

Determination of Gallic Acid in Tea by a Graphene Modified Glassy Carbon Electrode

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The determination of gallic acid (GA) content by a graphene modified glassy carbon electrode (graphene/GCE) was studied. The electrochemical behavior of GA on this electrode was studied by cyclic voltammetry (CV), and the standard curve was constructed by differential pulse voltammetry (DPV). The results indicate that graphene has a good catalytic effect on GA in phosphate buffer (PBS) and shows a linear response toward GA in the 8.0×10^{-8} to 2.0×10^{-5} mol·L⁻¹ concentration range. The detection limit is 1.2×10^{-9} mol·L⁻¹. This proposed determination for GA on graphene/GCE was carried out in the presence of potentially interfering compounds such as sorbic acid, tartaric acid, ascorbic acid and glucose. The content of GA in green tea was determined by this method, and the recovery was 97.9% - 100.6% with satisfactory results.

Keywords: Gallic acid; Differential pulse voltammetry; Graphene; Electrochemical determination

1. INTRODUCTION

Gallic acid (GA), 3, 4, 5-trihydroxybenzoic acid (Figure 1), is a type of phenolic acid. It can be found in many plants such as tea leaves, gallnuts, sumac, etc. [1, 2]. GA is not only a raw material used in industry (such as in tanning, ink dyes and manufacturing of paper) but it is also widely used in the food and pharmaceutical industry due to its broad range of bioactivities and pharmacological activities, including anti-inflammatory, antihistaminic and antitumor activities [3,4]. Therefore, this study for quantitative determination of GA in food and medicine is necessary.

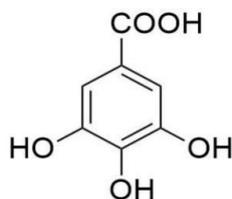


Figure 1. Molecular structure of GA

In the past few years, some techniques have been used successfully for the determination of GA in different samples, for example, HPLC [5, 6], high-performance thin-layer chromatography [7], the pulse perturbation technique [8], electrochemical sensors and nanosensors [9-17]. Electrochemical techniques have focused more attention on the electrochemical oxidation of hydroxyl groups. The direct electrochemical oxidation of GA is also possible.

Nanosensors have attracted attention because they are reliable, ultrasensitive and low cost, especially for drug and food analysis [18, 19]. Compared to other nanosensors, graphene has been widely used as an electrode material because of its unique electrochemical properties and important technological applications. A graphene modified glassy carbon electrode (graphene / GCE) is simple to make, reusable, and inexpensive to prepare [18, 19]. Although several electrochemical methods have been developed for GA determination, to the best of our knowledge, GA determination by graphene/GCE has not been reported.

In this work, the analysis of GA by an electrochemical sensor based on graphene is described. The results indicate that graphene has a good catalytic effect on GA in PBS. This sensor is selective for GA even in the presence of some potentially interfering compounds. The modified graphene / GCE is highly reproducible, stable and sensitive, which indicates that it has promise for novel applications in the detection of GA in tea samples.

2. EXPERIMENTAL INFORMATION

2.1 Apparatus and reagents

Voltammetry measurements were carried out using CHI660D electrochemical work stations (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The three-electrodes used in the electrochemical experiments are the graphene / GCE used as a working electrode, the saturated Ag/AgCl electrode and a Pt wire, which is used as a reference and counter electrode. The ultrasonic cleaner (Kunshan, China) is the KH-100DB, and the pH of the solution was adjusted by using a pH meter (module PHS-3B, Shanghai, China). Agilent1220 HPLC system was used. A quartz subboiling high-purified water distiller (SYZ-550) (Jiangsu, China) was also used.

