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Electrochemical Sensors for Food Safety

Lingwen Zeng, Lei Peng, Dazhi Wu and Baoguo Yang

Abstract

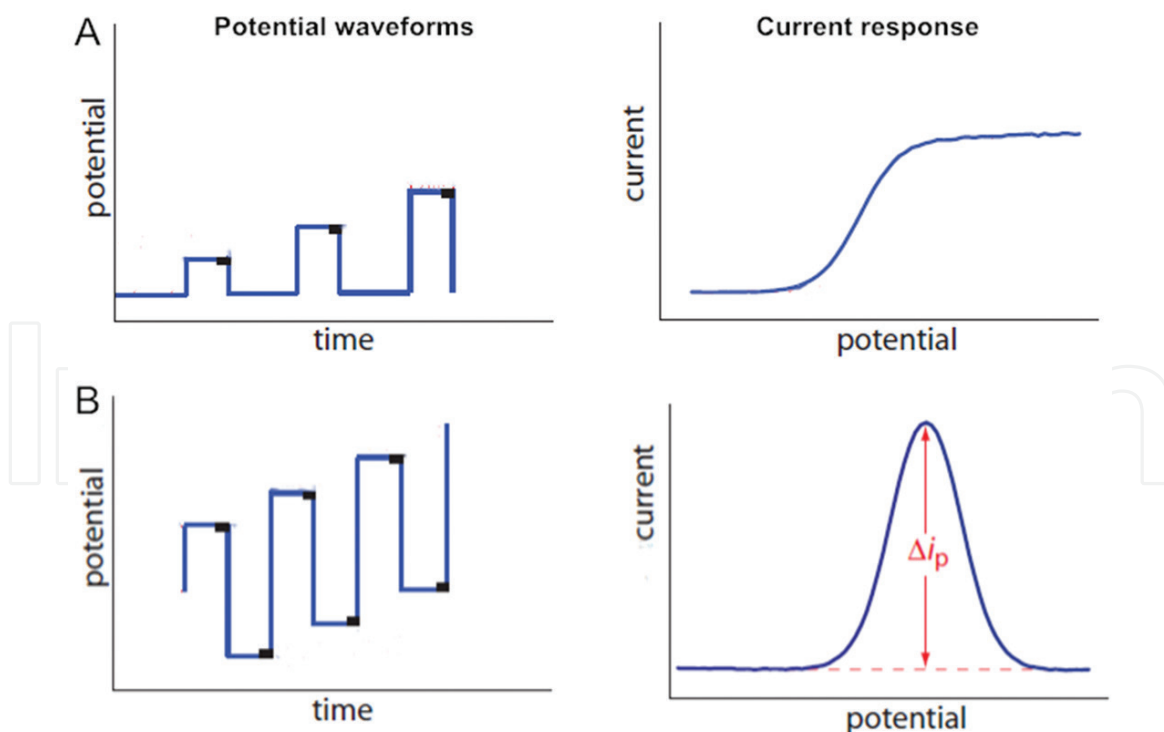
Food safety poses an increasing threat to human health worldwide. The development of analytical methods and techniques to ensure food safety is therefore of great importance. Electrochemical sensors provide unique opportunity to realize sensitive, accurate, rapid, and portable detection for food safety. They have the potential to overcome the restrictions and limitations of traditional methods. In this chapter, we review the progress of electrochemical sensors for the detection of food contaminants including heavy metals, illegal additives, pesticide residues, veterinary drug residues, biological toxins, and foodborne pathogen. Future perspectives and challenges are also discussed.

Keywords: electrochemical sensors, cyclic voltammetry, linear sweep voltammetry, differential pulse voltammetry, square wave voltammetry, food safety, detection

1. Introduction

Food safety has become a global public health concern affecting both mostly developing countries and developed countries. In addition, foodborne diseases negatively impact the economy, trade, and industries of affected countries. For example, melamine has been detected in infant formula (milk powder) in China, leading to more than 290,000 infants suffering from severe health problems such as urinary tract stones [1]. Early and accurate detection of food safety is therefore very important for preventing, controlling, and mitigating the impact of potential outbreaks. Many analytic methods, including chromatography methods such as gas chromatography (GC) [2], high performance liquid chromatography (HPLC) [3], gas chromatography-mass spectrometer (GC-MS) [4], and liquid chromatography-mass spectrometer (LC-MS) [5], and immunological detection, such as enzyme linked immunosorbent assay (ELISA) [6] and lateral flow immunoassay [7], have been employed for food safety detection. Although those traditional methods are relatively sensitive and specific, they are expensive, laborious, and time-consuming and require well-trained personnel [8, 9], which make them incompatible for developing countries and areas are lacking equipped facilities and specialists. It is therefore urgent to develop rapid, accurate, sensitive, and online technologies for food safety detection.

