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FEATURE ARTICLE

Doped Glassy Carbon: A New Material for Electrocatalysis

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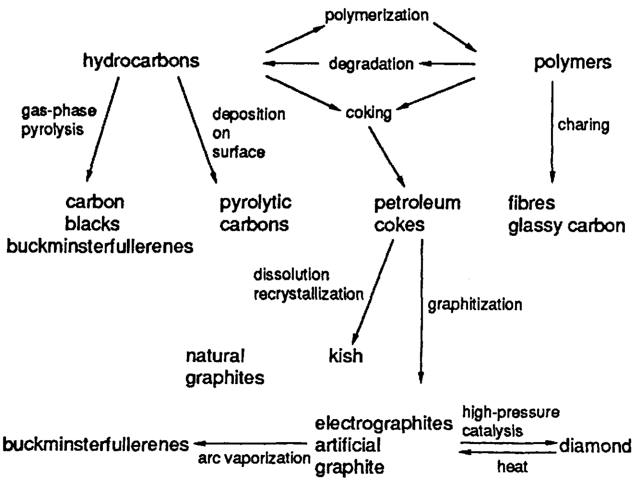
Glassy carbon is an important material for electrochemical catalysis, particularly as an electrode material. Current methods for the preparation of glassy carbon are described, together with a discussion of recent progress in the modification of the surface of glassy carbon. Surface modification of glassy carbon, with the intent of mediating its electrochemical behaviour, remains an important research topic. Methods to achieve this goal, including surface absorption of electrochemically active species, covalent attachment of active species and coating the surface of glassy carbon with thin films, are reviewed briefly. We describe a new low-temperature approach to preparing homogeneously modified, rather than surface modified, glassy carbon, using the thermolysis of poly(phenylene diacetylene)s as the carbon solid precursor. This methodology is compatible with the introduction of a wide variety of heteroatoms, including nitrogen, silicon and fluorine, and allows the preparation of thin films of glassy carbon. The incorporation of platinum in various oxidation states is described and the electrochemical response of the platinum-doped glassy carbons is described.

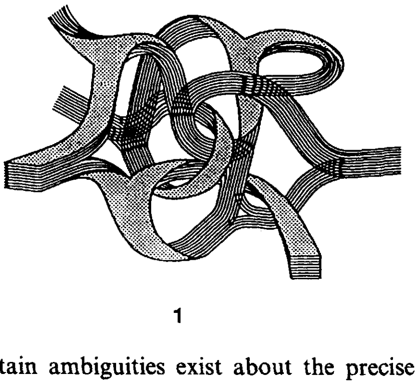
Keywords: *Feature article*; *Glassy carbon*; *Electrocatalyst*; *Electrode material*; *Platinum*

Graphitic carbons have found widespread use in electrochemical systems owing to their high electrical conductivity, good corrosion resistance, and reasonable mechanical and dimensional stability. Specific applications of graphitic carbons include its use as an electrode, as electrocatalyst supports, and as bipolar electrode separators. Because of the high ash content of natural graphites, most graphitic carbons that are used in electrochemical applications are prepared from hydrocarbon sources. A unique feature of synthetic graphites is the wide variety of microstructures accessible, depending upon the source of the carbon precursors and the method of preparation (Scheme 1).[1] A detailed discussion of synthetic graphites is beyond the scope of this paper, however, the conventional preparation and physical properties of various carbons have been thoroughly reviewed by Kinoshita.[2]

Of these various forms of carbon, glassy or vitreous carbon (GC) is the most important for use as an electrode. Glassy carbon derives its name from exhibiting fracture behaviour similar to glass, from having a disordered structure over large dimensions (although it contains a graphitic microcrystalline structure), and because it is a hard shiny material, capable of high polish. Glassy carbon is particularly useful in electrochemical applications because of its low electrical resistivity, impermeability to gases, high chemical resistance, and because it has the widest potential range observed for carbon electrodes.[3] Glassy carbon was first prepared by Yamada and Sato in 1962 by the high-temperature pyrolysis of phenolic resins,[4] and later by Davison who used cellulose as the starting material.[5] A model for the structure of glassy carbon has been proposed by Jenkins and Kawamura.[1] They concluded that glassy carbon (**1**) consists of long microfibrils that twist, bend, and interlock to form interfibrillar bonds, and that these microfibrils are randomly oriented.



