Chapter 6

Modified Electrodes for Determining Trace Metal Ions

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Additional information is available at the end of the chapter

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Abstract

Due to all the advantages of low cost, speed, and simplicity, electrochemistry has always represented a perfect choice to be selected in quantitative analysis particularly in the case of metal ions but with the drawback of specificity and sensitivity. With the arrival of nanomaterials, the problem of sensitivity and limit of detection has been overcome and a great variety of applications of electrochemistry especially in trace analysis are highlighted. Layers of materials can be arranged and manipulated to make the methods more specific to targeting analytes The opportunity is there for both older and newer methods to be beneficial in a large number of applications with superb analytical performance. This knowledge of modified electrodes can inspire newer and greater innovative applications of electrochemistry with the promising extension to other areas under current interests.

Keywords: modified electrodes, ASV, nanomaterials, metal ion analysis

1. Introduction

A number of techniques have been employed for the determination of trace metal ions including atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and electrochemical techniques. Spectroscopic techniques are very expensive and need preconcentration as well as extraction that are time-consuming with danger of losses and contamination [1]. Electroanalytical techniques, particularly anodic stripping voltammetry (ASV), can be considered as the most powerful techniques due to their excellent detection limits, high sensitivity, capacity for multielement determination, high speed, simplicity, and relatively low cost [2] not to mention their innovative opportunities. It is important to be noted right at the very first here that voltammetry is not the only technique to be used for modified electrodes but other electrochemical techniques can be applied as well, especially potentiometry.

The selection of a proper electrode material is crucial in voltammetry. For the past six decades, mercury has been the most commonly used electrode material in various configurations for electrochemical determination of trace metal ions. Despite advantages of formation of amalgam and high overvoltage for gases among others, there have been numerous attempts to replace well-known toxic mercury with some other nontoxic or less-toxic electrode material [3]. Nowadays, numerous new electrode materials and methods have been developed, especially those concerning electrode modifications in particular with nanomaterials.

2. Background of modified electrodes

In general especially in the past, an electrode can be any electroconducting materials that were started by metals such as platinum or gold. Later, glassy carbon has been used with a number of advantages in particular ease to use and wide potential range. After that, carbon paste has been applied due to the fact that it is easy to prepare. Various substances have been mixed to attract the analytes especially metal ions to be collected at electrode surface and increase the sensitivity. With an introduction of nanomaterials and conducting polymers, for example, the surface areas for preconcentrating metal ions have been dramatically increased, making the method perfect for trace metal analysis in accordance with simplicity and low cost of electrochemical methods. Consequently, at present, there are a great number of research articles involving the development of new methods using a variety of modified electrodes to be applied with various areas as well as samples. To make this chapter simple but specific, the use of enzymes in the form of biosensors is not mentioned here. Those who are interested can obtain those specific stories in detail in a large number of available references [4]. We also have to say that modified electrodes can be used with a great variety of analytes, but metal ions are under the focus here. However, for the sake of abundant available applications and promising characteristics in adapting to metal ion analysis, the determinations of other analytes will be concisely included.

3. Types of substrate electrodes

Due to the fact that there are vast types of available and investigated substrates, the most recent and the most popular are discussed here. Other less frequently used electrodes such as carbon fiber or carbon cloth are not included. The readers are recommended to further study corresponding articles for more details.

3.1. Glassy carbon electrode (GCE)

Glassy carbon electrodes (GCEs) are prepared by means of a carefully controlled heating program of premodeled polymeric resin body in an inert atmosphere [5]. Unlike many nongraphitizing carbons, it is impermeable to gases and also resistant to acid attack. The structure of glassy carbon consists of graphite planes randomly organized in a complex topology. Glassy carbon possesses isotropic properties and does not require a particular orientation in the electrode device. The properties of carbonaceous materials significantly depend on the

manufacturing processes involved. Surface treatment is usually employed to create its active and reproducible surface to enhance analytical performances. Another way is to include certain additional activation steps such as electrochemical, chemical, vacuum heat, or laser treatment.

Carbon electrodes offer a useful and environmentally friendly alternative to substitute mercury electrodes with a narrow cathodic range or noble metal surfaces with limitations in terms of reproducibility, formation of oxide layers during voltammetric procedures and relatively low cost [6]. It becomes one of the most commonly used substrates due to its wide potential window with low background and its chemical stability. Electrode modification can then be applied to improve its performance in terms of sensitivity, selectivity, and reproducibility.

