

Determination of Catechol by Cetyltrimethylammonium Bromide Functionalized Graphene Modified Electrode

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ABSTRACT: A simple and sensitive electrochemical sensor was prepared by using electrodeposition of the cetyltrimethylammonium Bromide (CTMAB) functionalized Graphene (GR) on the glassy carbon electrode (GCE) to determine Catechol (CC) in water. The performance of the CTMAB functionalized GR sensor was studied and the analysis conditions of the CC were optimized. The experimental results showed that, compared with bare GCE, the redox peak current of CC on the modified electrode was obviously enhanced. Under the optimized conditions, the oxidation and reduction peak current all showed a good linear relationship with the concentration of CC from 5 $\mu\text{mol/L}$ to 1000 $\mu\text{mol/L}$. The detection limit of oxidation peak is 2.92 $\mu\text{mol/L}$, and that of reduction peak is 2.44 $\mu\text{mol/L}$. The recovery was founded to be in the range of 92.70 %~101.80 %. Moreover, the sensor could be used for the determination of CC in real samples with satisfactory results. And the mechanism of the sensitization of CC detected by CTMAB-GR modified GCE was discussed preliminarily.

Keywords: Cetyltrimethylammonium Bromide; Catechol; Graphene; Electrochemical Determination

1. Introduction

Catechol (1, 2-dihydroxybenzene, CC) was the isomeric form of dihydroxybenzene moiety. It was generally used in almost all conceivable applications like cosmetics, antioxidants, oil refineries, coal tar, plastic, leather, paint, steel and pharmaceutical industries [1]. The CC can cause headache, fatigue, kidney damage decrease in liver function. Recent studies revealed that the CC induces the DNA damage and can cause cancer in humans. Because of the widespread use of CC and its harmfulness, it was necessary to establish a sensitive and rapid method for detection of CC. Currently, the main methods used to determine CC and its derivatives include high-performance liquid chromatography (HPLC) [2], spectrophotometry [3], electrochemiluminescence [4], chemiluminescence [5], capillary electrophoresis [6] and electrochemical method [7, 8]. Although these methods have their own advantages, the capillary electrophoresis methods probably suffer from complex manipulations and the HPLC separations might be time-consuming. Some spectrophotometric procedures are complex, and some methods requires long heating times or non-aqueous media and so on. Electrochemical methods become more and more popular due to the advantages of simple operation, fast response, low cost, high sensitivity and selectivity.

Recently, carbon nanotubes, metal sulfides and quantum dots have been developed to make the surface of working electrode or as electrode materials [9, 10]. However, the materials are expensive to produce, complicated to manufacture and of limited production. In the latest years, GR has contributed to the fabrication of sensitive sensors due to its physical and electrochemical properties; one of the most surprising is its very specific electrical properties. It attracts interest of many scientists in the field of biological, physical, chemical [11]. A large number of studies have shown that GR has become one of the most ideal electrode materials due to its high specific surface area and high conductivity. And surfactants can effectively prevent the aggregation of nanomaterial and allow them to be well dispersed in water due to surfactants' amphipathic nature. Such as Hexadecyltrimethylammonium bromide (CTMAB), sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate, they are widely used in many analytical methods. The sensitivity, selectivity and reproducibility of the analytical methods were significantly improved when using it as functional materials for the functionalization of graphene [12], for example Zhang et al. prepared a sodium dodecyl benzene sulfonate modified electrode for the selective determination of dopamine [13]. Therefore, they were good dispersants and functionalities in the

preparation of nanomaterial reagents.

In this paper, CTMAB and GR were as materials and GCE was as the basal electrode to prepare the new and simple CTMAB-GR/GCE. And the performance of the sensor of GR functionalized with CTMAB and optimized the analysis condition of CC was studied.

The result showed that the modified electrode was demonstrated to have a quick response, low detection limit and fewer disturbances to detect CC and was successfully applied to the actual sample testing. The procedure for the preparation of the CTMAB-GR/GCE and detection mechanism for CC was as Fig.1.

