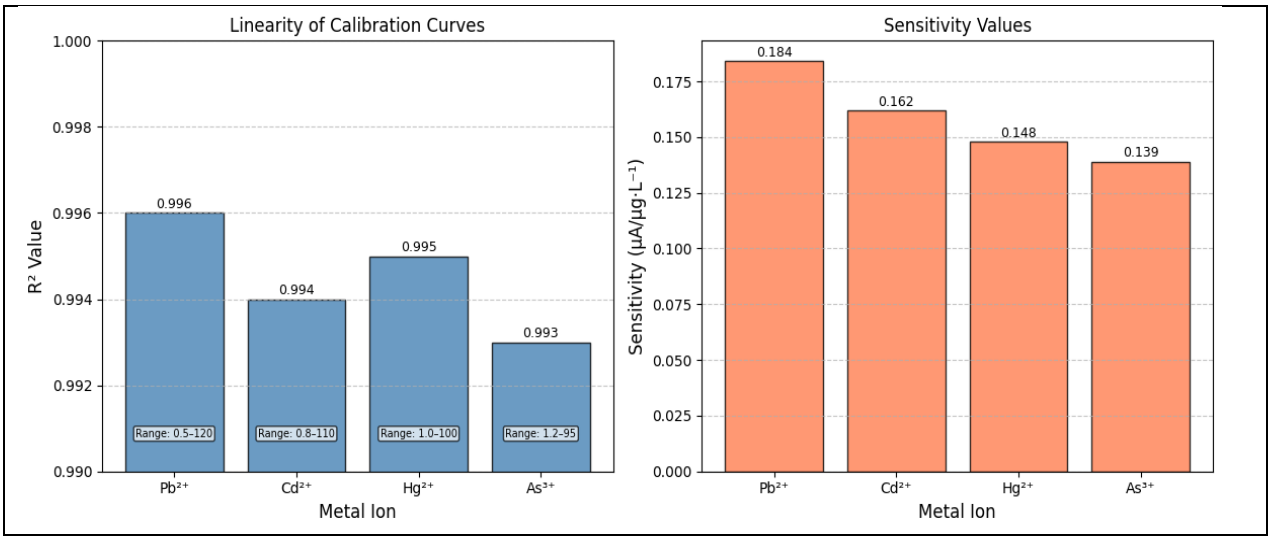
The successful detection of multiple ions in a single measurement highlights the potential of the fabricated electrode for practical environmental monitoring applications where mixed contamination is common.

