Int. J. Electrochem. Sci., 13 **(2018)** 396 – 409, doi: 10.20964/2018.01.09

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Ferrocene/graphene modified glassy carbon electrode for Chloromycetin detection

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Received: 7 March 2017 / *Accepted:* 25 September 2017 / *Online Published:* 1 December 2017

In this study, we used ferrocene/graphene to modify a glassy carbon electrode, which was fixed with an appropriate amount of Nafion solution. The -C-O-C- and -COOH functional groups were detected in the ferrocene/graphene composite using IR spectroscopy, which indicated that graphene was oxidized to graphene oxide, making it more hydrophilic, dispersible and compatible with polymers, thus increasing the chloromycetin detection rate. A scan rate of 0.05 V/s is ideal. The optimal conditions for chloromycetin detection were found using Cyclic voltammetry (CV): a scan rate of 0.05 V/s, pH 6.47, and 0.1 mol/L PBS buffer solution. Differential pulse voltammetry(DPV) shows that the concentrations of chloromycetin are 2×10^{-6} - 3.2×10^{-5} mol/L, and there is a good linear relationship between the peak current and the concentration: I_{pa}(μ A)=2.44772 c(μmol/L) -46.14375, r = 0.993; the detection limit is 4.5×10^{-8} mol/L. This modified electrode has good stability, repeatability and operability and can be applied to detect actual samples.

Keywords: Ferrocene/graphene-modified electrode; Detection; Chloromycetin; Cyclic voltammetry; Differential pulse voltammetry.

1. INTRODUCTION

Chloromycetin, also known as an amphenicol, is an antibiotic first isolated from microbial metabolites by Ehrlich and others in 1947. It is stable when it is dried and relatively stable in weakly acidic and neutral solutions[1]. Because of its broad antibacterial spectrum, chloromycetin is effective, inexpensive and widely used in clinical situations. Owing to the therapeutic use of the drug combinations of chloromycetin, it has some toxicity; in addition, because of its quick development speed, a simple and reliable method to monitor the quantities in pharmaceutical formulations remains necessary[2].

Graphene, a novel carbon nanomaterial, is a graphite film of a single layer that consists of closely packed together C atoms[3]. It has excellent electrical conductivity and a large specific surface area, which can be widely used in energy storage, sensors and modified electrodes and other fields. Ferrocene is a chemically stable metal compound, which is commonly used in antibacterial applications, catalysis, electrochemistry, and other fields. Its unique chemical structure makes it a good electron transfer mediator. Because of its electrochemical performance, high repeatability and good reversibility, ferrocene can be used as a redox-active center to detect small biomolecules.

Graphene has a unique honeycomb structure and nano-function, which opens up new roads for combining it with biological and electrochemical sensors[5]. However, because of its unitary structure and intrinsic properties, graphene has been greatly restricted in many areas. Therefore, it is imperative to develop more and better graphene derivatives to better apply graphene to electrochemical sensors. Currently, many graphene derivatives have been developed, such as fullerenes, alkoxy graphite, carbon nanotubes and graphene oxide. Although they are not widely used, they can be applied in a certain range of biosensors. It is envisioned that with the advance of science and technology, graphene-infused biosensors will become more prominent in some fields and irreplaceable in many others because of its high performance.

Graphene oxide biosensors prepared with functionalized graphene can be well applied in the detection of human blood. Graphene has a large specific surface area and excellent electrical conductivity, which supplies the appropriate atmosphere for oxidation enzymes and improves the absorption of enzymes on the surface.

Yang-Rae Kim explored the idea of using a graphene-modified electrode to detect dopamine in a system of vitamins. Their results showed that the current of the oxidation peak and concentration were linearly correlated when the DA concentration was 4~100 μmol/L in 1 mmol/L vitamin solution. Additionally, the presence of vitamins had no significant effect on the electrochemical analysis results of DA. Fu Haiying prepared an electrochemical sensor to detect uric acid using the conjugate synergies of ionic liquids, thionine and graphene and performed electrochemical detection using differential pulse voltammetry. Simultaneously, they detected the related performance for UA on this electrochemical sensor in the presence of vitamins. The experiment conclusions showed that this graphene electrochemical sensors had excellent selectivity, low detection limits and operability. The graphene electrochemical sensors were applied to detect the actual content of uric acid in the body and achieved desired results. Jiang Bingying detected cocaine using a graphene/AuNP composite-modified screen printed electrode. The results showed that the modified electrode could sensitively detect cocaine with a limitation of less than 1 nM.

