Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts

Jean Pinson*[a] and Fetah Podvorica[b]

Received 16th December 2004
First published as an Advance Article on the web 23rd February 2005
DOI: 10.1039/b406228k

Surface chemistry is the topic of this *tutorial review*. It describes the electrochemical reduction of aryl diazonium salts on carbon, silicon or metals which leads to the formation of an aromatic organic layer covalently bonded to the surface. The method which permits such a modification is set forth. The proof for the existence of the organic layer is brought forward. The grafting mechanism and the covalent bonding between the surface and the aryl group are discussed. The formation of mono or multilayers depending on the experimental conditions is rationalized. Finally some examples of the possible uses of this reaction are given.

Introduction

Many objects of our daily life are made with metals covered with polymers, for example home appliances are made of steel covered with a polymeric layer which prevents corrosion and improves aesthetics. These metal–polymer objects are made by deposition of a polymer on a metal sheet either from a liquid (roll-coating), from a sheet of solid polymer (roll bonded cladding), or by cataphoresis. In these cases only weak bonds are formed between the polymer and the iron surface. There are however cases were it would be desirable to establish a strong bond between carbon, metals or semiconductors and the organic layer for example in the biomedical field (prostheses, stents,…), in the field of sensors, in protection against corrosion,... There are relatively few methods allowing the formation of such strong bonds, mostly on metal surfaces. The methods allowing the covalent modification of surfaces: carbon,[1,2] silicon and semiconductors[3] and metals[4] have been partly reviewed.

By reference to organic chemistry the formation of a C–C bond between a carbon pertaining to the surface of the solid and a carbon from an organic molecule would seem quite easy to achieve, this is however not the case. The relatively few methods which permit this reaction involve the electrochemical oxidation of amines RNH_2 on carbon (but also on Pt or p- or n-Si) to give modified surfaces which can be summarized as: ***Surf***–NHR (where ***Surf*** represents the surface of carbon, metal or semiconductor). In a similar way alcohols ROH can be attached to carbon surfaces[2] to give ***Carbon***–OR modified surfaces. The electrochemical oxidation of carboxylates $RCOO^-$—the Kolbe reaction—is one of the oldest electro-organic reactions, it leads to the formation of the RR dimer. However, if the oxidation of carboxylates is performed on a GC (Glassy Carbon) or HOPG (Highly Oriented Pyrolitic Graphite) electrode the surface is derivatized to ***Carbon***–R. The oxidative electrolysis of hydrazides also leads to the formation of modified carbon surfaces. The reaction of gas phase hydrogen radicals gives hydrogenated carbon: ***GC***–H.[5] Under ultrahigh vacuum conditions, hydrogen free diamond reacts thermally with alkenes and fluorine, chlorine,

---

*jean.pinson@alchimer.com

Jean Pinson

Jean Pinson was born in Paris in 1940. He graduated from Ecole Nationale Supérieure des Industries Chimiques in Nancy (France) in 1963. He obtained his Ph.D. from the former Université de Paris in 1969. After a posdoctoral stay at the University of Oklahoma he joined Université Paris 7 where he was full professor until October 2004. He is now working for Alchimer, a company involved in surface coating through chemistry and electrochemistry.

Fetah Podvorica

Fetah Podvorica was born in Dumosh, Podujevë, Kosovo in 1968. He graduated from the albanian speaking University of Prishtina in 1993, which at that time was operating in private apartments as albanian students were not allowed to attend the official University. He received his DEA (Master's degree) from Université Paris 7 in 1997 and prepared his Ph.D. (2000) at the same University working with Professor Pinson. Now he is associate professor of Physical Chemistry at the University of Prishtina, Kosovo. He has spent sabbaticals at the Ecole Nationale Supérieure de Physique et Chimie in Paris and at the Université Paris 7. His research concerns surface chemistry, particularly the modification of conducting surfaces with organic groups.

perfluorobutyl; alkyl terminated diamonds have been prepared from hydrogen-terminated diamond under photochemical irradiation. Diamond films can be modified with perfluorooctyl groups under irradiation.[6]

The SiH bond of hydrogenated silicon is not a very strong bond, ($D°$(SiH) $\approx$ 330–380 kJ mole^{-1}, by comparison $C_{aromatic}$–H = 460 kJ mole^{-1}) and it is therefore easier to derivatize hydrogenated silicon than carbon. Quite a number of thermal, chemical, electrochemical and photochemical methods[3] are available which also permit one to obtain modified porous silicon. Among these methods are the photochemical, thermal or chemical activation of alkenes, the photochemical or mechanical activation of alkyl halides, the electrochemical activation of Grignard reagents. These reactions lead to ***Si***–R surfaces where R is an alkyl chain with possible end functions.

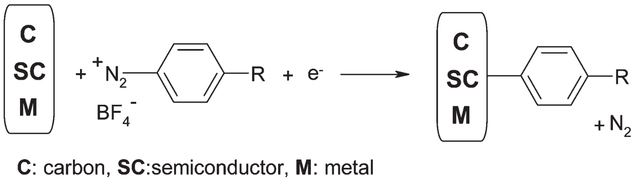
The modification of metal surfaces is even more difficult than that of carbon. Self Assembled Monolayers (SAMS)[7] form spontaneously from thiols on gold or copper but the gold–organic bond is quite weak (ΔG_{ads} = −21 kJ mol^{-1} for octanethiol in hexane) and this is the very reason why the alkyl chains can organize on the surface. On industrial metals such as iron the bond is even weaker, making this reaction of little practical use.

Two methods are available for the formation of a strong bond between a metal and an organic molecule. The first one, which has been reviewed recently,[4] involves the electrochemical reduction of vinylic compounds $H_2C{=}CHR$, in aprotic medium, it leads to a ***Metal***–Polymer structure. A variety of metals (nickel, iron,…) can be covalently bonded to a thin ($\approx$10 nm) polymeric layer. The reduction of diazonium salts is the second method, and this constitutes the subject of the present review.

The electrografting of aryl diazonium salts

Let us first give an overview of the method and let us show how it can be implemented. The modification of surfaces by electrochemical reduction of diazonium salts can be summarized on carbon,[8] metal[9] or semiconductor[10] as shown in Scheme 1.

The method is quite simple: a diazonium salt ArN_2^+($c \approx 1$ to 10 mM) dissolved in an aprotic medium with a supporting electrolyte (acetonitrile ACN + 0.1 M NBu_4BF_4) or in acidic aqueous medium[11] (for example H_2SO_4 0.1 M) is reduced, using the surface to be modified as a cathode. The potential of this cathode is set with the help of a potentiostat at the potential of the voltammetric peak of the diazonium or at more cathodic (more negative) potential for a variable period of time (seconds to minutes). After thorough rinsing of the electrode in an ultrasonic bath in order to remove any chemical which could be only weakly adsorbed, it is possible to observe the aryl group bonded to the surface by the different methods described hereafter.



Scheme 1

Diazonium salts (BF_4^- ^+N_2Ar) are easily and rapidly prepared in one step from a wide range of aromatic amines many of which are commercially available. The synthetic methods are well established and standard procedures can be found in practical organic chemistry textbooks. Tetrafluoroborates are particularly advisable as they are stable and there is no risk of explosion (upon heating, they undergo the Balz–Schiemann reaction leading to the fluoroaryl compound). The half life of solutions in aprotic or acidic medium is of the order of five days but diazonium salts are not stable in aqueous solution above pH $\approx$ 2–3. Synthetic flexibility is a characteristic of this method. As a number of different groups can be attached to the aromatic ring of the starting amine it is possible to obtain surfaces bearing a wide variety of functions (alkyl, halogenoalkyl, perfluoroalkyl, carboxylic, ester, cyanide, halides, nitro, alcohols, thiols, and more complicated structures including polyaromatics and compounds with triple bonds…).

