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Direct Modification of a Gold Electrode with Aminophenyl Groups by Electrochemical Reduction of in Situ Generated Aminophenyl Monodiazonium Cations

Joël Lyskawa and Daniel Bélanger*

Département de Chimie, Université du Québec à Montréal, Case Postale 8888, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3P8

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Aminophenyl groups were electrochemically grafted at the surface of a gold electrode by reduction of in situ generated aminophenyl monodiazonium cations. The in situ aminophenyl monodiazonium cations were generated by reaction of 1 equiv of *p*-phenylenediamine with 1 equiv of sodium nitrite in 0.5 M HCl, and their formation was confirmed by gas chromatography−mass spectrometry. The presence of aminophenyl groups at the surface of the gold electrode was demonstrated by electrochemistry and infrared and X-ray photoelectron spectroscopies. The formation of an inhomogeneous multilayered film was also evidenced by atomic force microscopy. Furthermore, grafted aminophenyl groups present at the gold electrode surface reacted with trifluoroacetic acid anhydride in dry tetrahydrofuran with a reaction yield of about 75% for the trifluoroacetylation of the amine groups.

Introduction

The modification of surfaces with specific chemical functionalities can result in potential application in chemical sensing,[1] microelectronics,[2] protection against corrosion,[3] and biosensing.[4] Since the past decade, the electrochemical reduction of aryldiazonium salts on conductive surfaces has been widely investigated.[5−13] This technique allows the covalent attachment of aryl groups bearing a terminal functionality such as alkyl, nitro, cyanide, carboxylic, ester, alcohol, thiol, and halogenated groups[6] to various surfaces (carbon,[7] metals[8] including gold,[8c,9] semiconductors,[10] and silicon[10,11]) through the generation of an aryl radical which then covalently binds to the electrode. Aminophenyl groups are extremely useful for the applications mentioned above. Unfortunately, their formation on conductive surfaces requires an initial grafting and a subsequent chemical step and can be performed via the electrochemical reduction of already grafted nitrophenyl groups or the hydrolysis of grafted 4-acetamidophenyl groups.[6,12] Also, the second step of the modification procedure, that is, conversion into NH_2, has been proven to be incomplete.[6,12] As a result of the numerous potential applications of such grafted aminophenyl groups,[1−4] a simpler grafting process would be much welcomed.

In this work, we show that the direct modification of a gold electrode with aminophenyl groups can be accomplished in one step by electrochemical reduction of in situ generated aminophenyl diazonium cations,[1b,13] generated from *p*-phenylenediamine. This work is significant because the selective diazotization of one amine group of *p*-phenylenediamine is achieved, and the resulting aminophenyl diazonium cations are directly used to graft aminophenyl groups at the surface of a gold electrode, thus avoiding a chemical step such as that required when grafted nitrophenyl groups are reduced to aminophenyl groups. A characterization of the resulting modified surfaces was performed by infrared reflection−absorption spectroscopy (IRRAS), X-ray photo-

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* To whom correspondence should be addressed. E-mail : belanger.daniel@uqam.ca. Fax: (514) 987-4054. Tel.: (514) 987-3000, ext. 3909.

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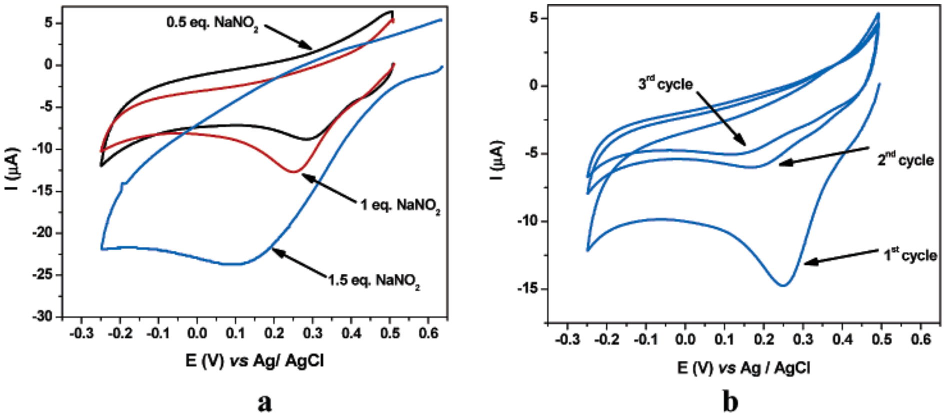
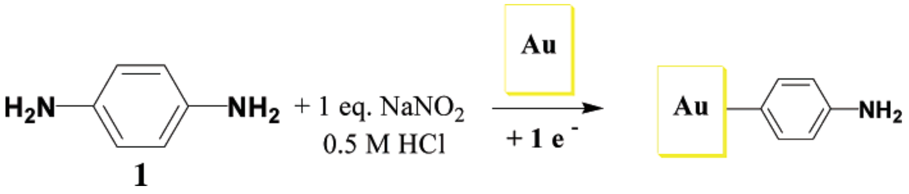


Figure 1. CVs obtained (a) as a function of the number equivalent of $NaNO_2$ introduced into the cell, (b) after addition of 1 equiv of $NaNO_2$, first and subsequent scans. Conditions: 5 mM [*p*-phenylenediamine], 0.5 M HCl, scan rate = 100 mV/s, Au (ϕ = 1 mm).

Scheme 1. Electrochemical Reduction of in Situ Generated Aminophenyl Diazonium Cations on Gold



electron spectroscopy (XPS), atomic force microscopy (AFM), and electrochemical techniques, which enable us to propose a chemical structure for the grafted layers. The chemical reactivity of aminophenyl surface groups, with a specific reactant for amine functionalities, is also described to further confirm their presence at the electrode surface and their usefulness as reactive sites for further functionalization.

