Recent Advances in Electrochemical Sensor and Biosensors for Environmental Contaminants

Li-Ping Mei, Pei Song, Yuan-Cheng Zhu, Yi-Fan Ruan, Xiao-Mei Shi, Wei-Wei Zhao, Jing-Juan Xu, and Hong-Yuan Chen

Contents

1 Introduction

Due to the development of society and technologies, the quality of human life has been obviously improved, especially in recent years. However, the following environmental issues are becoming increasingly serious. Numerous types of contaminants are released by modern factories, suburban farms, and even by urban communities, which are threatening human health and destroying the balance of

L.-P. Mei · P. Song · Y.-C. Zhu · Y.-F. Ruan · X.-M. Shi · W.-W. Zhao (✉)
J.-J. Xu · H.-Y. Chen (✉)
State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, China
e-mail: zww@nju.edu.cn; xujj@nju.edu.cn; hychen@nju.edu.cn

Inamuddin, A. M. Asiri (eds.), *Nanosensor Technologies for Environmental Monitoring*, Nanotechnology in the Life Sciences,
https://doi.org/10.1007/978-3-030-45116-5_1

ecosystems. In September 1996, the European Union adopted the Integrated Pollution Prevention and Control Directive, which could combine prevention and control of pollution to ensure a high level of environmental protection (O'Malley 1999). Up to now, almost all of the countries have promulgated several related laws to control the emission of environmental pollution.

Common environmental contaminants usually include heavy metal ions, organic contaminants, antibiotics, pathogens, gas pollutants, and so on. Heavy metals refer to those metal elements with a density larger than 5 g cm^{-3} and the atomic weights between 63.5 and 200.6 g mol^{-1} (Fu and Wang 2011; Srivastava and Majumder 2008), which are not biodegradable and easily accumulate in living organisms through food chains. Usually, heavy metal ions, such as copper, nickel, zinc, cadmium, mercury, chromium, and lead are released along with industrial wastewater and car exhausts to the outer environment. Excessive heavy metal ions can cause series of health problems, such as skin irritations, gastrointestinal distress, pulmonary fibrosis, and damage to the central nervous system, or even death (Paulino et al. 2006; Njau et al. 2000; Zhu et al. 2009; Bojdi et al. 2014; Metters et al. 2012). In addition, organic pollutions are also considered as other important environmental contaminants. Aromatic compounds are the most harmful to the human health and ecological environment among organic pollutions, such as phenolic compounds and polyaromatic hydrocarbons. Phenolic compounds are formed by hydroxyl substitution of hydrogen atoms on benzene rings in aromatic hydrocarbons. According to the number of hydroxyl groups, phenolic compounds can be divided into monophenols and polyphenols. Phenolic compounds in the environment come from a wide range of sources, including wastewater from chemical and pharmaceutical industries, degradation of organic pesticides, automobile exhaust, and so on. Phenolic compounds are commonly transmitted through water and air and can remain in the soil for a long time. Due to their carcinogenic, teratogenic, mutagenic, and other potential toxicity, phenolic compounds will cause serious harm to the ecological environment, animals, plants, and human health (Teh and Mohamed 2011; Su et al. 2011; Aksu 2005; Samanta et al. 2002; Falahatpisheh et al. 2001). Similarly, antibiotics, as one of the common pollutions, are the most useful drug for bacterial infection. However, antibiotics are not only used for disease treatment but also extensively used for growth-promoting of animals in animal husbandry (Martinez 2009; Smith et al. 2002). The release of antibiotics in the natural environment will lead to the selection of resistant bacteria, which may cause the appearance of super bacteria (Davies 1994). In addition to the above contaminants, gas pollutants mainly include carbon monoxide, nitric oxides, oxides of sulfur, and volatile organic compounds, and are derived from gaseous industrial emissions, such as the burning of coal, petroleum, and other fossil fuels, and automobile exhaust (Li et al. 2012). These gas pollutants may cause acid rain and damage the respiratory systems of humans and animals.

Highly sensitive detection of environmental pollutants can help to guide the pollution control and also protect humans from the damage of pollutants. In recent

years, environmentalists and analytical chemists have devoted plentiful of efforts to seek a sensitive detection method to measure and monitor the concentration of environmental pollutants. Up to now, much-advanced detection techniques have been developed, such as atomic spectroscopy (Hatch and Ott 1968), molecular spectroscopy (Xu et al. 2007), spectrophotometry (Baker et al. 2003), chromatography (Reemtsma 2003), mass spectrometry (Daughton 2001), electrochemistry method (Metters et al. 2012; Su et al. 2011), and so on. Although the accuracy and sensitivity of the previously reported methods are acceptable, the detection procedure of samples is usually expensive, complex, and time-consuming. These weaknesses are not suitable for the development toward civilianization and portability. Fortunately, electrochemistry methods, or electrochemical sensors, hold great promise to overcome the above disadvantage, due to their simplicity, rapid response, high sensitivity, small size, and low cost. Electrochemical sensors have been widely used to determine the amount of trace heavy metals ions in natural waters (Batley 1983), carcinogen (Barek et al. 2001), gas pollutants (Wan et al. 2018), and organic pollutants (Yang et al. 2018). Electrochemical biosensors have gradually emerged through an effective integration of specific biorecognition elements and electrochemical sensors. Benefit from the high selectivity of bio-recognition element, biosensors are worked without complex sample processing and can even be applied to multicomponent detection. Hence, the electrochemical sensors and biosensors have shown great potential for laboratory-based and on-site analysis of environmental contaminants.

This chapter has stated the important roles of electrochemical sensors and biosensors for environmental contaminants. We have summarized the common types, electrode materials, and composition of electrochemical sensors and biosensors. We have focused on the advances of electrochemical sensor technology in an update of electrode materials and fabricated strategies. In recent 5 years, applications of electrochemical sensors and biosensors in environmental problems and future trends have also been reviewed.

2 Fabrication

2.1 The Principles of Electrochemical Sensor and Biosensors

Electrochemical sensors and biosensors are devices that can sense the physical, chemical, or biological changes of analytes and convert them into measurable amperometry, voltammetry, impedance, or other electrochemical signals (Fig. 1). The electrochemical sensing system usually contains three electrodes: working electrode, counter electrode, and reference electrode. The working electrode is responsible for generating redox reaction of analytes and sensing redox signal. And the counter electrode is used to establish a closed circuit through electrolytic

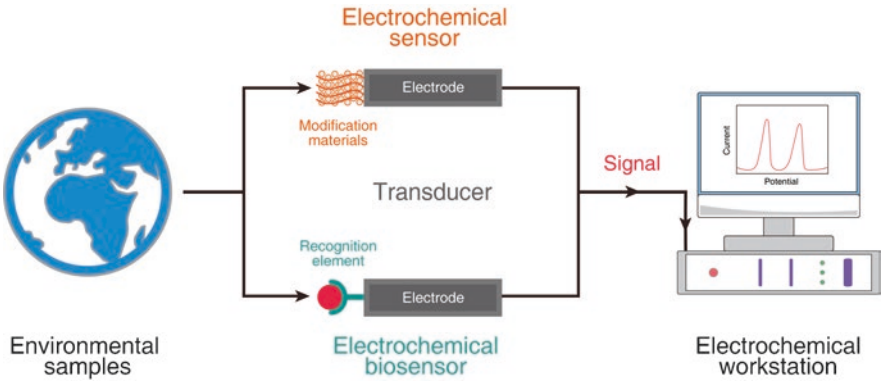

Fig. 1 The principle of electrochemical sensors and biosensors for environmental pollutions

solution so that the voltage/current can be applied to the working electrode. The reference electrode serves as a benchmark to maintain a known and stable operating potential.

The fundamental of electrochemical detection is redox reaction that occurs on the surface of work electrodes. Therefore, environmental contaminants with electrochemical activities can be directly sensed by electrochemical sensors. Voltammetry is the most widespread technology for electrochemical sensors, which can measure the current response to achieve a precise quantitative analysis of target analytes under an applied potential. Voltammetry exhibits a wide linear range that is from sub-ppb to ppm. A high concentration of analytes with ppm or ppb can be analyzed by cyclic voltammetry, differential pulse, or square-wave voltammetry techniques, while the analytes with low concentrations with ppb or sub-ppb can be measured by the stripping voltammetry techniques. The sensing process is mainly described as follows: First, a constant or variational voltage is applied to the working electrode that is immersed in the electrolyte containing various analytes. Then, redox reactions will occur on the electrode surface, resulting in the change of the current signal. Finally, the number of analytes can be obtained through the corresponding variations of electrical signals.

In order to improve selectivity and sensitivity for environmental pollutants, electrochemical biosensors were gradually developed, which involved high specificity biorecognition elements during their fabrication process. The biosensor is composed of a molecular recognition element and a conversion section. For environmental monitoring, the recognition element must specifically recognize one or several particular contaminants from a complex real sample without any interference. Therefore, enzymes, antibodies, and nucleic acids with high specificity are often used as the recognition element to modify the working electrode. Once the

target environmental pollutants are identified and captured by the recognition element, electric signals of modified electrodes will be immediately changed.

2.2 *Materials for Electrochemical Sensor and Biosensors*

As one of the most important parts of electrochemical sensors and biosensors, novel electrode materials are widely studied to improve the electrochemical catalytic activity of as-fabricated sensors and biosensors. Most electrochemical reactions are normally carried out on the surface of working electrodes, so the electrode materials should be chemically inert and with good electrical conductivity. Up to now, gold electrode (Shen et al. 2008; Lupu et al. 2009), glassy carbon electrode (Zhang et al. 2019a, b), and indium tin oxide (Fu et al. 2018; Vaishnav et al. 2015) are commonly used as substrate electrode to design high sensitive electrochemical sensors. Shen and co-workers have developed an enzyme-based electrochemical biosensor based on a modified gold electrode for sensitive detection of trace lead ions (Shen et al. 2008). Li's group has used glass carbon electrode as the substrate electrode to coat a carbon sphere and fabricate electrochemical sensor for the determination of dihydroxybenzene isomers (Yang et al. 2019a, b). Vaishnav and co-workers developed an indium tin oxide film electrochemical sensor, which exhibits improved performance for sensitive and selective detection of benzene (Vaishnav et al. 2015).

Meanwhile, many emerging materials are explored to modify the surface of the electrode, such as conducting polymers (Hatchett and Josowicz 2008; Ates 2013), metal-based nanomaterials (Wu et al. 2019; Li et al. 2019a, b), carbon nanotubes (Şenocak et al. 2019; Alam et al. 2019), graphene (Yi et al. 2019; Shao et al. 2010), and metal–organic framework nanomaterials (Cao et al. 2019; Lu et al. 2019a, b). This leads to the electrodes with good stability, huge specific area, improved redox performance, and recyclability. In the following paragraphs we introduce the application of these electrode materials in the construction of electrochemical sensors and electrochemical biosensors.

2.2.1 Conducting Polymers

Because of the delocalization of π-bonded electrons over polymeric backbone, the conducting polymers exhibit unique electronic properties, such as low ionization potentials and high electron affinities (Ates 2013). Owing to excellent electronic conductivity properties, operability, and low cost, conducting polymers are deemed to be one of the most attractive materials to modify the electrode surface. Liu and co-workers have explored the over-oxidized poly(3,4-ethylenedioxythiophene) films to replace Nafion films as the fixed layer for the modification of electrodes (Liu et al. 2011). Polypyrrole was utilized to enhance electrocatalytic currents in this system, attributing to its good conducting performance. Manisankar and coworkers have prepared poly(3,4-ethylenedioxythiophene)-modified electrodes

and fabricated electrochemical sensors for the detection of pesticides (Manisankar et al. 2005). The sensors show excellent performance toward the determination of pesticides. Recently, copolymer-based electrode was developed by in situ generation 3-poly(propylene thiophenoimine)-co-poly(3-hexylthiophene), which was applied to design a highly sensitive pyrene electrochemical sensor (Makelane et al. 2019). In addition, conducting polymers have been also applied to immobilize enzymes onto the electrode surface for the preparation of electrochemical biosensors, due to the unique cross-linking properties (Lin and Yan 2012).

