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## Modification of carbon surfaces with methyl groups by using ferrocene derivatives as redox catalysts of the oxidation of acetate ions

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### ABSTRACT

The effect of the structure of three different redox mediators on the oxidation of tetrabutylammonium acetate was studied in acetonitrile on glassy carbon and HOPG electrodes. The direct oxidation of acetate ion is essentially a carbocation process which allows in many instances the formation of products in solution. However a covalent modification of the carbon surface was possible when the oxidation process is mediated by ferrocene derivatives. The redox catalysis process occurs at lower potential values than the direct oxidation process, which triggers a radical chemistry allowing the grafting of carbon surfaces with methyl groups. Depending on the redox potential of the mediator as well as on the number of ferrocene redox centers present in its structure, the efficiency of the electrode modification process can be significantly increased. Atomic force microscopy images of HOPG modified surfaces, by using either a mediator containing one or two redox centers, were obtained to show the formation of aggregates distributed in a highly compact layer.

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### 1. Introduction

The relevance of covalent modification of carbon surfaces with organic moieties, for applications in nanotechnology and materials science, has been well recognized and reviewed [1–3]. Because of the great stability and chemical properties of the grafted organic layers, several organic electrochemical reactions have been used as a method to attach a wide variety of organic groups to carbon surfaces. For example, by using the well known reduction of aryl-diazonium salts [4], and the reduction of iodonium and sulfonium salts [5,6]. Alternatively, the electrochemical oxidation of amines [7,8], alcohols [9], and arylacetates [10] have also been used for the same purpose. Nevertheless the highest number of papers on electrochemical covalent grafting involves aryl-diazonium salts, the oxidation of carboxylates also allows the attachment of a wide variety of organic groups onto carbon surfaces. Although this oxidation method is based on salts of accessible carboxylic acids, it has only been explored on a limited number of compounds [10–14].

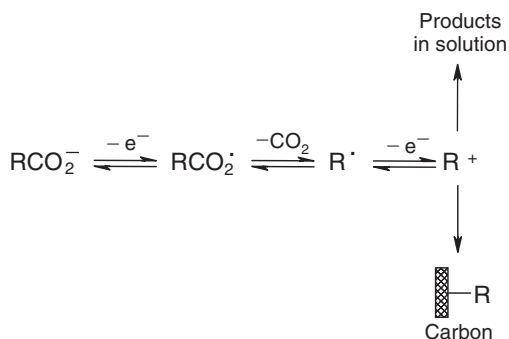
Nowadays there are two methods available to carry out the grafting of a carbon surface by oxidation of carboxylates. One of them is based on the direct oxidation of the carboxylate  $\text{RCOO}^-$ , which considers the intervention of a non-Kolbe process, in which the carbocations produced ( $\text{R}^+$ ) can react in solution, either with the acetonitrile to afford acetamides or acylamides [15–18], or with the  $\text{sp}^2$  carbon atoms of the electrode surface (Scheme 1). Glassy carbon and HOPG electrodes have been modified with aryl-methyl groups by using the direct method [10–14].

In a previous study on the direct oxidation of a series of aliphatic carboxylates (acetate–octanoate) on glassy carbon electrodes, it was demonstrated that carbocations were also involved in the mechanism [17], however, the grafting of alkylic groups on the surface was not possible. The disadvantage of the direct method as a tool to graft surfaces from oxidation of aliphatic carboxylates, was however overcome by implementing an indirect oxidation method [19]. In this particular case, acetate oxidation was induced by the oxidized form of ferrocene (**1**) as redox catalyst, being methyl radicals the responsible of the grafting process. The attachment of alkylic groups through C–N (amine oxidation) and C–O (alcohol oxidation) bonds has been reported previously, however, this is the first method of modification of carbon electrodes allowing the anchoring of alkylic moieties through C–C bonds. Alkyl modification is important because it reduces the tendency of the substrate oxidation under atmospheric conditions as

