



A graphene oxide modified carbon ceramic electrode for voltammetric determination of gallic acid

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ABSTRACT

In this paper, a new type of carbon ceramic electrode modified with reduced graphene oxide (RGO) was fabricated via sol-gel method. The constructed electrode was used in square wave voltammetric (SWV) determination of gallic acid (GA). The electrochemical properties of the fabricated electrode and voltammetric behavior of gallic acid were investigated by cyclic voltammetry (CV). The SWV investigation of GA was performed in Britton-Robinson buffer at pH 2 as a supporting electrolyte. Under the optimized SWV mode parameters, the oxidation peak current (best measured at 0.57 V vs Ag/AgCl) increased linearly in the wide concentration range from 0.51 to 46.40 $\mu\text{mol L}^{-1}$. The calculated values of LOD and LOQ were 0.0867 and 0.263 $\mu\text{mol L}^{-1}$, respectively. The presented results were obtained without any preconcentration procedure. During the experiment, the effect of common interfering molecules was also investigated. Finally, the usability of the proposed method was verified by the quantitative analysis of GA in red wine, black tea and white tea samples.

1. Introduction

Carbon ceramic electrode (CCE) that can be obtained in a simple way by the sol-gel method is a very attractive type of carbon-based electrodes. According to the literature, carbon ceramic electrodes can be used for determination of different biological substances e.g.: paracetamol [1], L-tyrosine [2], ascorbic acid [3], hydrazine [4] or estradiol [5]. CCEs possess unique features - they are porous and rigid, and they can be easily modified both on surface and in entire volume. The surface modification possesses the inability for easy refreshment of electrode surface. In case of surface damage, the new modifier layer must be prepared. The good alternative for this kind of modification is entire volume modification and it is the most important advantages of CCEs. They can be easily modified in entire volume by direct incorporation of modifier in silica matrix, which allows to eliminate the problem with the surface renewal.

Many examples of surface and entire volume modified carbon ceramic electrodes proposed by other researches can be found in the literature. Shamsipur and co-workers proposed surface modification of CCE using gold nanoparticles [6]. The surface of CCE can also be modified using copper nanoparticles or ionic liquid [7]. It is known, that entire volume modification is less complicated and faster when compared to surface modification procedure. In literature we can find examples where molecules such as buckyballs [8], mixed oxides SiO_2 /

SnO_2 [9] or Ru(II)-complex [10] were incorporated in silica matrix of CCEs. All of the mentioned reports show, that the modified carbon ceramic electrodes exhibit good analytical properties. In our previous papers it was proved that graphite enrichment by bismuth oxide [11] or zeolites [5] improves the electroanalytical quality of the CCEs. The carbon ceramic electrode can be also modified by replacement of graphite powder by other carbon material. It was confirmed that graphite replacement with carbon nanotubes allows to produce electrodes of higher stability, sensitivity and selectivity when compared to standard carbon ceramic electrode [12, 13]. Another carbon material worth of interest in this aspect is graphene. Because of its unique properties, in particular its ability to rapid electron transfer, a significant improvement in the electroanalytical quality of CCE should be expected. In the literature data, only few reports are dedicated to using of graphene for surface modification [14] and entire volume modification [15] of CCEs. It is worth to notice, that proposed electrode preparation procedure is faster and simpler in comparison with electrodes proposed by other researchers.

Gallic acid (GA, 3,4,5-trihydroxybenzoic acid) is one of the main polyphenolic acid that widely exists in tea and other plants such as sorghum, wheat, rice, corn, and fruits such as grapes and apples [16]. This acid exhibits strong antioxidant properties, as well as anti-cancer, anti-aging and bacteriostatic effects. Due to bioactive and pharmacological importance of GA, the development of sensitive and fast

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methods for its determination in real samples is essential. GA can be determined in various types of samples using different kinds of methods. According to the literature several methods such as: high performance liquid chromatography [17, 18], ultrahigh performance liquid chromatography [19], flow injection chemiluminescent analysis [20], reverse flow spectrophotometry [21] and photoelectrochemical platform [22] can be used for determination of GA. Nevertheless, most of these methods require time-consuming pretreatment steps, and expensive analytical instruments. In recent times, it is observed, that electrochemical methods can be a very good alternative for the mentioned advanced techniques. Conversely to the other techniques, they exhibit low-dose solvent consumption, less interference, and the possibility of the faster direct detection. Literature data show that GA and other phenolic compounds were determined in real samples via various electrochemical techniques using different electrodes e.g.: bare glassy carbon electrode [23, 24], polypyrrole modified glassy carbon electrode [25], carbon paste electrode modified with nanotubes [26], hanging mercury drop electrode [27], polyethyleneimine-functionalized graphene modified glassy carbon electrodes [28], indium-tin oxide electrodes [29] and boron-doped graphene electrode [30].

In this paper, the entire volume modification of the ceramic carbon electrode using reduced graphene oxide was conducted. The effect of such modification on CCE properties was studied by comparison of cyclic voltammograms of ferrocyanide model probe registered at ceramic electrodes with and without addition of graphene, marked as RGO-CCE and GP-CCE respectively. Moreover, for the first time, the square wave voltammetric procedure of GA at RGO-CCE was developed and validated. The optimized procedure was used for direct determination of analyte in real samples.

2. Experimental

2.1. Apparatus

The surface morphology of the GP-CCE and RGO-CCE was characterized by scanning electron microscopy (SEM, Nova NanoSEM 450, FEI) using a through lens detector (TLD) with an accelerating voltage of 10 kV. The SEM images were obtained with magnification of $35,000\times$.

