

Attachment of anthraquinone derivatives to glassy carbon and the electrocatalytic behavior of the modified electrodes toward oxygen reduction

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Abstract The electrochemical reduction of oxygen on glassy carbon (GC) electrodes modified with anthraquinones was studied using cyclic voltammetry (CV) and the rotating disk electrode (RDE) technique. Two methods were used in surface modification. The first method comprised immersion of the polished or anodically pretreated GC electrode in a solution containing 9,10-anthraquinone-2-carboxylic acid (AQ-2-COOH) or its anion (AQ-2-COO⁻) in dimethylsulfoxide (DMSO) or 9,10-anthraquinone-2-ethanoic acid (AQ-2-CH₂COOH) or its anion (AQ-2-CH₂COO⁻) in *N,N*-dimethylformamide (DMF). Alternatively, the surface of the GC disk was modified by anodic oxidation of AQ-2-COOH or AQ-2-COO⁻ in DMSO or AQ-2-CH₂COOH in DMSO or DMF or AQ-2-CH₂COO⁻ in DMF. The modified electrodes showed electrocatalytic activity toward oxygen reduction in 0.1 M acetate buffer pH (4.8), 0.1 M phosphate buffer

(pH 8) and 0.1 M NaOH. Atomic force microscopy (AFM) examination of the modified electrodes was carried out and the differences in surface morphology of various modifications were in evidence.

Keywords 9,10-Anthraquinone-2-carboxylic acid ·
9,10-Anthraquinone-2-ethanoic acid ·
Glassy carbon electrode · Oxygen reduction ·
Electrocatalysis

Introduction

The adsorption behavior of various quinones has been of considerable interest during recent decades. Early work by Yeager and coworkers showed that the quinone-modified electrodes are particularly attractive as electrocatalysts for O₂ reduction [1–4]. These systems are of practical importance regarding the electrosynthesis of hydrogen peroxide. Salimi et al. [5] reported the preparation and electrochemical characterization of glassy carbon (GC) modified with four 1,4-dihydroxy-9,10-anthraquinone derivatives. They stated that the anthraquinones used were strongly and irreversibly adsorbed on pre-anodized GC electrodes. They also studied the electrochemical behavior and stability of the modified electrodes in aqueous solutions of different pH and the optimum working pH was ca. 6–7. It was also found that the adsorbed anthraquinone derivatives show excellent electrocatalytic activity for the reduction of O₂ to H₂O₂ with overpotentials ranging from 560 to 650 mV lower than that of a bare glassy carbon electrode. In subsequent work, these authors used several anthraquinone-substituted podands in surface modification [6]. The electrochemical behavior and stability of the modified

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electrodes was studied in acidic aqueous solutions and they claimed that the optimum working pH was around 4.5. Analogous to their previous study, the electrocatalytic reduction of O_2 occurred at much lower overpotentials compared to that of an unmodified GC.

Manisankar et al. [7] studied the electrochemical properties of glassy carbon electrodes modified with 9,10-anthraquinone, its amino derivatives, and dyes. According to these authors, the reduction of oxygen proceeds by a two-electron pathway yielding hydrogen peroxide and pH 5–8 was found to be the optimum working pH by comparing the shift in oxygen reduction potential. The anthraquinone-modified GC electrodes possessed excellent electrocatalytic activities for oxygen reduction with overpotential ranging from 280 to 560 mV lower than that at a bare glassy carbon electrode.

Manisankar and Gomathi [8] reported the construction of modified carbon paste electrodes by incorporation of 9,10-anthraquinone derivatives and dyes in a graphite powder–paraffin oil matrix and a study of their electrochemical and catalytic behavior. They tested the stability of the modified carbon paste electrodes in acidic, neutral, and basic media. The authors examined the electrocatalytic ability of the modified electrodes for the reduction of oxygen to H_2O_2 and pH 7.0–8.0 was chosen as the optimum working pH by comparing the shift in oxygen reduction potential. The anthraquinone-incorporated carbon paste electrodes studied possess excellent electrocatalytic activity for oxygen reduction with a large decrease in overpotential compared to that of an unmodified carbon paste electrode.

Compton and coworkers have employed quinone-modified carbon electrodes for sonoelectrocatalysis of oxygen reduction and hydrogen peroxide production [9–11]. A variety of quinones were used and their electrocatalytic behavior was explored. Particular attention was paid to the issue of stability of the modified electrodes under insonation.

Vaik et al. [12] investigated the electrochemical reduction of oxygen on anodically pretreated glassy carbon and on oxidized GC electrodes grafted with anthraquinone. The oxidative pretreatment of polished GC electrode was made by oxidizing it at 1.75 V vs SCE for 10 s in 0.1 M KOH. Anthraquinone was grafted on these electrodes by electrochemical reduction of 10 mM solution of the corresponding diazonium salt (Fast Red AL Salt). The authors suggest that the surface oxidation increases the electrocatalytic activity of GC for oxygen reduction to hydrogen peroxide and the reduction of O_2 is considerably altered when oxidized GC electrodes are grafted with anthraquinone.

Vaik et al. [13] studied the electrochemical reduction of oxygen on glassy carbon electrodes modified with anthraquinone. Surface modification was performed by anodic oxidation of the carboxylate group in 4 mM solution of 9,10-anthraquinone-2-ethanoic acid (AQ- CH_2COOH) in

DMF. The modified electrode showed a pronounced electrocatalytic activity toward oxygen reduction in 0.1 M KOH. The authors found that the rate constant for the reaction between the semiquinone radical and oxygen showed little dependence on the point of attachment of the quinone.

It is apparent on the basis of the literature reports that the adsorption of anthraquinone derivatives to different carbon surfaces can occur irreversibly. Also, the covalent functionalization or covalent attachment to the graphite or carbon surface using anthraquinone derivatives was observed. However, to our knowledge, there is no literature on the adsorption or covalent attachment to the carbon surface by the physical contact or electrografting of a quinones carboxylate or quinone carboxylic or ethanoic acid and the use of these modified electrodes to study the reduction of oxygen. The purpose of the present work was to show the occurrence of a strong adsorption to the glassy carbon surface by immersion of the electrode in a solution of AQ-2-COOH or AQ-2-COO⁻ in DMSO or AQ-2- CH_2COOH in DMSO or DMF or AQ-2- CH_2COO^- in DMF and also to show the occurrence of covalent functionalization of the GC surface by anodic oxidation of these compounds. The reduction of oxygen on the modified electrodes was also investigated.