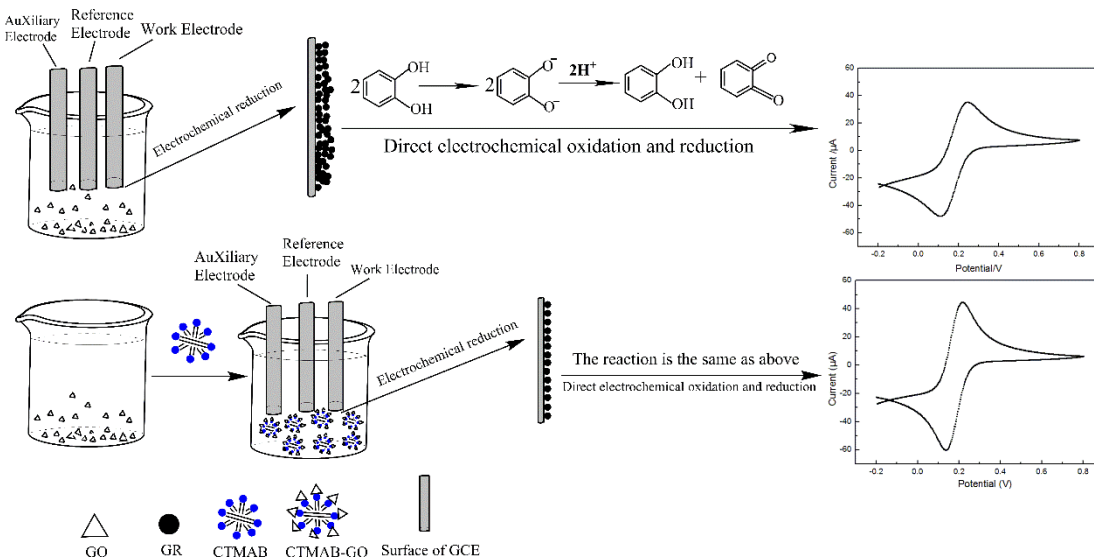


Fig.1 The procedure for the preparation of the CTMAB-GR/GCE and detection mechanism for CC.

2. Experimental

2.1. Instruments and reagents

PGSTAT302N electrochemical workstation (Metrohm Co., Ltd., China) was used to measure the cyclic voltammetric and electrochemical impedance spectroscopy. A three-electrode configuration was employed, the working electrode was CTMAB-GR/GCE (3 mm diameter, or GR/GC, CTMAB/GCE, GCE), saturated calomel electrode and platinum electrode (1 mm diameter) were served as the reference and counter electrodes, respectively; TENSOR27 type Fourier transform infrared spectrometer (BRUKER company, Germany); DX-2077X ray diffraction (Dandong Fang yuan Instrument Co., Ltd., China); Hitachi H-9000NA transmission electron microscope (TEM) (Hitachi High-Technologies Corporation, Tokyo, Japan).

CTMAB, potassium ferricyanide, ethanol and potassium chloride were purchased from Kelong (Chengdu, China) and Catechol (CC) was obtained from Mulan Town, Xindu District, and Chengdu Industrial Development Zone. Phosphate buffer solution (PBS) was prepared by mixing sodium dihydrogen phosphate and disodium hydrogen phosphate. Graphene oxide (GO) was synthesized from graphite powder by modified Hummers method [14, 15]. All other reagents were used for the analysis of pure reagents; all the solutions were prepared in double distilled water.

2.2. The pretreatment of the GCE

A GCE (diameter 3 mm) was polished with 1.0, 0.3, 0.05 μm alumina slurry in turn on a microcloth, followed by ultrasonic cleaning in ethanol and double-distilled water, each for 3 min. Finally, the electrode was treated in the 0.5 M H_2SO_4 by cycling the potential between -0.2 V and 0.8 V (scan rate: 100 mV/s) to obtain stable cyclic voltammetry curve.

2.3. Preparation of CTMAB-GR and Optimization of Preparation Conditions

100 mL GO aqueous solutions with a concentration of 0.5 mg/mL in six beakers, respectively. And then dispersed in an ultrasonic disperser for 1 hour, the GO colloids with good suspension stability were obtained. Different kind of CTMAB-GRs were prepared by ultrasonic dispersion for 1 h after adding 0.08 mg, 25.0 mg, 50.0 mg, 100.0 mg, 150.0 mg and 200.0 mg of CTMAB, respectively. Then they were electrochemically reduced on the surface of the electrode, CTMAB-GR/GCE was obtained. They were used to investigate the

response to 500 μ mol/L CC to determine the optimal dose of CTMAB.

2.4. The preparation of modified electrodes

The pretreated electrode was modified in a CTMAB-GR dispersion by cyclic voltammetry in the range from -1.4 to 0.6 V with 0.1 V/s scanning rate. After drying, the surface was rinsed thoroughly with double-distilled water and the electrode was stored in double-distilled water when not in use. Once prepared, the coated electrode was very stable and could be used for several weeks (with proper care).