3.2. Boron-doped diamond (BDD)

Boron-doped diamond (BDD) electrodes have also currently attracted much interest to be applied in a variety of areas due to their superior properties, including extreme robustness with a low level of background interference, less adsorption of polar molecules, and attractively wider potential window in aqueous media [7, 8]. It has been used to quantify manganese in tea [9] as well as lead in tap water [10] and river sediment. Anodic stripping voltammetry BDD has been proved to possess outstanding features [11] to determine silver [12] and simultaneous detection of lead and copper [13].

3.3. Fluorine-doped tin oxide (FTO)

Fluorine-doped tin oxide (FTO) has been applied continuously as a substrate with outstanding features of simplicity in layer-by-layer (LbL) fabrication and its compatibility with extensive building blocks including dyes, biomolecules, nanomaterials, and polymers [14]. In spite of the fact that it has been reported to be successfully applied in the analysis of biosubstances particularly DNA, it is also mentioned here in light of making its promising way to metal ion analysis.

3.4. Screen-printed electrode (SPE)

There are numerous possibilities to choose from for screen-printed electrode (SPE). The most popular material is still carbon. SPE has advantages of small size, low cost, simplicity as well as smaller amount of sample and waste. The problem of lower sensitivity can be solved by electrode modification, which also highlights its applications in a larger number of areas [15].

3.5. Carbon paste electrode (CPE)

Carbon paste is still widely used throughout the development of modified electrodes with certain reasons including superb quality of carbon as an electrode, low cost, and its simplicity [16]. With clever design, additional benefits can be reached including stability, reproducibility, and fast response time. This material has been found to be useful for the determination of both compounds and metal ions.

3.6. Silica

Silica, in particular mesoporous silica, has been increasingly used in modified electrode with features of inertness, high surface area, moderate cost, availability, and compatibility of being

anchored by various materials. It has been reported to be useful in the analysis of both biomolecules and metal ions [17].

4. Types of modified electrodes

A number of materials have been investigated to be used in preconcentrating metal ions as well as other substances and make electrochemistry unique and highlighted in the worlds of analytical chemistry and beyond. Thanks to the developments and arrivals of nanomaterials, the most widely used especially at the very beginning is metal nanoparticles such as silver or gold to increase the surface areas and in turn the sites for metal ions to deposit. Both conducting and nonconducting polymers have been used for a long time in modifying electrode surface to have more capabilities in supporting metal ions. Mesoporous silica with the advantage of surface areas as well has been used in the determinations of a number of metal ions. Another example of a neutral substance with greater surface areas in collecting metal ions is chitosan, a substance from shrimp. Currently, it is certain that the opportunity is there that a large number of substances are under investigations or even await the discovery. Finally, the combinations of a variety of materials have also been proved to be useful in further receiving the metals ions to a greater extent. The electrodes modified by aforementioned materials are then applied in stripping voltammetry, parameters are optimized, and then the methods are used with real samples. Normally, the results are compared with standard methods or the standard materials are used for verification. A number of spectroscopic and electrochemical methods can also be used to provide additional details of the analysis. At present, a very large number of research articles focus on the applications of modified electrodes in many areas especially in the analysis of a great variety of substances, in particular, metal ions. Also, a number of materials have been investigated in the form of layers and sublayers as well as specific pores as a specific substrate for particular analytes, hence, the new term of "molecular imprinted," which makes the method extremely specific.

The following materials that have been used in electrode modifications are not arranged with the criteria of the time of development. Rather, it is presented in the order of simplicity.

4.1. Unmodified electrode

With a superb characteristic of specific electrode such as screen-printed carbon electrode, metal ion can still be determined at trace level by in a very normal way [18].

4.2. Graphene

Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale and hexagonal lattice in which one atom forms each vertex. It is composed of a single layer of sp2 carbon in two dimensions. It is the basic structural element of other allotropes, including graphite, charcoal, carbon nanotubes (CNTs), and fullerenes. Graphene has a great variety of unusual beneficial properties including strength, heat and electricity conductivity, transparency, magnetic properties, and low cost [19].

