

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

Andi Eka Kartika<sup>1\*</sup>, Satria Putra Jaya Negara<sup>2</sup>

<sup>1,2</sup> Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Makassar, Makassar 90244, South Sulawesi, Indonesia.

\*Corresponding author: [andi.eka.kartika@unm.ac.id](mailto:andi.eka.kartika@unm.ac.id)

### 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<sup>1</sup>. 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<sup>2-4</sup>. 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)<sup>5,6</sup>, atomic absorption spectroscopy (AAS)<sup>7,8</sup>, and X-ray fluorescence (XRF)<sup>9,10</sup> 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<sup>11</sup>. 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<sup>12-14</sup>.

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 sensing<sup>15-17</sup>. 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 doping<sup>18</sup>, functionalization with chelating ligands or polymers<sup>19,20</sup>, and hybridization with metal nanoparticles or other functional materials have been extensively explored<sup>21</sup>. 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 20<sup>th</sup> 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 electrodes<sup>22</sup>.

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 interface<sup>23</sup>. 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 monitoring<sup>24-27</sup>. There are several examples of heavy metal determination that have been reported such as<sup>28</sup> successfully developed ultrasensitive electrochemical sensors based on chitosan-mediated Fe-Al MMON nanocomposites for simultaneous detection of Pb<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> 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 (Cd<sup>2+</sup>) at 0.4 ppb, lead (Pb<sup>2+</sup>) at 2.5 ppb, copper (Cu<sup>2+</sup>) at 7.3 ppb, and mercury (Hg<sup>2+</sup>) at 0.7 ppb<sup>29</sup>.

The analytical performance of voltammetric sensors is commonly evaluated using parameters such as limit of detection (LOD), sensitivity, selectivity, linearity, stability, and reproducibility<sup>30,31</sup>. 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 sites<sup>32-36</sup>. 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 lattice<sup>37</sup>. Each carbon atom possesses four valence electrons, three of which participate in strong in-plane sp<sup>2</sup> hybridized bonding, while the remaining electron contributes to a delocalized  $\pi$ -electron system above and below the graphene plane<sup>38</sup>. This unique electronic structure endows graphene with exceptional properties, including high surface area, excellent electrical conductivity, and outstanding mechanical strength<sup>39,40</sup>. These characteristics make graphene particularly attractive as a working electrode material in voltammetric sensing applications.

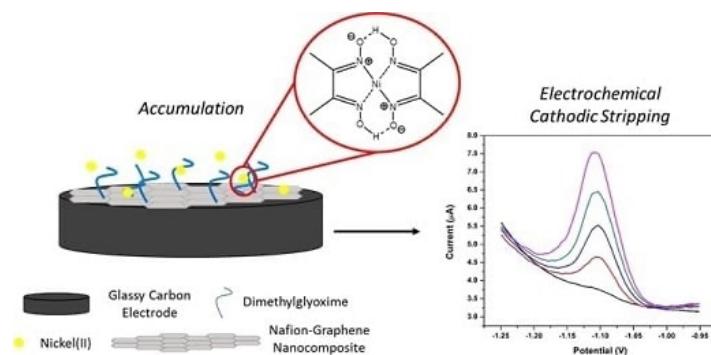
Graphene can be engineered into various structural forms, such as graphene nanoribbons, nanosheets, nanoplates, and three-dimensional (3D) graphene architectures<sup>41</sup>. While these structural variations influence electrochemical behavior, comparative studies systematically correlating graphene 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