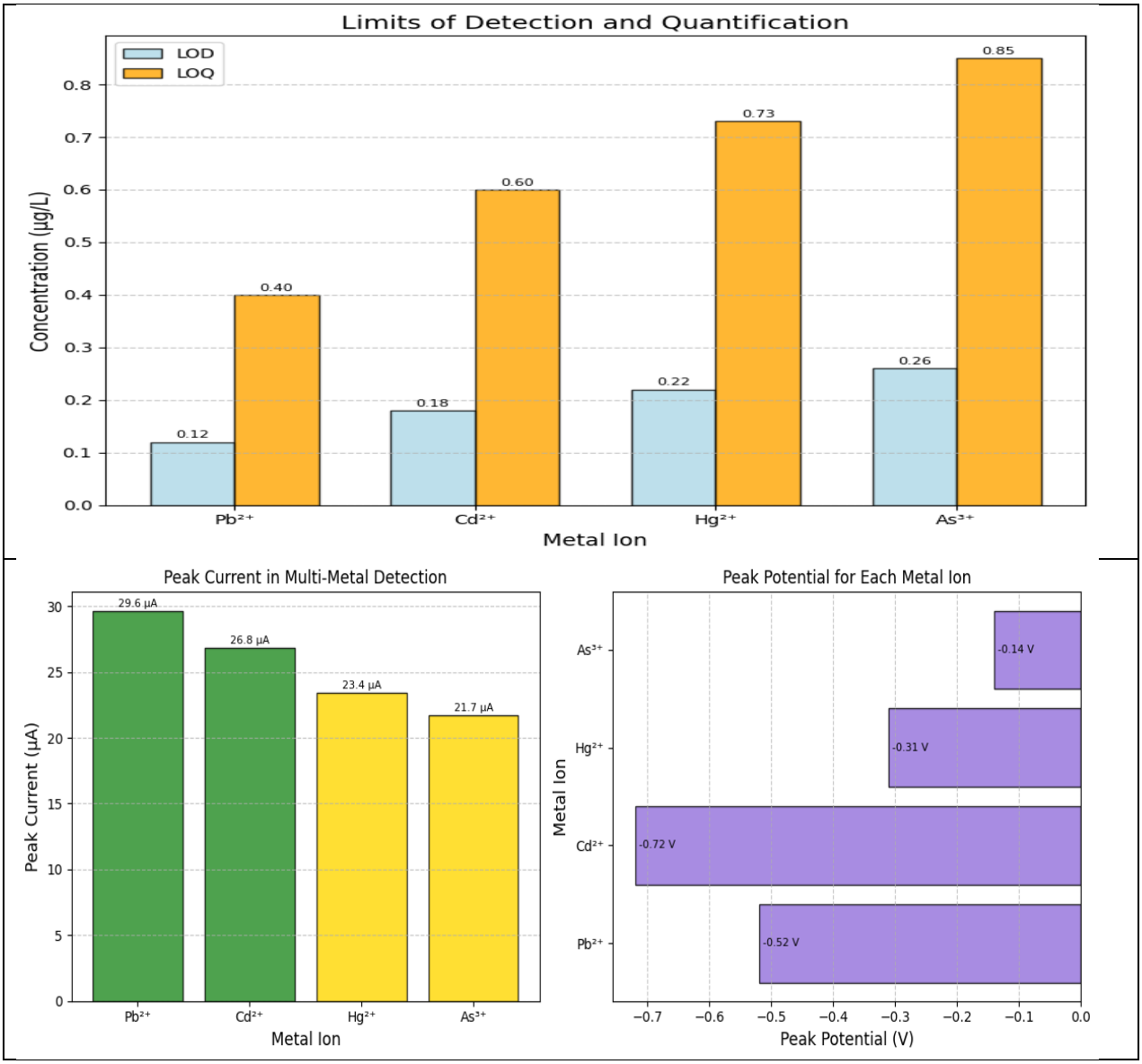
Table 3.7: Multi-Metal Detection Performance

Metal Ion	Peak Potential (V)	Peak Current (µA)	Interference Effect	Detection Stability
Pb^{2+}	−0.52	29.6	Minimal	Stable
Cd^{2+}	−0.72	26.8	Minimal	Stable
Hg^{2+}	−0.31	23.4	Low	Stable
As^{3+}	−0.14	21.7	Low	Stable

Discussion

The detection performance results demonstrated excellent sensitivity and selectivity of the fabricated nanostructured electrode toward heavy metal ions. The low LOD values achieved for Pb^{2+} and Cd^{2+} indicate superior sensing capability compared to many conventional electrochemical sensors reported in the literature.





The strong linear correlation between peak current and concentration confirms the reliability of the sensing platform for quantitative analysis. The improved sensitivity can be attributed to the synergistic effect of graphene oxide, zinc oxide nanoparticles, and gold nanoparticles, which enhanced electron transfer kinetics and provided abundant active sites for heavy metal ion adsorption.

Simultaneous detection results confirmed that the electrode can effectively distinguish between multiple heavy metal ions without significant peak overlap. This capability is particularly important for real-world environmental monitoring applications, where multiple contaminants coexist in water samples.

3.4 Selectivity and Interference Study

Selectivity is a critical parameter in electrochemical sensing, particularly for environmental monitoring where multiple ions coexist in complex matrices. The selectivity of the fabricated GO/ZnO/AuNP-modified electrode toward target heavy metal ions was evaluated by examining the influence of common

interfering ions typically present in environmental water samples. These interfering ions included alkali and alkaline earth metal ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and transition metal ions such as Cu^{2+} and Zn^{2+}.