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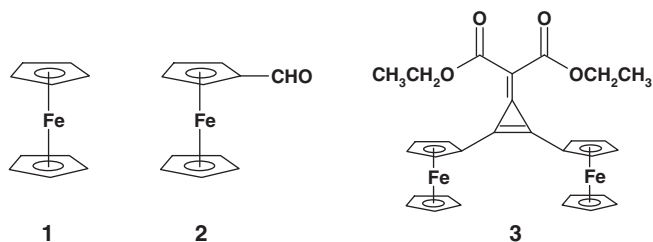
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**Scheme 1.** Mechanism of direct oxidation and carbon surface modification.

well as in aqueous conditions [20]. Relevant advantages in the use of mediators like **2** and **3** are shown in this work, in which the redox catalyzed oxidation of acetate ions and the grafting of glassy carbon and HOPG electrodes are discussed. Compounds **1** and **2** are used to compare the role of the redox potential of mediators on the grafting process, while compound **3** was used to evaluate the presence of multiple redox centers in the mediator structure. Cyclic voltammetry as well as atomic force microscopy (AFM) were used to obtain further insights on the mediated grafting of carbon surfaces.



## 2. Experimental

### 2.1. Chemicals

Acetonitrile spectra grade (Merck Uvasol) was used as solvent, while recrystallized tetrabutylammonium hexafluorophosphate was the supporting electrolyte. Ferrocene (98%), ferrocenecarboxaldehyde (98%) and tetrabutylammonium acetate (98%) were Aldrich chemicals and they were used as received. Compound **3** (3-(diethoxycarbonyl)methylidene-1,2-diferrocenylcyclopropene) was synthesized according to a protocol previously reported [21]. The solutions of tetrabutylammonium acetate and the ferrocene derivatives were deoxygenated by dry argon bubbling. After this, the inert atmosphere was maintained over the solutions during each experimental run.

### 2.2. Instrumentation and electrodes

The electrochemical device consisted of a potentiostat Autolab PGSTAT 100 (Methrom) with positive feedback resistance compensation. A conventional three-electrode cell was used to carry out the voltammetric experiments. The work electrode was a 3 mm diameter glassy carbon disk (Sigradur G from HTW, Germany). This electrode was carefully polished with 0.3  $\mu\text{m}$  alumina powder and ultrasonically rinsed with distilled water and ethanol before each run. The counter electrode was a platinum mesh and the reference electrode an aqueous Saturated Calomel Electrode (SCE). A salt

bridge, containing 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  + acetonitrile solution, connected the cell with the reference electrode. All electrochemical experiments were performed at room temperature.

The HOPG was freshly cleaved with adhesive type before each experiment. A teflon cell with an arrangement of three-electrode as previously mentioned was used to perform the grafting over HOPG.

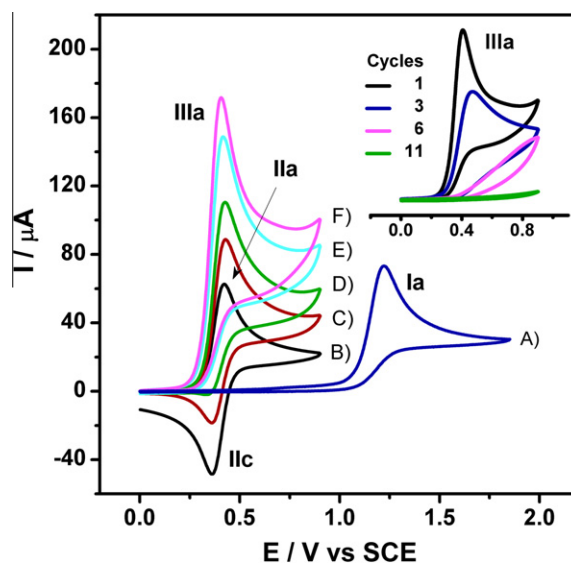
AFM images of both clean and grafted HOPG samples  $10 \times 10$  mm (Advanced Ceramics) were obtained with an Autoprobe CP Research (ThermoMicroscopes, from Veeco Group) instrument, in the tapping mode. The images were processed with ProScan program, version 2.0. All the experiments were performed with a scanner  $5 \mu\text{m}$  in  $x$ - $y$  and  $1.5 \mu\text{m}$  in  $z$  scan range. Silicon Veeco cantilever of  $45\text{--}55 \mu\text{m}$ ,  $0.2 \text{ Nm}^{-1}$  spring constant and  $10\text{--}16$  kHz resonance frequency in air were used. Typical scan rates were around 1–2 Hz.