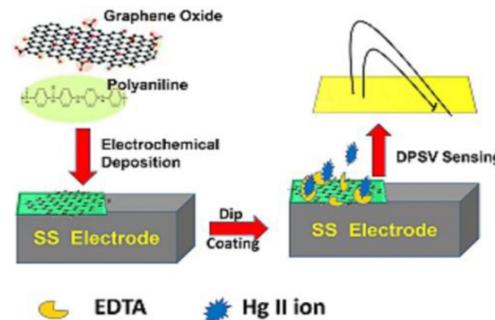
One of the key approaches to improving the performance of graphene-based voltammetric sensors is surface modification using chelating ligands<sup>42</sup>. Chelating ligands are molecules or ions containing multiple donor atoms, such as oxygen, nitrogen, or sulfur, which can simultaneously coordinate 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<sup>43</sup>. 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  $\text{Ni}^{2+}$  (LOD 1.5  $\mu\text{g L}^{-1}$ ) due to strong and specific Ni-DMG complexation, although their application is largely limited to single-analyte detection<sup>44</sup>. In contrast, EDTA-functionalized reduced graphene oxide sensors enable the simultaneous detection of multiple metal ions, such as  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , with low detection limits (1.02 and 2.52 ppb, respectively) and good stability (>90% signal retention), demonstrating greater versatility for environmental monitoring<sup>45</sup>. Similarly, rGO-TTU-based sensors show high sensitivity and low limits of detection for  $\text{Hg}^{2+}$  (0.02 mg  $\text{L}^{-1}$ ), together with strong selectivity and recyclability<sup>46</sup>.



**Figure 1.** Mechanism of  $\text{Ni}(\text{II})$  detection using a glassy carbon electrode modified with a Nafion-graphene-dimethylglyoxime nanocomposite.<sup>44</sup>

### 3.2 Modification with Ion-Selective Polymers

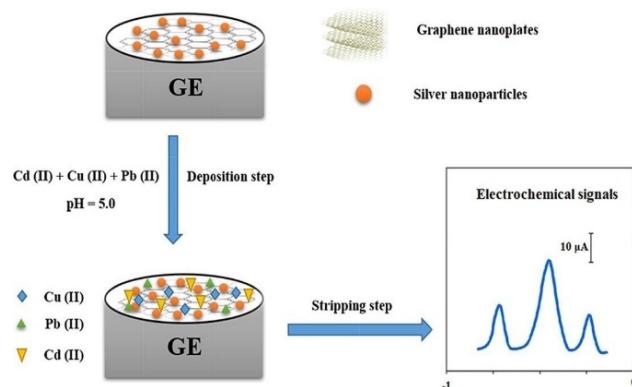
Applying ion-selective polymers as coatings on graphene has proven effective in enhancing voltammetric sensor performance; however, their analytical characteristics strongly depend on the polymer type and functionalization strategy employed. Ion-imprinted polymer (IIP)-graphene sensors, such as CS/GO-IIP systems, exhibit high selectivity and good reproducibility toward single target ions (e.g.,  $\text{Cu}^{2+}$ ), with moderate detection limits (0.15  $\mu\text{mol/L}$ ), but their applicability is generally restricted to specific analytes due to the imprinting process<sup>47</sup>. 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  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  with comparable or lower detection limits (down to sub- $\mu\text{M}$  or ppb levels) and successful implementation in real water and biological samples<sup>48</sup>. Biopolymer-based graphene sensors, particularly those functionalized with chitosan, demonstrate superior sensitivity for  $\text{Pb}^{2+}$  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<sup>49</sup>. 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  $\text{Hg}^{2+}$  with detection limits reaching 1 ppb, below the EPA regulatory threshold<sup>50</sup>. 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 <sup>50</sup>.

### 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  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  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 <sup>51</sup>. rGO/AgNPs-based sensors achieve ultra-low LODs down to the femtomolar–zeptomolar range for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ , 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 <sup>52</sup>. In contrast,  $\text{Fe}_3\text{O}_4$ /graphene-modified carbon paste electrodes offer balanced performance, combining low  $\text{ng L}^{-1}$  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 <sup>53</sup>. Similarly, AgNPs/GrNPs-modified graphite electrodes enable the simultaneous detection of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  with low detection limits of 59, 44, and 55  $\text{ng L}^{-1}$  for  $\text{Pb}(\text{II})$ ,  $\text{Bi}(\text{III})$ , and  $\text{Cu}(\text{II})$ , 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 <sup>54</sup>.



