

Indonesian Journal of Chemical Science and Technology (IJCST)

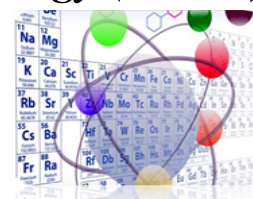
State University of Medan, <https://jurnal.unimed.ac.id/2012/index.php/aromatika>

IJCST-UNIMED 2026, Vol. 09, No. 1, Page; 168 – 179

Received : Jan 23rd, 2026

Accepted : Jan 30th, 2026

Web Published : Jan 31st, 2026



A Review: Modified Graphene-Based Voltammetry Sensors for Heavy Metal Detection in Water Samples

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ABSTRACT

Heavy metal contamination in aquatic environments poses a serious environmental and public health concern, requiring analytical methods that are sensitive, selective, and suitable for on-site analysis. Voltammetry electrochemical sensors have emerged as a promising alternative to conventional techniques due to their low cost, portability, rapid response, and high sensitivity. Graphene, with its high surface area, excellent electrical conductivity, and chemical stability, has been widely utilized as an electrode material to enhance sensor performance. However, pristine graphene often exhibits limited selectivity toward specific metal ions. To address this limitation, various surface modification strategies have been developed, including functionalization with chelating ligands, ion-selective polymers, nanoparticles, and composite materials. This review provides a comprehensive overview of recent advances in modified graphene-based voltammetry sensors for heavy metal detection in water samples, covering voltammetry principles, graphene modification strategies, analytical performance, and practical environmental applications.

Keywords: graphene, heavy metals, voltammetry sensor, surface modification

1. INTRODUCTION

Water covers almost 71% of the earth's parts and its existence is essential for living beings. However, many aquatic environments have been polluted by anthropogenic activities such as settlements, industry, and agriculture ¹. Of the various pollutants that pollute the waters, heavy metals are one of the most worrisome. The term heavy metal refers to metals that have a density of more than 5g/mL or solid metal elements that are toxic in small concentrations. Heavy metals continue to represent a significant risk to human health and environmental sustainability due to their inherent resistance to natural degradation. This characteristic allows them to endure in ecosystems for extended periods potentially centuries leading to their progressive accumulation within biological food webs ²⁻⁴. Consequently, the precise measurement of heavy metal concentrations in water, particularly at trace levels, is critically important for safeguarding human health and maintaining ecological balance.

Conventional analytical techniques such as inductively coupled plasma-mass spectrometry (ICP-MS) ⁵, atomic absorption spectroscopy (AAS) ^{7,8}, and X-ray fluorescence (XRF) ^{9,10} are widely employed for heavy metal detection due to their high sensitivity and accuracy. However, their practical application is often constrained by high operational costs, bulky instrumentation, time-consuming procedures, and limited suitability for on-site analysis.

In contrast, electrochemical sensing platforms, particularly voltammetry sensors, have emerged as attractive alternatives owing to their portability, rapid response, low cost, and compatibility with in-situ measurements ¹¹. Despite these advantages, the analytical performance of voltammetry sensors in complex water matrices is frequently limited by insufficient sensitivity and poor selectivity toward specific metal ions, highlighting the need for advanced electrode materials ¹²⁻¹⁴.

Among various electrode materials, graphene-based materials have attracted considerable interest due to their high surface area and excellent electrical conductivity, which are advantageous for enhancing electron

transfer and signal amplification in voltammetric sensing¹⁵⁻¹⁷. Nevertheless, pristine graphene often exhibits limited metal-ion recognition capability, necessitating further surface modification to achieve selective and sensitive detection.

To address these challenges, diverse graphene modification strategies including oxidation, heteroatom doping¹⁸, functionalization with chelating ligands or polymers^{19,20}, and hybridization with metal nanoparticles or other functional materials have been extensively explored²¹. These approaches have demonstrated markedly different effects on analytical performance, such as detection limits, sensitivity, selectivity, and operational stability, indicating that no single modification strategy is universally optimal.

