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Javier Cristobal Espinoza Vergara

`espinozajavier@docente.ubo.cl`

Universidad Bernardo O'Higgins <https://orcid.org/0000-0001-5171-911X>

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Assembly of Graphene on SAMs and their performance to ORR.

Javier Espinoza-Vergara^{*a}, Cristian Gino Ramirez^b.

^a Universidad Bernardo O'Higgins, Centro de Investigación y Desarrollo de Ciencias de la Ingeniería (CIDCI), Facultad de Ingeniería, Ciencia y Tecnología, Avenida Viel 1497, Santiago, Chile.

^b Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago, Av. L. B. O'Higgins, 3363, Santiago, Chile.

*Corresponding author. E-mail: espinoza.javier@docente.ubo.cl

ABSTRACT

Here we present a new class of molecularly assembled electrode systems, composed of chemically reduced oxidized graphene (CRGO). The hydrophobic immobilization between this graphitic nanostructure on terminal groups (CH_3) of molecular spacers was carried out using monolayers of self-assembled molecules (SAMs) of 4-Methylbenzenethiol (4-MBT), obtaining thus the $[\text{Au}/4\text{-MBT}/\text{CRGO}]$ electrode system. On the other hand, the electrochemical characterization that is carried out through cyclic voltammetry and Electrochemical Impedance Spectroscopy (EIS) shows how the presence of CRGO reestablishes the electronic transfer and reduces the charge transfer resistance between the redox probe $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and the electrode surface. Besides, the conductive images of AFM (AFM-c) reveal that the areas of greatest conductance are presented by CRGO nanostructures, immobilized on the graft of SAMs molecules in Au (111). Likewise, the characterization through Raman Spectroscopy indicated the presence of structural imperfections of this crystal lattice of carbon atoms, and a high number of localized defects on the surface of CRGO, due to the interaction that the CRGO nanostructure presents,

when the assembly is established with the graft of SAMs in Au. The catalytic activity of this electrode system was examined for the reduction of O₂ in aqueous media of NaOH and compared with that of Au (111) bare and Au (111) coated directly with Fe-phthalocyanine (FePc) molecules. The electrocatalytic studies carried out with [Au (111)/FePc] and [Au/4-MBT/CROG/FePc] electrodes show that the O₂ reduction takes place by transferring 4-electron to give water. In this paper, the characterization and application of a CRGO modified gold electrode, a novel electrode system, are proposed.

Keywords: CRGO; SAMs, AFM-c, Fe phthalocyanines, O₂ reduction reaction.

1. INTRODUCTION.

Graphene is currently one of the most intensively studied materials [1]. This single-atom-thick sheet of carbon sp²-hybridized carbon arrayed in a honeycomb pattern is the world's thinnest, strongest, and stiffest material. It is no wonder that this two-dimensional material is considered, from the application's viewpoint, to be even more promising than other nanostructured carbon allotropes, that is, 1-dimensional nanotubes and 0-dimensional fullerenes [2]. Because of its novel properties such as high specific surface area [3,4], high thermal and electrical conductivities [4,5], great mechanical strength [6], unprecedented pliability, and impermeability [7], graphene has found potential applications in many fields such as nanocomposites [2,8], batteries [9], supercapacitors [10], nanoelectronics [11], sensors [12,13], and biosensors [14], etc. According to the literature, graphene appears to be an ideal material for electrochemistry applications [15,16] because of its large surface area, low production costs, and excellent electric and electrochemical properties [17], as well as due to defective sites [16].

This principle is in accord with Banks and Compton's work, who suggested, that catalytic activity of graphite-based electrodes mostly comes from the edges and the defects in their structure [18]. It is known that molecules and atoms adsorbed on graphene surfaces serve as local doping sites that significantly alter the electronic properties of graphene [19,20]. Several techniques have been developed to study the interactions between molecules and graphene surfaces. For example, Raman spectroscopy has been widely employed to characterize the quality of the graphene surface and to detect molecules bound to graphene [21] and scanning tunneling microscopy has been used to image molecules on graphene [22]. However, it has been reported that electrochemical studies on chemically synthesized graphene suggest that graphene may have favorable electron transfer kinetics [23].

The immobilization of graphene layers in electrode systems through the molecular linker has been investigated through a diamine linker which was preassembled on GCE by electrostatic interaction between the positively charged amine and the negatively charged layers of graphene oxide (GO), has several benefits over the reported methods [24] in the construction of electrochemical sensors being used in the detection of various molecules such as dopamine and ascorbic acid, as well as in nitrogenous bases belonging to the chain of DNA [25]. Lately, several publications reported that graphene-based electrodes have shown electrocatalytic activity towards diverse compounds such as H_2O_2 , O_2 , and NADH, and much more [26,27].

On the other hand, the Self-Assembled Monolayers (SAMs) are organic assemblies that arrange themselves spontaneously on solid surfaces into crystalline or semicrystalline structures and the self-assembly method is one of the elegant methods for the fabrication of nanomaterials on conducting substrates [28,29,30]. The application of SAMs in microelectronics has gained significant attention, with the drive towards miniaturization in this area as well as in modified surfaces based on graphene [31]. Ramesha et al, reported the self-assembly of GO on Au substrate

through cystamine SAM by electrostatic interaction [32]. Viinikanoja et al. reported the in-situ spectro-electrochemical characterization of GO on Au electrode attached through mercapto-ethylamine linker [33]. Kim et al. reported the self-assembly of GO using the surface of ITO amine-terminated grafted followed by the electrochemical reduction of GO for the immobilization of horseradish peroxidase [34]. Building on previous studies, we aimed to develop modified electroactive surfaces based on Au–SAMs–graphene architectures, designed to serve as nanostructured supports for the immobilization of catalytically active molecules through π – π stacking interactions. These interactions occur between the aromatic carbon network of graphene and the extended π -conjugated systems of macrocyclic complexes, such as metal phthalocyanines. This approach seeks to obtain promising electrocatalysts for the oxygen reduction reaction (ORR), with the potential to achieve catalytic performance comparable to that of Pt-based electrodes [35].

In this article, we present a simple and effective method for fabricating a modified electrode system according to the way CRGO layers are arranged. First, the Au (111) electrodes are modified by the formation of SAMs of 4-MBT, for the subsequent hydrophobic adsorption of monolayers CRGO in their terminal groups CH₃. These systems are denoted as [Au/4-MBT/CRGO]. This electrode system is characterized by electrochemical techniques (cyclic voltammetry, EIS), spectroscopic (RAMAN, XPS), and scanning electron microscopy techniques such as STM (See the Supporting Information), AFM tapping and AFM conductive mode, which contributes to the study of the behavior of CRGO nanostructure immobilized on the SAMs of 4-MBT.

Based on the previous assembly of this electrode system, this document demonstrates that CRGO nanostructures can be functionalized with FePc through π - π stacking interactions between graphene aromatic carbons and of the macrocycle [36,37]. In this work, we have investigated the catalytic activity of FePc for O₂ reduction adsorbed directly on Au (111) and also onto CRGO nanostructures anchored on SAMs formed on Au (111).

