

**Aqueous UV-VIS spectroelectrochemical study of the
voltammetric reduction of graphene oxide on screen
printed carbon electrodes**

Carla Navarro Hernández^a, Maria Begoña González García^a, David Hernández Santos^a, M^a
Aranzazu Heras^b, Alvaro Colina^b, Pablo Fanjul-Bolado^{a*}

^aDropSens, S.L., Ed. CEEI, Parque Tecnológico de Asturias, 33428-Llanera, Asturias,
Spain

^bDepartment of Chemistry, Universidad de Burgos, Pza.Misael Bañuelos s/n, E-09001,
Burgos, Spain

*e-mail: pfanjul@dropsens.com

* To whom correspondence should be addressed.

Abstract

Two graphene oxide (GO) materials with different layer size and proportion of functional groups in the basal planes (hydroxyl and epoxy) and in the edges (carbonyl and carboxyl) were used to modify the surface of commercially available screen printed electrodes. Cyclic voltammetry in 0.1 M KNO_3 was evaluated as an easy to use electrochemical methodology to reduce GO attached to the surface of screen-printed electrodes (SPEs). A cathodic peak related to the reduction of GO was identified, and the peak potential was correlated to the difficulty to reduce GO to Electrochemically Reduced Graphene Oxide (ERGO) depending on the functional groups present in the basal plane and in the edges of the original GO monolayers. Time resolved UV-VIS absorption spectroelectrochemistry in near-normal reflection mode on a screen-printed electrode is used for the very first time as an *in-situ* characterization technique for real time monitoring unambiguously the electrochemical reduction of graphene oxide.

Keywords: Graphene Oxide, Electrochemically Reduced Graphene Oxide, screen-printed electrodes, cyclic voltammetry, Raman spectroscopy, UV-VIS Spectroelectrochemistry.

1. Introduction

It is well known that the aromatic lattice of graphene where each atom of carbon is bonded to other three in a sp^2 hybridization structure, is discontinued by oxygen based functional groups in graphene oxide (GO). These functional groups are mainly hydroxyl and epoxy ones located in the basal planes [1,2] while usually carboxylic and carbonyl groups are distributed in the edges [3]. GO is generally produced by chemical methods involving oxidation and exfoliation steps where the defects in form of functional groups are decorating the ordered ideal graphene structure [4-5]. These functional groups are highly hydrophilic and very useful to functionalize graphene surface with other molecules. GO also forms stable and homogeneous aqueous dispersions preventing aggregation by stacking of the monolayers due to the repulsive interactions between functional groups of different monolayers. Stable and homogeneous dispersions of GO are very useful for easy electrode modification by dip-coating or drop-casting [6-7]. However a later reduction step is necessary to partially recover both the inherent mechanical and electrical conductivity properties of graphene [8], and the surface morphology with the ideal ordered sp^2 hybridization structure [9-11]. Chemical reduction of GO usually needs later cleaning steps while thermal reduction of GO typically provokes the structural damage of the graphene [12]. The third more used method is the electrochemical reduction that avoids the drawbacks of the previous ones, and allows us to have a higher control of the reduction process [13-15]. Therefore, in

this work we made use of an easy voltammetric method to electrochemically reduce GO fixed in the electrode surface. The effect of functional groups in the monolayers, determined from the XPS analysis of different GO, on the reduction process can be clearly observed using electrochemical techniques.

Raman Spectroelectrochemistry has been widely used to study the reduction of GO, providing very valuable information about the process [16-17]. Raman and FTIR spectroelectrochemistry have been combined in the same study to follow the reduction process of a GO film, obtaining information about the dependence of the process on the solvent, being more efficient in organic solvents than in aqueous solution [18]. A different approach has been to use the color changes occurring during GO reduction (from black to brown) to follow a chemical reduction process of GO in solution [19]. However, to the best of our knowledge, the *in-situ* UV-VIS spectroscopic study of the electrochemical reduction of GO deposited on an electrode surface has not been yet performed. Therefore, here, UV-VIS spectroelectrochemistry has been selected as an *in-situ* and real time characterization technique because a more complete and specific information can be obtained. The miniaturized three electrode cell of Screen Printed Electrodes that only needs a drop of electrolyte solution makes easy and reproducible the experimental setup in comparison with conventional electrodes [20].

