Int. J. Electrochem. Sci., 12 **(2017)** 8622 – 8641, doi: 10.20964/2017.09.39

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Review

Recent Advances in Chemically Modified Electrodes, Microfabricated Devices and Injection Systems for the Electrochemical Detection of Heavy Metals: A review

Guo Zhao[1,2], *Hui Wang*[1,2], *Gang Liu*[1,2,*]

[1] Key Lab of Modern Precision Agriculture System Integration Research, Ministry of Education of China, China Agricultural University, Beijing 100083 P.R. China
[2] Key Lab of Agricultural Information Acquisition Technology, Ministry of Agricultural of China, China Agricultural University, Beijing 100083 P.R. China
[*]E-mail: pac@cau.edu.cn

Received: 24 May 2017 / *Accepted:* 5 July 2017 / *Published:* 13 August 2017

Heavy metal (HM) ion pollution has become a serious environmental problem in both developed and developing countries and will inevitably pose a threat to humans and ecosystems as a result of HM enrichment in organisms through the food chain. Therefore, HM detection and monitoring are currently attracting increasing attention. However, current analytical methods (based on spectroscopy) to detect HMs are often expensive and tedious and can only be performed by trained personnel. Electrochemical methods for the in situ detection of HMs are some of the most promising alternative methods, featuring easy adaptability, low power costs, short analytical times and high sensitivity. Chemically modified electrodes, which are based on combined electrochemical methods, have been widely used to offset the weaknesses of spectroscopic methods. In this paper, we review different types of materials that have been used to modify electrodes for HM detection. The material characteristics that improved the electrocatalytic activity of the modified surfaces are discussed. Additionally, recent trends in the detection of HMs using electrochemical methods with various types of microfabricated devices and injection analysis systems are highlighted. Finally, the challenges and future perspectives regarding HM determination in real samples using electrochemical methods are critically reviewed, and effective approaches are presented.

Keywords: Chemically modified electrodes, electrochemical detection, heavy metal ions, nanomaterials, microfabricated sensors, injection system

1. INTRODUCTION

Pollution by heavy metals (HMs) in the environment, such as in water and soil, is a serious problem because of the undegradability of HMs, which can cause them to accumulate in ecological systems over time and endanger human health through the food chain. The existence of HMs at trace levels in environmental samples threatens both ecological systems and human health [1, 2]. Most of the standard techniques for the trace-level analysis of HMs use large-scale equipment based in the laboratory, such as inductively coupled plasma mass spectrometry (ICP-MS) [3-7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8-13] and atomic absorption spectrometry (AAS) [14-17], which are all reliable and sensitive for the analysis of HMs. However, there are some disadvantages, including expensive hardware and their time-consuming and labourious operation. Moreover, only one type of HM can be analysed at one time using some of these laboratory-based analysis methods. Additionally, these techniques require specific preparation steps [18] before HM determination, which can limit their application in on-site detection. Therefore, developing an accurate, fast, simple method for the routine detection of HMs in samples is required.

Increasing attention has been paid to the use of electrochemical methods for HM detection because of the excellent characteristics of these methods for on-site detection, such as high sensitivity, low power requirements and short analytical times [19]. Electrochemical methods are considered to be some of the most effective methods for HM detection and are alternatives to spectroscopic methods [20, 21].

Compared with other electrochemical methods, stripping voltammetric analysis, which is regarded as one of the most effective ways to realize HM detection, has several excellent characteristics, such as easy operation, low cost and high sensitivity, and it can simultaneously detect several HMs [22].

Three-electrode systems that consist of a counter electrode (CE), a reference electrode (RE) and a working electrode (WE) are usually used to perform the electrochemical determination. The WE usually plays a key role in the electrochemical detection of HMs because the chemical reaction occurs on the WE surface. The specific recognition and accumulation of HMs can be realized by modifying the WE using different types of materials [23, 24]. Due to the good chemical and physical properties of the chemically modified electrodes, they are widely used for electrochemical HM detection and can dramatically improve the accumulation efficiency of HMs without interference compared with the traditional electrochemical methods [25]. The type of material used to modify the electrode is an important factor in producing reliable, high-performance electrochemical sensors. Thus, advances in new materials for modifying electrodes have a positive impact on analytical techniques. Moreover, using combinations of different types of materials to modify electrodes can further improve the analytical performance of the electrodes, including their sensitivity, stability and anti-interference performance.

Alternatively, with the development of microengineering technology, different types of microfabricated devices have been developed to improve the analytical performance of conventional electrodes and realize HM detection. Mass transport has been enhanced due to analyte diffusion on the electrode surface, which changes from linear to radial when the dimensions of the electrodes are reduced. Furthermore, compared with traditional macroelectrodes, microelectrodes have several excellent characteristics, such as enhanced signal-to-noise ratios, low capacitive currents, a decreased ohmic drop and high rates of mass transport [26-28]. With the development of injection analysis systems, the combination of an injection analysis system and an electrochemical technique presents an effective method for the rapid screening and on-site detection of HMs [29]. In this case, a sample plug tip is directly injected onto the surface of the working electrode, which is immersed in a large volume of blank solution in the injection analysis system [30, 31]. The combination of injection analysis systems and electrochemical techniques can effectively improve the precision and efficiency of electrochemical HM detection. Investigations are on-going for the development of sensing strategies, such as chemically modified electrodes, microfabricated devices and injection analysis systems, to realize the determination of trace HMs in various real samples, such as the entire environment and living systems. Therefore, the aim of the present review is to critically analyse methods for detection of HMs using various modified electrodes, microfabricated devices and injection analysis systems. This review also attempts to critically review available publications describing the materials for electrode modifications, available electrodes, their methodology and applications. Moreover, the aim of the present review is to provide a general overview regarding recent trends in the development of devices and systems for the determination of HMs that are based on microfabrication and injection analysis technologies.

2. CHEMICALLY MODIFIED ELECTRODES FOR THE DETECTION OF HMs

2.1. Carbon-based materials for modifying electrodes

Undoubtedly, the synthesis of nanomaterials and the understanding of their basic properties have substantially developed in the field of nanotechnology. Carbon nanotubes and graphene and its derivatives, which are carbon-based nanostructures, have attracted considerable interest regarding the modification of electrodes for electrochemical analysis because they can effectively improve the electrochemical performance of the electrodes [32, 33]. In the development of electrochemical sensors, nanomaterials are used to modify the surfaces of working electrodes of catalysts to catalyse the redox process occurring at the electrode surface [34]. Carbon-based nanomaterials have been regarded as exceptional candidates for improving electrochemical sensors [35-37] because of their excellent electrical, chemical and physical properties.

2.1.1 Carbon nanotubes

A nanotube is a nanometre-scale tube-like structure. Due to the extraordinary characteristics of carbon nanotubes (CNTs), they are regarded as a viable nanomaterial in electrochemistry and electrode modification. Since CNTs were invented in 1991, they have attracted significant attention for applications in various fields. Because of the extraordinary characteristics of CNTs, such as low electrode fouling, high electron-transfer rate, a large effective detection surface and high electrocatalytic activity [38], their potential applications have been investigated by numerous researchers in recent years [39], and these properties make them attractive as substrates for the detection of HMs [40-42].

Multiwalled carbon nanotubes (MWCNTs) are a type of CNT that exhibit excellent properties, such as good chemical stability, an increased electrode surface area, significant mechanical strength and a fast electron-transfer rate [43]. MWCNTs have attracted considerable attention in the field of material science for electrode modification and as an electrode component to improve the sensitivity and anti-interference properties of electrodes. Bagheri et al. [44] used a triphenylphosphine/MWCNT composite carbon ionic liquid electrode to simultaneously and sensitively detect Cd(II), Pb(II) and Hg(II) using square-wave anodic stripping voltammetry (SWASV). Mandil et al. [45] modified a screen-printed electrode with various brands of MWCNTs and bismuth films for the trace detection of Zn(II), Pb(II) and Cd(II). An engineered MWCNT material was synthesized by Li et al. [46] via doping with nitrogen and grafting thiol groups onto an activated MWCNT matrix to improve the detection sensitivity for lead and cadmium ions using SWASV. The functionalization of MWCNTs can effectively improve the selectivity and sensitivity of HM detection.

Huang et al. [47] developed a novel, facile, green method to fabricate an electrochemical sensor modified by a hybrid nanocomposite, which was composed of two-dimensional graphene oxide (GO) sheets and one-dimensional MWCNTs. Cd(II) and Pb(II) were simultaneously detected with differential pulse anodic stripping voltammetry (DPASV) measurements, and the detection limits of Pb(II) and Cd(II) were 0.2 and 0.1 μg L^{-1}, respectively.

Table 1. Comparison of the LODs of electrodes modified with carbon nanotubes for the detection of heavy metals.