2. EXPERIMENTAL SECTION

2.1 Materials.

Single-layer Graphene Oxide 60 mL dispersion in water (500 mg/L) flake size: 0.3-0.7 μ m was purchased from Graphene Supermarket. Graphene oxide chemically reduced (CRGO), was synthesized according to a method described in the literature (See the Supporting Information). FePc (90%) and hydrazine monohydrate (98%), were obtained from Sigma Aldrich. Potassium hexacyanoferrate (II) trihydrate and Potassium hexacyanoferrate (III) were obtained from Merck. The reagents and solvents were of analytical grade and were used without further treatment. The working electrode was a thin vapor-deposited Au film deposited on glass (12×12 mm slides purchased from Arrandee, Germany). Gold slides were annealed using an H₂ flame, to obtain preferential Au (111) orientation. The reference electrode was a saturated calomel electrode (SCE) and a platinum wire of 5 cm² geometrical area served as the counter electrode.

2.2 Apparatus

Electrochemical experiments were conducted with nanopure water solutions purified with a Millipore Milli-Q Biocel Ultrapure water system fed with distilled water. For electrochemical measurements, solutions were purged with ultra-pure nitrogen for 30 min before each measurement. Electrochemical experiments, linear and cyclic voltammetry, and electrochemical impedance spectroscopy (EIS), were performed with Autolab PGSTAT AUT85730, using a conventional three-electrode electrochemical cell. On the other hand, EIS was performed in a solution of 2.5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and was recorded at the equilibrium potential ($E_{\text{eq}} = -0.18$ V), with an amplitude of 10 mV rms and in the frequency range between 10 mHz and 10 kHz.

The AFM images were obtained using the model DIMENSION 3100 with Bruker IV nanoscope electronics. For the measurements of AFM-conductive, a gold-coated silicone tip was used, allowing the local electrical conductivity to be measured exactly in the same area of the sample, which is analyzed in topography and phase-contrast images. The sample was connected electrically to support using a polarization potential of 500 mV since without this connection it would not be possible to monitor and appreciate the current differences of the CRGO. Besides, on the other hand, surface characterization was achieved by STM with an ECM-2 microscope (Veeco, USA) using a constant height module and commercial cut Pt-Ir tips.

Raman Spectroscopy Equipment Jobin-Yvon LabRam HR 800 dispersive spectrometer, coupled to an Olympus BXFM optical microscope. The detector used is a CCD cooled to -70 °C. Laser lines used: 532 nm. Diffraction networks used: 600 lines / mm. Laser Powers on samples: 0.5-4 mW. Objectives of the microscope used: 50 $\times$ and 100 $\times$. XPS experiments were performed in a PHI 5500 Multi-technique System (from Physical Electronics) with a

monochromatic X-ray source (Aluminium K alfa line of 1486.6 eV energy and 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d_{5/2} line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analyzed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.85 eV of Pass Energy and 0.8 eV/step for the general spectra and 23.5 eV of Pass Energy and 0.1 eV/step for the spectra of the different elements. All Measurements were made in an ultra-high vacuum (UHV) chamber pressure between 5×10^{-9} and 2×10^{-8} torr.

2.3. Electrodes Modification.

Gold substrates were immersed in an absolute ethanol solution containing 0.2 mM of aromatic thiol (4-MBT) for 5 minutes at ambient temperature [38]. The electrodes were then washed with ethanol to remove weakly adsorbed molecules and were then dried in a stream of high-purity N₂. The SAMs were formed by chemisorption of sulfur head group of aromatic thiols on Au(111), this substrate is denoted as [Au/4-MBT].

2.4. Assembly of CRGO on the [Au/4-MBT] electrode system through the incubation method.

Substrates [Au/4-MBT] were immersed in dispersion with a concentration of 1 mg/mL of CRGO in DMF in an incubation system, where these nanostructures hydrophobically adsorbed onto [Au/4-MBT] electrode surfaces for 24 h under stirring and at room temperature. Then, this electrode system was sonicated and thoroughly rinsed with Mili-Q water and then dried under N₂ gas flow, finally obtaining the electrode system [Au/4-MBT/CRGO]. Subsequently, the non-covalent functionalization of FePc on CRGO was carried out through the Vapor Deposition technique, where these complexes were vaporized in a high vacuum chamber, using low pressures at the order of 10^{-6} Torr. and at a temperature of 600 °C, obtaining the electrode system [Au/4-MBT/CRGO/FePc].

3. RESULTS AND DISCUSSION.

3.1. Characterization of SAMs 4-MBT on Au(111).

To follow the formation of SAMs on the gold electrode, Fig. 1 shows the comparison of the cyclic voltammetry profile of the bare and modified Au (111) surfaces with the SAMs graft, carried out in a de-aerated aqueous in 0.1 M NaOH at 0.05 V/s. Fig. 1a illustrates the cyclic voltammogram of the bare Au (111) electrode obtained after annealing the Au sample with H₂ flame. The *I* vs *E* profile shows the typical shape in alkaline electrolyte for an Au (111) electrode with atomically smooth surfaces (111). However, Figure 1b illustrates the voltammetric response for the process of reductive desorption or stripping process of 4-MBT from Au (111) surface. In particular, the reductive desorption curve for 4-MBT shows a single rather sharp cathodic peak located at - 0.72 V, suggesting that the 4-MBT species is chemisorbed on the gold electrode by adapting mainly a single type of surface domain on the gold substrate. Besides, the characteristics of this single reduction peak show a greater homogeneity in packing. The molecular structure of 4-MBT suggests that significant lateral intermolecular interactions (π -stacking) could be taking place between thioaromatic moieties once the SAMs are formed, which ultimately strongly influences the stability and the desorption process of this graft [39, 40]. The electrical charge density associated with the monolayer was found to be 40.11 $\mu\text{C cm}^{-2}$, is a lower value than the charge of other monolayers of aromatic thiols of the same size, such as the 4-aminothiophenols (4-ATP) on Au (111), with a value of 66 $\mu\text{C cm}^{-2}$ [41].

Therefore, this could be attributed to the fact that the molecules are with a lower degree of packing on the Au (111) surface, due to the incubation time of the Au (111) surface in the ethanolic solution with 4-MBT, compared to other thiols of the same size [42,43].