Scheme 1



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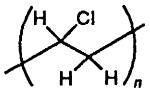
While certain ambiguities exist about the precise molecular structure of glassy carbon, this model does take into account the relatively low density of glassy carbon, *ca.* 1.5 g cm^{-3} compared with 2.3 g cm^{-3} for graphite (which suggests the existence of voids), the impermeability of glassy carbon to gases (which suggest that these voids are not connected), and the isotropic conductivity observed for glassy carbon.

The current approach used for the conventional preparation of glassy carbon solids involves the careful pyrolysis of one of a variety of polymeric materials including poly(vinyl chloride) (**2**), poly(vinylidene chloride) (**3**), cellulose (**4**), phenolic resin (**5**), poly(furfuryl alcohol) (**6**), and poly(acrylonitrile) (**7**).[1,6]



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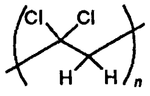

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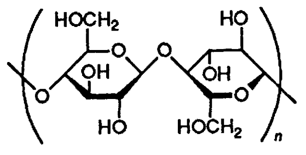

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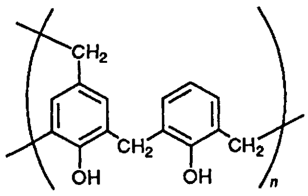

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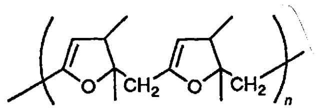

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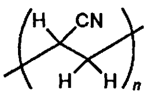

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The processing requirements for the preparation of glassy carbon are quite exacting. A typical procedure using a phenol–formaldehyde resin entails first preparing a solution of the resin in methanol. The methanol solution is then poured into a mould and the solution heated at 0.3 °C h^{-1} to 90 °C to drive off the methanol. The moulds are cooled and the solid removed. The solid is then heated at 2 °C h^{-1} to 1000 °C, then heated further at 0.5 °C h^{-1} to 3000 °C. The size of an artifact produced in this way is limited to *ca.* 3 mm in thickness.[1] Other representative approaches to other forms of glassy carbon include the rapid carbonization (4 s) of droplets of polymerized furfuryl alcohol in a thermal reactor followed by further thermal treatment at 1600 °C to produce *ca.* 40 μm particles of glassy carbon;[7] and alternatively, forcing a solution of poly(acrylonitrile) (8%) in aqueous sodium thiocyanate solution (50%) through a spinneret hole (with guide rollers adjusted to stretch the fibre by a factor of 3) into a coagulating bath of aqueous sodium thiocyanate solution (10%) followed by gradual heating to 2500 °C to produce carbon fibre composed of a graphitic outerlayer with a glassy carbon core.[1] It is important to note that all current approaches to synthetic graphites, including glassy carbon solids, require extensive heat treatment (1000–3000 °C).

The chemical transformations that occur on the formation of glassy carbon are, of course, dependent on the starting polymer. In general, thermal treatment of **2**–**7** to *ca.* 500 °C results in the loss of small molecules such as carbon monoxide, carbon dioxide, hydrogen chloride, hydrogen cyanide, water, and small hydrocarbons. Above 700 °C, the loss of hydrogen results in the formation of carbon–carbon bonds and a highly cross-linked structure.[6] The extreme thermal requirements for these syntheses yield glassy carbon with $<0.5\%$ of any element other than carbon, independent of the precursor material.

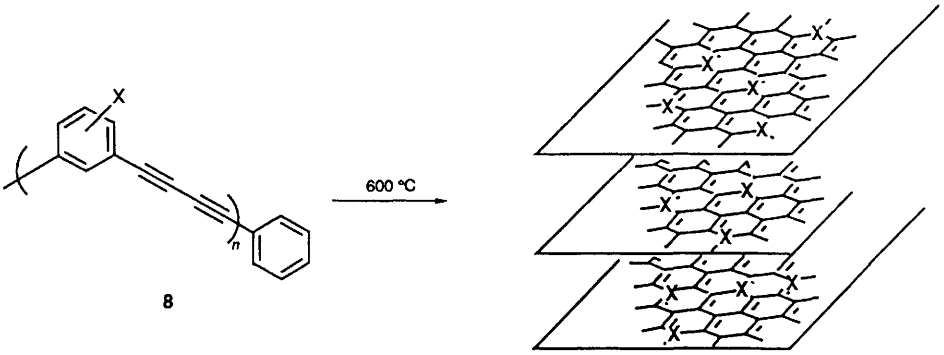
Modification of Glassy Carbon Electrodes

The first application of glassy carbon as an electrode was reported in 1965.[8] As noted earlier, glassy carbon is a versatile electrode material because it is chemically inert with a wide potential range and also because it is non-porous and can be polished.[3] Although glassy carbon operates well as an electrode material, deriving desired catalysis often requires chemical modification of the surface. Notably, the electrochemical properties of glassy carbon are strongly influenced by its thermal and chemical history and by its exposure to reactive species.[9–13] Indeed, most electrochemical reactions require the interaction of ions and/or molecules with the electrode surface and, as a result, are strongly dependent on the composition and structure of the electrode surface.