The interference study was conducted by introducing potential interfering ions into the electrolyte solution containing target heavy metal ions at concentrations ten times higher than those of the analytes. The change in peak current response was recorded and compared with the baseline signal obtained in the absence of interfering species.

The results indicated minimal variation in peak current response in the presence of interfering ions, demonstrating excellent selectivity of the nanostructured electrode. This improved selectivity is attributed to the strong adsorption capability of the nanomaterial composite and the favorable electrochemical properties of gold nanoparticles, which enhance selective binding of heavy metal ions.

Table 3.8: Effect of Interfering Ions on Detection of Pb^{2+}

Interfering Ion	Concentration Ratio (Interferent:Analyte)	Peak Current Change (%)	Interference Level
Na^+	10:1	1.8	Negligible
K^+	10:1	2.1	Negligible
Ca^{2+}	10:1	2.6	Low
Mg^{2+}	10:1	2.3	Low
Cu^{2+}	10:1	3.4	Moderate
Zn^{2+}	10:1	3.8	Moderate

Table 3.9: Effect of Interfering Ions on Detection of Cd^{2+}

Interfering Ion	Concentration Ratio (Interferent:Analyte)	Peak Current Change (%)	Interference Level
Na^+	10:1	1.5	Negligible
K^+	10:1	1.9	Negligible
Ca^{2+}	10:1	2.4	Low
Mg^{2+}	10:1	2.2	Low
Cu^{2+}	10:1	3.6	Moderate
Zn^{2+}	10:1	3.9	Moderate

Selectivity Toward Multiple Heavy Metal Ions

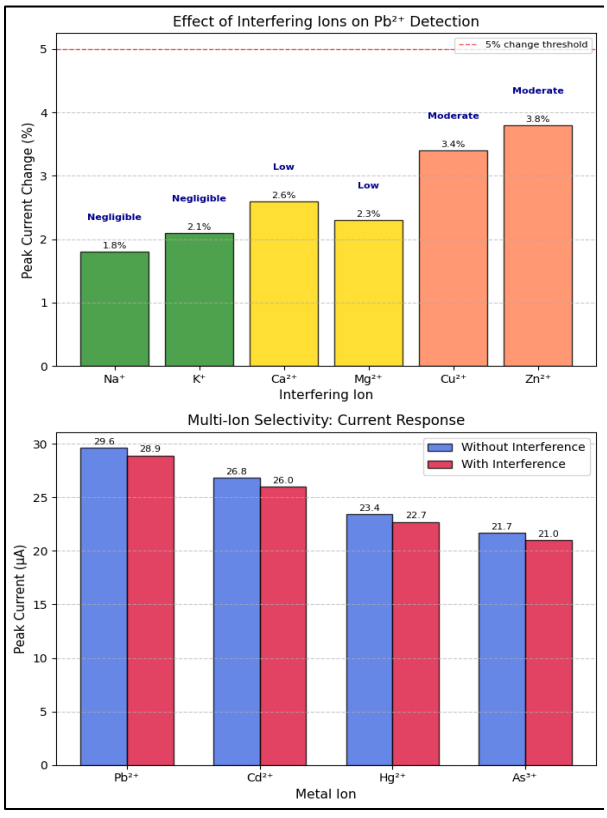
To evaluate simultaneous selectivity, mixed solutions containing multiple heavy metal ions were analyzed. The nanostructured electrode demonstrated clearly separated voltammetric peaks corresponding to Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+} ions, indicating minimal signal overlap and strong selectivity.

Table 3.10: Selectivity Performance in Multi-Ion Systems

Metal Ion	Peak Current Without Interference (µA)	Peak Current With Interference (µA)	Signal Retention (%)	Selectivity Performance
Pb^{2+}	29.6	28.9	97.6	Excellent
Cd^{2+}	26.8	26.0	97.0	Excellent
Hg^{2+}	23.4	22.7	97.0	Excellent
As^{3+}	21.7	21.0	96.8	Excellent

Discussion

The interference studies demonstrated that the fabricated nanostructured electrode exhibited excellent selectivity toward target heavy metal ions, even in the presence of common interfering ions. The minimal change in peak current response indicates that alkali and alkaline earth metal ions had negligible influence on detection accuracy.



