

Application of Graphene-based Electrochemical Sensors in The Detection of Pesticide Residues

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Abstract

This study intends to investigate the utilization of graphene-based electrochemical sensors for detecting pesticide residues. By means of literature investigation and experimental examination, the working principle, performance and practical application of graphene electrochemical sensors are comprehensively researched. We find out that due to its special electric and chemical characteristics, graphene can sense pesticide residues with high sensitivity and selectivity. The sensor can quickly and accurately detect the pesticides in the sample, and it also shows great promise for simultaneously detecting multiple types of pesticides. Actual sample testing has shown some initial results. Graphene based electrochemical sensors have a wide range of applications in the field of pesticide residue detection, and they are expected to become an alternative to traditional detection methods, which will provide strong support for food safety and environmental protection.

Keywords

Graphene; Electrochemical sensor; Pesticide residue; Detection; Application.

1. INTRODUCTION

1.1. Background of the study

Pesticide residues are widely present in agricultural products and the environment, on the one hand, they will directly endanger the health and safety of consumers, causing latent acute and chronic poisoning problems, on the other hand, it will also bring great challenges to ecological coordination, and may interfere with the reputation of international trade in agricultural products, if you want to protect food safety and environmental health, you must do fast, sensitive and accurate detection of pesticide residues, although the accuracy of traditional detection methods is good, but usually with the help of large instruments and equipment, the operation is cumbersome and time-consuming. It is difficult to respond to emergencies with rapid screening and immediate monitoring in the field.

However, traditional electrode materials have some performance shortcomings, such as low sensitivity, weak selectivity, poor stability, and easy to be interfered with by the matrix, and these defects are still the main obstacles that restrict their practical application and popularization. Graphene is a two-dimensional honeycomb lattice structure formed by a layer of carbon atoms through sp^2 hybrid orbitals, known as the "king of new materials", it has unique physical and chemical properties, such as huge specific surface area, excellent conductivity, excellent electron migration performance, good chemical stability and very easy to implement functional transformation. This makes it an excellent foundation for building efficient electrochemical sensing interfaces. This project mainly studies how to improve the detection

speed of pesticide residues in food or the environment, reduce the testing cost, and make up for the shortcomings of traditional detection methods.

1.2. Research objectives

The project focuses on improving the detection speed of pesticide residues hidden in food or the environment, and reducing the cost of related detection, making up for the loopholes of traditional detection methods, and includes some characteristics and advantages of graphene-based electrochemical sensors. Then compare them with traditional detection methods to summarize the improvements that graphene brings to electrochemical sensors.

2. LITERATURE REVIEW

2.1. The importance of pesticide residue testing

Pesticides are contained in the food, which is due to the biological chain and biological aggregation effect, aquaculture animals eat plankton with pesticide residues, aquatic products will have pesticide residues, crops are cultivated, transported, stored, if crops or pesticides are not properly disposed of, let them touch each other, it will also cause crops to have pesticide residues, and in the environment with pesticide harmful pollution sources, it may also make pesticide residues in food, from the perspective of harm, Organophosphorus pesticide residues and organochlorine pesticide residues will bring different degrees of harm to people, and organophosphorus pesticide residues in food will poison people's respiratory tract, stomach, skin tissue, reduce people's physical fitness, and acetylcholine in serum cannot be completely decomposed due to the reduction of enzyme activity. Eating food with organophosphorus pesticide residues for a long time will cause rapid heartbeat, continuous sweating, muscle twitching and other phenomena, causing central nervous system disorders, liver function decline, white blood cell swallowing ability becomes smaller, and will also promote cells to produce cancerous or malformations and other diseases. In severe cases, it can lead to death[1].

2.2. Traditional detection methods for pesticide residues

Traditional detection methods for pesticide residue detection include gas chromatography (GC), gas-mass spectrometry (GC/MS), high-performance liquid chromatography (HPLC), liquid mass spectrometry (HPLC/MS), tandem mass spectrometry (MS/MC), thin layer chromatography (TLC), supercritical fluid chromatography (SFC), etc., which can complete the qualitative and quantitative detection of pesticide residues, which is the standard detection method stipulated by the state, and now mainly relies on GC, GC/MS, HPLC, HPLC/MS [2].

