Int. J. Electrochem. Sci., 12 **(2017)** 8504 – 8515, doi: 10.20964/2017.09.48

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Simultaneous Quantitation of Caffeic Acid and Ferulic Acid Based on Graphite-like C_3N_4/chitosan Modified Film

Lijun Jing[1], *Jun Lin*[1], *Qiqi Fei*[1], *Haowei Tang*[3], *Xiaodi Yang*[1,*], *Chong Sun*[2,*]

[1] Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China and Changzhou Innovation & Development Institute of Nanjing Normal University, Changzhou 2130000, China
[2] Institute of Agricultural Products Processing, Jiangsu Academy of Agricultural Sciences, Nanjing 210014, P. R. China
[3] Nanjing Foreign Language School, Nanjing 210008, China
[*]E-mail: yangxiaodi@njnu.edu.cn, sunchong0106@163.com

Received: 18 May 2017 / *Accepted:* 11 July 2017 / *Published:* 13 August 2017

Caffeic acid (CA) and ferulic acid (FA), as the simple phenolic acids, widely exist in plants and food. In this experiment, a novel method based on graphite-like carbon nitride (g-C_3N_4) and chitosan (CS) was applied to determinate CA and FA in food samples. X-Ray diffraction (XRD), fourier transform infrared spectrometer (FTIR), ultraviolet visible spectrophotometer (UV-*vis*) and transmission electron microscope (TEM) were illustrated that g-C_3N_4 was synthesized successfully and had a unique two-dimensional structure. Under the optimized conditions, including the scan rate, pH and so on, the modified electrode had a sensitive response to CA and FA in the range of 1-30 μg/mL and 5-30 μg/mL with the detection limits of 0.354 μg/mL and 4.964 μg/mL (S/N=3), respectively. The electrochemical method showed satisfactory results and provided a new approach to determinate phenolic acids with many advantages, such as rapid response, easy operation, low cost and highly sensitive.

Keywords: Graphite-like carbon nitride; Caffeic acid; Ferulic acid; Electrochemical determination

1. INTRODUCTION

Phenolic acids are a kind of organic acids containing phenol rings and they have many pharmacological functions [1, 2]. Caffeic acid (CA) and ferulic acid (FA), as the simple phenolic acids, widely exist in plants and food. CA can be used as antibacterial and antiviral drugs, and is mainly gotten from tomatoes and potatoes. The content of CA in the human body principally depends on the intake of coffee. FA is usually applied for the treatment of cardiovascular and cerebrovascular diseases. Due to its good antioxidant activity and antibacterial property, FA is also used for food preservative. Now, FA is added in sports food because it can stimulate the secretion of hormones. Thus, more and more attention has been attracted for their content in medicine and food at present. Many medicaments prefer to choose CA and FA as the key indicators of their quality. And they have been approved as a food additive in many countries to improve the nutrition. As the result, it is important to establish a convenient and sensitive method to determinate CA and FA.

Up till the present moment, various analytical methods are applied for the determination of phenolic acids, such as photochemical method, chromatography, electrochemical analysis and so on. Fourier transform near infrared spectroscopy (FT-NIR) was used to prove CA in Radix Salvia Miltrorrhiza extract solutions by Wenlong [3]. Coralie Martin and his colleagues utilized ultraviolet visible spectrophotometer (UV-*vis*), fluorescence spectroscopy and Raman spectra to analyze CA and other hydroxycinnamic acids in white wines [4]. Chromatography is the major method to detect CA and FA for its high sensitivity and good selectivity. Bartnik and Males all used thin-layer chromatographic (TLC) for the qualitative analysis of CA and FA [5, 6]. Xu et al. and had selected high performance liquid chromatography (HPLC) and ultra-high performance liquid chromatography (UPLC) as the analytical instruments to detected CA or FA [7-10]. Lee used capillary chromatography (CE) for the determination of CA and FA [11]. Recently, phenolic acids were also identified by mass spectrum (MS), capillary electrophoresis-electrospray ionization mass spectrum (CE–ESI/MS), UPLC–MS/MS and high performance liquid chromatography-diode array detector-electrospray ionization mass spectrometer (HPLC-DAD-ESI-MS^n) [12-14]. However, these methods all carried out with specific instruments, complex operation and a mass of organic solvents, which would be environment unfriendly. In contrast with these methods, electrochemical analysis was a superior method due to its low cost, fast response, good sensitivity and selectivity [15]. JerônimoRaimundo Oliveira-Neto and his colleagues found that the determination of CA in coffee samples with electrochemistry and chromatography had no difference [16]. Until now, there were few reports about the analysis of phenolic acids by electrochemical method.

