1

Attachment of Organic Layers to Materials Surfaces by Reduction of Diazonium Salts

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1.1
A Brief Survey of the Chemistry and Electrochemistry of Diazonium Salts

Aromatic diazonium salts ($ArN_2^+ X^-$) are easily synthesized in an acidic aqueous medium (HBF_4) starting from an amine in the presence of $NaNO_2$, and in an aprotic medium ($ACN + HBF_4$ in ether) in the presence of *t*-butylnitrite or in $ACN + NOBF_4$ [1–2]. As many aromatic amines are available commercially, the preparation of a large number of diazonium salts can be easily carried out. They can be isolated and characterized, but they can be used directly in the solution where they have been prepared [3].

The chemistry of aromatic diazonium salts [1, 4, 5] is dominated by the electrophilic character of the azo group; they react with aromatic amines and phenols to give azo dyes (C-coupling) that are important coloring materials [6]. Aliphatic diazonium salts are extremely unstable and up to now only a few examples of grafting on carbon black involving the diazonium salt of 2-aminoethanesulfonic acid and 4-bromobenzylamine have been reported [1, 7].

As we will see below, when a diazonium reacts with a surface, with a few reported exceptions, the diazonium group is lost and the radical reacts with the surface, therefore grafting involves a homolytic dediazonation step; in this respect the dediazonation reactions are important for discussing the grafting mechanism. This dediazonation can take place heterolytically to give Ar^+ cations, or homolytically to give $Ar^·$ radicals [8]; these spontaneous reactions can be slowed down by reducing the temperature to below 5 °C. The Sandmeyer reaction (1.1) is a first example of an important dediazonation reaction involving a radical; the reduction of the diazonium salt by cupric chloride or bromide ArCl, (Br) gives an aryl radical that abstracts a chlorine (bromine) atom from CuCl (Br) to give ArCl (Br), as shown in the reaction.

$$ArN_2^+Cl^- + CuCl \rightarrow ArCl + N_2 \qquad (1.1)$$

A second important dediazonation reaction of diazonium salts in relation to grafting is the Gomberg–Bachman reaction; in the presence of a base the diazonium group is lost to give radicals that couple to other aromatic groups, dimers and a number of other coupling products are obtained [9, 10]. The Pschorr reaction is the intramolecular reaction of an aryl radical with an aryl group, the radical is produced, for example, by reduction of a diazonium salt by Cu(0) [11]. Merwein reactions also rely on the formation of radicals [12]. Solvolytic dediazonations are another example, they can take place in a heterolytic or homolytic manner, that is, through the intermediacy of an aryl cation or an aryl radical [13–17]; heterolytic dediazonation takes place in solvents of low nucleophilicity (H_2O), while a homolytic mechanism is observed in solvents of increased nucleophilicity (HMPT, pyridine), in a number of solvents, such as MeOH, EtOH, DMSO, both mechanisms can be observed [14]. For example, in ethanol a slow heterolytic mechanism is observed in an acid medium and a 50 times faster homolytic one in a basic medium [14]. For a given solvent, electron-withdrawing substituents in the aromatic ring favor homolytic dediazoniations [14].

In an aqueous acidic medium and in aprotic non-nucleophilic solvents diazonium salts are present, but at neutral and basic pHs [13–17] equilibria between the diazohydroxide and diazoates are established; they are displaced toward the formation of diazoates; equilibrium and rate constants have been measured [13]. In the presence of alcohols, diazoethers Ar–N=N–OEt [13, 18] , and in the presence of amines, triazenes Ar–N=N-(NR$_2$) are obtained. These derivatives can also be used for surface modification. For example, diazohydroxides can spontaneously dediazonize and the ensuing radical attaches to the surface of gold [19]. Triazenes are interesting because they are transformed into diazonium salts in an acid medium; in 2% HF the oxidized silicon surface is transformed into Si–H and aryldiethyltriazenes are transformed into aryldiazonium salts, followed by spontaneous grafting of the aryl species to the silicon surface [20]. They can also generate aryldiazonium salts in the presence of electrogenerated acid produced by oxidation of hydrazine [21].

Prior to the discovery of the electrografting reaction, the reduction of diazonium salts $ArN_2^+ X^-$ had been investigated in an aqueous medium at mercury electrodes [22]. In an aqueous acidic medium two waves are observed; the first is a one-electron wave, while the overall process involves four electrons on the second wave and leads to phenylhydrazine. The formation of the aryl radical was confirmed by coulometry, on a mercury pool, at the potential of the first wave, that provided, nearly exclusively, phenylmercuric chloride and diphenylmercury by reaction of phenyl radicals with mercury. Note that these mercury compounds can be viewed as the result of electrografting on a liquid metal. The involvement of radicals [23] during the electrochemical reduction (on the first wave) of aryldiazonium salts was also observed through the Pschorr synthesis of phenanthrene [24], and also by electron spin resonance (ESR) in ACN in the presence of a spin-trap [25].

1.2
The Different Methods that Permit Grafting of Diazonium Salts

In this section we describe the many methods that permit the grafting of diazonium salts, on many substrates, through a variety of experimental conditions.

1.2.1
Electrochemistry

This is the first method that was used for grafting (electrografting) diazonium salts [26–29]. Electrochemistry of diazonium salts in an aprotic medium is very simple, a single, broad, one-electron wave is observed at potentials close to 0 V vs SCE as presented in Table 1.1.

The attachment of the ensuing aryl radical (1.2) + (1.3) (Figure 1.1) to the carbon or metal substrate translates in the fast disappearance of the wave due to the blocking of the electrode by the organic layer formed on it. This is, most likely, the reason for the broadness of the wave; the surface is modified while the voltammogram is recorded. Sometimes a prepeak is observed; on gold, it has been

Table 1.1 Some reduction potentials on GC of benzenediazonium salts in ACN.

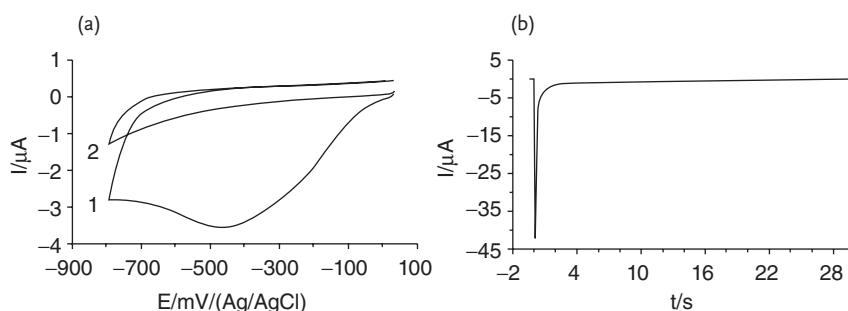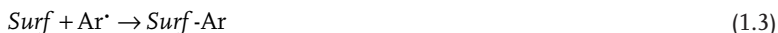| Diazonium salt	Reduction potential, V vs SCE
4-Nitrobenzenediazonium	+0.20 [27]
4-Bromobenzenediazonium	+0.02 [27]
Benzenediazonium	−0.06 [27]
4-t-Butylbenzenediazonium	−0.10 [30]
4-Methylbenzenediazonium	−0.16 [30]
4-Diethylaminobenzenediazonium	−0.56 [31]

Figure 1.1 (a) Cyclic voltammogram and (b) chronoamperometry of 4-nitrobenzenediazonium ($c = 5$ mM) in ACN + 0.1 M NBuBF4: 1, first and 2, second scan. Gold electrode ($d = 1$ mm), $\nu = 100$ mV s^{-1}, reference Ag/AgCl.

assigned to the reduction on the different crystallographic facets of gold, for example, the diazonium salt $^+N_2–C_6H_4–S–C_6F_{13}$ presents three voltammetric peaks on polycrystalline gold at +0.14, +0.03 and ~−0.45 V vs (Ag/Ag$^+$), that are assigned respectively to Au (111), Au (100) and Au (110) + Au (331) [32].

$$ArN_2^+ + 1e^- \rightarrow Ar^\bullet + N_2 \tag{1.2}$$

$$Surf + Ar^\bullet \rightarrow Surf\text{-}Ar \tag{1.3}$$

$$Ar^\bullet + 1e^- \rightarrow Ar^- \tag{1.4}$$

The Ar$^\bullet$ radical is responsible for the grafting reaction, its formation and its further evolution are, therefore, important in the context of surface modification. It has been shown, by simulation of the voltammograms, that the reduction of the benzenediazonium cation (1.2) is a concerted reaction, which means that, during the electrochemical reduction at the peak potential, there are no intermediates between the diazonium cation and the radical; this also means that the radical is formed directly on the surface, which is a very favorable situation for the grafting reaction [33]. This radical can be reduced, in turn, to an anion (1.4) that is unfavorable for the grafting reaction. The reduction potential of Ar$^\bullet$ has been measured not only by simulation of the voltammetric curves: $E = -0.64$ V vs SCE [33], but also from the number of electrons consumed at different potentials for the reduction of benzenediazonium, diphenyliodonium and triphenylsulfonium salts, which all provide a phenyl radical upon reduction: $E = -0.95$ V vs SCE [34]. The standard redox potential has been measured by simulation of the voltammograms [33]: $E°(Ph^\bullet/Ph^-) = +0.05$ V vs SCE; it has also been calculated by DFT methods: $E°(Ph^\bullet/Ph^-) = -0.26$ V vs SCE [35]. These indicate that the reduction of Ar$^\bullet$ is quite easy, which means that during electrografting the potential should not be too negative in order to prevent the reduction of the radical. This is shown by the reduction of different diazonium salts at -1.0 V vs SCE (at a potential where the radical is reduced to an anion), on a mercury electrode, in acetonitrile; azobenzenes were obtained in good yields but no mercury compounds were reported [36].

