Surface Effect on Fe (III)Poly-(Tetraaminophenyl) Porphyrin Modified Electrodes After Electrocatalytic Reactions. An Electrochemical and Atomic Force Microscopy Study

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In this work, Fe(III)-poly-*m*-TAPP and Fe(III)-poly-*p*-TAPP films were deposited by electropolymerization on different surfaces, e.g. Au(111), Highly Oriented Pyrolytic Graphite (HOPG), glassy carbon and graphite were studied. Atomic force microscopy (AFM) was utilized to monitor the surface generated on the different substrates before and after performing electrochemical reactions at the modified assemblies. To this purpose two electrochemical reactions were studied, namely the electrooxidation of nitrite and electroreduction of oxygen in order to determine porphyrin structural differences and the effect on film morphology when the modified electrode was used as electrocatalyst in redox processes. First, the electropolymerization mechanism depends on the position of the amino group in the porphyrin backbone. The amino group in *para* position generates a greater amount of oligomers upon the electrode surface, as evidenced by AFM images obtained at HOPG and Au(111). In general all modified electrodes showed electrocatalytic activity toward O_2 electroreduction and NO₂⁻ electrooxidation. Fe (III)-poly-*p*-TAPP modified electrode is better electrocatalysts than Fe (III)-poly-*m*-TAPP for both reactions in acid and neutral media, respectively. Second, AFM images illustrated how film morphology was affected after being used as electrocatalyst. Fe (III)-poly-m-TAPP film is affected to a greater extent and usually forms aggregates on the electrode surface whereas Fe (III)-poly-*p*-TAPP films exhibited agglomerates and smooth morphology, but in general its deterioration is more homogeneous. Finally, this study showed how both porphyrin polymer films maintain their electrocatalytic properties after successive voltammetric cycles, demonstrating in some degree their stability.

Keywords: Porphyrin, Electropolymerization, AFM, Modified electrode, Electrocatalytic process

1. INTRODUCTION

In recent years, electroactive surface characterization and reactions of polymer modified electrodes using scanning techniques have significantly advanced taking advantage of instrumental and methodological developments in this field, particularly the progress made in the use of atomic force (AFM) and scanning tunneling (STM) microscopy techniques [1].

Structure determination is an important issue for the subsequent determination of electronic properties of the various prepared films or conductive polymers. Only after a clearly established morphology the studies can proceed and, ultimately, clarify the performance and interaction of the obtained structures in some reactions of applied interest [2].

STM has been used in many studies about porphyrin deposition conducted on different substrates such as metals, HOPG, semiconductors and also in different environments, e.g. ultra-high vacuum (UHV) or solutions [2-3]. Some in situ studies have used AFM and STM. However, in the electropolymerization process streaky STM images are obtained, reflecting the difficulty for the electron to tunnel through the usually thick porphyrin films; consequently AFM is needed to monitor the obtained morphologies [4]. Nevertheless, the ex situ STM technique has been employed to identify the growth stages of a porphyrin film by electropolymerization on Au(111) electrodes [5].

On the other hand, among the molecules of interest amenable to study their morphology, porphyrins and metalloporphyrins can be highlighted. They have been increasingly used for the fabrication of modified electrodes because of their prospective application as chemical sensor, in microelectronic devices, photoconductors and power transformers [6-9] as well as for their electrocatalytic activity toward different reactions, e.g. NO [10-12] and O₂ [13] reduction, alcohols oxidation [14] and its study in biological media as biosensors [15].

In addition, porphyrins electropolymerization is a well-established approach for films preparation. The film thickness can be controlled by monitoring the electropolymerization charge. Moreover, reproducibility of the film properties is good [16,17].

In this work, poly-tetra (*x*-aminophenyl) porphyrin (Fe (III) poly-*x*-TAPP) (where x = m, p) Fe (III) chloride electrochemically deposited on Au(111) and HOPG was obtained. The covered surface of the various substrates will be characterized by AFM. This technique is the most appropriate to precisely monitor topography changes. Consequently a detailed study on the effect of two electrochemical reactions, namely nitrite electrooxidation and oxygen electroreduction, was conducted aimed at determining porphyrin structural differences and the effect on films morphology after use in oxidation/reduction electrocatalytic reactions.

