Recent Progress of Electrochemical Sensors in Food Analysis

Zhaoxia Shi 1, Ling Xia 2 and Gongke Li 2, *  

1 Henan Key Laboratory of Biomolecular Recognition and Sensing, College of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, China; shizhaoxia@sqnu.edu.cn  
2 School of Chemistry, Sun Yat-sen University, Guangzhou 510006, China; xialing@mail.sysu.edu.cn  
* Correspondence: cesgkl@mail.sysu.edu.cn

Abstract: Electrochemical sensors have the advantages of being sensitive, stable, selective, simple, fast, and cost-efficient, and they have attracted much attention in food analysis. Electrode modification materials are very important for the performance of electrochemical sensors. This review summarizes the type of electrode modification material (metal nanoparticles/metal oxides, conductive polymers, carbon materials, and the metal-organic framework and its composite materials) and the application progress of electrochemical sensors in food analysis, mainly including the detection of food additives, pesticide residues, veterinary drugs residue, heavy metals, and mycotoxins in food in the recent ten years. Moreover, the application of electrochemical sensors is prospected.

Keywords: electrochemical sensors; nanomaterials; food safety; analysis

1. Introduction

Food safety issues have always been the focus of public concern. However, in recent years, various food safety problems still occurred such as: “Sudan red”, “clenbuterol”, and “melamine”, which seriously threatened human health. In order to protect people’s life and safety, the development of a fast, sensitive, and reliable food safety analytical method is the priority among priorities of many researchers. Traditional food safety detection techniques mainly included gas chromatography, liquid chromatography, gas chromatography-mass spectrometry, and liquid chromatography-mass spectrometry [1,2]. These methods have shortcomings such as a long detection cycle, complicated operation, and expensive instruments, which are difficult to meet the needs of rapid analysis of food. Electrochemical sensors have various advantages such as their high sensitivity, good selectivity, fast analysis speed, simple equipment, and ability to monitor in complex systems, which have wide application prospects in the field of food safety analysis [3,4].

For an electrochemical sensor, the sample analysis process mainly includes two stages: recognition and signal conversion. Recognition was carried out via the recognition element, which was usually determined via the electrode modification material. Signal conversion refers to the process of converting the analytes into a measurable electrical signal, then the signal was output through the instrument, which could be used as the basis of quantitative analysis. The detection principle is based on the electrochemical REDOX reaction to detect the tested substance, and the modified electrode material was commonly used to identify the separate components. An electrochemical sensor is an electronic instrument that could be used to detect the target quantitatively based on the REDOX process. The molecular recognition element is the sensing element of the target molecule. In the detection system, it can recognize the target molecule specifically or sensitively, generate corresponding physical and chemical reactions on the electrode surface, and then these reactions are converted into electrical, thermal, light, or other easily recognized signals to achieve the qualitative or quantitative detection of the target object [5]. If it is a bare electrode, that is to say, without modification material, the performances were limited, including sensitivity and selectivity. Therefore, electrode modification materials play a decisive role.
in the performance of the identification element. Electrode modification materials usually have high conductivity and good catalytic activity, which can accelerate the electrode signal transmission and amplify the detection signal, achieving the purpose of highly sensitive analysis. Therefore, electrode modification materials with the characteristics of a large specific surface area, good conductivity, and ease of functionalization for electrode modification should be preferred. With the continuous development of materials science, especially nanomaterials and biomaterials, electrochemical sensing technology has also achieved rapid development. Scheme 1 lists the main framework of this review, including the types of electrode modification materials and the application of electrochemical sensor in food analysis. Electrochemical sensors based on various nanomaterials are widely used in the detection of food additives, pesticide and veterinary drug residues, heavy metal ions, mycotoxins and other target substances of different categories, and fast and accurate detection results were achieved. This review mainly summarizes the application of electrochemical sensors based on metal oxides, the metal organic framework, carbon materials, conductive polymers and their composite materials in the field of food analysis.

Scheme 1. Nanomaterial-constructed electrochemical sensors in food analysis.

2. Electrode Material

Electrode modification materials play a decisive role in electrode performance. Electrode modification materials usually have high conductivity and good catalytic activity, which can accelerate electrode signal conduction; amplifies the detection signal; and lastly, achieves the purpose of highly sensitive detection. Hazardous substances in food are the detection objects of electrochemical sensors. Modified electrodes recognize the response caused via changes in certain molecules and then convert the response into detectable information. Therefore, the modified electrode material must have the ability to recognize molecules. At present, metal nanoparticles/metal oxides, conductive polymers, carbon materials, the metal-organic framework and its composite materials and other functional materials have been widely used to build the electrochemical sensor. In addition to utilizing
the recognition capabilities of the modified electrode material, for some substances that are difficult to detect specifically by using the modified material alone, other kinds of affinity reagents are sometimes used in the construction of the sensor, such as aptamers, antibodies, or molecularly imprinted polymers. This paper mainly reviews the food safety electrochemical sensors based on the recognition ability of nanomaterials. Only some application examples involve the use of affinity agents, so other types of affinity agents will not be introduced in detail.

2.1. Metal Nanoparticles/Metal Oxides

In the field of electrochemical sensors, precious metals (gold, silver, platinum, etc.) as catalysts were first used in the electrochemical catalytic process. However, the high cost of precious metal catalysts limited their extensive use in practical applications. At the same time, the phenomenon of “electrode poisoning” was unavoidable in the catalytic process of precious metal catalysts [6]. The good performance of metal oxides in electrocatalytic activity, adsorption properties, electron transport properties, etc., has attracted much attention and been applied to many fields, and the morphology and size of metal oxides are easy to control [7–9]. Metal oxide-based electrochemical sensors have advantages of low cost, simple construction, and easy operation. Electrochemical sensors based on metal oxides have attracted much attention in the field of electrochemical analysis [10,11]. The substance to be detected reacts on the surface of the metal oxide-based electrochemical sensor and generates the corresponding electrical signal. By analyzing the strength of the electrical signal, the concentration of the substance could be calculated, then the purpose of detecting whether the substance exceeds the standard or is safe was realized [12]. Compared with the traditional precious metal catalyst, the metal oxide catalyst is more convenient to use and operate [13,14]. The metal elements, such as Fe, Co, Cu, are large reserves of rich resources. Therefore, metal oxides can be widely used as catalysts without the limitation of cost and reserves.

