

Covalent Modification of Carbon Surfaces by Aryl Radicals Generated from the Electrochemical Reduction of Diazonium Salts

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Abstract: Electrochemical reduction of a wide variety of aromatic diazonium salts on carbon electrodes (glassy carbon, highly oriented pyrolytic graphite) leads to the covalent attachment of the corresponding aromatic radicals. The films thus deposited on glassy carbon surfaces require mechanical abrasion to be removed. Cyclic voltammetry, X-ray photoelectron spectroscopy, polarization modulation IR reflection absorption spectroscopy, Auger spectroscopy, and Rutherford backscattering spectroscopy allow the characterization of the overlayer and an estimate of the surface coverage. The latter can be controlled through diazonium concentration and electrolysis duration. The mechanism of derivatization is discussed on the basis of the kinetic data obtained from cyclic voltammetry and preparative electrolysis. This versatile method of surface modification may find applications in the field of carbon–epoxy composites as attested by the successful binding of grafted *p*-aminophenyl groups with epichlorhydrin.

Modification of carbon surfaces is an important objective in electrochemistry and material science. Most important from the industrial point of view is the surface modification of carbon fibers aiming to improve the mechanical properties of carbon composite materials, particularly carbon–epoxy composites. These mechanical properties depend not only on the intrinsic characteristics of each of the components but also of those of the interface between them. It is thus anticipated that chemical modification of the carbon surface may improve the properties of the composite.² In this connection, chemical binding of the carbon surface with the epoxy resins commonly used in the manufacturing of composites is of particular interest.³ More generally, active attention is currently paid to covalently modified electrodes for catalytic or analytical purposes and also in view of biotechnological applications. Most of the methods used for modifying the carbon surface involve vigorous oxidation processes leading to the formation of carboxylic, quinonic, ketonic or hydroxylic groups on the surface⁴ that can then be coupled with the molecule to be attached. The main procedures so far employed in this purpose are as follows: (i) treatment

by boiling oxidizing acid solutions such as H₂SO₄ or HNO₃,^{5a} which also results in an increase of the specific surface area of carbon;⁵ (ii) oxidation by air or oxygen at 500–800 °C^{5a} or by radio frequency O₂ plasmas⁶ that likewise causes roughening of the carbon surface^{6c} and may eventually lead to degradation of the fiber; and (iii) electrochemical oxidation using the carbon fibers as anode in an aqueous solutions at the O₂ evolution potential^{3,7} or in HNO₃ or K₂Cr₂O₇ solutions.⁸ All of these procedures lead to the formation of oxygenated functional groups on the carbon surface whose nature and number are difficult to identify and control. It would therefore be desirable to design a more versatile and less drastic way of modifying carbon surfaces. A first attempt in this direction consisted of electrochemical oxidation of amines leading to the formation of surface carbon–nitrogen bonds.⁹ The modifying layer was shown to be a compact packing of amino groups. Then, starting from *ω*-diamines (ethylenediamine or triethylenetetramine) it was possible to preserve one of the two amino groups for further reaction with the epoxy groups of the resin.

We describe here another versatile method for modifying

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carbon surfaces, namely the electrochemical reduction of diazonium salts, which leads to covalent attachment of aryl radicals onto the carbon surface. Grafting of 4-nitrophenyl radicals on glassy carbon (GC) has been described in preliminary reports.¹⁰ GC and highly oriented pyrolytic graphite (HOPG), grafted by the same diazonium reduction method, have been recently characterized by Raman spectroscopy.¹¹ This surface modification method has been recently used for attaching glucose oxidase on carbon surfaces,^{10c} for electrochemical differentiation between dopamine and ascorbic acid,^{12a} and for diminishing protein adsorption.^{12b} In the present work, we have shown the generality of the method by reacting diversely substituted phenyl radicals and other aryl radicals with glassy carbon. We have also examined the possibility of electrochemically and chemically modifying substituents borne by the grafted aryl groups with particular emphasis on the reaction of amine substituents with epichlorohydrin as a model for the binding of carbon fibers to epoxy resins.

The electrochemistry of some diazonium salts has been previously investigated on mercury in sulfolane,^{13a,b} nitromethane,^{13c} acetone,^{13d} and dimethylformamide^{32e} and on platinum and gold in acetonitrile.^{13f} The reduction is very easy, and adsorption of reactant and/or intermediates was suspected to take place in all cases. The homogeneous reduction of diazonium salts is also very easy, and rate constants of the reaction with outersphere electron donors have been measured.¹⁴ Whether the reduction involve the intermediacy of the diazenyl radical or produce concertedly the aryl radical¹⁵ and dinitrogen remains an unsettled problem in electrochemical as well as in homogeneous studies, although diazenyl radicals have been characterized in thermal and photodissociation of azoalkanes.¹⁶

Results and Discussion

The various diazonium salts that we have used to derivatize glassy carbon (GC) electrodes are listed in Table 1. Particular care was taken to analyze the derivatization process and characterize the resulting electrode coating in the case of **1** and **2**. GC and highly oriented pyrolytic graphite (HOPG) with the basal plane exposed to the solution were both used as electrode material. HOPG was found to allow a more complete characterization of the grafted species and estimation of the resulting film thickness.

