Spontaneous Attachment of Amines to Carbon and Metallic Surfaces

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Primary alkylamines attach spontaneously from acetonitrile (ACN) solutions onto glassy carbon and metallic surfaces (Au, Pt, Cu, and Fe). The surface concentration of the organic layer measured from the integration of cyclic voltammograms appears close to or lower than that of a compact monolayer. The rate of the attachment depends on the concentration of the primary amino compound; it reaches a maximum after 3 h of immersion for the most concentrated solutions (20 mM). The modified surfaces have been characterized by cyclic voltammetry (CV), energy dispersive X-ray spectrometry (EDX), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (ATR). The possible reaction mechanisms are discussed.

Introduction

This paper investigates the attachment of organic layers to carbon and metal surfaces. A limited number of methods permit such a reaction. The most popular is the spontaneous attachment of thiols on gold and some other metals (self-assembled monolayer, SAMS);[1] it leads to a bond between sulfur and metal, which is not very strong and therefore permits the organization of the layer. The electrochemical reduction of vinylic compounds,[2] and of diazonium salts[3] leads to a strong bonding of an unorganized multilayer on carbon and metals. The electrochemical oxidation of alcohols[4] ROH on carbon leads to **C−OR** modified carbon while the electrochemical oxidation of amines which will be described in some more details below leads to **C**, **Au**, or **Pt−NHR** assemblies on carbon, gold, and platinum, respectively.

On carbon, attachment of primary and secondary alkylamines has been achieved by electrochemical oxidation.[5] Upon oxidation of a primary amine, RNH_2, on a glassy carbon (GC) or carbon fiber electrode, one can observe the attachment of the $RNH-$ group to the surface of the electrodes as shown in Scheme 1.

Attachment of the amino group was demonstrated through the observation of the electrochemical signal of reporting groups such as the nitro group: upon oxidation of 4-nitrobenzylamine on a GC electrode, thorough rinsing of the electrode in an ultrasonic bath and transfer in an ACN + 0.1 mol·L^{-1} NBu$_4$-BF$_4$ solution, it was possible to observe the reversible signal of the nitrobenzyl group.[5a,b,c] Other reporting groups were also used such as anthracene or anthraquinone.[5a] The grafting was also demonstrated by XPS through the increase of the N1s signal after oxidation of the amines[5a,b,c] but also through the observation of the F1s signal after further derivatization of a surface modified by oxidation of ethylenediamine,[5a] SIMS (secondary ion mass spectroscopy) measurements confirmed the attachment of 2-amino 4-methylthiazole to the surface of fibers.[5a] With secondary amines, the surface concentration of amino groups

SCHEME 1
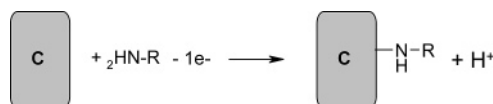
SCHEME 2: Z ≡ electron withdrawing groups on the carbon fiber surface such as carboxyl or carbonyl functional groups.
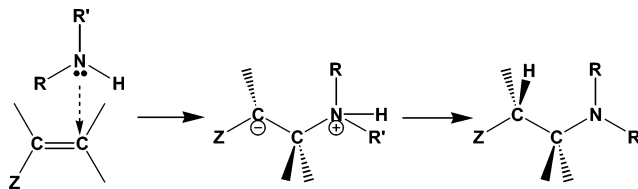
was lower than with primary amines and tertiary amines hardly graft at all.[5b,c]

The spontaneous reaction of *n*-butylamine with carbon films obtained by pyrolysis of cellophane[6a] was investigated by IR spectroscopy, the formation of highly stable (up to 400°C) carboxylic-ammonium salts was established. Later on, it was shown[6b] that the attachment of amines to carbon fibers could also be achieved without electrochemistry and this was assigned to a Michael-like reaction between the amines acting as a nucleophile and double bonds of the carbon structure (Scheme 2). In a similar way, nucleophilic addition of primary and secondary amines on buckminsterfullerene has been observed.[7] Grafting of amino groups without electrochemistry was also achieved by polishing carbon surfaces in the presence of ammonia and further reaction with N-hydroxysuccinimide ester.[8] More recently, the partial intercalation of 4-nitrobenzylamine into graphite powder and multiwalled nanotubes was observed.[9]

On metals, Herlem[10a,b] has shown that the oxidation of pure ethylenediamine on a Pt or Au electrode leads to the formation of a polyethyleneimine-like polymer strongly attached to the metallic surface. More recently,[5c] we have shown that it is possible to achieve the modification of gold and platinum surfaces by electrochemical oxidation of various amines. The grafting of amino groups was characterized by cyclic voltammetry through the observation of the reversible signal of

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SCHEME 3
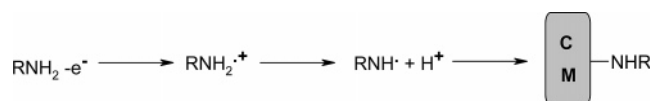
nitrobenzyl groups, through the blocking of the electrode resulting from the deposition of the organic layer and through XPS and IRRAS (infrared reflection absorption spectroscopy) for a large number of primary, secondary, and tertiary amines including nitrobenzylamines. On gold and platinum electrodes, the amount of grafted nitrobenzyl groups could be measured by integration of the cyclic voltammograms. The surface concentrations were similar to that observed on carbon. The electrochemical bonding of amines on a smooth gold electrode was also observed by use of ^{14}C− labeled compounds.[10c] The first step leads to losely adsorbed species; it is followed by a process leading to strongly attached molecules. The attachment of the amino group was initially assigned to the radical-cation formed upon oxidation of the amine but more recent investigations[5c] indicated (through the IRRAS examination of deuterated amines attached to Pt) that the radical obtained after deprotonation of the radical−cation (Scheme 3) is responsible for the attachment reaction.

As amines are oxidized at relatively high anodic potentials, only noble metals (gold and platinum) and carbon can be derivatized through this electrochemical reaction and this constitutes a serious drawback of the method.

On titanium and aluminum (two metals which are covered by native oxides and hydroxides), an interesting spontaneous reaction was observed between the metal and diamines such as 3-aminomethyl-3,5,5-trimethylcyclohexylamine or poly(oxopropylene diamine).[11] Using various analytical techniques (differential scanning calorimetry, DSC; IRRAS, inductively coupled plasma spectroscopy, ICP; and polarized optical microscopy, POM), the authors have shown that a chemical reaction of the diamine monomers takes place with the surface along with a partial dissolution of the metallic oxide/hydroxide layer. Then, metallic ions diffuse through the liquid organic layer to form an organometallic complex by coordination bonding of the two nitrogens with metal atoms. When the complex's concentrations are higher than their solubility limits, these complexes may partially precipitate to form needle sharp crystals; their structures were determined by NMR (nuclear magnetic resonance). However, no such phenomena were observed on gold.