Because of the desire to impart selectivity to electrochemical reactions and to control electron transfer kinetics, several investigators have utilized adsorption or covalent bonding of catalysts to the glassy carbon surface. The intent of these modifications is to control the interaction of molecules and ions with the electrode surface. These superficially chemically modified electrodes (CMEs) include the incorporation of a variety of molecular catalysts and mediators by adsorption, covalent bonding, or incorporation in a polymer film and the many approaches have been reviewed.[14–18] The catalyst can then act as an electron-transfer mediator, an adsorption site (*e.g.* Pt particles), or as a promoter of multistep reactions (*e.g.* O_2 reduction). The effects of such alterations can enhance the electrocatalytic properties of an electrode by changing its selectivity toward electroactive species, by modification of the reaction rate, or by increasing the corrosion resistance of the surface. These surface modifications have resulted in the use of glassy carbon electrodes for many important electrocatalytic reactions including dioxygen reduction, the hydrogen evolution reaction (HER), methanol oxidation, glucose oxidation, biosensors, *etc.* It should be noted that in most of the examples of the preparation and chemistry of CMEs described below, the underlying goal is the *surface* modification of the glassy carbon electrode.

Alternative approaches for effecting control of the catalytic activity of carbon-based electrodes involves the preparation of materials that incorporate an electroactive species both in the interior and on the surface of the electrode. These approaches include the preparation of composite electrodes where an electroactive species is added to a conductive material such as carbon black and the mixture is then bound in a polymeric matrix.[18–22] An attractive feature of these composite electrodes is that they offer high stability for catalysis and an easily renewable surface by simple polishing of the electrode.

We have pursued an alternative approach to the preparation of modified glassy carbon materials by the synthesis of new carbon solids which contain elements other than carbon.[23–25] These dopants are incorporated into the carbon solid and significantly modify the structure and surface energy of the electrode surface which ultimately controls the interaction of small molecules with the surface. These new doped glassy carbon materials (DGC) exhibit excellent behaviour for electrocatalysis.[24,25] We have found that the incorporation of dopants, including halogens and metals, on the molecular level in a carbon precursor, a poly(buta-1,3-diynyl-1,3-phenylene), (**8**), followed by thermolysis at relatively low temperatures (< 600 °C), results in a conductive, dimensionally stable carbon matrix containing the dopant (**9**) (Scheme 2).[24] We have also found that the thermolysis of carbon precursor systems that are doped with metals results in the formation of metal particles of controlled composition, size and catalytic activity.[25] The glassy carbon precursors are soluble in typical organic solvents allowing the preparation of thin, continuous films (< 1 μm thick) of DGC materials on a variety of substrates including conventional glassy carbon and high-surface-area carbons. Exposure of metallic dopants or a new heteroatom-



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Scheme 2

doped carbon-based surface at the electrode–solution interface then imparts catalytic properties to the underlying material.

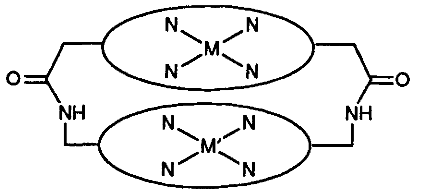
The fundamental novelty of our approach is the synthesis of new carbon matrices which, by necessity, result in the formation of new carbon-based surfaces rather than the superficial chemical modification of conventional glassy carbon. The resulting DGC materials are extremely robust and the surface is easily renewable. Importantly for the demands of different electrocatalytic chemistries, the composition of the solid can be varied, effectively changing the surface of the electrode.

A brief discussion follows of selected reports concerning the chemical modification of electrode surfaces (CMEs) with catalysts by three primary methods: chemisorption, covalent attachment, and entrapment in polymers adsorbed or covalently attached to the electrode surfaces. The focus of the discussion concerning CMEs is the historical development of methodology for the modification of carbon surfaces by these many methods with the goal of deriving desired electrocatalysis. These reports prompted our efforts in the preparation of DGC materials and we detail their synthesis, characterization and remarkable electrocatalytic activity later in this article.