The formation of the layer can be easily detected, as shown in Figure 1.1, through the disappearance of the reduction wave of the diazonium salt; chronoamperometry is also very characteristic, instead of a decrease in the current according to a Cotrell law, a very sharp decrease is observed due to the fast blocking of the surface.

1.2.2
Reducing Substrate, Homolytic Dediazonation, Reaction with the Substrate

Table 1.1 exemplifies the easy reduction of diazonium salts; if the substrate has reducing capabilities an aryl radical will be formed, close to the electrode, by simply dipping the substrate in the solution of the diazonium salt. In some other examples, where the substrate is less reducing, it is difficult to differentiate a reduction by the substrate from a spontaneous dediazonation. Indeed, a spontaneous homolytic dediazonation is another route for the formation (in solution) of

aryl radicals. But the substrate can also react chemically with the diazoniums salt or the aryl cation Ar$^+$ (and not the radical) and two examples are described in the section on the grafting mechanism.

Metals such as iron and copper can reduce diazonium salts and 4-nitrophenyl layers are obtained by dipping copper, iron, nickel and zinc in a solution of the corresponding salt [37]. The grafting process is in agreement with a redox reaction: grafting is more efficient on zinc than on iron, and even more than on nickel; this trend follows the open-circuit potential order E_{OCP}(Zn) < E_{OCP}(Fe) < E_{OCP}(Ni) and, on a selected metal, grafting is more difficult with less-easily reduced diazonium salts. Benzenediazonium tetrafluoroborate has been reacted in ACN with various metals (Al, Ca, Cr, Cu, Fe, Ga, In, Mg, Li, Na, or Zn), nitrogen evolution was observed, indicating the reduction of the diazonium salt. With copper a ionization-dissolution was evidenced at high concentration and the formation of a complex $[Cu(N_2C_6H_5) (NC–CH_3)_3]^+$ was demonstrated [38]. On gold a spontaneous grafting occurs in acidic [19, 39, 40] solution but the mechanism is unclear. These results indicate that the redox properties of both partners (diazonium + metal) are involved in the grafting reaction.

On glassy carbon, the mechanism seems to follow a reductive path as the easily reducible 4-nitro, 4-trifluoromethyl, or 4-bromobenzenediazonium (Ep = +0.20, −0.34, −0.35 V vs SCE, respectively) are grafted spontaneously, but not the diazonium salts of diethyl, amino diphenyl, triphenyl aniline (Ep = −0.42, −0.35 and −0.45 V, respectively) [41] nor *N,N*-diethylaminobenzenediazonium (Ep = −056 V vs SCE) [31]. Moreover, a jump in the open circuit potential of the carbon electrode was observed upon addition of the 4-nitrobenzenediazonium salt in solution [41, 42]. These features point to an electron transfer mechanism and to the intermediacy of the aryl radical. Spontaneous grafting of diamond has also been observed [43, 44]; the reaction time necessary to obtain a monolayer (72 h in an ACN saturated solution of 4-nitrobenzenediazonium) [43] is more in agreement with a homolytic spontaneous dediazonation than with an electron transfer from the surface. Carbon nanotubes (CNTs) can also be modified spontaneously [45]. In pure water (where diazoates should be present), the mechanism has been assigned (through a careful kinetic analysis and ESR measurements) to a spontaneous homolytic dediazonation [46].

Spontaneous grafting can also be achieved on hydrogenated silicon, the substrate reduces the diazonium salt to a radical [47], this is described in more detail below. At a scanning electrochemical microscope SECM tip the pH can be modified and fluoride ions transformed into HF that etches the native oxide of a Si wafer, 4-nitrobenzenediazonium can be grafted spontaneously in the holes [48].

1.2.3
Reducing Reagent

As diazonium salts are very easily reduced, a number of reducing reagents can be used. Hypophosphorous acid (H_3PO_2) has been used to functionalize the surface of carbon powder [49–54], polymers (polypropylene, polyethylterephthalate,

polyetheretherketone) and inorganic compounds (TiN, SiC, SiO$_2$, SiOC) [55]. Iron powder has also been used as a reducing agent for the grafting of diazoniums alone or diazonium and vinylics [56]; in this last case, the process is very efficient as even the surface of glass or Teflon can be modified. Gold surfaces have been modified in the presence of ascorbic acid [40]. With these methods, the radical is produced in solution and there should be no limitation to the growth of the layers, but no data about the thicknesses are given.

1.2.4
Neutral and Basic Media

In a neutral aqueous medium diazohydroxides are obtained, they rapidly deprotonate to diazoates that decompose radicals [13]; these radicals react spontaneously with metals [57] and graphene sheets [58]. In basic and neutral media, diazoniums are transformed directly into diazoates; gold surfaces have been modified in this way [19, 40]. Iron oxide magnetite, Fe$_3$O$_4$, nanoparticles have been capped by aryl groups, by adding the 2-hydroxyethylbenzenediazonium tetrafluoroborate (BF$_4$, N$_2$–C$_6$H$_4$–(CH$_2$)$_2$–OH) directly in the pH 9 solution where the nanoparticles are formed [59]. Carbon nanotubes have been modified spontaneously in a diazoate solution at pH 11 [60]. In these cases, a homolytic dediazonation is known to take place [13, 14].

1.2.5
Ultrasonication

Grafting of various inorganics and polymers (see above) has been achieved under ultrasonication [55]. Diamond nanoparticles have also been modified under ultrasonication by 4-nitrophenyl groups in acidic aqueous solution [44]. ITO has been modified by 4-nitrobenzenediazonium, in water, at different frequencies, the lowest one (20 kHz) was shown to be the most efficient [61]. A mechanism has been proposed, based on the known formation of reducing radicals (H$^{\bullet}$, R$^{\bullet}$ from adventitious impurities), these radicals should reduce the diazonium salt [61].

1.2.6
Heating and Microwave

The surface of polyethylterephtalate has been modified by heating an aqueous solution of sulfanilic acid at 70 °C in the presence of NaNO$_2$ [62]; under these conditions a heterolytic cleavage of the diazonium cation should be favored. Thermal reactions, using *in situ* generated aryl diazonium salts, have permitted the derivatization of SWCNTs (single wall carbon nanotubes) at 60 °C in dichlorobenzene for 15 h [45], and MWCNTs (multiwall carbon nanotubes) at 80 °C in concentrated sulfuric acid in the presence of ammonium persulfate and 2,2-azoisobutyronitrile [63]. A microwave-assisted surface modification of CNTs and nanohorns has been described [64–66]. Heating aryldiazonium tetrafluorobo-

rates to obtain fluoroaryl derivatives is the Balz–Schiemann reaction [67], it is likely that some fluorinated aryls are formed during these grafting reactions.

1.2.7
Mechanical Grafting

Silicon covered with its native oxide can be mechanically scribed with a diamond tool in the presence of the diazonium salt of 4-aminobenzoic acid. This leads to patterning of the surface with aryl groups. It is likely that radicals are generated due to the breaking of chemical bonds of the silicon substrate [68]. The formation of an aryl radical could be related to a reduction of the diazonium salt by silicon itself or by the Si radical. A ball milling grinding procedure has been described to functionalize glassy carbon spheres [69]. It should be used carefully as diazonium salts are known to be explosive (except tetrafluoroborates [67]).

1.2.8
Photochemistry

It is also possible to derivatize surfaces by photolysis of charge transfer complexes between diazonium salts and electron-donating compounds, such as dimethoxybenzene. Upon irradiation, this charge transfer complex gives aryl radicals [70] that are able to bind to various polymers and inorganic substrates [55]. Direct photochemistry (245 nm) of 4-(2-(4′-pyridinyl)ethynyl)benzene diazonium salt in acetonitrile has permitted the anchoring of monolayer films onto indium-tin-oxide (ITO) glass slides [71].

1.3
The Different Substrates, Diazonium Salts, and Solvents that Can Be Used

The grafting of diazonium salts on glassy carbon (GC) and highly ordered pyrolytic graphite (HOPG) has been compared with that of amines, azides and olefins bearing ferrocene moieties, dense layers have been obtained with diazonium salts [72].

1.3.1
Substrates

GC was the first substrate to be electrografted by diazonium salts but, step by step, the scope of substrates that can be modified by this reaction has been enlarged to the point where all categories of substrates have been surface modified. The different substrates are listed in Table 1.2.

Some investigations have compared grafting on various substrates [178, 179], for example, grafting of 4-sulfobenzenediazonium tetrafluoroborate has been compared on gold and GC; the 4-sulfophenyl layers are shown to be far less

Table 1.2 The different substrates that have been grafted by reaction with diazonium salts.