2. EXPERIMENTAL PART

2.1 Reagents

Tetra(*x*-aminophenyl) porphyrin (Fe (III)-*x*-TAPP) (where x = m, p) Fe (III) chloride were obtained from MidCentury Co. and used without further purification. N,N'-dimethylformamide, DMF, (Fluka p.a.> 99.5%) was treated with anhydrous Na₂CO₃ and then doubly distilled at reduced pressure

under argon atmosphere. Tetrabutylammonium perchlorate, TBAP, (Fluka, 99%) was recrystallized from a 2:1 ethanol-water solution and dried at 60 °C under vacuum.

HCl 0.1 M and phosphate buffer solution (PBS prepared from 0.1 M NaCl, 2.6 mM KCl, 0.04 M Na₂HPO₄ and 0.01 M KH₂PO₄) with pH 7.4 were used as base electrolyte. Aqueous solutions were prepared using Milli-Q water and were deoxygenated before each measurement by bubbling argon gas (99.99%). All the experiments were carried out at room temperature. All chemicals were supplied by Merck and used without further purification.

2.2 Electrodes and electrochemical measurements

Electrochemical measurements were performed using an Autolab potentiostat-galvanostat (PGSTAT30). The reference electrode was changed depending on the solvent. An Ag/AgCl/1M TMACl in CH3CN/DMF (3:1) reference electrode was used in DMF solutions whose potential was always measured compared to the SCE and a SCE reference electrode was employed in aqueous solution. All the potentials were quoted to this electrode.

The working electrodes were flame-annealing Au(111) plates (0.4 cm², ArrandeeTM), highly oriented pyrolytic graphite plates (HOPG, 0.5 cm², SPI Supplies), a glassy carbon disc (GC, 0.7 cm², CHI instrument) and a graphite electrode patent N°68.718-PCT, Chile (G, 0.51 cm²). A platinum ring was employed as counter electrode.

2.3 Preparation of electrodes modified with Fe (III)-poly(x-TAPP).

The electropolymerization was carried out by consecutive potential cycles (50 cycles) at 0.2 $V \cdot s^{-1}$ in a DMF + 0.1 M TBAP solution containing 0.1 mM (*x*-TAPP) Fe(III) chloride. After the polymerization, the modified electrodes were carefully rinsed with DMF to remove the excess of electrolyte and finally with Milli-Q water. Then the electropolymerized film was stabilized in base electrolyte solutions by consecutive potential cycles between the potential limits where the nitrite oxidation and dioxigen reduction are carried out.

2.4 AFM measurement

AFM imaging was made in air at room temperature with a NanoScope V controller Multimode microscop (from Digital Instrument, Santa Barbara, CA, Bruker) operating in resonant mode using etched silicon tips (RTESP, 215-254 kHz and 20-80 N/m.). Images were taken at high resolution and scan rate of 0.5-1 Hz.

3. RESULTS AND DISCUSSION

3.1 Preparation of the Fe (III)-poly(m-TAPP) and Fe (III)-poly(p-TAPP) electropolymerized films.

Fe (III)-poly-*m*-TAPP and Fe (III)-poly-*p*-TAPP films were prepared on four different electrode substrates, *viz*. G, GC, HOPG and Au(111). The corresponding potential window selected for

the production of each film and voltammograms obtained during monomer electropolymerization in the optimum working conditions have been described elsewhere [5,18,19]

Polymer obtention depends on different variables such as solvent in which the monomer or complex is dissolved, potential scan rate, potential range in which the polymer is obtained, and the substrate on which the polymer is deposited [5,16-24].

Figure 1 shows the structure of the complexes used in the current work. The phenyl groups in *meso* position, which are substituted in *ortho* (2,*o*), *meta* (3,*m*) or *para* (4,*p*) position by amino groups, are perpendicular to the porphyrin macrocyclic ring. This fact does not prevent the electropolymerization since study of different complexes M (M = Mn, Fe, Co, Ni and Cu)-tetra (*x*-*aminophenyl*) porphyrin (*x*-TAPP) (where x = o, m, p) predict that when amino substituents are in *ortho* and *para* position the electropolymerization is favored. By contrast when the amino substituents are in *meta* position the electropolymerization kinetics changes. This can be seen in polymerization charge *vs*. electropolymerization-time plots [5,19,23]



Figure 1. Structure of M- Tetra(*3* - aminophenyl)porphyrin (TAPP) (where the group amino can be in position *2,3 and 4* and M = transition metal).