In recent years acting as excellent catalysts, metal oxides have been increasingly used in constructing electrochemical sensors. For example, Zhang et al. [15] synthesized hollow carbon spheres via a hydrothermal reaction, then Co$_3$O$_4$ nanowires were assembled successfully on the surface of the hollow carbon spheres (as shown in Figure 1A). The obtained composite materials were used to build a gas sensor for detecting acetone, which exhibited an enhanced catalytic performance even at lower operating temperatures. In addition, the sensor showed long-time stability, a larger response intensity, and excellent selectivity. Das et al. [16] successfully synthesized Co$_3$O$_4$ with an average diameter of 31.97 nm and used it to prepare electrochemical sensors for the electrochemical detection of H$_2$O$_2$, which showed fast response speed and high sensitivity. Wu et al. [3] synthesized polystyrene spheres via polyreaction in an oxygen-free environment, then used it as a template to synthesize 3D hierarchical porous Co$_3$O$_4$ materials (as shown in Figure 1B). The as-synthesized materials-based gas sensor exhibited an excellent sensing performance to NH$_3$ gas at room temperature, with a low detection limit of 0.5 mg/mL. Metal nanoparticles/metal oxides generally exhibit good catalytic activity, good biocompatibility, and excellent electron transport kinetics. In the field of electrochemical sensing, metal nanoparticles/metal oxides have been considered as a kind of excellent modified electrode material by many researchers. Due to the high surface reactivity, large surface area, and various valence states, nanometal oxides show an excellent catalytic performance. In a word, metal oxide nanoparticles are a kind of cheap, low toxic, and stable nanomaterial, which has been widely used in electrochemical sensors and show an excellent performance. However, there are many kinds of nano-metal oxides with different catalytic properties. For the future work of researchers, it is suggested to try to study more metal oxides, and for the same kind of metal oxide, it can be controlled by changing the synthesis conditions to prepare the morphology of particles, such as rods, fibers, fusiform, etc., and conduct in-depth research on its reaction mechanism.
2.2. Conducting Polymer

Conducting polymers are widely used in constructing electrochemical sensors because of their excellent conductivity and good stability. Conducting polymers, such as polydopamine (PDDA), polypyrrole (PPy), and polymerization (3,4-Vinyl dioxthiophene) (PEDOT) have the advantages of high conductivity, good environmental stability, good film forming performance, and easy preparation. These properties aroused great interest in researchers to promote its application in electrochemical sensors. For instance, Dipankar et al. [17] reported the synthesis of rod-like PPy-Ag nanocomposites (Figure 2A). Firstly, they obtained PPy with the assistance of sodium cholate as a surfactant. Then, the rod-like PPy-Ag nanocomposite exhibited excellent sensitivity for the determination of dopamine. In addition, Shao’s group [18] reported a sensor platform which was based on the Au nanoparticles/Ti3C2Tx/PDDA composite (Figure 2B). In this work, Ti3C2Tx-PDDA was synthesized via a simple solvent reaction. After the Ti3C2Tx suspension was modified on the surface of the electrode via the drop-coating method, Au NPs were deposited on the surface of the electrode via potentiostatic deposition. Benefitting from the catalytic activity of Au NPs, the large area, and the excellent electrical conductivity of Ti3C2Tx, the sensor demonstrated cocatalytic oxidation of nitrite ions. Future research on conducting polymers should focus on the design and synthesis in order to achieve the specific detection of target objects, which depends only on the design of the functional groups on the surface of the material, rather than the action of the specific affinity agent.
2.3. Carbon-Based Material

Carbon materials usually have characteristics of high conductivity, good thermal stability, good biocompatibility, and good electrocatalysis performance, which make it an ideal modified electrode material. For instance, both one-dimensional carbon nanotubes and two-dimensional graphene carbon materials have been widely used for electrical analysis. To illustrate, Zhang’s group [19] synthesized a phosphor-doped graphene composite and used it as an electrode modification material to construct the electrochemical sensor (Figure 3A). The sensor exhibited high selectivity for the detection of acetaminophen. The good conductivity of the modified electrode sped up the electron transfer, showing good electrocatalytic activity to the oxidation of acetaminophen. Zhu’s group [20] constructed a carbon fiber microelectrode based on the Au nanoparticles RGO-MWCNTs (Multi-walled Carbon Nanotubes, MWNTs) nanocomposite, which realized the simultaneous detection of three kinds of dihydroxybenzoic acid isomers (Figure 3B). The synergistic effect between Au nanoparticles and RGO-MWCNTs reduced the overpotential, showing an enhancement effect in electrocatalysis and improving the peak shape of dihydroxybenzoic acid (DHBA).

![Figure 3. (A) Scheme of phosphorus-doped graphene for acetaminophen detection in pharmaceutical tablet [19]; Copyright 2018 Elsevier. (B) schematic illustration of synthesis process and morphological characterization of RGO-MWCNTs/Au and application for the determination of 2,3-DHBA, 2,5-DHBA, and 2,6-DHBA [20]. Copyright 2019 Elsevier.](image)

Carbon-based composites have been used in electrochemical sensors for many years. We think that the future research direction of carbon-based materials should focus on how to use the characteristics of carbon-based materials to prepare portable electrodes and how to synthesize new composite materials, such as graphene paper electrodes, graphene aerogel composites, and carbon-based quantum dots.

2.4. Metal-Organic Framework and Its Composite Materials

Organic–inorganic hybrid materials, also called metal–organic frameworks (MOFs), are made of an organic ligand bound to a metal ion or a group of metal ions [21,22] (Figure 4A). Due to the diversity of metal ions and organic ligands, different MOFs materials could be prepared by selecting different metal ions and organic ligands. Then, their structure, morphology, and chemical properties also exhibited differences. Therefore, MOFs have many outstanding features such as pore diameter adjustability, high porosity, a large specific surface area, and biocompatibilities. These features make MOFs
show a wide range of applications in the field of electrochemical sensing. Wu et al. [23] reported a Cu-MOFs modified electrode for the electrochemical detection of L-tyrosine. Porous Cu-MOFs provided a large number of active sites for adsorbing L-tyrosine. The prepared sensor showed high sensitivity and superior stability for the detection of L-tyrosine. Gao et al. [24] synthesized a Prussian blue/MWCNTs/ZIF-67 composite material and constructed a modified electrode based the material for detecting acetaminophen. The negatively charged MWCNTs were used as the carrier to fix the Prussian blue with a positive charge, thus avoiding the agglomeration of Prussian blue effectively and improving the stability, conductivity, and catalytic activity of composite materials. Coupling these benefits with the porous, large specific surface area of MOF, the modified electrode showed high stability and superior selectivity to the detection of acetaminophen. Mao’s group [25] prepared an iron phthalocyanine/ZIF-8(Pc-Fe/ZIF-8) composite successfully and constructed an electrochemical sensor based the material for the detection of trichloroacetic acid (Figure 4B). As an electrode material, ZIF-8 has porous structure, a large specific surface area, and strong adsorption capacity. At the same time, Pc-Fe (II) could accelerate the electron transfer at the electrode interface during the sensing process. Therefore, the modified electrode exhibited a low detection limitation and high sensitivity. Combining MOFs with other functional materials would not only have the superior properties of MOFs and the other functional materials, but also produces synergistic effects to obtain an enhanced sensing performance. Therefore, the combination of MOFs with other functional materials has become a research hotspot recently.