Modified electrode	Method	Linear range	Detection limit	Reference
PPh3/MWCNTs/IL/CPE	SWASV	Pb(II) Cd(II) Hg(II) 0.1-150.0 nM	Pb(II) Cd(II) Hg(II) 0.06 nM 0.092 nM 0.074 nM	44
BiF/MWCNT-Nafion/SPE	SWASV	Pb(II) Cd(II) Zn(II) 2.4-19.2 nM	Pb(II) Cd(II) Zn(II) 0.7 nM 1.5 nM 11.1 nM	45
Engineered MWCNTs/GCE	SWASV	Pb(II) Cd(II) 2-50 μg/L	Pb(II) Cd(II) 0.3 μg/L 0.4 μg/L	46
Bi/G/MWCNTs/GCE	DPASV	Pb(II) Cd(II) 0.5-30 μg/L	Pb(II) Cd(II) 0.2 μg/L 0.1 μg/L	47
Bi/CMWCNTs-β-CDNafion/GCE	SWASV	Pb(II) Cd(II) 1-100 μg/L	Pb(II) Cd(II) 0.21 μg/L 0.13 μg/L	48
Bi/MWCNT-EBP-NA/GCE	SWASV	Pb(II) Cd(II) 1-50 μg/L	Pb(II) Cd(II) 0.08 μg/L 0.06 μg/L	49
Sn/MWCNTs-NaDBS/GCE	DPASV	Zn(II) Cd(II) 5-100 μg/L	Zn(II) Cd(II) 0.9 μg/L 0.8 μg/L	50

According to the desired properties of the surfaces of various modified electrodes, the effect of CNTs in diverse composites is different. For example, the nanocomposite of carboxylic-acid-functionalized MWCNT–β-cyclodextrin–Nafion (CMWCNTs–β-CD–Nafion) was used to modify the glassy carbon electrode (GCE) surface to simultaneously detect Pb(II) and Cd(II). The direct electron transfer of the electrode modified with CMWCNTs–β-CD–Nafion was significantly enhanced due to an efficient electroconducting tunnel [48].

To improve the detection performance, different types of polymers have been used to disperse MWCNTs, such as sodium dodecyl benzene sulfonate, polyaniline and Nafion, by exploiting the surface wrapping effect [49, 50]. In recent years, Nafion has been widely used to modify the electrode surface due to its attractive antifouling, ion-exchange and permselective properties [51], and MWCNTs can be dispersed by adding Nafion. Moreover, the GCE modified by the dispersion of MWCNTs and Nafion was used to improve the HM sensing performance in the presence of surfactants, including Triton X-100 and sodium dodecyl sulfate (SDS) [52]. A comparison of the detection limit and linear range data are listed in Table 1, which shows different kind of electrodes for the HMs detection.

2.1.2 Graphene and its derivatives

Graphene is a type of nanomaterial with a 2D structure that consists of a single layer of carbon atoms. Graphene is a popular nanomaterial that is widely used to modify different types of electrodes for electrochemical analysis due to its remarkable characteristics, such as high tensile strength and electrical conductivity. Different chemically modified electrodes have been developed by introducing various moieties onto graphene to improve the HM detection performance [53].

A solid-state carbon diffusion method was used by Wang et al. [54] to synthesize graphene thin films by treating nickel–carbon mixed layers that were thermally co-sputtered onto silicon substrates. The working electrodes were modified by Bi/graphene thin films and then used to detect trace amounts of Cu(II), Cd(II) and Pb(II) in acetate buffer solutions [54].

A sensitive, facile, disposable sensing platform was introduced by Huangfu et al. [55] to detect trace levels of Pb(II) and Cd(II). A screen-printed electrode (SPE) was modified by a graphene-poly(sodium 4-styrenesulfonate) composite film (GR/PSS/Bi/SPE) to fabricate this sensing platform. The sensitivity and linearity of GR/PSS/Bi/SPE was improved compared with the bare SPE by providing more absorption sites because of the functionalization of graphene with negatively charged PSS. The detection limits of the GR/PSS/Bi/SPE were determined to be 0.042 μg/L and 0.089 μg/L for Cd(II) and Pb(II), respectively, in the linear range of 0.5 to 120 μg/L [55].

A ZnO–reduced graphene oxide (ZnO–RGO)-composite-modified GCE developed by Lu et al. [56] was successfully used to detect Pb^{2+} in water samples. The electrospinning $Zn(Ac)_2$–polyacrylonitrile–polyvinyl pyrrolidone precursor was used to prepare ZnO nanotubes, and then the ZnO–RGO composite was obtained by mixing the reduced graphene oxide (RGO) with the ZnO nanotubes [56]. Activated graphene (AG) was used by Lee et al. [57] to modify a Bi film GCE that was plated in situ for the trace detection of Pb(II), Cd(II) and Zn(II) using DPASV. The chemical activation of GO was used to prepare the AG, and pores were created using KOH [57].

Potassium permanganate ($KMnO_4$) and concentrated sulfuric acid (H_2SO_4) were used to simultaneously oxidize and exfoliate graphite for the synthesis of graphite oxide using the Hummers method [58]. Polar oxygen functional groups, such as hydroxyls, carbonyls and epoxies, were introduced via an acid treatment to create hydrophilic graphite oxide sheets, i.e., GO. These GO sheets were easy to disperse with numerous solvents and were also soluble in water using mild sonication.

Subsequently, several methods have been used to reduce the GO to graphene, including thermal reduction, electrochemical reduction [59] and the addition of reducing agents [60]. To immobilize the GO on the electrode surface, electrochemical reduction can be conducted using reducing scans and a sweeping potential ranging from 0 to -1.5 V, which may be the one of the most convenient methods to modify electrodes with RGO [59].

Table 2. Comparison of the LODs of electrodes modified with graphene and its derivatives for the detection of heavy metals.

Modified electrode	Method	Linear range (μg/L)	Detection limit (μg/L)	Reference
AG–NA/GCE	DPASV	Pb(II) Cd(II) Zn(II) 5-100	Pb(II) Cd(II) Zn(II) 0.05 0.07 0.57	[57]
NH_2–GO/AM	SWASV	As(III) 1-10	As(III) 0.162	[66]
L-cys/GR–CS/GCE	DPASV	Pb(II) Cd(II) 0.56-67.2	Pb(II) Cd(II) 0.12 0.45	[67]
ERGO–TH–MES/GCE	SWASV	Pb(II) Cd(II) 1-40	Pb(II) Cd(II) 0.05 0.1	[68]
Nafion–G/GCE	DPASV	Pb(II) Cd(II) 0.5-50 1.5-30	Pb(II) Cd(II) 0.02 0.02	[69]
GO/MWCNTs/Nafion/GCE	DPASV	Pb(II) Cd(II) 0.5-30	Pb(II) Cd(II) 0.2 0.1	[47]
GO/DTT/SPCE	SWASV	Cd(II) Pb(II) Cu(II) Hg(II) 1-2.5	Cd(II) Pb(II) Cu(II) Hg(II) 7.1 1.9 0.4 0.7	[64]
GR/PSS/Bi/SPE	DPASV	Cd(II) Pb(II) 0.5-120	Cd(II) Pb(II) 0.042 0.089	[55]
Bi–GCPE	SWASV	Cd(II) Pb(II) 0.1-50	Cd(II) Pb(II) 0.07 0.04	[70]
Hg(II)/GO/GCE	SWASV	Pb(II) 0.005-0.07 and 0.1-10	Pb(II) 0.00013	[71]
Bi/GR–β-CD–Nafion/GCE	SWASV	Cd(II) 1-500 and 800-2000	Cd(II) 0.3	[72]

Electrodes modified by the RGO or RGO composites combined with other materials have numerous excellent characteristics, such as improved resolution and selectivity, and they have therefore been widely used to modify electrodes to detect HMs with satisfactory results [60-62]. An electrochemical sensing platform was constructed that used the RGO composite and tin nanoparticles (SnNPs) to modify a glassy carbon sheet (GCS), i.e., G-Sn/GCS. The G-Sn/GCS was developed using constant potential electroreduction after drop-casting a composite of RGO and SnNPs. The obtained electrochemical sensing platform was successfully used for the trace detection of HMs with detection limits of 0.52 nM for Cu(II), 0.60 nM for Pb(II) and 0.63 nM for Cd(II) in the linear range from 10 nM to 100 nM [63]. For the electrode modification, diaminoterthiophene was used by Choi et al. [64] to dope GO to construct a disposable sensor, and this disposable sensor was successfully used to simultaneously detect Hg(II), Cu(II), Cd(II) and Pb(II). Xiong et al. [65] reported an RGO–Fe_3O_4-nanocomposite-modified electrode using a one-pot and simple synthesis method, and the Fe_3O_4 was small in size. Under optimized conditions, the RGO–Fe_3O_4-modified GCE was used for the individual and simultaneous determination of Hg(II), Cd(II) and Pb(II) using SWASV. The experimental results show that the proposed modified electrode can provide satisfactory accuracy for the analysis and detection of HMs. A comparison of the detection limit and linear range data given in Table 2 suggests that the electrochemical sensor, which is based on the Bi/graphene-poly(sodium 4-styrenesulfonate)-nanocomposite-modified screen-printed electrode, yields better results for the simultaneous trace analysis of Pb(II) and Cd(II).