On iron, a reaction was observed with amines (at 60−75°C, 16 h)[12] and the resulting surface was investigated by XPS spectroscopy. Based on these studies, several types of iron−oxygen bonds were discussed.

On crystalline silicon Si(001) and Si(111), the bonding of trimethylamine (TMA) and dimethylamine (DMA) under ultrahigh vacuum, has been characterized by XPS, IR, and density-functional computational methods.[13a] It was shown that TMA forms stable dative bonded adducts on both silicon surfaces. These adducts are highly ionic, indicating a high degree of donation from N to Si. Corresponding studies on DMA on Si-(001) show only dissociative adsorption via cleavage of the NH bond. More generally, the ability of silicon to act as an electron acceptor has been implicated in the interaction of molecules such as ammonia and phosphine with silicon surfaces.[13b,c,d]

As concerns the possible applications, the electrochemical attachment of amines to carbon has been used for various applications: electrochemically modulated liquid chromatography,[14] suppression of protein adsorption at GC electrodes,[15]

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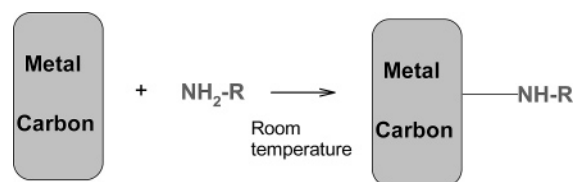
specific electrodes for the reduction of CO_2,[16] electrochemical preparation of ion exchange carbon fiber,[17] chemical sensors,[18] attachment of polyoxometalates through the electrochemical oxidation of 4-aminobenzoic acid,[19a] formation of multilayer films of Fe(III) tetrakis(p-sulfonatophenyl) porphyrin and cationic polymer diazo-resins through the electrochemical oxidation of aminobenzenesulfonic acid[19b] in water, and the formation of zirconium-phosphonate multilayers on alkylamines derivatized GC.[19c] The reaction of amines with metal oxides has been used for adhesion improvement.[20]

It is the purpose of the present paper to show that the attachment of amino groups to metallic surfaces can be achieved without electrochemical oxidation by simple dipping of the metallic plate into a solution of the amine as sketched in Scheme 4. This will make the grafting of amines to easily oxidized industrial and coinage metals (Fe, Cu) possible, which are oxidized at potentials less positive than the amines. 11-Aminoundecanoic acid was examined in order to determine if the deprotonation of the carboxylic group could influence the grafting of the amino group through a possible adsorption by the carboxylic or carboxylate group. In addition, after grafting, this carboxylic group could be used for further modification of the surface.

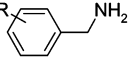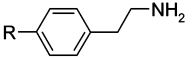The alkylamines used for the modified surfaces are shown in Scheme 5.

The modified surfaces will be termed by the symbol of the metal followed by the symbol of the amine, for example **PtnHex**. Previous experiments[5c] dealing with the oxidation mechanism of aliphatic amines were performed in dimethylformamide (DMF), which is less acidic than acetonitrile (ACN), but we observed that electrografting is more efficient in ACN likely due to differences of solvation of the amines. Therefore, the experiments described in this paper were performed in ACN.

Results

Infrared Spectroscopy. The attachment of amines (after dipping (120 min) of surfaces in 15 mM solution of amines in ACN) to the different surfaces was characterized by IR spectroscopy. The spectra for *n*- hexylamine are shown in Figures 1 and 2, and Figures S1−S3 (see the Supporting Information). The results are summarized in Table 1.

The above IR spectra clearly indicate the presence of the amino group on the surface of the different metals. Primary amines present two NH stretching bands (asymmetric and symmetric vibrations) in the 3500−3000 cm^{-1} range. These bands are observed for all the amines investigated even if the two bands are somewhat merged in the case of 4NB and 11AU. Secondary amines show only one band in the NH stretching region, and this is what is observed in agreement with the expected structure of the modifying layer indicated in Scheme 4. Other signatures of the amino group (Figures S1−S5 and Tables S1−S4, see the Supporting Information) on the surface are the NH stretching (**AuBz**, **Pt4NB**, **Fe4NB**, **AunHex**, **PtnHex**, **Cu11AU**, **AucyHex**, **PtcyHex**, **CucyHex**, **FecyHex**), CN stretching (**Fe4NB**, **Cu4NB**) and NH deformation (**AuBz**, **PtBz**, **FeBz**, **Cu4NB**, **Pt4NB**, **Fe4NB**, **AunHex**, **PtnHex**,

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SCHEME 5

	R = H	Bz
R⟨benzylamine⟩NH₂	R = 4-nitro	4NB
	R = 3-nitro	3NB
	R = 4-fluoro	4FB
R⟨phenethylamine⟩NH₂	R = 4-nitro	4NPE
n-Hexylamine	*n*-C₆H₁₅N	*n*Hex
11-Aminoundecanoic acid	C₁₁H₂₃NO₂	11AU
Cyclohexylamine	cycloC₆H₁₃N	*cy*Hex
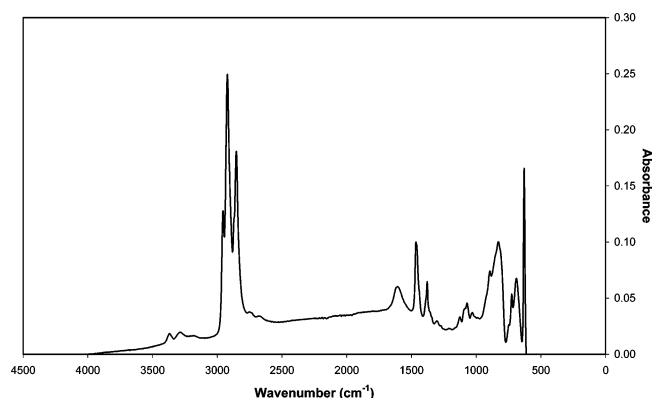
Figure 1. ATR spectrum of *n*-hexylamine (*n***Hex**) (neat liquid).
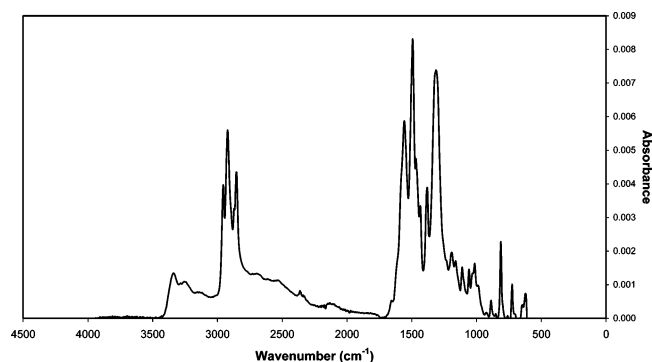
Figure 2. ATR spectrum of *Fen***Hex**.

