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William Richard, David Evrard, Pierre Gros. New insight into 4-nitrobenzene diazonium reduction process: Evidence for a grafting step distinct from NO<sub>2</sub> electrochemical reactivity. *Journal of electroanalytical chemistry and interfacial electrochemistry*, 2012, vol. 685, pp.109-115. 10.1016/j.jelechem.2012.09.014 . hal-00744350

**HAL Id: hal-00744350**

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**To link to this article** : DOI:10.1016/j.jelechem.2012.09.014  
URL : <http://dx.doi.org/10.1016/j.jelechem.2012.09.014>

**To cite this version :**

Richard, William and Evrard, David and Gros, Pierre *New insight into 4-nitrobenzene diazonium reduction process: Evidence for a grafting step distinct from NO<sub>2</sub> electrochemical reactivity.* (2012) Journal of Electroanalytical Chemistry, vol. 685 . pp. 109-115.  
ISSN 1572-6657

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# New insight into 4-nitrobenzene diazonium reduction process: Evidence for a grafting step distinct from NO<sub>2</sub> electrochemical reactivity

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## ABSTRACT

Electrochemical and spectroscopic investigations were performed in order to clarify the mechanism of 4-nitrobenzene diazonium reduction on glassy carbon in protic medium. The number and nature of the electron transfer processes were found to be strongly correlated to the electrode surface state. On polished electrode two different reduction peaks were observed. Selective electrolyses realized at the corresponding potential definitely proved that the grafting process actually occurs at a potential distinct from NO<sub>2</sub> electroreduction, this latter inducing the presence of the quasi-reversible NO/NHOH redox couple at the electrode surface. These results were confirmed by XPS analyses. Furthermore, voltammetric experiments using Fe(CN)<sub>6</sub><sup>3-</sup> showed that the electrochemical properties of the modified electrode strongly depend on the potential applied for grafting, which modulates the nitro group oxidation state. All the results suggested that the electrode functionalization was more efficient when grafting and NO<sub>2</sub> reduction were performed separately.

### Keywords:

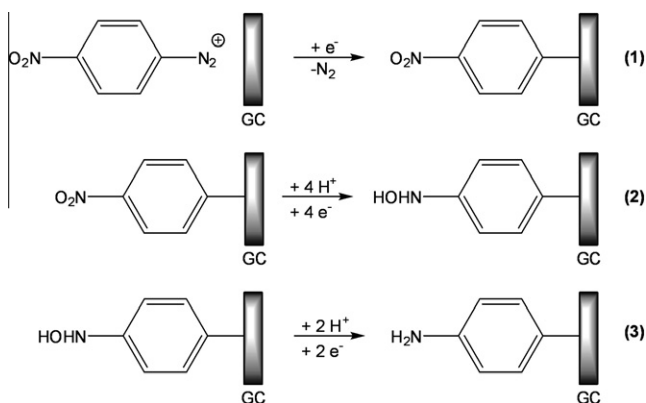
4-Nitrobenzene diazonium  
Electrode functionalization  
Grafting process  
Reduction mechanism  
Cyclic voltammetry

## 1. Introduction

Among all the numerous strategies reported in the literature for carbon-based surface modification, diazonium grafting is probably the most promising one since it provides an easy covalent way to immobilize additional functional group of interest. Since the first report by Pinson and coworkers in the early 1990s [1], functionalization via diazonium reduction has received an increasing interest and the numerous studies devoted to explore the wide range of its potentialities have been recently reviewed [2–4]. The immobilized group affords specific chemical and physicochemical properties to the surface which are exploited in many application fields such as molecular electronics [5,6], energy conversion [7–9] and chemical [10–12] or biological [13,14] sensing. Depending on the aim of the work, it can also be used for further modification using chemical reaction such as click chemistry [15–17] and amine/carboxyl condensation [18,19] or to directly interrogate the functionalized surface.

Because it is commercially available and bears an electroactive NO<sub>2</sub> moiety, 4-nitrobenzene diazonium (NBD) is concerned with many applications, both as an electrochemical probe to characterize a surface or to modify its intrinsic properties. On the one hand, it has been used to evidence the difference of reactivity between

graphene single and multilayers [20], to identify diamond surface terminations and measure the density of hydrogen atoms bonded to the surface [21] or to illustrate nanoscale patterning of carbon surface [22]. On the other hand, NBD was reported to modify the electrical properties of graphene field-effect transistors [23] or to help at covalent immobilization of organometallic model of enzyme onto carbon surface [24]. All these applications need the electrochemical reactivity of NBD to be clearly defined and this is the reason why it has been extensively investigated in both organic and aqueous media [25–30]. It is nowadays well established that the reduction of the nitro moiety in protic medium leads to the formation of hydroxylamine (NHOH) group [31] which belongs to the reversible nitroso/hydroxylamine (NO/NHOH) redox couple. Moreover, further reduction results in amination of the hydroxylamine groups (Scheme 1). In aprotic solution, NO<sub>2</sub> can be reversibly converted into radical anion (NO<sub>2</sub><sup>-•</sup>) [32]. Despite numerous comparative works on the influence of the electrolyte salt or the effect of substrate material [31,33,34], the whole reduction mechanism of NBD still remains unclear and gave rise to contradictory interpretations in the literature. Particularly our attention was drawn on diazonium grafting and NO<sub>2</sub> first reduction step. Depending on the authors, one or two irreversible peaks are reported for NBD reduction (Table 1). Brooksby and Downard noticed that the first, smaller peak was not always present and that its corresponding current varied from one experiment to another [31]. On the contrary Baranton and Belanger systematically noticed a first reduction peak distinct from that assigned to diazonium reduction [33,35]. Since the origin of this first peak remains unknown, many