2.2. Nanoparticle-based materials for modifying electrodes

Compared with bulk materials, nanoparticles (NPs) have several remarkable electronic, physical and chemical properties [73-91]. The nature of the material used for synthesis plays an important role in the properties of NPs. Generally, several stabilizers have been used to prepare the NPs using the chemical reduction of metal salts. The stability and solubility of the NPs can be improved by these stabilizers, which are attached to the NP surface. The presence of NPs in the modified material is sensitive to the change on the electrode surface. The use of NPs in the modification of electrodes has numerous advantages, such as controllable functionalization of the desired groups, increased mass transport rates, better control of the NP surface and high surface area, which can enhance the electron kinetics of the electrode.

In recent years, metal NPs (MNPs) have attracted significant interest in the modification of electrodes for the analysis of HMs, such as gold [73-86], silver [87, 88], tin [63] and Fe_3O_4 [89-91] NPs, which have unusual chemical and physical properties. The modified electrodes based on MNPs show high sensitivity towards the detection of HMs compared with bare electrodes. Additionally, MNP-based modified electrodes can help minimize overlapping target analyte signals, which are caused by similar redox potentials, thus providing ideal peak-to-peak separations. This paper describes several examples of MNP-based electrodes to identify and analyse HMs.

Laffont et al. [73] reported a GCE modified with gold NPs (AuNPs/GCE) to develop an electrochemical sensor for Hg(II) using the SWASV method and a chloride desorption step. Under optimized conditions, the experimental results show that the chloride desorption step can effectively improve the analysis performance of the gold NP modified electrode for the trace detection of Hg(II) in the analysis procedure. In another example, Hezard et al. [79] used a AuNPs/GCE to detect trace amounts of Hg(II) using SWASV. A detection limit of 0.42 nM for Hg(II) was obtained in the linear range from 0.64 to 4.00 nM under optimized conditions. In addition, a AuNPs/GCE was introduced by Kamyabi et al. [81] to detect trace levels of As(III) in water samples using ASV and the detection limit of the AuNPs/GCE was calculated to be 0.18 μg/L. A silver-NP-deposited GCE was developed by

Sivasubramanian et al. [87] to detect Pb(II) in the picomolar concentration range using SWASV. An electrode modified with bismuth–silver bimetallic NPs was developed by van der Horst et al. [88] for the detection of Pd, Pt and Rh in the presence of dimethylglyoxime (DMG). This was used to construct a nanosensor, and an acetate buffer solution (0.2 M, pH 4.7) was used as the supporting electrolyte. The stripping peak current signal of the differential pulse adsorptive was linear with Pd, Pt and Rh, in the range of 0.2 to 1.0 ng/L (n = 3) (deposition time: 60 s). The detection limits for Pd, Pt and Rh were 0.19 ng/L, 0.20 ng/L and 0.22 ng/L, respectively. Lee et al. [63] introduced a SnNP-modified RGO glassy carbon sheet (GCS) (G-Sn/GCS) using an electrodeposition method to simultaneously detect Cu(II), Pb(II) and Cd(II) at trace levels. A highly linear response was obtained in the range of 10 nM to 100 nM using G-Sn/GCS for the determination of Cu(II), Pb(II) and Cd(II), and their limits of detection were 0.52 nM, 0.60 nM and 0.63 nM, respectively.

Recently, magnetic magnetite (Fe_3O_4) NPs has attracted considerable interest for the identification and removal of HMs due to their advantages and unique properties [92-95]. An impinging stream-rotating packed bed reactor was used by Fan et al. [89] to continuously prepare Fe_3O_4 NPs, which were used to modify an electrode to detect Cd(II), Hg(II), Pb(II) and Cu(II). SWASV was utilized to evaluate the electrochemical characteristics of the Fe_3O_4-NP-modified electrode for HM detection. Under optimized conditions, the experimental results demonstrated that this electrode could satisfy the requirements for the individual detection of Cd(II), Hg(II), Pb(II) and Cu(II). A facile surfactant-free hydrothermal method was successfully used by Li et al. [90] to prepare the Fe_3O_4 with a nanoplate-stacked structure. The electrochemical characteristics of the proposed nanoplate-stacked-Fe_3O_4-modified electrode for detecting Zn(II), Cu(II), Cd(II), Hg(II) and Pb(II) were studied using SWASV. The results demonstrated that the nanoplate-stacked-Fe_3O_4-modified electrode could be used for the trace detection of Zn(II), Cu(II), Cd(II), Hg(II) and Pb(II). In other work, Zhou et al. [91] reported a Fe_3O_4-chitosan-NP-modified electrode for the determination of Cd(II), Cu(II), Hg(II) and Pb(II) using SWASV. In experiments, this electrode displayed a dramatic electrochemical response towards Cd(II), Cu(II), Hg(II) and Pb(II).

In addition, two thoria (ThO_2)-NP-modified carbon paste electrodes were developed by Pereira et al. [96] using the ASV method to sensitively detect the total inorganic arsenic in water samples. The results confirm that thoria-based NP electrodes could be used to directly detect inorganic arsenic in acidic solutions.

AuNPs, which are used for electrode modification in combination with other materials, have been the subject of numerous investigations to detect HMs. An AuNP-array-modified gold electrode was developed by Gao et al. [74] for the simultaneous determination of Pb^{2+}, Cu^{2+} and Hg^{2+} in the presence of macromolecule contaminants using SWASV. The modified electrode was obtained using the following procedure. First, the gold electrode was modified with a AuNP array using electrodeposition, and then a mercaptoethanesulfonate (MES) monolayer was coated onto the electrode surface. The results demonstrated that the modified electrode could significantly improve the sensitivity compared with a bare electrode.

The electrodes modified with composites consisting of AuNPs and other materials, including RGO decorated with AuNPs [75], DNAzyme and ordered mesoporous carbon–AuNPs [78], p-aminothiophenol/AuNP-decorated $HxTiS_2$ nanosheets [82], AuNPs grown on carbon nanofibres [88], AuNP–graphene–selenocysteine composites [76] and Au–Cu bimetallic NPs [97], were used to detect various types of HMs. A comparison of the detection limit and linear range data are listed in Table 3, which shows different kind of modified electrodes for the HMs detection.

Table 3. Comparison of the LODs of electrodes modified with nanoparticle-based materials for the detection of heavy metals.

Modified electrode	Method	Linear range	Detection limit	Reference
AuNPs–GC electrode	SWASV	Hg(II) 0.4-6 nM	Hg(II) 80 pM	73
Au-GN-SeCys/GCE	SWASV	Pb(II) Cd(II) 1-100 μg/L	Pb(II) Cd(II) 0.05 μg/L 0.08 μg/L	76
AuNPs–GCE	SWASV	Hg(II) 0.64-4 nM	Hg(II) 0.42 nM	79
AuNPs/GCE	SWASV	As(III) 0.5-600 μg/L	As(III) 0.18 μg/L	81
Silver nanoparticles/GCE	SWASV	Pb(II) 1-10 μM	Pb(II) 10 pM	87
Bi-AgF/GCE	DPASV	Pb(II) Pt(II) Rh(III) 0.2-1 ng/L	Pb(II) Pt(II) Rh(III) 0.19 ng/L 0.2 ng/L 0.22 ng/L	88
G-Sn/GCS	DPASV	Pb(II) Pb(II) Cu(II) 10-100 nM	Pb(II) Pb(II) Cu(II) 0.63 nM 0.6 nM 0.52 nM	63
Fe_3O_4/GCE	SWASV	Pb(II) 0.3-1.3 μM	Pb(II) 0.119 μM	89
Bi-AgF/GCE	DPASV	Pb(II) Cu(II) Hg(II) 1-100 μg/L	Pb(II) Cu(II) Hg(II) 0.16 μg/L 0.15 μg/L 0.14 μg/L	74
Au–Cu bimetallic nanoparticles/GCE	SWASV	As(III) 10-100 μg/L	As(III) 2.09 μg/L	97

2.3. Polymer-based materials for modifying electrodes

Several organic polymers, including chelating and conducting polymers, have been used to fabricate electrochemical sensors to detect HMs. The two types of modification method involving polymers are the post-modification of polymerized products on electrodes and copolymerization of monomers. The conductive/electroactive polymers most commonly used to modify electrodes to detect HMs include polyaniline (PANI) [98-103], poly(*p*-aminobenzene sulfonic acid) (poly(*p*-ABSA)) [104, 105], polypyrrole (PPy) [106, 107], poly(sodium 4-styrenesulfonate) (PSS) [108], poly(4-vinylpyridine) (PVP) [109], poly-**L**-lysine (PLL) [110], poly(pyrocatechol violet) (poly(PCV)) [111], poly(allylamine hydrochloride) (PAH) [112], poly(1,8-diaminonaphthalene) (Poly (1,8-DAN)) [113] and poly(2,5-dimercapto-1,3,4-thiadiazole) (PDMcT) [114]. The use of polymer nanocomposites has been motivated by the growing number of scientists exploring “active states of polymer nanocomposites” who have been inspired by the ability of polymer nanocomposites to promote electron transfer in electrochemical reactions and by their large surface area and high electrical conductivity, which lead to improved selectivity and sensitivity and lower detection limits [98-114].