TABLE 1: IR Spectra of Metals Derivatized by
n-**hexylamine (*n*Hex)**[a]

	*n*Hex[b]	*Aun*Hex	*Ptn*Hex	*Cun*Hex	*Fen*Hex
NH₂, NH[c] stretching	as 3358 w s 3273 w	3310 w	3311 m	3310 m	3312 m
CH₃[d] stretching	as 2955 m	2954 m	2955 m	2953 m	2952 m
CH₂[d]	as 2922 s s 2851 s	2918 s 2852 s	2920 s 2851 s	2919 s 2851 s	2918 s 2851 s
NH deformation	1623 w	1654 w	1648 w	1653 vw	1630 vw
NH[e] bending	823 s 723 w	819 m 721 w	820 m 711 m	819 m 721 w	818 m 723 m

[a] ATR spectrum, wavenumbers in cm⁻¹. [b] Neat liquid. [c] By comparison 3392 and 3325 cm⁻¹ in dilute C₂Cl₄ solutions.[23] [d] By comparison $\nu a(CH_3) = 2966$, $\nu a(CH_2) = 2921$ and $\nu a(CH_2) = 2852$ cm⁻¹ for pentane and heptanethiol.[24] [e] From ref 22.

FenHex, **CunHex**, **Cu11AU**, **AucyHex**, **PtcyHex**, **CucyHex**, **FecyHex**). These signatures leave little doubt about the presence of the amino group on the different surfaces. The presence of the R group of the RNH₂ molecule is also attested by the

presence of the CH₂ stretching vibrations for *n*- and cyclo-hexylamine, of the COOH signature for 11-aminoundecanoic acid and by the vibrations corresponding to the aromatic ring and the nitro group for benzylamine and its 4-nitro derivative. Altogether these spectra provide a strong evidence for the attachment of the amines on the different metals investigated; they also indicate that the attachment takes place without cleavage of the R substituent (Scheme 4).

XPS Spectrum. The derivatization of 11-aminoundecanoic acid was performed both in neutral and basic ACN (after dipping (120 min) of surfaces in 15 mM solution of amines in ACN, see the Experimental Section) to determine whether the presence of a negative charge on the end of the molecule would influence its reaction with the surface through the orientation of the molecule. The survey spectra (Figure S6, see the Supporting Information) of copper and iron surfaces derivatized by reaction with 11-aminoundecanoic acid indicate the presence of both iron or copper and iron oxides, of carbon, oxygen, and nitrogen. Detection of the Fe2p3/2 from iron (706.5 eV) as well as its oxide (710.6 eV) and Cu2p3/2 from copper (933 eV) indicates that the organic layer is thinner than the analysis depths of XPS (∼10 nm) on these metallic substrates (iron and copper respectively), and that iron oxide is present despite the care taken during the preparation of the sample (see the Experimental Section). One can observe an important increase of the background intensity at energies higher than the Fe2p and Cu2p which is due to inelastically scattered photoelectrons. The carbon C1s region presents two peaks, the positions of which are summarized in Table S5 (Supporting Information). The carbon C1s peak observed at 285 eV for all the four samples can be assigned to the 10 carbon chain and that at 288.5 eV to the carbon of the carboxylic group (by comparison icosanoic acid presents a signal at 289.14 eV).[25]

Oxygen presents two components (Table S5, Supporting Information). On iron, that at lower binding energy (∼529.7 eV) is related to iron surface oxide (FeOOH is observed at 530.1−531.8 eV[26]). On copper, the signal at 531.0 eV is much smaller and corresponds to Cu₂O (530.5 eV[27]) while that at higher energy (∼532 eV) should correspond to the carboxylic group (hexanedioic acid appears at 532.8 eV[28]). Finally, no difference can be observed between the neutral and basic medium, indicating that the charge on the carboxylic groups does not influence the reaction through a possible different adsorption of the molecule.

Nitrogen presents (Figure 3) a main N1s component at 400 eV (peak B) which appears identical whether the sample is prepared under neutral or basic conditions (Table S5, Supporting Information). This signal certainly corresponds to some amine hydrogen bonded to the end carboxylic group of *Fe*11AU. This amine would remain attached despite vigorous ultrasonic rinsing.
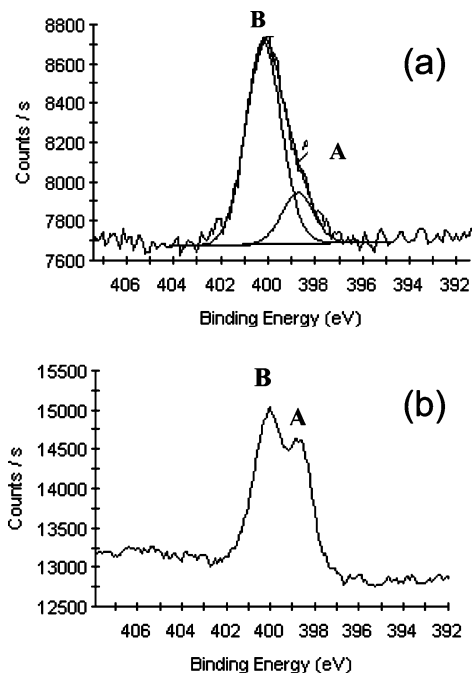
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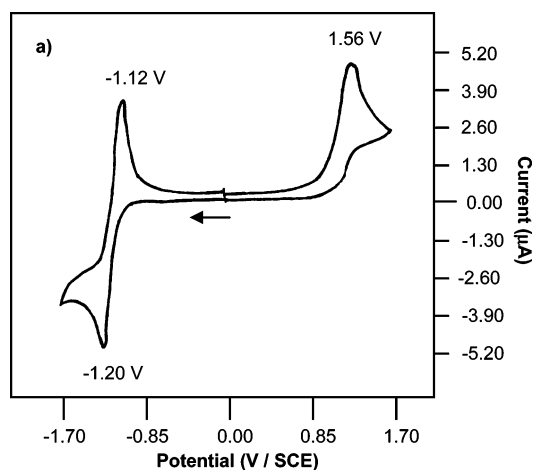**Figure 3.** XPS spectra (N1s component) or (a) *Fe***11AU** and (b) *Cu***11AU** in neutral ACN.

