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Grafting of Nitrophenyl Groups on Carbon and Metallic Surfaces without Electrochemical Induction

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The grafting of 4-nitrophenyl groups on carbon or metallic surfaces without externally applied electrochemical induction is described. Clean surfaces of glassy carbon (GC), copper, nickel, iron, and zinc substrates were dipped in a solution of 4-nitrobenzene diazonium tetrafluoroborate salt in acetonitrile. After the modified surfaces were rinsed, they were analyzed by FT-IRRAS, cyclic voltammetry, XPS, and AFM. The main result of this investigation is the spontaneous formation of a multilayer coating without electrochemical induction regardless of the substrate used. Influence of immersion time and of 4-nitrobenzene diazonium tetrafluoroborate salt concentration on the grafting were also investigated.

Introduction

Surface modification of conductive surfaces via the attachment of organic molecules with specific end functionalities can lead to various possible applications (lubrication, adhesion, protection against corrosion, sensors, biomedical applications, etc.). In addition, the bonding, structure, and conductivity of the organic overlayer raise some interesting chemical and electrochemical problems. The methods leading to a covalent attachment of organic layers on conductive surfaces are relatively scarce. They involve the oxidation of amines,[1] alcohols,[2] carboxylates,[3] and hydrazides[4] which are restricted to no-oxidizable surfaces such as carbon or platinum, and the reduction of vinylic compounds[5] and diazonium[6−26] salts which have been applied to a variety of industrial, coinage, and noble metals. Electroreduction of diazonium salts provides a convenient way of covalently grafting aryl groups on carbon,[6−21] metals,[22−24] and semiconductors.[25,26] It shows several interesting features. First, the possibility of using this process with oxidizable metals: the reduction potential is always set negative to the open circuit potential of the metal (even if the reduction potential of the diazonium salt is positive to this open circuit potential[22]). This prevents any oxidation of the substrate metal during the grafting reaction. Therefore, this reaction could be extended to a large variety of engineering metals such as copper, nickel, zinc, and some of the corresponding alloys.[22] Second, diazonium salts are either commercially available or can be easily obtained in one step from widely available aromatic amines; thus substituents can be varied

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at will on the aryl ring. This allows introduction of a large variety of chemical functions on the metallic or carbon surface which, for example, can be focused on controlling electron transfer (protection against corrosion) or controlling adsorption of molecules (biological field or chemical sensors).[23,24] Third, this process does not require specially dry solvents or the exclusion of oxygen (diazonium salts are reduced before dioxygen). The mechanism of the electrografting of diazonium salts has been extensively reported in the literature:[6−10] it involves a reductive electron transfer to the diazonium salt concerted with the cleavage of dinitrogen[6g] leading to the generation of aryl radicals, followed by the binding of these radicals to the surface via covalent bonds.[22e] The success of this grafting essentially hinges upon the fact that the aryl radicals are not reduced at the potential at which they are produced.

Recent studies[22c,d] have been devoted to the protection of metallic surfaces against alteration by electrografting. Quite interesting results have been obtained related to the protection of iron with organic layers deposited via this process: the electrografted layers decrease the corrosion currents and shift corrosion potentials in a positive direction. Moreover, as the chemical covalent bonds generated by the grafting reaction enhance the attachment of the layer to the substrate, they should limit its possible delamination during the corrosion process.

Grafting of aryl groups to carbon and metallic substrates without any electrochemical induction forms the subject of the present contribution. We will show that dipping the substrate into an appropriate diazonium salt solution results in its coverage by an organic aryl layer. The spontaneous grafting of diazonium salts has been already observed on carbon black (the process has been patented for the production of inks[21]) and on carbon nanotubes.[19a,c,d,e] The spontaneous grafting has been more recently observed on gold[19f] and on Si (heavily doped n- or p-type Si, hydrogenated Si(111) or Si(100) and on polycrystalline Si), GaAs, and Pd.[19g] Recently, Cu and oxide Cu surfaces[27] were also derivatized with aryl layers by immersion in diazonium salt solution in both aqueous and acetonitrile media. Compared to the electrochemical reaction, this procedure provides a simpler and more versatile method for the elaboration of organic

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layers attached to the substrate. The ease of the process could render its application attractive in the industrial field.

We have investigated the grafting of 4-nitrobenzene diazonium tetrafluoroborate salt (noted PNBD) on surfaces with different chemical reactivities to precisely determine the conditions of spontaneous grafting. Iron, zinc, copper, nickel, and glassy carbon were used as surfaces and acetonitrile was used as solvent. First, the presence of aryl groups on the substrate after its immersion into a diazonium salt solution in acetonitrile will be demonstrated by transfer experiments where the signature of the nitrophenyl groups could be observed after thorough rinsing of the substrate. The presence of nitrophenyl groups on the surface will be observed by cyclic voltammetry, but also by Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) and X-ray photoelectron spectroscopy (XPS). The presence of an organic layer will be evidenced by atomic force microscopy (AFM). Second, the influence of diazonium salt concentration and immersion time on the grafting will be studied. The modified surfaces will be referred to as, for example, 0.1-modified ***GC*NO$_2$**, by the concentration (expressed in mM) of the diazonium salt used for the derivatization followed by the symbol of the substrate and by that of the aryl substituent or simply as ***Zn*NO$_2$**, ***Cu*NO$_2$**, etc.

Experimental Section

Chemicals and Substrates. Acetonitrile (99.8%, noted ACN), NBu_4BF_4 (99%), $K_3Fe(CN)_6$ (99%), KCl (99%), 4-nitrobenzene diazonium tetrafluoroborate salt (98%, noted PNBD), nitrobenzene (99%), and 4-nitroaniline (99%) were obtained from Aldrich and were used as received. Glassy carbon, iron (99.5%), zinc (99.95%), nickel (99.9%), and copper (99.99%) were obtained from Goodfellow. Aqueous solutions were prepared with ultrapure Milli-Q water (Millipore Milli-Q water purification system). All electrolytic solutions were routinely deaerated with argon during 20 min before each measurement.

The electrodes consisted of 1-mm-diameter wire (or 3-mm-diameter glassy carbon rod) embedded into glass tubes; before use, they were manually polished with 15-, 3-, and then 1-μm diamond paste. Then they were sonicated in deaerated acetone (1 min) and then in deaerated ACN solution for 10 min. This was followed by their immersion into deaerated 10, 1, or 0.1 mM PNBD salt in ACN (10 mL) over a period of 1 min, 6 min, or 1 h. Substrates thus modified will be noted as 0.1-modified, 1-modified, and 10-modified. After immersion, substrates were thoroughly rinsed with pure deaerated ACN in an ultrasonic cleaner for 10 min and then with pure deaerated acetone (for 10 min under sonication) to ascertain that any organic material only weakly adsorbed on the surface would be removed. Some experiments were performed in a glovebox containing less than 2 ppm of dioxygen, the electrodes were then polished manually in the glovebox and immediately immersed in the solution of PNBD.

