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Design of New Electrochemical Sensors and Detection Application of Chemical Feedstock Residues

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The contamination of chemical residues with great harm, long duration, and wide range of action has increasingly become the focus of research. Taking electrochemical sensor as research basis, a new three-electrode electrochemical sensor is designed based on the decomposition principle of chemical enzyme media. The electrode system of this sensor brings in the graphene nanocomposites with excellent conductivity and ZnSe quantum dots with good enzyme immobilization. It not only guarantees the activity of acetylcholinesterase, but also reduces the impedance and improves the accuracy and sensitivity of the detection system. By adopting the designed detection system, based on the inhibitory effects of chemical ions and enzyme media, it is available to test the chemical ions. The test results show that the average recovery rate of chemical ions is between 94% and 108% when using the optimal detection conditions determined in the dissertation, and the deviation value is less than 0.01, indicating that the sensor can accurately detect the actual chemical feedstock residues.

1. Introduction

With the rapid rise of modern industry, the consequent chemical feedstock pollution, chemical ion pollution and heavy metal pollution have become increasingly serious, seriously threatening the safety of air, water, and soil. Therefore, it has become increasingly important to accurately detect, measure and control the chemical feedstock residues. At present, since people's environmental protection concepts and health concepts have been strengthened, the research and control of chemical residues have been concerned by some researchers. The detection and analysis techniques have received more and more attention (Hart and Wring, 2010). Current measuring methods mainly include spectroscopic analysis, mass spectrometry, and electrochemical analysis (Alizadeh and Amjadi, 2011). The first two traditional detection methods have complicated pretreatment processes, long detection cycles, and clumsy detection instruments, while the electrochemical sensors, acting as a rapid detection technology for chemical ions, meet the demand for scientific research and practical operation and has increasingly become a research hotspot for detecting chemical substances. Maksymiuk (2006) has designed an acetylcholine biosensor to detect phosphorus content in chemical substances. Based on electrochemical principles to detect organophosphorus pesticide residues, Yantasee et al. (2008) have adopted acetylcholine as an electrode media and obtained the detection limits of various pesticides. Du et al. (2016) have detected parathion-methyl in vegetable samples in combination with electrochemical analysis by means of hydrotalcite’s extraction ability. Existing studies have shown that the research of electrochemical sensors can help guide the treatment and improvement of chemical feedstock residuals and have positive significance for environmental protection.
Therefore, this dissertation takes the acetylcholinesterase sensor as the research object and constructs the chemical substance detection model to detect chemical ions, providing a new efficient and convenient way for the monitoring and quantitative detection of chemical contamination residues.

2. Electrochemical Sensor

Based on the principle of electrochemistry, combined with electrodes and other physics components, electrochemical sensors measure the solution concentration by electrochemical information analysis.

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Currently, electrochemical sensors are widely used in chemical, pharmaceutical and other fields due to their advantages of fast detection speed, high precision, and low cost (Banerjee et al., 2017; Choudhary et al., 2015; Dong, 2017; Guan et al., 2018). For the detection of chemical feedstock residues, the commonly used detection methods are electrochemical enzyme biosensors and enzyme-free electrochemical sensors. The main characteristics of the two are shown in Table 1 below.

Table 1: The advantages of electrochemical biosensors

Item	Advantages
Electrochemical biosensors	Small volume, Continuous monitoring; Quick response and low sample usage; The cost of the instrument is much lower than that of large analytical instruments;
No enzymatic electrochemical sensors	Good stability; Good reproducibility; It's not restricted by dissolved oxygen;

Among them, the electrochemical enzyme biosensor uses a chemical enzyme as a carrier electrode, which can efficiently and rapidly measure solution concentration. There are two main points for the carrier role of chemical enzymes: (1) chemical feedstock have inhibitory effects on enzymes; (2) enzymes have a catalytic effect on the reaction process of chemical feedstock. Based on the above two aspects, there are two kinds of electrochemical enzyme biosensor designs, that is, enzyme-inhibiting electrochemical biosensors and enzyme-catalyzed electrochemical biosensors.

