*Mini Review*

# Application of Carbon Based Material for the Electrochemical Detection of Heavy Metal Ions in Water Environment

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In recent years, the preparation and application of carbon materials and their composites have been widely studied, and remarkable progress has been made in the detection of environmental pollutants, especially in the study of heavy metal analysis methods in water. In this paper, the research status of various kinds of carbon materials used in the detection of heavy metal ions in water is reviewed, and the preparation, performance, mechanism, advantages and disadvantages of the electrochemical detection methods with carbon material-modified electrodes are categorically analysed. The excellent electron transport properties of carbon materials give them a natural advantage in the development of electrochemical test methods for heavy metal ions that are conducive to the online, in situ and real-time detection of heavy metal ions in water. However, research on carbon-modified electrodes is just in its infancy, and there are some problems, such as poor anti-interference ability and selectivity, poor electrode reusability, and less practical research applications. It is necessary to continue the development and preparation of new composite electrodes that are modified with carbon materials to further improve the selectivity and anti-interference ability of electrochemical testing methods, increase the service life of electrodes and research applications in unconventional environments, and expand the application scope of graphene-based composite electrodes.

## 1. INTRODUCTION

The rapid development of modern industry has led to the demand for a large number of metals because they are used in a variety of products, such as batteries, pigments, photographic films, automotive fuels, steel, as well as a variety of explosives and coating materials [1–3]. Although the

industry is necessary, the impact of heavy metals on environmental pollution cannot be ignored because of its potential harm to the stability of the environment and to human safety, which has aroused widespread concern [4–10]. Toxic heavy metal ions, especially $Pb^{2+}$ and $Cd^{2+}$, are widely used in metallurgy, photographic materials and the electronic industry, and it is inevitable that these industrial processes produce a variety of wastewater. The $Pb^{2+}$ and $Cd^{2+}$ heavy metals are usually bioavailable; thus, they are absorbed by microorganisms and gradually accumulate in the food chain. Due to the expansion of organisms from low to high levels and a long metabolic cycle, the heavy metals finally reach a harmful level in species of high-nutrition organisms [11,12]. High concentrations of the $Pb^{2+}$ and $Cd^{2+}$ heavy metals can lead to movement, language and hearing impairment and even directly lead to death. The World Health Organization limits the amount of $Cd^{2+}$ in drinking water standards to no more than 5 μg/L and $Pb^{2+}$ to no more than 10 μg/L. The harm of these metals to human health is obvious, so there is an urgent need for a fast and economic method with high sensitivity and selectivity for the determination of $Pb^{2+}$ and $Cd^{2+}$ in drinking water and the environment [13–17].

Heavy metals are commonly known as high-density metals (more than 4.5 $g/cm^3$), which can pose a threat to the environment and organisms. Some metal elements are necessary for the health of human beings in ultrasmall amounts, but at high levels they are toxic (zinc, copper, manganese, nickel); in contrast, heavy metals do not benefit human health (cadmium, mercury, lead) [18–23]. At uncertain concentrations, heavy metals have many adverse effects on health and lead to various diseases. Heavy metals may come from industrial processes, such as smelting, or from waste decomposition, diet, medicine, etc. Heavy metal pollution is different from many organic pollutants because metals do not decay into harmless compounds over time [24–33]. Due to the large number of industrial uses of heavy metals and their cumulative effects in humans and other organisms, there are an increasing number of analytical methods that can be used to monitor the presence of heavy metals in the environment and in biological matrices, such as blood, sweat and urine. The complex relationship between the levels of metal elements in the body and toxic pathological effects continues to drive the development of better analytical tools with increased sensitivity and selectivity to heavy metals [34–42].