## 3. Results and discussion

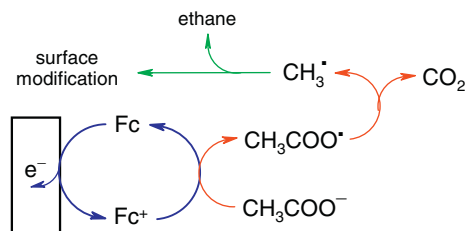
### 3.1. Grafting of glassy carbon by oxidation of acetate ion mediated by compound **1**

The voltammetric signal corresponding to the direct oxidation of acetate ( $\text{Ac}^-$ ) in acetonitrile (Fig. 1A) ( $E_p = 1.21 \text{ V/SCE}$  at  $0.1 \text{ V s}^{-1}$ ), is chemically irreversible and it involves carbocations as intermediates, which react with the acetonitrile to afford N-methyldiacetamide as the product [19]. On the other hand, the typical reversible voltammogram of ferrocene ( $E_{\text{IIa-IIIc}}^0 = 0.392 \text{ V/SCE}$ ) can also be observed in Fig. 1B (peaks IIa–IIc). When different amounts of acetate ion ( $\text{Ac}^-$ ) were added to the ferrocene solution (curves C–F), the current intensity was increased while the reversible behavior changed gradually towards a chemically irreversible behavior (peak IIIa). The maximum current value was about three times the initial current for pure ferrocene and it was achieved at an approximate acetate concentration of 40 mM.

This result has been interpreted in our previous study [16] in the framework of a Kolbe decarboxylation process in which the activation step is promoted by the oxidized form of ferrocene



**Fig. 1.** Direct oxidation of tetrabutylammonium acetate 4 mM (curve A) and oxidation of ferrocene 2 mM at different concentrations of acetate ion (curves B–F): (B) 0 mM, (C) 5.7 mM, (D) 10.7 mM, (E) 23.1 mM, (F) 41.2 mM. Insert: successive cycles obtained at the last solution composition and by bubbling the solution between each cycle. All the experiments were carried out in acetonitrile + 0.1 M  $n\text{-Bu}_4\text{NPF}_6$ , at  $0.1 \text{ V s}^{-1}$ , on a glassy carbon electrode ( $\phi = 3 \text{ mm}$ ).



**Scheme 2.** Mechanism of mediated oxidation and carbon surface modification.

(Fc), which is the ferrocenium ion ( $\text{Fc}^+$ ). In this reaction the acetate ion ( $\text{CH}_3\text{COO}^-$ ) transfers one electron to  $\text{Fc}^+$  to regenerate Fc and to afford a highly reactive acyloxy radical ( $\text{CH}_3\text{COO}^\bullet$ ), which is cleaved in methyl radicals ( $\text{CH}_3^\bullet$ ) and  $\text{CO}_2$ . In this way, the turnover in which the redox pair  $\text{Fc}/\text{Fc}^+$  is involved, explains the increase in the oxidation current, which implies that each ferrocenium ion ( $\text{Fc}^+$ ) can oxidize several molecules of acetate ion. The limit in the oxidation current achieved is related to a slow rate of homogeneous electron transfer between the species  $\text{RCOO}^-$  and  $\text{Fc}^+$  [19,22].

The most relevant feature of the mediated reaction is the fact that, the current intensity decreases steadily by cycling (insert in Fig. 1), such as in the case of typical electrode inhibition processes [23]. In this way, after 11 successive voltammetric cycles (with stirring between each one), the glassy carbon electrode was totally blocked with an organic layer. The structure of this layer was stated to be highly compact [23], as shown by capacitance measurements, which were obtained from cyclic voltammetry experiments at different scan rates in the solvent-electrolyte system, for both, clean glassy carbon ( $C_{\text{clean}} = 20.8 \mu\text{F cm}^{-2}$  at  $0.2 \text{ V/SCE}$ ) and modified glassy carbon ( $C_{\text{modified}} = 12.7 \mu\text{F cm}^{-2}$  at  $0.2 \text{ V/SCE}$ ) electrodes. This sort of difference has been also found for other modified electrodes with organic layers [24,25] and is a consequence of the decrease of the dielectric constant of the organic film and the increase of its thickness. On the other hand, this result suggests also that the grafting of larger aliphatic chains could be complemented by performing a deeper and precise analysis in terms impedance measurements and equivalent circuits.

