

Covalent modification of Graphitic Carbon Substrates by Non-Electrochemical Methods

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Abstract: New methods for modifying graphitic carbon surfaces without electrochemical assistance, and without the deliberate formation of carbon surface oxygen functionalities, have emerged in the past decade. The approaches rely on spontaneous reactions of aryldiazonium salts, primary amines, ammonia and iodine azide at room temperature, chemical reduction of aryldiazonium salts, reactions of alkenes and alkynes at elevated temperatures, and photochemical reactions of alkenes, alkynes, azides and diazirines. This review describes the methodology and scope of these reactions at graphitic carbon materials (excluding carbon nanotubes), examines mechanistic possibilities and future prospects.

Keywords: spontaneous grafting, photochemical grafting, thermal grafting, aryldiazonium salt, amine, azide, alkene, alkyne

Introduction

Grafting molecular layers to surfaces enables control of the interfacial structures, properties and reactivities of surfaces, while maintaining the properties of the bulk material. Graphitic carbons have many attractive characteristics, including ease-of-handling, low-cost, high mechanical stability and good electrical conductivity. The material is readily available in a number of forms including high surface area felts and cloths suitable as supports for combinatorial chemistry [1, 2], carbon powders useful for chromatography [3], glassy carbon (GC) [4], a convenient material for planar electrodes and very smooth films of pyrolysed photoresist [5] suitable for applications in molecular electronics [6, 7, 8]. Another advantage of graphitic carbon is that the surface can be easily modified by methods which give very stable molecular coatings, attached by strong C-C [9] or C-N covalent bonds. For systems studied in detail, the attached coatings have been shown to be largely unaffected by elevated temperatures [10, 11] and extended sonication in aggressive solvents [10, 11, 12, 13]. In electrochemical investigations, grafted layers have also been shown to withstand cycling over a wide potential range [14, 15, 16].

The first example of electrochemically-assisted covalent modification of carbon was reported in 1990 [17], and since then many studies have explored this general approach to grafting. In the electrochemical method, a solution-based radical is generated at the electrode (substrate) surface by reduction or oxidation of the modifier. The radical appears to couple to the surface with formation of a covalent bond to a surface carbon. The most studied reaction is reduction of an aryldiazonium cation to yield an aryl radical which binds to the surface [10, 12]. The modification of carbon surfaces by this route is a very active field of research and has been reviewed recently [18, 19]; aspects pertinent to this review are discussed briefly below. Reduction of iodonium salts leading to grafting of phenyl and alkynyl groups [11, 20], and oxidation of primary amines [17, 21, 22, 23, 24] and arylacetates [15, 25] giving amine and methylene-based radicals respectively, are other approaches to electrografting.

Continued interest in developing new methods for covalently modifying carbon surfaces can be attributed to a number of factors. Different attachment methods rely on the reactions of different functional groups and hence access to a broad range of

attachment methods widens the choice of commercially available or easily synthesized modifiers. This increases the range of groups that can be attached and clearly this is important when designing interfaces with selected chemical or physical properties. A second consideration is that different film structures (monolayer vs multilayer or close-packed vs loosely packed) may result from different modification strategies. For example, electrochemical grafting tends to lead to multilayer or polymeric films, and it may be difficult to limit the grafting to a monolayer [26, 27, 28]. Different attachment strategies also lend themselves more or less easily to patterning, an important consideration for applications of modified carbon surfaces in areas such as sensors and molecular electronics. Finally there is a need for methods which are more convenient than electrografting for particular samples.

Several interesting non-electrochemical approaches for covalent attachment of organic modifiers to graphitic carbons have been reported in the last decade and are the subject of this review. The selected methods involve spontaneous room temperature reactions, and those promoted by chemical reducing agents, heat or UV irradiation. Methods involving deliberate oxidation of the carbon surface to generate surface oxygen functionalities are not included in the review, neither are modification methods for carbon nanotubes. In the first section, the chemical structure of graphitic carbon surfaces is briefly discussed and the following sections are organised according to the modifier, describing modification methods involving aryldiazonium salts, primary amines, ammonia, alkenes and alkynes, and azides and diazirines.

Chemical structure of graphitic carbon surfaces

Graphitic materials incorporate basal plane and edge plane carbon sites in a spatial arrangement and relative abundance that depends on the particular material. Highly ordered pyrolytic graphite (HOPG) and cut carbon nanotubes each present two types of surfaces: one at which only basal plane sites are significant and a second at which only edge plane sites are important. The surfaces of other graphitic carbons, for example GC, carbon black and pyrolysed photoresist film (PPF) incorporate a mixture of edge and basal plane carbons. For the modification methods of interest in this review, the limited

evidence available indicates that the basal plane of HOPG is unreactive (see following sections), pointing to the prime importance of edge plane sites.

A generally accepted model for the edge plane of graphitic carbon is shown in Fig. 1. Both armchair and zigzag sites are present, terminated with hydrogen or various oxygen functionalities. The relative abundances of these depends on the material's preparation method and its post-treatment [4]. The presence of surface radicals (or σ dangling bonds) is also commonly assumed; heat [29], argon RF plasma treatment and mechanical abrasion [30] have been suggested to increase the abundance of surface σ radicals.

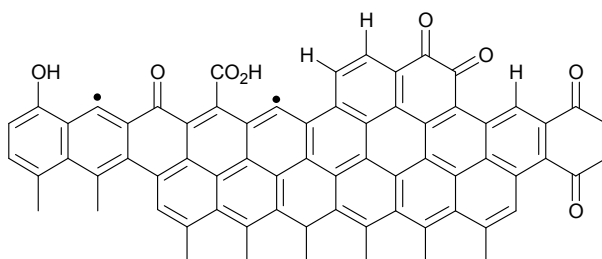


Fig. 1 Representation of the graphitic carbon edge plane.

Recently a new model for the oxygen-free sites of graphitic edge planes has been proposed in a study which attempts to reconcile diverse aspects of the chemistry and physics of graphitic carbons [31]. As shown in Fig. 2, in addition to H-termination, the important structures are benzyne-like at armchair sites (with the singlet ground state being most common) and carbene-like at zigzag sites (with triplet state being most common). To date such structures have not featured in mechanistic considerations of the grafting reactions described below, but provide an interesting avenue for future investigations.

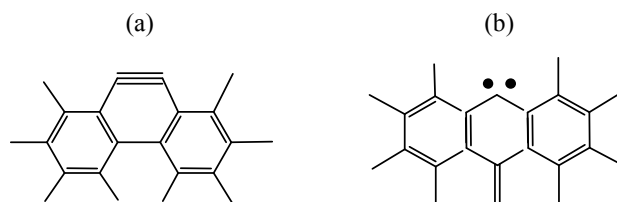


Fig. 2 Radovic's proposal for oxygen-free sites for the graphitic edge plane [31]. (a) Benzyne structure at armchair site and (b) Carbene structure at zigzag site.