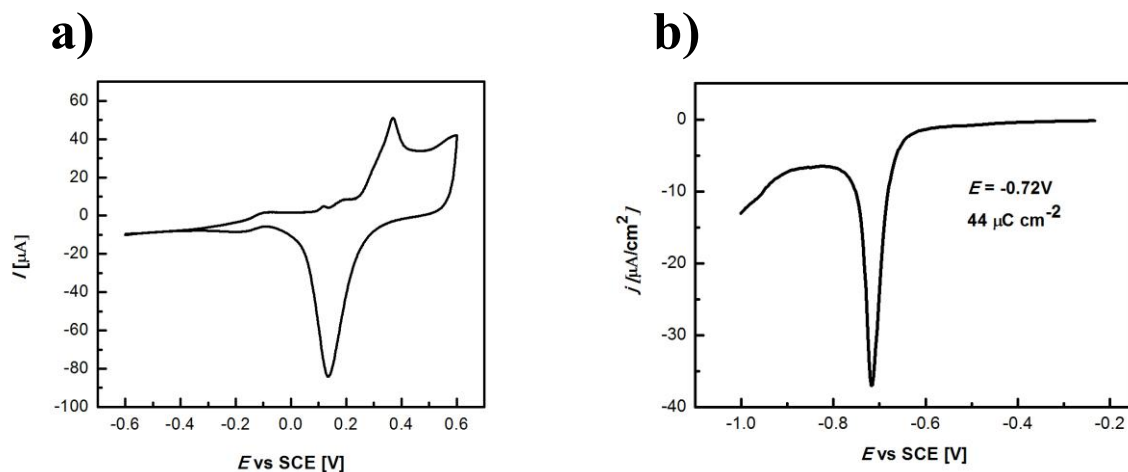


Fig. 1 Cyclic voltammograms for: (a) Unmodified Au (111) electrode and b) Reductive desorption of 4-MBT in a 0.1 M NaOH solution saturated in N_2 ; at a sweep speed of 50 mVs^{-1} .

Also, the modification of the electrode was confirmed using X-ray photoelectron spectroscopy (XPS). Fig. 2a shows the elemental analysis by XPS is shown that allows characterizing the species present on the surface through the general spectra of the [Au/4-MBT] electrode system where appears the characteristic signals of Au $4f_{5/2}$ and Au $4f_{7/2}$ (84 and 88 eV respectively), C 1s (284.5 eV) and S 2p (162 eV), a result of the spontaneous formation of 4-MBT SAMs. In figure, 2b the S (2p) spectrum consists of two peaks at 161.13 and 162.0 eV (assigned to the orbital doublet arising from S $2p_{3/2}$ and S $2p_{1/2}$ attributed to the Au-S bond and a peak at 163.04 eV that could indicate unbound (RSH) on the surface [44].

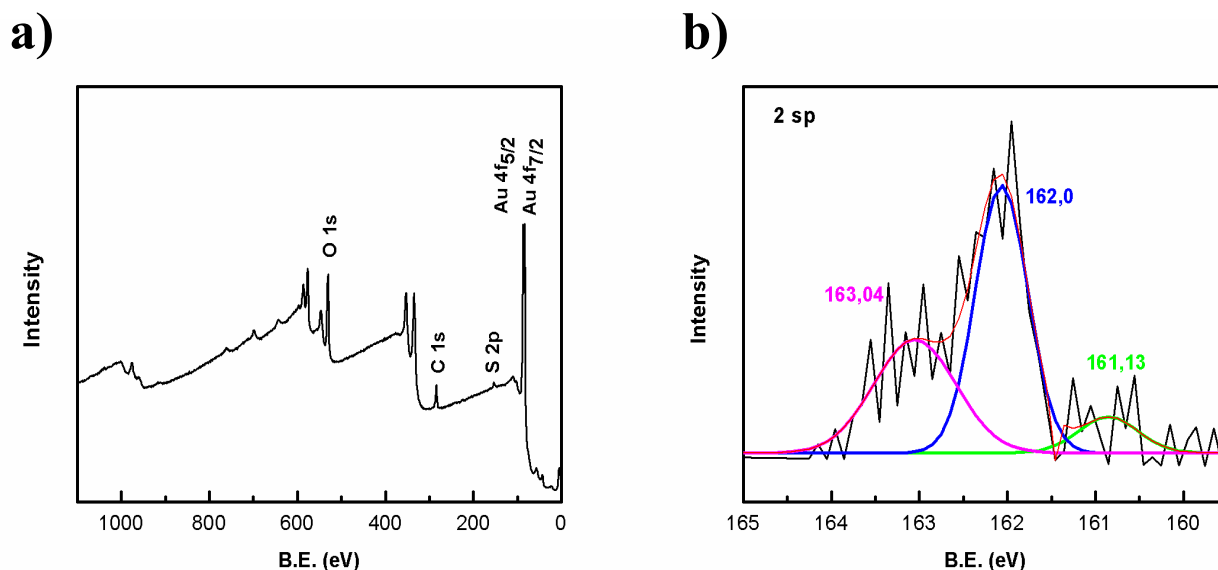


Fig. 2 XPS spectra of the [Au/4-MBT] electrode system: a) General, and (b) high resolution S 2p signal.

3.2. Electrochemical characterization of CRGO assembled on the [Au/4-MBT/CRGO] electrode system.

The second stage in the construction of the assembled system was the incorporation of the CRGO nanostructure through a hydrophobic interaction on the terminal methyl groups ($-\text{CH}_3$) of the 4-MBT monolayer to form the electrode system [Au/4-MBT/CRGO].

The electrochemical characterization of the electrode system [Au/4-MBT/CRGO] and its references; Pristine Au (111) and [Au/4-MBT] were carried out using cyclic voltammetry and electrochemical impedance spectroscopy. Fig. 3a shows the electrochemical behavior of surfaces before and after the assembly of CRGO on the 4-MBT SAMs, where the voltammetric response reflected the structural differences of the surfaces of the three systems, where well-defined redox peaks are observed for the pristine Au electrode (black line) with the peak-to-peak separation (ΔE_p) about 60 mV compared with the voltammetry curves for [Au/4-MBT] (red line) with ΔE_p about

278 mV which reveals a process of greater irreversibility since SAMs that significantly decrease electron transfer kinetics (ET) between the electrode and the redox probe in solution.

On the other hand, the cyclic voltammetry of the [Au/4-MBT/CRGO] electrode system (green line) with ΔE_p about 115 mV, shows a behavior with a much faster ET kinetics than the [Au/4-MBT] system suggesting that ET heterogeneous is largely restored by graphene sheets. This result shows the great contribution of CRGO nanostructures to the conductivity of the system, which benefits ET, which is highly decreased by a graft of SAMs on Au (111) due to its hydrophobic end groups [50]. The results obtained by cyclic voltammetry were also confirmed through Electrochemical Impedance Spectroscopy (EIS) whose results are summarized in Table 1 using the same redox probe $[\text{Fe}(\text{CN})_6]^{3-/4-}$, displayed in the Nyquist diagrams of figure 3b. In these plots, it is possible to distinguish two regions: at high frequency, the kinetically controlled region, which is characterized by a half-circle, where the diameter of this corresponds to the electron transfer resistance (R_{CT}); a smaller diameter of the semicircle indicates a faster electronic transfer. At low frequency, we found the diffusion-controlled region, where the straight line or Warburg line is located. The impedance spectra were fitted to the Randles' equivalent circuit shown in Fig. 3c. In the model, R_s is the solution resistance, R_{CT} corresponds to the electron-transfer resistance, Q represents the double-layer capacitance and Z_w is the Warburg impedance, which represents a kind of resistance to mass transfer [45].