**Scheme 1.** The three possible reduction steps for NBD in aqueous media.

authors assumed both NBD grafting and  $\text{NO}_2$  reduction reactions to occur simultaneously [3,30,31,36–38]. Only very recently Cline et al. [27] suggested a grafting process to occur at less cathodic potential although without providing further details on the grafted species. These discrepancies are certainly the reason why a high cathodic overpotential is systematically applied to ensure the interface modification (Table 1). Nevertheless a full comprehension

of NBD reduction mechanism is of critical interest since the chemical and electrochemical properties of the resulting modified surface strongly depend on the nature of the functional group borne on the organic layer.

In this work, we present simple considerations based on cyclic voltammetry and potentiostatic grafting experiments to definitely clarify (i) the conditions inducing a double cathodic signal and (ii) the reactions occurring at both reducing steps in order to provide a fully understood tool to chemists aiming at surface functionalization. Electrochemical results are confirmed and completed by XPS analyses highlighting the relationship between the potential used for grafting and the major chemical group present onto the electrode surface. Finally the evolution of the functional group redox state, which depends on the potential applied to the electrode, has been evidenced by means of cyclic voltammograms using  $\text{FeCN}_6^{3-/4-}$  as a redox probe.

## 2. Experimental

### 2.1. Chemicals

All products were used as received. 4-nitrobenzene diazonium (NBD) tetrafluoroborate ( $\text{C}_6\text{H}_4\text{N}_3\text{O}_2\text{BF}_4$ , 97%) was purchased from Aldrich. Potassium ferricyanide(III) ( $\text{K}_3\text{Fe}(\text{CN})_6$ , 99% powder) was

**Table 1**  
Literature survey on NBD grafting and reduction steps.

Medium/conditions	Substrate	$E_p$ (V) <sup>a</sup>	Attribution	$E_g$ (V) <sup>b</sup>	Ref.
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 2 mM	GC	−0.08 irrev <sup>c</sup> −1.28 rev	Diazonium reduction $\text{NO}_2$ reduction into radical anion	−0.88	[54]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 1 mM	GC	0.08 irrev −1.17 rev	Diazonium reduction $\text{NO}_2$ reduction	ocp <sup>d</sup>	[55]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 5 mM	GC	0.02 irrev No further investigation	Diazonium reduction	From −0.2 to −1.2 <sup>e</sup>	[46]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 2 mM	GC	0.03 irrev No further investigation	Diazonium reduction	ocp	[45]
ACN, 0.1 M $\text{Et}_4\text{NClO}_4$ 1.8 mM	GC	0.2 irrev −1.19 rev	Diazonium reduction	−0.6	[32]
ACN, 0.1 M $\text{Et}_4\text{NClO}_4$ 1.8 mM	HOPG	0.27 irrev −1.2 rev	Diazonium reduction No discussion		[32]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 1 mM	GC	−0.07 irrev −1.22 rev	Diazonium reduction $\text{NO}_2$ reduction into radical anion	−0.72	[30]
ACN, 0.1 M $\text{Et}_4\text{NBF}_4$ 1 mM	GC	0.41 irrev 0.06 irrev	Unattributed Diazonium reduction	0.06, −0.24	[33]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 2 mM	GC	−0.02 irrev −1.17 rev	Diazonium reduction $\text{NO}_2$ reduction into radical anion	− <sup>f</sup>	[3]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 1 mM	GC	0.08 irrev −0.89 irrev −1.16 rev	Diazonium reduction No discussion No discussion	−0.17, −0.42, −0.67	[38]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ , after $\text{NO}_2$ grafting	Carbon nanofiber	−0.04 irrev −1.18	Diazonium reduction $\text{NO}_2$ reduction into radical anion	−0.04, −0.6	[36]
ACN, 0.1 M $\text{Et}_4\text{NBF}_4$ 1 mM	GC	0.46 irrev 0.1 irrev	Unattributed Diazonium reduction	0.1, −0.2	[35]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 0.59 mM	PPF	0.19 irrev −0.15 irrev	Unattributed Diazonium reduction	−0.3	[31]
ACN, 0.1 M $\text{Bu}_4\text{NBF}_4$ 2 mM	GC	0.49 irrev 0.05 irrev −0.6 irrev	Unattributed Diazonium reduction	0.53	[27]
0.1 M $\text{H}_2\text{SO}_4$ after $\text{NO}_2$ grafting	GC	0.48 irrev 0.1 irrev	Unattributed Diazonium reduction	0.1, −0.2	[35]
0.5 M HCl 1 mM	GC	0.4 −0.34 irrev	Diazonium reduction $\text{NO}_2$ reduction into amine	−0.72	[29]
0.1 M $\text{H}_2\text{SO}_4$ 0.89 mM	PPF	−0.03 irrev	Diazonium reduction	−0.3	[31]
0.1 M $\text{H}_2\text{SO}_4$ 1.5 mM	GC	−0.14 irrev −0.49 irrev	Diazonium reduction $\text{NO}_2$ reduction into amine	−0.2	[36]