Results and Discussion

Grafting. It has been recently suggested that the high instability of the monodiazonium salt of *p*-phenylenediamine prevents its synthesis.[8d] However, this contradicts an earlier report that indicated that the diazotation of one amine group of *p*-phenylenediamine can be achieved.[14] To clarify this situation and because of our interest in preparing an aminophenyl modified electrode surface in one step, the diazotation of *p*-phenylenediamine was investigated. The formation of such a modified electrode would involve the electrochemical reduction of aminophenyl diazonium generated in situ from the corresponding diamine (**1** in Scheme 1) in acidic media. For this study, *p*-phenylenediamine **1** (5 mM) was solubilized in aqueous HCl (0.5 M), and adequate amounts of sodium nitrite were added to generate the mono-aryldiazonium salt in the electrochemical cell (in situ). The influence of the number of equivalents of $NaNO_2$ added to the electrochemical cell containing the diamine solution was first investigated by cyclic voltammetry (Figure 1).

Upon addition of 0.5 equiv of $NaNO_2$ to the *p*-phenylenediamine solution, the open circuit potential of the Au electrode increases from 0.32 to 0.50 V. In this solution, the cyclic voltammograms (CVs) of the Au electrode exhibits a well-defined cathodic peak at 0.25 V vs Ag/AgCl (Figure 1a). The intensity of the reduction peak is higher when 1 equiv of $NaNO_2$ is added which suggests a diazotation of the starting diamine with higher yield.

The corresponding CV (see also Figure 1b, 1st cycle) exhibits a well-defined reduction peak assigned to the formation of the aryl radical, which then attaches to the surface (Scheme 1). This electrochemical response is analogous to the ones obtained for the electrochemical reduction of substituted aryl diazonium cations.[6] The second and third cycles of a set of consecutive CVs (Figure 1b) exhibit a slight shift of the cathodic peak to more negative potentials and lower currents, consistent with the passivation of the gold electrode due to the formation of a grafted layer. A similar behavior has been previously reported for the electrochemical reduction of several diazonium salts at both carbon and gold electrodes.[5−9,11,12] When more than 1 equiv of $NaNO_2$ is added to the mixture, the open circuit potential is shifted to 0.70 V and the CV shows a broad cathodic peak that is more intense and shifted to more negative potential (Figure 1a). The larger peak current in the presence of 1.5 or 2 equiv of sodium nitrite might be indicative of a smaller grafting efficiency as was recently shown for the grafting of various aryl groups on glassy carbon electrode.[13] Indeed, it will be shown below that the amount of grafted aminophenyl groups is smaller when more than 1 equiv of sodium nitrite is used.

The formation of the aminophenyl monodiazonium cations in solution upon addition of 1 equiv of sodium nitrite was confirmed by gas chromatography−mass spectrometry (GC-MS). For this purpose, a mixture of the monodiazonium cations, generated from the *p*-phenylenediamine after addition of 1 equiv of sodium nitrite in a 6 M HCl solution, and an excess of potassium iodide was heated at 100 °C during 3 h[15] (Scheme 2). After cooling and extraction with dichloro-

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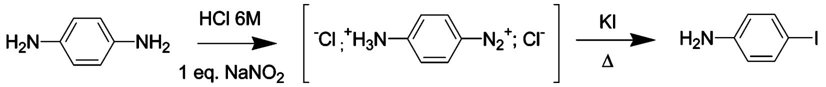
Scheme 2. Reaction between the Monodiazonium Salt in Situ Generated from *p*-Phenylenediamine and Potassium Iodide



methane, the formation of 4-iodoaniline, 4-chloroaniline, and 1-chloro-4-iodobenzene were observed by GC-MS (note that 1,4-diodobenzene was not detected) with a 90% yield for the mono-substituted compounds and 10% for the disubstituted product considering peak surface areas (Figure SI 1, Supporting Information). This clearly demonstrates the preferential formation of the monodiazonium salt from the *p*-phenylenediamine upon addition of 1 equiv of $NaNO_2$ in the solution rather than the bisdiazonium cations. Thus, these results suggest that the bisdiazonium species are generated in very low yield in the electrochemical cell. The formation of the monodiazonium salt in these conditions (e.g., 1 equiv of both the diamine and $NaNO_2$) will be also confirmed by XPS (vide infra).

The above results confirm the earlier claim concerning the possibility of forming the aminophenyl monodiazonium cations from *p*-phenylenediamine[14] when a quantitative number of equivalents of the amine and $NaNO_2$ are used to generate the monodiazonium. Presumably, the formation of the bisdiazonium cations is more difficult for electrostatic reasons and also because the second amine group of the aminophenyl monodiazonium will be less reactive toward diazotation.

When a gold electrode is modified potentiostatically at −0.4 V during 400 s in a 5 mM acidic solution of **1** containing 1 equiv of $NaNO_2$, one can visually observe the formation of an orange film on the electrode. This observation suggests that the growth of multilayers occurred on the gold surface. Following modification, the electrode was subsequently ultrasonicated in water and acetone during 5 min to remove any adsorbed and loosely attached species on the surface. During this cleaning procedure, the unprotonated form of aminophenyl groups is regenerated (p*K*a of soluble aniline = 4.63). It is noteworthy that such films can withstand longer ultrasonic treatment (1 h in water and acetone), which is consistent with the existence of a strong bond or interactions between the metal and the aromatic species. This is in agreement with previous observation for substituted phenyl modified gold electrode.[9]

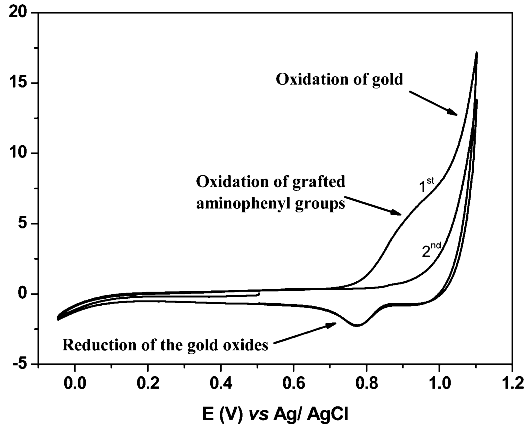


Figure 2. Cyclic voltammetric response of a gold electrode modified by aminophenyl groups in 0.5 M H_2SO_4 at a scan rate of 20 mV/s.

