Electrochemical Derivatization of Carbon Surface by Reduction of in Situ Generated Diazonium Cations

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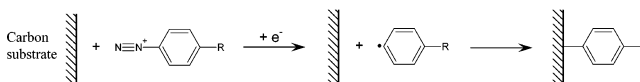*Received: August 11, 2005; In Final Form: October 14, 2005*

The derivatization of a glassy carbon electrode surface was achieved by electrochemical reduction of several in situ generated diazonium cations. The diazonium cations were synthesized in the electrochemical cell by reaction of the corresponding amines with $NaNO_2$ in aqueous HCl. The versatility of the method was demonstrated by using six diazonium cations. This deposition method, which involves simple reagents and does not require the isolation and purification of the diazonium salt, enabled the grafting of covalently bounded layers which exhibited properties very similar to those of layers obtained by the classical derivatization method involving isolated diazonium salt dissolved in acetonitrile or aqueous acid solution. Cyclic voltammetry and electrochemical impedance spectroscopy carried out in aqueous solutions containing electroactive redox probe molecules such as $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+}$ confirmed the barrier properties of the deposited layers. The chemical composition of the grafted layers was determined by X-ray photoelectron spectroscopy and surface coverage in the range 3×10^{-10} to 6×10^{-10} mol cm^{-2} was estimated for films grown in our experimental conditions.

Introduction

The electrochemical and chemical modification of carbon by reduction of diazonium salts attracted a lot of interest in the past decade.[1–5] Savéant and Pinson were the first to demonstrate that the reduction of an aryl diazonium cation afforded the corresponding aryl radical, which can further react with a carbon atom of the carbon substrate to yield the covalent bonding of this aryl group according to Scheme 1.[6] Very recently, Pinson and Andrieux have demonstrated that the generation of the aryl radical is a concerted process, which involves the electron transfer and the cleavage of dinitrogen before the formation of the covalent bond.[7] This modification procedure is very attractive because it avoids the use of oxidative conditions which can lead to the detrimental oxidation of the carbon substrate[8,9] and also because it allows the presence of selected functional groups on the aryl groups. The large variety of substituted aryl groups that were grafted at the carbon electrode surface was recently reviewed.[10] The specific substituent on the aryl group can be used to impart useful properties to the modified electrode and to elaborate more complex chemical structures that can have various applications.[10,11] For example, ionizable substituents such as $-COOH$, $-SO_3H$, and $-N(C_2H_5)_2$ can be used to bind metal complexes that can be further chemically reduced to generate metal/metal oxide species.[12,13] Ionizable groups can also provide charge selectivity properties that are useful for sensing applications.[14] The substituent also could be chosen to allow further chemistry such as to immobilize enzyme[15] and electroactive groups[16] and to perform combinatorial chemistry.[17]

On the other hand, a major disadvantage of the modification approach based on aryl diazonium salt is that the synthesis of the salt is required. Indeed, the synthesis and isolation of the diazonium salt are not always straightforward. The synthesis is

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SCHEME 1

commonly carried out in acidic media from the corresponding amine by using $NaNO_2$ as a reactant.[1,18–20] On the other hand, it might be interesting to have a modification procedure that will avoid this synthesis by using the amine as a precursor. Interestingly, the chemical modification of carbon powder, which makes use of an amine and relies on the in situ generation of the diazonium salt (addition of sodium nitrite in water or $NOBF_4$ in acetonitrile), has been investigated in great detail by the groups of Tour,[21] Compton,[22] and Bélanger[23] and is now industrially exploited by the Cabot Corporation.[24,25] Moreover, Morita et al.,[26] Blankespoor et al.,[27] and very recently our group[28] reported that an aromatic amine can be transformed into a diazonium by a standard diazotization procedure[29] and that the resulting solution can be used to modify carbon[26,27] or gold[28] electrode by electrochemical reduction.

In this work, we report the modification of glassy carbon electrode by electrochemical reduction of a diazonium salt generated in situ in the aqueous deposition solution without the isolation of the diazonium salt. The versatility of the method was demonstrated by using several diazonium salts. More specifically, the electrochemical modification was performed with the following in situ generated salts: 4-bromophenyldiazonium, 4-chlorophenyldiazonium, 4-nitrophenyldiazonium, 4-trifluoromethylphenyldiazonium, 4-carboxyphenyldiazonium, 4-sulfophenyldiazonium, and 4-diazo-*N*,*N*-diethylaniline. The modification was followed by cyclic voltammetry and the modified electrodes were characterized by cyclic voltammetry and electrochemical impedance spectroscopy in the presence of electroactive species and also by X-ray photoelectron spectroscopy to determine the surface coverage of aryl groups. The

resulting modified electrodes were compared with those obtained by electrochemical reduction of acidic and nonaqueous solutions containing the dissolved diazonium salt.

Experimental Section

The diazonium cations used for the derivatization of the glassy carbon electrode were identified as follow: 4-bromophenyl-diazonium (Br-PD), 4-chlorophenyldiazonium (Cl-PD), 4-ni-trophenyldiazonium (NO$_2$-PD), 4-trifluoromethylphenyldiazo-nium (CF$_3$-PD), 4-carboxyphenyldiazonium (COOH-PD), 4-sul-fophenyldiazonium (SO$_3$H-PD), and 4-diazo-*N,N*-diethylaniline (DEA-PD).

Reagents. Tetraethylammonium tetrafluoroborate (NEt$_4$BF$_4$) (Aldrich) was dried by heating at 80 °C under vacuum for 24 h. Potassium ferricyanide, potassium ferrocyanide, potassium chloride, hydrochloric acid, hexaamineruthenium(III) chloride, para-substituted anilines used for diazonium salt synthesis, sodium nitrite, tetrafluoroboric acid, 4-diazo-*N,N*-diethylaniline tetrafluoroborate, 4-nitrophenyl diazonium tetrafluoroborate, and 4-bromophenyl diazonium tetrafluoroborate were used as received from Aldrich.