<sup>a</sup> Cathodic peak potential obtained from CV experiment. All the potential values are referred to SCE.

<sup>b</sup> Potential used for electrochemical grafting.

<sup>c</sup> irrev: Irreversible; rev: reversible.

<sup>d</sup> ocp: Open-circuit potential.

<sup>e</sup> In this work, different potential values were applied for grafting, together with different electrolysis times.

<sup>f</sup> No grafting potential is provided in this work since it is a review.

obtained from Sigma–Aldrich. Tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ , 98%), potassium dihydrogenophosphate ( $\text{KH}_2\text{PO}_4$ ), di-potassium hydrogenophosphate ( $\text{K}_2\text{HPO}_4$ ) and acetonitrile (extra dry) were supplied by Acros Organics.

Sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) was purchased from Fischer Chemical. Acid solutions were prepared by dilution of hydrochloric acid (HCl 37%) from VWR using Milli-Q water (18 M $\Omega$  cm), and were deaerated by bubbling Nitrogen during 10 min. A gas stream was maintained over the solutions during experiments.

## 2.2. Apparatus

All the electrochemical experiments were performed at room temperature using a Metrohm  $\mu$ -Autolab II potentiostat interfaced to a personal computer and controlled with NOVA 1.7 software package. A classical three-electrode glass cell was used with a Metrohm platinum rod and a Radiometer saturated calomel electrode (SCE) connected to the cell by a capillary as counter and reference electrode, respectively. All the potentials are given with respect to SCE. Working electrode was a 3 mm diameter glassy carbon (GC) rotating disk electrode from Radiometer.

XPS measurements were performed with a K alpha spectrometer from Thermo Scientific, using the monochromatized Al K $\alpha$  line at 1486.6 eV. A fixed analyser pass energy of 50 eV was used for N(1s) core level scans. The binding energy scale was calibrated to  $284.5 \pm 0.1$  eV for the main C(1s) feature. Experiments used GC plate (5.5 mm diameter) from Mersen as substrate material.

## 2.3. Electrode modification

Prior to modification, GC electrodes and GC plates were manually polished to a mirror-like finish successively with 9  $\mu\text{m}$ , 3  $\mu\text{m}$  and 1  $\mu\text{m}$  diamond powder from Presi on a cloth polishing pad. After each step, the electrode was thoroughly rinsed with Milli-Q water and sonicated in ethanol for 5 min in order to remove any impurity.

In order the influence of GC surface state to be evaluated, some electrodes were only coarsely polished with 9  $\mu\text{m}$  diamond powder. For the sake of clarity, this kind of electrode is referred to as “unpolished electrode”.

Freshly polished electrode was modified from acetonitrile + 0.1 M  $\text{Bu}_4\text{NBF}_4$  or 0.1 M HCl (pH 1) solutions both containing 2.5 mM NBD, either by constant potential electrolysis at 0.3 V during 300 s or by simply dipping the electrodes into the solution for the same duration. After modification, the electrode was carefully rinsed with Milli-Q water before and after sonication in ethanol during 5 min to remove weakly adsorbed moieties. The same procedure was used for GC plate modification.