The CV response of the gold modified electrode in a 0.5 M H_2SO_4 solution does not exhibit any electroactivity between 0 and 0.8 V (Figure 2). Thus, one can rule out the formation of polyaniline or oligomers of polyaniline, which are electroactive in this potential range and are usually generated by electrochemical oxidation of aniline.[16] However, an oxidation wave is observed at around 0.9 V, which could be assigned to the irreversible oxidation of aminophenyl (e.g., aniline) groups grafted at the gold electrode surface. This value is in agreement with the ones obtained for oxidation of aniline to its radical cation form during the polymerization process of polyaniline in acidic media.[17] However, the electrochemical oxidation of the grafted aminophenyl groups does not appear to lead to the formation of a polyaniline layer presumably due to the fact that the electrochemically generated radicals cannot efficiently recombine or react with another aniline unit because they are not close enough to each other. Interestingly, the formation of surface confined aniline dimers and polyaniline by electrochemical oxidation of the aniline terminated alkylthiol chain of a monolayer film was recently reported.[18] In this case, the orientation of the aniline monomer at the end of the alkyl chain favored the coupling reaction between the aniline units.

Barrier Effect. The blocking behavior of the resulting modified gold electrodes was investigated by electrochemical measurements in the presence of ferri/ferrocyanide as an electroactive redox probe. Figure 3a shows CVs before and after the modification of gold electrode by the electrochemical reduction of in situ generated aminophenyl diazonium cations together with that recorded for a gold electrode modified by in situ generated 4-nitrophenyl diazonium cations.[19] One can note for the latter electrode that nitrophenyl groups could have been partially reduced to NH_2 during the electrochemical grafting step.[20]

The CV response of the bare electrode in the presence of the ferri/ferrocyanide redox couple is significantly affected by both grafted layers. When the same conditions are used for the modification, Figure 3a shows the more important suppression of the electrochemical response of the $[Fe(CN)_6]^{3-/4-}$ redox system in the case of the electrode modified by aminophenyl groups than for that modified by nitrophenyl groups. These results were confirmed by electrochemical impedance measurements (Figure 3b). Indeed, the charge-transfer resistance, estimated from the diameter of the semicircle of the Nyquist plot,[7c] is higher for the aminophenyl modified electrode than for nitrophenyl, reveal-

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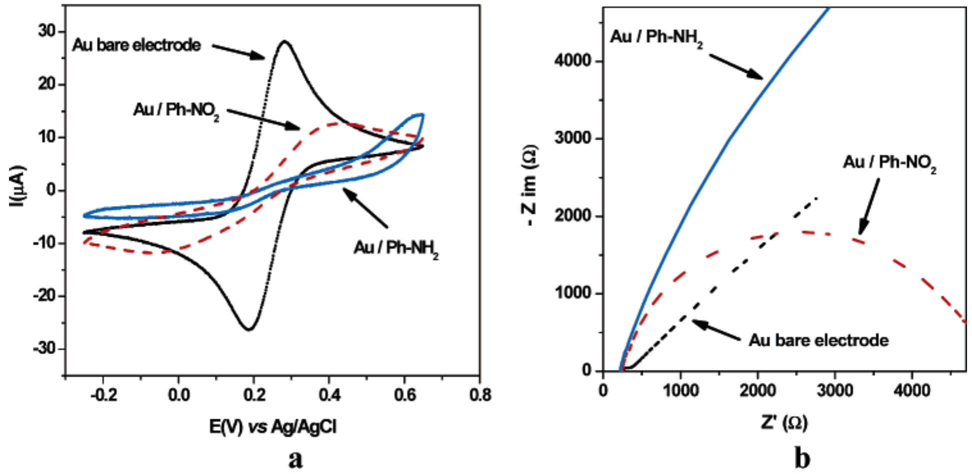

Figure 3. (a) CVs at a scan rate of 50 mV/s and (b) Nyquist plots of gold electrodes ($\phi = 1$ mm) modified by in situ generated X-phenyl diazonium cation ($X = NO_2$ or NH_2) in 0.5 M HCl, $E_{\mathrm{applied}} = -0.4$ V vs Ag/AgCl during 400 s; $C_{\mathrm{Fe(III)/Fe(II)}} = 5$ mM, pH = 7.

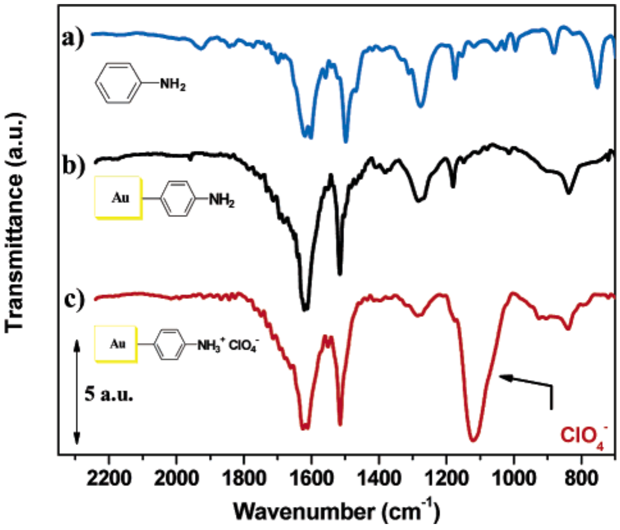

Figure 4. (a) IR spectrum of aniline (NaCl window) and IRRAS spectra of (b) aminophenyl modified gold electrode and (c) aminophenyl modified gold electrode after immersion in 0.5 M $HClO_4$ solution.

ing a stronger barrier effect for the former. These results suggest that the aminophenyl layer is more compact than the one consisting of nitrophenyl groups.[21] Thus, the electrochemical reduction of in situ generated aminophenyl diazonium cations leads to the formation of a strongly attached surface film, which passivates the gold electrode.