2.3. The development trend of pesticide residue detection technology in the future

Nowadays, many pesticide residue detection technologies such as chromatography, spectroscopy, and immunoassay technology are used in food testing, and these technologies have their own suitable categories and scenarios, but there are certain limitations [3]. High cost, low sensitivity, long pretreatment time, cumbersome steps, equipment is not portable and other conditions will affect the detection results, and electrochemical methods can solve these problems, so now there has been a certain application in the detection, but the current electrode production process is more complicated, which also hinders the commercialization process of sensor detection, and the use of new electrical materials to make electrochemical sensors is the inevitable trend of its application to pesticide detection. However, there are still many difficulties to overcome in building an electrochemical sensor with good selectivity and sensitivity [4].

2.4. Graphene-based electrochemical sensors

Graphene is a two-dimensional structure material, it is stacked by a layer of carbon atoms using sp² hybrid orbitals, graphene has good physical and chemical properties, strong stability, good thermal conductivity, large electron mobility, low resistivity, etc., so graphene has a wide range of applications in electricity, medicine, optics, catalysis, sensors, etc., and can also use graphene surface defects to compound it with other substances to add new physical and chemical properties and functions. Therefore, graphene has great advantages in the application of electrochemical sensors [5].

3. PRINCIPLE OF GRAPHENE-BASED ELECTROCHEMICAL SENSOR DETECTION OF PESTICIDE RESIDUES

3.1. Interaction mechanism between graphene and pesticide residues

When graphene interacts with pesticide residues, the electron transfer mechanism is very important, graphene has good conductivity, electrons move very fast inside it, when pesticide molecules are adsorbed to graphene, there may be direct electron transfer, this electron transfer is affected by the electrical properties of graphene itself on the one hand, and on the other hand, it is also affected by the chemical structure of pesticide molecules, some pesticide molecules containing nitro or halogen substituents usually show strong electron reception characteristics, Stable complexes can be formed with graphene through electron transfer [6]. This mechanism provides a theoretical basis for graphene-based electrochemical sensors, which can be used to detect signal changes due to electron transfer to measure the sensitivity of pesticide residues.

3.2. Generation and conversion of electrochemical signals

When the pesticide residue is close to the graphene electrochemical sensor, the key to the formation of the electrochemical signal lies in the electron transfer and interface reaction between the pesticide molecule and the graphene, when the sensor operates, the pesticide molecule will adhere to the surface of the graphene modified electrode through physical adsorption or chemical bonding, and then under the influence of the applied electric field, those active functional groups in the pesticide molecule, such as N=N, C=O, etc., will carry out redox reactions. As a result, electrons flow from pesticide molecules to the graphene substrate or move in the opposite direction [7, 8]. Specifically, the current electrochemical sensor performs a qualitative analysis of the concentration of pesticide residues by measuring the Faraday current generated by the redox reaction, and the potential sensor relies on observing the change of the electrode surface potential to reflect the presence and concentration of pesticide molecules [9]. When researchers want to improve the efficiency and accuracy of signal conversion, they often implement functional treatment on graphene electrodes, and when using nano gold particles or metal oxide nanomaterials, the specific surface area of the electrode can be significantly increased, and more active sites will be given to promote electron transfer [10].

3.3. Factors affecting detection performance

When graphene-based electrochemical sensors are used to detect pesticide residues, they are affected by many factors, the shape of graphene, the sensor production process and the detection environment are key factors, the first point, the shape of graphene has important significance for the detection performance, relevant studies have shown that single-layer graphene, multi-layer graphene, graphene quantum dots and graphene quantum dots of different shapes of graphene materials, there are obvious differences in adsorption capacity and electron transfer ability, single-layer graphene has a relatively large surface area and good conductivity, so the detection sensitivity is generally relatively high [6]. Graphene quantum dots have many functional groups at the edges and have unique photochemical properties, which are