Grafting using aryldiazonium salts

Aryldiazonium salts are very useful and versatile reagents for functionalising conducting and semiconducting surfaces with a variety of functional groups. The unique characteristics of the aryldiazonium cation are the very strong electron-withdrawing effect of the diazonium moiety and the high stability of dinitrogen as a leaving group. These factors account for relative ease of reduction of aryldiazonium salts; for example the chemically irreversible electroreduction of the benzenediazonium and *p*-nitrobenzenediazonium cations occurs at $E_p^{\text{red}} = -0.06$ and 0.20 V, respectively (vs SCE, in 0.1 M Bu_4NBF_4 - acetonitrile) [10, 32]. The electroreduction of aryldiazonium salts has been shown to proceed through a concerted mechanism in which electron transfer and dinitrogen loss are concomitant [32]. Because aryldiazonium cations are reduced at relatively high potentials, the subsequent reduction of the aryl radical generated at the electrode surface does not occur [32].

It is well-established that electroreduction of aryldiazonium salts on carbon can lead to multilayer film growth [26, 27, 28, 33]. The thickness of the layer (typically ranging from one monolayer, *ca.* 1 nm, to over 20 nm) may be partially controlled by the concentration of aryldiazonium salt and by the amount of charge consumed. It is assumed that an oligophenylene-like structure forms by reaction of the electrogenerated aryl radicals that react first with the electrode surface, and then with the already grafted phenyl groups. However, many workers have noted, particularly on the basis of X-ray photoelectron spectroscopy (XPS) analysis, that films grafted by electroreduction of aryldiazonium salts contain reduced nitrogen species which cannot be explained by a pure oligophenylene film structure. Recent reports provide firm evidence for the presence of azo groups within films [34, 35, 36] and Pinson and co-workers have proposed a film formation mechanism, shown in Fig. 3, which accounts for the formation of multilayer films incorporating azo links [34].

terminated and in all cases, binding of a phenyl group converted a sp^2 -carbon to sp^3 . Calculations showed that there are large adsorption energies at both types of edge site, however bonding at the basal plane is significantly weaker. These results are consistent with experiments which have shown that the yield of the electrografting reaction is significantly greater on GC than on basal plane graphite [10] and faster at edge plane graphite than at the basal plane [37], although it is not clear whether electrografting at basal plane graphite occurs at pristine graphene sheets or only at defect sites. Hence both theory and experiment support the conclusion that strong covalent bonds can be formed between aryl groups and the edge plane of graphitic carbons, but the mechanism of bond formation remains to be elucidated.

Electrografting is not a convenient method for some forms of graphitic carbon, for example, powders. Recognising that aryldiazonium salts can be readily reduced in homogeneous solution using chemical reducing agents, Compton and co-workers reacted graphite powder with aryldiazonium salts in the presence of hypophosphorous acid (H_3PO_2) [38]. Characterisation of the resulting materials confirmed the expected covalent grafting reactions. In principle, any sufficiently strong reductant could be suitable for this modification method, however, hypophosphorous acid has been the reductant of choice. Indeed, concentrated hypophosphorous acid solutions have long been used for deamination of $ArNH_2$ to ArH , from the ArN_2^+ intermediate [39]. Applications of this method, reported by Compton's group, include the modification of graphite powder with species showing pH-dependent behaviour for use as reagentless pH sensors [40], and step-wise reaction of nitrophenyl-modified graphite powder to give the poly-L-cysteine-functionalised material that could be useful for the extraction of heavy metals [41]. More recently the same authors have demonstrated a simple and convenient method for preparation of gram quantities of graphite powder modified with aminophenyl groups; the strategy involves reduction of immobilised nitrophenyl groups with alkaline ferrous sulphate [42]. An interesting application of the methodology is the functionalisation of mesoporous carbon with arylsulfonate groups, affording a highly active protonic catalyst [43].

Although the homogeneous reduction method has led to the preparation of derivatised carbon materials, the use of a specifically added reductant may be avoided

through the so-called “spontaneous” modification, as discussed in the following paragraphs. A recent report by Toupin and Bélanger (described below), comparing the spontaneous and chemical reduction methods, shows that under the conditions used in their study, addition of reducing agent to the graphite powder-aryldiazonium salt mixture had no effect on the nature or yield of product [44]. However this may simply be a consequence of the particular conditions used; the relative advantages of the chemical reduction vs spontaneous method for graphitic carbon substrates needs further investigation. Modification of insulating materials such as glass and polytetrafluoroethylene (PTFE) via homogeneous reduction of aryldiazonium salts is an interesting and potentially very useful new extension of the method [45].

The first reports of spontaneous attachment of aryl radicals to planar carbon surfaces appeared in 2005 [46, 47]. Prior to this time however, the spontaneous modification of carbon blacks by aryl radicals derived from aryldiazonium cation precursors had been patented and used for interesting industrial applications in the manufacturing of inks and toners [48]. Spontaneous grafting from aryldiazonium salts was also reported earlier on metals, semiconductors and on carbon nanotubes [49, 50].

The spontaneous grafting to GC, carbon black and PPF from acetonitrile and aqueous acid solutions of aryldiazonium salts has been studied by electrochemical and spectroscopic techniques. The studies show that the films grafted spontaneously have the same characteristics as those grafted electrochemically, but in general, films are thinner and form more slowly by the spontaneous route. For example, in their study aimed at confirming covalent bonding between GC and aryl groups, Combellas and co-workers employed time-of-flight secondary ion mass spectroscopy (ToF-SIMS) to examine films electrografted and spontaneously grafted from solutions of aryldiazonium salts (2 mM in 0.1 M Bu_4NBF_4 - acetonitrile) [47]. The spontaneously grafted films of $-\text{C}_6\text{F}_{13}$ and $-\text{Br}$ phenyl derivatives gave qualitatively similar spectra to those grafted electrochemically, although for the same preparation times, signals were much weaker after spontaneous grafting.

Pinson and co-workers made a detailed investigation of spontaneous grafting from solutions of *p*-nitrobenzenediazonium tetrafluoroborate onto iron, zinc, copper, nickel and GC [46]. To effect grafting, clean substrates were dipped in deaerated acetonitrile

solutions containing 0.1 - 10 mM diazonium salt for 1- 60 min followed by cleaning by sonication. Spontaneous grafting was confirmed, on all surfaces, by electrochemical and spectroscopic techniques. Fourier transform infrared reflection absorption spectroscopy (FTIRRAS) and XPS revealed the expected signals for an immobilized nitrophenyl film and the absence of signals attributable to the diazonium moiety. These results point to a film formation mechanism that involves dinitrogen loss from the aryldiazonium cation and covalent grafting. The immersion time of the GC substrate in the modification solution was found to have a significant effect on the surface concentration of nitrophenyl groups, as estimated from the charge associated with the nitrophenyl reduction peak in cyclic voltammetry. The surface concentration tripled for immersion times ranging from 1 to 60 min, reaching a maximum value of $(5.8 \pm 0.2) \times 10^{-9} \text{ mol cm}^{-2}$. This effect was also found for iron although much less pronounced and over longer time periods. Atomic force microscopy of the iron surface showed that the surface became rougher with increasing immersion time. On GC, thicker films were obtained when the concentration of the diazonium salt was increased over two orders of magnitude while keeping the immersion time constant. Again this was less pronounced on iron. The film grafted to GC from 0.1 mM diazonium salt solution was not blocking to ferricyanide voltammetry, suggesting patchy coverage, however films prepared from 1 and 10 mM modifier solutions completely blocked the redox response. Reduction of nitrotoluene (in acetonitrile) was observed at all GC surfaces implying that the hydrophobic surface film is permeable to that redox probe. These results are qualitatively similar to those obtained for electrografted films, consistent with very similar film properties and structure for both grafting methods, although electrografted films are generally thicker.

