

Comparative Study of Screen-Printed Electrodes Modified with Graphene Oxides Reduced by a Constant Current

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» Abstract
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1 **COMPARATIVE STUDY OF SCREEN-PRINTED ELECTRODES MODIFIED WITH**
2 **GRAPHENE OXIDES REDUCED BY A CONSTANT CURRENT**

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ABSTRACT

A comparative study of several screen-printed electrodes modified with electrochemically reduced graphene oxides (ERGO) by means of a constant current has been carried out. The ERGOs were produced from graphene oxides (GO) with different controlled functional groups contents and locations. The experimental reduction conditions were optimized for each particular GO to generate ERGO-modified electrodes with the aim of improving the performance of the dopamine redox process. The ERGO-modified electrodes exhibited a larger electroactive area, a higher reversibility of the redox process, faster kinetics, and greater double-layer capacitance. Analysis of the reduction degree and residual functional groups by means of X-ray photoelectron spectroscopy (XPS) after and before reduction enabled us to determine the relation between the electrochemical behaviour and morphology of the electrodes. A hydrazine-reduced graphene oxide showed the best analytical performance with a higher sensitivity ($0.259 \mu\text{A}/\mu\text{M}$ vs. $0.090 \mu\text{A}/\mu\text{M}$ in the case of a bare electrode), and a linear range from 1-100 μM . It was found that both the experimental reduction conditions and starting graphene material are critical for obtaining a modified electrode with a suitable electrochemical behaviour and properties and that a constant current is a suitable technique for the reduction of graphene oxides, especially for screen-printed electrodes.

Keywords: Graphene; graphene oxide; electrochemically reduced graphene oxide; screen-printed electrodes; galvanostatic reduction

1 1. INTRODUCTION

2 Graphene, a two-dimensional carbon material with highly useful properties including a large surface
3 area and high mechanical, thermal and chemical stabilities, has emerged as a very interesting material
4 for electrochemical applications, especially in (bio)sensors due to its excellent properties such as high
5 electron conductivity, fast heterogeneous electron-transfer rate at the graphene sheet edges and basal-
6 plane defect sites, large surface area and good biocompatibility.[1-4] The most suitable graphene
7 material for modifying electrochemical sensors is graphene oxide (GO) due to its high capacity to be
8 dispersed in aqueous solvents that allows a more efficient electrode modification. GO is usually
9 produced by the oxidation of graphite, a methodology based on the Hummers [5] or Brodie method, [6]
10 which is considered to be the best alternative for the preparation of graphene on a large scale.[7]
11 Additionally, the preparation of GO can be modified by using graphites with different crystalline
12 structures or by different preparation methods [8] giving rise to graphene materials of different sheet
13 size, structure and properties, variables that can also be tuned to improve the electrochemical
14 performance of electrodes.

15 Although several studies on GO improving electrode properties have been reported [9,10], in most
16 cases a previous GO reduction is carried out in order to decrease the number of oxygen-based
17 functional groups to obtain better electrochemical properties.[11,12] And again the properties of the
18 reduced graphene oxides are influenced not only by the parent GO but also by the reduction process
19 followed.[13] Several authors have reported that the electrocatalysis is influenced by the orientation of
20 the graphene sheets with respect to the electrode surface, the C/O atomic ratio, or the synthesis route of
21 the material.[14] For instance, graphene nanoribbons with different oxidation degrees were employed
22 for the optimization of the detection of several analytes, showing how the graphene structure had a
23 significant effect on the electrochemical detection[15-16]. For these reasons, a lot of work remains to
24 be done before the use of the graphene materials for electroanalytical applications, and particularly, for
25 sensors, is standardized and the analysis of the morphology of graphene material for use in these
26 applications is optimized.

1 For the development of sensors and biosensors, screen-printed electrodes (SPEs) are among the most
2 widely used platforms due to the low cost of their fabrication, high sensitivity, and their easily modified
3 surfaces with compounds such as proteins or nanomaterials, that increase their active area and
4 electrocatalytical properties.[17-18] There are already a number of commercial SPEs modified with
5 graphene that have the advantage of being readily available for their electrochemical measurements,
6 but with the disadvantage of there being no control over the amount and type of nanomaterial
7 employed. In consequence, in situ modification of SPEs with graphene is the most widely employed
8 procedure by means of either direct adsorption (with or without the aid of a polymer) or
9 electrodeposition. It is worth mentioning that SPEs have pseudoreference electrodes, usually silver-
10 made. This fact needs to be taken into account because these electrodes are not ideally polarizable
11 electrodes, and therefore, a shift in their potential during the measurements could occur in some
12 experimental conditions. The reduction of GO for use in SPEs is usually performed by means of a
13 previous tedious chemical reduction process or by applying a potential scan or a constant reduction
14 potential.[19-21] In such cases it is possible that the potential applied to reduce the GO will vary for
15 different electrodes in the preparation step. Our alternative strategy to eliminate this problem is to
16 reduce GO-modified SPEs by means of galvanostatic reduction by applying a specific reduction current
17 (I_{red}). The applied current remains constant throughout the experiment and changes to the silver
18 pseudoreference electrode will not have any effect in the reduction of GO. This could happen in acidic
19 or chloride-containing media, where silver could be easily oxidized. The application of a constant
20 current for the generation of nanomaterials on screen-printed electrodes has been already proven useful.
21 For instance, gold nanoparticles were electrodeposited from a gold solution by means of a constant
22 current [22]. These nanostructured SPEs have been used for several (bio)sensing applications [23-25].
23 The reduction of graphene-modified SPEs by the application of a constant current remains to be
24 studied.

25 The aim of this work was to study the electrochemical performance of ERGO-modified screen-printed
26 electrodes and, particularly, the effect of different graphenes on the electrochemical behaviour of

1 dopamine using the modified electrodes. Dopamine was selected because it is one of the most widely
2 used model analytes for the characterization of electrodes and would facilitate a comparison between
3 our results and the results obtained with other graphene or electrode materials. Screen-printed carbon
4 electrodes (SPCEs) were modified using three GOs with different content and location of defects and
5 functional groups. Electrochemically reduced graphene oxides were obtained by in situ electrochemical
6 reduction using a constant current and the effect on the electrochemical process of dopamine was
7 studied under several experimental conditions (reduction current, reduction time, pH, GO amount) by a
8 multifactorial design. The main novelty of our work lies on that a reduction current is used to prepare
9 ERGO instead of the potential-controlled reduction usually employed. As explained, this reduction
10 method may be more suitable for SPEs containing pseudoreference electrodes that could vary under
11 different experimental conditions. The galvanostatic method allows to carry out the reduction using
12 aggressive conditions (acidic or basic media with the application of high currents) with a higher control
13 of the current flowing between the electrodes. Kinetic and electrode parameters for the dopamine
14 electrochemical process were estimated for the different ERGO-modified SPCEs. The results obtained
15 for the ERGO-modified SPCEs have been explained in terms of their structural data measured by XPS.
16 Finally, the analytical characteristics of these modified electrodes for the determination of dopamine
17 were obtained.

18 **2. EXPERIMENTAL**

19 **2.1. Reagents and solutions**

20 Sodium hydroxide (99%), sulfuric acid (98%), phosphoric acid (85%), and ethanol (absolute) were
21 purchased from Merck. Dopamine hydrochloride was purchased from Sigma-Aldrich. Ultrapure water
22 obtained with a Millipore Direct Q5™ purification system from Millipore Ibérica was used throughout
23 the work. A phosphate buffer solution (PB) was prepared with H₃PO₄ (85%) and NaOH up to a pH of
24 7. Dopamine working solutions were prepared in 0.1 M H₂SO₄.

