Electrochemistry Communications 43 (2014) 51–54

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Permselectivity and preconcentration properties of taurine/graphite oxide electrode coatings: Analytical perspectives

Barbara Brunetti *, Elio Desimoni

DeFENS, University of Milan, Via Celoria 2, I-20133 Milan, Italy

ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form 4 March 2014
Accepted 14 March 2014
Available online 22 March 2014

Keywords:
Chemically modified electrodes
Taurine
Permselectivity
Voltammetry

ABSTRACT

A glassy carbon electrode is modified by the formation of a taurine/graphite oxide film. The procedure involves potentiostatic oxidation of taurine in a pH 7 solution. The modified electrode presents attractive features such as permselectivity against anions and preconcetration of cation species leading to an increased selectivity and sensibility respect to a bare electrode. Potential analytical applications are investigated.

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1. Introduction

Electrode modification still receives a continuously growing attention thanks to the conferred appealing features, such as increased sensitivity and selectivity. Amongst the possible modifiers, are worth mentioning sulphonated species, such as Nafion, poly(p-aminobenzene sulfonic acid), cysteic acid and so on [1]. Most of these species are deposited by electrochemical oxidation, both potentiostatically or by cycling the potential.

Another sulphonated species, taurine (2-aminoethanesulfonic acid), was recently used as a modifier for determining pharmaceuticals [2–5]. Taurine was electropolymerized onto plain glassy carbon electrodes (GCEs) [2] or modified GCE [3–5] cycling the potential in a wide range. However, it is also well known [6–8] that this procedure leads to the formation of oxygen-containing functionalities and consequently to a graphite oxide film. In both these cases, enhanced sensitivity towards cationic species, but not permselectivity against anionic ones was seen at the relevant electrodes.

In this work, the surface modification of GCE was obtained by potentiostatic deposition from a taurine solution. After having assessed the best modification procedure, prospective analytical applications were investigated. The results are described and discussed in the light of the existing literature.

2. Experimental

2.1. Materials and apparatus

Ultrapure water was obtained by passing house-distilled water through a Simplicity 185 water purification system (Merck Millipore, USA). Taurine and the other reagents (Sigma-Aldrich, Italy) were of analytical grade and used as received.

Voltammetric analyses were performed using a μ-Autolab Type III potentiostat (Metrohm-Autolab) connected to a 663VA stand through an IME663 interface and computer-controlled using GPES v. 4.9 software. All measurements were conducted using a three-electrode cell equipped with a glassy carbon electrode (2 mm diameter, Metrohm), an Ag/AgCl (3 M KCl) reference electrode and a platinum counter electrode.

The morphological examination was carried out with an optical inverted microscope XDS-3 MET (Optika Microscopes) connected to a digital USB camera and computer-controlled by the Optika Vision Pro software.

Experiments were conducted at room temperature (22 ± 2 °C).

2.2. Preparation of the modified electrodes

Glassy carbon electrodes were mirror polished with alumina slurry, removing residual polishing material by ultrasonication.

The preparation of the taurine/graphite oxide modified electrode (TME) was achieved in a $2 \cdot 10^{-3}$ M taurine solution (supporting electrolyte: pH 7 phosphate buffer) keeping the potential at 2.0 V

* Corresponding author.
E-mail address: barbara.brunetti@unimi.it (B. Brunetti).

http://dx.doi.org/10.1016/j.elecom.2014.03.009
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for 300 s. After the modification, the electrode was rinsed with water and dried at room temperature.

Every experiment was performed by using a newly prepared electrode. At the end, electrodes were cleaned with an alcohol/water wet cloth and polished as described above.

3. Results and discussion

3.1. Surface modification of the electrode

Accordingly to literature results, taurine could be electropolymerized directly onto GCE [2] or GCE modified with different species, such as carbon nanotubes [3], TiO_2-graphene nanocomposite [4], and zirconia nanoparticles [5]. The reported procedures involve cycling the potential in pH 7 phosphate buffer containing 2 mm taurine, in very wide potential ranges, from − 1.5 V to 2.0 V [2,4,5] or even to 2.5 V [3]. As evidence of the deposition, Authors reported a voltammetric pattern characterized by an increase of a peak height ascribed to taurine, along with the observation of a coloring of the electrode. An increased sensitivity respect to the bare GCE was reported for all the considered analytes. However, it is also well known [6–8] that cycling the potential of a GCE in such a wide range leads to the surface formation of oxygen-containing functional groups (OH^-, etc). An analogous coloration of the surface was observed even in this case and the colored film was ascribed to the formation of a porous graphite oxide film [8–11].