Since the mechanism of spontaneous grafting seems to be closely related to that of the electrochemical protocol (involving dinitrogen loss from the diazonium salt) the nature of the redox reaction in the spontaneous protocol is an important question. Vautrin-UI and co-workers [51] have started to address this question by carefully examining the reactivity of a range of *para* substituted benzenediazonium salts toward different substrates. The reduction peak potentials (*vs* SCE) of the benzenediazonium derivatives (2 mM solution in 0.1 M Bu₄NBF₄ - acetonitrile) ranged from +0.03 V for -NO₂ to -0.56 for the -Et₂N derivative. Although the substrates investigated included GC

most of the study dealt with metals, with open circuit potentials (OCPs) in acetonitrile solution: Zn (-0.50 V), Fe (-0.10 V) and Ni (+0.30 V). These compare with GC with an OCP of +0.63 V in the same conditions [46]. The main conclusion of this interesting study is that for metal substrates, both the nature of the substrate and the aryldiazonium salt are important in the extent and morphology of surface modification. For example, with the relatively difficult to oxidise nickel substrate and difficult to reduce $\text{-Et}_2\text{N}$ derivative, no grafting was observed even after 15 h of immersion in the diazonium salt solution. On the other hand, using zinc, the most easily oxidised substrate, and the easily reduced nitrobenzenediazonium salt, small islands of organic matter could be seen by AFM after 5 min immersion, and longer immersion times yielded a thick non-uniform film. With the same diazonium derivative, grafting is slow on nickel but after 2 h immersion, a homogenous modification of small grain is obtained. Therefore it seems that while grafting is favoured at more easily oxidised surfaces (zinc) the resulting layers are less regular than at the less easily oxidised surfaces (nickel). This was confirmed using the iron substrate that has intermediate redox properties and yielded a film of intermediate homogeneity in an intermediate immersion time. Finally, and interestingly, although electrochemically induced modification is possible at SnO_2 , no grafting was obtained by dipping the semi-conductor in the aryldiazonium solution, presumably because this surface is too difficult to oxidize.

These findings are consistent with spontaneous grafting at metals occurring through redox reactions between the substrate and the aryldiazonium salt. Surface oxidation products (presumably dissolved metal ions or surface oxides) could not be detected but this is perhaps not unexpected considering the amounts involved may be very small. The absence of homogeneity in some of the films may be assigned to the formation of anodic and cathodic zones on the metal surfaces which, even before reaction, were not oxide-free. However, the implications of these results for the mechanism of spontaneous grafting at GC are not obvious because the very positive OCP of GC, compared with the metal substrates, raises the question of whether GC is thermodynamically able to reduce aryldiazonium cations. These questions have very recently been addressed by Toupin and Bélanger [44], as described below.

In our studies of spontaneous grafting to GC and PPF surfaces using 10 mM aryldiazonium salts, we found that for acetonitrile solutions of the *p*-nitrobenzene derivative, no film formed on PPF even after 120 min immersion time (in the dark and in the absence of air) [52]. Under the same conditions, the surface concentration of nitrophenyl groups on GC reached $32 \times 10^{-10} \text{ mol cm}^{-2}$. Using 0.14 M H_2SO_4 as the solvent, grafting occurred spontaneously on both surfaces, although the concentration of nitrophenyl groups was lower on PPF. AFM depth profiling of films grafted to PPF showed a maximum thickness of 3.8 nm, and a linear relationship between surface concentration of nitrophenyl groups and film thickness. The surface concentration per monolayer thickness of nitrophenyl groups was $(3.2 \pm 0.5) \times 10^{-10} \text{ mol cm}^{-2}$, close to that previously determined for electrochemically grafted layers [28], suggesting a similar film structure after spontaneous and electrochemical grafting. Spontaneous grafting of carboxyphenyl groups to PPF from acidic solutions of the corresponding diazonium salt was also successful. At present we are unable to explain the different reactivity of GC and PPF towards spontaneous grafting, and the different reactivity of PPF in acetonitrile and aqueous acid solutions. The OCP of PPF is less positive than that of GC and hence the reducing power of the substrate seems unlikely to be a factor [53]. In fact, the lack of a relationship between film formation and OCP suggests that the generation of radicals proceeds via a different mechanism at carbon than at metals, or that there is another essential step, besides electron transfer, that controls the process. Adsorption of the diazonium cation is one possibility under investigation.

Toupin and Bélanger have undertaken detailed studies of the spontaneous reaction between Vulcan carbon black and aryldiazonium salts in aqueous solution [35, 44]. Surface modification was established by elemental analysis, XPS and nitrogen adsorption. Reduced nitrogen species were detected in the films and the authors propose the presence of some diazo linkages between the phenyl group and the carbon surface. This linkage is assumed to arise from coupling of the diazonium salt *ortho* to a surface phenolic functionality, giving the structure shown in Fig. 4. The thermal stability of the modified layers was examined using XPS and thermogravimetric analysis coupled to mass spectrometry (TGA-MS). Significant loss of material only occurred at temperatures

above 200 °C, confirming that carbon samples are modified with strong covalent bonds to the surface [35].

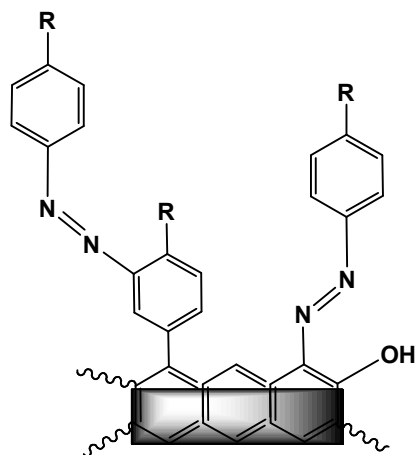


Fig. 4. Surface linkage of aryl groups through a C-C (left) or C-diazo bond *ortho* to a hydroxyl activated carbon (right) [35].

In order to gain insight into the mechanism of the spontaneous grafting reaction, Toupin and Bélanger compared the yield of immobilised nitrophenyl groups after spontaneous grafting of the *in situ* prepared *p*-nitrobenzenediazonium cation and after grafting of the pre-prepared diazonium salt in the presence of hypophosphorous acid as reducing agent [44]. Both types of reaction were carried out before and after oxidation of carbon black in refluxing nitric acid, and after heat treatment of the oxidised material at 1000 °C in argon. Important results of this very interesting study are that the grafting yields of all reactions were very similar and that the extent of reaction is limited, probably to close to monolayer coverage (assuming that some grafting occurs on the basal plane). Furthermore, increasing the reaction time and increasing the concentration of reagents did not increase the yield of reaction. Based on these results the authors suggest some mechanistic possibilities for the spontaneous reaction of aryldiazonium salts with carbon substrates in aqueous acid. They propose that the carbon π -electron system acts as a nucleophile, transferring electrons and leading to the decomposition of the aryldiazonium cations. They also suggest that the same reaction may occur with oxidised carbon but in this case, the surface oxygen functionalities undergo a concerted decarboxylation by an arenium ion mechanism. They note however, that the analogous

homogeneous reaction between 9-anthroic acid and *p*-nitrobenzenediazonium ion does not lead to decarboxylation.

