



# Electrochemical characterization of electrochemically reduced graphene coatings on platinum. Electrochemical study of dye adsorption



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## ABSTRACT

Reduced graphene oxide coatings were synthesized by cyclic voltammetry on Pt electrodes. Electrochemically reduced graphene oxide was analyzed by scanning electrochemical microscopy for the first time. The redox mediator influences the electrochemical response; thus  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  gave a similar response and  $\text{Fe}^{3+}$  gave the poorest response. Pt electrodes coated with reduced graphene oxide were also used in the electrochemical adsorption (performed by cyclic voltammetry) of different dyes (Methylene Blue, Procion MX-2R and Amaranth). Electrochemical methods proved to be useful to monitor the adsorption of dyes on the surface of graphene materials. After adsorption, with Methylene Blue and Procion MX-2R, the appearance of a stable redox pair (with 1 electron transfer) was observed. This redox pair was adsorption controlled since the intensity of the redox pair was proportional to the scan rate used. Electrochemical adsorption multiplied by 3 the electrical charge of the Methylene Blue adsorbed on the surface of reduced graphene oxide when compared with simple adsorption at open circuit potential. In the case of Procion MX-2R, the increase obtained was even higher, with a 6-fold increase.

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## 1. Introduction

Since the discovery of graphene by Novoselov et al. [1], graphene has emerged as a revolutionary material in the field of physics and materials science due to its electronic [2], optical [3], thermal [4] and mechanical properties [5,6]. Different methods of production have been used for the production of graphene and derivatives [7,8]. High quality graphene crystals are obtained from mechanical exfoliation (the first method reported by Novoselov et al.) [1], however its production is limited to low quantities only useful for basic studies. This is why other methods with higher production capacity have been used, for instance: chemical vapour deposition [7,8] or chemical methods [7–9]. Among chemical methods, the production of graphene oxide (GO) is of particular interest due to the low production costs and its versatility. The reduction of GO allows the deposition of reduced graphene oxide

(RGO) on different substrates. The reduction can be performed thermally, photocatalytically, chemically, electrochemically, etc. [10]. Electrochemical reduction is of particular interest because its ease of operation and control, and no additional reagents such as dangerous reductants (for instance hydrazine) are needed [10]. The applications of graphene and derivatives in chemistry and electrochemistry are varied and numerous and include energy storage [7], sensors [7], oxygen reduction reaction [11] or photocatalysis [12] among others.

Scanning electrochemical microscopy (SECM) is a powerful technique that has been used to test the electroactivity of samples ranging from biological applications [13] to materials characterization such as corrosion processes [14]. Some studies have focused on the electrochemical characterization of graphene, graphene oxide and reduced graphene oxide by SECM [15–21]. However, the characterization by SECM of RGO obtained by electrochemical methods has not been reported in bibliography. This is the reason why electrochemical characterization by SECM of RGO deposited on Pt electrochemically was performed in this paper.

The interaction of graphene with organic molecules has been shown to be of interest; for instance the doping (n or p) of graphene with aromatic molecules has been demonstrated [22]. Graphene and derivatives have also been shown to be good

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adsorbents for dyes due to the  $\pi$ – $\pi$  stacking interaction between graphene and aromatic compounds [23,24]. These materials could have applications in dye-sensitized biosensors [25] or charge transfer complexes [26–28]. In this paper, the electrochemical adsorption of different dyes by cyclic voltammetry (CV) is proposed as a method to monitor the adsorption of the dye and a more efficient way of adsorbing dyes than open circuit adsorption. The RGO/dye complexes were also later characterized by CV in order to evaluate the adsorption products as well as its electrochemical properties.

## 2. Experimental

### 2.1. Reagents and materials

All reagents used were of analytical grade.

For the synthesis: Monolayer graphene oxide (GO) powders were acquired from Nanoinnova Technologies S.L. (Spain). Lithium perchlorate ( $\text{LiClO}_4$ ) was purchased from Merck. Pt wires (0.5 mm diameter, 99.99% purity) were acquired from Engelhard–Clal. The effective length of the electrodes used (where reaction occurred) was 2 cm (total area of  $0.31 \text{ cm}^2$ ). The area of the electrodes was controlled with Teflon<sup>®</sup>.

For the characterization: Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and potassium chloride (KCl) were purchased from Merck. Hexaammineruthenium (III) chloride ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ ), potassium ferrocyanide (III)  $\text{K}_3\text{Fe}(\text{CN})_6$  and iron (III) sulfate pentahydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ) were used as received from Acros Organics. Methylene Blue (MB), Procion MX-2R (PMX2R) and Amarant (AM) were purchased from Panreac, Zeneca and Fluka, respectively.

When needed, solutions were deoxygenated by bubbling nitrogen ( $\text{N}_2$  premier X50S). Ultrapure water was obtained from an Elix 3 Millipore–Milli-Q Advantage A10 system with a resistivity near to  $18.2 \text{ M}\Omega \text{ cm}$ .

