DETERMINATION OF KOJIC ACID BASED ON A POLY(L-ARGININE)-ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE MODIFIED ELECTRODE

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Received March 1, 2019

A sensitive electroanalytical method for determination of kojic acid has been investigated on the basis of the enhanced electrochemical response at poly(L-arginine)-electrochemically reduced graphene oxide modified glassy carbon electrode fabricated by cyclic voltammetry. The glassy carbon electrode, poly(L-arginine) modified glassy carbon electrode, electrochemically reduced graphene oxide modified glassy carbon electrode, and poly(L-arginine)-electrochemically reduced graphene oxide modified glassy carbon electrode were characterized by electrochemical impedance spectroscopy. The electrochemical behaviors of kojic acid were studied by cyclic voltammetry and differential pulse voltammetry in detail. Under optimal experiment conditions, the sensitive oxidation peak of kojic acid was appeared at 1.07 V and the calibration curves for kojic acid were obtained in the range of $7.50 \times 10^{-7} - 1.00 \times 10^{-4}$ mol L⁻¹ and $1.00 \times 10^{-9} - 5.00 \times 10^{-7}$ mol L⁻¹ with a detection limit of 1.0×10^{-9} mol L⁻¹ (at an S/N of 3). This method has been applied to the determination of kojic acid in the rice wine samples with satisfactory results

INTRODUCTION

Kojic acid (5-hydroxy-2-(hydroxymethyl)-4H-pyran-4-one), a natural organic acid produced biologically by several species of fungi¹ attracts enormously attention in recent years due to its striking commercial value. The most extensive practical applications of kojic acid have been found in cosmetic preparations and food industry. Using as cosmetic skin-whitening and radio protective agents, kojic acid has inhibitory effect on the formation of melanin by inhibiting tyrosinase formation.^{2,3} In the production of food, kojic acid has traditionally been used as food additive to prevent enzymatic browning since it is an effective inhibitor of polyphenol oxidase, the

critical chemical substance that is responsible for spoilage.⁴ Apart from these two outstanding applications, kojic acid also possesses many other potential industrial applications reviewed by Mohamad⁵ and Lajis.⁶ Despite the wide and vital use of kojic acid, however, it at high doses is toxic.⁷ According to available literature, kojic acid could cause toxicity to liver and kidneys.⁸ Therefore, the amount of kojic acid in different products must be controlled by convenient, rapid and sensitive analytical methods.

So far, various methods have been applied for the analysis of kojic acid, including high-performance liquid chromatography,⁹⁻¹¹ capillary electrophoresis,¹² ion-pair liquid chromatography,¹³ spectrophotometric method.¹⁴ In addition, electro-

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analytical method has been regarded as a promising alternative to the aforementioned requirements for selective and sensitive analysis of kojic acid since it displays high stability, high selectivity, low detection limit, small cost, rapid analysis and simple use.¹⁵ However, direct electrochemical oxidation of kojic acid at bare electrode surface is hindered by high overpotential and slow electrode kinetics. Therefore, chemically modified electrodes are expected to lower the overpotential of kojic acid oxidation in comparison to the bare electrode. Up to now, many papers reporting on different types of modified electrodes can be found for performing kojic acid electrochemical detection. For example, in the 90's, Shih¹⁶ used disposable screen-printed polypropylene modified carbon electrode to analysis kojic acid for the first time. Then, in 2007 and in 2009, Yang¹⁷ and Liu¹⁸ investigated the potential application of PVP (polyvinylpyrrolidone) modified acetylene black paste electrode and carbon nanotube/alizarin red S modified electrode in the determination of kojic acid, respectively. Furthermore, in 2011, Yang¹⁹ used hollow CuO/Fe₂O₃ hybrid microspheres immobilized in chitosan matrix as modifiers to detect of kojic acid and obtained noteworthy results. In the same year, Wang²⁰ applied molecularly imprinted polymer modified electrode for assay of kojic acid showing excellent sensitivity and selectivity.