26 **2.2. Apparatus and electrodes**

1 *X-ray photoelectron spectroscopy (XPS):* Analyses of the GOs and ERGOs were carried out on a
2 SPECS system operating under 10^{-7} Pa with a Mg-K α X-ray source (100 W). A Shirley background
3 function was used to adjust the background of the spectra. To calculate the functional groups of the
4 samples, the XPS C1s peaks were curve-fitted by combining the components and by minimizing the
5 total square-error fit. Curve fitting of the C1s spectra was performed using a Gaussian–Lorentzian peak
6 shape after performing a Shirley background correction [26]. The resulting spectra show the binding
7 energy of the C=C (sp^2) at 284.5 eV. The chemical shifts of +1.0, +2.0, +3.0 and +5.0 eV were
8 assigned to C (sp^3) hybridisation, C–OH, C–O–C and COO functional groups,
9 respectively[27]. Similarly, the O1s and N1s were deconvoluted in the following ranges. In the O1s
10 spectra, the peak at 533 eV was assigned to C–OH groups while the peak at 531 eV was ascribed to C–
11 O–C and COO groups [28,29]. In the N1s spectra, the peak at 400.3 eV was assigned to
12 pyrrolic nitrogen, the peak at 398.7 eV to pyridinic nitrogen and the peak at 401 eV to
13 graphitic nitrogen [30].

14 *Voltammetric measurements:* Voltammetric measurements were performed on an μ -Autolab type 2
15 (Metrohm) potentiostat/galvanostat controlled by Autolab GPES 4.9. All measurements were carried
16 out at room temperature.

17 *Screen-printed carbon electrodes:* The SPCEs, (ref.110) were purchased from DropSens (Spain). These
18 electrodes incorporate a conventional three-electrode configuration, printed on ceramic substrates (3.4
19 x 1.0 cm). Both the working (disk-shaped 4 mm diameter) and the counter electrodes are made of
20 carbon inks, whereas the pseudoreference electrode and electric contacts are made of silver. An
21 insulating layer was printed over the electrode system, leaving uncovered the electric contacts and a
22 working area which constitutes the reservoir of the electrochemical cell, with an actual volume of 50
23 μ L.

24 25 **2.3. Synthesis of parent graphene oxides and partially reduced graphene oxides**

1 *Synthesis of GOs:* The GOs used in this work were prepared from two synthetic graphites (a
2 commercial graphite powder –GO1- and a carbochemical graphite –GO2-) [8,31] by the modified
3 Hummers method [30,32]. This method makes use of the Hummers reagents with additional amounts
4 of NaNO₃ and KMnO₄. Concentrated H₂SO₄ (360 mL) was added to a mixture of graphite (7.5 g) and
5 NaNO₃ (7.5 g), and the mixture was cooled down to 0 °C using an ice bath. KMnO₄ (45 g) was added
6 slowly in small doses to keep the reaction temperature below 20 °C. The solution was heated up to 35
7 °C and stirred for 3 h, at which point 3% of H₂O₂ (1.5 L) was added slowly, which produced a
8 pronounced exothermal effect up to 98 °C. The reaction mixture was then stirred for 30 min and next
9 centrifuged. The remaining solid material was then washed with 600 mL of water and centrifuged
10 again, this process being repeated until the pH was neutral. A colloidal suspension of GO sheets in
11 purified water (1 mg mL⁻¹) was prepared in 1-L batches, and kept under ultrasound treatment for 10 h.
12 Then the suspension was centrifuged, the supernatant was filtered over cellulose and the solid was
13 discarded.

14 *Synthesis of partially reduced graphene oxide:* GO1 was previously reduced with hydrazine
15 monohydrate in an aqueous solution in the presence of a base [30,33,34] to yield a partially reduced
16 graphene GO1pr. In brief, 500 mL of an aqueous solution of GO1 (1 mg mL⁻¹) was loaded into a 2-L
17 round-bottomed flask and hydrazine hydrate (5 mL, ratio 100 : 1), ammonia (200 µL) and toluene (10
18 mL) were then added. Finally, the solution was heated in an oil bath at 100 °C under a water-cooled
19 condenser for 24 h. The base was added to the reaction solution to increase the pH to around 10; at this
20 pH the electrostatic repulsions of GO1 sheets are maximised. Toluene was added to the reaction
21 mixture to avoid the agglomeration of graphene sheets upon water evaporation. Dialysis membranes
22 were used to purify GO1pr. The sample was introduced into the membranes, which were in turn
23 inserted into containers with Milli-Q water. The water was replaced until the conductivity of the
24 water was the same as that of the Milli-Q water.

25 *AFM characterization of the parent graphene materials used in this work:* The AFM images and
26 profiles of GO1, GO2 and GO1pr were obtained by depositing a drop of a water suspension of the

1 samples onto the surface of mica (**Figure 1**). The sheets were imaged using a Cervantes atomic force
2 microscope from Nanotec Electronica™ operating under ambient conditions. Microcantilevers with
3 nominal spring constants of $k = 40$ N/m and a resonance frequency of $f = 300$ kHz were used to image
4 the sheets. WSxM software was employed to control the atomic force microscope as well as for the
5 data processing of the acquired images. The size and height of the samples were measured by means of
6 AFM imaging and profiling. GO1 exhibit a larger sheet size compared to GO2 (500 nm and <100 nm,
7 respectively), while the treatment with hydrazine to yield GO1pr have no influence in the lateral size of
8 the sheet.

9 *TEM characterization of the parent graphene materials used in this work:* TEM observations of the
10 parent graphene materials used in this work, GO1, GO2 and GO1pr, were performed on a JEOL 2000
11 EX-II instrument operating at 160 keV. Suspensions of the GO were deposited on standard holey
12 carbon copper grids using the drop cast method and loaded into the microscope. The images recorded
13 are depicted in **Figure 2**.

14

15 **2.4. Modification of screen-printed electrodes with graphene**

16 **2.4.1 Graphene drop casting**

17 The electrode surface was modified with graphene oxide by drop casting 6 μ L of a suspension of the
18 specific GO prepared in H₂O:ethanol (8:2) over the surface of the working electrode and dried at room
19 temperature overnight. The volume and H₂O:ethanol ratio were optimized to ensure that the surface of
20 the working electrode was completely cover with GO.

21 **2.4.2 Graphene reduction and experimental design**

22 GO-modified SPCEs were electrochemically reduced by a constant current (galvanostatic reduction) to
23 form the partially reduced graphenes labelled ERGOX, where X refers to the parent graphene oxide
24 used (1, 2 or 1pr). **Table 1** shows the reduction conditions and the nomenclature of each modified-
25 electrode used. A graphical diagram of the modification with GO and reduction of SPCEs is shown in
26 **Figure 3**. Briefly, the reduction was carried out by applying a constant cathodic current for a specific

1 period of time after dropping an aliquot of 40 μL of the reduction solution onto the electrochemical cell
2 of the modified-SPCEs. Three different reduction media (H_2SO_4 0.1 M, PB 0.1 M pH 7 and NaOH 0.1
3 M) were used for the reduction of the GO-modified SPCEs and an experimental design based on a full
4 factorial design to evaluate the influence of the reduction current, time and GO concentration on the
5 electrochemical behaviour of the dopamine redox process was carried out. The peak potential
6 separation between the anodic and cathodic peaks was specially considered, in addition to the
7 magnitude of the peak and capacitive currents. In this design, a set of 9 experiments were performed in
8 duplicate for each reduction media and GO material. The initial conditions of the experimental design
9 are shown in **Table 2**. All statistical and graphical analyses were carried out with Minitab 16 (Minitab
10 Inc.).