In this paper, a ferrocene-functionalized graphene-modified electrode is used to detect the content of chloromycetin in actual water samples. The recommended methods in pharmacopoeias to determine chloromycetin in pharmaceuticals involve UV-spectroscopy and HPLC, but these methods have limited selectivity and are often subjected to interferences from the components of the matrix. The currently used methods to determine chloromycetin in animal food samples, milk, meat or tissues and fluids of treated cattle are LC-MS, GC-MS, HPLC, planar chromatography, etc. Zhou [6] used colloidal gold immunochromatography to quickly detect chloromycetin residues in food; however, its early experimental steps are notably

complex, and it cannot be used to quantitatively analyze chloromycetin. Tyagi [12] used a liquid chromatographic method with electrospray ionization tandem mass spectrometric (LC-ESI-MS-MS) detection and identification to determine chloromycetin in shrimp tissue. Taka [13] determined chloromycetin in honey using LC-MS/MS. Sai [1] analyzed CAP in drinking water samples by a novel photonic sensor using a self-cross-linked imprinting close-packed opal (CPO) as a recognition element. However, these methods are laborious and require high-cost instruments.

Graphene has a large surface area, good dispersivity and strong electric conductivity. Ferrocene can participate in the gain and loss of electrons and undergo redox reactions. This new assembled modified electrode perfectly combines the advantages of graphene and ferrocene. In addition, this electrode has a simple structure, it is easy to make, and the manufacture cost is low. In the detection of chloromycetin, it has a low detection limit, and there is a good linear relationship in a wide linear range. It is convenient, economically efficient and effective, which contributes to its practicability.

2. EXPERIMENTAL

2.1. Chemicals and solutions

Chloromycetin, Al_2O_3 powder, and polyvinylidene fluoride (PVDF) were purchased from Aladdin. The chloromycetin stock solutions were prepared in 0.1 M PBS buffer solution. Graphite and Nafion solution（15%）were received from Sigma. The Nafion solution was directly used and required cryopreservation. $Na_2HPO_4 \cdot 12H_2O$ (AR) and NaH_2PO_4 (AR) were ordered from XiLong Chemical Industry. They were dissolved in double distilled water and can be formulated to different pH values by combining them with a PBS buffer solution (0.1 M) in different proportions.

2.2. Apparatus and measurements

The entire electrochemical measurements were performed with a CHI630D Electrochemical Workstation with a professional software package (Shanghai CH Instrument Company, China). The three-electrode system in a 10-mL one-compartment voltammetric cell included a bare glassy carbon electrode (GCE, 3 mm in diameter, Model MF-2012, BAS) or a modified GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode in this setup.

The FT-IR spectra were recorded on an IR-Affinity-1 Fourier Transform Infrared Spectrophotometer (Thermo Fisher/Finnigan-Cahn-Nicolet, American). A temperature magnetic stirrer (KeXi, Jintan) was used to disperse the raw material and promote the formation of the composite material. Different solutions were prepared for the pHS225 pH meter (LeiCi, Shanghai). The ultrasonic process was performed using a KQ-500 Bonifier (500 W, Kunshan ultrasonic instruments Co., Ltd.)

Cyclic voltammetry (CV) was used for preliminary studies on the electrochemical behavior of chloromycetin.

Differential pulse voltammetry (DPV) was used to develop the electroanalytical methodology and determine chloromycetin in real samples.

The AC impedance (EIS) method is based on a measurement of the response of the electrochemical cell to a small-amplitude alternating potential (or current). The procedure is performed over a wide range of frequencies. The response is established through the complex-impedance plot, and the result can be interpreted in terms of an equivalent electrical circuit. If the surface changes, the impedance signal will be modified, and the differences in the signal before and after the modification of the electrode can be used to understand the electrode/solution behavior.

2.3. Preparation of 0.1 M PBS buffer solution

Solution A consists of 7.8011 g NaH_2PO_4 (accurately weighed), which was fully dissolved with double distilled water in a 500-mL volumetric flask. Solution B was made using the same method, where 17.9 g $Na_2HPO_4 \cdot 12H_2O$ was fully dissolved. According to the experiment and literature, 500 mL each of different PBS buffer solutions with different pH values was prepared.

2.4. Preparation of the ferrocene/graphene composite material

We accurately weighed 0.004 g ferrocene, completely dissolved it with anhydrous ethanol, added 0.02 g graphene while slowly stirring, continued stirring for 3 h in a water bath at 25 ℃, added 0.356 g graphite powder and 0.038 g polyvinylidene fluoride (PVDF), sonicated the mixture for 1 h to evenly distributed them in the composite material, and further stirred the mixture for 12 h at room temperature (we kept the mixture away from air and shaded it from light).