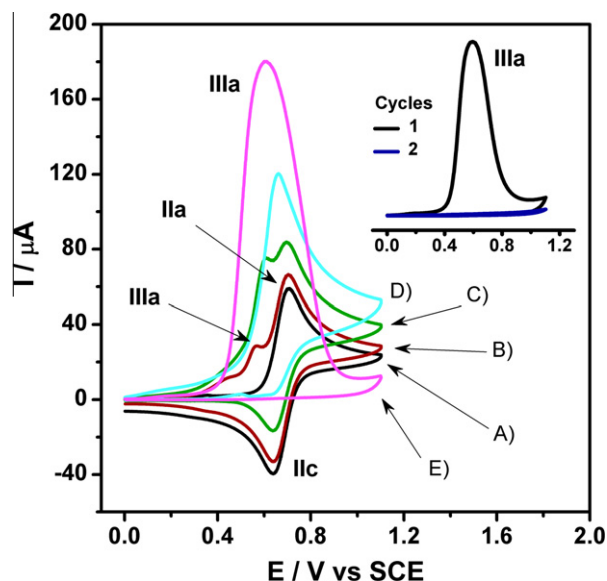
Since the inhibited state of the electrode was not affected by ultrasonic rinsing in several solvents, it was proposed that the electrode inhibition is due to the covalent attachment of methyl radicals ( $\text{CH}_3^\bullet$ ), generated as a product of decarboxylation of the acyloxy radicals ( $\text{CH}_3\text{COO}^\bullet$ ) (Scheme 2).

The radical nature of the grafting proposal was mainly supported by the fact that the grafting of the carbon surface occurred in the ferrocene mediated process and not in the direct oxidation process (carbocationic). In agreement with this fact, the typical product of the direct carbocationic pathway (N-methyldiacetamide) was not detected in the reaction between ferrocenium tetrafluoroborate and tetrabutylammonium acetate in acetonitrile under an inert atmosphere.

### 3.2. Grafting of glassy carbon by using mediators **2** and **3**

With the aim of obtaining information about the role of the structure of the mediator on the process of covalent modification of glassy carbon surfaces, ferrocenecarboxaldehyde (**2**) and 3-(diethoxycarbonyl)methylidene-1,2-diferrocenylcyclopropene (**3**) were tested. The ferrocene derivative **2** is a mediator possessing a redox potential closer to the signal of acetate oxidation, meanwhile compound **3** is a molecule which presents two redox centers that have the possibility of participating in the redox loops.

In the case of ferrocenecarboxaldehyde (**2**) ( $E_{\text{IIa-IIIc}}^0 = 0.673 \text{ V/SCE}$ ), it presents a more positive oxidation potential than ferrocene



**Fig. 2.** Oxidation of ferrocenecarboxaldehyde 2 mM at different concentrations of acetate ion: (A) 0 mM, (B) 1 mM, (C) 2.9 mM, (D) 6.7 mM, (E) 16.7 mM. Insert: successive cycles obtained at the last solution composition and by bubbling the solution between each cycle. All the experiments were carried out in acetonitrile + 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, at  $0.1 \text{ V s}^{-1}$ , on a glassy carbon electrode ( $\phi = 3 \text{ mm}$ ).