11 **2.5. Electrochemical characterization of the modified screen-printed electrodes**

12 **A) Evaluation of the control of the dopamine electrochemical process**

13 Cyclic voltammograms for 1×10^{-4} M of dopamine were recorded at different scan rates (10, 25, 50, 100,
14 250, 500 mV/s), and both the anodic and cathodic peak currents were plotted versus the scan rate or the
15 root of the scan rate. Taking into account the linearity of these plots, the determinant control of the
16 electrochemical process was obtained. As it is widely known [35], for a diffusion-controlled process,
17 the peak current is directly proportional to the square root of the scan rate ($i_p \propto v^{1/2}$) and for an
18 adsorption-controlled process, the peak current is directly proportional to the scan rate ($i_p \propto v$).

19 In a different method for obtaining information on the control of the process, the logarithm of the peak
20 current versus the logarithm of the scan rate was represented. As explained previously [36], a slope
21 near 0.5 can be expected for a diffusion-controlled process, while a slope near to 1 can be expected for
22 an adsorption-controlled process.

23 **B) Study of the reversibility of the dopamine electrochemical process**

1 The peak separation (ΔE_p) was calculated and represented versus scan rate (v). Considering the
2 variation of the peak separation, the reversibility of the electrochemical process is estimated. For
3 irreversible systems, ΔE_p varies with the scan rate. Therefore, for comparison purposes of the ERGO-
4 modified SPCEs, the peak separation at 100 mV/s (ΔE_{p100}) was employed. For a reversible system, as
5 known, this difference is close to $59/n$ mV, while that for an irreversible process the difference is
6 greater.

7 **C) Estimation of the electroactive area and roughness factor**

8 Using the data from the CV experiments, the Randles-Sevcik equation for an irreversible process was
9 employed to estimate the area of the electroactive electrode:

$$10 \quad i_p = (2.99 \times 10^5) n^{3/2} \alpha^{1/2} A C D^{1/2} v^{1/2} \quad (1)$$

11 where i_p is the peak current intensity (A), n is the number of electrons transferred in the electrochemical
12 reaction, α is the transfer coefficient (0.5), A is the electrode area (cm^2), C is the bulk concentration of
13 the analyte (mol/cm^3), D is the diffusion coefficient of the analyte ($0.67 \times 10^{-5} \text{ cm}^2/\text{s}$ in H_2SO_4 0.1
14 M)[37], and v is the scan rate (V/s).

15 To estimate the roughness factor (f) the following equation was employed:

$$16 \quad f = A/A_g \quad (2)$$

17 where A is the experimentally calculated electroactive electrode area and A_g is the geometric area of
18 the working electrode (0.126 cm^2 for SPCEs).

19 **D) Estimation of kinetic parameters for dopamine using modified-SPCEs**

20 The heterogeneous rate constant, k^0 , was estimated using the Nicholson method [38] where the peak
21 separation (ΔE_p) (mV) is related to a dimensionless function (ψ) and this function is related to the rate
22 constant:

$$23 \quad \psi = k^0 (D_O/D_R)^{a/2} (RT)^{1/2} (\pi n F D_O v)^{-1/2} \quad (3)$$

1 where D_O is the diffusion coefficient for the dopamine ($0.67 \times 10^{-5} \text{ cm}^2/\text{s}$), D_R is the diffusion
2 coefficient for dopaminequinone (approximated to the dopamine diffusion coefficient) (cm^2/s), α is the
3 transfer coefficient ($\alpha=0.5$), R is the universal gas constant (J/mol K), T is the absolute temperature
4 (K), n is the number of electrons transferred, F is the Faraday constant (C/mol) and v is the scan rate
5 (V/s). To estimate the gamma function the following equation developed by Swaddle et al. [39] was
6 employed:

$$\ln \psi = 3.69 - 1.16 \ln(\Delta E_p - 59) \quad (4)$$

8 **E) Estimation of the double-layer capacitance**

9 The capacitive current obtained in cyclic or linear voltammetry can be described by the following
10 equation [35]:

$$11 \quad |i_c| = A \cdot C_{dl} \cdot v \quad (5)$$

12 where i_c is the capacitive current (A), A is the electrode area (cm^2), C_{dl} is the double-layer capacitance
13 (F/cm^2) and v is the scan rate (V/s). To estimate the C_{dl} , several cyclic voltammograms of the
14 electrolytic medium (H_2SO_4 0.1M) were recorded at different scan rates (10, 25, 50, 100, 250, 500
15 mV/s). Capacitive currents obtained at a specific potential versus scan rate were represented. In this
16 case, a potential near the standard potential of dopamine (+0.3 V) was selected and C_{dl} values were
17 obtained using equation 5.

18 **2.6. Electrochemical measurements**

19 For the optimization and electrochemical characterization of the modified electrodes, cyclic
20 voltammetric experiments were performed using 40 μL of dopamine $1 \times 10^{-4} \text{ M}$ in H_2SO_4 0.1 M. CV
21 was carried out from -0.2 to +0.7 V at a scan rate of 0.1 V/s with a step potential of 2 mV (unless stated
22 otherwise).

1 For the analytical characterization, a series of calibration plots for dopamine were recorded using the
2 different modified electrodes. Briefly, 40 μL of dopamine of the specific concentration in H_2SO_4 0.1 M
3 was added to the electrode and square-wave voltammetry was performed from 0 to +0.6 V. Square-
4 wave parameters were optimized, the best results being obtained at a frequency of 20 Hz, an amplitude
5 of 40 mV and a step potential of 10 mV. The limit of detection was calculated as the concentration
6 corresponding to three times the standard deviation of the estimate.

7 **3. RESULTS AND DISCUSSION**

8 **3.1. Optimization of the reduction conditions to obtain ERGO-modified SPCEs**

9 Graphene materials with different characteristic were used in this work as parent materials to prepare
10 GO-modified electrodes. Although all of them were used in the form of monolayers, GO1 exhibit a
11 larger sheet size than GO2 (> 500 nm and <100 nm, respectively). This is related to the fact that,
12 although both samples exhibit a similar atomic C/O ratio (2.2, **Table 3**), GO2 has a larger amount of
13 COOH groups, located at the edges of the sheet. On the other hand, the reduction of GO1 with
14 hydrazine to yield GO1pr increases the C/O ratio up to 2.8 while incorporating a certain amount of
15 nitrogen (7.8 atomic %) from the decomposition of hydrazine [30]. As a consequence, an
16 indiscriminate partial reduction of the functional groups present in GO1 is achieved (C/O ratio of 2.8),
17 accompanied by a partial reconstruction of the sp^2 carbon content (from 36.7 % to 43.0%). The size of
18 the sheets is, however, not affected during reduction. From these materials, the GO-modified
19 electrodes were prepared by drop casting and subsequent electrochemical reduction, while the
20 efficiency of the electrode was measured from the electrochemical behaviour of the dopamine redox
21 process, as illustrated in **Figure 3**.