2.5. Experimental method

The electrochemical experiments were performed in an electrochemical cell with a three-electrode configuration with PGSTAT electrochemical workstation (Autolab). The electrocatalytic activity of the CTMAB-GR/CGE electrode toward CC was examined by measuring cyclic voltammograms (CVs) in 0.2 M PBS solution containing 500 μ mol L⁻¹ CC. Then CVs were employed to optimize the experimental conditions and differential pulse voltammetry (DPV) at initial potential -0.2 V, terminate the potential 0.6 V, to detect different concentrations of CC solution. The electrochemical impedance spectra (EIS) were carried out in 5 mmol/L Fe (CN)₆^{3-/4-} solution containing 0.1 mol L⁻¹ KCl. The initial potential was 0.2 V and the frequency range was from 10⁻² Hz to 10⁵ Hz.

3. Results and Discussion

3.1. The characterization of GO

GO was characterized by infrared (IR) spectra and X-ray diffraction (XRD), respectively; and the cyclic voltammograms of a GO-modified GCE in GO dispersion at a scan rate of 50 mV/s was drawn. All the test results prove that GO and GR were successfully prepared in this study [16].

3.2. Surfactant selection

The common surfactant - Cetyltrimethylammonium bromide and twelve alkyl sodium sulfate were used for surfactant selection to functionalize GO, and the dispersibility of GO and functional GO were compared each other, the results show that SDS functionalized GO (SDS-GO) has the worst dispersibility and was agglomerated in the solution, the non-functionalized GO also dispersed and settled in the solution, which was obviously separated from the supernatant. Only CTMAB-GO was well-distributed in the solution with no delamination, so CTMAB was chosen as a functionalized surfactant.

3.3. Optimization of modification conditions of CTMAB-GR/GCE.

During the preparation of modified electrode, the amount of CTMAB had a significant impact on the electrochemical performance of functionalized GR, so the amount of CTMAB was optimized; the result was shown in Fig.2 and Fig.3.

As shown in Fig. 2, the dosage of CTMAB had a great impact on the redox peak current of CC, the redox peak current was largest when the quantity of CTMAB was 50.0 mg, so 50.0 mg of CTMAB were chosen as the best preparation conditions of the modified electrodes.

3.4. The characterization of CTMAB-GR

The energy spectra of the restored GR and the CTMAB-GR showed that the atomic percentage of C in GR was 48.86% (Fig.3). While the atomic percentage of C in CTMAB-GR was 57.76% and element N was newly emerged, the content of it was 15.48%. Since C and N were present in CTMAB, it was shown that CTMAB was successfully bound to GR.

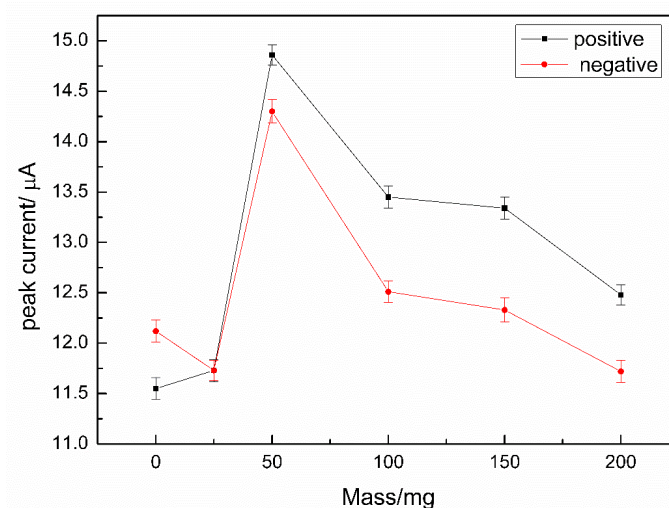


Fig.2 The effect of surface active agent mass on the peak current.

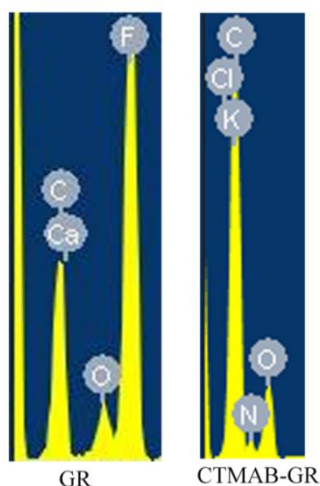


Fig.3 The spectra of GR and CTMAB-GR

3.5. Characterization of electrochemical behavior of CTMAB-GR/GCE

1) Characterization of cyclic voltammetry

The cyclic voltammetry (CV) of bare GCE, GR/GCE and CTMAB-GR/GCE in the 500 $\mu\text{mol/L}$ CC was investigated, respectively. As shown in Fig.4, the peak shape of CC was not good enough and the peak current was small on the bare GCE (a), and they were better on the GR/GCE (b). But on the CTMAB-GR/GCE(c), the peak shape was more symmetrical, the peak current significantly increased and the oxidation peak potential was shifted negatively, the reduction peak potential was shifted positively, the result indicated that the CTMAB-GR had significant electrocatalytic effect on the redox of CC.