Graphene (GR), a 2D nanomaterial with single layer sp² hybridized carbon atoms, has been widely applied to modify electrode for its large surface area, excellent electrical conductivity, low cost, outstanding mobility charge carriers, and fast electron transfer rate.^{21,22} The graphene modified electrode shows great promise for the analysis of many kinds of material such as folic acid,²³ baicalein,²⁴ dopamine,²⁵ hydrogen peroxide,²⁶ and environmental samples²⁷ etc. Compared to the uncontinuous graphene oxide, reduced graphene oxide on the GCE surface has better electron transfer ability.²⁸ Meanwhile, it is an effective way to modulate the film-forming and electronic properties of graphene by assembly of the carbon-carbon bonds with different groups, such as carboxyl groups, amino groups, ionic liquids, and so on. Among them, amino acids with amine and carboxylic acid functional groups have been intensively used owing to their effectiveness in the oxidation of different substances.^{29,30} To the best of our knowledge, there is no report can be found to use reduced graphene oxide combined with amino

groups for the determination of kojic acid. Even though, reduced graphene oxide³¹ and amino groups³² used as modifiers separately for the analysis of kojic acid were available, the linear ranges and detection limits still need to improve. Based on these facts, therefore, we report the application of a poly(L-arginine)-graphene chemically modified electrode in the determination of kojic acid. Moreover, in spite of some different ways available to modify the electrode surface, the way of electropolymerization has been proved to be the most effective and convenient. Electropolymerization provides uniform, simplicity and controllable film thickness and allows adjusted deposition by changing electrochemical polymerization parameters.

In the present work, we apply electrochemically reduced graphene oxide and L-arginine as modifiers to fabricate glassy carbon electrode by electropolymerization. The electrochemical property of kojic acid at the poly(L-arginine)-electrochemically reduced graphene oxide modified glassy carbon electrode (PLA-ERGO/GCE) were studied in great detail by cyclic voltammetry and differential pulse voltammetry. The PLA-ERGO/GCE has high electrochemical activity towards kojic acid oxidation without significant interference in the presence of some other electroactive species. Moreover, this method was examined for the voltammetric determination of kojic acid in rice wines with satisfactory results.

EXPERIMENTAL

1. Reagents and Materials

Kojic acid (98%) was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China) L-arginine acid was purchased from Bio Life Science & Technology Co. (Shanghai, China). The kojic acid and L-arginine acid stock dispersions of 5.00×10^{-3} mol L⁻¹ were prepared with doubly distilled deionized water and stored at 4.0 °C away from light. The kojic acid standard solutions (7.50×10^{-7} – 1.00×10^{-4} mol L⁻¹ and 1.00×10^{-9} – 5.00×10^{-7} mol L⁻¹) were diluted freshly using HClO₄ solution (0.1 mol L⁻¹) prior to use. Graphene oxide (2 mg mL⁻¹) purchased from XFNANO Materials Technology Co. (Nanjing, China) was dispersed in pH 5.5 phosphate buffer solutions (PBS) to get 1 mg mL⁻¹ dispersion before used. The phosphate buffer solution (PBS) at pH 5.5 was prepared by using the stock solutions of 0.1 mol L⁻¹ Na₂HPO₄·NaH₂PO₄ and the pH was adjusted with appropriate amounts of Na₃PO₄ and H₃PO₄. All other chemical reagents (such as HClO₄, H₂SO₄, Na₂HPO₄, NaH₂PO₄, Na₃PO₄, H₃PO₄) were analytical-reagent and all these aqueous solutions were prepared using doubly distilled deionized water. All measurements were carried out at room temperature (23.0 ± 2.0 °C).

2. Apparatus

All cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on a BAS100B/W electrochemical workstation (BAS group, USA) with a conventional three-electrode system consisting of a glassy carbon working electrode (3 mm in radius), a platinum wire counter electrode, and a KCl-saturated Ag/AgCl reference electrode. Acidity was obtained using a digital pH/mV meter (PHS-3C, Shanghai Leici Device Works, China) and sonication was carried out by a KQ-250B Ultrasonic Cleaner (Kunshan, China).

3. Fabrication of PLA-ERGO/GCE

Prior to modification, the bare glassy carbon electrode (GCE) was first polished to a mirror-like smoothness with 0.05 μm Al_2O_3 powder on a polishing cloth, then the electrode was rinsed with nitric acid (1:1), ethanol and doubly distilled deionized water in sequence. Finally, the electrode was sonicated for 10 min in doubly distilled deionized water and dried at room temperature. After the above treatment, physically adsorbed materials were removed from the electrode surface. Then, the clean GCE was immersed in 10 mL polymerization solution prepared by mixing 5 mL of graphene oxide, 2.50 mL of $5 \times 10^{-3} \text{ mol L}^{-1}$ L-arginine acid stock dispersions, and 2.50 mL of pH 5.5 PBS and conditioned by cyclic sweeping from the potential of 2.5 to -2.4 V at the scan rate of 140 mV s^{-1} for 8 cycles. After polymerization, rinsing the modified electrode with doubly distilled deionized water carefully and drying in air, the PLA-ERGO/GCE modified electrode is ready.