To date, various analytical techniques have been used for heavy metal detection, such as inductively coupled plasma mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), atomic absorption spectroscopy (AAS), and atomic emission spectroscopy (AES) [43–46]. These methods have good sensitivity and accuracy for heavy metal detection. However, they usually need professional operators and the samples require complex, time-consuming pretreatment processes; furthermore, the instruments are expensive and have high maintenance costs [47–49]. Compared with traditional methods, an electrochemical determination has the advantages of a low price, easy integration, simple operation, high selectivity, high sensitivity and convenient use.

For many environmental testing and analysis methods, the traditional laboratory tests are complex and cumbersome; additionally, they require complex instruments and have high operating costs. At the same time, the sample pretreatment process is complex, time-consuming and requires multistep processing, which limits the detection of samples [50–53]. In addition, physical and chemical changes may occur during the sampling process. Electrochemical analysis methods have been widely used in the analysis of environmental pollutants because of their excellent characteristics (high sensitivity, short analysis time, ease of use, ease of transport, low cost of instruments, easy-to-handle samples, etc.). The

advantages of electrical analysis technology, which is usually due to a compact electrochemical analysis system that has almost no moving parts, can be integrated. In addition, due to the small noise associated with microelectrodes, they can also be miniaturized [54–57]. In recent years, the development of electrochemical analysis has been very rapid, and all kinds of new electrochemical analysis methods and technologies have been emerging. This method usually uses the sample to be tested as an integral part of the chemical cell for determination. The classification of electrical analysis methods according to different electrical parameters is shown in Figure 1. Electroanalytical chemistry is based on electrical parameters, such as potential, current, charge and conductance, between an electrode and a measured substance. Electrochemical detection consists of a working electrode, reference electrode, and auxiliary electrode system. According to different measurements, a traditional electrochemical analysis method can be divided into a potential analysis, Coulomb analysis, conductivity analysis, voltammetry method and polarography method [58–61].
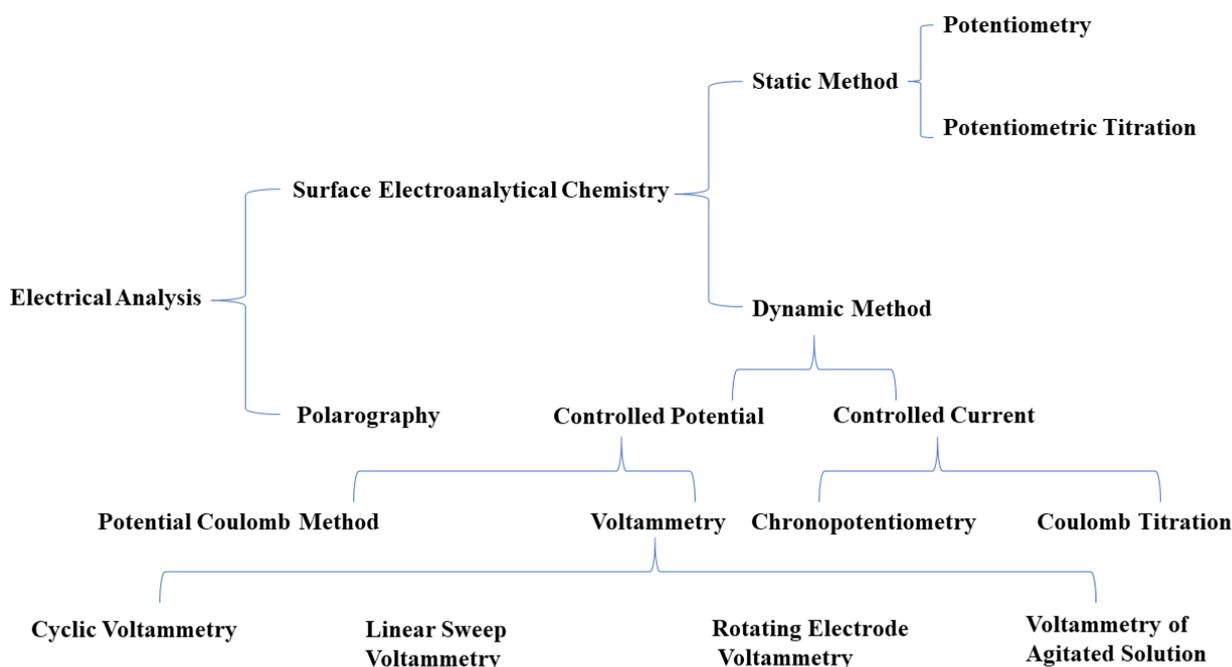
**Figure 1.** Electrical analysis method for heavy metal ions detection.

