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Electrocatalytic oxidation of kojic acid at a reduced graphene sheet modified glassy carbon electrode

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ABSTRACT

A simple procedure has been developed to prepare a glassy carbon (GC) electrode modified with reduced graphene sheets (RGSs) (RGSs/GC). The electrocatalytic oxidation of kojic acid on the RGSs/GC electrode in 0.2 M HAc–NaAc buffer solution has been studied using cyclic voltammetry and chronoamperometry. Compared with the unmodified GC electrode, a decrease in overpotential and large enhancement of oxidation current for kojic acid oxidation has been achieved with the RGSs/GC electrode. The kinetic parameters of the kojic acid oxidation reaction electrocatalyzed by RGSs have also been calculated. The diffusion coefficient of kojic acid has been estimated as 1.5×10^{-5} cm^2 s^{-1} for the experimental conditions, using chronoamperometry. The transfer coefficient for electron transfer and the number of electrons transferred in the overall reaction have been calculated to be 0.53 and 1, respectively. Under the optimized conditions, the oxidation peak current was proportional to kojic acid concentration in the range of 0.01–0.14 mM with a current sensitivity of 42.9 μA mM^{-1} and correlation coefficient of 0.9950, suggesting that RGSs are a potential electrode material for electrochemical sensors for kojic acid detection.

1. Introduction

Kojic acid (5-hydroxy-2-(hydroxymethyl)-4-pyrone, is a natural metabolic product of several species of *Aspergillus*, *Acetobacter*, and *Penicillium* [1,2]. Kojic acid and some of its derivatives are used in cosmetic preparation to achieve a skin-lightening effect [1]. In everyday life, it is widely used as food additive and preservative [1]. In addition, kojic acid has also been used as an antibiotic, pesticide, and analytical chemical (in the determination of thorium and rare earths) [1]. Moreover, because the 4-pyrone in kojic acid molecules has aromaticity like benzene, kojic acid may have adverse effect on human health and is possible to be a carcinogenic [3]. Therefore, the development of a convenient, economical, rapid and sensitive method for the determination of trace amounts of kojic acid in different samples is highly desirable.

Up to now, various methods such as high-performance liquid chromatography (HPLC) [4–6], stopped-flow method [7], and ion pair liquid chromatography [8], have been reported for the quantification of kojic acid. Among several techniques, electrochemical techniques offer the opportunity for portable, economical, sensitive, and rapid methodologies for the determination of kojic acid. However, the oxidation of kojic acid is kinetically sluggish, and a relatively high overpotential is required at the carbon electrodes. Accordingly, during the last decade, many affords have been made to lower the overpotential of the kojic acid oxidation [3,9–11].

Recently, a new class of large surface-to-volume ratio, high conductivity carbon material, graphene, has attracted increasing attention for optoelectronic devices [12], supercapacitors [13], gas sensor [14], pH sensor [15], and chemical sensor [16]. Graphene is the name given to a flat monolayer of carbon atoms firmly packed into a honeycomb-like crystalline lattices in a two dimensional fashion [17]. This unique nanostructure material has low manufacturing cost [18], high surface area [19], excellent electrical conductivity [20], unique graphitized basal plane structure [17], and strong mechanical strength [17]. Such properties indicate that graphene may be a good electrocatalyst or a support for electrocatalysts. Thus, in the past years, graphene-oriented electrochemistry, bioelectrochemistry as well as electrocatalysis have greatly stimulated research interests [21–42]. One of important works towards understanding the electrochemical reactivity of graphene is from Kampouris and Banks [43], who have assumed that the electrocatalytic nature of graphene resides in electron transfer from the edge of graphene. However, to the best of our knowledge, the electrocatalytic activity of graphene towards the oxidation of kojic acid has not been studied.

In the current study, we present, for the first time, the properties of reduced graphene sheets (RGSs) for electrocatalysis for the oxidation of kojic acid. The electrocatalytic ability of RGSs was

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thoroughly investigated by cyclic voltammetry (CV), chronoamperometry, and linear sweep voltammetry (LSV). RGSs showed significantly electrocatalytic activity towards the oxidation of kojic acid.

2. Experimental

2.1. Chemical and materials

Concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrazine (N_2H_4), acetic acid (HAc), and sodium acetate (NaAc) were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Kojic acid (analytical grade) was purchased from Shanxi Sciphar Biotechnology Co., Ltd. For the synthesis of RGSs, nature graphite powder (99.99%) was purchased from Beijing Chemical Company. Water used was Milli-Q water (MiliQ, USA). 0.2 M HAc–NaAc buffer solutions with various pH values were prepared by mixing stock standard solutions of HAc and NaAc. Ultra-high purity nitrogen (N_2, 99.99%) gas was purchased from Qingdao Heli Gas Co. and used for the deaeration of solution.

2.2. Synthesis of RGSs

Graphene oxide (GO) was prepared from graphite according to the Hummers method [44]. In brief, concentrated H_2SO_4 (46 mL) and $NaNO_3$ (1 g) were added into the 250 mL flask filled with graphite (1 g) at room temperature, followed by addition of solid $KMnO_4$ (6 g) slowly at 0 °C (ice bath). After increase of temperature to 35 °C, the mixture was stirred by magnetic stirring bar for 2 h, followed by slow addition of Milli-Q water, which produced a rapid increase in solution temperature up to a maximum of 100 °C. The reaction was maintained at 98 °C for a further 15 min, and then terminated by addition of more Milli-Q water (200 mL) followed by H_2O_2 (20 mL). The solid product was separated by centrifugation at 5000 rpm, and then washed three times with Milli-Q water and air dried at 50 °C for 24 h.