Figure 4. (A) Crystal structure of MOF-74 [21]; Copyright 2012 American Association for the Advancement of Science. (B) schematics of ZIF-8 and PcFe@ZIF-8 synthesis process, and the electrochemical sensing mechanism for trichloroacetic acid determination [25]. Copyright 2019 American Chemical Society.
In conclusion, the selection of electrode modification materials is a key step in the
design of electrochemical sensors. Therefore, the performance of electrochemical
sensors can be improved by modifying materials with electrodes. Nanomaterials have
a high specific surface area, which can improve the load capacity of various signal sources,
thus improving the sensitivity. In addition, nanomaterials have the characteristics
of easy surface modification, which provide convenience for chemical modification. These
advantages also broaden the application field of nanomaterials but also provide the premise
for the construction of sensitive sensors. The main application types of nanomaterials in
electrochemical sensors are listed in Table 1.

Table 1. The main application types of nanomaterials in electrochemical sensors.

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Sensors</th>
<th>Sample</th>
<th>Analytes</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal nanoparticles /metal oxides</td>
<td>Co3O4@rGO/GCE</td>
<td>Packaged milk, milk</td>
<td>Chloramphenicol</td>
<td>0.55 µM</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>MgO/GCE</td>
<td>powder, honey samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiO2/Au NTAs/GCE</td>
<td>Water</td>
<td>Cd(II), Pb(II)</td>
<td>0.062 µM, 0.24 µM</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>AgNPs-Pdop@Gr</td>
<td>Natural Water</td>
<td>Bisphenol A</td>
<td>6.2 nM</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>meso-MFI-CuO/GCE</td>
<td>Catechol-spiked water</td>
<td>Catechol</td>
<td>0.10 µM</td>
<td>[29]</td>
</tr>
<tr>
<td>Carbon-based materials</td>
<td>rGO/Pd@PPy NPs/GCE</td>
<td>Serum</td>
<td>Ascorbic acid,  Epinephrine, I-tyrosine</td>
<td>0.049 µM, 0.056 µM, 0.047 µM</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>EB-Ppy-BSA/GCE</td>
<td>Tea and chicken</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>α-Fe2O3/ PAN NTs/GCE</td>
<td>Human urine</td>
<td>Uric acid</td>
<td>0.038 µM</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>PPy@Cellulose /GCE</td>
<td>Commercial fruit</td>
<td>Ascorbic acid</td>
<td>0.75 µM</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>Pt/PEDOT-PBNPs/GCE</td>
<td>Human blood samples</td>
<td></td>
<td>1.4 µM</td>
<td>[34]</td>
</tr>
<tr>
<td>Conducting polymer</td>
<td>FeCo@pyrolysis carbon-Surface engineering /GCE</td>
<td>Soil, groundwater, industrial effluent</td>
<td>Cr(VI)</td>
<td>0.15 µM</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>MnFe2O4/GO/GCE</td>
<td>Water sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MoS2/f-MWCNTs/GCE</td>
<td>Milk, powdered milk, and honey samples</td>
<td>Chloramphenicol</td>
<td>0.015 µM</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>Polytyramine/sol-gel/f-MWCNT/AuNPs MIP/PGE</td>
<td>Urine and plasma</td>
<td>Ketamine</td>
<td>0.70 nM</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>Graphene/Nano-Au/GCE</td>
<td>Beef, fish, and milk powder</td>
<td>Diethylstilboestrol</td>
<td>9.8 nM</td>
<td>[38]</td>
</tr>
<tr>
<td>Metal-organic framework-based materials</td>
<td>UiO-66-NH2@PANI-co-ANAA/GCE</td>
<td>Milk and human urine</td>
<td>H2O2, dopamine</td>
<td>0.60 µM, 0.30 µM</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Fe-MOF@mesoporous Fc3O4@mc/GCE</td>
<td>River water and human serum</td>
<td>Pb2+, As3+</td>
<td>2.3 pM, 6.7 pM</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>AuNp@MOF/CPE</td>
<td>No</td>
<td>Bisphenol A</td>
<td>0.038 nM</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>Au@Cu-MOF/N-GQDs/GCE</td>
<td>Apple juices</td>
<td>Patulin</td>
<td>4.5 pM</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>PtNP/MIL-101(Fe)/GCE</td>
<td>Powder and pasteurized milk</td>
<td>Aflatoxin M1</td>
<td>6.1 pM</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Note: GCE: Glassy carbon electrode; NTAs: Nanotube arrays; Pdop: Polydopamine; Au-PEDOT: Gold-poly(3,4-ethylenedioxythiophene); PPy: Polypyrrole; EB: Electron beam; PAN NTs: Polyaniline nanotube; PEDOT-PBNPs: Poly(3,4-ethylenedioxythiophene)-Prussian blue nanoparticles; f-MWCNTs: Functionalized multiwalled carbon nanotubes; MIP/PGE: Molecularly imprinted polymer/pencil graphite electrode; CPE: Carbon paste electrode; N-GQDs: Nitrogen-doped graphene quantum dots.

3. Application of Electrochemical Sensors in Food Safety

Food safety is closely related to human beings, which is a serious issue in many
countries. Much attention is focused on the security of food as it is a social hotspot.
Therefore, how to monitor food quality has become the focus of some researchers. One of
various analysis methods, electrochemical sensing technology, has been extensively applied
in the field of food safety detection due to its benefits of being simple, quick, accurate, and
having sensitive equipment. This paper mainly reviews its applications in the detection of
food additives, pesticide residues, veterinary drugs residue, heavy metals, and mycotoxins.
3.1. Food Additives

Food additives can both improve the flavor and extend the shelf life of food. However, excessive use will cause serious harm to human health. There are many methods for the detection of food additives, such as high-performance liquid chromatography (HPLC), chromatography and mass spectrometry, spectrophotometry, etc. [46–48]. These methods have achieved the accurate and sensitive detection of some food additives, but these methods have shortcomings such as complex operation, high cost, long analysis time, and so on. Therefore, it is very important to establish a fast, simple, efficient, and sensitive analytical method for the detection of food additives. Electrochemical analysis methods have been widely used in food safety detection (such as pigment, antioxidant, antibiotic, and so on) because of its advantages of easy operation, cheap price, high sensitivity, and good selectivity.