2.5. Preparation of the ferrocene/graphene-modified electrode

A bare glassy carbon electrode was polished with 1, 0.3, and 0.05 μm aluminum oxide powder in the same direction on wet suede; ultrasonic cleaning was performed for 3 minutes with ethanol and distilled water, and then, the electrode was naturally dried. We pipetted 8 μL prepared ferrocene/graphene composites on the polished bare glassy carbon electrode, spread it evenly and dried the product under natural conditions. We also pipetted 15% Nafion solution using a micro-injector, dispersed it onto the surface of the ferrocene/graphene composites at room temperature and naturally dried them. The ferrocene/graphene-modified electrode was placed in a buffer solution (pH 6.47) until the composite formed a layer of polymer film; then, we reduced the potential for one minute, and the ferrocene/graphene-modified electrode was completed.

2.6. Experimental procedure

In 20 mL buffer solution that contained a certain amount of chloromycetin, we used a 217 calomel electrode as the reference electrode, a 213 Pt electrode as the auxiliary electrode, and the ferrocene/graphene-modified glassy carbon electrode as the working electrode, which formed a three-electrode system.

The electrochemical operating parameters were set as follows:
AC resistance parameter settings (EIS):
Init E (V) = 0 Maximum frequency (Hz) =1.5×10^{6}
Minimum frequency (Hz) = 0.05 Amplitude (V) = 0.005
Cyclic voltammetry parameter settings (CV):
Init E (V)=0.6 High E (V)=0.6
Low E (V)=-0.2 Final E (V)=0
Initial Scan=Negative Scan Rate (V/s)=0.001~0.02
Sweep Segments=2 Sample Interval=0.001
Quiet Time (sec)=2 Sensitivity (A/V)=1×10^{-4}
Differential pulse voltammetry parameter settings (DPV):
Init E (V）=-0.2 Final E (V)=0.6
Incr E (V）=0.005 Amplitude (V)=0.05
Pulse Width (sec)=0.05 Sampling Width=0.04
Pulse Period (sec)=0.1 Quiet Time (sec)=30
Sensitivity (A/V)=1×10^{-4}

3. RESULTS AND DISCUSSION

3.1. AC impedance characterization of the modified electrodes

In this experiment, we measured the impedance of three types of modified electrodes in the buffer solution of 1×10^{-5} mol/L chloromycetin: ferrocene/graphene-modified electrode, ferrocene/graphite-modified electrode and graphite-modified electrode. The electrochemical impedance spectroscopy characterizes the impedance changes of different electrode surfaces, and the electron transfer impedance values reflect the characteristics of the test solution and electrode interface. A smaller electron transfer impedance indicates a greater electron transfer rate on the modified electrode surface. z' is the real part of the impedance on the interface between the test liquid and the electrode; z'' is the imaginary part of the impedance on the interface between the test liquid and the electrode. Figure 1 shows that the ferrocene/graphene-modified electrode has a significantly smaller impedance than the ferrocene/graphite-modified electrode and graphite-modified electrode, and the graphite-modified electrode has a larger impedance than the ferrocene/graphite-modified electrode. This result is probably caused by the presence of ferrocene, which provides the media and platforms to accelerate the electron transfer rate in the solution. Zhang [28] used nano cobalt modified glassy carbon electrode (CoNP/GCE) to study the electrochemical behavior of chloromycetin and determine chloramphenicol content in eye drops. The AC impedance spectra of GCE and CoNP/GCE showed that charge transfer resistance in bare GCE is obviously larger than that of CoNP/GCE, it indicated that nano cobalt enhanced the electron transport. Meanwhile, the electron transfer impedance of CoNP/GCE is much bigger than ferrocene/graphene-modified GCE, which nearly reaches 4000 Ω.