As shown previously, **1** exhibits, in a CH₃CN + 0.1 M *n*-Bu₄-BF₄ solution on a GC electrode, a broad and irreversible cathodic peak, which disappears after two cycles.^{10a} On HOPG, the

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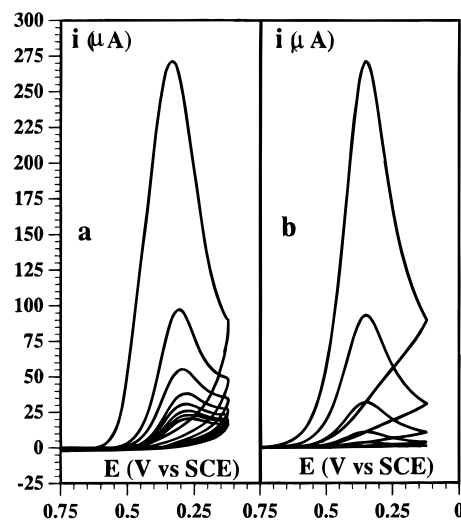


Figure 1. (a) Repetitive cyclic voltammetry of an HOPG electrode in a 1.8 mM solution of **1** in CH₃CN + 0.1 M Et₄ClO₄. Scan rate: 0.2 V/s. (b) Simulation of self-inhibition (see text).

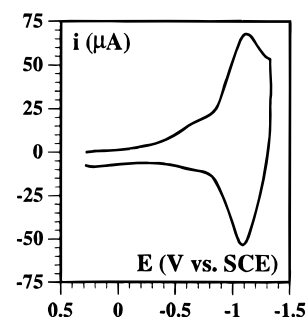


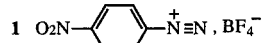
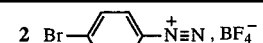
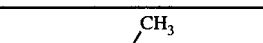
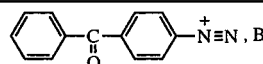
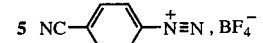
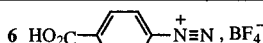
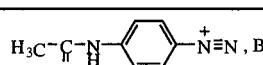
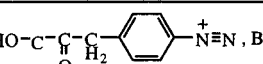
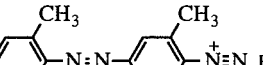
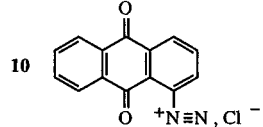
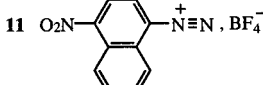
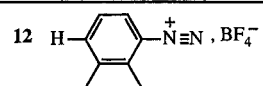
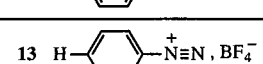
Figure 2. Cyclic voltammogram after derivatization at -0.35 V, from 1.8 mM solution of **1**, of a 0.28 cm² HOPG electrode in CH₃CN + 0.1 M Et₄NClO₄. Scan rate: 0.2 V/s.

disappearance of the peak (Figure 1) is slower. In the first case, the attachment of 4-nitrophenyl radicals was proved by the reversible wave observed in the cyclic voltammetry of the electrode transferred to a pure electrolyte solution, by analysis of the surface by X-ray photoelectron spectroscopy (XPS),^{10a} and more recently by Raman spectroscopy.¹¹ Figure 2 shows the cyclic voltammogram obtained under similar conditions on HOPG. The main wave is a reversible wave, located in the same potential range as that of nitrotoluene ($E^0 = -1.20$ V vs SCE). We also note the presence of a small reversible pre-wave at a slightly more positive potential as in the case of glassy carbon.^{10a}

The presence of NO₂ groups on the surface is also revealed by polarization modulation IR reflection absorption (PMIRRAS).^{17a,b} The signals obtained on GC and HOPG are the same (Figure 3). The two bands in the spectrum are very close to the antisymmetric and symmetric vibrations of the nitro group in nitrobenzene.¹⁷ The presence of the nitro groups on the surface of HOPG or GC electrodes is also revealed by XPS (Figure 4). Before grafting of the 4-nitrophenyl groups, the HOPG surface does not show a nitrogen signal. After grafting, rinsing in water, ethanol, and acetone, and drying, the main signal, at 406 eV, can be assigned to the NO₂ group. There is, however, a small signal at 400 eV, corresponding to a reduced nitrogen functionality. Similar results were obtained at a GC electrode with the difference that the signal at 401 eV is already

