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Direct electrodeposition of reduced graphene oxide on carbon fiber electrode for simultaneous determination of ascorbic acid, dopamine and uric acid

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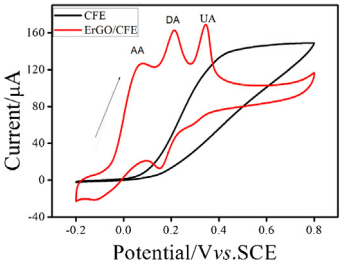
HIGHLIGHTS

- The ErGO/CFE was fabricated by a simple electrodeposition method.
- The ErGO/CFE shows high electron transfer kinetics in CV response.
- The ErGO/CFE shows high sensitivity and selectivity for simultaneous determination of AA, DA and UA.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrochemically reduced graphene oxide (ErGO) modified carbon fiber electrode (CFE) was fabricated by a simple electrodeposition method. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) had been used to investigate the electrochemical behavior of ErGO/CFE toward ascorbic acid (AA), dopamine (DA) and uric acid (UA). Compared to the bare CFE, the ErGO/CFE showed higher catalytic activity toward electrochemical oxidation of AA, DA and UA. In the CV curves, three well and distinct peaks with large peak potential separation of 116 mV, 167 mV and 283 mV between AA–DA, DA–UA and AA–UA were observed. In the DPV curves, the corresponding peak potential separations were 198 mV, 163 mV and 361 mV between AA–DA, DA–UA and AA–UA also observed. DPV was used as the analytical technique to acquire the linear calibration curves for AA, DA and UA with the concentration ranges of 8–2016.45 μM, 1.5–224.82 μM, 6–899.3 μM, respectively, in the individual detection of each component. The detection limits were 4.5 μM, 0.77 μM and 2.23 μM for AA, DA and UA indicating that the ErGO/CFE can be achieved with high sensitivity and selectivity for simultaneous determination of these three biomolecules.

1. Introduction

Ascorbic acid (AA), dopamine (DA) and uric acid (UA) play important roles in physiological function of organisms. AA is commonly used in large scale as an antioxidant in food, animal feed, pharmaceutical formulations and cosmetic applications [1]. Meanwhile AA has direct participation in many biological reactions and its deficiency can be related to symptom of some diseases, e.g. scurvy [2]. It also has been used for prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [3]. DA is an important neurotransmitter that belongs to the catecholamine family and has been given extensive attention in clinical research

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due to its involvement in motor and cognitive function [4]. Abnormal DA concentration in the brain may lead to serious disease, such as Parkinson's disease and addiction [5,6]. UA is the final oxidation product of urine metabolism and is excreted in urine [7]. Abnormal concentration of UA in human body is symptom of several diseases such as gout, hyperuricemia and Lesch–Nyhan syndrome [8,9]. Therefore, the sensitive and reliable determination of AA, DA and UA is an important topic not only in the field of biomedical chemistry but also for diagnostic and pathological research. In present, electrochemical methods have been extensively used for the determination of these three molecules. However, as we know, the three biological molecules oxidation potentials are almost the same at traditional electrodes which results in severely overlapped voltammetric response [10]. It is difficult to simultaneously determine them at the traditional electrodes, so various chemically modified electrodes have been developed.

Graphene, a one-atom-thick sp^2-bond carbon sheet recently has been attracted extensive interest because of its ideal two-dimensional structure [11], unique electronic properties [12], thermal properties [13], mechanical properties [14] and optical properties [15]. It is always applying in many fields such as nanoelectronics, nanoelectromechanical devices, nanocomposites, sensors, ultracapacitors, solar cells and liquid crystal devices [16–18]. Furthermore, graphene oxide (GO) and reduced graphene oxide (RGO) have also been used for modified electrodes. GO with single-layered is an intriguing nanomaterial with tremendous potential for electronic applications. Many reports are related to the application of graphene oxide based materials in supercapacitors [19]. Compared to graphene oxide, the reduced graphene oxide has better conductivity. Studies indicate that biological activity of the RGO modified electrode shows a better electrochemical response [20]. Wang et al. reviewed the application of RGO in electrochemical catalysis [21], Chen and Tang also reviewed the application of RGO in electrochemical sensor [22]. To the best of our knowledge, there are no reports which use the electrodeposition method to obtain RGO for simultaneous determination of AA, DA and UA.