Considering the number of works dealing with graphene and graphene oxide based materials in different areas, the voltammetric reduction of GO is an easy, clean and efficient method. Moreover complementary information provided by *in-situ* time-resolved UV-VIS absorption spectroelectrochemistry has been used as characterization tools to shed more light on this important reduction process.

2. Experimental

2.1 Instrumentation

Voltammetric measurements were performed with a portable bipotentiostat/galvanostat mSTAT400 (DropSens, Spain) controlled by DropView 8400 2.1 software. UV-VIS Spectroelectrochemistry was carried out with SPELEC instrument (DropSens, Spain) used in combination with a reflection probe, working in a near normal reflection configuration in a reflection cell (DRP-REFLECELL., DropSens, Spain).

Raman spectroscopy was performed using a WITEC alpha300 RA. Elemental analysis was developed with a LECO-CHNS-932 microanalyzer. XPS measurements of GO were carried out on SPECS system operating under 10^{-7} Pa connected to a MgK α X-Ray source (100 W). Atomic Force Microscopy (AFM) analysis of GO sheets was carried out using a Cervantes atomic force microscope from Nanotec Electrónica (Spain) under ambient conditions. GO monolayers were deposited on mica substrates by drop casting evaporated in room temperature, washed with ultrapure water and dried with nitrogen.

2.2 Reagents and solutions

Graphene Oxide was obtained from a chemical oxidation and wet exfoliation process of highly crystalline graphite [22]. These samples were provided by CSIC-Incar as 1000 ppm ready to use aqueous solutions prepared in ultrapure water by sonication. This solution was diluted 1:1 with dimethylformamide (DMF) previously to the electrode modification.

Potassium nitrate was provided by Sigma-Aldrich (Spain). Sodium hydroxide, DMF, hydrochloric acid fuming (37%), were purchased from Merck (Germany). All other chemicals employed were of analytical reagent grade. Ultrapure water obtained with a

Milli-RO 3 plus/Milli-Q plus 185 purification system from Millipore Ibérica S.A was used throughout this work.

2.3 Screen-printed electrodes (SPEs)

The DropSens´ electrodes incorporate a three-electrode cell configuration printed on ceramic substrates (dimensions: 3.4 x 1.0 x 0.05 cm; length x width x height) and were previously described [21]. Both working (disk-shaped 4 mm diameter) and counter-electrodes are made of carbon inks, whereas pseudoreference electrode and electric contacts are made of silver.

SPEs were modified by drop-casting of 10 µl of Graphene Oxide dispersions on the working electrode surface, leaving it to dry at room temperature. The solvent has to be completely evaporated before the electrochemical assays. Voltammetric measurements on SPEs were performed by placing a 50 µl drop of the corresponding electrolyte solution to the working area.

3. Results and Discussion

Two different GO materials obtained from the same highly crystalline graphite are used during this work. GO1 was obtained from a parent graphite with a bigger grain size (20-80 µm) and GO2 was produced from a smaller graphite crystal (2-20 µm) following in both cases a modified Hummers method [22]. AFM characterization of GO sheets obtained at the end of the process showed a lateral size of the monolayer corresponding to 644 ± 25 nm (n = 66 layers) for GO1, in comparison with the 320 ± 25 nm (n = 88 layers) for GO2.

As it is shown in Table 1 the elemental analysis of both materials in terms of %C and %O is quite similar. However, from the XPS analysis we can deduce that higher sp^2

hybridization is observed in GO1 than in GO2. This fact is in agreement with the monolayer size measured by AFM, since the basal plane of the monolayer is bigger in GO1 than in GO2. The XPS analysis of the functional groups showed a high amount of epoxy groups in GO1 mainly formed in the basal plane of the graphene monolayer. However a high proportion of $-COOH$ groups formed mainly in the edges of the graphene planes are present in GO2, with a smaller monolayer size and consequently a higher proportion of edges than in GO1. Both materials showed very large numbers of oxygen functionalities with a C/O ratio close to 2, typical of GO [22].