Due to the excellent characteristics of PANI, such as good environmental stability, high conductivity and facile preparation, it has been widely used for electrode modification using an electrochemical method to construct a porous structure [115, 116]. Wang et al. [100] reported a graphene ultrathin-film electrode modified with a bismuth NP and polyaniline porous layer, which was used to detect Cd(II) and Pb(II) using SWASV in acetate buffer solutions. Chen et al. [101] modified a GCE with Bi, Nafion and tethered polyaniline (PANI)–2-mercaptoethanesulfonate (MES) (Bi/Nafion/PANI–MES/GCE) to improve the Cd(II) and Pb(II) detection sensitivity. The results indicate that the Bi/Nafion/PANI–MES/GCE exhibited better detection performance than the Bi/Nafion/PANI/GCE and Bi/Nafion/GCE. Promphet et al. [103] developed a screen-printed carbon electrode (SPCE) that was modified with graphene/polyaniline/polystyrene (G/PANI/PS) nanoporous fibres using the electrospinning fabrication method to construct an electrochemical sensor for the simultaneous analysis of Cd(II) and Pb(II). In another example, a GCE modified with Nafion, poly(2,5-dimercapto-1,3,4-thiadiazole) (PDMcT) and MWCNTs was developed by He et al. [114] to detect Cd and Pb. Under optimized conditions, the stripping peak current was linear for concentrations of HMs in the range of 0.05 to 20 μg/L for Cd(II) and 0.1 to 22 μg/L for Pb(II). The detection limits were 0.05 μg/L for Pb(II) and 0.03 μg/L for Cd(II). The experimental results demonstrated that the proposed modified electrode satisfied the requirements for the detection of Pb(II) and Cd(II) in water samples. A graphene–polyaniline (GR/PANI)-nanocomposite-modified electrode was fabricated by Ruecha et al. [102] to construct an electrochemical sensor using reverse-phase polymerization in the presence of polyvinylpyrrolidone (PVP) for the simultaneous trace-level determination of Pb(II), Cd(II) and Zn(II). The relationship between the metal ion concentration and the anodic current was linear in the range of 1 to 300 mg/L. The limits of detection were 0.1 mg/L, 1.0 mg/L and 0.1 mg/L for Cd(II), Zn(II) and Pb(II), respectively.

Due to its good biocompatibility, water solubility and redox activity, polypyrrole is one of the most commonly used electrode modifiers for the electrochemical analysis of various HMs. A polypyrrole membrane functionalized by an iminodiacetic acid (IDA-PPy) that contains carboxyl groups was utilized to modify a carbon paste electrode (CPE) that was developed by Alex Joseph et al. [107] to fabricate an electrochemical sensor for the trace determination of Cd(II) using DPASV. In another case, a GCE modified with overoxidized 2-mercaptoethanesulfonate (MES)-tethered polypyrrole, Nafion and Bi was developed by Chen et al. [106] to detect Pb(II) and Cd(II). Under optimum conditions, the linear range was from 0.05 to 35 μg/L for Pb(II) and 0.1 to 25 μg/L for Cd(II), and the limits of detection (S/N = 3) were 0.03 μg/L for Pb(II)and 0.04μg/L for Cd(II).

Poly(*p*-aminobenzene sulfonic acid) is a widely used polymer for the modification of electrodes to detect HMs. A novel sensor based on a GCE modified with a bismuth/poly(*p*-aminobenzene sulfonic acid) (Bi/poly(*p*-ABSA)) film was developed by Wu et al. [104] for the simultaneous determination of Zn(II), Pb(II) and Cd(II) using DPASV. Under optimized conditions, the relationship between the stripping peak current and HM concentration was linear in the range of 1.0 to 110.0 μg/L for Zn(II) and Cd(II) and in the range of 1.0 to 130.0 μg/L for Pb(II). The limits of detection for Zn(II), Cd(II) and Pb(II) were 0.62 μg/L, 0.63 μg/L and 0.80 μg/L, respectively. Wang et al. [105] reported GCE modified with a stannum film/poly(p-aminobenzene sulfonic acid)/graphene composite using the electrodeposition of exfoliated GO and the electropolymerization of *p*-

aminobenzene sulfonic acid (*p*-ABSA). This modified electrode was used to detect trace levels of Cd(II) using SWASV.

Due to the low diffusion coefficient on the surface of modified electrodes, sluggish electron kinetics were obtained on the polymer-modified electrodes. Therefore, ion exchange polymers have been investigated to rectify this issue. A poly(sodium 4-styrenesulfonate)-modified mercury film electrode was introduced by Monterroso et al. [108] to directly determine trace-level HMs using SWASV. Moreover, the permselectivity and ion-exchange properties of the modified electrode were investigated. In other work by Jia et al. [117], Nafion and poly(sodium 4-styrenesulfonate) were developed to produce a composite to modify an electrode for the simultaneous determination of Pb(II) and Cd(II), and the composite performance was also investigated. Under optimized conditions, the detection limits were 93 ng/L and 71 ng/L for Pb(II) and Cd(II), respectively, with a deposition time of 10 min. As shown in Table 4, the detection limit and linear range of different kind of modified electrodes for the HMs detection were compared.

Table 4. Comparison of the LODs of electrodes modified with polymer-based materials for the detection of heavy metals.

Modified electrode	Method	Linear range	Detection limit	Reference
Bi/PANI/graphene electrode	SWASV	pb(II) 0.1-1.1 μM	Pb(II) 0.33 nM	100
Bi/Nafion/PANI-MES/GCE	SWASV	Pb(II) Cd(II) 1-30 μg/L 1-20 μg/L	Pb(II) Cd(II) 0.05 μg/L 0.04 μg/L	101
G/PANI/PS nanoporous fibe/SPCE	SWASV	Pb(II) Cd(II) 10-500 μg/L	Pb(II) Cd(II) 3.30 μg/L 4.43μg/L	103
Bi/Nafion/ PDMcT-MWCNTs/GCE	DPASV	Pb(II) Cd(II) 0.1-22 μg/L 0.05-20 μg/L	Pb(II) Cd(II) 0.03 μg/L 0.05μg/L	114
G/PANI nanocomposite-modified electrode	SWASV	Pb(II) Cd(II) Zn(II) 1-300 μg/L	Pb(II) Cd(II) Zn(II) 0.1 μg/L 0.1 μg/L 1 μg/L	102
IDA-PPy/CPE	DPASV	Pb(II) 5 nM-1 μM	Pb(II) 9.6 nM	107
Bi/Nafion/OPPy–MES/GCE	SWASV	Pb(II) Cd(II) 0.05-35 μg/L 0.1-25 μg/L	Pb(II) Cd(II) 0.03 μg/L 0.04 μg/L	106
Bi/poly(p-ABSA)/GCE	SWASV	Pb(II) Cd(II) Zn(II) 1-130 μg/L 1-110 μg/L 1-110 μg/L	Pb(II) Cd(II) Zn(II) 0.8 μg/L 0.63 μg/L 0.62 μg/L	104
poly(p-ABSA)/GR/GCE	DPASV	Cd(II) 1-70 μg/L	Cd(II) 0.05 μg/L	105
PSS-TMFE	SWASV	Pb(II) 100 μM-2 M	Pb(II) 0.26 nM	108
GC/NA-PSS/BiFE	SWASV	Pb(II) Cd(II) 1-50 μg/L	Pb(II) Cd(II) 93 ng/L 71 ng/L	117

2.4. Ionic-liquid-based materials for modifying electrodes

Ionic liquids (ILs) are commonly used materials with great promise in the area of electrochemistry. ILs have been widely used as electrode modifiers and electrochemical solvents [118, 119] in the fabrication of electrochemical sensors for electrochemical analysis and exhibit satisfactory analysis performance because of their excellent characteristics, including wide electrochemical windows, low volatility, good intrinsic conductivity, thermal stability and high viscosity [120-123].

Table 5. Comparison of the LODs of electrodes modified with ionic-liquid-based materials for the detection of heavy metals.