For XPS and AFM measurements, metallic disks of 15 mm diameter and 1 mm thick were used. Substrates of 20 × 35 mm^2 and 1 mm thick were used for FT-IRRAS experiments. All the samples were polished before each experiment with a polishing machine (RotoPol-31 Struers equipment) with a permanent diamond disk and then with 9-, 6-, 3-, and 1-μm diamond pastes. The polished samples were then carefully rinsed in deaerated acetone (10 min) and then deaerated acetonitrile (10 min) under sonication before their introduction in the PNBD solution. These substrates were then processed as the substrates used for electrochemical tests.

Apparatus. Electrochemical measurements were carried out with a conventional three-electrodes cell and a Princeton Applied Research Inc. potentiostat/galvanostat model 273 from EGG. All electrochemical analyses were performed at room temperature. A gold wire was used as a counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode, which was dipped in a separated bridge containing the electrolytic solution free of any other compound. All potentials are given versus the saturated calomel electrode (SCE).

FT-IRRAS spectra were obtained with a NICOLET Magna IR 860 spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Experiments were performed with an angle of incidence of 80° and the measurement chamber was continuously purged during acquisition of spectra. Each FT-IRRAS spectrum of grafted substrates results from the co-addition of 500 interferograms at a resolution of 4 cm^{-1} and from the difference of the bare substrate spectrum in the same conditions. The spectrum of 4-nitrobenzene diazonium tetrafluoroborate salt was recorded as KBr pellet in transmission mode.

XPS experiments were carried out with a VG Instruments 220i spectrometer by using an unmonochromated Al Kα X-ray source (incident energy 1486.6 eV). A source power of 15 kV and 20 mA was used. The dimensions of the X-ray beam were 7 mm per 8 mm. The pressure in the analysis chamber was 10^{-9} Pa. Calibration in binding energy (BE) was achieved using the Ag $3d_{3/2}$ and Ag $3d_{5/2}$ transitions (368.3 and 374.3 eV, respectively). The BE resolution of the spectrometer was estimated to 0.2 eV. The binding energy values were corrected using the C_{1s} signal of contamination carbon at 285 eV. The angle “Θ”, defined as the angle between the electron kinetic energy analyzer and the sample surface, was fixed at 90° for all the XPS experiments.

AFM images were obtained with a Nanoscope III (Digital Instrument) operating in the tapping mode using monocrystalline silicium tips. The frequency was 280 kHz ± 20 Hz. The spring constant of the cantilever was 40 N/m and the scan frequency was 1.5−2 Hz. Height of the layers was measured by carefully creating dips in the layer with a metallic pin and measuring the profile over this dip. The mean roughness was obtained from a Nanoscope IIIa software and represents the arithmetic average of the deviation from the center plane

$$R_S = \frac{\sum_{i=1}^{N} |Z_i - Z_{cp}|}{N}$$

where Z_{cp} is the Z value of the center plane, Z_i is the current Z value, and N is the number of points within a given area. Therefore R_S should be equal to zero for a perfect plane.

Results

Electrochemical Behavior of PNBD in ACN Solution. For the sake of comparison, the electrochemical behavior of PNBD (2 mM in ACN + 0.1 M NBu_4BF_4) was investigated by cyclic voltammetry on the different electrode surfaces.

With easily oxidized metals, the available potential range is restricted. The open circuit potentials (OCP) of the different substrates investigated were measured in a 2 mM PNBD solution in ACN (+ 0.1 M NBu_4BF_4): ***GC*** +0.63; ***Ni*** +0.30; ***Fe*** −0.05; ***Cu*** −0.15; and ***Zn*** −0.50 V. Therefore, when electroreduction of PNBD occurs in a potential range positive to the metal oxidation, cyclic voltammograms cannot

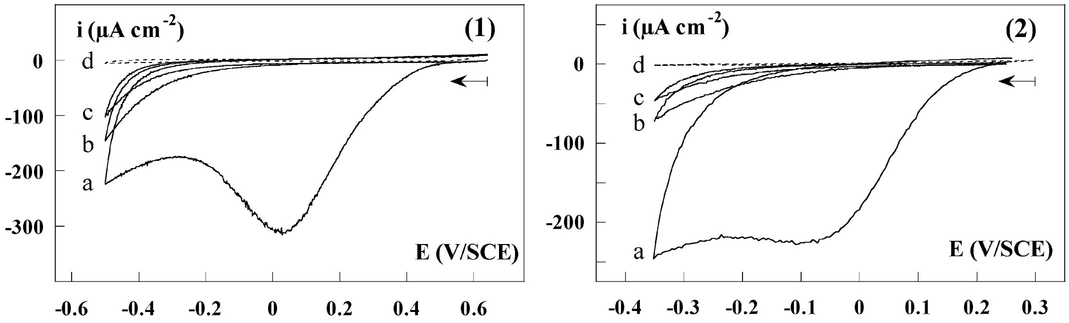

Figure 1. Cyclic voltammograms of 2 mM PNBD in ACN + 0.1 M NBu_4BF_4 on (1) GC and (2) nickel: (a) first cycle, (b) second cycle, and (c) third cycle. Cyclic voltammograms 1(d) and 2(d) are obtained in ACN + 0.1 M NBu_4BF_4 solution free of diazonium salt. Scan rate 0.2 V s^{-1}.