Figure 4. Cyclic voltammetry ($v = 0.1$ V s^{-1}, reference SCE): (a) of an ACN + 0.1 M NBu$_4$BF$_4$+ 9.11 mM solution of 4-nitrobenzylamine on a clean carbon electrode, first scan to negative potential.

In any case, it cannot correspond to an ammonium salt obtained by reaction of an amino group with the terminal carboxylic acid as this species should appear at about 402 eV (402.2 eV for trimethylammonium on Si[13a]) (besides the vibration at >3400 cm^{-1} is somewhat out of the range expected for an ammonium bond). The component at approximately 398.5 eV (peak A) certainly corresponds to the secondary amine bonded to the metal by comparison with electrografted butylamine on gold and platinum[5c] which present the same features at, respectively, 398.1 and 397.9 eV. Other comparisons can be made with dimethylamine on Si[13a] (398.9 eV), with iron phthalocyanine at 399.1 eV,[29] with iron pyrrole at 398.8 eV,[30] but also with aniline on copper (under vacuum at 397.5 eV).[31]

Cyclic Voltammetry. To observe the spontaneous grafting of amines to various surfaces we reacted 4-nitrobenzylamine (4NB) with different surfaces as its nitro group can be easily characterized by cyclic voltammetry.[32] Figure 4 shows the voltammogram of 4-nitrobenzylamine in an ACN + NBu$_4$BF$_4$ 0.1 M solution on a GC electrode, it presents an anodic peak at
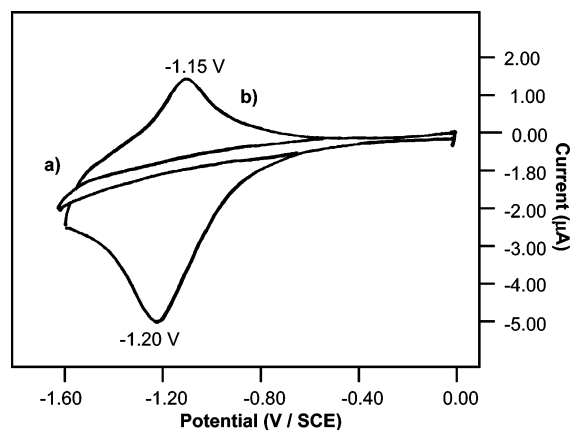

Figure 5. Cyclic voltammetry ($v = 0.1$ V.s^{-1}, reference SCE): (a) of an ACN + 0.1 M NBu$_4$BF$_4$ solution on a clean platinum electrode; (b) of an ACN + NBu$_4$BF$_4$ 0.1 M solution on a platinum electrode modified by dipping for 120 min in a 18.2 mM solution of 4-nitrobenzylamine in ACN, rinsed and transferred to this solution: *Pt***4NB**.

$E_{pa} = +1.56$ V/SCE. As explained in the Introduction[5c] this wave corresponds to the electrografting process of the amine. On the cathodic side, the reversible system located at $E° = -1.15$ V/SCE (measured as the midpoint between the cathodic and anodic peaks) corresponds to the one electron reversible system nitrophenyl D nitrophenyl radical anion. The nitro group of 4-nitrobenzylamine can, therefore, be used as a reporting group to characterize the grafting of the amine.

On gold and platinum, it is not possible to completely observe the electrochemical oxidation of the amine as it occurs after the onset of the oxidation of the metal itself. But after dipping the metals in the solutions of 4-nitrobenzylamine, it was possible to demonstrate the formation of **Au4NB**, **Pt4NB**. These materials are characterized by cyclic voltammetry. Figure 5 shows the voltammogram of a platinum electrode which has been dipped (without any electrochemical induction) in a solution of 4-nitrobenzylamine ($c = 18.22$ mM) in ACN for 2 h at room temperature, thoroughly rinsed in acetone/ethanol in an ultrasonic bath for 10 min and transferred to a ACN + NBu$_4$BF$_4$ 0.1 M solution: **Pt4NB**. The similarity between the redox potentials of the reversible system $E°($**Pt4NB**$) = -1.18$ V/SCE with that of 4-nitrobenzylamine at $E° = -1.16$ V/SCE on Pt clearly indicates that the amine has been strongly attached to the surface, strongly enough to resist ultrasonic rinsing. The same behavior is observed on gold where the reversible couple of the 4-nitrobenzylamino group is observed at $E°($**Au4NB**$) = -1.16$ V/SCE, while that of 4-nitrobenzylamine is observed at $E° = -1.14$ V/SCE, on carbon $E°($**C4NB**$) = -1.16$ V/SCE, on copper $E°($**Cu4NB**$) = -1.14$ V/SCE, and on iron $E°($**Fe4NB**$) = -1.18$ V/SCE. These last two metals cannot be electrografted as they are much oxidized than the amine.

The voltammograms of Figures 5 and 6 and Figures S7 − S9 (see the Supporting Information) show the reversible wave of the nitrobenzyl group where the anodic and cathodic peaks are of similar height (taking in account the proper baseline for the forward and backward scans). Upon further scanning, the voltammogram rapidly disappears due to the protonation of the small amount of radical anion generated on the surface by residual water of the solvent.

The shape of the voltammograms also deserves some comments. The voltammogram of a one electron reversible couple involving a fast electron transfer and a mass transport to and from the electrode by diffusion should present a cathodic and an anodic peaks separated by 60 mV. This is the case of the
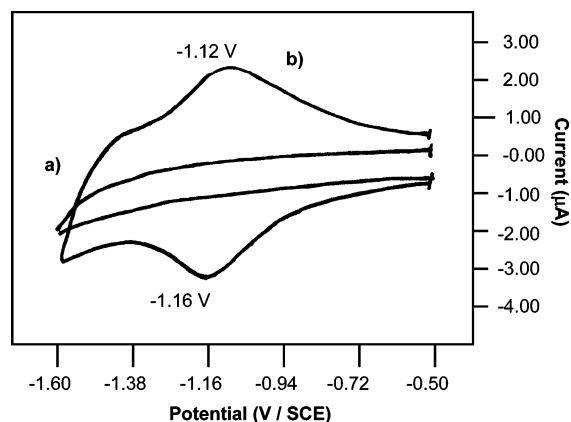
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Figure 6. Cyclic voltammetry ($v = 0.1$ V.s^{-1}, reference SCE): (a) of an ACN + 0.1 M NBu$_4$BF$_4$ solution on a clean copper electrode; (b) of an ACN + NBu$_4$BF$_4$ 0.1 M solution on a Cu electrode modified by dipping for 2 h in a 9.11 mM solution of 4-nitrobenzylamine in ACN, rinsed and transferred to this solution, *Cu*4NB.