very advantageous when selectively detecting certain pesticide molecules [10]. In the process of production, the degree of graphene dispersion, the degree of functional modification, and the form of compounding with other nanomaterials will directly affect whether the sensor is stable and repeatable. Graphene quantum dots synthesized by bottom-up method usually have a relatively balanced size distribution and good chemical stability, but the cost of this method is high and the process is complicated, and although the top-down method is simple and easy to implement, it may damage part of the structure of graphene materials, thereby affecting their electrochemical properties [11]. Under high temperature or strong acidic conditions, the oxygen-containing functional groups on the surface of graphene may degrade, which will weaken the adsorption capacity of graphene. In the case of high ionic strength, the increase in background current may obscure the tiny signal of the target molecule, thus interfering with the accuracy of the detection [11, 12]. Therefore, when applying it in detail, all the factors mentioned above should be taken into account, and the sensor should maximize its detection efficiency by improving the experimental conditions.

4. RESEARCH PROGRESS ON THE DETECTION OF PESTICIDE RESIDUES BY GRAPHENE-BASED ELECTROCHEMICAL SENSORS

4.1. Graphene-based electrochemical sensor with high sensitivity

Electrochemical sensors have high sensitivity, but although some things have electrical activity, the current reaction is not large, if it is directly used for detection, the sensitivity will be lower, at this time with graphene, gold nanoparticles, β -cyclodextrin and these functional nanomaterials, can make the detection signal larger, graphene oxide (GO) is oxidized graphene, its properties are more active than graphene, various properties are also better, use GO, gold nanoparticles, β -cyclodextrin to modify electrochemical sensors, A sensor that can significantly expand the detection signal of the berberine electrochemical sensor has been made, and the sensitivity of this sensor has indeed been greatly improved through design experiments [13]. The manufacturing principle of the sensor is shown in Figure 1.

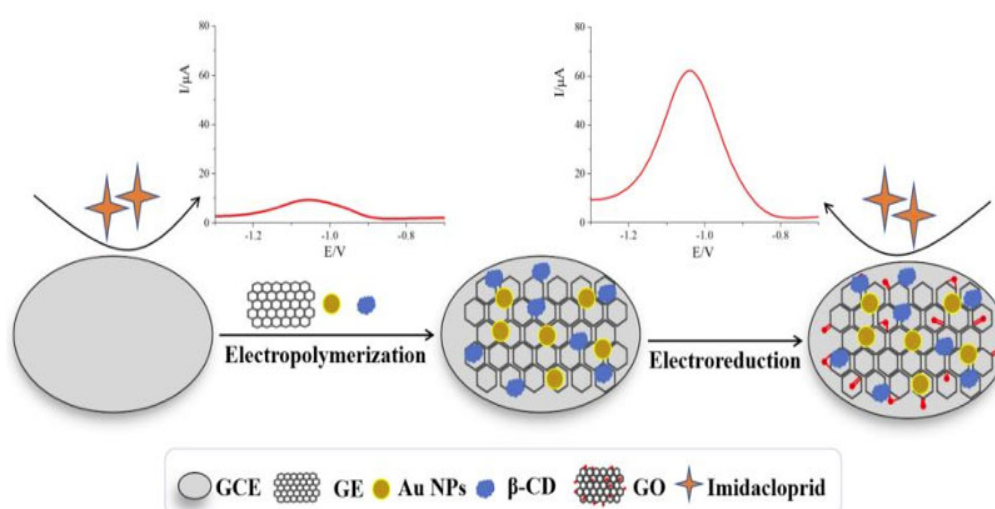


Figure 1. Manufacturing method for imidacloprid detection sensors [13]

4.2. Graphene-based electrochemical sensors with high stability and accuracy

The electrochemical sensor based on heme chloride reduced graphene oxide modified glass-carbon electrode and the use of sodium zirconia modified nanomaterials can realize the rapid detection of two pesticide residues in water, dicholon and octanulic sulfate as shown in Figure

2, and the materials are characterized by scanning electron microscopy, ultraviolet-visible absorption spectroscopy and X-ray photoelectron spectroscopy in the experimental process, and pesticide residues are detected, and the peak current is found to be a linear relationship directly proportional to the concentration of pesticide residues, and the detection limit is lower than that of conventional detection methods. The relative standard deviation is small when performing a large number of replicates, and the rate of response reduction detected after prolonged electrode placement is low [4]. It can be proved that the graphene-based electrochemical sensor has good stability and its accuracy in practical application is also credible.