Electrochemical sensors are designed by modifying the surface of traditional electrodes to construct chemically modified electrodes. Compared with an unmodified electrode, the response of the modified electrode is significantly improved. Therefore, the modifying material on the electrode plays a key role in selectivity and enrichment, which improves the sensitivity and reduces the detection time [62,63]. In the detection step, the modified electrode improves the electron transfer. The modified materials may be metal oxides, metal nanoparticles, carbon materials, conductive polymer films, and

biomolecules. Depending on the natural properties of these materials, the modifier can be adsorbed, covalently bonded, dripped, or even dispersed into a conductive matrix on the electrode surface.

Nanomaterials are usually solid materials composed of very fine particles with a size between 1-100 nm. Compared with bulk materials, nanomaterials have the advantages of a large specific surface area, more active sites on the surface, and a high ability for heavy metal enrichment. A 0.03 ppb thallium ion can be detected with a bismuth nanoparticle-modified membrane electrode [64]. Hu et al. [65] realized a simultaneous electrochemical determination of $Pb^{2+}$ and $Cd^{2+}$ at the ppb concentration level with anthraquinone/clay nanocomposites. Dai et al. [66] realized highly sensitive $Pb^{2+}$ detection, which was induced by iodine ions with a $Fe_3O_4$ nanoparticle-modified electrode and reduced the detection limit to 0.04 nm. The conductivity of the nanomaterials mentioned above is not ideal, and they need to be evenly loaded on the electrode surface to meet the requirements of the electrode conductivity test, so more efficient preparation technology of the electrode materials is highly required. In recent years, carbon nanomaterials have been widely studied in the field of heavy metal electroanalytical chemistry. Luo et al. [67] found that CNTs can effectively improve the electrochemical response signal of bismuth film electrodes to $Cd^{2+}$. CNT-based composite materials can effectively improve the adsorption and analysis performance of heavy metals.

Carbon nanomaterials, including fullerenes, CNTs and graphene, are indispensable materials in nanoscience and technology (Figure 2). In 1985, British spectrologist Kroto [68] and others discovered fullerene, while in 1991, Iijima [69] observed CNTs with electron microscopy. In 2004, the Geim [70] group successfully stripped graphene by a physical mechanical method, which enriched the carbon nanomaterial family. Graphene has a single honeycomb-like two-dimensional structure composed of carbon atoms. Because it is only one atom thick, it can be regarded as a basic building block to form other graphite-related structural carbon materials of various dimensions. Graphene can not only warp to form zero-dimensional fullerene but also curl to form one-dimensional CNTs. Due to the excellent electrical, thermal and mechanical properties of graphene and the unique physical and chemical properties of large carbon nanomaterials, researchers at home and abroad have conducted extensive and in-depth research. The above research has led to many achievements in energy conversion, energy storage, catalysis, carbon fibre, sensing and other applications.
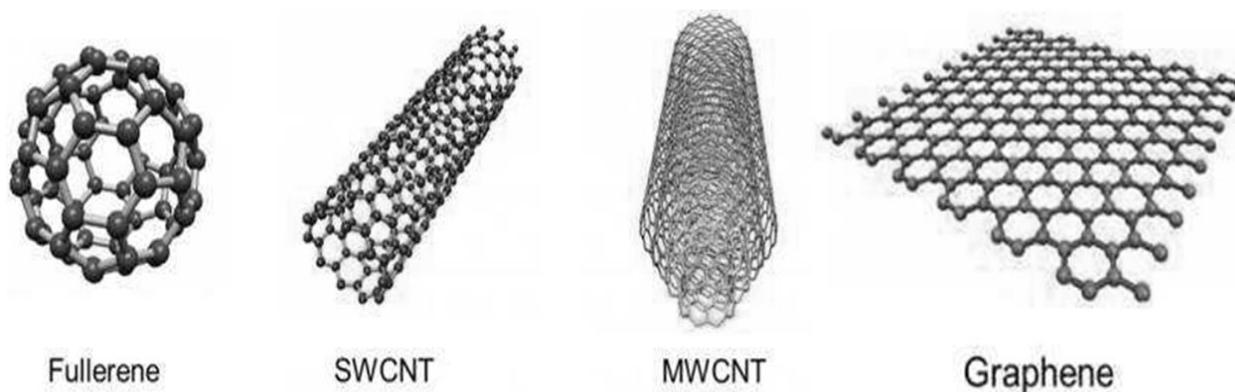