Modified electrode	Method	Linear range	Detection limit	Reference
BiF/N/IL/G/SPCE	SWASV	Pb(II) Cd(II) Zn(II) 0.1-100 ng/L	Pb(II) Cd(II) Zn(II) 0.06 ng/L 0.06 ng/L 0.09 ng/mL	124
IL/Gr/CPE	SWASV	Ti(Ⅰ) Pb(II) Hg(II) 1.25 μM-200 μM	Ti(Ⅰ) Pb(II) Hg(II) 0.357 μM 0.45 μM 0.386 μM	125
HAP-CILE	SWASV	Pb(II) Cd(II) 1 μM-100 μM	Pb(II) Cd(II) 0.2 μM 0.5 μM	126
IL-SPE	SWASV	Pb(II) Cd(II) 1-80 μg/L	Pb(II) Cd(II) 0.1 μg/L 0.08μg/L	127

A Nafion/IL/graphene-composite-modified screen-printed carbon electrode was developed by Chaiyo et al. [124] to construct a novel electrochemical sensor that was highly sensitive and both easy and inexpensive to fabricate. This disposable electrode was capable of the trace analysis of Pb(II), Cd(II) and Zn(II) due to its fast electron transfer kinetics and excellent conductivity. Furthermore, a new composite electrode was fabricated by Bagheri et al. [125] using graphene, 1-n-octylpyridinum hexafluorophosphate (OPFP) and [$2,4\text{-}Cl_2C_6H_3C(O)CHPPh_3$] for the simultaneous detection of Hg(II), Pb(II) and Tl(I) at trace levels using SWASV. Li et al. [126] reported a hydroxyapatite-modified carbon IL electrode with the IL N-octylpyridium hexafluorophosphate (OPPF6) as the binder for the simultaneous detection of Cd(II) and Pb(II) at trace levels. The linear range of the modified electrode was 1×10^{-9} mol/L to 1×10^{-7} mol/L for both Cd(II) and Pb(II), and the corresponding limits of detection were 2×10^{-10} mol/L and 5×10^{-10} mol/L, respectively.

An IL-doped SPE was modified with RGO using electrochemical reduction to construct a disposable electrochemical sensor for the determination of Cd(II) and Pb(II) [127]. Under optimized conditions, the stripping peak current exhibited a linear relationship with the concentration of both Cd(II) and Pb(II) in the range of 1.0 to 80.0 μg/L, and the corresponding detection limits were 0.10 μg/L and 0.08 μg/L, respectively. The results demonstrated that this modified electrode could detect trace levels of Cd(II) and Pb(II) due to the electrode's dramatic physical and chemical properties, including a wide electrochemical window, high sensitivity and stability, good ionic and electronic conductivity and a large surface area. A comparison of the detection limit and linear range data are listed in Table 5, which shows different kind of electrodes modified with ionic-liquid-based materials for the detection of HMs.

3. MICROFABRICATED DEVICES FOR THE DETECTION OF HMs

In recent years, numerous researchers have reported microfabricated sensors and the application of new electrode materials, structures and module packages [8,9]. The microfabricated sensors exhibit several excellent characteristics, such as good uniformity, low cost, high signal-to-noise ratio and increased mass transport, compared with traditional electrodes [10]. Thus, different types of microfabricated sensors have been developed to achieve the quantitative analysis of HMs [128-135]. Because of the development of miniaturized technologies and the significant advantages of microfabricated sensors, such as good reliability, easy operation and high throughput [136, 137], their application has attracted considerable interest in HM detection.

An on-chip device based on a microfabricated three-electrode system was developed by Zhang et al. [130] to realize the simultaneous determination of Pb(II) and Cd(II) utilizing SWASV integrated with a vibration motor. The reference electrode was surrounded by a gold electrode with a U-shaped structure, which was used as the counter electrode to provide shielding from potential electromagnetic influence. A cover layer produced by master-mould-based polydimethylsiloxane (PDMS) was bonded onto the glass substrate to organize an integrated measurement cell and a compact module. Moreover, a coin-sized vibration motor was installed in the module to provide an alternate vibration function for stirring. The detection of Pb(II) and Cd(II) was conducted using differential pulse stripping voltammetry (DPSV). A linear response for both Pb(II) and Cd(II) was observed in the range of 10 μg/L to 80 μg/L. The limits of detection were 1.2 μg/L for Pb(II) and 0.7μg/L for Cd(II), with a deposition time of 325 s without vibration. With vibration, the detection limits for Pb(II) and Cd(II) were 0.25 μg/L and 0.11 μg/L, respectively.

In similar work reported by Am Jang's group [138], a polymer lab chip sensor based on bismuth was developed for the in situ detection of Cd(II) utilizing SWASV. The results demonstrated that this electrochemical lab chip sensor has potential for use in environmental monitoring applications because of its numerous advantages, including its ease of use, the portability of the analysis system and its low cost.

In another study, densely packed iridium ultramicroelectrode arrays (UMEAs) were developed by Xudong Xie to detect trace levels of Cd(II) and Pb(II) in water samples. Silicon technology was used to manufacture the designed UMEAs, which consisted of four separate working electrode arrays. Each array contained 1012 disc-shaped iridium ultramicroelectrodes (UMEs), and the diameter and interelectrode distance were 1.8 μm and 25 μm, respectively. The ultramicroelectrode array chip was successfully used to analyse Cd(II) and Pb(II) in aqueous solution [139] due to its high signal-to-noise ratio and mass transport rate.

Silva et al. [140] reported a microsensor based on a mercury-electroplated-iridium microelectrode array. The microsensor was successfully used to detect Cu(II), Cd(II) and Pb(II) at trace levels using SWASV. An array (42×42) of 6-μm-diameter iridium microdiscs was used to construct the proposed sensors, which were produced using microfabrication processing techniques.

4. INJECTION ANALYSIS SYSTEMS FOR THE DETECTION OF HMs

Anodic stripping voltammetry (ASV) is one of the most commonly used voltammetric techniques for the trace analysis of HMs [1]. The combination of on-line systems and ASV is an effective method for on-site analysis considering the cost efficiency, precision, speed and degree of automation of the system. Thus, numerous on-line systems based on ASV and continuous flow techniques [141-144] have been reported, such as the flow-injection analysis (FIA) methodology [145-149], which has been used most often for these systems. In addition to FIA, sequential-injection analysis (SIA) methodologies have been developed to resolve the issues of the existing methods [150, 151]. Additionally, SIA is an on-line analysis technique that can be used for detection in real samples and for sample pretreatment. In recent years, the application of SIA for both physical handling and chemical pretreatment of the real samples has been further developed to satisfy the multi-step and complex operational requirements of sample handling, in contrast with earlier SIA investigations with simple determinations [152, 153].

Kefala et al. [154] reported a bismuth film electrode modified with a polymer to realize the simultaneous on-line detection of Zn(II), Pb(II) and Cd(II) utilizing SWASV in combination with the SIA system. The experimental results showed that the combination of the bismuth film electrode modified with a polymer and the SIA method met the requirements for the on-line analysis of HMs at trace levels. Moreover, this system is a sensitive, environmentally friendly platform for on-line analysis and can also decrease the interference from surface-active compounds.

A thermostated electrochemical flow cell (EFC), which was designed by dos Santos et al. [155] to improve the efficiency and reduce the cost of sample handing, was combined with the bismuth-film-modified SPE. An analysis platform consisting of an EFC and the modified SPE was used to simultaneously detect Pb(II) and Cd(II) using SWASV in several tap water and wastewater samples. Moreover, the flow-batch analysis (FBA) approach was developed to automate the procedure of this analysis platform.

In work by Punrat et al. [156], a sequential injection system, a computer-controlled system and an electrochemical detector were used to construct an automated analysis system for the determination of Hg(II) using SWASV [156]. This automated analysis system, which was highly sensitive, convenient and cost-efficient, could quantitatively analyse Hg(II).

5. CHALLENGES IN REAL SAMPLE ANALYSIS

Currently, HM contamination is considered one of the main environmental problems, particularly in water and soil. ASV, one of the most commonly used electrochemical techniques, has attracted considerable attention for HM detection because of its efficiency and ease of use. Several investigations have been reported on new materials and electrode modifications to realize highly sensitive HM detection using ASV [157-171]. The application of the chemically modified electrodes can effectively improve the electrode sensitivity. However, the electrochemical determination of HMs in real soil and water samples faces several challenges because of the interaction effects amongst the HMs and an unknown matrix effect in real samples. Besides the major interferences that cause interaction effects amongst HMs, other interferences exist, which may decrease or increase the stripping responses of target HMs. Therefore, the detection results for target HMs in real samples may be inconsistent with the actual values. Electrochemical detection methods have been developed to reduce the effect of the matrix on real samples, including sample preparation before detection and the application of multiple standard addition methods. Moreover, chemometrics methods have been used to validate the ability of the electrochemical methods to determine trace levels of HMs in real samples.