Modern electrochemistry provides powerful analytical techniques for sensors, with the advantages of instrumental simplicity, low cost, and miniaturization, work on-site, and the ability to measure pollutants in complex matrices with minimal sample preparation [10]. Electrochemical sensors and methods are developed as suitable tools for different applications, including bioprocess control, agriculture, and military, and, in particular, for food quality control. Voltammetric techniques, such

**Figure 1.**

Potential waveforms and their respective current response for (A) differential pulse voltammetry (DPV) and (B) square wave voltammetry (SWV).

as cyclic voltammetry (CV) [10], linear sweep voltammetry (LSV) [11], differential pulse voltammetry (DPV) [12], and square wave voltammetry (SWV) [13], have been widely used in food analysis. Among these voltammetric techniques, DPV and SWV are commonly used, as low detection limits and multiplex analysis can be achieved with the two methods. These two techniques involve potential waveforms and their respective current response are shown in **Figure 1A**. The waveform of DPV consists of pulses of constant amplitude superimposed on a staircase waveform. This method has the highest sensitivity in electrochemistry because the charging current can be ignored against faradaic current, and their ratio is obtained as large. Moreover, SWV consists of symmetrical square-wave pulses superimposed on a staircase waveform. During each square wave cycle, the current is sampled twice, just before the end of each forward and each backward pulse followed by subtraction of the currents. The peak current heights (values) obtained by the two methods are directly proportional to the concentrations of the analyte. Amperometry is another important electrochemical analysis method in which the potential of the working electrode is constant and the resulting current from faradic processes occurring at the electrode is monitored with a function of time. In this method, the current is integrated over relatively longer time intervals, so it gives an improved signal to noise ratio [14].

Electrochemical sensors can be used as food safety monitoring tools in the assessment of biological/ecological quality or for the chemical monitoring of both inorganic and organic pollutants. In this chapter we provide an overview of electrochemical sensor systems for food safety applications, and in the following sections, we describe the various electrochemical sensors that have been developed for food safety detection.

2. Heavy metals

Heavy metals (HMs) are currently defined as metals with a specific gravity greater than 5 g cm^{-3} , which are considered as a serious source for polluting the

biosphere throughout the world and causing many healthy and physiological diseases due to their prolonged half-life, non-biodegradability, and potential of accumulation in different parts of the human body [15, 16]. Heavy metals like cadmium, lead, arsenic, chromium, and mercury are considered as hazardous elements even at low concentrations [17–19]. Therefore, sensitive and selective determination of toxic heavy metals with cost-effective and convenient procedures is of paramount importance.

Due to the speed of detection, low cost, high sensitivity, and easy adaptability for in situ measurement [20], electrochemical sensors have attracted great interest in the detection of heavy metal ions for food safety.

For many years, anodic stripping voltammetry (ASV) at the mercury and its modified electrode was extensively applied to the determination of trace metal ions for the extensive cathodic potential range [21, 22]. However, the disposal of the mercury-containing device and the incorrect handling can lead to the formation of mercury vapors that are toxic and represent a significant health and environmental hazard [23]. Therefore, various mercury-free electrodes have been developed in the past few decades. For example, a nanostructured bismuth film electrode (nsBiFE) has been prepared for ASV detection of multiple heavy metals, in which the detection limits of 0.4 and 0.1 $\mu\text{g L}^{-1}$ are obtained for Cd^{2+} and Pb^{2+} , respectively [24]. Similar to bismuth, antimony nanoparticles have also been proven to be highly sensitive and reliable for tracing analysis of heavy metals [25]. To take into real application, more and more electrochemical sensors based on screen-printed carbon electrode (SPCE) have been fabricated for trace heavy metal detection in food safety as it is inexpensive, portable, and easy for mass production [26, 27].

