Microchimica Acta (2019) 186: 171
https://doi.org/10.1007/s00604-019-3248-5

REVIEW ARTICLE

Graphene-derived nanomaterials as recognition elements for electrochemical determination of heavy metal ions: a review

Yinxiu Zuo[1,2] · Jingkun Xu[1,3] · Xiaofei Zhu[1] · Xuemin Duan[1] · Limin Lu[2] · Yongfang Yu[2]

Received: 1 November 2018 / Accepted: 5 January 2019 / Published online: 12 February 2019

Abstract

This review (with 155 refs.) summarizes the progress made in the past few years in the field of electrochemical sensors based on graphene-derived materials for the determination of heavy metal ions. Following an introduction of this field and a discussion of the various kinds of modified graphenes including graphene oxide and reduced graphene oxide, the review covers graphene based electrodes modified (or doped) with (a) heteroatoms, (b) metal nanoparticles, (c) metal oxides, (d) small organic molecules, (e) polymers, and (f) ternary nanocomposites. Tables are provided that afford an overview of representative methods and materials for fabricating electrochemical sensors. Furthermore, sensing mechanisms are discussed. A concluding section presents new perspectives, opportunities and current challenges.

Keywords Electrochemical sensor · Metal · Metal oxide · Polymer · Cadmium · Lead · Mercury · Graphene oxide · Reduced graphene oxide

Introduction

Heavy metal ions (e.g. those of Cd, Pb, and Hg), and semimetals (e.g. As) are highly toxic and may cause serious damage to health. Owing to growing concerns in this area, many international and national organizations have defined maximum contaminant levels for drinking water. For example, the maximum permissible levels set by the World Health Organization (WHO) for Cd and Pb are 0.003 and 0.010 mg L^{-1}, respectively [1]. Electrochemical sensors are very promising for heavy metal monitoring, as they offer desirable characteristics such as sensitivity, selectivity, inexpensiveness, robustness, and field-deployability [2].

Graphene and its derivatives, including graphene oxide (GO), reduced graphene oxide (rGO), and three-dimensional (3D) graphene, are widely used in electrochemistry [3]. Graphene consists of a one-atom-thick planar sheet comprising a closely packed honeycomb carbon lattice. By definition, graphene contains only sp^2 carbons without oxygen (or nitrogen). Pristine graphene has a high electron transfer rate, a large surface area (2630 m^2 g^{-1}) [4], and a high conductivity (64 mS cm^{-1}) [5, 6]. Although some studies [7, 8] claim that pristine graphene was used, in fact they used graphite, GO or rGO. GO, a monolayer of graphite oxide, contains many defects and numerous oxygen functional groups, mostly in the form of hydroxyl and epoxy groups on the basal plane, with smaller amounts of carboxyl, carbonyl, phenol, lactone, and quinone groups at the sheet edges [9]. Compared with pristine graphene, the polar oxygen functional groups provide GO with good dispersibility in many polar solvents, particularly in water (concentration < 1 mg mL^{-1}). In addition, the oxygen functional groups serve as sites for immobilizing various electroactive species via covalent or noncovalent bonds. However, the large amount of oxygen functional groups in GO causes some loss of electrical conductivity, which may

✉ Xuemin Duan
duanxuemin@126.com

✉ Limin Lu
lulimin816@hotmail.com

[1] Jiangxi Provincial Key Laboratory of Drug Design and Evaluation, School of Pharmacy, Jiangxi Science and Technology Normal University, Nanchang 330013, Jiangxi, China

[2] Key Laboratory of Crop Physiology, Ecology and Genetic Breeding, Ministry of Education, Institute of Functional Materials and Agricultural Applied Chemistry, College of Science, Jiangxi Agricultural University, Nanchang, Nanchang 330045, China

[3] School of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China

limit the direct application of GO in electrically active materials and devices [9].

Reduced graphene oxide (rGO) is obtained by the chemical/electrochemical reduction of GO. The charge transportation ability of rGO is enhanced compared with that of GO owing to the removal of some oxygen-containing functional groups and partial remediation of the sp^2 conducting structure. Moreover, the chemical and electrical properties of rGO are tunable and the content of oxygen functional groups and defects is sufficient for facilitating analyte adsorption [10]. Although rGO and its composites have been widely employed as sensing materials [11], the dispersion ability remains challenging.

In addition to these two-dimensional (2D) nano-carbon materials, 3D graphene has received considerable interest owing to its outstanding properties, such as an interconnected porous structure, an enormous specific surface area, good mechanical stability, and flexibility to tailorable surface chemistry [12]. Based on these advantages, 3D-graphene-based sensors have been exploited for the electrochemical sensing of heavy metal ions. However, 3D graphene shows an inferior sensing ability for heavy metal ions [13] owing to the restricted diffusion of aqueous analytes in the hydrophobic 3D connected framework [12]. To improve the sensing ability, various active species have been introduced on the 3D framework of graphene [12]. An excellent review related to 3D-graphene-based electrochemical sensors has been published by Baig et al. [14]. A summary of the merits and disadvantages of graphene, GO, rGO, and 3D graphene are listed in Table 1.

In general, the direct use of pristine graphene or graphene derivatives for electrochemical sensing suffers from low sensitivity, interference from other substrates, and easy agglomeration. Therefore, sensors based on graphene-derived nanomaterials have been widely investigated [15, 16]. Although Gan et al. has addressed the preparation of sensors based on various 2D nanomaterials and their sensing properties for heavy metal ions [17], a systematic investigation of the mechanisms by which graphene-derived nanomaterials achieve improved detection of heavy metal ions is still needed. Our review is organized according to the type of sensing elements, which are classified as heteroatom-doped graphene, metal-modified graphene, metal oxide-modified graphene, organically modified graphene, polymer-modified graphene, and ternary graphene-based nanocomposites. Corresponding hybrid materials are also introduced.

Sensors using heteroatom-doped graphene and GO

Heteroatom (N, S, F, etc.) doped graphene can exhibit various new or improved electromagnetic, physicochemical, optical, and structural properties [18]. For example, Xing et al. synthesized N-doped graphene via a one-step electrochemical strategy. The incorporation of pyridine-like N and pyrrole-like N in graphene was found to greatly enhance the performance for electrochemical determination of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} compared with rGO. The detection limit were estimated to be 0.05 μM for Cd^{2+} and Hg^{2+}, and 0.005 μM for Pb^{2+} and Cu^{2+}. [19]. Liu et al. reported a nanocarbon paste electrode modified with N-doped graphene for trace Pb and Cd determination using square wave anodic stripping voltammetry. The presence of N atoms in graphene increased the number of catalytically active sites and enhanced the electron transfer ability of the modified electrode [20]. In the presence of dibenzyl disulfide and a silica template, Manna et al. synthesized S-doped porous rGO by thermal annealing, and the material was used for efficient removal and electrochemical determination of Hg^{2+}. As shown in Fig. 1, the presence of a large amount of thiophenic S and the porous structure provided a detection limit as low as 0.5 nM [21]. Antony et al. reported fluorinated GO for the simultaneous detection of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} using square wave anodic stripping voltammetry. The incorporation of F into GO improved the sensitivity owing to the interactions between electron-donating F and electron-deficient heavy metal ions [22].

Table 1 Summary of the merits and disadvantages of graphene, GO, rGO and 3D graphene for heavy metal ion sensing

Type of carbon material	Merits	Disadvantages
graphene	high electron transfer rate; large surface area; high conductivity	easy agglomeration; inferior solvent dispersion ability
GO	good dispersibility in many polar solvents; large surface area; many oxygen functional groups	poor conductivity
rGO	easy preparation method; large surface area; conductivity approximately 4-fold greater than that of GO	inferior solvent dispersion ability
3D graphene	interconnected porous structure; enormous specific surface area; good mechanical stability	hydrophobic 3D framework

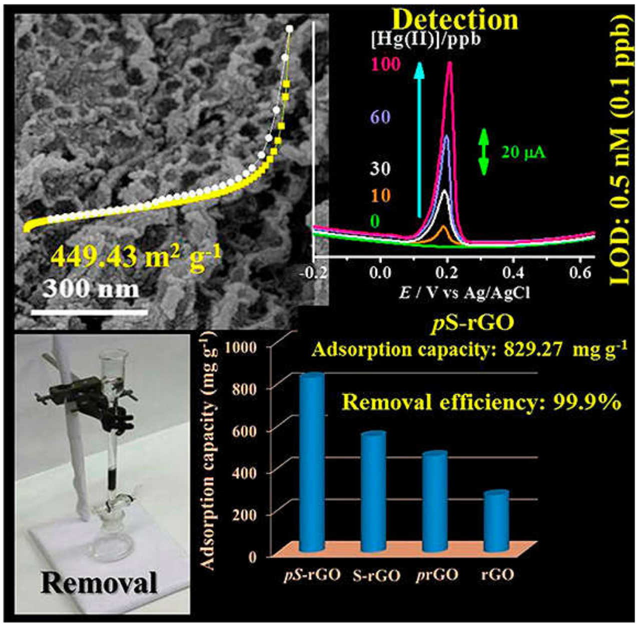

Fig. 1 The morphology of S-doped porous rGO and application in Hg^{2+} electrochemical sensing and removing. Reproduced from [21] with permission of ACS

Sensors using metal-modified graphene

Graphene modified with noble metal nanoparticles (NPs) has been used for heavy metal ions sensing because noble metal NPs exhibit high catalytic activity via the size effect. Moreover, graphene can transfer electrons acquired from catalytic process of the metal NPs to electrodes, which may accelerate the catalytic process [23]. Among NPs that form nanocomposite with graphene, Au NPs are the most widely applied for the detection of metal ions because they offer the advantages of high chemical stability and easy preparation processes [15]. For example, Au NPs decorated graphene synthesized via electrodeposition method was used for sensitive determination of Hg^{2+}. Compared with their bulk electrode counterpart, Au NP modified electrodes are promising because they can eliminate the memory effect and increase the sensitivity for heavy metal ion detection [15]. The detection limit for Hg^{2+} was estimated to be 0.03 pM, which is well below the guideline value set by the WHO [24]. In addition to Hg^{2+} electroanalysis, Au NPs/rGO nanocomposites have also been widely used for the analysis of As^{3+}. For instance, Liu et al. utilized an Au NPs-electroreduced graphene oxide (ERGO) composite film for the determination of As^{3+}. The obtained good sensitivity (limit of detection = 2.7 nM) was attributed to the formation of Au–As intermetallic compounds that enhance the efficiency for cathodic preconcentration of As(0) [25]. Moreover, the effect of the supporting electrolyte (0.20 M aqueous $HClO_4$, 0.20 M aqueous HCl, or 0.10 M aqueous H_2SO_4) on the magnitude of the detected signal was also evaluated. The detection performance in 0.20 M aqueous HCl was better than that in the other two supporting electrolytes, which was attributed to improved electron kinetics resulting from the complexation of Cl^- ions with As^{3+}. However, the detection of inorganic As in highly acidic media could cause problems such as hydrogen evolution or undesirable corrosion reactions [26].

In addition to Au NPs, graphene decorated with Ag NPs has also been used in heavy metal ion sensing. For example, Sang et al. synthesized Ag NPs/rGO via an in situ method. A nanocomposite-modified glassy carbon electrode was used for simultaneous electrochemical sensing of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, and this modified electrode showed excellent selectivity [27]. However, expensive materials like Au and Ag are of limited practicality when fabricating macroelectrodes, which require large amount of material, owing to cost considerations [28].

Alternatives like Bi NPs or Sn NPs have also been used in heavy metal ion sensing. For example, Sahoo et al. prepared Bi NPs modified rGO sheets via an in situ method [29]. Lee et al. decorated rGO with Sn NPs via an electrodeposition method and realized electrochemical sensing of Cd^{2+}, Pb^{2+} and Cu^{2+} using square wave anodic stripping voltammetry [30]. Sn has similar electroanalytical properties to Bi, but it is less toxic and cheaper [31].

Apart from metal NPs, metal films have also been hybridized with graphene to construct sensors for heavy metal determination. For example, Ping et al. fabricated an electrochemical sensing platform based on a screen-printed electrode modified with an electrochemically rGO. After in situ plating with a Bi film, the electrode was used for the simultaneous determination of Cd^{2+} and Pb^{2+} [32]. The mechanism of Cd^{2+} and Pb^{2+} detection at the surface of Bi based electrode involves the capacity of Bi to form a "fused alloy" with heavy metal ions [33]. Compared with a previously widely used Hg film, Bi is less toxic to the environment and has excellent mechanical stability [33]. Unfortunately, compared with the Hg-modified electrode, the Bi-modified electrode has various limitations, such as a narrow potential window (below the oxidation potential of Bi) and easy oxidation upon contact with air [34].