Fullerene          SWCNT          MWCNT          Graphene

**Figure 2.** Structure of carbon nanomaterials.

## 2. FULLERENE BASED ELECTROCHEMICAL SENSOR FOR HEAVY METAL IONS DETECTION

Fullerene C60 is a 32-faceted body composed of 12 five-membered rings and 20 six-membered rings. Its diameter is approximately 0.7 nm. As soon as C60 was discovered, chemists began to explore the possibility of its application in catalysis. At present, fullerenes and their derivatives are mainly used as catalysts in the field of catalytic materials. Because fullerenes are electron deficient and electrophilic, they can stabilize free radicals through adsorption on the fullerene surface. Hirschon et al. [71,72] studied the activity and selectivity of fullerenes in the cracking of methane to produce high carbon hydrocarbons and hydrogen. They found that compared with activated carbon and carbon black, soot containing 12% C60 in a toluene extraction had a higher methane conversion and selectivity for low-carbon olefins and a lower reaction temperature than that of other carbon materials.

C60 itself is a solid molecule with a large $\pi$ bond. Its HOMO orbital can reversibly accept six electrons [73]. Since the discovery of fullerenes, the redox behaviour and electrochemical properties of fullerenes have attracted the interest of scientists. In 1992, six reversible reduction peaks of C60 were obtained in a toluene solution containing 15-20% acetonitrile at - 10 °C with TBAPF6 as the supporting electrolyte [74]. The above results confirmed that C60 had the three lowest unoccupied orbitals and could accept six electrons. Thus, it is a weak oxidant. Winkler et al. [75] produced redox active thin films by electrochemical reduction in solutions containing palladium acetate and C60 or C60 derivatives (including p-diazo-hexyl-ring derivatives, pyrrolidine derivatives and pyrrole salts). The results showed that due to the partial reduction of C60, it had electrochemical activity in the negative voltage region. In addition, C60 has a cage-like $\pi$-electronic structure. Like paraffin, it will be electrophilically attacked by electron-releasing molecules such as amines, proteins and enzymes. Therefore, C60 can be used for the establishment of sensors. However, fullerene has not been used for electrochemical heavy metal-ion sensing so far. Interestingly, fullerene has shown some advantages when used for fluorescence detection. For example, Kumar et al. [76] reported copper-ion fluorescence detection using a fullerene-ferrocene-based donor-bridge-acceptor dyad.

## 3. CARBON NANOTUBE BASED ELECTROCHEMICAL SENSOR FOR HEAVY METAL IONS DETECTION

CNTs can be regarded as hollow structures formed by the curling of graphite sheets, and the ends are sealed by pentagons and hexagons. As an ion concentrator and excellent sensing platform, carbon nanotubes have a more effective detection area and faster electron transfer rate than ordinary carbon materials because of their unique tubular structure [77]. However, a carbon nanotube-modified electrode will produce a large background current when detecting trace amounts of heavy metal ions, which will affect the detection signal. In this case, a carbon nanotube can be used to reduce the signal-to-noise ratio and improve the response signal by an acidification and oxidation treatment, an organic molecular modification, a polymer modification or a metal material modification.