4.3. Graphene oxide

Graphene can be prepared in a modified way to obtain different and beneficial properties in new forms including thermally reduced graphene, partially reduced graphene, or even electrochemically reduced graphene (ErGO). Normally, this is the arrangement of oxygen in the structure, hence the name graphene oxide that is really helpful in collecting metal ions and providing better selectivity, resolution, as well as precision. With the addition of other substance that can form the bond via conjugation with graphene, electrocatalization as well as electroluminescence (ECL) can be facilitated. This modified graphene derivatives can be use satisfactorily in both waste water treatment via adsorption [20] as well as analysis in only one step [21] in addition to the development of new batteries [21, 22] and improvement of antibacterial properties [23].

4.4. Metals

Metal and metal alloys can also be used in the analysis of different species such as nitrite but the applications for metal ions are focused here. Moreover, as a typical case,only metal that can satisfactorily substitute mercury namely bismuth is emphasized.

In 2000, a new type of electrode called bismuth film electrode (BiFE) consisting of a thin film of bismuth deposited on a carbon substrate has been proposed as an alternative to mercury electrodes in ASV [24]. The main advantage of electrochemical properties of bismuth film electrodes in comparison with mercury film electrodes (MFEs) is that Bi is more environmentally friendly with less toxicity in addition to simple preparation, high sensitivity, well-defined and separated stripping signals, and insensitivity to dissolved oxygen (which is an essential property for on-site monitoring). The superior stripping performances of bismuth-based electrodes derive from their ability to form "fused" alloys with other metals similar to mercury [24].

There are three common ways to generate a bismuth film including (i) by preplating it from an acidic solution which is called an ex situ preparation, (ii) by codeposition with the analyte which is commonly known as an in situ setup and (iii) by electrode modification of a film, such as Bi_2O_3(s) or BiF_3, to generate the Bi(s) coating [25]. Ex situ plating was found to be easier to manage because the conditions can be different from analytical or stripping conditions, and there are no interferents in depositing; however, it is more susceptible to the change of electrode surface during electrode transfer and more steps make the method take longer time. Another advantage of ex situ methods is that the electrode can be regenerated at any time. Also, the potential can be better controlled due to the fact that, for in situ preparation, the stripping of bismuth needs to be performed at the potential more positive than bismuth oxidation and after that bismuth is replated [26].

4.5. Metal complexes

A number of metal complexes have been immobilized on the substrate to attract or react with other substances. Due to the fact that it already contains metals, this type of modification substance is normally used for the determination of organic and inorganic compounds especially via electrocatalysis [27]. Cobalt phthalocyanin has been widely and continuously

investigated and applied for the analysis of ascorbic, diethyl stilbestol, and acetaminophen [28]. Manganese porphyrins have been extensively investigated [29]. As a matter of fact, porphyrins themselves can accommodate metal ions really well and, with the increase of surface areas, should be able to be used in the analysis of metal ions [30].

4.6. Metal nanoparticles

There was a wonderful review for metal nanoparticles for the determination of arsenic, chromium, lead, cadmium, and antimony [31]. Mixing metal nanoparticles with a wide range of compounds can allow the analytical performances of the methodology to be greatly improved in various aspects especially sensitivity due to larger amount of analytes collected.

4.7. Metal compound nanoparticles

Due to the fact that there are a great variety of metal compound nanoparticles that have been used in metal ion analysis especially recently [32], only modified magnetic iron oxide nanoparticles (M-MIONPs) for mercury determination are mentioned here as an example.

It is well known that mercury in the lowest levels of concentrations is dangerous for human health due to its bioaccumulation in body and toxicity. Modified magnetic iron oxide nanoparticles (M-MIONPs) with 2-mercaptobenzothiazole (MBT) was found to be able to absorb mercury (II) ion satisfactorily from polluted surface water with advantages of speed, cost-effectiveness, simplicity, capability, ease of preparation, and safety [33]. Modification by 2-mercaptobanzothiazole could increase absorption percentage up to 98.6% compared with 43.47% for magnetic iron oxide nanoparticles (MIONPs) alone. Salt concentrations and pH were found to have no profound effect on mercury ion accumulation with high loading capacity of 590 μg/g. This proves that the capability of metal compound nanoparticles in attracting analytes can be greatly improved by combining them with additional compounds.

4.8. Organic compounds

Organic compounds that can be used normally or after polymerization are provided in the topic of polymers. All kinds of organic compounds that can attract metal ions can be used well in metal ion determination. The stronger bond obtained from the compounds, the better they can be applied in accumulating metal ions. Ketones and quinones form another group of interest with specific interaction with certain metal ions [34]. Additionally, all organic compounds can be made nanostructured by mounting in a multilayer form on substrate electrode. A few popular compounds are exemplified as follows.