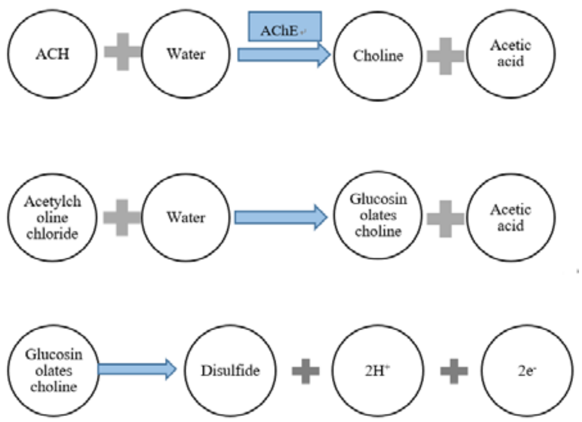


Figure 1: To determine the working principle of chemical raw material testing.

Table 2: Classification of enzyme fixation techniques

Category	Paraphrase	Characteristics
Adsorption method	The non-covalent action binds the enzyme to the carrier	The enzyme activity recovery is high; Enzymes fall off easily;
Embedding method	The physical action will bury the enzyme	The enzyme activity retention rate was high; It is not suitable for measurement of large or large molecular substrate.
Covalent method	The enzyme is fixed by an irreversible covalent bond	The enzyme activity is difficult to guarantee;
Crosslinking method	Cross-linking of the enzyme molecules through a multifunctional reagent or crosslinking agent	The operation is simple and the enzyme film thickness is controllable; Reduction of enzyme activity
Electric polymerization	The electro polymerization processes the enzymes into the polymer	The enzyme electrode reproducibility is better;

The working principle of enzyme-inhibiting electrochemical biosensors to measure chemical feedstock is shown in Figure 1 below. The detection mechanism of chemical contamination is that the chemical ion concentration is positively correlated with the concentration of hydrolyzed products, that is, the chemical ions produced by the decomposition of AchE inhibition effect are reduced and the current formed is reduced.

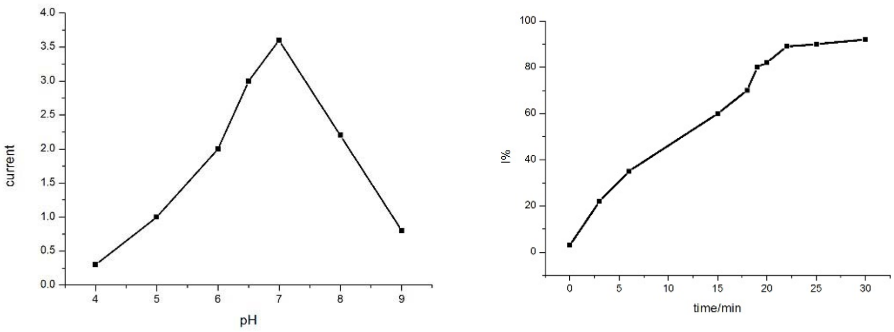
The commonly used media in enzyme-catalyzed electrochemical biosensors are organophosphorus hydrolases. These enzymes can drive chemical substances to generate organic substances such as alcohols. The catalytically generated products possess electrical activity that can be detected by sensors. Based on this principle, the ion detection of corresponding chemical substances is measured. Bartolomeo and Grilli (2015) have designed an OPH-based microbial sensor and detected the content of chemical contamination (sulphide).

In order to ensure the activity and reusability of enzymatic media, the study of enzyme immobilization has become a research hotspot. At present, there are mainly five kinds of enzyme immobilization techniques, as shown in Table 2.