2.2.2 Metal-Based Nanomaterials

With the rapid development of technologies, metal nanomaterials have been widely used in various fields of catalysis, biomedicine, energy, and environmental analysis. Currently, metal nanomaterials with different compositions and morphologies are successfully synthesized, in which some of them act as the electrode-modified materials used for the fabrication of electrochemical sensors and biosensors. Rahman and coworkers have synthesized the gold–silver alloy nanoparticles and fabricated an electrochemical sensor for the detecting of pyrene with the low detection limit of 0.1 μM (Latif ur et al. 2015). Poliana and coworkers have constructed an electrochemical sensor with high sensitivity for the quantitative analysis of phenolic compounds, which is on the strength of zinc oxide nanocomposites-modified glass carbon electrode (Freire et al. 2016). The synthesized zinc oxide nanoflowers can be used to effectively enhance the current response and reduce the separated peaks during the process of electrochemical oxidation of phenolic compounds. Magnetic ferroferric oxide nanoparticles were synthesized and utilized to fabricate an electrochemical sensor for simultaneous detection of multiple heavy metal ions (Wu et al. 2019). The integration between as-prepared magnetic ferroferric oxide nanoparticles and multiwalled carbon nanotubes has effectively improved the performance of electrochemical sensor. Meanwhile, the metal-based nanomaterials are served as electrode materials and also used to fabricate electrochemical biosensors. Gu's group has used multisegment gold/platinum nanowire and nanoparticle hybrid arrays as the electrode materials and developed antibiotics electrochemical biosensors with excellent analytical properties, in which L-cysteine and penicillinase were considered as biological recognition molecules for tetracycline and penicillin, respectively (Li et al. 2019a, b).

2.2.3 Carbon Nanotubes

The carbon nanotubes consist of sp^2 carbon units, which is different from the traditional carbon fibers. There are two categories in the family of carbon nanotubes: single-wall carbon nanotubes and multiwall carbon nanotubes. Carbon nanotubes possess excellent mechanical and electronic properties and can be used in the sensing field. Alam and coworkers have developed an electrochemical sensor for

detecting of lead ions in drinking water using the modified multiwall carbon nanotubes (Alam et al. 2019). Benefit from high electron transfer efficiency of multiwall carbon nanotubes, the sensors exhibit high sensitivity and selectivity for the analysis of lead ion. Ahmet and coworkers have synthesized single-wall carbon nanotubes-based hybrid material and designed an electrochemical sensor with excellent analysis performance for the determination of serine (Şenocak et al. 2019). Sun's group has developed an ultrasensitive electrochemical aptasensor for chlorpyrifos using ordered mesoporous carbon/ferrocene hybrid multiwall carbon nanotubes as electrode materials, which could be provided to enhance the sensitivity of the developed biosensor (Jiao et al. 2016).

2.2.4 Graphene

Graphene and its derivatives have attracted tremendous attention from researchers in recent years, due to their special physical and chemical properties of good electric conductivity, strong mechanical strength, and large surface area (Shao et al. 2010). These excellent features make them as good candidate electrode materials for the construction of electrochemical sensors and biosensors. Although the basic building unit of graphene is similar to zero-dimension fullerenes and one-dimension carbon nanotubes, the two-dimensional structure of graphene and its derivatives result in an enlarged specific surface area. Surface modification of working electrodes through graphene can significantly increase the effective electrode area and enhance response signals of electrochemical sensors and biosensors. Furthermore, graphene oxide composite materials have been prepared and used as the modification electrode materials for the fabrication of sensitive electrochemical sensor, which have been applied to simultaneously determine a variety of heavy metal ions (Yi et al. 2019). Recently, porous three-dimensional graphene framework has also been investigated to enhance the mechanical property. Shi and coworkers have synthesized a novel three-dimensional graphene framework/bismuth nanoparticles film with rapid electron transfers ability, remarkably large active area, excellent structure stability, and high mass transfer efficiency, which have been utilized to design a heavy metal ions electrochemical sensor with enhanced analytical performance (Shi et al. 2017). Similarly, Sethuraman and coworkers have developed an electrochemical catechol biosensor based on reduced graphene oxide-metal oxide composite and enzyme, in which the introduced graphene nanocomposites were provided to improve the sensitivity of catechol biosensors (Sethuraman et al. 2016).

2.2.5 Metal–Organic Frameworks

The metal–organic framework is an organic-inorganic hybrid material with intramolecular pores formed by self-assembly of organic ligands and metal ions or clusters through coordination bonds. In recent years, metal–organic frame materials have captured considerable attention, because of their characteristics of porosity,

large specific surface area, structural and functional diversity, and unsaturated metal sites. Various metal–organic framework materials have been prepared, and have important applications in the fields of hydrogen storage, gas adsorption and separation, sensors, drug release, catalytic reaction, and so on. With the increasing number of metal-organic framework materials and the gradual rise of composite metal–organic framework materials, metal–organic framework materials will have inestimable application prospects. However, there are only a few studies on the application of metal-organic framework materials as electrode materials in the fabrication of electrochemical sensors and biosensors. Based on as-prepared graphene aerogel–metal organic frameworks, Wang's group has developed an effective electrochemical sensor for simultaneous detection of heavy metal ions (Lu et al. 2019a, b). Owing to the synergy effect of graphene and metal-organic frameworks, the sensors show high sensitivity and selectivity. Cao and coworkers have utilized hierarchically porous copper-based metal–organic framework materials to construct an electrochemical glyphosate sensor, which exhibits high sensitivity with the ultralow detection limit of 1.4×10^{-13} mol L^{-1} (Cao et al. 2019).

3 Application of Environmental Contaminants

Currently, many efforts have been devoted to the research and developments of technologies toward a decrease or detection of the impacts of environmental pollutions (Maduraiveeran and Jin 2017). The potential of electrochemical sensors and biosensors was explored for detecting commonly environmental contaminants including heavy metal ions, phenolic compounds, polyaromatic hydrocarbons, pesticides, antibiotics, pathogens, gas pollutants, and so on (Fig. 2). Due to their simplicity, accuracy, and portability, electrochemical sensors and biosensors have been widely demonstrated to be useful for the recognition and quantitative analysis of specific compounds (Ramnani et al. 2016; Rotariu et al. 2016; Saidur et al. 2017). The detailed applications of electrochemical sensors and biosensors in the detection of environmental pollutions are depicted as follows.

3.1 Heavy Metal Ions

When the specific gravity of metals is larger than 5 and metals with a density greater than 4.5 g cm^{-3}, the metals can be generally defined as heavy metals, containing gold, silver, copper, iron, mercury, lead, cadmium, and so on (Bansod et al. 2017; Cui et al. 2015; Zhang et al. 2019a, b). Heavy metals can cause chronic poisoning when the accumulation reaches a certain extent in the living organism. However, heavy metals usually involve lead, cadmium, mercury, chromium, metalloid

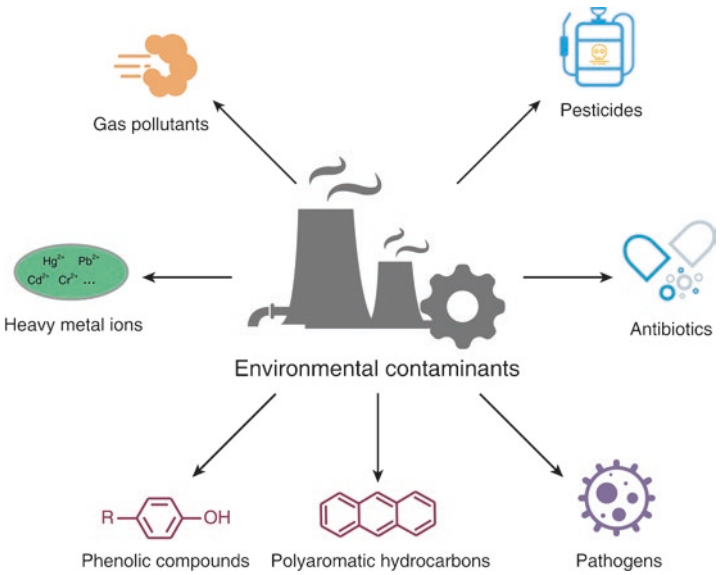

Fig. 2 The classification of commonly environmental pollutions

arsenic, and other crucial biological poisonous heavy elements in the matter of environmental contaminants. Heavy metals are very hard to biodegrade and can be easily accumulated in vivo through the biomagnification effect of the food chain. Thus, the aggregated heavy metals can cause some irreversible damages to human beings, because they can lead to chronic poisoning and inactivation of enzymes and proteins in the human body. Due to the increasing industrial activities of human beings, heavy metal ions have become a significantly serious environmental problem that cannot be ignored. Therefore, it is urgent to develop an efficient, rapid, sensitive, accurate, and highly selective approach for the determination of heavy metal ions.

Compared with the traditional methods (Liu et al. 2017; Barbosa et al. 2016; Liang et al. 2000; Sun et al. 2017), electrochemical technique can be regarded as one of the most potential methods for the detection of heavy metal ions, due to its simplicity, rapid, high selectivity, and sensitivity. The process of electrochemical determination of heavy metal ions primarily involves two parts: recognition process and signal translation process. The detection mechanism of heavy metal ion electrochemical sensors and biosensors are both mainly based on the conversion of the specific recognition reaction between recognition element and target analytes to a measurable electrochemical signal (Saidur et al. 2017). And the generated signal response is related to the concentration of studied analyte, so heavy metal ions can be quantitatively analyzed by electrochemical sensors and biosensors.

3.1.1 Lead Ions

Lead ions, as one of the most toxic metallic pollutants, can accumulate in living organisms through the food chain and cause a series of adverse effects on human health (Wang et al. 2018; Dolati et al. 2017; Zhou et al. 2016). Due to the potential threats of lead ions to public health, many countries and organizations have strict hygiene regulations on the content of lead ions in drinking water. The maximum limit for lead ions contaminant in drinking water has been set to be 72 nM by the U.S. Environmental Protection Agency, while the International Agency for Research on Cancer has defined the safety limit of lead ion as 48.26 nM in food and drinking water (Guo et al. 2015). Thus the development of a novel analytical approach is significant for effective and routine detection of lead ions in the environment.

Currently, various lead ions electrochemical sensors and biosensors have been developed for highly selective and sensitive determination of lead ions. Zhang and coworkers have prepared $Mn_{1-x}Zn_xFe_2O_{4s}$-modified electrodes and used for directly electrochemical detection of lead ions, and the analytical performance of this sensor was enhanced by the introduction of zinc ion and Nafion (Zhang et al. 2019a, b). Additionally, several electrochemical biosensors have also been designed for the effective determination of lead ions. For example, Wei and coworkers have proposed a highly sensitive lead ion electrochemical aptasensor, which is based on gold nanoparticles-modified graphene nanocomposite as a signal probe to achieve ultrasensitive determination of lead ions (Fig. 3) (Wang et al. 2019a, b).

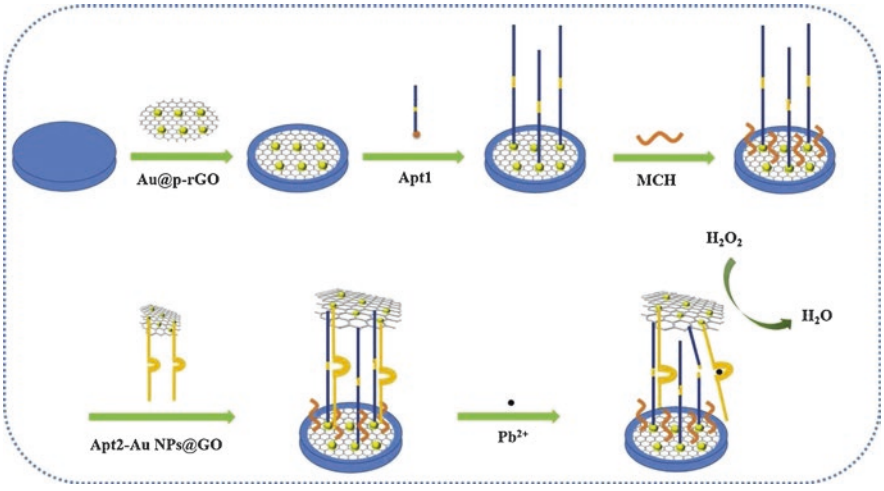

Fig. 3 The scheme of fabrication of lead ion electrochemical aptasensor. Note the Au@p-rGO was prepared and supplied to immobilize the aptamer, which showed excellent electrocatalytic activity toward H_2O_2. Based on this, a highly sensitive electrochemical aptasensor was constructed and exhibited good performance for the detection of lead ions. *Au@p-rGO* Gold-modified porous reduced graphene oxide, *Apt1* sulfydryl-labeled substrate strand, *Apt2* sulfhydryl-labeled catalytic strand, *MCH* 6-mercapto-1-hexanol. Reprinted from Wang et al. (2019a, b), with permission from Elsevier

3.1.2 Cadmium Ions

Cadmium ion is also one of the heavy metal pollutions that easily accumulates in the environment through the food chain (Si et al. 2018). It is highly toxic and endangers the health of humans and the environment. Thus, it is of great importance for researchers to develop a rapid, convenient, low-cost, and high-efficiency technique to monitor and detect trace amounts of cadmium ions in the environment.