22 As an initial test, it was demonstrated in the case of the GO1-modified electrode that further reduction
23 of the electrode using a reduction current to generate ERGO-modified electrodes under two different
24 conditions (ERGO1A, ERGO1B) improves the performance of the electrode (**Figure 4**). This was
25 measured by comparing the lower peak potential separation and a higher peak current obtained for the

1 dopamine redox process to the GO-modified or bare electrodes. This shows that galvanostatic reduction
2 is an useful electrochemical technique for the reduction of GO-modified electrodes, especially in the
3 case of screen-printed electrodes incorporating a pseudoreference electrode. It is known that the
4 experimental reduction conditions influence electrochemical behaviour, particularly in so far as the
5 differences in functional groups of the graphene materials to be reduced are concerned, which include
6 in this work the characteristics of the parent GO-x. Thus, an experimental design to obtain the most
7 suitable experimental conditions for the reduction of graphene oxide was performed. In accordance
8 with the aims of this work, the multifactorial experiments were designed using as factors the GO
9 concentration, reduction current and reduction time for the available parent graphene materials (GO1,
10 GO2, GO1pr) and for reduction media (H₂SO₄ 0.1 M, PB 0.1 M pH 7, NaOH 0.1 M). The initial values
11 for the design can be found in **Table 2**. As a response, the peak potential separation between anodic
12 and cathodic processes was specially considered, in addition to the peak and capacitive currents for
13 choosing the most suitable conditions, once a cyclic voltammetry has been performed with the
14 parameters described in Section 2.6. In the event that, with the initial design, no optimal values for ΔE_p
15 were found, a new multifactorial design was performed taking into account the factors that had a
16 positive effect on the previous design.

17 In general, the most significant effect on the responses was obtained for both the concentration of each
18 particular parent graphene material and the reduction current, while the influence of the reduction time
19 was minimal (data not shown). Therefore, 60 s was chosen as the most suitable reduction time. On the
20 other hand, it is worth noting that the conditions that produced a low ΔE_p , generally, produced high
21 peak currents. After performing these experimental designs, the most suitable ERGO-modified
22 electrodes for further studies were chosen. A nomenclature for these electrodes has been used for the
23 sake of convenience in the rest of the manuscript and is shown in **Table 1** together with that of the
24 parent GO-SPCEs.

25 It is interesting to note that the optimized results for the GO2-modified electrodes, with the highest
26 number of acid groups, were obtained for the reduction only in NaOH (ERGO2A) and PB 0.1M (pH7,

1 ERGO2B and ERGO2C). In contrast for the GO1rp-modified electrodes, which have a very small
2 number of acid groups, an acid media is proposed (H₂SO₄, ERGO1pr), the GO1-modified electrodes
3 being the most versatile material in this regard (reduction efficient in H₂SO₄ -ERGO1A-, NaOH-
4 ERGO1B- and PB 0.1M -ERGO1C-).

5 The chemical modifications that occurred during the preparation of the screen-printed electrodes were
6 determined by means of XPS measurements (**Table 3**). In all cases, the electrochemical reduction of
7 the parent GO-SPCEs led to the partial reconstruction of its carbon sp² structure as a consequence of
8 the elimination of certain oxygen-containing functional groups (a higher C/O ratio in all cases). The
9 extent of the reduction depended however on the type of GO and the reduction conditions applied.

10 For the GO1x series, the use of an acid medium led to a lower degree of reduction in the graphene
11 materials (lower C/O) with only a partial reconstruction of the carbon sp² structure. It is also interesting
12 to mention that there was a marked effect in the reduction of the C=O and COO groups (down to 9-
13 11% and 5-6% respectively), while the C-O groups were hardly reduced in any of the media.

14 In the case of the GO2x series, the different reduction conditions gave rise to different results.
15 Reduction with NaOH (ERGO2A) was slightly more efficient than with PB under the same
16 experimental electrochemical reduction conditions (ERGO2B), with a further reduction of the C-O
17 groups (down to 13.7 %). However, the reconstruction of the sp² carbon network was not so efficient
18 due to the formation of a larger amount of sp³ carbon atoms. When the I_{red} is increased from -10 μA
19 (ERGO2B) to -100 μA (ERGO2C), an enhanced reduction of the graphene material is achieved. It is
20 observed however the formation of a larger amount of sp³ carbon atoms and a larger number of COO
21 groups in more heterogeneous surroundings (larger FWHM).

22 In ERGO1pr, a larger reduction was achieved when compared to the parent graphene material. This
23 included a decrease in the nitrogen-containing functional groups (derived from the chemical treatment
24 of GO1 to produce parent GO1pr). However, the nitrogen content of the reduced sample was still of the

1 order of 4.0 %, indicating that this procedure is not selective to the reduction of these types of
2 functional groups.

3 **3.2. Electrochemical characterization of modified screen-printed electrodes**

4 Reduction has an effect in electrochemical performance, which will be discussed later in detail. In
5 particular, a study of the electrochemical process of dopamine at the surface of ERGO-modified SPCEs
6 was performed following the procedure explained in **section 2.5A**. **Figure 5** shows the CVs of
7 dopamine when the scan rate is varied using modified electrodes with different grades of reversibility
8 (ERGO1A and its parent materials GO1-200, as examples).

9 From the above results, a linear relation between the peak current (both cathodic and anodic) and the
10 square root of the scan rate is apparent, suggesting that the dopamine electrochemical reaction is
11 diffusion-controlled (data not shown). The diffusion-controlled process is also determined by
12 representing the logarithm of the peak current versus the logarithm of the scan rate. The slope values
13 obtained (summarized in **Table 1**) are, in all cases, close to 0.5, in the range of values expected for
14 diffusion-controlled processes.

15 The decreases in the ΔE_{p100} values after the galvanostatic reduction of all the GO-SPCEs (**Table 1**)
16 indicates that further reduction of GO-modified electrodes enhances the reversibility of the
17 electrochemical process of dopamine. Thus, while the GO-SPCEs show values between 280-300 mV,
18 suggesting that an irreversible process is in play, the ERGO-SPCEs exhibit ΔE_{p100} values below 150
19 mV (better reversibility). Theoretically, an improved reversibility should yield a better analytical
20 signal, especially using techniques such as differential-pulse or square-wave voltammetry, where, by
21 the characteristics of the applied potential pulses, reversible processes are enhanced. The best examples
22 were obtained for all the types of graphene materials ERGO1A (54.2 mV), ERGO2C (52.8 mV) and
23 ERGO1pr (56.3 mV)). If the values of the series ERGO1x and ERGO2x are compared respectively, it
24 seems that reversibility is more affected by the reduction process applied in each case than by the type
25 GO-SPCE reduced, with differences of ΔE_{p100} depending on the type of treatment applied at each GO-

1 SPCE. More noticeable is the reduction in ΔE_{p100} observed in ERGO2C with respect to that of
2 ERGO2B (the same reduction media but at a higher reduction current). It seems therefore that a higher
3 reduction current improves reversibility and at least $-10 \mu\text{A}$ is needed to obtain a more reversible
4 process. A possible explanation for this could be the formation of a graphene material in which there is
5 still an appreciate presence of functional groups (in the case of ERGO2C, more COO groups in more
6 heterogeneous surroundings –higher FWHM-, **Table 3**).

7 Using the cyclic voltammetric data with the different scan rates and the procedure explained in **section**
8 **2.5C**, an estimation of the electroactive working area (A) for the modified and unmodified electrodes
9 was performed. **Table 1** shows the numerical values for A estimated from the Randles-Sevcik equation.
10 From the values obtained, a general rule can be deduced: modification with graphene materials
11 increases the electroactive area compared to bare electrodes, and the reduction of GO using some
12 experimental conditions further enhances this electroactive area. Taking into account the geometric
13 area of the bare working electrode (0.12 cm^2) and the roughness factor (**Table 1**), it seems that the
14 rough carbon is partially passivated due to surface contaminants or to the organic binder of the carbon
15 ink as observed by other authors [40] and modification with GO or ERGO improves the electroactive
16 area. For voltammetric techniques, the analytical signal (limiting or peak current) is usually
17 proportional to the electrode area. This fact implies that a higher electroactive area can produce an
18 increment in the analytical signal. However, the capacitive or background current is also proportional
19 to the electrode area. Thus, while at certain levels the enhancement of the electroactive area may
20 involve an improvement in the sensitivity, in other cases, the increased area may produce a decrease in
21 the signal/background ratio resulting in a lower analytical sensitivity. Specifically, no significant
22 difference in the electroactive area can be seen for GO1pr, whereas a significant increment is observed
23 for the reduced GO1 and GO2 materials. The effect of a lower pH on the electroactive area is not
24 significant (similar values of A in the ERGO1x series), though a greater increase on the electroactive
25 area seems occur with a higher reduction current (more negative currents, higher value of A in
26 ERGO2C than in ERGO2B). Particularly noteworthy is the increase in electroactive area in ERGO1B.