Choi et al. [78] used unmodified carbon nanotubes and acidified carbon nanotube-modified electrodes to measure copper ions in deionized water, tap water and river water by square-wave anodic stripping voltammetry. They found that different aqueous solutions did not affect the selectivity of copper detection. The acidified CNT-modified electrode had a lower detection limit and wider linear range than the unmodified CNT electrode. They believed that this was due to the exfoliation of the carbon nanotube bundle and the improvement of the interfacial viscosity during the oxidation process. Li et al. [79] acidified carbon nanotubes and then mixed them with nitrogen in a mercaptanization method to place N, S and other elements on their surface, which helped to enrich heavy metals and improved the detection limit towards heavy metals.

In addition, organic molecules with heavy metal adsorption groups can be used to modify carbon nanotubes, which can not only ensure a fast electron transfer rate but also capture as many heavy metal ions as possible to improve the detection effect. Liang et al. [80] used a MWCNT-modified GC electrode that was further modified by inositol hexaphosphate to detect copper(II) in trace water by a differential pulse ASV method. Inositol hexaphosphate could not only interact with oxidized MWCNTs but also be fixed on the ITO surface. A large number of MWCNTs were dispersed on the ITO surface to form a three-dimensional network. Inositol hexaphosphate has six phosphate radicals that can capture metal ions, and the compound formed by inositol hexaphosphate and copper ions was the most stable. Other ions demonstrated little interference with copper ions, so the modified electrode could selectively detect copper ions. Wang et al. [81] used MWCNTs (TCA-MWCNTs) modified by heterothiocalixarene to detect $Pb^{2+}$. The electrode combined the selective recognition characteristics of heterothiocalixarenes with the excellent conductivity and large active area of CNTs, thus greatly improving the sensitivity and specificity during analytical determination.

Afkhami et al. [82] used MWCNTs and prepared Schiff base-modified carbon paste electrodes to detect mercury and lead ions in different bodies of water, with detection limits of $9.0 \times 10^{-4}$ and $6.0 \times 10^{-4}$ μM, respectively. Pan et al. [83] used GC electrodes modified with hydroxyapatite (HAP) and CNTs to detect cadmium(II), and the performance of GCE, HAP and CNT were compared. The sensitivity of the HAP CNT-modified GC electrode to $Cd^{2+}$ was significantly enhanced. Hasan et al. [84] used carbon paste electrodes modified with triphenylphosphine, and multiwalled carbon nanotubes to detect multiple ions at the same time, and the electrode had excellent performance and could be reused.

Polymer-dispersed CNTs are also a common method to reduce background current and improve detection performance. Perfluorinated sulfonic acid, polyaniline and chitosan polymers can not only inhibit the aggregation of carbon nanotubes but also contain groups that can coordinate and adsorb heavy metals on the polymer surface, enhance the dissolution signal, improve the sensitivity and reduce the detection limit. A PAMAM CNT composite prepared by Hayati et al. [85] had a good adsorption effect on nickel, arsenic, zinc and cobalt ions in solution. Nguyen et al. [86] used 1,8 naphthalene amine- and multiwalled carbon nanotube-modified electrodes to detect mercury ions and achieved good detection results. Anandhakumar et al. [87] used a CNT and Nafion-modified GC electrode to detect lead(II) in water, and the detection limit reached 1 nM.