Sb film electrodes exhibiting similar electroanalytical performance to the Bi film electrodes have also been applied to heavy metal sensing. For example, Ruengpirasiri et al. used GO-Sb film-modified electrode for the simultaneous determination of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} [35]. In situ preparation of Sb films can be conducted in a wider pH range than Bi films because bismuth hydroxide will form at pH 4, which results in irreproducible measurements [36, 37]. Thus, Sb film electrodes are a valuable and complementary alternative to Bi film electrodes for measurement under an oxidative potential or in acidic media (e.g. determination of Cu^{2+} and Hg^{2+}). However, the toxicity of Sb metal ions, especially Sb^{3+}, cannot be ignored completely [36]. The overview on metal-modified graphene as sensing material for electrochemical sensing of heavy metal ions was displayed in Table 2.

Sensors using metal-oxide-modified graphene

As an alternative to metal NPs and metal films, metal oxides have frequently been used in heavy metal ion sensing owing to their large surface areas and high electrocatalytic activities. The sensing mechanism of metal oxide for heavy metal ion is strong adsorption ability, or electrocatalytic activity, or both simultaneously [28, 55–57]. However, most metal oxides have inferior conductivities and stabilities, which are unfavorable for electron transfer during the detection process and decrease the long-term stability of the electrode. However,

Table 2 Overview on metal-modified graphene as sensing material for electrochemical sensing of heavy metal ions

Electrode	Sensing ions	Linear range	LOD	Ref.
Au NPs/graphene/GCE	Hg^{2+}	0.12-29.9 pM	0.03 pM	[24]
Au NPs/graphene/GCE	Hg^{2+}	1-150 nM	0.6 nM	[38]
Au NPs/rGO/CPE	Hg^{2+}	4.99–31.92 nM	1.25 nM	[39]
Au NPs/rGO/GCE	As^{3+}	0.01-5 μM	2.7 nM	[25]
Au NPs/rGO/CPE	As^{3+}	13.35-266.95 nM	1.74 nM	[40]
Au NPs/rGO/GCE	As^{3+}	4-26.69 pM	1.33 pM	[41]
Au NPs/graphene/GCE	Pb^{2+}	10-150 nM	0.8 nM	[42]
Au NPs/graphene/GCE	Cu^{2+}	5-100 nM	0.028 nM	[43]
Au NPs/rGO/Au electrode	Cu^{2+}	0.02-1 μM	8 nM	[44]
Au NPs/rGO/GCE	Cd^{2+}	1-12 μM	31.81 nM	[45]
	Pb^{2+}		12.69 nM	
	Cu^{2+}		27.42 nM	
	Hg^{2+}		20.7 nM	
dendritic Au/GO/GCE	Fe^{3+}	0.007-1 μM	1.5 nM	[46]
Au NPs/rGO/GCE	Fe^{3+}	0.03-3 μM	3.5 nM	[47]
Au NPs/rGO/GCE	Fe^{3+}	0.03-3 μM	3.5 nM	[47]
Au NPs/rGO/GCE	CH_3Hg^+	13.92-111.32 nM	0.56 nM	[48]
Ag NPs/rGO/GCE	Cd^{2+}	0.05-3.5 μM	0.254 μM	[27]
	Pb^{2+}	0.05-2.5 μM	0.141 μM	
	Cu^{2+}	0.05-3.5 μM	0.178 μM	
	Hg^{2+}	0.5-3 μM	0.285 μM	
Ag NPs/GO/GCE	As^{3+}	13.33-375.19 nM	0.24 nM	[49]
Pt NPs/rGO/GCE	As^{3+}	10-100 nM	1.1 nM	[50]
Bi NPs/rGO/CPE	Zn^{2+}	1.53-6.12 μM	0.26 μM	[29]
	Cd^{2+}	0.18-1.07 μM	0.025 μM	
	Pb^{2+}	0.097-0.58 μM	2.65 nM	
	Cu^{2+}	0.31-1.57 μM	0.41 μM	
Bi nanosheets/GO/GCE	Fe^{3+}	0.01-20 μM	2.3 nM	[51]
Sn NPs/rGO/glassy carbon sheets	Cd^{2+}	10-100 nM	0.63 nM	[30]
	Pb^{2+}		0.6 nM	
	Cu^{2+}		0.52 nM	
Bi film/rGO/SPE	Cd^{2+}	8.9-53.38 nM	4.45 nM	[32]
	Pb^{2+}	4.83-28.96 nM	7.12 nM	
Bi film/graphene/GCE	Zn^{2+}	0.015-1.53 μM	0.028 μM	[52]
	Cd^{2+}	0.0089-0.89 μM	1.6 nM	
	Pb^{2+}	0.00483-0.48 μM	0.53 nM	
Bi film/graphene/GCE	Cd^{2+}	0.062-1.068 μM	4.18 nM	[53]
Bi film/graphene nanosheets/GCE	Cd^{2+}	0.00445-0.89 μM	3.11 nM	[54]
	Pb^{2+}	0.48-480 nM	0.22 nM	
Sb film/GO/SPE	Cd^{2+}	0.3-1.5 μM	0.054 μM	[35]
	Pb^{2+}	0.1-1.3 μM	0.026 μM	
	Cu^{2+}	0.3-1.5 μM	0.06 μM	
	Hg^{2+}	0.1-1.3 μM	0.066 μM	

GCE, glassy carbon electrode; CPE, carbon paste electrode; SPE, screen printed electrode when a metal oxide is combined with graphene, the nanocomposite is expected to provide a new electrochemical platform for heavy metal ion sensing [58]. Up to now, Fe_3O_4, ZnO, MnO_2, Cu_2O, Fe_2O_3, SnO_2, TiO_2, and Co_3O_4-based graphene nanocomposites have been successfully applied to the detection of heavy metal ions in aqueous solution. The morphology and average size of the metal oxide can greatly influence the performance of the modified electrode. As shown in Fig. 2, Sun et al. synthesized rGO decorated with three different shapes of Fe_3O_4 via a one-step in-situ co-precipitation method. The sensitivity for analysis of Pb^{2+} decreased in the following order: band Fe_3O_4/rGO > spherical Fe_3O_4/rGO > rod Fe_3O_4/rGO [59]. Karthik et al. synthesized Co-doped ZnO/rGO as a heavy metal ion sensor for Cd^{2+} and Pb^{2+}. Compared with ZnO/rGO, Co-doped ZnO/rGO exhibited better catalytic activity toward Cd^{2+} and Pb^{2+} sensing with detection limits of 8.36 nM for Cd^{2+} and 4 nM for Pb^{2+} [60].

Compared with monometallic oxides, bimetallic oxides exhibit better electrochemical activity owing to electron hopping between different valence states of metals in oxygen sites [61]. Huang et al. compared the detection performance of $NiCo_2O_4$ with those of Co_3O_4 and NiO. $NiCo_2O_4$ exhibited better performance for electrochemical determination of Pb^{2+} and Cu^{2+} than the other two materials [62]. Based on this concept, Xiong et al. used a 1,6-hexanediamine (HDA)- functionalized $MgFe_2O_4$/rGO composite for the electrochemical determination Cu^{2+}. The amino group in HDA has high activity for coordination with heavy metal ions. The detection limit was estimated to be 0.2 nM with a sensitivity of 0.0172 μA nM^{-1} [63]. The same group investigated polyethyleneimine (PEI) (or ethanediamine (EDA)) functionalized $CoFe_2O_4$/rGO composite for electrochemical detection of ultra-trace Cu^{2+}, and explored the interaction mechanism. Cyclic voltammetry and X-ray photoelectron spectroscopy results indicated that the interaction between the composite and Cu^{2+} involved an adsorption control process [64]. Zhou et al. synthesized GO incorporating mesoporous $MnFe_2O_4$ for the electrochemical determination of Pb^{2+}. The mesoporous structure of $MnFe_2O_4$ increased the specific surface area of GO and enhanced the electrochemical activity toward Pb^{2+} analysis [65]. The overview on metal oxide-modified graphene as sensing material for electrochemical sensing of heavy metal ions was shown in Table 3.

Sensors using organically modified graphene

The modification of graphene with organic molecules is believed to increase the sensitivity and selectivity of graphene-based electrochemical sensors for heavy metal ion through two different recognition mechanisms, namely, chemical affinity and cavity entrapment (or both simultaneously). Various kinds of organic molecule including small organic molecules (containing electron-rich groups such as –OH, –SH, and –NH_2) and caged molecules (calixarenes and cyclodextrins) have been investigated [1]. For instance, Muralikrishna et al. synthesized L-cysteine functioned GO by reacting the carboxyl groups in graphene with the amino group in L-cysteine. This material was used for the simultaneous electrochemical determination of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+}. The oxygen–containing groups of GO and the electron donor group in L-cysteine facilitated the adsorption process of heavy metal ions [81]. Yuan et al. reported high–density 2-amino-5-mercapto-1,3,4-thiodiazole (AMT)–grafted GO prepared via an amidation reaction between GO and AMT under strong basic conditions. The high grafting density was attributed to the high density carboxyl groups on GO. The detection signal during electroanalysis of Cu^{2+} was amplified by the abundant N, O, and S donor atoms of AMT.

To exploit the coordination between heavy metal ions and N atoms in piperazine, our group synthesized piperazine–grafted GO through nucleophilic ring–opening of epoxy groups on GO with the amino groups of piperazine. After chemical reduction by ascorbic acid, the modified glassy carbon electrode was used for the detection of Hg^{2+} with a detection limit of 0.2 nM [82]. Based on the same synthetic mechanism, Zhou et al. reported cysteamine-functionalized GO for the selective determination of Hg^{2+}. In addition to

Fig. 2 Preparation processes of three shapes of Fe_3O_4/rGO by adjusting the mole ratio of Fe^{2+}/Fe^{3+} via in-situ co-precipitation method. Reproduced from [59] with permission of Elsevier

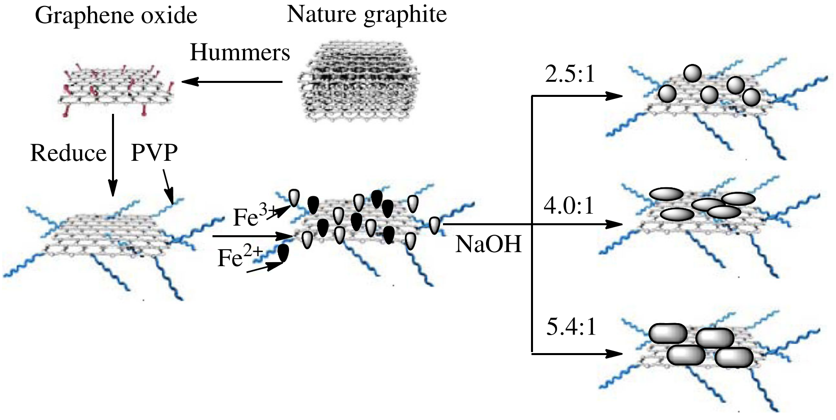

Table 3 Overview on metal oxide-modified graphene as sensing material for electrochemical sensing of heavy metal ions