1 Although the used GO concentration used is higher than other cases, the same occurs for the non-
2 reduced GO-modified electrode, the increase in area being approximately 54%. Analysis of the XPS
3 data suggests that the increase in electroactive area may be influenced by the degree of reduction
4 achieved, but it seems that a high amount of oxygenated groups needs to be maintained in the structure
5 after reduction these values to be increased.

6 Given the somewhat irreversible character of the dopamine redox process, the rate transfer constant (k^0)
7 was calculated following the Nicholson method explained in **section 2.5D**. The results can be found in
8 **Table 1**. In all cases, higher rate constants were found in the ERGO-modified electrodes than in the
9 GO-modified or bare electrodes, for all the reaction media. This may be a result of the increase in
10 electron transfer capacity resulting from the reduced graphene surface due to the increased amount of
11 Csp^2 and a smaller number of oxygenated groups in the structure of the material (**Table 3**). If the
12 reduced series are compared, it is observed that ERGO1 experienced the greatest increase in k^0
13 compared to the other graphene materials. Furthermore, none of the modified electrodes achieved a
14 complete reversible redox process (a theoretical value of 0.02 cm/s for k^0) but the ERGO1A electrode
15 produced a k^0 of 9.9×10^{-3} cm²/s, very close to that of the theoretical value. According to the XPS data,
16 this material is the one to experience the lowest reconstruction of the carbon sp² structure after
17 reduction. Its enhanced amount of remaining C-O groups compared to the other reduced graphene
18 materials could be a possible explanation for its higher rate transfer constant.

19 The double-layer capacitance, C_{dl} , was estimated following the procedure described in **section 2.5E**.
20 Values obtained for C_{dl} for each modified electrode are shown in **Table 1**. In general, a significant
21 increment of the C_{dl} is observed after the modification of SPCEs with GO and a further increment is
22 obtained after the electrochemical reduction to obtain ERGO. These data are consistent with those
23 found by other authors [41]. A higher C_{dl} entails a higher capacitive current, i.e. a higher contribution
24 to the measured current from non-faradaic processes. The capacitive current does not contain analytical
25 information of the system but difficult the measurement of small faradaic currents associated with low
26 concentration of analytes, and therefore, could affect to the sensitivity of the method. Generally, SPCEs

1 modified with ERGO2 generated the lowest capacitances, while a trend is observed for an increment in
2 C_{dl} using more negative reduction currents. As in the previous cases, the increment in C_{dl} is affected by
3 the reaction media in which the reduction of each specific GO is achieved. For the GO1 series, an
4 increment in the basicity during reduction seems to significantly increase the C_{dl} values
5 (ERGO1A<ERGO1B<ERGO1C), which also matches with the increase in the degree of reduction
6 achieved (**Table 1**). However, for the GO2 series the C_{dl} values obtained for ERGO2A and ERGO2B,
7 with a higher reduction degree than those of the GO1 series, are much lower. Additionally, ERGO2C,
8 in which according to the XPS data the reduction process led to lower degree of reduction and a more
9 heterogeneous heteroatomic structure, exhibits one of the highest C_{dl} values. A comparable value was
10 obtained for ERGO1pr, with certain nitrogen functional groups. It seems therefore that an increase in
11 the sp^3 carbon content and a decrease in the oxygenated groups after the reduction produced a smaller
12 increment in C_{dl} , while on the contrary, a loss of Csp^3 groups and an increment in heteroatomic groups,
13 produced a greater increase in C_{dl} .

14 **3.3. Study of the analytical performance for dopamine determination**

15 A study of the analytical characteristics for dopamine determination was performed by measuring
16 different concentrations of dopamine (10^{-6} M - 10^{-3} M) using several ERGO-modified, GO-modified
17 and bare electrodes for comparison. Square-wave voltammetry was chosen as the most suitable
18 electrochemical technique and the experimental parameters were optimized (data in **section 2.6**). The
19 results obtained for the linear range, sensitivity (slope of the calibration plot) and detection limits are
20 shown in **Table 4** and calibration plots for ERGOpr1 are shown in **Figure 6**. Generally, no relationship
21 was found between the best electrochemical properties (higher area, reversibility, rate constant) of the
22 ERGO-modified electrodes and the best analytical characteristics. Furthermore, with certain
23 exceptions, no significant improvement in the analytical performance was found for most of the
24 ERGO-modified SPCEs compared to the non-reduced or bare electrodes. It is probable that, despite the
25 slightly lower electroactive area and the sluggish kinetics of the electron transfer, the lower capacitance

1 of the double layer has a significant effect on the lower detection limits of the GO-modified SPCEs and
2 especially of the bare SPCEs.

3 As mentioned previously, there are exceptions where ERGO-modified electrodes show better analytical
4 characteristics than bare electrodes: ERGO2C and ERGO1pr (these electrodes contain the highest
5 heterogeneous heteroatomic structure –together with nitrogen functional groups of COO-). For
6 ERGO2C, a higher sensitivity (see the slope of the calibration plot) is found when determining
7 dopamine. This ERGO-modified electrode showed the highest reversibility (lowest ΔE_{p100}) of all the
8 electrodes employed. It seems that the application of -100 μA for the reduction current generates a
9 graphene surface that promotes the electron transfer. However, a lower reproducibility is found with
10 this electrode, probably due to a difficult control of the reduced surface by using a high current.

11 For ERGO1pr, calibration plot shown in **Figure 6**, also a significant increase on the sensitivity is found
12 compared to GO-modified and bare electrodes. XPS data for this ERGO-modified electrode did not
13 show a significant difference in the oxygen groups compared to other ERGO-modified electrodes. The
14 only difference is the presence of nitrogen containing groups in its structure (**Table 3**). Considering that
15 GO1pr-modified electrode also contains nitrogen groups and no improvement is observed in the
16 analytical sensitivity it seems that the reconstruction of the carbon sp^2 structure during the
17 electrochemical reduction of GO1pr combined with the presence of certain nitrogen containing groups
18 plays an important role in the sensitivity of the electrode.

19 In electrochemical terms, the electron transfer rate is only slightly increased, C_{dl} is higher, and the
20 increase in the electroactive area is small (~15%) compared to the unreduced GO1pr electrodes. The
21 reversibility of the process is significantly higher (ΔE_{p100} of 172.8 mV versus 300.7 mV), and if this
22 improvement is not due to faster kinetics, the redox process of dopamine may follow a different
23 mechanism in this case possibly due to the interaction between the nitrogen-containing groups and
24 reduced oxygen-containing groups of the ERGO film. It could also be due to the increased activity
25 obtained with ERGO films or the presence of nitrogen containing groups in the structure that allow a

1 closer interaction with dopamine. On the other hand, with the ERGO1pr electrodes, a smaller linear
2 range is observed, only up to 100 μM . This evidences that the electroactive surface has become
3 saturated with lower concentrations of dopamine than the other electrodes (up to 0.5 or 1 mM). This
4 would be in agreement with a different interaction of dopamine with nitrogen functional groups of the
5 ERGO1pr.