Infrared spectroscopy (IR) studies revealed that absorptions due to $-NH_2$ groups stretching in the TAPP monomer between 3200-3600 cm⁻¹, are strongly reduced and still exist in the polymer spectrum. This corroborates that H₂-*o*-TAPP and M-*o*-TAPP polymerize through the amino groups in an aniline-like mechanism [16,24]. This mechanism consists of a polymeric growth via an aniline radical-cation formation that dimerizes preferentially in *para* head-tail oriented position (in the benzene ring) with respect to nitrogen. The subsequent oxidation of the dimer allows the addition of another monomer molecule resulting in the formation of a trimer and so on [26,27]. From the above data it can be stated that due to steric hindrance of the porphyrin ring, it is reasonable to admit that the polymer chain does not grow through each aniline group (4 aniline groups) in the porphyrin structure but through just two of them, opposite each other with respect to the porphyrin ring. A probable skeletal structure obtained by electropolymerization has been reported when amino substituents are in *ortho* position [24]. It can be inferred that when the amino substituents are in *meta* position in the complex, if the mechanism of polymerization proceeds in a head-to-tail manner, there would be a greater steric effect caused by the presence of the porphyrin ring and this effect would be responsible for the complex to undergo lower electropolymerization on different substrates. However, when the complex possesses the amino substituents in *para* position, it seems to go through another electropolymerization mechanism. Possibly the electropolymerization mechanism of these complexes occur by oxidation of an amino group and subsequent *ortho* coupling. A similar mechanism has been reported for the electropolymerization of metal tetraamino phtalocyanines and aminophenylporphyrins [22,28,29].

Prior to voltammetry studies the modified electrodes were stabilized between 0 V– -0.8 V for reduction and 0 V- 1.2 V for oxidation in argon saturated solutions of 0.1 M HCl and PBS, pH 7.4, at 0.1 V·s⁻¹ until a stable profile was obtained. No redox couple was depicted for the central metal or porphyrin ring. This behavior has been already reported for these films [18,19]. On the other hand, Chen *et al.* observed that films obtained from acidic solutions in which the complex is dissolved and then the Fe-poly(*o*-TAPP) is stabilized in nitrogen-saturated H₂SO₄ solution, they presented a reversible Fe(III)/Fe(II) redox couple corresponding to the central metal [21]. When Cu-poly (*x*-TAPP) and Ni-poly (*x*-TAPP) (where x = o, p) are stabilized in NaClO₄ or HClO₄, a redox couple corresponding to the porphyrin ring was obtained [17].

This is in agreement with the fact that the attained film depends on the solvent in which the monomer or complex was dissolved, and the polymers, being the same, present different capacitive stabilization responses indicating a great modification in their electrical characteristics. This might be produced by a protonation phenomenon in the oligomeric chains of the film.

3.2 Electrochemical reduction of O_2 on electrodes modified with Fe(III)-poly(m-TAPP) and Fe(III)-poly(p-TAPP).

Figures 2 and 3 depict I vs. E curves obtained at $0.1 \text{ V} \cdot \text{s}^{-1}$. The thin black line corresponds to unmodified electrodes and the thick black line to poly-(*m*-TAPP) modified electrodes. The thick grey line is for poly-(*p*-TAPP) modified electrodes. In general, an overpotential decrease and higher currents are seen in both figures. These results clearly indicate the existence of an electrocatalytic process in 0.1 M HCl (Fig. 2) and PBS, pH 7.4, (Fig. 3) aqueous solutions saturated with dioxygen at different modified electrodes. Moreover, it was demonstrated that in both media electrodes modified with poly-*p*-TAPP are better electrocatalysts than poly-*m*-TAPP.