Electrode	Sensing ions	Linear range	LOD	Ref.
band Fe_3O_4/rGO/GCE	Pb^{2+}	0.4-1.5 μM	0.17 μM	[59]
Fe_3O_4 rose like and spherical/rGO/GCE	Pb^{2+}	0.05-1.5 nM	0.082 nM	[66]
Fe_3O_4/rGO/GCE	Cd^{2+}	0.4-0.8 μM	0.056 μM	[67]
Fe_3O_4/rGO/SPE	As^{3+}	0.027-4 μM	1.33 nM	[68]
Fe_3O_4/rGO/GCE	As^{3+}	0.00013-67.4 nM	0.0016 nM	[69]
Fe_3O_4-rGO/GCE	Cd^{2+}	0.1-1.7 μM	28 nM	[70]
	Pb^{2+}		8 nM	
	Hg^{2+}		17 nM	
Fe_3O_4-rGO/GCE	Cr^{3+}	0.2-2 nM	-	[71]
Fe_2O_3/graphene/Bi/GCE	Zn^{2+}	0.015-1.53 μM	1.68 nM	[72]
	Cd^{2+}	0.0089-0.89 μM	0.71 nM	
	Pb^{2+}	4.83-482.6 nM	0.34 nM	
SnO_2/rGO/GCE	Cd^{2+}	0.3-1.2 μM	0.1015 nM	[73]
	Pb^{2+}		0.1839 nM	
	Cu^{2+}		0.2269 nM	
	Hg^{2+}		0.2789 nM	
TiO_2–graphene/Nafion/GCE	Cd^{2+}	0.6-32 μM	2 nM	[74]
	Pb^{2+}	0.01-32 μM	0.1 nM	
CeO_2/graphene/GCE	Cd^{2+}	0.2-2.5 μM	0.1944 nM	[75]
	Pb^{2+}		0.1057 nM	
	Cu^{2+}		0.1636 nM	
	Hg^{2+}		0.2771 nM	
Co_3O_4/rGO/chitosan/GCE	Pb^{2+}	1-200 nM	0.35 nM	[76]
MnO_2/rGO/GCE	As^{3+}	1.33-667.37 nM	0.67 nM	[77]
ZnO–rGO/SPE	Cd^{2+}	0.089-0.71 μM	1.42 nM	[78]
	Pb^{2+}	0.048-0.39 μM	0.82 nM	
ZnO/rGO/GCE	Pb^{2+}	2.4-480 nM	0.48 nM	[79]
Co-doped ZnO/rGO/GCE	Cd^{2+}	0.089-0.8 μM	8.36 nM	[60]
	Pb^{2+}	0.048-0.43 μM	4 nM	
PbO/rGO/GCE	As^{3+}	-	10 nM	[80]
1,6-hexanediamine functionalized $MgFe_2O_4$/rGO/GCE	Cu^{2+}	2-1000 nM	0.2 nM	[63]
polyethylenimine functionalized $CoFe_2O_4$/rGO/GCE	Cu^{2+}	0.003-0.1 μM	0.02 nM	[64]
$MnFe_2O_4$/GO/GCE	Pb^{2+}	0.2-1.1 μM	0.0883 μM	[65]

GCE, glassy carbon electrode; *SPE*, screen printed electrode

interacting with the Au electrode surface through the formation of Au–S bonds, the residual mercapto groups in cysteamine can selectively interact with Hg^{2+} [83]. Göde et al. functionalized rGO with calixarenes using 1-ethyl-3-(3-dimethylaminoprophy) carbondiimide hydrochloride (EDC) and *N*-hydroxy succinimide (NHS) to activate the carboxylic acid (–COOH) groups on rGO. The nanocomposite was used for simultaneous determination of Fe^{3+}, Cd^{2+}, and Pb^{2+}. As shown in Fig. 3, the 3D basket, cup, or bucket shapes of calixarenes can effectively entrap metal ions and the

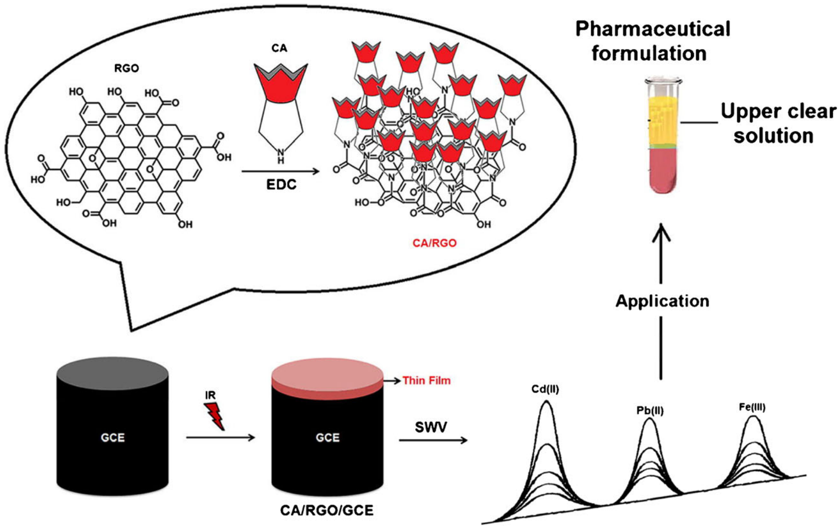

Fig. 3 Preparation of calixarene/rGO/GCE and nano-sensing of the guest metal ions. Reproduced from [84] with permission of Elsevier

Table 4 Overview on organically modified graphene as sensing material for electrochemical sensing of heavy metal ions

Electrode	Sensing ions	Linear range	LOD	Ref.
β-CDs/rGO/GCE	Pb^{2+}	1-100 nM	0.5 nM	[88]
hydroxypropyl-β-CDs/rGO/GCE	Cd^{2+} Pb^{2+}	0.5-9 nM 0.1-9 nM	0.0673 nM 0.092 nM	[89]
β-CDs/NH_2-rGO/GCE	Cu^{2+}	0.03-100 µM	2.8 nM	[90]
N-graphene/chitosan/Au electrode	Pb^{2+}	0.1-100 µM	66.4 nM	[86]
NH_2-graphene/chitosan/GCE	Cu^{2+}	0.4-40 µM	0.064 µM	[91]
thiolated thionine/rGO/Bi film/GCE	Cd^{2+} Pb^{2+}	8.9-355.8 nM 4.83-193.05 nM	0.89 nM 0.24 nM	[92]
7,7,8,8-tetracyanoquinodimethane/graphene/glassy carbon disc electrodes	Cu^{2+}	1-10000000 nM	0.63 nM	[93]
1,2-Bis(N'-benzoylthioureido) benzene/rGO/GCE	Pb^{2+}	0.000063-39 mM	25.1 nM	[94]
κ-carrageenan/L-cysteine/GO/GCE	Cd^{2+} Pb^{2+}	5-50 nM	0.58 nM 1.08 nM	[95]
carboxymethyl cellulose/glutathione/rGO/GCE	Cd^{2+}	2-20 nM	0.05 nM	[96]
N-[(1-pyrenyl-sulfonamido)-heptyl]-gluconamide/rGO/Au electrode	Hg^{2+}	0.1-4 nM	0.1 nM	[85]
IL/graphene/Se-doped CPE	Cu^{2+} Sb^{3+}	2-70 µM 2-40 µM	0.66 µM 0.043 µM	[97]
IL/rGO/Au nanodendrites/GCE	Fe^{3+}	0.3-100 µM	35 nM	[98]
IL/graphene/CPE	Tl^{+} Pb^{2+} Hg^{2+}	1.25-200 nM	0.257 nM 0.45 nM 0.386 nM	[99]
Bi/IL/rGO/SPE	Cd^{2+} Pb^{2+}	8.9-711.67 nM 4.83-386.1 nM	0.71 nM 0.48 nM	[100]
L-cysteine/graphene/GCE	Cd^{2+} Pb^{2+}	4.98-597.8 nM 5.02-299.7 nM	4 nM 0.58 nM	[101]
L-leucine/GO/Nafion/Au electrode	As^{3+}	66.7-667.4 µM	6.67 µM	[102]
sodium dodecyl benzene sulfonate/3D graphene/GCE	Pb^{2+}	0.48-970 nM	0.0145 nM	[103]
4-carboxyphenyl diazonium tetrafluoroborate/rGO/Au electrode	Pb^{2+} Cu^{2+}	0.4-20 nM 1.5-20 nM	0.4 nM 1.5 nM	[104]
trithiocyanuric acid/rGO/Au electrode	As^{3+}	2.67-133.5 nM	0.72 nM	[105]
3,8-diaminobenzo[c]cinnoline/GO/GCE	Cd^{2+} Pb^{2+}	4.45-222.4 nM 2.41-120.66 nM	1.07 nM 1.01 nM	[106]
GOdoped diaminoterthiophene/SPCE	Cd^{2+} Pb^{2+} Cu^{2+} Hg^{2+}	0.0089-22.24 nM 0.0048-12.07 nM 0.016-39.34 nM 0.005-12.46 nM	0.063 nM 0.0092 nM 0.0063 nM 0.0035 nM	[107]
carboimidazole-rGO/GCE	Pb^{2+} Hg^{2+}	5–10000 nM 0.6–9000 nM	3 nM 0.2 nM	[108]
piperazine-rGO/GCE	Hg^{2+}	0.4–12000 nM	0.2 nM	[82]
p-aminophenyl-GO/GCE	Cd^{2+} Cu^{2+}	0.01-0.5 nM	3.3 pM	[109]
2-amino-5-mercapto-1,3,4-thiodiazole-GO/CPE	Cu^{2+}	0.1-1000000 µM	0.04 µM	[110]
rhodamine B hydrazide-GO/Au electrode	Cu^{2+}	0.1-50 nM	0.061 nM	[111]
L-cysteine-GO/GCE	Cd^{2+} Pb^{2+} Cu^{2+} Hg^{2+}	0.4-2 µM 0.4-1.2 µM 0.4-2 µM 0.4-2 µM	3.26 nM 2.01 nM 4.11 nM 5.55 nM	[81]
calixarene-rGO/GCE	Fe^{3+} Cd^{2+} Pb^{2+}	0.1-10 nM	0.02 nM	[84]
cysteamine-GO/Au electrode	Hg^{2+}	5-40 nM	3 nM	[83]

Table 4 (continued)

Electrode	Sensing ions	Linear range	LOD	Ref.
carboxylate-graphene/GCE	UO_2^{2+}	0.05-5 µM	-	[112]
NH_2-GO/Au microelectrode	As^{3+}	13.35-133.47 nM	2.16 nM	[87]
GO/4-aminophenyl/Au electrode	Pb^{2+}	1-30.3 nM	1 nM	[113]
	Cu^{2+}	10-58.8 nM	10 nM	
	Hg^{2+}	10-58.8 nM	5 nM	
alkyl-GO/Au substrate	Cu^{2+}	2-100 µM	2.7 µM	[114]

CD, cyclodextrin; *IL*, ionic liquid; *GCE*, glassy carbon electrode; *CPE*, carbon paste electrode; *SPE*, screen printed electrode; *SPCE*, screen printed carbon electrode

oxygen–containing groups can form complexes with the metal ions, thus increasing the sensitivity and selectivity of the sensor for these metal ions [84].

Yu et al. fabricated *N*-[(1-pyrenyl-sulfonamido)-heptyl]-gluconamide (PG) modified graphene for ultrasensitive and selective sensing of heavy metal ions. Owing to the large π system of pyrene, a stable interaction can occur between the pyrene residue and graphene. Whereas functional groups such as hydroxyls and imines in glucose can act as coordination sites for Hg^{2+} during the detection process [85]. Magerusan et al. used an N–doped graphene/chitosan nanocomposite for selective Pb^{2+} detection. The electron-donating functional groups such as hydroxyls and amines in chitosan and the N doping groups in rGO can easily coordinate electron-deficient heavy metal ions. Moreover, positively charged chitosan can interact with negatively charged rGO to increase the stability of the nanocomposite [86]. Yang et al. constructed an As^{3+} sensor with excellent selectivity using an Au microelectrode decorated with amino-functionalized GO. Benefited from the synergetic effect of the strong adsorption capability of NH_2-GO and the excellent electrocatalytic ability of Au microwire, resulting in a low detection limit of 2.16 nM [87]. The overview on organically modified graphene as sensing material for electrochemical sensing of heavy metal ions were listed in Table 4.

Sensors using polymer modified graphene

Polymers with a high number of reactive sites allows for analyte preconcentration on the electrode surface and are thus expected to increase the sensitivity when used for heavy metal ion sensing. Among the various types of polymers, conducting polymers have received much attention owing to their superior electrical conductivities and anti-fouling capabilities [115]. Moreover, the morphology of the conducting polymers (fiber, wire, film, or particle) and the dopants are related to the detection performance (sensing range, limit of detection, and response/recovery time) of the modified electrode [116, 117]. Conducting polymers including polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) have been widely used in heavy metal determination. For example, in our previous work, we synthesized PEDOT nanorods/GO nanocomposite via interfacial polymerization as a new electrode material for electrochemical detection of Hg^{2+}. The specific doping and de-doping properties of PEDOT could be controlled by varying the deposition potential, providing a selective sensing platform for Hg^{2+} determination. Moreover, in the nanocomposite, the PEDOT nanorods can function as electro-active sites to facilitate electron transfer during the determination process [118]. Dai synthesized PPy/GO nanocomposites via in situ chemical oxidation polymerization, and phytic acid molecules were functionalized with nanocomposites through electrostatic attraction. Owing to the presence of phosphoric acid groups in phytic acid and N-containing groups in PPy, the sensor was utilized for the simultaneous determination of Cd^{2+} and Pb^{2+} with detection limits of 19 and 1.98 nM, respectively [119]. Muralikrishna et al. described PANI/GO hydrogels for highly sensitive electrochemical determination of Pb^{2+}. The hydrogels were synthesized through in situ polymerization of aniline in the presence of GO nanosheets followed by hydrogel formation at an elevated temperature [120].

