



Graphene nanoribbon-based electrochemical sensors on screen-printed platforms



Aída Martín^a, Javier Hernández-Ferrer^b, María Teresa Martínez^b, Alberto Escarpa^{a,*}

^a Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, E-28871 Alcalá de Henares, Madrid, Spain

^b Instituto de Carboquímica ICB-CSIC, Miguel Luesma Castán, 4, 50018 Zaragoza, Spain

ARTICLE INFO

Article history:

Received 31 July 2014

Received in revised form 13 November 2014

Accepted 13 November 2014

Available online 15 November 2014

Keywords:

Graphene oxide nanoribbons
reduced graphene nanoribbons
multiwalled carbon nanotubes
electrochemical sensor
screen-printed electrodes
uric acid
ascorbic acid and levodopa

ABSTRACT

In this work, oxidized graphene nanoribbons (GNRox) and reduced graphene nanoribbons (GNRred) were explored for the construction of disposable electrochemical sensors on screen-printed platforms for the sensing of ascorbic acid (AA), levodopa (LD) and uric acid (UA).

GNRred demonstrated improved electroanalytical performance in comparison not only with the carbon screen printed electrodes (CSPEs), but also with other related carbon nanomaterials such as multi-walled carbon nanotubes (MWCNTs) and GNRox. MWCNTs served as the carbon source for GNRox which was further reduced to form GNRred.

The excellent electrocatalysis exhibited by this carbon nanomaterial toward AA, LD and UA allowed a fast (100 s), selective (at +0.08, +0.27 and +0.39 V, respectively), and accurate determination (with recoveries between 97 to 101%) of these analytes in urine samples.

Excellent intra-electrode repeatability (RSD < 5%, n = 10), inter-electrode reproducibility (RSD < 13%, n = 5 electrodes) and stability of the sensor (the electrode maintained 93 ± 3% of its signal after 15 days) were also demonstrated, becoming this electrochemical sensor a valuable tool for clinical routine uric acid assessment.

Tailored graphene nanoribbons on screen-printed platforms become a new generation of disposable graphene-based electrochemical sensors for POC testing applications.

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1. Introduction

Graphene is a two dimensional lattice of carbon atoms bonded by sp² hybridization. This structure provides the material its extraordinary properties [1–3], such as high surface area, excellent thermal and electrical conductivities, optical transparence, high mechanical strength and high elasticity, among others. Of these listed properties, its large surface area and its high electrical conductivity have been exploited, for its application in electrochemistry, although others, such as the impurities content could play an important role [4]. This general definition and properties describe the theoretical or pristine graphene, however, considering synthesized graphenes, graphene family includes a broad variety of terms that describe different materials with different physical structure and properties [5].

Basically, the most applied graphenes in analytical electrochemistry present as main sources graphite or carbon nanotubes (CNTs) in top-down scheme synthesis. On the one hand, the

oxidation and exfoliation of graphite yield graphene oxide (GO), this material loses the aromaticity and the heterogeneous electron transfer (HET) rate is lower than in pristine graphene. Furthermore, the reduction of GO via chemical, thermal or electrochemical treatments generate reduced graphene oxide (GR) [6]. Although this material recovers the aromaticity and increases the HET compared with GO [7], GR material presents defects and new heteroatoms in the carbon lattice compared with the pristine graphene [8]. These GO and GR materials cover more than half of the analytical literature about graphene in electrochemical applications (see selected reviews [5,9–15]). On the other hand, from the opening process of CNTs, graphene nanoribbons (GNRs) are produced [16]. These graphitic structures are dimensionally limited in the basal plane x–y, from a few to some hundred nanometers, because the diameter of the CNT limits the final dimension. Although many synthetic processes have been described in the literature [17–20] for synthesizing GNRs, again, the oxidation step to open the CNT and the reduction process of the generated nanoribbon are the most cited in analytical electrochemistry.

In contrast with pristine graphene, GNRs obtained by chemical oxidation of CNTs are really promising in electrochemistry,

* Corresponding author. Fax: +34 91 885 49 71.

E-mail address: alberto.escarpa@uah.es (A. Escarpa).

because of the edge chemistry involved in GNR. Pristine graphene has an inert chemical surface, without defects and they exhibit poor electrochemical behavior [21], on the contrary, these graphene nanoribbons are more reactive. This reactivity can be caused by the adsorption of analytes via π - π stacking interaction, and by electrostatic or hydrogen bond interactions with functionalities of the target molecules and the oxygen moieties located at the edges of the graphene material [22]. Remarkably, however GNRs have scarcely been explored, in the relevant literature, as electrochemical transducers for sensing or biosensing applications [5] tailored graphene nanoribbons seem to be a useful tool in electrochemistry [22,23].

