

Application of nanomaterial-modified electrochemical sensors in pesticide residue detection

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Abstract. Nowadays, the frequent application of insecticides leads to pesticide remnants detected in plentiful amounts of many foods, such as fruits and edibles. Even though the remains of the compounds produced by pesticides are tracked, the tremendous toxicity is sufficient to endanger human life and health. Thus, detecting pesticide residue in different vegetable and fruit foods is essential. Determine the number of leftover pesticides in different vegetable and fruit foods to avoid serious illnesses brought about by exposure to pesticides so that people's physical and mental health and product quality and safety are ensured. Therefore, this article is about nano-porous materials based-electrochemical sensors used to detect pesticide residues in food. This article briefly introduces the mechanism and composition of electrochemical sensors, the classification of electrochemical nanomaterials, and the utilization of nanomaterials in electrochemical sensors. Nano-porous materials have a high specific surface area, adsorption, and catalytic properties to ensure accurate, accurate, and reliable detection. This article discusses metal nanomaterials with variable sizes, shape, surface, and physical and chemical features and their implementation in the detection of electrochemical sensors. It also introduces metal oxide nanomaterials with the characteristics of cheap and easy preparation and the detection range of this material. It also introduces the properties of carbon nanomaterials, carbon nanotubes, graphene, and carbon dots. Subsequently, this article summarizes the progress of nano-porous materials based on electrochemical sensors in pesticide residues. It also introduces the opportunities and challenges that nanomaterial-modified electrochemical sensors will face in pesticide detection and looks forward to reducing the harm of pesticides to the environment and human health in the future.

Keywords: Nanomaterials, Electrochemical sensors, Pesticide residue detection, Modified electrode.

1. Introduction

Pesticides are chemicals that change the metabolism and growth and development of organisms and have a variety of classifications, which could be divided into inorganic pesticides, organic pesticides, and so on. Pesticides are extensively employed in vegetables, fruits, and other crops to prevent and eliminate pests. However, pesticides are not completely acting on a specific organism or are only harmful to a certain organism. Different pesticides also have an enormous impact on other organisms. The influence of different pesticides is also various. Pesticide residues are specific substances converted or produced when pesticides are used. Pesticide residues may affect people's safety. Pesticide residues may be absorbed by the human body, leading to disease, food poisoning, and other hazards. Therefore, we should detect pesticide residues and clearly understand pesticide residues.

The detection of pesticides has spectroscopy, enzyme inhibition, chromatography, rapid detection technology, and so on. Among them, chromatography occupies the major position. In recent years, there have been some more detection methods. Electrochemical sensors transmit and output content

by converting other signals into electrical signals, and electrochemical sensors could also improve detection efficiency and accuracy. Nanomaterials-based electrochemical sensors change the properties of the original electrochemical sensors by using nanomaterials and improved their specific surface area, catalytic efficiency, and detection ability. First of all, this article is about the application of nanocomposites based on electrochemical sensors in the field of pesticide residue detection. Secondly, the application of nano-porous materials based on electrochemical sensors in pesticide residue detection is studied in this paper. At last, pesticide residues are detected based on the characteristics of nano-porous materials, such as a decent area of surface, extraordinary catalysis efficiency, and outstanding adsorptive capacity.

2. Electrochemical sensors

2.1. Mechanism and composition of electrochemical sensors

The basic mechanism of electrochemical sensors is to carry out technical analysis through experiments, transform the chemical change process shown in the experiment into an electrical signal, and output the content of pesticide residues in the detection [1], as shown in **Fig. 1**. It is the result of transforming the pesticide residue value into an electrical signal output into the detection content through the electrochemical sensor. It converts the chemical parameters into a specific electrical signal, and ensures the susceptibleness of the electrochemical sensors, to identify the residual content of the specified pesticide. At the same time, the composition of electrochemical sensors is mainly composed of a transmission module and a recognition module. The transmission module is used for transforming the signal into an electrical signal, and the recognition module is used to identify whether the chemical substance is the pesticide detected. And the core of the electrochemical sensors is also the electrode.