Synthesis of Cl-PD, CF$_3$-PD, COOH-PD, and SO$_3$H-PD. Para-substituted aniline (17 mmol) was dissolved in 11.5 mL of 50% w/w aqueous tetrafluoroboric acid solution. After the solution was cooled to −3 °C, 2.4 g (34 mmol) of NaNO$_2$, dissolved in cold water, was slowly added to the mixture.[18] The solution was filtered. The slurry was cooled below −3 °C to favor crystallization, filtered by suction, washed with ice water and cold ether, and finally dried under vacuum. The diazonium salt was kept in a desiccator at 3 °C over phosphorus pentaoxide. The diazonium functional group was detected by IR at about 2290 cm^{-1}.[30]

Electrode Preparation and Modification. Working electrodes made of glassy carbon were obtained from Bioanalytical Systems Inc. (Model MF-2012; diameter 3 mm). Platinum gauze of ca. 1 cm^2 was used as counter electrode. All potentials were reported versus the reference electrode Ag/AgCl (saturated KCl). The glassy carbon electrode surface was cleaned by polishing with Buehler 1 and 0.05 μm alumina slurry (Tech-Met Canada). After each polishing the electrode was washed with Nanopure water (18.2 MΩ cm) by sonication and kept in water. Prior to the electrochemical derivatization, the electrode was sonicated in acetonitrile or water depending on the derivatization method. Electrochemical modification of glassy carbon electrode was carried out in deaerated acetonitrile containing 1 mM diazonium salt and 0.1 M NEt$_4$BF$_4$ in the case of classical derivatization or in deaerated water containing 1 mM diazonium salt and 0.5 M HCl. The carbon electrode surface modification with in situ generated diazonium cations was performed in two steps: first, 400 μL of 0.1 M NaNO$_2$ (final concentration: 2 mM) was added to the electrolytic solution (20 mL) containing 1 mM amine and 0.5 M HCl under stirring at room temperature. Second, the mixture was left to react for about 5 min prior to the electrochemical modification. After modification, the electrode was rinsed abundantly with Nanopure water and sonicated in Nanopure water for 30 s. The solutions containing the various electroactive probes were hexaamineruthenium (1 mM; 0.1 M KCl, adjusted to pH 3 with concentrated HCl) to probe the *N,N*-diethylaniline (DEA) film and ferricyanide/ferrocyanide (5 mM; 0.1 M KCl, adjusted at pH 7 with a 1 M KOH solution) for the other films. All solutions were deaerated with extra dry nitrogen during 15 min. The relative electroactivity of the modified electrode, which is inversely related to its blocking properties, was quantified by cyclic voltammetry in the presence of redox probe species. The parameter I_{rel} is defined as:

$$I_{rel}(\%) = \frac{i_{pa} \text{ with a film}}{i_{pa} \text{ for a bare electrode}} \times 100 \quad (1)$$

where i_{pa} is the intensity of the anodic peak current. Electrochemical impedance spectroscopy measurements were performed at open circuit potential in 5 mM Fe(CN)$_6^{3-}$, 5 mM Fe(CN)$_6^{4-}$, 0.1 M KCl, adjusted to pH 7 with KOH. The frequency range was 100 kHz to 0.05 Hz, using a 20 mV sine-wave amplitude.

Instrumentation and Procedure. Electrochemical measurements were performed in a one-compartment cell with a three-electrode configuration. Cyclic voltammetry and chronoamperometry were carried out with use of either a potentiostat or galvanostat electrochemical interface SI1480 (Solartron Instruments) interfaced with a PC, and the electrochemical setups were controlled with DC Corrware (Scribner Associates, version 2.8d) software. Electrochemical impedance spectroscopy (EIS) experiments were performed with electrochemical interface SI1480 and a frequency response analyzer SI1255B (Solartron instruments) controlled by Zplot software (Scribner Associates, version 2.8d). The Zview software (Scribner Associates, version 2.8d) was used to analyze the electrochemical impedance data.

X-ray photoelectron spectra (XPS) were obtained on glassy carbon plates (GLCP-10; The Electrosynthesis Co.) with a VG Escalab 220i-XL equipped with a hemispherical analyzer and an Al anode (Kα X-rays at 1486.6 eV) used at 12−14 kV and 10−20 mA. The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below 10^{-9} Torr. XPS survey spectra were recorded with a pass energy of 100 eV and an energy increment of 1 eV whereas the pass energy was 20 eV and the energy increment was 100 meV for the core level spectra. Core level spectra were used to evaluate the atomic concentrations of the species present at the glassy carbon electrode surface. The atomic concentrations (at. %) of each individual element were determined from the relative peak areas of the spectra and the corresponding sensitivity factors according to:

$$\text{at. \%} = \frac{A_i/s_i}{\sum_i A_i/s_i} \quad (2)$$

where A_i is the peak area of the element i and s_i is the sensitivity factor for this element. For example, values of 1, 1.8, 2.93, 1.68, 4.43, 2.84, and 8.52 were used for C 1s, N 1s, O 1s, S 2p, F 1s, Br 3d, and Na 1s, respectively.

FTIR measurements were performed with a Michelson series FTIR spectrometer (Bomem Hartmann & Braun) MB series.

Computational Methods. The quantum chemical calculations were performed with the Gaussian 98[31] package for density functional calculation. Spin densities for each substituted phenyl radical were determined by optimization with a Hartree−Fock calculation followed by a Møller−Plesset correlation energy correction (MP2). This optimization was carried out at the MP2/6-31G* level of theory without influence of the solvent. The ionic character of the molecules was taken into account when it was applicable.

Results and Discussion

Cyclic Voltammetry in the Presence of Diazonium Cations. The reduction of diazonium salts was analyzed under different conditions by cyclic voltammetry. In Figure 1, the cyclic voltammograms at a glassy carbon electrode of in situ
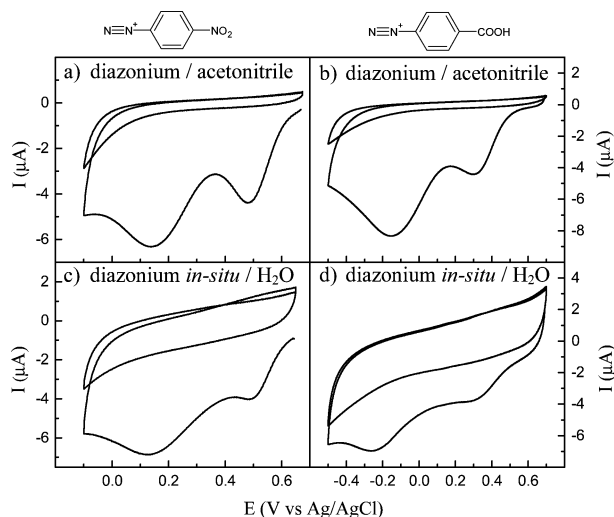
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Figure 1. Cyclic voltammograms for the reduction of 1 mM N_2^+-$(C_6H_4)NO_2$ (a, c) and 1 mM $N_2^+(C_6H_4)COOH$ (b, d) recorded at a scan rate of 50 mV s^{-1}. Cyclic voltammograms a and b are obtained in acetonitrile with 0.1 M $(Et)_4NBF_4$ as supporting electrolyte and voltammograms c and d are obtained in aqueous medium with 0.5 M HCl as supporting electrolyte (see Experimental Section for exact composition of the solution). The first two cycles are shown.

generated diazonium species in aqueous acidic medium are compared to those obtained for diazonium salts in acetonitrile. Parts a and c of Figure 1 show the first two cycles recorded during the reduction of NO$_2$-PD salt in acetonitrile and for the in situ generated salt in aqueous solution, respectively, and parts b and d of Figure 1 show the cyclic voltammograms recorded under the same conditions for COOH-PD. The first cycle of each cyclic voltammogram presents two reduction peaks. During the second cycle, these redox waves disappeared and the cyclic voltammogram only exhibits a very small reduction current, which suggests the presence of the grafted layer. This grafted layer restrains further electrochemical reduction of the diazonium salt, and consequently, its own growth. Interestingly, the cyclic voltammetry behavior of the in situ generated diazonium cation is similar to that of the diazonium salt in acetonitrile. This demonstrates the usefulness of the in situ generated approach for the grafting of aryl groups at carbon surface.[26−28] A detailed characterization of the cyclic voltammetry behavior of several in situ generated diazonium salts and the resulting modified electrodes is presented below to demonstrate the versatility of this approach.