Graphite-like carbon nitride (g-C_3N_4) was a two-dimensional material and had the honeycomb mesh structure which was similar to graphene [17]. It was composed of carbon and nitrogen atoms with sp^2 hybrid orbitals [18]. In g-C_3N_4, each layer piled up one by one and it was beneficial for the transfer of electron among different layers [19]. It was well known that g-C_3N_4 had many advantages, such as predominant photocatalytic activities [20]. Nowadays, g-C_3N_4 has been used in photocatalyst and fluorescent probe [21, 22]. Due to its large specific surface area, strong adsorption ability and well electro-conductibility, it can be applied to the electrochemical determination.

In this paper, we attempted to employ g-C_3N_4 to construct modified electrode for the determination of CA and FA. g-C_3N_4 was one-step synthesized by heating melamine directly and was characterized by X-Ray diffraction (XRD), fourier transform infrared spectrometer (FTIR), UV-vis and transmission electron microscope (TEM), respectively. Then, CA and FA were quantitatively analyzed by the modified electrode which was based on g-C_3N_4 and chitosan (CS). The prepared electrode was employed to determinate CA and FA in real samples, such as juice, coffee and so on. This method showed satisfactory results and provided a new ideal for the detection of phenolic acids.

2. EXPERIMENTAL SECTION

2.1. Materials

Melamine (> 99.0%), caffeic acid (CA, > 99.0%) and ferulic acid (FA, > 99.5%) were all purchased from Aladdin Reagent Co., Ltd in Shanghai. CS, KCl, $K_3Fe(CN)_6$, $K_4Fe(CN)_6\cdot 3H_2O$, $CH_3COONa\cdot 3H_2O$, CH_3COOH, CH_3CH_2OH, NaOH and HCl were provided by Sinopharm Chemical Reagent Co., Ltd in Nanjing. 3, 4-ethylenedioxythiophene (EDOT) and poly (sodium-p-styrenesulfonate) (PSS) were obtained from D&B Corp. in Shanghai. Carboxyl graphene (CGr) was purchased from Nanjing XFNANO Materials Tech Co.,Ltd. All solutions were prepared with ultra-pure water. Acetate buffer solutions (ABS) were prepared by $CH_3COONa\cdot 3H_2O$ and CH_3COOH, and various pH values were adjusted with HCl and NaOH.

2.2. Synthesis of g-C_3N_4

In the experiment, g-C_3N_4 was synthesized by melamine which was heated directly at 520 ℃ for 4 h in muffle [23] and the color of product was turned from white to primrose. To prepare nanosheets of g-C_3N_4, g-C_3N_4 bulk was ground into fine particles and then dissolved in ultra-pure water with the concentration of 600 μg/mL. Before used, the suspension needed to be ultrasound for 6 h [24, 25].

2.3. Preparation of g-C_3N_4/CS/GCE

Prior to each electrode modified, glass carbon electrodes (GCE, D=3 mm) should be polished by 0.3 and 0.05 μm α-$A1_2O_3$ slurry, and then washed ultrasonically with absolute ethanol for 30 seconds and cleaned with ultra-pure water for few times. After that, GCE was dried at room temperature. 4 μL of prepared g-C_3N_4 nanosheets were dropped on the surface of the undefiled GCE and dried in the air. Then, g-C_3N_4/GCE was modified with 5 μL of 1% CS and dried at room temperature. Thus, the g-C_3N_4/CS/GCE was prepared. CGr/CS/GCE was modified according to g-C_3N_4/CS/GCE. Poly-3,4-ethylenedioxy-thiophene/g-C_3N_4/CS/GCE (PEDOT/g-C_3N_4/CS/GCE) was prepared by electro-polymerized on the g-C_3N_4/CS/GCE in a solution which contained 0.01 M EDOT and 0.1 M PSS [26].

2.4. Pretreatment of real samples

In the experiment, practical water samples were obtained from Xuanwu Lake, Qinhuai River, Changjiang River and tap-water. Juice (Nongfu Spring) and coffee (Nestle) samples were purchased from local supermarket. Before detection, samples were pretreatment as following. Practical water samples were filtrated for three times to remove insoluble impurities and pH values were adjusted to 4.5 by ABS. 1.00 g coffee powered was dissolved in 100 mL ultra-pure water and 2 mL solution was added into 50 mL volumetric flask and diluted with ABS (pH=4.5) to the mark line. And 2 mL of juice was diluted with ABS (pH=4.5) to 50 mL.