TABLE 2: Surface Concentration of 3- and 4-Nitrobenzylamino (3NB and 4NB) Groups on GC Electrodes (*C*3NB and *C*4NB)^a

	Γ x 10^{10} mol cm^{-2}	
	electrochemical grafting 30 min	spontaneous grafting 30 min
4-nitrobenzylamine	4.0	1.4
3-nitrobenzylamine	6.4	1.9

^{a} Concentration of the amines: $c = 5$ mM.

4-nitrobenzylzamine/4-nitrobenzylzamine radical anion couple of Figure 4. But one observes that the peak separations are equal or lower than 60 mV for all electrodes. The voltammograms presents a shape that is typical of a confined redox couple (for example, compare the shape for 4-nitrobenzylamine in solution in Figure 4 with that of 4-nitrobenzylamino group bonded to the platinum surface in Figure 5b). Both of these features are related to the fact that the species do not diffuse to and from the electrode and are attached to the surface of the electrode (for a fast electron transfer, the peak separation should be zero for a species which does not diffuse).

We also investigated the possible spontaneous modification by *N*-methyl 3-nitrobenzylamine and by *N*,*N*-dimethyl-3-nitrobenzylamine but no modification of the surface could be observed, indicating that secondary and tertiary amines are much less reactive than primary amines.

Surface Concentration of the Organic Layers. Integration of the voltammogram of attached 3- or 4-nitrobenzylamino (3NB and 4NB) and 4-nitrophenylethylamino (4NPE) groups permits to measure the amount of electricity consumed for the reduction. As the reduction of the nitrophenyl group is known to be monoelectronic,[32] it is possible to deduce the number of nitrophenyl groups attached to the surface. The surface concentrations are given in mol cm^{-2} of geometrical area.

Tables S6−S11 (Supporting Information) summarize the surface concentration of nitrophenyl groups obtained by im-

mersion of metallic surfaces in 3- and 4-nitrobenzylamines as well as 4-nitrophenylethylamine solutions of two different concentrations. Figures 7, S10, and S11 (see the Supporting Information) illustrate these data. The surface concentration of the most compact layer of 4-nitrobenzylamino and 4-nitrophenylethylamino groups can be obtained from molecular models[33] $\Gamma = 4.8 \ 10^{-10}$ and $5.3 \ 10^{-10}$ mol cm^{-2}. The surface concentrations increase with time and reach a plateau after 2 h for ~20 mM solutions and 3 h for ~10 mM solutions. The values of the plateaus range from 7 to 14 10^{-10} mol cm^{-2}. This corresponds to a value close to a monolayer. The highest surface concentrations of the different substrates are obtained on gold and platinum, they are similar to these or lower on carbon, copper, and iron.

We also compared the surface concentrations obtained by electrochemical and spontaneous grafting for equal reaction times. The results are reported in Table 2, they clearly indicate that the electrografting is more efficient; the surface concentration is about three times higher for the same reaction time.

Finally the surface concentrations obtained during the grafting of different metals by 4-nitrobenzylamine was investigated in the presence of nitrogen or oxygen dissolved in the solution. The results (Table S12, Supporting Information) indicate little difference in the surface concentration of 4-nitrobenzylamine. This shows that the surface of the materials is already oxidized during the experiment (in agreement with the XPS spectra) despite the care taken to prevent oxidation and that further oxidation by bubbling oxygen changes neither the reaction nor its kinetics.

Influence of the Oxidation of the Surface.

As described in the Experimental Section, great care was taken to prevent the oxidation of the surface between polishing and grafting. However, under such conditions, it is not possible to completely suppress the formation of oxides as shown in the XPS spectrum above in the preceding paragraph concerning the surface concentrations in the presence or absence of dioxygen. We, therefore, made experiments to completely reduce or oxidize the surface before grafting. Surfaces of Fe, Cu, Au, Pt, and GC were reduced electrochemically (see the Experimental Section) by cycling to −3.0 V/SCE and oxidized either by cycling to +2.0 V/SCE in ACN (mild oxidation) or by cycling under the same conditions in 0.4 M aqueous sulfuric acid in the presence of dioxygen (strong oxidation). The results for 3-nitrobenzylamine are shown in Table 3 altogether with the results obtained without previous treatment of the surfaces. The reaction conditions were the same as previously described. For Fe, Cu, and GC the results clearly indicate smaller surface concentration after reduction of the surface and conversely a larger surface concentration after electrochemical oxidation of the surface in ACN. On the contrary, for Au and Pt, reduction or mild oxidation lead to a little change, but after stronger oxidation (electrochemical oxidation in aqueous sulfuric acid) the amount of grafting is significantly smaller.

In parallel, we examined by EDX (a semiquantitative method) the reduced and oxidized surfaces before and after derivatization

TABLE 3: Surface Concentration of 3-nitrobenzylamino Groups after Immersion in a 16.5 mM 3-Nitrobenzylamine Solution in ACN^a

surface	Γ x 10^{10} (mol cm^{-2}) Au	Γ x 10^{10} (mol cm^{-2}) Pt	Γ x 10^{10} (mol cm^{-2}) Fe	Γ x 10^{10} (mol cm^{-2}) Cu	Γ x 10^1 (mol cm^{-2}) GC
reduced	10.9	10.3	5.5	3.9	4.0
oxidized	10.5^b (3.6)^c	10.8^b (3.2)^c	14.1^b	13.5^b	12.1^b
without treatment	11.2	11.7	9.0	9.3	7.9