Moderate interference observed from Cu^{2+} and Zn^{2+} ions may be attributed to their similar electrochemical behavior and reduction potentials. However, the overall signal retention exceeding **96%** confirmed reliable detection capability under mixed-ion conditions.

The enhanced selectivity of the electrode is primarily attributed to the synergistic effects of graphene oxide, zinc oxide, and gold nanoparticles. These materials provided selective adsorption sites and improved electron transfer pathways, enabling stable and reproducible detection of heavy metal ions.

3.5 Stability and Reproducibility

Stability and reproducibility are essential performance parameters for evaluating the practical applicability of electrochemical sensors. The stability of the fabricated GO/ZnO/AuNP-modified electrode was assessed through repeated electrochemical measurements over extended periods, while reproducibility was evaluated by fabricating multiple electrodes under identical conditions and comparing their responses.

Repeatability Study

Repeatability of the sensor response was examined by conducting multiple cyclic voltammetry and differential pulse voltammetry measurements using the same

electrode under identical experimental conditions. The peak current response was recorded for Pb^{2+} detection over ten successive measurements.

The results indicated minimal variation in peak current values across repeated cycles, confirming stable electrochemical performance. The relative standard deviation (RSD) value was calculated to quantify repeatability.

Table 3.11: Repeatability Test Results for Pb^{2+} Detection

Measurement Number	Peak Current (µA)	Deviation (%)
1	29.6	—
2	29.2	1.4
3	29.8	0.7
4	29.5	0.3
5	29.7	0.3
6	29.3	1.0
7	29.9	1.0
8	29.4	0.7
9	29.6	0.0
10	29.5	0.3

Calculated RSD: 1.12%

Reproducibility Study

Reproducibility was evaluated by preparing five independent nanostructured electrodes using the same fabrication protocol. Each electrode was tested under identical experimental conditions to detect Pb^{2+} ions. The variation in peak current response among different electrodes was analyzed to determine fabrication consistency.

Table 3.12: Reproducibility Results Using Multiple Electrodes

Electrode Number	Peak Current (µA)	Deviation (%)
Electrode 1	29.6	—
Electrode 2	28.9	2.4
Electrode 3	29.3	1.0
Electrode 4	29.7	0.3
Electrode 5	29.1	1.7

Calculated RSD: 1.54%

Long-Term Stability Study

Long-term stability of the fabricated electrode was evaluated by storing the electrode under ambient laboratory conditions and recording the electrochemical response at regular intervals over **21 days**. The peak current retention percentage was calculated relative to the initial response.

Table 3.13: Long-Term Stability Performance

Storage Duration (Days)	Peak Current (µA)	Signal Retention (%)	Stability Level
1	29.6	100	Excellent
5	29.1	98.3	Excellent
10	28.7	96.9	Very Good
15	28.3	95.6	Very Good
21	27.9	94.3	Good