The two GO were used to modify the surface of the working electrode of screen printed carbon electrodes by drop-casting using the DMF/H₂O dispersion where these highly hydrophilic materials are solubilized. The electrochemical reduction of GO was carried out by cyclic voltammetry in 0.1 M KNO₃ scanning the potential from 0.00V to -1.30V vs. Ag pseudoreference electrode at 0.050 V/s [9,14]. A cathodic peak emerged at -0.95V for GO1 and at -0.80V for GO2 (Fig.1), both related to the irreversible electrochemical reduction of some oxygen-containing groups of GO in the basal plane such as epoxide, hydroxyl, aldehydes and peroxides since the reduction of carbonyl, carboxy and ester groups (generally distributed in the edges of the monolayer) takes place at more negative potentials [15]. As can be observed in the voltammograms, a lower overpotential is needed to reduce GO2 than to reduce GO1. This behavior can be rationalized in terms of a higher amount of hydroxyl groups in the basal plane of GO2 that would be easier to be reduced in comparison with the main epoxy groups localized in the basal plane of GO1. The *in-situ* monitoring of spectral changes occurred during the voltammetric reduction of GO can be easily carried out by UV-VIS spectroelectrochemistry and it is shown accordingly to our knowledge for the very first time in this work. GO (brownish colored material) is transformed to ERGO (black

colored material) leading to an increase of absorbance in the full UV-VIS range that is observed during the electrochemical reduction (Fig.2), with higher absorbance values at shorter wavelengths. The corresponding voltabsorptogram obtained at 300nm for GO1 is shown in Figure 3A. Absorbance does not change the initial zero value up to the overpotential is negative enough to reduce the GO to ERGO, around -0.75V. From this potential downwards, absorbance increases until the reduction is completed at -1.30V. Absorbance does not decrease in the backward scan, indicating that an irreversible reduction of GO has taken place under these experimental conditions. The derivative voltabsorptogram at 300nm (Figure 3B) exhibits a full correlation with the cyclic voltammogram indicating that the two signals are related to the same process. Moreover, the same experiment was performed using an electrode without GO deposited on the surface. In this case, a reduction peak was also observed at -0.88 V. However, there is no change in the spectra during the experiment because no GO is deposited on the electrode, demonstrating that spectroelectrochemistry provides unambiguous information on the process taking place at the electrode.

In-situ Raman monitoring of the process is very useful since the same area of the electrode surface is sampled during the electrochemical reduction. GO and ERGO were characterized by Raman Spectroscopy. Raman spectra provide information on the main structural changes taking place during the electrochemical reduction of GO. Considering the peak intensity of D and G bands of GO1, an increase of I_D/I_G ratio from 1.13 to 1.22 after the experiment was observed, demonstrating that the reduction of GO1 has taken place. This behavior is attributed to the increase of defect concentration and to a decrease in the average size of the sp^2 domains in ERGO compared to GO [2].

4. Conclusions

Cyclic voltammetry has been demonstrated to be a simple and efficient method for the electrochemical reduction of GO on the surface of screen printed electrodes. The peak potential of the cathodic peak, identified with graphene oxide reduction is related to the presence of reducible epoxy or hydroxyl functional groups in the basal plane. Thus, GO with a lower monolayer size and a high proportion of hydroxyl functional groups in the basal plane is easier to be reduced than graphene oxide with a high proportion of epoxy groups in the basal plane. A new approach for the *in-situ* characterization of graphene materials by time resolved UV-VIS absorption spectroelectrochemistry in reflection mode using screen printed electrodes is introduced. It easily allows us to confirm in real time not only the material colour change (brown-GO to black-ERGO) but the potential at which the reduction is occurring. The use of miniaturised screen-printed electrodes allows a fast and easy analysis with a simple experimental setup for UV-VIS absorption spectroelectrochemistry in comparison with the use of conventional electrodes.

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6. References

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CAPTIONS FOR FIGURES AND TABLES

Figure 1. Cyclic voltammograms in 0.1 M KNO_3 of GO1 (blue line) and GO2 (red line) modified screen printed electrodes.

Figure 2. Evolution of UV-VIS absorption spectra during electrochemical reduction of the GO1 modified screen printed electrode.

Figure 3. (A) Voltabsorptogram at 300 nm for the electrochemical reduction of GO1 and (B) comparison of derivative voltabsorptogram at 300 nm and the corresponding cyclic voltammogram of GO1.

Table 1. Elemental and XPS characterization of GO1 and GO2 sheets.