GA was purchased from Sigma-Aldrich (Shanghai, China). Green tea was bought from a local supermarket that can be directly used. Samples of tea liquid and quantitative amounts of pH3.0 PBS buffer solution were taken into volumetric flask and constant-volumed 20 mL to be measured, respectively. Graphene was made in 2012 by our team. Its preparation method in the laboratory and spectra of IR, SEM and TEM to characterize it were reported in a previous publication [20]. Thus, 0.5 mg graphene flour was dispersed in 1.0 mL of double-distilled water under ultrasonic stirring to form a homogeneous solution. PBS was obtained using a solution of sodium phosphate dibasic ($0.20 \text{ mol}\cdot\text{L}^{-1}$) and citric acid ($0.10 \text{ mol}\cdot\text{L}^{-1}$). Other chemicals used in this work were of analytical grade which have been used directly without especial purification. Double-distilled water was used in our experiments.

2.2 Preparation of the graphene / GCE

Before modification, GCE was polished carefully with a polishing cloth and suspension of alumina slurry. Then, GCE was rinsed with nitric acid (volume ratio 1:1), absolute ethanol and distilled water in an ultrasonic bath for 1 min, respectively. A specific amount of graphene suspension droplets were dropped on the surface of the electrode by a micropipette. After drying under an infrared lamp, the graphene modified electrode was obtained. The graphene modified electrode can be used for multiple determinations by scanning in PBS (pH=3.0).

2.3 Experimental methods

Electrochemical experiments were carried out by a typical three-electrode system connected to the CHI660D. Cyclic voltammetry (CV) or differential pulse voltammetry (DPV) methods are used to study the electrochemical test of GA. The scanning curve was recorded when the electrode was immersed in the measured liquid. After each scan, the electrode was placed in PBS (pH=3.0) and scanned until the peak was no longer detected and stored for the next use.

3. RESULTS AND DISCUSSION

3.1 The amount of graphene

The thickness of graphene on the surface of GCE has a great influence on the determination of GA. Graphene / GCEs were prepared on GCE by removing 1-10 μ L graphene (0.5 mg \cdot mL⁻¹) with a liquid pipette. The experimental results for the determination of GA under the same conditions showed that the oxidation peak current (i_{pa}) of GA increased with an increase in volume in the range of 1 to 5 μ L, and the peak decreased with an increase in concentration in the range of more than 5 μ L. This result may be due to an increase in the number of reaction sites on the surface of GCE, as the electron transfer rate and the reaction sensitivity increased. On the other hand, a continuous increase of the concentration results in a thicker graphene coating, and hindered electronic transmission, increased difficulty in substrate diffusion to the surface of the electrode, and decreased oxidation peak current was observed. This is consistent with the provisions publication [21].

3.2 Study of the electrochemical behavior of GA

Figure 2 shows the voltammetric curves for the same concentration of GA on bare (Figure 2, a) and graphene modified electrodes (Figure 2, c) under the same conditions, and the voltammetric curve of a solution of PBS (pH=3.0) on graphene modified electrodes is included for comparison (Figure 2, b). It can be seen that (Figure 2, b), there is no oxidation peak was observed in the absence of GA at a graphene / GCE in the potential window range from -0.4 to 1.2 V. There is only a small oxidation peak (8.4 μ A) observed for the bare electrodes (curve a), while a large oxidation peak (27.96 μ A) was

observed from graphene / GCE (curve c). The results showed that peak current improved significantly, suggesting that the graphene / GCE provided large surface area and enhancing the peak current for the detection of GA.

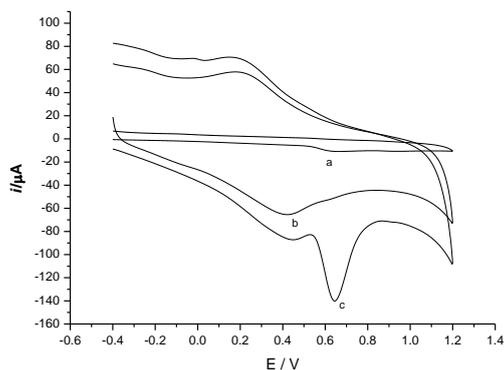


Figure 2. Cyclic voltammograms (CVs) of (a) bare GCE and (c) graphene / GCE with $8 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ GA in PBS (pH=3.0). Cyclic voltammogram of (b) graphene / GCE without GA in PBS (pH=3.0).