He’s group [49] prepared an electrochemical sensor based on Au nanoparticles/RGO/Cu-MOFs for the detection of sodium nitrite (Figure 5). Yang et al. [50] established an electrochemical sensor for Sudan I based on the nanohybrids of graphene-ZnSe quantum dots. An enrichment effect on Sudan I of the sensor was significantly enhanced via the hybrids of ZnSe and the graphene quantum dots, which also improved electrocatalytic activity for Sudan I’s oxidation. Liu et al. [51] prepared a MnO₂/graphene supported on an Ni foam electrode by using ultrasonic impregnation and electrochemical deposition. Pb(II) in the aquatic environment was detected using the resultant electrode. On the Ni foam, graphene and MnO₂ were deposited, which increased the active surface area and aided in electron transport. Erady et al. [52] reported a Bi/MWCTs/CTAB composite modified electrode for the detection of caffeic acid. The composite showed a good catalytic effect on caffeic acid, where the detection limit was as low as 0.157 nmol/L. Wang et al. [53] synthesized carbon nanotubes/polypyrrole composites and used it to build a modified electrode for detecting carmine, where the detection limit was 1 nmol/L and could detect carmine content in fruit drinks.

![Figure 5. The preparation process of Au nanoparticles/RGO/Cu-MOFs composite material and the application for the detection of sodium nitrite [49]. Copyright 2019 Elsevier.](image-url)
electrochemical detection of food additives will focus on the research and development of new materials, studying the mechanism of electrochemical detection and conducting research on a new method of electrochemical detection.

3.2. Pesticide Residue

In agricultural production, pesticides play an important role in improving the production, harvest, and quality of agricultural products. However, pesticide residues not only contaminate the ecological environment, but also harm people’s health. Benefits including speed to real-time analysis features in the electrochemical approach can be used as a suitable tool for identifying pesticide residues in agricultural goods, such as benzimidazoles, organophosphorus, and organochlorine.

Lu et al. [54] constructed an electrochemical sensing system based on a reticulated bimetallic Pd@Au nanowire composite for malathion detection (Figure 6A). The nanowire network structure not only provided multiple electronic pathways, which was beneficial to improve the electrical conductivity of the composite, but also provided a larger electroactive specific surface area due to the self-interconnection of the nanowire. Song et al. [55] synthesized Ag nanoparticle-modified N-fluorine co-doped monolayer 2D MoS$_2$ nanocomposites and constructed an electrochemical method for detecting the residue of organophosphorus pesticides in food (Figure 6B). The material accelerated electron transport and obtained a high electroactive specific surface area, which realized the high sensitivity detection of monocrotophos and chlorpyrifos. Duan et al. [56] constructed an electrochemical sensing system of pentachloronitrobenzene based on the NiCo$_2$O$_4$@ZnO/ZnCo$_2$O$_4$ microspheres and molecularly imprinted polymers to achieve a highly sensitive and selective detection of pentachloronitrobenzene (Figure 6C). Dong et al. [57] designed and synthesized a ZnFe$_2$O$_4$/SWCNTs nanocomplex and used it to construct an electrochemical sensing platform for the simultaneous detection of both carbendazim and thiabendazole. The ZnFe$_2$O$_4$/SWCNTs composites have excellent electrocatalytic activity and a specific surface area where the sensitive detection of carbendazim and thiabendazole was realized.

Figure 6. (A) TEM image of Pd@Au NWs network and the electrochemical behaviors of the nanosensor [54]; Copyright 2019 Elsevier. (B) schematic illustration for determination of monocrotophos and chlorpyrifos [55]; Copyright 2018 Elsevier. (C) the preparation process of MIP/NiCo$_2$O$_4$@ZnO/ZnCo$_2$O$_4$/GCE and electrochemical detection of pentachloronitrobenzene [56], Copyright 2021 Elsevier.
3.3. Veterinary Drugs Residue

Animal husbandry is an important part of the national economy, and veterinary medicine is essential in its development process. Veterinary drugs can prevent, diagnose, and treat animal diseases, regulate animal physiological functions, and improve product quality [58]. In addition to pesticide residues, the residues of veterinary drugs are also issues that need close attention. The residues of veterinary drugs refer to the residues of prototype drugs or their metabolites, including impurities related to veterinary drugs that accumulate or remain in livestock, poultry bodies, or products (such as eggs, milk, meat, etc.) after the use of drugs [59]. In food with animal residues exceeding the standard, the drugs will accumulate continuously in the body, and accumulation to a certain concentration will cause a variety of acute poisoning [60]. Compared with pesticide residues, the detection of veterinary drug residues is more complicated, which further increases the difficulty of detection. Therefore, it is necessary to strengthen the research on the detection methods of animal residues and devote time and attention to the development of highly sensitive and high accuracy analysis and detection technology of agricultural residues, which could quickly and accurately detect drug residues in products. Electrochemical analysis is an ideal method.

Deroco et al. [61] constructed an electrochemical sensor based on a carbon black nanoparticle-modified electrode and used it to detect Amoxicillin and Nimesulide simultaneously, which exhibited characteristics of being simple and having a low cost (Figure 7A). The film showed an excellent electrocatalytic activity to the electron transfer processes, and the proposed sensor presented better electrocatalytic activity to the electrooxidation of both Amoxicillin and Nimesulide, where the detection limits were 0.12 µmol/L and 0.016 µmol/L. George et al. [62] synthesized a samarium vanadate/carbon nanofiber composite and built the electrochemical sensor based the composite material for sulfadiazine analysis (Figure 7B), where the synergistic effect of the combination of samarium vanadate and carbon nanofiber accelerated charge transfer and generated more surface-active sites, which was conducive to the effective detection of antibiotics. De Araujo et al. [63] applied an electrochemical method to investigate the electrochemical behavior of xylazine and achieved an accurate quantitative method of xylazine by using the differential pulse voltammetry (Figure 7C). This work demonstrated the potential of electrochemistry for the clinical analysis of xylazine. In addition, de Araujo et al. [64] also fabricated a device which could scribe graphene on a polymeric polyetherimide substrate by using a laser, of which the device was used to detect xylazine sensitively based on electrochemical principles. As a veterinary drug, xylazine was associated with drug-facilitated crimes. The scratch on the sensor presented a highly porous characteristic, which contributed to the enhancement of the electroactive area. The sensor showed high sensitivity, selectivity, and accuracy and was successfully applied to analyze xylazine in practical samples, including beverage and urine samples. The work indicated that the electrochemical portable device could be a portable and low-cost alternative sensor for on-site quick testing.