Table 1 summarizes some data gathered from the above figures. Comparison of results in 0.1 M HCl and PBS, pH 7.4 revealed a greater electrocatalytic effect in acid medium, potential shift (ΔE) between 0.46 - 0.15 V, meanwhile potential shifts are lower, ΔE between 0.18 V - 0.01 V, in neutral medium. Comparison of the respective modified electrode surfaces led to a potential shift (ΔE) trend as follows:

In acid medium: HOPG > G \cong GC > Au(111)

In neutral medium: $G > GC \cong HOPG \cong Au(111)$



Figure 2. Curves I (μ A) *vs* E (V) in dioxygen – satured 0.1 M HCl to 0.1 V·s⁻¹ for the reduction of O₂ on unmodified electrodes (thin black line) and different modified electrodes A) G, B) GC, C) HOPG y D) Au(111) with poly - Fe(III)-*m*-TAPP (thick black line) y poly -Fe(III)-*p*-TAPP (thick grey line).

Current peak vs. scan rate studies for the best system (HOPG modified) of O_2 saturated acid solutions exhibited a current increase proportional to scan rate. A peak current vs. (scan rate)^{1/2} plot for the modified electrodes gave a straight line, indicating that the electrocatalytic process is diffusion controlled [30-32].

In general, O_2 can be reduced via a two-electron reaction to H_2O_2 or a four-electron process to H_2O [33]. This electrochemical reduction in aqueous medium has been widely studied on electrodes modified with porphyrin and other transition metal azamacrocycles [21,30-35]. The relationship between peak current and scan rate for a typical irreversible reaction enable the number of transferred electrons to be determined [32]. Among the more active systems for O_2 that display a defined current peak, G/Fe(III)-poly (*p*-TAPP) in PBS was chosen. The number of electrons *n* found for the reduction of dioxygen was 2. This result demonstrated that under these conditions O_2 was reduced to H_2O_2 through a two-electron pathway.

On the other hand, experiments carried out in acid medium presented some drawbacks when the scan rate potential was increased because the obtained curves showed no well-defined peak current, preventing thus the determination of the number of transferred electrons. Similar systems studies accomplished by Chen *et al.* in acid medium revealed that the main product in dioxygen electroreduction was H_2O and very little H_2O_2 [21]. **Table 1.** The onset potential for the O₂ reduction on the electrodes used. E1 corresponds to the bare electrode and E2 to the modified electrode. It is also reported the potential difference $\Delta E = E2 - E1$.

Electrode	E1 (V)	E2 (V)	$\Delta E (V)$	
	F	Fe(III)-poly(<i>m</i> -TAPP) in PBS		
GRAPHITE	-0,210	-0,100	0.110	
GLASSY CARBON	-0,250	-0,220	0.030	
HOPG	-0,050	-0,040	0.010	
Au(111)	-0,150	-0,100	0.050	
	I	Fe(III)-poly(<i>p</i> -TAPP) in PBS		
GRAPHITE	-0,210	-0,030	0.180	
GLASSY CARBON	-0,250	-0,190	0.060	
HOPG	-0,050	-0,020	0.030	
Au(111)	-0,150	-0.180	0.030	
	F	Fe(III)-poly(<i>m</i> -TAPP) in HCl		
GRAPHITE	-0.100	0.150	0.250	
GLASSY CARBON	-0.380	-0.150	0.230	
HOPG	-0.210	0.200	0.410	
Au(111)	-0.200	-0.050	0.150	
	I	Fe(III)-poly(<i>p</i> -TAPP) in HCl		
GRAPHITE	-0.100	0.200	0.300	
GLASSY CARBON	-0.380	-0,100	0.280	
HOPG	-0.210	0.250	0.460	
Au(111)	-0.200	-0.030	0.170	



Figure 3. Curves I (μ A) *vs* E (V) in dioxygen – satured PBS pH 7,4 solution to 0.1 V·s⁻¹ for the reduction of O₂ on unmodified electrodes (thin black line) and different modified electrodes A) G, B) GC, C) HOPG y D) Au(111) with poly - Fe(III)-*m*-TAPP) (thick black line) y poly - Fe(III)-*p* -TAPP (thick grey line).

Figures 4A and 4B depict voltammograms obtained at 0.1 V·s⁻¹ for the electrooxidation of nitrite at Au(111) and HOPG in PBS, pH 7.4. The thin black line corresponds to bare electrodes and the thick black line to poly-(*m*-TAPP) modified electrodes. The thick grey line is for poly-*p*-TAPP modified electrodes.