Materials and methods

The tetramethylammonium salts of anthraquinone carboxylic and ethanoic acids (TMA⁺AQ-2-COO⁻ and TMA⁺AQ-2- CH_2COO^-) were prepared in a glass apparatus (Schlenk tube) under reduced pressure and inert atmosphere (N_2). A mixture of 25.22 mg of AQ-2-COOH(β^-) (99%, TCI America) or 26.7 mg of AQ-2- CH_2COOH (synthesized as described in [13]) and dissolved in 5 ml of methanol and 27 μ l of tetramethylammonium hydroxide (TMAOH, 25 wt % solution in water; Aldrich) was added to the system. After a few minutes of solvent evaporation, the dry salts of TMA⁺AQ-2-COO⁻ and TMA⁺AQ-2- CH_2COO^- were obtained.

Glassy carbon (GC) disk electrodes with geometrical surface area (A) of 0.2 or 0.25 cm² were employed for the cyclic voltammetry (CV) and the rotating disk electrode (RDE) measurements. The electrodes were polished before use to a mirror finish by abrasion with emery paper followed by 1.0, 0.3, and 0.05 μ m alumina slurries and cleaned by sonication in Milli-Q water (Millipore) for 15 min. A Pine Instrument Co. rotating disk electrode and MSRX speed control unit were used. Pt gauze served as counter electrode and a saturated calomel electrode (SCE) was used as a reference. All the potentials are referred to this electrode. All experiments were carried out at room temperature (25 ± 1 °C).

The electrochemical measurements were carried out with an AFCBP1 bipotentiostat (Pine Instrument Company) and the surface morphology studies were performed using an atomic force microscope TopoMetrix® AFM Explorer.

The solutions of modification of GC were made up in DMSO (<0.05% water; Merck) or DMF (<0.05% water; Merck) containing 0.1 M sodium perchlorate (NaClO₄; Merck), saturated with N₂ (99.95%; White Martins), and by adding AQ-2-COOH, or AQ-2-CH₂COOH, or dry TMA⁺AQ-2-COO⁻, or dry TMA⁺AQ-2-CH₂COO⁻ to achieve a final concentration of 4 mM. The solutions were treated in an ultrasonic bath for 2 min under N₂ bubbling. The use of different solvents is due to different solubilities of anthraquinone derivatives. The derivatization of the polished or anodically pretreated GC electrode surface (repetitive potential cycling for 50 times between 0 and 1.5 V when the solvent used was DMSO or between 0 and 1.7 V when the solvent used was DMF at 100 mV s⁻¹) was made by immersion in the solution of anthraquinone derivatives during 3 or 42 h or by anodic oxidation of these anthraquinones by repetitive potential cycling for 50 times between 0 and 1.5 V when the solvent used was DMSO or between 0 and 1.7 V when the solvent used was DMF at 100 mV s⁻¹. The electrodes modified by anodic oxidation of the carboxylic substituent are designated as GC/AQ and GC/AQCH₂ for electrografting with AQ-2-COO⁻ and AQ-2-CH₂COO⁻ (or AQ-2-CH₂COOH), respectively. The electrodes modified by immersion (adsorption) are denoted as GC/AQ-2-COO⁻, GC/AQ-2-COOH, GC/AQ-2-CH₂COO⁻, and GC/AQ-2-CH₂COOH.

The modified electrodes were electrochemically characterized by cyclic voltammetry and oxygen reduction was studied in 0.1 M acetate buffer at pH 4.8 (acetic acid [Fluka] ≥ 99% + sodium acetate [Merck] 99%), 0.1 M phosphate buffer at pH 8 (NaH₂PO₄[Merck] 99–102% + NaOH [Merck] 99.99%), and 0.1 M NaOH (99.99%; Merck) in Milli-Q water. The solutions were saturated with N₂ or O₂ (99.95%; White Martins). A continuous flow of gases was maintained over the solution during the electrochemical measurements.

Results and discussion

Surface modification

The electrochemical oxidation of AQ-2-COO⁻ was studied in dimethylsulfoxide. Figure 1 shows typical cyclic voltammograms at different scan rates recorded with the stationary glassy carbon electrode. An anodic peak was observed at approximately 1.35 V vs SCE. The current increase observed at $E > 1.5$ V can be attributed to the

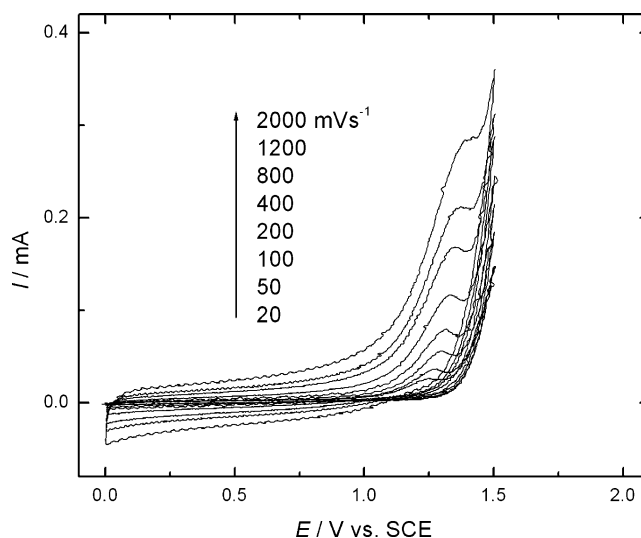


Fig. 1 Electrochemical oxidation of AQ-2-COO⁻ on a GC electrode in N₂-saturated DMSO containing 4 mM AQ-2-COO⁻ (dry carboxylate) and 0.1 M NaClO₄ at various sweep rates. Each curve corresponds to the second potential scan. The electrode was polished before each experiment. $A=0.25$ cm²

discharge of the solvent. The AQ-2-COO⁻ peak oxidation current decreased during repetitive potential cycling (Fig. 2) showing the progress of electrode functionalization. However, the quinone surface concentrations did not reach full coverage even after 50 cycles as the oxidation current at the end of the experiment was still measurable. This is probably due to steric hindrance, as previously observed [14]. As a result, processes other than surface grafting can take place such as Kolbe coupling yielding a dimer or nucleophile attack, if the carbonium ion is formed [15]. The