Bismuth and mercury have the ability to form alloys with many heavy metals, which helps to distinguish adjacent peaks and enhance the dissolution signal. However, the toxicity of mercury limits its application in heavy metal detection. Bismuth with low toxicity is widely used in heavy metal

analysis. Mandil et al. [88] prepared MWCNT Bi film-modified screen-printed electrodes for the determination of Pb(II), Cd(II) and Zn(II) ions in water; under optimal test conditions, the lowest detection limits of the three ions were 0.7 nM, 1.5 nM and 11.1 nM, respectively. Cerovac et al. [89] used a BiOCl/MWCNT-GCE to detect lead and cadmium ions in water samples, and in a HAc/NaAc buffer solution at pH 4, the detection limits were 1.9 pg/L and 4.0 μg/L, respectively. Ouyang et al. [90] reported zinc and cadmium ion detection limits that were lower than 2 ppb, and the detection limit of lead ions reached 0.12 ng/L.

Table 1 summarizes recently developed carbon nanotube-based electrochemical sensors for heavy metal-ion determination.

**Table 1.** Recently developed carbon nanotube-based electrochemical sensors for heavy metal-ion determination.

| Materials | Method | Target | Reference |
|---|---|---|---|
| MWCNT-peptide | CV | $Cd^{2+}$, $Hg^{2+}$ | [91] |
| MWCNT-PPh3-IL | SWASV | $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$ | [84] |
| MWCNT-Pt-Fe(III) | ASLSV | $As^{3+}$ | [92] |
| SWCNT-PhSH-Au | SWASV | $Hg^{2+}$ | [93] |
| MWCNT-Au | DPV | $As^{3+}$ | [94] |
| SPCNT-Au | SWASV | $Hg^{2+}$ | [95] |
| CNTs-Bi | SWASV | $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$ | [78] |
| MWCNT-Chit-SH | SWASV | $Hg^{2+}$ | [96] |
| CNTs | OSWSV | $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cu^{2+}$ | [97] |
| Cu-IIP-CNT-MCPE | DPASV | $Cu^{2+}$ | [98] |
| $Zn_3(PO_4)_2$-MWCNTs-DNA | EIS | $Hg^{2+}$ | [99] |
| MWCNTs-Schiff base | SWASV | $Pb^{2+}$, $Hg^{2+}$ | [100] |
| L-MWCNTs-CPE(IL) | DPASV | $Cd^{2+}$ | [101] |
| MWCNTs-NA-Bi-SPE Pb | DPASV | $Pb^{2+}$, $Zn^{2+}$, $Cd^{2+}$ | [102] |

## 4. GRAPHENE BASED ELECTROCHEMICAL SENSOR FOR HEAVY METAL IONS DETECTION

The reason why graphene has good conductivity is that in a single-layer graphene structure, each carbon atom can give an unbound electron. These unbound electrons move back and forth in the plane of graphene, and the electron conduction rate in graphene is $8 \times 105$ m/S faster than that in general semiconductors. At the same time, graphene, as a kind of $sp^2$ hybrid carbonaceous material, has good superconductivity. In this section, the research progress of graphene and its composites in the detection of heavy metal ions in recent years is reviewed in detail. We discuss the influence of different types of composite materials on the detection ability of several important heavy metal ions, and reveal the application potential of graphene-based composite materials for heavy metal detection and the current research direction of heavy metal detection.

In recent years, graphene has been widely studied for applications in the field. It has been used in a solid-phase extraction of heavy metal ions in water and has also been combined with atomic absorption and other analytical methods to detect trace or ultratrace heavy metals in water. Deng et al.

[103] and Long et al. [104] used GO solid phase extraction atomic fluorescence spectrometry and GO solid phase extraction plasma emission spectrometry to detect $Cd^{2+}$ and $Pb^{2+}$ in water. The detection limits of $Cd^{2+}$ and $Pb^{2+}$ with GO-AFS were 0.002 ng/mL and 0.01 ng/mL, respectively. The detection limits of $Cd^{2+}$ and $Pb^{2+}$ with GO-ICP-OES were 0.15 ng/mL and 0.6 ng/mL, respectively. Shimirani et al. [105] prepared magnetic graphene composites for the preconcentration of cadmium ions and developed a magnetic solid phase extraction coupled with flame atomic absorption spectrometry for the determination of trace Cd in water and vegetables. The detection limit of this method was 0.32 ng/mL, and the detection range was 1.1 ~ 150 ng/mL. The recovery of the sample was 93.1% - 102.3%. The above method has a wider detection range than other preconcentration methods, and it is simple, sensitive, and suitable for water environments; furthermore, it may help in the development of more electrochemical analysis methods.