6 A comparison of the analytical results obtained by the ERGO1pr screen-printed electrode with those of
7 other previously published works on the determination of dopamine shows that the lower values of the
8 linear range are of a similar order to those of most of these complex electrodes (**Table 5**).

9 Although the carbon nanofiber-modified pyrolytic graphite electrode has a much lower value (0.05
10 μM), these electrodes have a bigger size than screen-printed electrodes and need a conventional
11 electrochemical cell for them to work. The ERGO1pr-modified screen-printed electrode has similar
12 analytical characteristics to other screen-printed electrodes reported and possesses a fairly high
13 sensitivity compared to that of other electrodes. In short, the ERGO1pr-modified screen-printed
14 electrode developed in this work offers a similar analytical performance and the inherent advantages
15 provided by miniaturization.

16 **4. CONCLUSIONS**

17 A comparative study of several screen-printed electrodes modified with electrochemically reduced
18 graphene oxides or partially reduced graphene oxides with different morphologies by galvanostatic
19 reduction was carried out. We have reported that galvanostatic reduction (the application of a current
20 for a given time) is a suitable electrochemical technique for the reduction of graphene oxide, especially
21 in the case of screen-printed electrodes containing a pseudoreference electrode. In general terms it was
22 found that when the electrode is modified with graphene oxides with enhanced acid groups, modified
23 electrodes showed a higher electroactive area, more reversibility, faster kinetics, but also a higher
24 double-layer capacitance. Although these parameters may have a significant influence on the analytical
25 determination of different species, in the case of dopamine, the best analytical characteristics (highest

1 sensitivity) were obtained with a graphene oxide previously reduced with hydrazine. This fact indicates
2 that the interaction between the analyte and the graphene may be more decisive to the analytical
3 determination than the improvement of the electrochemical properties (electroactive area, faster
4 kinetics, etc.). This work shows that the use of different graphene materials and reducing conditions
5 can be used as a tool for tuning their electrochemical properties.

6

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10

2 **Table 1.** Electrochemical data estimated for ERGO, GO and bare screen-printed electrodes

Electrode	Reduction medium	[GO] ($\mu\text{g/mL}$)	I_{red}^* (μA)	Area, A (cm^2)	Cdl ($\mu\text{F/cm}^2$)	ΔE_{p100} (mV)	k^o (cm/s)	Slope (an/cat) (log i_p vs. log v)	Roughness factor
ERGO1A	H ₂ SO ₄ 0.1 M	125	-10	0.141 ± 0.012	85 ± 43	54.2	9.9×10^{-3}	0.49 / 0.45	1.13
ERGO1B	NaOH 0.1 M	200	-10	0.138 ± 0.013	155 ± 21	81.0	4.1×10^{-3}	0.52 / 0.43	1.10
ERGO1C	PB 0.1 M (pH 7)	125	-10	0.113 ± 0.013	190 ± 13	85.5	2.1×10^{-3}	0.49 / 0.42	0.90
ERGO2A	NaOH 0.1 M	100	-10	0.088 ± 0.001	27 ± 27	125.3	1.3×10^{-3}	0.43 / 0.38	0.70
ERGO2B	PB 0.1 M (pH 7)	100	-10	0.095 ± 0.01	48 ± 36	145.1	1.6×10^{-3}	0.48 / 0.43	0.76
ERGO2C	PB 0.1 M (pH 7)	100	-100	0.116 ± 0.04	164 ± 14	52.8	5.4×10^{-3}	0.56 / 0.40	0.92
ERGO1pr	H ₂ SO ₄ 0.1 M	100	-10	0.088 ± 0.01	146 ± 32	172.8	7.9×10^{-4}	0.48 / 0.40	0.70
GO1-125	-	125	-	0.109 ± 0.01	16.2 ± 0.2	280.1	3.8×10^{-4}	0.48 / 0.45	0.87
GO1-200	-	200	-	0.104 ± 0.004	25 ± 5	280.7	3.8×10^{-4}	0.52 / 0.48	0.83
GO2-100	-	100	-	0.083 ± 0.004	62 ± 25	280.4	4.3×10^{-4}	0.46 / 0.39	0.69
GO1pr-100	-	100	-	0.076 ± 0.007	46 ± 10	300.7	3.6×10^{-4}	0.47 / 0.44	0.61
SPCE	-	-	-	0.074 ± 0.005	26 ± 10	294.6	3.6×10^{-4}	0.47 / 0.41	0.59

3 *Reduction time of 60 s in all cases.

1 **Table 2.** Initial values for the different parameters employed in the multifactorial design to
2 optimize the reduction conditions

<u>Parameter</u>	<u>Minimum value</u>	<u>Maximum value</u>	<u>Center value</u>
[GO]	1 µg/mL	100 µg/mL	50.5 µg/mL
Reduction current	-10 µA	-1 µA	-5.5 µA
Reduction time	60 s	900 s	480 s

3

1 **Table 3.** XPS data for specific ERGO and GO-modified electrodes

Sample	XPS		C1s									
	C/O	N	Csp2		Csp3		C-O		C=O		COO	
		%	%	FWHM	%	FWHM	%	FWHM	%	FWHM	%	FWHM
GO1	2.2	-	36.7	1.4	9.4	1.1	26.1	1.1	17.0	1.1	10.8	1.5
ERGO1A	3.4	-	43.4	1.5	13.1	1.2	27.7	1.1	9.9	1.1	5.9	1.1
ERGO1B	4.4	-	49.3	1.5	11.5	1.2	22.2	1.1	11.3	1.1	5.6	1.1
ERGO1C	4.5	-	52.8	1.5	12.2	1.2	21.4	1.1	8.9	1.1	4.8	1.1
GO1pr	2.8	7.1	43.0	1.3	23.1*	1.2	17.2*	1.1	8.9	1.3	7.8	1.6
ERGO1pr	4.4	4.0	52.5	1.6	17.5*	1.2	15.5*	1.1	6.5	1.2	7.8	1.6
GO2	2.2	-	36.8	1.4	14.7	1.3	24.7	1.1	11.1	1.1	12.7	1.3
ERGO2A	6.9	-	58.9	1.4	17.2	1.1	13.7	1.1	5.8	1.1	4.4	1.1
ERGO2B	4.5	-	58.1	1.5	11.8	1.1	16.1	1.1	7.6	1.1	5.9	1.1
ERGO2C	5.0	-	56.6	1.4	14.0	1.1	15.8	1.2	6.7	1.1	7.6	1.5

2

* Including C-N bonds from hydrazine

- 1 **Table 4.** Analytical characteristics for the different screen-printed electrodes employed in this work
- 2 (bare SPCE, GO and ERGO-modified electrodes).