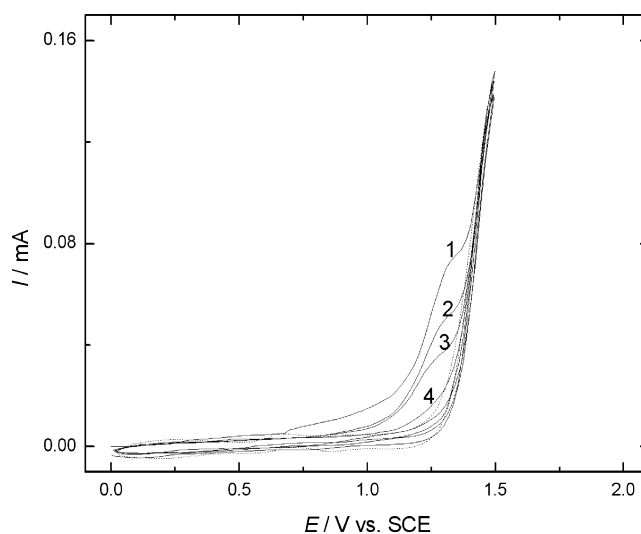


Fig. 2 Electrochemical grafting behavior of AQ-2-COO⁻ on a GC electrode in N₂ saturated DMSO containing 4 mM AQ-2-COO⁻ (dry carboxylate) and 0.1 M NaClO₄ at $v=100$ mV s⁻¹. Curves (1–4) correspond to the first, second, third, and fifth potential scans. Dotted curve corresponds to the 50th potential scan of GC in the presence of 0.1 M NaClO₄/DMSO. $A=0.25$ cm²

electrochemical oxidation of AQ-2-COOH in dimethylsulfoxide was not observed in the same potential range by repetitive cycling (data not shown). However, the electrochemical oxidation of AQ-2-CH₂COOH in *N,N*-dimethylformamide or dimethylsulfoxide was observed as a single oxidation peak at approximately 1.18 V (DMF) or 1.24 V (DMSO) vs SCE (very near to the peak potential of electrooxidation of AQ-2-CH₂COO⁻ [13]), shown in Fig. 3. It is important to mention that in the 50th cycle for the case of AQ-2-CH₂COOH a small decrease in peak current occurred, followed by a displacement of the peak to a more positive potential. Theoretical calculations (HF/6-31G*) of HOMO orbital for different anthraquinone derivatives showed the inexistence of HOMO orbital populating the acidic carboxylic moiety in the case of AQ-2-COOH molecule, for the other derivatives, HOMO orbital populates the acidic or anion carboxylic moiety. These results can suggest a possible explanation for the electrooxidation observed in the case of AQ-2-CH₂COOH molecule.

Surface modification of carbon electrodes by electrochemical oxidation of arylcarboxylates is well established [14, 16–21]. Various compounds have been attached to carbon surface using this method and the mechanism proposed is as follows [14]:

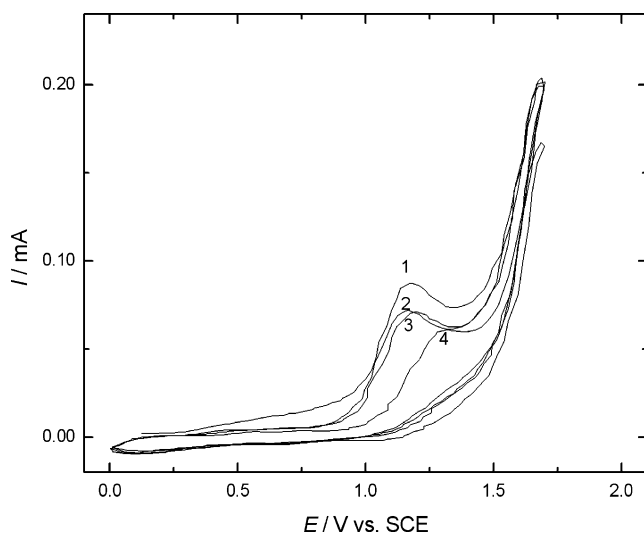


Fig. 3 Electrochemical grafting behavior of AQ-2-CH₂COOH on a GC electrode in N₂-saturated DMF containing 4 mM AQ-2-CH₂COOH and 0.1 M NaClO₄ at $\nu=100$ mV s⁻¹. Curves (1–4) correspond to the first, second, third, and 50th potential scans. $A=0.2$ cm².

The carbocation formed (R⁺) reacts with the carbon surface to yield a C–C bond [14].

The anodic oxidation behavior observed in Figs. 1 and 2 corresponds to irreversible charge transfer to AQ-2-COO⁻, followed by the chemical attachment of products to the GC surface, i.e., an EC mechanism. Similar electrooxidation behavior shown in Fig. 3 suggests the same mechanism for AQ-2-CH₂COOH. On the basis of these preliminary results it appears that the electrooxidation of AQ-2-COO⁻ and AQ-2-CH₂COOH is a suitable method for the covalent attachment of these quinones to glassy carbon surface.

Quinone adsorption or attachment, stability of these surfaces and the effect of pH on the electrochemical behavior of modified electrodes were characterized by cycling the electrode between 0 and -1.2 or -1.25 V for 100 cycles (100 mV s⁻¹) in oxygen-free 0.1 M acetate buffer (pH 4.8), 0.1 M phosphate buffer (pH 8.0) and 0.1 M NaOH. The modified electrodes were treated in an ultrasonic bath for 20 min. in DMSO or DMF before these measurements to ensure the removal of weakly bound quinones. Figure 4a–c shows the stable cyclic voltammetric response of GC/AQ-2-COOH, GC/AQ, and GC/AQCH₂ electrodes, respectively, at different sweep rates. The values of redox potential (E_f) of surface bound quinones were -0.38 (pH 4.8), -0.54 (pH 8) and -0.92 V (pH 13), for GC/AQ-2-COOH, GC/AQ, and GC/AQCH₂, respectively. These values were relatively close to the values for adsorbed ($E_f=-0.40$ V in 0.1 M acetate buffer (pH 5) and $E_f=-0.62$ V in 0.1 M phosphate buffer (pH 8) [6]) or covalently attached anthraquinone ($E_f=-0.845$ V in 0.1 M NaOH [22]). The surface concentrations of the quinones ($\Gamma_{\text{AQ-2-COOH}}$, Γ_{AQ} , and Γ_{AQCH_2}) were determined by charge integration under the background corrected cathodic peaks (at a scan rate of 10 mV s⁻¹) and the values of 2.6×10^{-10} , 1.5×10^{-10} and 2.1×10^{-10} mol cm⁻² were found.