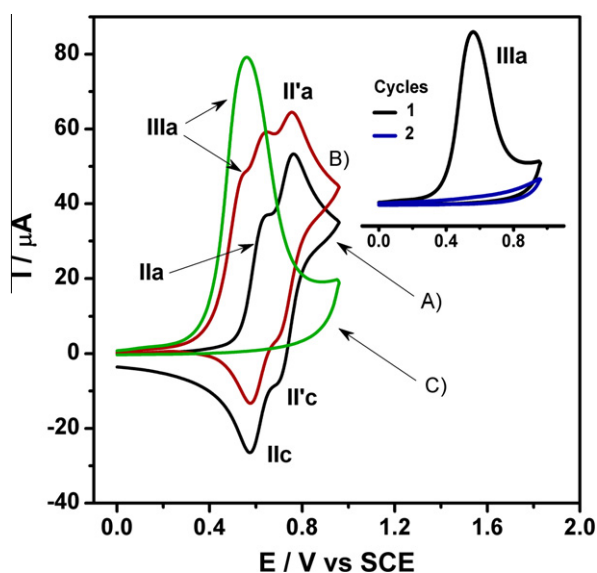
(**1**) ( $E_{\text{IIa-IIIc}}^0 = 0.392 \text{ V/SCE}$ ). Fig. 2A shows the reversible oxido-reduction wave of compound **2** in pure acetonitrile (peaks IIa–IIIc) and in the presence of several concentrations of acetate ion (curves B–E). As in the case of the system where ferrocene was the mediator, the lost of reversibility of signal IIa–IIIc and the increment in the current intensity by increasing the acetate concentration is evidence of the redox catalysis nature of the oxidation process. However, contrasting with the electrochemical behavior observed for ferrocene, in the present case it was furthermore observed the appearance of a pre-peak at low concentrations of acetate (peak IIIa). According to the theoretical description of cyclic voltammetry for redox catalyzed systems [26], this kind of pre-peaks is the result of a combined effect of a high rate of the homogeneous electron transfer and a low substrate concentration. It means that at the level of this pre-peak and at low acetate concentrations ( $\leq 3 \text{ mM}$ ), the current is limited by the diffusion of the acetate ion, which implies that this substrate is rapidly consumed by the species  $\mathbf{2}^*$  generated by oxidation of **2**. Such situation is overcome at higher substrate concentrations, where the pre-peak IIIa becomes the principal peak. The potential difference between pre-peak IIIa and the oxidation peak IIa ( $0.138 \text{ V}$  at  $0.1 \text{ V s}^{-1}$ ) support the fast nature of the homogeneous electron exchange among  $\text{CH}_3\text{COO}^-$  and  $\mathbf{2}^*$ . In the case of derivative **1** and by increasing the scan rate, the corresponding homogeneous process was characterized by the transition of the chemically irreversible behavior to the reversible behavior ( $k_h \approx 80 \text{ M}^{-1} \text{ s}^{-1}$ ) [19,22], however, in the case of compound **2**, such transition was not achieved, at least in the range of scan rate explored ( $0.1\text{--}10 \text{ V s}^{-1}$ ).

Although this interpretation arises from a situation in which the reactants, intermediates and products do not interact with the electrode, it must be recognized that in the acetate–ferrocenecarboxaldehyde system the reaction mechanism is much more complicated because of the competition between the homogeneous processes and the surface reactions giving rise to the electrode inhibition (Scheme 2). As it is shown in Fig. 2, this surface phenomenon predominates as long as the acetate concentration is high enough, which is illustrated through the voltammogram obtained at an acetate concentration of 16.7 mM (curve E). At this particular condition, where the maximal current intensity is achieved as a

result of the catalytic reaction, the reactions of methyl radicals with the surface predominate significantly over the reactions of this intermediate in solution. This last proposal is consistent with the symmetry of the oxidation peak and by the fact that the current at the inversion potential (1.1 V/SCE) is almost zero (insert in Fig. 2).

For electrode inhibition processes, repetitive cyclic voltammetry have demonstrated to be very useful to characterize the inhibition phenomenon [23]. Thus, from an analysis of successive voltammetric cycles, obtained with argon bubbling between each one (insert in Fig. 2) it was demonstrated that the electrode inhibition is highly efficient, because only one voltammetric cycle is necessary to block totally the electrode surface. This is revealed by the fact that the current intensity in cycle 2 is essentially zero.