6. CONCLUSION AND FUTURE PERSPECTIVES

This review summarizes carbon-based, NP-based, polymer-based, and IL-based materials for modified electrodes and microfabricated devices and injection systems to detect HMs using electrochemical techniques. The electrodes modified by these materials exhibited numerous remarkable electrochemical properties, such as high sensitivity, stability and anti-interference properties, to improve the HM-detection performance of electrochemical techniques. Applying these advancements in chemically modified electrodes in commercial applications to solve real environmental problems is highly desirable. However, several fabrication procedures for the modified electrodes are complicated and tedious, which restrict their commercial adoption and further application in practise. To successfully commercialize these modified electrodes, several existing problems must be solved to ensure that these electrochemical sensors are reproducible, cost efficient and suitable and affordable for consumer use. Furthermore, with the development of microfabricated sensors and injection analysis systems, the combination and integration of chemically modified electrodes with automatic and miniaturized systems can become an exciting new research field and is expected to be widely used in future real-world applications.

ACKNOWLEDGEMENTS
This work was supported by the General Program of the National Natural Science Foundation of China (no. 31671578) and by the National High Technology Research and Development Program of China (no. 2013AA102302).

References

1. H.G. Seiler, H. Sigel, A. Sigel, New York, 1998.
2. L. Rassaei, F. Marken, M. Sillanpää, M. Amiri, C.M. Cirtiu, M. Sillanpää, *Trends Anal. Chem.*, 30 (2011) 1704.
3. S. Caroli, G. Forte, A.L. Iamiceli, B. Galoppi, *Talanta*, 50 (1999) 327.
4. A.T. Townsend, K.A. Miller, S. McLean, S. Aldous, *J. Anal. Atomic Spectrom.*, 13 (1998) 1213.
5. R.S. Amais, A. Virgilio, D. Schiavo, J.A. Nóbrega, *Microchem. J.*, 120 (2015) 64.
6. S. Cerutti, M.F. Silva, J.A. Gásquez, R.A. Olsina, L.D. Martinez, *Spectrochim. Acta Part B: Atomic Spectrosc.*, 58 (2003) 43.
7. S. Wang, X. Dong, B. Dai, M. Pan, S. He, J. Wang, *J. AOAC Int.*, 98 (2015) 218.
8. A.N. Anthemidis, G.A. Zachariadis, C.G. Farastelis, J.A. Stratis, *Talanta*, 62 (2004) 437.
9. W. Li, P. Simmons, D. Shrader, T.J. Herrman, S.Y. Dai, *Talanta*, 112 (2013) 43.
10. L. Zhao, S. Zhong, K. Fang, Z. Qian, J. Chen, *J. Hazard. Mater.*, 239-240 (2012) 206.
11. M.M. Özcan, F.Y. Al Juhaimi, *Environ. Monit. Assess.*, 184 (2012) 2373.

12. E. Ünlü, B. Gümgüm, *Chemosphere*, 26 (1993) 2055.
13. I.J. Cindric, I. Krizman, M. Zeiner, S. Kampic, G. Medunic, G. Stingeder, *Food Chem.*, 135 (2012) 2675.
14. P. Pohl, *Trends Anal. Chem.*. 28 (2009) 117.
15. J. Gasparik, D. Vladarova, M. Capcarova, P. Smehyl, J. Slamecka, P. Garaj, R. Stawarz, P. Massanyi, *J. Environ. Sci. Health A*, 45 (2010) 818.
16. G. Kaya, C. Ozcan, M. Yaman, *Bull. Environ. Contam. Toxicol.*, 84 (2010) 191.
17. H. Mohammed, S. Sadeek, A.R. Mahmoud, D. Zaky, *Microchem. J.*, 128 (2016) 1.
18. D. Zhao, X. Guo, T. Wang, N. Alvarez, V.N. Shanov, W.R. Heineman, *Electroanalysis*, 26 (2014) 488.
19. B. Bansod, T. Kumar, R. Thakur, S. Rana, I. Singh, *Biosens. Bioelectron.*, 94 (2017) 443.
20. A. Afkhami, H. Bagheri, A. Shirzadmehr, H. Khoshsafar, P. Hashemi, *Electroanalysis*, 24 (2012) 2176.
21. R. Ouyang, Z. Zhu, C.E. Tatum, J.Q. Chambers, Z.L. Xue, *J. Electroanal. Chem.*, 656 (2011) 78.
22. J. Wang, *Wiley-VCH Verlag GmbH & Co. KGaA*, 2007.
23. I. Bontidean, C. Berggren, G. Johansson, E. Csoregi, B. Mattiasson, J.R. Lloyd, K.J. Jakeman, N.L. Brown, *Anal. Chem.*, 70 (1998) 4162.
24. D. Pan, Y. Wang, Z. Chen, T. Lou, W. Qin, *Anal. Chem.*, 81 (2009) 5088.
25. Y. Wei, C. Gao, F.L. Meng, H.H. Li, L. Wang, J.H. Liu, X.J. Huang, *J. Phys. Chem. C*, 116 (2012) 1034.
26. F. Davis, S.P.J. Higson, *Environ. Sci.: Process. Impacts*, 15 (2013) 1477.
27. D. Salvatore, M.A. Baldo, B. Carlo, *Curr. Anal. Chem.*, 4 (2008) 215.
28. G. Herzog, V. Beni, *Anal. Chim. Acta*, 769 (2013) 10.
29. T.F. Tormin, R.R. Cunha, R.A.B. da Silva, R.A.A. Munoz, E.M. Richter, *Sens. Actuators B: Chem.*, 202 (2014) 93.
30. M.S.M. Quintino, L. Angnes, *Electroanalysis*, 16 (2004) 513.
31. J. Wang, Z. Taha, *Anal. Chem.*, 63 (1991) 1053.
32. A.K. Geim, K.S. Novoselov, *Nat. Mater.*, 6 (2007) 183.
33. M.R. Shahmiri, A. Bahari, H. Karimi-Maleh, R. Hosseinzadeh, N. Mirnia, *Sens. Actuators B: Chem.*, 177 (2013) 70.
34. D.A.C. Brownson, C.E. Banks, *Analyst*, 135 (2010) 2768.
35. J. Wang, *Electroanalysis*, 17 (2005) 7.
36. Y. Shao, J. Wang, H. Wu, J. Liu, I.A. Aksay, Y. Lin, *Electroanalysis*, 22 (2010) 1027.
37. M. Zhou, Y. Zhai, S. Dong, *Anal. Chem.*, 81 (2009) 5603.
38. N. Jadon, R. Jain, S. Sharma, K. Singh, *Talanta*, 161 (2016) 894.
39. L. Cui, J. Wu, H. Ju, *Biosens. Bioelectron.*, 63 (2015) 276.
40. Q. Wan, F. Yu, L. Zhu, X. Wang, N. Yang, *Talanta*, 82 (2010) 1820.
41. S. Cerovac, V. Guzsvány, Z. Kónya, A.M. Ashrafi, I. Švancara, S. Rončević, Á. Kukovecz, B. Dalmacija, K. Vytřas, *Talanta*, 134 (2015) 640.
42. Y. Wei, R. Yang, X. Chen, L. Wang, J.H. Liu, X.J. Huang, *Anal. Chim. Acta*, 755 (2012) 54.
43. A. Afkhami, H. Ghaedi, T. Madrakian, M. Rezaeivala, *Electrochim. Acta*, 89 (2013) 377.
44. H. Bagheri, A. Afkhami, H. Khoshsafar, M. Rezaei, A. Shirzadmehr, *Sens. Actuators B: Chem.*, 186 (2013) 451.
45. A. Mandil, R. Pauliukaite, A. Amine, C.M.A. Brett, *Anal. Lett.*, 45 (2012) 395.
46. X. Li, H. Zhou, C. Fu, F. Wang, Y. Ding, Y. Kuang, *Sens. Actuators B: Chem.*, 236 (2016) 144.
47. H. Huang, T. Chen, X. Liu, H. Ma, *Anal. Chim. Acta*, 852 (2014) 45.
48. G. Zhao, H. Wang, G. Liu, Z. Wang, *Int. J. Electrochem. Sci.*, 11 (2016) 8109.
49. G. Zhao, Y. Yin, H. Wang, G. Liu, Z. Wang, *Electrochim. Acta*, 220 (2016) 267.
50. Y.Q. Tian, N.B. Li, H.Q. Luo, *Electroanalysis*, 21 (2009) 2584.
51. J. Wang, *Electroanalysis*, 17 (2005) 1341.