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Table 1. Derivatization of GC Surfaces by Electrochemical Reduction of Diazonium Salts

| diazonium salt | E_p^b | XPS signal (eV), atom _{orbital} (group) | PMIRRAS bands (cm ⁻¹) (group) | E^0_{Ar} (rev) E^p_{Ar} (irr) |
|--|---------|--|---|---|
| 1  | 0.20 | 406, N _{1s} (NO ₂) | 1485, 1265 (NO ₂) | - 1.19 (rev) |
| 2  | 0.02 | 71, Br _{3d} (Br) | - | - 2.5 (irr) |
| 3  | - 0.10 | 200, Cl _{2p} (Cl) | - | - |
| 4  | 0.09 | - | - | - 1.72 (rev) |
| 5  | 0.16 | - | - | - 2.42 (rev) |
| 6  | 0.10 | 288, C _{1s} (CO ₂ H) | 1540 (CO ₂ ⁻) | - |
| 7  | - 0.10 | 288, C _{1s} (CO) 400, N _{1s} (NH) | - | - |
| 8  | - 0.07 | 288, C _{1s} (CO) | - | - |
| 9  | 0.06 | 202, N _{1s} (N=N) | - | - 1.39 (irr) |
| 10  | 0.32 | - | - | - 0.94 (rev) |
| 11  | 0.37 | 406, N _{1s} (NO ₂) | - | - 1.09 |
| 12  | 0.08 | - | - | - 2.49 |
| 13  | - 0.06 | - | - | - |

^a 0.1 mM in CH₃CN + 0.1 M *n*-Bu₄BF₄. ^b Irreversible cyclic voltammetric peak potential at 0.2 V/s in V vs SCE. ^c Standard potential for reversible surface waves or peak potential at 0.2 V/s for irreversible surface waves in V vs SCE. Temperature 20 °C.

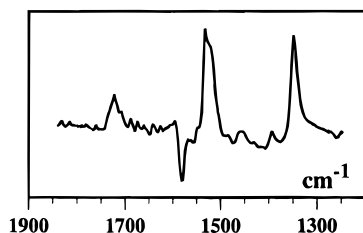


Figure 3. PMIRRAS spectrum of a GC or HOPG electrode derivatized from a 1.8 mM solution of **1** in CH₃CN + 0.1 M Et₄NClO₄.

present on the ungrafted surface. Derivatization of carbon fibers by the same technique also resulted in the appearance of the characteristic N_{1s} XPS signals of NO₂ at 406 eV.

The coatings thus grafted are extremely difficult to remove from the electrode surface. Ultrasonic rinsing of GC electrodes for 15 min in CH₃CN, (CH₃)₂NCHO, (CH₃)₂SO, benzene, benzonitrile, acetone, ethanol, methanol, CH₂Cl₂, and CHCl₃

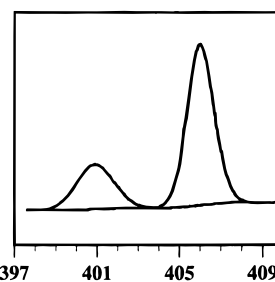


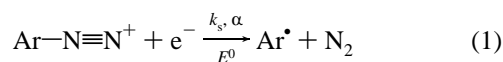
Figure 4. XPS spectrum of an HOPG electrode derivatized from a 2 mM solution of **1** in CH₃CN + 0.1 M Et₄NClO₄. The base line is the spectrum obtained before grafting.

leaves the cyclic voltammetric signal unchanged. Rinsing HOPG-grafted surfaces by the same solvents (without ultrasonication that would destroy the HOPG structure) leads to the same result. The film also remained stable after 6-month exposure to atmospheric air. With GC electrodes, the only way

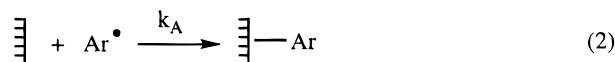
of getting rid of the film is to use abrasive paper to clean up the surface.

In Auger spectroscopy, the only peak that can be detected on a freshly cleaved HOPG plate is that of carbon. After electrolysis of **1** and rinsing, the bands of O and N appear. These bands remain intact upon heating at 700 K under vacuum. They disappear only when the temperature is raised to 1400 K.

These observations point to a covalent attachment of the 4-nitrophenyl radicals onto the carbon surface according to the following mechanism.



E^0 , k_s , and α are the standard potential, standard rate constant, and transfer coefficient of the rate-determining electron transfer.



The success of the derivatization of the carbon surfaces by electrochemical reduction of diazonium salts essentially hinges upon the fact that the aryl radicals produced by reaction 1 are not reduced at the potential at which they are produced¹⁸ and may thus react with the surface. This is at variance with what occurs upon reduction of aryl halides, the reduction potential of which is more negative than -1 V/SCE. In the latter case, the radical formed upon cleavage of the radical anion is reduced to an aryl anion at the electrode or in solution.¹⁹

That the grafting of the surface of the HOPG basal plane is homogeneous is indicated by the even aspect of the 100 nm \times 100 nm images obtained in scanning tunneling microscopy (STM) shown in the Supporting Information.