In the case of compound **3**, which contains two redox centers of ferrocene, two consecutive and overlapped reversible voltammetric signals were observed (Fig. 3A). The redox potential corresponding to each signal ( $E_{\text{IIa-IIc}}^{\circ} = 0.612$  and  $E_{\text{II'a-II'c}}^{\circ} = 0.722$  V/SCE) is comparable in magnitude with the redox potential of mediator **2** ( $E_{\text{IIa-IIc}}^{\circ} = 0.673$  V/SCE). When tetrabutylammonium acetate was added to a solution of **3** (curves B and C), an increase in the current intensity of both signals was observed as well as the appearance of a pre-peak at 0.584 V/SCE (peak IIIa), which becomes the principal signal at a concentration of 5.2 mM (curve C). Under these conditions the current intensity is a maximum and the oxidation wave presents a symmetrical pattern which is typical for an electrode inhibition processes in which the rate of the surface reaction overcomes significantly the rate of the homogeneous reactions [23]. In agreement with this, all the area of the electrode is essentially covered during the first voltammetric scan (Fig. 3, insert), as revealed by the fact that the current intensity for the second scan is similar to the background. Such behavior is quite similar to that described and interpreted above for the system containing mediator **2**, however, in this case, the presence of two redox centers in the mediator structure makes the grafting of the electrode at smaller concentrations of acetate ion more efficient than in the case of mediator **2**.



**Fig. 3.** Oxidation of 3-(diethoxycarbonyl)methylidene-1,2-diferrocenylcyclopropane 1 mM at different concentrations of acetate ion: (A) 0 mM, (B) 1.6 mM, 5.2 mM. Insert: successive cycles obtained at the last solution composition and by bubbling the solution between each cycle. All the experiments were carried out in acetonitrile + 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, at 0.1 V s<sup>-1</sup>, on a glassy carbon electrode ( $\phi = 3$  mm).

**Table 1**

Potential of mediator, acetate ion concentration and number of cycles need to modify glassy carbon surfaces.

Mediator	$E^{\circ}/V^a$	[Acetate]/mM	Number of cycles
1	0.392	40.2	10
2	0.673	16.7	1
3	0.612, 0.722	5.2	1

<sup>a</sup> All the measurements were carried out in acetonitrile + 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, at 0.1 V s<sup>-1</sup>, on glassy carbon electrode ( $\phi = 3$  mm), and referred to SCE.

The main characteristics of the electrode inhibition process obtained from the acetate oxidation mediated by the different ferrocene derivatives **1–3** is shown in Table 1. By comparing the relationship of concentrations of acetate ion to mediator against the number of cycles needed to achieve total electrode inhibition, it can be inferred that the grafting efficiency is favored by several factors: (a) the presence of more than two ferrocene redox moieties in the mediator structure, which contribute statistically to the increase of the free radical population at the interface; (b) high rates of homogeneous electron transfer between the acetate ion and ferrocenium derivatives, as revealed from the fact that reversibility of waves IIIa, for mediators **2** and **3**, was never trapped except for mediator **1**, in the scan rate range of 0.1–10 V s<sup>-1</sup>; (c) with the driving force of the homogeneous electron transfer, which is favored by narrow separations between the oxidation potential of acetate ion and mediators, such as it was the case for the systems with mediators **2** and **3** with respect to mediator **1**.

In all the cases considered here the inhibited state of the electrode was not affected by vigorous ultrasonic rinsing in solvents such as ethanol or acetone, which implies that the electrode inhibition is due to the strong adsorption of organic groups whose binding mode can be considered as covalent [27,28]. Nevertheless the use of one or other mediator could be more or less consuming of time and acetate ion, the ultimate state of the modified electrode must be comparable independently of the mediator used. In this framework, AFM offers an additional means to characterize the morphology of the modified surface.