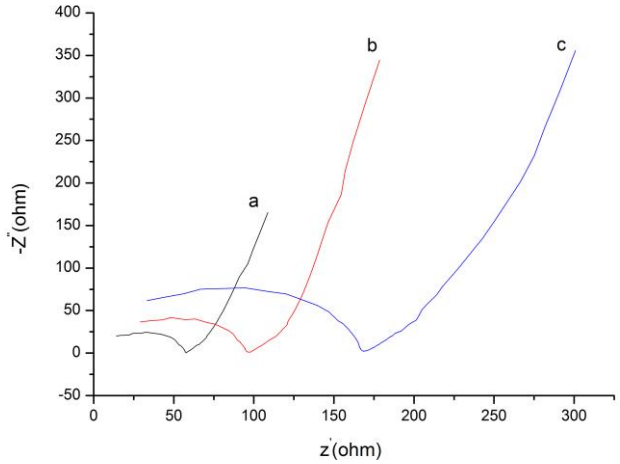


Figure 1. AC impedance spectra of the (a) ferrocene/graphene-modified electrode, (b) ferrocene/graphite-modified electrode and (c) graphite-modified electrode in 0.1 mol/L PBS buffer solution (pH 6.47) containing 1×10^{-5} mol/L chloromycetin.

3.2. Electrochemical behavior of chloromycetin on the modified electrodes

We separately prepared three different electrodes: a bare glassy carbon electrode, a graphene-modified electrode, and a ferrocene/graphene-modified electrode; then, we detected their CV diagrams in a PBS buffer solution containing 1×10^{-5} mol/L chloromycetin (pH 6.47) at a scan rate of 0.005 V/s.

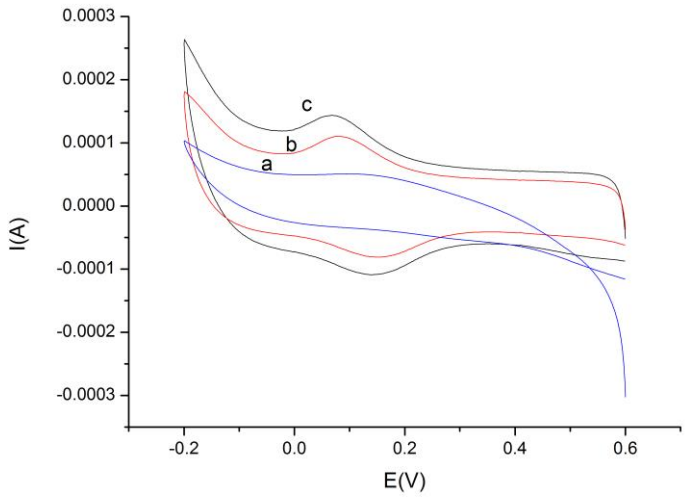


Figure 2. Cyclic voltammograms of the (a) bare glassy carbon electrode, (b) graphene-modified electrode and (c) ferrocene/graphene-modified electrode in 0.1 mol/L PBS buffer solution (pH 6.47) with 1×10^{-5} mol/L chloromycetin at a scan rate of 5 mV/s.

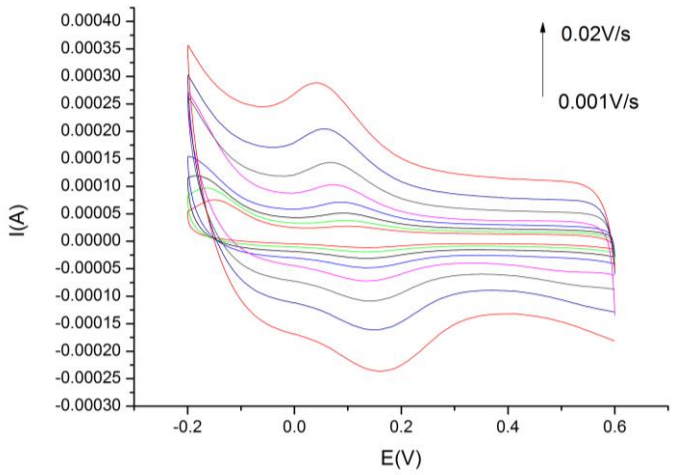
Figure 2 shows that chloromycetin had no obvious redox peaks on the bare glassy carbon electrode (a), which implies that almost no electrochemical reaction occurred. Similarly, the curve of the graphene-modified electrode shows that chloromycetin has a significant redox peak, and the peak difference is 0.107 V, which is small. For the bare glassy electrode modified with ferrocene/graphene

composites, the peak current value on this sensor significantly increases, and the difference between the peaks decreases to 0.0058 V, which proves the excellent reversibility of this electrochemical reaction. On the one hand, the honeycomb lattice structure makes graphene have a relatively large surface area, which increases the electron transfer rate and speeds up the reaction progress; on the other hand, the ferrocene plays the role of the media: it cooperates with the graphene substrate to form a larger conjugated system, which accelerates the electron transfer between chloromycetin and the glassy carbon electrode and increases the detection sensitivity. Wang [26] detected chloromycetin using multi-walled carbon nanotube modified glassy carbon electrode (MWNTs/GCE) . Compared with the bare GC electrode, the peak current is obviously increased high, and the peak potential shifted negatively, which showed that MWNTs has an electrocatalytic effect on chloromycetin, the electrode reaction of chloromycetin is changed from two-step reduction to one-step reduction, and the overpotential of the reaction is decreased, so sensitivity is greatly improved.