Among them, CTMAB-GR has a strong electrocatalysis on the detection of CC, the catalytic mechanism is as follows: (Fig.1). First of all, GO itself is negatively charged because it has oxygen-containing functional groups such as hydroxyl or carboxyl groups, when GO was functionalized with cationic surfactant CTMAB, its charge was neutralized to zero, and then reducing the possibility of agglomeration. Secondly, the micelles formed by CTMAB improve the interface state between GO and water, which makes the compatibility among them enhanced. Instead of agglomeration, GO is homogeneously dispersed in water. Thirdly, surfactants have a controlling effect on the nanometer size of nanomaterial [17]. The addition of CTMAB makes the GO more delicate and uniform, and the ultrasonic wave has a stripping effect on the layered nanomaterial. Therefore, during the ultrasonic preparation of CTMAB-GO, the number of GO layers will be less than that of the non-functionalized GO, the specific surface area is larger and therefore exhibits higher electrochemical activity when it is electrochemically reduced to CTMAB-GR on the electrode surface and used for CC detection. The method of electrochemical reduction on GCE with CTMAB-GO has the advantages of simple, rapid, low cost and more sensitive detection than the method of CdTeQDs/GR [16] modified electrode which we used in the past.

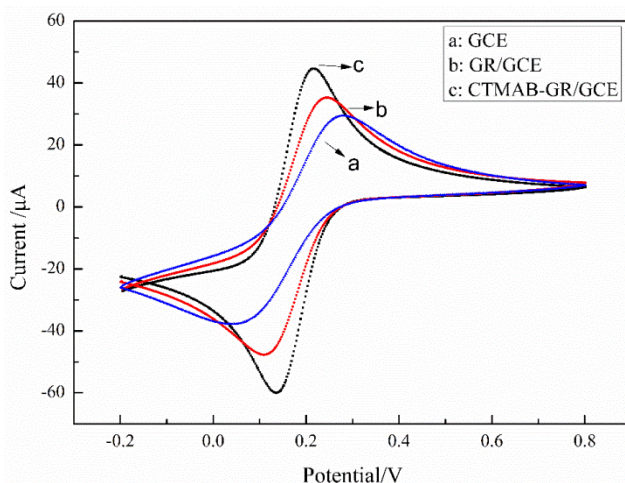


Fig.4 Cyclic voltammograms of GCE (a), GR/GCE (b), CTMAB-GR/GCE (c) in PBS (pH = 7.0) containing 0.5 mM CC.

2) Characterization of EIS

The Electrochemical impedance spectra (EIS) of bare GCE, GR/GCE and CTMAB-GR/GCE was investigated, respectively (Fig.5). The electronic properties of the modified films were evaluated by EIS pattern. The high-frequency semicircle part and the low frequency linear part of Nyquist indicate the electrotransfer limited process and the controlled diffusion process respectively. Meanwhile, the diameter of the semicircle represents the electron transfer resistance.

The radius of the semicircular part of the curve corresponding to the bare GCE was the largest (A), and that of GR/GCE was somewhat smaller (B), indicating that the GR enhances the electrical conductivity of the electrode, and the radius of the CTMAB-GR/GCE decreased obviously and became to the smallest (C). The result showed that CTMAB-GR greatly promoted the electron transfer rate on the electrode.

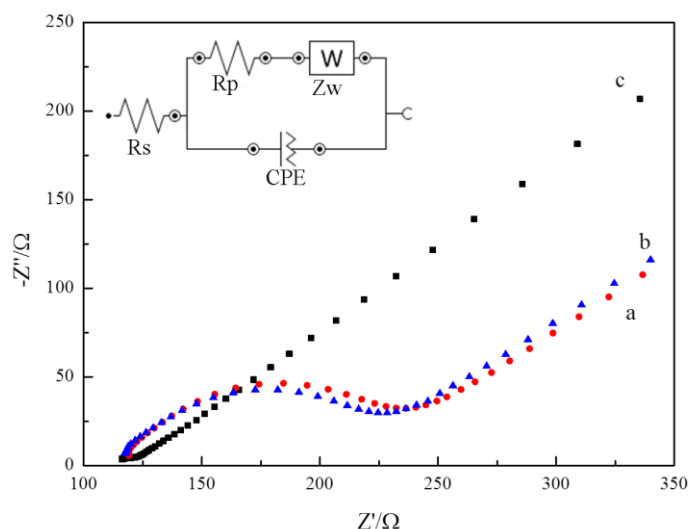


Fig.5 Electrochemical impedance spectroscopy (EIS) of GCE (a), GR/GCE (b) and CTMAB/GR/GCE (c).