This review evaluates recent advances in modified graphene-based voltammetry sensors for heavy metal detection in water samples, with particular emphasis on comparative performance analysis, emerging performance trends, key advantages and limitations of different modification strategies, and existing research gaps that must be addressed to facilitate practical environmental applications.

2. THEORETICAL BASIS: VOLTAMMETRY TECHNIQUES

Voltammetry is an electroanalytical technique that identifies and quantifies electroactive species by monitoring current responses as a function of an applied potential. Originating from polarography developed by Jaroslav Heyrovský in the early 20th century, voltammetry has evolved significantly with the decline of mercury-based electrodes due to environmental and safety concerns, giving rise to modern solid-state and nanomaterial-modified electrodes²².

A voltammetric system typically consists of three electrodes: a working electrode, a reference electrode, and a counter electrode. Among these, the working electrode is the critical component where redox reactions of the target analyte occur. The magnitude of the measured current is governed by electron transfer kinetics, mass transport, and surface interactions at the electrode solution interface²³. Consequently, the physicochemical properties of the working electrode surface play a decisive role in analytical performance.

Voltammetry offers several advantages over conventional spectroscopic techniques such as AAS and ICP-OES, including high sensitivity, low instrumental cost, wide linear dynamic range, portability, and potential for in situ and real-time monitoring²⁴⁻²⁷. There are several examples of heavy metal determination that have been reported such as²⁸ successfully developed ultrasensitive electrochemical sensors based on chitosan-mediated Fe-Al MMON nanocomposites for simultaneous detection of Pb²⁺, Cd²⁺, and Hg²⁺ at the parts per trillion level. The DPV method shows the highest sensitivity with good detection limits. The sensor has also been successfully applied its practical potential in water quality monitoring. In addition, a straightforward yet highly effective electrochemical sensor based on voltammetry has been successfully developed. This sensor is capable of simultaneously detecting four hazardous heavy metals in water and exhibits excellent sensitivity and stability. It can detect cadmium (Cd²⁺) at 0.4 ppb, lead (Pb²⁺) at 2.5 ppb, copper (Cu²⁺) at 7.3 ppb, and mercury (Hg²⁺) at 0.7 ppb²⁹.

The analytical performance of voltammetric sensors is commonly evaluated using parameters such as limit of detection (LOD), sensitivity, selectivity, linearity, stability, and reproducibility^{30,31}. Among these, sensitivity and selectivity are most strongly influenced by the surface characteristics of the working electrode. In this context, electrode modification with nanostructured materials has emerged as an effective strategy to enhance electron transfer, increase active surface area, and introduce selective binding sites³²⁻³⁶. Graphene and its derivatives have attracted particular attention as electrode modification materials due to their exceptional electrical conductivity, high surface area, mechanical stability, and ease of functionalization. When integrated into voltammetric systems, graphene-modified electrodes significantly improve current response, lower detection limits, and enhance selectivity toward heavy metal ions, especially when combined with metal nanoparticles, polymers, or metal-organic frameworks. As a result, graphene-based voltammetric sensors represent a powerful and promising platform for sensitive and selective heavy metal detection in environmental water samples.

3. GRAPHENE AND ITS MODIFICATIONS

Graphene is a two-dimensional (2D) nanomaterial consisting of a single atomic layer of carbon atoms arranged in a hexagonal honeycomb lattice³⁷. Each carbon atom possesses four valence electrons, three of which participate in strong in-plane sp² hybridized bonding, while the remaining electron contributes to a delocalized π -electron system above and below the graphene plane³⁸. This unique electronic structure endows graphene with exceptional properties, including high surface area, excellent electrical conductivity, and outstanding mechanical strength^{39,40}. These characteristics make graphene particularly attractive as a working electrode material in voltammetric sensing applications.