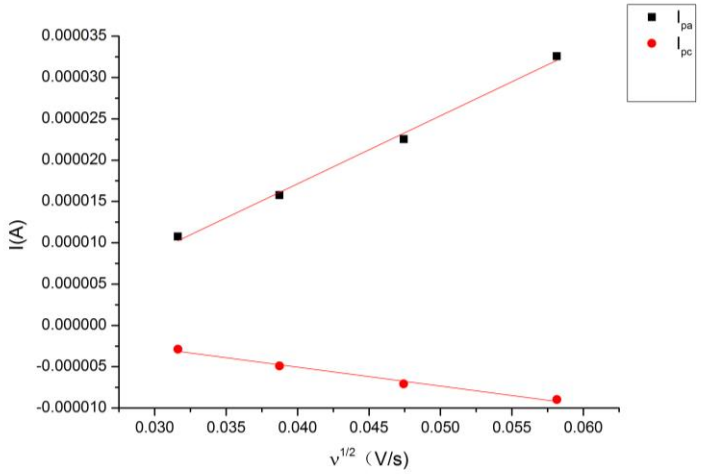
3.3. Effect of the scan rates on the electrochemical behavior of chloromycetin

The cyclic voltammetry diagram of 1×10^{-5} mol/L chloromycetin was measured at different scan rates (the bottom liquid of the PBS buffer solution; pH 6.47) as shown in Figure 3(a). According to the experiment, the peak current value significantly increases when the scan rate gradually increases from 0.001 V/s to 0.02 V/s. Simultaneously, the oxidation peak slightly moves in the positive direction, whereas the reduction peak moves in the negative direction.

In the experiment, we tested the linear relationship between the peak current (oxidation peak current I_{pa} and reduction peak current I_{pc}) and the scan rate in 0.1 mol/ L PBS buffer solution with 1×10^{-5} mol/L chloromycetin. As shown in Figures 3(b) and 3(c), when the scan rate is 0.001-0.005 V/s, the redox peak current and square root of the scan rate are positively correlated, which shows that the redox behavior of chloromycetin on the ferrocene/graphene-modified electrode is controlled by diffusion. When the scan rate is 0.005-0.02 V/s, the redox peak current and scan rate have a positive correlation. The results show that in the range of 0.005-0.02 V/s, the redox behavior of chloromycetin on the ferrocene/graphene-modified electrode is controlled by adsorption. To reduce the background current and enhance the signal-to-noise ratio, we selected 0.005 V/s as the appropriate scan rate. Xin [27] used nanogold-tiania nano needle modified glassy carbon electrode (Au-TiO_2/GCE) for chloromycetin detection, the cyclic voltammetry curves at different scan rates indicated that the reduction peak current of chloromycetin increases with the increasing of scan rate. Within a slow scan rate range, the peak current is proportional to the square root of the scan rate, indicating that the electrode reaction is a diffusion-control process. And when the can rate is too high, the charging current is too large, which is unfavorable to determine the peak current.



(a)



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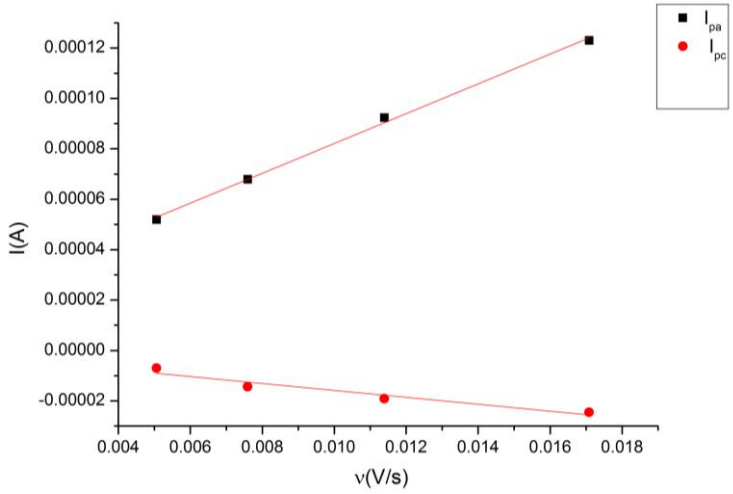


(c)

Figure 3(a). Cyclic voltammogram of the ferrocene/graphene-modified electrode in 0.1 mol/L PBS buffer solution (pH 6.47) containing 1×10^{-5} mol/L chloromycetin with a scan rate of 0.001-0.02 V/s; (b) diagram of the redox peak current and square root of the scan rate; (c) diagram of the redox peak current and scan rate.