52. L. Agui, P. Yanez-Sedeno, J.M. Pingarron, *Anal. Chim. Acta*, 622 (2008) 11.
53. M. Mallesha, R. Manjunatha, C. Nethravathi, G.S. Suresh, M. Rajamathi, J.S. Melo, T.V. Venkatesha, *Bioelectrochemistry*, 81 (2011) 104.
54. Z. Wang, P.M. Lee, E. Liu, *Thin Solid Films*, 544 (2013) 341.
55. C. Huangfu, L. Fu, Y. Li, X. Li, H. Du, J. Ye, *Electroanalysis*, 25 (2013) 2238.
56. Y.Y. Lu, M.N. Chen, Y.L. Gao, J.M. Yang, X.Y. Ma, J.Y. Liu, *Chin. J. Anal. Chem.*, 43 (2015) 1395.
57. S. Lee, S. Bong, J. Ha, M. Kwak, S.K. Park, Y. Piao, *Sens. Actuators B: Chem.*, 215 (2015) 62.
58. W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.*, 80 (1958) 1339.
59. M.J. McAllister, J.-L. Li, D.H. Adamson, H.C. Schniepp, A.A. Abdala, J. Liu, M. Herrera-Alonso, D.L. Milius, R. Car, R.K. Prud'homme, I.A. Aksay, *Chem. Mater.*, 19 (2007) 4396.
60. S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, *Carbon*, 45 (2007) 1558.
61. M. Lv, X. Wang, J. Li, X. Yang, C.A. Zhang, J. Yang, H. Hu, *Electrochim. Acta*, 108 (2013) 412.
62. S. Xiong, S. Ye, X. Hu, F. Xie, *Electrochim. Acta*, 217 (2016) 24.
63. P.M. Lee, Z. Chen, L. Li, E. Liu, *Electrochim. Acta*, 174 (2015) 207.
64. S.M. Choi, D.M. Kim, O.S. Jung, Y.B. Shim, *Anal. Chim. Acta*, 892 (2015) 77.
65. S. Xiong, B. Yang, D. Cai, G. Qiu, Z. Wu, *Electrochim. Acta*, 185 (2015) 52.
66. M. Yang, T.J. Jiang, Y. Wang, J.H. Liu, L.N. Li, X. Chen, X.J. Huang, *Sens. Actuators B: Chem.*, 245 (2017) 230.
67. W. Zhou, C. Li, C. Sun, X. Yang, *Food Chem.*, 192 (2016) 351.
68. Z. Li, L. Chen, F. He, L. Bu, X. Qin, Q. Xie, S. Yao, X. Tu, X. Luo, S. Luo, *Talanta*, 122 (2014) 285.
69. J. Li, S. Guo, Y. Zhai, E. Wang, *Anal. Chim. Acta*, 649 (2009) 196.
70. W. Wonsawat, S. Chuanuwatanakul, W. Dungchai, E. Punrat, S. Motomizu, O. Chailapakul, *Talanta*, 100 (2012) 282.
71. Q. Zhao, Y. Chai, R. Yuan, J. Luo, *Sens. Actuators B: Chem.*, 178 (2013) 379.
72. G. Zhao, H. Wang, G. Liu, *Int. J. Electrochem. Sci.*, 11 (2016) 1840.
73. L. Laffont, T. Hezard, P. Gros, L.E. Heimbürger, J.E. Sonke, P. Behra, D. Evrard, *Talanta*, 141 (2015) 26.
74. X. Gao, W. Wei, L. Yang, T. Yin, Y. Wang, *Anal. Lett.*, 38 (2005) 2327.
75. P.M. Lee, Z. Wang, X. Liu, Z. Chen, E. Liu, *Thin Solid Films*, 584 (2015) 85.
76. A.F. Al-Hossainy, A.A.I. Abd-Elmageed, A.T.A. Ibrahim, *Arab. J. Chem.*, (2015).
77. A. Wong, C.A. Razzino, T.A. Silva, O. Fatibello-Filho, *Sens. Actuators B: Chem.*, 231 (2016) 183.
78. Y. Zhou, L. Tang, G. Zeng, C. Zhang, X. Xie, Y. Liu, J. Wang, J. Tang, Y. Zhang, Y. Deng, *Talanta*, 146 (2016) 641.
79. T. Hezard, K. Fajerwerg, D. Evrard, V. Collière, P. Behra, P. Gros, *J. Electroanal. Chem.*, 664 (2012) 46.
80. L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan, S. Yao, *Electrochim. Acta*, 115 (2014) 471.
81. M.A. Kamyabi, A. Aghaei, *Electrochim. Acta*, 206 (2016) 192.
82. X. Gan, H. Zhao, X. Quan, Y. Zhang, *Electrochim. Acta*, 190 (2016) 480.
83. A.O. Idris, N. Mabuba, O.A. Arotiba, *J. Electroanal. Chem.*, 758 (2015) 7.
84. H. Wan, Q. Sun, H. Li, F. Sun, N. Hu, P. Wang, *Sens. Actuators B: Chem.*, 209 (2015) 336.
85. E. Bernalte, C.M. Sánchez, E.P. Gil, *Sens. Actuators B: Chem.*, 161 (2012) 669.
86. B. Zhang, J. Chen, H. Zhu, T. Yang, M. Zou, M. Zhang, M. Du, *Electrochim. Acta*, 196 (2016) 422.
87. R. Sivasubramanian, M.V. Sangaranarayanan, *Talanta*, 85 (2011) 2142.
88. C. van der Horst, B. Silwana, E. Iwuoha, V. Somerset, *J. Electroanal. Chem.*, 752 (2015) 1.
89. H.L. Fan, S.F. Zhou, J. Gao, Y.Z. Liu, *J. Alloys Compd.*, 671 (2016) 354.

90. W.J. Li, X.Z. Yao, Z. Guo, J.H. Liu, X.J. Huang, *J. Electroanal. Chem.*, 749 (2015) 75.
91. S.F. Zhou, X.J. Han, Y.Q. Liu, *J. Alloys Compd.*, 684 (2016) 1.
92. Y. Sun, W. Zhang, H. Yu, C. Hou, D.S. Li, Y. Zhang, Y. Liu, *J. Alloys Compd.*, 638 (2015) 182.
93. Y.F. Sun, W.K. Chen, W.J. Li, T.J. Jiang, J.H. Liu, Z.G. Liu, *J. Electroanal. Chem.*, 714 (2014) 97.
94. Y.M. Liu, X.J. Ju, Y. Xin, W.C. Zheng, W. Wang, J. Wei, R. Xie, Z. Liu, L.Y. Chu, *ACS Appl. Mater. Interfaces*, 6 (2014) 9530.
95. Y.F. Shen, J. Tang, Z.H. Nie, Y.D. Wang, Y. Ren, L. Zuo, *Sep. Purif. Technol.*, 68 (2009) 312.
96. F.J. Pereira, M.D. Vázquez, L. Debán, A.J. Aller, *Talanta*, 152 (2016) 211.
97. M. Yang, Z. Guo, L.N. Li, Y.Y. Huang, J.H. Liu, Q. Zhou, X. Chen, X.J. Huang, *Sens. Actuators B: Chem.*, 231 (2016) 70.
98. Z. Wang, E. Liu, X. Zhao, *Thin Solid Films*, 519 (2011) 5285.
99. A. de Barros, C.J.L. Constantino, N.C. da Cruz, J.R.R. Bortoleto, M. Ferreira, *Electrochim. Acta*, 235 (2017) 700.
100. Z. Wang, L. Li, E. Liu, *Thin Solid Films*, 544 (2013) 362.
101. L. Chen, Z. Su, X. He, Y. Liu, C. Qin, Y. Zhou, Z. Li, L. Wang, Q. Xie, S. Yao, *Electrochem. Commun.*, 15 (2012) 34.
102. N. Ruecha, N. Rodthongkum, D.M. Cate, J. Volckens, O. Chailapakul, C.S. Henry, *Anal. Chim. Acta*, 874 (2015) 40.
103. N. Promphet, P. Rattanarat, R. Rangkupan, O. Chailapakul, N. Rodthongkum, *Sens. Actuators B: Chem.*, 207, Part A (2015) 526.
104. Y. Wu, N.B. Li, H.Q. Luo, *Sens. Actuators B: Chem.*, 133 (2008) 677.
105. Z. Wang, H. Wang, Z. Zhang, X. Yang, G. Liu, *Electrochim. Acta*, 120 (2014) 140.
106. L. Chen, Z. Li, Y. Meng, P. Zhang, Z. Su, Y. Liu, Y. Huang, Y. Zhou, Q. Xie, S. Yao, *Sens. Actuators B: Chem.*, 191 (2014) 94.
107. A. Joseph, S. Subramanian, P.C. Ramamurthy, S. Sampath, R.V. Kumar, C. Schwandt, *Electrochim. Acta*, 137 (2014) 557.
108. S.C.C. Monterroso, H.M. Carapuça, A.C. Duarte, *Talanta*, 65 (2005) 644.
109. Z. Jyh-Myng, C. Mu-Jye, *Anal. Chim. Acta*, 320 (1996) 43.
110. S.C. Monterroso, H.M. Carapuca, A.C. Duarte, *Talanta*, 68 (2006) 1655.
111. M.A. Chamjangali, H. Kouhestani, F. Masdarolomoor, H. Daneshinejad, *Sens. Actuators B: Chem.* 216 (2015) 384.
112. C.P. Silva, H.M. Carapuça, *Electrochim. Acta*, 52 (2006) 1182.
113. F.E. Salih, A. Ouarzane, M. El Rhazi, *Arab. J. Chem.*, (2015).
114. X. He, Z. Su, Q. Xie, C. Chen, Y. Fu, L. Chen, Y. Liu, M. Ma, L. Deng, D. Qin, Y. Luo, S. Yao, *Microchim. Acta*, 173 (2011) 95.
115. S. das Neves, M.A. De Paoli, *Synth. Metals*, 96 (1998) 49.
116. H.N. Dinh, J. Ding, S.J. Xia, V.I. Birss, *J. Electroanal. Chem.*, 459 (1998) 45.
117. J. Jia, L. Cao, Z. Wang, *Electroanalysis*, 19 (2007) 1845.
118. M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.*, 8 (2009) 621.
119. X. Niu, H. Zhao, M. Lan, *Electrochim. Acta*, 56 (2011) 9921.
120. J. Huang, A.F. Hollenkamp, *J. Phys. Chem. C*, 114 (2010) 21840.
121. M.C. Buzzeo, C. Hardacre, R.G. Compton, *Chemphyschem*, 7 (2006) 176.
122. A.M. Navarro-Suárez, J.C. Hidalgo-Acosta, L. Fadini, J.M. Feliu, M.F. Suárez-Herrera, *J. Phys. Chem. C*, 115 (2011) 11147.
123. H. Khani, M.K. Rofouei, P. Arab, V.K. Gupta, Z. Vafaei, *J. Hazard. Mater.*, 183 (2010) 402.
124. S. Chaiyo, E. Mehmeti, K. Žagar, W. Siangproh, O. Chailapakul, K. Kalcher, *Anal. Chim. Acta*, 918 (2016) 26.
125. H. Bagheri, A. Afkhami, H. Khoshsafar, M. Rezaei, S.J. Sabounchei, M. Sarlakifar, *Anal. Chim. Acta*, 870 (2015) 56.