Due to their simplicity and cost-efficiency, electrochemical sensors have been frequently used in cadmium ion detection in recent 5 years (Si et al. 2018; Zhao et al. 2016). For example, a novel cadmium ions electrochemical sensor on account of reduced graphene oxide–gold nanoparticles–tetraphenylporphyrin nanoconjugates has been proposed by Si and coworkers (Si et al. 2018). The cadmium ions can be effectively detected, according to the coordination effect between cadmium ions and porphyrin. The sensitivity of the as-developed electrochemical sensor could be enhanced by the introduced Au nanoparticles.

3.1.3 Mercury Ion

As one of the most toxic heavy metal contaminants, accumulated mercury ion can cause serious adverse effects on human and environmental health. The mercury ions determination has attracted extensive attention to environmental monitoring. In recent 5 years, numerous literatures based on electrochemical detection mercury ions have been reported (Akbari Hasanjani and Zarei 2019; Xu et al. 2018; Isa et al. 2017; Wang et al. 2016). For example, Li and coworkers have constructed a highly sensitive electrochemical biosensor for the quantitative analysis of mercury ions, in which the electrical signals have been amplified by the synergistic effect between DNA-based hybridization chain and silver@gold core–shell nanoparticles with a positive charge (Li et al. 2016). This mercury ions electrochemical biosensor shows excellent performance with a low detection limit of 3.6 nM. Subsequently, He's group has utilized the specific thymine-Hg^{2+}-thymine base pair to fabricate a highly sensitive mercury ions electrochemical biosensor (Fig. 4) (Yu et al. 2019). Toluidine blue integrated with hybridization chain reaction could effectively realize mercury ions signal amplification. The developed biosensor exhibited a remarkable response for mercury ions, which includes a low detection limit of 0.2 pM and a wide linear range from 1 pM to 100 nM.

3.1.4 Arsenic Ions

Arsenic ion is also considered as a category of toxic environmental pollution, which can bring about various health and environmental issue, such as the skin, kidneys, urinary bladder, and lungs (Kato et al. 2016; Jaishankar et al. 2014). Therefore, it is necessary to develop a convenient, rapid, and efficient approach for quantitative analysis of arsenic ions in the environment. In contrast with traditional spectroscopy

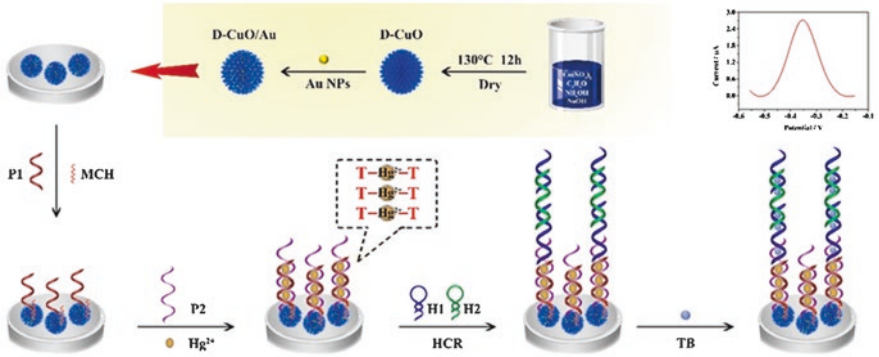

Fig. 4 The fabrication of the mercury ions electrochemical biosensor. Note CuO dandelion-like microspheres modified with Au nanoparticles were prepared and used as electrode materials to enhance the analytical properties of biosensors. And toluidine blue, as redox indicator, was integrated with the hybridization chain reaction for signal amplification. *D-CuO-Au* gold nanoparticle modified dandelion-like copper oxide, *P1* thiolated probe; *P1: other oligonucleotide H1 and H2* two hairpin DNA, *HCR* hybridization chain reaction, *TB* toluidine blue. Reprinted from Yu et al. (2019), with permission from Elsevier

methods (Kempahanumakkagari et al. 2017), electrochemical methods are more suitable for the monitor of arsenic ion content in terms of their easy operation, low-cost, and high sensitivity. For example, Gumpu and coworkers have fabricated a preeminent sensor for electrochemical determination of arsenite and arsenate, on the basis of ruthenium bipyridine–graphene oxide nanocomposite modified electrode (Fig. 5) (Gumpu et al. 2018). This as-developed sensor exhibits excellent properties toward the determination of arsenic(III) and arsenic(V) with the detection limits of 21 nM and 34 nM, respectively.

3.1.5 Simultaneous Detection of Heavy Metal Ions

As well known, common heavy metal ions in the environment mainly include lead, cadmium, mercury, arsenic, and other metal ions. Although numerous literatures on electrochemical detection heavy ions have been reported (Cui et al. 2015; Si et al. 2018; Akbari Hasanjani and Zarei et al. 2019; Kato et al. 2016), it is still important in terms of research significance of the simultaneous monitor for various heavy metal ions due to the complexity of actual samples. As illustrated in Fig. 6, Ferreira's group has investigated the impacts of the incorporation of gold nanoparticles into layer-by-layer films of emeraldine salt polyaniline and sodium montmorillonite clay mineral and constructed an electrochemical sensor for simultaneous several heavy metal ions detection (de Barros et al. 2017). Electrochemical sensors exhibited high performance toward the detection of trace-level cadmium, lead, and copper ions with the induced gold nanoparticles.

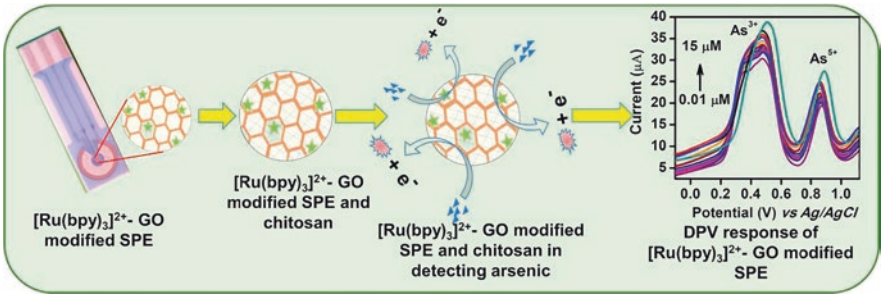

Fig. 5 Schematic of electrochemical detection of arsenic ions. Note a preeminent sensor for electrochemical determination of arsenite and arsenate, on the basis of ruthenium bipyridine–graphene oxide nanocomposite ($[Ru(bpy)_3]^{2+}$-GO)-modified electrode. And $[Ru(bpy)_3]^{2+}$-GO was used as interface and promoted electron transfer rates. Reprinted from Gumpu et al. (2018), with permission from Elsevier

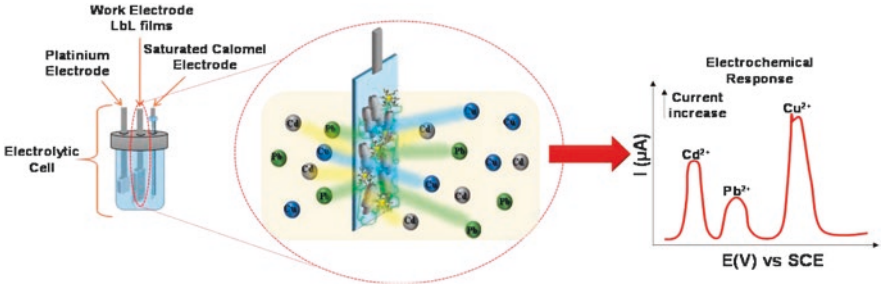

Fig. 6 Schematic of simultaneous electrochemical detection of several heavy ions. Note the impacts of the incorporation of gold nanoparticles into layer-by-layer films of emeraldine salt polyaniline and sodium montmorillonite clay mineral have been investigated. On the basis of this, an electrochemical sensor was constructed for simultaneous detection of cadmium, lead, and copper ions by square wave anodic stripping voltammetry. Reprinted from Barros et al. (2017), with permission from Elsevier

3.2 Phenolic Compounds

Phenolic compounds are prototype poisons substances and are as one of the 129 priority controlled pollutants identified by the US Environmental Protection Agency, which has great potential harm to human health and ecological environment (Huang et al. 2016; Xie et al. 2006). Phenolic compounds, as one of the main pollutants, are mainly derived from dye, pesticide, petrochemical, and other enterprises discharged wastewater, which are widely distributed in the natural environment (Gan et al. 2017). It is of great significance for precise analysis of trace phenolic compounds in the real sample.

Common analytical methods for phenolic compounds mainly involve spectrophotometry (Han et al. 2014), high-performance liquid chromatography (Hofmann et al. 2015), gas chromatography (Kovács et al. 2011), and electrochemical

technologies (Freire et al. 2016; Gan et al. 2017). In contrast, electrochemical methods have attracted increasing attention among the determination of phenolic compounds because of their easy operation, simplicity, preeminent selectivity, and low cost (Wee et al. 2019). Different electrochemical sensors have been fabricated for the quantified analysis of phenolic compounds in recent 5 years (Govindhan et al. 2015; Jiang et al. 2019; Camargo et al. 2018; Lima et al. 2018). Generally, oxidation signals of phenolic compounds are often recognized through conventional bare electrodes with high over potentials. In terms of the development of various electrode materials or optimizing the experimental conditions, many efforts have been devoted to magnifying measurable signals for the electrochemical detection of phenolic compounds (Lima et al. 2018; Maikap et al. 2016; Huang et al. 2015). For example, a titanium dioxide-based electrochemical sensor was designed for the detection of bisphenol A, in which high-energy {0 0 1}-exposed titanium dioxide single crystals were served as the electrode material to amplify the signal (Fig. 7) (Pei et al. 2018). This as-fabricated sensitive sensor obtained excellent performance toward the bisphenol A with a low detection limit of 3.0 nM.

Phenolic catalytic enzymes are involved during the development of electrochemical biosensors, which can be used to effectively catalyze oxidation phenolic compounds (Apetrei et al. 2013; Roychoudhury et al. 2016). Tyrosinase, laccase, and polyphenol oxidase are commonly applied to construct phenolic biosensors, which have advantages of rapid response, high sensitivity, and selectivity, long-term stability (Andreescu and Sadik 2004). As a significant polyphenol oxidase, laccase can oxidize the phenolic hydroxyl to generate the measurable signal (Rodríguez-Delgado et al. 2015). For instance, Jiang and coworkers have constructed a new electrochemical biosensor for simultaneous determination of catechol and hydroquinone (Fig. 8) (Jiang et al. 2019). Meanwhile, tyrosinase has the capacity for the oxidization of mono and diphenol compounds among the most phenolic biosensors, which is due to its two copper atoms within the active sites (Sethuraman et al. 2016).