A large variety of materials have been modified by this method: carbon (GC,[8,11] HOPG,[8,12,13] pyrolized photoresists,[14] pyrolized Teflon,[15] carbon fibers,[11] carbon blacks,[16] carbon nanotubes,[17] diamond[18]), semiconductors (Si,[10,19] GaAs[20]), and metals[9,21](including noble metals such as Au and Pt). In contrast to many of the methods quoted in the introduction, this reaction is a reductive electrolysis and can therefore be performed on oxidizable substrates such as industrial metals (Fe, Zn, Ni, Co,[21] Cu,[21,22] Pd.[20] have been derivatized in this way). As we shall see below the reduction takes place at very low cathodic potentials and even easily reduced functions such as nitro groups can be used as substituents, for the same reason exclusion of dioxygen from the solution is not mandatory. As stated above, the reaction can be achieved in the order of minutes.

These different characteristics make the method appealing for the modification of a variety of surfaces by many different organic functional groups. In the following, we shall discuss the electrochemistry of the diazonium salts associated with the grafting reaction, the characterization of the functional groups, the bonding of the organic layer, its structure and some applications of the method. In addition, recent works have shown that it is possible to derivatize surfaces without electrochemistry by simple immersion of the surface in a diazonium solution.[17,20,22]

Electrochemistry of diazonium salts, the grafting mechanism

Through which mechanism does this reaction occur? Which are the intermediates? Examination of the electrochemical behaviour of diazonium salts and of some related compounds can shed some light on these questions.

Fig. 1 shows the voltammogram of 4-nitrobenzene diazonium tetrafluoroborate in ACN + 0.1 M NBu_4BF_4 on a glassy carbon electrode (a material on which electrochemistry of these compounds is the most simple). It shows (Fig. 1a) a

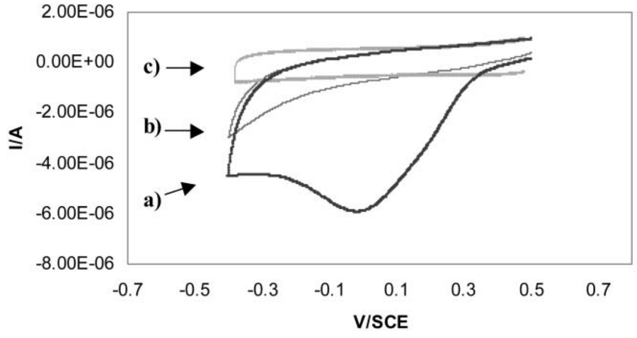


Fig. 1 Glassy carbon disk electrode (d = 3 mm) in ACN + 2 mM $^{+}N_2C_6H_4NO_2\ BF_4^-$ + 0.1 M NBu_4BF_4 a) first and b) second scan and c) the same electrode in ACN + 0.1 M NBu_4BF_4.

broad irreversible wave at Ep = −0.02 V/SCE (Ep, peak potential), the fact that the voltammetric wave is irreversible indicates that an irreversible reaction (*i.e.* the cleavage of dinitrogen) is associated with the electron transfer. On the second scan (Fig. 1b), the wave disappears nearly completely and this is indicative of the blocking of the surface by the organic groups which become attached to the surface. The very low cathodic reduction potential is characteristic of diazonium salts;[8] for example 4-nitronaphthenyl diazonium tetrafluoroborate is reduced at Ep = 0.37 V/SCE and 4-methylbenzene diazonium is reduced at Ep = −0.18 V/SCE.

Let us look in more detail at the electrochemistry of diazonium salts. For this purpose, it is interesting to compare the electrochemical behaviour of diazonium salts with the well-established electrochemistry of aryl halides which is summarized below in a very simplified manner on glassy carbon. These compounds which never show any sign of attachment of the aryl group to the surface are reduced by two electrons according to Scheme 2.

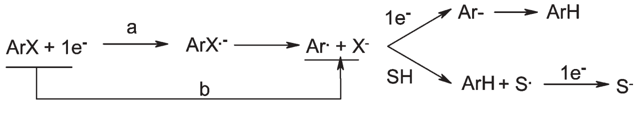
The radical anion is formed after the transfer of one electron from the electrode (path a) and will diffuse away from this electrode. Depending on the length of its lifetime it will give rise to the aryl radical closer (shorter) or farther (longer) from the electrode. If the radical is formed far from the electrode it will react through an hydrogen atom abstraction with the solvent or be reduced by the parent radical anion, but it will have no chance of diffusing back to the surface and reacting with it. If the cleavage of the radical is very fast or even more so if the electron transfer is concerted with the cleavage of the halogen (path b) the radical will be formed very close to the surface or "on the surface", respectively. But the radical $Ar^\bullet$ is much more easily reduced (as we will see below) than the parent aryl halide (for example 4-bromonitrobenzene is quite easily reduced at Ep = − 0.98 V/SCE, but 2-chloronaphthalene is reduced at: Ep = −2.26 V/SCE) and therefore the radical will be reduced to the aryl anion before having a chance to react with the surface. The difference in behaviour of the very easily reduced diazonium cations allows an explanation as to why they react with the surface while aryl halides do not. Analysis of the voltammogram of benzenediazonium[23] has permitted the establishment of the following mechanism for the formation of the phenyl radical (Scheme 3).

The phenyl radical is produced directly "on the electrode" through an electron transfer concerted with the cleavage of dinitrogen to give the phenyl radical. But, in contrast to aryl halides, at the very low cathodic reduction potential of the diazonium the phenyl radical is not reduced and can react with the surface. The reduction wave of the phenyl radical is observed in cyclic voltammetry, as a very small wave negative to the wave of (more cathodic than) the diazonium itself at Ep = −0.64 V/SCE. This wave of the radical is small because most of the radical has reacted by the time the potential is negative (cathodic) enough to make this reduction possible. From the simulation of the voltammogram it was possible to obtain the thermodynamic redox potential of the phenyl radical/phenyl anion couple: E° = 0.05 V/SCE.

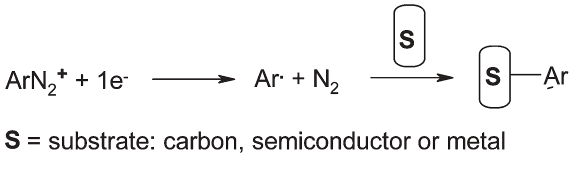
Therefore the particular behaviour of diazonium salts is related both to their easy reduction (which is itself related to the very strong electron-withdrawing character of the diazonium group σ = + 1.91) and to the concertedness of the electron transfer–dinitrogen cleavage which ensures that the formation of the radical takes place "on the surface" itself.

The comparison between the electrochemical reduction of aryl halides and diazoniums gives confidence in the fact that the radical is the species responsible for the attachment of the aryl group to the surface, but one can always wonder if other species such as aryl radical-anions or anions could bind to the surface. As for radical anions, they can be easily rejected as the diazoniums which cannot give rise to radical anions can be electrografted. On the contrary, radical-anions are easily obtained from aromatics or aromatic halides and to the best of our knowledge, no grafting reaction has ever been observed. Anions can be produced under very dry conditions from aromatics such as anthracene, but no grafting to the surface is observed when they are produced by electrochemistry.