### 2.2. Synthesis of reduced graphene oxide on Pt

An Autolab PGSTAT302 potentiostat/galvanostat was used to perform cyclic voltammetry (CV) as well as electrochemical impedance spectroscopy (EIS) measurements. GO was reduced on the surface of Pt by CV. The solution used for the synthesis contained ultrapure water,  $3 \text{ g L}^{-1}$  GO and  $0.1 \text{ M LiClO}_4$  (supporting electrolyte). Pt electrodes were pretreated with a flame treatment to clean their surface [29]. A three-electrode configuration was used for the synthesis: a Pt wire was used as counter electrode and Ag/AgCl (3.5 M KCl) was used as reference electrode. To perform the electrochemical synthesis, the potential was cycled between  $+0.6 \text{ V}$  and  $-1.4 \text{ V}$  at  $50 \text{ mV s}^{-1}$  for 40 scans.

### 2.3. Field emission scanning electron microscopy (FESEM)

A Zeiss Ultra 55 FESEM was used to observe the morphology of the samples, using an acceleration voltage of 3 kV. Energy dispersive X-ray (EDX) measurements were performed between 0 and 10 kV.

### 2.4. Electrochemical characterization by cyclic voltammetry (CV)

After synthesis, the electrodes were characterized by CV in  $0.5 \text{ M H}_2\text{SO}_4$  to test their characteristic capacitive behavior. Electrodes were also tested with different redox systems ( $0.01 \text{ M Ru}(\text{NH}_3)_6^{3+}/0.1 \text{ M KCl}$ ;  $0.01 \text{ M Fe}(\text{CN})_6^{3-}/0.1 \text{ M KCl}$  and  $0.02 \text{ M Fe}^{3+}/0.5 \text{ M H}_2\text{SO}_4$ ) to test their reversibility and therefore the electrochemical behavior of the electrode surface.

### 2.5. Electrochemical impedance spectroscopy (EIS)

The same configuration used for the synthesis of RGO on Pt was used for the EIS characterization of the electrodes in  $0.5 \text{ M H}_2\text{SO}_4$  solution.

The experimental results were also fitted using a non-linear least squares fitting minimization method by ZView software (version 2.7).

### 2.6. Scanning electrochemical microscopy (SECM)

SECM measurements were carried out with a scanning electrochemical microscope of Sensolytics. A three-electrode configuration cell consisting of a  $25\text{-}\mu\text{m}$ -diameter Pt microelectrode, a Pt wire auxiliary electrode and Ag/AgCl (3.5 M KCl) reference electrode. Measurements were performed with the same redox systems used in the CV characterization:  $0.01 \text{ M Ru}(\text{NH}_3)_6^{3+}/0.1 \text{ M KCl}$ ;  $0.01 \text{ M Fe}(\text{CN})_6^{3-}/0.1 \text{ M KCl}$  and  $0.02 \text{ M Fe}^{3+}/0.5 \text{ M H}_2\text{SO}_4$ . All the experiments were carried out in an inert nitrogen atmosphere.

The samples were glued to microscope slides with epoxy resin. The microelectrode operated at a potential of  $-0.4 \text{ V}$ ,  $0 \text{ V}$ ,  $-0.1 \text{ V}$  for the  $0.01 \text{ M Ru}(\text{NH}_3)_6^{3+}/0.1 \text{ M KCl}$ ,  $0.01 \text{ M Fe}(\text{CN})_6^{3-}/0.1 \text{ M KCl}$  and  $0.02 \text{ M Fe}^{3+}/0.5 \text{ M H}_2\text{SO}_4$  systems, respectively. At these potentials, the oxidized form of the redox mediator (Ox) is reduced (Red) at a diffusion controlled rate. Approach curves were obtained by recording the tip reduction current as the microelectrode tip was moved in z direction (approaching the sample). Approach curves give us an indication of the surface's electroactivity. These curves were compared to the theoretical ones (positive and negative feedback models). The substrate's surface in all the measurements was at their ocp.

### 2.7. Electrochemical behavior of dyes on the surface of Pt/RGO electrodes

The electrochemical behavior of different dyes was tested by means of CV. Solutions containing  $5 \cdot 10^{-3} \text{ M}$  of MB, PMX2R and AM and  $0.5 \text{ M H}_2\text{SO}_4$  were used for this purpose. A three-electrode configuration was used. Potential was cycled between  $-0.2 \text{ V}$  and  $+0.7 \text{ V}$  for 100 scans to produce the adsorption of the dyes. An experiment was also performed at ocp in the same conditions to evaluate the spontaneous adsorption of dyes during 1 hour. The potential evolution during ocp adsorption was monitored by means of chronopotentiometry (zero current). The electrodes were characterized previously and after dyes' adsorption in  $0.5 \text{ M H}_2\text{SO}_4$  solutions to determine possible adsorption products on the surface of RGO. To evaluate dye adsorption, the electrodes were rinsed with water several times in order to eliminate the dye not adsorbed. The electrodes were also characterized at different scan rates to determine if the processes were diffusion or adsorption controlled and determine the number of electrons involved.

## 3. Results and discussion

### 3.1. Field emission scanning electron microscopy (FESEM)

Fig. 1 shows the FESEM micrographs and EDX analysis of the Pt/RGO electrode obtained by means of cyclic voltammetry, sweeping the potential from  $+0.6 \text{ V}$  to  $-1.4 \text{ V}$  for 40 scans. The whole surface of the Pt electrode was coated by RGO sheets; in Fig. 1-a RGO sheets deposited on Pt have been magnified for better observation. EDX was used to analyze chemically the composition of the sample (Fig. 1-b). C, O and Pt appeared in the spectrum; C and O arise from GO. The presence of Pt is due to the penetration of the X-ray that is in the order of  $\mu\text{m}$ , much higher than the

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