IRRAS. Figure 4 shows the IRRAS spectrum of an aminophenyl modified gold plate (Figure 4b) together with the spectrum of aniline (Figure 4a) for comparison. One can observe some difference between the two spectra, which give important information about the nature of the deposited film. The presence of aminophenyl groups on the metallic surface is clearly confirmed by three bands at about 1600, 1500, and 1250 cm^{-1}. The intense band at 1617 cm^{-1} is attributed to the angular deformation of N—H in NH_2 and to the C=C bond stretch in aromatic rings. This band could also be the result of the presence of phenyl multilayers.[22,23]

The strong band at 1515 cm^{-1} also reveals the presence of aromatic ring in the film (C=C stretching) whereas the one at 1273 cm^{-1} corresponds to C—N aromatic vibration. All these characteristic bands are also observed in the aniline spectrum, which unambiguously confirms the immobilization of aminophenyl groups on the gold electrode. The broad band at 908 cm^{-1} and the single band at 837 cm^{-1} are assigned to the out of plane vibration of aromatic C—H. These bands reveal the presence of 1,4 disubstituted and 1,2,4 trisubstituted phenyl moieties according to the growth of a phenyl multilayer on the meta position during the electrochemical process.[5,8a,22] It should be noted that the characteristic bands of polyaniline at 1578 and 1140 cm^{-1} associated to the quinone-ring stretching[24] and the band used by Chiang and MacDiarmid[25] to estimate the polyaniline doping state, respectively, are not observed in the spectrum, which again rules out the formation of such polymer on the gold electrode during the grafting step.

The spectrum of the aminophenyl modified electrode (Figure 4a) exhibits three weak bands at 3440, 3385, and 3230 cm^{-1} (not shown) which correspond to N—H bond elongation in agreement with the ones observed in the same spectral region for aniline. Furthermore, the bands associated with the C—H aromatic stretch are attenuated by the phenyl multilayers as demonstrated by Kariuki and McDermott.[22] It is noteworthy that the band at 2230 cm^{-1}, due to the N≡N stretch of the diazonium salt, is absent in the spectra shown in Figure 4b,c, which is consistent with the loss of the diazonium group during the reduction process and suggests the covalent attachment of aryl groups to gold.

An additional proof of the presence of the aminophenyl functionality on the gold surface was obtained when the modified electrode was immersed in a 0.5 M $HClO_4$ solution for 1 h to generate the ammonium perchlorate salt. After rinsing with diluted $HClO_4$ (1 mM) and treatment in an ultrasonic bath with acetone for 5 min, the IRRAS spectrum of the resulting modified electrode was characterized by a strong band at 1120 cm^{-1} (Figure 4c). This band, which is not observed for the aminophenyl modified electrode could,

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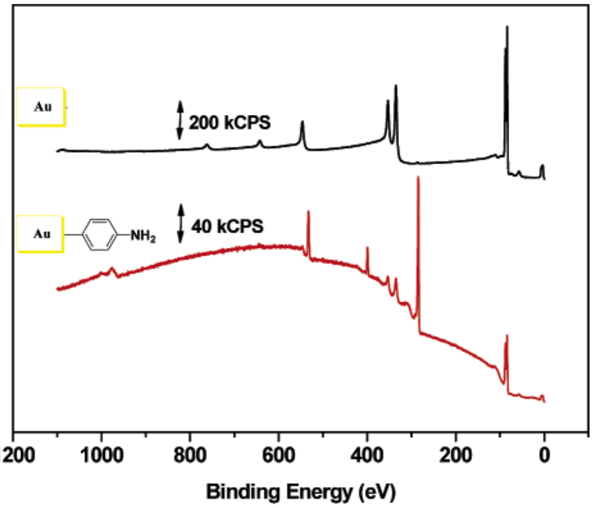


Figure 5. XPS survey spectra of a gold electrode before and following modification by aminophenyl groups.

therefore, be attributed to the presence of perchlorate, the counterions, in the film.[26] Hence, the IRRAS data provide compelling evidence for the grafting of aminophenyl groups on the gold electrode by the electrochemical reduction of in situ generated aminophenyl diazonium.

XPS. The grafting of aminophenyl groups on the gold surface was further characterized by XPS measurements. Figure 5 shows the survey spectra of gold electrodes before and after modification by aminophenyl groups. The spectrum of the bare gold electrode presents the characteristic Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks at 84 and 88 eV, respectively. Small traces of carbon are detected at 284.6 eV (C 1s) due to the adsorption of organic contaminants during and after the cleaning process. After electrochemical derivatization, the intensities of the Au peaks decreased significantly whereas those of carbon, nitrogen, and oxygen increased dramatically. In addition, the presence of a grafted layer is confirmed by the increase of the background, following modification, which is due to the inelastic scattering of the photoelectrons by the grafted layer. The thickness of the deposited layer was estimated to be about 10−15 nm from the attenuation of the Au 4f peaks.[9a] Oxygen traces may be explained by the formation of coadsorbates following the interactions between amino groups, atmospheric carbon dioxide, and water. Indeed, a C 1s peak appears at 288.2 eV, assigned to HCO_3^-, when modified gold plates are exposed to air.[27] In addition, the peak at 399.4 eV is attributed to the presence of an organic film containing nitrogen functionality at the gold surface. Additional information about the nature of the film can be deduced from the N 1s and C 1s core level spectra (Figure 6).