Compared with the bare GCE (1.74 k Ω), the electron transfer resistance values (R_p) of GR/GCE (666 Ω) and CTMAB-GR/GCE (49.9 Ω) gradually decreased.

3) Optimization of pH of supporting electrolyte

There were 2 phenolic hydroxyl groups in the structure of CC, which has certain acidity in the solution. Therefore, the pH of the solution has a great influence on its detection. The investigation was carried out in different pH value ranging from 4.0~8.0. As shown in Fig.6 and Fig.7, as the pH gradually increases from 4.0 to 6.0, the anodic peak current and cathodic peak current increase substantially. When the pH was increased from 6.0 to 8.0, these two peaks current gradually decreased, indicating that CC was easier to be oxidized and reduced under acid condition. Considering the sensitivity of the determination of CC, the pH of 6.0 was selected as the optimum value.

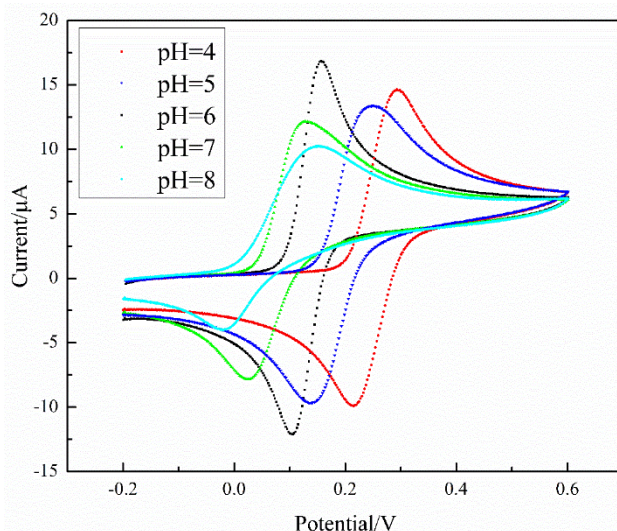


Fig.6 Cyclic voltammograms of different pH (4.0,5.0,6.0,7.0,8.0)

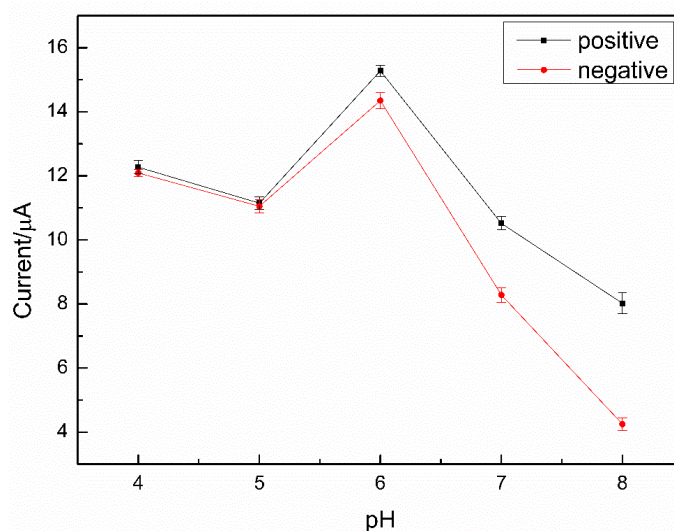


Fig.7 The effect of pH to peak current

The redox peak potential shifts negatively with the increasing of pH, the potential and pH showed a good linear relationship (Fig.8). The results show that protons are involved in the electrode reaction. The linear regression equations could be expressed as:

$$E_{pa} \text{ (mV)} = 476.8 - 46.2pH \text{ (R} = 0.9700\text{)}$$

$$E_{pc} \text{ (mV)} = 455.7 - 58.8pH \text{ (R} = 0.9800\text{)}$$

The slope of the linear relationship between E_{pc} and pH was close to the theoretical value of -58.5 mV / pH . According to the equation: $dE_p / dpH = 2.303mRT / nF$ (m and n are the number of protons and electrons in the reaction) [18], m/n was accumulated as 0.78 and 0.93, respectively. The latter is about 1, it is shown that the electrochemical reaction process is a reaction process with the equal number of electrons and protons.