4. Electrochemical Measurements

The PLA-ERGO/GCE modified electrode as working electrode was first activated in 10 mL blank solution prepared by mixing 5 mL of pH 7.0 PBS and 5 mL of doubly distilled deionized water by cyclic sweeps from -0.2 to 0.8 V at the scan rate of 180 mV s^{-1} for 1 cycle until the stable CV background curve was obtained. Electrochemical measurements were subsequently conducted by transferred electrodes into 10 mL buffer solution containing 5 mL of $0.2 \text{ mol L}^{-1} \text{ HClO}_4$, 3 mL of doubly distilled deionized water, and 2 mL proper concentration of kojic acid standard solutions. Cyclic voltammograms were carried out in the potential range from 0.4 to 1.4 V at the scan rate of 100 mV s^{-1} after 240 s quiet time. After every measurement, the PLA-ERGO/GCE modified electrode was washed with doubly distilled deionized water and removed the adsorptive substances by successive CV sweeps via taking it into the above mentioned blank solution. Optimized DPV parameters were as follows: potential increment 8 mV , pulse amplitude 40 mV , pulse width 60 ms , and pulse interval 100 ms .

RESULTS AND DISCUSSION

Characterization of PLA-ERGO/GCE

The electron transfer capability of the four electrodes including bare GCE, poly(L-arginine) modified glassy carbon electrode (PLA/GCE), PLA-ERGO/GCE and electrochemically reduced

graphene oxide modified glassy carbon electrode (ERGO/GCE) were investigated by electrochemical impedance spectroscopy (EIS) with an electroactive redox probe $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Fig. 1 depicts the typical electrochemical impedance spectra of bare GCE (1), PLA/GCE (2), PLA-ERGO/GCE (3) and ERGO/GCE (4) modified electrodes in 10 mL PBS containing $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ and $1.0 \text{ mol L}^{-1} \text{ KCl}$. In the high frequency region, the electron transfer resistance (R_{et}) can be quantified from the semicircle diameter.³³ The GCE and PLA/GCE with higher semicircle diameters have higher resistance and lower electron conductivity. The electron conductivity of PLA-ERGO/GCE was found to be significantly improved which is due to a huge interface electron transfer of reduced graphene oxide expanding the electron transfer passage of the redox probes to the electrode surface. Meanwhile, the EIS of ERGO/GCE is almost a straight line indicating the fastest electron transfer kinetics. However, the film on the surface of the graphene-modified electrode is liable to come off in absence of L-arginine that incorporated in graphene sheets could effectively enhancing the stability of the graphene adhesion. All above results strongly suggest that the PLA-ERGO/GCE is most suitable for determination.

Electrochemical Detection of Kojic Acid Using Different Electrodes

The electrochemical activity of a bare GCE (curve 1), a PLA/GCE (curve 2) and a PLA-ERGO/GCE (curve 3) for the kojic acid oxidation investigated by means of CV in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ at the scan rate of 100 mV s^{-1} are shown in Fig. 2. The CV of kojic acid ($1.00 \times 10^{-5} \text{ mol L}^{-1}$) at PLA-ERGO/GCE exhibits a remarkable oxidation peak centered at $+1.2 \text{ V}$, while the oxidation current at the bare GCE and PLA/GCE are poor and relatively weaker, respectively. The above results presented the PLA-ERGO/GCE electrode exhibited a highly catalytic activity toward kojic acid oxidation. Such increased electrochemical activity is ascribed to a synergistic enhancement of reduced graphene and L-arginine acid, not only the individual role of large surface area provided by the graphene. Further, no obvious electrocatalytic reduction response of kojic acid was observed suggesting an irreversible reaction of kojic acid at the modified electrode.

Fig. 1 – Electrochemical impedance spectra of GCE (1), PLA/GCE (2), PLA-ERGO/GCE (3) and ERGO/GCE (4) in 5.0×10^{-3} mol L $^{-1}$ K $_3$ [Fe(CN) $_6$], 1.0 mol L $^{-1}$ KCl solution.

Fig. 2 – Cyclic voltammograms of kojic acid on GCE (1), PLA/GCE (2) and PLA-ERGO/GCE (3) at a scan rate of 0.10 V s $^{-1}$ in 0.1 mol L $^{-1}$ HClO $_4$.

Optimum of Analytical Condition

The electrochemical performance of the PLA-ERGO/GCE electrode toward the oxidation of kojic acid can be affected by various parameters, such as scanning potential, solution pH and scan rate. These parameters were optimized based on the oxidation peak current by cyclic voltammetry in the following work.