	Class of materials
Diamond Reviews on the surface modification of diamond include the derivatization with diazonium salts [73–74].	Boron-doped diamond [75, 76]
	Surface-hydrogenated diamond [77–81]
	Nano diamonds [43, 44, 82, 83]
	Diamond nanowires [84]
HOPG	[27, 85, 86]
Graphene	Graphene [58, 87–94]
	Graphene nanoribbons [95]
Carbon nanotubes A large number of papers and some reviews have been published concerning the modification with diazonium salts [96–99]. See Chapter 4	Carbon nanotubes [45, 100–103], nanohorns [104], peapods [105]
Pyrolyzed photoresists [106–107] (PPF, a very flat carbon surface)	[108–112]
Glassy carbon Most of the investigations have been performed on this substrate [113–114].	Glassy carbon plates [26, 27, 115, 116] or spheres [117]
Carbon fibers	Carbon fibers [27, 118–120], nanofibers [121], carbon felts [122–124]
Carbon black (see also Chapter 14, "Patents and Industrial Applications")	[125–130]
Porous carbon	Mesoporous carbons [131–135]
Semiconductors [136–137]	Flat hydrogenated silicon [28, 48, 138–143], porous silicon [144], silicon nanoparticles [145]. AsGa [47]
	InAs/GaAs quantum dots [146]. Ge nanowires [147]
Metals [31, 37, 148]	Precious metals: gold [39, 149–151], platinum [152, 153], silver [112, 154].
	Coinage metals: copper [155, 156], nickel [157, 158] Industrial metals: iron [29, 57, 159–164], stainless steel [165, 166], aluminum [156], nanoparticles [167–172].
Oxides	ITO (indium tin oxide) [173–175], SnO_2 [31], TiO_2 [176], SiO_2, SiOC [55], Fe_3O_4 nanoparticles [59].
Nitride	TiN, TaN [55]
Carbides	SiC [55]
Polymers	Polyethylene, polypropylene, polyetheretherketone [55], Teflon® [177]

electrochemically stable on gold than on GC. The instability is due to cleavage of the bond between the sulfonate functional group and the phenyl ring [180, 181].

Electrografting of different types of carbon materials hsa been compared, for example, on HOPG the reaction is faster on the edges that on the basal plane. On the basal plane, electrografting, which was followed by AFM, takes place only at defects and the layer grows from this initial nucleus [86]; after 20 cycles in a 1 mM solution, a uniform 1 nm layer is observed [182]. Graphene flakes grafted with diazonium salts are predominantly modified on the edge [183], as could be expected by comparison with HOPG, and single graphene layers react faster than bilayers [58]. On diamond, the efficiency of electrografting also depends on the surface terminations (-H, -OH, -O–O-, . . .), the H-terminated surface being the most reactive [184].

1.3.2
Diazonium Salts

$^+N_2$ Ar-R	References
R = 4-nitro	The 4-nitrophenyl groups have a reversible cyclic voltammetry wave at $E°$ ~—1.20 V vs SCE in ACN, two strong IR bands at ~1340 and ~1520 cm^{-1} and a characteristic XPS signal at 406 eV [27].
R = alkyl, perfluoroalkyl, alcoxy, aryl, halogens, carboxyl, nitrile	[27, 30, 110, 125, 148]
R = SO$_3$H	[180]
R = −N(C$_2$H$_5$)$_2$ or −N(C$_6$H$_5$)$_2$	[185]
R = −BO$_3$H	[186, 187]
R = maleimide	[188]
R = −CHO	[189]
R = NH$_2$ R = −CH$_2$−NH$_2$ NH$_2$ groups can be obtained by reduction of nitro groups [190]	The monodiazonium salt of *p*-phenylenediamine (NH$_2$–C$_6$H$_4$–N$_2$$^+$) cannot be isolated, but it can be prepared in solution by using only one equivalent of a diazotation reagent. In an acidic medium the amino group is protonated and does not react with the diazonium salt [191–193].
R = 1-(2-thienyl) and 1-(2-bisthienyl)	[194]
R = −C$_6$H$_4$−C≡C−C$_6$H$_4$−R′	[20, 195–198]
Ar = anthraquinone	[199, 200]
Ar = phenothiazine	[201]
Ar = 1,10-, and 5-aminophenanthroline, 3-aminopyridine, 6-aminoquinoline	[202, 203]

(Continued)

$^+N_2$ Ar-R	References
Ar–N_2^+ = CoCp(η^5-C$_5$H$_4$N$_2$)$^{2+}$ and Mn(CO)$_3$(η^5-C$_5$H$_4$N$_2$)$^+$	[204]
R = Ruthenium complexes of bi and terpyridine	[205–208]
R = Osmium complexes	[209, 210]
R = Proteins	[211–213]

Very often these substituents are introduced to perform further reactions on the layer, for example, phenylazide or phenylacetylenediazonium salts have been prepared for further click chemistry [214, 215].

Two diazonium salts can be grafted together, the percentage of the most easily reduced salt being higher in the layer than in the solution [216, 217]. It is also possible to grow layers on top of one another, for example, a layer of polynitro or polybromophenylene can be grown on top of a layer of polyphenylene [218], and a layer of a pinacol ester of a phenylboronic acid on top of a layer of 4-nitro phenyl groups [219].

1.3.3
Solvents

Acetonitrile as an aprotic solvent and aqueous acid as a protic solvent have been most often used. Hydrofluoric acid (2%) permits, at the same time, the transformation of the oxidized SiO$_2$ surface of silicon into SiH, and that of aryl triazenes into diazonium salts that attach to the SiH surface [20]. 1-(2-Bisthienyl)-4-aminobenzene is insoluble in water but it can be solubilized from a β-cyclodextrin aqueous solution [220]; the diazonium salt (or more likely the diazoether [221]) can be grafted while still in the cyclodextrin cage. CNTs have been modified and debundled at the same time in concentrated sulfuric acid [222, 223], "on water" [224], and without solvent in the presence of aniline and isoamylnitrite [225]. Even if the diazonium salts are more stable in an acidic medium, grafting can be observed at neutral [57] or basic pH [19]; diazoates are formed that can be grafted spontaneously or electrografted to give similar layers to those obtained from diazonium salts.

Ionic liquids can be used for the grafting of diazonium salts on glassy carbon [226, 227] and graphene sheets [228]. A *p*-butyldiazonium salt having a bis(trifluoromethanesulfonyl)amidates (Tf$_2$N$^-$) counter anion, and being, therefore, both the substrate and the solvent, has been grafted spontaneously and by electrochemistry on glassy carbon [229]. 4-Nitrobenzenediazonium has been electrografted to carbon electrodes in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [227]. The surface concentration of grafted

4-nitrophenyl groups decreases with the viscosity of the ionic liquid, but no explanation was proposed for this experimental fact [230].

Finally, these investigations indicate that there are no very large differences between the grafting in different solvents.

1.4
Evidence for the Presence of a Bond between the Substrate and the Organic Layer

1.4.1
Stability of the Layer

One of the interesting points with diazonium salts is the formation of a bond between the surface (carbon, metal, semiconductor, oxide) and the organic layer. The formation of C or Si(surface)–C(organic layer) is only an extension of the *C*–C and *Si*–C bonds of organic chemistry, where a single C or Si atom is replaced by the whole carbon or silicon substrate. More surprising is the formation of a *Metal*(surface)–carbon(layer) bond; however, organomercury compounds have been known for a long time and can even be isolated [231, 232]; in addition, a number of organometallics are known, including noble metals, for example, gold can be bonded to aryl groups [233, 234]. As this bulk metal–organic layer bond is somewhat unusual, efforts have been made to characterize the *metal*–carbon and *carbon*–carbon bonds of the modified surfaces.

The stability of the layer is a strong indication of the existence of a bond and this stability has been tested in different ways.

Ambient stability. The layers obtained from diazonium salts are stable: for six months under ambient conditions on both glassy carbon GC [27] and Si [235], but also under ultrasonication in solvents and under harsh conditions: successive ultrasonic rinsings of GC electrodes for 15 min in ten different organic solvents leaves the cyclic voltammetric of the nitrophenyl group signal unchanged [27] and silicon samples modified with 4-dodecylphenyl groups resist exposure to 40% HF or NH_4F for up to 10 min [28].

Thermal stability. TGA (thermal gravimetric analysis) and XPS analysis of modified carbon black and mesoporous carbon [135] show that the layer of 4-nitrophenyl groups is stable above 200 °C and that the cleavage occurs in the 300–500 °C range [129]. The loss of the organic layer is observed in the 150–200 °C range for chlorophenyl-modified SWCNTs [100, 236–237]. Therefore, upon annealing at 500 °C, the spontaneous grafting of CNTs is partially reversible [238]. On 316 stainless steel the IR bands of the polyphenylene film can be observed up to 400 °C [166].

Electrochemical stability. The ferro/ferricyanide reversible redox system is blocked (disappears) by the layers obtained from different diazonium salts (4-carboxy, 4-nitro, 4-diethylamino and 4-bromo-benzenediazonium); the electrode must be polarized to very negative (−2 V vs SCE) or very positive (1.8 V vs SCE) potentials

to restore the signal of the probe [239], but an XPS analysis indicated that the layer is not completely removed [240].