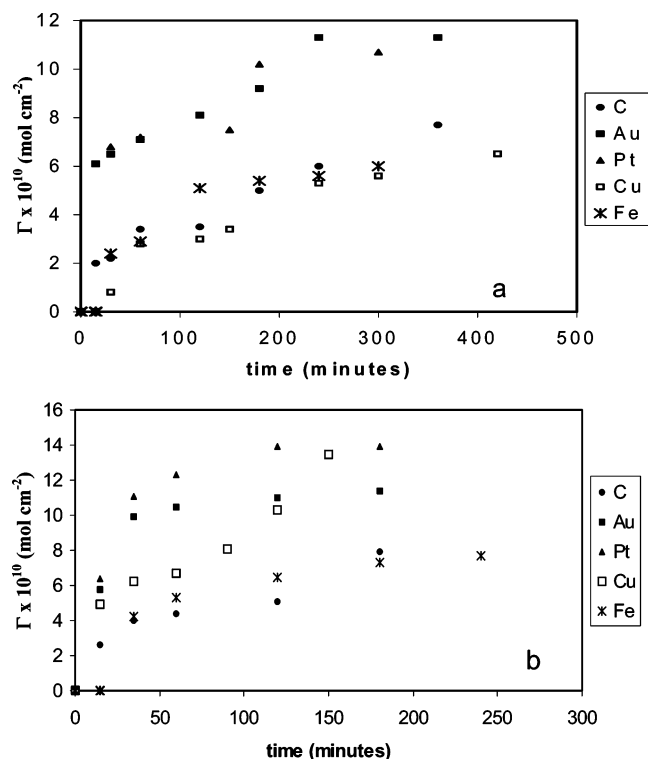^{a} Time of immersion = 240 min. ^{b} Mild oxidation, ^{c} Strong oxidation (see text).

Figure 7. Surface concentration (Γ in mol cm^{-2})of 4-nitrobenzylamino groups on carbon, gold, platinum, copper and iron as a function of immersion time in an ACN solution of 4-nitrobenzylamine: (a) $c =$ 9.11 mM, (b) $c =$ 18.22 mM.

by 4-fluorobenzylamine (the fluoro group is more easily observed in this technique than the nitro group). The spectra are shown in Figures 8 and S12 (see the Supporting Information).

For Fe, Cu, and GC, a notable increase of the oxygen content is observed after the oxidation of the surface and conversely a decrease after reduction. After modification of the oxidized surface of iron by 4-fluorobenzylamine the peak of fluorine is clearly observed on the spectrum at the same time as the signal of oxygen decreases. On the contrary, after reduction of the surface, no fluorine signal is observed. The same observation can be made on Cu and GC.

On Au and Pt, which are more difficult to oxidize, an oxidation process of the surface by cycling to positive potential scans in sulfuric acid aqueous solution is needed to increase the oxygen amount (strong oxidation). After this strong oxidation process no modification by 4-fluorobenzylamine was detected, but a modification is clearly observed by EDX on a Au or Pt surface free of oxides.

Discussion

The results of cyclic voltammetry (through the observation of the reversible signal of the nitrophenyl group), IR spectroscopy (through the signature of the secondary amine and its substituents) and XPS (through the observation of an N1s signal which can be assigned to the secondary amine bonded to the metal), EDX (through the observation of the fluorine signal) provide convergent evidences of the spontaneous bonding of amines to carbon and metal surfaces. The reaction is not very fast, but there are many applications where a complete coverage of the surface is not mandatory, in such cases minutes are sufficient to obtain the desired coverage. In addition, previous oxidation of the surfaces of Fe and Cu permits to obtain increased concentrations of the amino groups. Besides, this is
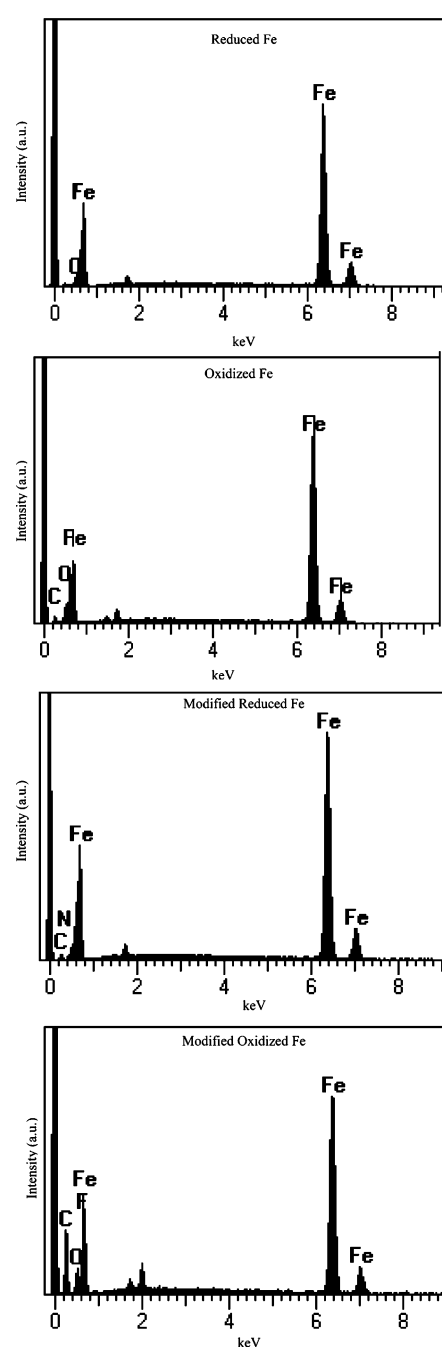

Figure 8. EDX spectra of (a) iron reduced surface by scanning, in ACN/0.1M NBu$_4$BF$_4$, to -3.0 V/SCE, (b) iron oxidized surface by scanning, in ACN/0.1M NBu$_4$BF$_4$, to $+2.0$ V/SCE, (c) reduced iron surface modified by dipping in 15 mM 4-fluorobenzylamine solution in ACN, $t =$ 240 min, d) oxidized iron surface modified by dipping in 15 mM 4-fluorobenzylamine solution in ACN, $t =$ 240 min.

the only way to attach amino groups to the surface of industrial metals which are oxidizable to be electrografted (they are oxidized at potentials less positive than the amines). The above examples point to the fact that a large variety of organic groups can be bonded through this method, including groups which can be further modified by chemical reactions such as carboxylic groups of **Fe**-11AU. In addition, the attachment of the amino group results from a chemical reaction, not from a mere physisorption. As primary amines are widely available commercially, this method should prove of some interest for the attachment of organic layers to metals.

Let us discuss the structure of the bonded species. Strong attachment of the amino group to the carbon of metals is

demonstrated by the fact that the organic layer remains bonded even after ultrasonication. The formation of a N-metal bond is observed by XPS through the N1s peak at 398.8 eV on iron and copper. The species which is bonded is a secondary amino group with a single NH bond as observed by IR (a single NH stretching bond).