**Figure 3.** Illustration of electrode sensor modified with graphene nanoplate & silver nanoparticles <sup>54</sup>.

### 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.

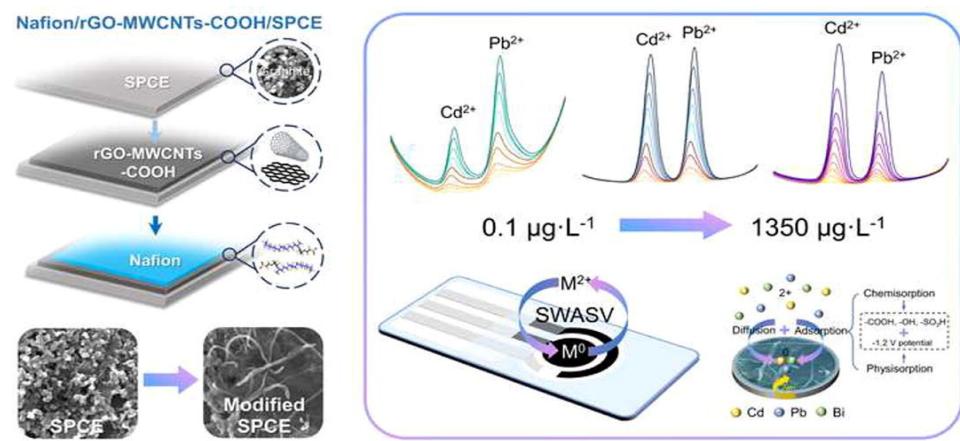
For example, electrochemically modified graphene/bismuth nanocomposite electrodes exhibit strong capability for the simultaneous detection of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  using stripping voltammetry, achieving low detection limits (1.80  $\mu\text{g/L}$  for  $\text{Zn}^{2+}$ , 0.18  $\mu\text{g/L}$  for  $\text{Cd}^{2+}$ , and 0.11  $\mu\text{g/L}$  for  $\text{Pb}^{2+}$ ) 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 <sup>55</sup>.

Further improvements in sensitivity and practical applicability have been demonstrated using micro-patterned rGO/CNT composite electrodes. These sensors enable independent detection of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  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 <sup>56</sup>.

In addition, graphene-based composites integrated with hydrosulfonyl (–SH) functionalized covalent organic frameworks (COFs) offer enhanced selectivity and sensitivity toward  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  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<sup>57</sup>.

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 Cd<sup>2+</sup> and Pb<sup>2+</sup> 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 Cd<sup>2+</sup> and 0.02 µg/L for Pb<sup>2+</sup>) over a broad concentration range (0.1-1350 µg/L), and its performance has been successfully validated in tap water and lake samples<sup>58</sup>.



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

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<sup>59</sup>.

### 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 Analytics	Voltmetry Method	Detection Limit (LOD)	Selectivity	Sample	Ref.
1	GCE/graphene-Bi	Zn(II) Cd(II), Pb(II)	<i>differential pulse anodic stripping voltammetry</i> (DPASV)	Zn(II) = 1.80 $\mu$ g/L Cd(II) = 0.18 $\mu$ g/L Pb(II) = 0.11 $\mu$ g/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	<sup>55</sup>
2	Modified Au Electrode [Ru(bpy) <sub>3</sub> ] <sup>2+</sup> -GO	Cd(II), Pb(II), As(III) Hg(II)	<i>differential pulse voltammetry</i> (DPV)	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	<sup>60</sup>
3	CPE/Fe <sub>3</sub> O <sub>4</sub> NPs-Graphene	Pb(II), Bi(III) Cu(II)	<i>Square-wave anodic stripping voltammetry</i> (SW-ASV)	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	<sup>53</sup>
4	Electrode Graphite/AgNPs/G rNPs	Cd (II), Cu (II), Pb (II)	<i>square wave anodic stripping voltammetry</i> (SWASV)	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	<sup>54</sup>
5	<i>Electrode Laser-Induced Graphene Fiber</i> (LIGF)	Cd(II) Pb(II)	<i>Square Wave Anodic Stripping Voltammetry</i> (SWASV)	Cd(II) and Pb(II) are 0.4 $\mu$ g/L	There is a decrease in selectivity if Bi(III) is added above 1000 $\mu$ g/L.	Drinking water and tap water	<sup>61</sup>
6	GCE/rGO-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Cd(II) Cu(II)	<i>Pulse Voltage Differential</i> (DPV)	Cd <sup>2+</sup> : LOD = 0.31 nM LOQ = 1.02 nM	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -rGO sensor is selective against Cd <sup>2+</sup> and Cu <sup>2+</sup> despite the presence of interfering ions	Lake water and tap water	<sup>62</sup>