3.4. Heavy Metal

Among many pollutants, heavy metal ions are an important category [65], such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and so on [66–68]. Numerous studies have shown that their presence posed a major threat to human health [69], affecting the food chain and the stability of ecosystems [70,71]. At present, there are many published reports about the detection of trace heavy metal ions using methods such as inductively plasma-coupled mass spectrometry [72], atomic fluorescence spectrometry [73], HPLC [74], etc. Although these technologies have the advantages of high sensitivity and high selectivity, there are still some shortcomings when they are used as heavy metal detection methods. For example, the detection cost is too high, the operation procedure is complex, the detection time is too long, and the detection is difficult in the actual environment and real-time analysis. Electrochemical methods were used by many researchers to analyze the concentration of heavy metal ions in water. For instance, Smruti et al. [75] prepared silver and platinum composite particles
(Ag@Pt NPs) from biological extracts via microwave radiation technology, constructed a biosensor, and applied them to the detection of Pb\(^{2+}\) in environmental water samples collected from rivers, domestic water supply, and sewage treatment plants (Figure 8A). Yun’s team [76] prepared an electrochemical sensor based on sodium carboxymethylcellulose/Silver nanoparticles (CMS/Ag NPs), which was successfully applied to the detection of Hg\(^{2+}\) and S\(^{2-}\) in lake and tap water samples. Ting et al. [77] synthesized a novel coupling of graphene quantum dots and gold nanoparticles (Au NPs), and electrochemical methods were established based on the material for detecting heavy metal ions (Hg(II) and Cu(II)), which showed low detection limits and high sensitivity (Figure 8B). Wang’s group [78] assembled and synthesized the T-base functional Au NPs/rGO electrode, and the constructed electrochemical biosensor was used to determine mercury ions in water (Figure 8C). The sensor has excellent selectivity for Zn(II), Cd(II), Pb(II), Cu(II), Ni(II), Co(II) and other heavy metals. It has been applied to the determination of Hg(II) in actual environmental samples successfully.

Figure 7. (A) The principle of the electrochemical sensor for detecting amoxicillin and nimesulide simultaneously based on carbon black [61]; Copyright 2018 Elsevier. (B) schematic diagram of the synthetic process of SmV/CNF and the application of detecting sulfadiazine [62]; Copyright 2021 Elsevier. (C) electroanalytical method for xylazine quantification [63]. Copyright 2019 Elsevier.

The key to electrochemical sensors for the detection of agricultural/pharmaceutical residues and heavy metal ions in food is the loading of signal factors and the development of sensing strategies. Although, based on the direct interaction between the object to be measured and the electrode modification material, the constructed non-biological sensor has the advantages of low cost, simple operation, and good stability, compared with biosensors based on enzymes, aptamers, antibodies, and other recognition molecules, there is still room for further improvement in specific detection. Therefore, in order to achieve a high sensitivity detection of actual food samples, it is necessary to develop new nanomaterials and the construction of highly sensitive sensing strategies, as well as the development of more stable and reliable sensing modes that are not affected via environmental factors.
were linearly correlated, and the aptasensor was applied for the determination of AFB1 in peanuts and corn samples. Tang et al. [82] established an electrochemical aptamer-based peroxidase. At last, they found concentrations of AFB1, and the electrochemical signals peanut and corn samples (Figure 9A), with a detection limit of 0.33 ng/L. At first, the Hg\textsuperscript{2+} detection based on GQD-AuNP [77]; Copyright 2015 Elsevier. (Figure 8.

**Figure 8.** (A) Schematic diagram of Ag@Pt NPs-based electrode for the detection of Pb\textsuperscript{2+} content in environmental water samples collected from rivers [75]; Copyright 2020 Elsevier. (B) principle of Hg\textsuperscript{2+} detection based on GQD-AuNP [77]; Copyright 2015 Elsevier. (C) the principle of the biosensor for detecting Hg\textsuperscript{2+} based on functionalized hymidine [78]. Copyright 2016 Elsevier.

### 3.5. Mycotoxins

Mycotoxins are a class of toxic secondary metabolites produced by fungi growing in food or feed. It has caused serious pollution and has become one of the main factors threatening global food safety [79,80]. Mycotoxins not only contaminate grain and cereal agricultural products directly, such as corn, wheat, barley, peanuts, oats, rice, and feed, but also contaminate animal foods through the food chain indirectly, such as milk, meat, and eggs. Contaminated food not only reduces its own nutritional value greatly, but also brings great threats to the health and life of humans and animals. There are many kinds of mycotoxins in food, among which the common and representative mycotoxins are aflatoxins (AFs), zearalenone (ZEN), ochratoxin A (OTA), okadaic acid (OA), microcystin-LR (MC-LR), cylindrospermopsin (CYN), and saxitoxin (STX). The development of a simple, efficient, accurate, and reliable mycotoxin detection method is an important way to prevent and solve the problem of food contamination. Electrochemical sensors have broad prospects in detecting mycotoxin because of their characteristics.

Wang et al. [81] established an electrochemical aptasensor based on DNA-AuNPs-HRP nanoprobes, and the aptasensor was used to detect the content of aflatoxin B1 (AFB1) in peanut and corn samples (Figure 9A), with a detection limit of 0.33 ng/L. At first, the authors immobilized the complementary strand (cDNA) of the AFB1 aptamer (Apt) on the surface of the electrode, which was modified with gold nanoparticles. The specific recognition between AFB1 and Apt was utilized with the catalytic action of horseradish peroxidase. At last, they found concentrations of AFB1, and the electrochemical signals were linearly correlated, and the aptasensor was applied for the determination of AFB1 in peanuts and corn samples. Tang et al. [82] established an electrochemical aptamer-based method for the determination of the OTA by using different affinities of MoS\textsubscript{2} for ssDNA and dsDNA. In addition, MoS\textsubscript{2} possessed peroxidase-like activity, which plays an important effect in amplifying the electrochemical signal of the REDOX system. At last, the aptasensor possessed a linearity range of 1.0 pmol/L–2.5 nmol/L and the detection limit of 0.57 pmol/L. Wang et al. [83] also used aptamers as specific receptors to build a label-free aptasensor for the detection of CYN (Figure 9B). The aptasensor showed high specificity toward CYN, indicating that electrochemical-based aptasensors could be used as an alternative method for monitoring the content of toxins in food. Singh and colleagues [84]
combined electrochemical sensing with microfluidic chip, and then designed and developed an electrochemical microfluidic biochip for the detection of OA (Figure 9C). They immobilized an aptamer specific to OA on the screen-printed carbon electrode which was modified via the gold nanocomposite. The detection limit of the fabricated aptasensor was 8 pmol/L. This work provided a new thought and method for the construction of electrochemical sensors, indicating that microfluidic-based electrochemical aptasensors were very promising for on-field assays and broadened the mind about combining electrochemistry with other techniques.