The reaction of amines with oxidized carbon surfaces has already been observed by Zawadski.[6a] Bonding of butylamine on these carbon materials with a high surface concentration of carboxylic groups was assigned to the formation of carboxylate-ammonium salts. This is supported by the fact that the attachment of butylamine to the carbon is very slight after outgassing at 600°C, but increases tremendously when the carbon film is oxidized with oxygen at 300°C. This is certainly not the case in our experiments as no XPS peak is observed which could correspond to an ammonium group at 402 eV,[5c] in addition there is no IR indication of the presence of an ammonium group (which presents broad band in the 2700–2500 cm^{-1} range). On carbon fibers, the surface of which is much less oxidized and is closer to that of GC, which was used in this investigation, Buttry[6b] observed the grafting of amines (including secondary amines at the difference of our experiments) albeit at higher temperature (120°C in neat 1,6-diaminohexane) and longer reaction times (15 h) than in this study. Two types of attached structures were observed (starting from primary amines) either secondary amines (in the case of 1,6-diaminohexane or 2-aminoanthraquinone) or quarternary ammonium starting from dimethylaminomethyl ferrocene. As indicated above we can reject the formation of ammonium species. In this investigation, a structure similar to that of Scheme 2 (where a nitrogen is bonded to the carbon) could be possible.

On iron three different structures were proposed for amines on passive oxy-hydroxy iron films by Incorvia.[12] These structures involve (i) the coordination of a NH$_2$ group to FeOH, (ii) FeO−NH$_3$R$^+$, and (iii) FeOH RNH$_3^+$ FeOH. None of these structures correspond to what we observe. The first one involves a primary amine, and we have shown that a secondary amino group is bonded to the material; the two others imply ammonium ions which have been rejected on the basis of the XPS spectrum.

In agreement with our observations we propose the structure of Scheme 1 for the attached amino species on carbon and metals. On metals, the hydrogen is likely lost as water in the grafting process, as discussed below.

Let us now examine the possible mechanisms. On carbon, the mechanism which was proposed by Buttry[6b] is shown in Scheme 2, it involves a Michael reaction between the amine and electron deficient double bonds on the surface of carbon. The same mechanism could be operative in our case, albeit with shorter times and lower temperatures. It is not known if Buttry[6b] has tried to perform the reaction at a lower temperature, but Table 3 clearly shows an increased efficiency of the grafting reaction upon oxidation of the GC surface, indicating an attack of nitrogen on oxidized carbons. Most likely both mechanisms (the Michael reaction of Scheme 2 and a nucleophilic attack on oxidized carbons) occur in parallel. Another explanation for the different reaction conditions between the experiments reported in this paper and that of Buttry[6b] could originate from the difference of reactivity between carbon fibers and glassy carbon.

As concerns the reaction mechanism of amines with metals, the reaction of aniline with copper (110) has already been observed[31] under high vacuum (10^{-9} to 10^{-7} mbar) at 293K. The XPS spectra obtained after reaction of aniline with copper

SCHEME 6
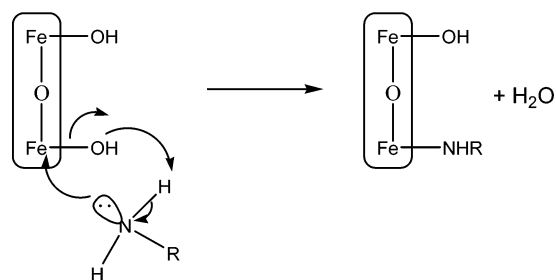
were assigned to a C$_6$H$_5$NH$^-$ species, and this was confirmed by STM measurements. There is some similarity between these vacuum experiments and our results giving confidence in our own observations concerning the attachment of amines to metal surfaces but the mechanism observed in a solvent is certainly very different from that operating under high vacuum.

The mechanism described by Roche[11] for the reaction of amines with metal oxides has been rejected on gold as no reaction was observed by these authors. The same is probably true for platinum.

Another possibility would involve an electron transfer as in the case of electrografting of amines. Upon electrochemical oxidation, an aminyl radical RNH•, obtained by deprotonation of an initial radical-cation RNH$_2$•$^+$, has been deemed responsible for the attachment reaction. The formation of a radical cation is difficult under our present experimental conditions. On iron, for example, the oxidant could be iron oxide, i.e., Fe^{2+} or Fe^{3+}, but in view of the oxidation potential of the amines and the rest potentials of iron ($\sim$0V/SCE) the electron exchange seems improbable. To test this possibility, we have tried to oxidize *n*-hexylamine ($E_p = 1.40$V/SCE at 0.1 V s^{-1}) with electrogenerated ferricinium ($E° = 0.040$ V/SCE) and no reaction was observed. In addition, bubbling of oxygen in the solution did not change the surface concentrations as indicated by the results (Table S12, Supporting Information).

In our opinion, for Fe and Cu a possible mechanism would involve a nucleophilic substitution of a M−OH group (M = metal) by RNH$_2$ to give MNHR (Scheme 1) and H$_2$O as sketched in Scheme 6. This mechanism would be in agreement with the results of Table 3. Indeed, strong oxidation of the surface leads to higher surface coverage of the amino group. This mechanism is also in agreement with the observations of Davies[31] who found that, on a clean surface, a limited reaction takes place with aniline under high vaccuum but that "in the presence of chemisorbed oxygen efficient oxy-dehydrogenation takes place with water desorption".

On Au and Pt, reduction or moderate oxidation (see the Experimental Section) of the surfaces only leads to small changes of the surface coverages. On the contrary, strong oxidation of the surface leads to a decrease of surface concentrations. The mechanism must, therefore, be different from that which is operating on Fe and Cu. During the reaction of dimethylamine with Si(001) and (111), Hamers[13a] observed a dissociative adsorption via the cleavage of the NH bond.[34] A similar mechanism would be operative in our case where the bonding of the nitrogen to the metal would decrease the strength of the NH bond. On Si, Hamers[13a] observed that the hydrogen binds to Si to give SiH, we do not know the fate of the hydrogen lost during the binding to Au or Pt. This mechanism is also somewhat similar to that described for the chemisorption of CO on metals[35] where the carbon binds to different sites of Pd, but

also to the dissociative adsorption of alkyldiynes on Pt[35a−c] where a CH bond is cleaved while the carbon binds to three Pt atoms.