2.5. Methods

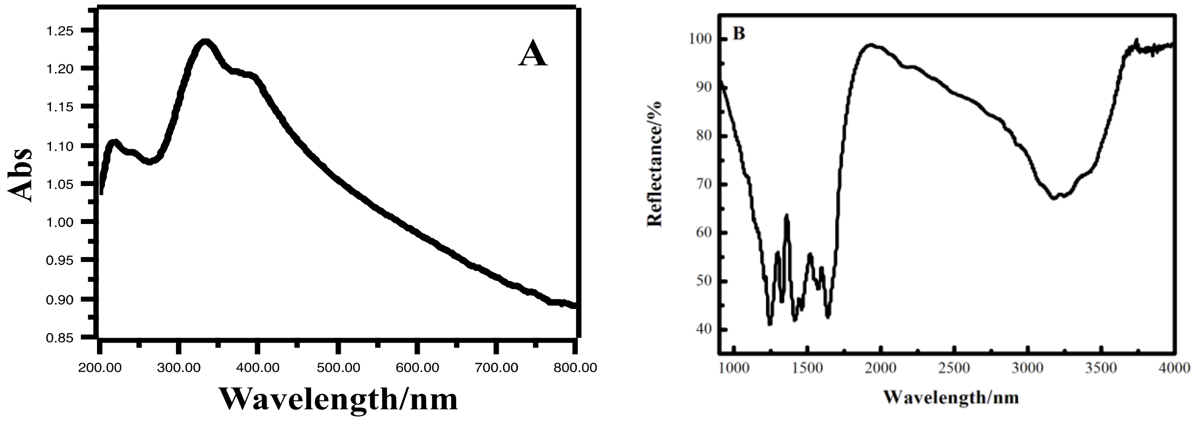
CHI660D electrochemical station was bought from CH Instruments, Chen hua in Shanghai, China. A three-electrode system was applied in the experiment with a modified electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode. Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were performed to indicate the properties of modified electrode.

H-7650 TEM (Audiocodes, Suzhou) was used to show the structure of synthetic materials. The spectrograms of g-C_3N_4 were displayed by UV-*vis* (Thermo Evolution 201, American) and FTIR (Cary 5000, Varian, American). XRD (D/max 2500/PC, Japan) revealed the atomic or molecular structure of g-C_3N_4. The pH meter was obtained from Mettler Toledo in Shanghai to adjust the pH value of ABS. HPLC with 2489 ultraviolet (UV) dual channel detector was purchased from Waters. Acetonitrile, ultra-pure water and trifluoroacetic acid were chose as mobile phase by 20:80:0.1 (V/V/V). The detecting wavelength was 270 nm and the flow rate was 0.5 μL/min. HPLC was applied to detected CA and FA simultaneously and the results would be compared with that of electrochemical method.

3. RESULTS AND DISCUSSION

3.1. Representations of g-C_3N_4

To determine the structure of g-C_3N_4, the UV-*vis* and FTIR were studied and showed in Figure.1 (A and B). From the UV-*vis* spectra of g-C_3N_4, absorption peaks at 220 nm and 320 nm were observed, which were the characteristic absorption of π-π* and n-π* transition respectively [27, 28]. The FTIR image displayed that the material had been synthesized successfully. Hydrogen bond was existed in the suspension by the bond of H-N at 3174 cm^{-1} and the stretching vibrations of C-N and C=N was observed at 1637 cm^{-1} and 1299 cm^{-1} [29-31]. In the TEM image (Figure.1C), g-C_3N_4 was discovered to have a unique two-dimensional layered feature structure.



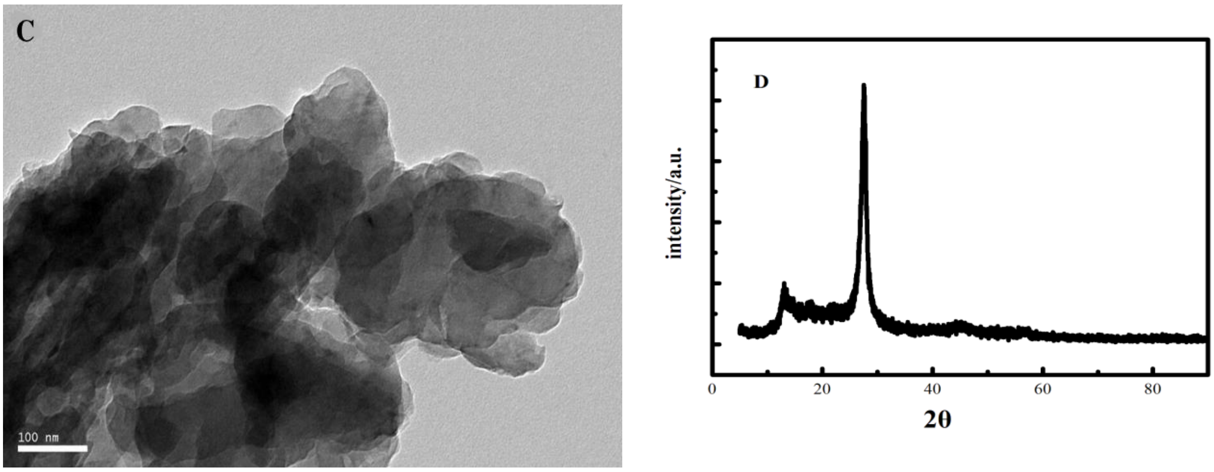


Figure 1. (A) UV-*vis* image of g-C_3N_4. (B) FTIR image of g-C_3N_4. (C) TEM image of g-C_3N_4. (D) XRD pattern of g-C_3N_4.