Considering the first cyclic voltammogram, the intensity of the first peak at the most positive potential is variable for a set of experiments. This reduction peak was previously noticed in aqueous and acetonitrile media, but its origin is not yet clearly understood.[32] The second cathodic peak at lower potential corresponds to the reduction of the aryldiazonium cations to a radical which then binds covalently to the carbon surface.[7] The peak potential, E_p, corresponding to the reduction of NO$_2$-PD is 0.14 V for both the diazonium salt in acetonitrile (Figure 1a) and the in situ generated diazonium cations in aqueous acidic solution (Figure 1c). Figure 2a reports the peak potential for the reduction of the different diazonium salts in acetonitrile and for the in situ generated species in aqueous medium. It can be seen that NO$_2$-PD, Cl-PD, Br-PD, and CF$_3$-PD have the same reduction potential in both acetonitrile and aqueous media. This behavior indicates that the in situ reduction mechanism that leads to the modification of the carbon surface is similar to that in acetonitrile medium. On the other hand, in the case of COOH-
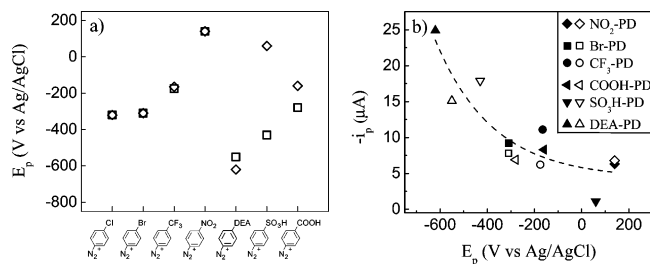

Figure 2. (a) Peak potential (E_p) for the diazonium reduction in acetonitrile (□) and in situ generated diazonium in aqueous media (◇) for various diazonium cations. (b) Peak current versus peak potential for the reduction of diazonium cations in acetonitrile (solid symbols) and generated in situ in aqueous medium (open symbols).
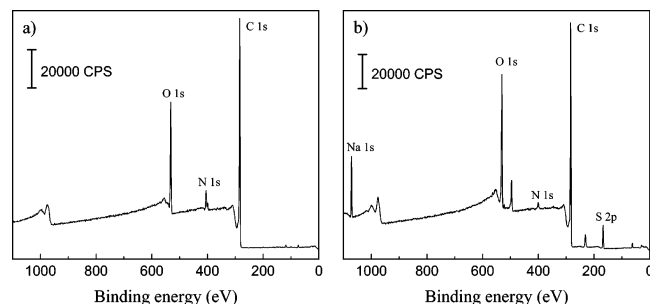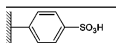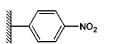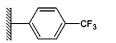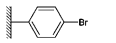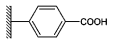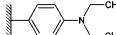

Figure 3. XPS survey spectra for 4-nitrophenyl (a) and 4-sulfophenyl (b) modified glassy carbon electrodes at E_p for 240 s with the corresponding in situ generated diazonium cations in 0.5 M HCl.

PD $E_p = -0.12$ V in acetonitrile (Figures 1b and 2a), and $E_p = -0.28$ V for the in situ generated diazonium (Figures 1d and 2a). A difference in the reduction potential was also evidenced for two other species (DEA-PD and SO$_3$H-PD) (Figure 2a). The peculiar behavior of COOH-PD, SO$_3$H-PD, and DEA-PD observed for the reduction of the in situ generated species will be discussed below. A close examination of the cyclic voltammograms also revealed that the intensity of the peak current (i_p) increased as the cathodic peak potential is more negative (Figure 2b). This is the observed trend for cyclic voltammograms recorded for both diazonium reduction in acetonitrile and in situ generated diazonium in aqueous medium, despite some scattering of the data. Since the grafting of a blocking layer can inhibit further electron transfer, a smaller cathodic peak current might reflect a more efficient grafting process.[33]

X-ray Photoelectron Spectroscopy (XPS). Glassy carbon electrodes modified by electrochemical reduction of the in situ generated diazonium cations were characterized by X-ray photoelectron spectroscopy. The electrodes were modified by applying a potential corresponding to the peak potential recorded by cyclic voltammetry for 240 s. Typical XPS survey spectra obtained for 4-nitrophenyl and 4-sulfophenyl grafted layers are presented in Figure 3. The C 1s and O 1s peaks are observed at 285 and 530 eV together with those expected N 1s (406 eV) and S 2p (168 eV) peaks for 4-nitrophenyl and 4-sulfophenyl modified electrodes, respectively. The presence of N 1s and Na 1s peaks at 400 and 1070 eV, respectively, is also noticeable. In addition, core level spectra were also recorded and used to estimate the elemental atomic composition of the surface of each modified electrode (Table 1). With the exception of the DEA modified electrode, which case will be discussed below, the atomic ratio of a typical element with respect to carbon for each grafted layer is between 4% and 8%. These values translate in surface concentration on the range 3×10^{-10} to 6×10^{-10} mol cm^{-2},[13] which is lower than that corresponding to a close-packed monolayer. This seems to suggest that the efficiency for the
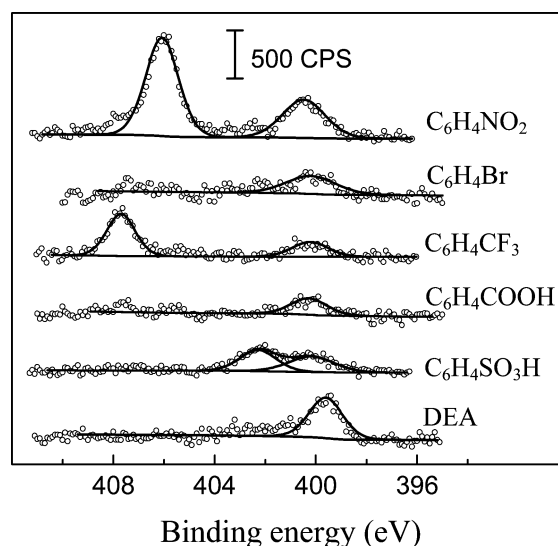
TABLE 1: Atomic Composition of the Glassy Carbon Surface Modified by Electrochemical Reduction of in Situ Generated Aryldiazonium Salts