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

#### 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.

#### REFERENCES

1. Xiang H, Cai Q, Li Y, Zhang Z, Cao L, Li K, Yang H (2020) Sensors Applied for the Detection of Pesticides and Heavy Metals in Freshwaters. *J Sensors* 2020:1–22
2. Lace A, Cleary J (2021) A Review of Microfluidic Detection Strategies for Heavy Metals in Water. *Chemosensors* 9:60
3. Dag N, Arici OK (2021) Heavy Metals in Soils Pb (Lead), Hg (Mercury), Cd (Cadmium), As (Arsenic) Effects on Human Health. *Int J Environ Trends* 5:48–59
4. Sulthana SF, Iqbal UM, Suseela SB, Anbazhagan R, Chinthaginjala R, Chitathuru D, Ahmad I, Kim T (2024) Electrochemical Sensors for Heavy Metal Ion Detection in Aqueous Medium: A Systematic Review. *ACS Omega* 9:25493–25512
5. Chen Y, He M, Chen B, Hu B (2021) Thiol-grafted magnetic polymer for preconcentration of Cd, Hg, Pb from environmental water followed by inductively coupled plasma mass spectrometry detection. *Spectrochim Acta Part B At Spectrosc* 177:106071
6. Ahmad H, Koo BH, Khan RA (2022) Enrichment of trace Hg(II) ions from food and water samples after solid phase extraction combined with ICP-OES determination. *Microchem J* 175:107179
7. Daşbaşı T, Saçmacı Ş, Ülgen A, Kartal Ş (2015) A solid phase extraction procedure for the determination of Cd(II) and Pb(II) ions in food and water samples by flame atomic absorption spectrometry. *Food Chem* 174:591–596
8. Kassim NSA, A. I. S. M. Ghazali S, Liyana Bohari F, A. Z. Abidin N (2022) Assessment of heavy metals in wastewater plant effluent and lake water by using atomic absorption spectrophotometry. *Mater Today Proc* 66:3961–3964
9. Zhou S, Yuan Z, Cheng Q, Zhang Z, Yang J (2018) Rapid in situ determination of heavy metal concentrations in polluted water via portable XRF: Using Cu and Pb as example. *Environ Pollut* 243:1325–1333
10. Tighe M, Bielski M, Wilson M, Ruscio-Atkinson G, Peaslee GF, Lieberman M (2020) A Sensitive XRF Screening Method for Lead in Drinking Water. *Anal Chem* 92:4949–4953
11. Shi Y, Zhang S, Zhou H, Dong Y, Liu G, Ye W, He R, Zhao G (2025) Recent Developments in Heavy Metals Detection: Modified Electrodes, Pretreatment Methods, Prediction Models and Algorithms. *Metals (Basel)* 15:80
12. Dai X, Wu S, Li S (2018) Progress on electrochemical sensors for the determination of heavy metal ions from contaminated water. *J Chinese Adv Mater Soc* 6:91–111
13. Ding R, Cheong YH, Ahamed A, Lisak G (2021) Heavy Metals Detection with Paper-Based Electrochemical Sensors. *Anal Chem* 93:1880–1888
14. Yang Z (2024) Voltammetry for quantitative determination of trace mercury ions in water via acetylene black modified carbon paste electrode. *Alexandria Eng J* 87:107–113
15. Ambrosi A, Chua CK, Latiff NM, Loo AH, Wong CHA, Eng AYS, Bonanni A, Pumera M (2016) Graphene and Its Electrochemistry – An Update. *Chem Soc Rev* 45:2458–2493
16. Urade AR, Lahiri I, Suresh KS (2023) Graphene Properties, Synthesis and Applications: A Review. *JOM* 75:614–630
17. Abdelshafi NA, Darwish HW, Alanazi AS, Naguib IA, Elkhouly HH, Khodary NS, Mohamed EH (2024) Voltammetric analysis of pholcodine on graphene-modified GNPs/PTs with green assessment. *BMC Chem* 18:48
18. ZHENG Z, YANG X, LI J, ZHANG X, MUHAMMAD I, GENG L (2021) Preparation and properties of graphene

nanoplatelets reinforced aluminum composites. *Trans Nonferrous Met Soc China* 31:878–886