Mechanical stability. The Si–C bond has been tested by AFM; even after scratching the multilayer, the signal of a very thin layer can be detected by XPS [241]. Some mechanical tests have been performed on composites, including modified carbons; the existence of a bond between the carbon and the modifying organic layer is expected to improve the mechanical properties of the composite [242–245]. The debonding shear stress of carbon fibers imbedded in epoxy resins has been measured, it increased from 71 MPa for an untreated fiber to 116 MPa for a fiber modified with 4-aminophenyl groups [242]. Polystyrene/ SWCNT nanocomposites where the SWCNTs are functionalized by reaction with diazonium compounds, have demonstrated improved properties [243]. A polystyrene/carbon nanosheets composite has been prepared by modifying graphene with the diazonium salt of 2-(4-aminophenyl)ethanol, and attaching polystyrene by ATRP polymerization [244]. This treatment resulted in a 15 °C increase in the glass transition temperature of polystyrene compared to the pure polymer and up to 70% and 57% increases in the tensile strength and Young's modulus, respectively. The improved stability of the coating of drug eluting stent, upon surface modification of the stent with diazonium salts, is described in Chapters 6 and 14.

1.4.2
Spectroscopic Evidence for a Bond

XPS. The signature of the iron–aryl bond has been observed on iron plates electrografted with the diazonium salt of 4-aminobenzoic acid; a minor component of the C 1s peak, centered at 283.3 ± 0.1 eV, is assigned to a carbide type of carbon [159]. On oxidized copper an XPS peak appears at 532.8–533.0 eV assigned to a *Cu*–O-aryl bond [156]. On ITO an O 1s peak at 532.70 eV has been tentatively assigned to In or *Sn*–O–C(aryl) bond (but the nitro group appears at the same position) [61].

Raman. *In situ* spectroscopy indicated that the spectra of electrografted 4-nitroazobenzene were quite different from that of the free molecule. The intensity of the Raman bands associated with the grafted phenyl-NO$_2$ moiety varied as the substrate was polarized between ~0 to −1200 mV vs SCE, implying an electronic interaction between the π system of the graphitic substrate and the electrografted molecules [246]. On sp^2 carbons (graphene) the formation of a bond by reaction with a diazonium salt results in the formation of an sp^3 carbon, and this can be observed by Raman as a D line at ~1600 cm^{-1} [58, 89, 247]. By surface-enhanced Raman scattering (SERS), the signature of the *Au*(nanoparticles)–C(aromatic) bond has been observed as a small band at 422 cm^{-1}, its assignment was confirmed by DFT calculations. The same band has also been detected by HREELS (high-resolution electron energy loss spectroscopy) [248].

Table 1.3 Some bond energies between surface and aryl groups.

Examples	Bond energies (kJ mol^{-1}) and geometry
Si–C_6H_4	−292.6, upright, atop [250]
Fe–C_6H_4	−171.4, upright, bridge [250]
Au C_6H4	−100.3, upright, atop [250]
(*Au*–C_6H_4) vs (*Au*-S–C_6H_4)[a]	−14.2 [251]
$C_{graphene}$-C_6H_4	−24 [94]
Two -C_6H_4 groups in para on a graphene ring	−264 [94]

a)   Bonding energy difference between a phenyl group and a thiophenyl group on gold.

ToF-SIMS. A spectrum has been obtained for a layer of 4-perfluorohexylphenyl groups on GC. Fragments have been assigned the following structure; (CH_2CH_2 $C_6H_3C_6F_{13}C_6H_4C_6F_{13}$)$^+$, that represents both the carbon surface (CH_2CH_2–) and the organic layer (-$C_6H_3C_6F_{13}$–$C_6H_4C_6F_{13}$) [249].

DFT (Density Functional Theory) calculations are in perfect agreement with the existence of a bond between the substrate and the organic layer, they are described in detail in Chapter 2. Table 1.3 gives some of the interesting bond energies that have been calculated, including a comparison with phenylthiol on gold.

These few examples clearly indicate the possibility of a bond between the surface (graphene, nanotubes, metal, semiconductors) and the aryl groups; their energy is very variable and, as could be expected, much lower on gold than on carbon. These theoretical calculations are in good agreement with the experimental data.

Self-assembled monolayers (SAMs) of thiols on gold have been extensively investigated, and it was, therefore, interesting to compare the stability of SAMs with the layers obtained from diazonium salts. On a gold surface, the stability upon scanning to positive or negative potentials as well as upon storage in the laboratory atmosphere was found to be somewhat higher for carboxyphenyl layers than for 3-mercaptopropionic acid or 4-mercaptobenzoic acid SAMs [179, 252]. The thermal stability of the modified surfaces was also higher with diazonium salts than with thiols [253]. These experimental data are in good qualitative agreement with the theoretical calculations above, the binding energy of aryl layers is somewhat higher than that of the thiol layers and their experimental stability is also somewhat higher.

1.5
From Monolayers to Multilayers

The grafting of diazonium salts by electrochemistry or another method does not generally provide monolayers, in contrast to SAMs on gold. Multilayers are

generally obtained with thicknesses ranging from a few nanometers to microns. When considering electrografting, the radicals produced via reaction (1.2) either attach to the surface (1.3) or react with the first grafted aryl group, this reaction is responsible for the growth of the layer. As the layer grows, the electron transfer through the layer becomes more and more difficult and finally stops. At this point, as we will see below, there is still a possibility for the layer to grow through a chain reaction but after a certain time this reaction also stops (its turnover is not known). The reaction is self-limiting. However, thicker layers (over 100 nm) can be obtained, as we will see below, if an electron relay (a redox couple) is included in the chain. Such limitations of the thickness of the layer should not exist when the radicals are produced in solution (by a reducing agent, by ultrasonication, in basic solution or by increasing the temperature), but the layers obtained on gold from 4-nitrobenzenediazonium (10 mM) in basic solution are only 1.6 nm after 1 h reaction, or 3.8 nm on PPF after 2 h, which is not very thick [19, 254]. Under these conditions, the grafting yield is probably very low; most of the radicals produced in the solution will form dimers via the Gomberg–Bachmann reaction [9]. To observe grafting of SiO_2, SiC, SiOC, under ultrasonication in aqueous solution, very large concentrations of the diazonium salts were used (~0.2 M), a precipitate was formed in the solution but the thickness of the layer was not very large, as judged from the IR spectrum [55].

These dimers and oligomers are always formed during the grafting reaction (electrochemical or other) and remain deposited on the surface, for example, they account for 64% of the IR absorption when gold is electrografted with 4-nitro benzenediazonium tetrafluoroborate ($c = 2.5$ mM only). Therefore, the sample must be rinsed carefully under ultrasonication or refluxed, to be certain that these deposited products have been removed and that only a grafted layer is examined [252].

In the literature the characterization of the layers is not always clear. A good characterization of the layer should include d (nm) the thickness of the layer, Γ_{surf} the number of groups directly attached to 1 cm^2 of the surface and Γ_{vol} the number of aryl groups in the layer over 1 cm^2 of the surface. The experimental value of Γ_{surf} can be compared with the value that can be easily estimated from molecular models for the closest possible packing (that is obtained by dividing 1 cm^2 by the surface occupied by one molecule without possible rotation): for 4-nitrophenyl groups: $\Gamma_{surf} \sim 12.5 \times 10^{-10}$ mol cm^{-2}. However, this value does not take into account the surface crystallography and has no physical significance, it should be taken only as an inaccessible landmark for comparison with experimental measurements.

1.5.1
Monolayers

They can be obtained by various methods. With electrografting the thickness of the layer can be controlled through the charge consumed during the electrografting step. On hydrogenated silicon [255], a charge Q^* was determined (depending on the grafting potential) above which the decay of the current under potentiostatic
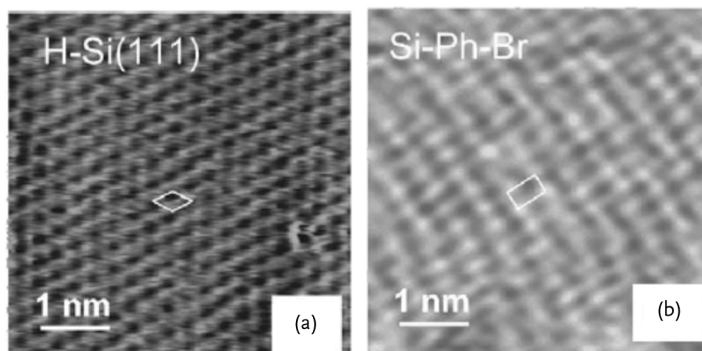
Figure 1.2 STM image of (a) a hydrogenated Si–H monocrystalline surface and (b) the same surface modified by bromophenyl groups. Reprinted from reference [255] with permission of Elsevier Science & Technology Journals.

conditions did not follow a Cottrell law, by limiting the charge at Q^* during the electrolysis it was possible to obtain monolayers. $\Gamma_{surf} \sim 5 \times 10^{-10}\,mol\,cm^{-2}$ was determined by Rutherford backscattering and $\Gamma_{surf} = 6.72 \times 10^{-10}\,mol\,cm^{-2}$ was obtained from the STM image. Note that this physically significant value corresponds to a complete monolayer on silicon, within the difference of the calculated value above. This STM image showed an organized monolayer deriving from the SiH surface by a $(1\sqrt{3})R30$ transformation [255] (Figure 1.2). Such an organized surface is unexpected as the very reactive phenyl radicals should be unselective. This was explained either by an easier grafting in the vicinity of a first grafted aryl group or by π-stacking interactions. This is the only organized surface observed after reduction of diazonium salts, other examples with different groups and substrates would certainly be interesting. Using the same method to control the film thickness on hydrogenated diamond, monolayers have been obtained and characterized by AFM and angle-resolved XPS, which indicated an oriented arrangement of the nitrophenyl groups, with NO_2 groups preferentially located on the top of the layer [76] PPF, a particularly flat carbon surface was derivatized with biphenyl and stilbene groups through a single voltammetric scan from +0.1 to −0.1 V vs SCE and a line profile was recorded by AFM after scratching the layer by contact mode AFM. The thicknesses of the layers were close to that of a monolayer [108].