3. Detection Application of Chemical Feedstock Residues

3.1 Research on Detection Conditions of Chemical Feedstock Residues

The pH value, potential and chemical substances' suppression time of the electrochemical detection system are all related to the detection performance of the enzyme sensor. Therefore, this dissertation takes the pH value and chemical substances' suppression time as the research object and optimizes the relevant detection conditions. The optimization results are shown in Figure 2. It can be seen from the figure that when the pH value is 7.0, the electrode current value is the largest; when the chemical substances' suppression time reaches 16 mins, the current is gradually stable. Thus, the optimal chemical substances' suppression time is 16 mins.



(A) (B)

Figure 2: Effects of pH(A) and inhibition time(B) on the response ofAChE/F-ZnSe/GR-Chi/GCE

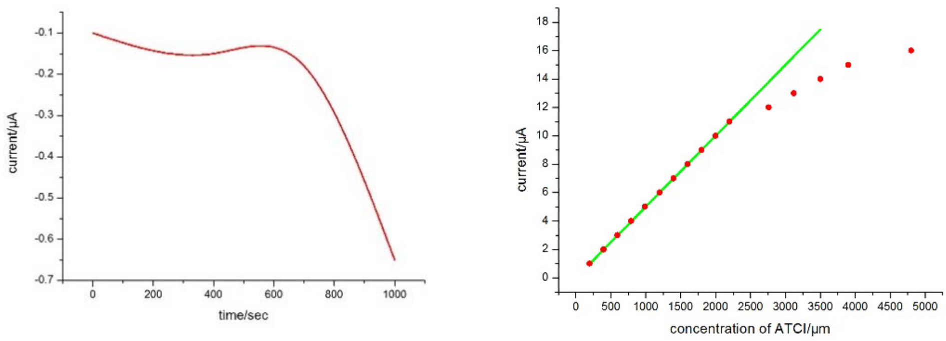


Figure 3: Current - time diagram of the electrode

In order to further study the sensitivity of the electrode to ATCl, the current-time relation of the electrode gets analyzed in this dissertation. The obtained curve is shown in Figure 3. As can be seen in Figure 3, the three-electrode response is faster, and the current stays stable 12 seconds after adding ATCL to the electrode, indicating that the graphene has good conductivity. The response current has a linear relation with the ATCL concentration, and the correlation coefficient is 0.98. However, after the concentration of ATCL is greater than 1100 μM, the positive correlation between the two decreases, indicating that the enzyme catalysis is about to reach saturation. Therefore, the optimal amount of ATCl in the electrode system should be 1100 μM.

The stationary phase of the relation between the current size and the ATCL concentration can be expressed by the following Lineweaver-Burk equation (Sanoit et al., 2009): $1/I_{ss}=1/I_{max}+K_m^{app}/I_{max}{}^c$.

Among them, I_{ss}—the steady-state current of the solution to be tested; I_{max}—the maximum current of the solution to be tested; C—the maximum concentration of the solution to be tested. The obtained k_m^{app} constant value is 0.12MM. Kalimuthu et al., (2012) and Frag et al., (2018) has obtained the coefficients, which are respectively 0.23MM and 0.31MM. Compared with the above research results, the three-electrode electrochemical detection system has a friendlier adsorption force for ATCL.

3.2 Design of New Electrochemical Sensor

In this thesis, a glassy carbon electrode has been used to prepare the electrode together with graphene-chitosan suspension and F-ZnSe QDs solution. Based on the three-electrode system, the electrochemical detection system is designed. The three-electrode system includes the working electrode, counter electrode and reference electrode. The principle of the three-electrode electrochemical electrode is shown in Figure 4 below. The film-forming ability of chitosan can uniformly disperse graphene and form a positive charge carrier. By virtue of the electrostatic attraction, the positive charge carrier can combine with the negative charge carrier F-ZnSe QDs, along with fusing acetylcholinesterase, so as to form a multi-layered surface film. In this way, good conductivity and electrode sensitivity can be ensured.