It was of special interest to compare the cyclic voltammetric behavior of the electrografted GC electrodes with those modified by short-time (or long-time) immersion and also the behavior of the modified electrodes at different pH. The GC electrode was either polished or repetitively cycled in a quinone-free solution at 100 mV s⁻¹ for 50 scans before immersion. The stable cyclic voltammetric response of a GC/AQ-2-COOH (GC polished and cycled 50 times in DMSO followed by immersion during 3 h in solution of AQ-2-COOH) at acetate buffer pH 4.8 (Fig. 4a) showed well-defined redox peaks with reversible characteristics. The cyclic voltammetric behavior of a GC/AQCH₂ (GC cycled 50 times in DMSO in the presence of AQ-2-CH₂COOH) or GC/AQ-2-COO⁻ (GC polished and cycled 50 times in DMSO followed by immersion during 3 h in solution of AQ-2-COO⁻) in acetate buffer at pH 4.8 appeared with a small displacement of redox peaks to more negative potential (-0.42 V) and with twice the value of

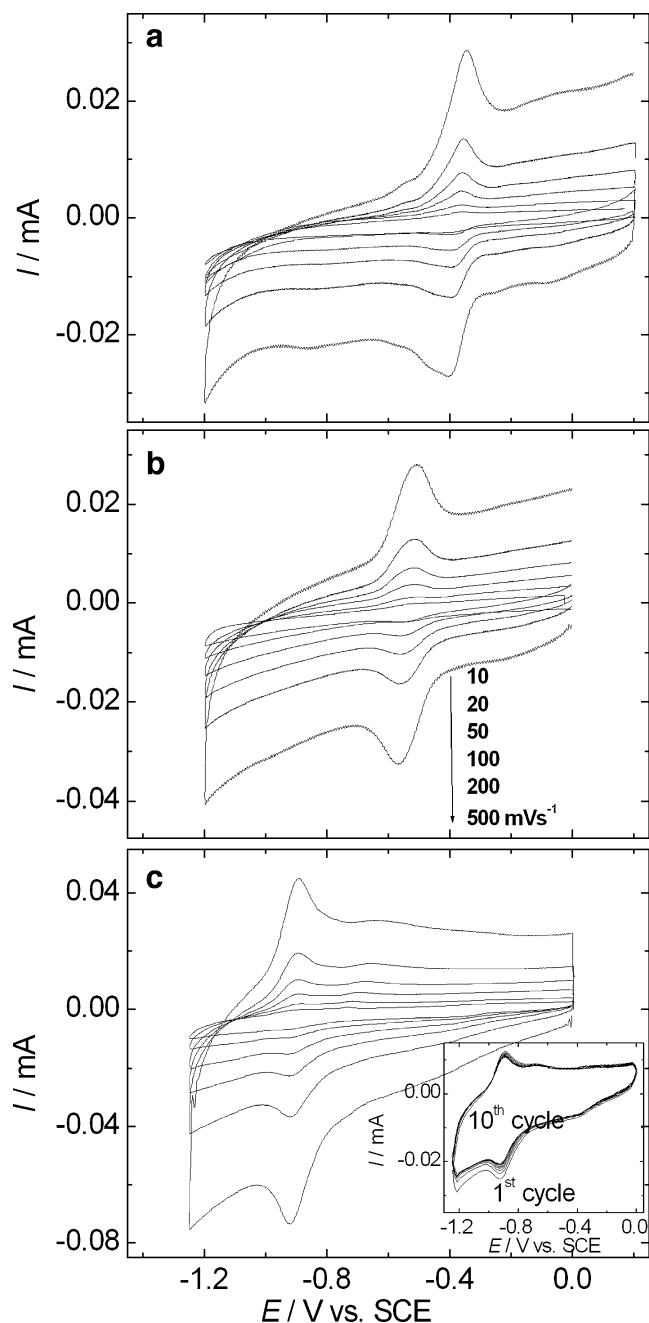


Fig. 4 Cyclic voltammograms for anthraquinone-modified GC electrodes: **a** GC/AQ-2-COOH (polished GC electrode repetitively cycled for 50 times at 100 mV s^{-1} between 0 and 1.5 V in DMSO containing 0.1 M NaClO_4 , followed by immersion in 4 mM AQ-2-COOH in DMSO + 0.1 M NaClO_4 during 3 h) in N_2 -saturated 0.1 M acetate buffer at pH 4.8; **b** GC/AQ (electrografted from 4 mM AQ-2-COO⁻; Fig. 2) in N_2 -saturated 0.1 M phosphate buffer (pH 8), and **c** GC/AQCH₂ (electrografted from 4 mM AQ-2-CH₂COOH, Fig. 3) in N_2 -saturated 0.1 M NaOH. Sweep rate: 10, 20, 50, 100, 200, and 500 mV s^{-1} . Inset: ten repetitive cyclic voltammograms for GC/AQCH₂ in N_2 -saturated 0.1 M NaOH and sweep rate 100 mV s^{-1} . $A=0.2 \text{ cm}^2$

peak currents to that presented in Fig. 4a. The stable cyclic voltammetric response of a GC/AQ (GC cycled 50 times in DMSO in the presence of AQ-2-CH₂COO⁻) in 0.1 M

phosphate buffer at pH 8 (Fig. 4b) showed well-defined redox peaks and the same reversible characteristic. The stable cyclic voltammetric response of a GC/AQCH₂ (GC cycled 50 times in DMF in the presence of AQ-2-CH₂COOH) in 0.1 M NaOH (Fig. 4c) showed also a well-defined redox behavior. Inside the Fig. 4c are shown ten repetitive cyclic voltammograms to evidence the stability of the modified electrode with respect to the quinone response. The parameters of the response on the potential scan rate showed in Fig. 4 that satisfied the criteria for electrochemical reversibility were $dE_{pc}/d(\log\nu) \approx 0$, I_{pc} increased linearly with ν , the peak current ratio ($-I_{pa}/I_{pc}$) ≈ 1 and $\Delta E_p = E_{pa} - E_{pc} \approx 30 \text{ mV}$ ($n=2$ electrons). We could observe the displacement of the redox potential to more negative values with increasing the solution pH, in agreement with previous observations [5–7]). The stable cyclic voltammetric response of a GC/AQ-2-COO⁻ (GC polished and immersed by 42 h in solution of AQ-2-COO⁻ or GC polished and cycled 50 times in DMSO followed by immersion during 42 h in solution of AQ-2-COO⁻) in 0.1 M NaOH was similar to that presented in Fig. 4c with slightly smaller peaks. The cyclic voltammetric response of a GC/AQ-2-COOH (GC polished and immersed by 42 h in solution of AQ-2-COOH or GC polished and cycled 50 times in DMSO followed by immersion during 42 h in solution of AQ-2-COOH) in 0.1 M NaOH was featureless. The difference can be attributed to the more effective detachment of the adsorbed AQ-2-COOH or AQ-2-COO⁻ in basic solutions as reported by Salimi et al. [5, 6]. The cyclic voltammetric behavior of a GC/AQ-2-CH₂COOH (GC polished and immersed by 42 h in solution of AQ-2-CH₂COOH or GC polished and cycled 50 times in DMF followed by immersion during 42 h in solution of AQ-2-CH₂COOH) in 0.1 M NaOH was similar to that presented in Fig. 4c. The presence of CV peaks for GC/AQ-2-COOH, GC/AQ-2-COO⁻, GC/AQ-2-CH₂COOH and GC/AQ-2-CH₂COO⁻ indicates the strong adsorption of these AQ derivatives to glassy carbon as previously observed with other anthraquinone derivatives [5–8].