	C 1s [a]	C − F [a] C − O [a]	N 1s[b] 400	N 1s[b] 406	O 1s	Br 3d	F 1s	S 2p	Na 1s	$\frac{R}{C}$ [d]	Γ [e] (mol.cm^{-2})
⌬—SO₃H	74.5 (80.3)[c]		0.9 (1.3)[c]		17.0 (14.7)[c]			**4.6**[f] (3.7)[c]	2.4 (-)[c]	0.046	3.4×10^{-10}
⌬—NO₂	78.8		1.7	**3.8**[f]	15.7					0.07	5.1×10^{-10}
⌬—CF₃	70.5 (84.9)[c]	**4.3**[f] (2.5)[c]	0.5 (-)[c]		11.1 (6.3)[c]		12.2 (6.3)[c]			0.061	4.5×10^{-10}
⌬—Br	84.8		1.3		9.5	**4.4**[f]				0.052	3.8×10^{-10}
⌬—COOH	76.2	**5.8**[f]	0.9		17.0					0.076	5.5×10^{-10}
⌬—N(CH₃)(C₂H₅)	90.3		**2.4**[f]		7.3					0.027	2.0×10^{-10}

[a] C 1s corresponds to the peak at 284.5 eV, C−F corresponds to the peak at 292.3 eV (attributed to the CF₃ groups), and C−O corresponds to the peak at 288.9 eV (attributed to the COOH groups). [b] N 1s 400 corresponds to the peak attributed to amino groups or azo-bridge and N 1s 406 corresponds to the peak attributed to nitro groups. [c] Values in parentheses correspond to the atomic ratio after an additional rinsing of the electrode (see text for details). [d] R/C: ratio of the intensity of the characteristic element peak over that of the C 1s peak. [e] The surface concentration, Γ in mol·cm^{-2}, is calculated from the following equation: $\Gamma = R/C \times 7.3 \times 10^{-9}$.[35] [f] Bold characters correspond to the characteristic element for each grafted layer.

grafting of these in situ generated diazonium salts is similar. However, the cyclic voltammetry data (Figure 2b) suggested that some differences should be observed for the grafting efficiency. The grafting efficiency or the surface coverage, which can be determined from the XPS data, appears to be related to the intensity of the cathodic peak current as the *R/C* (ratio of the intensity of the characteristic element peak over that of the C 1s peak) decreases when the cathodic peak current increases. The grafting efficiency may also be related to the spin density. This latter was calculated with Gaussian 98[31] and the spin densities obtained for the six carbon atoms of the phenyl group are reported in Table SI1 of the Supporting Information. The calculation was carried out for the radicals obtained by reduction of the in situ generated diazonium salts. The plots of the surface concentration and the cathodic peak current versus spin density of the carbon 1 (see Scheme SI1 in the Supporting Information for atoms numbering details) for the different grafted molecules are linear except for SO₃⁻ and DEA groups (Figures SI1 and SI2, Supporting Information) which do not follow this trend. The correlation is obviously not perfect since other factors can contribute to the grafting efficiency. These factors included the dipole moment of the aryl radical[33] and hydrophobicity/hydrophilicity effects. Finally, the lower surface concentration, determined from the N 1s core level spectrum, for the grafting of DEA groups can be presumably attributed to the competition with the hydrogen evolution reaction at the negative potential used for the reduction of DEA-PD.

Figure 4 presents the N 1s core level spectra of the different grafted glassy carbon electrode. The 4-nitrophenyl modified electrode presents a N 1s peak at 406 eV, which is characteristic of NO₂ groups on the surface.[1,34] The DEA modified electrode is characterized by a peak at 399.5 eV, which is due to the presence of the N-(C₂H₅)₂ substituent.[35] As previously observed for most electrodes modified by electrochemical reduction of diazonium salt, an additional nitrogen peak is observed at 400 eV on all the electrodes with an atomic concentration near 1%. This component can be attributed to the presence of a C−N=N−C linkage at the surface of the electrode as a consequence of the electrode modification.[36] In the case of 4-nitrophenyl modified electrode, the origin of this peak also can be linked to the reduction of the nitro groups to amino groups in the XPS analysis chamber during the measurements[37] or during the electrochemical grafting step in aqueous medium.[34] However, the latter can be ruled out because the grafting was

Figure 4. N 1s core level spectra recorded on glassy carbon electrodes modified by electrochemical reduction of in situ generated diazonium salts.

performed at a potential for which the electrochemical reduction of nitro groups cannot occur. Interestingly, a peak was also observed at 408 eV for the electrode modified with CF₃ groups. This peak might be related to the presence of nitrate.[38] However, the presence of nitrate (originating from the oxidation of nitrite) in the electrolyte used for the in situ generation of diazonium is unlikely and thus the exact source of the N 1s signal observed at 408 eV is unknown. Afterward, the C₆H₄CF₃ modified electrode was sonicated in acetonitrile for 30 min and then abundantly rinsed with acetonitrile and water. The N 1s core level spectra obtained before and after this treatment are presented in the Supporting Information (Figure SI3). The atomic ratios obtained for the so cleaned electrode are reported, in parentheses, in Table 1. Interestingly, this treatment entirely removed the nitrogen species that were still present on the electrode surface despite the initial water cleaning procedure used after the grafting step (see the Experimental Section). This suggests that those species which generate signals at 400 and 408 eV are not strongly bound to the electrode surface and that, in this case, the formation of the azo group is unlikely. Presumably, the species giving rise to the peak at 400 eV result from the adsorption of reaction products coming from the
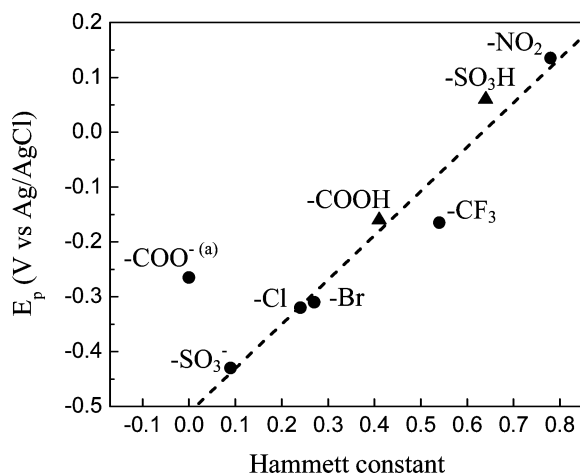
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Figure 5. Variation of the reduction peak potential versus Hammett constant for various diazonium salts: ●, aryl diazonium salts reduced by the in situ route; ▲, aryl diazonium salts reduced in acetonitrile. Superscript a: E_p measured during the reduction of COOH-PD in aqueous medium is plotted with the Hammett constant of the COO^- group and reported with the label $-COO^-$.