Figure 4. Voltammograms ciclyc of electrooxidation of nitrite 1 mM in PBS pH 7,4 solution to 0.1 $V \cdot s^{-1}$ on unmodified electrodes (thin black line) and different modified electrodes A) Au(111) and B) HOPG with poly - Fe(III)-*m*-TAPP) (thick black line) y poly -Fe(III)-*p* -TAPP (thick grey line).

Figure 4A corresponds to the electrochemical response of both polymer modified surfaces. An overpotential decrease of about 0.1 V and current enhancement, in comparison to the same process at a

bare electrode, characteristic of an electrocatalytic effect, was observed [19]. This electrocatalytic effect is not so clear in Fig. 4B. When Au(111) was modified with poly-*m*-TAPP, the nitrite oxidation potential shifts to more positive potentials. This behavior has been previously observed. Apparently nitrite modifies the modified surface leading to a decrease of nitrite electrooxidation kinetics [19]. On the other hand, when Au(111) was modified with poly-p-TAPP the response of the modified or unmodified electrode was very similar, but the oxidation current increased at the modified electrode. There are many explanations for these features. The clean surface of each electrode is different including the adsorption of water and electrolytes. On the other hand, on each surface, a different kind of polymer is probably formed. It is not possible to elucidate double layer effects or porosity of the coating and many other factors that can be playing a role in the final behavior. In fact, depending on the composition of the surface, different kinds of polymers can be obtained [36]. Also, differences in electrocatalytic response to nitrite oxidation at glassy carbon due to a difference in the method of modifying the surface with cobalt phthalocyanine has been determined [37], indicating that all the factors are playing a role. During polymerization, the grafting of the film would depend on surface defects, the possible affinity of higher filled orbitals of the metal and the chain, and the presence of OH (among other factors) [38]. These few examples reveal the complexity of the analysis of the electrocatalytric behavior of the modified electrodes. However, it may be mentioned that no adsorption of nitrite occurs because in all cases the current is diffusion controlled. [19]. Finally it was conclude that poly-*p*-TAPP modified electrodes are better electrocatalysts than poly-*m*-TAPP.

3.4 AFM Characterization of electrodes modified with Fe (III)-poly(m-TAPP) and Fe (III)-poly(p-TAPP).

Previous work demonstrated that electrodes modified with M-poly-*x*-TAPP (where x = o, m, p) presented stability problems after frequent use in some electrocatalytic reactions [17-20,23,25,39,40]. In order to study the effect of electrocatalytic reactions on Fe (III)-poly-*m*-TAPP and Fe(III) poly-*p*-TAPP, two ordered surfaces were selected and morphologically characterized, namely Au(111) and HOPG. AFM studies were accomplished on modified electrodes before and after being subjected to O₂ electroreduction and nitrite electrooxidation, respectively.

Figures 5A, 5B, 6A and 6B show typical high-resolution images obtained by AFM and the corresponding and representative cross section of the electropolymerized porphyrin films selected for this study on HOPG and Au(111) electrodes. In a previous work STM and cyclic voltammetry techniques revealed that, in general, thin films are obtained. Also, in the electropolymerization early cycles, direct formation of porphyrin radical occurs on the bare electrode surface producing 2D islands growth. Subsequently a lateral growth takes place by the addition of new oligomers on the edges of the 2D islands, producing finally a 3D growth [5]. Figure 5A and 5B show that the HOPG surface is completely covered by polymer particles of similar size, around 40-60 nm, although the height of poly-*p*-TAPP is nearly twice (10 - 14 nm) as much as that of poly-*m*-TAPP (6 - 8 nm) corroborating thus that during the electropolymerization poly-*p*-TAPP undergoes greater 3D growth than poly-*m*-TAPP.

When the polymers were deposited on Au(111) electrodes (Figs. 6A and 6B) both modified electrodes were completely coated by a uniform distribution of particles. Furthermore, the difference in the growth of 3D poly-*p*-TAPP on this substrate is even greater as compared to poly-*m*-TAPP. This can be appreciated from the corresponding cross sections shown in Figs.6A and 6B. These results prove that poly-*p*-TAPP grows more and this may be due, as discussed above, to the fact that the polymerization mechanism is affected by the position of the amino group in the porphyrin backbone.