Oxygen reduction on modified glassy carbon (GC) electrodes

Figure 5a–c show the cyclic voltammetry results in 0.1 M acetate buffer (pH 4.8), 0.1 M phosphate buffer (pH 8.0) and 0.1 M NaOH in the presence or absence of O₂ for quinone-modified GC electrodes prepared from AQ-2-COOH by immersion during 3 h or AQ-2-COO⁻ and AQ-2-CH₂COOH by anodic oxidation. For comparison purposes, the CV results for a bare GC electrode are also shown.

It can be seen in Fig. 5 that the redox peaks of the different AQ species superposed on the response of bare

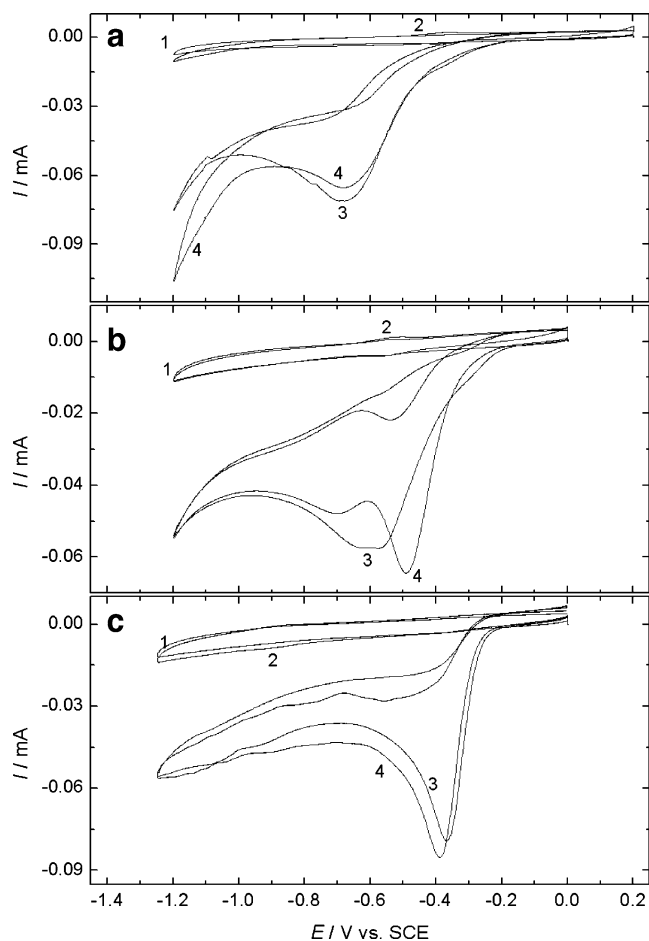


Fig. 5 Cyclic voltammograms for: **a** GC/AQ-2-COOH ($\Gamma_{\text{AQ-2-COOH}} = 2.6 \times 10^{-10} \text{ mol cm}^{-2}$) and for a bare GC electrode in 0.1 M acetate buffer at pH 4.8: (1) bare GC electrode in N_2 -saturated solution, (2) GC/AQ-2-COOH electrode in N_2 -saturated solution, (3) bare GC electrode in O_2 -saturated solution, (4) GC/AQ-2-COOH electrode in O_2 -saturated solution; **b** GC/AQ ($\Gamma_{\text{AQ}} = 1.5 \times 10^{-10} \text{ mol cm}^{-2}$) and for a bare GC electrode in 0.1 M phosphate buffer at pH 8: (1) bare GC electrode in N_2 -saturated solution, (2) GC/AQ electrode in N_2 -saturated solution, (3) bare GC electrode in O_2 -saturated solution, (4) GC/AQ electrode in O_2 -saturated solution; and **(c)** GC/AQCH₂ ($\Gamma_{\text{AQ}} = 2.1 \times 10^{-10} \text{ mol cm}^{-2}$) and for a bare GC electrode in 0.1 M NaOH: (1) bare GC electrode in N_2 -saturated solution, (2) GC/AQCH₂ electrode in N_2 -saturated solution, (3) bare GC electrode in O_2 -saturated solution, (4) GC/AQCH₂ electrode in O_2 -saturated solution. $\nu = 20 \text{ mV s}^{-1}$; $A = 0.20 \text{ cm}^2$

glassy carbon in N_2 saturated solutions show very small current compared to the currents of O_2 reduction. In Fig. 5a, the O_2 reduction peak appears at around -0.68 V . We can observe a small decrease in the peak current for the modified electrode, however, with a much larger current at more negative potential than -0.9 V (Fig. 5a). At pH 8 (Fig. 5b), the O_2 reduction peak on a bare GC electrode is observed at around -0.6 V and the peak is displaced to a more positive potential (-0.49 V) for the modified electrode showing a slightly larger peak current. In 0.1 M NaOH (Fig. 5c), the O_2 reduction peak at ca. -0.37 V corresponds

to a bare GC electrode and there is a small shift of the reduction peak to a more negative potential (-0.39 V) on the modified electrode.

The effect of these AQ species to O_2 reduction is relatively small and occurs in a very narrow potential range and is dependent on pH and also on the quinone compound used. In some cases, the blocking behavior of GC surface by AQ compounds either adsorbed or grafted is evident and this leads to a decrease in the reduction current in comparison with bare GC. Using the GC surface cleaning and modification procedures mentioned above, it was not possible to observe much lower overpotentials for O_2 reduction on the modified electrodes compared to that of a bare GC electrode. These results are not in agreement with those reported in [5–7]. To better understand the cyclic voltammetry results, we performed experiments using a rotating GC disk electrode.

Figure 6a–c shows the RDE results for O_2 reduction on quinone-modified GC and bare GC electrodes in 0.1 M acetate buffer (pH 4.8), 0.1 M phosphate buffer (pH 8.0), and 0.1 M NaOH and the reduction behavior of the quinone-modified GC electrodes in O_2 -free solutions. The disk currents of the quinone-modified electrodes in de-aerated solutions were featureless. The oxygen reduction wave commences at potentials more negative than ca. -0.2 V in these solutions; however, the overall reduction behavior differs at different pHs. At pH 4.8, the disk current depends on the type of the adsorbed (or grafted) AQ. AQ carboxylate anions adsorbed (AQ-2-COO⁻ or AQ-2-CH₂COO⁻) and grafted quinones (AQ or AQCH₂) produce a decrease in the total reduction current between -0.3 and -1.2 V in comparison with bare GC (data not shown). However, when acidic AQ derivative (AQ-2-COOH or AQ-2-CH₂COOH) is adsorbed, a slight current increase is observed between -0.3 and -1.2 V as compared to that of the bare GC (Fig. 6a).

