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## Characterization of the surface redox process of caffeic acid adsorbed at glassy carbon electrodes modified with partially reduced graphene oxide

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### ABSTRACT

This paper describes for the first time the caffeic acid (CA) electrochemical oxidation in 1.0 M HClO<sub>4</sub> and phosphate buffer solutions (PBS) of different pH at glassy carbon electrodes (GCE) modified with electrochemically partially reduced graphene oxide (GCE/ePRGO) using cyclic and square wave voltammetries. A quasi-reversible surface redox couple was found in all reaction media at this modified electrode. The Box-Behnken design (BBD) statistical experiments and the surface methodology (RSM) were used to optimize experimental variables to generate the GCE/ePRGO. Atomic force microscopy (AFM) and electrochemical impedance spectroscopy (EIS) were used as the techniques to characterize the surface of modified electrodes. EIS was also used to determine a tentative electrochemical area for the GCE/ePRGO.

The Frumkin adsorption isotherm was the best which describes the specific interaction of CA with GCE/ePRGO. The thermodynamic and kinetics of the surface redox couple were studied in 1.0 M HClO<sub>4</sub>. Therefore, we used the methods of the “quasi-reversible maximum” and the “splitting of the net SW voltammetric peak” to obtain information about the thermodynamic and kinetics of this surface redox couple. Averages values obtained for the formal potential and the anodic transfer coefficient were (0.638 ± 0.005) V and (0.58 ± 0.06), respectively. A value of 40 s<sup>-1</sup> was obtained for the overall formal rate constant. For comparison, CA electrochemical responses were also studied at bare GCE, and GCE modified with a dispersion of graphene oxide (GCE/GO).

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### 1. Introduction

Caffeic acid or 3-(3,4-dihydroxyphenyl)-2-propenoic acid (CA) is a phenolic acid (Fig. 1), which is found in various agricultural products such as coffee [1], teas [2], potatoes, grains, vegetables, fruits and orange juices [3]. CA is also often found in herbs [4] or wines [5].

Thus, CA is a biomolecule derived from plants. It has a variety of interesting properties, including *anti*-inflammatory, anticancer, anti-depressive, antiviral, antioxidant, anti-pruritic, and anti-tumor effects [6–11].

Moreover, it is usual to determine the antioxidant activity of a given matrix based on the total polyphenolic content (TPC), without the individual contribution of the different components. The CA is often chosen as a reference compound to evaluate the TPC [12]. Thus, it is of great interest to study the CA electrochemical behavior at different electrode surfaces. Giacomelli et al. [13], studied the CA electro-oxidation in aqueous solutions in the pH range from 2.0 to 8.5 at bare glassy carbon

electrodes (GCE) to propose an electro-oxidation mechanism in aqueous solutions and to characterize the probable products. These authors found that the electrode process is diffusion controlled, and that two electrons are involved in the CA electro-oxidation mechanism at all pH's studied. They proposed that the corresponding o-quinone should be the main product formed. However, they also found that the stability of the o-quinone electrochemically generated depends on the pH, being greater at pH ≤ 5.5. Therefore, these authors proposed that the CA electro-oxidation mechanism is 2e<sup>-</sup>, 2H<sup>+</sup> at pH lower than about 5.5. Moreover, a variety of methods has also been developed to determine CA in real samples [14–17]. In this sense, the modification of electrode surfaces with nano-materials has been studied in order to increase their conductivity properties, and their electro-catalytic activities [14, 15,18].