4.8.1. Crown ether

Crown ether is a macrocyclic compound with a pore of specific size to accommodate metal ions. With derivation, its selectivity can be greatly increased. This characteristic combined with different potential of stripping makes the methodology suitable for simultaneous determination of metal ions which can face or cause interferences in other techniques [35].

Strategies can also be designed to let the compounds to form self-assembled monolayers (SAM) on metal electrodes or to be immobilized on other monolayers [36, 37].

4.8.2. Schiff bases

Schiff bases are defined as the substances that contain the C=N moiety. With their specific capability in forming complexes with metal ions, Schiff bases can help increase the quantity of analytes on the electrode surface. Typical examples are potentiometric determination of Co(II) [38] and cyclic voltammetric analysis of Al(III) [39].

4.9. Polymers

Two cases of 2-mercaptobenzothiazole and diazonium are stated here for the vision about the applications with the use of materials in this group that can be in both monomeric and polymeric forms. Moreover, certain polymers can also be used for the purpose of molecular imprint [40].

4.9.1. 2-mercaptobenzothiazole

2-mercaptobenzothiazole (MBT) has been found in both monomer and polymer forms with the capabilities of collecting metal ions. Modification of nano-TiO_2 modified with 2-mercaptobenzothiazole (MBT) was found to be capable of collecting metal ions including Cd(II), Cu(II), and Pb(II) followed by elution with nitric acid and analysis by flame AAS [41]. Adsorption process as well as analytical conditions was optimized to obtain the dynamic range in ng/ml of 0–25.0 for Cd, 0.2–20.0 for Cu and 3.0–70.0 for Pb. The method was applied to the determination of Cd(II), Cu(II), and Pb(II) in water and ore samples. Obviously, this can also be applied to the analysis by electrochemistry without any need for elution. As a matter of fact, this is the topic under investigations of our group at present.

Poly(2-mercaptobenzothiazole) (PMBT) modified glassy carbon electrode has been fabricated and employed for the determination of specific organic compounds namely dopamine (DA), uric acid (UA), and nitrite (NO_2^-) in pH 6 phosphate buffer [42]. PMBT was found to catalyze oxidation of the compounds and shift the potentials to more negative which in turn resulted in well-defined and well-separated differential pulse (DP) peaks and made them possible to be simultaneously analyzed. SEM also revealed that continuous PMBT was formed with nano-scaled particles of 15–25 nm diameters. With optimized conditions, dynamic linear range in μmol/l was found to be 0.8–45 for DA, 0–165 for UA, and 60–1000 for NO_2^- with excellent linearity and submicromolar detection limits. Moreover, using standard addition, the methodology could be applied well with the real samples of urine and serum. Once again, due to the fact that the compound can react with metal ions well, this could shed some lights on simultaneous analysis of metal ions as well.

4.9.2. Diazonium

The modification through the electrochemical or chemical reduction of aromatic diazonium derivatives has been extensively investigated on a variety of carbon substrate including glassy carbon [43, 44], graphite [45], graphene [46], and carbon nanotube [47]. It has been proved to immobilize a great variety of functional groups onto carbon materials with simplicity and versatility to be used in metal analysis in a number of areas. Another advantage is long-term stability both in air and organic solvents. The high stability of the diazonium-modified electrodes

and the versatility of the diazonium modification method are particularly attractive for stripping analysis. Carbon modified by the reduction of aromatic diazonium derivatives was first used as an electrode for electrochemical stripping analysis of heavy metals [44]. Diazobenzoic acid was reduced on GCE to obtain benzoic acid modified GCE to simultaneously analyze Cd^{2+} and Pb^{2+}. The sensitivity of stripping peaks for both metals was increased up to six times with satisfactory analytical performances including 0.5–50 μg/l linear range, submicrogram per liter detection limits, and superbly low relative standard deviation especially for Cd^{2+}. The method was successfully used in determining the metals in sewage samples. The detection of Cd^{2+} by ASV on BDD electrode based on simple and selective electrochemical reduction of Cd^{2+} on diazonium-modified BDD electrode has been developed with analytical performance interference study as well as verification by analyzing standard material. The method was then applied to the analysis of Cd in tap water [43].