Graphene can be engineered into various structural forms, such as graphene nanoribbons, nanosheets, nanoplates, and three-dimensional (3D) graphene architectures⁴¹. While these structural variations influence electrochemical behavior, comparative studies systematically correlating graphene morphology with sensor

performance parameters such as sensitivity, selectivity, and stability remain limited. This lack of standardized comparison makes it difficult to identify the most effective graphene configuration for practical heavy metal detection.

To enhance the analytical performance of graphene-based voltammetric sensors, surface modification is essential. Such modifications aim to improve not only sensitivity and electron transfer efficiency, but also selectivity, operational stability, and applicability in real water samples. Common strategies include functionalization with selective ligands, polymer coatings, incorporation of metal or metal oxide nanoparticles, and formation of graphene-based composites. However, many studies primarily emphasize improved detection limits without providing comprehensive comparisons of selectivity, reproducibility, and long-term performance.

3.1 Modification with Chelating Ligands

One of the key approaches to improving the performance of graphene-based voltammetric sensors is surface modification using chelating ligands ⁴². Chelating ligands are molecules or ions containing multiple donor atoms, such as oxygen, nitrogen, or sulfur, which can simultaneously coordinate metal ions to form stable complexes. The selection of an appropriate chelating ligand is therefore crucial, as its affinity and specificity directly govern sensor selectivity ⁴³. Numerous chelating ligands have been successfully integrated with graphene-based materials to enhance sensor sensitivity, selectivity, and practical applicability. DMG-functionalized Nafion graphene electrodes exhibit excellent selectivity and ultra-trace detection of Ni²⁺ (LOD 1.5 µg L⁻¹) due to strong and specific Ni–DMG complexation, although their application is largely limited to single-analyte detection ⁴⁴. In contrast, EDTA-functionalized reduced graphene oxide sensors enable the simultaneous detection of multiple metal ions, such as Pb²⁺ and Cd²⁺, with low detection limits (1.02 and 2.52 ppb, respectively) and good stability (>90% signal retention), demonstrating greater versatility for environmental monitoring ⁴⁵. Similarly, rGO-TTU-based sensors show high sensitivity and low limits of detection for Hg²⁺ (0.02 mg L⁻¹), together with strong selectivity and recyclability ⁴⁶.

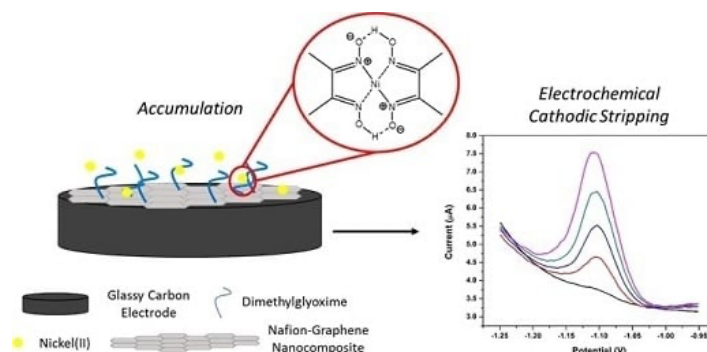


Figure 1. Mechanism of Ni(II) detection using a glassy carbon electrode modified with a Nafion–graphene–dimethylglyoxime nanocomposite. ⁴⁴