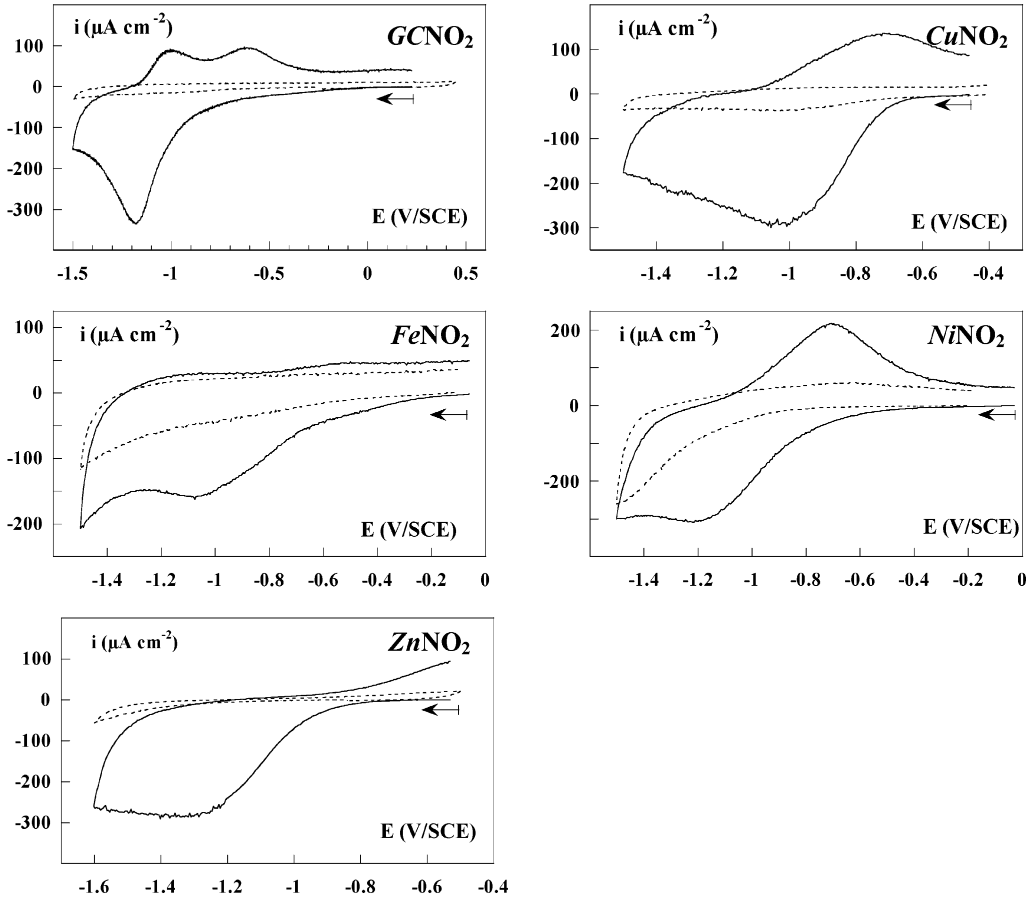

Figure 2. Cyclic voltammograms on bare (dashed line) and 10-modified (full line) electrodes in ACN + 0.1 M NBu_4BF_4. Scan rate 0.2 V s^{-1}. Modification of electrode surface consisted of dipping the electrode in a 10 mM PNBD solution in ACN for 1 h.

be properly observed. Figure 1 shows consecutive cyclic voltammograms obtained on glassy carbon and nickel. On the first cycle, voltammetric responses present a cathodic process close to 0 V attributed to the reduction of the diazonium salt into an aryl radical.[22] Repetitive cycling into the 2 mM PNBD solution leads to complete disappearance of the cathodic peak of the diazonium salt starting from the second cycle. This indicates a complete blocking of the electrode by the organic layer produced during the initial cycle under the above experimental conditions.

Evidence of the Spontaneous Grafting. Modification of the different electrodes without electrochemical induction was first accomplished with the procedure described in the Experimental Section, by immersing samples in a 10 mM deaerated diazonium solution for 1 h. Samples were then analyzed by the following methods as diagnostic of grafting: electrochemistry, FT-IRRAS, XPS, and AFM.

Electrochemical Analysis of Nitrophenyl Groups. After immersion, the reacted electrodes were rinsed as described in the Experimental Section and then transferred into an ACN + 0.1 M NBu_4BF_4 solution for electrochemical analysis. Grafting of diazonium salt on the surfaces was ascertained through the observation of the electrochemical system of nitrophenyl groups in aprotic solution (acetonitrile) as already reported in the literature.[6−10,22]

Figure 2 shows cyclic voltammograms obtained on the different surfaces under investigation, before and after immersion in the PNBD solution. Whatever the electrode, the voltammograms acquired after immersion exhibit a cathodic process at about −1.1 V corresponding to the

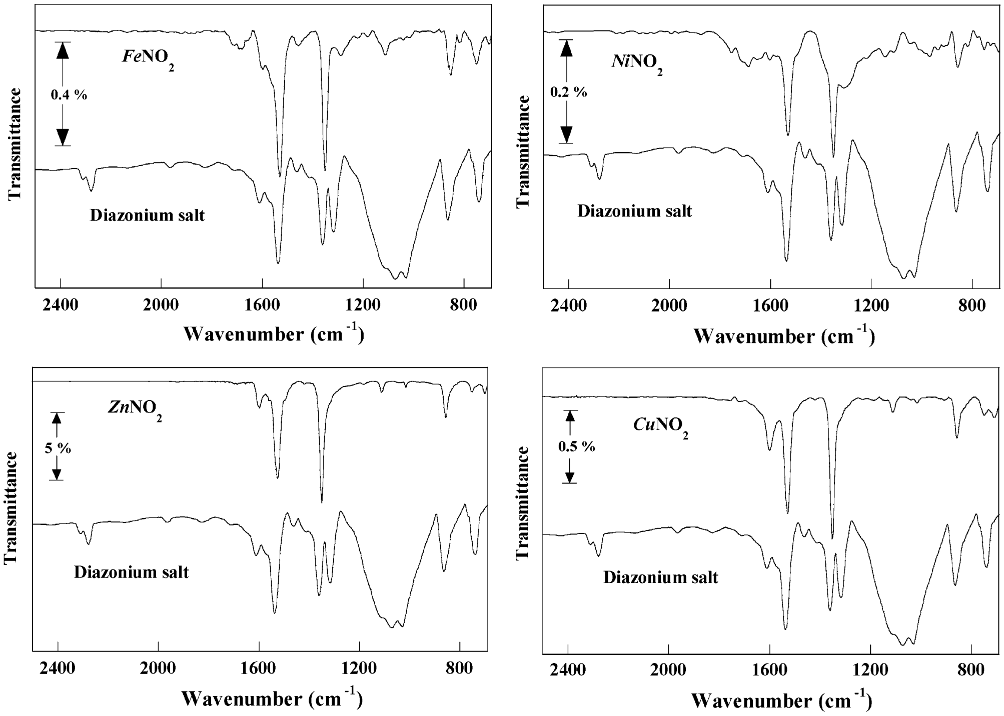

Figure 3. FT-IRRAS reflection spectra of 10-modified substrates. FT-IR transmission spectrum of 4-nitrophenyl diazonium salt in KBr pellet is also presented. Modification of surfaces consisted of dipping the material in 10 mM PNBD solution in ACN for 1 h. Note that the transmittance scale corresponds to the spectrum of modified electrode and the scale is different for the salt spectrum.

reduction of nitrophenyl groups grafted to the surface into the corresponding radical anions. These radical anions are oxidized during the reverse scan (oxidation process between −1.1 and −0.45 V, depending on the electrode). Even on electrode materials not easily oxidized, the modification occurs spontaneously. We can also notice that cyclic voltammograms are close to those previously reported for nickel, copper, and zinc electrodes with nitrophenyl groups electrochemically grafted.[22a,c,d]

FT-IRRAS Analysis. Figure 3 is relative to FT-IRRAS reflection spectra of iron, nickel, zinc, and copper surfaces (***Fe*NO$_2$**, ***Ni*NO$_2$**, ***Zn*NO$_2$**, and ***Cu*NO$_2$**) after immersion in an acetonitrile solution containing 10 mM PNBD; the parent diazonium salt spectrum in KBr pellet is also reported as a reference. Evidence for the presence of nitrophenyl group on the metallic surfaces is clearly observed through (i) two strong bands due to the nitro groups at about 1350 and 1530 cm^{-1} (symmetric and asymmetric stretching respectively), the difference $\nu_{\text{asymmetric}} - \nu_{\text{symmetric}} = 180$ cm^{-1} being what could be expected for a solid[28a] (159 to 177 cm^{-1}); (ii) a band at about 700 cm^{-1} attributable to an NO$_2$ out-of-plane bending vibration;[28b] (iii) the C═C stretching modes of aromatic rings between 1440 and 1550 cm^{-1}; and (iv) the C−H bending modes of aromatic rings between 1150 and 800 cm^{-1}.

We can notice that the symmetric stretching due to NO$_2$ groups of the diazonium salt gives an additional band at 1316 cm^{-1} whereas only one band is observed when attached on grafted surfaces: this splitting has already been reported for aromatic nitro-compounds and is attributed to coupling effects[28c] between NO$_2$ symmetric vibration mode and ring vibration modes. The band observed on the spectrum of the diazonium salt at 860 cm^{-1} is linked to C−H out of plane deformation bands and is assigned to 1,4-disubstituted aromatic rings. This band is still observed on all the grafted substrates at about 855 cm^{-1}; it could be attributed to 1,4-disubstitued but also to trisubstitued aromatic rings.