SAM$_S$ of thiols on polycrystalline gold[1] provide self-assembled monolayers, on the contrary, oxidation of vinylic compounds[2] and reduction of diazonium salts[3] lead, in most cases, to unorganized multilayers. The measurements of surface concentrations which are reported above point to the formation of monolayers during the spontaneous attachment of amines. This is in agreement with the observations concerning the reaction of aniline with copper surfaces under vacuum where the reaction is limited to a monolayer.[31] For the spontaneous grafting of amines, the formation of multilayers is unlikely as it is difficult to imagine the reaction through which the primary amine could react, for example, on the alkyl group of hexylamine. Therefore, the values of Tables 3 and S6−S11 can confidently be taken as a realistic representation of the surface concentration.

We can discuss the possible organization of the spontaneously grafted amine layers, indeed, during the reaction of aniline with Cu (110), organized domains were observed by STM.[31] Our experiments were performed on polycristalline metals and a definitive answer should rely on future STM examination of modified monocrystals. However, some insight on a possible organization can be obtained from the IR spectra. The IR spectra of SAMs, where long alkyl chains are adsorbed on a gold surface, present a shift of the asymmetric and symmetric CH$_2$ bands to low wavenumbers[24] as the length of the chain increases. The value is close to that of the liquid for $n = 5$ and close to that of a crystal for $n = 21$. For n-hexylamine the positions of the CH$_2$ bands do not change from the neat liquid to the grafted surface indicating a disordered structure and for amino 11-undecanoic acid on copper the CH$_2$ bands are very small, and it is therefore, impossible to detect any organization of the layer. The CH$_2$ bands of neat n-hexylamine are the strongest bands of the spectrum (intensity ν_{as}(CH$_2$)/ intensity of the ∼1470 cm^{-1}band = 3.3) while they become smaller when the amine is attached to the metal (the same ratio is equal to 1.2 for **FenHex**; 1.4 for **CunHex**, 1.8 for **PtnHex;** and 1.7 for **AunHex**). This indicates, in application of the selection rules on a surface, that the alkyl chains are close to the normal surface.

Experimental Section

Amines were commercial compounds and used without further purification. 3 and 4- nitrobenzylamines were obtained from their hydrochloride ammonium salt by dissolving 500 mg in 10 mL of water, adding 0.18 mL of concentrated NaOH (40%), extracting with 3 × 10 mL of toluene, drying the organic layer, and evaporating under vacuum. The amine is not very stable and was kept under argon at −20°C and used as rapidly as possible. ACN, (Merck) was reagent rate quality and used without further purification. n-Bu$_4$NBF$_4$ was from Fluka (puriss 99%).

GC was obtained from Tokai, gold was evaporated on glass surfaces previously covered with a chromium layer, platinum was evaporated on glass, copper, and iron 99.98% and 99.9% of purity were obtained from Goodfellow.The electrodes were previously described.[5c]

The surfaces used for all the experiments were carefully polished with 1 μm diamond paste and rinsed in deoxygenated ethanol for 10 min and acetone under ultrasonication. The solutions were deoxygenated during the reaction. At the end of this reaction (modification of the electrodes) the samples were thoroughly rinsed in deoxygenated ethanol and acetone under

sonication for 10 min. The electrodes were regenerated by polishing again. The reaction of amino 11-undecanoic acid (11AU) was performed in ACN (neutral ACN) and in ACN after addition of stoichiometric amount of NBu$_4$OH (basic ACN).

The EDS spectra were also recorded on purposely reduced and oxidized surfaces. The surfaces (Fe, Cu, Au, and Pt) were reduced, in ACN/0.1 M NBu$_4$BF$_4$, by cycling to −3.0 V/SCE (10 cycles). The electrodes were maintained in deoxygenated solution after cycling; the amines were then added in the ACN solution. In a similar way oxidation reactions were performed by cycling to 2.0 V/SCE in ACN/0.1 M NBu$_4$BF$_4$ (mild oxidation). Strong oxidation of Au and Pt was achieved by dipping in a nondeoxygenated 0.4 M aqueous sulfuric acid for 15 min and then by cycling in the same solution to 2.0 V/SCE (10 cycles). The modified surfaces were kept under nitrogen and the spectra were recorded as fast as possible after their preparation.

The IR spectra were recorded on a Bruker Tensor 27 used in the total infrared reflection mode for Figures 1 and 2 and S1−S3 (Supporting Information). The spectrometer was equipped with a Durascope accessory (from Sens IR Technology) where the sample is pressed against a diamond window. This accessory is a micro ATR system which makes use of a diamond base sampling platform. The same Au, Pt, Cu, Fe plates were used for recording the background and the spectra. The spectra of 4-nitrobenzylamine (Figure S4) and 11-aminoundecanoic acid (Figure S5) were recorded on an IR spectrometer as previously described.[5c]

The XPS spectra were recorded on a Thermo VG Scientific Escalab 250 fitted with a microfocused, monochromatic Al Kα X-ray source. An X-ray beam of 650 μm size was used at a power of 10 mAx15 kV. Spectral calibration was determined by setting the C−C/C−H C1s peak at 285 eV. The surface composition was determined using the manufacturer's sensitivity factor. The particular concentration of a particular element A (%) was computed using the following:

$$\%A = \frac{(I_A/S_A)}{\sum (I_n/S_n)} \, 100$$

where I$_n$ and s$_n$ are the integrated peak areas and sensitivity factors, respectively

The EDX spectra were recorded using a JEOL JSM-6300 field emission scanning electron microscope equipped with an energy-dispersive X-ray (EDX) microanalyzer operating at 15 kV.

The surface concentration, Γ, given in Tables 2 and 3 and S6−S11 and Figures 7 and S10−S11 (see the Supporting Information) were calculated from the area of the cathodic peak after subtraction of the baseline. We did not use the surface of both cathodic and anodic peaks as the surface of the anodic peak maybe decreased by the protonation of the radical anion. The surface concentrations are given by reference to the geometrical surface of the electrode.

Conclusion

A simple method for the attachment of amines to carbon and metallic surfaces is described, it only requires dipping of the metallic coupon in an ACN solution of the amine. This method was exemplified with different amines and various metals including easily oxidizable metals such as copper and iron. The organic layer is strongly bonded to the surface as it resists ultrasonication. The grafting of the organic group was ascer-

tained by cyclic voltammetry, IR, XPS, and EDX. The formation of monolayers is deduced from the integration of the voltammograms. Mechanisms for this reaction are proposed both on carbon and metals. Further applications of this method are currently under investigation.

Supporting Information Available: ATR spectra, IRRAS spectra, XPS spectra, cyclic voltammetry, surface concentration, and EDS spectra for modified surfaces with alkylamines. This material is available free of charge via the Internet at http://pubs.acs.org.

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