Besides conducting polymers, other electroactive polymers including Nafion, poly(dimethylsiloxane) (PDMS), polydopamine, poly-L-lysine (PLL), polyallylamine, and polyethyleneimine have also been used in heavy metal ion sensing. For example, Li et al. reported a Nafion–graphene nanocomposite for ultrasensitive determination of Cd^{2+}, with a detection limit of 0.044 nM [121]. The addition of Nafion can increase the mechanical robustness of the electrode and avoid interference from anionic in the sample (NO_3^-, SO_4^{2-}, or CO_3^{2-}). Chałupniak et al. prepared a microfluidic lab-on-a-chip platform for heavy metals preconcentration and electrochemical detection based on a GO-PDMS nanocomposite. The use of GO–PDMS significantly improve the sensitivity for the electrochemical detection of heavy metals with a low detection limit of 0.34 pM [122]. Guo et al. prepared an electrode modified with an GO and chitosan hybrid matrix through drop casting, and a PLL film was coated on the electrode through electropolymerization via a

Table 5 Overview on polymer modified graphene as sensing material for electrochemical sensing of heavy metal ions

Electrode	Sensing ions	Linear range	LOD	Ref.
PEDOT/GO/GCE	Hg^{2+}	0.01-3 μM	2.78 nM	[118]
phytic acid functionalizedPPy/GO/GCE	Cd^{2+} Pb^{2+}	0.044-1.33 μM 0.024-0.72 μM	0.019 μM 1.98 nM	[119]
PPy/rGO/glassy carbon macroelectrodes	Hg^{2+}	5-60 nM	4 pM	[127]
PPy-graphene/β-CDs/SPCE	Hg^{2+}	1-300 nM	0.47 nM	[128]
cysteine-functionalizedGO/PPy/SPCE	Pb^{2+}	0.00676-67.57 nM	0.34 pM	[129]
PANI/graphene/SPCE	Zn^{2+} Cd^{2+} Pb^{2+}	0.015-4.59 μM 0.0089-2.67 μM 4.83 nM-1.45 μM	0.015 μM 0.89 nM 0.48 nM	[130]
graphene/PANI/polystyrene/SPCE	Cd^{2+} Pb^{2+}	0.089-4.45 μM 0.048-2.41 μM	0.039 μM 0.016 μM	[131]
PANI/GO/GCE	Pb^{2+}	0.2-3500 nM	0.04 nM	[120]
poly(1,5-diaminonaphthalene)/rGO/Pt patterned electrodes	Pb^{2+}	0.97-3.38 nM	0.97 nM	[132]
Nafion-graphene/GCE	Cd^{2+}	1.78-133.44 nM	0.044 nM	[121]
Nafion-graphene/Bi film/GCE	Cd^{2+} Pb^{2+}	13.34-266.88 nM 2.41-241.31 nM	0.18 nM 0.097 nM	[133]
Nafion-rGO/silicon (Si) substrates	Cd^{2+} Pb^{2+} Cu^{2+}	50-300 nM	1.69 nM 0.39 nM 2.16 nM	[134]
Nafion/IL/graphene/SPCE	Zn^{2+} Cd^{2+} Pb^{2+}	0.00153-1.53 μM 0.89-889.59 nM 0.48-482.63 nM	1.38 nM 0.53 nM 0.39 nM	[135]
GO–poly(dimethylsiloxane)/SPCE	Pb^{2+}	1.21-377.05 nM	0.34 pM	[122]
cysteine-polydopamine-rGO/GCE	Cd^{2+} Pb^{2+}	3.56-400.32 nM 1.93-217.18 nM	0.89 nM 0.58 nM	[136]
poly-L-lysine/chitosan/rGO	Cd^{2+} Pb^{2+} Cu^{2+}	0.44-88.96 nM 0.24-48.26 nM 0.79-157.37 nM	0.089 nM 0.097 nM 0.31 nM	[123]
polyallylamine/graphene/GCE	Cu^{2+}	0.5-50 μM	0.35 μM	[124]
polyethyleneimine/rGO/GCE	Cu^{2+}	1-70 μM	0.3 μM	[125]
glutaraldehyde–glutaraldehyde/ poly(diallyldimethylammonium chloride)-rGO/GCE	Hg^{2+}	0.03-5 μM	7.7 nM	[137]

GCE, glassy carbon electrode; *SPCE*, screen printed carbon electrode; *IL*, ionic liquid

cyclic voltammetry method. The amino and hydroxyl groups in this system effectively coordinated metal ions. Moreover, the PLL films which had excellent permselectivity, good stability, strong adherence to the electrode surface, and an increased amount of active sites enhanced the electrocatalytic activity of the modified electrode. When used for the simultaneous electrochemical detection of Cd^{2+}, Pb^{2+}, and Cu^{2+}, detection limits of 0.089, 0.097, and 0.31 nM, respectively, were obtained [123]. Liu et al. constructed polyallylamine-hydrochloride-functionalized via a non-covalent method. The $–NH_2$ functional groups of polyallylamine hydrochloride improved the performance or trace detection of Cu^{2+}, with a relatively low detection limit of approximately 0.35 nM [124]. Through nucleophilic substitution reactions between the surface-exposed epoxy groups in GO and the active amine groups in PEI, Hu et al. synthesized PEI-rGO nanocomposites. When combined with Nafion, the hybrid modified electrode showed selectivity for Cu^{2+} electrochemical determination, with a detection limit of 0.3 μM [125]. In conclusion, polymer-modified interfaces have many outstanding merits, but the application of these systems is still limited by potential swelling or denaturation of the polymers during prolonged accumulation times and slow diffusion across the films [126]. In addition, the overview on polymer modified graphene as sensing material for electrochemical sensing of heavy metal ions was showed in Table 5.

Sensors using ternary graphene-based nanocomposite

Compared with binary graphene-based nanocomposites, ternary or quaternary graphene nanocomposites such as metal-

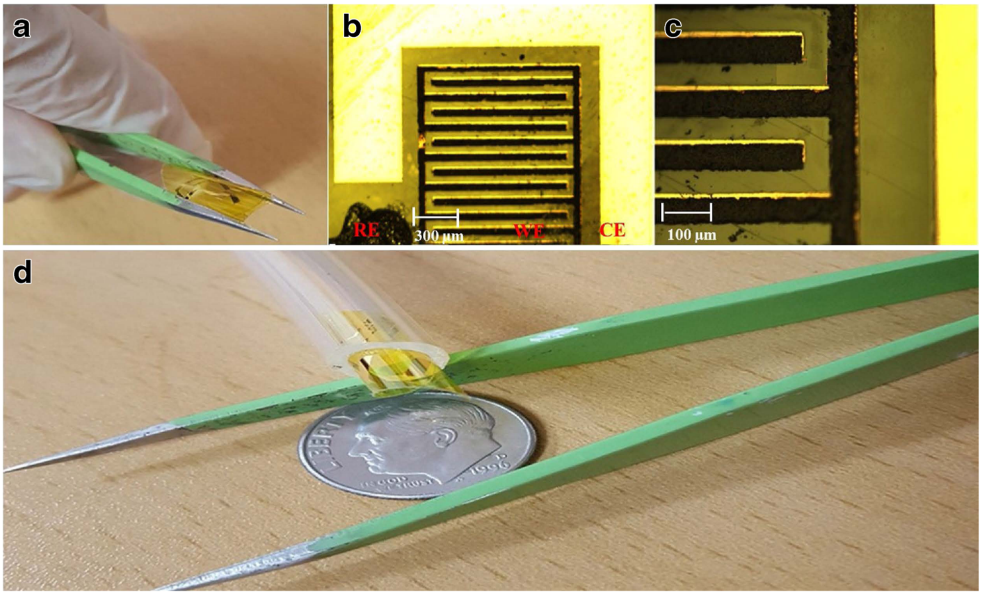

Fig. 4 Photographs of the fabricated miniaturized, integrated, and flexible heavy metal ion sensor with micro-patterned rGO and a CNT composite working electrode. Photo images (**a**, **d**) of a fabricated flexible heavy metal ion sensor, (**b**) microscope image of 3 electrodes, and (**c**) working electrode. (Gap size: 50 µm, total effective working electrode area: 1.5 mm^2, total working electrode thickness: ~1 µm). Reproduced from [141] with permission of Elsevier

conducting polymers, metal-carbon nanotube (CNT) or conducting polymer-CNT hybrid with graphene show better performance [23]. For example, Dong et al. constructed an Au NPs/PANI/graphene modified electrode for sensitive detection of Pb^{2+}. Compared with Au NPs, PANI, or graphene modified glassy carbon electrodes, the ternary hybrid showed improved detection performance, which was attributed to the synergetic effects of these three materials [138]. Moreover, PANI can function as a protective layer for Au NPs, avoiding interparticle aggregation via van der Waals attraction [1].

Wang et al. reported that the passivation of modified electrodes is problematic real sample analysis because various surface-active species may be adsorbed on the electrode. However, fouling of the electrode can be effectively alleviated by modification of the electrode with a dialysis membrane layer, such as Nafion, PLL, or cellulose acetate. Commonly used membrane modification methods usually involve a solvent evaporation procedure, which results in unsatisfactory homogeneity and reproducibility of the membrane. Therefore, they adopted an electrodeposition method to modify rGO/glassy carbon electrode with *p*-aminobenzene sulfonic acid. Compared with the afore-mentioned modification method, this electropolymerization method had the advantages of strong adhesion, controllable film thickness, uniform structure, and good stability. After in-situ plating a stannum film, the sensor was used for the sensitive determination of trace Cd^{2+} [139].

Cui et al. prepared thiazole-derivative functionalized graphene decorated with SnO_2 NPs and compared the influence of different halogen anions (F, Cl, or I) on the detection performance of the composite. The F@SnO_2/thiazole derivative-functionalized graphene exhibited superior performance for the detection of Cu^{2+} than the other two materials [140]. Recently, sensors based on a flexible substrate have gained attention, owing to their potential application as wearable sensors to monitor heavy metal ion in sweat, saliva, tears, or other body fluids. For example, Xuan et al. fabricated a fully integrated, miniaturized, and flexible electrochemical sensor based on a micro-patterned rGO and CNT composite on a flexible Au substrate as a working electrode (Fig. 4). After plating with a Bi film, the sensor exhibited separated and well-defined stripping peaks for Cd^{2+} and Pb^{2+} [141].

Sensors based on films have also received attention owing to their potential as disposable electrodes for heavy metal ion sensing. For example, Dong et al. synthesized a sandwich structured ionic liquid-CNT-graphene film via an effective inkjet printing method for electrochemical determination of Cd^{2+} and Pb^{2+}. The sensor exhibited high sensitivity, a wide linear range, and a low detection limit owing to the synergetic effects of these materials including fast charge transferability, sufficient surface active sites, and a large surface area [142]. Table 6 shows the overview on ternary or quaternary graphene-based nanocomposite as sensing material for electrochemical sensing of heavy metal ions.

