RHBr/RGO composite material as an enhanced sensing platform can detect Cu$^{2+}$ with high selectivity

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Abstract: This work reports a simple and efficient electrochemical detection method, using RHBr/RGO nanocomposite electrode material modified GCE to detect trace Cu$^{2+}$. A simple and effective assembly method is used to prepare RHBr/RGO composite materials. After characterization by DPV and EIS, we discussed and optimized some factors that affect the detection of chemical sensors. Then DPV was used to evaluate the analytical performance of RHBr/RGO/GCE in the detection of Cu$^{2+}$. Using optimal experimental factors, the linear response range of the sensor to Cu$^{2+}$ concentration is 4×10$^{-7}$~1×10$^{-5}$ M, and the detection limit is 3.9 nM (S/N = 3).

1. Introduction

Cu$^{2+}$ is a ubiquitous heavy metal and an essential element in living organisms [1]. Excessive copper intake and severe deficiency in organisms can lead to diseases, for instance neurological diseases and Menke syndrome [2]. Therefore, exploring a more efficient and accurate method to determine and monitor Cu$^{2+}$ in biological and environmental samples has become an urgent issue. Compared with the developed metal ion detection method, the electrochemical detection method based on electrode materials has the advantages of relatively low cost, simple instrument, high sensitivity, and low detection limit, so it has great development prospects.

RGO is attractive to the field of electroanalysis due to its low-cost raw material preparation, excellent electrocatalytic activity, low electronic noise, and especially large theoretical specific surface area [3]. Recently, graphene-based electrode materials have been widely studied as a highly efficient and convenient electrochemical sensor platform for high-sensitivity detection of common metal ions [4-10]. Here, we report for the first time a new Cu$^{2+}$ sensor based on RHBr/RGO nanocomposite electrode material modified GCE. The experimental results show that, compared with the GCE and RGO/GCE modified electrodes, the proposed electrode RHBr/RGO/GCE has a strong affinity for Cu$^{2+}$, and the analysis of Cu$^{2+}$ shows a strong peak current response.
2. Experimental

2.1. Chemicals and materials
GO comes from XFNANO (Nanjing, China). RHBr (our research group has synthesized). $10^{-2}$ M Cu(NO$_3$)$_2$ solution was used to prepare Cu$^{2+}$ solutions with different concentrations. Buffer solutions of different pH were prepared by mixing CH$_3$COONa and CH$_3$COOH as supporting electrolytes. All the solvents and drugs we used in the experiment are of analytical grade. The water used in all experiments requiring water is ultrapure water.

2.2. Synthesis of RHBr/RGO
The RHBr solution was joined dropwise to the GO solution and ultrasonically dispersed for 3 h. The mixture was reduced with hydrazine monohydrate at 50 °C for 4 hours with stirring.

2.3. Fabrication of RHBr/RGO modified electrode
Before modifying GCE, polish the bare GCE with alumina powder, then rinse thoroughly with ultrapure water after each grinding, and sonicate in ethanol, HNO$_3$ and ultrapure water for 5 minutes, and then air dry at room temperature. Finally, the RHBr/RGO dispersion was directly dropped on the surface of thepretreated GCE and weathered in air at indoor temperature.

2.4. Apparatus
The EQUINOX55 FTIR spectrometer was used to characterize the FTIR within the range of 4000-400 cm$^{-1}$. All electricity experiments were tested on the CHI660 electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).

3. Results and discussion

3.1. Representation of RHBr / RGO
As can be seen from Figure 1, FTIR spectroscopy is used to characterize RGO, RHBr and RHBr/RGO. For RGO: the peaks at 1735.72, 1623.65, 1225.87 and 1054.04 cm$^{-1}$ belong to the absorptions of C=O, C=C, epoxy C–O and alkoxy C–O, respectively. For RHBr: The absorption at 3278 cm$^{-1}$ is attributed to the tensile vibration of the O-H. The peaks at 1720 cm$^{-1}$ and 1680 cm$^{-1}$ belong to the characteristic peak of C = O. After assembly, the characteristic peaks of RGO and RHBr both appeared in the infrared spectrum of RHBr / RGO, which indicated that the assembly of RGO and RHBr was successful.