3.3 Optimum Conditions for the Determination of GA

3.3.1 Optimal pH

Figure 3 shows CVs for the determination of GA in different pH solutions under the same conditions with scanning rate of $0.1 \text{ V} \cdot \text{S}^{-1}$ after 25 s. The results show that the oxidation peak potential of GA decreased with an increase in pH [16]. The linear equation is $E_{\text{pa}} = 0.91 - 0.10 \text{ pH}$, $R = 0.9976$, which indicates that the reaction on the modified electrode involves protons. We can further see that the oxidation peak current reached its maximum value at pH=3.0, so a pH of 3.0 was selected for this experiment.

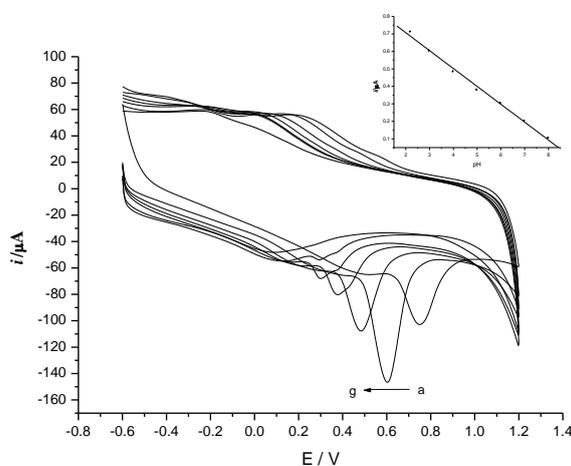


Figure 3. CVs of $8 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ GA at a graphene / GCE at different pH. Insert is linear relationship between oxidation peak potential of GA and pH (a - g: 2.2, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0). Scan rate: $0.1 \text{ V} \cdot \text{s}^{-1}$ with stirring 25s.

3.3.2 Optimum Scanning Rate

The oxidation peak current of GA increased with an increase in scanning rate (Figure 4). The oxidation peak current of GA (i_{pa}) has a linear relationship with the scanning rate (Insert of Figure 4), as shown in equation: $i_{pa}=4.17\times 10^{-6}+2.23v$ ($V\cdot S^{-1}$), and the correlation coefficient is $R=0.9973$. This demonstrates that the oxidation of GA is an adsorption-controlled process [22] on the graphene/GCE. With an increase in the scanning rate, the peak deformation was poor, and the sensitivity was reduced. Therefore, a scanning rate of $0.1 V\cdot S^{-1}$ was selected for further studies.

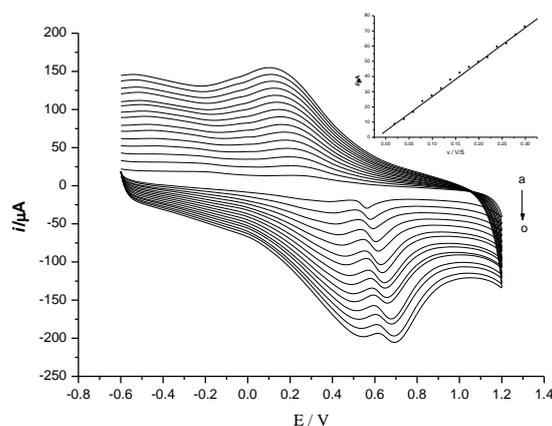


Figure 4. CVs of $8.00\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ GA in PBS (pH=3.0) at a graphene / GCE at different scan rate. Insert is the plot of peak currents of GA versus scan rates (a ~ o: 0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16, 0.18, 0.2, 0.22, 0.24, 0.26, 0.28, 0.3 $V\cdot S^{-1}$).

3.3.3 Determination of the Optimum Stirring Time

Because GA is adsorbed on the surface of graphene / GCE, the adsorption time of GA has a great influence on the determination of the optimum stirring time. Under the same conditions, the peak current of GA oxidation was recorded. The results show that i_{pa} of GA increases gradually with stirring time from 10 to 25 seconds and reaches its maximum at 25 seconds; therefore, the best adsorption time is 25 seconds.