The relative intensity of the band located at 860 cm^{-1} (calculated with respect to the band at 1350 cm^{-1}) on the FT-IRRAS spectrum of the modified surfaces is weaker than that obtained on the FT-IR spectrum of the diazonium salt. This is likely due to a modification of the substitution during the layer formation but also to the fact that the spectrum is dominated by vibrational modes perpendicular to the surface of the sample, as was already observed with the electrochemically modified surfaces.[22d] But the most striking feature is the absence of the stretching N≡N mode near 2280 cm^{-1} whatever the grafted surface. This suggests that the grafting without electrochemical induction occurs with the loss of nitrogen, as was already reported for the grafting with electrochemical induction.[22] We can also emphasize the fact that the transmittance signal is weak on iron and even weaker on nickel which seems to indicate that the layer is thin on these metals.

XPS Results. Figure 4 shows the N1s regions pertaining to XPS spectra of samples that were immersed in a 10 mM PNBD solution in ACN for 1 h. XPS spectra of nonmodified substrates are also presented.

XPS spectra of all the grafted surfaces reveal two peaks. The first peak at the highest binding energy around 406 eV can be undoubtedly attributed to NO$_2$. This peak is totally absent on all the nongrafted surface spectra; this confirms

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(28) (a) Nyquist, R. A. *Interpreting Infrared, Raman and Nuclear Magnetic Spectra*; Academic Press: New York, 2001; Volume 2, p 173. (b) Socrates, G. *Infrared Characteristic Group Frequencies, Tables and Charts*; Wiley: New York, 1994. (c) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Methuen & Co: London, 1968; p 228.

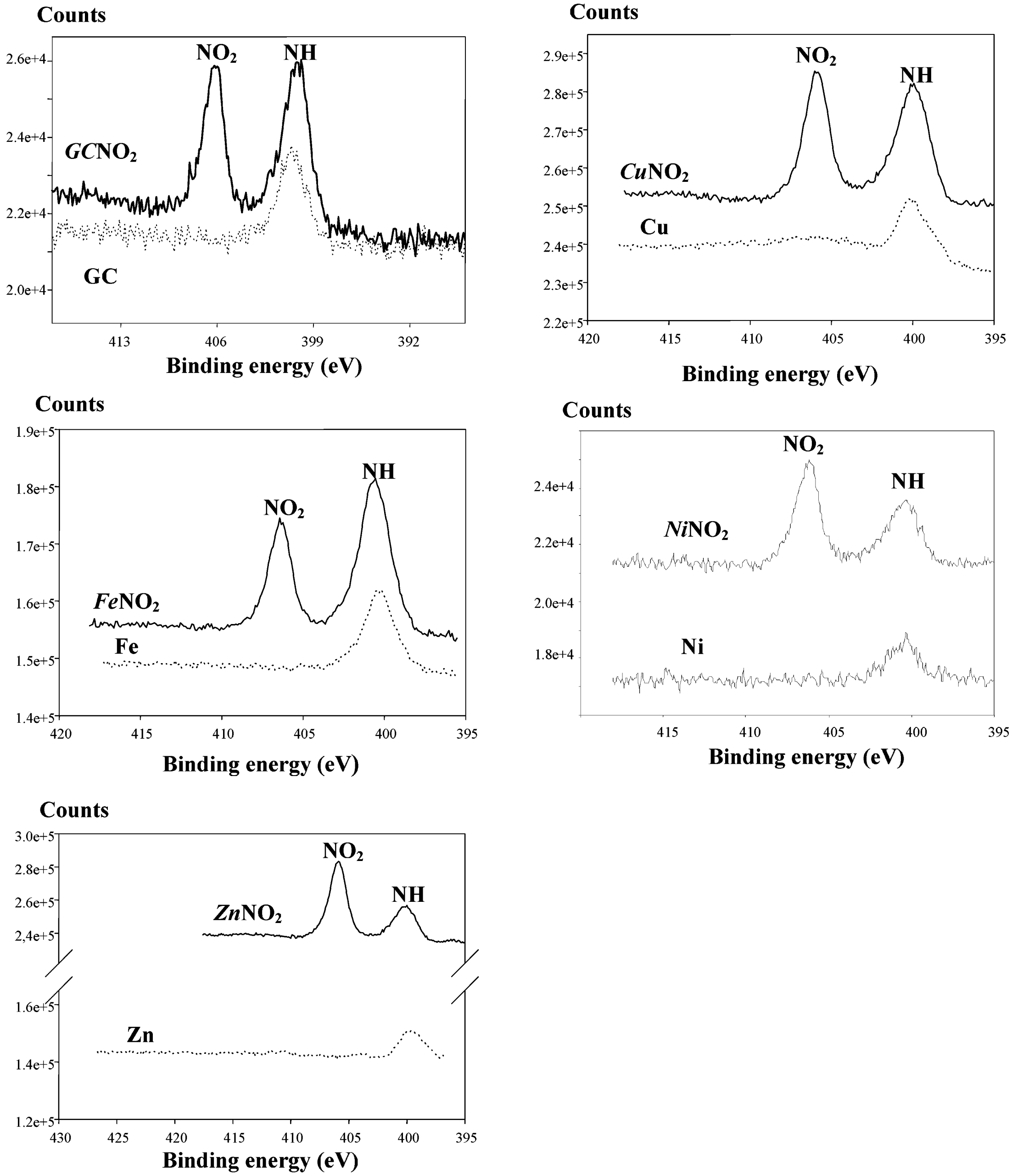

Figure 4. XPS spectra of N1s region of bare and 10-modified surfaces. Modification of surfaces was accomplished by dipping the material in a 10 mM PNBD solution in ACN for 1 h.

that all modified substrates present the NO_2 function onto their surfaces. The second peak around 400 eV can be assigned, on one hand, to the atmospheric nitrogen (this peak is always evidenced when the sample is prepared apart from the preparation chamber of the XPS spectrometer) and, on the other hand, to reduced nitrogen (amines). Actually, amine groups can come from chemical reduction of NO_2 under the X-ray beam during XPS experiment, as already reported in the literature.[29a] The reduction phenomenon is clearly evidenced in Figure 5: after 120 scans, the photoelectron peak around 406 eV (attributed to NO_2) is changed almost entirely into a photoelectron peak around 400 eV (attributed to NH_2), as already observed on silica surfaces.[29a] So, to avoid this chemical reduction under the photon beam, the number of scans (such as the acquisition time) for obtaining the N1s signal was chosen at 50 for all our experiments.

Concerning the other nitrogen species potentially present on these samples, from the literature,[8b,29b] the N1s photoelectron peak of the diazonium N_2^+ should be located at 402 eV. No peak appears at this binding energy on grafted surface spectra, which reveals the loss of N_2^+ during the grafting process.