In this work, graphene oxide was directly electrodeposited at a constant potential on the carbon fiber electrode to obtain the reduced graphene oxide modified electrode (ErGO/CFE). The obtained ErGO/CFE was used for simultaneous determination of AA, UA and DA. The basic characteristics of the ErGO electrode were studied in details. Cyclic voltammetry and differential pulse voltammetry were employed to investigate the electrochemical behaviors of AA, DA and UA at the proposed electrode. The reusability and stability of the ErGO electrode were also studied.

2. Experimental

2.1. Reagents

Graphite powder, disodium hydrogen phosphate, sodium dihydrogen phosphate, lithium perchlorate, potassium ferrocyanide, potassium ferricyanide and potassium chloride were purchased from Sinopharm Chemicals Reagent Co., Ltd., China. Ascorbic acid, dopamine and uric acid were purchased from Acros Organics. All these chemicals were of analytical reagent grade and used as received. The solutions of AA, DA and UA were freshly prepared with 0.1 M phosphate buffer solutions (PBS; pH 7.0). The double-distilled water was used throughout all the experiments.

2.2. Apparatus

The morphology of obtained electrode was studied by scanning electron microscope (SEM) (S-4700, Hitachi High Technologies Corporation, Japan). Cyclic voltammetry and differential pulse voltammetry measurements were carried out using a CHI650D electrochemical workstation (Shanghai Chenhua Instrument Plant, China) with a standard three-electrode. The CFE (360 μm diameter) (CeTech Co., Ltd.) and its modified electrode were used as working electrodes. CFEs were rinsed thoroughly with ethanol and water by ultrasonication each for 15 min before experiments. Platinum foil with an area of 1 cm × 1 cm and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The areas of working electrode and counter electrode immersed in the solution were 1.2 cm × 360 μm and 0.5 cm × 1 cm, respectively. All the experiments were carried out at room temperature.

2.3. Preparation of graphene oxide

Graphene oxide (GO) was synthesized from graphite by modified Hummers method [23]. Firstly, 0.5 g $NaNO_3$ and 1.0 g graphite powder were added into a 24 mL H_2SO_4 solution (0 °C). Under vigorous agitation, 3.0 g $KMnO_4$ was added slowly to keep the temperature of the suspension lower than 20 °C. Successively, the reaction system was transferred to a 35 °C water bath and stirred for 60 min. Secondly, 46 mL of double-distilled water was mixed into the above solution and further stirred at 98 °C for 15 min. Additional 140 mL of double-distilled water was added and followed by a slow addition of 10 mL H_2O_2 (30%) turning the reaction to stop. After the above reactions, the final product was washed by HCl (5%) until sulfate ions could not be detected with $BaCl_2$. The final product was then dried in vacuum for 12 h at 40 °C. Lastly, 60 mg the product GO was dispersed into 10 mL double-distilled water under ultrasonic homogenizer for 120 min so that the impurities in the GO solution were centrifuged. After the GO solution was purified by centrifugal machine for 15 min, we got target GO solution with the concentration was estimated to be 3 mg/mL.

2.4. Preparation of the ErGO/CFE electrode

The electrochemically reduced graphene oxide (ErGO) modified electrode as prepared by electrolyzing the 3 mg/mL GO aqueous suspension containing 0.1 M lithium perchlorate on the CFE at a consistent potential of −1.2 V for 5000 s (shown in Scheme 1). After electrodeposition, the ErGO electrode was washed with double-distilled water and then immersed in double-distilled water for 30 min to remove the residual GO absorbed on the electrode.

3. Results and discussion

3.1. Basic characterizations of ErGO

The morphology of CFE and obtained ErGO/CFE was investigated by SEM. Fig. 1 shows that there are obvious differences between the two electrodes. From Fig. 1(A), we can observe a quite smooth surface of CFE, while in Fig. 1(B) and (C) the surface of ErGO/CFE is wholly covered with three-dimensional structures. How do the three-dimensional structures form? It is apparently that graphene oxide was reduced at the consistent potential. With an increasing electrodeposition time, the reduced graphene oxide sheets on CFE surface would increase. The reduced graphene oxide sheets interconnected with each other and as a result, the three-dimensional structures formed on the surface of ErGO/CFE. It can be believed that the three-dimensional structures enlarge the surface area of the ErGO/CFE which could provide a high area for the affinity adsorption of AA, DA and UA.

Fig. 2 compares the cyclic voltammetric (CV) responses at the two electrodes in 2.5 mM $Fe(CN)_6^{3-/4-}$ + 0.1 M KCl solution. The CV curve of bare CFE shows a pair of poor redox peaks, suggesting the sluggish electron transfer at the interface of the carbon fiber. While