Figure 6. Cyclic voltammograms recorded in aqueous 5 mM Fe-$(CN)_6^{3-/4-}/0.1$ M KCl, pH 7, at a scan rate of 50 mV s^{-1} for a bare glassy carbon electrode (- - -) and 4-nitrophenyl and 4-carboxyphenyl (—) glassy carbon electrodes modified at E_p for 30 s.

electrochemically generated radicals since a decrease in the amount of $C_6H_4CF_3$ species present on the surface of the electrode is also noticed (Table 1). The N 1s core level spectrum of the 4-sulfophenyl modified electrode also exhibits a peak at 402 eV. To get some insight into the nature of the species responsible for the presence of this peak, the electrode was rinsed in a 10^{-4} M KOH solution for 24 h. The N 1s spectrum of the resulting electrode is characterized by the loss of this peak at 402 eV and, in addition, the Na 1s peak earlier observed on the survey spectrum also disappeared (Table 1, as well as Figure SI3 in the Supporting Information). These observations can be explained as follows. Considering that the in situ generation of SO$_3$H-PD is carried out in a 0.5 M HCl solution containing 1 mM sulfanilic acid, the sulfanilic acid is in the $NH_3^+(C_6H_4)SO_3^-$ form and consequently an ionic association can occur between the ammonium and the sulfonate group of two different diazonium cations. Presumably, some of the ammonium groups were preserved during the in situ generation of diazonium due to this ionic association and this led to a grafted layer composed of $C_6H_4SO_3^-$ groups interacting with the ionized form of sulfanilic acid. Finally, the presence of Na$^+$ at the surface of the as-deposited layer and its elimination after the base treatment can be explained by the electrostatic interaction of Na$^+$ with sulfonate groups. It should be noted that the disappearance of the N 1s peak at 402 eV is accompanied by a decrease in the sulfur content, which is in agreement with a removal of sulfanilic acid from the electrode surface. Moreover, and in contrast with the 4-trifluoromethylphenyl modified electrode described above, the azo species, covalently bound to the surface and characterized by a N 1s peak at 400 eV, are present and resist the KOH treatment.

Effect of the Aqueous Solvent. The reduction potential E_p of in situ generated SO$_3$H-PD and COOH-PD is shifted negatively in comparison with the observed E_p in acetonitrile medium whereas a positive shift of the reduction potential can be seen for DEA-PD. Previous studies have demonstrated that the reduction potential of substituted diazoniums correlates very well with the Hammett constant of the substituents.[7,33] A similar correlation can be seen in Figure 5, which shows the plot of the cathodic peak potential as a function of the Hammett constant of various substituents including the dissociated forms
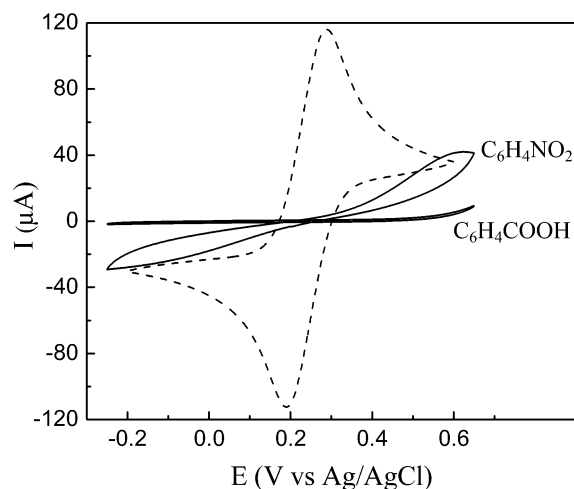
of the carboxylic and sulfonic acid derivatives. A linear relationship is verified for all the substituents investigated in this work, including the SO$_3$H and SO$_3^-$ forms of SO$_3$H-PD, but not for COO$^-$ for which the poor correlation suggests that it is not in the COO$^-$ form. Considering that the pK_a values of benzoic acid, COOH-PD, and surface grafted 4-carboxyphenyl are about 4.2,[39] 2.4,[40,41] and 2.8,[36] respectively, the COOH-PD in the deposition solution is present in its undissociated form under our experimental conditions, as confirmed by the XPS data which do not demonstrate any evidence for the presence of Na$^+$ at the surface of 4-carboxyphenyl modified electrode. The negative shift of the reduction peak potential observed for the reduction of in situ generated COOH-PD could be explained by a different solvation in acetonitrile and aqueous medium, linked to the hydrophilic properties of carboxylic acid substituent.

Barrier Effect of the Grafted Layer. The cyclic voltammogram of soluble electroactive species provides a convenient tool to study the presence of grafted films and their blocking properties. The influence of the glassy carbon electrode modification conditions on the cyclic voltammetric response of $Fe(CN)_6^{3-/4-}$ oxido-reduction was investigated for different layers grafted by electrochemical reduction of the in situ generated diazonium cations. In addition to the nature of the substituent on the diazonium, both the diazonium reduction time and the reduction potential were varied. The reduction time was set at 30 or 240 s and the electrochemical modification potential was either the cathodic peak potential E_p of each diazonium or 0.3 V more negative than E_p. Finally, it should be noted that the DEA grafted layers exhibited a nonblocking effect for $Fe(CN)_6^{3-/4-}$ redox system reactions and instead were characterized in the presence of $Ru(NH_3)_6^{3+}$.

Figure 6 shows the cyclic voltammograms recorded at bare glassy carbon electrode and 4-nitrophenyl and 4-carboxyphenyl modified electrodes. The voltammogram of the $Fe(CN)_6^{3-/4-}$ redox system presents a quasireversible behavior at the bare electrode with an apparent redox potential of 0.23 V. The 4-nitrophenyl and 4-carboxyphenyl modified glassy carbon electrodes exhibit a significant blocking behavior for the oxidation and reduction reactions of the $Fe(CN)_6^{3-/4-}$ redox system. For the same grafting conditions, the blocking effect appears to be more important for the 4-carboxyphenyl modified electrode. It should be noted that in previous work, the
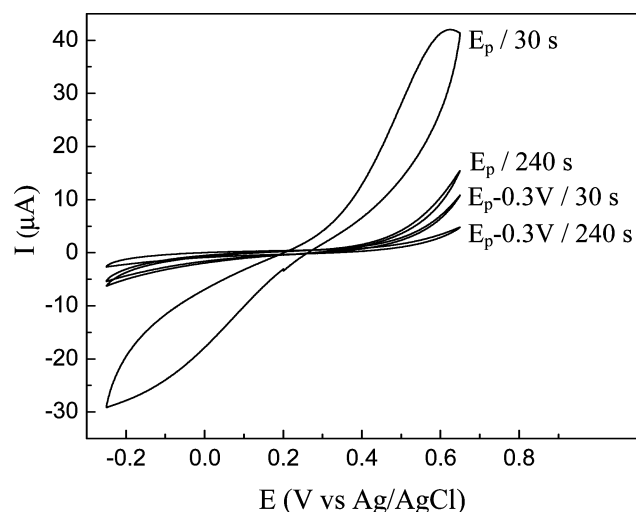
Figure 7. Cyclic voltammograms recorded in aqueous 5 mM Fe-$(CN)_6^{3-/4-}$/0.1 M KCl, pH 7, at a scan rate of 50 mV s^{-1} for a 4-nitrophenyl modified glassy carbon electrodes for various reduction conditions: at the cathodic peak potential for 30 s (E_p/30 s), at the cathodic peak potential for 240 s (E_p/240 s), at a potential 0.3 V more negative than E_p for 30 s ($E_p - 0.3$ V/30 s), and at a potential 0.3 V more negative than E_p for 240 s ($E_p - 0.3$ V/240 s).