3.4. Effect of the pH value on the electrochemical behavior of chloromycetin

We obtained a differential pulse voltammetry (DPV) chart for different pH values in the PBS buffer solution of 1.0×10^{-5} mol/L chloromycetin, which shows that the peak currents change when the pH changes. As shown in Figure 4, when the pH value changes from 5.60 to 6.47, the peak current value increases as the pH value increases; when the pH value continues to increase from 6.47 to 7.17, the peak current gradually decreases.

The possible causes for this situation are that the modified electrodes fixed with Nafion film repulse neutral and anionic particles. At pH<6.47, the H^+ concentration in the bottom solution gradually increases with the decrease in pH, so the adsorption capacity of chloromycetin on the modified electrode significantly decreases. When pH<6.47, the peak current increases with increasing pH. When pH>6.47, as the pH value continues to increase, the OH^- content in the solution gradually increases, which charges a part of the chloromycetin and decreases the amount of adsorbed chloromycetin on the modified electrode; thus, the peak current value is reduced. Chai [25] demonstrated that under acidic or alkaline conditions, changes in the surface charge distribution of the chloramphenicol molecule cause its adsorption on the electrode surface.

The amount of added charge is increased, so that the peak current of the reduction is increased

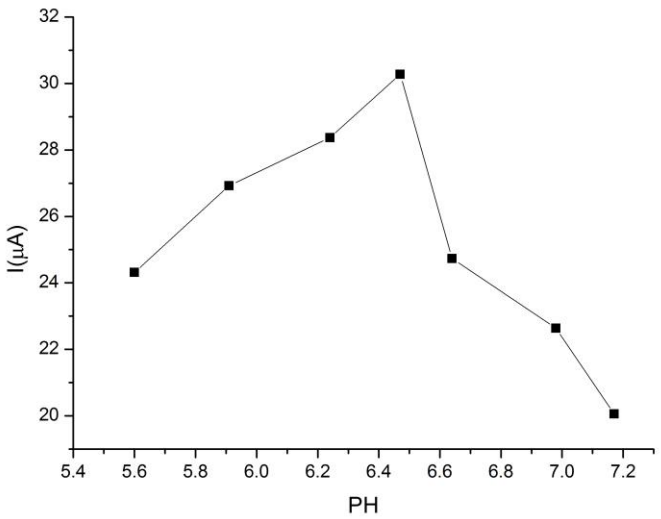


Figure 4. Relationship between the pH value and the peak current in a solution of 1×10^{-5}mol/L chloromycetin.

3.5. Determination of the selectivity for chloromycetin

3.5.1. Differential pulse relationship of chloromycetin with different concentrations

At room temperature, we prepared 0.1 mol/L PBS buffer solution (pH 6.47) containing different concentrations of chloromycetin. The differential pulse voltammetry charts were determined in this solution. As shown in Figure 5, the peak current value gradually increases with the increase in concentration of chloromycetin because in a certain range, when the chloromycetin concentration

increases, its diffusion rate in the test solution and adsorption rate on the ferrocene/graphene-modified electrode increase; thus, the peak current value increases. When the chloromycetin concentration is notably small (1.25×10^{-6} mol/L), the oxidation peak current value remains at -0.7188 μA, which indicates that the ferrocene/graphene-modified electrode has high sensitivity in chloromycetin detection.