The homogeneity of the coating is confirmed by the analysis of the successive current–potential curves observed upon repetitive linear scanning of the electrode surface (Figure 1a) as developed below. The decrease of the peak current indicates that progressive passivation takes place as a consequence of electrode derivatization. We may analyze this phenomenon according to the mechanism depicted by reactions 1–3 (the main reaction that destroys the aryl radical in solution is likely to be H-atom transfer from the solvent¹⁹) under the assumption that the derivatized portion of the surface has become totally inactive toward reduction of the diazonium cation. As established in detail elsewhere,²⁰ the surface coverage, θ ($= \Gamma/\Gamma^0$ where Γ and Γ^0 are the surface concentration and maximal surface concentration of grafted radicals respectively) and current (i) – potential (E) curves can then be obtained from the following set of equations

$$\frac{i_n}{\text{FSC}^0 \sqrt{\alpha F \nu D / RT}} = (1 - \theta_n) \psi \quad \text{with} \\ \theta_n = \theta_{n-1}^* + p \int_0^{\alpha F \nu / RT} (1 - \theta_n) \psi d\eta$$

where D is the diffusion coefficient, C^0 the initial concentration of diazonium salt in the solution, and ν the scan rate. The

(18) (a) The oxidation potential of PhLi in tetrahydrofuran has been reported to be -0.3 V vs SCE.^{18b} This points to an easy reduction of Ph \cdot even though this value is certainly more positive than the standard potential of the Ph \cdot /Ph $^-$ couple since Ph $^-$ is strongly ion-paired by Li $^+$. (b) Jaun, B.; Schwartz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

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subscript n in i_n and θ_n indicates the running number of the cycle. θ_{n-1}^* is the relative coverage at the end of the preceding cycle and is equal to 0 for the first cycle. The parameter $p = [k_A/(k_A + \sqrt{Dk})](C^0/\Gamma^0)\sqrt{RTD/\alpha F \nu}$ is a measure of the competition between the surface and solution reactions of the radical and of the matching between the diffusion flux of diazonium cations and the area occupied by the grafted radical. The dimensionless function ψ , required to compute i_n and θ_n , is given by the following integral equation

$$\psi \exp\left[\frac{\alpha F}{RT}(E_{(t)} - E^R)\right] = 1 - \frac{1}{\sqrt{\pi}} \int_0^{\alpha F \nu / RT} \frac{\psi}{\sqrt{\alpha F \nu t / RT - \eta}} d\eta$$

where $E_{(t)}$ is the electrode potential, which is a repetitive triangular function of time, and E^R is a scan rate-dependent reduction potential of the diazonium cation defined as

$$E^R = E^0 + (RT/\alpha F) \text{Ln}(k_s/\sqrt{\alpha F \nu D / RT})$$

Figure 1b shows the simulation of the HOPG cyclic voltammograms of Figure 1a according to the above mechanism and assumes a value of the parameter p equal to 0.3; $\alpha = 0.45$ results from the peak width of the first scan voltammogram; $D = 10^{-5}$ cm 2 s $^{-1}$ from the voltammetry of molecules of similar size; and $\Gamma^0 = 12.5 \times 10^{-10}$ mol cm $^{-2}$ from a geometrical calculation of the closest packing of 4-phenyl nitro groups on the surface. Thus

$$k_A/(k_A + \sqrt{Dk}) = 0.56$$

meaning that 56% of the radicals produced by reduction of the diazonium cations react with the carbon surface while 44% escape and react in the solution. The surface carbons bearing the aryl group most likely pass from a sp 2 to a sp 3 hybridization.

As seen in Figure 1, the simulation of the first three repetitive voltammograms is quite satisfactory. Then, upon further cycling, the simulated peaks decrease significantly faster than the experimental peaks. The experimental voltammograms tend toward a limiting behavior that is practically reached after the seventh cycle. We also notice that the peak potential exhibits a small but distinct negative shift, at the highest diazonium concentrations, while it is not predicted to vary from one scan to the next in the framework of the above mechanism and assumptions. These observations point to the concept that, when the grafted film tends to saturation, the electrode is not totally inert toward reduction of the diazonium cations even though the derivatization reaction becomes inefficient for steric reasons. Under such conditions, constrained diffusion of the incoming diazonium cations toward the small gaps between the grafted radicals still allow their reduction.²¹ It is also predicted that constrained diffusion competes more efficiently with electron transfer than linear diffusion and thus results in an apparent slowing down of the charge transfer kinetics, which translates into a negative shift of the peak potential.²¹

With GC electrodes, the saturation of the surface is more rapid than with HOPG electrodes; the second scan voltammogram is very small compared to the first. The kinetics of derivatization may nevertheless be investigated using the variation of the first scan peak current with the scan rate and the diazonium concentration. Indeed, the amount of radicals produced at the electrode increases with the bulk concentration of diazonium salt and/or when the scan rate decreases. The degree of inhibition increases accordingly. More precisely, the ratio, i_p/i_p^0 of the observed peak current over the peak current in

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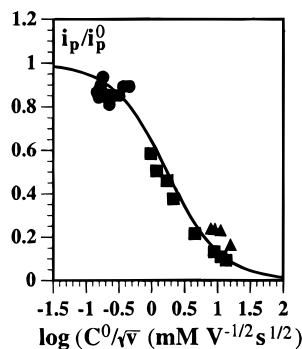