4.10. Chitosans (natural polymers)

Chitosan (CTS), poly-[1,4]-N-D-glucosamine, is one of the most abundant natural polymers. Its pKa is about 6.5; therefore, at lower pH solutions (>pKa), its primary amines are protonated, making it a cationic polyelectrolyte that is soluble in aqueous solution. At higher pH (>pKa), these amines are deprotonated which, in turn, makes chitosan neutral and insoluble [48]. The reasons that chitosan can be applied well in the analysis of drug substances, environment pollutants, industrial materials, and food compounds are that they can form the film well and attach strongly to the surfaces. They are also hydrophilic, compatible with biological substances, mechanical resistant, and capable to be further modified [49].

4.11. Clay

It has long been known that cationic metals can be strongly absorbed on clay materials with negative charge. A large number of scientists especially in the areas of environments have extensively studied the adsorption of metal ions on the clay particles. This characteristic also benefits the determination as well as elimination of metal ions [50, 51].

4.12. Mesoporous silica

Mesoporous materials are described as materials whose pore diameters lie in the range between 2 and 50 nm [52]. These materials are in focus due to the fact that they have abundant surface areas, they can absorb metal ion very fast, and their pore size as well as pore arrangement can be well-controlled. Moreover, they can be chemically modified with other functional groups to be able to better attract large variety of metal ions for the purpose of simultaneous analysis and removal for various samples [53].

4.13. Charcoal

Due to the fact that different kinds of charcoal can specifically adsorb metal ions on their surface [54, 55], they should work well in collecting metal ions. The increase of both surface areas and specificity from modifications can facilitate better analytical performances. Even though there have not yet been recent reports about their applications in metal ion analysis, the opportunity

is there to apply charcoals onto substrates as a new methodology to reach the objective of using readily obtained and low-cost materials in both analysis and removal of metal ions.

4.14. Carbon nanotube

Carbon nanotubes are tube-form materials with the diameter at nanometer level discovered by a Japanese scientist, Sumio Iijima, in 1991. They can be classified into single-walled (SWCNT) and multiwalled (MWCNT) with different properties especially in terms of metallic and magnetic behavior. They can be prepared by chemical vapor deposition (CVD), arc discharge, or laser vaporization. They can be applied in a large number of areas especially modified electrodes. Carbon nanotubes can be mounted either alone or mixed with other materials on any substrate electrode but preferably GCE. MWCNT is normally more satisfactory due to its advantages of highly ordered structure, light weight strength as well as thermal and electrical conductivity. In particular, the multi-walled have been extensively used in the determination of organic compounds [56] or metal ions either by electrochemistry [57] or spectroscopy [58, 59]. Their advantages in analysis mainly derive from the capabilities to adsorb metal ions [60]. This property makes it suitable to be applied in the areas of energy [61]. Furthermore, with large surface areas of carbon nanotubes, a number of substances can be mounted on them either single layer or multilayer to increase the capability to preconcentrate metal ions before their determinations [62].

4.15. Mixed or multilayered modification

Mixed materials can be used to determine both organic and inorganic substances including metal ions with the only reason of selectivity improvement. Despite of the fact that there are increasing methods to determine compounds such as H_2O_2 or glycerol, the combination of modified materials has been proved to facilitate the determination of trace metals. The good example is the use of bismuth, polystyrene sulfonate (PSS), and carbon nanopowder (CnP) in the determination of cadmium and lead [63]. This group can be further researched with the keyword "nanocomposites" [23, 64].

4.16. Biomolecules

Certain biomolecules including DNA, peptides, algae, and cell among numerous others can be used to determine specific metal ions. However, the experimental procedures can be much more complicated and difficult. The readers are recommended to obtain more information from an available review [65].

5. Roles of trace metal ions

Heavy metal contaminations have become one of the environmental issues of global concern due to the serious harm to human health. They have been main contribution for environmental problems caused by their ecological toxicity in a number of areas worldwide. Heavy metals and their products have been extensively distributed in natural surroundings, and they continued their cycles in accumulating in living organisms before passing on to human.

Among those not easily removed from the environment are cadmium, mercury, copper, lead, silver, zinc, and arsenic [41]. Lead and cadmium are responsible for the damage of kidney and nervous as well as circulation systems [66]. Lead particularly has the greatest effects on children due to the fact that it causes irreversible neurological disorders. The limits of lead and cadmium in drinking water set in the USA are 0.015 and 0.005 mg/l respectively [67]. Therefore, control and accurate determination of trace metals in environment is of paramount importance.