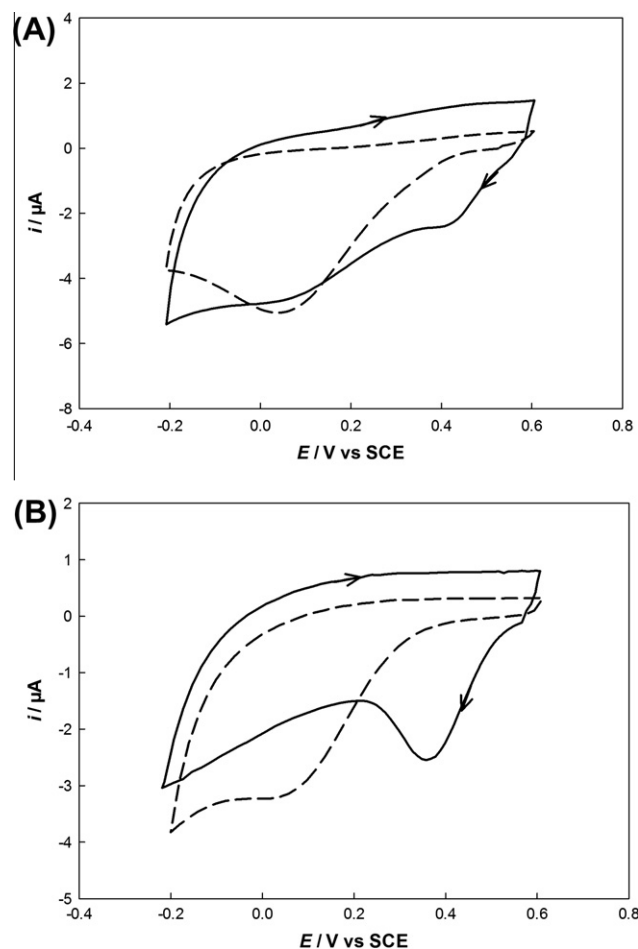
## 2.4. Solution preparation

Most cyclic voltammograms were recorded in 0.1 M HCl (pH 1). pH modification between 0 and 2 was also performed using HCl solution at the corresponding concentration. For higher pH value, 0.1 M solutions of  $\text{KPF}_6$  (pH 3.6), carbonate buffer (pH 5 and 6) and phosphate buffer (pH 7) were used.

## 3. Results and discussion

### 3.1. Influence of GC surface state

Fig. 1 presents the cyclic voltammograms (CVs) recorded on bare GC electrode in 0.1 M HCl (Fig. 1A) and in acetonitrile (Fig. 1B) both containing 2.5 mM NBD. On a properly polished



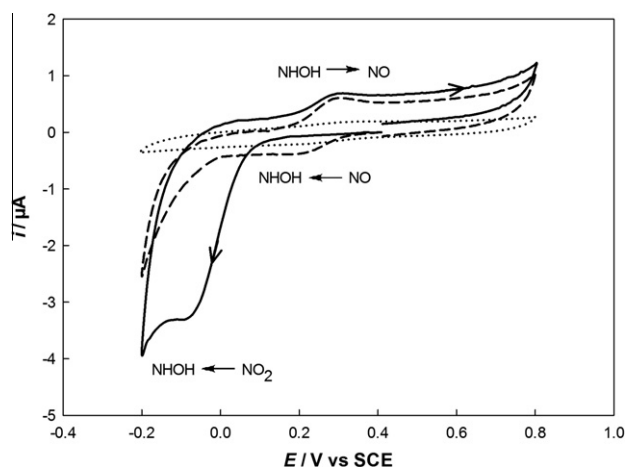
**Fig. 1.** Cyclic voltammograms recorded in 0.1 M HCl (A) and in acetonitrile (B) solutions both containing 2.5 mM NBD. Solid lines: polished GC electrode (see Section 2.3); dashed lines: unpolished GC electrode. Scan rate: 100 mV s $^{-1}$ .

electrode (as described in the Experimental Section) a cathodic signal was systematically observed around 0.4 V in both solutions (solid lines). Furthermore a second signal was recorded around 0.05 V in HCl (Fig. 1A, solid line), thus proving that two distinct processes actually occurred in aqueous solvent. Although a standard potential  $E^\circ = 0.05$  V has been found by Andrieux and Pinson, a contribution from phenyl radical reduction could hardly be invoked, the same authors reporting a corresponding small peak at  $-0.64$  V [39], far beyond the potential range used here. Moreover, the rather slow scan rate used here is not favorable to the observance of radical species. In comparison no more reduction reaction was observed in acetonitrile (Fig 1B, solid line) in the same potential range. This last result is in accordance with literature data indicating that  $\text{NO}_2$  reduction in aprotic solution did not afford NHOH groups formation but rather led to the corresponding radical anion at very negative potential [32]. Consequently, in aprotic medium the cathodic peak observed around 0.4 V corresponds to NBD grafting. On unpolished electrode only one cathodic peak was noticed whatever the electrolytic solution (dashed lines). Clearly the presence of the peak at 0.4 V is strongly correlated to the surface state, in accordance with the work by Cline et al. [27]. However, the hypothesis proposed by these authors that the multiple peaks could be the result of different carbon sites seems to be caught out: assuming that the solvent has no influence on these sites, the latter hypothesis fails at accounting for the differences reported here. It is noteworthy that all these peaks disappeared on the second scan (not shown) whatever the medium and the

electrode preparation, as a consequence of a blocking process of the GC surface. All these results were also observed when experiments were conducted with a diazonium concentration ten times lower. Once the conditions leading to the observation of two reduction peaks are clarified, an important question arises: since in aqueous media a peak is observed at 0.05 V whatever the surface state of the electrode, does a unique reaction occur on first and second peaks in the case of properly polished electrode, or is there two distinct reduction reactions? In other words, do electrolyses performed at both potentials lead to a same or different grafted layer? To answer these questions, several grafting experiments were performed at different potentials.