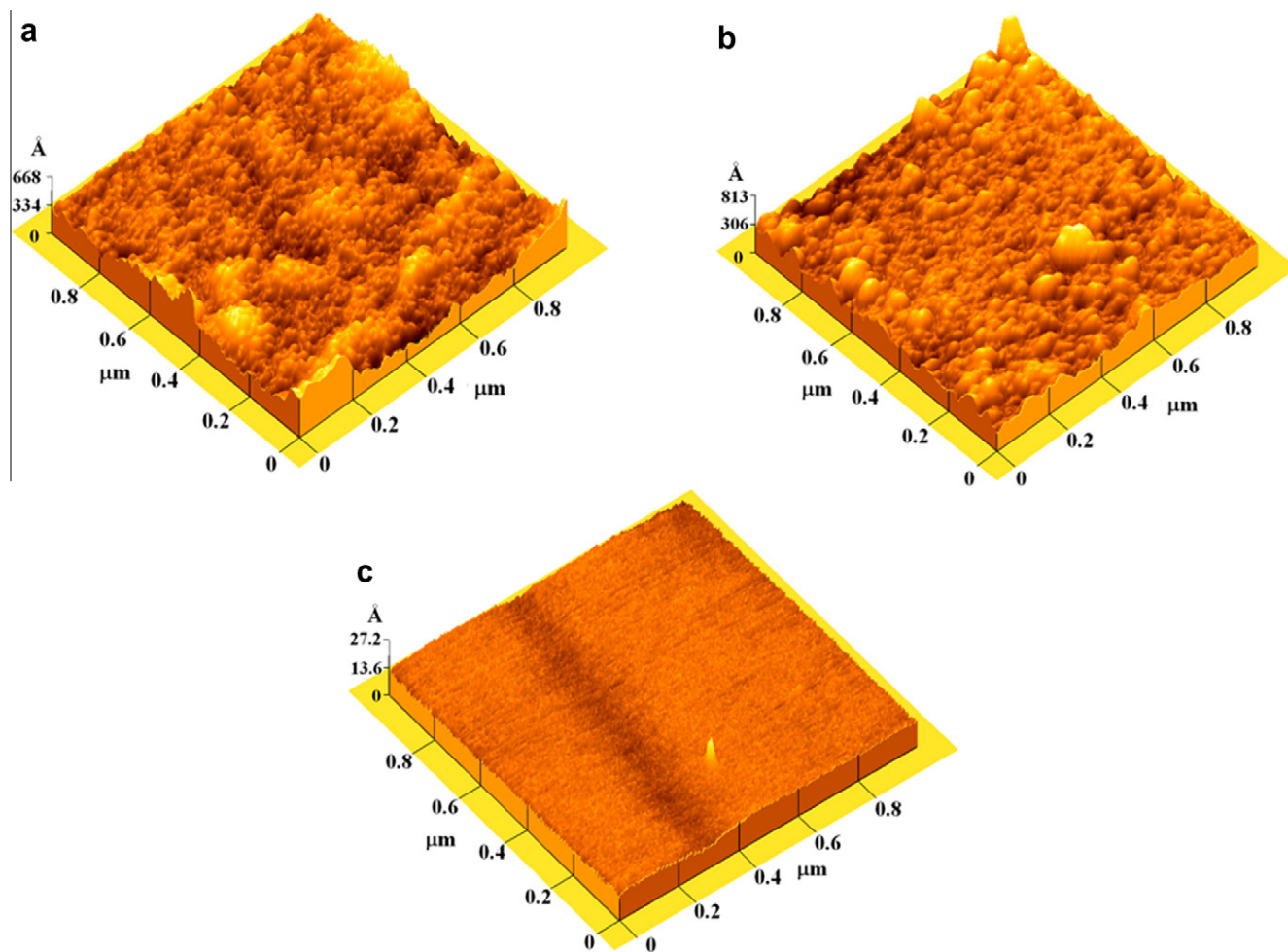
### 3.3. AFM study of HOPG modified surfaces

The modification of surfaces of HOPG was carried out following the cyclic voltammetry procedure used to modify glassy carbon electrodes. That is, the total suppression of the oxidation current by cycling was indicative that the HOPG electrode was completely blocked. Thus, once the maximum coverage was reached, the modified HOPG surface was carefully rinsed several times with two solvents, acetonitrile and acetone, and dried at room temperature. Ultrasonic cleaning was avoided since it destroys the HOPG surface.

Since the electrochemical behavior was similar in the case of mediators **2** and **3**, it was decided to compare only the morphology of the modified surfaces by using mediators **1** and **3**. Fig. 4 shows AFM images obtained on clean HOPG and after inhibition of the surface by oxidation of acetate mediated with compounds **1** and **3**. In both cases, an array of large hillocks was obtained. Table 2 resumes the principal data obtained from the analysis of AFM images of modified HOPG surfaces.