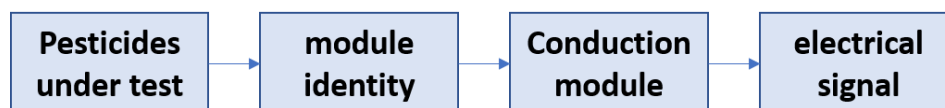


Fig. 1 Electrochemical sensors workflow schematic diagram

2.2. Electrochemical sensors classification

(1) Current-mode chemical sensor

These electrochemical sensors are mainly based on redox properties for qualitative or quantitative analysis.

(2) Potentiometric chemical sensor

These electrochemical sensors are based on the specific linear relationship obtained by the potential difference when the substance to be measured reaches stability in the electrolyte solution.

(3) Conductive chemical sensor

The type of electrochemical sensors determines the solution concentration by the conductivity of the electrolyte solution.

2.3. Application of nanomaterials in electrochemical sensors

Nano-porous materials have chemical tunability, which could change the stability and properties of electrochemical sensors. Cui et al. [2] prepared yolk-shell nanostructures that show good stability and catalytic effect. At the same time, the large specific surface area of nano-porous materials increases the recognition probability and the sensitivity of detection, which could improve the accuracy of pesticide residue detection. Porous polymer materials such as Conjugated microporous polymers (CMPs) also have photocatalytic properties. Xu et al. [3] showed that the main factors affecting the photocatalytic reaction are poor utilization of visible light, high photogenerated electron-hole recombination rate and high band gap energy.

3. Nanomaterial-based electrochemical sensors

3.1. Metal and metal oxide nanomaterials

3.1.1 Metal nanoparticles

Metal nanomaterials have the general characteristics of nanomaterials such as dielectric confinement effect, surface effect and quantum size effect [4]. The sensor based on metal nanoparticles has the merits of high specific surface area and the excellent speed of transferring electrons. Therefore, the electrochemical sensors based on metal nanoparticles could significantly heighten the limit of detection, stability and sensitivity when detecting the target [5].

Gao X. Y. et al. [6] prepared nano-porous gold (NPG) through chemical etching of Au/Ag concentrated binary alloy in sulfuric acid and modified glass carbon electrode (GCE), which was formatted to an NPG/GCE electrode for the simultaneous determination of parathion-methyl and carbendazim. Under the effective combination of NPG and GCE, the electrochemical properties of NPG/GCE for methyl and carbendazim were studied by differential pulse voltammetry (DPV). The results of this sensor determination showed prominent selectivity and stability. The limit of detection (LOD) of parathion-methyl and carbendazim were 0.02 $\mu\text{mol/L}$ and 0.24 $\mu\text{mol/L}$, respectively. Kumaravel et al. [7] deposited silver/Nafion composite on GCE by means of the electrochemical deposition method, and then prepared TiO_2 /Nafion composite solution coated electrode by drop coating method to the formation of a homogeneously layered mold on the electrode surface (Fig. 2). The Nafion/nano TiO_2 /GCE nanocomposite electrode was prepared under the effective combination of the two. The electrode has a good electrocatalytic activity for imidacloprid. The electrode was applied to the electrochemical sensing of imidacloprid, and the minimum LOD was 0.25 $\mu\text{mol/L}$.

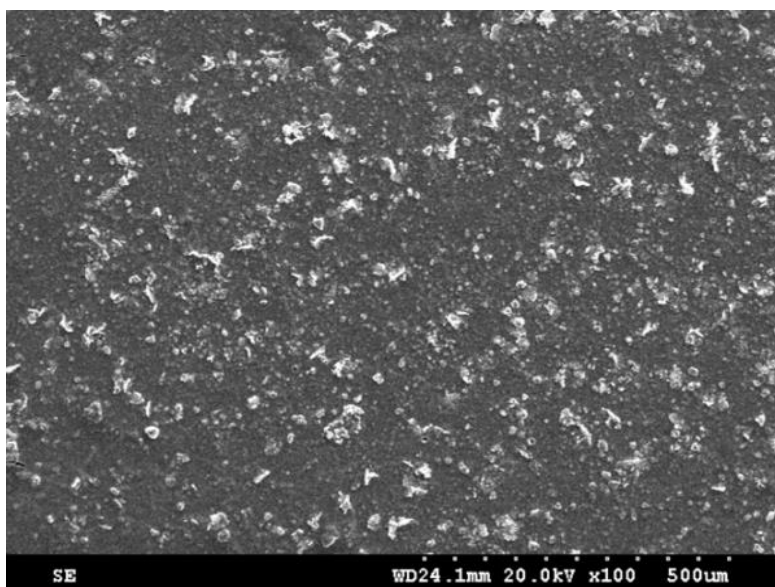


Fig. 2 SEM image of nAg/nTiO₂ composite modified GCE [7].