3.4 Standard curve and detection limit

The standard curve of GA was determined by CV and DPV. The experimental results showed that the DPV method was more sensitive than the CV method. Therefore, a standard curve of GA was determined by DPV. The results are shown in Figure 5. It can be seen that the response of graphene/GCE increased for various concentrations ranging from 0.02 to $10 \mu\text{mol}\cdot\text{L}^{-1}$. The presented sensors have good catalytic activity for GA which is very comparable with previously reported GA sensors [10-17]. The i_{pa} of GA has a good linear relationship ($y = 1.1\times 10^{-6} + 1.01c$) within the concentration range of 2.0×10^{-8} to $2.0\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in pH=3.0 PBS. The correlation coefficient is $R = 0.9963$. When the standard

addition method was used to increase the concentration to $1.2 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$, The i_{pa} of GA appeared, so the detection limit was $1.2 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$.

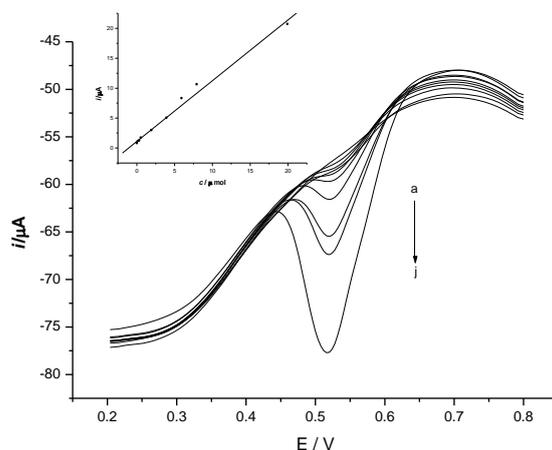


Figure 5. DPV curves of different concentrations of GA in PBS (pH=3.0). Insert is linear relationship between GA concentration and oxidation peak current of GA. (Each of the numbers from a to j corresponds to a concentration of 8.0×10^{-8} , 2.0×10^{-7} , 4.0×10^{-7} , 6.0×10^{-7} , 8.0×10^{-7} , 2.0×10^{-6} , 4.0×10^{-6} , 6.0×10^{-6} , 8.0×10^{-6} , $2.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, respectively)

The comparison of the proposed sensor with other reported sensors for the determination of GA have been done. The results are shown in Table 1.

Table 1. Comparison of different electrodes for GA

| Electrode | Method | Linear range ($\mu\text{mol} \cdot \text{L}^{-1}$) | LOD ($\mu\text{mol} \cdot \text{L}^{-1}$) | Reference |
|----------------------|-------------|--|---|-----------|
| GCE/PEI-rGO | LSV | 0.58-58 | 0.41 | 10 |
| GCE/PEP | DPV | 1-20 | 0.06 | 11 |
| GE/TH/NICF | Amperometry | 4.99-1200 | 1.66 | 12 |
| CPE/SiO ₂ | DPV | 0.8-100 | 0.25 | 13 |
| AgNP/Delph/GCE | Amperometry | 0.60-625.80 | 0.28 | 14 |
| Graphene/PM | Amperometry | 0.1-728.9 | 0.027 | 15 |
| ASPCE | Amperometry | 0.01 -1799.6 | 0.031 | 16 |
| APTS@GO/PP | DPV | 0.006-2000 | 0.0017 | 17 |
| AH-SDS/GCE | DPV | 0.08-20 | 0.0012 | This work |

Compared with several modified electrodes, the proposed method was better or comparable to those previous reported methods [10-17]. It showed a wide linear range and a low LOD. The results indicate that graphene has a good catalytic effect on GA.