3.2 Modification with Ion-Selective Polymers

Applying ion-selective polymers as coatings on graphene has proven effective in enhancing voltammetric sensor performance; however, their analytical characteristics strongly depend on the polymer type and functionalization strategy employed. Ion-imprinted polymer (IIP)–graphene sensors, such as CS/GO-IIP systems, exhibit high selectivity and good reproducibility toward single target ions (e.g., Cu²⁺), with moderate detection limits (0.15 µmol/L), but their applicability is generally restricted to specific analytes due to the imprinting process ⁴⁷. Conductive polymer-graphene composites, including polyglycine- and polyaniline-based electrodes, offer broader applicability by improving electron transfer kinetics and increasing electroactive surface area, enabling simultaneous or multi-ion detection of Hg²⁺ and Pb²⁺ with comparable or lower detection limits (down to sub-µM or ppb levels) and successful implementation in real water and biological samples ⁴⁸. Biopolymer-based graphene sensors, particularly those functionalized with chitosan, demonstrate superior sensitivity for Pb²⁺ detection, achieving ultra-low detection limits (as low as 0.05 ppb); however, their performance tends to be more susceptible to matrix interferences due to nonspecific interactions ⁴⁹. Furthermore, hybrid systems combining conductive polymers, graphene oxide, and chelating agents, such as PANI/GO/EDTA composites, integrate efficient electron transfer, enlarged active surface area, and strong metal-ligand complexation, resulting in low charge-transfer resistance, high electrochemical stability, and enhanced selectivity toward Hg²⁺ with detection limits reaching 1 ppb, below the EPA regulatory threshold ⁵⁰. Overall, these comparisons highlight the trade-off between selectivity, versatility, sensitivity, and practical applicability among different polymer–graphene sensor architectures.

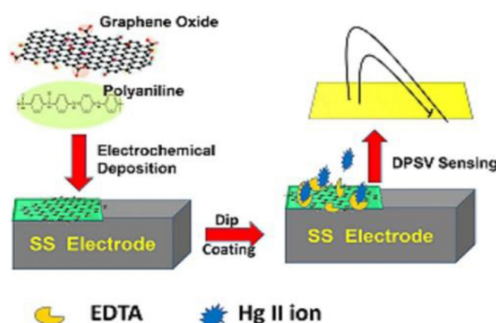


Figure 2. Illustrative schematic of the preparation process and detection mechanism of polyaniline polymer modified electrode ⁵⁰.

3.3 Modification with Nanoparticles

A comparative evaluation of graphene–nanoparticle-based voltammetric sensors highlights clear differences in analytical performance depending on the nanoparticle system and electrode architecture. The 3D GF/BiNP framework exhibits excellent sensitivity for Pb^{2+} and Cd^{2+} with very low detection limits (0.02 and $0.05 \mu\text{g L}^{-1}$, respectively), along with good stability and reproducibility, making it suitable for multi-metal detection at trace levels ⁵¹. rGO/AgNPs-based sensors achieve ultra-low LODs down to the femtomolar–zeptomolar range for Cu^{2+} , Cd^{2+} , and Hg^{2+} , benefiting from strong synergistic effects between graphene conductivity and AgNP catalytic activity; however, reports on long-term stability and performance in complex real matrices remain limited ⁵². In contrast, Fe_3O_4 /graphene-modified carbon paste electrodes offer balanced performance, combining low ng L^{-1} detection limits, good selectivity against interfering ions, high reproducibility ($\text{RSD} \leq 5.25\%$), and demonstrated applicability across diverse real samples including tap, bottled, river, and seawater ⁵³. Similarly, AgNPs/GrNPs-modified graphite electrodes enable the simultaneous detection of Cd^{2+} , Cu^{2+} , and Pb^{2+} with low detection limits of 59 , 44 , and 55 ng L^{-1} for Pb(II) , Bi(III) , and Cu(II) , respectively. The sensor exhibits good selectivity in the presence of potentially interfering metal ions and maintains stable performance for up to 30 days in tap water samples, underscoring its strong practical applicability ⁵⁴.

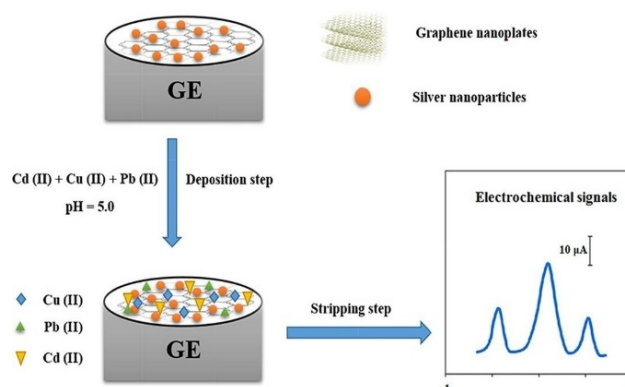


Figure 3. Illustration of electrode sensor modified with graphene nanoplate & silver nanoparticles ⁵⁴.