It was benefit for the electron transfer between layer and layer [31]. XRD was applied to illustrated that g-C_3N_4 had two characteristic diffraction peaks at 13.06° and 27.46 ° in Figure.1D. They represented (100) and (002) planes that were corresponding to the inner layer-packing motif and the interlayer accumulation with conjugate aromatic system, respectively. The result was consistent with the literature [32-34]

3.2. Electrochemical characterizations of g-C_3N_4/CS/GCE

To investigate the electrochemical properties of different modified electrodes, EIS and CV were chosen. In this research, GCE, CGr/CS/GCE, PEDOT/g-C_3N_4/CS/GCE and g-C_3N_4/CS/GCE acted as working electrodes separately. EIS was used to detect the conductivity of modified electrodes in 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ (1:1) including 0.1 M KCl because the interface electron-transfer resistance (R_{et}) of modified electrode could be calculated by the semicircle diameter [35]. The EIS images showed that g-C_3N_4/CS/GCE (in Figure.2A) had a smaller semicircle in contrast to other modified electrodes, which indicated that g-C_3N_4/CS/GCE had the better conductivity for the detection of targets. It could be inferred that the unique layered feature structure of g-C_3N_4 enhanced the electron transfer between the modified electrode surface and ferricyanide. CV images shown in Figure.2B investigated the electrochemical responses of different electrodes in 0.1 M KCl solution containing 1 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ (1:1) at scan rate of 100 mV/s. Compared with other electrodes, g-C_3N_4/CS/GCE and GCE presented a pair of good redox peak, while the redox currents at g-C_3N_4/CS/GCE were enhanced obviously than GCE. The results certified that g-C_3N_4 and CS had been modified on GCE successfully and g-C_3N_4/CS/GCE processed good conductivity, which was in accord with the conclusion of EIS. From DPV of Figure.2C, CA and FA were detected simultaneously by g-C_3N_4/CS/GCE, GCE and PEDOT/g-C_3N_4/CS/GCE in the potential range from 0 to 0.7 V in ABS (pH = 4.5). FA could not be distinguished from CA when CGr/CS/GCE were be used. The peak currents of CA and FA at g-C_3N_4/CS/GCE were sharper and higher than others because of its strong adsorption capacity and the hydrogen bond between g-C_3N_4 and targets. As a result, g-C_3N_4/CS/GCE was used to detect CA and FA at the same time in aqueous solutions.