Table 1. Carbon/Nitrogen Atomic Ratio Evaluated by XPS of the Film Generated at the Gold Electrode Surface as a Function of the Number of Equivalents of $NaNO_2$ Added to the Deposition Solution

$NaNO_2$ (number of equivalents)	C/N atomic ratio
0.5	9.5
1	9.5
1.5	24.1
2	26.2

The N 1s core level spectrum can be well-fitted with two components located at 399.4 and 400.1 eV (Figure 6a). The 399.4 eV component is consistent with the presence of amino groups at the electrode surface.[28] A peak with a similar binding energy has been reported for an aminophenyl film obtained by the reduction of grafted nitrophenyl groups.[8a,29,30] The smaller component at 400.1 eV, often observed and prone to debate, may be attributed to the formation of azo bridges[3a,9a,28] in the film. It is well-known that diazonium is prone to coupling resulting in the formation of an azobenzene derivative, which might be involved in the film growth.[31] Furthermore, such azo bridges could be formed at the surface and within the film.[3a,9a] The origin of this peak could also be attributed to the formation of ammonium salt, but this hypothesis is unlikely because the counterion (Cl^-) was not observed in the film by XPS (N 1s ammonium bicarbonate excluded because it is usually observed at 401.2 eV[27]). The nitrogen fraction involved in azo bridge could be estimated to be 13% relative to surface area of the two N 1s components, that is, one azo group for every 12 phenyl rings. The absence of characteristic peaks for the diazonium function at 403.8 and 405.1 eV demonstrates that the diazonium cation has undergone a chemical transformation during the electrochemical process.[10]

The C 1s core level spectrum (Figure 6b) can be fitted with at least three components at 284.4, 284.9, and 285.5 eV. The two first components are attributed to carbon of aromatic rings, and these two components were also observed in the case of gold electrode and carbon powder modified by nitrophenyl groups.[32] The 285.5 eV peak is assigned to the carbon attached to the amino groups.[28] One can note that the intensity of this peak decreases and that the C/N ratio

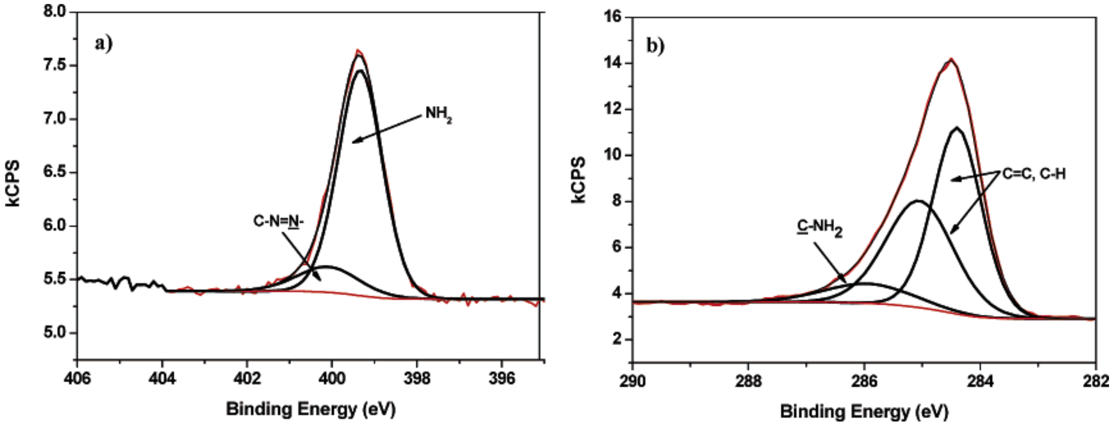
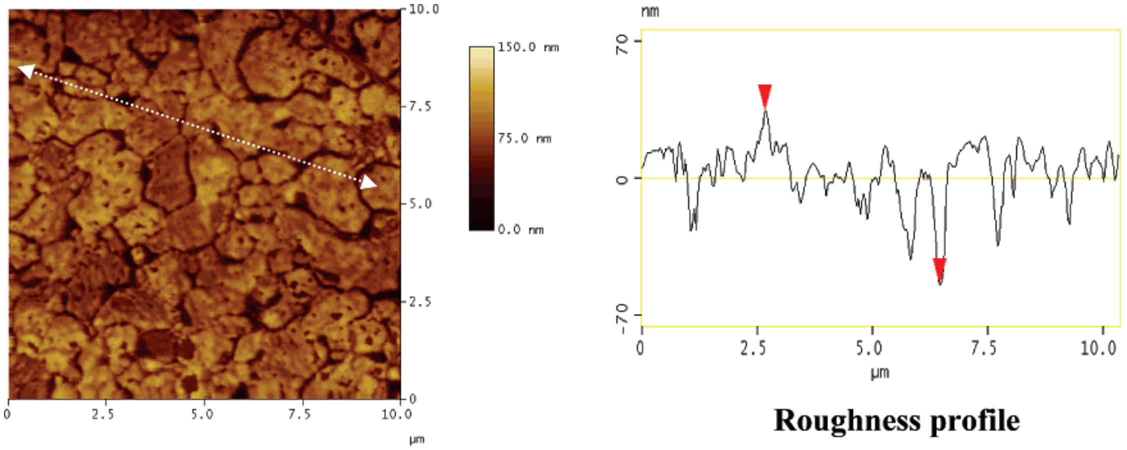


Figure 6. XPS core level spectra of gold electrodes modified by aminophenyl groups: (a) N 1s and (b) C 1s.