Conclusions and perspectives

Graphene-based nanocomposites have been widely investigated as chemical sensors with high sensitivity and selectivity. We reviewed the sensing principles of graphene-based hybrids, including heteroatom-doped graphene, metal-modified graphene, metal-oxide-modified graphene, organically modified graphene, polymer-modified graphene, and ternary graphene based nanocomposite, which provide sensitive, selective and stable platforms for heavy metal ions determination. On one hand, searching for new materials and new

Table 6 Overview on ternary or quaternary graphene-based nanocomposite as sensing material for electrochemical sensing of heavy metal ions

Electrode	Sensing ions	Linear range	LOD	Ref.
Au NPs/PANI/graphene/GCE	Pb^{2+}	0.5-10 nM	0.1 nM	[138]
Bi NPs/PANI/graphene/silicon substrates	Cd^{2+}	0.33-1000 nM	0.33 nM	[143]
	Pb^{2+}			
Sn film/poly(p-aminobenzene sulfonic acid)/graphene/GCE	Cd^{2+}	8.9-622.71 nM	0.44 nM	[139]
Au NPs/chitosan/graphene/GCE	Pb^{2+}	2.41-482.63 nM	4.83 pM	[144]
Au NPs/IL/GO/GCE	Hg^{2+}	0.1-100 nM	0.03 nM	[145]
Au NPs/graphene/selenocysteine/Bi film/GCE	Cd^{2+}	4.45-444.8 pM	0.71 pM	[146]
	Pb^{2+}	2.41-241.31 pM	0.24 pM	
azacrown ether/Au NPs/rGO/CPE	Cu^{2+}	0.00787–1.18 μM	1.57 nM	[147]
benzothiazole-2-carboxaldehyde/Fe_3O_4/GO/GCE	Cd^{2+}	0.7-800 nM	0.3 nM	[148]
	Pb^{2+}	0.3 nM-430 nM	0.1 nM	
2-aminobenzothiazole/fluorine@SnO_2/graphene/GCE	Cu^{2+}	2-1000 nM	0.3 nM	[140]
curcumin/MnO_2/graphene/GCE	Hg^{2+}	0.249-5.982 μM	0.096 μM	[149]
Au NPs/CNT/GO/SPE	Hg^{2+}	0.00249-1.25 μM	1 nM	[150]
Bi NPs/nanoporous carbon/graphene/GCE	Cd^{2+}	0.08-0.8 μM	4.1 nM	[151]
	Pb^{2+}	0.06-0.6 μM	3.2 nM	
Bi film/CNT/rGO/Au substrate	Cd^{2+}	0.18-1.78 nM	5.34 pM	[141]
	Pb^{2+}	0.097-0.97 nM	0.97 pM	
xanthate/CNT/graphene/CPE	Cu^{2+}	0.02-11.1 μM 31.1-111.1 μM	9.5 nM	[152]
poly(O-toluidine)/CNT/GO	Pb^{2+}	0.1-1000000 nM	0.089 nM	[153]
Nafion/calcium lignosulfonate/porous graphene/GCE	Cd^{2+}	0.05-5 μM	0.003 μM	[154]
	Pb^{2+}		0.01 μM	
Nafion/IL/graphene/Bi film/SPCE	Zn^{2+}	0.00153-1.53 nM	1.38 pM	[135]
	Cd^{2+}	0.89-889.6 pM	0.53 pM	
	Pb^{2+}	0.48-482.63 pM	0.39 pM	
IL/CNT/graphene film	Cd^{2+}	0.001-1 μM	0.1 nM	[142]
	Pb^{2+}		0.2 nM	
Ru(II)-tris(bipy)-GO/AChE/Pt	Cd^{2+}	0.02-0.7 μM	0.07 μM	[155]
	As^{3+}	0.05-0.8 μM	0.03 μM	

IL, ionic liquid; *GCE*, glassy carbon electrode; *CPE*, carbon paste electrode; *SPE*, screen printed electrode; *SPCE*, screen printed carbon electrode

methodologies to control the morphology and structure of sensing materials to fabricate new sensors is an important direction for graphene-based sensors. On the other hand, optimizing the performance of current sensor systems, including sensitivity, selectivity, and stability, is of equal importance. Furthermore, the development of flexible or wearable sensors for detecting heavy metal ions in real samples or human body fluids is an important endeavor.

Acknowledgments We are grateful to the National Natural Science Foundation of China (21665010, 51762020 and 31741103), the Outstanding Youth Fund of Jiangxi Province (20162BCB23027), the Natural Science Foundation of Jiangxi Province (20171BAB203015, 20171ACB20026 and 20181BAB206015), the Jiangxi Provincial Department of Education (GJJ170662), and the One Hundred Person Yuan Hang Project (2017) for their financial support of this work. Yinxiu Zuo is greatly acknowledged Yunyong Hu for his support and encouragement during this writing process.

Compliance with ethical standards The author(s) declare that they have no competing interests.

References

1. Aragay G, Pons J, Merkoci A (2011) Recent trends in macro-, micro-, and nanomaterial-based tools and strategies for heavy-metal detection. Chem Rev 111(5):3433–3458. https://doi.org/10.1021/cr100383r

2. Rassaei L, Marken F, Sillanpää M, Amiri M, Cirtiu CM, Sillanpää M (2011) Nanoparticles in electrochemical sensors for environmental monitoring. TrAC-Trend Anal Chem 30(11):1704–1715. https://doi.org/10.1016/j.trac.2011.05.009
3. Xu JH, Wang YZ, Hu SS (2017) Nanocomposites of graphene and graphene oxides: synthesis, molecular functionalization and application in electrochemical sensors and biosensors. A review. Microchim Acta 184(1):1–44. https://doi.org/10.1007/s00604-016-2007-0
4. Wu S, He Q, Tan C, Wang Y, Zhang H (2013) Graphene-based electrochemical sensors. Small 9(8):1160–1172. https://doi.org/10.1002/smll.201202896
5. Pumera M (2009) Electrochemistry of graphene: new horizons for sensing and energy storage. Chem Rec 9(4):211–223. https://doi.org/10.1002/tcr.200900008
6. Chen X, Wu G, Jiang Y, Wang Y, Chen X (2011) Graphene and graphene-based nanomaterials: the promising materials for bright future of electroanalytical chemistry. Analyst 136(22):4631–4640. https://doi.org/10.1039/c1an15661f
7. Li F, Liu S, Wu T, Zhang Q, Dong X, Niu L (2018) Disposable graphene sensor with an internal reference electrode for heavy metals stripping analysis. Anal Methods 10(17):1986–1992. https://doi.org/10.1039/c8ay00221e
8. Chao H, Fu L, Li Y, Li X, Du H, Ye J (2013) Sensitive stripping determination of cadmium(ii) and lead(ii) on disposable graphene modified screen-printed electrode. Electroanal 25(9):2238–2243. https://doi.org/10.1002/elan.201300239
9. Chen D, Feng H, Li J (2012) Graphene oxide: preparation, functionalization, and electrochemical applications. Chem Rev 112(11):6027–6053. https://doi.org/10.1021/cr300115g
10. Naveen MH, Gurudatt NG, Shim YB (2017) Applications of conducting polymer composites to electrochemical sensors: a review. Applied Mater Today 9:419–433. https://doi.org/10.1016/j.apmt.2017.09.001
11. Fang Y, Wang E (2013) Electrochemical biosensors on platforms of graphene. Chem Commun 49(83):9526–9539. https://doi.org/10.1039/c3cc44735a
12. Zhao D, Zhang L, Siebold D, DeArmond D, Alvarez NT, Shanov VN, Heineman WR (2017) Electrochemical studies of three dimensional graphene foam as an electrode material. Electroanal. 29(6):1506–1512. https://doi.org/10.1002/elan.201700057
13. 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. https://doi.org/10.1016/j.aca.2017.03.013
14. Baig N, Saleh TA (2018) Electrodes modified with 3D graphene composites: a review on methods for preparation, properties and sensing applications. Microchim Acta 185(6):283. https://doi.org/10.1007/s00604-018-2809-3
15. Waheed A, Mansha M, Ullah N (2018) Nanomaterials-based electrochemical detection of heavy metals in water: current status, challenges and future direction. TrAC-Trend Anal Chem 105:37–51. https://doi.org/10.1016/j.trac.2018.04.012
16. Shao Y, Wang J, Wu H, Liu J, Aksay IA, Lin Y (2010) Graphene based electrochemical sensors and biosensors: a review. Electroanal 22(10):1027–1036. https://doi.org/10.1002/elan.200900571
17. Gan X, Zhao H, Schirhagl R, Quan X (2018) Two-dimensional nanomaterial based sensors for heavy metal ions. Microchim Acta 185(10):478. https://doi.org/10.1007/s00604-018-3005-1
18. Wang X, Sun G, Routh P, Kim DH, Huang W, Chen P (2014) Heteroatom-doped graphene materials: syntheses, properties and applications. Chem Soc Rev 43(20):7067–7098. https://doi.org/10.1039/c4cs00141a
19. Xing H, Xu J, Zhu X, Duan X, Lu L, Wang W, Zhang Y, Yang T (2016) Highly sensitive simultaneous determination of cadmium (II), lead (II), copper (II), and mercury (II) ions on N-doped graphene modified electrode. J Electroanal Chem 760:52–58. https://doi.org/10.1016/j.jelechem.2015.11.043
20. Liu XS, Li ZJ, Ding RM, Ren BB, Li YH (2016) A nanocarbon paste electrode modified with nitrogen-doped graphene for square wave anodic stripping voltammetric determination of trace lead and cadmium. Microchim Acta 183(2):709–714. https://doi.org/10.1007/s00604-015-1713-3
21. Manna B, Raj CR (2018) Nanostructured sulfur-doped porous reduced graphene oxide for the ultrasensitive electrochemical detection and efficient removal of Hg(II). ACS Sustain Chem Eng 6(5):6175–6182. https://doi.org/10.1021/acssuschemeng.7b04884
22. Thiruppathi AR, Sidhureddy B, Keeler W, Chen A (2017) Facile one-pot synthesis of fluorinated graphene oxide for electrochemical sensing of heavy metal ions. Electrochem Commun 76:42–46. https://doi.org/10.1016/j.elecom.2017.01.015
23. Meng FL, Guo Z, Huang XJ (2015) Graphene-based hybrids for chemiresistive gas sensors. TrAC-Trend Anal Chem 68:37–47. https://doi.org/10.1016/j.trac.2015.02.008
24. Gong J, Zhou T, Song D, Zhang L (2010) Monodispersed Au nanoparticles decorated graphene as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II). Sensor Actuat B-Chem 150(2):491–497. https://doi.org/10.1016/j.snb.2010.09.014
25. Liu Y, Huang Z, Xie Q, Sun L, Gu T, Li Z, Bu L, Yao S, Tu X, Luo X, Luo S (2013) Electrodeposition of electroreduced graphene oxide-Au nanoparticles composite film at glassy carbon electrode for anodic stripping voltammetric analysis of trace arsenic(III). Sensor Actuat B-Chem 188:894–901. https://doi.org/10.1016/j.snb.2013.07.113
26. Gao C, Huang XJ (2013) Voltammetric determination of mercury(II). TrAC-Trend Anal Chem 51:1–12. https://doi.org/10.1016/j.trac.2013.05.010
27. Sang S, Li D, Zhang H, Sun Y, Jian A, Zhang Q, Zhang W (2017) Facile synthesis of AgNPs on reduced graphene oxide for highly sensitive simultaneous detection of heavy metal ions. RSC Adv 7(35):21618–21624. https://doi.org/10.1039/c7ra02267k
28. Welch CM, Compton RG (2006) The use of nanoparticles in electroanal: a review. Anal Bioanal Chem 384(3):601–619. https://doi.org/10.1007/s00216-005-0230-3
29. Sahoo PK, Panigrahy B, Sahoo S, Satpati AK, Li D, Bahadur D (2013) In situ synthesis and properties of reduced graphene oxide/Bi nanocomposites: as an electroactive material for analysis of heavy metals. Biosens Bioelectron 43:293–296. https://doi.org/10.1016/j.bios.2012.12.031
30. Lee PM, Chen Z, Li L, Liu E (2015) Reduced graphene oxide decorated with tin nanoparticles through electrodeposition for simultaneous determination of trace heavy metals. Electrochim Acta 174:207–214. https://doi.org/10.1016/j.electacta.2015.05.092
31. Molina J, Cases F, Moretto LM (2016) Graphene-based materials for the electrochemical determination of hazardous ions. Anal Chim Acta 946:9–39. https://doi.org/10.1016/j.aca.2016.10.019
32. Ping J, Wang Y, Wu J, Ying Y (2014) Development of an electrochemically reduced graphene oxide modified disposable bismuth film electrode and its application for stripping analysis of heavy metals in milk. Food Chem 151:65–71. https://doi.org/10.1016/j.foodchem.2013.11.026
33. Arduini F, Calvo JQ, Palleschi G, Moscone D, Amine A (2010) Bismuth-modified electrodes for lead detection. TrAC-Trend Anal Chem 29(11):1295–1304. https://doi.org/10.1016/j.trac.2010.08.003
34. Pan D, Wang Y, Chen Z, Lou T, Qin W (2009) Nanomaterial/ionophore-based electrode for anodic stripping voltammetric determination of lead: an electrochemical sensing platform toward