With respect to the more limited extent of modification by spontaneous- than electrografting (at planar carbon substrates), Toupin and Bélanger reason that a spontaneous reaction that proceeds via electron transfer from the π system of the carbon will be accompanied by an increase in the OCP of the substrate to a point where the reaction can no longer proceed. This is in contrast to metal substrates, where a galvanic process would maintain an effectively constant driving force for the reduction reaction (as for electrografting at constant applied potential). Finally, the authors note that because the reaction products and yields were the same in the presence and absence of hypophosphorous acid, it appears that under their reaction conditions, grafting is governed by electron transfer from the carbon substrate, even in the presence of the reducing agent. This point needs further investigation using a wide range of reaction conditions: certainly it is difficult to understand why addition of a chemical reducing agent could not, in principle, lead to thick, multilayer films. Indeed using a gold substrate and iron powder as the reducing agent, aryl films close to 20 nm in thickness have been grafted from aryl diazonium salt solutions [45].

In summary, for graphitic carbon substrates which have significant edge plane content, simply immersing the substrate in a solution of aryl diazonium salt is a practical method for covalently grafting aryl films. The intimate structure of the films grafted to planar substrates appears to be the same as for films obtained with electrochemical induction, although the spontaneously grafted films are thinner. The details of the factors that control spontaneous grafting of aryl diazonium salts at GC, carbon black and PPF are not entirely clear. In particular the differences between spontaneous grafting at GC and PPF do not seem to be related to the OCP of each material, and it is possible that different mechanisms for formation of radicals are operative in aqueous acid and acetonitrile. The importance of the semi-catalytic reaction mechanism, shown in Fig. 3, has not been elucidated. This mechanism shows that after an initial formation of radicals, reaction A can lead to continued film growth without further addition of radicals, and hence result in multilayer films without continued electron transfer from the substrate.

In addition to the solution methods described above, solvent-free conditions have also been used for functionalisation of high surface area graphitic carbon using aryldiazonium salts [54, 55]. The procedures followed those used for carbon nanotubes [49] and involved addition of isoamyl nitrite to a dry mixture of ordered mesoporous carbon and aniline derivative, and after 1 h at room temperature, heating the stirred reaction mixture to 70 °C. The presence of the expected groups on the modified carbons was confirmed with FTIR spectroscopy, thermogravimetric analysis, scanning and transmission electron microscopy, and nitrogen adsorption. Grafting aryl groups to the surface gave measurable changes in pore size; this straightforward method for pore size manipulation and the stable attachment of functional groups suggests that the material could be developed for applications in chemical sensing, catalysis and separation.

Very recently, we have exploited the spontaneous reaction of aryldiazonium salts with GC and PPF to prepare surfaces patterned with phenyl derivatives [52]. Microcontact printing onto the carbon substrate using patterned PDMS stamps inked with diazonium salt solutions gave covalently attached nitrophenyl, carboxyphenyl and aminophenyl groups. Although the procedures have not been optimised, patterns with line widths down to 50 μm were readily generated and imaged. Microcontact printing is a very simple approach to patterning and it will be interesting to explore the full scope of the method.

Grafting using primary amines

The electrooxidation of primary amines at carbon, gold and platinum electrodes is chemically irreversible and leads to covalent grafting of an organic layer at the surface. The standard electrode potentials for the oxidation of primary alkylamines in acetonitrile fall in the range of *ca.* 1.49 to 1.54 V *vs* SCE [56] and hence electrografting is not possible at easily oxidised metals. It has been demonstrated [17, 23] that the electrooxidation of primary amines yields the radical cation that quickly deprotonates giving a radical with tautomeric forms. XPS spectra of modified metallic electrodes show peaks which can be assigned to metal-nitrogen bonding indicating that covalent attachment occurs through the amine nitrogen atom (Fig. 5). Electrografting of secondary

amines gives significantly lower surface coverages and no grafting occurs with tertiary amines, consistent with the progressively lower reactivities of the radical cations of these species.

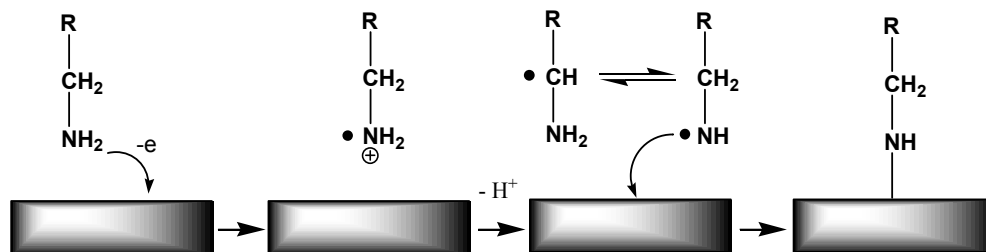


Fig. 5 Proposed mechanism for the electrografting of primary alkyl amines [57].

Buttry and colleagues have studied the thermal reaction of amines with carbon fibre [58]. Fibre was successfully modified with primary, secondary and tertiary amines by refluxing in the neat amine or in a concentrated tetrahydrofuran solution for 15 h to 5 days. For 1,6-diaminohexane, evidence of modification was obtained from FTIR-attenuated total reflectance (FTIR-ATR) spectroscopy, AFM and pH-dependent electrostatic binding of ferricyanide. The electrochemical response of the ferri/ferrocyanide couple allowed estimation of the amine surface coverage, giving $5 \times 10^{-11} \text{ mol cm}^{-2}$. To address the question of reaction mechanism, grafting of [(dimethylamino)methyl]ferrocene was also examined in detail because formation of an amide bond through reaction with surface oxygen functionalities is not possible with a tertiary amine. Electrochemical analysis of the treated fibres showed the response of the immobilized ferrocenyl group (surface coverage $\approx 5 \times 10^{-11} \text{ mol cm}^{-2}$), but at a more positive potential than in solution; the positive shift is consistent with the effect of a quaternized nitrogen which would result from nucleophilic attack of the amine at electrophilic C=C sites on the carbon surface. XPS analysis in the N 1s region of the modified fibres was also consistent with a quaternized nitrogen. The reaction was shown to be favoured in the presence of an acid catalyst leading the authors to propose a Michael-like reaction between amines and the carbon surface (Fig. 6). Supporting this proposal, the aromatic amine, 2-aminoanthraquinone, was also successfully grafted and XPS data were consistent with the presence of an amine, but not with an amide nitrogen.

The surface coverage of anthraquinone ($6 \times 10^{-11} \text{ mol cm}^{-2}$) was very similar to that measured after electrochemical modification of the carbon fibres by oxidation of 0.05 mM 2-aminoanthraquinone at 0.9 V vs SCE for 40 s.