The above discussion concerns carbon surfaces, but it can be extended to metal surfaces with however some differences. In order to create metal–carbon bonds, one should work with surfaces as free as possible from oxides, for this purpose it is necessary to polish carefully the surface which should then be rinsed in a deoxygenated solvent and immediately grafted in a deoxygenated solution. Another difference with carbon stems from the easy oxidation of industrial metals. For example with iron it is not possible to observe the voltammogram of 4-nitrobenzenediazoniums as in Fig. 1, as its reduction takes place at a potential more anodic (more positive) than the oxidation of the metal. This is, however, of little practical importance: the peak potentials can be estimated from the



Scheme 2



Scheme 3

values on carbon and during the grafting reaction the potential is always set cathodic to the oxidation of the metal. Besides when the reduction potentials can be measured on carbon and metals little difference is observed.

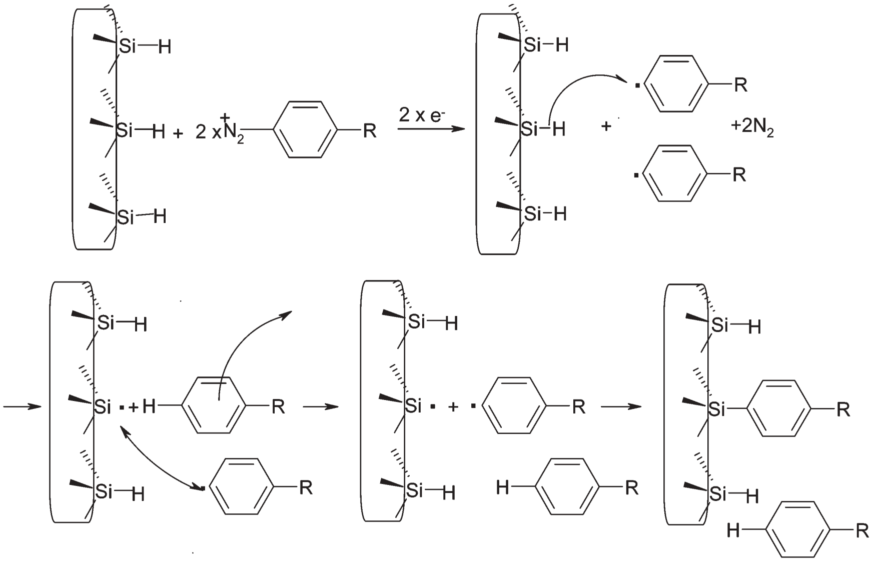
Under ambient conditions, silicon is covered by a layer of SiO_2, but it is possible[10] to prepare monocrystalline surfaces of hydrogenated silicon (such as Si(111)). This hydrogenated silicon surface can be electrografted as sketched in Scheme 4. Upon reduction of ArN_2^+ on this surface an aryl radical is formed which abstracts an hydrogen atom from the surface to produce a silyl radical. Recombination of a silyl radical with an aryl radical produces a modified silicon surface. This mechanism is reasonable, as the SiH bond is weaker than the aromatic C–H bond as indicated above and also because the cleavage of dinitrogen being concerted with the transfer of the electron, radicals are formed "on the surface" and therefore prone to react with surface silyl radicals.

More recently,[17,20,22] it has been shown that diazonium salts spontaneously bind to different surfaces such as carbon black,[16] Si, GaAs, Pd[20] (in ACN) and Cu[22] (in ACN and aqueous H_2SO_4). A spontaneous electron transfer between the substrate and the diazonium salt has been deemed responsible for the formation of the radical in the case of silicon and copper (open circuit potential of ***Cu***: −0.306 mV/SCE in 100 mM H_2SO_4 and. −0.531 mV/SCE in ACN). A mechanism has been proposed on silicon similar to that which occurs under electrochemical stimulation. This purely chemical grafting of surfaces is very interesting as it does not require electrochemical equipment. The electrons necessary for the reduction of the diazonium salt are most likely provided by the metal which should become positively charged; this should lead to an oxidation of the surface (on very thin −90 nm copper layers an important corrosion of the surface is easily observed). It should therefore be checked that this oxidation of the surface permits surfaces of the same quality as that obtained by electrochemistry to be achieved.

Characterization of the organic layer

Once the electrografting reaction has been achieved and after thorough rinsing of the sample (only strongly bonded organic layers must remain on the surface), one must ascertain the presence of the organic layer. A number of electrochemical and spectroscopic techniques have been used for this purpose; let us present the main proof for the presence of the attached organic layer.

As electrochemistry has been used to attach the organic groups to the surface it can also be used to characterize the organic groups bonded to the surface if these groups are electroactive.[8] In this respect, nitrophenyl groups are excellent reporting groups. Electrografting of 4-nitrobenzenediazonium as in Fig. 1 provides a surface modified with 4-nitrophenyl groups. After thorough rinsing of the sample and transfer to a solution containing only the solvent and supporting electrolyte (ACN + 0.1 M NBu_4BF_4) one should be able to observe the voltammetric signal of the nitrophenyl group. Nitrobenzene is reversibly reduced, in aprotic medium, by one electron to its stable radical-anion at rather low cathodic potential ($E^\circ = -1.20$ V/SCE), it is therefore easy to observe the 4-nitrophenyl group attached to the surface. This is shown in Fig. 2: the reversible voltammogram of the attached 4-nitrophenyl groups is located at the same position ($E^\circ = -1.17$ V/SCE) as for nitrobenzene itself. On this voltammogram the cathodic and anodic peaks are located at the same potential (giving rise to the symmetrical shape of the voltammogram) indicating that the species undergoing the redox process do not diffuse to and from the electrode and are therefore bonded to the surface. Upon repetitive scanning of this reversible wave, it rapidly disappears due to the protonation of the radical-anion of the 4-nitrophenyl group by residual water. The same type of characterization has been achieved on Si(111)[10,19] and on metals.[9,21] If the modified carbon electrode is transferred to an aqueous acidic solution (instead of ACN), the nitro group will be reduced irreversibly by 4 to 6 electrons to the hydroxylamine or



Scheme 4

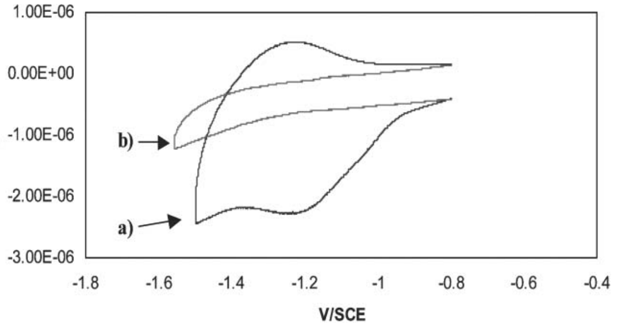


Fig. 2 a) Glassy carbon disk electrode ($d = 3$ mm) electrografted with 4-nitrophenyl groups and transferred in an ACN + 0.1 M NBu_4BF_4 solution; b) same untreated glassy carbon disk electrode in an ACN + 0.1 M NBu_4BF_4 solution.

amino group, giving rise to a higher irreversible wave.[11,24,25] On the second scan, this wave completely disappears, the nitrophenyl group has been reduced to an aminophenyl group which has no electrochemical reduction signal. Other electrochemically[8] active reporting groups have been be used to demonstrate the presence of the organic layer such as 4-bromophenyl, 4-cyanophenyl, 4-phenylazophenyl, naphthyl, anthraquinone, 4-benzoylphenyl.