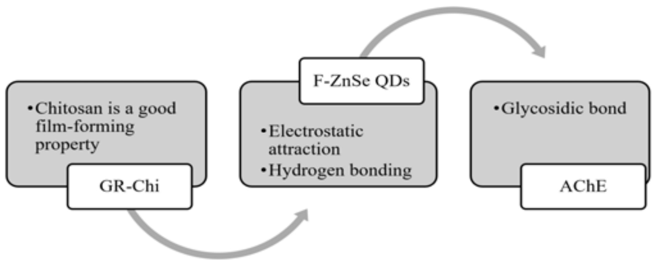


Figure 4: Schematic diagram of three electrode electrochemical electrodes

The relation between chemical ions and enzymes is as follows: $M\%=((I_1-I_2)/I_1)\times100\%$

Among them, M%—the inhibition ratio of chemical ions to the enzyme; I_1—The current value before the inhibition of the enzyme; I_2—the current value after inhibition of the enzyme;

3.3 Detection and Results Analysis of Chemical feedstock residues

The test water is taken from a certain water area in Jiangsu, to ensure that the water sample is neutral, and the soil sample is taken from a chemical plant pilot area in Jiangsu. Weigh 0.01316 g of methyl parathion and dissolve it in a 50 mL volumetric flask and then conduct constant volume with ethanol. The main steps are shown in Figure 5. According to the research of Pescheck et al., (2014) and Ge et al., (2015) the graphene is prepared by oxidation method. Based on the research and preparation of F-ZnSe QDs, a borated functional ZnSe quantum dot is extracted and prepared.

The spectrum chart of graphene oxide obtained by the spectral analysis method is shown in Figure 6. It can be seen from Figure 6 that the graphene oxide reaches the absorption peak at the wavelength of 230 nm, while the graphene reaches the absorption peak at the wavelength of 280 nm. Since the peak value shifts back, the chemical bond C=O has stronger absorption capacity than the chemical bond C—C, and the electrons after oxidation reach the conjugate stat, leading to a reduction of the absorption peak.

The electrochemical impedance diagrams of four electrodes in the same content (0.1m) of K+1 solution obtained in this dissertation are shown in Figure 7. As can be seen from Figure 7, the resistance value of bare electrode is about 210. After compositing Nano materials to the electrode surface, the resistance value decreases. After compositing acetylcholinesterase to the electrode surface, the resistance value increases to 1600. This is mainly because the enzyme media are resistance material. The increase in resistance indicates that acetylcholinesterase is well composited on the electrode surface.

According to the optimal detection conditions, the chemical ion model of the chemical feedstock is tested. From the current response detection results (Fig. 8) after the three-electrode electrochemical detection system goes through chemical ion suppression, it can be found that the inhibition rate of enzyme media is positively correlated with the current intensity. The reason is that as the concentration of chemical ions increases, the inhibitory effect of the enzyme media increases, and the hydrolysate concentration of the chemical substance decreases, so the current formed becomes weaker and weaker.