The use of graphene in several areas of science has grown in recent years. The great interest in this material is based on its outstanding physical properties such as quantum electronic transport, high mobility, and high elasticity [19]. Graphene derivatives are also very important for the development of various investigations [20–24]. Graphene oxide (GO) is an oxidized form of graphene, which contains polar organic groups such as epoxide, carbonyl, carboxyl, and hydroxyl among

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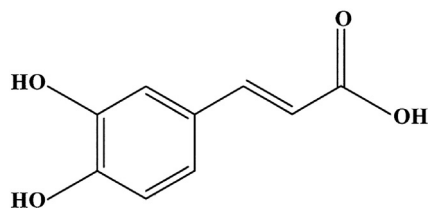


Fig. 1. Chemical structure of caffeic acid.

other, allowing its reduction by different routes. These polar organic groups have high hydrophilicity, making that the GO can be easily dispersed in aqueous suspensions [25]. When the GO is reduced through an appropriate process, the reduced graphene oxide (RGO) formed is similar to graphene. However, it still contains residual oxygen and other hetero-atoms, and structural defects [26]. The resulting RGO has been used as starting material for the fabrication of various modified electrodes [27–30], which were then used as electrochemical sensors to determine different analytes in various matrices. Thus, sensors based on immobilized RGO at different electrodes have been developed to determine nitromethane in complex real samples [31], sulfide in fruits [32] or gatifloxacin in tablets and human urine samples [30]. Different RGO modified electrodes have also been used to quantify CA. Thus, Filik et al. [33], have developed a glassy carbon electrode (GCE) modified with a Nafion/RGO composite film to determine CA in white wine samples. Moreover, Vilian et al. [34], studied the CA electrochemical oxidation at a GCE modified with chemically reduced GO using different electrochemical techniques. This modified electrode was further used to determine CA in wine samples.

In this paper, we study for the first time the CA electrochemical oxidation in 1.0 M HClO<sub>4</sub> and phosphate buffer solutions (PBS) of different pH at a GCE modified with electrochemically partially reduced graphene oxide (GCE/ePRGO). Cyclic (CV) and square wave voltammeteries were the electrochemical techniques used. A surface quasi-reversible redox couple was found in all reaction media at this modified electrode. The Box-Behnken design (BBD) statistical experiments and the surface methodology (RSM) were used to optimize experimental variables to generate the GCE/ePRGO [35]. Atomic force microscopy (AFM) and electrochemical impedance spectroscopy (EIS) were used to characterize the surface of modified electrodes. EIS was also used to determine a tentative electrochemical area for the GCE/ePRGO.

On the other hand, the main objective of this work is to perform for the first time a complete characterization of the thermodynamic and kinetics of the surface redox couple in 1.0 M HClO<sub>4</sub> at glassy carbon electrodes modified with electrochemically partially reduced graphene oxide. Therefore, we used the methods of the “quasi-reversible maximum” and the “splitting of the net SW voltammetric peak” to obtain information about the thermodynamic and kinetics of the superficial redox couple [36–43]. The adsorption isotherm which best describes the specific interaction of CA with the surface of the modified electrode is also discussed. For comparison, CA electrochemical responses were also studied at bare GCE, and GCE modified with a dispersion of GO (GCE/GO).

## 2. Experimental

### 2.1. Reagents

CA, KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, HCl, trisodium salt of ethylene diamine tetraacetic acid, ferrocene, K<sub>4</sub>[Fe(CN)<sub>6</sub>] and K<sub>3</sub>[Fe(CN)<sub>6</sub>] were purchased from Sigma-Aldrich. HClO<sub>4</sub>, ethanol, methanol, acetic acid, KCl and KNO<sub>3</sub> were Merck p.a. Acetonitrile was Sintorgan, HPLC degree. Ultrapure water ( $\rho = 18 \text{ M}\Omega \text{ cm}$ ) was obtained from a Millipore-Milli Q system. Stock solutions of CA ( $1 \times 10^{-3} \text{ M}$ ) were prepared in ethanol, protected from light, and kept in the refrigerator. PBS were prepared

using 0.1 M Na<sub>2</sub>PO<sub>4</sub>H (Merck p.a.) and 0.1 M KPO<sub>4</sub>H<sub>2</sub> (Merck p.a.). Working solutions were prepared daily by adding different aliquots of the CA stock solution to 1 M HClO<sub>4</sub> aqueous solution or the corresponding PBS of different pH. All reagents were used as received. The percentage of ethanol in all solutions was 5%.