In addition, Talan et al. [8] prepared AuNPs by the Frens method and attached them to the fluorine-doped tin oxide (FTO) conductive glass surface by deposition of drop coating. Since AuNPs have high conductivity and specific resistance, fixing AuNPs could amplify the detection electrochemical signal, which is conducive to the improvement of sensing performance. AuNPs could also utilize their ion-ion interaction force to immobilize chlorpyrifos antibody, and this material was used in sensor construction. The LOD of the electrochemical immunoassay based on FTO conductive glass of chlorpyrifos could reach 10 M, and the chlorpyrifos concentration ranged from 1 fM to 1 μM .

3.1.2 Metal oxide nanomaterials

Compared with noble metal and other metal composites, metal oxides have the benefit of cost-effective and simple development, and nanometal oxides also have unique properties such as low toxicity, good stability, wide energy band gap and good biocompatibility [9].

Wang et al. [10] utilized hydrothermal to prepare cobalt oxide/reduced graphene oxide (CoO/rGO) nanocomposite. The material has good electrochemical activity and could be used in electrode modification to directly catalyze the oxidation of carbofuran (CBF) and carbaryl (CBR) oxidation. Under the optimum conditions, the LOD of CBR and CBF were 7.5 $\mu\text{g/L}$ and 4.2 $\mu\text{g/L}$, respectively. The response showed a superior linear correlation with CBR and CBF concentration from 0.5 $\mu\text{M/L}$ to 200 $\mu\text{M/L}$ and from 0.2 $\mu\text{M/L}$ to 70 $\mu\text{M/L}$, respectively. Parham et al. [11] fixed zirconia nanomaterials on the carbon pulp electrode by direct synthesis, and used zirconia to detect methyl parathion (MP) pesticides due to its strong affinity for phosphate groups in MP. The LOD of the sensor obtained by square wave voltammetry (SWV) was 2.0 ng/mL.

Wang et al. [12] prepared molecularly imprinted polymers (MIPs) based on two-dimensional Sn_3O_4 nanoplates and modified them on the electrode surface. Through a series of characterization techniques, it was found that the MIPs/ $2\text{DSn}_3\text{O}_4$ modified electrode has a two-dimensional structure, which could significantly enhance the electrode's surface area, improving the rates of transferring electrons and effectively detecting the chlorhexidine in honey. The current response showed a good linear correlation with chlorhexidine concentration from 0.025-2.5 $\mu\text{mol/L}$, and the minimum LOD was 0.0032 $\mu\text{mol/L}$. The principle of the preparation of two-dimensional Sn_3O_4 nanoplates was shown in Fig. 3.



Fig. 3 Preparation principle of MNZ imprinted 2D Sn_3O_4 nanosheets [12].

Zhao et al. [13] synthesized nitrogen-doped carbon sheets embedded with zirconia nanoparticles (ONCSs-ZrO₂NPs) for the electrochemical detection of MP. The obtained ONCSs process favorable conductivity, high area of a specific surface, excellent mechanical stability, and the group of nitrogen-containing functional could accelerate the ability to transfer electrons and strengthen the wetting ability of the electrode surface, thus a suitable microenvironment was supplied for the redox reaction of MP. Based on the synergistic interaction between the zirconia nanoparticles and the nitrogen-doped carbon sheet, the LOD of MP could reach 0.115 ng/mL.