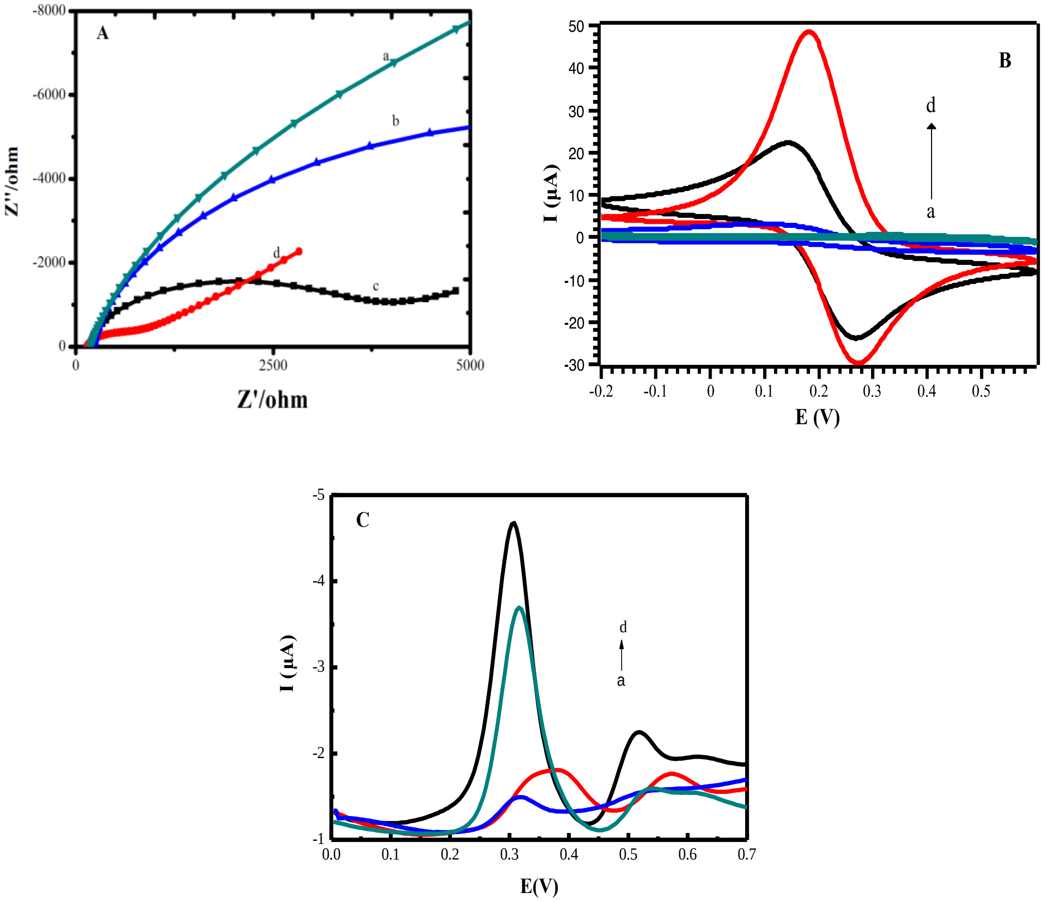


Figure 2. (A) EIS measurements of (a) CGr/CS/GCE, (b) PEDOT/g-C_3N_4/CS/GCE, (c) GCE, (d) g-C_3N_4/CS/GCE in 5 mM $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ (1:1) including 0.1 M KCl. (B) CV images of (a) CGr/CS/GCE, (b) PEDOT/g-C_3N_4/CS/GCE, (c) GCE, (d) g-C_3N_4/CS/GCE in 1 mM $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ (1:1) including 0.1 M KCl. Scan rate: 100 mV/s. (C) DPV of different electrodes (a) CGr/CS/GCE, (b) PEDOT/g-C_3N_4/CS/GCE, (c) GCE, (d) g-C_3N_4/CS/GCE in ABS (pH = 4.5) containing 10 μg/mL CA and FA.

3.3 Optimization of the electrolyte and modifying quantity

There were too many factors affecting the activity of modified electrodes, such as electrolyte and the modified quantity of g-C_3N_4. In this work, CA and FA were detected in phosphate buffer solution (PBS, pH=7.0) and acetic acid buffer solution (ABS, pH=4.5) respectively. The study verified that the oxidation currents and reduction currents of both CA and FA in ABS were much stronger than that in PBS due to the faintly acidity of CA and FA. Therefore, ABS was chosen as the electrolyte.

Modified quantity of g-C_3N_4 also influenced the peak currents of CA and FA. In this experiment, 600 μg/mL was chosen as the concentration of g-C_3N_4 and 5μL CS was deposited on modified electrode. Hence, the relationship between the amount of g-C_3N_4 and response currents of targets was researched. The result discovered that the peak current of CA increased with the augment of g-C_3N_4 before 4 μL. When the quantity was greater than 4 μL, the peak current would gradually decrease because g-C_3N_4 was aggregated on GCE, which could hinder the electron transfer between layer and layer. Therefore, the peak current was reduced. However, there was little effect on FA because the peak current of FA was far less than that of CA and change was not obvious. During the study, 4 μL g-C_3N_4 in 600 μg/mL was used to be immobilized on every electrode.

3.4 Effect of the pH of buffer solution and scan rate

The pH of buffer solution as a vital element about the properties of modified electrode was studied and a series of ABS with the pH value from 2.5 to 8.5 were prepared. As revealed in Figure.3, with the enhancement of pH, the response currents had changed. The peak currents of CA and FA all increased with the pH value range from 2.5 to 4.5, which due to the band of carboxyl and nitrogen. When the pH value was greater than 4.5, the currents declined sharply. Thus, the value of 4.5 was chosen as the best pH value.