### 2.2. Apparatus

CV and SWV experiments were performed with an AutoLab PGSTAT 101 potentiostat, controlled by the NOVA1.9 electrochemical software. EIS experiments were performed with an AutoLab PGSTAT 30 potentiostat, controlled by the FRA 4.9 software.

The electrodes were inserted into the cell through holes in its Teflon cover. The working electrodes were a bare GCE and both modified GCE/GO and GCE/ePRGO. A platinum wire and Ag/AgCl, 3 M NaCl (BAS, RE-5B) were used as counter and reference electrodes, respectively. In CV, the scan rate ( $v$ ) was varied from 0.025 to 0.200 V s<sup>-1</sup>. In SWV, the amplitude ( $\Delta E_{\text{SW}}$ ) was varied from 0.025 to 0.100 V, the staircase step ( $\Delta E_s$ ) was 0.005 V, and the frequency ( $f$ ) was varied from 5 to 90 Hz.

EIS measurements were performed in solutions containing equal concentrations ( $1 \times 10^{-3} \text{ M}$ ) of reduced and oxidized forms of the [Fe(CN)<sub>6</sub>]<sup>4-3-</sup> redox couple, with 0.1 M KCl as the supporting electrolyte. An amplitude sine wave perturbation of 5 mV was applied to electrodes, whereas the dc potential was set at the formal potential of the redox couple, i.e.,  $E_f^0 = 0.250 \text{ V vs. Ag/AgCl}$ . The ac frequency was varied from 0.5 Hz to 10 kHz. Both, the in-phase ( $Z'$ ) and out-phase ( $Z''$ ) impedance components were extracted from experimental data. Nyquist plots were fitted from a non-linear fitting using two equivalent circuits (see below) [44,45], which can be defined into the FRA electrochemical impedance software. The characteristic parameters of both circuits were extracted from these fittings (see below). Most electrochemical measurements were performed at 25 °C, except those where the effect of temperature on voltammetric signals was studied.

Atomic force microscopy (AFM) images were obtained by using Agilent Technologies 5500 AFM (Agilent Technologies, CA, USA) working in acoustic AC mode using Si probes with force constants around of 40 N/m and resonance frequency in the range of 300–350 kHz (MikroMasch®, HQ: NSC15/AL BS). The experiments were performed in stationary dry-air atmosphere. Images were treated and analyzed using Gwyddion, open source software for the visualization and analysis of scanning probe microscopy data.

### 2.3. Preparation of graphene oxide dispersions

GO was synthesized from graphite flakes by using an improved method respect to that developed by Marcano et al. [46]. Thus, 9.0 g of KMnO<sub>4</sub> was added at a 9:1 mixture of H<sub>2</sub>SO<sub>4</sub> / H<sub>3</sub>PO<sub>4</sub> concentrated (180:20 cm<sup>3</sup>) with stirring. 1.5 g of graphite flakes were then added to form a uniform suspension, which was stirred and heated at 50 °C during 12 h. The mixture was cooled at 5 °C and poured onto ice (200 cm<sup>3</sup>) with 30% H<sub>2</sub>O<sub>2</sub> (1.5 cm<sup>3</sup>). The filtrate was centrifuged at 4000 rpm during 30 min and the precipitated solid was washed several times with a solution of 30% HCl and subsequently with water. The resulting solid was dispersed in water and dialyzed (dialysis membrane of regenerated cellulose with a molecular weight cut-off around 12–14 kD; Spectra/Por®) against water (18 MΩ cm) until the conductance of the dialyzed solution do not change after 6 h.

### 2.4. Preparation of electrodes

GCE were polished with alumina slurries of 0.30 and 0.05 μm during 1 min each one, and sonicated in water during 30 s. The polished GCE was modified with a GO dispersion (GCE/GO) by dropping an aliquot of  $10 \times 10^{-3} \text{ cm}^3$  of the dispersion on the top of the electrode and allows drying during 30 min at 37 °C. The GCE/ePRGO was generated by cycling the GCE/GO in the potential range between -0.200 V and

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