It is observed in these results that the R_s element (resistance due to the electrolyte) is not affected by the chemical transformations (reactions) that occur at the interface, as it represents the bulk solution properties, due to this it practically does not undergo significant changes after of the modification of the Au (111) substrate. On the other hand, the R_{CT} exhibits a significant variation when incorporating the different components of the assembly, since this depends on the electronic characteristics of the electrode/electrolyte interface. The [Au/4-MBT] electrode system presents

the highest R_{CT} value of 135.78 Ω , showing that the monolayer has lower conductivity and that it imposes a barrier to the electronic transfer from the interface to the electrode, due to the high degree of compaction and homogeneity of the packing in the molecular arrangement, on the one hand, and also due to the hydrophobic conditions mentioned above. When assembling CRGO to the [Au/4-MBT] system, the R_{CT} value decreased significantly to 89.76 Ω . This phenomenon occurs due to the high electrical conductivity that the CRGO nanostructure presents, restoring electronic transport through it [46], obtaining a higher electrochemical activity than the [Au/4-MBT] system, as also seen in the voltammogram of the figure 3a.

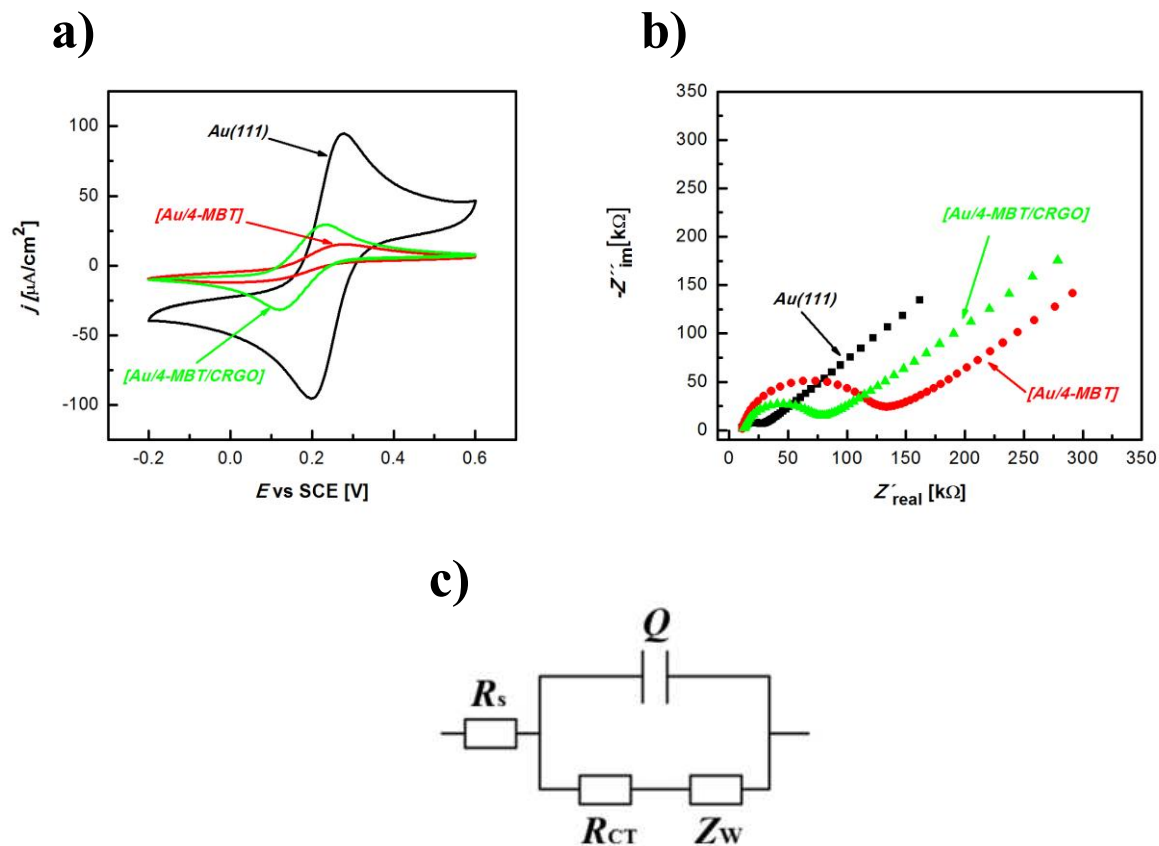


Fig. 3 Electrochemical characterization through a) cyclic voltammetry curves, b) impedance spectroscopy Nyquist curves, in a 0.1 M KNO_3 solution in the presence of 2.5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and c) Randles circuit model proposed of Au electrode surfaces.

Table 1

Summary of estimated electrochemical impedance parameters obtained for all electrode systems.

Electrode	R_s (k Ω)	R_{CT} (k Ω)
Au (111)	10.31	27.16
[Au/4-MBT]	10.87	135.78
[Au/4-MBT/CRGO]	10.33	89.76

3.3. Morphological and topographic characterization of the [Au/4-MBT/CRGO] electrode system through Atomic Force Microscopy (AFM tapping mode).

AFM images of Fig. 4a show that the CRGO immobilized on the 4-MBT SAMs shows regions with a high degree of folding, a behavior that has been described in the literature, due to the high π -conjugation of the graphitic nanostructure [47]. The cross-sectional analysis of image 4 a) represents the height profiles of figures 4 b and c). Figure 4b confirms the stacking of CRGO nanostructures that are arranged on the surface of the [Au/4-MBT] electrode system with an approximate value of 4,12 nm indicating the presence about 4 layers of CRGO. On the other hand, the analysis of the cross-section of figure 4 c), confirms the folding of this nanostructure with a value of 8.05 nm, indicating the presence of CRGO multilayers in this area. It should be noted that both the stacking and the folding of CRGO established an important role since that the abundance of graphitic edge planes/defects is essentially responsible for the fast ET kinetics, active electrocatalytic for ORR, and other biosensing properties [48,49].

