



Chemically versus electrochemically reduced graphene oxide: Improved amperometric and voltammetric sensors of phenolic compounds on higher roughness surfaces

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ABSTRACT

The electrochemistry of hydroquinone (HQ), catechol (CT), and dopamine (DP) on a glassy-carbon electrode (GCE) modified with chemically (CRGO) and electrochemically reduced graphene oxide (ERGO) was investigated and compared for the development of amperometric and voltammetric sensors. Cyclic voltammetric measurements showed higher current on the CRGO-modified GCE, which can be explained by the higher number of sheets compared with ERGO-modified as revealed by SEM images as well as higher roughness surface monitored by AFM, indicating a higher electroactive area. Electrochemical impedance spectroscopy (EIS) revealed that both modified surfaces presented a very similar behavior (Nyquist plots) and lower resistance to electron transfer in comparison with the unmodified GCE. Considering both modified electrodes for sensing purposes, differential-pulse voltammetry (DPV) in unstirred solutions and amperometry under hydrodynamic solutions showed higher sensitivity and lower limit of detection (LOD) values for HQ, CT and DP on the CRGO-modified GCE. These results indicate that the effect of surface rugosity and electroactive area of RGO modified electrodes contribute to the improvement of sensing characteristics of phenolic compounds using either DPV or amperometric detection under flow conditions. DPV and amperometry provided LOD values between 1 and 5 nmol L⁻¹ and 12 and 55 nmol L⁻¹, respectively, while the latter offers much faster responses resulting in theoretical analytical frequency higher than 1000 h⁻¹.

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1. Introduction

Carbon materials have been widely used in electroanalysis due to their low cost, wide potential window and good electrocatalytic activity [1]. Graphene is one among the variety of carbon materials, extensively studied in various applications in the past few years [2–5]. Reduced graphene oxide (RGO) is a two-dimensional material formed of sp² hybridized carbon atoms with a densely packed hexagonal structure with oxy-functional groups. These characteristics give the RGO important properties for use as electrochemical sensors, due to properties such as excellent adsorptivity and conductivity, high strength and good flexibility for chemical modification [6].

The graphene oxide (GO), precursor of RGO, can be reduced on various substrates and through various ways (thermal, photocatalytic, chemical, and electrochemical processes), yielding modified surfaces [7]. Examples of applications of RGO are the construction of a supercapacitor by reduction of GO using a copper plate forming highly conductive carbonaceous films [6], platinum electrodes coated with electrochemically reduced GO to study adsorption of dyes [7] and rGO/bimetallic platinum and palladium catalyst for electro-oxidation of methanol [8].

Electrochemical reduction of GO has received more attention in recent years over the other methods since it is a green approach and the thin film of reduced graphene oxide can easily be prepared by this method on conducting electrode substrate for electrocatalytic applications [9–11]. The electrochemically reduced GO is confined with a lower number of oxygen functionalities and is more conductive than the RGO prepared by other methods [12].

A study correlating the potential range used for the electrochemical reduction of the GO to RGO structure was performed

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[13]. It was observed that the structural disorder of RGO decreased and electrical conductivity significantly increased in the initial part of the reduction process between 0 and -0.5 V, connected with desorption of hydroxyl and formation of carboxyl groups. In the potential range from -1.0 V to -1.4 V, $-\text{COOH}$ was completely reduced to $\text{C}=\text{O}$, and from -1.6 V to -1.8 V the reduction of $\text{C}=\text{O}$ was observed [13].

Catechol (CT), dopamine (DP) and hydroquinone (HQ) are phenolic compounds of environmental and biological interests and DP has been commonly used as model analyte [14]. In the literature there are some works using different electrochemical techniques and RGO-based electrodes, including electrochemically (ERGO) and chemically reduced graphene oxide (CRGO) to determine DP in some matrices. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using electrodes modified with ERGO were applied to determine DP obtaining detection limits (LD) of $3 \mu\text{mol L}^{-1}$ [15] and $0.5 \mu\text{mol L}^{-1}$ [16], the latter work applied in urine samples. CV and DPV techniques combined with a CRGO-modified electrode was applied to determine DP, obtaining LD values of $2.64 \mu\text{mol L}^{-1}$ [17] and $0.6 \mu\text{mol L}^{-1}$ [18], respectively, the latter applied to blood serum samples. Another work reported the detection of CT employing a CRGO-modified electrode with a LD value of $0.01 \mu\text{mol L}^{-1}$ using DPV [19] while a second work showed a LD value of $0.1 \mu\text{mol L}^{-1}$ for CT on a ERGO-modified electrode using DPV [20]. Hence, there are different investigations demonstrating the feasibility of ERGO- and CRGO-modified electrodes for phenolic compounds; however, to our knowledge, there is not a comparison between the two procedures.