3.2. Carbon nanomaterials

In recent years, carbon nanomaterials stimulate extensive research in various fields from theory to more practical applications. Widely employed in electrochemistry, they deem a material of great significance for the reason that their excellent structure and scalable production performance [14]. It could be used as a kind of modified electrode material with good conductivity, rich carbon source, adjustable active sites, high mechanical strength, high electron transfer rate, stable structure, high

specific surface area [15]. carbon nanomaterials could better analyze the electrical analysis signal of compounds [16]. However, there are also some shortcomings, such as low catalytic activity. At present, carbon materials used in electrochemical sensors are carbon nanotubes, graphene, carbon quantum dots and so on. The research on electrochemical sensors for detecting pesticides based on different carbon nanomaterials electrocatalysts is described as follows.

3.2.1 Carbon nanotubes

Carbon nanotubes are a kind of quantum material of one dimension, possessing a unique form. Radial magnitude could reach the nanometer level, and the magnitude of the axial is micron level. Through sp^2 hybridization, the three carbon atoms surrounding each one completely joined together. Carbon nanotubes, also known as buckytubes, belong to the fullerene carbon system, a new kind of carbon material with a complete molecular structure at the nanometer level. Carbon nanotubes have two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Carbon nanotubes possess unique metal or semiconductor conductivity, a vast area of a particular surface, mechanical vigor of the highest caliber, good adsorption capacity, and electron conduction ability, which could be used for chemically modified electrodes to detect pesticide residues.

Satar Tursynbolat et al. [17] developed an ultra-sensitive electrochemical sensor based on polydopamine/carboxyl a multi-tiered system of carbon nanotube composites. The nanocomposite-modified GCE could be used for the detection of metronidazole. Carboxylic MWCNTs (MWCNTs-COOH) were successfully used for the quantitative measurement of metronidazole in actual drug samples for the reason that they had prominent specific surface area, remarkable surface hardness, excellent electroconductibility and high chemical durability. Polydopamine could be applied to the surface of MWCNTs-COOH by facile electro-polymerization. Under the optimized conditions, the linear range was 5-5000 $\mu\text{mol}/\text{dm}^3$ and the detection limit was 0.25 $\mu\text{mol}/\text{dm}^3$.

Although carbon nanotubes could exhibit satisfactory performance, it has been found that the combination of carbon nanotubes with other conductive materials could achieve a synergistic sensitization effect to obtain better performance. For instance, Huo et al. [18] investigated a new electrochemical sensor for the detection of malathion by using a composite material composed of SWCNTs and CuO nanowires. Because SWCNTs with network structure had strong adsorption capacity for malathion and a good affinity between CuO NWs and malathion, electron transport capacity was enhanced. The performance of CuO NWs-SWCNTs nanocomposites was significantly improved and the stability was good, which provided a basis for the electrochemical quantitative detection of malathion. Under the optimal conditions, the detection range was 0-600 nmol/L, and the detection limit was 0.3 nmol/L.

3.2.2 Graphene

Graphene, as a novel carbon-based nanomaterial, namely a monolayer graphite sheet, is an infinite expansion of six-membered ring benzene units, formed by sp^2 hybrid carbon atoms, forming a two-dimensional crystal material. It has been used as an active catalytic material for fuel cells, supercapacitors, lithium-ion batteries, and solar cells [19] due to its suitable mechanical strength, large surface area, stable chemical properties, high conductivity, and ultra-high electron mobility.

Xie et al. [20] triumphantly prepared an electrochemical biosensor based on graphene/chitosan/parathion by using the inhibition of organophosphorus pesticides (Ops) on the activity of acetylcholinesterase (AChE) and the excellent conductivity of graphene. The detection of 11 Ops was realized, and the detection limit range was 0.012 ng/mL-0.23 ng/mL.

In addition, graphene oxide (GO) and reduced graphene oxide (RGO) are two imperative members of the graphene family. Electrochemical sensors based on GO, rGO, and functionalized graphene was constructed and used for the detection of various analytes [21].

Li et al. synthesized graphene by the Hummers method and used chitosan as a fixing agent to modify it on a GCE to achieve a highly selective detection of dopamine (DA), with a linear range of 5-200 μM . They also proposed a mechanism for the selective adsorption of DA and the repulsion of

interfering substances such as ascorbic acid (AA) [22]. As shown in **Fig. 4**, there was a π - π conjugation effect between DA containing aromatic ring structure and graphene surface, which promoted DA to approach and adsorb on the electrode surface, accelerated the electrochemical catalytic process of graphene electrode to DA, and had an obvious electrochemical response. On the contrary, ascorbic acid was far away from the interface due to no adsorption due to the absence of an aromatic ring structure, and its electrochemical activity was inhibited without an obvious electrochemical response.