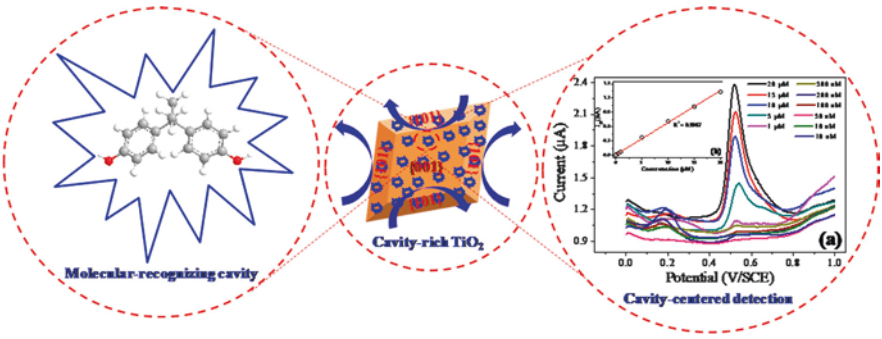

Fig. 7 Schematic of electrochemical detection of bisphenol A. Note high-energy {0 0 1}-exposed titanium dioxide single crystals were prepared and served as the electrode material to amplify the signal. The fabricated electrochemical sensor was applied for the detection of bisphenol A with wide linear range. Reprinted from Pei et al. (2018), with permission from American Chemical Society

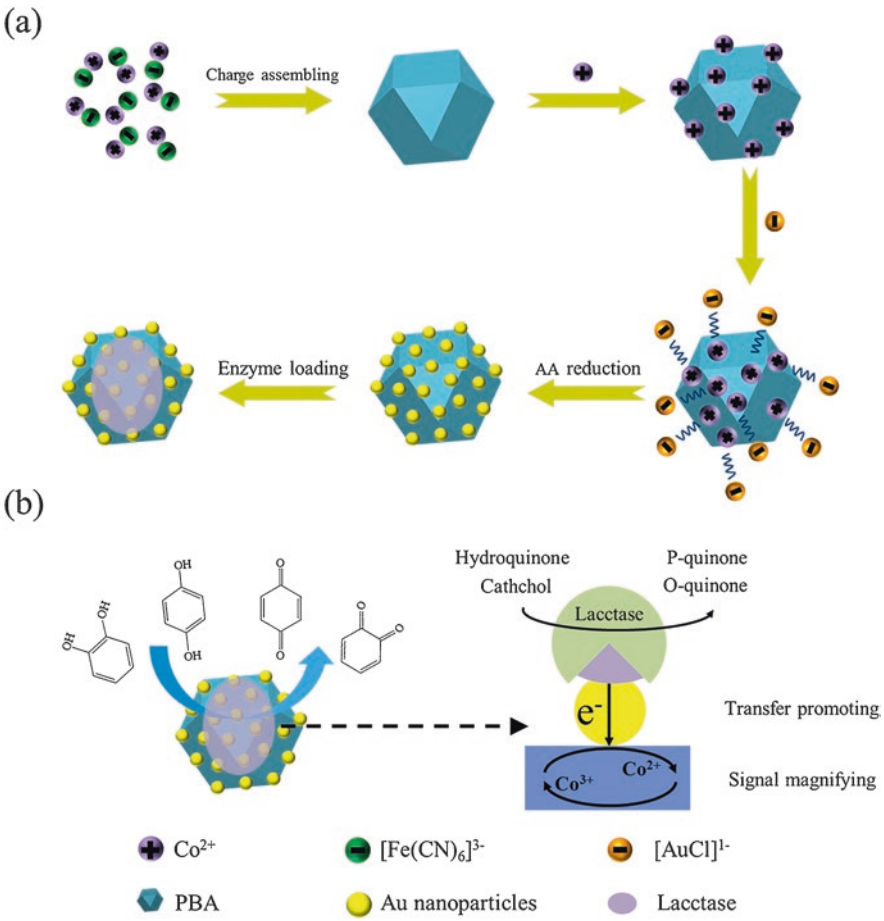

Fig. 8 Lactase-based electrochemical biosensor for the simultaneous detection of catechol and hydroquinone. Note each prepared Prussian blue analog crystal with the high surface area can be a benefit for the combination of enzyme center and Prussian blue analog crystal, which can accelerate the electron transfer. Based on the synergy between electrode materials, the as-prepared phenolic biosensor was designed and obtained simultaneous detection for the trace hydroquinone and catechol with high sensitivity under various applied potentials. *PBA* Prussian blue analog. Reprinted from Jiang et al. (2019), with permission from Elsevier

A highly selective biosensor was built for the electrochemical determination of catechol on the basis of enzyme-modified electrode (Sethuraman et al. 2016).

Simultaneous determination of phenolic isomers is of great significance due to the coexistence of them in actual samples. However, similar physicochemical properties of phenolic isomer would result in the overlapping peak potentials, which is a key obstacle for their quantitative analysis (Huang et al. 2016). Some researchers have carried out electrochemical pretreatment on the surface of screen-printed electrode through different methods and obtained a fine peak separation of hydroquinone and catechol (Wang et al. 2010).

3.3 Polyaromatic Hydrocarbons

Polyaromatic hydrocarbons are volatile hydrocarbons and important environmental and food pollutants commonly generated by incomplete combustion of coal, oil, wood, tobacco, organic polymer compounds, and other organic compounds (Makelane et al. 2019). Up to now, more than 200 kinds of polyaromatic hydrocarbons, such as benzo α pyrene, benzo α anthracene, and so on, are easily carcinogenic, and widely distributed in the environment (Tovide et al. 2014). A large number of polyaromatic hydrocarbons in the environment are worrying because they are known to be highly toxic and have adverse health effects at low concentrations. Thus the determination of polyaromatic hydrocarbons in food, seawater, and lakes has aroused intensely research interest. To date, electrochemical sensor has been considered as a vital analysis tool for environmental determination, which is mainly based on the electrooxidation behavior of polyaromatic hydrocarbons (Makelane et al. 2019; Tovide et al. 2014). Iwuoha's group has exploited an anthracene electrochemical sensor based on graphenated polyaniline nanocomposite (Tovide et al. 2014). The amount of anthracene could be directly quantified through the electrooxidation behavior of anthracene on the surface of the modified electrode.

3.4 Pesticides

Generally, pesticides refer to chemicals extensively used in agriculture to control diseases and insect pests and regulate plant growth. Pesticides are the most affluent among the whole environmental contaminants, which are widely presented in atmosphere, water, soil, food, and plants (Uniyal and Sharma 2018; Kaur and Prabhakar 2017; Kumar et al. 2015). It is well known that pesticides are highly toxic and have an adverse impact on human's health and ecological balance. Therefore, it is vitally important to exploit a highly sensitive, facile, and low-cost approach for the accurate determination of pesticides in the environmental samples.

Traditionally, the detection methods of pesticides are general mass spectrometry (Chamkasem and Harmon 2016) and chromatography (Berijani et al. 2006), but these methods have some disadvantages of time-consuming, require a professional operation, and expensive. As a novel analytical method, electrochemical analytical technologies have been also extensively used due to their simplicity, sensitivity, and selectivity (Pérez-Fernández et al. 2019). In recent 5 years, various electrochemical sensors have been fabricated and applied for the quantitative analysis of pesticides through the direct redox reaction (Şenocak et al. 2019; Kaur and Prabhakar 2017; Xu et al. 2019). As shown in Fig. 9, a novel pesticide electrochemical sensor has been proposed based on the copper metal–organic frameworks modified electrode (Cao et al. 2019). Oxidation–reduction reaction could occur on the modified electrode surface, which would lead to an obvious signal response. When glyphosate combined with the modified electrode surface, glyphosate–copper ion complex

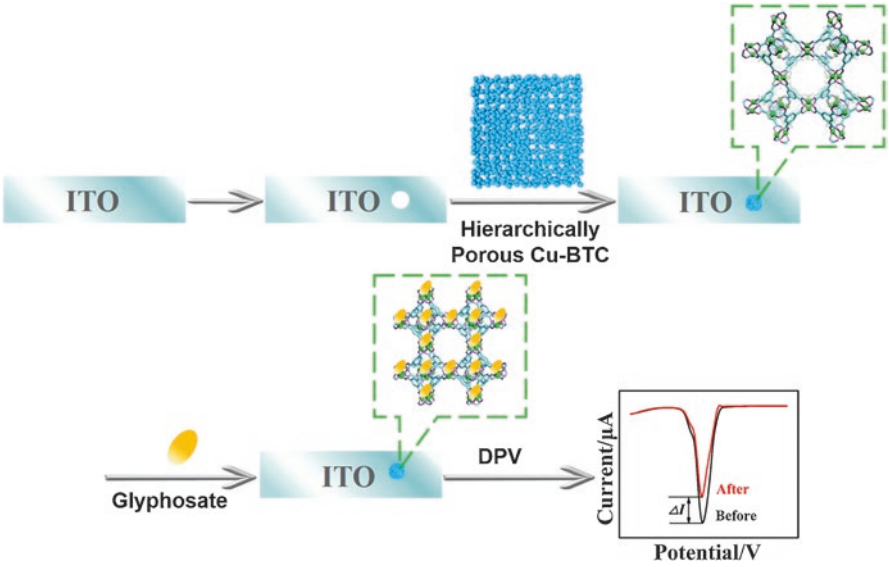

Fig. 9 The principle of the glyphosate electrochemical sensor. Note a novel pesticide electrochemical sensor has been proposed based on the copper metal–organic frameworks modified electrode. When glyphosate combined with the modified electrode surface, glyphosate–copper ion complex would be produced because of adsorption of glyphosate on the metal center of copper metal–organic frameworks. And the generated complex could impede the electron transfer, causing a decrease of primary response current. The reduced current value is related to the reacted glyphosate concentration, so current changes before and after the reaction of a modified electrode with glyphosate could be utilized to detect the amount of glyphosate in real samples. *DPV* differential pulse voltammetry. Reprinted from Cao et al. (2019), with permission from Elsevier

would be produced because of adsorption of glyphosate on the metal center of copper metal–organic frameworks. Afterward, the generated complex could impede the electron transfer, causing a decrease of primary response current for the modified electrode. The reduced current value is related to the reacted glyphosate concentration, so current changes before and after the reaction of modified electrode with glyphosate were utilized to detect the amount of glyphosate in real samples. This as-developed electrochemical sensor exhibits excellent performance toward the determination of glyphosate.

In addition to the direct electrochemical sensor detection of pesticides, various electrochemical biosensors, including DNA-based biosensor (Eissa and Zourob 2017), enzyme sensors (Lu et al. 2018), immunosensors (El-Moghazy et al. 2018; Li et al. 2019a, b), and aptasensors (Roushani et al. 2018), have been also constructed and used for the highly sensitive detection of pesticides. According to the oxidation of guanine moieties, the electrochemical biosensors have been also developed for organophosphorus pesticide detection. As a recognition molecule, DNA is anchored on the modified electrodes surface in the fabrication process of DNA-based electrochemical biosensors (Eissa and Zourob 2017). The amount of

organophosphorus pesticides can be quantified by monitoring the variation of redox characterizations of DNA that mainly refers to the oxidation of the guanine base. However, DNA-based electrochemical sensors are mainly based on the interactions between analytes and nitrogen bases, which can alter the electrochemical response of guanine base of DNA, so they have no specificity during the detection process. And DNA electrochemical sensors cannot achieve the simultaneous detection of several pesticides, thus there are few works about DNA electrochemical sensors for pesticide detection in recent 5 years. As prompted by the above limitations of DNA sensors, novel biomolecules and recognition strategies for the development of biosensors have been explored by researchers.

Enzymatic-based electrochemical biosensors for the detection of pesticides can be mainly based on the catalytic activity of organophosphorus hydrolase and the inhibition of several enzymes activity existed in pesticides, such as butyrylcholinesterase, acetylcholinesterase, tyrosinase, and so on (Cahuantzi-Muñoz et al. 2019). For the organophosphorus electrochemical biosensor, organophosphorus hydrolase enzyme is usually used to catalyze the hydrolysis of P-based bonds of organophosphorus, which will generate toxic products along with two protons. Because the released protons can result in a change of current or potential, organophosphorus hydrolase-based electrochemical biosensors have been fabricated and used for the detection of organophosphorus. Mulchandani and coworkers have proposed a highly sensitive electrochemical biosensor for paraoxon and methyl parathion based on organophosphorus hydrolase (Mulchandani et al. 2001). Based on the inhibition of acetylcholinesterase, Gao's group has fabricated and employed as a highly efficient electrochemical biosensor for the measurement of organophosphorus pesticides (Lu et al. 2019a, b).