We have also compared the photoelectron peaks of the metallic substrates for bare and modified surfaces (Figure S1, Supporting Information). All the photoelectron peaks (Zn2p, Fe2p, Cu2p, Ni2p) display a significant decrease of their intensity between the bare and the grafted substrate, obviously indicating that the metallic surface is covered by

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(29) (a) Mendes, P.; Belloni, M.; Ashworth, M.; Hardy, C.; Nikitin, K.; Fitzmaurice, D.; Critchley, K.; Evans, S.; Preece, J. *Chem. Phys. Chem.* **2003**, *4*, 884. (b) Nakayama, Y.; Takahagi, T.; Soeda, F.; Ishitani, A.; Shimomura, M.; Okuyama, K.; Kunitake, T. *Appl. Surf. Sci.* **1988**, *33/34*, 1307.

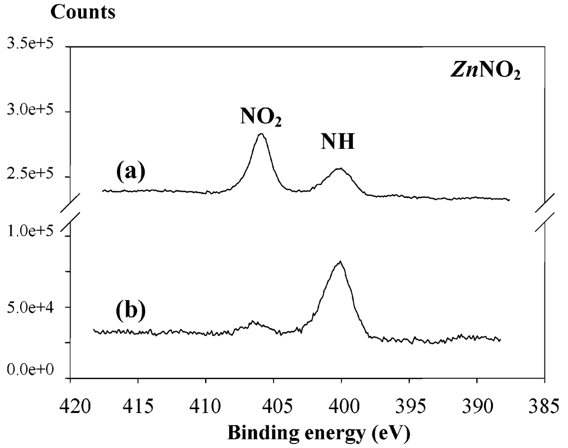

Figure 5. XPS evidence of the reduction of NO_2 groups into NH_2 under the X-ray beam: (a) spectrum obtained after 50 scans, and (b) spectrum obtained after 120 scans. Zinc surface was modified by immersion in a 10 mM PNBD solution in acetonitrile for 1 h.

the organic layer. Although the decrease of the total Fe2p intensity is not so obvious on the spectrum of the grafted substrate, the determination of the peak area underlines this decrease: the intensity of the Fe(0) contribution is 66 000 counts for the bare substrate (and 36 000 counts for the grafted one) and the Fe(II) peak is 53 000 counts for the bare substrate (and 40 000 counts for the grafted one).

In conclusion, these two types of XPS data (results obtained from the N1s and from the “substrate” photoelectron peaks) clearly show the presence of the NO_2 function onto GC, nickel, iron, zinc, and copper surfaces, indicating the spontaneous formation of an organic coating on the different materials. Moreover, these results agree with those obtained by FT-IRRAS: the grafting of the nitrophenyl groups without electrochemical induction occurs with the loss of nitrogen.

The characterizations of the modified surfaces by electrochemistry, FT-IRRAS and XPS, clearly show the spontaneous formation of an organic layer on all the substrates studied. However, the question of linkage type existing between the layer and the substrate is not elucidated. Even if the organic layer resists sustained ultrasonic rinsing, one can wonder whether the layer is covalently bound to the surface or simply physisorbed. A beginning answer can be given by using nitrobenzene (NB) or 4-nitroaniline (noted NA) instead of PNBD in the immersion solution. Experiments were also conducted with NB or NA by using the procedure already described for PNBD. We chose to dip the electrodes in a 10 mM NB or NA solution (in acetonitrile) for 1 h. After immersion, electrodes were rinsed with pure deaerated ACN in an ultrasonic cleaner for 10 min. Electrodes were then transferred into an acetonitrile solution (containing 0.1 M NBu_4BF_4 as supporting electrolyte) free of any other compound and characterized by cyclic voltammetry. Voltammograms obtained on electrodes thus treated differ strongly from those obtained on electrodes immersed in PNBD solution (examples on GC and Fe electrodes, Figure S2). Only electrodes immersed in PNBD solution present a redox process linked to nitrophenyl/nitrophenyl radical anion couple. These results clearly show that there is no film on the electrodes after their immersion in NB or NA solutions followed by their ultrasonic rinsing. With the diazonium precursor, the layer resists ultrasonic rinsing and, in that case, nitrophenyl groups are certainly covalently bonded on the different surfaces. These results also indicate that the aryl layer is not linked to the surface via nitro groups. Moreover, the formation of the aryl film is accompanied with the loss of N_2^+, as indicated by FT-IRRAS and XPS measurements.

Modification of Grafting Parameters. The above results show the formation of an organic layer when the substrate is immersed in a 10 mM PNBD solution for 1 h. We have then studied the influence of grafting parameters, such as PNBD concentration and immersion time, on the occurrence of the grafting and on the properties of the layers.

Influence of the Immersion Time on the Grafting. Experiments were performed to establish the relation between substrate immersion time in the PNBD solution and the quantity of nitrophenyl groups present on the surface. Glassy carbon and iron electrodes were immersed into a 10 mM PNBD solution (in ACN) for 1 min, 6 min, and 1 h. Electrodes were then thoroughly rinsed as described in the Experimental Section and characterized by cyclic voltammetry in a pure electrolytic solution (ACN + 0.1 M NBu_4BF_4). The evolution of the cyclic voltammograms on GC and Fe as a function of immersion time is shown in Figure 6. We notice that, whatever the immersion time, grafting occurs on the different surfaces, as revealed by the presence of the reduction peak characteristic of nitrophenyl groups at about −1.1 V. On glassy carbon (***GC*NO$_2$**), increasing the immersion time leads to a marked increase of the current peak intensities, indicating an increased amount of nitrophenyl groups on the surface. On iron (***Fe*NO$_2$**), the evolution is more limited, there is practically no evolution of the voltammograms with the immersion time up to 1 h. However, increasing the immersion time of the iron electrode in the PNBD solution up to 6 h leads to the observation of a quasi-reversible process; the height of the peak is similar to that observed on ***GC*NO$_2$**. Table 1 summarizes the surface concentrations deduced from integration of the electrical charge under the nitrophenyl reduction peak of ***GC*NO$_2$** and ***Fe*NO$_2$**. This calculation mode was already used to estimate the amount of nitrophenyl groups grafted in the case of electrochemically modified surfaces.[9f,22a] With this method, the amount of electroactive nitrophenyl groups grafted on GC varies from 2.0 to 5.8 10^{-9} mol cm^{-2} for immersion times ranging from 1 to 60 min. This surface coverage corresponds to approximately 1 to 4 monolayers present on the surface[6a] (from molecular models,[30] a monolayer on a perfect plane would correspond to a surface concentration of $\Gamma = 1.35\ 10^{-9}$ mol cm^{-2}). On iron, the thickness of the layer would correspond to 2 to 6 monolayers for immersion times between 1 and 6 h. These results tend to indicate the spontaneous formation of multilayers regardless of the nature of the substrate.

The evolution of layer morphology with immersion time was observed by AFM on grafted iron. The thickness and the roughness of organic layers of ***Fe*NO$_2$** for different immersion times into ACN + 10 mM PNDB solution are gathered in Table 2. These data point to a continuous growth

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(30) *Alchemy 2000*; Tripos, Inc: St Louis, MO.