### 3.2. Influence of grafting potential

In order to identify the reduction process occurring around 0.4 V, a constant potential electrolysis was performed at 0.3 V during 300 s in the 2.5 mM NBD-containing HCl solution with a freshly polished GC electrode. This potential was chosen in order the corresponding reaction to be diffusion-controlled. The resulting modified electrode was rinsed as described in the Experimental Section. Then two successive CVs were recorded in a diazonium-free HCl solution (Fig. 2). On the first cycle (solid line), a reduction peak was observed at  $-0.1$  V on the forward scan. Comparatively no significant cathodic current was shown in the same potential range without NBD in the electrolysis solution (dotted line). This last result proves that the electrolysis performed at 0.3 V with NBD leads to a grafting process inducing the presence of redox species at the electrode surface. Then a quasi-reversible signal was recorded at 0.20 V on the following cycle (dashed line), corresponding to the redox nitroso/hydroxylamine couple as already mentioned [32]. It is noteworthy that this signal was visible only from the first reverse scan, contrary to the observation by Ortiz et al. who performed NBD reduction at  $-0.72$  V and thus noticed this signal from the first cathodic sweep [29]. Practically no cathodic current was observed on the first forward scan before the electrode potential decayed to  $-0.1$  V. Consequently no hydroxylamine moiety was produced during the constant potential electrolysis at 0.3 V. Reduction of  $\text{NO}_2$  into NHOH actually occurred at  $-0.1$  V during the first CV. The corresponding peak dramatically decreased on the second CV indicating that most of the accessible  $\text{NO}_2$  functions were reduced during the first scan. All these results clearly indicate that (i) NBD grafting occurred during the electrolysis at 0.3 V,

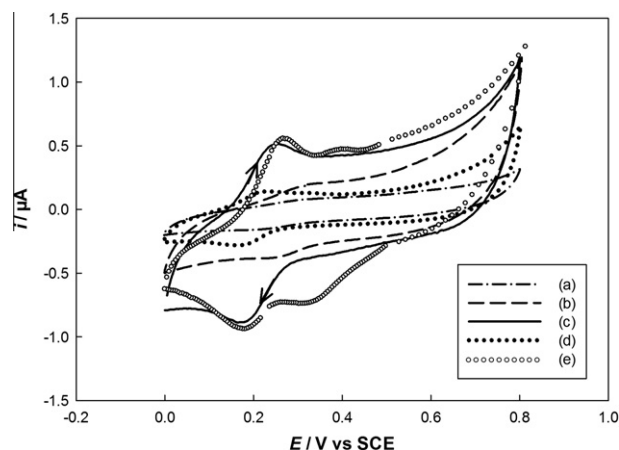


**Fig. 2.** Cyclic voltammograms recorded in 0.1 M HCl on polished GC electrode modified by electrolysis at 0.3 V during 300 s in 0.1 M HCl (dotted line) and in 2.5 mM NBD-containing 0.1 M HCl solution (solid line: first scan; dashed line: second scan). Scan rate:  $50 \text{ mV s}^{-1}$ .

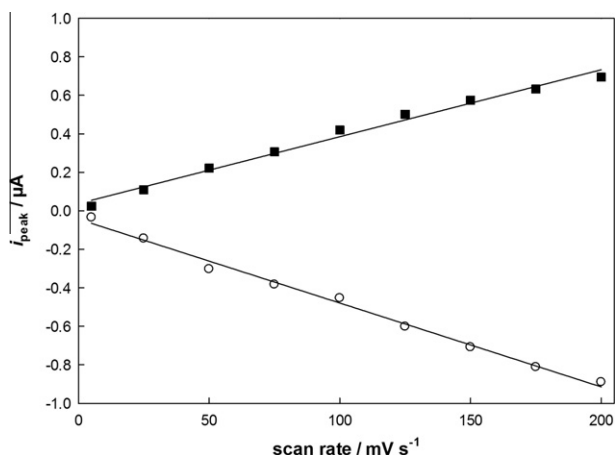
which is a much higher potential than those usually reported for NBD potentiostatic grafting (see Table 1 for an overview of grafting potential values) and, (ii) at this potential the  $\text{NO}_2$  moiety does not experience any reduction into NHOH. Thus, on carefully polished GC substrate, it is possible to distinguish NBD grafting from  $\text{NO}_2$  reduction, contrary to what was suggested by Brooksby and Downard or by the group of Saveant who performed NBD reduction at  $-0.3$  V [31] and  $-0.2$  V [36] respectively.

Fig. 3 shows CV recorded in a diazonium-free HCl solution with a polished GC electrode modified by constant potential electrolysis at 0.3 V during 300 s in the 2.5 mM NBD-containing HCl solution (curve b). The voltammogram exhibited a more capacitive response than that observed on a clean polished GC electrode (curve a), thus confirming that a grafting process actually occurred during the electrolysis at 0.3 V. Contrary to that observed in Fig. 2 (dashed line), no reversible signal corresponding to the redox nitroso/hydroxylamine couple was recorded in this case. The main reason is that the lowest potential applied during the CV was 0 V, thus avoiding the reduction of  $\text{NO}_2$  into NHOH group as demonstrated before. Only a little, bad-defined reversible system was observed around 0.27 V on both grafted and unmodified electrodes and was assumed to belong to the quinone redox system often observed on GC after polarization [40–42]. The same behavior was obtained when the electrolysis at 0.3 V was performed in acetonitrile containing 2.5 mM NBD. This last result proves once again that the reaction occurring at 0.3 V corresponds to a grafting process which leaves  $\text{NO}_2$  groups unchanged, this latter being reduced at a more cathodic potential as shown in Fig. 1.