![Figure 1. FTIR spectrum of RHBr, RGO and RHBr/RGO](image-url)
3.2. Electricity properties of RGO/GCE, GCE and RHBr/RGO/GCE

The diameter of the semicircle in the EIS diagram represents the resistance when electrons transfer on the pole. The shorter the dimension of the semicircle, this indicates that the resistance of the electronic when it is transferred on the electrode is smaller, and the faster the electron moves on the electrode. This in turn indicates that the conductivity of the nanocomposite electrode material used to modify the electrode is better. Compared with GCE, the semicircle diameter of RHBr/RGO is significantly reduced (Figure 2A), which indicates that RGO's good conductivity accelerates the movement of electrons on the electrode. The experimental results show that the high conductivity of the RHBr/RGO nanocomposite electrode material we proposed significantly promotes the transfer of electrons on the pole surface, which helps to enhance the detection sensitivity of the pole. Figure 2B shows the DPV analysis characteristics of GCE, RGO/GCE and RHBr/RGO/GCE. Compared to the response current of GCE, the response current of RGO/GCE to Cu$^{2+}$ is significantly improved, which is attributed to the good conductivity of RGO. Interestingly, when using RHBr / RGO / GCE, the strongest peeling peak appeared. The results show that RHBr/RGO/GCE has better response performance than RGO/GCE and GCE.

![Figure 2. A): EIS plots of RGO/GCE, GCE and RHBr/RGO/GCE; B): DPASV bights of GCE, RGO/GCE and RHBr/RGO/GCE.](image)

3.3. Optimization of the detection conditions

The pH of the buffer solution dielectric in the DPV electrochemical detection has an effect on the response peak current during the detection. It can be seen from Figure 3A that the dissolution current of the electrode will gradually increase as the pH value of the electrolyte solution increases. When the pH of the electrolyte solution is 4.5, the dissolution current of the pole is the highest. In addition, when the pH of the electrolyte solution is greater than 4.5, the dissolution current of the electrode increasingly decreases. Therefore, we take 4.5 as the optimal pH value in the following detection process. The accumulated potential has an important influence on the peak current of the electrode during the DPV detection process. The optimal cumulative potential was optimized during the experiment. As shown in Figure 3B, when the stacking potential is within the range of -0.1 to -1.3 V, the elution peak current of the electrode gradually becomes higher. When the time exceeds 300s, the peak current of the electrode changes little. Therefore, we take 300s as the optimal accumulation time in the following detection process.
3.4. Interference study
Because there are some other interfering metal ions coexisting in the solution, their presence may affect the Cu\textsuperscript{2+} detection current in the actual sample detection. Therefore, the selectance of the RHBr/RGO/GCE was also studied in this work. As can be seen from Figure 3D, the interference metal ions that may be present in these solutions have little effect on the stripping reaction of Cu\textsuperscript{2+}. This shows that the RHBr / RGO / GCE based on the DPV method we proposed has a very high selectivity for Cu\textsuperscript{2+} detection.

3.5. Detection of Cu\textsuperscript{2+}
Therefore, we conducted DPV experiments on the basis of optimal experimental conditions. As shown in Figure 4A, in the range of $4 \times 10^{-7}$ to $1 \times 10^{-5}$ M, with the increase of copper concentration, the peak current of anode dissolution increases significantly. The detected current value is linear correlation to the concentration of Cu\textsuperscript{2+} in the solution. The linear equation (Figure 4B) is $i_{pc} = 3.08 C_{Cu(II)} - 12.90$, and the correlation coefficient is 0.999. The detection limit of Cu\textsuperscript{2+} is $3.9 \text{ nM}$ ($S/N = 3$).
Figure 4. (A) DPASV responses of the RHBr/RGO/GCE for the detection of different concentrations of Cu^{2+} in acetate buffer solution; (B): Corresponding linear calibration chart of the dissolution peak current of Cu^{2+}.

4. Conclusions
In short, RHBr/RGO nanocomposite electrode materials have been obtained by us through a simple method. GCE modified with RHBr/RGO nanocomposite electrode material has been proved to be able to detect Cu^{2+} in solution by DPV method. The experimental results show that, compared with GCE and RGO/GCE modified electrodes, RHBr / RGO / GCE has a higher sensitivity for the detection of Cu^{2+}. More importantly, our proposed RHBr / RGO / GCE has a very high selectivity for the detection of Cu^{2+}. It is expected that new nanomaterials can provide great potential for the manufacture of electrochemical sensors.

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Notes
The writers declares that there is no competitive economic interest.

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