As for immunosensors, measurable signals can be changed along with the organophosphorus concentrations because of the high specificity of organophosphorus antibodies to analytes (El-Moghazy et al. 2018). As shown in Fig. 10, an amino-modified metal-organic framework-based electrochemical immunosensor has been proposed for the simultaneous detection of pesticides triazophos and thiacloprid with high sensitivity (Yang et al. 2019a, b). With the assistance of specific monoclonal antibodies, Pérez-Fernández and coworkers have exploited a competitive immunosensor for the electrochemical determination of imidacloprid on screen-printed carbon electrodes (Pérez-Fernández et al. 2019).

Although enzymatic sensors and immunosensors have been widely used, they still possess several disadvantages of expensive. As a newly emerged method, aptasensors have appeared in the field of environmental monitoring to conquer the above limitations, which is mainly based on the folding of induced oligodeoxynucleotides aptamers. The combination of detected targets and nucleic acid aptamer on the electrode surface can alter its folding and flexibility, resulting in the electronic gain and loss of the redox-labeled substrates (Roushani et al. 2018). Consequently, an induced electrical signal will be generated and recorded, which is proportional to the concentration of pesticides. For instance, a high specific impedimetric biosensor was developed on the basis of aptamer modified platinum nanoparticles microwires for the detection of atrazine and acetamiprid (Fig. 11) (Madianos et al. 2018).

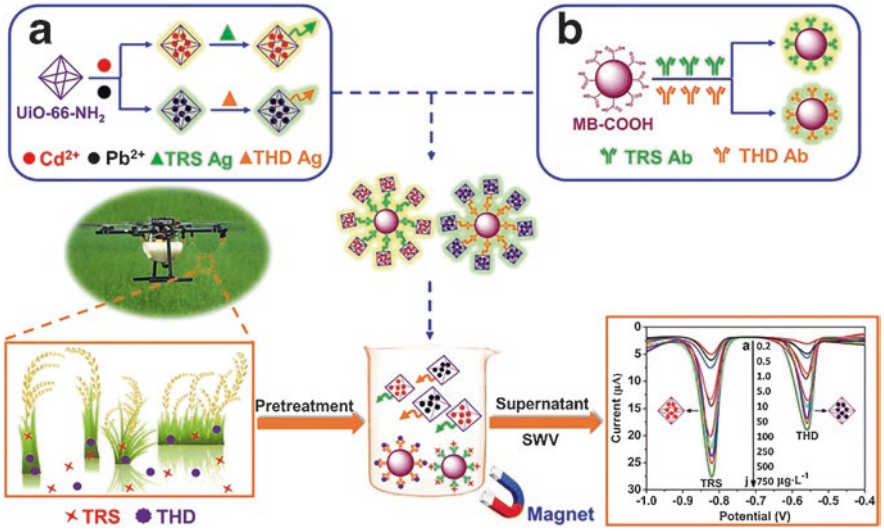

Fig. 10 The fabrication of the glyphosate electrochemical immunosensor. Note amino-modified metal–organic framework nanoparticles were prepared to capture metal ions. Based on the specific binding of antigens to antibodies, a highly sensitive electrochemical immunosensor was constructed and for the simultaneous detection of pesticide triazophos and thiacloprid with a low limit of detection. *UiO-66-NH₂* amino-modified metal–organic framework, *TRS* triazophos, *THD* thiacloprid, *Ag* antigen, *Ab* antibody, *MB-COOH* magnetic bead, *SWV* square wave voltammetry. Reprinted from Yang et al. (2019a, b), with permission from Springer

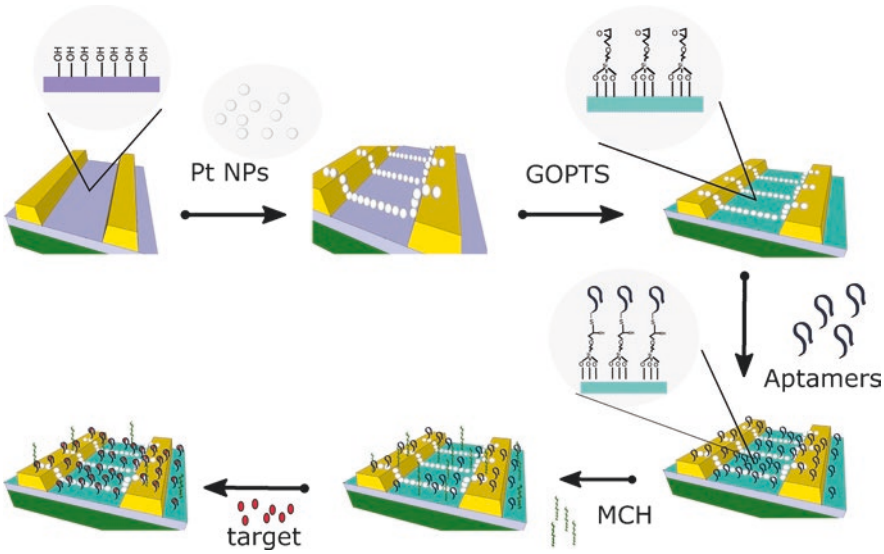

Fig. 11 The fabrication and application of aptasensor. Note a high specific impedimetric biosensor was developed on the basis of aptamer modified platinum nanoparticles microwires. The aptasensor exhibited excellent performance toward the detection of atrazine and acetamiprid. *Pt NPs* platinum nanoparticles, *GOPTS* (3-glycidyloxypropyl)triethoxysilane, *MCH* 6-mercapto-1-hexanol. Reprinted from Madianos et al. (2018), with permission from Elsevier

3.5 Antibiotics

As a drug of inhibition and sterilizing bacteria, antibiotics have been widely used in medical and health, livestock and poultry breeding, agricultural production and other industries, and promoting the economic development of the society (Liu et al. 2018; Chen et al. 2019; Zhou et al. 2019). Antibiotics are mainly used as feed additives in livestock and poultry breeding, which are used to prevent and treat animal diseases and accelerate animal growth. However, the unreasonable use of antibiotics in livestock and poultry industry has been very common, highly sensitive detection of antibiotics is vitally necessary to regulate this phenomenon.

The detection of antibiotics is generally trace analysis due to their relatively low concentration in wastewater, which often needs highly sensitive instruments for accurate detection. According to the previously reported work (Batrawi et al. 2017), the main detection techniques of antibiotics are chromatography and its combination, enzyme immunoassay, capillary electrophoresis, and so on. The above-mentioned methods not only have the advantages of high sensitivity, accuracy, enhanced analytical efficiency, low detection limit, and strong specificity but possess the shortcomings of expensive instruments, tedious operation, need for professional operators, complex sample handling, and high cost. Therefore, these methods are difficult to become a conventional detection technique. At present, electrochemical sensors and biosensors have attracted increasing attention in antibiotics detection, based on their merit of low cost, easy miniaturization, biocompatibility, high sensitivity, and rapid response.

Electrochemical antibiotics sensors and biosensors are mainly based on the direct redox reactions of antibiotics or chemical reactions between targets and immobilized recognition elements, such as, antigen, enzyme, aptamer, cell, small molecular, macromolecule chemicals, antibody, and so on, which will cause the variations for the detectable properties of the work electrode, such as potential, response current, and resistance. In the recent 5 years, various electrochemical sensors and biosensors have been constructed for the detection of various antibiotics (Sun et al. 2019; Wang et al. 2019a, b; Liu et al. 2019). For example, a highly sensitive electrochemical sensor has been developed and applied for the detection of ciprofloxacin in view of the coordination interaction between ciprofloxacin and copper ions (Fig. 12a) (Fang et al. 2019) Lu's group has synthesized various metal–organic framework as label-free bioplatforms for the construction of sensitive electrochemical oxytetracycline aptasensors (Fig. 12b) (Zhou et al. 2019).

3.6 Pathogens

Pathogens refer to microorganisms, including bacteria, viruses, rickettsia, and fungi, parasites, or other vectors that can cause diseases in humans, animals, and plants (Silva et al. 2018). Pathogen infections are deemed to be a significantly serious

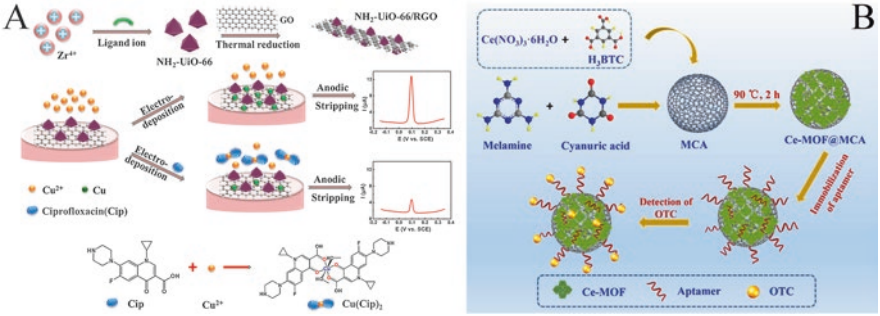

Fig. 12 Electrochemical (**a**) sensor and (**b**) biosensor for different antibiotics. Note a highly sensitive electrochemical sensor has been developed and applied for the detection of ciprofloxacin based on the coordination interaction between ciprofloxacin and copper ions (**a**). Various metal–organic frameworks were synthesized and used as label-free bioplatforms for the construction of sensitive electrochemical oxytetracycline aptasensors (**b**). Zr^{4+} Zirconium ions, *NH_2-UiO-66-RGO* amino-modified metal–organic framework supported on reduced graphene oxide, *MCA* melamine and cyanuric acid, *Ce-MOF* Ce-based metal–organic framework. A reprinted from Fang et al. (2019), with permission from American Chemical Society; B reprinted from Zhou et al. (2019), with permission from Elsevier

issue for global health, which can cause thousands of deaths and tremendous morbidity around the world (Campuzano et al. 2017). Therefore, it is urgent to develop an efficient method for the accurate detection of pathogens. Compared with the traditional approaches, diverse electrochemical biosensors have been also constructed and used to detect pathogens, due to their advantages of simplicity, inexpensive, sensitivity, and easy miniaturization (Hou et al. 2018; Jijie et al. 2018). The principle of pathogen electrochemical biosensors is mainly based on the specific recognition between various identification elements and targets, which can lead to the change of detectable signal. For instance, Guo and coworkers have fabricated a facile, label-free, cheap electrochemical *Escherichia coli* biosensor with satisfactory performance, while the electrochemical signals were amplified through rolling circle amplification and peroxidase-mimicking DNAzyme (Fig. 13) (Guo et al. 2016).