Effect of Scanning Potential

To determine the optimal scanning potential range, CVs were first recorded in the potential range from 1.0 to 1.6 V by keeping the low potential at 0.4 V and the maximum peak current appeared at 1.4 V. Then, CVs were recorded in the potential range from 0.1 to 0.6 V and the maximum peak current occurred at 0.4 V. In view of the above determination results, 0.4–1.4 V was chosen as the best determination potential range.

Effect of pH

Different types of buffer solution with different pH value obviously influenced the oxidation peak current of kojic acid. Therefore, oxidation kojic acid at the PLA-ERGO/GCE electrode was evaluated in various solutions including H $_2$ SO $_4$, HClO $_4$ and NaH $_2$ PO $_4$ -Na $_2$ HPO $_4$. The maximum oxidation peak current was found in 0.1 mol L $^{-1}$ HClO $_4$, therefore this solution was selected for the electrochemical detection of kojic acid.

Effect of Scan Rate

The effect of scan rate on the peak current of 1.00×10^{-5} mol L $^{-1}$ kojic acid was investigated at

different scan rates from 0.02 V s $^{-1}$ to 0.40 V s $^{-1}$ in 0.1 mol L $^{-1}$ HClO $_4$ solution. As CVs shown in Fig. 3, the electrochemical oxidation peak current gradually increases as the scan rate increased and the logarithm of the current was found to be proportional to the logarithm of the scan rate linearly. The corresponding equation is $\lg I = 0.1684 + 0.6455 \lg V$, with the linear regression coefficient $R = 0.9950$. This clearly proves that the electrooxidation process of kojic acid at PLA-ERGO/GCE electrode is mainly controlled by diffusion. The scan rate of 100 mV s $^{-1}$ with the best oxidation peak shape was used for the optimal measurement condition.

It also could be noted that the oxidation peak potentials shifts positively in the scan rate range from 20 mV s $^{-1}$ to 400 mV s $^{-1}$. The electrochemical oxidation peak potential varies linearly with the scan rate: $E_{pa} = 0.8574 + 0.0294 \ln v$ ($R = 0.9926$). According to Laviron's equation³⁴:

$$E_{pa} = E^0 + \left(\frac{RT}{\alpha nF} \right) \ln \left(\frac{RTk^0}{\alpha nF} \right) + \left(\frac{RT}{\alpha nF} \right) \ln v \quad (1)$$

the slope of E_{pa} versus $\ln v$ is $\frac{RT}{\alpha nF}$, where R is gas constant, T is temperature, α is the transfer coefficient and is general 0.5, F is Faraday constant, and n is the transferred electron number. The value of this slope is equal to 0.0294 in this oxidation process. Therefore, n of kojic acid oxidation can be calculated as 1.6.

The current and time of the diffusion process obey the Cottrell equation (Cottrell 1902), i.e. $I_d = nFAD^{1/2}C_0(\pi t)^{-1/2}$, where I_d is the limit diffusion current, n is the transferred electron number, F is Faraday constant, A is the electrode area, D is the diffusion coefficient, and C_0 is the solution concentration. Based on the linear relationship

between the limit diffusion current and $t^{1/2}$, the values of the diffusion coefficient of the bare GCE and the PLA-ERGO/GCE were calculated and shown in Table 1. It can be seen, the diffusion coefficient of the PLA-ERGO/GCE is much larger than that of the bare GCE indicating an excellent sensitivity of this modified electrode. This result is consistent with the above experimental results.

Quantitative Analysis of Kojic Acid

In comparison to CV method, DPV is of higher sensitivity and resolution since the charging

current has a small contribution to the background current.³⁵ Therefore, DPV was employed to investigate the dependency between the oxidation peak current and the concentration of kojic acid in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$. DPVs of different concentrations of kojic acid at the PLA-ERGO/GCE were recorded in Fig. 4. The peak current of kojic acid increased linearly with the increased concentration in the range of $7.50 \times 10^{-7} - 1.00 \times 10^{-4} \text{ mol L}^{-1}$ and $1.00 \times 10^{-9} - 5.00 \times 10^{-7} \text{ mol L}^{-1}$. The corresponding linear equations and correlation coefficients were shown in Table 2. In addition, the detection limit ($S/N = 3$) is as low as $1.0 \times 10^{-9} \text{ mol L}^{-1}$.

Fig. 3 – Cyclic voltammograms of kojic acid at various scan rates [1-15: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 240, 280, 320, 360, 400 mV s^{-1}].