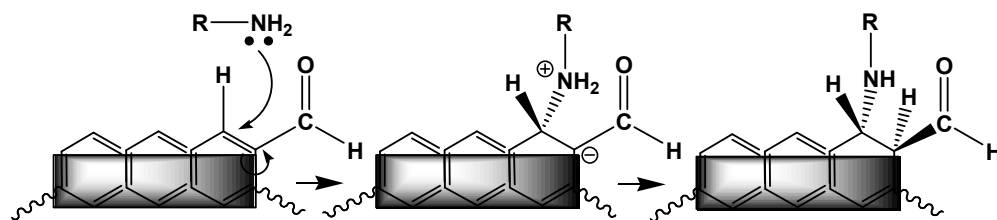


Fig. 6 Michael-like reaction of alkyl amines on a carbon substrate. The amine adds α to a carbon atom bearing an electron-withdrawing group [58].

Gallardo and co-workers recently reported a study of the spontaneous attachment of alkylamines to glassy carbon and metallic surfaces (Au, Pt, Cu, Fe) [57]. In contrast to Buttry's approach [58], the modification procedure involved simply dipping the samples into acetonitrile solutions of the amines (*ca.* 15 mM) at room temperature. Grafting of primary amines to all surfaces was confirmed by IR and XPS data. At metallic surfaces, a nitrogen-metal bond was detected by XPS, and IR revealed the formation of a secondary amino group. After spontaneous grafting of 4-nitrobenzylamine, followed by cleaning by sonication, the reversible reduction of surface nitrophenyl groups was detected. The observation of film electrochemistry after sonication confirms the strong attachment of the amine to the substrates. Electrochemically determined maximum surface concentrations of nitrophenyl groups were of the order of $10 \times 10^{-10} \text{ mol cm}^{-2}$ for all surfaces. Spontaneous reactions of secondary and tertiary were also attempted but no modification of any substrate was observed.

Comparing spontaneous and electrografting of primary amines, Gallardo and co-workers found that on GC, platinum and gold, spontaneous grafting proceeded slowly compared with electrografting. Note that copper and iron cannot be electrografted because they are more easily oxidized than 4-nitrobenzylamine or other aliphatic amines. On GC, 30 min spontaneous grafting from a 5 mM solution of 4-nitrobenzylamine gave a surface concentration of attached groups of $1.4 \times 10^{-10} \text{ mol cm}^{-2}$, whereas under the same conditions, electrografting gave $4.0 \times 10^{-10} \text{ mol cm}^{-2}$. Oxidation of GC, Fe and Cu

substrates prior to spontaneous grafting increased the surface concentration of attached film, compared with that at a polished surface, whereas reduction decreased the surface concentration. For polished GC, the coverage increased from $8 \times 10^{-10} \text{ mol cm}^{-2}$ to $12 \times 10^{-10} \text{ mol cm}^{-2}$ after mild oxidative pretreatment at 2 V vs SCE in acetonitrile, and decreased to $4 \times 10^{-10} \text{ mol cm}^{-2}$ when the electrode had received a prior reducing treatment (-3 V vs SCE in acetonitrile). The mechanism of grafting on carbon was briefly discussed by the authors. They propose that two mechanisms could proceed in parallel: a Michael reaction (Fig. 6) and nucleophilic attack on oxidized carbon. The latter, involving a surface ketone, would yield an imine link to the surface. Note however that the observed increase in surface grafting after mild oxidation could also be due to an increase in electron withdrawing surface groups (oxidised carbon functionalites) promoting the Michael reaction.

These studies provide convincing evidence for the covalent attachment of primary amines to carbon, however the mechanism for the non-electrochemical and electrochemical grafting reactions appear to be different. Electrochemical grafting is more rapid and gives higher surface concentrations; there is no evidence that thermally-induced or spontaneous room temperature reactions result in multilayer films, unlike electrochemically-assisted grafting [59, 60]. The latter aspect of the non-electrochemical methods may be advantageous for some applications, as is the possibility of grafting to easily oxidisable metals, not amenable to electrochemical grafting.

Grafting using ammonia

Moiroux, Savéant and co-workers have reported a very simple method for reacting ammonia with GC [61]. Polishing GC in the presence of ammonia gives a surface that readily reacts with activated esters resulting in a modifier layer coupled to the surface via amide bonds. The modified surfaces are stable to sonication suggesting that amine groups are covalently attached to the surface. The authors propose that abrasion of the GC surface generates dangling bonds that react with ammonia. This reaction is analogous to, but technically much simpler than, that reported earlier by Anson [62] and Murray [30] who generated oxide-free carbon by treating edge plane graphite and GC with argon

plasma and exposing the reactive surfaces to amine vapour. In this earlier work, modification of GC surfaces was also effected by polishing in the presence of alkenes. [30]

In Moiroux and Savéant's initial study, electroactive phthalimide and ferrocene derivatives of N-hydroxysuccinimide (NHS) esters were coupled with amine modified GC, giving electrochemically-determined maximum surface coverages of $4.7 \times 10^{-10} \text{ mol cm}^{-2}$ and $2.5 \times 10^{-10} \text{ mol cm}^{-2}$, respectively. To demonstrate the utility of the amine-modified GC, the material was used as a platform for assembly of tethers suitable for attachment of a wide range of biomolecules [61]. In later work, polyethyleneglycol chains were attached to GC through the same modification strategy for electrochemical studies of chain flexibility [63]. For immobilisation of a di-iron complex bearing a reactive N-hydroxysuccinimide ester functionality, Talarmin and co-workers compared the reactivity of a GC electrode functionalised by polishing in the presence of ammonia, with an electrode modified with aminophenyl groups by electrografting from a solution of nitrobenzenediazonium salt, followed by reduction of the grafted nitrophenyl groups [64]. The latter approach gave a higher yield of immobilised iron complex and better-defined voltammograms, leading the authors to comment that polishing in the presence of ammonia may give ill-defined surface sites with various functional groups. Hence while the spontaneous attachment of amino groups by polishing in the presence of ammonia is straightforward and useful, it does not allow a facile way to control the number of amino functionalities at the carbon surface.

Grafting using alkenes and alkynes

The thermally- and photolytically-assisted grafting of alkynes and alkenes to graphitic carbon materials has recently been demonstrated by several groups. In general, the procedures are similar to those employed for covalent modification of silicon and diamond surfaces. McCreery was the first to report modification of graphitic carbon, in the form of PPF, by thermal reaction with alkynes and an alkene [65]. The method was demonstrated using alkynes with the following substituents: Zn(II) porphyrin, ferrocenyl, trifluorotolyl and 5-chloropentyl, and with a Zn(II) porphyrin alkene derivative. Grafting

was carried out under an inert atmosphere using alkynes and alkene as neat liquids, or after dissolution in THF and drop-coating. XPS analysis of all grafted layers gave the expected elemental compositions, and voltammetric analysis of surfaces reacted with the electroactive porphyrin and ferrocene derivatives showed the expected redox couples. Monitoring the voltammetry of surfaces prepared by reaction with the Zn(II) porphyrin with the alkyne linker showed that maximum surface concentration ($3.0 \times 10^{-10} \text{ mol cm}^{-2}$) was obtained for a substrate grafting temperature of 330 °C and grafting time of 3 min. When lower temperatures were used, longer grafting times were required, however prolonged heating at 330 °C led to some dimerisation of the alkyne. AFM depth profiling of the film revealed an average thickness of $1.42 \pm 0.38 \text{ nm}$, consistent with monolayer coverage of porphyrin in a tilted configuration. Surface IR studies provided strong evidence for a reaction between the alkyne and carbon surface, rather than simple physisorption of the modifier. Bands attributable to the alkyne group were absent after the grafting reaction and spectra confirmed the tilted configuration of the porphyrin rings. This is in contrast with the flat-on-the-surface adsorption observed for the porphyrin without an alkyne linker. The atomic percentages determined by XPS did not change after sonication of surfaces in acid or base, also indicating strongly attached layers.