Vibrational spectroscopies (FTIRRAS—Fourier Transform InfraRed Reflection Absorption Spectroscopy—and Raman) are very useful in characterising the surface groups. Again, the nitrophenyl group is an excellent reporting group, through the two strong bands at ≈ 1530 and $1350\ \text{cm}^{-1}$ (antisymmetric and symmetric stretching), it can be easily characterized. 4-Benzoylphenyl,[9] dimethylamino[12] groups have also be characterized by FTIRRAS. These techniques also allow the demonstration of the fact that the diazonium salts are not merely adsorbed on the surface through the absence of the $^+N_2$ stretching[13,21,26] which should be located in the 2300–2130 cm^{-1} region. The IR beam reflected by the surface is polarized perpendicularly and the spectra are dominated by vibrational modes with components perpendicular to the sample surface, from these selection rules it is possible to determine the orientation of the molecule on the surface, as has been done with SAM's. A quantitative exploitation of this phenomenom should permit the structure of the aryl layer to be determined with precision. Raman spectroscopy has been used by McCreery[13,26] to examine these organic layers in great detail. The attachment of 4-nitrophenyl or 4-nitrophenylazophenyl layers to GC, edge or plane HOPG were demonstrated through a complete assignment of the spectra. Integration of the peaks allowed the determination of the surface concentration of the nitrophenyl groups. It was also possible to observe the reduction of the nitro groups described above.

XPS (X-ray Photoelectron Spectroscopy) is obviously a technique of choice to characterize the surface after grafting, it has been widely used by the different groups interested in this reaction.[8,22,24] Again the nitrophenyl group appears as an excellent reporting group: its N1s peak is located at 406 eV well apart from other N1s peaks such as amines which appear at 400 eV. Many other groups have been observed by this technique[20–22] such as F-, Br-, I-, C_6F_{13}- and HOOC-C_6H_5. Attenuation of the signal related to the atoms of the surface (in the case of metals or semiconductors) allows an estimation of the thickness of the organic layer.

RBS (Rutherford BackScattering), a technique which measures the energy of $^4He^+$ ions backscattered by the atoms of the surface, has permitted[9,10,21] the observation of the presence of Br and I atoms after electrografting of the corresponding benzenediazonium ions. In addition this technique is quantitative as it allows the determination of the number of heavy atoms on the surface and therefore the surface concentration.

AFM (Atomic Force Microscopy),[9,12,14,25] and STM[19] (Scanning Tunneling Microscopy) have allowed the observation of the modifications of the surface after electrografting. The images clearly evidence the formation of a layer of variable height and roughness (depending on the grafting conditions).

The convergent results of these different techniques and some others (EDS[27]—Energy Dispersion Spectroscopy—, capacitance measurements,[10,19] ellipsometry[20]) leave little doubt about the presence on the different surfaces (carbon, Si, metals) of the aryl-R groups bearing the R- substituents of the starting benzenediazonium salt.

Bonding of the organic layer

We have depicted the different experiments which prove that a substituted aryl layer can be observed on top of the substrate: what is the evidence indicating the formation of a covalent bond between the substrate and the aryl layer? The first indication is the strength of this bond which resists ultrasonic cleaning in a variety of solvents[8] (ACN, dimethylformamide, dimethyl sulfoxide, benzene, benzonitrile, acetone, methanol, ethanol, dichloromethane and chloroform for 15 minutes each) on carbon and metals and is stable for a month in ambient conditions. On Si, 4-bromophenyl layers resisted 40% HF for 2 minutes and 10 M NH_4F for 1 minute.[10,19] On GaAs (chemically grafted)[20] the layer resisted concentrated HCl and NH_4OH for 5 minutes. The 4-nitrophenyl modified carbon samples could be heated, in UHV, up to 700 K without losing the Auger signal of the aromatic layer.[8] The potential range in which these layers are stable has been investigated,[28] it spans from 2.6 to 5.6 V depending on the substituent (4-diethylamino and 4-bromo, respectively). These layers can only be removed by mechanical polishing or by scratching with an AFM tip. This resistance to aggressive reagents, to many organic solvents, to temperature clearly excludes a weak bond such an hydrogen bond or a van der Waals interaction.

On silicon, a ionic bond is difficult to imagine and is unlikely in view of the XPS position of the Si2p signal of the grafted layer and that of Si–H which are nearly identical even under conditions where the signal is mainly surface sensitive (detector at grazing incidence).[10] In the case of a ***Si***–$C_6H_4NO_2$ surface an estimate of the shift of the Si signal is expected to be less than 1 eV; these data clearly support the existence of a covalent bond between Si and the organic group.

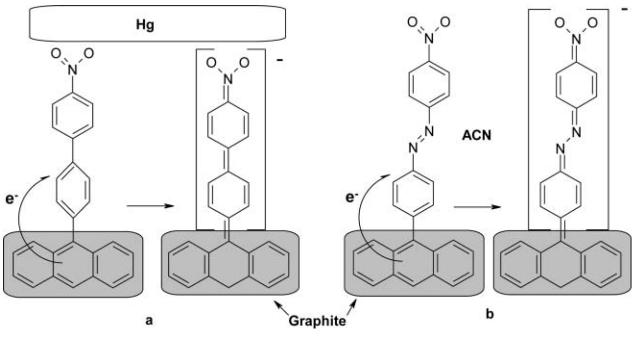
On carbon, the same XPS observation can be done and a similar conclusion can be drawn. But in addition, some additional proof of a covalent bond has been brought forward.

McCreery[29] has attached monolayers of biphenyl and nitrobiphenyl to very flat graphitic carbon obtained by pyrolysis of a photoresist. A mercury contact was established on the top of the layer (Scheme 5a). Upon varying the potential between the mercury on top of the monolayer and carbon at the bottom he was able to observe conductance switching of this junction. The same author[26] attached nitroazobenzene (NAB) to a GC surface in an electrochemical cell and observed the Raman spectrum of the layer. The attached NAB spectra were quite different from the free NAB spectra in solution and could be monitored as a function of potential. In the potential range between *ca.* +200 to *ca.* −1000 mV/SCE the intensity of the Raman bands associated with the phenyl-NO_2 moiety varied significantly. In both of these experiments, the resistance switching and the changes of the Raman spectra were consistent with a change of structure of the electrografted biphenyl, nitrobiphenyl, nitrophenyazophenyl (NAB) groups to quinoid structures containing a C=C double bond between the aromatic group and the graphitic substrate (Scheme 5). These two experiments imply a strong electronic coupling between the π system of the graphitic substrate and the electrografted molecules and support the existence of a bond between carbon and the organic layer.

A different kind of evidence was obtained from ToF-SIMS[30] (Time of Flight Secondary Ions Mass Spectroscopy). Examination of a nitrophenyl modified GC surface under a Ga^+ ion beam indicated the presence of fragments at *m*/*z* 500 which were assigned the following structure: $[CHC_6H_3NO_2C_6H_5NO_2C_6H_3NO_2C_6H_4NO_2]^-$; the final carbon being likely part of the substrate.

On iron, XPS has permitted[31] evidence of the ***Fe***–C_6H_4COOH bond to be brought forward. A small C1s signal is observed at 283 $\pm$ 0.1 eV which corresponds to a carbide type carbon. Variation of the Tilt of Angle of the electron beam relative to the surface normal indicated that the COOH rich layer is located on top of the carbide rich aryl–iron interface. This is in agreement with the existence of a Fe–C covalent bond.

The above data indicate that the aryl layer is attached through a strong bond to carbon, silicon, and metals excluding a mere physisorption. In addition, they point to the covalent character of this bond in agreement with what could be expected on C and Si, but maybe more surprisingly on metals.



Scheme 5

Monolayers or multilayers

Until now we have used purposely the rather vague term of aryl layer. We shall now define the structure of this layer and try to provide an answer to the following questions: i) is it possible to measure and control the thickness of this layer? ii) is it possible to obtain random or organized monolayers but also thicker layers (how thick)?