3.7 Gas Pollutants

Gas pollutants are one of the major pollutants, mainly including formaldehyde, nitrogen oxides, carbon monoxide, hydrogen sulfide, sulfur dioxide, ammonia, and so on (Wei et al. 2018; Trivedi et al. 2018). The released gas pollutants into the air not only cause environmental pollution but also pose a threat to human health. To date, various gas sensors have been fabricated and used for the detection of toxic gases. The electrochemical sensor is one of the most common sensors for detecting toxic and harmful gases, due to their serious of merits, such as easy miniaturization,

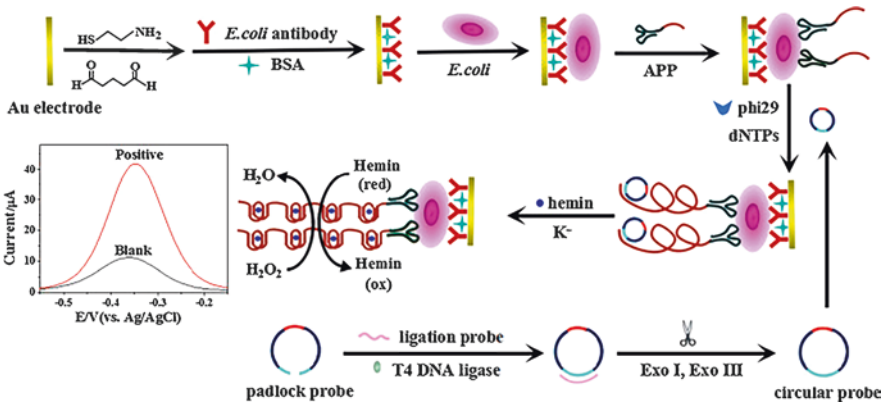

Fig. 13 Fabrication and application of electrochemical *E. coli* biosensor. Note a facile, label-free, cheap electrochemical *E. coli* biosensor was fabricated on the gold electrode. The developed sensors indicated satisfactory performance, and the electrochemical signals were amplified through rolling circle amplification and peroxidase-mimicking DNAzyme. *BSA* bovine serum albumin, *APP* aptamer-primer probe, *Exo I* exonuclease I, *Exo III* exonuclease III, *red* reduction state, *ox* oxidation state. Reprinted from Guo et al. (2016), with permission from Elsevier

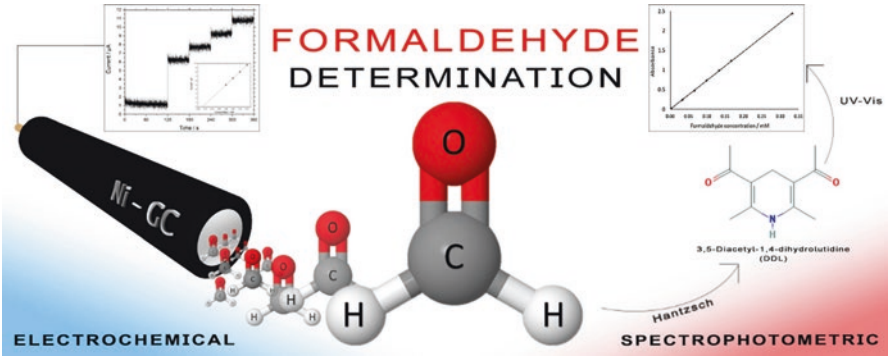

Fig. 14 Detection of formaldehyde by electrochemical oxidation. Note nickel metal were prepared and severed as electrode materials. The as-designed electrochemical sensors showed excellent performance for the directly electrochemical oxidation of formaldehyde. Reprinted from Trivedi et al. (2018), with permission from Elsevier

inexpensive, good linearity and repeatability, long-term stability, and so on. The detecting principle of electrochemical gas sensors is based on electrochemical activity of the measured gas, which can be utilized to electrochemically oxidize or reduce the toxic gases, to distinguish the gas composition and detect the gas concentration. As depicted in Fig. 14, nickel–metal-modified electrodes were prepared and considered as work electrode for the determination of formaldehyde through directly electrochemical oxidation (Trivedi et al. 2018).

4 Conclusions and Perspectives

Electrochemical sensors and biosensors have been considered an effective analytical tool and have been applied for the detection of various environmental pollutants, owing to the remarkable performance of rapid response, high sensitivity, and selectivity. In this chapter, we have summarized their latest developments of electrochemical sensors and biosensors for environmental contaminants detection in the past 5 years. On the one hand, a number of novel electrode materials have been synthesized, which have significantly improved the sensitivity and selectivity of the electrochemical sensors. On the other hand, new biosensing strategies have been proposed and have been applied to fabricate electrochemical biosensors for the detection of various pollutants.

Although electrochemical sensors and biosensors have achieved satisfactory achievements in the detection of environmental pollutants, there are still some important challenges to be resolved. In order to better meet the needs of electrochemical sensors and biosensors in practical applications, some efforts should be made from the following aspects: (1) Novel electrode materials. The synthesis of new nanomaterials is of great significance for the fabrication of electrical sensors and biosensors, which can effectively enhance analytical performance. (2) Miniaturization. The development of portable sensors can improve work efficiency and reduce the consumption of reagents and manpower. (3) Combined with other spectral analysis techniques, such as Raman spectroscopy, the wide detection range and enhanced accuracy can be achieved. In brief, it is our research directions and goals to develop electrochemical sensors and biosensors with excellent performance and apply them to environmental and life analysis in the future.

Acknowledgments Financial support from the National Natural Science Foundation of China (Grant 21675080), the Natural Science Foundation of Jiangsu Province (Grant BK20170073) is appreciated.

References

Akbari Hasanjani HR, Zarei K (2019) An electrochemical sensor for attomolar determination of mercury(II) using DNA/poly-L-methionine-gold nanoparticles/pencil graphite electrode. Biosens Bioelectron 128:1–8. https://doi.org/10.1016/j.bios.2018.12.039

Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. Process Biochem 40:997–1026. https://doi.org/10.1016/j.procbio.2004.04.008

Alam AU, Howlader MMR, Hu N-X, Deen MJ (2019) Electrochemical sensing of lead in drinking water using β-cyclodextrin-modified MWCNTs. Sensors Actuators B Chem 296:126632. https://doi.org/10.1016/j.snb.2019.126632

Andreescu S, Sadik OA (2004) Correlation of analyte structures with biosensor responses using the detection of phenolic estrogens as a model. Anal Chem 76:552–560. https://doi.org/10.1021/ac034480z

Apetrei IM, Rodriguez-Mendez ML, Apetrei C, de Saja JA (2013) Enzyme sensor based on carbon nanotubes/cobalt(II) phthalocyanine and tyrosinase used in pharmaceutical analysis. Sensors Actuators B Chem 177:138–144. https://doi.org/10.1016/j.snb.2012.10.131

Ates M (2013) A review study of (bio)sensor systems based on conducting polymers. Mater Sci Eng C 33:1853–1859. https://doi.org/10.1016/j.msec.2013.01.035

Baker A, Inverarity R, Charlton M, Richmond S (2003) Detecting river pollution using fluorescence spectrophotometry: case studies from the Ouseburn, NE England. Environ Pollut 124:57–70. https://doi.org/10.1016/S0269-7491(02)00408-6

Bansod B, Kumar T, Thakur R, Rana S, Singh I (2017) A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms. Biosens Bioelectron 94:443–455. https://doi.org/10.1016/j.bios.2017.03.031

Barbosa VMP, Barbosa AF, Bettini J, Luccas PO, Figueiredo EC (2016) Direct extraction of lead(II) from untreated human blood serum using restricted access carbon nanotubes and its determination by atomic absorption spectrometry. Talanta 147:478–484. https://doi.org/10.1016/j.talanta.2015.10.023

Barek J, Cvačka J, Muck A, Quaiserová V, Zima J (2001) Electrochemical methods for monitoring of environmental carcinogens. Fresen J Anal Chem 369:556–562. https://doi.org/10.1007/s002160100707

de Barros A, Constantino CJL, da Cruz NC, Bortoleto JRR, Ferreira M (2017) High performance of electrochemical sensors based on LbL films of gold nanoparticles, polyaniline and sodium montmorillonite clay mineral for simultaneous detection of metal ions. Electrochim Acta 235:700–708. https://doi.org/10.1016/j.electacta.2017.03.135

Batley GE (1983) Electroanalytical techniques for the determination of heavy metals in seawater. Mar Chem 12:107–117. https://doi.org/10.1016/0304-4203(83)90074-9

Batrawi N, Wahdan S, Al-Rimawi F (2017) A validated stability-indicating HPLC method for simultaneous determination of amoxicillin and enrofloxacin combination in an injectable suspension. Sci Pharm 85:6. https://doi.org/10.3390/scipharm85010006

Berijani S, Assadi Y, Anbia M, Milani Hosseini M-R, Aghaee E (2006) Dispersive liquid–liquid microextraction combined with gas chromatography-flame photometric detection: very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. J Chromatogr A 1123:1–9. https://doi.org/10.1016/j.chroma.2006.05.010

Bojdi MK et al (2014) Synthesis, characterization and application of novel lead imprinted polymer nanoparticles as a high selective electrochemical sensor for ultra-trace determination of lead ions in complex matrixes. Electrochim Acta 136:59–65. https://doi.org/10.1016/j.electacta.2014.05.095

Cahuantzi-Muñoz SL et al (2019) Electrochemical biosensor for sensitive quantification of glyphosate in maize kernels. Electroanalysis 31:927–935. https://doi.org/10.1002/elan.201800759

Camargo JR et al (2018) Electrochemical biosensor made with tyrosinase immobilized in a matrix of nanodiamonds and potato starch for detecting phenolic compounds. Anal Chim Acta 1034:137–143. https://doi.org/10.1016/j.aca.2018.06.001

Campuzano S, Yáñez-Sedeño P, Pingarrón MJ (2017) Molecular biosensors for electrochemical detection of infectious pathogens in liquid biopsies: current trends and challenges. Sensors 17:2533. https://doi.org/10.3390/s17112533

Cao Y et al (2019) An electrochemical sensor on the hierarchically porous cu-BTC MOF platform for glyphosate determination. Sensors Actuators B Chem 283:487–494. https://doi.org/10.1016/j.snb.2018.12.064

Chamkasem N, Harmon T (2016) Direct determination of glyphosate, glufosinate, and AMPA in soybean and corn by liquid chromatography/tandem mass spectrometry. Anal Bioanal Chem 408:4995–5004. https://doi.org/10.1007/s00216-016-9597-6

Chen C et al (2019) Amoxicillin on polyglutamic acid composite three-dimensional graphene modified electrode: reaction mechanism of amoxicillin insights by computational simulations. Anal Chim Acta 1073:22–29. https://doi.org/10.1016/j.aca.2019.04.052

Cui L, Wu J, Ju H (2015) Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials. Biosens Bioelectron 63:276–286. https://doi.org/10.1016/j.bios.2014.07.052

Daughton CG (2001) Emerging pollutants, and communicating the science of environmental chemistry and mass spectrometry: pharmaceuticals in the environment. J Am Soc Mass Spectrom 12:1067–1076. https://doi.org/10.1016/S1044-0305(01)00287-2

Davies J (1994) Inactivation of antibiotics and the dissemination of resistance genes. Science 264:375. https://doi.org/10.1126/science.8153624

Dolati S, Ramezani M, Abnous K, Taghdisi SM (2017) Recent nucleic acid based biosensors for Pb^{2+} detection. Sensors Actuators B Chem 246:864–878. https://doi.org/10.1016/j.snb.2017.02.118

Eissa S, Zourob M (2017) Selection and characterization of DNA aptamers for electrochemical biosensing of carbendazim. Anal Chem 89:3138–3145. https://doi.org/10.1021/acs.analchem.6b04914

El-Moghazy AY et al (2018) Ultrasensitive label-free electrochemical immunosensor based on PVA-co-PE nanofibrous membrane for the detection of chloramphenicol residues in milk. Biosens Bioelectron 117:838–844. https://doi.org/10.1016/j.bios.2018.07.025

Falahatpisheh MH, Donnelly KC, Ramos KS (2001) Antagonistic interactions among nephrotoxic polycyclic aromatic hydrocarbons. J Toxicol Environ Health A 62:543–560. https://doi.org/10.1080/152873901300007833

Fang X et al (2019) Nanocomposites of Zr(IV)-based metal–organic frameworks and reduced graphene oxide for electrochemically sensing ciprofloxacin in water. ACS Appl Nano Mater 2:2367–2376. https://doi.org/10.1021/acsanm.9b00243

Freire PG et al (2016) Morphology of ZnO nanoparticles bound to carbon nanotubes affects electrocatalytic oxidation of phenolic compounds. Sensors Actuators B Chem 223:557–565. https://doi.org/10.1016/j.snb.2015.09.086

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92:407–418. https://doi.org/10.1016/j.jenvman.2010.11.011

Fu C et al (2018) A homogeneous electrochemical sensor for Hg^{2+} determination in environmental water based on the T–Hg^{2+}–T structure and exonuclease III-assisted recycling amplification. Analyst 143:2122–2127. https://doi.org/10.1039/C8AN00462E

Gan T et al (2017) Flexible graphene oxide-wrapped SnO_2 hollow spheres with high electrochemical sensing performance in simultaneous determination of 4-aminophenol and 4-chlorophenol. Electrochim Acta 250:1–9. https://doi.org/10.1016/j.electacta.2017.08.043

Govindhan M, Lafleur T, Adhikari B-R, Chen A (2015) Electrochemical sensor based on carbon nanotubes for the simultaneous detection of phenolic pollutants. Electroanalysis 27:902–909. https://doi.org/10.1002/elan.201400608

Gumpu MB, Veerapandian M, Krishnan UM, Rayappan JBB (2018) Electrochemical sensing platform for the determination of arsenite and arsenate using electroactive nanocomposite electrode. Chem Eng J 351:319–327. https://doi.org/10.1016/j.cej.2018.06.097