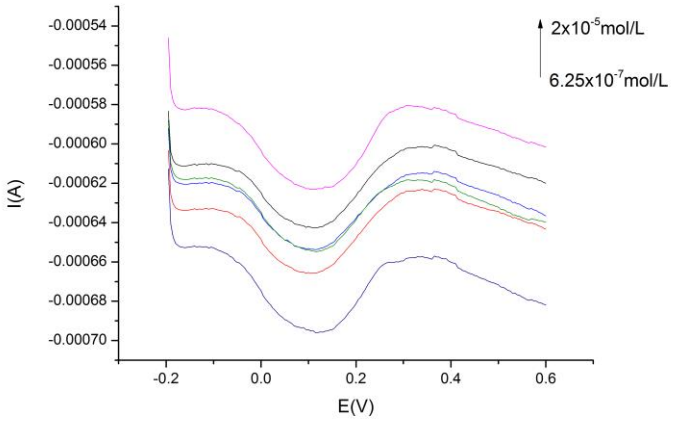
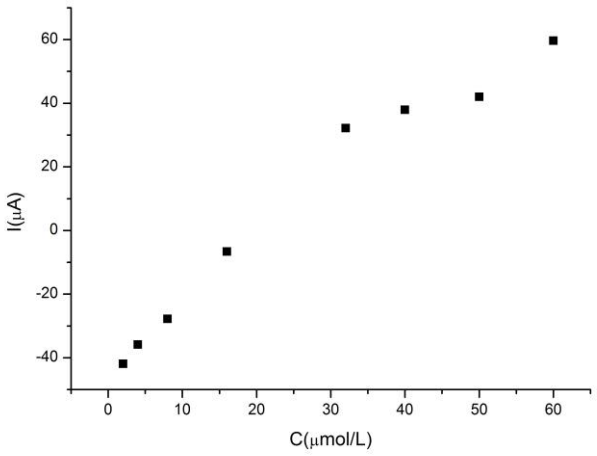


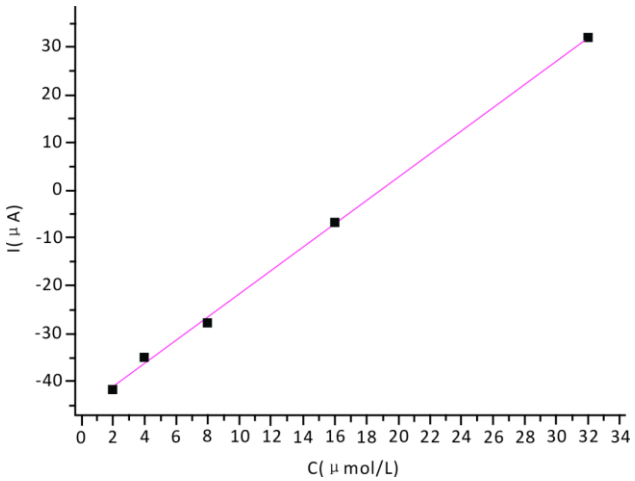
Figure 5. Differential pulse voltammogram of chloromycetin with different concentrations in 0.1 mol/L PBS buffer solution (pH 6.47).

3.5.2. Linear range and detection limit of chloromycetin

As shown in Figure 6, within a certain range, there is a linear relation between the peak current and the chloromycetin concentration; however, there is no significant linear relationship when the chloromycetin concentration is large. In the range of 2×10^{-6} ~3.2×10^{-5} mol/L, there is a good linear relationship between the peak current and chloromycetin concentration: I_{pa} (μ mol/L)= 2.44772c-46.14375 (μmol/L), r = 0.993. The detection limit is three times the standard deviation, so the limit of detection of chloromycetin on the ferrocene/graphene-modified electrode is 4.5×10^{-8} mol/L.



(a)



(b)

Figure 6. (a) Diagram of the oxidation peak current and concentration of chloromycetin in 0.1 mol/L PBS buffer solution, pH 6.47; (b) Linear relationship between oxidation peak current and chloromycetin concentration.

3.6. Reproducibility of the ferrocene/graphene-modified electrode

With 10 continuous scans in PBS buffer solution containing chloromycetin (pH 6.47), the relative standard deviation of the oxidation peak current is only 3.6%, which indicates that the modified electrode has good reproducibility for the detection of chloromycetin. In addition, for the glassy carbon electrode modified with the same batch of ferrocene/graphene composites, after two weeks, the test results decreased by 7.5%, which indicates that the ferrocene/graphene-modified electrode has good stability and reproducibility.

3.7. Interference experiments

Table 1. Relative standard deviation of the additive substance.