heavy metals. Anal Chem 81(12):5088–5094. https://doi.org/10.1021/ac900417e

35. Ruengpiraširi P, Punrat E, Chailapakul O, Chuanuwatanakul S (2017) Graphene oxide-modified electrode coated with in-situ antimony film for the simultaneous determination of heavy metals by sequential injection-anodic stripping voltammetry. Electroanal 29(4):1022–1030. https://doi.org/10.1002/elan.201600568
36. Zhang XZ, Qu KM, Li DP (2015) Advance in the stripping voltammetry using alloy electrodes for the determination of heavy metal ions. Int J Electrochem Sci 10(10):8497–8512
37. Wang T, Yue W (2017) Carbon nanotubes heavy metal detection with stripping voltammetry: a review paper. Electroanal 29(10):2178–2189. https://doi.org/10.1002/elan.201700276
38. Ding L, Liu Y, Zhai J, Bond AM, Zhang J (2014) Direct electrodeposition of graphene-gold nanocomposite films for ultrasensitive voltammetric determination of mercury(II). Electroanal 26(1):121–128. https://doi.org/10.1002/elan.201300226
39. Sahoo PK, Sahoo S, Satpati AK, Bahadur D (2015) Solvothermal synthesis of reduced graphene oxide/Au nanocomposite-modified electrode for the determination of inorganic mercury and electrochemical oxidation of toxic phenolic compounds. Electrochim Acta 180:1023–1032. https://doi.org/10.1016/j.electacta.2015.09.018
40. Sahoo S, Sahoo PK, Satpati AK (2017) Gold nano particle and reduced graphene oxide composite modified carbon paste electrode for the ultra trace detection of arsenic (III). Electroanal 29(5):1400–1409. https://doi.org/10.1002/elan.201600676
41. Li WW, Kong FY, Wang JY, Chen ZD, Fang HL, Wang W (2015) Facile one-pot and rapid synthesis of surfactant-free Au-reduced graphene oxide nanocomposite for trace arsenic (III) detection. Electrochim Acta 157:183–190. https://doi.org/10.1016/j.electacta.2014.12.150
42. Lee PM, Wang Z, Liu X, Chen Z, Liu E (2015) Glassy carbon electrode modified by graphene–gold nanocomposite coating for detection of trace lead ions in acetate buffer solution. Thin Solid Films 584:85–89. https://doi.org/10.1016/j.tsf.2015.03.017
43. Wang S, Wang Y, Zhou L, Li J, Wang S, Liu H (2014) Fabrication of an effective electrochemical platform based on graphene and AuNPs for high sensitive detection of trace Cu^{2+}. Electrochim Acta 132:7–14. https://doi.org/10.1016/j.electacta.2014.03.114
44. Liu M, Pan D, Pan W, Zhu Y, Hu X, Han H, Wang C, Shen D (2017) In-situ synthesis of reduced graphene oxide/gold nanoparticles modified electrode for speciation analysis of copper in seawater. Talanta 174:500–506. https://doi.org/10.1016/j.talanta.2017.06.054
45. Gnanaprakasam P, Jeena SE, Premnath D, Selvaraju T (2016) Simple and robust green synthesis of Au NPs on reduced graphene oxide for the simultaneous detection of toxic heavy metal ions and bioremediation using bacterium as the scavenger. Electroanal 28(8):1885–1893. https://doi.org/10.1002/elan.201600002
46. Han H, Pan D, Wang C, Zhu R (2017) Controlled synthesis of dendritic gold nanostructures by graphene oxide and their morphology-dependent performance for iron detection in coastal waters. RSC Adv 7(26):15833–15841. https://doi.org/10.1039/c6ra27075a
47. Zhu Y, Pan D, Hu X, Han H, Lin M, Wang C (2017) An electrochemical sensor based on reduced graphene oxide/gold nanoparticles modified electrode for determination of iron in coastal waters. Sensor Actuat B-Chem 243:1–7. https://doi.org/10.1016/j.snb.2016.11.108
48. Xu Y, Zhang W, Shi J, Zou X, Li Y, Haroon Elrasheid T, Huang X, Li Z, Zhai X, Hu X (2017) Electrodeposition of gold nanoparticles and reduced graphene oxide on an electrode for fast and sensitive determination of methylmercury in fish. Food Chem 237:423–430. https://doi.org/10.1016/j.foodchem.2017.05.096
49. Dar RA, Khare NG, Cole DP, Karna SP, Srivastava AK (2014) Green synthesis of a silver nanoparticle-graphene oxide composite and its application for As(III) detection. RSC Adv 4(28):14432–14440. https://doi.org/10.1039/c4ra00934g
50. Kempegowda R, Antony D, Malingappa P (2014) Graphene platinum nanocomposite as a sensitive and selective voltammetric sensor for trace level arsenic quantification. Inter J Smart Nano Mater 5(1):17–32. https://doi.org/10.1080/19475411.2014.898710
51. Hu X, Pan D, Lin M, Han H, Li F (2016) Graphene oxide-assisted synthesis of bismuth nanosheets for catalytic stripping voltammetric determination of iron in coastal waters. Microchim Acta 183(2):855–861. https://doi.org/10.1007/s00604-015-1733-z
52. Lee S, Park SK, 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. https://doi.org/10.1016/j.jelechem.2016.02.003
53. Lin X, Lu Z, Zhang Y, Liu B, Mo G, Li J, Ye J (2018) A glassy carbon electrode modified with a bismuth film and laser etched graphene for simultaneous voltammetric sensing of Cd(II) and Pb(II). Microchim Acta 185(9):438. https://doi.org/10.1007/s00604-018-2966-4
54. Wang J, Chen X, Wu K, Zhang M, Huang W (2016) Highly-sensitive electrochemical sensor for Cd^{2+} and Pb^{2+} based on the synergistic enhancement of exfoliated graphene nanosheets and bismuth. Electroanal 28(1):63–68. https://doi.org/10.1002/elan.201500447
55. Cui L, Wu J, Ju H (2015) Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials. Biosens Bioelectron 63:276–286. https://doi.org/10.1016/j.bios.2014.07.052
56. Campbell FW, Compton RG (2010) The use of nanoparticles in electroanal: an updated review. Anal Bioanal Chem 396(1):241–259. https://doi.org/10.1007/s00216-009-3063-7
57. Arino C, Serrano N, Diaz-Cruz JM, Esteban M (2017) Voltammetric determination of metal ions beyond mercury electrodes. A review. Anal Chim Acta 990:11–53. https://doi.org/10.1016/j.aca.2017.07.069
58. Khan M, Tahir MN, Adil SF, Khan HU, Siddiqui MRH, Al-warthan AA, Tremel W (2015) Graphene based metal and metal oxide nanocomposites: synthesis, properties and their applications. J Mater Chem A 3(37):18753–18808. https://doi.org/10.1039/c5ta02240a
59. Sun Y, Zhang W, Yu H, Hou C, Li D, Zhang Y, Liu Y (2015) Controlled synthesis various shapes Fe_3O_4 decorated reduced graphene oxide applied in the electrochemical detection. J Alloy Compd 638:182–187. https://doi.org/10.1016/j.jallcom.2015.03.061
60. Karthik R, Thambidurai S (2017) Synthesis of cobalt doped ZnO/reduced graphene oxide nanorods as active material for heavy metal ions sensor and antibacterial activity. J Alloy Compd 715:254–265. https://doi.org/10.1016/j.jallcom.2017.04.298
61. Lu XF, Gu LF, Wang JW, Wu JX, Liao PQ, Li GR (2017) Bimetal-organic framework derived $CoFe_2O_4$/C porous hybrid nanorod arrays as high-performance electrocatalysts for oxygen evolution reaction. Adv Mater 29(3):1604437. https://doi.org/10.1002/adma.201604437
62. Yu XY, Yao XZ, Luo T, Jia Y, Liu JH, Huang XJ (2014) Facile synthesis of urchin-like $NiCo_2O_4$ hollow microspheres with enhanced electrochemical properties in energy and environmentally related applications. ACS Appl Mater Interfaces 6(5):3689–3695. https://doi.org/10.1021/am4060707
63. Xu J, Li Z, Yue X, Xie F, Xiong S (2018) Electrochemical detection of Cu(ii) using amino-functionalized $MgFe_2O_4$/reduced

graphene oxide composite. Anal Methods 10(17):2026–2033. https://doi.org/10.1039/c8ay00452h

64. Xiong S, Ye S, Hu X, Xie F (2016) Electrochemical detection of ultra-trace Cu(ii) and interaction mechanism analysis between amine-groups functionalized CoFe$_2$O$_4$/reduced graphene oxide composites and metal ion. Electrochim Acta 217:24–33. https://doi.org/10.1016/j.electacta.2016.09.060

65. Zhou SF, Han XJ, Fan HL, Huang J, Liu YQ (2018) Enhanced electrochemical performance for sensing Pb(II) based on graphene oxide incorporated mesoporous MnFe$_2$O$_4$ nanocomposites. J Alloy Compd 747:447–454. https://doi.org/10.1016/j.jallcom.2018.03.037

66. Mahmoudian MR, Alias Y, Basirun WJ, Woi PM, Sookhakian M, Jamali-Sheini F (2015) Synthesis and characterization of Fe$_3$O$_4$ rose like and spherical/reduced graphene oxide nanosheet composites for lead (II) sensor. Electrochim Acta 169:126–133. https://doi.org/10.1016/j.electacta.2015.04.050

67. Sun YF, Chen WK, Li WJ, Jiang TJ, Liu JH, Liu ZG (2014) Selective detection toward Cd^{2+} using Fe$_3$O$_4$/RGO nanoparticle modified glassy carbon electrode. J Electroanal Chem 714-715: 97–102. https://doi.org/10.1016/j.jelechem.2013.12.030

68. Chimezie AB, Hajian R, Yusof NA, Woi PM, Shams N (2017) Fabrication of reduced graphene oxide-magnetic nanocomposite (rGO-Fe$_3$O$_4$) as an electrochemical sensor for trace determination of As(III) in water resources. J Electroanal Chem 796:33–42. https://doi.org/10.1016/j.jelechem.2017.04.061

69. Devi P, Sharma C, Kumar P, Kumar M, Bansod BKS, Nayak MK, Singla ML (2017) Selective electrochemical sensing for arsenite using rGO/Fe$_3$O$_4$ nanocomposites. J Hazard Mater 322:85–94. https://doi.org/10.1016/j.jhazmat.2016.02.066

70. Xiong S, Yang B, Cai D, Qiu G, Wu Z (2015) Individual and simultaneous stripping voltammetric and mutual interference analysis of Cd^{2+}, Pb^{2+} and Hg^{2+} with reduced graphene oxide-Fe$_3$O$_4$ nanocomposites. Electrochim Acta 185:52–61. https://doi.org/10.1016/j.electacta.2015.10.114

71. Prakash A, Chandra S, Bahadur D (2012) Structural, magnetic, and textural properties of iron oxide-reduced graphene oxide hybrids and their use for the electrochemical detection of chromium. Carbon 50(11):4209–4219. https://doi.org/10.1016/j.carbon.2012.05.002

72. Lee S, Oh J, Kim D, Piao Y (2016) A sensitive electrochemical sensor using an iron oxide/graphene composite for the simultaneous detection of heavy metal ions. Talanta 160:528–536. https://doi.org/10.1016/j.talanta.2016.07.034

73. Wei Y, Gao C, Meng FL, Li HH, Wang L, Liu JH, Huang XJ (2012) SnO$_2$/reduced graphene oxide nanocomposite for the simultaneous electrochemical detection of cadmium(ii), lead(ii), copper(ii), and mercury(ii): an interesting favorable mutual interference. J Phy Chem C 116(1):1034–1041. https://doi.org/10.1021/jp209805c

74. Zhang H, Shuang S, Wang G, Guo Y, Tong X, Yang P, Chen A, Dong C, Qin Y (2015) TiO$_2$–graphene hybrid nanostructures by atomic layer deposition with enhanced electrochemical performance for Pb(ii) and Cd(ii) detection. RSC Adv 5(6):4343–4349. https://doi.org/10.1039/c4ra09779c

75. Xie YL, Zhao SQ, Ye HL, Yuan J, Song P, Hu SQ (2015) Graphene/CeO$_2$ hybrid materials for the simultaneous electrochemical detection of cadmium(II), lead(II), copper(II), and mercury(II). J Electroanal Chem 757:235–242. https://doi.org/10.1016/j.jelechem.2015.09.043

76. Zuo Y, Xu J, Jiang F, Duan X, Lu L, Xing H, Yang T, Zhang Y, Ye G, Yu Y (2017) Voltammetric sensing of Pb(II) using a glassy carbon electrode modified with composites consisting of Co$_3$O$_4$ nanoparticles, reduced graphene oxide and chitosan. J Electroanal Chem 801:146–152. https://doi.org/10.1016/j.jelechem.2017.07.046

77. Devi P, Bansod B, Kaur M, Bagchi S, Nayak MK (2016) Co-electrodeposited rGO/MnO$_2$ nanohybrid for arsenite detection in water by stripping voltammetry. Sensor Actuat B-Chem 237:652–659. https://doi.org/10.1016/j.snb.2016.06.124