The nitro group is a good reporter group as it gives a one-electron reversible system in ACN and a mixed 6-electron wave for amine and a 4-electron wave for hydroxylamine in an aqueous medium [256]. The thickness of a nitrophenyl layer prepared by chronoamperometry (with different times), on PPF, at a potential located 150 mV negative to the voltammetric peak was measured by AFM [256]. At the same time, a cyclic voltammogram of the 4-nitrophenyl derivatized surface was recorded in $0.1\,M\,H_2SO_4$. By integration of the voltametric(s) peak(s) of the nitrophenyl groups in aprotic or aqueous media, it is, therefore, possible to estimate the number of nitro groups in the layer. With this method, a

voltammetrically determined surface coverage of $-Ar-NO_2$ groups is obtained: $\Gamma_{surf} = (2.5 \pm 0.5) \times 10^{-10}\,mol\,cm^{-2}$ for a film thickness (measured by AFM scratching) equivalent to a monolayer. This experimentally determined surface coverage corresponds to $21 \pm 3\%$ [256] of the close-packed monolayer at a plane surface mentioned above. Note that this value is not very different from that determined above on Si(111) [255]. As we will see in Chapter 4, this integration of the voltammograms of redox active groups, should only be used to determine Γ_{surf} with monolayers, or at least very thin layers [257].

By non-electrochemical methods, the simple control of the concentration and the reaction time should permit one to obtain monolayers and the example above that gives a 1.6 nm layer on gold is not far from a monolayer [19]. The homogeneity should then be checked by AFM.

Monolayers can also be obtained by tuning the structure of the diazonium salt. For example, $^+_2N-C_6H_4-S-S-C_6H_4-H$ or Cl has been electrografted to a carbon surface giving a bilayer, subsequently the S–S- bond was cleaved electrochemically at $-1.3\,V$ vs SCE, yielding a near monolayer of phenyl thiolate ($Carbon-C_6H_4-S^-$, $\Gamma_{surf} = 4 \times 10^{-10}\,mol\,cm^{-2}$) in agreement with the AFM measurements of the film thickness [258]. The same experiment was performed on SWCNTs and MWCNTs and the cleavage of the multilayer to a monolayer was ascertained by TEM [259]. This formation–degradation procedure was extended to a hydrazone-substituted benzenediazonium, $^+N_2-C_6H_4-C=N-NH-C(=O)-CH_2-N(CH_3)_3^+$ that gave a rather thin layer of only 1.9 nm, indicating a protective effect of the hydrazone group to the attack of aryl radicals. In addition, the hydrazone group is easily cleaved in an acidic medium to give a benzaldehyde monolayer ($Carbon-C_6H_4-CHO$, $\Gamma_{surf} = 4 \times 10^{-10}\,mol\,cm^{-2}$) [260].

Steric effects can be used to limit the growth of the layer. Using 3,5-bis-*tert*-butyl benzenediazonium (with two bulky *tert*-butyl groups) it was possible to obtain a monolayer that was characterized by IR and ellipsometry ($d = 1\,nm$ on gold) [261]. The *tert*-butyl groups prevent a further attack on the grafted group by an aryl radical. The steric effect was also effective in limiting the growth of the layer obtained from 4-([triisopropylsilyl]ethynyl)benzenediazonium salt, but in this case deprotection by cleavage of the silyl group provides a 4-ethynylphenyl layer that is able to react through click chemistry [262]. The influence of steric effects on the thickness of the layers was demonstrated with diversely substituted benzenediazonium salts; in particular with 2-ethyl or 2,6-dimethyl derivatives grafting does not takes place, the Ar⁺ radical being deactivated by steric hindrance. This experimental result was supported by DFT calculations, indicating that 2,6-dimethyl substitution decreases the binding energy by more than 50% and causes the Cu atom connected to carbon to move out of the surface by as much as 0.6 Å [30].

1.5.2
Layers of Medium Thickness

If special care is not taken and/or if diazonium salts such as those described above are not used, multilayers of variable thickness are obtained whatever the substrate,

the diazonium, and the grafting method. When grafting takes place spontaneously (chemically) by simple dipping of a substrate into a solution of the diazonium salt, the parameters controlling the thickness of the layer are the concentration of the solution and the immersion time. For example, the 4-nitro polyphenylene layer on iron increases from 2.8 nm (after 1 min) to 9.7 nm (after 360 min) (10 mMsolution in ACN) and from 2.6 to 5.2 nm by increasing the concentration of the diazonium salt from 0.1 to 10 mM (reaction time 1 h) [37]. On GaAs, d increases from 1.0 (after 1 h) to 2.8 nm (after 6 h) (0.5 mM solution of 4-phenylazobenzenenediazonium tetrafluoroborate) [47]. The thickness of the layers as well as the surface concentration Γ_{vol} (obtained from the integration of the voltammograms) have been measured during the spontaneous modification of gold by 4-nitrobenzenediazonium [39]. The curves (Γ_{vol} and d vs immersion time, Figure 1.3) present a shape similar to that obtained under electrografting conditions.

When the diazonium salt is reduced in solution, the thickness of the layer should not be self-limited as the radicals are produced in solution and the layer should grow until consumption of all the diazonium salt but, as indicated above, the obtained layers are thin, likely due to the low yield of the reaction; in addition few data are available in the literature.

In the case of electrografting (150 mV negative to the voltammetric peak), the same parameters are operative: the thickness of the layer obtained on PPF from 4-(4′-nitrophenylazo) benzenediazonium cation in ACN increases rapidly for 200 s and then reaches a plateau of 6.2 nm (Figure 1.3) [257]. However, the potential is
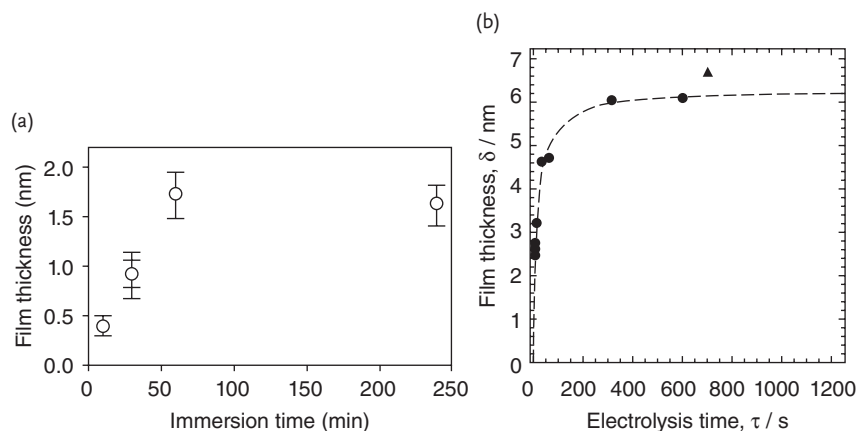

Figure 1.3 Films obtained (a) from 4-nitrobenzenediazonium by spontaneous grafting on gold, thickness (d) versus immersion time (c = 10 mM in 0.1 M H$_2$SO$_4$ at 25 °C, under nitrogen in absence of light), and (b) electrografting of 4-nitroazobenzene on PPF, thickness versus electrolysis time (c = 10 mM in 0.1 M H$_2$SO$_4$, E = 150 mV negative to the voltammetric peak). Adapted with permission from references [39] and [257]. Copyright 2005 and 2009 American Chemical Society.

an additional parameter and this is exemplified by the increase in the thickness of the layer obtained on PPF after a single voltammetric scan to +0.22, +0.02, −0.12, −0.22 and −0.42 V vs SCE from 1.0 to 1.9, 2.1, 2.3, and 2.6 nm, respectively (with 1 mM 4-(4′-nitrophenylazo) benzenediazonium cation) [108]. On Si, the thickness of the layer was shown to increase exponentially with the potential (80 mM 4-nitrobenzenediazonium in DMF) [241]. Some variations of the thickness are also found with different substrates (35, 40 and 60 nm on Cu, Ni and Zn, respectively) [148]. The thickness of the layer also depends on the way the potential is imposed to the electrode. Electrografting can be achieved by cyclic voltammetry, by chronoamperometry, but more recently the use of potential pulses has been found very efficient for the growth of the layers. For example, a 300 nm film of 4-vinylpyridine and 4-nitrobenzenediazonium has been obtained on n-doped silicon by using very short pulses (0.1–1 s) of 5–20 V between anode and cathode [263]. In another example, (2 mM 4-nitrobenzenediazonium in ACN on gold), an enhancement of the sweep rate by 10 or 100 leads to a film thickness of 400 and 900 nm, respectively [264]. This increased thickness has been assigned to the formation of porous layers more easily penetrable by the solvent + electrolyte system [264].