3.7. Effect of scan rate on peak current and peak potential

1) Effect of scan rate on peak current

As shown in Fig.9 and Fig.10, the redox peak current of CC improved with the increase of scan rate. Both of the oxidation peak current (I_{pa}) and reduction peak current (I_{pc}) of CC showed a good linear relationship with the scan rate from 50 to 700 mV/s. The equations can be expressed as:

$$I_{pa}(\mu\text{A}) = 0.0405v + 15.97252 \text{ (R} = 0.9827\text{)}$$

$$I_{pc}(\mu\text{A}) = -0.0358v - 15.58314 \text{ (R} = 0.9739\text{)}$$

It meant the oxidation of CC on CTMAB-GR/GCE was a typical adsorption controlled electrode process. Although the quicker the scanning rate was, the larger the peak current was, high scanning rate corresponded to a big background current, which had an adverse influence on the electrochemical determination, so in this experiment, we chose 50 mV/s as the optimal scanning rate.

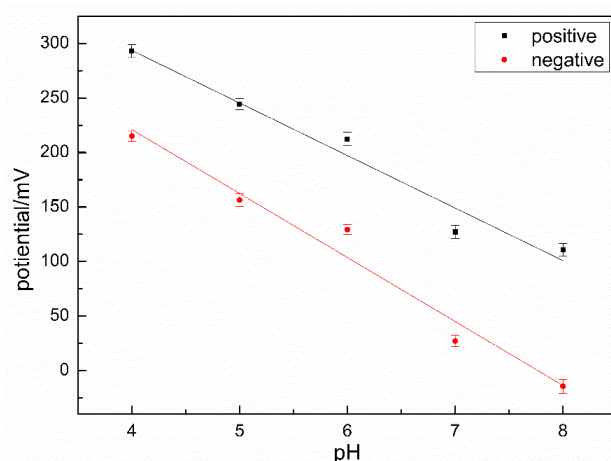


Fig.8 The effect of pH to peak potential

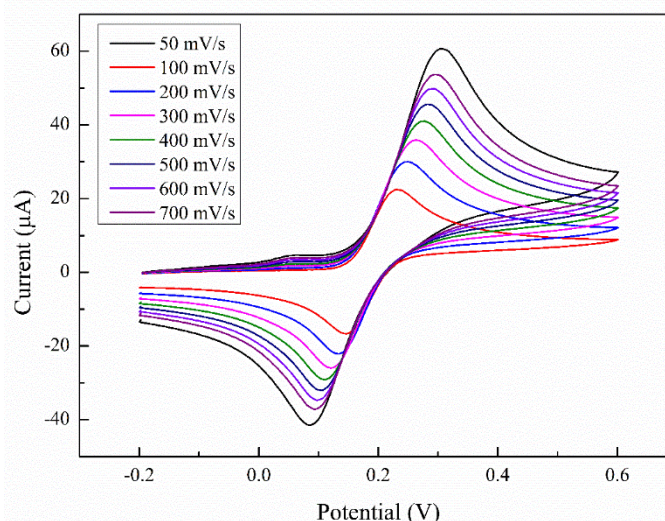


Fig.9 CVs of different scan rate in 500 $\mu\text{mol/L}$ CC (a-g: 50, 100, 200, 300, 400, 500,600and 700 mV/s)

2) Effect of scan rate on peak potential

The Fig.11 shows that the peak potential was linear with the logarithm of the scanning rate over the range of 0.05V/s to 0.2 V/s. While the linear equation can be expressed as follows as the scanning rate: 200 mV/s ~700 mV/s.

$$E_{pa}(\text{V}) = 0.30655 + 0.08821 \log v(\text{V/s}) \quad (R=0.9986)$$

$$E_{pc}(\text{V}) = 0.08419 - 0.07063 \log v(\text{V/s}) \quad (R=0.9982)$$

According to the Laviron model [19], the slope value of the equations of E_{pa} and E_{pc} can be expressed as $2.303RT/(1-\alpha)$ nF and $-2.303RT/\alpha nF$, the ratio of the slope of E_{pa} and E_{pc} was $\alpha/\alpha-1$, then we calculated based on the linear regression equation of logarithm of peak potential and scanning rate. Electron transfer coefficient (α) was 0.56.