3.5 AFM Characterization of electrodes modified with Fe (III)-poly(m-TAPP) and Fe (III)-poly(p-TAPP) after electroreduction of O_2 .

Figures 5(C, D, E and F) and 6(C, D, E and F) show typical high-resolution images obtained by AFM and the corresponding cross sections after O_2 electroreduction in acid (HCl) and neutral (PBS) medium at both modified electrodes.

3.5.1 In acid medium, 0.1 M HCl

A deterioration of the polymer film was observed in acid medium (Figs. 5E, 5F and 6E, 6F) after being used several times for O_2 electroreduction. The behavior of each electrode was as follows.

1.- HOPG/poly-*m*-TAPP tends to form agglomerates of polymer films ranging from 200 to 300 nm in size and 8 to 10 nm in height, leaving deep cavities between them. On the other hand, HOPG/poly-*p*-TAPP presents flaky-shaped structures ranging from 50 to 100 nm in size and 3 to 10 nm in height with cracks between them corresponding to HOPG steps, yielding deep cavities on the modified surface.

2 .- Au(111)/poly-*m*-TAPP presents agglomerates of polymer film ranging from 20 to 30 nm in size and 4 to 6 nm in height , but, although particle size exhibits the same distribution, a height increase was observed. On the other hand, Au(111)/poly-*p*-TAPP film tends to be more homogeneous showing smaller structures ranging 10 - 20 nm in size and height decrease ranging from 4 to 6 nm. Moreover, the large cavities found in polymers obtained at HOPG are absent in both modified electrodes.

Usually, after O_2 reduction, films obtained on both HOPG and Au(111) exhibited a general effect, *i.e.* a significant deterioration of the film after being utilized as electrocatalyst substrate. This effect was observed at neutral pH but proved to be stronger at acid pH. Nevertheless, a considerable amount of porphyrin remained on the surface with a distribution other than the initial one.

3.5.2 In neutral medium, PBS

In neutral medium (Figs. 5C, 5D and 6C, 6D) deterioration of the polymer film is different to that in acid medium. No agglomerates were observed for HOPG/poly-*m*-TAPP, instead a scattering of islands over the electrode surface ranging from 20 to 30 nm in size and 1 to 4 nm in height was seen. On the other hand, HOPG/poly-*p*-TAPP is no longer flaky, but rather agglomerates in the range 50-100 nm in size and 4-12 nm in height. On both electrodes these particles leave large cavities between them.

Au(111)/poly-*m*-TAPP and Au(111)/Fe(III)-poly-*p*-TAPP electrodes comparison revealed that both present a similar effect in which agglomerates of various sizes are formed.

In conclusion, the poly-*p*-TAPP presents in almost all cases a more homogeneous deterioration whereas poly-*m*-TAPP shows agglomerates that would block active sites that might directly affect its electrocatalytic activity.



Figure 5. AFM images and representative cross section corresponding to the modified HOPG electrodes: **A**) and **B**) after cyclic voltammetric electropolimerization. **C**) and **D**) after of electroreduction of O_2 in PBS. **E**) and **F**) after of electroreduction of O_2 in HCl.

A) $Fe(III)$ -poly(m-TAPP) (3x3µm)	
C) Fe(III)-poly(m-TAPP) (3x3µm)	

E) Fe(III)-poly(m-TAPP) $(3x3\mu m)$

- B) Fe(III)-poly(p-TAPP) (3x3μm)D) Fe(III)-poly(p-TAPP) (3x3μm)
- **F**) Fe(III)-poly(p-TAPP) $(3x3\mu m)$

3.6 AFM Characterization of electrodes modified with Fe(III)-poly(m-TAPP) and Fe(III)-poly(p-TAPP) after electrooxidation of NO_3^- .

Figures 7(A, B, C and D) depict typical high-resolution images obtained by AFM along with the corresponding and representative cross section after NO_2^- electrooxidation in neutral medium (PBS) at both modified electrodes.