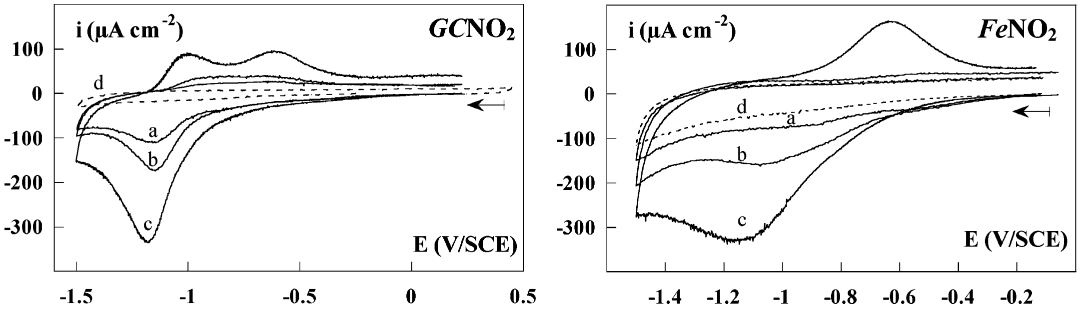

Figure 6. Influence of electrode immersion time in 10 mM PNBD (in ACN) on the cyclic voltammograms obtained after transfer in a pure electrolytic solution (ACN + 0.1 M NBu_4BF_4). Cyclic voltammograms on ***GC*NO₂** after soaking the sample for (a) 1 min, (b) 6 min, and (c) 1 h. Cyclic voltammograms on ***Fe*NO₂** after electrode immersion for (a) 1 min, (b) 1 h, and (c) 6 h. Cyclic voltammograms noted (d) are obtained on bare electrodes. Scan rate 0.2 V s^{-1}.

Table 1. Influence of Electrode Immersion Time on the Electrical Charge (Corresponding to the Integration of the Reduction Peak of Nitrophenyl Groups) and on the Surface Coverage of *GC*NO₂ and *Fe*NO₂

substrate	immersion time[a] (min)	Q (μC cm^{-2})[b]	Γ (mol cm^{-2})[c]
glassy carbon	1	189 ± 12	$(2.0 \pm 0.2)\ 10^{-9}$
	6	274 ± 12	$(2.8 \pm 0.2)\ 10^{-9}$
	60	564 ± 12	$(5.8 \pm 0.2)\ 10^{-9}$
iron	60	320 ± 33	$(3.3 \pm 0.3)\ 10^{-9}$
	360	756 ± 33	$(7.8 \pm 0.3)\ 10^{-9}$

[a] Grafting was achieved in 10 mM PNBD in ACN. [b] Q, representing the electrical charge, is calculated by integration of the voltammetric peak corresponding to the reduction of nitrophenyl groups. [c] Γ is the surface coverage and is calculated as $\Gamma = Q/FA$, where F is the Faraday and A is the geometric area of the electrode.

Table 2. AFM Characteristics of 10-Modified *Fe*NO₂ as a Function of Immersion Time

immersion time (min)	thickness of the layer ±1.5 nm	roughness ±0.3 nm	height of the protruding features ±1.5 nm
0		0.6	
1	2.8	0.7	2.2
5	3.2	0.8	2.6
30	4.8	0.9	3.1
60	5.2	1.2	3.9
120	7.4	3.0	5.0
360	9.7	3.9	7.4

of the layer, which becomes rougher and rougher with time due to the formation of higher and higher heaps. However, the evolution of the thickness with immersion time is not very pronounced: between 1 and 6 h of immersion, the thickness is only doubled. This weak increase of thickness could be explained by a non-homogeneous coverage of the surface at low immersion time. As immersion time increases, holes in the layer are filled and the growth also goes on at molecules already grafted, as shown by the increase of the roughness and of the height of protruding features. The obtained results may also provide an estimation of the number of monolayers present on the surface. Indeed, if one assumes that the length of one monolayer fits with the height of a nitrophenyl group standing up on a surface (0.66 nm according to molecular models) then the thickness of the layers described in Table 2 would correspond to 4 to 15 monolayers.

Influence of PNBD Concentration on the Grafting. The effect of PNBD concentration on the spontaneous grafting was also investigated. This was conducted by varying the PNBD concentration by 2 orders of magnitude (0.1 to 10 mM), and by keeping the immersion time constant (1 h). Figure 7 shows the electrochemical response in a pure electrolytic solution of ***GC*NO₂** and ***Fe*NO₂** prepared from the different PNBD solutions. Cyclic voltammograms reveal that grafting occurs on the different electrodes, but is less pronounced on iron as already observed. As the PNBD concentration decreases, so do the surface of the nitrophenyl group reduction peak and the surface coverage. The estimation of the thickness of the layer on ***GC*NO₂**, deduced from the integration of the reduction peak, gives values ranging from 1 to 4 monolayers for PNBD concentration going from 0.1 to 10 mM. On iron, this estimation was not possible, as cyclic voltammogramms are too close to the background current to lead to reliable measurements.

AFM Results. AFM images recorded on iron after its immersion into 0.1, 1, and 10 mM PNBD solution for 1 h are shown in Figure 8 and their characteristics are reported in Table 3. Progressive modification of the surface is clearly observed. The untreated iron surface shows the grooves due to the polishing with diamond particles. After dipping in a 0.1 mM solution of PNBD, little surface modifications are observed: the grooves are still visible but the blurred aspect indicates the presence of a thin organic film. One observes only separate islands of organic layers with an average height of the protruding features of 2.6 nm indicating the local formation of multilayers. As PNBD concentration increases (up to 10 mM), the density of these islands becomes more important, the average height of the layer increases as well as the height of the protruding features and therefore the roughness. After contact with a 1 mM solution, a large number of small heaps are visible with diameters of the order of 10 nm; as the concentration is increased to 10 mM, the heaps grow in size (about 100 nm) and coalesce. At the same time, most of the grooves disappear. In conclusion, the characteristics of these images demonstrate the formation of an organic layer whatever the diazonium concentration. They also show that increasing the concentration of diazonium salt leads to thicker and, apparently, more compact layers.

Electrochemical Response of Redox Probes on Grafted Electrodes. We have also studied the behavior of two redox probes on GC modified electrode: ferricyanide in aqueous medium and nitrotoluene in organic medium (acetonitrile). This analysis was restricted to ***GC*NO₂**, as the ferri/ferrocyanide couple is located at potentials positive to the oxidation of other substrates. The ferri/ferrocyanide couple

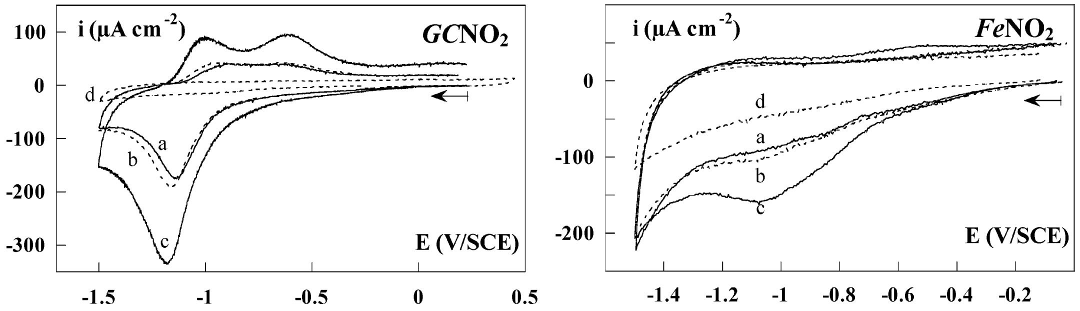

Figure 7. Influence of PNBD concentration on the cyclic voltammograms obtained after transfer of the electrode in a pure electrolytic solution (ACN + 0.1 M NBu_4BF_4). Cyclic voltammogramms of ***GC*NO$_2$** and ***Fe*NO$_2$** prepared by 1 h immersion in (a) 0.1 mM, (b) 1 mM, and (c) 10 mM PNBD solution (in ACN). Figures noted (d) show voltammograms of bare electrodes. Scan rate 0.2 Vs^{-1}.