Figure 5. Cyclic voltammetry of a GC electrode in a solution of **1** in $\text{CH}_3\text{CN} + 0.1 \text{ M } n\text{-Bu}_4\text{BF}_4$. Variations of the normalized peak current (toward the value with no inhibition) with **1** concentration and scan rate (\bullet , $[\mathbf{1}] = 0.1 \text{ mM}$, ν from 0.07 to 0.5 V/s; \blacksquare , $[\mathbf{1}] = 5 \text{ mM}$, ν from 0.05 to 0.4 V/s; \blacktriangle , $[\mathbf{1}]$ from 0.2 to 6 mM, $\nu = 0.2 \text{ V/s}$). Solid line: simulation of self-inhibition (see text).

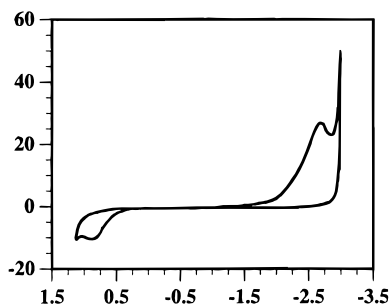


Figure 6. Cyclic voltammetry after derivatization at -0.1 V vs SCE, from a 2 mM solution of **2**, of a 0.28 cm^2 HOPG electrode in $\text{CH}_3\text{CN} + 0.1 \text{ M Et}_4\text{NClO}_4$. Scan rate: 0.2 V/s.

the absence of inhibition is a decreasing sigmoid function of log of the same dimensionless parameter p defined earlier. Fitting of the experimental results with the theoretical curve (Figure 5) leads to (taking the same values for D and Γ^0)

$$k_A/(k_A + \sqrt{Dk}) = 0.84$$

meaning that 84% of the radicals produced by reduction of the diazonium cations react with the carbon surface while 16% escape and react in the solution. It thus appears that the GC surface is more reactive toward 4-nitrophenyl radicals than the basal plane of HOPG. Since GC surfaces contain both edge and basal planes, it follows that edge carbons are more reactive than basal carbons.

The reduction of **2** gives rise to a similarly strong attachment of 4-bromophenyl radicals on HOPG and GC surfaces and allows an additional type of spectroscopic characterization using Rutherford backscattering (RBS)²² to be carried out. Repetitive cyclic voltammetry of **2** (see the Supporting Information) exhibits the same kind of self-inhibition decrease of the peak current as in the case of **1**. Once grafted by reduction of **2**, rinsed with the same series of solvents as described above, and transferred into a pure electrolyte solution, a HOPG electrode gives rise to a voltammogram (Figure 6) that exhibits an irreversible surface wave at a potential close to that of bromobenzene. Upon scan reversion an anodic wave corresponding to the irreversible oxidation of bromide ions is observed. These observations indicate that the 4-bromophenyl radicals, produced by the reduction of **2**, are attached on the electrode surface. Similar observations were made with GC electrodes. Ultrasonication in the same solvents cannot eliminate the electrode coating, which requires abrasion to be

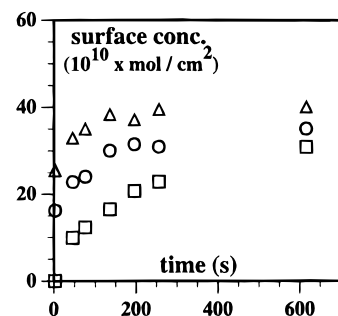


Figure 7. Derivatization of a GC electrode by 4-nitrophenyl radicals generated upon electrolysis at -0.6 V vs SCE of a solution of **1** in $\text{CH}_3\text{CN} + 0.1 \text{ M } n\text{-Bu}_4\text{BF}_4$ and ultrasonic rinsing in H_2O , EtOH, and acetone. Variation of the surface coverage with the electrolysis duration and with the concentration of **1**: 0.2 (\square), 1 (\circ), 5 (\triangle) mM.

removed. XPS of a grafted surface exhibits the characteristic signal of Br_{3d} at 71 eV. Retrodiffusion of He^+ ions by a surface derivatized by reduction of **2** gives an RBS signal at 1.7 MeV characteristic of the presence of Br atoms. In this case too, the homogeneous character of the coating is attested by the large-scale ($200 \text{ nm} \times 200 \text{ nm}$) STM images shown in the Supporting Information.