This behavior is similar to that described for stationary electrode with the exception of the potential range between -0.55 and -0.9 V to GC/AQ-2-COOH modified electrode (Fig. 5a) in which case was observed a current decrease in comparison with bare GC. These results characterize the presence of AQ on the GC surface that produce a surface blocking to O_2 reduction in the case of AQ adsorbed in the anionic form or AQ grafted (disk current decreases in comparison with bare GC) or catalyzing O_2 reduction in the case of acidic AQ adsorbed (disk current increases in comparison with bare GC). A pre-wave at modified electrodes (this is absent on bare GC) in 0.1 M phosphate buffer (pH 8.0) is observed at around -0.52 V (Fig. 6b) and a smaller disc current compared to bare GC at more negative potential than -0.6 V . In this case, there is a good agreement between these results and the results obtained with a stationary GC electrode (Fig. 5b). This behavior also

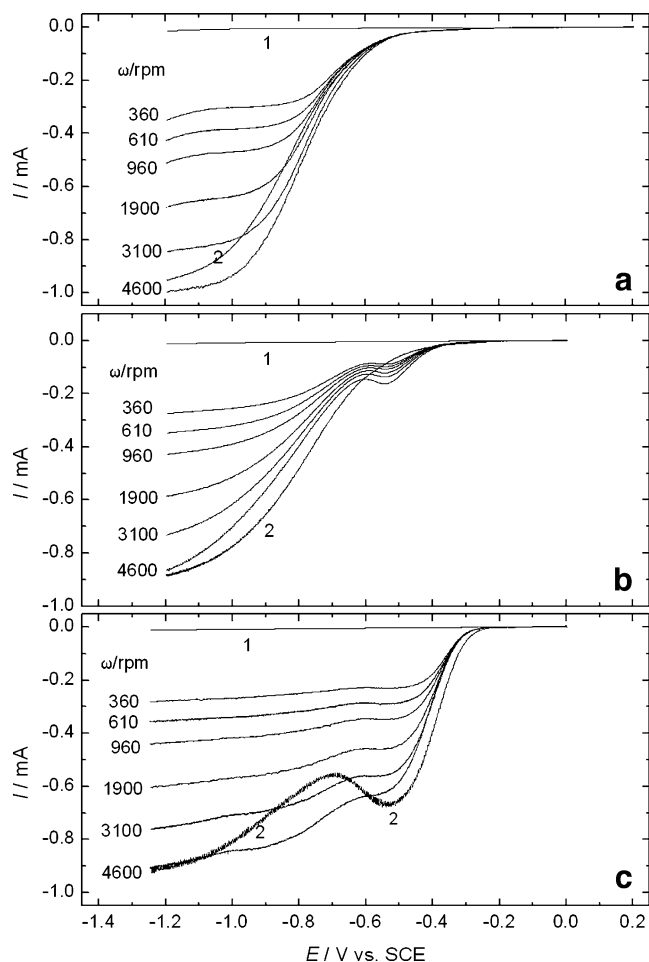
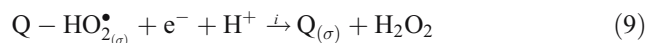
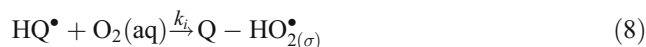
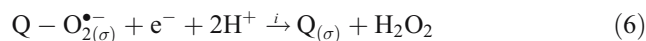
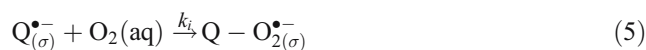


Fig. 6 Voltammetry curves for: **a** GC/AQ-2-COOH electrode ($\Gamma_{AQ-2-COOH} = 2.6 \times 10^{-10} \text{ mol cm}^{-2}$) in N_2 - (1, $\omega=4,600 \text{ rpm}$) or O_2 -saturated 0.1 M acetate buffer (pH 4.8) at various rotation rates, (2) bare GC in O_2 -saturated solution ($\omega=4,600 \text{ rpm}$), and other $I-E$ curves correspond to the GC/AQ-2-COOH electrode in O_2 -saturated solution; **b** GC/AQ ($\Gamma_{AQ} = 1.5 \times 10^{-10} \text{ mol cm}^{-2}$) in N_2 - (1, $\omega=4,600 \text{ rpm}$) or O_2 -saturated 0.1 M phosphate buffer (pH 8) at various rotation rates, (2) bare GC in O_2 -saturated solution ($\omega=4,600 \text{ rpm}$), other $I-E$ curves correspond to the GC/AQ electrode in O_2 -saturated solution; and **c** GC/AQCH₂ ($\Gamma_{AQ} = 2.1 \times 10^{-10} \text{ mol cm}^{-2}$) in N_2 - (1, $\omega=4,600 \text{ rpm}$) or O_2 -saturated 0.1 M NaOH at various rotation rates, (2) bare GC in O_2 -saturated solution ($\omega=4,600 \text{ rpm}$); other $I-E$ curves correspond to the GC/AQCH₂ electrode in O_2 -saturated solution. $v=20 \text{ mV s}^{-1}$; $A=0.2 \text{ cm}^2$

supports the presence of AQ on the GC surface that catalyzes O_2 reduction until around -0.6 V , and at more negative potentials a surface blocking to O_2 reduction occurs.

In 0.1 M NaOH, a pre-wave is observed at ca. -0.5 V (Fig. 6c) with smaller reduction current compared to that of bare GC, but at $E < -0.6 \text{ V}$ exists an increase in disk current, the behavior similar to that shown in Fig. 5c. This behavior supports again the presence of AQ on the GC disk that produces a surface blocking to O_2 reduction until around -0.6 V and at more negative potentials surface redox catalysis of O_2 reduction is observed.

We consider that the electrocatalytic reduction of oxygen on GC electrodes modified with anthraquinone derivatives follows a mechanism shown below [23]. According to this mechanism, an electrochemically generated semiquinone (reaction 4, where $Q_{(\sigma)}$ means a quinone species attached/adsorbed to a carbon electrode surface) reacts with molecular oxygen, forming an intermediate superoxo species ($Q - O_{2(\sigma)}^{\bullet-}$, reaction 5). This intermediate reacts with a proton and a second electron producing hydrogen peroxide (reaction 6). As supposed by Wass et al. [23] Reactions 4 to 6 correspond to the reduction of O_2 in solutions with $\text{pH} > \text{p}K_a$ of the semiquinol present as a radical anion; however, at $\text{pH} < \text{p}K_a$ the semiquinol formed by reaction 7 undergoes reaction 8, in which case the superoxo intermediate is protonated ($Q - HO_{2(\sigma)}^{\bullet}$, reaction 8). This species reacts with a second electron and a proton producing hydrogen peroxide (reaction 9).