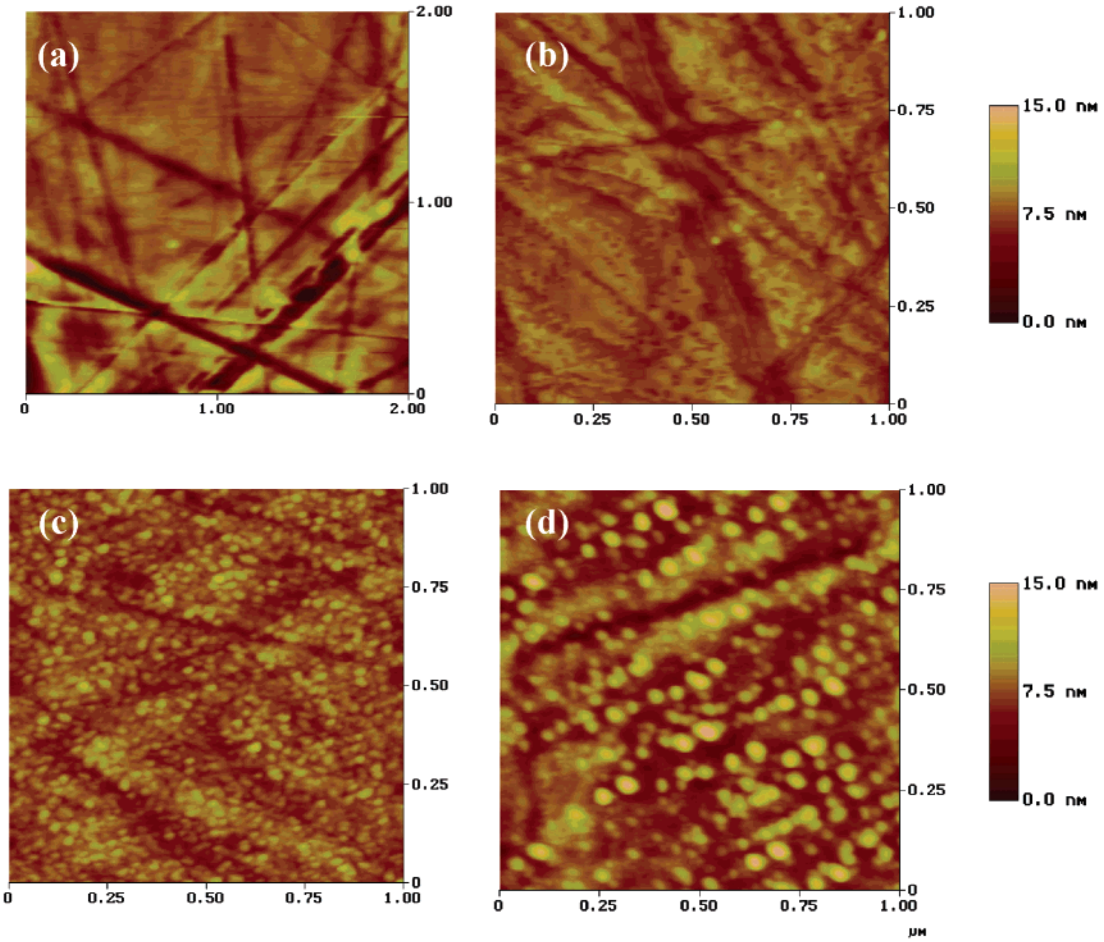

Figure 8. AFM images of (a) bare iron and (b) 0.1-modified, (c) 1-modified, and (d) 10-modified ***Fe*NO$_2$**. Iron disk was dipped in PNBD solution for 1 h.

Table 3. AFM Characteristics of *Fe*NO$_2$ as a Function of PNBD Concentration[a]

concentration PNBD (mM)	thickness of the layer ± 1.5 nm	roughness ± 0.3 nm	height of the protruding features ± 1.5 nm
bare iron	0	0.6	
0.1	2.6	0.9	2.3
1	4.4	1.1	3.0
10	5.2	1.5	3.9

[a] The samples were dipped in the PNBD solution for 1 h.

in a 0.1 M KCl aqueous solution presents a reversible system located at $E° = + 0.19$ V on bare GC electrode. Figure 9 illustrates the response of ferri/ferrocyanide on ***GC*NO$_2$** in a 0.1 M KCl + 1.6 mM $Fe(CN)_6^{3-}$ aqueous solution. Cyclic voltammograms on bare and 0.1-modified ***GC*NO$_2$** electrode have the same shapes: the direct reduction of ferricyanide is accomplished with practically no modification of the redox potentials or the peak currents intensities. However, on 1- and 10-modified electrodes, the ferri/ferrocyanide redox system disappears. This behavior is similar to that observed on electrodes modified by 4-nitrophenyl groups[7,31] via electrochemical reduction of the corresponding diazonium salt: the absence of the electrochemical response of $Fe(CN)_6^{3-/4-}$ couple was first attributed to the hydrophobicity

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(31) Cabet-Deliry, E.; Chaussé, A.; Griveau, S.; Mercier, F.; Pinson, J.; Vautrin-Ul, C. Submitted to *J. Mater. Chem.*

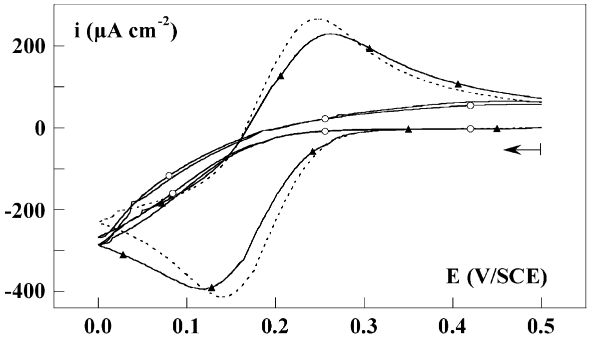

Figure 9. Cyclic voltammograms on (- - -) bare GC, (▲) 0.1-modified, (──) 1-modified, and (○) 10-modified ***GC*NO₂** in 0.1 M KCl aqueous solution containing 1.6 mM $Fe(CN)_6^{3-}$. Scan rate 0.2 V s^{-1}. Modification of electrode surface consisted of dipping the electrode in a 0.1, 1, or 10 mM PNBD solution in ACN for 1 h.

of the film and later to change of GC electronic properties during reductive grafting leading to a decrease of the rate of electron transfer. In contrast to what is observed with ferri/ferrocyanide, the nitrotoluene/nitrotoluene radical anion couple is clearly observed on ***GC*NO₂** as on a clean GC surface and there is very little difference between the two voltammograms, while this same couple is slightly slower on ***Fe*NO₂** than on a clean iron electrode (Figures S3 and S4, Supporting Information). This behavior would imply that nitrotoluene diffuses in the organic layer which would not be possible to ferricyanide due to hydrophobicity of the organic layer. The slowness of the response of the ferri/ferrocyanide couple on the modified electrodes can also be attributed to repulsive interactions between the hydrophobic film and the hydrophilic probe. This prevents the ferricyanide from penetrating the film and interacting with the electrode. These results agree with those obtained by AFM: at low PNBD concentration (0.1 mM), the layer is very thin and not homogeneous. Defects allow access to the underlying GC, so that the ferri/ferrocyanide couple is still observed. As PNBD concentration increases (1 to 10 mM), holes are filled and the surface does not present any uncovered place, preventing the redox probe from approaching the electrode surface.