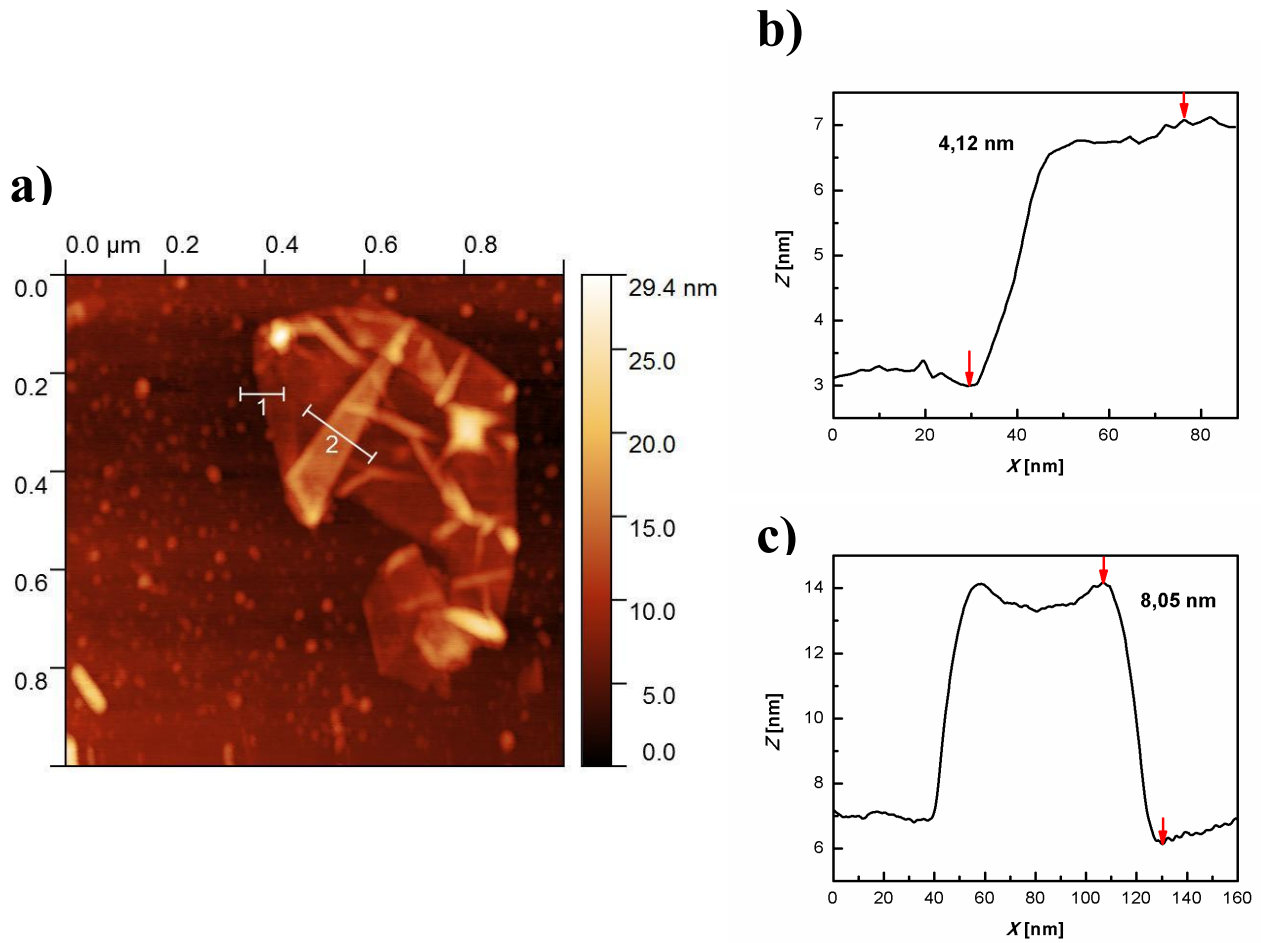


Fig. 4 a) 1 $\mu\text{m} \times 1 \mu\text{m}$ image of AFM tapping of the [Au/4-MBT/CRGO] electrode system, with its corresponding height profiles b) and (c).

3.4. Characterization of conductivity of the [Au/4-MBT/CRGO] electrode system through AFM-c.

The local organization of graphene within the [Au/4-MBT/CRGO] electrode system, together with the spatial distribution of its electrical conductivity, was investigated at the nanometric scale by conductive atomic force microscopy (AFM-c). This technique enables the simultaneous characterization of surface topography and local electrical properties. During the

measurements, the AFM operates in contact mode using a conductive probe that scans the sample surface while a bias voltage is applied between the conductive tip and the electrode. The resulting current flowing through the tip-sample interface is continuously monitored, allowing the local electrical response of the surface to be correlated directly with its morphological features. Consequently, AFM-c provides valuable information regarding the spatial distribution, connectivity, and electrical heterogeneity of conductive domains at the nanoscale.

Figures 5a and 5b present the conductivity maps obtained for the [Au/4-MBT/CRGO] system. The images reveal a high surface population of CRGO, manifested as regions of enhanced electrical response and represented by the brightest areas in the conductivity maps. These highly conductive domains exhibit current values of approximately 20 nA, indicating the presence of electrically active graphene-based regions distributed across the modified electrode surface. The contrast observed in the conductivity images therefore provides direct evidence of the heterogeneous but spatially distributed incorporation of CRGO within the 4-MBT self-assembled monolayers (SAMs).

A more detailed examination of the conductivity contrast, particularly in Figure 5c, reveals local current variations of approximately 4.5 nA. These variations are associated with the presence of CRGO domains on the grafted SAM and reflect differences in the local electrical transport pathways across the modified surface. Such variations in current may arise from the heterogeneous spatial arrangement of the graphene sheets, their degree of contact with the underlying molecular layer, and the local electronic coupling between the CRGO and the Au/4-MBT interface. Thus, the AFM-c measurements provide not only evidence for the presence of CRGO, but also complementary information concerning its local electrical interaction with the functionalized electrode.

Importantly, the conductivity distribution observed by AFM-c is consistent with the electrochemical behavior previously described for this system. In particular, the enhanced and spatially heterogeneous conductivity detected at the nanoscale can be correlated with the electrochemical responses obtained by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Likewise, the spatial distribution of the conductive domains is consistent with the morphological information obtained from scanning tunneling microscopy (STM). Taken together, these complementary characterization techniques indicate that the incorporation of CRGO into the Au/4-MBT architecture modifies both the surface morphology and the local electronic properties of the electrode. The AFM-c results therefore provide nanoscale experimental evidence linking the organization of CRGO on the SAM-functionalized Au surface to the macroscopic electrochemical response of the [Au/4-MBT/CRGO] electrode system. The corresponding electrochemical results are presented in the Supporting Information.