In a second example of the thermally-assisted reaction of an alkene with a graphitic carbon substrate, Godet and co-workers used amorphous carbon films, grown using plasma decomposition of methane and graphite sputtering in Ar-H₂ [66, 67]. After sputtering, films were subjected to various times of argon ion bombardment and thermal annealing under ultrahigh vacuum, giving eight distinct surfaces with oxygen atomic percent ranging from 0.8 to 5.8 [67]. Reaction with ethyl undecylenate was carried out overnight in the neat liquid alkene under an inert atmosphere at 120 or 160 °C. Evidence for surface modification was obtained from XPS measurements of surfaces before and after reaction with alkene. Changes in the spectra after reaction with the alkene were consistent with the expected ester-terminated layer and the magnitude of attenuation of the argon signal (argon is implanted in the amorphous carbon film during preparation) was consistent with a grafted monolayer of 1.6 nm thickness. Further evidence for the presence of an ester-terminated film was obtained by converting the ester to the carboxylic acid and coupling with 4-aminomethylpyridine and 2-aminoethylferrocenyl-

methylether. These reactions also led to the expected changes in XPS spectra. The thermal stability of the ester layer was tested by heating under vacuum and monitoring the XPS spectra. No changes were observed on heating up to 180 °C, and the layer appeared largely intact at 345 °C, suggesting that the ester is indeed covalently grafted to the surface. Detailed analysis of XPS spectra afforded estimates of the surface concentration of grafted ester, pyridine and ferrocene groups. Surface concentrations of attached molecules ranged from $< 0.2 \times 10^{14} \text{ cm}^{-2}$ ($< 3 \times 10^{-11} \text{ mol cm}^{-2}$) for amorphous carbon samples with the highest oxygen content, to $4.3 \times 10^{14} \text{ cm}^{-2}$ ($7 \times 10^{-10} \text{ mol cm}^{-2}$) for amorphous carbon samples with the lowest oxygen content. As expected, surface concentrations of coupled pyridine and ferrocene groups were in all cases lower than of those of the parent ester modified surface.

McCreery's study [65] described above provides convincing evidence for the formation of covalently attached monolayers through thermal reaction with alkynes and alkenes with PPF, and the results of Godet and co-workers obtained at amorphous carbon support that conclusion [66, 67]. The mechanism of the reaction is not clear however. Godet reports that thermal grafting reaction does not proceed at the basal plane of freshly cleaved HOPG, pointing to the involvement of edge plane sites [67]. The authors outline several possibilities based on mechanisms proposed for thermal reactions of similar species at diamond [68, 69, 70] and silicon [71, 72] surfaces, and the earlier work of Mazur and Murray, who proposed that surface carbon radicals form when carbon substrates are heated under vacuum or are abraded in the absence of air [29, 30]. Figures 7-9 depict possible reaction pathways.

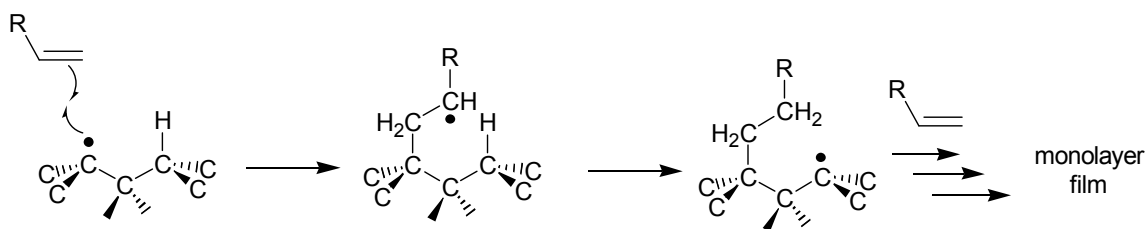


Fig. 7 Proposed mechanism for the addition of alkenes to a H-terminated sp^3 carbon surface.

Figure 7 shows the type of mechanism proposed for thermal reactions of alkenes at H-terminated diamond, germanium and silicon surfaces. The reaction could be initiated by C-H bond homolysis, or adventitious radicals associated with the carbon substrate. While this mechanism is unlikely to be important for reactions at PPF films with their relatively low sp^3 carbon content, it cannot be discounted at the amorphous carbon films of Godet and co-workers which have some sp^3 carbon content, significant bulk hydrogen levels but an unknown amount of surface hydrogen coverage [66, 67].

Figure 8 shows representative cycloadditions on H-terminated sp^2 carbon edge sites with alkenes and alkynes, as proposed by McCreery's group [65]. The reactions are analogous to the well-established cycloaddition reactions of alkenes and alkynes with Si(100)-2 x 1 and Ge(100)-2 x 1 surfaces and are a possible reaction pathway at PPF and amorphous carbon films.

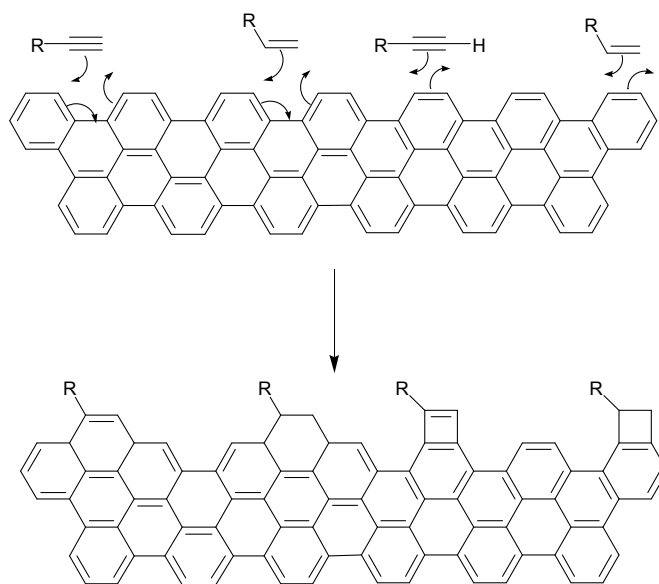


Fig. 8 Proposed mechanism for cycloadditions reactions of alkenes and alkynes on H-terminated sp^2 carbon edge sites [65].