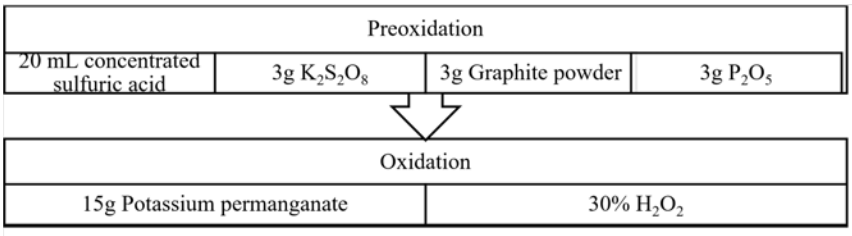


Figure 5: Preparation of graphene oxide

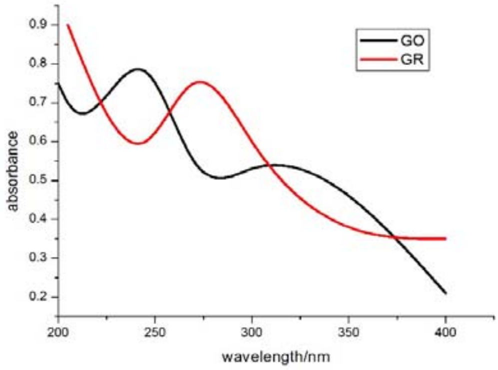


Figure 6: UV-visible absorption spectra of differentgraphene oxide and graphene

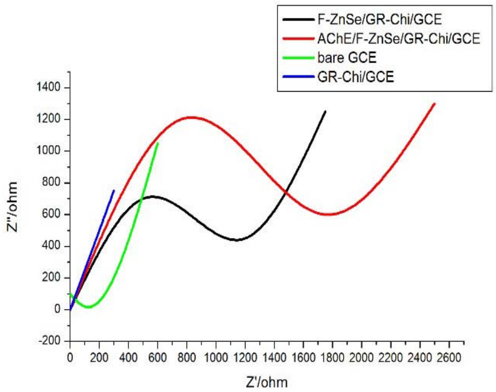


Figure 7: Electrochemical impedance spectra of modified electrodes (frequency range: 10^5hz-10^{-1}hz)

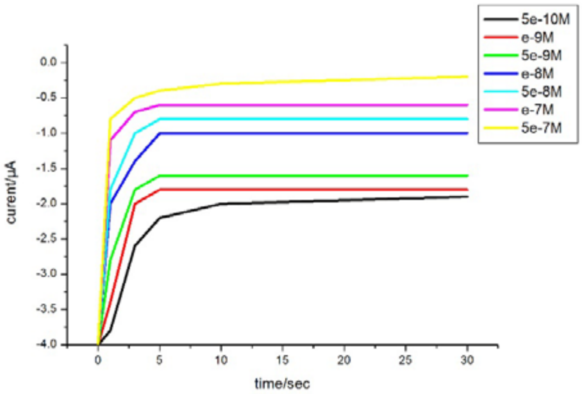


Figure 8: Current response test results

In order to demonstrate the effectiveness of the three-electrode electrochemical detection system, the standard addition method is adopted to measure the organophosphorus ions in the chemical feedstock residues. Different Nano-level MPs are added to the chemical substance samples, and the three-electrode sensors are used for detection. The results are shown in Table 3. The average recovery rate is greater than 94% and less than 108%, while all deviation values are less than 0.01. Therefore, the sensor can accurately detect the actual samples.

Table 3: Actual sample recovery experiment results (n=3)

Sample	Taken (nM)	Found (nM)	Recovery (%)	RSD (%)
	1	0.95	95	4.76
Chemicals	10	10.75	107.5	3.86
	100	95.69	95.69	5.18

4. Conclusions

In the current society, people's health concepts and environmental protection concepts have been continuously strengthened, and the analysis technology for chemical feedstock residues has also received increasing attention from researchers. The traditional analysis methods depend heavily on large-scale precision instruments. Meanwhile, the high detection cost and complicated detection procedures make it difficult to apply the detection technology in the actual chemical feedstock residues. This paper uses the detection method of electrochemical enzyme biosensor as a research basis and has constructed a high-sensitivity biosensor. The main conclusions are as follows:

(1) A new three-electrode acetylcholinesterase biosensor has been constructed. The electrode system of this sensor adopts the graphene-chitosan nanocomposite and ZnSe quantum dots, which ensures the activity of acetylcholinesterase, reduces the impedance, and improves the accuracy and sensitivity of the detection system. (2) The detection conditions get optimized. Through the experiments, the optimal chemical substances' suppression time is16 mins, and the optimal amount of ATCl in the three-electrode system should be 1100 μM. (3) The effectiveness of the sensor gets verified. By using the established detection system, based on the inhibitory effect of chemical ions and enzyme media, the chemical ions are detected. The detection results show that the average recovery rate is greater than 94% and less than 108%, indicating that the sensor has good conductivity and the enzyme media has good coverage performance. Thus, this sensor can accurately detect the actual chemical feedstock residues.

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