3. Illegal additives

Addition of inedible substances and abuse of food additives are the prominent problems affecting food safety [28]. Typical illegal additives include melamine, clenbuterol, and Sudan I. These illegal actions may pose great threat to human health. For the detection of these chemicals, various nanomaterial-based biosensors have been developed. Various approaches aiming at analyzing specific chemical contaminants and illegal additives have been developed [29–31]. Li et al. developed a gold nanoparticles (AuNPs)-decorated reduced graphene oxide (RGO) modified electrode for detection of Sudan I in food samples including chili powder and ketchup sauce, demonstrating satisfactory sensitivity, selectivity, and recovery [11]. A sensitive and selective electrochemical sensor based on MIL-53@XC-72 nanohybrid modified glassy carbon electrode (GCE) was also fabricated to determine melamine with a linear range from 0.04 to 10 μM and detection limit of 0.005 μM ($\text{S/N} = 3$) [32]. In addition, the sensor displayed excellent reproducibility, high stability, selectivity, and good recoveries for the determination of melamine in liquid milk. The synergistic effect of nitrogen-doped graphene (NGR) and nitrogen-doped carbon nanotubes (NCNTs) has also been investigated and applied to prepare an electrochemical sensor for simultaneous and sensitive determination of caffeine and vanillin [33]. Electrochemical sensors have also been developed for many other food additives, such as sunset yellow [34, 35].

4. Pesticide residues

Pesticides, including fungicides, herbicides, and insecticides, are widely used in most food production to control pests that would otherwise destroy or reduce food

production [36]. In the area of agriculture, the usage of insecticides, herbicides, molluscicides, and fungicides has an increasing importance. However, many pesticides are toxic and can cause many health problems when consumed by animals and humans, such as bone marrow disorders, carcinogenicity, infertility, cytogenic effects, neurological diseases, and immunological and respiratory problems. Hence, pesticide residue detection is very important for food safety [37].

To date, many methods have been applied to determine pesticide residues in food samples. Electrochemical methods provide the elucidation of processes and mechanisms of redox reaction of pesticides and their residues [38]. They are sensitive, reliable, and fast. They can be easily miniaturized and integrated with other analytical methods [39, 40]. A magneto-actuated enzyme-free electrochemical sensor based on magnetic molecularly imprinted polymer was developed, and it showed outstanding analytical performance for the detection of methyl parathion in fish, with a limit of detection of as low as $1.22 \times 10^{-6} \text{ mg L}^{-1}$ and recovery values ranging from 89.4 to 94.7% [41]. Da Silva and coworkers [42] developed an acetylcholinesterase (AChE) biosensor for rapid detection of carbaryl in tomato samples by using electrode modified with reduced graphene oxide (rGO). The electrochemical response increased as the concentration of acetylthiocholine chloride increased, while the response decreased in the presence of AChE inhibitor OPs with a linear response to the inhibition of the thiocholine oxidation process for carbaryl concentrations from 10 to 50 nmol L^{-1} and 0.2 to 1.0 mol L^{-1} . Compared with AChE, organophosphorus hydrolase (OPH) enzymes catalyze the hydrolysis of organophosphorus pesticides (OPs) with a high turnover rate, can potentially be reused, and are, therefore, suitable for continuous monitoring of OPs [43, 44].

5. Veterinary drugs

Veterinary drugs mainly include antimicrobial drugs, antiparasitic drugs, and growth promoters, which are extensively used for treatment and prevention of diseases in animals, promotion of animal growth, and feed efficiency [45]. But the possible presence of veterinary drugs in animal-derived foods is one of the key issues for food safety, which arouses great public concern. So it is very important to develop quick and accurate methods to detect veterinary drug residues in animal-derived food, and their quantity must be less than the maximum residue limits (MRL) defined in many countries on the basis of food safety [46].

Electrochemical sensors have drawn considerable attention in many fields such as food safety, disease diagnosis, and environmental monitoring [47, 48]. Lin et al. [49] developed a hybrid CNT-modified electrode for simultaneous determination of toxic ractopamine and salbutamol in pork samples. Conzuelo et al. developed a novel strategy to construct disposable amperometric affinity biosensors by recombinant bacterial penicillin-binding protein (PBP) tagged by an N-terminal hexahistidine tail that was immobilized onto Co^{2+} -tetradentate nitrilotriacetic acid (NTA)-modified screen-printed carbon electrodes (SPCEs) for the specific detection and quantification of β -lactam antibiotic residues in milk, which was accomplished by means of a direct competitive assay using a tracer with horseradish peroxidase (HRP) for the enzymatic labeling [50]. The sensor showed limits of detection with the low part-per-billion level for the antibiotics tested in untreated milk samples and a good selectivity against other antibiotic residues frequently detected in milk and dairy products. In addition, Wang et al. proposed a simple, rapid, and highly sensitive homogeneous electrochemical strategy for the detection of ampicillin based on target-initiated T7 exonuclease-assisted signal amplification. This biosensor showed a low detection limit of 4.0 pM toward ampicillin with an

excellent selectivity, which has been successfully applied to assay antibiotic in milk. Importantly, the sensor system could avoid the tedious and time-consuming steps of electrode modification, making the experimental processes much simpler and more convenient, which has great potential for the simple, easy, and convenient detection of antibiotic residues in food safety field [51].