Figure 9 represents the pathway proposed in the 1970s by Mazur and Murray [29, 30] for the reaction of alkenes with oxide-free carbon, produced by heat treatment under vacuum or by surface abrasion in an inert atmosphere. Removal of surface oxygen functionalities from edge plane sites and exposure of bulk carbon is suggested to result in surface radicals. The treated surfaces react at room temperature with alkenes giving

stable attached layers. The temperature used to activate the surface in Mazur's study (1020 °C) is significantly higher than that used for the thermal grafting reactions of McCreery and Godet, however the effectiveness of lower activating temperatures was not reported by Mazur. Hence this reaction pathway cannot be discounted for the thermal grafting of alkenes and alkynes.

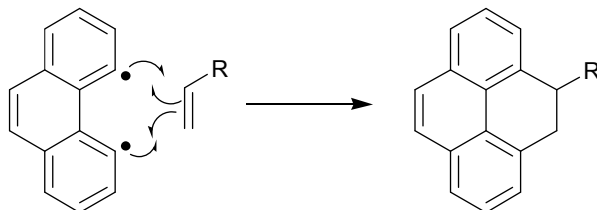


Fig. 9 Radical-based reaction of alkene with oxide-free, edge plane carbon.

Photografting of alkenes to H-terminated GC substrates has been utilized by Hamers' group to prepare stable biorecognition layers [73]. The grafting methodology followed that previously established for functionalisation of diamond surfaces, beginning with treatment of GC with hydrogen plasma followed by drop-coating the surface with alkene and irradiating with UV light (254 nm) in an inert atmosphere. Trifluoroacetamide- and *tert*-butoxycarbamate- protected 10-aminodec-1-ene were grafted by this procedure giving amine functionalized surfaces for subsequent covalent attachment of biotin and DNA oligonucleotides. Surface concentrations of biomolecules were found to be close to those expected for close-packed monolayers (based on the geometric area of the GC surface): 88 % of a close-packed monolayer for DNA, and 78 % for avidin bound at the biotin-modified surface. The packing of the photografted amine tether layer was not investigated and cannot be deduced from the surface concentrations of biomolecules because the packing of these relative large molecules is presumably not limited by the number of tether sites. However, based on the surface concentration of DNA, the surface concentration of amine groups was at least $(4.67 \pm 0.07) \times 10^{-11} \text{ mol cm}^{-2}$.

More recently, Hamers has reported a detailed study of the photografting of an alkene to H-terminated amorphous carbon thin films [74]. Films were prepared by DC magnetron sputtering and electron-beam evaporation giving amorphous materials with a high sp^2 carbon content. Following the same procedure as described above for photografting to H-terminated GC surfaces, trifluoroacetamide- protected 10-aminodec-

1-ene was attached to the amorphous carbon film surface. The loss of the double bond of the alkene group during grafting was confirmed by IRRAS indicating that the alkene was not simply physisorbed to the surface. Estimates of surface concentration derived from XPS measurements gave a lower limit value of *ca.* 1×10^{-9} mol cm⁻² (based on the geometric surface area) which was assumed to correspond to a close-packed monolayer of modifier. Note however that the thickness of the grafted layer was not reported and hence the possibility of multilayer formation (with loosely packed modifiers) cannot be discounted. After reaction of the amine layer with DNA oligonucleotides, repeated cycles of hybridization and denaturing with a complementary sequence were made. There was no detectable loss of DNA from the surface, indicating highly stable layers under the reaction conditions. Quartz crystal microbalance wafers were also coated with amorphous carbon films and functionalized with DNA using the same methodology, allowing DNA hybridization to be studied in real time.

We have taken a very simple approach to photografting of alkenes to GC and PPF surfaces [75]. The carbon substrate was not treated with hydrogen plasma, and photolysis (254 nm) was carried out in air using carbon substrates that had been spin coated with neat alkene (1-decene, ethyl- 10-undecylenate and *1H, 1H, 2H*-perfluoro-1-decene) or an acetonitrile solution of the alkene (1-undecylenic acid). The method was also demonstrated using the alkyne, ethynylferrocene. Surface topographical and depth-profiling measurements using AFM, water contact angle measurements and voltammetry of redox probes at the modified surfaces indicated that loosely-packed monolayers were formed by photolysis of 1-decene, ethyl-10-undecylenate and 1-undecylenic acid. Significantly thicker films were formed by photolysis of *1H, 1H, 2H*-perfluoro-1-decene and ethynylferrocene. For the latter modifier, the electrochemistry of the attached ferrocenyl group gave a surface concentration of *ca.* 3.6×10^{-10} mol cm⁻² for a film thickness of (3.0 ± 0.2) nm, consistent with a loosely packed multilayer. Further reactions of the grafted layers were examined. The surface prepared by photografting 1-undecylenic acid was shown to react with activated amines, and that prepared from 1-decene was activated by photolysis in the presence of oxalyl chloride and subsequently reacted with amines in high yield.

Detailed consideration of the mechanism for photografting alkenes and alkynes to GC, PPF, and H-terminated GC and amorphous carbon has not been included in the above studies. Alkenes do not absorb at the wavelength employed for photografting and no grafting occurred in the absence of UV irradiation [75], hence the UV activation of the carbon surface appears to be involved in the initiation of grafting. Hamers suggests that the mechanism of grafting on H-terminated amorphous carbon is likely to be analogous to that operative at H-terminated diamond surfaces [74]. The surface of hydrogen-plasma treated GC has been shown to have sp^3 diamond-like character [76, 77] and so reaction at these sites is expected. For H-terminated diamond, it is proposed that grafting is initiated by photoemission of electrons from the surface to the liquid phase, forming radical anions that abstract H atoms from the surface [78]. The surface radical can react with the alkene, as shown in Fig. 7. The authors point out that charge neutrality must be maintained for the diamond material, and hence reactions such as loss of protons from the surface or transfer of electrons back to the surface via oxidation of liquid phase species must also be involved.

The importance of hydrogen abstraction in photochemical reactions of alkenes and alkynes with polished GC and PPF surfaces is difficult to assess. The amount of H-terminated sp^3 carbon at the surface of these materials is unknown but is generally considered to be low. Hydrogen abstraction from sp^2 edge sites is also a possibility but would be considerably less energetically favourable than abstraction from sp^3 carbon. However only loosely packed photografted layers are formed on these surfaces [75], possibly indicating that reaction occurs through hydrogen abstraction. On the other hand, assuming that the alkene or alkyne can be reduced by photoemitted electrons, the radical produced is expected to be able to react directly with the surface in the same manner (as yet unknown) as for the spontaneous reactions of aryl radicals with graphitic carbon. After coupling, various deactivation pathways could operate, including transfer of an electron back to the surface and hydrogen abstraction from another alkene molecule.

Grafting using azides and diazirines

When irradiated with UV light, azides and diazirines eliminate dinitrogen to generate reactive nitrenes and carbenes, respectively. Kuhr and co-workers have developed this

approach for covalently grafting biotin to graphitic carbon surfaces [79, 80, 81, 82]. Photobiotin, which is the nitroaryl azide derivative of biotin, gives the corresponding nitrene on irradiation. The singlet state can insert into O-H and N-H bonds and the triplet into C-H bonds, giving several pathways for grafting to a graphitic carbon surface. Using this chemistry, Kuhr's group demonstrated two methods for generating micron-scale patterns of biotin on GC surfaces. In their first approach to photopatterning, a GC surface coated with a film of photobiotin was exposed to a laser diffraction pattern (325 nm) for 60 s, resulting in 5 μm lines of biotin, with a spacing of 10 μm [79, 80]. In their second method, UV laser light (325 nm) was focused on the photobiotin-coated GC surface and the GC was moved in the controlled manner to 'write' covalently-attached biotin features on the surface, with line widths of 5 -10 μm [82]. A similar approach to biotin patterning has also been reported based on irradiation of the photobiotin surface through a mask [83]. The biotin-derivatised surfaces react with avidin-tagged enzymes, providing a general and versatile method for enzyme immobilization on carbon surfaces.