3.8. Linear range and limit of detection

Under the optimal conditions, a series of different concentrations of CC solutions were measured by CV to investigate the linear range and limit of detection at the potential of -0.2 ~ 0.6 V. The oxidation peak current and reduction peak current were correspondingly enhanced with the increase of the concentration (Fig.12). When the concentration of CC was in the range of 5.0 $\mu\text{mol L}^{-1}$ to 1000 $\mu\text{mol L}^{-1}$, both of the peak current of oxidation and reduction showed a good linear relationship with the concentration and the relationship can be expressed by

the following equations:

$$I_{pa} (\mu A) = 0.0242C - 0.219 (\mu mol / L) (R = 0.9962),$$

$$I_{pc} (\mu A) = -0.0246C + 0.2016 (\mu mol/L) (R=0.9946).$$

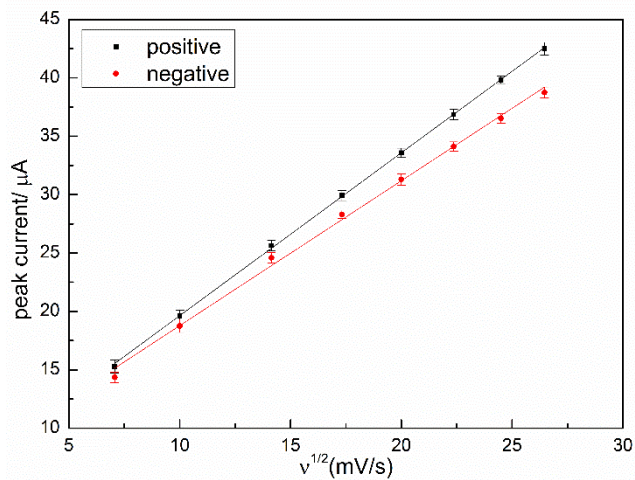


Fig.10 The relationship between peak current and $v^{1/2}$

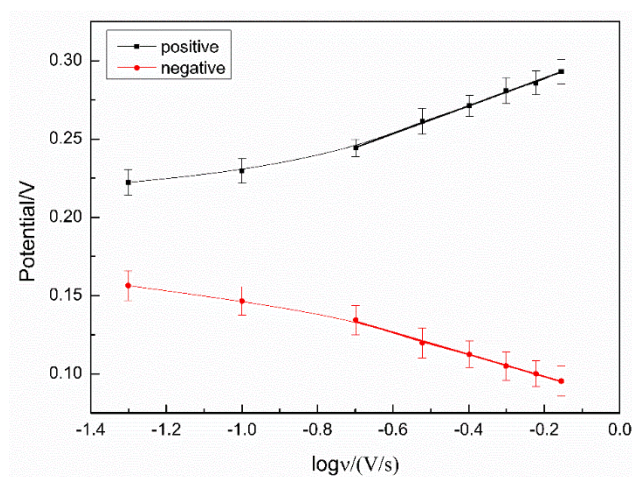


Fig.11 The relationship between E_p and $\log v$

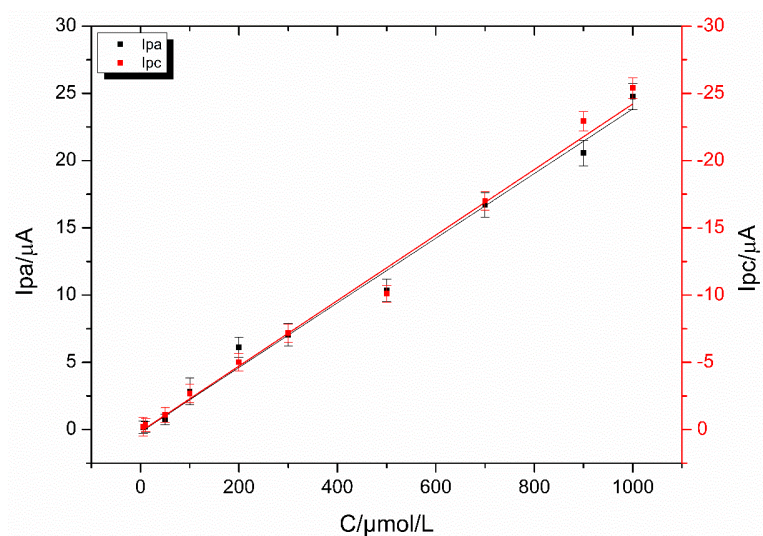


Fig.12 The linear relationship CC (5.0 $\mu mol/L \sim 1000 \mu mol/L$) and peak current

The detection limits was 2.92 $\mu mol/ L$ and 2.44 $\mu mol/ L$, respectively.