6. Biological toxins

Mycotoxins are fungal secondary metabolites that have toxic effects on humans and animals. Generally, mycotoxins can be easily found in agriculture crops, dairy products, including milk and cheese, and alcohols [52]. Mycotoxins enter human or animal bodies through consumption of contaminated animals or industrial food products. Crops and food products that are highly susceptible to mycotoxin contamination include alcoholic beverages, wheat, corn, barley, sugarcane, cottonseed, peanuts, rice, sugar beets, sorghum, and hard cheese [53].

Many review articles have focused on mycotoxin detection using different transduction methods [54, 55]. However, only a few review articles have reported on the use of nanomaterials for the electrochemical (EC) sensing of mycotoxins [56]. The present review summarizes the recent developments of nanomaterial-based EC biosensors for mycotoxin detection. It describes the importance of mycotoxin detection and the current progress and necessity of POC analysis of food toxins [56]. Finally, it illustrates the role in mycotoxin detection of EC sensors based on carbon and graphene metal nanoparticles (NPs) combined with different recognition elements, such as aptamers, antibodies, and molecularly imprinted polymers (MIPs) [57, 58]. These sensors exhibited additional analytical merits such as a shortened analysis time with simplified analytical procedures and portability. As such, EC sensors are now acknowledged as promising options for the trace-level identification of mycotoxins in food processing and manufacturing industries.

7. Microbial pathogens

Microbial pathogens include bacteria, viruses, and protozoa, and failure to detect them can have severe impacts on public health and safety. In the food or water services industries, legislation developed by the appropriate associated regulatory bodies to monitor and control the presence of these microorganisms is vital. Rapid and cost-efficient detection methods, with high-throughput capacity, are essential to implement effective monitoring systems to protect human health [59]. In 2012, the Environmental Protection Agency (EPA) released new Recreational Water Quality Criteria recommendations for protecting human health in waters designated for primary contact recreation [60]. Guner et al. developed an electrochemical sensor for the detection of *E. coli* using a pencil graphite electrode that was modified with multi-walled CNT (MWCNT), chitosan, polypyrrole (PPy), and AuNPs. Anti-*E. coli* monoclonal antibody was immobilized on the hybrid bionanocomposite, and the detection range was from 3×10^1 to 3×10^7 CFU/mL of *E. coli* [61]. Gao et al. describe a novel electrochemical biosensor based on mouse monoclonal antibody immobilized on self-assembled monolayers (SAM)-modified gold (Au) electrodes for the detection of *Listeria monocytogenes* (LM) and the detection range is from 10^2 to 10^6 CFU/mL. More importantly, this biosensor could apply to detect LM in milk without sample pretreatment, which is a straightforward and reliable method for analysis of LM with a simple operation and sensitivity at a low cost [62]. SPCEs were modified with iron/gold core/shell nanoparticles (Fe@Au) conjugated with anti-salmonella antibodies to develop

an electrochemical biosensor for Salmonella detection. The biosensor was performed by square-wave anodic stripping voltammetry through the use of CdS nanocrystals and its calibration curve was established between 1×10^1 and 1×10^6 cells/mL with the detection limit of 13 cells/mL. The developed method showed that it is possible to determine the bacteria in milk at low concentrations and is suitable for the rapid (less than 1 h) and sensitive detection of *S. typhimurium* in real samples. Therefore, the developed methodology could contribute to the improvement of the quality control of food samples [63].

8. Summary

Food safety is undoubtedly one of the major global concerns. In this chapter, we summarize some representative electrochemical sensors toward food contaminants such as heavy metals, illegal additives, pesticide residues, veterinary drug residues, biological toxins, and foodborne pathogen. These electrochemical sensors for food safety detection continue to show many advantages including rapid response, field applicability, high sensitivity, high selectivity, and online analysis. Moreover, electrochemical sensors are much cheaper and easier to be miniaturized, which may play a key role on quality control in food processing, improving product quality and safety. However, the stability of the electrochemical sensors is still a challenging problem. Recently, we have developed an electrochemical instrument and a number of electrochemical sensors for the detection of heavy metal ions with excellent sensitivity and reproducibility. The instrument and sensors are being commercialized with satisfactory user feedback.

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