126. Y. Li, X. Liu, X. Zeng, Y. Liu, X. Liu, W. Wei, S. Luo, *Sens. Actuators B: Chem.*, 139 (2009) 604.
127. Z. Wang, H. Wang, Z. Zhang, G. Liu, *Sens. Actuators B: Chem.*, 199 (2014) 7.
128. G.H. Hwang, W.K. Han, J.S. Park, S.G. Kang, *Sens. Actuators B: Chem.*, 135 (2008) 309.
129. I. Cesarino, C. Gouveia-Caridade, R. Pauliukaitė, É.T.G. Cavalheiro, C.M.A. Brett, *Electroanalysis*, 22 (2010) 1437.
130. W. Zhang, H. Zhang, S.E. Williams, A. Zhou, *Talanta*, 132 (2015) 321.
131. C. Kokkinos, A. Economou, *Talanta*, 84 (2011) 696.
132. N. Spano, A. Panzanelli, P.C. Piu, M.I. Pilo, G. Sanna, R. Seeber, A. Tapparo, *Anal. Chim. Acta*, 553 (2005) 201.
133. C. Kokkinos, A. Economou, *Sens. Actuators B: Chem.*, 229 (2016) 362.
134. A. Jang, Z. Zou, K.K. Lee, C.H. Ahn, P.L. Bishop, *Talanta*, 83 (2010) 1.
135. C. Kokkinos, A. Economou, *Talanta*, 125 (2014) 215.
136. D. Gerhold, T. Rushmore, C.T. Caskey, *Trends Biochem. Sci.*, 24 (1999) 168.
137. H. Zhu, M. Snyder, *Curr. Opin. Chem. Biol.*, 7 (2003) 55.
138. W. Jung, A. Jang, P.L. Bishop, C.H. Ahn, *Sens. Actuators B: Chem.*, 155 (2011) 145.
139. X. Xie, D. Stüben, Z. Berner, J. Albers, R. Hintsche, E. Jantzen, *Sens. Actuators B: Chem.*, 97 (2004) 168.
140. P.R.M. Silva, M.A. El Khakani, M. Chaker, A. Dufresne, F. Courchesne, *Sens. Actuators B: Chem.*, 76 (2001) 250.
141. E. Muñoz, S. Palmero, M.A. García-García, *Talanta*, 57 (2002) 985.
142. A. Economou, P. Fielden, *Analyst*, 121 (1996) 1903.
143. C. Kokkinos, A. Economou, N.G. Goddard, P.R. Fielden, S.J. Baldock, *Talanta*, 153 (2016) 170.
144. M. Kim, J.W. Lim, H.J. Kim, S.K. Lee, S.J. Lee, T. Kim, *Biosens. Bioelectron.*, 65 (2015) 257.
145. S. Jaenicke, R.M. Sabarathinam, B. Fleet, H. Gunasingham, *Talanta*, 45 (1998) 703.
146. Z. Lukaszewski, B. Karbowska, W. Zembrzuski, *Electroanalysis*, 15 (2003) 480.
147. A. Izquierdo, M.D.L. de Castro, M. Valcárcel, *Electroanalysis*, 6 (1994) 894.
148. Z. Ramshani, A.S.G. Reddy, B.B. Narakathu, J.T. Wabeke, S.O. Obare, M.Z. Atashbar, *Sens. Actuators B: Chem.*, 217 (2015) 72.
149. T.D.C. Oliveira, J.M. Freitas, R.A. A. Munoz, E.M. Richter, *Talanta*, 152 (2016) 308.
150. C.E. Lenehan, N.W. Barnett, S.W. Lewis, *Analyst*, 127 (2002) 997.
151. U. Injang, P. Noyrod, W. Siangproh, W. Dungchai, S. Motomizu, O. Chailapakul, *Anal. Chim. Acta.* 668 (2010) 54.
152. A. Economou, *Trends Anal. Chem.*, 24 (2005) 416.
153. C. Henriquez, L.M. Laglera, M.J. Alpizar, J. Calvo, F. Arduini, V. Cerda, *Talanta*, 96 (2012) 140.
154. G. Kefala, A. Economou, *Anal. Chim. Acta*, 576 (2006) 283.
155. V.B. dos Santos, E.L. Fava, N.S. de Miranda Curi, R.C. Faria, O. Fatibello-Filho, *Talanta*, 126 (2014) 82.
156. E. Punrat, S. Chuanuwatanakul, T. Kaneta, S. Motomizu, O. Chailapakul, *J. Electroanal. Chem.*, 727 (2014) 78.
157. R.W. Murray, A.G. Ewing, R.A. Durst, *Anal. Chem.*, 59 (1987) 379.
158. B. Nigović, *Anal. Bioanal. Chem.*, 384 (2006) 431.
159. C.Y. Liu, J.P. Yao, H.W. Tang, S.P. Zhu, J.F. Hu, *Anal. Bioanal. Chem.*, 386 (2006) 1905.
160. I. Švancara, K. Vytřas, J. Barek, J. Zima, *Crit. Rev. Anal. Chem.*, 31 (2001) 311.
161. A. Wei, L. Pan, W. Huang, *Mater. Sci. Eng.: B*, 176 (2011) 1409.
162. L. Jiang, Y. Wang, J. Ding, T. Lou, W. Qin, *Electrochem. Commun.*, 12 (2010) 202.
163. N.F. Atta, S.A. Darwish, S.E. Khalil, A. Galal, *Talanta*, 72 (2007) 1438.
164. X.C. Song, X. Wang, Y.F. Zheng, R. Ma, H.Y. Yin, *J. Nanoparticle Res.*, 13 (2011) 5449.
165. H. Gao, X. Qi, Y. Chen, W. Sun, *Anal. Chim. Acta*, 704 (2011) 133.
166. B. Fang, C. Zhang, W. Zhang, G. Wang, *Electrochim. Acta*, 55 (2009) 178.

167. Z. Linting, L. Ruiyi, L. Zaijun, X. Qianfang, F. Yinjun, L. Junkang, *Sens. Actuators B: Chem.*, 174 (2012) 359.
168. F. Meng, W. Shi, Y. Sun, X. Zhu, G. Wu, C. Ruan, X. Liu, D. Ge, *Biosens. Bioelectron.*, 42 (2013) 141.
169. J. Tashkhourian, M.R.H. Nezhad, J. Khodavesi, S. Javadi, *J. Electroanal. Chem.*, 633 (2009) 85.
170. C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, *Chem. Rev.*, 105 (2005) 1025.
171. I.M. Al-Akraa, A.M. Mohammad, M.S. El-Deab, B.E. El-Anadouli, *Int. J. Electrochem. Sci.*, 8 (2013) 458.