6. Stripping techniques for metal ion determination

For voltammetry, stripping techniques are the most widely used in metal ion analysis [2, 3] and normally the main objective of developing new ASV methodology for is to improve the analytical performances in determining trace metal ions including higher reproducibility, higher sensitivity, more convenience, better speed, lower cost, and environmentally friendlier conditions. The methods are optimized as well as standardized and then applied to the analysis of a great variety of real samples. Their brief practical aspects are presented as follows.

7. Optimizations of stripping voltammetry

After the modified electrode of interest is fabricated and its characteristics such as wettability are clearly defined, involving parameters are optimized such as electrolyte and electrolyte concentrations, pH and buffer to use, concentration of modifying agent and involving materials, deposition potential, deposition time, scan rate, and interferences. The optimized method is then applied with standards to obtain analytical performances followed by methods validations. Finally, real samples can be analyzed in comparison with other standard methods.

8. Comparison of voltammetry with other methods

The comparison of voltammetry with normal electrode has been comprehensively discussed, especially for the speciation of arsenic [68]. Spectroscopic methods can provide the best limit of detection (LOD) but with high cost. With higher LOD, voltammetry is a better choice. Due to much greater sensitivity achieved by using modified electrodes, previous obstacles can be overcome and makes a large number of methods in the past applicable to real sample analysis by electrochemistry.

9. Study of metal ligand interaction and surface

Once practical approaches have been clearly proved to be applicable, the next important step is delving into involving interactions in order to lay the brick for future development of modifying materials as well as metal species to be determined. Methods such as X-ray crystallography, cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and

quantum calculations can be helpful in understanding collecting interaction and bond formation between metal ions and coordinating atoms [69, 70].

In addition, normally surface method such as Scanning Electron Microscopy (SEM) as well as Transmission Electron Microscopy (TEM) can be employed to follow the change of the surface during modifications and EIS has also proved to be helpful in checking the conductivity of electrode materials [71].

10. Comparison of analytical performances for individual analyte

To picture the figures of merit and analytical performances and to compare a wide range of modified electrodes, a number of investigations have been summarized in **Tables 1–5**). The decision has been made to arrange the research items with the criteria of individual analyte with a wide range of publication periods to suit specific areas of researchers and to

Entry	Modified electrode	Methods	Ion/compound	Linear range (mol/l)	LD (nmol/l)	Ref
1	Fe_3O_4 NPs-CS[a]/GCE	DPV[j]	Bisphenol A (BPA)	0.05–30.0	8.0	[72]
2	CMK-3/nano-CILPE[b]	LSV[k]	Bisphenol A (BPA)	0.2–150	50.0	[73]
3	Fe_3O_4 NPs-CB[c]/GCE	DPV	Bisphenol A (BPA)	0.0001–50.0	0.031	[74]
4	Au NPs/SGNF[d]/GCE	LSV	Bisphenol A (BPA)	0.08–250.0	35.0	[75]
5	Au NPs-GR[e]/GCE	DPV	Bisphenol A (BPA)	0.0001–100	50.0	[76]
6	Fe_3O_4 NPs-PANAM[f] / GCE	AMP[l]	Bisphenol A (BPA)	0.01–3.07	5.0	[77]
7	RGO[g]/CNT[h]/Au NPs/SPE[i]	DPV	Bisphenol A (BPA)	0.00145–1.49	0.8	[78]

[a]CS: chitosan.
[b]CMK-3/nano-CILPE: ordered mesoporous carbon modified nano-carbon ionic liquid paste electrode.
[c]CB: carbon black.
[d]SGNF: stacked graphene nanofibers.
[e]Au NPs-GR: gold nanoparticles dotted graphene.
[f]PANAM: poly(amidoamine).
[g]RGO: reduced graphene oxide.
[h]CNT: carbon nanotubes.
[i]SPE: screen-printed electrode.
[j]DPV: Differential Pulse Voltammetry
[k]LSV: Linear Scan Voltammetry
[l]AMP: Amperometry

Table 1. Analytical performances of various modified electrodes for BPA determination.