3.4 Modification with Composite Materials

Various graphene-based composite materials have been extensively investigated to enhance electrochemical sensor performance across a wide range of applications, from biomarker detection to heavy metal monitoring. These improvements primarily arise from the synergistic integration of graphene's high electrical conductivity and large surface area with the complementary chemical or structural functionalities of secondary materials.

For example, electrochemically modified graphene/bismuth nanocomposite electrodes exhibit strong capability for the simultaneous detection of Zn^{2+} , Cd^{2+} , and Pb^{2+} using stripping voltammetry, achieving low detection limits ($1.80 \mu\text{g/L}$ for Zn^{2+} , $0.18 \mu\text{g/L}$ for Cd^{2+} , and $0.11 \mu\text{g/L}$ for Pb^{2+}) and wide linear ranges (1 – $100 \mu\text{g/L}$). This performance is attributed to the alloy-forming ability of bismuth with heavy metals, which enhances stripping efficiency, combined with graphene's role in improving surface area and electron transfer ⁵⁵.

Further improvements in sensitivity and practical applicability have been demonstrated using micro-patterned rGO/CNT composite electrodes. These sensors enable independent detection of Cd^{2+} and Pb^{2+} in drinking water with detection limits of 0.6 ppb and 0.2 ppb , respectively, while maintaining good stability and reliability, highlighting their suitability for real-sample analysis ⁵⁶.

In addition, graphene-based composites integrated with hydrosulfonyl ($-\text{SH}$) functionalized covalent organic frameworks (COFs) offer enhanced selectivity and sensitivity toward Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} ions due to strong sulfur–metal coordination. These sensors achieve low detection limits (0.2 – $1.1 \mu\text{g/L}$), good

stability (signal variation <5%), and high recoveries (>95%) in real sample analysis, demonstrating promising potential for coastal and environmental monitoring applications ⁵⁷.

Similarly, a three-dimensional hybrid rGO/MWCNTs-COOH network fabricated on screen-printed carbon electrodes provides a highly conductive and vertically oriented structure that facilitates efficient electron transfer and simultaneous adsorption of Cd²⁺ and Pb²⁺ ions. With the additional stabilization from Nafion coating and in-situ bismuth film formation, this sensor delivers ultra-low detection limits (0.04 µg/L for Cd²⁺ and 0.02 µg/L for Pb²⁺) over a broad concentration range (0.1-1350 µg/L), and its performance has been successfully validated in tap water and lake samples ⁵⁸.

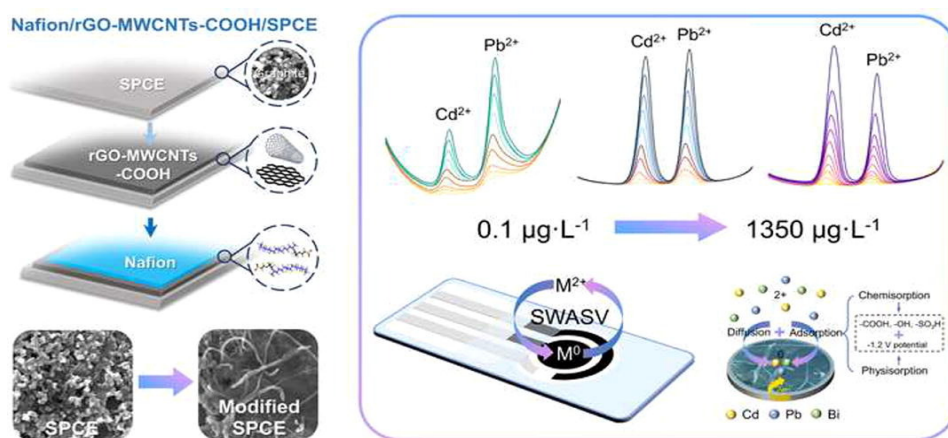


Figure 4. Schematic illustration of the electrochemical detection using a Nafion/rGO-MWCNTs-COOH-modified SPCE ⁵⁸.