78. Zhang W, Xu Y, Zou X (2017) A ZnO–RGO-modified electrode coupled to microwave digestion for the determination of trace cadmium and lead in six species fish. Anal Methods 9(30): 4418–4424. https://doi.org/10.1039/c7ay01574g

79. Lu YY, Chen MN, Gao YL, Yang JM, Ma XY, Liu JY (2015) Preparation of zinc oxide-graphene composite modified electrodes for detection of trace Pb(II). Chin J Anal Chem 43(9):1395–1401. https://doi.org/10.1016/s1872-2040(15)60862-3

80. Ramesha GK, Sampath S (2011) In-situ formation of graphene-lead oxide composite and its use in trace arsenic detection. Sensors Actuat B-Chem 160(1):306–311. https://doi.org/10.1016/j.snb.2011.07.053

81. Muralikrishna S, Sureshkumar K, Varley TS, Nagaraju DH, Ramakrishnappa T (2014) In situ reduction and functionalization of graphene oxide withl-cysteine for simultaneous electrochemical determination of cadmium(ii), lead(ii), copper(ii), and mercury(ii) ions. Anal Methods 6(21):8698–8705. https://doi.org/10.1039/c4ay01945h

82. Zuo Y, Xu J, Xing H, Duan X, Lu L, Ye G, Jia H, Yu Y (2018) Simple and green synthesis of piperazine-grafted reduced graphene oxide and its application for the detection of Hg(II). Nanotechnology 29(16):165502. https://doi.org/10.1088/1361-6528/aaaf4a

83. Zhou H, Wang X, Yu P, Chen X, Mao L (2012) Sensitive and selective voltammetric measurement of Hg^{2+} by rational covalent functionalization of graphene oxide with cysteamine. Analyst 137(2):305–308. https://doi.org/10.1039/c1an15793k

84. Gode C, Yola ML, Yilmaz A, Atar N, Wang S (2017) A novel electrochemical sensor based on calixarene functionalized reduced graphene oxide: application to simultaneous determination of Fe(III), Cd(II) and Pb(II) ions. J Colloid Interf Sci 508:525–531. https://doi.org/10.1016/j.jcis.2017.08.086

85. Yu C, Guo Y, Liu H, Yan N, Xu Z, Yu G, Fang Y, Liu Y (2013) Ultrasensitive and selective sensing of heavy metal ions with modified graphene. Chem Commun 49(58):6492–6494. https://doi.org/10.1039/c3cc42377h

86. Magerusan L, Socaci C, Coros M, Pogacean F, Rosu MC, Gergely S, Pruneanu S, Leostean C, Pana IO (2017) Electrochemical platform based on nitrogendoped graphene/chitosan nanocomposite for selective Pb^{2+} detection. Nanotechnology 28(11):114001. https://doi.org/10.1088/1361-6528/aa56cb

87. Yang M, Jiang TJ, Wang Y, Liu JH, Li LN, Chen X, Huang XJ (2017) Enhanced electrochemical sensing arsenic(III) with excellent anti-interference using amino-functionalized graphene oxide decorated gold microelectrode: XPS and XANES evidence. Sensor Actuat B-Chem 245:230–237. https://doi.org/10.1016/j.snb.2017.01.139

88. Zhan F, Gao F, Wang X, Xie L, Gao F, Wang Q (2016) Determination of lead(II) by adsorptive stripping voltammetry using a glassy carbon electrode modified with β-cyclodextrin and chemically reduced graphene oxide composite. Microchim Acta 183(3):1169–1176. https://doi.org/10.1007/s00604-016-1754-2

89. Lv M, Wang X, Li J, Yang X, Ca Z, Yang J, Hu H (2013) Cyclodextrin-reduced graphene oxide hybrid nanosheets for the simultaneous determination of lead(II) and cadmium(II) using square wave anodic stripping voltammetry. Electrochim Acta 108:412–420. https://doi.org/10.1016/j.electacta.2013.06.099

90. Li Y, Sun G, Zhang Y, Ge C, Bao N, Wang Y (2013) Sensitive and selective stripping voltammetric determination of copper(II) using a glassy carbon electrode modified with amino-reduced graphene

oxide and β-cyclodextrin. Microchim Acta 181(7-8):751–757. https://doi.org/10.1007/s00604-013-1082-8

91. Mo Z, Liu H, Hu R, Gou H, Li Z, Guo R (2017) Amino-functionalized graphene/chitosan composite as an enhanced sensing platform for highly selective detection of Cu^{2+}. Ionics 24(5): 1505–1513. https://doi.org/10.1007/s11581-017-2309-1
92. Li Z, Chen L, He F, Bu L, Qin X, Xie Q, Yao S, Tu X, Luo X, Luo S (2014) Square wave anodic stripping voltammetric determination of Cd^{2+} and Pb^{2+} at bismuth-film electrode modified with electroreduced graphene oxide-supported thiolated thionine. Talanta 122:285–292. https://doi.org/10.1016/j.talanta.2014.01.062
93. Piek M, Fendrych K, Smajdor J, Piech R, Paczosa-Bator B (2017) High selective potentiometric sensor for determination of nanomolar con-centration of Cu(II) using a polymeric electrode modified by a graphene/7,7,8,8-tetracyanoquinodimethane nanoparticles. Talanta 170:41–48. https://doi.org/10.1016/j.talanta.2017.03.068
94. Abraham AA, Rezayi M, Manan NSA, Narimani L, Rosli ANB, Alias Y (2015) A novel potentiometric sensor based on 1,2-bis(n’-benzoylthioureido)benzene and reduced graphene oxide for determination of lead (ii) cation in raw milk. Electrochim Acta 165: 221–231. https://doi.org/10.1016/j.electacta.2015.03.003
95. Priya T, Dhanalakshmi N, Thennarasu S, Thinakaran N (2018) A novel voltammetric sensor for the simultaneous detection of Cd^{2+} and Pb^{2+} using graphene oxide/kappa-carrageenan/L-cysteine nanocomposite. Carbohyd Polym 182:199–206. https://doi.org/10.1016/j.carbpol.2017.11.017
96. Priya T, Dhanalakshmi N, Thennarasu S, Thinakaran N (2018) Ultra sensitive detection of Cd (II) using reduced graphene oxide/carboxymethyl cellulose/glutathione modified electrode. Carbohyd Polym 197:366–374. https://doi.org/10.1016/j.carbpol.2018.06.024
97. Liu R, Lei C, Zhong T, Long L, Wu Z, Huan S, Zhang Q (2016) A graphene/ionic liquid modified selenium-doped carbon paste electrode for determination of copper and antimony. Anal Methods 8(5):1120–1126. https://doi.org/10.1039/c5ay02945g
98. Li F, Pan D, Lin M, Han H, Hu X, Kang Q (2015) Electrochemical determination of iron in coastal waters based on ionic liquid-reduced graphene oxide supported gold nanodendrites. Electrochim Acta 176:548–554. https://doi.org/10.1016/j.electacta.2015.07.011
99. Bagheri H, Afkhami A, Khoshsafar H, Rezaei M, Sabounchei SJ, Sarlakifar M (2015) Simultaneous electrochemical sensing of thallium, lead and mercury using a novel ionic liquid/graphene modified electrode. Anal Chim Acta 870:56–66. https://doi.org/10.1016/j.aca.2015.03.004
100. Wang Z, Wang H, Zhang Z, Liu G (2014) Electrochemical determination of lead and cadmium in rice by a disposable bismuth/electrochemically reduced graphene/ionic liquid composite modified screen-printed electrode. Sensor Actuat B-Chem 199:7–14. https://doi.org/10.1016/j.snb.2014.03.092
101. Zhou W, Li C, Sun C, Yang X (2016) Simultaneously determination of trace Cd^{2+} and Pb^{2+} based on L-cysteine/graphene modified glassy carbon electrode. Food Chem 192:351–357. https://doi.org/10.1016/j.foodchem.2015.07.042
102. Liu L, Wang CY, Wang GX (2013) Novel cysteic acid/reduced graphene oxide composite film modified electrode for the selective detection of trace silver ions in natural waters. Anal Methods 5(20):5812–5822. https://doi.org/10.1039/c3ay40888d
103. Qiu N, Liu Y, Guo R (2016) A novel sensitive electrochemical sensor for lead ion based on three-dimensional graphene/sodium dodecyl benzene sulfonate hemimicelle nanocomposites. Electrochim Acta 212:147–154. https://doi.org/10.1016/j.electacta.2016.06.136
104. Wang B, Luo B, Liang M, Wang A, Wang J, Fang Y, Chang Y, Zhi L (2011) Chemical amination of graphene oxides and their extraordinary properties in the detection of lead ions. Nanoscale 3(12):5059–5066. https://doi.org/10.1039/c1nr10901d
105. Yuan YH, Zhu XH, Wen SH, Liang RP, Zhang L, Qiu JD (2018) Electrochemical assay for As (III) by combination of highly thiol-rich trithiocyanuric acid and conductive reduced graphene oxide nanocomposites. J Electroanal Chem 814:97–103. https://doi.org/10.1016/j.jelechem.2018.02.039
106. Çelik GK, Üzdürmez AF, Erkal A, Kılıç E, Solak AO, Üstündağ Z (2016) 3,8-diaminobenzo[c]cinnoline derivatived graphene oxide modified graphene oxide sensor for the voltammetric determination of Cd^{2+} and Pb^{2+}. Electrocatal 7(3):207–214. https://doi.org/10.1007/s12678-015-0297-3
107. Choi SM, Kim DM, Jung OS, Shim YB (2015) A disposable chronocoulometric sensor for heavy metal ions using a diaminoterthiophene-modified electrode doped with graphene oxide. Anal Chim Acta 892:77–84. https://doi.org/10.1016/j.aca.2015.08.037
108. Xing H, Xu J, Zhu X, Duan X, Lu L, Zuo Y, Zhang Y, Wang W (2016) A new electrochemical sensor based on carboimidazole grafted reduced graphene oxide for simultaneous detection of Hg^{2+} and Pb^{2+}. J Electroanal Chem 782:250–255. https://doi.org/10.1016/j.jelechem.2016.10.043
109. Gupta VK, Yola ML, Atar N, Ustundağ Z, Solak AO (2013) A novel sensitive Cu(II) and Cd(II) nanosensor platform: graphene oxide terminated p-aminophenyl modified glassy carbon surface. Electrochim Acta 112:541–548. https://doi.org/10.1016/j.electacta.2013.09.011
110. Yuan X, Chai Y, Yuan R, Zhao Q, Yang C (2012) Functionalized graphene oxide-based carbon paste electrode for potentiometric detection of copper ion(ii). Anal Methods 4(10):3332–3337. https://doi.org/10.1039/c2ay25674f
111. Kang M, Peng D, Zhang Y, Yang Y, He L, Yan F, Sun S, Fang S, Wang P, Zhang Z (2015) An electrochemical sensor based on rhodamine B hydrazide-immobilized graphene oxide for highly sensitive and selective detection of Cu(ii). New J Chem 39(4): 3137–3144. https://doi.org/10.1039/c5nj00157a
112. Ziółkowski R, Górski Ł, Malinowska E (2017) Carboxylated graphene as a sensing material for electrochemical uranyl ion detection. Sensor Actuat B-Chem 238:540–547. https://doi.org/10.1016/j.snb.2016.07.119
113. Zhang Y, Qi M, Liu G (2015) C-C bonding of graphene oxide on 4-aminophenyl modified gold electrodes towards simultaneous detection of heavy metal ions. Electroanal 27(5):1110–1118. https://doi.org/10.1002/elan.201400591
114. Zhang W, Wei J, Zhu H, Zhang K, Ma F, Mei Q, Zhang Z, Wang S (2012) Self-assembled multilayer of alkyl graphene oxide for highly selective detection of copper(ii) based on anodic stripping voltammetry. J Mater Chem 22(42):22631. https://doi.org/10.1039/c2jm34795d
115. March G, Nguyen T, Piro B (2015) Modified electrodes used for electrochemical detection of metal ions in environmental analysis. Biosensors 5(2):241–275. https://doi.org/10.3390/bios5020241
116. Kuilla T, Bhadra S, Yao D, Kim NH, Bose S, Lee JH (2010) Recent advances in graphene based polymer composites. Prog Polym Sci 35(11):1350–1375. https://doi.org/10.1016/j.progpolymsci.2010.07.005
117. Hui Y, Bian C, Xia S, Tong J, Wang J (2018) Synthesis and electrochemical sensing application of poly(3,4-ethylenedioxythiophene)-based materials: a review. Anal Chim Acta 1022:1–19. https://doi.org/10.1016/j.aca.2018.02.080
118. Zuo Y, Xu J, Zhu X, Duan X, Lu L, Gao Y, Xing H, Yang T, Ye G, Yu Y (2016) Poly(3,4-ethylenedioxythiophene) nanorods/graphene oxide nanocomposite as a new electrode material for

the selective electrochemical detection of mercury (II). Synthetic Met 220:14–19. https://doi.org/10.1016/j.synthmet.2016.05.022