As found by Wass et al. [23], using quantum chemistry calculations, two distinctly different structures were predicted for the critical chemical step depending on the protonation of the quinone site (catalytic site present as $Q^{\bullet-}$ or HQ^{\bullet} in reactions (5) and (8), respectively). These authors suggest the reduction of O_2 on protonated semiquinones to have a much higher activation barrier than that of the radical anion sites, therefore explaining the experimentally observed decrease in electrocatalytic activity in acidic media for grafted quinones.

On the bases of the results obtained in this work, it is clear that at low pH, for example 4.8, most probably the adsorbed or attached anthraquinone semiquinone radical is protonated, resulting in a significantly lower electrocatalytic activity for O_2 reduction (and H_2O_2 production). At pH 8

and in 0.1 M NaOH, most probably the adsorbed or attached anthraquinone semiquinone radical is not protonated, resulting in a significant electrocatalytic activity for O_2 reduction (and H_2O_2 production) in the range of potentials coinciding with the formation of the anthraquinone semiquinone radical. This behavior is better observed in hydrodynamic experiments. We consider that the oxygen reduction current results from the following contributions: (1) native surface quinone-type groups on GC, (2) adsorbed or attached anthraquinone groups, and (3) heterogeneous glassy carbon surface [22–24]. Therefore, at pH 8 and 13, the adsorption or attachment of anthraquinone derivatives can decrease the catalysis of oxygen reduction in other potential range due to a decrease in surface coverage of native quinone groups or the heterogeneous glassy carbon surface itself.

Nagaoka et al. [25] reported that quinone-modified electrodes (juglone and 9,10-phenanthrenequinone adsorbed on GC) do not mediate oxygen reduction at pH 5–6. Wass et al. [23] suggested that anthraquinone groups attached have pK_a slightly higher than 5.3. Degrand [26] demonstrated that the rate constant for oxygen reduction on a polymeric film of anthraquinone significantly increased for $pH > 4.5$. Rao and Hayon [27] reported pK_a values changing from 3.2 to 5.4 to semiquinone radicals and radical anions of 12 quinones in aqueous solution. Thus, our electrochemical results suggest the pK_a values of

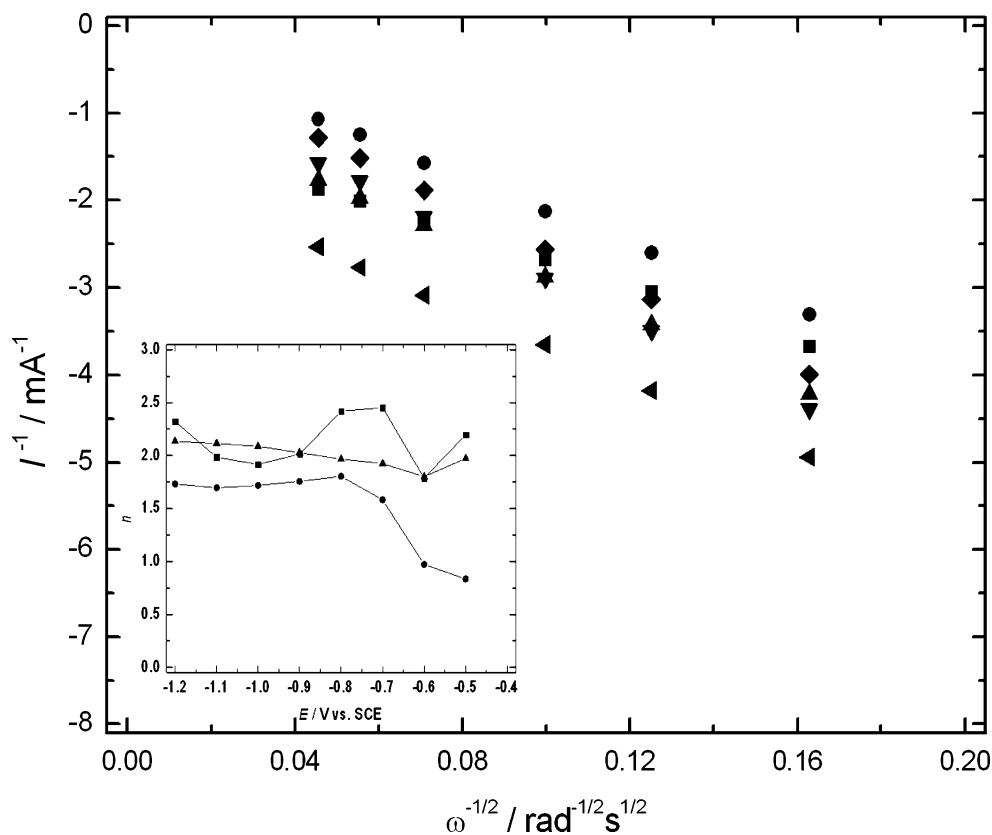
the anthraquinone derivatives adsorbed or attached to GC surface to be larger than 4.8 and lower than 8 on the bases of the experimental observation that at pH 4.8 the electrocatalysis of oxygen reduction by quinones did not occur and at pH 8 the electrocatalytic effect was present. The determination of kinetic parameters of oxygen reduction on GC electrodes modified with anthraquinones was outside the scope of this article. A detailed kinetics analysis at various pHs was carried out in a separate work (Jürmann, et al. 2007, submitted for publication).

The number of electrons transferred per O_2 molecule (n) was calculated from the Koutecky–Levich (K-L) equation [28]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{dl}} = -\frac{1}{nFkc_{O_2}^b} - \frac{1}{0.62nFD_{O_2}^{2/3}\nu^{-1/6}c_{O_2}^b\omega^{1/2}}, \quad (X)$$

where j_k and j_{dl} are the kinetic and diffusion limited current densities, respectively; k is the overall rate constant for O_2 reduction, D_{O_2} is the diffusion coefficient of oxygen ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) [29], $c_{O_2}^b$ is its concentration in the bulk ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$) [29], and ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$) [30]. From the data in Fig. 7, a

Fig. 7 Koutecky–Levich plot for oxygen reduction on a GC/AQ-2-COOH electrode in O_2 -saturated 0.1 M acetate buffer (pH 4.8) at -0.8 V (◐) and -1.0 V (◑), a GC/AQ electrode in O_2 -saturated 0.1 M phosphate buffer (pH 8) at -0.8 V (◒) and -0.9 V (◓), and a GC/AQCH₂ electrode in O_2 -saturated 0.1 M NaOH at -0.6 V (◔), and -0.8 V (◕). The inset shows the potential dependence of the number of electrons transferred per O_2 molecule on GC/AQ-2-COOH (◐), GC/AQ (◑), and GC/AQCH₂ (◓) electrodes



value of n close to 2 was found in a large range of potentials for all the electrodes studied.