19. Sheng Z, Cao M, Hong Y, Wang S, Fan Z, Xiong J, Yang H, Deng C (2018) Preparation of Functionalized Graphene Nano-platelets and Use for Adsorption of Pb<sup>2+</sup> from Solution. *J Wuhan Univ Technol Sci Ed* 33:1395–1401

20. Pushpanjali PA, Manjunatha JG, Hareesha N, Amrutha BM, Raril C, ALOthman ZA, Alanazi AM, Pandith A (2022) Fabrication of poly(L-Aspartic acid) Layer on graphene nanoplatelets paste electrode for riboflavin sensing. *Mater Chem Phys* 276:125392

21. Beyyavaş E, Aslanoglu M (2025) An Electrochemical Platform Constructed with Tantalum Nanoparticles and Graphene Nanoplatelets for the Voltammetric Sensing of Ritodrine. *Electroanalysis*. <https://doi.org/10.1002/elan.12029>

22. Wenzel TJ (2013) Douglas A. Skoog, Donald M. West, F. James Holler, and Stanley R. Crouch: Fundamentals of analytical chemistry, 9th ed., international ed. *Anal Bioanal Chem* 405:7903–7904

23. Kounaves SP (1997) Voltammetric Techniques. *Handb. Instrum. Tech. Anal. Chem.*

24. Gafurov ZN, Kanyukov AO, Kagilev AA, Sinyashin OG, Yakhvarov DG (2021) Electrochemical methods for synthesis and in situ generation of organometallic compounds. *Coord Chem Rev* 442:213986

25. Alyamni N, Abot JL, Zestos AG (2024) Perspective—Advances in Voltammetric Methods for the Measurement of Biomolecules. *ECS Sensors Plus* 3:027001

26. Yang Q, Nagar B, Alvarez-Diduk R, et al (2021) Development of a Heavy Metal Sensing Boat for Automatic Analysis in Natural Waters Utilizing Anodic Stripping Voltammetry. *ACS ES&T Water* 1:2470–2476

27. Bressi V, Chiarotto I, Ferlazzo A, Celesti C, Michenzi C, Len T, Iannazzo D, Neri G, Espro C (2023) Voltammetric Sensor Based on Waste-Derived Carbon Nanodots for Enhanced Detection of Nitrobenzene. *ChemElectroChem*. <https://doi.org/10.1002/celc.202300004>

28. Sengupta P, Pramanik K, Sarkar P (2021) Simultaneous detection of trace Pb(II), Cd(II) and Hg(II) by anodic stripping analyses with glassy carbon electrode modified by solid phase synthesized iron-aluminate nano particles. *Sensors Actuators B Chem* 329:129052

29. Naseri M, Mohammadniaei M, Ghosh K, et al (2023) A Robust Electrochemical Sensor Based on Butterfly-shaped Silver Nanostructure for Concurrent Quantification of Heavy Metals in Water Samples. *Electroanalysis*. <https://doi.org/10.1002/elan.202200114>

30. Jjagwe J, Olupot PW, Kulabako R, Carrara S (2024) Electrochemical sensors modified with iron oxide nanoparticles/nanocomposites for voltammetric detection of Pb (II) in water: A review. *Heliyon* 10:e29743

31. Chatzithanasiou E, Liava V, Golia EE, Girousi S (2024) Analytical Applications of Voltammetry in the Determination of Heavy Metals in Soils, Plant Tissues, and Water—Prospects and Limitations in the Co-Identification of Metal Cations in Environmental Samples. *Analytica* 5:358–383

32. Filippidou MK, Chatzandroulis S (2023) Microfluidic Devices for Heavy Metal Ions Detection: A Review. *Micromachines*. <https://doi.org/10.3390/mi14081520>

33. Ivanišević I (2023) The Role of Silver Nanoparticles in Electrochemical Sensors for Aquatic Environmental Analysis. *Sensors* 23:3692

34. Sati A, Ranade TN, Mali SN, Ahmad Yasin HK, Pratap A (2025) Silver Nanoparticles (AgNPs): Comprehensive Insights into Bio/Synthesis, Key Influencing Factors, Multifaceted Applications, and Toxicity—A 2024 Update. *ACS Omega* 10:7549–7582