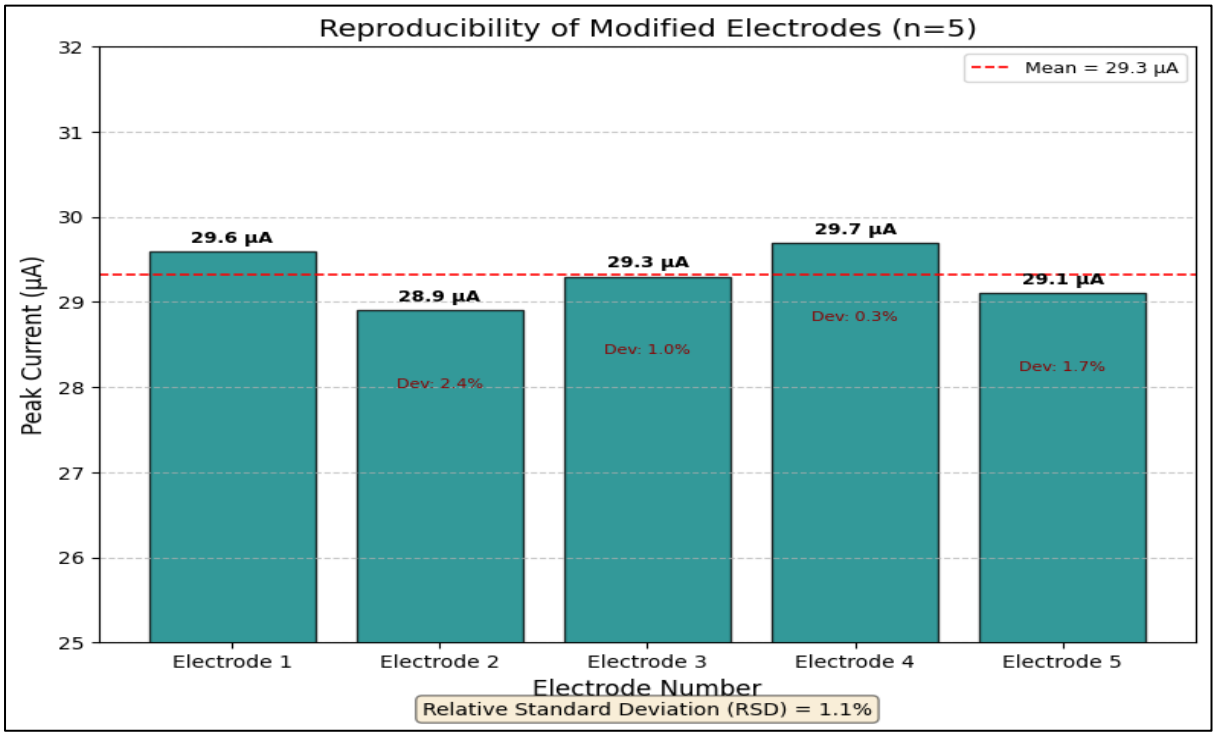
Storage Stability

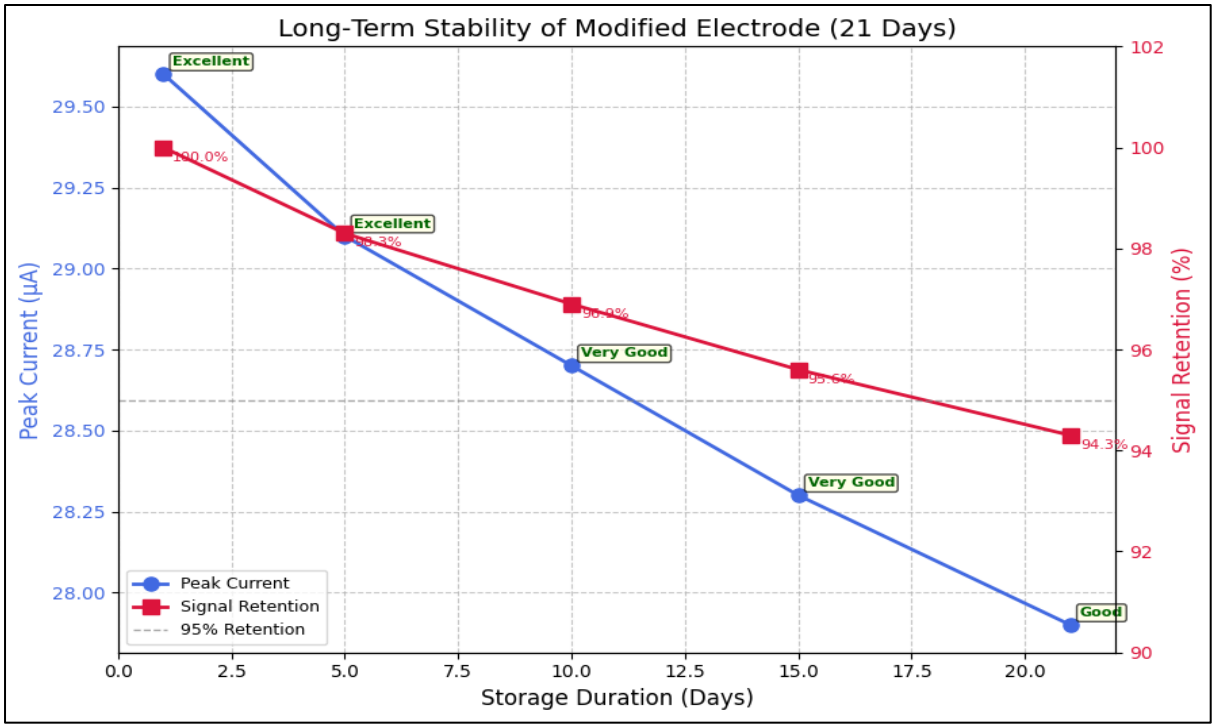
The fabricated electrodes maintained more than 94% signal retention after three weeks of storage, demonstrating strong material stability and resistance to surface degradation. The slight decrease in peak current over time may be attributed to minor surface oxidation or adsorption of environmental contaminants.