A drawback of the photobiotin approach is that the grafting of biotin was found to be patchy [79, 82]; this may be attributed to the poor reactivity of the nitrene with the GC surface which is expected to present a low concentration of C-H and O-H bonds. On the other hand, the carbene generated photolytically from diazirines can insert into C-C and C=C bonds and hence is expected to react with high yield at carbon surfaces. Using a (trifluoromethyl)diazirine derivative of biotin and their maskless photolithography methods, Kuhr and co-workers obtained a significantly more homogeneous surface coverage of immobilized biotin than when using photobiotin, confirming that carbene-generating species are a better choice than nitrene-generating species for photografting reactions at graphitic carbons [81].

Very recently, the spontaneous reaction of iodine azide with PPF was reported by Devadoss and Chidsey as a route to the preparation of azide-modified graphitic carbon [84]. To obtain the maximum surface concentration of grafted azide, PPF samples were immersed in a 10 mM acetonitrile solution of the azide for 60 min or longer at room temperature. Characterisation of the modified surfaces by XPS showed the expected N1s signals and an estimated surface concentration of $(7.3 \pm 1.4) \times 10^{13}$ molecules cm^{-2} ((1.2

$\pm 0.6) \times 10^{-10} \text{ mol cm}^{-2}$). The grafting reaction was proposed to proceed at the edge plane sites via a Hassner-type addition to C=C bonds, followed by elimination of HI, Fig. 10.

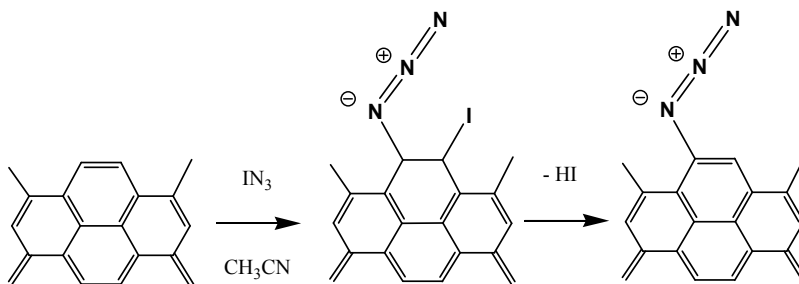


Fig. 10 Proposed mechanism for reaction of iodine azide with PPF [84].

The azide terminated surface gives a versatile platform for reaction with alkyne derivatives via ‘click’ chemistry. XPS monitoring of the reaction with ethynylferrocene suggested 100 % yield and the electrochemically determined surface concentration of ferrocene groups ($2.0 \times 10^{13} \text{ molecules cm}^{-2}$) was in reasonable agreement with XPS data. No ferrocene could be detected after similar experiments at a basal plane graphite surface, whereas at edge plane graphite, the surface concentration of ferrocene groups was approximately double that at PPF. These findings support the grafting mechanism shown in Fig. 10. The utility of the modification method was further demonstrated by successful reaction of the azide-modified PPF surface with 1-ethynyl-4-(trifluoromethyl)-benzene. Using XPS, the triazole linker was shown to be stable to acid hydrolysis, indicating that the approach should have wide synthetic applicability. One obvious drawback is the care required during preparation and grafting of the potentially explosive iodine azide.

Concluding remarks

The modification methods described above are a useful addition to the well-established electrochemical methods for covalent grafting to carbon surfaces. Methods relying on reducing agents in homogeneous solution, spontaneous and thermally-promoted reactions have a practical advantage when the sample dimensions or form make an electrochemical approach difficult, or when electrochemical instrumentation is not available. (Note however that with respect to grafting from aryldiazonium salts and amines,

electrochemical methods are faster and give easier control of film thickness.) Non-electrochemical methods can also offer practical advantages when patterning of surfaces is required. Combining photochemical attachment strategies with standard photolithography techniques gives a straightforward approach to patterning modifiers. Considering the higher yield for attachments proceeding via the formation of a carbene than a nitrene, patterned grafting via photolytic generation of carbenes is an approach that could be further explored. Microcontact printing onto graphitic carbon surfaces using the spontaneous reaction of aryldiazonium salts [52] is a simple method that we are developing in ongoing work. Although we previously reported patterning methods using soft lithography and electrochemical grafting procedures [85], microcontact printing is a more straightforward (although currently less controllable) approach which may be extended to other modifiers which graft spontaneously at room temperature.

An attractive aspect of the new grafting methods is the range of groups that have been attached. In particular, grafting aliphatic modifiers directly to carbon surfaces via reactions involving alkenes and alkynes complements the electrochemical and non-electrochemical methods for attachment of aromatic species. Fabrication of interfaces with particular functionality is clearly simplified when there is a range of surface reactive groups that can be used to introduce the functionality to the surface. Grafting procedures which reliably result in no more than monolayer coverage are of particular interest and layers grafted by UV and heat treatment of alkenes and alkynes appear promising in this regard.

The mechanisms of the non-electrochemical grafting reactions are generally not well-understood and further progress in this area will no doubt lead to better control of reactions and a better understanding of their scope. The reactions range from those where activation of the modifier is independent of the surface (photografting based on azides and diazirines) to those where the surface is intimately involved in initiation of the reaction (photografting of alkenes and alkynes). For other reactions, classical organic chemistry between edge plane and the modifier has been proposed (thermal grafting of alkynes and alkenes to PPF, spontaneous grafting of iodine azide to the same substrate and thermal grafting of amines to carbon fibres and GC). The mechanism of initiation of spontaneous grafting of aryl groups from aryldiazonium salts requires further

investigation. The nature of graphite edge plane sites that react with radicals, and the mechanisms for those reactions are also not understood.

There is one brief report of spontaneous grafting onto GC from iodonium salts [20]. A low surface coverage of grafted nitrophenyl groups was detected after immersion of a GC electrode into a 2 mM solution of 3,3'-dinitrodiphenyliodonium in 0.1 M Bu₄NBF₄ - acetonitrile for 10 min. Electrografting from iodonium salts provides a route for surface attachment of both aryl and alkynyl groups [11, 20] and it would be interesting to establish the scope of the spontaneous reaction. Iodonium cations are reduced at considerably more negative potentials than aryldiazonium cations, hence it seems unlikely that they could be reduced by the carbon substrate. More detailed examination of spontaneous grafting from iodonium salt solutions may offer mechanistic insights that are also relevant to spontaneous grafting from aryldiazonium salts.

In summary, there is considerable scope for further development of these non-electrochemical methods for modifying graphitic carbon substrates. Gaining a better understanding of the reaction mechanisms will lead to increased opportunities for exploitation of the methods.

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