4-nitrophenyl modified electrode was found to present a higher barrier effect than a 4-carboxyphenyl modified electrode.[36] In this previous work, the diazonium reduction was carried out at constant potential (-0.7 V vs Ag/AgCl) independently of the para substituent of the diazonium salt. Therefore, a larger overpotential was used for the NO$_2$-PD reduction than for COOH-PD, which may be the cause of the higher barrier effect observed for 4-nitrophenyl modified glassy carbon electrodes. In the present study, the reduction potential was set either at the peak potential observed for each diazonium salt or at a constant overpotential relative to E_p, to avoid the effect of the variation of the overpotential. Figure 7 and Table 2 show that the blocking effect increases (e.g., I_{rel} decreases) as the applied potential is made more negative and with an increase of the reduction time. This trend is observed for all grafted layers and demonstrates that, first, in the investigated time range, the growth of the grafted layer by electrochemical reduction of the

in situ generated diazonium cations is not self-limited, and second, that it is possible to obtain a relative control of the layer thickness by controlling two parameters of the diazonium reduction: the applied potential and the reduction time. Finally, there is no direct correlation between the surface coverage, as indicated by the R/C values, and the blocking behavior, as indicated by the I_{rel} values, because a factor such as hydrophobicity can play a significant role and influence the observed electrochemical response.[42]

Furthermore, the blocking effect of grafted layers formed by electrochemical reduction of in situ generated NO$_2$-PD was compared to that obtained by modification with the NO$_2$-PD directly dissolved in acetonitrile and in a 0.5 M HCl aqueous solution. The I_{rel} values obtained for these modification conditions are reported in Table 3. The electrodes modified by reduction of the diazonium salt directly dissolved in a 0.5 M HCl solution exhibit a blocking behavior similar to that obtained with an electrode modified by the in situ route. This observation leads to the conclusion that the introduction of sodium nitrite in the electrolyte used for the in situ reduction does not appear to affect the electrode modification process and the electrochemical reduction seems to generate similar grafted layers whether the diazonium cations are obtained in situ or separately by a prior synthesis. However, when the electrode modification is carried out in acetonitrile, a slightly higher blocking effect (e.g., smaller I_{rel} values) toward the Fe$(CN)_6^{3-/4-}$ redox reaction is observed. As a consequence, the layer grafted in acetonitrile medium can be considered as being more compact and homogeneous than layers obtained in aqueous medium.[42,43]

The blocking effect of the grafted layer on a glassy carbon electrode was also evaluated by electrochemical impedance spectroscopy in a 5 mM Fe$(CN)_6^{3-/4-}$ pH 7 solution (Figure 8). The Nyquist plot for a bare glassy carbon electrode reported in Figure 8 (insert) presents a typical shape, with a semicircle in the high-frequency domain characteristic of an interfacial charge-transfer mechanism and a straight line with a slope near unity in the low-frequency domain characteristic of a semi-infinite diffusion phenomenon. The charge transfer calculated from the semicircle diameter is 22 Ω. The Nyquist plots a and b in Figure 8 were obtained for two electrodes modified by reduction of NO$_2$-PD generated in situ at E_p for 30 and 240 s,

TABLE 2: I_{rel} and R_{CT} Obtained for Aryl Modified Glassy Carbon Electrodes

	E_p for 30 s		E_p for 240 s		$E_p - 0.3$ V for 30 s		$E_p - 0.3$ V for 240 s	
	I_{rel} (%)	R_{CT} (Ω)	I_{rel} (%)	R_{CT} (Ω)	I_{rel} (%)	R_{CT} (Ω)	I_{rel} (%)	R_{CT} (Ω)
—SO$_3$H	46.1	2.4×10^5	26.2	6.3×10^5	16.7	4.1×10^5	6.4	1.1×10^6
—NO$_2$	36.2	5.8×10^4	13.3	1.8×10^5	9.3	5.3×10^5	4.1	2.2×10^6
—CF$_3$	31.9	3.9×10^5	12.1	2.3×10^6	1.8	5.9×10^6	1.7	2.6×10^7
—Br	15.7	4.0×10^5	1.5	1.7×10^6	1.0	3.4×10^6	0.7	4.1×10^6
—COOH	8.0	4.5×10^5	3.3	6.9×10^5	2.9	2.6×10^6	1.9	2.6×10^6
—N(CH$_3$)(CH$_3$)	99.5 [a]	–	88.0 [a]	–	80.1 [a]	–	70.3 [a]	–

[a] The values reported for I_{rel} in the case of DEA modified electrode are obtained in a 0.1 M KCl and 1 mM Ru$(NH_3)_6^{3+}$ at pH 3.

TABLE 3: I_{rel} Obtained for Glassy Carbon Electrodes Modified with Grafted 4-Nitrophenyl Layer Reduction in Situ Generated of Diazonium Cations, and by Reduction of the Diazonium Salt Dissolved in 0.5 M HCl Aqueous Solution and in Acetonitrile

	I_{rel} (%)			
	E_p for 30 s	E_p for 240 s	$E_p - 0.3$ V for 30 s	$E_p - 0.3$ V for 240 s
NO$_2$−PD in situ generated in 0.5 M HCl	35.6 ± 1.0	15.3 ± 1.8	9.3 ± 0.8	4.1 ± 0.4
NO$_2$−PD dissolved in 0.5 M HCl	35.0 ± 2.3	14.6 ± 0.8	10.1 ± 1.0	4.5 ± 0.4
NO$_2$−PD dissolved in acetonitrile	28.9 ± 0.6	10.7 ± 1.7	3.7 ± 1.2	2.1 ± 0.6

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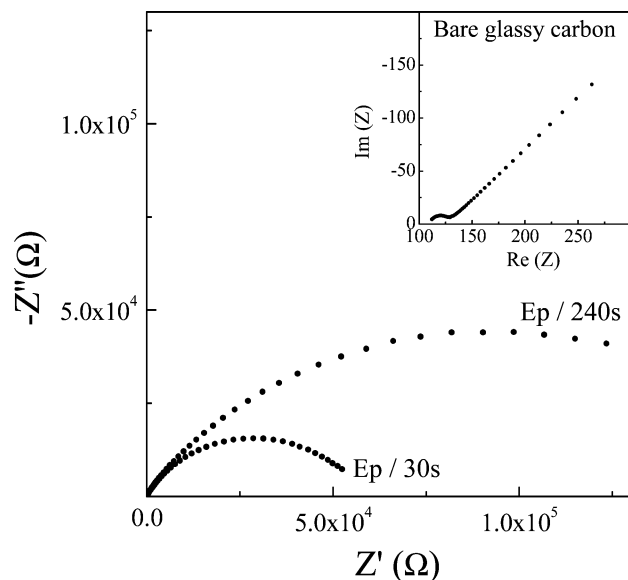**Figure 8.** Nyquist representation of the electrochemical impedance spectroscopy data in aqueous 5 mM $Fe(CN)_6^{3-/4-}$/0.1 M KCl, pH 7, for a bare glassy carbon electrode (insert) and 4-nitrophenyl modified glassy carbon electrodes at the cathodic peak potential for 30 s (E_p/30 s) and at the cathodic peak potential for 240 s (E_p/240 s).