In authors' opinion, GNR is an under exploited carbon nano-material full of properties which needs to be demonstrated. The most relevant and expected promises derived from the use of these carbon nanomaterials in electrochemical sensing should be: (i) The electrocatalytic effect induced by graphene materials might have an effect on the redox capacity of analytes and, consequently, on the decrease of the detection potentials, which would improve the overall *selectivity* of the analysis. (ii) Enhancement of faradaic currents, since the large surface area of graphene detectors would permit rapid redox conversion. This implies the increase in *sensitivity* in the analytical procedure. (iii) Increase the resistance to passivation originated from the greater surface area of the graphene-based detectors. It implies better *reproducibility* in analysis, because of the lower electrode fouling.

To demonstrate the analytical potency of GNRs, the detection of the three target analytes (AA, LD and UA) has been chosen. Remarkably, these electroactive molecules with high clinical significance which has been scarcely reported in the bibliography using these nanomaterials [22,24,25].

In this paper, the analytical performance of two GNR materials, oxidized graphene nanoribbons (GNRox) (44% wt. oxygen content) and reduced graphene nanoribbons (GNRred) (14% wt. oxygen content) has been studied to build electrochemical sensors on the carbon screen-printed (CSPE) platforms in the detection of AA, LD and UA.

2. Experimental

2.1. Materials and Reagents

Graphene materials were synthesized from multiwall carbon nanotubes (MWCNTs) via the longitudinal unzipping method [16]. Using these GNRox (44% wt. oxygen content), the chemical reduction with N_2H_4/NH_3 [26] yielded GNRred (14% wt. oxygen content). These carbon nanomaterials have been previously characterized [22]. Briefly, GNR features could be summarized as follows (see Table 1): using atomic force microscopy (AFM),

GNRox showed height profiles of 0.8 nm (with sizes of layers of 200 nm x 150 nm) while in GNRred the height was 1.2 nm (with sizes of layers of 120 nm x 50 nm), suggesting the presence of one and three layers in GNRox and GNRred, respectively. Considering the results obtained by XPS, Raman and IR spectroscopy techniques, GNRox showed high percentage of carboxyl and alcohol groups while the content of sp^2 carbons and defects in the structure was increased in GNRred. Furthermore, Raman data showed the presence of additional edges (more defects) and small layers in GNRred, being consistent with the results found in AFM.

Levodopa or L-3,4-dihydroxyphenylalanine (LD) and uric acid (UA) were purchased in Sigma Aldrich (St. Louis, MO, USA). Ascorbic acid (AA) was obtained in Fluka Chemika (Buchs, UK). Sodium dihydrogen phosphate and disodium hydrogen phosphate used to prepare phosphate buffered solution (PBS), as well as, potassium hexacyanoferrate (III) were purchased in Panreac (Badalona, Spain).

Standard solutions were prepared in 0.10 M phosphate buffered solution (PBS) at pH=7.4 adjusted with NaOH. All working solutions were well protected from light and daily prepared. Mixtures of 5 mM AA, 0.05 mM LD and 0.05 mM UA in 0.1 M PBS at pH= 7.4, were explored to study precision parameters. Urine samples recollected from healthy individuals were 50 and 100-fold diluted with the buffer solution before analysis. All solutions were prepared with Milli-Q water from a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Apparatus and measurements

Field emission scanning electron microscopy (FE-SEM) images were obtained on a JEOL Model JSM6335F equipment working at 5 kV. The aluminum mount stubs used for the FE-SEM analysis were obtained from Electron Microscopy Sciences (Hatfield, UK). Direct determination of oxygen was carried out with a Flash 1112 analyzer from Thermo Fisher Scientific.

All electrochemical measurements were performed, at room temperature, on an USB-based portable electrochemical station μ -Stat 100 potentiostat controlled by PSLite 1.6 software and on a carbon screen-printed electrode (CSPE), which integrates the three-electrode system, a carbon working electrode of 4 mm diameter as well as a carbon counter and silver (Ag) pseudo-reference electrodes (Dropsens, Oviedo, Spain).

2.3. Methods

2.3.1. Preparation of graphene modified electrode

GNRred was dispersed to obtain a 0.5 mg mL⁻¹ dispersion in water/NH₃ (1% v/v) by ultrasonication in a bath for 30 min, followed by tip sonication using a VCX130, (Sonics, Newtown, USA)

Table 1
Analytical characteristics of the GNRred s and GNRox.

TECHNIQUE		MATERIAL	
		GNRred	GNRox
Microscopy	TEM	Stacked layers	Folded layers
	AFM	1.2 nm height 3–4 layers 120 nm × 50 nm	0.8 nm height 1 layer 200 nm × 150 nm
Spectroscopy	Raman	High content of defects. Small layers	High sp^3 content
	IR	ν_{CO} (weak)	ν_{CO} (strong)
	XPS	ν_{CO} (weak) 15% C=O 10% C–O 47% Csp^2 10% Csp^3	ν_{CO} (strong, broad) 46% C=O 26% C–O 2% Csp^2 19% Csp^3
Others	Oxygen content	14%	44%

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