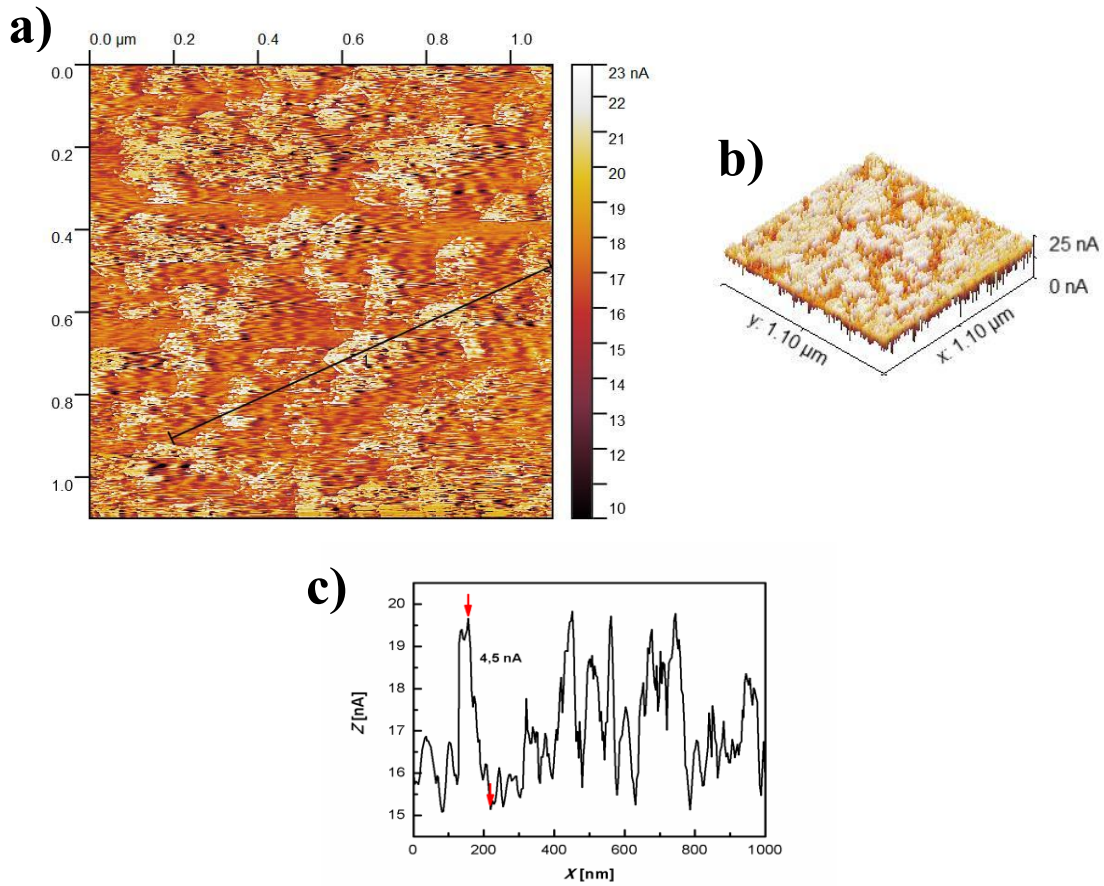


Fig. 5 AFM-c images of [Au/4-MBT/CRGO] electrode system: a) 2D view ($1\ \mu\text{m} \times 1\ \mu\text{m}$), b) a 3D view of surface and c) electrical current cross-section analysis.

3.5. Characterization by Raman Spectroscopy of the [Au/4-MBT/CRGO] electrode system.

This technique is considered one of the most effective tools in the structural determination of Graphene on various surfaces, since it is used to analyze the number, and orientation of layers, the quality and types of edge, and the effects of disturbances, such as electric and magnetic fields, deformation, doping, disorder and chemical functionalization [50,51]. Figure 6 shows the typical bands at $1348.57\ \text{cm}^{-1}$ and $1590.86\ \text{cm}^{-1}$ are presented, corresponding to D and G, respectively, in the first-order zone of graphitic materials. The D band, typically observed at around $1350\ \text{cm}^{-1}$, is associated with a defect-activated breathing mode of six-membered carbon rings and becomes Raman-active because of structural disorder, defects, edges, or disruption of the translational

symmetry of the sp^2 carbon lattice. In contrast, the G band, located at approximately 1580 cm^{-1} , originates from the in-plane stretching vibration of sp^2 -hybridized carbon atoms. Therefore, an increase in the D-band intensity relative to the G band (I_D/I_G) is generally indicative of a higher degree of structural disorder and a reduction in the size of the ordered sp^2 domains. In CRGO, this behavior can be associated with the introduction of oxygen-containing functional groups during oxidation, which disrupt the sp^2 carbon network and generate sp^3 -hybridized carbon sites. However, the I_D/I_G ratio should be interpreted primarily as a measure of structural disorder and defect density rather than as a direct quantitative measure of the sp^3 carbon fraction. [51,52]. On the other hand, the Raman spectra also exhibit a 2D band centered at an average wavenumber of 2694.27 cm^{-1} , characterized by a relatively weak intensity and an asymmetric line shape. The position, linewidth, and shape of the 2D band are highly sensitive to the electronic and structural environment of graphene. In particular, interactions with the underlying substrate and molecular adsorbates, such as self-assembled monolayers (SAMs), can induce charge transfer, interfacial doping, and localized strain, resulting in measurable shifts and broadening or asymmetry of the 2D feature. Therefore, the observed modification of the 2D band in the graphene/SAMs/Au assembly can be associated with interfacial electronic interactions and local structural perturbations arising from the molecular grafting process. However, the changes in the 2D band should not be considered as direct evidence of defect density alone; rather, they should be interpreted together with the D and G bands, particularly the I_D/I_G ratio, to distinguish structural disorder from strain- and doping-related effects [53,54,55,56].

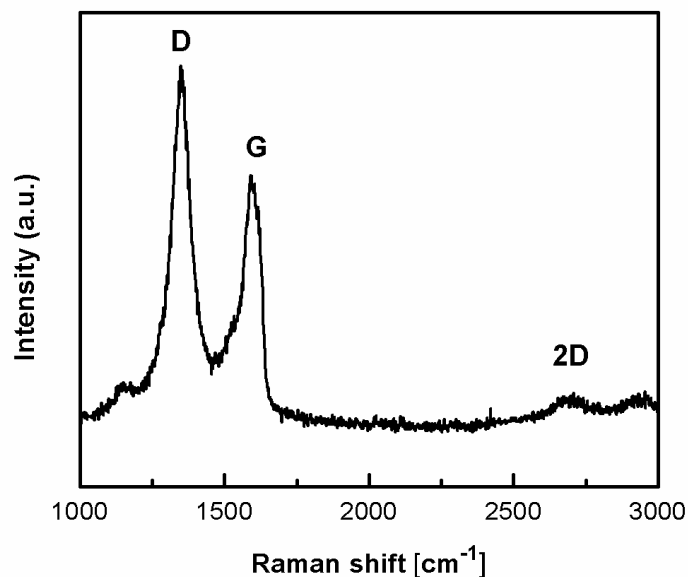


Fig. 6 Raman spectra of the [Au/4-MBT/CRGO] electrode system.

3.6. Characterization of the [Au/4-MBT/CRGO/FePc] electrode system through X-ray photoelectron spectroscopy (XPS).

X-ray photoelectron spectroscopy (XPS) was employed to further explore the interactions between CRGO and FePc. Figure 7a shows the elemental analysis by XPS data of the [Au/4-MBT/CRGO/FePc] electrode system, where the peaks of C, N, O, and Fe can be found, revealing that the FePc molecules have been successfully anchored on the nanostructure CRGO. Fig. 7 b shows the Nitrogen (N 1s) region for the assembled electrode, where a peak located at 398.10 eV is attributed to the pyridine nitrogen atoms of the FePc macrocycle [57]. Instead, figure 7c shows a peak located at 709.2 eV, which corresponds to the Fe 2p emission. This is consistent with the type of iron found in FePc in the Fe (II) state bound to the surface of CRGO by physical adsorption [58]. The deconvolution of the C 1s region presented in figure 7d shows four contributions: a lower energy band (284.31 eV) attributed to the C=C bond of the SAMs [59], the main band centered at 284.60 eV attributed to the C=C of the graphitic nanostructure of CRGO

and two less intense bands located at 287.50 and 289.89 eV attributed to C-O (hydroxyls-epoxides) and -O-C=O (carboxylates) respectively bonds, the latter belonging to the remaining oxygenated groups of CRGO [60].