This discussion relies on the measurement of the thickness of the layer and this has been most often achieved through AFM and XPS experiments and by measurements of surface concentration Γ of aryl reporting groups (by integration of cyclic voltammograms, Raman and RBS signals). It should be pointed that a value of Γ can be interpreted in different ways whether one assumes (or not) a close-packing of the aryl groups at the surface of the substrate: for a given Γ, the more compact the layer the thinner it will be and conversely the more disperse the aryl groups on the surface the thicker the aryl layer. The surface concentration of a close-packed monolayer Γ_{CPML} of phenyl (or 4-substituted phenyl) groups can be easily estimated from molecular models: $\Gamma_{CPML} = 1.35 \times 10^{-9}$ mol cm^{-2}.

There is an agreement between the different groups interested in this method that it is possible to increase and control the thickness of the layer by controlling the charge passed during the grafting electrolysis (although the yield of the reaction is not unity[8] and may vary from one substrate to the other); controlling the charge is equivalent to controlling the electrolysis time and the current, but these reactions are performed (as stated above) at controlled potential and therefore the two parameters which can be used are the electrolysis time and grafting potential. The third parameter is the concentration of the diazonium salt. It should be added that the conditions vary from one paper to another making precise comparisons between the results somewhat difficult, in addition there is a possibility that different substrates (for example different carbon substrates with different surface structures and reactivities) lead to different results.

We shall first examine the results obtained on carbon using ACN as a solvent. With 4-nitrophenyl groups electrografted on GC (a surface with a roughness which depends on the polishing conditions) in ACN at a potential located 0.8 V more cathodic than the voltammetric peak (a rather cathodic potential), it was observed by integration of the voltammetric signal that Γ increased with time (up to 600 s) and concentration (0.2, 1 and 5 mM) to reach a limiting value ($\Gamma = 3–4 \times 10^{-9}$ mol cm^{-2} of geometric area)[8] close to Γ_{CPML} of a close-packed monolayer if one takes into account the roughness of the surface. Increasing the electrolysis time from 10 to 100 minutes did not significantly increase Γ.[25] The same order of magnitude for Γ was obtained by Bélanger[24] (5 mM solution, 0.65 V cathodic to the voltammetric peak, 240 s, $\Gamma = 1.8 \times 10^{-9}$ mol cm^{-2}), and also by McCreery[13] (1 mM, $\approx$0.5 V negative to the voltammetric peak, 600 s, $\Gamma = 0.65 \times 10^{-9}$mol cm^{-2}). The potential dependence of Γ has been examined by Downard,[25] she observed that the surface concentration increased as the grafting potential becomes more cathodic ($\Gamma = 6 \times 10^{-10}$, 12×10^{-10}, 19×10^{-10} mol cm^{-2} of geometric area at potentials 0.25, 0.50 and

0.75 V negative to the voltammetric peak, respectively). Taking into account the roughness of the substrate, these values of Γ are lower than that corresponding to a close-packed monolayer. The basal plane of HOPG is a better substrate for such investigations as its real surface is very close to its geometric surface, integration of the cyclic voltammogram ($\Gamma^{8,13} = 1.6 \times 10^{-9}$ mol cm^{-2}), of the Raman spectrum ($\Gamma^{13} = 1.2 \times 10^{-9}$ mol cm^{-2}) and of the RBS spectra ($\Gamma^{8} = 1.8 \times 10^{-9}$ mol cm^{-2}) gave values close to one another and close to the surface concentration of a close-packed monolayer Γ_{CPML}. But as stated above, these values can also correspond to a less compact and thicker monolayer. HOPG surfaces were examined by AFM during the derivatization (after 1 to 5 cycles between −0.1 and −0.9 V/SCE) with 4-diethylaminophenyl groups[12] (from 0.5 mM solutions). The initial nucleation was observed at cleavage steps forming ≈1. 5 nm high "humps", it was followed by nucleation at defects of the basal plane where clusters of molecules are observed the height of which vary from 0.7 to 2.5 nm (*i.e.* about 1 to 4 aryl groups high—the height of a 4-nitrophenyl group is 0.71 nm). Using a 5 mM concentration of the diazonium salt, the height of these protruding features reached 5 to 15 nm. The growth of the layer on the basal plane continues as the islands of grafted layers grow larger and larger. After 5 cycles a continuous layer is observed with protruding features which can reach a height of nearly 8 nm. This picture of the aryl layer obtained by AFM or STM is quite different from that of a monolayer which emerged from integration of voltammograms or spectra.[8,13,24] In order to solve this problem, Downard[25] examined very carefully both the surface concentration measured by integration of the voltammogram of 4-nitrophenyl groups and the height of the layer obtained by AFM. The layers were produced on atomically flat pyrolyzed photoresists films by electrolysis of 4-nitrobenzenediazonium (c = 0.71 mM) at a potential 0.15 V negative to the voltammetric peak (a potential not very cathodic). At different electrolysis times, a linear correlation was observed between Γ and the height of the layer d. After 600 s the surface concentration reached a value of $\Gamma = 1.2 \times 10^{-9}$ mol cm^{-2} a value close to Γ_{CPML} but the height of the layer d measured by AFM was about 4 aryl groups high. It was therefore concluded that the compactness of this layer was 21% of a close-packed monolayer and its height equivalent to 4 aryl groups. It is however somewhat intriguing that all the measurements of Γ by integration of voltammograms or spectra, under various conditions and on different carbon substrates, always gave a value lower or close to that of a close-packed monolayer Γ_{CPML}.

Organic layers of 4-nitrophenyl groups bonded (2 mM solutions of the diazonium, 300 mV cathodic to the voltammetric peak, 300 s) to different metals (Au, Pt, Ni, Cu, Zn) have been examined by AFM, XPS and RBS.[21] Comparable thicknesses were obtained through the different methods for these different samples: 6 to 10 layers of nitro phenyl groups. Protuding features are observed as on carbon but the layers are much more homogeneous if the plates are polished immediately before grafting with the exclusion of dioxygen.

We have seen that in the preceding examples that multilayers are always observed by AFM even if integration of voltammograms or of spectra indicate the formation of monolayers. Is it possible to observe real monolayers by AFM? This has been achieved by McCreery,[14] on pyrolyzed photoresist, after a single voltammogram (from +0.2 to −0.4 V/SCE; 1 mM solution of various diazoniums such as stilbene or biphenyl,…). The presence of a monolyer was checked by measuring its height by scratching the layer with the AFM tip on a small surface and measuring the height of the step by non-contact AFM. The most interesting result concerning monolayers obtained by reduction of diazonium salts was reported by Allongue[19] on Si(111). By controlling the charge consumed during the electrolysis and by choosing the electrolysis potential at the peak potential, it was possible to obtain not only a monolayer but an organized monolayer. STM images of ***Si***–C_6H_4Br surfaces show 5 × 5 nm domains of organized molecules with a rectangular 3.8 × 6.5 Å unit cell which corresponds to a $(1 \times \sqrt{3})$R 30° modification of the Si(111) unit cell. It is somewhat surprising to observe (Fig. 3) an organization of the aryl groups as once they are bonded to the surface they cannot move and therefore cannot reorganize, but a Monte Carlo simulation indicated that the formation of organized domains is possible if there is a higher probability of grafting a molecule in the neighbourhood of a first attached molecule than far from this molecule. This could be due to either an electronic effect through the silicon or to stacking interactions of the aromatic molecules. This investigation and the resulting STM image demonstrates that it is possible to obtain **covalently bonded, self organized monolayers** of aryl groups.