To get further information on the grafted layer, the modified electrode was held at  $-0.1$  V during 300 s in diazonium-free HCl solution. A CV was then recorded (Fig. 3, curve c) highlighting another redox activity centered at 0.20 V. The influence of the potential scan rate on both cathodic and anodic peak currents is shown in Fig. 4A. The linear variation observed for potential scan rates from 5 to  $200 \text{ mV s}^{-1}$  suggests that the electroactive species involved in the reaction did not diffuse from the bulk solution but rather were grafted onto the electrode surface [43]. On the other hand the peak potential difference (ca. 80 mV) suggested a quasi-reversible redox system. The 80 mV value observed was probably due to the electron transfer resistant properties of the grafted layer. The evolution of both peak potentials as a function of pH



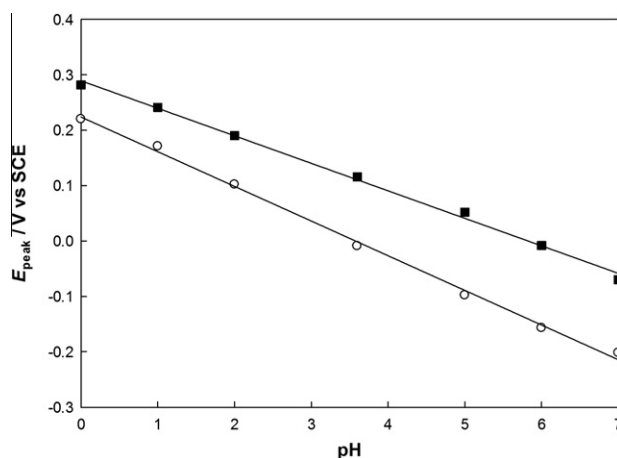
**Fig. 3.** Cyclic voltammograms recorded in 0.1 M HCl on: (a) bare GC electrode; (b) GC electrode modified by electrolysis at 0.3 V during 300 s in 2.5 mM NBD-containing 0.1 M HCl solution (GC- $\text{NO}_2$  electrode); (c) electrode polarized at  $-0.1$  V during 300 s in diazonium-free 0.1 M HCl solution (GC-NHOH electrode); (d) GC electrode dipped in 2.5 mM NBD-containing 0.1 M HCl solution during 300 s and polarized at  $-0.1$  V during 300 s in diazonium-free 0.1 M HCl solution; (e) GC electrode modified by two successive electrolyses during 300 s at 0.3 V and  $-0.1$  V in 2.5 mM NBD HCl solution. Scan rate:  $50 \text{ mV s}^{-1}$ .



**Fig. 4A.** Influence of the potential scan rate on both cathodic (white circles) and anodic (black squares) peak currents observed at 0.20 V on the CV recorded in 0.1 M HCl solution with GC-NHOH electrode.

(Fig. 4B) confirmed the presence of a pH-dependent redox process. The experimental slopes ( $-50$  and  $-63$  mV per decade for anodic and cathodic peaks, respectively) were very close to the theoretical one which corresponds to a one proton/one electron exchange [44]. It was verified that CV was identical to that obtained with a clean GC electrode (Fig. 3, curve a) when the first electrolysis at 0.3 V was performed without NBD. All these data are in agreement with the presence of the NHOH/NO reversible couple whose apparent standard potential is consistent with literature data [31]. Keeping in mind that the second electrolysis at  $-0.1$  V was performed in a NBD-free HCl solution, all these results demonstrate undoubtedly that  $\text{NO}_2$  group was already present onto GC surface at the end of the first electrolysis. Actually, the diazonium function was reduced at 0.3 V and the grafted nitro moiety was further reduced into hydroxylamine group at  $-0.1$  V. For the sake of clarity, the corresponding modified electrodes were indicated as GC- $\text{NO}_2$  and GC-NHOH, respectively.