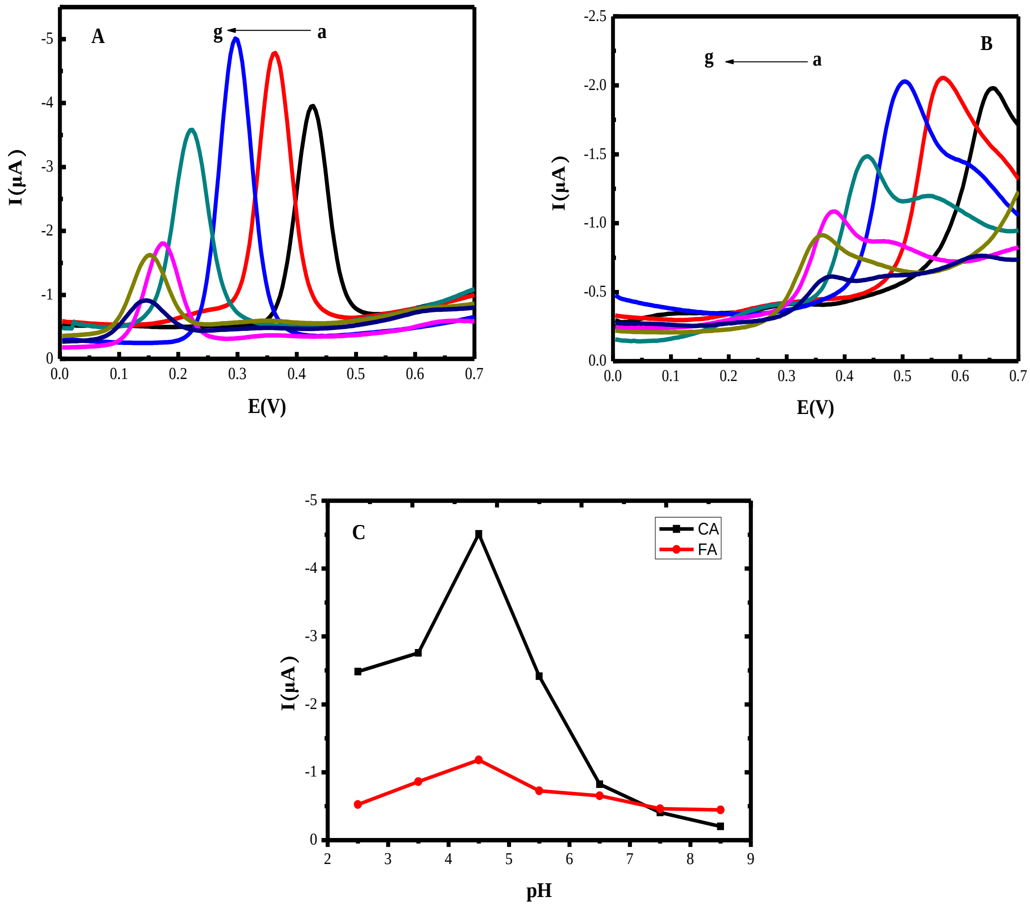


Figure 3. (A) DPVs of g-C_3N_4/CS/GCE in 0.1 M ABS including 10 μg/mL CA at different pH (a-g) as: 2.5, 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5, respectively. (B) DPVs of g-C_3N_4/CS/GCE in 0.1 M ABS including 10 μg/mL FA at different pH (a-g) as: 2.5, 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5, respectively. (C) The relationship between pH values and peak currents for 10 μg/mL CA and FA.

Figure.4 illustrated the influence of the scan rates for the detection of CA and FA. It was found that both the reduction peak current (I_{pc}) and oxidation peak current (I_{pa}) of two acids all enhanced with augment of scan rates and the potential of CA and FA had deviated. Thus, the error of potential was enlarged. As shown in thumbnails, the peak currents were linear with scan rates in the range from 20 to 250 mV/s due to the results for CA: I_{pa} (μA) = 0.3456 - $0.2697v^{1/2}$ (R^2 = 0.9988), I_{pc} (μA) = -0.1825 + $0.2019v^{1/2}$ (R^2 = 0.9996); FA: I_{pa} (μA) = 0.3243 – $0.08793v^{1/2}$ (R^2 = 0.9951), I_{pc} (μA) = 0.2450 + $0.08235v^{1/2}$ (R^2 = 0.9932). The reaction on g-C_3N_4/CS/GCE was mainly controlled by diffusion that was agrees with the conclusions reported by Zhang and Masek [15, 36]. In this experiment, 100 mV/s was applied to scan rate.