Table1. Performance comparison of the fabricated electrode in CC with other electrodes.

Electrodes	Method	Linear range ($\mu\text{mol/L}$)	Detection limit ($\mu\text{mol/L}$)	References
Pt/ZrO ₂ -RGO/GCE	DPV	1-400(I _{pa}); 1-1000(I _{pc})	0.4	1
RGO-MWNTs ^a /GCE	DPV	5.5-540	1.8	8
BG ^b /GCE	DPV	1-75	0.2	7
CdTe QDs/GR/GCE	DPV	30-1000	18.28	16
AuNPs-MPS ^c /CPE	SWV ^e	30-1000	1.1	20
Au@NG-PPy ^d /GCE	Amperometric	0.1-0.9	0.0016	21
CTMAB/GR/GCE	CV	5.0-1000	2.92(I _{pa}); 2.44(I _{pc})	This paper

^a MWNTs: multi-wall carbonnanotubes ^bBG: Boron-doped grapheme ^c AuNPs-MPS: gold nanoparticles mesoporous silica modified carbon paste electrode ^d Au@NG-PPy: gold nanoparticles decorated nitrogen doped grapheme covalently grafted polypyrrole ^e SWV: square wave voltammetry

The comparison of CTMAB-GR/GCE with other modified electrodes for the determination of CC was listed in Table 1. It can be seen that the CTMAB-GR/GCE offers a lower detection limit and wider linear range than other modified electrodes. Moreover, this method is based on cyclic voltammetry, the redox peaks have a good linear relationship with the concentration, which can be detected simultaneously and compared with each other to obtain more accurate detection results.

4. Reproducibility and stability

The stability and reproducibility of the CTMAB-GR/GCE were measured by CV under the optimized conditions. The 1000 $\mu\text{mol/L}$ CC was investigated in seven successive measurements using the same CTMAB-GR/GCE and the relative standard deviation (RSD) of the oxidation peak current was 0.45%. Meanwhile, the same concentration of CC was also measured by four same electrodes of CTMAB-GR/GCE and the RSD was 0.41%. The results indicate that the CTMAB-GR/GCE had a wonderful reproducibility. The modified electrode was placed at room temperature for a period of time. Analysis results show that the electrode response did not change significantly, indicating that the electrode has good stability.

5. Interference experiment

Under the optimized conditions, the various possible interfering species were investigated. The fixed concentration of CC is 500 $\mu\text{mol/L}$, and the maximum relative error is less than 5%. The experiment results showed that no interference could be observed for the following compounds: 180-fold K⁺, Na⁺, Ca²⁺, Fe³⁺, Al³⁺, NO³⁻, Cl⁻, Mg²⁺, SO₄²⁻, 100-fold of glucose, ascorbic acid and 50-fold of glutamic acid, bisphenol A, resorcinol and hydroquinone. These results indicated the modified electrode had good selectivity and the present method was adequate for the determination of CC in the solution with these interfering species.

6. Real samples analysis

CTMAB-GR/GCE was applied to determine the CC in a real industry and lake water (collected from Chengdu University of Technology, China) and Surface water (collected from IT Avenue Pi country Chengdu city Sichuan province). CC was not detected in these industry and lake water, then addition recovery was used to verify the reliability of this method (Table 2). Each sample solution undergoes three parallel determinations, and the RSD was 5% below, which demonstrated the reliability of the proposed method. The recovery of CC was in the range from 92.70 % ~ 101.80 %, which indicated that the modified electrode was suitable for accurate and sensitive determination of CC in real samples.

Table 2. The determination of CC in industry water and lake water.

Samples	Added CC ($\mu\text{mol/L}$)	Found CC ($\mu\text{mol/L}$)	RSD (%)	Recovery (%)
Industry water	10.00	10.18	4.81	101.8
		9.94		99.40
		9.27		92.70
		15.23		101.5
Lake water	15.00	15.07	1.13	100.5
		14.89		99.27
		20.17		100.9
		20.04		100.2
Surface water	20.00	19.92	0.62	99.60

7. Conclusions

In this paper, a novel and simple CTMAB-GR/GCE modified electrode to detect CC was prepared and the electrocatalytic redox behaviors of CC were also studied by CV. The modified electrode improved the absorptivity and electrocatalytic redox activity for CC because of the larger surface area, more efficient electron transfer rate of CTMAB-GR than GR modified by CTMAB before. Additionally, the modified electrode had a fast response and good stability and reproducibility, the recovery was in the range from 92.70 % to 101.80 %, when it was used to analyze the real samples. The result was satisfactory.

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