![Figure 9.](image)

**Figure 9.** (A) The principle of the electrochemical aptasensor for detecting aflatoxin B1 [81]; Copyright 2020 Elsevier. (B) fabrication process of a label-free aptasensor for the detection of cylindrospermopsin based on recognition-induced switching of the aptamer [83]; Copyright 2014 American Chemical Society. (C) the fabrication process of microfluidic electrochemical aptasensors and the application in detecting Okadaic Acid [84]. Copyright 2019 Elsevier.

At present, most of the research on the electrochemical detection of mycotoxins are electrochemical immunosensors. Mycotoxins are haptons, which are reactionogenicity but not immunogenicity, and they cannot directly stimulate the animal body to produce antibodies. The general method is to conjugate the mycotoxin with the carrier protein to form a complete antigen with immunogenicity, so that the corresponding antibody can be obtained via the immune reaction. Therefore, the key to establishing the electrochemical immunosensing strategy for mycotoxins lies in the support of carrier proteins. In the next few years, the research focus is likely to be on the support performance of different nanomaterials for carrier proteins, the simultaneous detection of multiple mycotoxins, and the development of portable sensing strategies.

### 3.6. Others

There are also some other harmful substances in food, such as small biological molecules including dopamine (DA), ascorbic acid (AA), and hydrogen peroxide, which plays an extremely important role in the human body [85]. However, the content level of some small biological molecules in the human body leads to a series of diseases, such as a lack of AA will lead to scurvy, and the high content of ureic acid in the human body may
lead to hyperuricemia and other diseases. Therefore, it is necessary to develop an analytical method that could accurately detect the content of small biological molecules in the human body. The electrochemical method could make full use of the REDOX ability of small biological molecules and quickly detect the content of small biological molecules. Moreover, the electrochemical method is a promising method because of its simple preparation, convenient testing, low cost, fast response, and high sensitivity [86,87].

Urhan et al. [88] prepared Ni nanoparticle-modified reduced graphene oxide (Ni NPs/rGO) nanocomposites on an indium tin oxide electrode via the co-deposition technique, which was used for the highly sensitive detection of glucose (Figure 10A). The electrode showed a high electrocatalytic performance and excellent anti-interference ability. Xiong et al. [89] constructed an enzyme-free H₂O₂ electrochemical sensor by fixing Au NPs on an indium tin oxide (ITO) substrate. The sensor showed a fast current response to H₂O₂ in the concentration range of 0.03–1 mmol/L. Pd has a relatively large abundance compared to other precious metals, such as Au and Pt, and could be used as a relatively inexpensive alternative for a variety of electrochemical sensing and biosensing platform applications [90]. Paulraj et al. [91] successfully synthesized Ag-doped polyaniline nanocomposites via a solid mechanical–chemical oxidative polymerization process, which overcame the weakness of the easy aggregation of silver nanoparticles and used it for the electrochemical detection of H₂O₂ and DA (Figure 10B). The detection limits were 0.03 µmol/L and 0.12 µmol/L, respectively.

In this part, we have summarized the application of electrochemical sensors in the detection of different categories of target substances such as food additives, pesticide residues, veterinary drug residues, heavy metal ions, mycotoxins, etc. From the previously mentioned, we now know that the establishment of a simple and rapid detection of the content of various harmful substances in food and the establishment of a fast and highly sensitive electrical analysis method for food quality monitoring is of great significance. The modified electrode material with good performance can give the sensor many excellent characteristics. The catalytic performance and selectivity of modified electrode materials used in food safety detection needs to be improved. Therefore, the development of electrode materials with better performance and their use in food safety detection will be the mainstream direction of future research. The main application modes of electrochemical sensors in food analysis in the recent ten years are listed in Table 2.