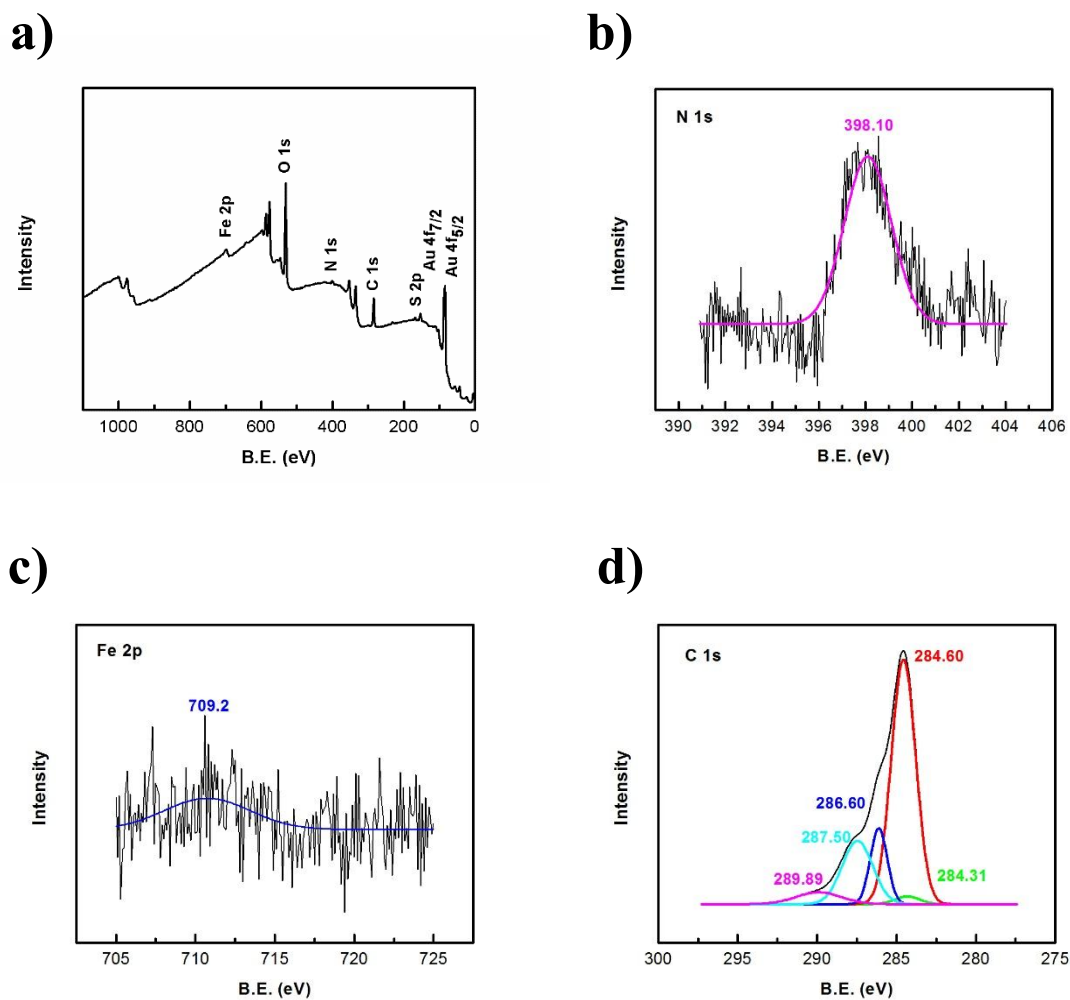


Fig. 7 XPS spectra a) general and high resolution of the [Au/4-MBT/CRGO/FePc] electrode system in the zones: b) N 1s, c) Fe 2p and d) C1s.

3.5 Electrocatalysis of the O₂ reduction reaction in the [Au/4-MBT/CRGO/FePc] electrode system.

In this section the study of electrocatalytic activity for ORR was carried out obtaining the electrochemical response (cyclic voltammetry and polarization curves) of the self-assembled electrodes obtained in each stage of construction, considering them as reference systems, towards the final assembly as illustrated in the scheme in Fig. 8.

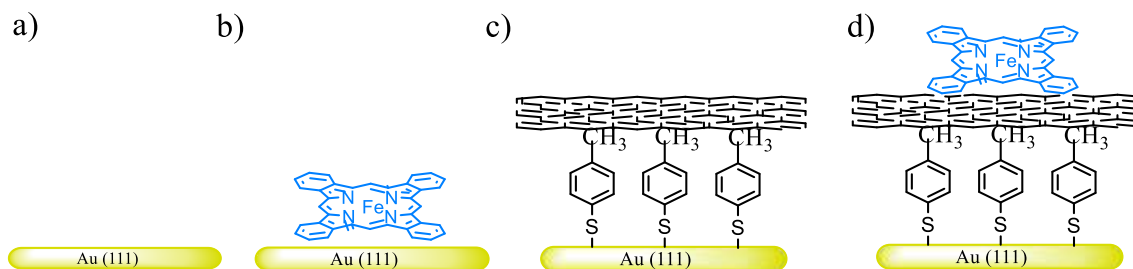


Fig. 8 Scheme of the different electrode configurations for the study of ORR. a) Au(111), b) [Au (111)/FePc], c) [Au/4-MBT/CRGO] and d) [Au/4-MBT/CRGO/FePc].

Figure 9 shows the cyclic voltammograms of the [Au/4-MBT/CRGO/FePc] electrode system, comparing it with the rest of the reference systems. The electrochemical response for ORR changes markedly at the [Au(111)/FePc] and [Au/4-MBT/CRGO/FePc] electrodes; in both, cathodic processes corresponding to the irreversible reduction of molecular oxygen are observed. This process is favored on both surfaces by the presence of the FePc complex. When comparing the voltammetric responses for ORR in Fig. 9, in the [Au(111)/FePc] systems (red curve) and [Au/4-MBT/CRGO/FePc] (blue curve), it was observed that the cathodic process is displaced towards positive potentials in the cyclic voltammogram for the [Au/4-MBT/CRGO/FePc] electrode system which starts at -0.040 V showing a cathodic peak of greater intensity in the

current density compared to the [Au(111)/FePc], where the voltammetric response of this cathodic process starts in -0.115 V.

This displacement of 75 mV to more positive potentials values shows that the [Au/4-MBT/CRGO/FePc] electrode system has the better electrocatalytic performance to carry out the ORR process. However, the electrocatalytic activity of the [Au/4-MBT/CRGO] electrode system displayed a very poor electrocatalytic response for ORR starting at -0.200 V showing a narrower cathodic process, due to the absence of suitable active sites for the coordination of the O₂ molecule and its subsequent electro-reduction.

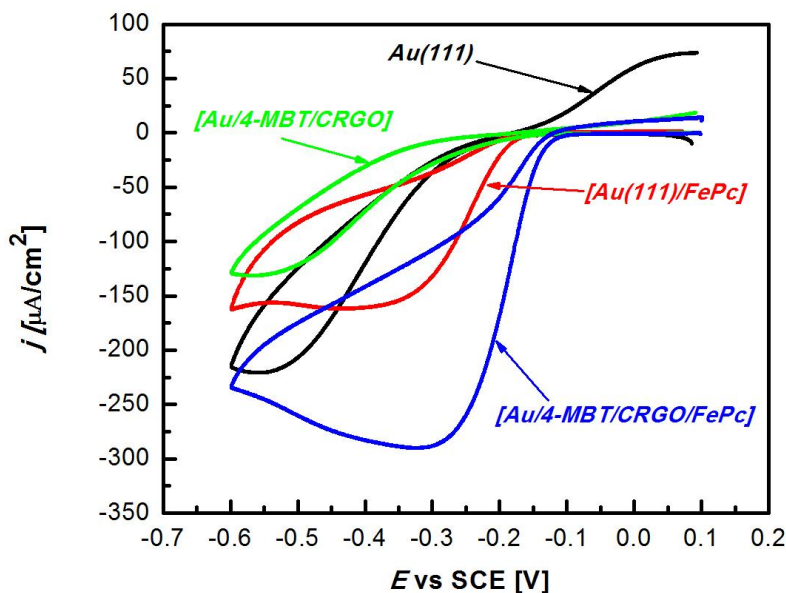


Fig. 9 Voltammetric response for ORR for a bare and modified Au (111) electrode with different configurations containing FePc. Measurements were carried out in a 0.1 M NaOH solution saturated with O₂ at 50 mV/s.