An estimate of the thickness of the films grafted by reduction of **1** or **2** could be obtained as follows. Integration of cyclic voltammograms of HOPG electrodes grafted with 4-nitrophenyl radicals and transferred, after rinsing with a series of solvents as described above, to a pure electrolyte solution (Figure 2) gives a surface concentration of $(16 \pm 2) \times 10^{-10} \text{ mol cm}^{-2}$, a value slightly larger than the closest packing concentration, $12.5 \times 10^{-10} \text{ mol cm}^{-2}$. Raman spectroscopy gave a number, $12 \times 10^{-10} \text{ mol cm}^{-2}$,¹¹ more like the closest packing concentration. RBS of HOPG electrodes grafted with 4-bromophenyl radicals^{21b} lead to a value of $(18 \pm 2) \times 10^{-10} \text{ mol cm}^{-2}$. In view of these values as well as of the observation, in the 4-nitrophenyl case, of a small prewave and of an additional N peak in XPS, we may conclude that the coverage is slightly larger than a monolayer. The supplementary amount of matter present in the film is likely to derive from the reaction of phenyl radicals with the substituted phenyl groups already attached on the surface either at the NO_2 nitrogen or at the ortho-carbons. The STM images and the self-inhibition phenomenon observed in the cyclic voltammetric reduction of **1** and **2** indicate a closed-packed arrangement of the phenyl groups on the surface rather than the formation of dendrites.

Determination of the surface concentration is more uncertain in the case of GC electrodes since the ratio of the geometrical to the actual surface area is not known. However, as depicted in Figure 7, where the surface concentrations are expressed in terms of geometrical area, the coverage can be varied up to saturation by changing the electrolysis time and/or the diazonium bulk concentration.

Starting from other diazonium salts we obtained similar derivatization of GC surfaces that were characterized by cyclic voltammetry (self-inhibition decrease of the diazonium reduction peak, surface wave of the grafted surface when the aryl group is reducible in the available potential range), XPS, or PMIRRAS as summarized in Table 1.

As an illustration of the effect of the size of the grafting radical on its maximal surface concentration on GC, we found with the nitronaphthalene derivative **11** a saturation surface concentration $\Gamma^0 = 15 \times 10^{-10} \text{ mol cm}^{-2}$, with reference to the geometrical surface area, instead of $\Gamma^0 = 41 \times 10^{-10} \text{ mol cm}^{-2}$ for the 4-nitrobenzene derivative **1**.

Several of the substituents placed para to the attachment point of the aryl radicals, as described in Table 1, may be chemically

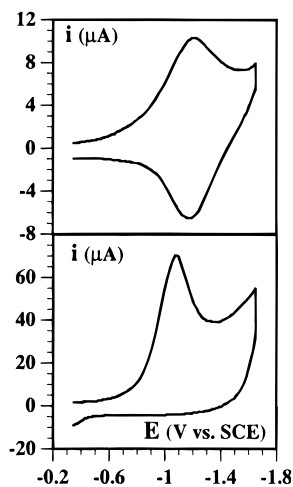
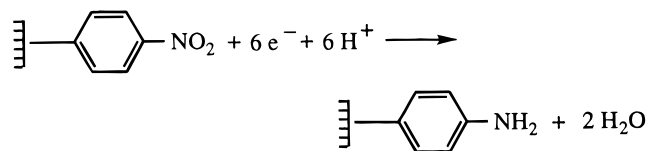


Figure 8. Cyclic voltammetry of a GC electrode derivatized by 4-nitrophenyl radicals from the reduction of **1** (see text) in $\text{CH}_3\text{CN} + 0.1 \text{ M } n\text{-Bu}_4\text{NBF}_4$ (a) and in $90:10 \text{ H}_2\text{O-EtOH} + 0.1 \text{ M KCl}$ (b). Scan rate: 0.2 V/s . Temperature: $20 \text{ }^\circ\text{C}$.

modified once the radical is grafted onto the carbon surface. The preparation of a surface derivatized by an aryl radical bearing a para NH_2 group (as in diaminodiphenyl sulfone, a classical hardener of epoxy resins) is of particular interest since its reaction with the epoxy groups of epoxy polymers may lead to improved carbon composite materials by strengthening the interface. We have found that this objective can be achieved either by reduction of the nitro groups on surfaces grafted with 4-nitrophenyl radicals (**1**) or by hydrolysis of grafted 4-acetamidophenyl groups (**7**).

Transformation of NO_2 groups into NH_2 groups could be carried out by two methods. In one of these, the electrode is first derivatized by 4-nitrophenyl radicals as described earlier, thus giving rise to the reversible cyclic voltammetric pattern of the grafted 4-nitrophenyl groups in a $\text{CH}_3\text{CN} + n\text{-Bu}_4\text{NBF}_4$ solution (Figure 8a). It is then transferred to a protic solution ($90:10 \text{ H}_2\text{O-EtOH} + 0.1 \text{ M KCl}$). The cyclic voltammetric wave then becomes irreversible and the peak height increases by a factor of *ca.* 6 (Figure 8b), suggesting that the classical reduction of NO_2 to NH_2 occurs within the grafted layer:

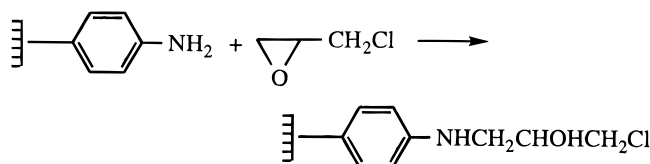


However, since the peak in $\text{H}_2\text{O-EtOH}$ is more narrow than in CH_3CN the ratio of the charge is less, *ca.* 4.5, indicating that the conversion of NO_2 into NH_2 is not complete.