In this work, surface modification of the GCE was obtained in a different way, i.e. by depositing taurine on the electrode surface at a fixed potential value. As a matter of fact, electropolymerization which is done by applying a constant potential (potentiostatic deposition) is a widely used technique too [12–14].

The influence of modification parameters (taurine concentration, deposition potential and time) on the electrode performances was evaluated comparing the cyclic voltammograms recorded at all the obtained sensors using dopamine as benchmark. As far as taurine concentration is concerned, values higher than $2 \cdot 10^{-3}$ M caused an increase in the background current and a slight drop in the electrode response. Likely, an excessive thickness of the layer could reduce the electrode conductivity. Electrodes obtained by deposition at potentials lower than 2.0 V exhibit a lower activity towards the benchmark species, but still increased respect that of a bare GCE.

In order to compare the selected procedure with those previously reported [2–5], some electrodes were also modified by cycling the potential in the reported ranges, obtaining a sensitivity lower than that of the sensor proposed in this paper.

3.2. Morphology

Morphological analysis by the optical microscope was performed to better understand the actual surface status of the modified electrodes. A color change was clearly observed for all the differently modified electrodes.

The taurine layer obtained in the chosen conditions (deposition at 2.0 V for 300 s) resulted indefinitely stable in every medium at whatever pH value, as reported in Fig. 1. On the contrary, layers grown at higher deposition potential and/or for longer times, underwent a quick swelling and subsequent detachment from the electrode surface after immersing the electrode in the test solution (Fig. 1).

Electrodes obtained by deposition at potentials lower than 2.0 V showed a lighter color such as those obtained following literature information [2,3]. In this last case, the coloration was also more uneven showing just circular spots.

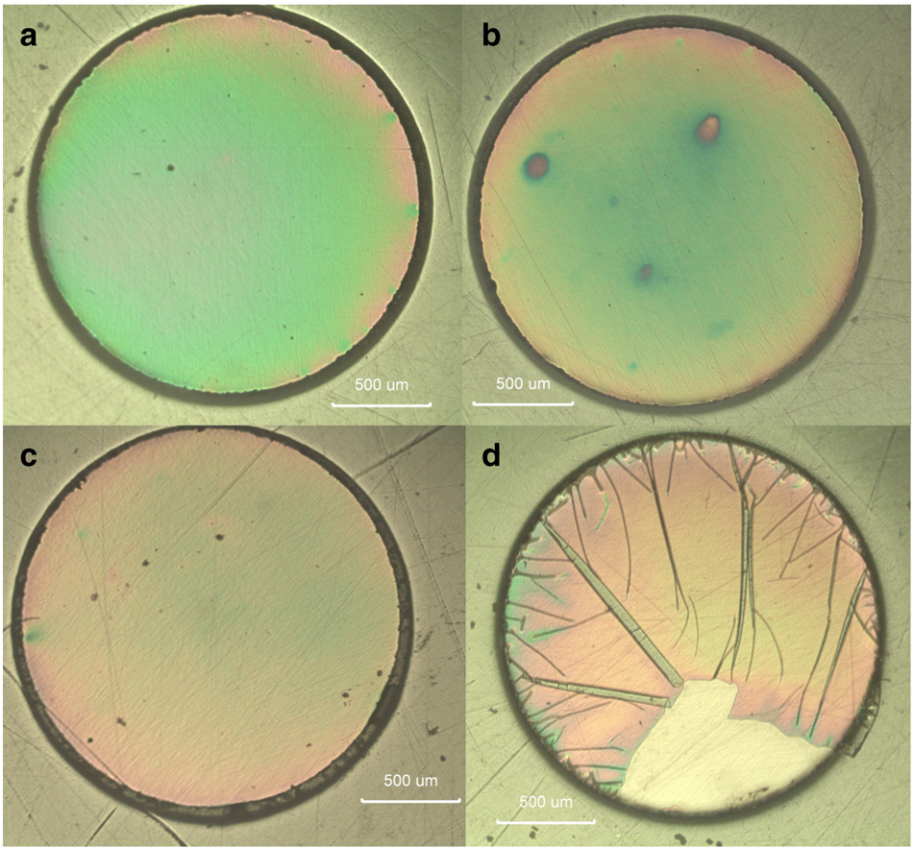

Fig. 1. Microscope images of a TME before (a) and after (b) immersion in a 10^{-3} M dopamine solution for 30 min. c and d refer to the corresponding images of an electrode obtained by deposition at 2.5 V for 300 s.

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