Kinetic studies were also performed to determine the Tafel slopes obtained from the inset Tafel plots corresponding polarization curves shown in Figure 10. The values of the Tafel slopes displayed in table 2 are 35 and 32 mV/decade for the [Au(111)/FePc] and [Au/4-MBT/CRGO/FePc] electrode system respectively. These values are in the reported range (between 30 and 40 mV/decade), this suggests that the determining stage of the reaction rate would be the same for ORR, which is catalyzed by macrocyclic Fe complexes through a 4-electron mechanism, indicating that the decisive step of the reaction corresponds to a slow electron transfer, preceded by a fast transfer [61, 62]. However, the value of the Tafel slope obtained for the [Au/4-MBT/CRGO] electrode system turned out to be close to 131 mV/decade, which suggests that the determining step of the reaction rate corresponds to the transfer of the first electron in the ORR mechanism.

Table 2.

Tafel slopes obtained from the RRO polarization curves in different Au electrode systems.

Electrode	[Au(111)/FePc]	[Au/4-MBT/CRGO]	[Au/4-MBT/CRGO/FePc]
Tafel Slopes (V/dec.)	-0.035	-0.131	-0.032

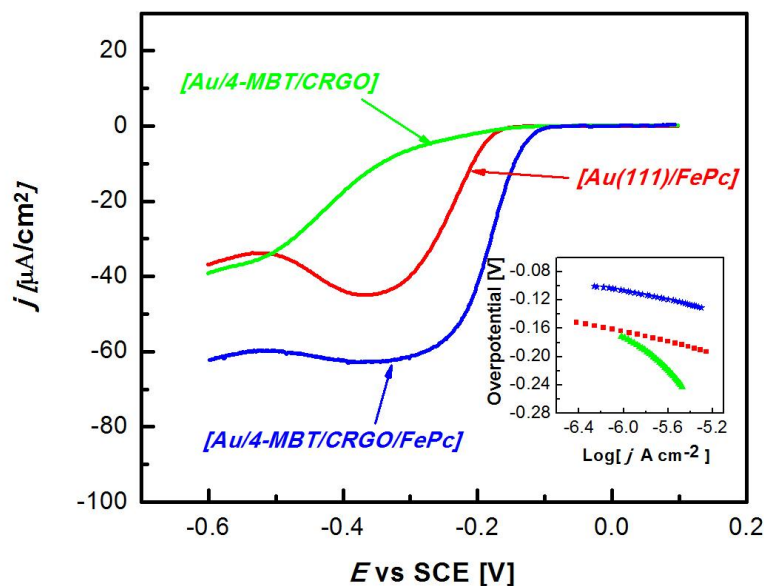


Fig. 10 Polarization curves for ORR at a scan rate of 2 mVs^{-1} in 0.1M NaOH solution saturated in O_2 for different Au electrode systems. Tafel plots obtained from the polarization curves from a). Insert: Tafel graph obtained from the polarization curves.

4. SCOPE AND OUTLOOK

The role of CRGO is not merely structural. Its incorporation produces a hierarchically heterogeneous interface in which folded and defect-rich graphitic domains provide locally conductive pathways across the electronically blocking 4-MBT layer. This is consistent with the local current contrast observed by conductive AFM and with the partial recovery of heterogeneous electron-transfer kinetics observed macroscopically by CV and EIS. The resulting conductive carbonaceous interface simultaneously provides a platform for non-covalent FePc immobilization, ultimately favoring the electrocatalytic response toward ORR. Beyond the specific application to FePc-catalyzed ORR, the present results highlight the broader potential of the $[\text{Au}/4\text{-MBT}/\text{CRGO}]$ assembly as a modular platform for the immobilization of electroactive molecules. Building on previous approaches for graphene immobilization on functionalized electrodes and graphene–

phthalocyanine systems, this work integrates a well-defined Au(111)/SAM/CRGO architecture in which the molecular linker provides surface anchoring, while CRGO restores efficient electronic communication and offers a π -conjugated interface for the subsequent non-covalent immobilization of FePc. The resulting [Au/4-MBT/CRGO/FePc] system improves the ORR response relative to directly adsorbed FePc on Au (111), while preserving the same overall reaction mechanism, supporting the concept of interfacial engineering rather than modification of the intrinsic catalytic pathway. This modular architecture could therefore be extended to other π -conjugated molecular catalysts. Nevertheless, the present study is limited to FePc and ORR on Au(111); future work should assess alternative catalysts and substrates, long-term stability, control of CRGO coverage and organization, and direct comparison with simpler graphene-based electrode architectures.

5. CONCLUSIONS.

- Cyclic voltammetry and electrochemical impedance spectroscopy results showed that the CRGO assembly on the [Au/4-MBT] electrode system favored electronic transport through this nanostructure, obtained conduction pathways for electrons between the electrochemical probe $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and the electrode, with a positive impact on the quality and properties of the [Au/4-MBT/CRGO] electrode assembly as a platform for fast electronic transfer in the study of the electrocatalysis of ORR, once functionalized with FePc.
- Characterization of the [Au/4-MBT/CRGO] electrode system through AFM-tapping, showed that the CRGO nanostructures are incorporated folded and segregated on the [Au/4-MBT] electrode system. The AFM-c study shows the conductivity mapping of the electrode system [Au/4-MBT/CRGO] is displayed and the contrast of the image clearly

showed that the areas of high conductance correspond to those where the CRGO layers are located.

- The electrode system [Au/4-MBT/CRGO/FePc], showed high electrocatalytic performance for ORR compared to the control system [Au(111)/FePc]; i.e., much higher current densities and a potential shift to more positive values of the ORR cathodic process. The analysis of the Tafel slope suggests for both electrode systems [Au (111)/FePc] and [Au/4-MBT/CRGO/FePc] the determining stage of the reaction rate would be the same for ORR through a 4-electron mechanism. Thus latter, indicates that the decisive step of the reaction corresponds to a slow electron transfer, preceded by a fast transfer. Therefore, it can be established that the mode of assembly of the FePc molecules does not change the mechanism of the reaction, or at least, does not change the Tafel slope.

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Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used SciSpace and Grammarly to improve the reference consultations and language and readability respectively. After using this tool/ service, the authors reviewed and edited the content as needed and took full responsibility for the content of the publication.

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