Roughness profile

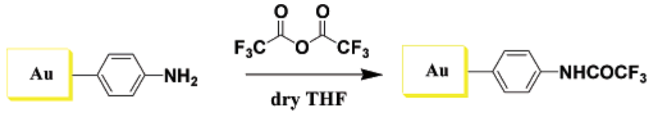
Figure 7. AFM image of an aminophenyl modified gold electrode. The roughness profile corresponds to the line drawn with two arrows on the AFM image. It should be noted that the bare gold electrode is relatively rough as well (see Figure SI 3, Supporting Information).

increases (Table 1) for gold electrodes modified after addition of 1.5 and 2 equiv of $NaNO_2$ into the electrochemical cell. Finally, the C 1s core level spectrum could be also fitted with an additional component at 284.1 eV (Figure SI 2, Supporting Information) which is in agreement with the formation of a Au−C bond as it was recently claimed by Pinson and co-workers for several metals modified by the same approach.[9,33] Nevertheless, it should be emphasized that a good fit can be also obtained without the presence of this additional low binding energy component.

Concerning the peak surface area ratios compiled in Table 1, one can observe a C/N ratio of 9.5 when 0.5 or 1 equiv of $NaNO_2$ is introduced in the cell. Although this ratio is higher than the one expected (carbon excess may be explained by the CO_2 adsorption), these results are in accordance with the generation of the monodiazonium salt which then attaches to the surface when less than 1 equiv of sodium nitrite is added to the solution.

When more than 1 equiv of $NaNO_2$ is used, one can observe that the C/N ratio increases dramatically in agreement with the generation of the bisdiazonium cations, which are unstable in our experimental conditions, at room temperature. Furthermore, the presence of chlorine in the XPS survey spectra for gold electrodes modified by using 1.5 or 2 equiv of sodium nitrite can be explained by the substitution of the diazonium functionality by chlorine in the deposited film. The latter will contribute to the increase of the C/N ratio (Table 1). Finally, the amount of grafted aminophenyl groups decreases substantially for the electrode modified in the presence of 1.5 or 2 equiv of sodium nitrite, as evidenced by the weaker attenuation of the Au 4f peaks in the survey spectra of these modified gold electrodes and as suggested by the observation of a larger anodic peak current for the CV recorded in this solution (vide supra, Figure 1a).

Scheme 3. Reaction of Grafted Aminophenyl Groups with TFAA



AFM. Visual inspection of the grafted electrode points to the formation of multilayers (vide supra). To have more information about the film morphology, AFM images of the modified gold electrodes were recorded in the tapping mode (Figure 7). Modification of the gold plate by the in situ generated diazonium salt is clearly evidenced. AFM investigations show the presence of a relatively inhomogenous and rough organic layer on the surface, as illustrated by the roughness profile of Figure 7, which shows an average thickness variation of about 25 nm over the line scan. Theses results indicate that the electrochemical process yields films much thicker than one monolayer. The formation of cracks could be explained by the hydrophilic properties of such film induced by the presence of amino groups. Presumably, water is incorporated in the film during its growth, and these cracks could be formed during drying of the deposited films when water evaporates.

Reactivity of Grafted Aminophenyl Groups. The direct grafting of aminophenyl groups can make possible further chemical derivatization which is crucial for biosensing applications.[34] To further demonstrate the presence of aminophenyl groups and the chemical reactivity of such grafted functions, gold electrodes modified by electrochemical reduction of in situ generated aminophenyl diazonium cations were immersed in a dry tetrahydrofuran THF solution of trifluoroacetic acid anhydride (TFAA, Scheme 3).[30]

The IRRAS spectra of the aminophenyl modified electrode before and following reaction with TFAA are shown in

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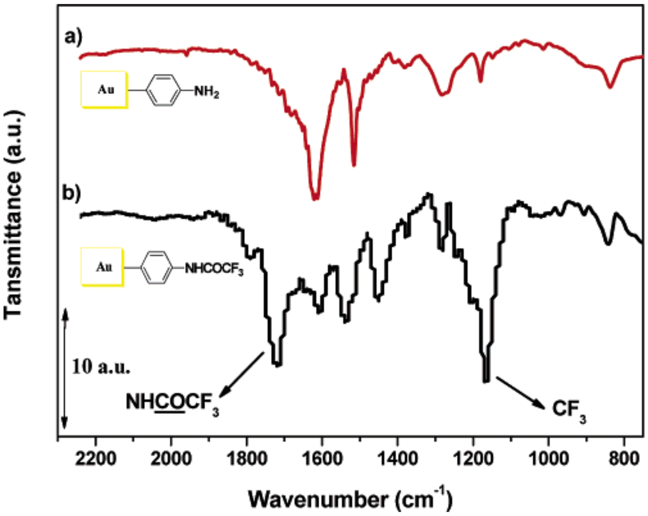


Figure 8. IRRAS spectra of (a) the aminophenyl modified gold plate and (b) aminophenyl modified gold plate after derivatization by TFAA.

Figure 8. The spectrum of the electrode after reaction with TFAA shows an intense peak at 1730 cm^{-1} that can be attributed to a carbonyl stretching vibration of the amide[23a,35] and a characteristic band of the CF_3 groups at 1170 cm^{-1},[23a,30] which confirms that the reaction occurred. The electrode surfaces were further characterized by XPS. The XPS survey spectrum of the aminophenyl modified electrode after reaction with TFAA (Figure 9a) exhibits a new peak around 690 eV, which is attributed to the presence of fluorine in the film. The F 1s core level spectrum (Figure 9b) could be very well fitted with a single component at 688.3 eV, which is assigned to the trifluoromethyl groups present at the surface.[30]

Table 2. Carbon/Nitrogen and Fluorine/Nitrogen Atomic Ratios Evaluated by XPS for the Aminophenyl Modified Gold Electrode after Reaction with TFAA as a Function of the takeoff Angle

takeoff angle (deg)	C/N atomic ratio	F/N atomic ratio
0	11.2	2.32
45	12.5	2.32
60	11.3	1.84
75	14.0	2.31