### Table 2. The application of electrochemical sensors in food analysis.

<table>
<thead>
<tr>
<th>Food Safety</th>
<th>Working Electrode</th>
<th>Analyte</th>
<th>Sample</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food additives</td>
<td>GN/TiO₂-CPE</td>
<td>Sunset yellow, tartrazine</td>
<td>Candy, royal jelly, ice cream, solid custard, soft drink</td>
<td>6.0 nM, 8.0 nM</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>MIP/PdAuNPs/ERGO/GCE</td>
<td>TBHQ</td>
<td>Edible oils</td>
<td>0.27 µM</td>
<td>[93]</td>
</tr>
<tr>
<td></td>
<td>AuNPs@COFs/GCE</td>
<td>Ractopamine</td>
<td>Pork and chicken</td>
<td>0.12 µM</td>
<td>[94]</td>
</tr>
<tr>
<td></td>
<td>AuNPs/Zr-MOF-Graphene/GCE</td>
<td>Sunset yellow and Sudan I</td>
<td>Soft drink and chili powder</td>
<td>0.1 µM, 0.1 µM</td>
<td>[95]</td>
</tr>
<tr>
<td></td>
<td>g-C₃N₄ NTs@MoS₂/GCE</td>
<td>Vanillin</td>
<td>Vanilla ice cream</td>
<td>4 nM</td>
<td>[96]</td>
</tr>
<tr>
<td></td>
<td>KSC@MoO₃/GCE</td>
<td>Hydroquinone and catechol</td>
<td>Environmental waters</td>
<td>0.063 µM, 0.059 µM</td>
<td>[97]</td>
</tr>
</tbody>
</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Food Safety</th>
<th>Working Electrode</th>
<th>Analyte</th>
<th>Sample</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pesticide residue</strong></td>
<td>CB-CTS-ECH/GCE</td>
<td>Herbicide</td>
<td>Environmental water</td>
<td>1.4 µM</td>
<td>[98]</td>
</tr>
<tr>
<td></td>
<td>Co-Ag BMNPs-PVP/GCE</td>
<td>Butralin</td>
<td>Honey and apple jam</td>
<td>32 nM</td>
<td>[99]</td>
</tr>
<tr>
<td></td>
<td>Gadolinium niobate/GCE</td>
<td>Aclonifen</td>
<td>River water and soil</td>
<td>1.2 nM</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>MnCo2O4/P-CN/GCE</td>
<td>Sulfadiazine</td>
<td>Water and urine</td>
<td>3.0 nM</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>WS2 nanosheets modified paper electrode</td>
<td>Nitrofurantoin</td>
<td>-</td>
<td>0.060 µM</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td>TGO@UiO-66/GCE</td>
<td>Paraoxon and Chlorpyrifos</td>
<td>Vegetable and Water</td>
<td>0.2 nM, 1.0 nM</td>
<td>[103]</td>
</tr>
<tr>
<td></td>
<td>Au@MWCNTs/GCE</td>
<td>-</td>
<td>-</td>
<td>0.0050 µM</td>
<td>[104]</td>
</tr>
<tr>
<td><strong>Veterinary drugs residue</strong></td>
<td>montmorillonite-acetylene black/CPME</td>
<td>Oxytetracycline</td>
<td>Fish shrimp</td>
<td>0.087 µM</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>PEI/TetX2/NP/GCE</td>
<td>Tetracycline</td>
<td>Milk</td>
<td>18 nM</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>apt/act/4-CP/GCE</td>
<td>Oxytetracycline</td>
<td>Milk</td>
<td>43 nM</td>
<td>[107]</td>
</tr>
<tr>
<td></td>
<td>RGO/GCE</td>
<td>Ciprofloxacin</td>
<td>Pharmaceutical Formulations and Bovine Milk</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ch-AuMIP/GCE</td>
<td>Ciprofloxacin</td>
<td>Tap water, mineral water, milk</td>
<td>0.21 µM</td>
<td>[109]</td>
</tr>
<tr>
<td><strong>Heavy metal</strong></td>
<td>ASPE-Poly (melamine)/g-C3N4</td>
<td>Pb2+, Cd2+</td>
<td>Water</td>
<td>80 nM; 0.020 µM</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>Gr/Zn/Zn(OH)2/GCE</td>
<td>Cu2+</td>
<td>Water</td>
<td>90.3 × nM</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>Au/SWNTs@MOF-199/GCE</td>
<td>Pb2+</td>
<td>-</td>
<td>25 pM</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td>MWNTs–COOH/UiO-66-NH2/MWNTs–COOH/GCE</td>
<td>Pb2+, Cd2+</td>
<td>Seawater, rainwater, air conditioning condensate</td>
<td>0.34 µM, 0.80 µM</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td>Amino acid/GCE</td>
<td>Zn2+, Cd2+, Cu2+, Hg2+</td>
<td>Water</td>
<td>8.9 pM, 5.8 pM, 3.0 pM, 5.9 pM</td>
<td>[114]</td>
</tr>
<tr>
<td></td>
<td>rGO-Alanine-PANI/GCE</td>
<td>Cd2+, Pb2+, Cu2+</td>
<td>Water</td>
<td>0.030 nM, 0.045 nM, 0.063 nM</td>
<td>[115]</td>
</tr>
<tr>
<td><strong>Mycotoxins</strong></td>
<td>rGO@SnO2/GCE</td>
<td>Patulin fungal toxin</td>
<td>Apple juice</td>
<td>0.66 nM</td>
<td>[116]</td>
</tr>
<tr>
<td></td>
<td>Au@Cu-MOF/N-GQDs/GCE</td>
<td>Patulin</td>
<td>Apple juice</td>
<td>0.45 pM</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>Zearalenone-pAb/AuNPs/MWCNT/PEI/CSPE</td>
<td>Zearalenone</td>
<td>Maize</td>
<td>0.47 pM</td>
<td>[117]</td>
</tr>
<tr>
<td></td>
<td>Mn2O3/GCE</td>
<td>Aflatoxin-B1</td>
<td>Corn extract</td>
<td>1.7 pM</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>Fe3O4/Fe@rGO/GCE</td>
<td>Patulin</td>
<td>Apple juice</td>
<td>0.20 pM</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>P-Arg-MIP on COOH-MWCNTs/GCE</td>
<td>Deoxynivalenol</td>
<td>Wheat flour</td>
<td>0.07 µM</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>AuNP/MnO2@GO</td>
<td>T-2 toxin</td>
<td>Beer</td>
<td>0.23 fM</td>
<td>[121]</td>
</tr>
<tr>
<td></td>
<td>CS-modified AuNPs/SPGE</td>
<td>Aflatoxin M1</td>
<td>Milk and serum</td>
<td>2.7 pM</td>
<td>[122]</td>
</tr>
</tbody>
</table>

Note: GN: Graphene nanosheets; CPE: Carbon paste electrode; MIP: Molecularly imprinted polymer; ERGO: Electrochemically reduced graphene oxide; TBHQ: Tertiary butylhydroquinone; g-C3N4 NTs@MoS2: Graphitic carbon nitride nanotubes-decorated MoS2 composite; ASPE: Pre-activated screen-printed carbon electrode; KSC: Keratinous-sludge biomass-derived carbon; CB-CTS-ECH: Carbon black-chitosan-epichlorohydrin; Co-Ag BMNPs-PVP: Co-Ag Bimetallic nanoparticles-poly(vinylpyrrolidone); MnCo2O4/P-CN: Manganese cobaltite/phosphorus-doped graphic carbon nitride nanosheet; TGO: TiO2 functionalized graphene oxide; CPME: Carbon paste microelectrode; rGO-Alanine-PANI: Polyaniline-alanine-reduced graphene oxide; PEI: Polyethyleneimine; 4-CP: 4-carboxyphenyl; CSPE: Carbon screen-printed electrodes; P-Arg-MIP: Molecularly imprinted poly(L-arginine); CS-modified AuNPs: Complementary strand of the aptamer-modified gold nanoparticles; SPGE: Screen-printed glassy electrodes.
4. Conclusions

As a kind of traditional analytical method, electrochemical sensors still play a role in food safety. Nanomaterials, especially metal nanomaterials, are ideal electrode modification materials for constructing electrochemical sensors. The exploration and development of new nanomaterials provides more possibilities for constructing a novel and specific electrochemical sensing platform. This review summarizes the latest advancements of electrochemical sensors based on various nanomaterials in food analysis. After reading the extensive literature in the field, we think the further development of electrochemical sensors in food analysis is mainly concentrated in the following aspects: (1) The miniaturization of an instrument: Electrochemical sensors are developing towards miniaturization, portability, and integration, which could realize real-time analysis and shorten the time
of the data output. (2) Detecting food samples on-line: Since the detection performance of sensors is easily affected by various factors, this requires us to develop new nanomaterials and build highly sensitive sensing strategies, but also develop more stable, more reliable, environment-free sensing modes to further promote their application in online food detection. (3) Development of novel sensing strategies: This includes ratiometric and dual-mode electrochemical sensors, which has a stronger anti-interference ability and practical application. (4) Big data and food safety detection: With the advent and rapid development of the era of big data, the era of big data provides a new opportunity for food safety analysis. Combining big data with food safety detection, applying it to the food supply chain, mining and analyzing food safety data, and carrying out food safety supervision have huge potential value.