Guo Y, Li J, Zhang X, Tang Y (2015) A sensitive biosensor with a DNAzyme for lead(II) detection based on fluorescence turn-on. Analyst 140:4642–4647. https://doi.org/10.1039/C5AN00677E

Guo Y et al (2016) Label-free and highly sensitive electrochemical detection of E. coli based on rolling circle amplifications coupled peroxidase-mimicking DNAzyme amplification. Biosens Bioelectron 75:315–319. https://doi.org/10.1016/j.bios.2015.08.031

Han XX et al (2014) Magnetic titanium dioxide nanocomposites for surface-enhanced resonance Raman spectroscopic determination and degradation of toxic anilines and phenols. Angew Chem Int Ed 53:2481–2484. https://doi.org/10.1002/anie.201310123

Hatch WR, Ott WL (1968) Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. Anal Chem 40:2085–2087. https://doi.org/10.1021/ac50158a025

Hatchett DW, Josowicz M (2008) Composites of intrinsically conducting polymers as sensing nanomaterials. Chem Rev 108:746–769. https://doi.org/10.1021/cr068112h

Hofmann T, Nebehaj E, Albert L (2015) The high-performance liquid chromatography/multistage electrospray mass spectrometric investigation and extraction optimization of beech (*Fagus*

sylvatica L.) bark polyphenols. J Chromatogr A 1393:96–105. https://doi.org/10.1016/j.chroma.2015.03.030

Hou Y-H et al (2018) A colorimetric and electrochemical immunosensor for point-of-care detection of enterovirus 71. Biosens Bioelectron 99:186–192. https://doi.org/10.1016/j.bios.2017.07.035

Huang YH et al (2015) One-pot hydrothermal synthesis carbon nanocages-reduced graphene oxide composites for simultaneous electrochemical detection of catechol and hydroquinone. Sensors Actuators B Chem 212:165–173. https://doi.org/10.1016/j.snb.2015.02.013

Huang J, Zhang X, Zhou L, You T (2016) Simultaneous electrochemical determination of dihydroxybenzene isomers using electrospun nitrogen-doped carbon nanofiber film electrode. Sensors Actuators B Chem 224:568–576. https://doi.org/10.1016/j.snb.2015.10.102

Isa IM et al (2017) Chloroplatinum(II) complex-modified MWCNTs paste electrode for electrochemical determination of mercury in skin lightening cosmetics. Electrochim Acta 253:463–471. https://doi.org/10.1016/j.electacta.2017.09.092

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7:60–72. https://doi.org/10.2478/intox-2014-0009

Jiang D et al (2019) Simultaneous biosensing of catechol and hydroquinone via a truncated cube-shaped au/PBA nanocomposite. Biosens Bioelectron 124–125:260–267. https://doi.org/10.1016/j.bios.2018.09.094

Jiao Y et al (2016) An ultrasensitive aptasensor for chlorpyrifos based on ordered mesoporous carbon/ferrocene hybrid multiwalled carbon nanotubes. RSC Adv 6:58541–58548. https://doi.org/10.1039/C6RA07735H

Jijie R et al (2018) Reduced graphene oxide/polyethylenimine based immunosensor for the selective and sensitive electrochemical detection of uropathogenic *Escherichia coli*. Sensors Actuators B Chem 260:255–263. https://doi.org/10.1016/j.snb.2017.12.169

Kato D, Kamata T, Kato D, Yanagisawa H, Niwa O (2016) Au nanoparticle-embedded carbon films for electrochemical As^{3+} detection with high sensitivity and stability. Anal Chem 88:2944–2951. https://doi.org/10.1021/acs.analchem.6b00136

Kaur N, Prabhakar N (2017) Current scenario in organophosphates detection using electrochemical biosensors. TrAC Trends Anal Chem 92:62–85. https://doi.org/10.1016/j.trac.2017.04.012

Kempahanumakkagari S, Deep A, Kim K-H, Kumar Kailasa S, Yoon H-O (2017) Nanomaterial-based electrochemical sensors for arsenic-a review. Biosens Bioelectron 95:106–116. https://doi.org/10.1016/j.bios.2017.04.013

Kovács Á, Mörtl M, Kende A (2011) Development and optimization of a method for the analysis of phenols and chlorophenols from aqueous samples by gas chromatography–mass spectrometry, after solid-phase extraction and trimethylsilylation. Microchem J 99:125–131. https://doi.org/10.1016/j.microc.2011.04.007

Kumar P, Kim K-H, Deep A (2015) Recent advancements in sensing techniques based on functional materials for organophosphate pesticides. Biosens Bioelectron 70:469–481. https://doi.org/10.1016/j.bios.2015.03.066

Latif ur R et al (2015) Synthesis, characterization, and application of Au–Ag alloy nanoparticles for the sensing of an environmental toxin, pyrene. J Appl Electrochem 45:463–472. https://doi.org/10.1007/s10800-015-0807-2

Li M, Li Y-T, Li D-W, Long Y-T (2012) Recent developments and applications of screen-printed electrodes in environmental assays—a review. Anal Chim Acta 734:31–44. https://doi.org/10.1016/j.aca.2012.05.018

Li Z et al (2016) Ultrasensitive electrochemical sensor for Hg^{2+} by using hybridization chain reaction coupled with ag@au core–shell nanoparticles. Biosens Bioelectron 80:339–343. https://doi.org/10.1016/j.bios.2016.01.074

Li X, Yuan Y, Pan X, Zhang L, Gong J (2019a) Boosted photoelectrochemical immunosensing of metronidazole in tablet using coral-like g-C_3N_4 nanoarchitectures. Biosens Bioelectron 123:7–13. https://doi.org/10.1016/j.bios.2018.09.084

Li Z, Liu C, Sarpong V, Gu Z (2019b) Multisegment nanowire/nanoparticle hybrid arrays as electrochemical biosensors for simultaneous detection of antibiotics. Biosens Bioelectron 126:632–639. https://doi.org/10.1016/j.bios.2018.10.025

Liang Q, Jing H, Gregoire DC (2000) Determination of trace elements in granites by inductively coupled plasma mass spectrometry. Talanta 51:507–513. https://doi.org/10.1016/S0039-9140(99)00318-5

Lima AP et al (2018) Influence of Al_2O_3 nanoparticles structure immobilized upon glassy-carbon electrode on the electrocatalytic oxidation of phenolic compounds. Sensors Actuators B Chem 262:646–654. https://doi.org/10.1016/j.snb.2018.02.028

Lin P, Yan F (2012) Organic thin-film transistors for chemical and biological sensing. Adv Mater 24:34–51. https://doi.org/10.1002/adma.201103334

Liu M et al (2011) A stable sandwich-type amperometric biosensor based on poly(3,4-ethylenedioxythiophene)—single walled carbon nanotubes/ascorbate oxidase/nafion films for detection of L-ascorbic acid. Sensors Actuators B Chem 159:277–285. https://doi.org/10.1016/j.snb.2011.07.005

Liu X et al (2017) Liquid spray dielectric barrier discharge induced plasma–chemical vapor generation for the determination of lead by ICPMS. Anal Chem 89:6827–6833. https://doi.org/10.1021/acs.analchem.7b01255

Liu X et al (2018) Recent advances in sensors for tetracycline antibiotics and their applications. TrAC Trends Anal Chem 109:260–274. https://doi.org/10.1016/j.trac.2018.10.011

Liu P et al (2019) An ultrasensitive electrochemical immunosensor for procalcitonin detection based on the gold nanoparticles-enhanced tyramide signal amplification strategy. Biosens Bioelectron 126:543–550. https://doi.org/10.1016/j.bios.2018.10.048

Lu X, Tao L, Song D, Li Y, Gao F (2018) Bimetallic Pd@au nanorods based ultrasensitive acetylcholinesterase biosensor for determination of organophosphate pesticides. Sensors Actuators B Chem 255:2575–2581. https://doi.org/10.1016/j.snb.2017.09.063

Lu M et al (2019a) Graphene aerogel–metal–organic framework-based electrochemical method for simultaneous detection of multiple heavy-metal ions. Anal Chem 91:888–895. https://doi.org/10.1021/acs.analchem.8b03764

Lu X, Tao L, Li Y, Huang H, Gao F (2019b) A highly sensitive electrochemical platform based on the bimetallic Pd@au nanowires network for organophosphorus pesticides detection. Sensors Actuators B Chem 284:103–109. https://doi.org/10.1016/j.snb.2018.12.125

Lupu S, Lete C, Marin M, Totir N, Balaure PC (2009) Electrochemical sensors based on platinum electrodes modified with hybrid inorganic–organic coatings for determination of 4-nitrophenol and dopamine. Electrochim Acta 54:1932–1938. https://doi.org/10.1016/j.electacta.2008.07.051

Madianos L, Tsekenis G, Skotadis E, Patsiouras L, Tsoukalas D (2018) A highly sensitive impedimetric aptasensor for the selective detection of acetamiprid and atrazine based on microwires formed by platinum nanoparticles. Biosens Bioelectron 101:268–274. https://doi.org/10.1016/j.bios.2017.10.034

Maduraiveeran G, Jin W (2017) Nanomaterials based electrochemical sensor and biosensor platforms for environmental applications. Trends Environ Anal 13:10–23. https://doi.org/10.1016/j.teac.2017.02.001

Maikap A, Mukherjee K, Mondal B, Mandal N (2016) Zinc oxide thin film based nonenzymatic electrochemical sensor for the detection of trace level catechol. RSC Adv 6:64611–64616. https://doi.org/10.1039/C6RA09598D

Makelane H, Waryo T, Feleni U, Iwuoha E (2019) Dendritic copolymer electrode for second harmonic alternating current voltammetric signalling of pyrene in oil-polluted wastewater. Talanta 196:204–210. https://doi.org/10.1016/j.talanta.2018.12.038

Manisankar P, Viswanathan S, Pusphalatha AM, Rani C (2005) Electrochemical studies and square wave stripping voltammetry of five common pesticides on poly 3,4-ethylenedioxythiophene modified wall-jet electrode. Anal Chim Acta 528:157–163. https://doi.org/10.1016/j.aca.2004.08.027

Martinez JL (2009) Environmental pollution by antibiotics and by antibiotic resistance determinants. Environ Pollut 157:2893–2902. https://doi.org/10.1016/j.envpol.2009.05.051

Metters JP, Kadara RO, Banks CE (2012) Electroanalytical sensing of chromium (III) and (VI) utilising gold screen printed macro electrodes. Analyst 137:896–902. https://doi.org/10.1039/C2AN16054D

Mulchandani P, Chen W, Mulchandani A (2001) Flow injection amperometric enzyme biosensor for direct determination of organophosphate nerve agents. Environ Sci Technol 35:2562–2565. https://doi.org/10.1021/es001773q

Njau KN, Woude MV, Visser GJ, Janssen LJJ (2000) Electrochemical removal of nickel ions from industrial wastewater. Chem Eng J 79:187–195. https://doi.org/10.1016/S1385-8947(00)00210-2

O'Malley V (1999) The integrated pollution prevention and control (IPPC) directive and its implications for the environment and industrial activities in Europe. Sensors Actuators B Chem 59:78–82. https://doi.org/10.1016/S0925-4005(99)00199-9

Paulino AT et al (2006) Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewaters. J Colloid Interface Sci 301:479–487. https://doi.org/10.1016/j.jcis.2006.05.032

Pei D-N, Zhang A-Y, Pan X-Q, Si Y, Yu H-Q (2018) Electrochemical sensing of bisphenol A on facet-tailored TiO_2 single crystals engineered by inorganic-framework molecular imprinting sites. Anal Chem 90:3165–3173. https://doi.org/10.1021/acs.analchem.7b04466

Pérez-Fernández B, Mercader JV, Checa-Orrego BI, de la Escosura-Muñiz A, Costa-García A (2019) A monoclonal antibody-based immunosensor for the electrochemical detection of imidacloprid pesticide. Analyst 144:2936–2941. https://doi.org/10.1039/C9AN00176J

Ramnani P, Saucedo NM, Mulchandani A (2016) Carbon nanomaterial-based electrochemical biosensors for label-free sensing of environmental pollutants. Chemosphere 143:85–98. https://doi.org/10.1016/j.chemosphere.2015.04.063