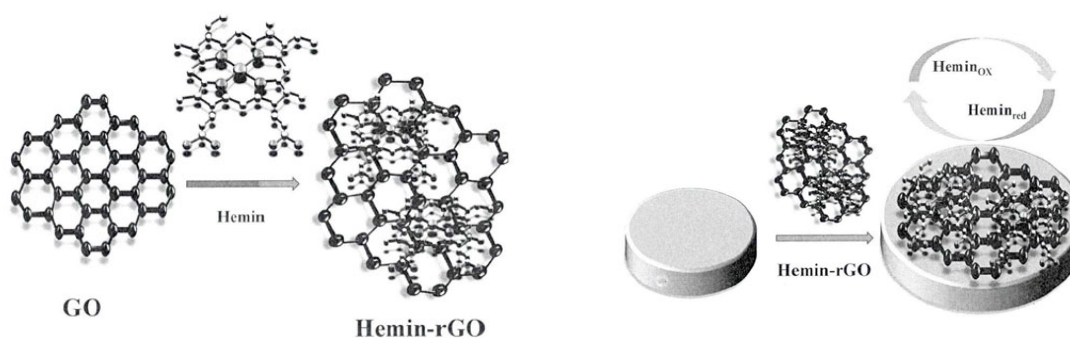


Figure 2. Hemin-rGO/GCE sensor assembly process and principle [4]

4.3. Selective composite sensors are made using graphene and other materials

A new type of composite sensor is constructed by composite use of cerium oxide and graphene to make modified electrode materials [14]. In the experiment, common interferences in soil, such as inorganic ions Mg^{2+} , Na^+ , Cl^- , CO_3^{2-} , SO_4^{2-} , organic small molecule glucose, nitro-containing p-nitrophenol, etc., have been systematically tested. The results showed that even if the interference concentration reached 20 times that of methyl parathion, the response current of the sensor was still small (relative standard deviation RSD=6.71%), indicating that the sensor had significant selective recognition ability for methyl parathion. This composite material (Gr/CeO₂) enhances the specific response to methyl parathion through dual action (physical adsorption and chemical catalysis) and inhibits the interference of other substances; Gr/CeO₂. The average recovery rate of /GCE sensor in soil spiking experiment was 102.2%~104.7%, Gr/GCE is 104.9%~108.8%. The nearly 100% recovery rate supports that the sensor can still accurately identify methyl parathion in complex soil substrates with minimal interference from other components. Gr/CeO₂/GCE has a detection limit as low as 0.0469 μM (S/N=3), Gr/GCE was 0.0988 μM . The very low detection limit means that the sensor's response signal to methyl parathion is significantly higher than the background noise, further supporting its selectivity.

At the same time, the experimental data show that there is room for optimization in the concentration, pH, enrichment potential and enrichment time of the modified solution.

5. CHALLENGES AND PROSPECTS OF GRAPHENE-BASED ELECTROCHEMICAL SENSORS FOR THE DETECTION OF PESTICIDE RESIDUES

5.1. Challenges

On the one hand, the stability and repeatability of the sensor itself have become a hot research category, graphene is classified into two-dimensional nanomaterials, its surface

properties are very sensitive to extremely subtle changes in the external environment, temperature, humidity and ion concentration in the solution will interfere with the working state of the sensor [10]. On the other hand, if graphene is stored for a long time or used frequently, it may oxidize or degenerate some structural degeneration, which will cause the signal response ability of the sensor to decrease, which reduces the real service life of the sensor, and also makes it calibrate more often in the field or laboratory conditions, and the cost increases [15].

The selectivity of sensors is still a technical difficulty that needs to be overcome urgently, graphite Alene has excellent conductivity and biocompatibility, but it can cause non-specific adhesion to many pesticide residues, which can cause disruption to the detection signal, especially for more complex matrix samples such as agricultural products or environmental water samples, where other coexisting components may compete for adsorption position with the analyte to be tested, resulting in deviations in the sensor's accuracy [10]. Different types of pesticide molecules vary greatly in structure and chemical properties, and it is still a difficult task to develop sensors that can effectively identify various pesticide residues.