Figure 6. AFM and representative cross section corresponding to the modified Au(111) electrodes: A) and B) after cyclic voltammetric electropolimerization. C) and D) after of electroreduction of O₂ in PBS. E) and F) after of electroreduction of O₂ in HCl. All the images have dimensions of (0.5x0.5µm)

A) Fe(III)-poly(m-TAPP)
C) Fe(III)-poly(m-TAPP)
E) Fe(III)-poly(m-TAPP)

B) Fe(III)-poly(p-TAPP)D) Fe(III)-poly(p-TAPP)F) Fe(III)-poly(p-TAPP)

Both electrodes modified with poly-*m*-TAPP present a further film deterioration. On Au(111) a particle distribution ranging from 100 to 200 nm in size and 30-50 nm in height, was observed. Beneath these very height particles, Au grains are found but when deposits on HOPG are surveyed, large agglomerates of polymer film ranging from 50 to 150 nm in size and 10 to 20 nm in height are seen, leaving between them valleys of homogeneous deposits ranging from 4 to 6 nm in height. Poly*p*-TAAP film on both HOPG and Au(111) presents a considerable loss of material that can be followed through the substantial decrease in the average height detected in the cross section (cross section Figs. 5B, 5D, 5F and 6B, 6D, 6F). On HOPG a preferential dissolution along the graphite steps, which is intensified at acid pH, appeared. On Au(111) a widespread loss across the whole electrode surface was observed.



Figure 7. AFM and representative cross section corresponding to the modified electrodes after of electrooxidation of NO_2^- in PBS.

A) Au(111)/Fe(III)-poly(m-TAPP)(3x3µm)B) Au(111)/Fe(III)-poly(p-TAPP)(0.5x0.5µm)C)HOPG/Fe(III)-poly(m-TAPP)(0.5x0.5µm)D)HOPG/Fe(III)-poly(p-TAPP)(0.5x0.5µm)

In general, the poly-*m*-TAAP film on HOPG also presents a widespread material loss, more intense at acid pH, generating large cavities over the film. Above all, what happens is a significant increase in the average size of the obtained agglomerates, indicating that the initially detached material redeposit yielding larger agglomerated particles. The above described situation is also true in the case of nitrite oxidation on both substrates at neutral pH (Fig. 7). In situ STM studies of Yoshimoto *et al.* confirmed adlayers structures of iron octaethylporphyrin (FeOEP) on Au(111) electrodes. The stability of these adlayers was investigated by examining the adlayer structure dependency on applied potential scan for O_2 electroreduction. It was observed that no reconstruction of adlayer structure occurred at Au(111) when the potential returned to its initial value. This suggests that FeOEP molecules did not desorbed from the electrode surface but are highly mobile on Au(111) surface [34]. This disagrees with ours results where the poly-*m*-TAPP oligomeric chains exhibited a behavior in which they are not desorbed from the electrode surface. On the other hand, poly-*p*-TAPP exhibited two phenomena, i.e. one wherein oligomers detachment into the bulk of the solution occurs and another in which the oligomers remain attached. Also, these oligomers would present mobility on the surface and a trend to form aggregates during O_2 electroreduction or NO_2^- electrooxidation reactions.

4. CONCLUSIONS

Fe(III)-poly-*m*-TAPP and Fe(III)-poly-*p*-TAPP films can be prepared by electropolymerization on different substrates, e.g. Au(111), HOPG, glassy carbon and graphite electrodes.

In general all modified electrodes showed electrocatalytic activity for O_2 electroreduction and NO_2^- electrooxidation. Nevertheless, we concluded that Fe(III)-poly-*p*-TAPP modified electrode is a better electrocatalyst than Fe(III)-poly-*m*-TAPP for both reactions in acid (HCl) and neutral medium (PBS).

The electropolymerization mechanism depends on the the amino group position in the porphyrin backbone. The amino group in *para* position generates a higher amount of oligomers on the electrode surface, as evidenced by AFM images obtained on HOPG and Au(111).

AFM images showed that film morphology is affected after use as electrocatalyst and that deposited oligomers present a high mobility on the electrode surface.

AFM images also revealed that Fe(III)-poly-*m*-TAPP film is most affected, and generally forms aggregates on the electrode surface.

AFM images showed that the film Fe(III)-poly-*p*-TAPP also presents agglomerates and smooth morphology, but overall deterioration is more homogeneous.

The polymeric films of both porphyrins maintain their electrocatalytic properties after repeated voltammetric cycles, showing some degree of stability.

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