35. Malik S, Singh J, Goyat R, Saharan Y, Chaudhry V, Umar A, Ibrahim AA, Akbar S, Ameen S, Baskoutas S (2023) Nanomaterials-based biosensor and their applications: A review. *Heliyon* 9:e19929

36. Bulemo PM, Kim DH, Shin H, et al (2025) Selectivity in Chemiresistive Gas Sensors: Strategies and Challenges. *Chem Rev* 125:4111–4183

37. Das S, Sudhagar P, Kang YS, Choi W (2015) Synthesis and Characterization of Graphene. In: *Carbon Nanomater. Adv. Energy Syst.* Wiley, pp 85–131

38. Yu W, Sisi L, Haiyan Y, Jie L (2020) Progress in the functional modification of graphene/graphene oxide: a review. *RSC Adv* 10:15328–15345

39. Geim AK (2009) Graphene: Status and Prospects. *Science* (80- ) 324:1530–1534

40. Adetayo A, Runsewe D (2019) Synthesis and Fabrication of Graphene and Graphene Oxide: A Review. *Open J Compos Mater* 09:207–229

41. Tiwari SK, Sahoo S, Wang N, Huczko A (2020) Graphene research and their outputs: Status and prospect. *J Sci Adv Mater Devices* 5:10–29

42. Mishyn V, Hugo A, Rodrigues T, et al (2022) The holy grail of pyrene-based surface ligands on the sensitivity of graphene-based field effect transistors. *Sensors & Diagnostics* 1:235–244

43. Gulcin İ, Alwasel SH (2022) Metal Ions, Metal Chelators and Metal Chelating Assay as Antioxidant Method. *Processes* 10:132

44. Pokpas K, Jahed N, Baker PG, Iwuoha EI (2017) Complexation-Based Detection of Nickel(II) at a Graphene-Chelate Probe in the Presence of Cobalt and Zinc by Adsorptive Stripping Voltammetry. *Sensors* 17:1711

45. Vasanthi Sridharan N, Mandal BK (2022) Simultaneous Quantitation of Lead and Cadmium on an EDTA-Reduced Graphene Oxide-Modified Glassy Carbon Electrode. *ACS Omega* 7:45469–45480

46. Sapari S, Razak NHA, Hasbullah SA, Heng LY, Chong KF, Tan LL (2020) A regenerable screen-printed voltammetric Hg(II) ion sensor based on tris-thiourea organic chelating ligand grafted graphene nanomaterial. *J Electroanal Chem* 878:114670

47. Wei P, Zhu Z, Song R, Li Z, Chen C (2019) An ion-imprinted sensor based on chitosan-graphene oxide composite polymer modified glassy carbon electrode for environmental sensing application. *Electrochim Acta* 317:93–101

48. Raril C, Manjunatha JG (2020) Fabrication of novel polymer-modified graphene-based electrochemical sensor for the determination of mercury and lead ions in water and biological samples. *J Anal Sci Technol* 11:3

49. Nguyen LD, Doan TCD, Huynh TM, Nguyen VNP, Dinh HH, Dang DMT, Dang CM (2021) An electrochemical sensor based on polyvinyl alcohol/chitosan-thermally reduced graphene composite modified glassy carbon electrode for sensitive voltammetric detection of lead. *Sensors Actuators B Chem* 345:130443

50. Mahadik M, Patil H, Bodkhe G, Ingle N, Sayyad P, Al-Gahaouri T, Shirsat SM, Shirsat M (2020) EDTA Modified PANI/GO Composite Based Detection of Hg (II) Ions. *Front Mater*. <https://doi.org/10.3389/fmats.2020.00081>

51. Shi L, Li Y, Rong X, Wang Y, Ding S (2017) Facile fabrication of a novel 3D graphene framework/Bi nanoparticle film for ultrasensitive electrochemical assays of heavy metal ions. *Anal Chim Acta* 968:21–29

52. Cheng Y, Li H, Fang C, Ai L, Chen J, Su J, Zhang Q, Fu Q (2019) Facile synthesis of reduced graphene oxide/silver nanoparticles composites and their application for detecting heavy metal ions. *J Alloys Compd* 787:683–693

53. El-Desoky HS, Beltagi AM, Ghoneim MM, El-Hadad AI (2022) The first utilization of graphene nano-sheets and synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a synergistic electrodeposition platform for simultaneous voltammetric determination of some toxic heavy metal ions in various real environmental water samples. *Microchem J* 175:106966