Moreover, the N 1s core level spectrum was affected by the chemical reaction. A comparison of the N 1s spectra before (Figure 6b) and following reaction with TFAA (Figure 9c) demonstrates the presence of a new component at 400.5 eV in addition to the amine peak at 399.4 eV. The former is attributed to the amide nitrogen of the modified electrode after the trifluoroacetylation of the amine group.[36,37] From the relative contribution of the two N 1s components at 400.5 and 399.4 eV, the yield of the trifluoroacetylation reaction could be estimated to 70%, if we assume that the diazo bridges (contribution at 400.1 eV, vide supra) are not affected by the reaction and still contribute to the peak at 400.5 eV. The reaction yield can be also confirmed by considering the F 1s and N 1s peaks, which gives an F/N ratio of 2.32 and consequently a yield of 77% for the transformation.

Furthermore, this ratio, as well as the N/C ratio, remained constant when the analysis was performed at takeoff angles of 0, 45, 60, and 75° (Table 2) which reveals that the chemical derivatization occurred not only at the film surface but also inside the film. These results suggest that TFAA diffuses inside the film, and this contrasts with the blocking behavior effect of the film to $Fe(CN)_6^{3-}$ (vide supra). This difference

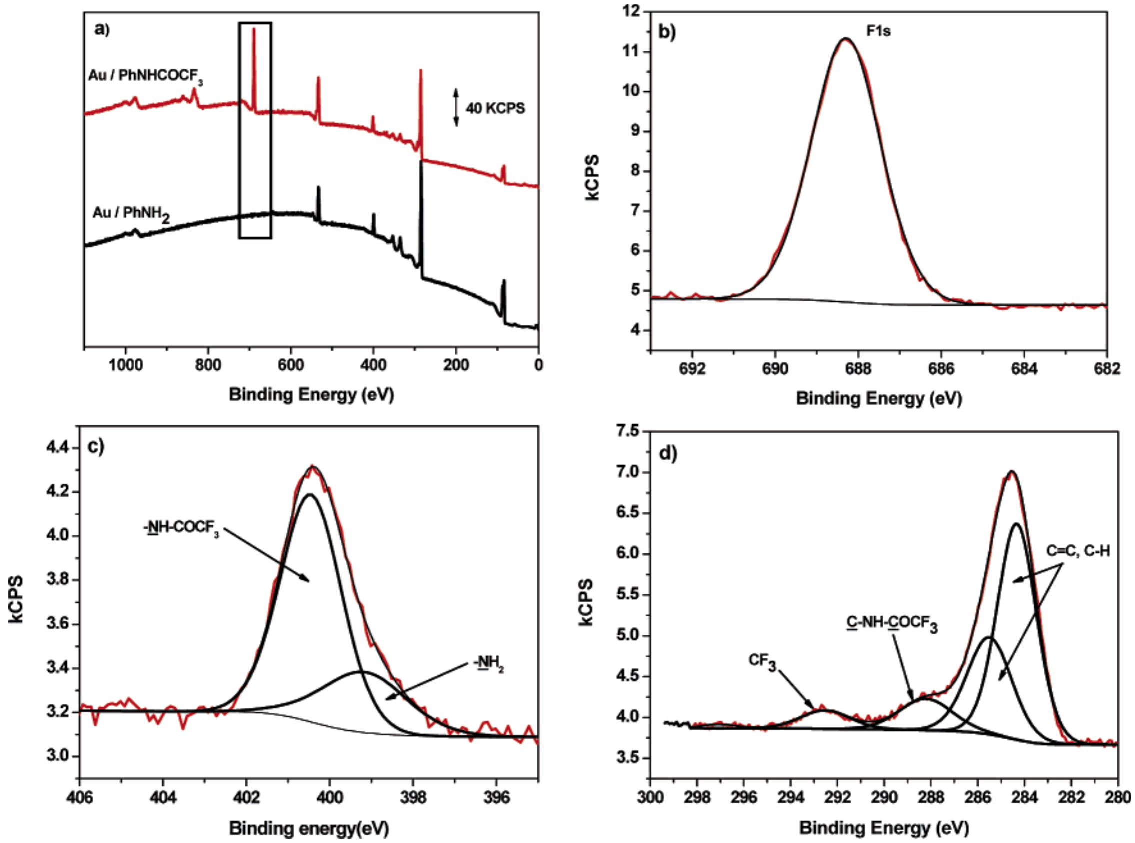
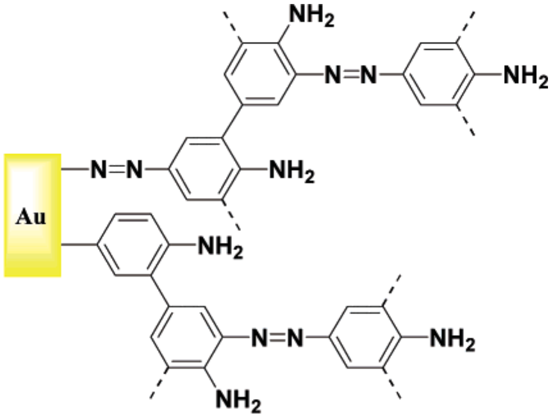


Figure 9. XPS measurements after chemical reaction of grafted aminophenyl groups with TFAA: (a) XPS survey spectra before and after reaction, (b) F 1s core level spectrum, (c) N 1s core level spectrum, and (d) C 1s core level spectrum of the grafted electrode after reaction.

Scheme 4. Proposed Structure of the Film Obtained by the Electrochemical Reduction of in Situ Generated Aminophenyl Diazonium Cation



could be explained by a difference in swelling in the two solvents (THF and water) that are used in these two sets of experiments.