The electrochemical growth of the layers on highly ordered pyrolytic graphite (HOPG) [116] is somewhat different from that on GC [86]; both have been examined by AFM (Figure 1.4). On GC, a rather irregular surface is observed with a thickness up to 20 nm after a 30 min electrolysis. whereas on HOPG the growth is very different since the nucleation takes place first on cleavage steps and then on defects of HOPG (CH$_3$CN, $c = 5$ mM 4-diazo N, N-diethylaniline). Subsequently, the growth of the layers extends from these initial nucleation sites [116].
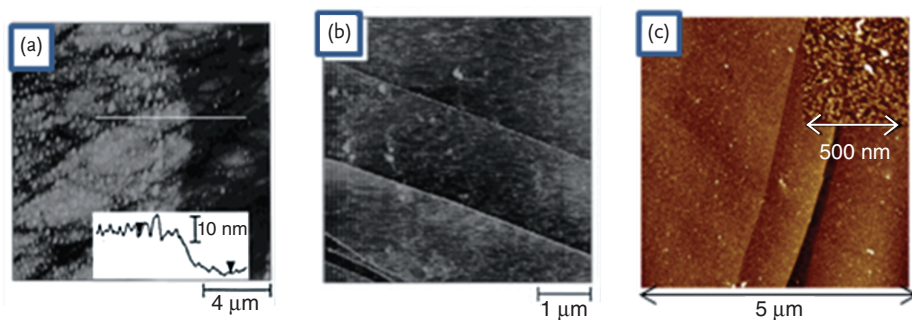

Figure 1.4 AFM image of: (a) a 4-nitrobenzenediazonium film deposited on a polystyrene-masked GC electrode at 0.2 V vs SCE for 30 min. The cross-sectional profile corresponds to the line scan through the image. (b) a HOPG substrate grafted in 0.5 mM diethylaniline following 4 cycles between −0.1 and −0.9 V vs SCE (0.1 M Bu$_4$NBF$_4$/CH$_3$CN). (c) HOPG substrate grafted in 1 mM 4-carboxybenzenediazonium following 20 cycles between 0 and −0.7 V vs Pt (0.1 M Bu$_4$NBF$_4$/CH$_3$CN). Adapted with permission from references [86] (a), [116] (b), and [182] (c). Copyright 1999 (a) and 2001 (b) American Chemical Society; Copyright 2010 (c) Elsevier.

However, after 20 voltammetric cycles (4-carboxybenzenediazonium, $c = 10^{-3}$ M) a uniform surface is obtained [182].

1.5.2.1 Thick Layers

In addition to monolayers and medium thickness layers (<20–30 nm) it is also possible to obtain thick layers (up to 1 μm). The thickest layers obtained by non-electrochemical methods (with iron as a reducing agent) reach about 20 nm [56]. The only foreseeable reason for the limited thickness of non-electrochemical layers is the low yield of the reaction, but it is clear that this point needs further investigation. As for electrochemically grown layers, the preparation of thick layers relies on the possible transfer of electrons from the electrode to the outer surface of the layer where the continuous growth should take place. This is possible if a redox system, that permits electron transfer from the electrode to the external surface of the layers, is included in the layer. Several such examples have been described. Very thick layers of poly 4-nitrophenylene have been obtained by repetitive scanning on gold, the relative thickness and the mass (measured by IR and QCM, respectively) increase with the negative limit of the voltammetric scan, particularly when the reduction peak of the nitrophenyl group is encompassed in the scan [265]. The effect of the switching potential (E_λ) was carefully investigated and is illustrated in Figure 1.5 [264]. The authors have considered the layers obtained from 4-nitrobenzenediazonium and have increased the negative limit of the voltammetric scan; if the scan only encompasses the peak corresponding to the reduction of the diazonium salt (E_{p1}) the layer remains in the 10 nm range, but as soon as the limit comes close to the peak corresponding to the nitro group ($E_{p2} = -1.4$ V vs SCE in ACN, corresponding to the reduction of the nitro group to its radical anion: $C_6H_4NO_2 \mathrel{<=>} \text{-}C_6H_4NO_2^{\cdot-}$) the layer thickness increases up to $d = 86$ nm. At more negative potentials, d remains constant. Starting from 4-methylbenzenediazonium with no redox groups, the layer remains in the 10 nm range. The reason for such differences originates in the possibility for the electrons to transfer through the layer at E_{p2} from one redox center to the other in the 4-nitrophenylene layer; a possibility that is not available for the 4-methylphenylene layer [264].

In a similar way, layers obtained by reduction of the diazonium salt of ruthenium bipyridine or terpyridine (Figure 1.5) give a linear plot for the surface concentration Γ_{vol} vs the charge, indicating that all the redox couples are active within the layer [205]. An efficient electron transfer is possible through the reversible Ru(0)/Ru(I) and Ru(II)/Ru(III) couples and the growth of the layer is not limited as with diazonium salts without electroactive substituents. Up to ~350 layers can be grown on the surface of carbon. This linear relation between the charge and Γ_{vol} is very different from the self-limiting behavior observed when no active redox couples are inserted in the layers. A related investigation [266] has presented the layers by reduction of the diazonium salt obtained from 2-([4′-aminophenyl]sulfanyl)-8-hydroxy-1,4-naphthoquinone in solution. In this layer, the anthraquinone group can act as a redox mediator: when the potential is set at −0.2 V vs SCE, anthraquinone is not able to transfer electrons through the layer and a surface
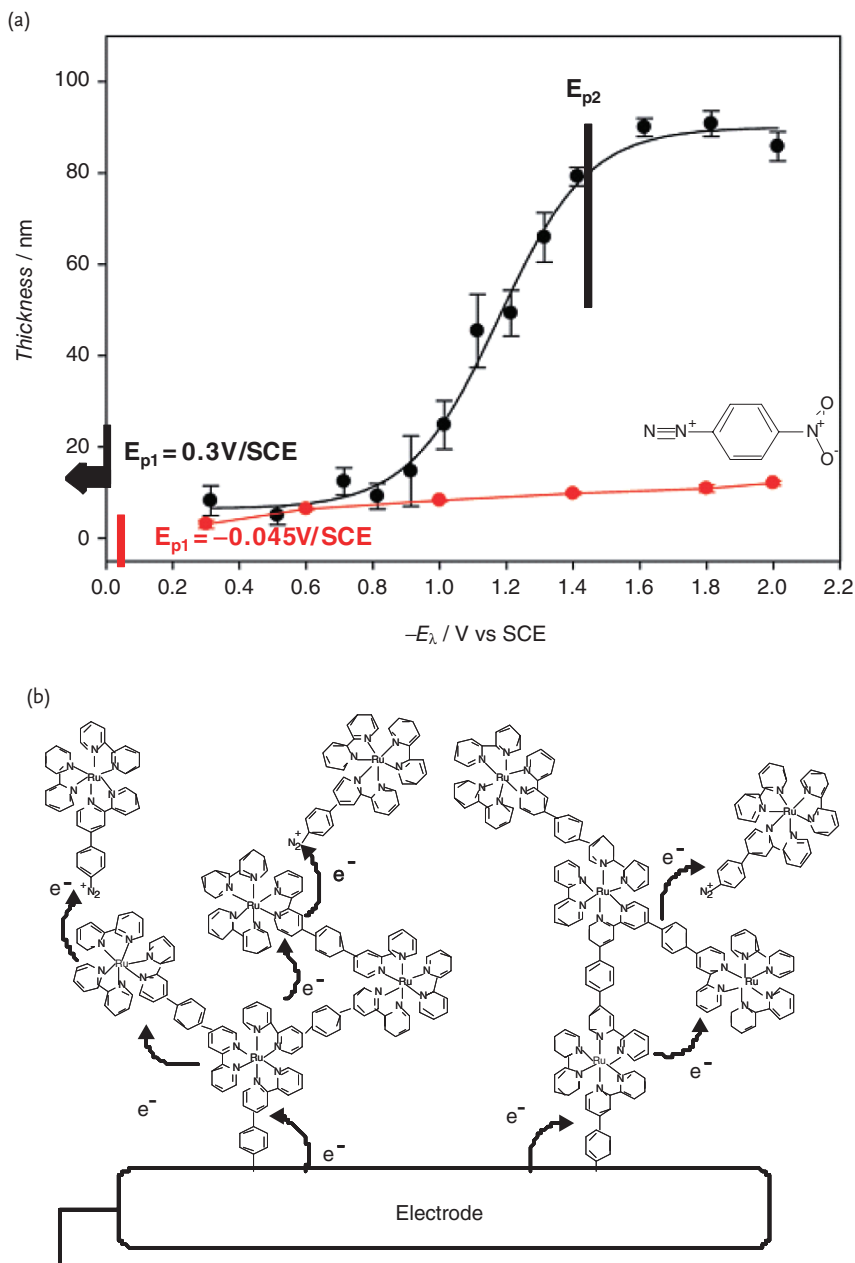
(a)

(b)

Figure 1.5 (a) Film thickness on gold surfaces, electrografted from 2 mM solutions of 4-nitro and 4-methyl benzenediazonium in 0.1 M Bu_4NBF_4/CH_3CN using 10 consecutive cyclic voltammetric cycles at a sweep rate of $1\,V\,s^{-1}$ for varying values of the negative limit (E_λ) of the scan. The peak potentials corresponding to the reduction of the diazonium salt (E_{p1}) and the nitro groups (E_{p2}) are indicated approximately. (b) A schematic representation of electron transfer through a layer of Ru complexes. Reprinted with permission from reference [264] (a). Copyright 2011 American Chemical Society; (b) courtesy of G. Bidan.

concentration of $\Gamma_{vol} = 3 \times 10^{-10}\,\text{mol}\,\text{cm}^{-2}$ is obtained, but if the potential is set at −0.5 V vs SCE anthraquinone acts as a redox mediator and the surface concentration increases to $\Gamma_{vol} = 9 \times 10^{-10}\,\text{mol}\,\text{cm}^{-2}$. At the difference of the above examples, micrometric layers can be obtained with benzenediazonium, without a substituent on the aromatic ring (~2 μm on copper and iron) on iron, copper and zinc, but not on carbon [218]. The reason for this unusual thickness is not clear but, in the light of Figure 1.5, one can wonder whether metallic salts that could act as redox relays are included in the layer.