All voltammetric measurements were performed using μ Autolab type II electrochemical analyzer (Metrohm Autolab B.V., Utrecht, The Netherlands) interfaced with an M164 electrode stand (*mtm anko*, Cracow, Poland) and controlled by GPES 4.9 software. A three-electrode cell consisted of GP-CCE or RGO-CCE as a working electrode, an Ag/AgCl/3 mol L⁻¹ KCl as a reference electrode, and a platinum wire as a counter electrode was used. All experiments were conducted at room temperature. The electrochemical impedance spectroscopic (EIS) measurements were performed with an Autolab PGSTAT 128 N potentiostat-galvanostat (Metrohm Autolab B.V., Utrecht, The Netherlands) with FRA2 (Frequency Response Analyzer) module controlled by FRA software (version 4.9) in conjunction with the electrodes stand.

2.2. Reagents and materials

Methyltrimethoxysilane (MTMS, pure 98%, Sigma Aldrich), methanol (CH₃OH, 99.8%, pure p.a., Avantor), hydrochloric acid (HCl, 36%, pure p.a., Avantor), graphite powder (GP, pure 99%, ALFA AESAR), reduced graphene oxide (RGO, Sigma Aldrich) were used for electrodes preparation.

The solution of 1×10^{-3} mol L⁻¹ potassium ferrocyanide (K₃[Fe(CN)₆], pure p.a., Avantor) dissolved in 1 mol L⁻¹ potassium chloride (KCl, pure p.a., Avantor) was used for the preliminary research. The standard stock solution of 1×10^{-3} mol L⁻¹ gallic acid (GA, C₇H₆O₅, pure 98.0%, Fluka) was obtained by dissolution of an appropriate amount of this reagent in water with the aid of an ultrasonic bath (15 min), and then was stored in a glass flask in fridge. The 0.04 mol L⁻¹ Britton-Robinson buffer solution (B-R) was prepared by

mixing of 0.04 mol L⁻¹ phosphoric acid (H₃PO₄, 85.0%, pure p.a., Avantor), 0.04 mol L⁻¹ acetic acid (CH₃COOH, 99.0%, pure p.a., Avantor), and 0.04 mol L⁻¹ boric acid (H₃BO₃, pure p.a., Avantor). The required pH value in the range from 2.0 to 12.0 was adjusted by 0.20 mol L⁻¹ sodium hydroxide (NaOH, pure p.a., Avantor).

2.3. Preparation of the bare CCE and RGO-CCE electrodes

For the fabrication of CCEs, the modified one step sol-gel procedure proposed by Lev and co-workers [31] was used. The bare electrode (GP-CCE) was prepared by mixing of 500 μ L of methanol (alcohol solvent) with 250 μ L of methyltrimethoxysilane (Si precursor) and 50 μ L of concentrated hydrochloric acid (catalyst). After 5 min of mixing 0.75 g of activated graphite powder was added and hand-mixed for additional 5 min using spatula. The obtained matrix was introduced into the Teflon body (ca. 3 mm of inner diameter) and then dried for 24 h at room conditions. The modified RGO-CCE was obtained in analogous procedure, but 0.05 g of graphite powder was replaced by reduced graphene oxide. As an electric contact in both cases a silver-painted copper wire was used. After 24 h of drying the surface of the electrodes was mechanical polished with 2500 grid silicon carbide paper, next rinsed with triply distilled water, and dried with argon.

2.4. Real sample preparation

The red wine samples (Castellani Merlot Venezie I.G.T.) were analyzed without pre-treatment. The analyzed tea samples were: black tea (Irving, 100 g) and white tea (Big-active, 50 g) both bought in Poland free market. Decoction of tea was prepared by boiling tea leaves (1 g) in distilled water (50 mL) for 20 min into 50 mL of distilled water, and after cooling the decoction was filtered using filter paper. Finally, the tea solutions used in analytical procedure were diluted 100 folds with B-R buffer (pH 2).

2.5. Measurement procedure

The behavior studies of potassium ferrocyanide and GA at GP-CCE and RGO-CCE were performed by cyclic voltammetry (CV). In CV mode the potential was swept over the range from 0.0 V to +0.6 V (for potassium ferrocyanide) and from +0.1 V to +1.3 V (for GA) at different scan rates (ν). Electrochemical impedance spectroscopic (EIS) measurement was performed in the frequency range of 100 kHz–0.01 Hz (50 points within the frequency range) in 0.1 mol L⁻¹ KCl containing 5 mmol L⁻¹ [Fe(CN)₆]^{3-/4-} redox probe.

For quantitative determination of GA square wave voltammetry (SWV) was used, and the scanning was performed in the potential range from 0 V to +1.65 V. To obtain the blank SW voltammograms, the following procedure was applied: 9 mL of the supporting electrolyte and 1 mL of the distilled water were poured into the cell, and the voltammograms were recorded under the inert atmosphere of the cell. The calibration curve was performed under optimized SWV parameters. The subsequent addition of the GA stock solution was transferred into the voltammetric cell with the supporting electrolyte. Each concentration from the calibration curve was measured in quintuplicate ($n = 5$).

Determination of GA in red wine samples was performed by direct addition of 40 μ L of sample to the electrochemical cell with B-R buffer at pH 2, and the SW voltammograms were recorded.

3. Results and discussion

3.1. Surface characterization

As can be seen in Fig. 1, the surface morphology of GP-CCE and RGO-CCE is slightly different. In case of bare electrode the graphite flakes tightly distributed in silica matrix can be observed (Fig. 1a). Whereas in case of RGO-CCE the pore formation between flakes is more

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