3.5 Analytical application

Samples of 2, 4, and 6 mL tea liquid and quantitative amounts of pH=3.0 PBS buffer solution (No. 1, 2, 3) were transferred into a volumetric flask and adjusted to constant volume. The oxidation peak currents were measured with the standard addition method, and the recovery rate was calculated. The results of the measurements and calculations are shown in Table 2. The results have been compared with standard method of HPLC.

Table 2. Results of the analysis of GA in samples (n=6)

| Sample | Added($\mu\text{mol}\cdot\text{L}^{-1}$) | Found($\mu\text{mol}\cdot\text{L}^{-1}$) | Recovery (%) |
|--------|--|--|---|
| 1 | 1.00 | 0.979 ^a ,0.985 ^b | 97.9 ^a , 98.5 ^b |
| 2 | 10.00 | 9.809 ^a ,10.29 ^b | 98.09 ^a , 102.9 ^b |
| 3 | 20.00 | 20.11 ^a ,19.92 ^b | 100.6 ^a ,99.6 ^b |

a: this work; b:HPLC method

It can be seen clearly that this proposed method was successfully applied to the determination of GA in tea samples. The analysis results obtained in this work were compared with those obtained by the HPLC method. Table 2 shows the measurement results obtained by the proposed method (Table 2a) and the HPLC method (Table 2b). The analysis results obtained using this proposed method were consistent with those obtained by the HPLC method. It can be seen that this sensor was successfully applied to the determination of GA.

3.6 Reproducibility

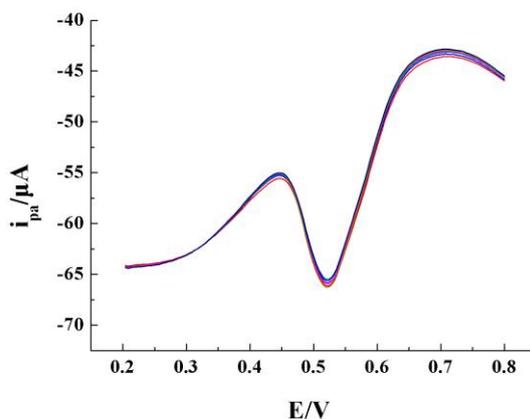


Figure 6. DPV curves for six times determination for $8.00 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ GA in PBS (pH=3.0) by a graphene / GCE

The reproducibility of the graphene / GCE was also investigated. The DPV method was used to determine $8.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ GA solution on graphene / GCE and was repeated 6 times (Figure 6).

The relative standard deviation of the oxidation peak current, measured six times, is RSD=1.33%, which shows that the graphene / GCE has good reproducibility.

3.7 Interference experiment

The interference experiment of GA with a concentration of $8.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ was carried out based on optimized conditions. The results showed that the presence of 150 times the typical expected concentration of Ca^{2+} , Fe^{3+} , Cu^{2+} , Na^+ , K^+ , PO_4^{3-} , CO_3^{2-} , Cl^- and NO_3^- , 100 times typical expected concentration of sorbic acid, tartaric acid, ascorbic acid and glucose, 10 times typical expected concentration of uric acid, salicylic acid, benzoic acid and phenol did not interfere with the determination of GA (the relative measurement error was less than 5%). Therefore, the present electrode has good selectivity.

From these above reports, it can be seen that graphene sensor can enhance the sensitivity of the electrode. It exploited a new way to determine GA in tea. It showed a wide linear range and a low LOD with several modified electrodes (Table 1), suggesting that this proposed method was suitable for the determination of GA. It also can be seen that this method has good recovery and precision in real samples from Table 2.

4. CONCLUSIONS

The results indicate that graphene has a good catalytic effect on GA in PBS and shows a response that is linear in the 8.0×10^{-8} to $2.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ GA concentration range. The detection limit is $1.2 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}$. This proposed determination for GA on graphene / GCE was carried out even in the presence of some potentially interfering compounds such as sorbic acid, tartaric acid, ascorbic acid and glucose. The modified electrode is highly reproducible, stable and sensitive. The content of GA in green tea was determined by this method, and the recovery was 97.9%-100.6% with satisfactory results.

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