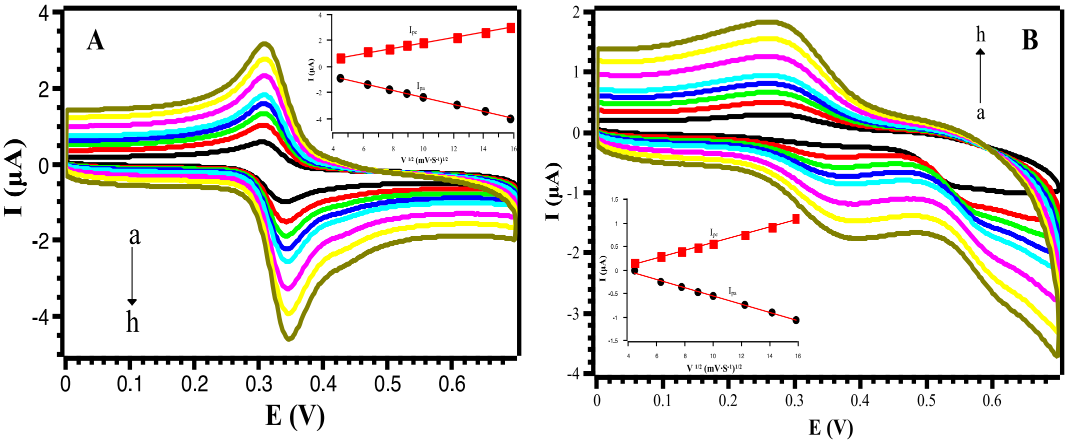


Figure 4. (A) CV images and the standard curves of CA; (B) CV images and the standard curves of FA. Scan rate were 20, 40, 60, 80, 100, 150, 200, 250 mV/s respectively (a~h).

3.5. Relation between the concentration and the response current

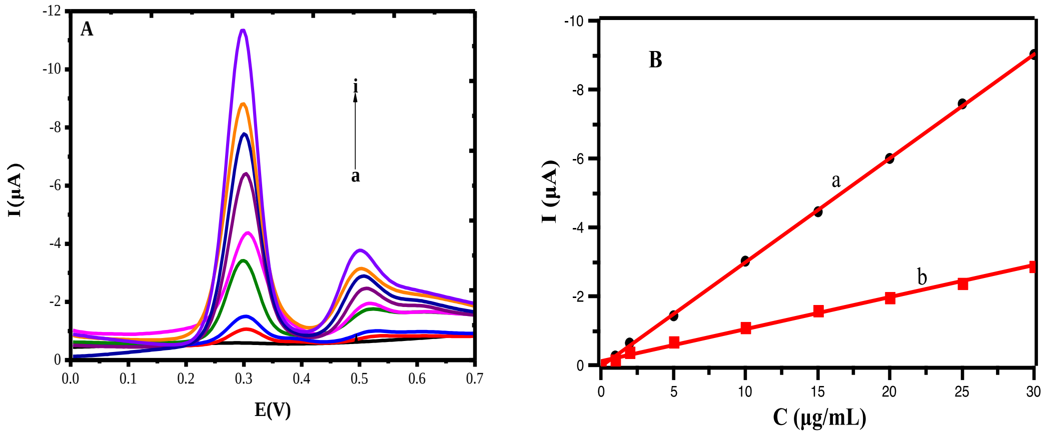


Figure 5. (A) The relation between the concentration and the response current of CA and FA, the concentrations were (a) 0 μg/mL, (b) 1 μg/mL, (c) 2 μg/mL, (d) 5 μg/mL, (e) 10 μg/mL, (f) 15 μg/mL, (g) 20 μg/mL, (h) 25 μg/mL, (i) 30 μg/mL. (B)The standard curves of CA (a) and FA (b).

Based on the above optimization conditions, the relation between the concentrations and the peak currents was investigated. DPV was used to determinate CA and FA in ABS (pH=4.5, Figure.5A). During the experiment, it induced that the peak currents of CA and FA had positive correlation with the concentrations in the range of 1-30 μg/mL (Figure.5B). The standard curve equation of CA was: I (μA) = -0.3020 C (μg/mL) + 0.0286 (R^2 = 0.9998) and the limit of detection (LOD) was 0.354 μg/mL (S/N=3). The standard curve equation of FA was: I (μA) = -0.0870 C (μg/mL) - 0.24024 (R^2 = 0.9988) and the LOD was 4.964 μg/mL (S/N=3). There were some different detection methods exhibiting in Table 1 to compare with this method. It was shown that this method processed a lower LOD than some analytical methods and could be used to monitor the amount of CA and FA at the same time. Nowadays, the determination of CA and FA with electrical analysis method was few. The method had simple operation and low detection limit. It provided a novel and practical idea for the detection for phenolic acids.

Table 1. Comparison of different methods to determinate CA and FA

Method	Targets	Linear range (μg/mL)	LOD (μg/mL)	Ref.
LDHf [a]/GCE	CA	1.261 – 32.427	0.468	[37]
PG [b]/GCE	CA	1.621 – 7.206	0.704	[38]
A new green bean tissue homogenate-based biosensor	CA	3.603 – 36.03	0.360	[39]
Micro-CE-ED [c]	CA	5.405 – 90.075	1.301	[40]
PPy-MWCNTs [d]/GCE	FA	0.645- 5.030	0.227	[41]
TLC [e] coupled with the paper-based colorimetric device	FA	77.676 – 135.933	6.991	[42]
CZE [f]	FA	2.427 – 485.475	14.389	[43]
GN [g]/GCE	FA	0.0971 – 9.710	0.0388	[44]
EPD-LuPc$_2$/ITO [h]	CA	0.180-1.801	11.187	[45]
	FA	0.194-1.942	1.342	
g-C_3N_4/CS/GCE	CA	1-30	0.354	This work
	FA	5-30	4.964	