Influence of Other Factors on Grafting. We have also checked the influence of the temperature during the soaking of the electrodes in the PNBD solution (10 mM in ACN) on the chemical grafting kinetics. The temperature range studied was 0−20 °C. Analysis of the substrates by cyclic voltammetry reveals that grafting occurs whatever the temperature. Moreover, the amount of electroactive nitrophenyl groups grafted increases with the temperature (data not shown).

The state of the substrate surface may also influence the grafting process: on easily oxidized metals such as iron, grafting could take place on an oxide layer despite the care taken during the preparation of the electrodes. We therefore achieved grafting experiments on iron, in a glovebox with an atmosphere of less than 2 ppm of O_2. There was no significant difference with the above results, obtained in laboratory atmosphere conditions.

Discussion

All the experiments described in the preceding section point to the spontaneous attachment of nitrophenyl groups on all studied surfaces: glassy carbon and metals, from easily oxidized iron to glassy carbon. Cyclic voltammetry allows observation of the reduction of the nitrophenyl moiety, FT-IRRAS spectra evidence the vibrations of the nitro groups, and these groups can also be observed through a separate peak in XPS; AFM shows the formation of a layer on top of iron, which continuously grows with time and concentration. These layers are strongly attached on the surfaces and can be obtained from rather dilute solutions starting from 0.1 mM and in times of minutes.

Film thickness measurements deduced from cyclic voltammetry and AFM both show the formation of multilayers on the surfaces. However, electrochemical data do not exactly correspond to those obtained by AFM: on iron, thicknesses calculated from voltammetry are equivalent to 2−6 monolayers, whereas AFM measurements point to thicker layers (5.2−9.7 nm, i.e., 8−15 monolayers, Tables 2 and 3). There is therefore a large difference between results obtained by the two methods. One can wonder about the origin of these discrepancies. A hypothesis would be that a part of the nitro groups is lost as nitrite ions due to aryl substitution during the growth of the layer. To check this hypothesis we looked for nitrite in the solution (see Supporting Information) and could not detect any. These results agree those obtained by McDermott[10b] during the electrochemical attachment of 4-diethylaminophenyl groups; the authors showed a simultaneous increase of the intensities of aromatic (C═C) band and of aromatic amines (phenyl−N) band on IRRAS spectra of GC modified electrodes when deposition time increased, indicating no loss of any function. One should therefore rationalize the fact that a number of nitro groups are still present in the layer. This number, evaluated by electrochemistry, corresponds approximately to only a very few monolayers. It is likely that these electrochemically detected groups are located at the electrode−layer interface and that the nitro groups further away from the electrode are not accessible to electron transfer. Another possible unlikely explanation would be the crowding existing in the layer which could push most of the nitro group out of planarity and would make them much more difficult to reduce (so difficult that their wave would be out of the electroactivity range). A last hypothesis could be the growth of further layer by simple adsorption of nitrophenyl groups on the initial layer. To conclude, these results tend to show that a part of the grafted nitrophenyl groups are electrochemically inactive, so that cyclic voltammetry does not allow a quantitative determination of all the surface groups. The above results also indicate that there remains a number of unsolved problems concerning the structure of these layers and we are currently investigating these problems.

The formation of the layer is accompanied by the loss of N_2^+, as indicated by XPS and FT-IRRAS measurements. This shows that a decomposition of the diazonium moiety occurs during the grafting. However, it is difficult to propose a mechanism that applies to all the materials used, as they differ in their physical and chemical properties. In a recent work,[13] the spontaneous reduction of diazonium salts on electrochemically reduced PTFE was ascribed to an open circuit potential-based mechanism. Lately, Hurley and

McCreery[27] showed the derivatization of Cu and oxide Cu surfaces with various aryl diazonium salts at open circuit potential (OCP) in aqueous and acetonitrile solutions. The authors showed the formation of mono- or muti-layer depending on diazonium salt used and deposition conditions. In all the deposition conditions studied, the layer is strongly attached to the surface. They proposed the formation of Cu−C and Cu−O−C linkage between the substrate and the phenyl ring on the basis of XPS measurements. The authors explain the multilayer formation as follows: an initial monolayer is formed, due to the reduction of the diazonium cation by metallic copper, then, subsequent diazonium cation in solution is reduced (thanks to electrons that can either tunnel through the attached phenyl layer or be conducted trough the conjugated π system) leading to a radical that attacks an attached phenyl ring. Another bonding possibility which leads to multilayer formation is azo coupling of diazonium cation with an attached ring. In the present study, an OCP mechanism could be applied in the case of iron, zinc, and copper, which have OCP more negative than the reduction potential of PNBD. The species then responsible for the first monolayer attachment to the surface should be the same radical involved in the electrochemical grafting reaction. It is more difficult to explain the reaction leading to the grafting on GC substrates. From XPS measurements,[8c,32] it is known that a typical polished GC surface presents graphitic regions but also various surface functional groups: phenolic, carboxyl, and carbonyl groups. Surface phenolic groups may undergo a coupling reaction with diazonium cations[7a,33] leading to the formation of azo derivatives. This could explain the formation of the initial organic layer on GC. Then, the formation of multilayers could be explained by the same kind of coupling reactions suggested above.

Conclusion

Dipping a carbon or metal sample into a solution of 4-nitrobenzene diazonium salt in acetonitrile results in the spontaneous formation of an aryl layer on the different surfaces. These aryl layers have been characterized through cyclic voltammetry, FT-IRRAS, XPS, and AFM, and all these methods point to the formation of an organic layer thicker than a monolayer under the grafting conditions used. This layer is strongly attached to the surface as it resists sustained ultrasonic rinsing. It is formed rather rapidly (for example in 5 min in a 10 mM solution as in Table 2) and could therefore be useful for practical applications. This paper mainly describes the formation of an organic layer without electrochemical induction. This electroless process could be applied to other diazonium salts. This could lead to the grafting of a large number of substituted aryl groups and could thus make this reaction interesting for further applications, as already reported for electrochemically generated layers.

Acknowledgment. S. Griveau is grateful to the *Conseil Général de l'Essonne* for providing financial support.

Supporting Information Available: XPS spectra of bare and modified surfaces, cyclic voltammograms of various samples, and investigation of the grafting solution for cleaved substituents (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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