At the other end of the range of thickness of the organic layer, very thick layers (100 nm) of 4-nitrophenyl groups were obtained[32] by scanning the potential to very cathodic potentials (+0.3 V to −2.9 V/SCE) for 20 cycles.

As a conclusion of this section, the different investigations have shown that it is possible by controlling the different parameters (charge and concentration or potential, time and concentration) to obtain either monolayers or multilayers. It should however be remembered that the different substrates are not equivalent and that formation of monolayers which is possible on pyrolized photoresists and Si(111) may not be possible on other substrates. For example, quite different growths are observed on the basal plane or the edge of HOPG;[12] glassy carbon is a disordered material consisting of phenyl rings and double bonds and the growth of the layers is

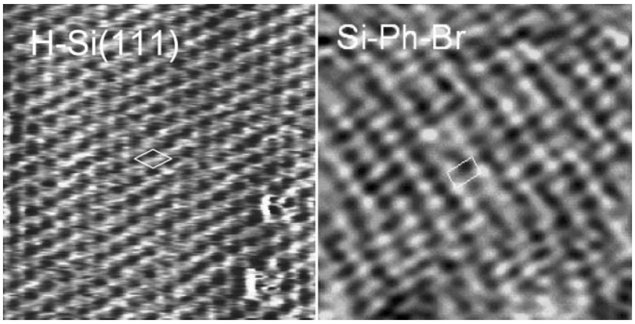


Fig. 3 STM image of surface (a) H-Si (111) and (b) modified with 4-bromophenyl groups bonded to Si(111). Reproduced from reference 19 with permission of Elsevier.

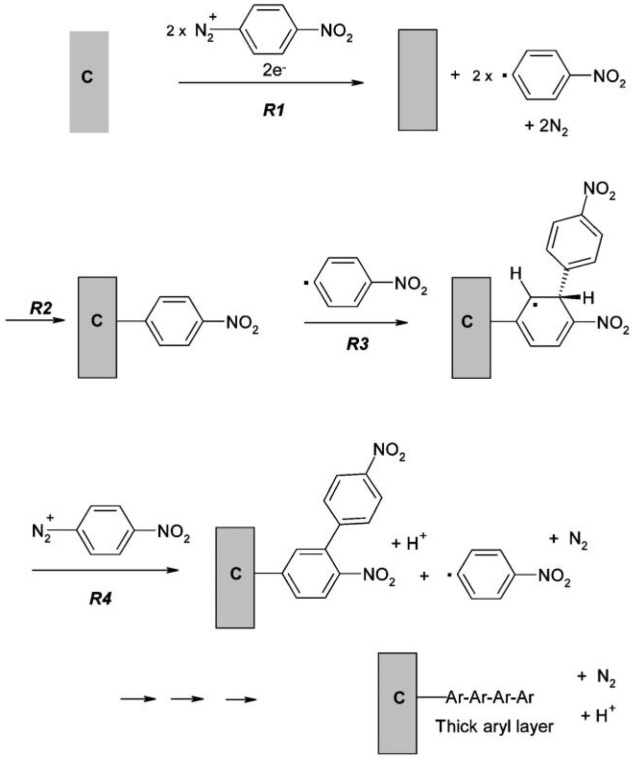
quite different from the basal plane of HOPG. Finally, AFM seems by far the best method to measure the thickness of the layers, there seems to be some unsolved problems concerning the interpretation of Γ mainly when it is derived from the integration of the voltammograms.

Stucture of multilayers

The preceding section has shown the possibility of growing multilayers on top of the different substrates, what can be the structure of these multilayers? are the successive layers bonded to each other or not?

The formation of organic layers bonded to the surface is due to the reaction of aryl radicals with the surface, the growth (observed for example by AFM[12]) of the layer is due to the same intermediate which attacks the first grafted aryl group as shown[30] in Scheme 6. This is a well-known organic reaction termed Aromatic Homolytic Substitution $S_{H.}$

The first step is the formation of a radical through a concerted electron transfer bond breaking reaction (reaction ***R1***), this radical binds to the surface (reaction ***R2***); another radical attacks the first grafted aromatic group (reaction ***R3***) to give a cyclohexadienyl radical. In order to recover the aromaticity this radical must lose an hydrogen radical (this is possible by abstraction of an hydrogen atom by an aryl radical) but more likely a proton and an electron. This last redox reaction is possible either through an electron transfer to the electrode and loss of a proton or by reoxidation of the cyclohexadienyl radical by a diazonium cation. Repetition of this reaction would lead to thick polyphenylene layers. If however two cyclohexadienyl radicals disproportionate as in Scheme 7, the formation of a cyclohexadiene group in the chain would interrupt the conjugation. In the case of S_H substitution the rates of the reaction on the different positions of the aromatic ring are not very different and the sensitivity to the donating or withdrawing character of the substituent is low, but for steric reasons attack *ortho* to the nitro group seems more likely.



Scheme 6

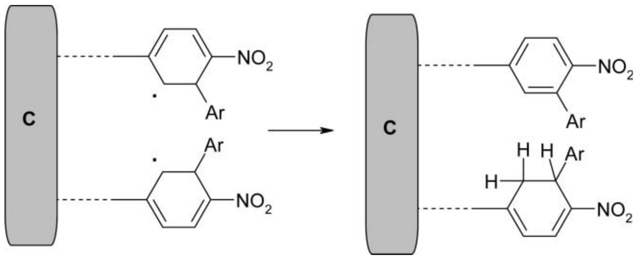
This mechanism which is in agreement with literature data concerning an aromatic substitution permits an explanation of the growth of polyphenylene layers even in cases when grafting takes place spontaneously[16,20,22] (without electrochemical induction). It could also explain the differences observed between electrochemically measured Γ and the height of the layers measured by AFM: some nitro groups would not pertain to nitroaromatic structures and would not be accounted in the integration of the nitroaromatic signal.

Another possibility has been proposed by Bélanger[28] for the growth of the layers. The voltammogram of $Fe(CN)_6^{3/4-}$ is reversible on a bare carbon electrode, but becomes very slow on electrodes modified with polyphenylene multilayers and the charge transfer resistance increases upon grafting the electrode. He observed the cleavage of aryl groups ($-C_6H_5COOH$, $-C_6H_5Br$,...) upon scanning the potential to very cathodic or very anodic potentials which translates in a rather sharp decrease of the transfer resistance and a return toward reversibility of the $Fe(CN)_6^{3/4-}$ couple. But for electrodes which seem completely degrafted along the preceding criteria, an XPS signal of the substituents can still be observed; the authors therefore concluded that there existed two kinds of aryl groups in the layer, some would be covalently bonded together and finally to the surface while the remainder of the film would be the result of the adsorption (π–π stacking) of reaction products coming from the electrogenerated radical. This was also supported by the observation of the XPS or CV signal of ferrocene in the polybromophenylene layers prepared in the presence of 4-aminophenylferrocene.

Although this is not an easy task more informations should be gathered to define the structure of these layer, a possibility would involve, for example, the derivatization of nanoparticles and the examination of the bonded layers by NMR which provides rich structural information.

Some applications and possible uses of electrografting of diazonium salts

Quite a number of different applications have been described for these covalently bonded organic layers, we shall review only some of them along a purely personal choice.