[a] Zn-Al-NO_3 layered double hydroxide film; [b] poly (glutamic acid); [c] microchip capillary electrophoresis with electrochemical detector; [d] polypyrrole-multiwalled carbon nanotube; [e] thin layer chromatography; [f] capillary zone electrophoresis; [g] graphene nanosheet; [h] electrophoretic deposition - lutetium bisphthalocyanine nanowires/indium tin oxide electrode

3.6. Specificity and reproducibility for the determination of CA and FA

To investigate the anti-interference properties for the determination of CA and FA, phenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, quercetin and kaempferol (all concentrations were 10 μg/mL) were added into the electrolytes in sequence. Compared the response currents of interferon with CA and FA, some interferon showed minimal influence, such as phenol, 2,4-dichlorophenol and kaempferol, which signal changes were less than 10%. However, the interferon, like quercetin, had greatly influenced because its molecular structure was resembled with CA and FA. It would be nice that quercetin was rare in real life. We found that the modified electrode had a good reproducibility and the relative standard deviation (RSD) was 3.6% by testing the same concentration of CA and FA with six electrodes. The stability of the modified electrode was evaluated by storage at 4℃ in fridge for 10 days. It retained 94.2% of original electrode.

3.7. Detection of real samples

For purpose of the feasibility of this method, it was investigated by analyzing CA and FA in real samples. The results of the determination were illustrated in Table 2. It could be seen that CA was detected directly. However, different from CA, FA has only a hydroxyl that would affect the activity of benzene ring and the building of hydrogen bonds [46, 47]. Therefore, the concentration of FA was too low to detect and it needed to be detected by standard addition method. In order to testify the properties of this method, HPLC was employed. From Table 3, it was easy to find that the relative deviation of two methods was less than 7%. Compared with HPLC, this method detected the real samples only with simple pre-processing and provided a satisfactory result. The method with cheap instrument and simple operation could be applied in actual life.

Table 2. The detection of CA and FA in real samples

Samples	**Found before adding (μg/mL)**		**Added (μg/mL)**	**Found after adding (μg/mL)**		**Recovery (%)**	
	CA	**FA**		**CA**	**FA**	**CA**	**FA**
Xuanwu	0.53±0.00	ND	10.00	10.68±0.24	12.52±0.35	101.54±2.34	125.16±3.46
Qinhuai	1.19±0.03	ND	10.00	11.14±0.06	10.81±0.01	99.50±0.31	108.06±0.14
Changjiang	2.00±0.03	ND	10.00	11.84±0.22	10.50±0.11	98.45±1.86	105.03±1.10
Tap-water	0.40±0.01	ND	10.00	10.99±0.01	9.53±0.02	105.98±0.05	95.25±0.15
Apple Juice	6.45±0.02	ND	10.00	17.02±0.06	10.28±0.03	105.70±2.59	102.83±0.33
Coffee	2.19±0.01	ND	10.00	12.23±0.17	10.33±0.11	100.40±1.98	103.30±1.10

Table 3. Comparison of the detection CA and FA by electrochemistry and HPLC

Standard samples	**1**		**2**		**3**	
	CA	**FA**	**CA**	**FA**	**CA**	**FA**
Electrochemistry	11.148	11.164	12.046	11.954	15.190	14.978
HPLC	11.090	10.821	12.036	12.399	14.205	14.813
Relative deviation (%)	0.522	3.17	0.08	3.59	6.93	1.11

4. CONCLUSION

To sum up, in this paper, graphite-like carbon nitride (g-C_3N_4) was synthesized by melamine and was fixed on the surface of GCE by ultrasound for 6 h. This modified electrode could be applied to detect CA and FA in solutions simultaneously. Under the optimal conditions, it showed a good linear relationship between the peak currents and concentrations of CA and FA. This method has some superior properties, such as simple operation, low detection limit, highly sensitive and better reproducibility. Finally, the method was employed to detect target objects in real samples with convenient pretreatment. The method provides a novel idea and technology for the detection of phenolic acids in food samples.

ACKNOWLEDGEMENT
The project is supported by the National Natural Science Foundations of China (21575067, 31601405), Natural Science Foundation Program of Jiangsu Province (BK20160591), the research funding of Jiangsu Administration of Environment Protection (2015020) and the research funding of Jiangsu Academy of Agricultural Sciences (6111681).

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