For the preparation of graphene oxide sheets, the obtained GO powders (0.1 g) were dispersed in 100 mL Milli-Q water with ultrasonic vibration for 2 h. Hydrazine (hydrazine:GO = 1:8 in weight) was subsequently added. Additional stirring at 95 °C afforded a black suspension of RGSs. Finally, RGSs were obtained by filtration of the product and drying at 50 °C for 24 h.

2.3. Characterization

Atomic force microscopy (AFM) image of the synthesized RGSs deposited on a freshly cleaved mica surface was taken with Nanoscope IIIa (Digital Instruments, USA) in tapping mode using. After sonicating for 5 min with an ultrasonic bath cleaner, a droplet of the RGSs suspension (0.01 g L^{-1}) was cast onto a freshly cleaved mica surface. The sample was kept at room temperature overnight to let the water evaporate.

Room temperature Fourier transform infrared (FT-IR) spectra of the synthesized graphene oxide sheets and RGSs were recorded in the range 4000–400 cm^{-1} with 2 cm^{-1} resolution on a Nicolet iS10 Fourier transform spectrometer (Thermo Fisher Scientific, USA) using the KBr pellet technique.

2.4. Preparation of the RGSs modified glassy carbon (RGSs/GC) electrode

The RGSs/GC electrode was used as the working electrode. Prior to the surface modification, the GC electrode (3 mm diameter) and the graphite electrode (3 mm diameter) were polished firstly with #2000 emery papers, then two kinds of alumina powders with the particle size of 1 and 0.05 μm with the use of a polishing cloth, and were cleaned with Milli-Q water in an ultrasonic bath for 10 min. As-synthesized RGSs were dispersed by sonication in Milli-Q water to form a homogenous suspension (1 g L^{-1}). The RGSs/GC electrode was prepared by casting the RGSs suspension (2 μL) on the GC electrode surface and evaporating the remaining water for 24 h at room temperature. After the modification, a robust film was formed on the GC electrode surface that contained 2 μg of RGSs.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a conventional two-compartment, three-electrode cell with the bare GC, the bare graphite, and the RGSs/GC electrode as working electrodes, a saturated calomel electrode (SCE) as reference electrode, and a Pt wire as counter electrode. The electrolytes, HAc–NaAc buffer solutions, were purged with pure N_2 for 20 min prior to the measurement. CV, LSV, and chronoamperometry were conducted with a computer-controlled electrochemical system (CHI 760C, CH Instruments, Inc., USA). All potentials were reported versus the SCE. All the experiments were conducted at room temperature 25 ± 2 °C.

3. Results and discussion

3.1. Characterization of the synthesized RGSs

AFM image confirm that evaporated dispersion of RGSs are comprised of isolated RGSs (Fig. 1). As shown, only individual flat RGSs with thickness of 0.7–0.8 nm were observed with lateral dimensions of several hundred nanometers for a single sheet. Nanosized RGSs contain a large amount of open graphitic edge

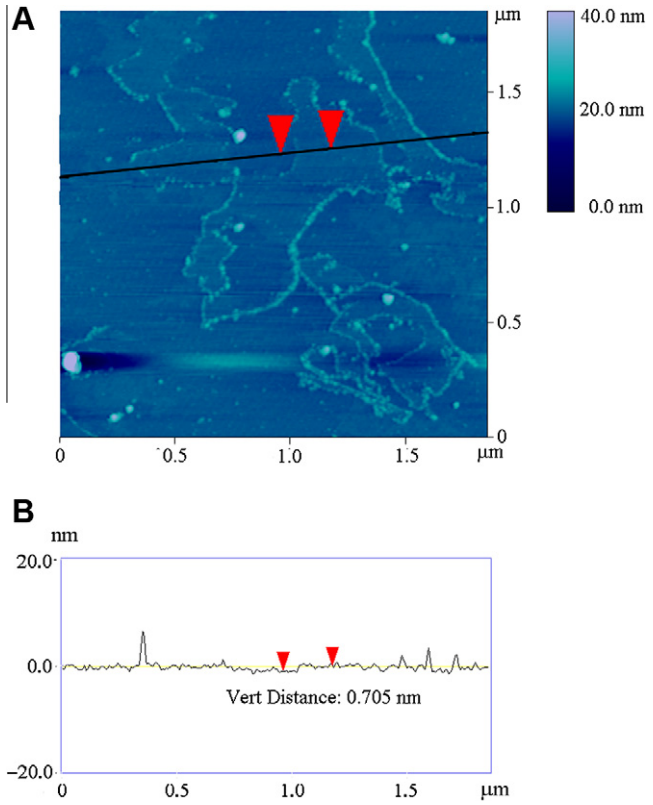

Fig. 1. AFM image of RGSs deposited on freshly cleaved mica. (A) Height image of the sample over the marked scanning area of 1900 × 1900 nm^2 and (B) section profile along the marked blank line, showing single layer of RGSs.