These results are confirmed by XPS. Starting from a clean GC plate where the $406 \text{ eV } \text{NO}_2 \text{ N}_{1s}$ signal is absent, 20 min of electrolysis at -0.7 V vs SCE in a 10 mM solution of **1** in $\text{CH}_3\text{CN} + n\text{-Bu}_4\text{NBF}_4$ resulted in the appearance of $6.4\% \text{ N}_{1s}$ signal at 406 eV ($\text{N}_{1s}(406 \text{ eV})/\text{N}_{\text{total}} = 0.67$). After 105 min of electrolysis at -1.4 V vs SCE in a $90:10 \text{ H}_2\text{O-EtOH} + 0.1 \text{ M KCl}$ solution on the same GC plate, the $\text{N}_{1s}(406 \text{ eV})$ peak decreases to 2.8% ($\text{N}_{1s}(406 \text{ eV})/\text{N}_{\text{total}} = 0.21$).

The resulting amino groups were then reacted with epichlorhydrin, a model for epoxy groups of epoxy resins components.^{9a} It was first checked that a clean GC plate dipped for 1 h in epichlorhydrin and ultrasonically rinsed in H_2O , EtOH , and acetone does not show any Cl_{2p} signal. A GC plate first treated to produce amino groups as described above was, after ultrasonic rinsing in H_2O , EtOH , and acetone, heated for 8 h at

$120 \text{ }^\circ\text{C}$ with epichlorhydrin.^{9a,23} It was then rinsed and dried in an oven at $120 \text{ }^\circ\text{C}$ for 1 h. Examination by XPS then showed an increase of the Cl_{2p} peak (200 eV) from 0% to 1.25% , thus indicating the occurrence of the following reaction.



4-Aminophenyl groups on the carbon surface may also be generated by hydrolysis of 4-acetamidophenyl groups²⁴ grafted by electrolysis at -0.6 V vs SCE during 15 min of the corresponding diazonium salt, **7**, in acetonitrile. After electrolysis of a 10 mM solution of **7** in $\text{CH}_3\text{CN} + n\text{-Bu}_4\text{NBF}_4$ at -0.6 V vs SCE during 15 min, the grafting of 4-acetamidophenyl groups was attested by an increase of the $400 \text{ eV } \text{N}_{1s}$ XPS signal from 1% to 9.6% and of the $288 \text{ eV } \text{C}_{1s}(\text{C=O})$ signal from 3.8% to 9.0% . The plate thus treated was then immersed in boiling $10\% \text{ H}_2\text{SO}_4$ for 3 h,²⁵ rinsed, and then reacted with epichlorhydrin as described earlier. The occurrence of the same reaction was attested by an increase of the Cl_{2p} peak (200 eV) from 0 to 1.8% .

Experimental Section

Glassy carbon electrodes were prepared from 3 mm carbon rods (Tokai Corp., Japan) embedded in epoxy resin (Torseal, Varian). Glassy carbon plates were from the same origin and the HOPG plates from Union Carbide (ZBY grade). Clean HOPG surfaces were prepared by removing a few graphite layers with adhesive tape.

Diazonium salts **1**, **2**, **3**, **9**, and **10** were of commercial origin (Aldrich) and used as received. The other diazonium salts were prepared by standard diazotization of the corresponding amines with NaNO_2 in acidic medium.^{10c,24}

4-Benzoylbenzenediazonium fluoborate, **4**: mp $164 \text{ }^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_2\text{BF}_4$: C, 52.73; H, 3.04; N, 9.46. Found: C, 52.72; H, 3.02; N, 9.59.

4-Cyanobenzenediazonium fluoborate, **5**: mp $150 \text{ }^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_7\text{H}_4\text{N}_3\text{BF}_4$: C, 38.74; H, 1.84; N, 19.37. Found: C, 38.68; H, 1.88; N, 19.24.

4-Carboxybenzenediazonium fluoborate, **6**: mp $138 \text{ }^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_7\text{H}_5\text{N}_3\text{O}_2\text{BF}_4$: C, 32.83; H, 1.95; N, 10.94. Found: C, 32.78; H, 2.03; N, 10.94.

4-Acetamidobenzenediazonium fluoborate, **7**:²⁶ mp $158 \text{ }^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_3\text{OBF}_4$: C, 38.58; H, 3.21; N, 16.88. Found: C, 38.65; H, 3.30; N, 17.01.

4-Phenylacetic acid diazonium fluoborate, **8**:²⁷ mp $135 \text{ }^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_8\text{H}_7\text{N}_2\text{OBF}_4$: C, 38.40; H, 2.80; N, 11.20. Found: C, 38.46; H, 2.88; N, 11.24.

4-Nitronaphthalenediazonium fluoborate, **11**: mp $186 \text{ }^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_{10}\text{H}_6\text{N}_3\text{O}_2\text{BF}_4$: C, 41.83; H, 2.09; N, 14.64. Found: C, 41.85; H, 2.14; N, 14.69.