Reemtsma T (2003) Liquid chromatography–mass spectrometry and strategies for trace-level analysis of polar organic pollutants. J Chromatogr A 1000:477–501. https://doi.org/10.1016/S0021-9673(03)00507-7

Rodríguez-Delgado MM et al (2015) Laccase-based biosensors for detection of phenolic compounds. TrAC Trends Anal Chem 74:21–45. https://doi.org/10.1016/j.trac.2015.05.008

Rotariu L, Lagarde F, Jaffrezic-Renault N, Bala C (2016) Electrochemical biosensors for fast detection of food contaminants—trends and perspective. TrAC Trends Anal Chem 7:80–87. https://doi.org/10.1016/j.trac.2015.12.017

Roushani M, Nezhadali A, Jalilian Z (2018) An electrochemical chlorpyrifos aptasensor based on the use of a glassy carbon electrode modified with an electropolymerized aptamer-imprinted polymer and gold nanorods. Microchim Acta 185:551. https://doi.org/10.1007/s00604-018-3083-0

Roychoudhury A, Basu S, Jha SK (2016) Dopamine biosensor based on surface functionalized nanostructured nickel oxide platform. Biosens Bioelectron 84:72–81. https://doi.org/10.1016/j.bios.2015.11.061

Saidur MR, Aziz ARA, Basirun WJ (2017) Recent advances in DNA-based electrochemical biosensors for heavy metal ion detection: a review. Biosens Bioelectron 90:125–139. https://doi.org/10.1016/j.bios.2016.11.039

Samanta SK, Singh OV, Jain RK (2002) Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. Trends Biotechnol 20:243–248. https://doi.org/10.1016/S0167-7799(02)01943-1

Şenocak A et al (2019) Highly selective and ultra-sensitive electrochemical sensor behavior of 3D SWCNT-BODIPY hybrid material for eserine detection. Biosens Bioelectron 128:144–150. https://doi.org/10.1016/j.bios.2018.12.052

Sethuraman V, Muthuraja P, Anandha Raj J, Manisankar P (2016) A highly sensitive electrochemical biosensor for catechol using conducting polymer reduced graphene oxide–metal

oxide enzyme modified electrode. Biosens Bioelectron 84:112–119. https://doi.org/10.1016/j.bios.2015.12.074

Shao Y et al (2010) Graphene based electrochemical sensors and biosensors: a review. Electroanalysis 22:1027–1036. https://doi.org/10.1002/elan.200900571

Shen L et al (2008) Electrochemical DNAzyme sensor for lead based on amplification of DNA–Au bio-bar codes. Anal Chem 80:6323–6328. https://doi.org/10.1021/ac800601y

Shi L, Li Y, Rong X, Wang Y, Ding S (2017) Facile fabrication of a novel 3D graphene framework/bi nanoparticle film for ultrasensitive electrochemical assays of heavy metal ions. Anal Chim Acta 968:21–29. https://doi.org/10.1016/j.aca.2017.03.013

Si Y et al (2018) rGO/AuNPs/tetraphenylporphyrin nanoconjugate-based electrochemical sensor for highly sensitive detection of cadmium ions. Anal Methods 10:3631–3636. https://doi.org/10.1039/C8AY01020J

Silva NFD, Magalhães JMCS, Freire C, Delerue-Matos C (2018) Electrochemical biosensors for Salmonella: state of the art and challenges in food safety assessment. Biosens Bioelectron 99:667–682. https://doi.org/10.1016/j.bios.2017.08.019

Smith DL, Harris AD, Johnson JA, Silbergeld EK, Morris JG (2002) Animal antibiotic use has an early but important impact on the emergence of antibiotic resistance in human commensal bacteria. Proc Natl Acad Sci 99:6434. https://doi.org/10.1073/pnas.082188899

Srivastava NK, Majumder CB (2008) Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. J Hazard Mater 151:1–8. https://doi.org/10.1016/j.jhazmat.2007.09.101

Su W-Y, Wang S-M, Cheng S-H (2011) Electrochemically pretreated screen-printed carbon electrodes for the simultaneous determination of aminophenol isomers. J Electroanal Chem 651:166–172. https://doi.org/10.1016/j.jelechem.2010.11.028

Sun Q et al (2017) A new electrochemical system based on a flow-field shaped solid electrode and 3D-printed thin-layer flow cell: detection of Pb^{2+} ions by continuous flow accumulation square-wave anodic stripping voltammetry. Anal Chem 89:5024–5029. https://doi.org/10.1021/acs.analchem.7b00383

Sun Y et al (2019) Novel three-dimensional electrochemical sensor with dual signal amplification based on MoS_2 nanosheets and high-conductive NH_2-MWCNT@COF for sulfamerazine determination. Sensors Actuators B Chem 281:107–114. https://doi.org/10.1016/j.snb.2018.10.055

Teh CM, Mohamed AR (2011) Roles of titanium dioxide and ion-doped titanium dioxide on photocatalytic degradation of organic pollutants (phenolic compounds and dyes) in aqueous solutions: a review. J Alloys Compd 509:1648–1660. https://doi.org/10.1016/j.jallcom.2010.10.181

Tovide O et al (2014) Electro-oxidation of anthracene on polyanilino-graphene composite electrode. Sensors Actuators B Chem 205:184–192. https://doi.org/10.1016/j.snb.2014.07.116

Trivedi D, Crosse J, Tanti J, Cass AJ, Toghill KE (2018) The electrochemical determination of formaldehyde in aqueous media using nickel modified electrodes. Sensors Actuators B Chem 270:298–303. https://doi.org/10.1016/j.snb.2018.05.035

Uniyal S, Sharma RK (2018) Technological advancement in electrochemical biosensor based detection of organophosphate pesticide chlorpyrifos in the environment: a review of status and prospects. Biosens Bioelectron 116:37–50. https://doi.org/10.1016/j.bios.2018.05.039

Vaishnav VS, Patel SG, Panchal JN (2015) Development of ITO thin film sensor for detection of benzene. Sensors Actuators B Chem 206:381–388. https://doi.org/10.1016/j.snb.2014.07.037

Wan H, Yin H, Lin L, Zeng X, Mason AJ (2018) Miniaturized planar room temperature ionic liquid electrochemical gas sensor for rapid multiple gas pollutants monitoring. Sensors Actuators B Chem 255:638–646. https://doi.org/10.1016/j.snb.2017.08.109

Wang S-M, Su W-Y, Cheng S-H (2010) A simultaneous and sensitive determination of hydroquinone and catechol at anodically pretreated screen-printed carbon electrodes. Int J Electrochem Sci 5:1649–1664

Wang N, Lin M, Dai H, Ma H (2016) Functionalized gold nanoparticles/reduced graphene oxide nanocomposites for ultrasensitive electrochemical sensing of mercury ions based on thy-

mine–mercury–thymine structure. Biosens Bioelectron 79:320–326. https://doi.org/10.1016/j.bios.2015.12.056

Wang L et al (2018) Sensitive and label-free electrochemical lead ion biosensor based on a DNAzyme triggered G-quadruplex/hemin conformation. Biosens Bioelectron 115:91–96. https://doi.org/10.1016/j.bios.2018.04.054

Wang M et al (2019a) Covalent organic framework-based electrochemical aptasensors for the ultrasensitive detection of antibiotics. Biosens Bioelectron 132:8–16. https://doi.org/10.1016/j.bios.2019.02.040

Wang Y et al (2019b) Electrochemical aptasensor based on gold modified graphene nanocomposite with different morphologies for ultrasensitive detection of Pb^{2+}. Sensors Actuators B Chem 288:325–331. https://doi.org/10.1016/j.snb.2019.03.010

Wee Y et al (2019) Tyrosinase-immobilized CNT based biosensor for highly-sensitive detection of phenolic compounds. Biosens Bioelectron 132:279–285. https://doi.org/10.1016/j.bios.2019.03.008

Wei P et al (2018) Impact analysis of temperature and humidity conditions on electrochemical sensor response in ambient air quality monitoring. Sensors 18:59. https://doi.org/10.3390/s18020059

Wu W et al (2019) Sensitive, selective and simultaneous electrochemical detection of multiple heavy metals in environment and food using a lowcost Fe_3O_4 nanoparticles/fluorinated multi-walled carbon nanotubes sensor. Ecotoxicol Environ Saf 175:243–250. https://doi.org/10.1016/j.ecoenv.2019.03.037

Xie T, Liu Q, Shi Y, Liu Q (2006) Simultaneous determination of positional isomers of benzenediols by capillary zone electrophoresis with square wave amperometric detection. J Chromatogr A 1109:317–321. https://doi.org/10.1016/j.chroma.2006.01.135

Xu HL et al (2007) Simultaneous detection and identification of multigas pollutants using filament-induced nonlinear spectroscopy. Appl Phys Lett 90:101106. https://doi.org/10.1063/1.2711537

Xu A et al (2018) Ultrasensitive electrochemical sensing of Hg^{2+} based on thymine-Hg^{2+}-thymine interaction and signal amplification of alkaline phosphatase catalyzed silver deposition. Biosens Bioelectron 104:95–101. https://doi.org/10.1016/j.bios.2018.01.005

Xu G et al (2019) Dual-signal aptamer sensor based on polydopamine-gold nanoparticles and exonuclease I for ultrasensitive malathion detection. Sensors Actuators B Chem 287:428–436. https://doi.org/10.1016/j.snb.2019.01.113

Yang S et al (2018) Advances in the use of carbonaceous materials for the electrochemical determination of persistent organic pollutants. A review. Microchim Acta 185:112. https://doi.org/10.1007/s00604-017-2638-9

Yang H et al (2019a) In situ construction of hollow carbon spheres with N, Co, and Fe co-doping as electrochemical sensors for simultaneous determination of dihydroxybenzene isomers. Nanoscale 11:8950–8958. https://doi.org/10.1039/C9NR01146C

Yang Y et al (2019b) An amino-modified metal-organic framework (type UiO-66-NH_2) loaded with cadmium(II) and lead(II) ions for simultaneous electrochemical immunosensing of triazophos and thiacloprid. Microchim Acta 186:101. https://doi.org/10.1007/s00604-018-3201-z

Yi W, He Z, Fei J, He X (2019) Sensitive electrochemical sensor based on poly(l-glutamic acid)/graphene oxide composite material for simultaneous detection of heavy metal ions. RSC Adv 9:17325–17334. https://doi.org/10.1039/C9RA01891C

Yu Y et al (2019) Dandelion-like CuO microspheres decorated with au nanoparticle modified biosensor for Hg^{2+} detection using a T-Hg^{2+}-T triggered hybridization chain reaction amplification strategy. Biosens Bioelectron 131:207–213. https://doi.org/10.1016/j.bios.2019.01.063

Zhang J, Sun X, Wu J (2019a) Heavy metal ion detection platforms based on a glutathione probe: a mini review. Appl Sci 9:489. https://doi.org/10.3390/app9030489

Zhang Y et al (2019b) High-performance electrochemical sensor based on $Mn_{1-x}Zn_xFe_2O_4$ nanoparticle/nafion-modified glassy carbon electrode for Pb^{2+} detection. J Electrochem Soc 166:B341–B348. https://doi.org/10.1149/2.0151904jes

Zhao G, Wang H, Liu G, Wang Z (2016) Box–Behnken response surface design for the optimization of electrochemical detection of cadmium by square wave anodic stripping voltammetry on bismuth film/glassy carbon electrode. Sensors Actuators B Chem 235:67–73. https://doi.org/10.1016/j.snb.2016.05.051

Zhou Q et al (2016) Highly sensitive electrochemical sensing platform for lead ion based on synergetic catalysis of DNAzyme and Au–Pd porous bimetallic nanostructures. Biosens Bioelectron 78:236–243. https://doi.org/10.1016/j.bios.2015.11.055

Zhou N et al (2019) Construction of Ce-MOF@COF hybrid nanostructure: label-free aptasensor for the ultrasensitive detection of oxytetracycline residues in aqueous solution environments. Biosens Bioelectron 127:92–100. https://doi.org/10.1016/j.bios.2018.12.024

Zhu Z et al (2009) Highly sensitive electrochemical sensor for mercury (II) ions by using a mercury-specific oligonucleotide probe and gold nanoparticle-based amplification. Anal Chem 81:7660–7666. https://doi.org/10.1021/ac9010809