Despite the enhanced analytical performance achieved by modified graphene-based voltammetry sensors. Several key challenges continue to limit their practical application for heavy metal detection in real water samples. Matrix effects remain a major concern, as natural organic matter, dissolved salts, and coexisting metal ions can compete with surface-bound chelating ligands or block active sites, resulting in signal suppression and peak distortion. Reproducibility is another critical issue, particularly for nanoparticle and composite-modified graphene electrodes, where variations in graphene quality, modifier loading, and fabrication protocols often lead to inconsistent sensor responses and batch-to-batch variability. Furthermore, long-term operational stability remains challenging due to ligand desorption, polymer degradation, nanoparticle aggregation, and electrochemical oxidation of graphene during prolonged cycling, which can significantly reduce sensor sensitivity over time. These limitations highlight the need for more robust surface immobilization strategies, standardized fabrication methods, and systematic long-term stability evaluations under realistic environmental condition ⁵⁹.

3.5 Modified Graphene Sensor Applications for Heavy Metal Detection

Graphene modification has proven to be a very effective approach in developing voltammetry sensors for heavy metal detection. The superior properties of graphene, such as large surface area and high electrical conductivity, can be further enhanced by the incorporation of other materials that have specific affinities for certain heavy metal ions. This modification strategy allows for increased sensitivity, selectivity, and lowering of the detection limits of voltammetry sensors, making it a promising tool for water quality monitoring and environmental analysis. The following table summarizes some examples of applications of modified graphene-based voltammetry sensors specifically designed for the detection of various heavy metal ions, based on the sources discussed.

Table 1. Applications of Modified Graphene-Based Voltammetry Sensors for Heavy Metal Ion Detection

No.	Modified Electrode Material	Target Analytcs	Voltmetry Method	Detection Limit (LOD)	Selectivity	Sample	Ref.
1	GCE/graphene-Bi	Zn(II), Cd(II), Pb(II)	<i>differential pulse anodic stripping voltammetry (DPASV)</i>	Zn(II) = 1.80 µg/L Cd(II) = 0.18 µg/L Pb(II) = 0.11 µg/L	Selective against Cd(II), Zn(II) and Pb(II) despite the presence of interfering ions (Fe(III), Co(II), Ni(II), Mn(II), Cu(II), and Cr(III))	Environmental water	⁵⁵
2	Modified Au Electrode [Ru(bpy) ₃] ²⁺ -GO	Cd(II), Pb(II), As(III) Hg(II)	<i>differential pulse voltammetry (DPV)</i>	Cd(II) = 2.8 nM Pb(II) = 1.41 nM As(III) = 2.3 nM Hg(II) = 1.6 nM	The sensor detects Cd(II), Pb(II), As(III) and Hg(II) simultaneously without interference demonstrating high selectivity for multi-ion analysis.	River water and tap water	⁶⁰
3	CPE/Fe ₃ O ₄ NPs-Graphene	Pb(II), Bi(III) Cu(II)	<i>Square-wave anodic stripping voltammetry (SW-ASV)</i>	Pb(II)= 59 ng/L Bi(III)= 44 ng/L Cu(II)= 55 ng/L	Selective in detecting Pb(II), Bi(III), and Cu(II) despite the presence of various other ions—as long as there is no EDTA or Triton X-100 in high concentrations.	Tap water, some samples of bottled mineral water, as well as river and sea water samples	⁵³
4	Electrode Graphite/AgNPs/G rNPs	Cd (II), Cu (II), Pb (II)	<i>square wave anodic stripping voltammetry (SWASV)</i>	Cd(II) = 5.0 ng Cu(II) = 4.1 ng Pb(II) = 1.0 ng	Highly selective and capable of detecting Cd(II), Pb(II), and Cu(II) simultaneously without interference from other metal ions	Tap water	⁵⁴
5	<i>Electrode Laser-Induced Graphene Fiber (LIGF)</i>	Cd(II) Pb(II)	<i>Square Wave Anodic Stripping Voltammetry (SWASV)</i>	Cd(II) and Pb(II) are 0.4 µg/L	There is a decrease in selectivity if Bi(III) is added above 1000 µg/L.	Drinking water and tap water	⁶¹
6	GCE/rGO-Ti ₃ C ₂ T _x	Cd(II) Cu(II)	<i>Pulse Voltage Differential (DPV)</i>	Cd ²⁺ : LOD = 0.31 nM LOQ = 1.02 nM	Ti ₃ C ₂ T _x -rGO sensor is selective against Cd ²⁺ and Cu ²⁺ despite the presence of interfering ions	Lake water and tap water	⁶²