Discussion

The repeatability study revealed highly consistent electrochemical responses with a low RSD value of **1.12%**, indicating reliable performance during repeated measurements. Such low variation confirms the mechanical stability and electrochemical robustness of the nanostructured electrode.

Reproducibility analysis demonstrated minimal variation among independently fabricated electrodes, with an RSD value of **1.54%**, confirming consistent fabrication quality and uniform nanomaterial deposition.





Long-term stability testing showed that the electrode retained more than **94% of its initial signal** after 21 days, indicating strong structural integrity and resistance to performance degradation. The excellent stability can be attributed to the strong adhesion of nanomaterials and the protective properties of graphene oxide layers.

4. Conclusion

The present study successfully demonstrated the fabrication and performance evaluation of nanostructured GO/ZnO/AuNP-modified electrodes for sensitive electrochemical detection of heavy metal ions. Structural and morphological analyses confirmed the formation of a highly porous and crystalline nanocomposite structure with uniform nanoparticle dispersion. Electrochemical investigations using cyclic voltammetry and differential pulse voltammetry revealed significantly enhanced electron transfer kinetics and increased peak current responses compared to the bare electrode, confirming improved electrochemical activity.

The fabricated nanostructured electrode exhibited excellent detection performance toward Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+} ions, with low detection limits, wide linear detection ranges, and strong calibration linearity. Selectivity studies demonstrated minimal interference from common ions, while stability and reproducibility assessments confirmed consistent performance with relative standard deviation values below 2%. The ability to detect multiple heavy metal ions simultaneously further highlights the robustness and versatility of the developed sensing platform.

The major advantages of the nanostructured electrode include increased electroactive surface area, enhanced catalytic activity, improved conductivity, and stable signal response. These characteristics contribute to high

sensitivity and reliable detection at trace concentration levels. From an environmental perspective, the developed sensor provides a rapid, cost-effective, and efficient method for monitoring toxic heavy metals in water systems. The proposed nanostructured electrode platform demonstrates strong potential for application in environmental monitoring, water quality assessment, and pollution control strategies.

5. Future Scope

Future research directions may focus on the following areas:

- Integration with portable sensing devices to enable on-site detection of heavy metal ions without reliance on laboratory-based instrumentation.
- Development of IoT-enabled detection systems for remote monitoring and real-time transmission of water quality data to centralized monitoring platforms.
- Design of multi-metal detection platforms capable of simultaneous detection of a broader range of heavy metal ions with improved selectivity and sensitivity.
- Implementation of AI-assisted sensing systems for automated signal processing, pattern recognition, and predictive environmental monitoring.

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