This section clearly demonstrate that it is possible to vary the thickness of the layers and, for example, one could prepare a thick layer from a diazonium salt containing a redox group, as in Figure 1.5, and cover it with a layer of differently substituted phenyl groups. This should allow one to tune both the thickness and the surface properties of the modifying layer.

1.6
Structure and Formation of Multilayers

Some questions arise about the structure of the layers: (i) what is their exact chemical structure? (ii) Are the layers organized (as e.g., SAMs) or not? (iii) Are they compact or do they include pinholes? (iv) Are they solvent sensitive? (v) How do they transfer electrons? Of course, there is no general answer to these questions and one must consider every particular case, but a broad general picture can be obtained from the different studies.

1.6.1
Chemical Structure

The general structure of the layers obtained by reduction of diazonium salts is that of a polyphenylene layer. The aryl groups are characterized by IR spectroscopy, either through the bands pertaining to the aromatic ring or through the signature of the substituents (−NO₂, −CF3, ...). Aromatic groups have also been observed by ToF-SIMS but the layer is not only of the Ar–Ar–Ar- . . . type, azo bonds (–N=N–) are also included in the layer. The formation of such bonds was first proposed to account for N 1s peaks in the XPS spectra [115]. Later, ToF-SIMS examination of layers grown (spontaneously or electrochemically) on carbon or metals indicated the presence of ions such as $-N=N-C_6H_4-CF_3$, Br^+ [267], their concentration was constant in the layer but increased at the outer surface. The presence of azo bonds was also evidenced by IR (~1450 cm⁻¹) [246]. The percentage of azo bonds in the layers has been estimated: 100% when the diazonium salt of Ru $(bipy)_2(apb)_2^+$ (bipy = bipyridine, apb = 4-(4′-aminophenyl)2,2′-bipyridine) is attached to the surface of GC [207]; between 25% and 40% when 4-nitrophenylbenzenediazonium is attached to GC [268–269]. A mechanism is presented below that accounts for the formation of –N=N– bonds.

1.6.2
The Spatial Structure of the Layers

The orientation of the first phenyl group on the surface (monolayer) has been calculated, for example, on gold, the 4-nitrophenyl ring should be tilted by 31° relative to the surface normal [250]. Monolayers of nitroazobenzene, azobenzene, nitrobiphenyl, biphenyl, and fluorene bonded to a PPF surface salt have been characterized by IR, using the selection rules for adsorbed molecules. The average tilt angle with respect to the surface normal for the various molecules varied from 31.0 ± 4.5° for nitroazobenzene to 44.2 ± 5.4° for fluorine, with the remaining groups exhibiting intermediate geometries [110], in excellent agreement with the calculated values. On diamond, angle-resolved XPS has shown that the nitro-groups of poly (4-nitrophenylene) are located at the outer part of the layer [76].

Concerning thicker layers, the question arises as to whether the layers are organized, for example, including only para-substitution or are they disorganized? The comparison of the IR spectrum of a layer obtained by reduction of benzenediazonium with that of poly(paraphenylene) clearly indicates that all the substitutions are not para and that the layer is disorganized (compound **9** in Figure 1.6). Raman spectra also indicate that the structure is isotropic (see Chapter 5).
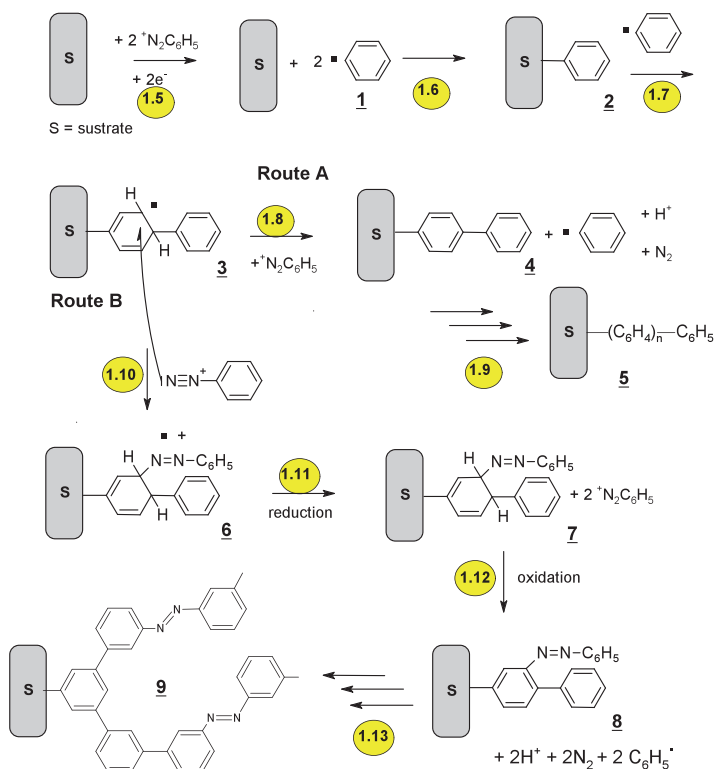

Figure 1.6 Mechanism of formation of multilayers.

1.6.3
Compactness of the Layers

We have seen above that a compact organized layer of aryl groups on a monocrystalline Si (111), surface corresponds to $\Gamma_{surf} = 6.72 \times 10^{-10}\,mol\,cm^{-2}$, and the STM image shows a compact layer. A value of $\Gamma_{surf} = 2.5 \times 10^{-10}\,mol\,cm^{-2}$ has been determined on PPF, which is not a monocrystal, but the similarity of the Γ_{surf} indicates that it should not be far from a compact layer. For thicker layers on different materials the presence of pinholes has been characterized. When examined by AFM, the 35–60 nm thick layers grown on metals show some mesoholes (~50 nm) [148]. Cyclic voltammetry, has also been used to evidence the presence of pinholes: the bulky *trans*[-η^2-dppe$_2$Ru(-C≡C–Ph)$_2$] complex presents a small sigmoidal signal on a C–C_6H_4–NH_2 layer, this was interpreted as resulting from widely spaced small diameter pinholes [270]. SECM, where the current is monitored on a micrometric electrode in solution while it approaches the surface, also permits one to monitor the presence of pinholes [271]. A layer containing ferrocenyl groups -Fc- (C–C_6H_4–$CONH$–CH_2–Fc or C–$NHCO$–Fc) was prepared and the response of various mediators of increasing potentials was examined. Decamethylferrocene is unable to oxidize the ferrocene attached to the surface and must, therefore, be oxidized directly on the surface accessible through pinholes. An electrochemical response was observed when the layer was prepared by reduction of the diazonium salt at low potential (–0.2 V vs SCE) but disappeared for thicker layers prepared at –1.0 V vs SCE. This interesting result indicates that thin layers include pinholes that are filled as the layer grows. A detailed analysis of SECM curves has been performed to investigate the structure of layers obtained from diazonium salts. These curves were recorded with different redox couples in solution (ferricyanide, phthalonitrile . . . with different $E°$) on top of 2–3 nm bromoethylphenyl layers attached to a gold substrate [272]. Macropores (diameter ~50 nm, density $3 \times 10^6\,cm^{-2}$) and nanopores (~10 nm, $7.5 \times 10^7\,cm^{-2}$) were taken into account and were deemed responsible for the major part of the current flowing through the system. Aqueous redox probes would be transported within large defects, while organic redox probes would be transported in meso- or nanopores.

If the layer electrografted on gold is not compact, gold can be "seen" through the holes and can be oxidized and reduced. The charge associated with Au oxide reduction was used to estimate the surface of the holes and the upper limit for the surface concentration Γ_{surf} of aryl groups directly attached to the Au surface after electrografting. Values for the surface concentration of the modifier were found in the range of $\Gamma_{surf} = 3–4 \times 10^{-10}\,mol\,cm^{-2}$ [273]. This is the same order of magnitude as the values reported above on monocrystalline Si and PPF.

On materials that are not monocrystalline, like PPF, Γ_{surf} is about half of what is measured on a Si monocrystal, this is probably related to number of sites that can be grafted and that are less numerous, at the same time there must be some places that react more slowly, or not at all, and that appear as pinholes, as described above. For example, on GC, edges of the structural units should be easier to

derivatize than the planes [86, 116]. However, in the parts that are grafted the thick layer appears as quite compact. Indeed, several substituents that are redox active, such as the nitro groups, are only partly detected. Γ_{volume} has been measured by integration of the nitro groups as a function of the film thickness. The results indicate that Γ_{volume} does not vary as a function of the thickness when d is larger than about 4 nm. Therefore, one must conclude that only a limited number of the nitro groups inside the layers are redox active and that this number does not increase as the layer grows [256, 257, 268]. In the same way the azo bonds in the 4-(4′-nitrophenylazo)phenyl layer are not detected by electrochemistry and are redox inactive [257]. As there is no loss of substituents during the growth of the film [37] these findings have been interpreted as resulting from a compact film structure in which solvent diffusion is limited [268]. There may also be spatial inhibition of the conformational changes that accompany the reduction [37].