The integration of the cathodic peak of the quasi-reversible system exhibited by GC-NHOH electrode (Fig. 3 curve c) gave an average surface coverage  $\Gamma = 1.5 \times 10^{-10}$  mol  $\text{cm}^{-2}$  (considering a two electron-exchange process), which is close to the value reported by many authors for a monolayer [31,32]. However, it has to be noticed that in the experimental self-inhibiting conditions used, the formation of a multilayer organic film was expected, so that the

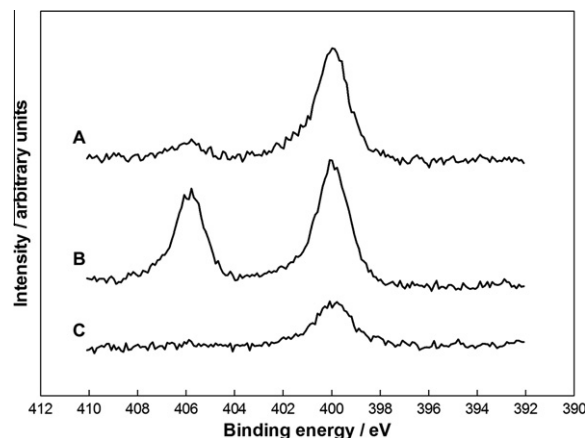


**Fig. 4B.** Influence of pH on both cathodic (white circles) and anodic (black squares) peak potentials on the CV plotted with GC-NHOH electrode. Scan rate:  $50$  mV  $\text{s}^{-1}$ .

$\Gamma$  value obtained may be correlated only to the accessible NHOH moieties. When GC electrode was simply dipped into NBD solution during 300 s without applying any potential and then experienced electrolysis at  $-0.1$  V in diazonium-free HCl, a similar redox system at 0.20 V was observed (Fig. 3, curve d). The corresponding very little surface coverage deduced from the integration of the cathodic peak (ca.  $3.5 \times 10^{-11}$  mol  $\text{cm}^{-2}$ ) is consistent with some NBD spontaneous grafting on GC leading to a submonolayer film [45–47]. The comparison between both  $\Gamma$  values clearly evidences that the reduction process at 0.3 V is associated to diazonium grafting, thus inducing a higher surface coverage. It is noteworthy that the NO/NHOH quasi-reversible system was also observed when both electrolyses at 0.3 and  $-0.1$  V were performed in 0.1 M HCl containing 2.5 mM NBD; however in this case, another ill-defined, quasi-reversible system ( $\Delta E = 75$  mV) around 0.36 V was noticed (Fig. 3, curve e). This latter may be explained by the presence of NO/NHOH redox systems that experienced different electronic environments due to the successive grafting. This last result is indicative of the formation of a thicker and non-homogeneous organic layer, which is in accordance with the work of Haccoun et al. [37] who reported the structural characteristics of the grafted layer to be potential and grafting time dependent. Consequently it seems better to separate the grafting and the  $\text{NO}_2$  reduction steps in order the functionalized electrode to be the most efficient. This is only possible on carefully polished GC electrodes, the surface state of which undergoes NBD first reduction peak to occur around 0.4 V.

### 3.3. XPS characterization

In order to confirm our proposal, XPS experiments were performed on bare GC, GC- $\text{NO}_2$  and GC-NHOH electrodes (Fig. 5). The spectrum recorded for GC- $\text{NO}_2$  exhibited two peaks at 405.9 and 399.9 eV (Fig. 5B), the former being slightly lower. Comparatively the first peak was not visible on bare GC spectrum (Fig. 5C). According to literature data, this first peak can be attributed to nitro groups [48,49]. This result undoubtedly proves our hypothesis that diazonium grafting occurred when electrolysis was performed at 0.3 V. The second peak at lower energy is more difficult to assign, since it can be assigned to several nitrogen-bearing groups. Ortiz et al. [29] suggested a complex contribution of various nitrogen reduced forms, namely  $\text{NH}_2$ , NHOH and azo groups. In our case, the presence of NHOH moieties is excluded by electrochemical measurements which did not exhibit the reversible NHOH/NO system on GC- $\text{NO}_2$  electrode (Fig. 3, curve b). Because of the long electrolysis time (ca. 300 s), we propose the peak at 399.9 eV to be assigned both to azo groups, in

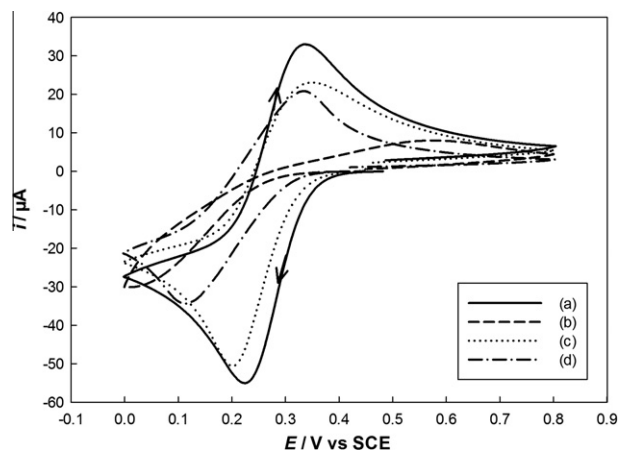


**Fig. 5.** X-ray photoelectron spectra of N(1s) core levels of: (A) GC-NHOH electrode; (B) GC- $\text{NO}_2$  electrode; (C) bare GC.