Finally, one can observe two new components at 288.2 and 292.5 eV on the C 1s core level spectrum (Figure 9d) after the chemical modification. The 288.2 eV peak is assigned to the carbonyl of trifluoroacetamide whereas the component at 292.5 eV is due to the carbon of trifluoromethyl groups.[28] Thus, IRRAS and XPS data provide compelling evidence of the reactivity of such grafted aminophenyl groups, which opens the way to the covalent coupling of other specific functionalities which can be useful for various applications such as for the immobilization of biomolecules.

Electrochemical and spectroscopic investigations confirm the presence of aminophenyl groups and their strong attachment to the gold surface. Furthermore, the growth of aminophenyl multilayers is clearly observed by AFM. The contribution of the azo bridge to the film growth was also suggested by XPS. Therefore, a chemical structure of the film obtained on the gold surface by the electrochemical reduction of in situ generated aminophenyl monodiazonium cations in acidic media can be proposed (Scheme 4). It involves three different subunits and processes. The first one is the direct grafting of aminophenyl units. The N 1s data suggests the formation of $C-N=N-C_6H_4-NH_2$ moieties at the surface.[9a] Finally, the formation of multilayers by reaction on already grafted groups[5,22] can be invoked to explain the formation of thick films.

Conclusion

The electrochemical reduction of in situ generated aminophenyl monodiazonium cations (from *p*-phenylenediamine) on gold in acidic media enabled the simple and efficient grafting of aminophenyl groups on the gold electrode surface in one step. The gold modified electrodes were characterized by several techniques such as XPS, IRRAS, and electrochemical measurements, which unambiguously show the multilayered nature of the aminophenyl film obtained and its robust attachment to the gold surface. Also, further chemical derivatization of such film was demonstrated and could presumably be extended to a reaction with the selected chemical or biological species. Interestingly, a complementary approach for the immobilization of proteins has been recently reported by Corgier et al., and in their procedure, rabbit immunoglobulin was functionalized with 4-carboxymethylaniline, diazotated, and electrochemically deposited on electrode.[1c] Finally, future experiments will examine the chemical modification of carbon powder by the aminophenyl diazonium salt generated from **1** without electrochemical induction,[38] and the results will be published in a forthcoming paper.

Experimental Section

Reagents. *para*-Phenylenediamine, *para*-nitroaniline, sodium nitrite, and trifluoroacetic acid anhydride, TFAA (Aldrich) were used as received. Aniline (Aldrich) was distilled twice before infrared spectroscopic investigations.

Electrode Preparation. Polycrystalline gold plates (used for XPS and IRRAS) from Arrandee (11 × 11 mm) were cleaned before each experiment using the following procedure: annealing with a butane flame, 1 min immersion in a 1:1 H_2SO_4/H_2O_2 mixture, 5 min of ultrasonic cleaning in nanopure H_2O, EtOH, and acetone, 50 cycles at 50 mV/s in 0.1 M H_2SO_4, and 5 min of ultrasonic cleaning in Nanopure H_2O, EtOH, and acetone. Gold electrodes ($\phi = 1$ mm) were cleaned by polishing with 0.05 μm alumina slurry. After each polishing, electrodes were washed by 5 min of consecutive ultrasonic treatment in Nanopure H_2O, EtOH, and acetone.

Equipment and Methods. Electrochemical experiments were performed using a potentiostat/galvanostat 263A (EG&G, Princeton Applied Research) and a frequency response analyzer Solartron 1250 controlled by a computer with the Corrware and Zplot (Scribner Associates, version 2.6b) softwares. A one-compartment electrochemical cell was used with a three-electrode configuration. The reference electrode was Ag/AgCl (saturated KCl), and the platinum gauze counter electrode was flame-cleaned before each experiment. The in situ diazonium reduction experiments were carried out in a 5 mM acidic solution (0.5 M HCl) of **1** or *para*-nitroaniline containing 1 equiv of sodium nitrite (unless otherwise stated) which was deaerated by bubbling with ultrapure nitrogen for 5 min prior to each experiment. The barrier properties of unmodified and modified gold electrodes were evaluated in a 5 mM $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$/0.1 M KCl aqueous solution, adjusted to pH 7 with 16 M NaOH. Electrochemical impedance spectroscopy experiments were carried out between 65 kHz and 50 mHz using a signal amplitude of 10 mV.

For XPS, IRRAS, and AFM measurements, the Au electrode was modified potentiostatically at −0.4 V for 400 s in a 5 mM acidic solution (0.5 M HCl) of **1** containing 1 equiv of sodium nitrite (unless stated otherwise). XPS measurements were carried out with an Axis-165 from Kratos Analytical equipped with an Al anode (monochromatic Kα X-rays at 1486.6 eV). The data were collected at room temperature, and the operating pressure in the analysis chamber was always below 10^{-9} Torr. The core level

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spectra were referenced to the Au $4f_{7/2}$ binding energy at 84 eV. Data treatment and peak-fitting procedures were performed using Casa XPS (version 2.2.107) software. IRRAS measurements were carried out with a ThermoNicolet Nexus 670 FT-IR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector. Experiments were performed with an incidence angle of 85°, and the measurement chamber was continuously purged with nitrogen during acquisition of spectra. IRRAS spectra were treated with OMNIC IR 6.0a software (ThermoNicolet Corporation). The aniline spectrum was recorded with NaCl windows in the transmission mode. AFM images were recorded at atmospheric pressure and temperature in the tapping mode using a Nanoscope III Dimension 3100 AFM instrument (Digital Instruments) with an etched silicon aluminium coated tip. GC-MS analyses were performed with a G 1800 B instrument from Hewlett-Packard equipped with a GCD system.

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Supporting Information Available: GC-MS investigation (GC profile and mass spectra), C 1s XPS core level spectrum of a gold electrode modified by aminophenyl groups, and AFM image of an unmodified gold electrode (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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