1.6.4
Swelling of the Layer

The structure of multilayers films also depends on the solvent [256, 257, 274, 275]. For example, the contact angle of a polycarboxyphenylene layer changes from ~25° after ultrasonication in water to ~65° after ultrasonication in petroleum ether. In water the carboxyl groups are exposed to the solvent, maximizing the hydrophilicity of the layer, while in petroleum ether a rearrangement of the film takes place with the aryl rings preferentially exposed, maximizing the hydrophobicity of the surface [274]. The same phenomenon can be observed through the measurement of the thickness (d) or through the blocking of redox probes [274]. These experiments indicate that after sonication in a "like" solvent (water for carboxyphenyl, and acetonitrile for methylphenyl films) the film has a swollen structure, whereas after sonication in an "unlike" solvent (petroleum ether and water for carboxyphenyl and methylphenyl, respectively), the film structure is more compact.

1.6.5
Electron Transfer through the Layers

The rate of electron transfer through the layers has been investigated [276–277]. Mixed monolayers of phenyl and carboxyphenyl groups have been prepared and the carboxyphenyl groups have been derivatized with ferrocene. With this system, the rates of electron transfer (k_{app}) measured for benzene/4-carboxybenzenediazonium = 40 deposited on carbon and gold were found to be equal to 10 and 68 s^{-1}, respectively, indicating that the rate depends on the substrate [178]. The rather slow heterogeneous rate constant k for the Fe(CN)$_6^{3-/4-}$ redox system at a layer obtained from 4-nitrobenzenediazonium on CC has been measured by SECM ($k = 2.6 \times 10^{-4}$ cm s^{-1}) [278].

Another important issue is the mechanism of electron transfer through these layers. The electron transfer was examined by two different methods (i) from the electrode through a ferrocene-derivatized layer to redox couples in solution and

(ii) in the reverse way from the electrode of a SECM, to redox couples, and to the ferrocene layer [270, 271]. The use of redox couples with variable redox potentials permit one to distinguish three electron transfer processes: through pinholes as described above, by electron transfer from one ferrocene to another through the layer, or from one aryl group to another when no ferrocenes are attached to these groups.

Electron transfer through the layers can also be observed in the dry state by measuring the conductivity of the films between carbon and mercury: $\sigma_{C6H5} = 2.45 \times 10^{-7}\,S\,cm^{-1}$ for a phenyl monolayer, $\sigma_{C12H10} = 1.03 \times 10^{-9}\,S\,cm^{-1}$ for a biphenyl monolayer, and $\sigma_{C18H14} = 4.10 \times 10^{-10}\,S\,cm^{-1}$ for a terphenyl monolayer [279], but also $\sigma_{PP} = 2.5 \times 10^{-6}\,S\,cm^{-1}$ for a polyphenyl layer [218]. For monolayers, the conduction is assigned to a tunneling process at low temperature, where the molecular conformations are apparently fixed. For the thicker terphenyl films at higher temperatures, conformational changes occur and involve a rotation of the phenyl ring. The coplanar conformer of terphenyl has a significantly higher conductivity [279].

Electron transfer has also been observed between the tip of an STM and an Os complex attached to gold, either through an S atom (SAM) or by reduction of a diazonium salt. The current flows through these devices go through a maximum at a potential close to the equilibrium potential of the complex [209].

1.6.6
The Formation Mechanism of Multilayers

A mechanism has been proposed for the formation of multilayers, including the formation of azo bonds [267] (Figure 1.6). Reaction (1.5) involves the monoelectronic reduction of two diazonium salts to give two aryl radicals via a concerted mechanism. These radicals have been observed by ESR [40] (see Chapter 7). One of these two radicals binds to the substrate (1.6), while the second one attacks the already grafted phenyl group **2** to give a cyclohexadienyl radical **3**, through reaction (1.7). At this point, the radical **3** can react with an aryl radical (route A) or diazonium cations (route B). Route A, through reactions (1.8) and (1.9), leads to a pure polyphenyl layer **5**. Reaction (1.8) is an electron exchange leading to the reoxidation of the cyclohexadienyl radical and reduction of a benzenediazonium. The formation of azo bonds (route B) in the polymeric chains begins by an attack of a diazonium cation on the cyclohexadienyl radical **3**. Reaction (1.10) gives rise to a radial cation **6** that should be readily reduced (1.11) to give **7**. This reduction can take place through an electron exchange with the metal, either connected or not (electron transfer can occur through the layer). Alternatively, an electron exchange with an aryl radical is possible. Reaction (1.12) involves the reoxidation of a cyclohexadiene; the driving force for this reaction being the restoration of the aromaticity and the conjugation of the two substituents. Alternatively, reactions (1.11) + (1.12), leading from **6** to **8**, amount to the reaction of two diazonium salts with **6** and to the formation of **8**, two phenyl radicals, two nitrogens, and two protons. The aryl radicals formed in reaction (1.8) and possibly (1.11) + (1.12) could now attack the

phenyl groups, as in reaction (1.7), leading to the growth of the chain through reactions (1.6) + (1.7) + (1.8) + (1.9) or (1.6) + (1.7) + (1.10) + (1.11) + (1.12) + (1.13). Reactions (1.8) and (1.11) + (1.12) are responsible for the chain mechanism. This mechanism explains not only the growth of polyphenyl layers but also the presence of azo bonds in these layers (in this case the reduction of diazonium salts occurs both by electron transfer through the layer and by a purely chemical chain mechanism) and during spontaneous grafting at long times (the only chain mechanism is operative) [42]. It is supported by literature data and, in particular, by a mechanism established for the formation of biphenyls [280]. A two-step mechanism has been proposed for the spontaneous grafting of carbon in ACN or 0.14 M H_2SO_4 [42] the fast first step being an electron transfer from the carbon substrate to the diazonium salt and attack of the radical on the surface, as in Figure 1.6. Involvement of a carbocation has been proposed in the second step, but in the author's view this slow step would more likely reflect the presence of the chain reactions described above.

On hydrogenated silicon a somewhat different mechanism [28] has been proposed for the attachement of the aryl radical (Figure 1.7).

A radical is formed by electron transfer from the hydrogenated Si surface. Subsequently, this radical abstracts a hydrogen atom from the surface to give a surface Si radical and an aromatic hydrocarbon. Reaction of another aryl radical with the silicon radical leads to an aryl group bonded to the surface, the growth of multilayers would follow the same mechanism as above. This mechanism is supported by the following observations: grafting of 4-nitrobenzenediazonium has been characterized *in situ* by IR with polarized light and a progressive increase of the two antisymetric and symmetric absorptions of the nitro-group was observed [142]. The surface silyl radicals of Figure 1.7 can be trapped [144] by purposely added compounds, for example, alkyl, arylseleno or thioether (R–[Se or S]–Ar), alkenes (CH_2=CH–R) and alkynes that trap the surface Si radicals to give surfaces such as *Si*–S–Ar and *Si*–CH_2–CH_2–R without any phenyl groups. In these experiments, the trapping agents overrun the phenyl radicals, most probably by a concentration effect.

Non-radical mechanisms have also been proposed for the attachment of 4-nitrophenyl groups to carbon black (Vulcan XC 72R) [281] and glassy carbon powders [282]. As a first possibility the carbon π system would play the role of the nucleophile for the decomposition of the diazonium ion and the oxygenated func-
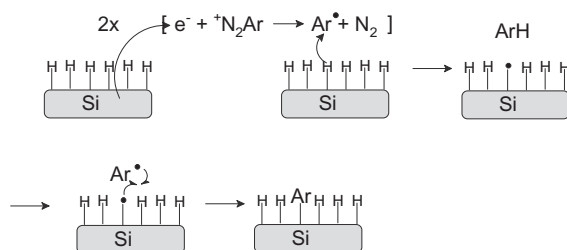

Figure 1.7 Electrografting mechanism of silicon.

tionalities would undergo a concerted decarboxylation by the arenium ion mechanism. This mechanism is based on the following observation: for highly oxygenated carbons, the XPS signal corresponding to oxygenated functions decreases upon spontaneous grafting [281]; but it cannot account for the formation of multilayers. The second possibility would be the heterolytic cleavage of the diazonium cation in pure water and addition of the cation to the carbon surface. This mechanism is supported by the different surface coverages obtained in the presence or absence of H_3PO_2 (that reduces the diazonium cation to the radical) [282], it is in line with the known heterolytic dediazonation in water [14].

1.7
Conclusion

The functionalization of surfaces by diazonium salts appears as a versatile and efficient method. It applies to many substrates, conducting or not, to a nearly endless list of diazonium salts, and through a large variety of methods (electrochemical or not). The layers that are formed are robust; their thickness can be varied from monolayers to microns. This is why they are now widely applied to modify surfaces for a variety of applications, including industrial applications, which are detailed in the next chapters. The mechanism is generally assigned to the attachment of a radical to the surface, but the possibility of a heterolytic reaction should be further investigated. The drawbacks of the method are the presence of pinholes and the fact that the layers seem mostly disorganized, but ongoing investigations indicate that it should be possible to obtain organized layers.

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