Naphthalenediazonium fluoborate, **12**: mp $142 \text{ }^\circ\text{C}$ dec (lit.²⁵ mp $110 \text{ }^\circ\text{C}$ dec). Anal. Calcd for $\text{C}_{10}\text{H}_7\text{N}_2\text{BF}_4$: C, 49.62; H, 2.89; N, 11.57. Found: C, 49.68; H, 2.87; N, 11.61.

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Benzenediazonium fluoborate, **13**. Anal. Calcd for $C_6H_5N_2BF_4$: C, 37.53; H, 2.60; N, 14.59. Found: C, 37.56; H, 2.63; N, 14.53.

Acetonitrile was Uvasol (Merck) and *n*-Bu₄NBF₄ was purissimum quality from Fluka. Epichlorhydrin (99%) was obtained from Aldrich.

For cyclic voltammetry we used a Taccussel GSTP 4 signal generator, a home-built potentiostat,²⁸ and an Itelec XY recorder.

XPS spectra were obtained with a Vacuum Generators ESCALAB MK1 spectrometer operated in the constant analyzer energy mode (20 eV). Unmonochromated Mg K α X-rays (1253.6 eV) were used. The power applied to the Mg anode was 200 W. The pressure in the analysis chamber was in the 10⁻⁸ mbar range. The analyzed surface was 10 mm \times 4 mm. The spectra were digitized, accumulated, and then treated according to standard procedures. Smoothing was avoided. Peak fitting was performed with Gaussian profiles. Peak areas were obtained from numerical integration or from the Gaussian component areas. Clean GC plates were first examined by XPS to control their surface composition. Oxygen was the main extraneous surface element detected on clean plates. Nitrogen (N_{1s} = 400 eV) was detected in a few cases. When a series of consecutive surface reactions were studied, the XPS experiments were performed on the same plate. After attachment of the radicals on the surface, the samples were cooled at liquid N₂ temperature during data acquisition and the evolution of the spectra was monitored as a function of time since we observed a slow degradation of the nitro groups under X-ray irradiation. Binding energies are referred to the main C_{1s} peak that was located at 285.0 eV to correct for the charging effect. Elemental percentages x_i were obtained from $x_i = (A_i/s_i)/\sum_i(A_i/s_i)$, where A_i and s_i are, respectively, the peak areas of the detected elements and the sensitivity coefficients. We used empirical sensitivities deduced from the study of stoichiometric compounds. This formula is correct for homogeneous samples only and was used to permit a rapid comparison of different samples.

The PMIRRAS setup was previously described.¹⁷ Rather than a grazing incidence angle, we chose an incidence angle of 55° for a better detection, taking into account the optical indexes of glassy carbon. The PMIRRAS spectra were recorded at 4 cm⁻¹ resolution by accumulating 200 scans. The normalized spectra were obtained by computing the ratio of the sample spectra to the carbon reference spectra.

RBS spectra were obtained with the Van de Graaf generator at the Groupe de Physique des Solides (Université Denis Diderot) using a 2 MeV ⁴He⁺ beam on several samples of HOPG treated as described above. Backscattered ions were detected at 165° off the incident beam. Excess amounts of surface bromine was determined by integration of the peak.

Conclusions

Electrochemical reduction of aromatic diazonium salts appears to be a general and versatile method for derivatizing carbon surfaces with a wide variety of unsubstituted or substituted aromatic radicals. The attachment of these films is persistent and strong. They require mechanical abrasion to be removed pointing to a covalent binding of the radicals to the surface. Cyclic voltammetry, X-ray photoelectron spectroscopy, polarization modulation infrared reflection absorption spectroscopy, and Rutherford backscattering spectroscopy have allowed the characterization the overlayer and an estimate of the surface coverage. The latter can be controlled through diazonium concentration and electrolysis duration and can be increased up to a saturation value slightly larger than a compactly packed monolayer. Analysis of the cyclic voltammetric data indicates that the kinetics of the derivatization involves self-inhibition of diazonium reduction by the attached radicals. Electrochemical reduction in aprotic medium of *p*-nitro substituents or hydrolysis of *p*-acetamido substituents leads to the formation of para NH₂ groups. These can be reacted successfully with epichlorhydrine showing that the grafting method may lead to improved carbon–epoxy composites where the carbon surface is attached to the epoxy resin by means of a series of covalent bonds.

Acknowledgment. This investigation was supported in part by the Ministère de l'Enseignement Supérieur et de la Recherche (France) under Contract No. 92T0208. We are grateful to Dr. G. Desarmot (Direction Scientifique des Matériaux, ONERA) for many helpful discussions. GC plates were kindly provided by Tokai Corp. We are grateful to Prof. B. Bent (Columbia University) for his help with the thermodesorption experiments and to C. Bilem and M. Leclerc for recording XPS spectra.

Supporting Information Available: STM images of HOPG electrodes after grafting of 4-nitro- and 4-bromophenyl groups (Figures S1a and S1b, respectively) (2 pages). See any current masthead page for ordering and Internet access instructions.

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