Scheme 7

The use of molecules in electronic circuits is a subject of much current interest. Molecular junctions are part of different possible molecular electronic devices. They are composed of molecules connected on both sides to a conductor as shown in Scheme 5a where nitroazobenzene molecules are sandwiched between a carbon surface and a mercury drop. McCreery[33] examined the behaviour of such devices. The carbon surface is a pyrolized photoresist deposited on Si, the organic group is nitroazobenzene (but also phenyl, fluorenyl, anthracenyl, biphenyl,…) bonded to the carbon by reduction of the corresponding diazonium salt; the other contact is made by a mercury drop or better by a deposited layer of titanium protected by a second layer of gold (note that there is no solvent or supporting electrolyte in the junction). If the potential between the two conductors is varied a conductance switching is observed.

As shown in Fig. 4, the initial junction is very resistant (≈600 MΩ, curve P), after a +4 V pulse (Ti relative to PPF), curve Q is obtained which corresponds to a 20 kΩ resistance. If the junction is maintained at 0 V it slowly returns to the initial state (curves after 1, 3, 6 and 60 minutes). Very interestingly, as deduced from the Raman spectra, curve P would correspond to the "phenyl" structure of the organic layer as shown in Scheme 5 while curve Q would correspond to the "quinoid" structure. The interest of covalently bonded aryl layers in such devices is their stability and the low energy barrier for the injection of electrons at the contact between the metal and organic molecule.

Nanotubes are currently investigated for their possible use in molecular electronics or for the formation of composite materials. However, a major problem stems from their difficult manipulation which is due to "roping". Sidewall derivatization could be a possible way to facilitate their solubility, their manipulation and therefore their use. Tour[17,34] was able to derivatize Single Wall NanoTubes (SWNT) electrochemically and thermally with a variety of diazonium salts. The reality of the modification was ascertained through IR spectroscopy (C=H stretching of t-BuC$_6$H$_4$– or C=O stretching of CH$_3$OOCC$_6$H$_4$– substituents) or EDS (Cl- or F-C$_6$H$_4$–) as well as by electronic transmission microscocopy. It was possible to show[35] that polyaryl chains can be grown on the wall of the nanotube. This was done by comparison of the XPS spectra of ***SWNT***–C$_6$H$_4$Br (which allows the measurement of n from the C$_n$/Br ratio) with the intensity of the Raman D-band (which indicates the number of carbons of the SWNT which have been transformed from sp^2 to sp^3 upon grafting). The intensity of the D band remained constant as n decreased, indicating that after the initial grafting, the bromophenyl groups are not added to the sidewall but to the substituent itself. In addition, values of n as high as 1 have been observed which are not compatible with the integrity of the SWNT (which was checked by Transmission Electron Microscopy). This is clearly the same phenomenon which has been observed during the formation of multilayers on HOPG discussed above.[12] The solubility[34] of SWNT was improved by grafting, the best result was obtained with 4-*tert*-butylphenyl groups. An interesting result[36] was obtained by modifying SWNTs with –C$_6$H$_4$COOC$_{10}$H$_{20}$OH moieties: these modified nanotubes were dispersed in a polystyrene matrix, examination of the viscoelastic properties of the composite demonstrated the formation of a percolated SWNT network structure (a real composite) while underivatized SWNTs led to a behaviour comparable to that of the unfilled polymer.

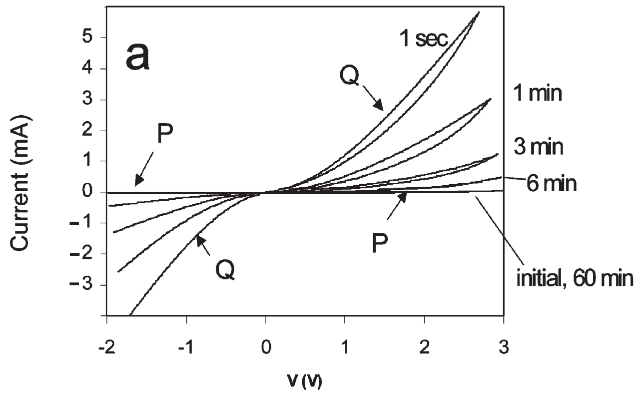
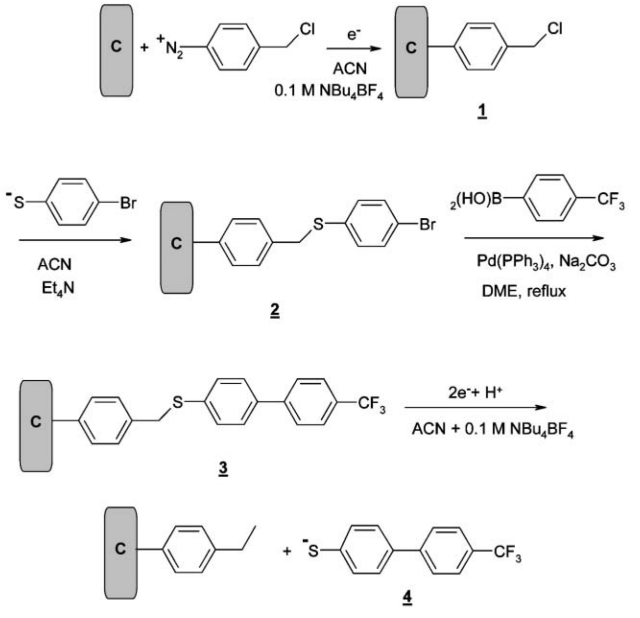


Fig. 4 i/V curve for a Au/Ti/NAB/PPF junction (at v = 1000 V s^{-1}) obtained before (curve P) and after a +4 V potential pulse lasting 5 s (curve Q) and return to V = 0 V. Reproduced from reference 33 with permission of the American Chemical Society.

Once a surface as been chemically modified by reduction of a diazonium salt, it may be interesting to perform further chemical modifications. Use of high surface carbon felts (1500 m^2 g^{-1}) as possible supports for combinatorial chemistry provides an example of such post-grafting modifications. A large part of combinatorial chemistry is performed on functionalized styrene–divinylbenzene beads; these beads undergo several successive chemical reactions before the final cleavage of the desired molecule from the bead. A similar set of reactions can be performed on carbon previously modified by a diazonium salt[27] as shown in Scheme 8.

The carbon felt is electrografted by a chloromethylphenyl group through the electrochemical reduction of the



Scheme 8

corresponding diazonium salt to give **1**, then chlorine undergoes a nucleophilic substitution by a bromobenzenethiolate molecule to yield **2**. This modified carbon is treated under the conditions of the Suzuki reaction to give **3**. As carbon is a conductive material it is possible to perform the final cleavage by electrochemical reduction of the C–S bond to obtain the final biphenyl. Post-functionalization of modified iron surfaces can also be achieved[37] by binding polymers in order to improve protection against corrosion.[38]

Preparation of derivatized electrodes which are able to respond specifically to a given substance is another use of the surfaces electrografted with diazonium salts. For example, in the extracellular fluids of the nervous central system measuring the concentration of dopamine down to the nanomolar level is a challenge in the presence of much higher concentrations of ascorbic acid (200–500 μM) as both compounds are oxidized in the same potential range. Carbon electrodes have been modified with *p*-phenylacetate[39] groups by electrografting of the corresponding diazonium salt. With such electrodes, it was possible to detect dopamine (20 μM) in the presence of ascorbic acid (2 mM) at pH 7.4 although the two compounds are oxidized at nearly the same potential. The same kind of selectivity was also observed[40] with electrodes modified with cathechol groups by post-funtionalization of 4-amino or 4-carboxy phenyl groups This selectivity results from electrostatic interaction between the anionic surface of the electrode and dopamine which, at this pH is a monocation while ascorbic acid is under its anionic form.

