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Nanomaterial-based electrochemical biosensors for food safety

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ABSTRACT

Currently, nano-biotechnology in the field of electrochemical biosensors has been a crucially novel strategy to construct simple and reliable monitoring systems for food safety. Due to the diversity of molecular species related to food safety, the characteristics of sensors must be designed according to concentration distribution level of target analyte, the specific reaction, the food source, and ease of operation. Therefore, the classification and characteristics of analytes for food safety (e.g., pesticides, veterinary drug residues, additives, inorganic and organic contaminants, pathogens and toxins) are clarified in this article. It focuses on an overview of electrochemical biosensors based on carbon nanotubes (CNTs), graphene (GR) and its derivatives, various metal nanoparticles, and polymers in food analyses. With the help of nanomaterials, the traditional advantages of electrochemical biosensors, such as rapidity, ease of fabrication and field applicability can be further improved. In addition, nanomaterials endow electrochemical biosensors with device miniaturization and high sensitivity and specificity, giving them great potential to assess the food safety on-site.

1. Introduction

With the development of modern agriculture and the food industry, the variety and quantity of food have increased dramatically. As a result, the safety of our food holds great socioeconomic impact and attracts global attention. The molecular species related to food safety are varied and complex [1]. Specifically, food safety is threatened by pesticides [2–4] and veterinary drug residues [5,6] in food, use of illegal additives [7,8], heavy metals [9,10], organic compounds [11–13], pathogens [14,15] and toxins. These species could give rise to foodborne diseases, seriously affecting human health and the profits of food businesses. The increasing demand for strict testing and controlling of harmful substances in foods leads to a boom in the research of food safety sensors.

Modern electrochemistry provides powerful analytical techniques for biosensors, with the advantages of instrumental simplicity, low cost and portability. Voltammetric techniques, encompassing cyclic voltammetry (CV) [16], linear sweep voltammetry (LSV) [17], differential pulse voltammetry (DPV) [5] and square wave voltammetry (SWV) [18], have been widely used in food analysis.

Due to the unique electrical and chemical properties of nanomaterials, electrochemical biosensors incorporating nanomaterials hold the potential to improve response speed, sensitivity and selectivity to meet the need of contaminant detection in complex food samples [19–23]. Our group recently presented several overviews of advances in electrochemical sensors and biosensors based on nanomaterials and nanostructures [24–26]. The latest and most significant development of enhanced electrochemical nanosensors and nanobiosensors for small molecules, enzyme-based biosensors, genosensors, immunosensors, and cytosensors were reviewed to broaden the interests of readers across various disciplines. Numerous functional nanomaterials produce a synergic effect on catalytic activity and signal transduction toward target analyte and lead to high selectivity based on specific recognition between molecules. Significantly, extensive research on the construction of functional nanomaterial-modified electrodes promotes the application of electrochemical biosensors in food safety. For example, Sundramoorthy et al. presented a comprehensive, state-of-the-art assessment of graphene applications in the food industry [27]. This article critically highlighted recent advances in graphene synthesis from foodstuffs, use of graphene for food analyses, and graphene-based analytical methods in detection of contaminants and toxins.

Our article focuses on recent developments in nanomaterial-based electrochemical sensors in food safety. The aim is to provide readers with a clear view of advances in areas ranging from electrode fabrication, strategies for signal amplification, and novel miniaturization techniques used in the electroanalytical sensors for food safety.

2. Diverse analytes for food safety

The analytes for food safety are numerous and complex. They can be roughly classified into three kinds: additives, chemical contaminants

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and microbial contaminants. It should be clarified that additives and contaminants need to be distinguished. This is because additives are added to produce popular flavor and color in food and drink products, but contaminants are not added intentionally. However, overconsumption of additives can lead to some undesirable consequences for consumers. For example, high doses of caffeine (1,3,7-trimethylxanthine) can cause severe side effects, including oversensitivity, irritability, anxiety, and insomnia, which gravely threaten people's health and, hence, lower their quality of life in the long run [28]. Worse still, too much intake of food or drinks containing caffeine is highly likely to induce a vicious cycle of addictive effect. In addition, because of widespread media reports on the harmful effects of various additives, the use of additives has been widely questioned by the public. The primary way to eliminate public concern and ensure food safety should be strict control of the concentration of additives in food, especially for foods geared toward growing children.

Chemical contaminants come from a variety of sources, especially from the chemical substances that control quality in food processing and storage, such as pesticide and veterinary drugs. For example, β-agonists have been used to improve the efficiency of feed utilization to enhance carcass leanness in livestock species. The family of β-agonists includes compounds such as clenbuterol, ractopamine, cimaterol, zilpaterol, and salbutamol [5]. However, toxic effects and numerous potential hazards of β-agonists, including cardiac palpitation, tachycardia, nervousness, muscle tremors, and confusion, have been reported [29].

Microbial contaminants of food or water cause food-borne disease, which takes a huge toll on human health and mortality. According to the reported article, some of the various bacterial pathogens that cause foodborne diseases are *Salmonella* (31%), *Listeria* (28%), *Campylobacter* (5%), and *Escherichia coli* O157:H7 (3%) [30]. Thus, it is important to design novel analytical methods for rapid, sensitive and low-cost detection of microbial contaminants.