				Cu: LOD = 0.18 nM LOQ = 0.62 nM			
7	GCE/LSG/PB-PEDOT	Cd(II)	<i>Pulse Voltage Differential (DPV)</i>	Cd(II) = 0.85 nM	Selectively detects Cd ²⁺ despite 10× concentrations of Mn ²⁺ , Pb ²⁺ , Ca ²⁺ , and Zn ²⁺ ions	Tap water and wastewater samples	63
8	Thymine-GO-Carbohydrazide (T-GO-C)	Hg ²⁺ (Mercury) Cr ⁶⁺ (Chrome Hexaval)	Differential Pulse Voltammetry (DPV) or Square Wave Voltammetry (SWV)	Linear detection range: above 5 ppb for both ions	Response to Hg ²⁺ & Cr ⁶⁺ remained stable despite bismuth disturbance	Standard solution; Intended for applications in drinking water or fields	64
9	GCE/rGO/Au-Bi	Pb(II) Cd(II)	<i>Differential Pulse Anodic Stripping Voltammetry (DPASV)</i>	Pb ²⁺ = 0.05 µM Cd ²⁺ = 0.02 µM	Selective despite the presence of interfering ions (K ⁺ , Ca ²⁺ , Fe ³⁺ , Fe ²⁺ , Co ²⁺ , Al ³⁺ , Mg ²⁺ , Mn ²⁺ , Ni ²⁺ , and Hg ²⁺) except Cu ²⁺ which degrades the signal	River water	65
10	Graphene Epitaxial (EG) electrode on silicon carbide (SiC) substrate	Cd(II) Cu(II) Hg(II) Pb(II)	<i>Square Wave Voltammetry (CSWV)</i>	Detection can be performed from 100–200 ppb		Real seawater	66
11	PVA/Chitosan-TRG/GCE)	Pb (II)	<i>square wave anodic stripping voltammetry (SWASV)</i>	0.05 ppb	selective to Pb ²⁺ at 50 ppb despite the presence of interfering ions with double concentrations.	Rivers and seawater	49
12	GCE/GR/GO	CD (II)	<i>differential pulse voltammetry (DPV)</i>	0.087 µM	selective to Cd ²⁺ in the presence of interfering ions, except Pb ²⁺ which causes interference	Tap water	67

4. CONCLUSION

Modification strategies for graphene-based sensors demonstrates that while chelating ligands and ion-imprinted polymers offer exceptional selectivity for single analytes, nanoparticle-based composites provide superior sensitivity for simultaneous multi-metal detection. Despite these achievements, significant challenges remain regarding matrix interference and long-term electrochemical stability. Future research must prioritize the development of standardized fabrication protocols and robust covalent functionalization to ensure sensor reliability in complex environmental matrices, ultimately enabling the deployment of cost-effective, portable devices for real-time water quality monitoring.

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