Chemisorption of Electrocatalytically Active Centres to Electrode Surfaces

In 1973, Lane and Hubbard reported the adsorption of various alkenes on a platinum electrode.[26,27] These alkenes could also serve as ligands for iron and platinum delivering the electroactive metal centre to the electrode surface. In 1964 Jasinski reported the reduction of O_2 in an alkaline electrolyte with an adsorbed cobalt phthalocyanine on a nickel electrode.[28,29] These reports, which demonstrated a possible alternative to expensive platinum-based fuel-cell systems, prompted a dramatic increase in research efforts on similar organometallic systems adsorbed on carbon electrodes for use in both alkaline and acid fuel cells.[30–48] The effectiveness of the different porphyrin or phthalocyanine complexes for oxygen reduction catalysis can be explained in part by a strong adsorption of the metalloporphyrin or metallophthalocyanine on the carbon electrode, the effective electron transfer activity of complex, and by the presence of axial ligation sites[46] where redox chemistry can be controlled. In general, higher O_2 reduction activities are obtained if the adsorbed phthalocyanines are subjected to thermal activation, often at elevated temperatures (600–800 °C), before use.[49–53] The heat treatments used often exceed the reported thermal stability of the phthalocyanine compounds themselves suggesting that the enhanced O_2 reduction activity is a consequence of formation of a species other than the original metalloporphyrin or metallophthalocyanine. Suggestions for the fate of the metal chelate on high-temperature treatment include the formation of metallic particles and the destruction of the periphery of the chelate ligand leaving the metal–N_4 moiety.[49,52,54–57]

Particularly informative studies of dioxygen reduction with metal porphyrins have been performed by Collman, Anson and co-workers.[34,39,58–60] Their investigations were focused on the catalytic properties of dimeric, homo- and heterobimetallic face-to-face porphyrins (**10**) with metal combinations including cobalt–cobalt, cobalt–iron, cobalt–silver, and cobalt–manganese. These complexes were conceived for the purpose of activating molecular dioxygen and the cofacial structure provided a framework for the stable binding of a dioxygen molecule. This approach led to an effective catalyst for the reduction of dioxygen to water in acidic solution. These bimetallic face-to-face porphyrins adsorbed on a graphite electrode reduced oxygen at a potential near +0.68 V *vs.* NHE in 0.5 mol dm^{-3} trifluoroacetic acid. Platinum, which is the most effective metal catalyst for this chemistry, operates at +0.63 V *vs.* NHE in trifluoroacetic acid. Although these complexes suffer decomposition too rapidly to allow their implementation in a fuel cell, the studies of these metalloporphyrins adsorbed on electrode surfaces demonstrate clearly that alternatives to the use of platinum for dioxygen reduction are possible.



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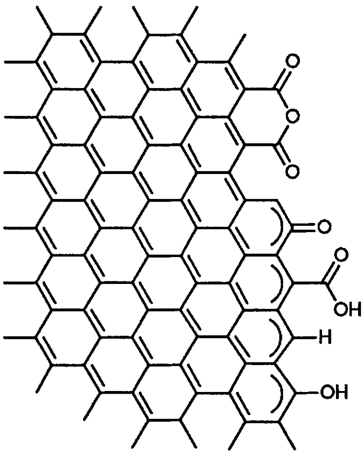
In addition to the ability to effect dioxygen reduction, iron, copper, nickel, and cobalt porphyrins and phthalocyanines, adsorbed onto glassy carbon or graphite electrode surfaces, have shown strong electrocatalytic effects for the oxidation of ascorbic acid[61] and hydrazine,[62,63] and the reduction of sulfur dioxide[64] and alkyl halides.[65,66]

Covalent Bonding of Electrocatalytically Active Centres to Electrode Surfaces

The affinity of most organometallic complexes or salts for a carbon surface is not high enough to prevent the rapid loss of the catalyst. An alternative to the often weak chemisorption of a catalyst to the electrode surface is the formation of a covalent bond between the catalyst and the carbon surface. However, on a typical glassy carbon surface, the density of chemical functionalities is low. Therefore, chemical treatment of the carbon surface is necessary to generate synthetically useful carboxylic acid and hydroxy groups on the edge planes (**11**).