Electrode	Linear range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$) / RSD (%)	Limit of detection (μM)
ERGO1pr	1 – 100	0.249 (3.4%)	0.09
ERGO1A	1 – 1000	0.072 (17.0%)	0.2
ERGO1B	5 - 500	0.082 (2.4%)	2.2
ERGO1C	5 - 500	0.081 (3.4%)	3.0
ERGO2A	5 – 500	0.114 (8.5%)	2.2
ERGO2B	5 – 1000	0.073 (6.5%)	1.0
ERGO2C	5 – 500	0.279 (22.1%)	4.6
GO1pr-100	5-500	0.085 (3.8%)	2.5
GO1-125	1-500	0.094 (4.4%)	0.5
GO1-200	5-500	0.093 (2.9%)	2.9
GO2-100	5 - 500	0.092 (1.6%)	3.1
SPCE	1-500	0.090 (2.1%)	0.3

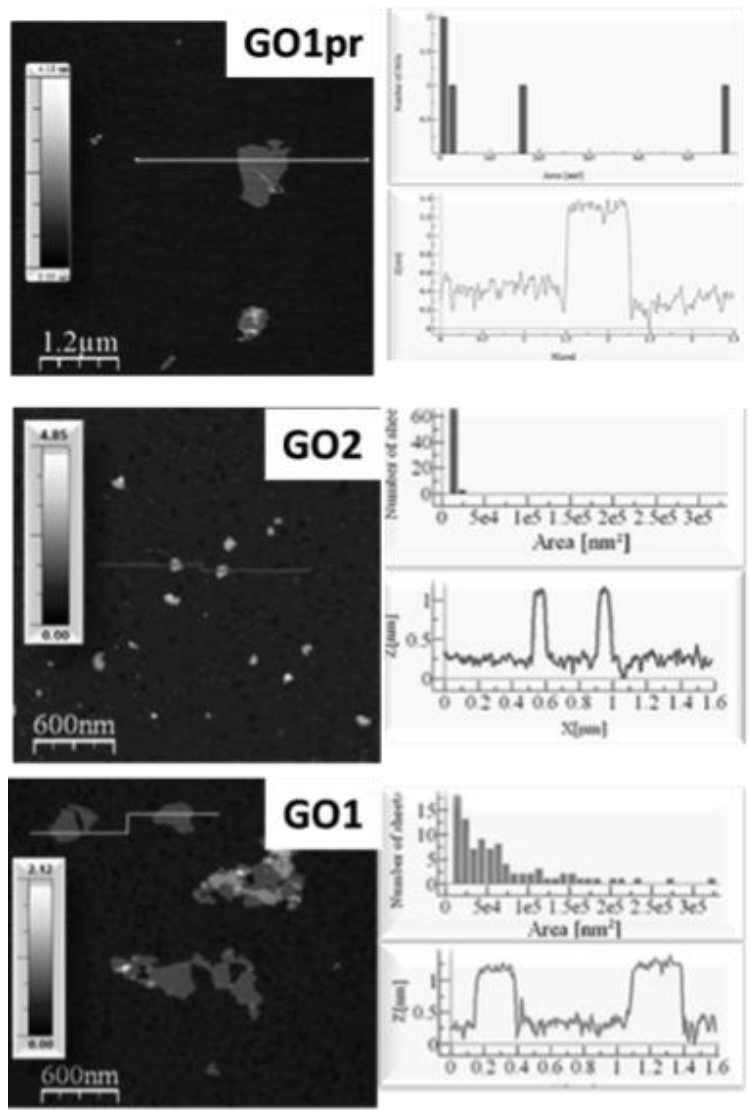
3

1 **Table 5.** Comparison of the analytical performance of different electrodes for the determination of
 2 dopamine

Electrode	Linear range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	Limit of detection (μM)	Reference
Oxidized glassy carbon	1.97 – 9.88	3.16	-	[42]
Mesoporous carbon nanofibers pyrolytic graphite	0.05 – 30	3.73	0.02	[43]
Pretreated glassy carbon	0.1 – 9	0.668	0.03	[44]
Graphite wax composite modified with Ni hexacyanoferrate film	1.5 – 1200	0.205	0.49	[45]
Glassy carbon modified with graphite-nanosheet-Nafion	0.5 - 10	3.695	0.02	[46]
Chitosan-Graphene glassy carbon	1 - 24	-	1	[47]
Hemin/Graphene oxide/glassy carbon	0.5 – 50	0.046	0.17	[48]
Zensor SPCE	5 - 1000	-	-	[49]
Graphene-SPE	0.5 - 2000	0.087	0.12	[19]
SPCE modified with electrochemically pretreated graphite/Nafion	0.5 – 70	0.74	0.023	[20]
DropSens SPCE	1 – 500	0.090	0.3	This work
ERGO1pr-SPCE	1 - 100	0.259	0.09	This work

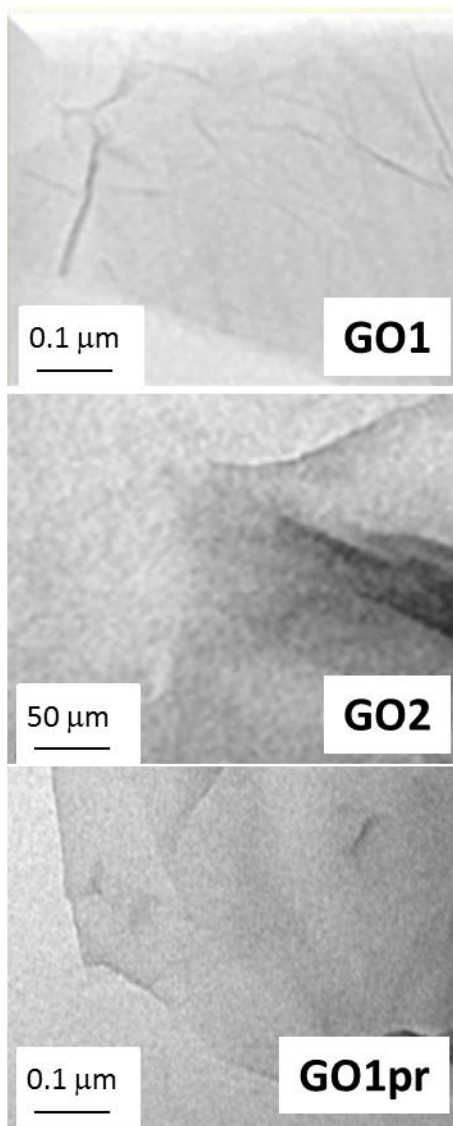
3

1 **Figure 1:** AFM images of the parent graphene materials.



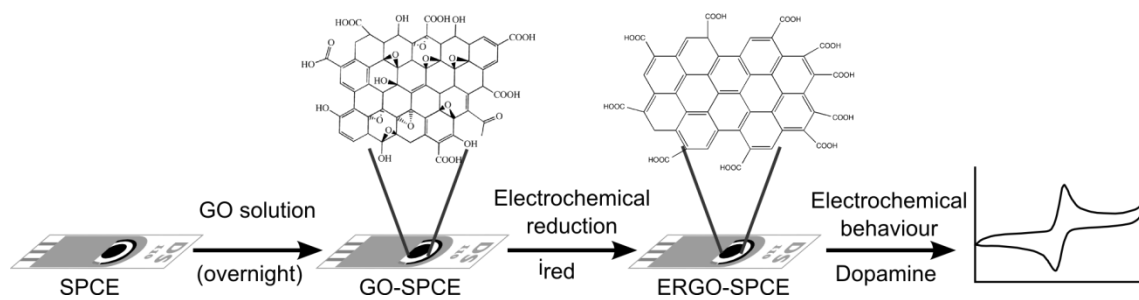
2

1 **Figure 2:** TEM images of the parent graphene materials.