Author Contributions: Z.S. Consult literature, Data curation, Investigation, and Writing—original draft preparation. L.X.: Visualization and Writing—review and editing. G.L.: Visualization, Resources, Funding acquisition, Supervision, Project administration, and Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: The work was supported by the State Key Program of National Natural Science of China (No. 22134007), and the National Natural Science Foundation of China (No. 21976213), respectively.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

10. Wang, M.; Sun, Y.; Yang, X.; Zhao, J. Sensitive determination of Amaranth in drinks by highly dispersed CNT in graphene oxide “water” with the aid of small amounts of ionic liquid. *Food Chem.* 2015, 179, 318–324. [CrossRef]


18. Wang, Y.; Zeng, Z.; Qiao, J.; Dong, S.; Liang, Q.; Shao, S. Ultrasensitive determination of nitrite based on electrochemical platform of AuNPs deposited on PDDA-modified MXene nanosheets. *Talanta* 2021, 221, 121605. [CrossRef]


34. Shalini, A.; Paulraj, P.; Pandian, K.; Anbalagan, G.; Jaisankar, V. Single pot synthesis, characterization of PPY@C composites modified electrode for the electrocatalytic determination of ascorbic acid in commercial fruit samples. *Surf. Interfaces 2019, 17, 100386. [CrossRef]


44. Hatamluyi, B.; Rezayi, M.; Beheshiti, H.R.; Boroushaki, M.T. Ultra-sensitive molecularly imprinted electrochemical sensor for patulin detection based on a novel assembling strategy using Au@Cu-MOF/N-GQDs. Sens. Actuators B Chem. 2020, 318, 128219. [CrossRef]
45. Jahangiri-Dehaghani, F.; Zare, H.R.; Shekari, Z. Measurement of aflatoxin M1 in powder and pasteurized milk samples by using a label–free electrochemical aptasensor based on platinum nanoparticles loaded on Fe-based metal-organic frameworks. Food Chem. 2020, 310, 125820. [CrossRef]
49. He, B.; Yan, D. Au/ERGO nanoparticles supported on Cu-based metal-organic framework as a novel sensor for sensitive determination of nitrite. Food Control 2019, 103, 70–77. [CrossRef]
52. Erady, V.; Mascarenhas, R.J.; Satpati, A.K.; Bhakta, A.K.; Mekhalif, Z.; Delhalle, J.; Dhasilo, A. Carbon paste modified with Bi decorated multi-walled carbon nanotubes and CTAB as a sensitive voltammetric sensor for the detection of Caffeic acid. Microchem. J. 2019, 146, 73–82. [CrossRef]
53. Wang, M.; Gao, Y.; Sun, Q.; Zhao, J. Ultrasensitive and simultaneous determination of the isomers of Amaranth and Ponceau 4R in foods based on new carbon nanotube/poly(pyrrrole) composites. Food Chem. 2015, 172, 873–879. [CrossRef]


70. Wimalawansa, S.J. The role of ions, heavy metals, fluoride, and agrochemicals: Critical evaluation of potential aetiologic factors of chronic kidney disease of multifactorial origin (CKDmfo/CKDu) and recommendations for its eradication. Environ. Geochem. Health 2016, 38, 659–678. [CrossRef]


73. Beltran, B.; Leal, L.O.; Ferrer, L.; Cerda, V. Determination of lead by atomic fluorescence spectrometry using an automated extraction/pre-concentration flow system. J. Anal. At. Spectrom. 2015, 30, 1072–1079. [CrossRef]


76. Xue, Y.; Ma, L.; Zhang, L.; Zhao, W.; Li, Z.; Li, Q. A green, rapid and efficient dual-sensors for highly selective and sensitive detection of cation (Hg²⁺) and anion (S²⁻) ions based on CMS/AgNPs composites. Polymers 2020, 12, 113. [CrossRef]


80. Chen, X.; Wu, H.; Tang, X.; Zhang, Z.; Li, P. Recent advances in electrochemical sensors for mycotoxin detection in food. Electroanalysis 2023, 35, e2021100223. [CrossRef]

81. Hui, Y.; Bini, W.; Ren, R.; Zhao, A.; Zhang, F.; Song, S.; He, Y. An electrochemical aptasensor based on DNA-AuNPs-HRP nanoprobes and exonuclease-assisted signal amplification for detection of aflatoxin B-1. Food Control 2020, 109, 106902. [CrossRef]


87. Xing, L.; Zhang, W.; Fu, L.; Lorenzo, J.M.; Hao, Y. Fabrication and application of electrochemical sensor for analyzing hydrogen peroxide in food system and biological samples. Food Chem. 2022, 385, 132552. [CrossRef]


92. Gan, T.; Sun, J.; Meng, W.; Song, L. Electrochemical sensor based on graphene and mesoporous TiO$_2$ for the simultaneous determination of trace colourants in food. Food Chem. 2013, 141, 3731–3737. [CrossRef] [PubMed]


101. Siriram, B.; Baby, J.N.; Hsu, Y.F.; Wang, S.F.; Benadict Joseph, X.; George, M. MnCo$_2$O$_4$ microflowers anchored on P-doped g-C$_3$N$_4$ nanosheets as an electrocatalyst for voltammetric determination of the antibiotic drug sulfadiazine. ACS Appl. Electron. Mater. 2023, 3, 3915–3926. [CrossRef]


111. Berrabah, S.E.; Benchettara, A.; Smaili, F.; Tabti, S.; Benchettara, A. Electrodeposition of zinc hydride on carbon graphite electrode for electrochemical determination of trace copper in water samples using square wave anodic stripping voltammetry. Mater. Chem. Phys. 2022, 278, 125670. [CrossRef]


114. Kokab, T.; Shah, A.; Ifitikhar, F.J.; Nisar, J.; Akhter, M.S.; Khan, S.B. Amino acid-fabricated glassy carbon electrode for efficient simultaneous sensing of Zinc(II), Cadmium(II), Copper(II), and Mercury(II) Ions. ACS Omega 2019, 4, 22057–22068. [CrossRef]


Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.