respectively. First, the semi-infinite diffusion in the low-frequency domain is no more apparent, and this phenomenon can be explained by the low current involved in the $Fe(CN)_6^{3-/4-}$ redox reaction on a modified electrode in the considered potential range. Indeed, the cyclic voltammograms for the modified electrodes for any modification conditions reveal an electron-transfer-limited process and not a diffusion limitation. Second, the Nyquist plot of modified electrodes consists of a depressed semicircle.[36] A simplified representation allows the charge-transfer resistance to be determined from the diameter of the semicircle. The charge-transfer resistance of modified electrodes varies from 10^4 to 10^7 Ω (Table 2), which represents a significant increase compared to the bare glassy carbon electrode and is consistent with the cyclic voltammetry data.

The blocking effect of the grafted layer can have several sources: (i) the physical barrier of the grafted layer that prevents the access of $Fe(CN)_6^{3-/4-}$ to the underlying glassy carbon electrode, (ii) the electrostatic repulsion, especially for 4-carboxyphenyl and 4-sulfophenyl grafted layers, (iii) the hydrophobic nature of the grafted layer in the case of 4-bromophenyl and 4-trifluoromethylphenyl groups, and (iv) the electron transfer limitation, which can vary with the grafted functionality.
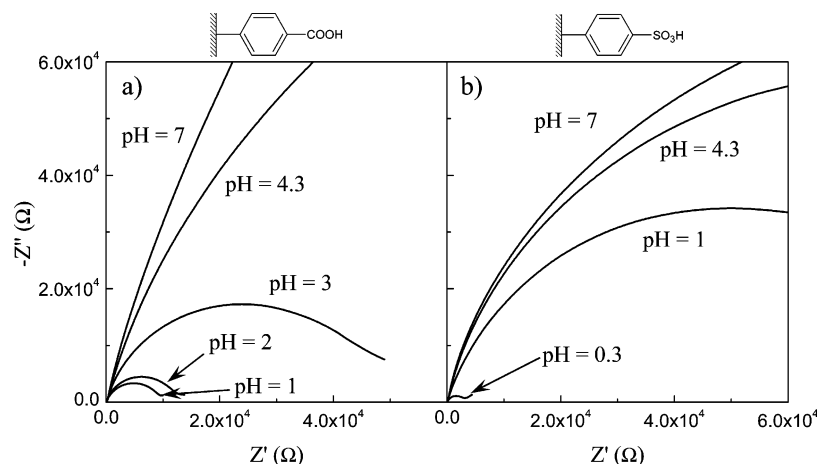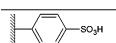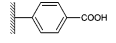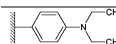
The influence of the above-mentioned electrostatic effect was studied for 4-sulfophenyl, 4-carboxyphenyl, and DEA modified electrodes in 5 mM $Fe(CN)_6^{3-/4-}$ solution at different pH values. The Nyquist plots obtained for 4-carboxyphenyl and 4-sulfophenyl grafted layers are presented in Figure 9, parts a and b, respectively. For these experiments, the pH of the $Fe(CN)_6^{3-/4-}$ solution was adjusted between appropriate values around the pK_a of the corresponding acid (e.g., benzoic acid for 4-carboxyphenyl modified electrode) to obtain a variation in the ratio of charged and neutral forms of the molecule grafted on the electrode surface. The charge-transfer resistances measured for each pH are reported in Table 4. For 4-carboxyphenyl and 4-sulfophenyl grafted layers, the decrease in pH is accompanied by a significant decrease in R_{CT}. For pH values low enough to consider that the grafted layer is neutral, the charge-transfer resistance of the modified electrode is in the range of 10^3 to 10^4 Ω. The same phenomenon is observed for the DEA grafted layer, and when the pH reaches the value of 12, R_{CT} is close to 10^3 Ω.

Because of the hydrophilic character of these layers, the charge-transfer resistance measured when the grafted layer is in the neutral state may be considered to be due to the steric hindrance or the physical barrier role played by the organic molecules. It is interesting to note that this value is about 1 to 2 orders of magnitude lower than that of R_{CT} measured for uncharged grafted layers such as 4-nitrophenyl, 4-bromophenyl, or 4-trifluoromethylphenyl. These three layers are more hydrophobic than 4-carboxyphenyl, 4-sulfophenyl, or DEA and this difference between the charge-transfer resistances of the modified electrode in their neutral state is consistent with the existence of an influence of the hydrophobic character of the grafted layer and the intensity of its blocking effect.

The variation of the R_{CT} values with pH can be used to estimate apparent pK_a values around 0.5, 3, and 10 for 4-sulfophenyl, 4-carboxyhenyl, and DEA grafted groups, respectively. In the case of the 4-sulfophenyl grafted layer, the apparent pK_a measured ($pK_a = 0.5$) is close to the pK_a of benzenesulfonic acid aqueous solution ($pK_a = 0.7$).[39] However, for both 4-carboxyphenyl and DEA grafted groups, a difference can be noticed between the apparent pK_a of the grafted layer and the pK_a of the corresponding molecule diluted in aqueous solution, benzoic acid, and N,N-diethylaniline, respectively. The apparent pK_a of the 4-carboxyphenyl grafted layer is shifted to a lower value than the pK_a value of benzoic acid in aqueous solution ($pK_a = 4.2$).[39] In the case of the DEA grafted layer, the apparent pK_a is positively shifted compared to the pK_a of

Figure 9. Nyquist representation of the impedance spectra in aqueous 5 mM $Fe(CN)_6^{3-/4-}$ at different pH values for (a) 4-carboxyphenyl modified glassy carbon electrode and (b) 4-sulfophenyl modified glassy carbon electrode.