Atomic force microscopy (AFM) examination of bare and modified GC surfaces

To clarify the difference between the adsorbed and attached anthraquinones on GC surfaces, the AFM topological images of bare GC (Fig. 8a), GC/AQ-2-COOH (Fig. 8b), GC/AQCH₂ (Fig. 8c), and GC/AQ-2-COOH surfaces (Fig. 8d) are shown. As expected, the bare GC surface is rather rough (Fig. 8a); however, when comparing with the Fig. 8b, the presence of adsorbed anthraquinone on the GC surface is clearly evident, showing plenty of small features superposed over the GC rough surface and covering the whole area of GC (cf. Fig. 8a,b). Looking at Fig. 8b, we can observe a certain disorder of surface features and also not a complete coverage of the GC surface by anthraquinone species. In Fig. 8c, plenty of small peaks superposed over the GC roughness is also observed, characterizing the attached anthraquinones, however, with a better ordering and a smaller number of voids than that observed in Fig. 8b. It is necessary at this point to consider that Fig. 8b and c was obtained without contact of the surface with the solution used in the electrochemical measurements (pH 4.8, pH 8 or NaOH). We can assume that there is the maximum

coverage by anthraquinones in these two cases. When the GC/AQ-2-COOH surface was allowed to contact with 0.1M NaOH, the presence of anthraquinone adsorbed at the GC surface is clearly observed (Fig. 8d) and we can see the presence of sparse small peaks superposed over the GC roughness, a fact that was electrochemically detected already (detachment of adsorbed AQ-2-COOH) for this kind of surface.

It is important to notice that the surface roughness is much larger for the modified GC electrodes compared to bare GC (see Fig. 8a–d). This observation suggests an adsorption or attachment of anthraquinones, which corresponds to a higher than a monolayer coverage. In fact, McDermott and McCreery detected this phenomena for different anthraquinones adsorbed on GC [31]. Our AFM results obtained with a bare GC are consistent with the results presented by Freund et al. [32], although McDermott et al. presented the STM images of better resolution for bare GC [33].

Conclusions

The electrocatalytic reduction of oxygen was studied on glassy carbon electrodes modified with anthraquinone derivatives. 9,10-Anthraquinone-2-carboxylic acid and

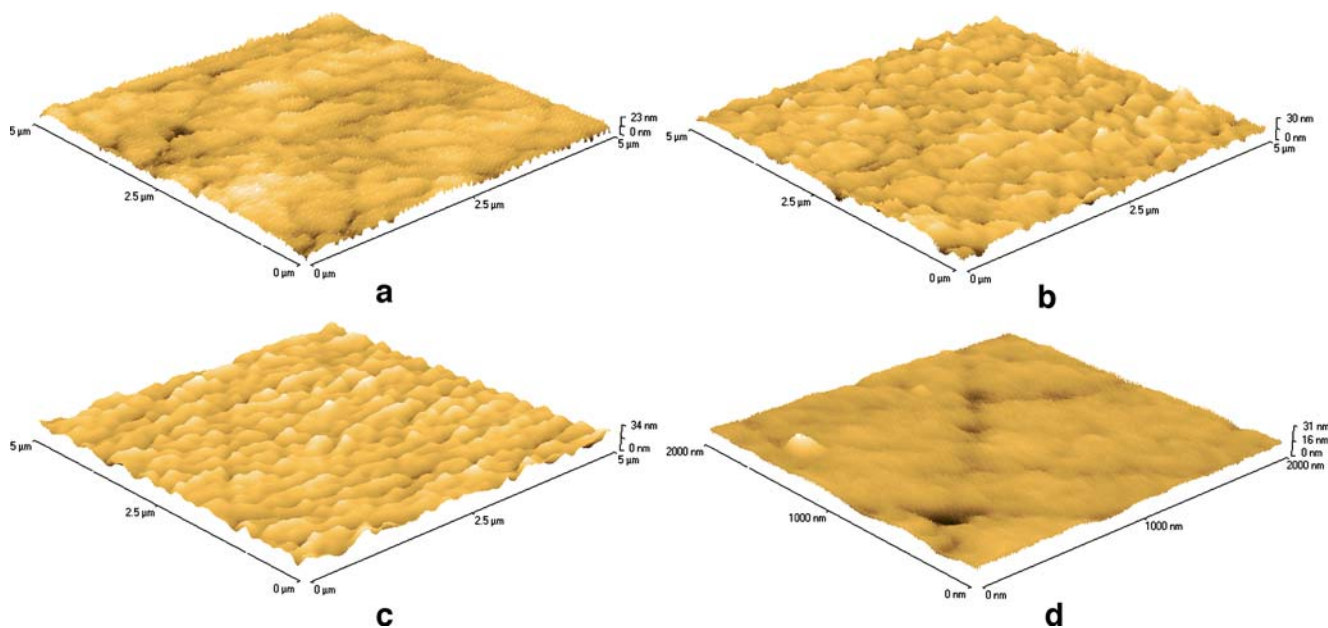


Fig. 8 AFM images for: **a** bare GC surface (polished GC electrode repetitively cycled for 50 times at 100 mV s^{-1} between 0 and 1.5 V in 0.1 M NaClO₄/DMSO); **b** GC/AQ-2-COOH surface (polished GC electrode repetitively cycled for 50 times at 100 mV s^{-1} between 0 and 1.5 V in 0.1 M NaClO₄/DMSO followed by immersion in 4 mM AQ-2-COOH/0.1 M NaClO₄/DMSO during 3 h. After this, the electrode was sonicated in DMSO for 20 min and dried with N₂); **c** GC/AQCH₂ surface (polished GC electrode repetitively cycled for 50 times at

100 mV s^{-1} between 0 and 1.5 V in 4 mM AQ-2-CH₂COOH/0.1 M NaClO₄/DMSO followed by sonication in DMSO for 20 min and drying with N₂); and **d** GC/AQ-2-COOH surface (polished GC electrode repetitively cycled for 50 times at 100 mV s^{-1} between 0 and 1.5 V in 0.1 M NaClO₄/DMSO followed by immersion in 4 mM AQ-2-COOH/0.1 M NaClO₄/DMSO during 3 h. After this, the electrode was sonicated in DMSO by 20 min, followed by CV and RDE voltammetry experiments in 0.1 M NaOH, again sonicated in

9,10-anthraquinone-2-ethanoic acid and their tetramethylammonium salts were used in surface modification. The two methods of modification employed were electrografting by anodic oxidation and immersion of the GC electrode in a solution containing a surface modifier.

The electrocatalytic activity towards O₂ reduction was slightly dependent on the modifier used, on the means of modification (electrografting vs immersion) and also on the pH of the solution. A difference in surface morphology between the electrodes modified with attached and adsorbed anthraquinones was found by AFM measurements and detachment of some layers could occur after immersion at different pHs depending on the modifier.

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