Fig. 4 – Differential pulse voltammograms of kojic acid at different concentrations [1-10: 7.50×10^{-7} , 1.00×10^{-6} , 2.50×10^{-6} , 5.00×10^{-6} , 7.50×10^{-6} , 1.00×10^{-5} , 2.50×10^{-5} , 5.00×10^{-5} , 7.50×10^{-5} , $1.00 \times 10^{-4} \text{ mol L}^{-1}$].

Table 1

The diffusion coefficient (D) of kojic acid with various electrodes

Electrodes	GCE	PLA-ERGO/GCE
D ($\text{cm}^2 \text{ s}^{-1}$)	1.754×10^{-7}	3.715×10^{-6}

Table 2

Linear ranges, regression equations, correlation coefficients and detection limits for individual determination of kojic acid on PLA-ERGO/GCE

Analyte	Linear ranges (mol L^{-1})	Linear regression eq. $I (\mu\text{A})$ $\rho (\text{mol L}^{-1})$	Corr. coeff.	Detection limit (mol L^{-1})
Kojic acid	$7.50 \times 10^{-7} - 1.00 \times 10^{-4}$	$lgI = 4.608 + 0.7880lg\rho$	0.9930	1.0×10^{-9}
	$1.00 \times 10^{-9} - 5.00 \times 10^{-7}$	$lgI = 2.335 + 0.1920lg\rho$	0.9982	

Table 3
Analytical results of KA in samples (n=5)

Analyte		Mean value $\rho / (\text{mol/L})$	RSD / (%)	Added $\rho / (\text{mol/L})$	Found $\rho / (\text{mol/L})$	Recovery / (%)
Rice wine	1	1.45×10^{-5}	3.0	1.5×10^{-5}	2.86×10^{-5}	94.0
	2	2.38×10^{-5}	2.9	2.5×10^{-5}	4.95×10^{-5}	103
Soy sauce	1	1.23×10^{-4}	3.2	1.0×10^{-4}	2.19×10^{-4}	96.0
	2	1.21×10^{-4}	3.0	1.5×10^{-4}	2.73×10^{-4}	101

Precision and Stability

The reproduction of the PLA-ERGO/GCE was evaluated at a fixed concentration of $1.00 \times 10^{-4} \text{ mol L}^{-1}$ kojic acid for 15 successive and repeated measurements in the same conditions. A relative standard deviation (RSD) value of 3.1% was obtained, revealing a satisfying repeatability of the modified electrode. The stability of the PLA-ERGO/GCE was studied by measuring the current and the potential responses at a kojic acid concentration of $1.00 \times 10^{-4} \text{ mol L}^{-1}$ over a period of 10 days. Under the same measurement conditions, the PLA-ERGO/GCE presented a good stability without significant changes of the peak potential and peak current.

Interference Studies

The influence of some foreign substances on the electrochemical oxidation of $1.00 \times 10^{-4} \text{ mol L}^{-1}$ kojic acid was investigated on the surface of the PLA-ERGO/GCE (approximately 5% relative error). For some common substances, ascorbic acid (0.1 mg), Cu^{2+} (0.2 mg), carmine (0.4 mg), and concentrations above 1.0 mg of K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , sucrose, glucose, L-tryptophan, L-threonine and oxalic acid, did not interfere with the kojic acid determination (the maximum concentration limit was not done), indicating an excellent selectivity of the developed method.

Sample Analysis

To evaluate the applicability of the above-presented method for kojic acid detection in real samples, two kinds of rice wine and soy sauce were diluted appropriately for determining by the

standard curve method and the results were presented in Table 3. The relative standard deviations (RSD) based on 5 repeated measurements ($n = 5$) were found to be 3.0, 2.9, 3.2 and 3.0, respectively. Then, the recovery measurements were carried out and the recoveries of the two kinds of rice wine and soy sauce are 94.0%, 103%, 96.0% and 101%, respectively. As a result of this work, the presented method is feasible for the determination of kojic acid content in real samples.

CONCLUSION

A more simple and sensitive electrochemical method based on kojic acid oxidation by cyclic voltammetry and differential pulse voltammetry was developed. Modification of GCE with the reduced graphene and L-arginine enhanced the catalytic activity of kojic acid oxidation, and interference from some common species was not observed. The advantages of these electrochemical methods were also demonstrated by successful application in the rice wine samples. As a conclusion, the proposed electrochemical method in this work can be an alternative good way to the determination of kojic acid.

Acknowledgements. This work was supported by the Key Project of Provincial Natural Science Research Foundation of Anhui Universities, China (Nos. KJ2018A0389 and KJ2016A642), and the Key Project of Anhui Universities Support Program for Outstanding Youth, China (No. gxyqZD2016111).

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