TABLE 4: R_{CT} Obtained for Aryl Modified Glassy Carbon Electrodes at Different pH Values

	R_{CT} (Ω)					
	pH = 0.3	pH = 1	pH = 2	pH = 3	pH = 4.3	pH = 7
�âSO$_3$H	3.1×10^3	9.6×10^4	–	–	1.7×10^5	2.4×10^5
�âCOOH	–	9.7×10^3	1.2×10^4	4.6×10^4	2.8×10^5	4.5×10^5

	pH = 7	pH = 8	pH = 10	pH = 12
�âN(CH$_3$)$_2$	38	65	1.7×10^2	1.1×10^3

N,N-diethylaniline (pK_a = 6.6).[39] A variation of the barrier effect of surfaces modified with carboxylic or amino groups with respect to pH was already observed by electrochemical impedance spectroscopy[44,45] or by cyclic voltammetry in a solution containing appropriate electroactive species.[36,46] Moreover, various methods were used to determine the pK_a of an ionizable group immobilized on a substrate.[47−51] In most of these studies, the apparent pK_a of the groups present at the electrode surface was shifted compared to the pK_a of the same molecule in solution. The apparent pK_a of the 4-carboxyphenyl layer was already evaluated in a previous work and was reported to be close to 2.8.[36] However, the source of this shift was not clearly identified. Burke and Barrett[48] observed that, in the case of polyelectrolyte multilayers, the pK_a of a surface amino group was positively shifted whereas it was negatively shifted for a surface carboxylic group immobilized on silica. This behavior is similar to that observed in the present work, but they attributed it to inhomogeneous polyelectrolyte coverage or to the influence of the silica substrate, and it is not certain that a carbon substrate would have the same influence. On the other hand, Wang et al.[47] observed a positive shift of the pK_a of self-assembled monolayers with carboxylic end groups, which is thought to be due to electrostatic interactions between neighbor carboxylic functional groups. Creager and Clarke[49] explained the positive shift observed for alkanoic acid monolayer by a simplified model involving the contribution of two effects: the first effect is the lower ion solvation due to a steric hindrance and the second one is an interfacial potential effect mostly generated by the ionization of the layer.[52,53] Another effect to consider is the conformation of the COOH group: the environment at the interface between the grafted layer and the electrolyte could generate a change in the COOH group conformation. In solution, carboxylic groups are under their most stable conformation (syn-conformation with O−H and C=O both on the same side of the C−O bound), but the peculiar environment of the layer/solution interface could force the carboxylic groups present in the grafted layer into an anti-conformation (O−H and C=O both on opposite side of the C−O bound).[51,54] The latter conformation would cause the dissociated form of the molecule to be more stable, and thus would decrease the pK_a of the grafted layer compared to that of the molecule in solution. Several factors can be invoked to explain a positive or a negative shift of the pK_a of an immobilized molecule on a substrate surface compared to its pK_a in solution and their possible combination as well as the unknown structure of the surface grafted layer make it difficult to provide a definitive explanation for the phenomenon observed in the present work.

General Discussion. This investigation was designed to demonstrate and confirm the possibility of modifying glassy carbon electrode by electrochemical reduction of in situ generated diazonium salt. This novel approach would present a significant advantage with respect to the method involving a diazonium salt because the isolation and purification of the diazonium salt would be avoided. As mentioned in the Introduction, the chemical modification (without externally applied electrochemical potential) of various carbon materials has been previously reported.[21−24] In these studies, it was shown that when a carbon substrate (e.g., carbon powder and carbon nanotubes) is left to react in a solution containing the in situ generated aryl diazonium, grafting of the aryl groups occurs. The grafting is observed whether or not a reducing agent (to reduce the diazonium cation) was added to the reaction mixture. Thus, it seems plausible to assume that electrochemical modification would be feasible if the electrolytic solution would consist of an in situ generated diazonium salt, as was very recently demonstrated for the covalent grafting of benzo-15-crown-5 ether,[26] phenyl nitrilotriacetic acid,[27] and 4-aminophenyl.[28] Furthermore, Kaufman et al.[55] recently reported that the chemical modification of carbon materials via an in situ generated aliphatic diazonium was possible despite the relative well-known instability of such diazonium species.[56] The results of the present study, which involves six different grafted species, demonstrate that the approach can be quite general and versatile. In addition, we believe that this approach could be eventually applied to several other molecules[57] and will facilitate the electrochemical modification of electrodes with diazonium salts. On the other hand, the modification procedure described in this study can be severely limited by the onset of hydrogen evolution reaction. This was demonstrated in this work for the electrochemical grafting of DEA that occurs at a relatively high negative potential. This problem will become even more acute for the grafting of molecules on metal surface[11] having a low overpotential for the hydrogen evolution reaction in acidic medium. Furthermore, the surface modification in aqueous medium limits the range of suitable groups for the derivatization. For example, this grafting route is not applicable to diazonium cations bearing hydrolyzable substituents.

The conventional modification procedure involving only a diazonium salt dissolved in acetonitrile or in acid aqueous medium might yield a grafted film containing less impurity than the one based on in situ generated diazonium. Interestingly, from the XPS data, it does not appear that reactants are entrapped in or at the surface of the glassy carbon electrode modified from an in situ generated diazonium. Finally, another parameter that might have some impact on the grafting process is the reaction time between the preparation of the deposition solution and the electrochemical grafting step. In the present study, the reaction time was set at about 5 min, based on the observation that the yellow electrolytic solution seems to become completely colorless after this short period of time when the in situ 4-nitrophenyl diazonium was generated. On the other hand, preliminary results with diazonium generated in situ in acetonitrile seem to indicate that much longer reaction time is needed prior to the electro-

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chemical grafting step. The result of this study will be reported elsewhere.[58]

Conclusion

Glassy carbon electrode surface was modified by electrochemical reduction of diazonium salts, either dissolved in acetonitrile or generated in situ in aqueous HCl solution. These two modification routes were studied by cyclic voltammetry, and the resulting grafted layers were characterized by cyclic voltammetry with a redox probe system. It appears that for diazonium cations with nonionizable substituents, the reduction is similar in both aqueous and acetonitrile media. The variation of the reduction potential of the substituted diazonium cations can be correlated with the Hammett constant of the substituents. The cyclic voltammetry in $Fe(CN)_6^{3-/4-}$ revealed that the layer obtained in aqueous medium was slightly thinner or less homogeneous than the one obtained in acetonitrile. XPS measurements for layers grafted by reduction of in situ generated diazoniums revealed that the lower the diazonium reduction potential is, the lower is the amount of grafted molecules at the carbon surface. This decrease in the amount of grafted molecules can be associated to an increase in the diazonium reduction current, which is linked to the barrier properties of the grafted layer. However, the amount of grafted molecules is quite comparable, which enabled us to differentiate several phenomena to explain the barrier effect of the grafted layer. Finally, the modification of carbon surface by reduction of in situ generated diazonium cations, which is a simple derivatization method, involving widely available amines, enables the grafting of molecules which are insoluble in nonaqueous solvent.

Supporting Information Available: Spin density for the aromatic carbons of each radicals obtained from reduction of in situ generated diazonium, calculated at the MP2/6-31G* level of theory; plots of the surface concentration and the cathodic peak current versus the spin density of C1; and N 1s core level spectra of glassy carbon electrode modified with $C_6H_4CF_3$ and $C_6H_4SO_3H$ before and after cleaning treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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