In terms of economy, the cost of graphene itself is high, and high-quality single-layer graphene cannot be commercially produced on a large scale, thereby weakening the ability of sensors to compete in the market [15]. From a policy point of view, the current standard recognition system for new sensor technology is not perfect, which hinders the comprehensive application of graphene electrochemical sensors in the field of environmental detection and food safety to a certain extent [10].

5.2. Future development direction

In order to break through the difficulties mentioned before, and to make the application of electrochemical sensors with graphene in the field of pesticide residue detection more common, future related research should focus on several places, first, after the use of new nanomaterial composite methods, the overall performance of the sensor will be greatly improved, and the graphene and metal nanoparticles such as gold and silver, tin dioxide, zinc oxide and other metal oxides or semiconductor quantum dots can be fused, which can not only improve the conductivity of the sensor and its catalytic effect, It can also consolidate its shape-selective adsorption ability for certain pesticide molecules [9]. At present, studies have pointed out that graphene-nano-gold composites have higher sensitivity and selectivity in detecting biomolecules such as dopamine, ascorbic acid, and uric acid, and this method is also suitable for the detection of pesticide residues [11].

The research and development of intelligent sensors will become the main trend of future research, combining microelectronic technology, artificial intelligence algorithms and wireless communication modules, which can achieve the function of sensor detection at any time, analyzing data and then transmitting it over long distances [9]. The intelligent sensor made of graphene can be placed in farmland or water sources to obtain changes in pesticide residues at any time, and send alarm messages to relevant government departments through the cloud platform.

Future research will need to streamline the production process of sensors and reduce manufacturing costs, on the one hand, optimizing the production method of graphene can improve yield and quality, and on the other hand, it is also practical to find low-cost replacement materials [11]. The government and academic circles should strengthen cooperation and create a consistent standardized verification system, so as to give policy help and technical support to the large-scale application of new sensors [10].

Graphene has a broad application prospect in the detection of pesticide residues with electrochemical sensors, but it is necessary to overcome many technical and non-technical obstacles in practical application [15].

6. CONCLUSION

This paper summarizes the research process of graphene-dependent electrochemical sensors for pesticide residue detection, and deeply analyzes its operating mechanism, advantages and difficulties. Alene has a special two-dimensional structure, large specific surface area, good conductivity and chemical properties on many surfaces, which make it good to make pesticide molecules attach and carry out electron transfer, greatly improving the sensitivity, stability and response speed of the sensor, compared with traditional detection methods, graphene electrochemical sensor has a very outstanding performance in the detection of the lower limit, linear range and response time, in the detection of such as imidacloprid, dicholon, octiphos, When it comes to various pesticide residues such as methyl parathion, it achieves the lower limit of detection from the micron level to the nano level, and has good repeatability and accuracy, and can be used for the detection of complex matrix samples in the actual environment.

Graphene composites such as Gr/CeO₂, graphene-gold nanoparticles, etc. have been functionally modified and synthesized, which further enhance the sensor's selectivity for the recognition of target pesticides, reduce the interference of coexisting substances, and improve the applicability of sensors in the real environment. However, when this technology is really put into application, it still encounters difficulties such as unstable graphene materials, limited selectivity, high manufacturing costs, and lack of a unified standard system.

In the future, we should focus on developing more material composite methods to improve the performance of sensors, promote the research of intelligent and miniaturized integrated systems, realize real-time collection and long-distance transmission of data, so that it can be used in online monitoring of farmland, water sources and other places, and improve the large-scale manufacturing method of graphene to reduce the cost of materials, add artificial intelligence algorithms to improve the processing capacity of signals, and the government, scientific research units and enterprises should jointly formulate corresponding testing standards and certification systems. To provide institutional support for technology transfer, electrochemical sensors relying on graphene have great potential in detecting pesticide residues, and are likely to become the main supplement or even alternative choice for current detection technologies and means, and then provide key technical support for the construction of an efficient, intelligent and green pesticide residue detection system.

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