accordance with the study by Doppelt et al. [50] and to amine groups generated by nitro reduction under the XPS beam [51,52]. It is noteworthy that a peak was recorded on bare GC at the same energy. This observation has been previously reported [32] but remains unexplained. The spectrum of GC-NHOH electrode exhibited the same two peaks at 405.9 and 399.9 eV (Fig. 5A). The first peak attributed to nitro group was significantly lower than that on GC-NO<sub>2</sub>, thus confirming the reduction of NO<sub>2</sub> groups when operating at -0.1 V. On the contrary, the intensity of the second peak at 399.9 eV remained nearly constant. However, the global amount of nitrogen decreased, indicating a loss of material. This fact has already been observed by Ortiz et al. [29] who proposed a fraction of the grafted phenyl groups to be cleaved from GC surface. Here, the fact that the peak at 399.9 eV remained constant whereas the peak corresponding to NO<sub>2</sub> group decreased indicates a conversion of this latter into another nitrogen-bearing function, namely NHOH. This is consistent with electrochemical data which indicate the presence of the NO/NHOH redox couple (Fig. 3, curve c). A little amination process could also be envisaged, although the reducing potential used was significantly too high. The presence of the peak at 405.9 eV, although lower than for GC-NO<sub>2</sub>, is in agreement with the hypothesis of a partial reduction of the nitro groups, the most accessible ones only being reduced at -0.1 V.

### 3.4. Electrochemical response towards redox probes

Finally, the response of the modified electrodes towards an electrochemical probe, namely Fe(CN)<sub>6</sub><sup>3-</sup>, was examined in 0.1 M HCl (Fig. 6). The electrochemical response of Fe(CN)<sub>6</sub><sup>3-/4-</sup> was almost totally suppressed on GC-NO<sub>2</sub> electrode (Fig. 6, curve b). Comparatively, the typical redox activity appeared on GC-NHOH (Fig. 6, curve c) although both anodic and cathodic peak currents were lower than those recorded on bare GC electrode (Fig. 6, curve a). These results strongly support the hypotheses proposed above and the blocking behavior of the functionalized electrode can thus be clearly explained. During the first electrolysis at 0.3 V, NBD was effectively grafted onto the electrode surface but the NO<sub>2</sub> moiety remained unchanged, providing a high electronic density interface which enhanced the electrostatic repulsion with ferricyanide anions. By applying -0.1 V, most of NO<sub>2</sub> groups were reduced into NHOH moieties. At pH 1, these latter are expected to be under their corresponding protonated form (assuming the pK<sub>a</sub> of hydroxylamine functions to be close to that of phenylhydroxylamine [53] ca. 1.96), thus making a more positively charged organic layer



**Fig. 6.** Cyclic voltammograms recorded in 0.1 M HCl containing 5 mM Fe(CN)<sub>6</sub><sup>3-</sup> on: (a) bare GC electrode; (b) GC-NO<sub>2</sub> electrode; (c) GC-NHOH electrode; (d) electrode obtained after two electrolyses in a 2.5 mM NBD-containing HCl solution at 0.3 and -0.1 V respectively. Scan rate: 50 mV s<sup>-1</sup>.

which favors mass transfer of ferricyanide anions to the electrode. Moreover, the material loss occurring during the electrolysis at -0.1 V should result in a thinner layer, thus contributing to some extent to a less pronounced barrier effect. Finally, when both electrolyses at 0.3 and -0.1 V were performed in NBD-containing solution, the resulting voltammogram of Fe(CN)<sub>6</sub><sup>3-</sup> exhibited a capacitive behavior, typical of a strong barrier effect resulting from a thick layer (Fig. 6, curve d). Indeed, in this case both diazonium grafting and NO<sub>2</sub> reduction into NHOH occur during the second electrolysis at -0.1 V in the presence of NBD. This is also true when a single electrolysis was performed at -0.1 V in NBD-containing solution; in this case the CV of Fe(CN)<sub>6</sub><sup>3-</sup> exhibited a rather more capacitive behavior, suggesting a highly disordered layer (not shown). The comparison between curves (c and d) demonstrates once again the interest of grafting NBD at higher potential than that commonly used in the literature.

## 4. Conclusion

This work demonstrates that NBD grafting actually occurs at 0.3 V on carefully polished GC and that this reaction is strongly correlated to the electrode surface state. This potential value is much less reducing than that usually reported for NBD potentiostatic grafting. XPS data proved that electrolysis at 0.3 V affords a NO<sub>2</sub> layer onto the electrode surface. Consequently on properly polished substrate it is possible to distinguish between diazonium grafting process and NO<sub>2</sub> electrochemical reduction reactions. Supplementary reduction of NO<sub>2</sub> into NHOH in protic solvent was clearly identified at -0.1 V. Moreover the electrochemical properties of the modified electrode were found to be strongly dependent on the grafting potential which modulates the nitro group oxidation state. This result is of dramatic importance for chemists aiming at surface modification since it allows a better control of the barrier effect induced by the organic layer.

## Acknowledgements

The authors thank Jerome Esvan from the Centre Inter-universitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT) for XPS measurements and fruitful discussion.

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