119. Dai H, Wang N, Wang D, Ma H, Lin M (2016) An electrochemical sensor based on phytic acid functionalized polypyrrole/graphene oxide nanocomposites for simultaneous determination of Cd(II) and Pb(II). Chem Eng J 299:150–155. https://doi.org/10.1016/j.cej.2016.04.083
120. Muralikrishna S, Nagaraju DH, Balakrishna RG, Surareungchai W, Ramakrishnappa T, Shivanandareddy AB (2017) Hydrogels of polyaniline with graphene oxide for highly sensitive electrochemical determination of lead ions. Anal Chim Acta 990:67–77. https://doi.org/10.1016/j.aca.2017.09.008
121. Li J, Guo S, Zhai Y, Wang E (2009) Nafion–graphene nanocomposite film as enhanced sensing platform for ultrasensitive determination of cadmium. Electrochem Commun 11(5):1085–1088. https://doi.org/10.1016/j.elecom.2009.03.025
122. Chalupniak A, Merkoci A (2017) Graphene oxide-poly(dimethylsiloxane)-based lab-on-a-chip platform for heavy-metals preconcentration and electrochemical detection. ACS Appl Mater Interfaces 9(51):44766–44775. https://doi.org/10.1021/acsami.7b12368
123. Guo Z, Li D, Luo X, Li Y, Zhao QN, Li M, Zhao Y, Sun T, Ma C (2017) Simultaneous determination of trace Cd(II), Pb(II) and Cu(II) by differential pulse anodic stripping voltammetry using a reduced graphene oxide-chitosan/poly-L-lysine nanocomposite modified glassy carbon electrode. J Colloid Interf Sci 490:11–22. https://doi.org/10.1016/j.jcis.2016.11.006
124. Liu H, Li S, Sun D, Chen Y, Zhou Y, Lu T (2014) Layered graphene nanostructures functionalized with NH_2-rich polyelectrolytes through self-assembly: construction and their application in trace Cu(ii) detection. J Mater Chem B 2(16):2212–2219. https://doi.org/10.1039/c4tb00104d
125. Hu R, Gou H, Mo Z, Wei X, Wang Y (2015) Highly selective detection of trace Cu^{2+} based on polyethyleneimine-reduced graphene oxide nanocomposite modified glassy carbon electrode. Ionics 21(11):3125–3133. https://doi.org/10.1007/s11581-015-1499-7
126. Suherman AL, Tanner EEL, Compton RG (2017) Recent developments in inorganic Hg^{2+} detection by voltammetry. TrAC-Trend Anal Chem 94:161–172. https://doi.org/10.1016/j.trac.2017.07.020
127. Zhao ZQ, Chen X, Yang Q, Liu JH, Huang XJ (2012) Beyond the selective adsorption of polypyrrole-reduced graphene oxide nanocomposite toward Hg^{2+}: ultra sensitive and selective sensing Pb^{2+} by stripping voltammetry. Electrochem Commun 23:21–24. https://doi.org/10.1016/j.elecom.2012.06.034
128. Palanisamy S, Thangavelu K, Chen SM, Velusamy V, Chang MH, Chen TW, Al-Hemaid FMA, Ali MA, Ramaraj SK (2017) Synthesis and characterization of polypyrrole decorated graphene/β-cyclodextrin composite for low level electrochemical detection of mercury (II) in water. Sensor Actuat B-Chem 243:888–894. https://doi.org/10.1016/j.snb.2016.12.068
129. Seenivasan R, Chang WJ, Gunasekaran S (2015) Highly sensitive detection and removal of lead ions in water using cysteine-functionalized graphene oxide/polypyrrole nanocomposite film electrode. ACS Appl Mater Interfaces 7(29):15935–15943. https://doi.org/10.1021/acsami.5b03904
130. Ruecha N, Rodthongkum N, Cate DM, Volckens J, Chailapakul O, Henry CS (2015) Sensitive electrochemical sensor using a graphene-polyaniline nanocomposite for simultaneous detection of Zn(II), Cd(II), and Pb(II). Anal Chim Acta 874:40–48. https://doi.org/10.1016/j.aca.2015.02.064
131. Promphet N, Rattanarat P, Rangkupan R, Chailapakul O, Rodthongkum N (2015) An electrochemical sensor based on graphene/polyaniline/polystyrene nanoporous fibers modified electrode for simultaneous determination of lead and cadmium. Sensor Actuat B-Chem 207:526–534. https://doi.org/10.1016/j.snb.2014.10.126
132. Nguyen TD, Dang TTH, Hoang T, Nguyen LH, Tran DL, Piro B, Pham MC (2016) One-step electrosynthesis of poly(1,5-diaminonaphthalene)/graphene nanocomposite as platform for lead detection in water. Electroanal 28(8):1907–1913. https://doi.org/10.1002/elan.201501075
133. Li J, Guo S, Zhai Y, Wang E (2009) High-sensitivity determination of lead and cadmium based on the Nafion-graphene composite film. Anal Chim Acta 649(2):196–201. https://doi.org/10.1016/j.aca.2009.07.030
134. Lee PM, Ng HW, Lim JD, Khun NW, Chen Z, Liu E (2016) Nanostructure restoration of thermally reduced graphene oxide electrode upon incorporation of Nafion for detection of trace heavy metals in aqueous solution. Electroanal 28(9):2037–2043. https://doi.org/10.1002/elan.201501099
135. Chaiyo S, Mehmeti E, Zagar K, Siangproh W, Chailapakul O, Kalcher K (2016) Electrochemical sensors for the simultaneous determination of zinc, cadmium and lead using a Nafion/ionic liquid/graphene composite modified screen-printed carbon electrode. Anal Chim Acta 918:26–34. https://doi.org/10.1016/j.aca.2016.03.026
136. Huang N, Zhang S, Yang L, Liu M, Li H, Zhang Y, Yao S (2015) Multifunctional electrochemical platforms based on the michael addition/schiff base reaction of polydopamine modified reduced graphene oxide: construction and application. ACS Appl Mater Interfaces 7(32):17935–17946. https://doi.org/10.1021/acsami.5b04597
137. Wang Y, Zhou L, Wang S, Li J, Tang J, Wang S, Wang Y (2016) Sensitive and selective detection of Hg^{2+} based on an electrochemical platform of PDDA functionalized rGO and glutaraldehyde cross-linked chitosan composite film. RSC Adv 6(74):69815–69821. https://doi.org/10.1039/c6ra10075a
138. Dong Y, Zhou Y, Ding Y, Chu X, Wang C (2014) Sensitive detection of Pb(ii) at gold nanoparticle/polyaniline/graphene modified electrode using differential pulse anodic stripping voltammetry. Anal Methods 6(23):9367–9374. https://doi.org/10.1039/c4ay01908c
139. Wang Z, Wang H, Zhang Z, Yang X, Liu G (2014) Sensitive electrochemical determination of trace cadmium on a stannum film/poly(p-aminobenzene sulfonic acid)/electrochemically reduced graphene composite modified electrode. Electrochim Acta 120:140–146. https://doi.org/10.1016/j.electacta.2013.12.068
140. Cui X, Fang X, Zhao H, Li Z, Ren H (2018) Fabrication of thiazole derivatives functionalized graphene decorated with fluorine, chlorine and iodine@SnO_2 nanoparticles for highly sensitive detection of heavy metal ions. Colloid Surfaces A 546:153–162. https://doi.org/10.1016/j.colsurfa.2018.03.004
141. 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 Actuat B-Chem 255:1220–1227. https://doi.org/10.1016/j.snb.2017.08.046
142. Dong S, Wang Z, Asif M, Wang H, Yu Y, Hu Y, Liu H, Xiao F (2017) Inkjet printing synthesis of sandwiched structured ionic liquid-carbon nanotube-graphene film: toward disposable electrode for sensitive heavy metal detection in environmental water samples. Ind Eng Chem Res 56(7):1696–1703. https://doi.org/10.1021/acs.iecr.6b04251
143. Wang Z, Li L, Liu E (2013) Graphene ultrathin film electrodes modified with bismuth nanoparticles and polyaniline porous layers for detection of lead and cadmium ions in acetate buffer solutions. Thin Solid Films 544:362–367. https://doi.org/10.1016/j.tsf.2013.02.098
144. Lu ZZ, Yang SL, Yang Q, Luo SL, Liu CB, Tang YH (2013) A glassy carbon electrode modified with graphene, gold

nanoparticles and chitosan for ultrasensitive determination of lead(II). Microchim Acta 180(7-8):555–562. https://doi.org/10.1007/s00604-013-0959-x

145. Zhou N, Li J, Chen H, Liao C, Chen L (2013) A functional graphene oxide-ionic liquid composites-gold nanoparticle sensing platform for ultrasensitive electrochemical detection of Hg^{2+}. Analyst 138(4):1091–1097. https://doi.org/10.1039/c2an36405k
146. Al-Hossainy AF, Abd-Elmageed AAI, Ibrahim ATA (2015) Synthesis, structural and optical properties of gold nanoparticle-graphene-selenocysteine composite bismuth ultrathin film electrode and its application to Pb(II) and Cd(II) determination. Arab J Chem. https://doi.org/10.1016/j.arabjc.2015.06.020
147. Ghanei-Motlagh M, Karami C, Taher MA, Hosseini-Nasab SJ (2016) Stripping voltammetric detection of copper ions using carbon paste electrode modified with aza-crown ether capped gold nanoparticles and reduced graphene oxide. RSC Adv 6(92):89167–89175. https://doi.org/10.1039/c6ra10267k
148. Dahaghin Z, Kilmartin PA, Mousavi HZ (2018) Simultaneous determination of lead(II) and cadmium(II) at a glassy carbon electrode modified with GO@Fe_3O_4 @benzothiazole-2-carboxaldehyde using square wave anodic stripping voltammetry. J Mol Liq 249:1125–1132. https://doi.org/10.1016/j.molliq.2017.11.114
149. Mejri A, Mars A, Elfil H, Hamzaoui AH (2018) Graphene nanosheets modified with curcumin-decorated manganese dioxide for ultrasensitive potentiometric sensing of mercury(II). fluoride and cyanide. Microchim Acta 185(12):529. https://doi.org/10.1007/s00604-018-3064-3
150. Martín-Yerga D, González-García MB, Costa-García A (2012) Use of nanohybrid materials as electrochemical transducers for mercury sensors. Sensor Actuat B-Chem 165(1):143–150. https://doi.org/10.1016/j.snb.2012.02.031
151. Cui L, Wu J, Ju H (2015) Synthesis of bismuth-nanoparticle-enriched nanoporous carbon on graphene for efficient electrochemical analysis of heavy-metal ions. Chem 21(32):11525–11530. https://doi.org/10.1002/chem.201500512
152. Yang F, He D, Zheng B, Xiao D, Wu L, Guo Y (2016) Self-assembled hybrids with xanthate functionalized carbon nanotubes and electro-exfoliating graphene sheets for electrochemical sensing of copper ions. J Electroanal Chem 767:100–107. https://doi.org/10.1016/j.jelechem.2016.01.005
153. Khan AAP, Khan A, Rahman MM, Asiri AM, Oves M (2016) Lead sensors development and antimicrobial activities based on graphene oxide/carbon nanotube/poly(O-toluidine) nanocomposite. Int J Biol Macromol 89:198–205. https://doi.org/10.1016/j.ijbiomac.2016.04.064
154. Yu L, Zhang Q, Yang B, Xu Q, Xu Q, Hu X (2018) Electrochemical sensor construction based on Nafion/calcium lignosulphonate functionalized porous graphene nanocomposite and its application for simultaneous detection of trace Pb^{2+} and Cd^{2+}. Sensor Actuat B-Chem 259:540–551. https://doi.org/10.1016/j.snb.2017.12.103
155. Gumpu MB, Veerapandian M, Krishnan UM, Rayappan JBB (2018) Amperometric determination of As(III) and Cd(II) using a platinum electrode modified with acetylcholinesterase, ruthenium(II)-tris(bipyridine) and graphene oxide. Microchim Acta 185(6):297. https://doi.org/10.1007/s00604-018-2822-6