54. Nourbakhsh A, Rahimnejad M, Asghary M, Younesi H (2022) Simultaneous electro-determination of trace copper, lead, and cadmium in tap water by using silver nanoparticles and graphene nanoplates as nanocomposite modified graphite electrode. *Microchem J* 175:107137

55. Lee S, Park S-K, Choi E, Piao Y (2016) Voltammetric determination of trace heavy metals using an electrochemically deposited graphene/bismuth nanocomposite film-modified glassy carbon electrode. *J Electroanal Chem* 766:120–127

56. Xuan X, Park JY (2018) A miniaturized and flexible cadmium and lead ion detection sensor based on micro-patterned reduced graphene oxide/carbon nanotube/bismuth composite electrodes. *Sensors Actuators B Chem* 255:1220–1227

57. Pan F, Tong C, Wang Z, Han H, Liu P, Pan D, Zhu R (2021) Nanocomposite based on graphene and intercalated covalent organic frameworks with hydrosulphonyl groups for electrochemical determination of heavy metal ions. *Microchim Acta* 188:295

58. Zhou J, Pan K, Qu G, Ji W, Ning P, Tang H, Xie R (2022) rGO/MWCNTs-COOH 3D hybrid network as a high-performance electrochemical sensing platform of screen-printed carbon electrodes with an ultra-wide detection range of Cd(II) and Pb(II). *Chem Eng J* 449:137853

59. Saqib M, Solomenenko AN, Hazra NK, Aljasar SA, Korotkova EI, Dorozhko E V., Vashisth M, Kar PK (2025) Electrochemical Detection of Heavy Metals Using Graphene-Based Sensors: Advances, Meta-Analysis, Toxicity, and Sustainable Development Challenges. *Biosensors* 15:505

60. Gumpu MB, Veerapandian M, Krishnan UM, Rayappan JBB (2017) Simultaneous electrochemical detection of Cd(II), Pb(II), As(III) and Hg(II) ions using ruthenium(II)-textured graphene oxide nanocomposite. *Talanta* 162:574–582

61. Jeong S-E, Kim S, Han J-H, Pak JJ (2022) Simple laser-induced graphene fiber electrode fabrication for high-performance heavy-metal sensing. *Microchem J* 172:106950

62. Mohanadas D, Rohani R, Abdul Rahman SF, Mahmoudi E, Sulaiman Y (2025) Highly Sensitive Titanium-Based

MXene-Reduced Graphene Oxide Composite for Efficient Electrochemical Detection of Cadmium and Copper Ions in Water. *J Compos Sci* 9:1–18

63. Machhindra LA, Yen YK (2022) A Highly Sensitive Electrochemical Sensor for Cd<sup>2+</sup> Detection Based on Prussian Blue-PEDOT-Loaded Laser-Scribed Graphene-Modified Glassy Carbon Electrode. *Chemosensors*. <https://doi.org/10.3390/chemosensors10060209>

64. Jayaraman N, Palani Y, Jonnalagadda RR, Shanmugam E (2022) Covalently dual functionalized graphene oxide-based multiplex electrochemical sensor for Hg(II) and Cr(VI) detection. *Sensors Actuators B Chem* 367:132165

65. Wang W-J, Lu X-Y, Kong F-Y, Li H-Y, Wang Z-X, Wang W (2022) A reduced graphene oxide supported Au-Bi bimetallic nanoparticles as an enhanced sensing platform for simultaneous voltammetric determination of Pb (II) and Cd (II). *Microchem J* 175:107078

66. Hajzus JR, Shriver-Lake LC, Dean SN, Erickson JS, Zabetakis D, Golden J, Pennachio DJ, Myers-Ward RL, Trammell SA (2022) Modifications of Epitaxial Graphene on SiC for the Electrochemical Detection and Identification of Heavy Metal Salts in Seawater. *Sensors*. <https://doi.org/10.3390/s22145367>

67. Shan Q, Tian J, Ding Q, Wu W (2022) Electrochemical sensor based on metal-free materials composed of graphene and graphene oxide for sensitive detection of cadmium ions in water. *Mater Chem Phys* 284:126064