Entry	Modified electrode	Methods	Ion/compound	Linear range (μg/l)	LD (μg/l)	Ref
1	CB-15-crown-5[a]/GCE	DPASV[j]	Pb/Cd	10.9–186.5/15.7–191.1	3.3/4.7	[35]
2	BiOCl[b]/MWCNT[c]/GCE	SWASV[k]	Pb/Cd	5–50/5–50	0.57/1.2	[79]
3	L-cys[d]/GR[e]-CS/GCE	DPASV	Pb/Cd	1.04–62.1/0.56–67.2	0.12/0.45	[80]
4	MWCNT/poly(PCV)[f]/GCE	DPASV	Pb/Cd	1.0–200.0/1.0–300.0	0.4/0.2	[81]
5	Bi-D24C8[g]/Nafion SPCE	SWASV	Pb/Cd	0.5–60/0.5–60	0.11/0.27	[2]
6	Bi/poly(p-ABSA)/GCE	DPASV	Pb/Cd	1.0–130/1.0–110.0	0.8/0.63	[82]
7	Bi-xerogel/Nafion/GCE	SWASV	Pb/Cd	1.04–20.72/0.56–11.24	1.3/0.37	[83]
8	Bi/CNT/SPE	SWASV	Pb/Cd	2–100/2–100	0.2/0.8	[84]
9	Bi_2O_3/GCE[h]	SWASV	Pb/Cd	2–250/1–150	0.26/0.52	[85]
10	BiF_4/CPE[i]	SWASV	Pb/Cd	20–100/20–100	9.8/1.2	[86]

[a]CB-15-crown-5, 4-carbox-ybenzo-15-crown-5.
[b]BioCl, bismuth-oxychloride.
[c]MWCNT, multi-walled carbon nanotube.
[d]L-cys, L-cysteine.
[e]GR, graphene.
[f]poly(PCV), poly(pyrocatecholviolet).
[g]D24C8, dibenzo-24-crown-8.
[h]Bi_2O_3/GCE, graphite-composite electrodes bulk-modified with Bi_2O_3.
[i]BiF_4/CPE, ammonium tetrafluorobismuthate bulk-modified carbon paste electrode.
[j]DPASV: Differential Pulse Anodic Stripping Voltammetry.
[k]SWASV: Square Wave Anodic Stripping Voltammetry.

Table 2 Analytical performances of various modified electrodes for Pd and Cd simultaneous determination.

Entry	Modified electrode	Methods	Ion/compound	Linear range (μM)	LD (μM)	References
1	Hb[a] microbelt/GCE	CV	H_2O_2	10–230	0.61	[87]
2	HRP[b]/DNA[c]-Ag/GCE	CV	H_2O_2	7.0–7.8	2	[88]
3	Cobalt oxide NPs/GCE	CV	H_2O_2	1–1000	0.6	[89]
4	Cyt c[d]/Ag NPs/GCE	CV	H_2O_2	8.5–130	9.8	[90]

Entry	Modified electrode	Methods	Ion/compound	Linear range (μM)	LD (μM)	References
5	Mb[e](Hb, HRP)/ SWCNT-CTAB[f]/GCE	CV[i]	H_2O_2	24.2–1670	8.07	[91]
6	Hb/undoped nanocrystalline diamond/GCE	CV	H_2O_2	2–25	0.4	[92]
7	Hb/PAN-co-PAA[g]/ GCE	CV	H_2O_2	–	4.5	[93]
8	Hb/chitosan and nano$CaCO_3$/GCE	CV	H_2O_2	–	8.3	[94]
9	Hb/nano-gold/ITO[h]	CV	H_2O_2	10–700	4.5	[95]
10	Hb/nano-Ag sol-gel/ GCE	CV	H_2O_2	1–250	0.1	[96]
11	Hb/nano-Ag-chitosan/ GCE	CV	H_2O_2	0.75–216	0.2	[97]

[a]Hb: Hemoglobin.
[b]HRP: Horseradish peroxidase.
[c]DNA: Deoxyribonucleic acid.
[d]Cyt c: Cytochrome c.
[e]Mb: Myoglobin.
[f]SWCNT-CTAB: Single walled carbon nanotubes-cetylramethylammonium bromide.
[g]PAN-co-PAA: poly(acrylonitrile-co-acrylic acid).
[h]ITO: Indium tin oxide.
[i]CV: Cyclic voltammetry.