3. Nanomaterials for electrochemical biosensors

Novel functional nanomaterials are the key components of many chemical and biological sensors, which are explored to improve the performance of existing devices or bring new perspective in food safety. The functions of nanomaterials are implemented for two purposes: to improve the response characteristics of the transducers and as the immobilization matrices for the bioreceptors. Nanomaterials used in electrochemical biosensors for food safety mainly include carbon-based nanomaterials, metal and metal oxide nanoparticles, magnetic nanoparticles and molecularly imprinted polymers.

3.1. Carbon nanotubes

Carbon nanotubes can be classified as single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs), according to the number of rolled layers. Both SWNTs and MWNTs are important materials to fabricate electrodes in biosensors, due to their unique mechanical, electrical and chemical properties. To improve their solubility and biocompatibility, CNTs can be functionalized with carboxyl or amino groups or form combinations with other materials, such as polymers, ionic liquids or metal nanoparticles. In the following sections, we illustrate the applications of CNT-based nanomaterials in the development of electrochemical sensors for food safety, shown in Table 1.

MWNTs are composed of multiply-nested graphene sheets, with variable diameters up to 100 nm [58]. MWNTs are strong candidates for biosensor applications, owing to large surface areas, unique physical properties, tunable lengths and moderate prices. MWNTs were often used to facilitate electron transfer between the electroactive species and the electrode, and moreover, various metal nanoparticles were added onto the MWNTs to generate additional electrocatalytic sites and to increase the sensitivity and detection limits of the electrodes. Through depositing gold nanoparticles by a multi-potential step technique at a MWNTs film, our group constructed an amperometric biosensor for determination of methyl parathion [2]. In this work, CdTe quantum dots were introduced to load a large amount of methyl parathion degrading enzyme. Extremely sensitive and perfectly selective response to methyl parathion has been achieved by using this dual-signal amplification strategy. Owing to high catalytic efficiency and strong adsorption capacity in electrochemical reaction, platinum nanoparticles (PtNPs) were used to make a sensitive electrode interface combining with MWNTs. A nano-composite of ZnO/Pt nanoparticles electrochemically has been deposited through layer-by-layer onto the surface of MWNTs modified GCE to build a trace sensor [49]. Copper nanoparticles were also used to decorate MWNTs to get a high performance electrochemical sensor for the detection of neotame [7]. By the formation of hydrogen bonds and weak hydrophobic interactions,β-cyclodextrin (β-CD) acted as a platform material to assemble APDC capped CuNPs and MWNTs on the electrode surface to increase the stability and reproducibility. Furthermore, it is a most common strategy to use stabilizers or protective capping agents to overcome the aggregation or precipitation of nanoparticles. Rahemi et al. proposed a new electroanalytical procedure for the monitoring of herbicide MCPA in natural waters, based on the incorporation of β-CD into MWNT and polyaniline film modified GCE [31]. The strategy of using β-CD as molecular receptor and MWNT as enhancer of electron transfer provided a new way of constructing electrodes for monitoring systems for food safety. Rotariu et al. fabricated a novel sensitive acetylcholinesterase (AChE) biosensor, which was based on the supramolecular arrangement resulting from the interaction of MWNTs and 7,7,8,8-tetracyanoquinodimethane (TCNQ) [59]. TCNQ molecules have two major roles: they serve as pillars for the MWNTs and function as electron acceptors for the oxidation of thiocholine. A sol–gel network was selected to stabilize the catalytic activity of the AChE and prevent enzyme leaching. SWNTs consist of single graphene sheets wrapped into cylindrical tubes, with diameters between 0.4 and 2.5 nm. Many studies have shown that SWNTs have high electrical conductivity, which can improve the signal-to-noise ratio, leading to ultrasensitive electrochemical sensors for the detection of food analytes. Yao et al. fabricated an enzyme-free methyl parathion electrochemical sensor based on carboxylic acid-functionalized SWNTsand β-CD modified glassy carbon electrode, which was successfully used for the trace analysis of methyl parathion in vegetable samples, with a low detection limit of 0.4 ng mL^{-1} [33].

The hybrid of carbon-based nanomaterials is another strategy to enhance the performance of food safety sensors. Lin et al. prepared a hybrid CNT-modified electrode for simultaneous determination of toxic ractopamine and salbutamol in pork sample [5]. This work discussed the optimized ratio for preparation of hybrid single-walled and multi-walled CNTs (SMWNTS). More compact structure of SMWNTS produced synergistic effects, resulting in good electrocatalytic properties to ractopamine and salbutamol. 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 [28]. In this work, the NGR–NCNTs nanocomposite was electrodeposited onto the GCE through potentiostatic method from the KCl aqueous solution containing homogeneous NGR–NCNTs.

In recent years, the combination of CNTs and molecularly imprinted polymers (MIPs) and the applications in food contaminants analyses have drawn more attention. The interaction between MIPs and analytes is based on steric matching and hydrophobic and electrostatic interactions similar to the Ag-Ab interaction [22]. MIPs are considered the artificial antibodies, which have great potential to replace natural biorecognition to improve the selectivity and stability of sensors. Prasad et al. prepared a double-template MIP nanofilm-modified pencil graphite electrode, which has been applied for the simultaneous analysis of glyphosate and glufosinate [3]. In the polymer layer, gold nanoparticles and CNT dispersants might form nanohybrids and exhibit an excellent

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