With both mediators, the morphology of the modified surfaces was similar, as it was revealed by the measurement of the rms. roughness ( $R_{\text{rms}}$ ) on images of  $1 \times 1 \mu\text{m}$  (64.8 Å for **1** and 69 Å for **3**). The average height ( $H_{\text{av}}$ ) of the hillocks was 205 Å for **1** and 221 Å for **3**. The average diameter ( $d_{\text{av}}$ ) of the hillocks obtained in AFM was measured by the profiling process subroutine. The result was  $262 \pm 69$  Å for compound **1** and  $300 \pm 57$  Å for compound





**Fig. 4.** Characterization of clean and modified HOPG surfaces by AFM; (a) HOPG modified by using mediator **1**, (b) HOPG modified by using mediator **3**, (c) Clean HOPG.

**Table 2**

Roughness rms, height average and average particle diameter obtained with AFM for clean and modified HOPG surfaces.

	$R_{rms}/\text{\AA}$	$H_{av}/\text{\AA}$	$d_{av}/\text{\AA}$
a	64.8	205	$262 \pm 69$
b	69	221	$300 \pm 57$
c	1.1	4.94	–

**3.** These results reveal that independently of mediator used, the properties of the modified surface are the same, which suggests that the choice of ferrocene derivative mediators is not critical and it will depend on the availability of the chemicals.

These results reveal the formation of multilayers whose formation can be attributed to the high population of methyl radicals generated during the mediated oxidation of acetate. This proposal is consistent with the fact that methyl radicals can extract hydrogen atoms from hydrocarbons to afford methane and alkyl radicals ( $\text{CH}_3 + \text{RH} = \text{CH}_4 + \text{R}^\cdot$ ) [29]. In this way, the formation of aggregates is possible when methyl radicals subtract hydrogen atoms from the attached groups, giving rise to transient grafted radicals, which next undergo subsequent coupling with the methyl radicals coming from the mediated oxidation of acetate. As a result of this coupling, attached aliphatic chains possessing primary and secondary carbons are formed, which open the possibility of dendritic growing of the attached layer. This sort of surface polymerization occurs until the layer is compact and thick enough to inhibit any electron transfer process.

#### 4. Conclusions

At our knowledge, the mediated oxidation of carboxylates is the sole method available to attach aliphatic chains on carbon surfaces through C–C bonds. Ferrocene derivatives have proved to be efficient as redox catalysts for the oxidation of acetate ions in acetonitrile. With respect to the direct oxidation process, this mediated process occurs at low potential values, which triggers a reaction between methyl radicals and the glassy carbon and HOPG surfaces. It is remarkable that such grafting is not possible by direct oxidation of acetate, which gives rise only to products derived from a carbocation chemistry. By comparing the electrochemical behavior of mediators **1–3**, it was established that the surface phenomena predominate by decreasing the separation between the redox potential of mediator and the peak potential of the acetate ion and by increasing the number of ferrocene moieties in the mediator structure. From the point of view of the number of voltammetric cycles required to achieve total electrode inhibition, mediator **2** and **3** have a similar behavior because in both cases it was required only one cycle. However, from the point of view of the acetate concentration required, the best mediator is **3**, because the total electrode inhibition is achieved with the lowest concentration of acetate ion. Other interesting feature of the modification of carbon surfaces by mediated oxidation of acetate ions consists in the fact that the electrode surface is blocked with a compact organic layer, which is microscopically constituted by an array of hillocks whose dimensions indicate the formation of aggregates. This feature of

the organic layer is explained by a dendritic growth owing to the reaction between methyl radicals in solution and the surface aliphatic groups that are gradually grafted. Such property is in agreement with our previous finding in which it was observed that the passage of molecules as small as molecular oxygen is not possible.

The compactness property of the modified electrodes by mediated oxidation of acetate is interesting because the method principle can be extrapolated to metals in order to form organic films which helps to prevent against corrosion processes. In other framework, carbon modified surfaces, by oxidation of acetate or longer aliphatic carboxylates, can be used to support phospholipids chains by non-covalent interactions, which are useful to simulate biological membranes. From a fundamental point of view, constant potential experiments, near to the onset of the oxidation wave, could be carried out to control the population of radical species at the electrode-solution interface and consequently to form the organic layer in a thermodynamically more favorable distribution.

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