Table 3. Analytical performances of various modified electrodes for H_{22} determination.

Entry	Modified electrode	Methods	Ion/compound	Linear range (nM)	LD (nM)	References
1	NN[a]HMDE[b]	CSV[f]	Iron	–	0.08	[98]
2	DHN[c]/HMDE	CSV	Iron	–	0.005	[99]
3	DHN[d](mercury coated, gold, micro-wire electrode)	CSV	Iron	–	0.1	[100]
4	5-Br-PADAP[d]HDME	DLSAV[g]	Iron	0.25–100	–	[101]
5	-(IL-rGO/AuNDs[e]/Nafion/ GCE)	SWV[h]	Iron	300–100,000	35	[102]

[a]NN: 1-nitroso-2-naphthol.
[b]DHN: 2,3-dihydroxynaphthalene.
[c]HDME: Hanging mercury drop electrode.
[d]5-Br-PADAP: 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol
[e]IL-rGO/Au NDs: ionic liquid-reduced graphene oxide supported gold nanodendrites.
[f]CSV: Cathodic stripping voltammetry.
[g]DLSAV: derivative linear sweep adsorption voltammetry
[h]SWV: Square wave voltammetry.

Table 4. Analytical performances of various modified electrodes for iron determination.

Entry	Modified electrode	Methods	Ion/compound	Linear range (μg/l)	LD (μg/l)	References
1	HMDE[a]	DPASV	Se (IV)	1.2–75	–	[103]
2	BiFE[b]	DPASV	Se (IV)	2.0–30	0.1	[104]
3	AuE[c] modified with poly 3,3′-diaminobenzidine 4HCl-Nafion	DPASV	Se (IV)	0.4–158	0.06	[105]
4	Screen printed graphite electrode	DPASV	Se (IV)	10–1000	4.9	[106]
5	Au NPs/BDD	DPASV	Se (IV)	10–100	–	[107]
6	Poly(3,3′- diaminobenzidine) film/AuE	DPASV	Se (IV)	7.9–79	0.78	[108]
7	Renewable silver annular band working electrode	DPASV	Se (IV)	1.0–10	0.15	[109]
8	AuNPs/E[d](GCE)	SWASV	Se (IV)	15–55	0.12	[110]

[a]HDME: Hanging Mercury Drop Electrode.

[b]BiFE: Bismuth film electrode.

[c]AuE: Gold electrode.

[d]E: Electrochemically prepared.

Table 5. Analytical performances of various modified electrodes for Se determination.

shed light on their upcoming research. Even though the focus is on metal ions, bisphenol A and hydrogen peroxide have been used as a model for the applications of modified electrodes in analyzing other compounds. Despite of the fact that two units of concentration are expressed, the advantage of modified electrodes in moving up to better sensitivity and specificity as well as their more useful and more innovative applications in the near future can be clearly seen.

11. Future trends

Electrochemistry has been used and studied for a long time, which lays great fundamentals for the development of newer electrochemical techniques. Valuable previous discoveries await their improvements by using modified electrodes. Innovations are underway to analyze metal ions with greater analytical performances as well as to suit simultaneous determinations. New compounds can be investigated and mixed or immobilized to increase the surface areas and serve species imprints which in turn require deeper investigations for the attractions and interactions between modified substrate and analytes. Modified electrodes should also work well with spectroscopic, separation, and other methods in a variety of ways. They have already been proved to facilitate reactions for energy research [111]. The new thing that has not been considered is the use of modified electrodes in organic synthesis to make it more specific [112]. Moreover, modified electrode has already found its ways in spectroelectrochemical

investigation [113]. Finally, new theoretical explanations can be adapted for better understanding and applications, which would be the stepping stones for more and greater inventions in the future.

12. Conclusions

Modified electrodes have been proved to be effective in the determination of a number of metals ions. With the speed, simplicity, and sensitivity of stripping voltammetry, the methods can be successfully applied to their analysis at trace level. Mixtures of various compounds await the art to manifest them in increasing the sensitivity for monitoring the concentrations of important metal ions. Additionally, the discovery of new nanomaterials would give stripping voltammetry a bright future. Furthermore, new electrochemical techniques such as EIS would assist the applications of modern modified electrodes in a great variety of areas. It is hoped that this article fires up researchers as well as opens up new opportunities in initiating and conducting new electrochemical research to be universally applicable in vast areas.

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