Conclusion

It is now well established that the electrochemical reduction of aryl diazonium salts on carbon, semiconductors and metals leads to the strong attachment of aryl groups to the surface. There is also evidence that this reaction can take place spontaneously and the parameters which govern this thermal reaction should be defined. A recent paper[22] suggests that grafting can also take place on surface oxides, this should be further investigated as it would broaden the scope of the possible uses of this reaction. The nature of the bond is most likely covalent, even on metals such as iron. However, its dissociation energy remains to be measured. Compact self assembled monolayers have been obtained on Si by controlling the parameters of the electrolysis but it is also possible on carbon or metals to obtain multilayers (up to 100 nm). The structure of these layers has been roughly established, but should be refined as the results of the different techniques are not completely coherent. Besides the applications of this reaction described in this paper many others have been developed for example in the field of catalysis and of the protection of metals against corrosion,… but much more is possible not only in the academic but also in the industrial field.

Acknowledgements

The authors are highly indebted to the many colleagues and coworkers who participated in these investigations and whose names appear in the references.

Jean Pinson*[a] and Fetah Podvorica[b]
[a] *Alchimer, Z.I. de la Bonde, 15 rue du Buisson aux Fraises, 91300, Massy, France. E-mail: jean.pinson@alchimer.com*
[b] *Chemistry Department of Natural Sciences Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, Prishtina, Kosovo*

References

1 A. J. Downard, *Electroanalysis*, 2000, **12**, 1085–1096.
2 H. Maeda, Y. Yamauchi and H. Ohmori, *Curr. Top. Anal. Chem.*, 2001, **2**, 121–133.
3 D. M. Wayner and R. A. Wolkow, *J. Chem. Soc., Perkin Trans. 2*, 2002, 23–34.
4 S. Palacin, C. Bureau, J. Charlier, G. Deniau, B. Mouanda and P. Viel, *Chem. Phys. Chem.*, 2004, **5**, 1468–1481.
5 T.-C. Kuo and R. L. McCreery, *Anal. Chem.*, 1999, **71**, 1533–1560.
6 T. Nakamura, M. Suzuki, M. Ishihara, T. Ohana, A. Tanaka and Y. Koga, *Langmuir*, 2004, **20**, 5846–5849 and references therein.
7 H. O. Finklea, *Electroanal. Chem.*, 1996, **19**, 109–335.
8 P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.-M. Savéant, *J. Am. Chem. Soc.*, 1997, **119**, 201–207.
9 A. Adenier, M.-C. Bernard, M. M. Chehimi, E. Cabet-Deliry, B. Desbat, O. Fagebaume, J. Pinson and F. Podvorica, *J. Am. Chem. Soc.*, 2001, **123**, 4541–4549.
10 C. Henry de Villeneuve, J. Pinson, M.-C. Bernard and P. Allongue, *J. Phys. Chem. B*, 1997, **101**, 2415–2420.
11 M. Delamar, G. Désarmot, O. Fagebaume, R. Hitmi, J. Pinson and J.-M. Savéant, *Carbon*, 1997, **35**, 801–807.
12 J. K. Kariuki and M. T. McDermott, *Langmuir*, 2001, **17**, 5947–5951 and references therein.
13 Y.-C. Liu and R. L. McCreery, *J. Am. Chem. Soc.*, 1995, **112**, 11254–11259.
14 F. Anariba, S. H. DuVall and R. L. McCreery, *Anal. Chem.*, 2003, **75**, 3837–3844.
15 C. Combellas, F. Kanoufi, D. Mazouzi, A. Thiébault, P. Bertrand and N. Médard, *Polymer*, 2003, **44**, 19–24.
16 J. M. Cooke, C. P. Galloway, M. A. Bissell, C. E. Adams, M. C. Yu, J. A. Belmont and R. M. Amici, *US Pat*, 6 110 9994 A, 2003 (to Cabot Corp.) and references therein.
17 C. A. Dyke and J. M. Tour, *Nano Lett.*, 2003, **3**, 1215–1218 and references therein.
18 J. Wang, M. A. Firestone, O. Auciello and J. A. Carlisle, *Langmuir*, 2004, **20**, 11450–11456.
19 P. Allongue, C. Henry de Villeneuve, G. Cherouvrier, R. Cortès and M.-C. Bernard, *J. Electroanal. Chem.*, 2003, **550–551**, 161–174.
20 M. P. Stewart, F. Maya, D. V. Konsynkin, S. M. Dirk, J. J. Stapelton, C. L. McGuiness, D. L. Allara and J. M. Tour, *J. Am. Chem. Soc.*, 2004, **126**, 370–378 and references therein.
21 M.-C. Bernard, A. Chaussé, E. Cabet-Deliry, M. M. Chehimi, J. Pinson, F. Podvorica and C. Vautrin-Ul, *Chem. Mater.*, 2003, **15**, 3450–3461.
22 B. L. Hurley and R. L. McCreery, *J. Electrochem. Soc.*, 2004, **151**, B252–B259 and references therein.
23 C. P. Andrieux and J. Pinson, *J. Am. Chem. Soc.*, 2003, **125**, 14801–14806.
24 C. Saby, B. Ortiz, G. Y. Champagne and D. Bélanger, *Langmuir*, 1997, **13**, 6805.
25 P. A. Brooksby and A. J. Downard, *Langmuir*, 2004, **20**, 5038–5045 and references therein.
26 T. Itoh and R. L. McCreery, *J. Am. Chem. Soc.*, 2002, **124**, 10894–10902.
27 E. Coulon, J. Pinson, J.-D. Bourzat, A. Commerçon and J.-P. Pulicani, *J. Org. Chem.*, 2002, **67**, 8513–8518.
28 M. D'Amours and D. Bélanger, *J. Phys. Chem.*, 2003, **107**, 4811–4817.
29 A. O. Solak, S. Ranganathan, T. Itoh and R. L. McCreery, *Electrochem. Solid-State Lett.*, 2002, **5**, E43–E46.
30 C. Combellas, F. Kanoufi, J. Pinson and F. Podvorica, *Langmuir*, 2005, **21**, 280–286.
31 K. Boukerma, M. M. Chehimi, J. Pinson and C. Blomfield, *Langmuir*, 2003, **19**, 6333–6335.

32 C. Bureau, E. Levy and P. Viel, *PCT Int. Appl.*, WO 03018212, 2003.
33 R. L. McCreery, J. Dieringer, A. O. Solak, B. Snyder, A. M. Novak, W. R. McGovern and S. DuVall, *J. Am. Chem. Soc.*, 2004, **126**, 6200–6210.
34 J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley and J. M. Tour, *J. Am. Chem. Soc.*, 2001, **123**, 6536–6542.
35 P. R. Marcoux, P. Hapiot, P. Batail and J. Pinson, *New J. Chem.*, 2004, **28**, 302–307.
36 C. A. Mitchell, J. F. Bahr, S. Arepalli, J. M. Tour and R. Krishnamoorti, *Macromolecules*, 2002, **35**, 8825–8830.
37 A. Adenier, E. Cabet-Deliry, T. Lalot, J. Pinson and F. Podvorica, *Chem. Mater.*, 2002, **14**, 4576–4585.
38 A. Chaussé, M. M. Chehimi, N. Karsi, J. Pinson, F. Podvorica and C. Vautrin-Ul, *Chem. Mater.*, 2002, **14**, 392–400.
39 A. J. Downard, A. D. Roddick and A. M. Bond, *Anal. Chim. Act.*, 1995, **317**, 303–310.
40 B. D. Bath, H. B. Martin, R. M. Wightman and M. R. Anderson, *Langmuir*, 2001, **17**, 7032–7039.