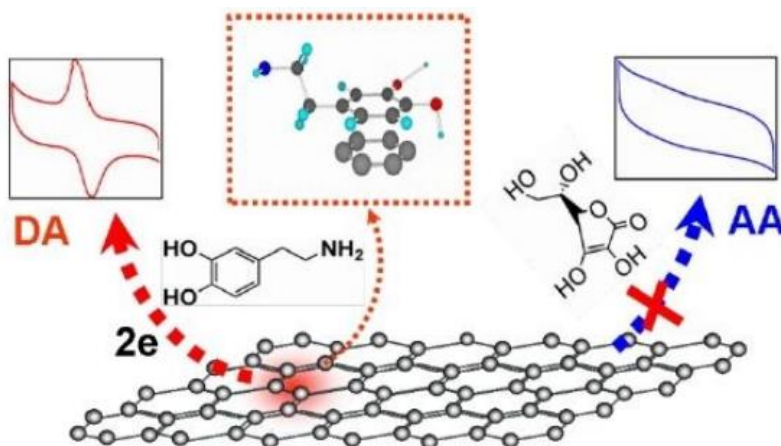


Fig. 4 A graphene-based interface-selective electrochemical catalysis of dopamine [22].

A novel voltammetric sensor based on monodisperse boron nitride quantum dots (BNQDs) and graphene oxide proposed by M.L. Yola et al [23], which successfully realized the simultaneous detection of parathion-methyl, diazinon and chlorpyrifos in water samples. The detection limits of the sensor for these three pesticides were 3.1×10^{-4} , 6.7×10^{-5} , and 3.3×10^{-5} nmol/L, respectively.

3.2.3 Carbon dots

Carbon dots (C-Dots) become a rising star in carbon nanomaterials due to their characteristic size of less than 10 nm [24]. Graphene Quantum Dots (GQDs), Carbon Nanodots (CNDs) and Polymer Dots (PDs) are the three main types of carbon dots. It is a quasi-spherical carbon nanoparticle without obvious lattice, mainly composed of sp^2/sp^3 carbon or amorphous carbon embedded in a sp^2 hybrid nanocrystalline region. C-Dots have the characteristics of low toxicity and environmental protection of carbon-based materials, high solubility in water, good biocompatibility, and excellent properties of nanomaterials. Carbon dots are expected to be more widely used in electrochemical sensor research.

A label-free and selective electrochemical biosensor based on GQDs and Au nanoparticle nanocomposite was developed by Tang et al [25]. Here, the oxidation current of the modified electrode was 16 times higher than that of the unmodified GCE. Besides, the oxidation current was linearly related to the concentration in the range of 0.001-10 μ M, which provided more possibilities for the detection of luteolin in pragmatic applications. The application of MoS_2 -CNTs@graphene oxide nanobelts, thiol- β -cyclodextrin and GQD nanocomposites modified GCE for the detection of quercetin by CV was first proposed by Zhao et al [26]. The sensor may have great potential in detecting more life samples due to its ultra-low detection limit of 8.2×10^{-4} μ M.

4. Conclusions and perspectives

In this article, the research progress of nanocomposites used in the detection of pesticide residues on the electrode of electrochemical sensors is reviewed. The principle, composition, and classification of electrochemical sensors are introduced. Around the metal, metal oxide, carbon nanotubes, graphene, graphene derivatives, C-Dots, and other nanomaterials, it is summarized that their application in electrochemical sensors has greatly improved the performance of the sensor. Such as metal and metal compounds have excellent electrocatalytic activity; carbon nanomaterials could expand the particular area of the surface and active sites of the material, and high conductivity is

conductive to accelerating electron transfer, improving the detection sensitivity, thereby improving the sensitivity, detection limit, and linear range, selectivity and other properties of the electrochemical sensors.

It is expected that the electrochemical sensors based on nanocomposites will provide more convenience for society, and could detect the content of pesticide residues conveniently and quickly, to reduce the harm of pesticides to the environment and human health.

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