Most heavy metal analyses are based on Bi-based graphene composite electrodes. Sahoo et al. [106] synthesized the active material of an RGO/Bi nanocomposite electrode in situ, which solved the problem in which a Bi-film electrode could not detect Cu2+. The above electrode was used to detect $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ in water, and the detection limits were 2.8 ng/mL, 0.55 ng/mL, 17 ng/mL and 26 ng/mL, respectively. Zhu et al. [107] modified a Bi-film electrode with nanogold and simultaneously detected $Cd^{2+}$ and $Pb^{2+}$ by SWASV. The detection limits were 0.1 ng/mL and 0.05 ng/mL, respectively, and the linear range was 0.5-40 ng/mL. Gao et al. [108] prepared an AlOOH-reduced GO material by a one-step hydrothermal method for the first time. This material combined AlOOH with the advantages of heavy metal enrichment and graphene electron transfer and had excellent electrochemical performance. In addition, AlOOH nanoflakes attached to graphene sheets could effectively prevent graphene accumulation and further improved the reaction activity. A drop coating of AlOOH nanoflakes on a glassy carbon electrode was used to detect $Cd^{2+}$ in water. The detection limit was $4.46 \times 10^{-11}$ M, and the detection range was 0.1-0.8 μM. The recovery with a standard addition was 96.3% - 102.2%, but this method demonstrated serious interference from humic acid in water.

Table 2 summarizes the recently developed graphene-based electrochemical sensors for heavy metal-ion determination.

**Table 2.** Recently developed graphene-based electrochemical sensors for heavy metal-ion determination.

| Materials | Method | Target | Reference |
|---|---|---|---|
| GO-Hg | SWASV | $Pb^{2+}$ | [109] |
| RGO-Bi | SWASV | $Cd^{2+}$ | [110] |
| RGO-Bi | DPASV | $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cu^{2+}$ | [111] |
| GR-Au | OSWSV | $Cu^{2+}$, $Pb^{2+}$ | [112] |
| RGO-Fe$_3$O$_4$ | CV | $Cr^{3++}$ | [113] |
| GR-Au | SWASV | $Hg^{2+}$ | [114] |
| GO-Cysteamine | ASV | $Hg^{2+}$ | [115] |
| SPGO-Au | SWASV | $Hg^{2+}$ | [116] |
| RGO-PbO | SWASV | $As^{3+}$ | [102] |
| GR-Nafion-PANI | SWASV | $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$ | [117] |
| L-cystine-GR-CS | DPASV | $Cd^{2+}$, $Pb^{2+}$ | [118] |
| Nitrogen-GR | DPASV | $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$ | [119] |
| L-cystine-Rgo | DPASV | $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$ | [120] |
| GR-BiF-Nafion-IL | SWASV | $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$ | [121] |

## 5. CONCLUSION

Because of its ultrahigh conductivity and extremely stable chemical properties, carbon materials combined with other detection technologies not only optimize detection means but also improve detection sensitivity. Carbon-modified electrodes show great application prospects, especially in electrochemical testing technology, which has obvious advantages in real-time, online and in situ analyses. Therefore, the continued development and preparation of new composite electrodes modified by carbon materials will become the research focus of scholars to improve the selectivity and anti-interference ability of electrochemical testing methods, increase the service life of electrodes and research application in unconventional environments, and expand the application scope of carbon-based composite electrodes.

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