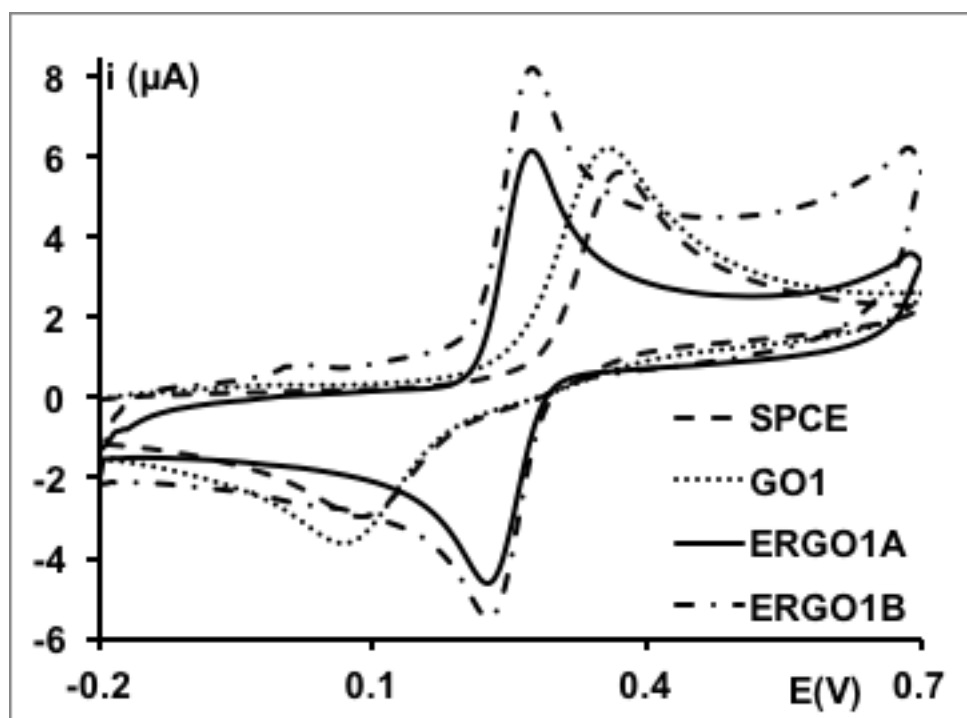


2

1 **Figure 3.** Modification procedure of screen-printed electrodes with electrochemically reduced
2 graphene oxides.

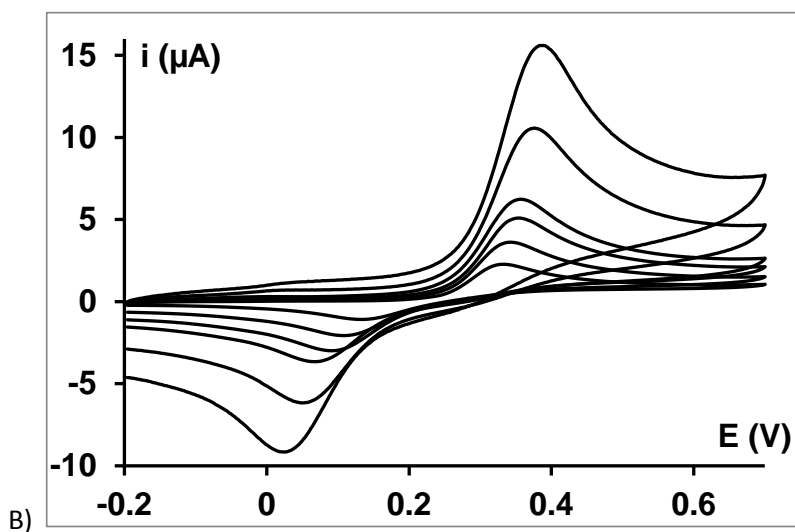
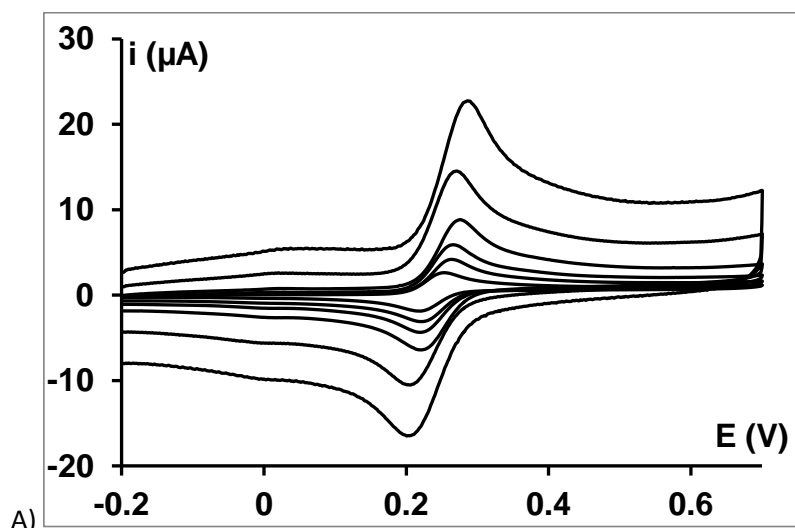


- 1 **Figure 4.** Cyclic voltammograms of dopamine at a bare SPCE (---), GO1-SPCE (...), ERGO1A (
2 —) and ERGO1B (- · - ·). Conditions: 1×10^{-4} M dopamine in H₂SO₄ 0.1 M. Scan rate: 0.1 V/s.

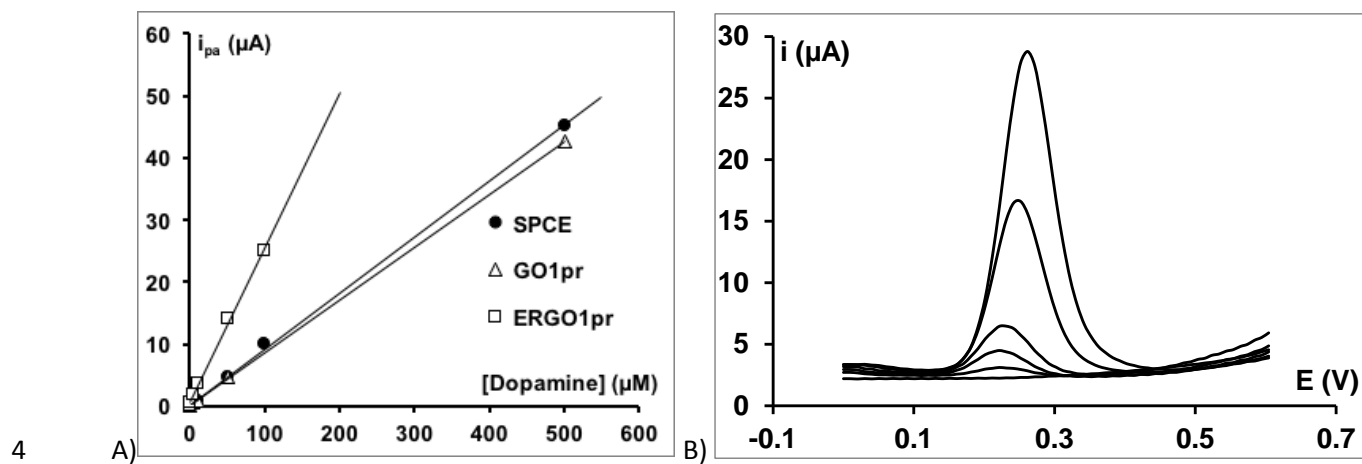


3

1 **Figure 5.** Cyclic voltammograms of 1×10^{-4} M of dopamine for different scan rates (10, 25, 50, 100,
2 250 and 500 mV/s for increasing currents, respectively) at a ERGO1A (A) and GO1-200 (B) modified
3 screen-printed electrodes.



- 1 **Figure 6.** (A) Calibration plot for different concentrations of dopamine at a SPCE (●), a GO1pr (△)
2 and a ERGO1pr (□) modified screen-printed electrodes. (B) Square-wave voltammograms for 0, 1, 5,
3 10, 50 and 100 μM of dopamine at a ERGO1pr-modified electrode.



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