The use of amperometric detection using RGO-modified electrodes is still scarcely reported although this technique offers high speed and sensitive detection under hydrodynamic conditions. Importantly, the combination of amperometric detection with batch-injection analysis (BIA) offers great promise to perform on-site determinations as the complete analytical system is portable, eliminating the external use of valves and pumps [21]. Additional advantages include the increase in speed and precision and reduction of sample volume and waste. BIA with amperometric detection using modified electrodes has been demonstrated [22–25].

The objective of this study was to compare the performance of a glassy-carbon electrode (GCE) modified with ERGO and CRGO towards the electrochemical response of the phenolic compounds, CT, DP and HQ, by cyclic voltammetry, DPV, and amperometric detection combined with fast BIA. Both electrode surfaces were characterized to further correlate with electrochemical responses obtained on each modified electrode.

2. Experimental

2.1. Materials

Graphene oxide (GO) used for ERGO and CRGO synthesis was laboratory prepared from graphite through the Hummers method. Hydroquinone (<99%) and catechol (<99%) were obtained from Fluka Analytical (Steinheim, Germany) and dopamine (<99%) from Acros (New Jersey, USA). All solutions were prepared with deionized water with a resistivity of at least $18 \text{ M}\Omega \text{ cm}$ obtaining from a Milli-Q purification system (Millipore, Bedford, MA, USA). To prepare the supporting electrolyte, perchloric acid (70% v/v) was obtained from Reagan (Rio de Janeiro, Brazil) was used. The stock solutions of the analytes were prepared every day before the experiments in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$.

2.2. Apparatus

The electrochemical measurements (voltammetry and amperometry) were performed with an Ivium potentiostat/galvanostat (VERTEX, Ivium, Eindhoven, Netherlands) interfaced to a personal computer, with appropriate software for data acquisition and treatment (IviumSoft 2.5). Electrochemical impedance spectroscopy (EIS) measurements were acquired with PGSTAT 128N (Eco Chemie – Metrohm). The working electrode was a modified or unmodified glassy-carbon disk ($\varnothing = 1.5$ mm, BASi Inc., USA). A miniaturized Ag/AgCl_(sat) [26] and a platinum wire were used as reference and auxiliary electrodes, respectively.

Scanning electron microscopy (SEM) analysis was performed using a Vega 3 LMU (TESCAN, Brno-Kohoutovice, Czech Republic) operated at 30 kV. The samples were dispersed in dimethylformamide and drop-casted on GCE (CRGO) or acquired directly from the ERGO-modified GCE.

Raman spectra from CRGO and ERGO modified electrodes were obtained using a LabRAM HR Evolution microscope (HORIBA, Kyoto, Japan) using a 532 nm Arion laser.

Atomic force microscopy (AFM) images were obtained from a Shimadzu Scanning Probe Microscope (SPM-9600) using the tapping-mode to study the sample surface.

2.3. ERGO synthesis

The ERGO synthesis was adapted from the literature [27,28], and consisted in preparing a 10 mL dispersion of commercial GO (1 mg mL^{-1}) in a 0.05 mol L^{-1} sodium phosphate solution. The dispersion was homogenized for 30 min in ultrasonic bath. Then, dissolved oxygen was removed by bubbling N_2 for 10 min. The electrochemical synthesis on a cleaned GCE was made by cyclic voltammetry (potential range from 0 to -1.7 V, 10 cycles and scan rate of 75 mV s^{-1}) in a cell with three electrodes.

2.4. Preparation of graphene oxide and its chemical reduction

The process of obtaining graphene oxide was performed in two steps. The first step was the oxidation of natural graphite using the oxidizing agent Mn_2O_7 , obtained by reaction of sulfuric acid and potassium permanganate. After the oxidation reaction period (75 min), 700 mL of deionized water with 3% hydrogen peroxide was added. Posteriorly, the formed solid was filtered, washed with HCl solution (5%) and water until neutral pH, and then dried in oven (60°C). The dried material prepared was named as graphite oxide (Gr-O). This approach is commonly called Hummers method [29]. After obtaining the Gr-O, this material was dispersed in water (in known proportions) using an ultrasonic bath which resulted in graphene oxide dispersions (GO).

For the chemical synthesis of RGO from GO, the reduction with NaBH_4 was used at a ratio of 1.0 mL of aqueous graphene oxide dispersion to 6.0 mg of NaBH_4 . The obtained black solid (CRGO) was then filtered, washed several times with distilled water and dried at 100°C for 24 h.

2.5. Preparation of the CRGO modified electrodes

A suspension of 0.5 mg mL^{-1} of CRGO in dimethylformamide was sonicated with a high frequency ultrasonic tip for 10 min, and then a drop of $20 \mu\text{L}$ was added to the cleaned surface of GCE. The electrode was then heated for 30 min at 60°C to obtain the modified electrode.

The cleaning of the GCE surface prior to the modification either with ERGO or CRGO was carried out by mechanical polishing using an alumina powder suspension ($0.3 \mu\text{m}$) and rinsed with deionized

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