Added substances	Concentration（mol/L）	RSD
Na^+	1×10^{-3}	3.46%
K^+	1×10^{-3}	2.08%
Mg^{2+}	1×10^{-3}	4.11%
Zn^{2+}	1×10^{-3}	3.87%
Cl^-	1×10^{-3}	1.12%
NO_3^-	1×10^{-3}	1.39%
CO_3^{2-}	1×10^{-3}	2.31%
sucrose	5×10^{-4}	3.77%
glucose	5×10^{-4}	2.99%
ascorbic acid	1×10^{-4}	1.64%

Under normal circumstances, if a substance is added and the error is no more than 5% compared with the previous detection, the added substance and the original substance have no

significant interference. Under optimal conditions, we detected the interference of some common inorganic and organic ions in the detection of 1×10^{-5} mol/L chloromycetin (pH 6.47). As shown in Table 1, the test results show that 100 times concentrations of Na^+, K^+, Mg^{2+}, Zn^{2+}, Cl, NO_3^-, and CO_3^{2-}, 50 times concentrations of sucrose and glucose, and 10 times concentration of ascorbic acid relative to the concentration of chloromycetin had no significant effect. This result shows that the ferrocene/graphene-modified electrode has good selectivity for the detection of chloromycetin.

3.8. Recovery rate of chloromycetin

Table 2. Determination of the chloromycetin recovery.

Sample	Theoretical value(mol/L)	Determined value(mol/L)	Relative standard deviation(%)	Recovery rate(%)
1	1.25×10^{-6}	1.18×10^{-6}	5.6	94.4
2	2.5×10^{-6}	2.36×10^{-6}	5.6	94.4
3	5×10^{-6}	4.78×10^{-6}	4.4	95.6
4	1×10^{-5}	9.47×10^{-6}	5.3	94.7
5	2×10^{-5}	1.88×10^{-5}	6	94

For 5 water samples from KongMu Lake, the test results of this method show that there is no chloromycetin in the water samples. We applied the stepwise dilution method to obtain certain concentrations of chloromycetin in the water samples, and the test results are shown in Table 2. Each sample had three parallel detections conducted for it; the relative standard deviation of the five groups of samples does not exceed 9%; the recovery rate is 94~109%, which indicates that this test method is correct and reliable, has a certain operability and can be applied to actual chloromycetin content detection.

3.9. Comparison with other methods

Chloromycetin residue detection methods include microbiological assay, immunoassay, instrumental analysis and so on. Among the instrumental analysis methods, electrochemical analysis methods are being used more and more widely. Chuanuwatanakul [19] used a boron-doped diamond thin-film (BDD) electrode by flow-injection analysis to determine chloromycetin in sterile eye drops and milk sample. Agüí [21] determined chloromycetin in milk at electrochemically activated carbon fibre microelectrode. Li [22] detected chloromycetin by electrochemical sensor based on molecularly imprinted polyaniline film. Yang [24] determined chloromycetin by a novel molybdenum disulfide (MoS_2) intercalated by self-doped polyaniline (SPAN) via ultrasonic exfoliating method.

Table 3 summarizes the electroanalytical method for chloromycetin determination from this study compared with other published methods. By comparision, the assembled graphene electrode in our article has a more simple structure, which is easy to manufacture at a low cost, it can also provide a wide linear range and a low detection limit. With its good repeatability, this electrode can be applied to detect chloromycetin in real samples.

Table 3. Comparison of the determination methods for chloromycetin

Method	Sensor	Linear range/M	Detection limit/M	Precision(RSD,%)
Voltammetry	assembled graphene-ferrocene modified glassy carbon electrode	2×10^{-6} to 3.2×10^{-5}	4.5×10^{-8}	3.6%
Spectrophotometry[1]	self-cross-linked imprinting close-packed opal	2×10^{-6} to 5.12×10^{-4}	–	within 4.9%
Square wave voltammetry[21]	activated carbon fiber microelectrode	1×10^{-7} to 1×10^{-5}	4.7×10^{-8}	–
Cyclic and square wave voltammetric method[20]	electrochemically pretreated glassy carbon electrode	1.0×10^{-7} to 7.0×10^{-5}	–	–
Differential pulse voltammetry[22]	the molecular-imprinted film of polyaniline molecule	–	–	2.7%
Amperometry applied to flow injection analysis[23]	2-mercapto-5-methylbenzimidazole self-assembled monolayer modified gold electrode	5×10^{-8} to 1×10^{-6}	4.4×10^{-5}	1.5%

4. CONCLUSION

In this study, we prepared a ferrocene/graphene composite-modified glassy carbon electrode, which can significantly increase the electron transfer rate, electrocatalytic performance and efficiency of chloromycetin detection. In addition, this composite material has a simple manufacture, short-time consumption, and good stability, and it can be well applied in practice to detect chloromycetin by cyclic voltammetry and differential pulse voltammetry. Moreover, this method has a low detection limit and a wide detection range. In the recovery test, the relative standard deviation is small with good feasibility and operability.

ACKNOWLEDGMENTS
This work was supported by the National Natural Science Foundation of China (nos. 21563011).

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