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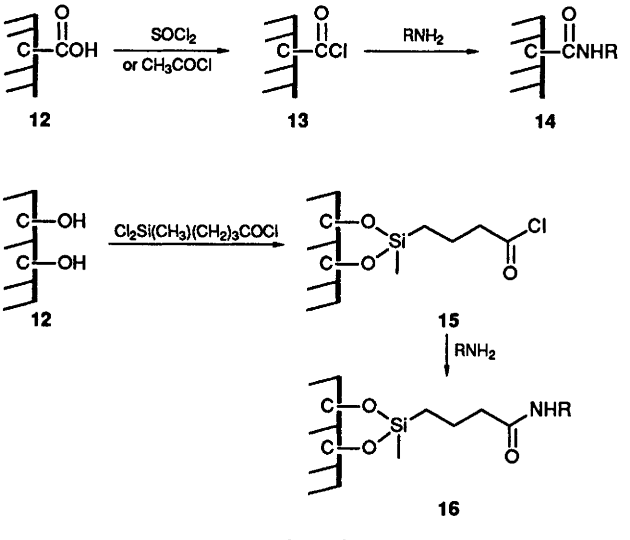
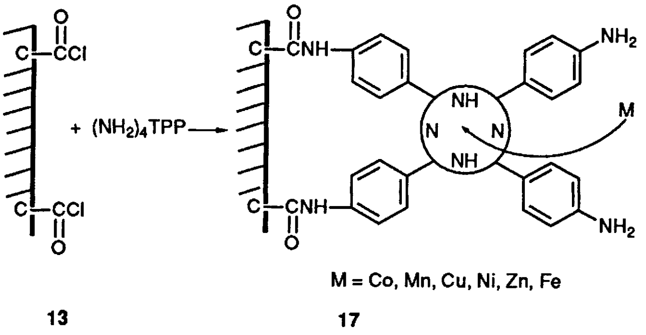
The carboxylic acid functionality on carbon, generated by thermal or oxygen plasma oxidation,[67] can be coupled with amines or alcohols[68] after activation with thionyl chloride,[69–72] acetyl chloride,[72] or following silanization[73] (Scheme 3). A dramatic example of the effect of surface-bound molecules on the course of the electrochemical reduction of ketones was reported by Miller and co-workers.[69] A graphite rod was heated in air at 160 °C to introduce oxygen functionality on the carbon surface. Subsequent treatment of the electrode with thionyl chloride followed by reaction of the activated surface with the methyl ester of L-phenylanaline gave an electrode that exhibited asymmetric induction for the reduction of carbonyl groups.



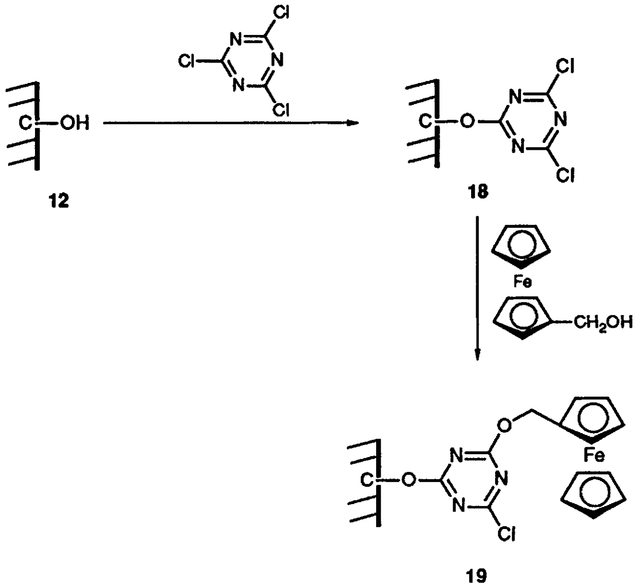
Scheme 3

Murray and co-workers used Miller's procedure[69] or silanization methodology for the introduction of acid chloride functionality onto a carbon surface and were able to immobilize tetra(aminophenyl)porphyrins and a variety of metal complexes onto glassy carbon electrodes.[70,71,74] The immobilized porphyrins were metallated with Co, Mn, Cu, Ni, Zn or Fe before or after surface immobilization (Scheme 4). These bound metalloporphyrins exhibited electrochemical redox reversibility and the redox potential of each metal complex was not greatly affected by the immobilization on the surface.[74] Anson and Koval were able to prepare a pyridine functionalized carbon electrode by activation of a graphite surface with thionyl chloride followed by reaction with 4-methylaminopyridine.[75] The electrode surface was effectively modified by reaction of the pyridine surface with (pentaammine)ruthenium(II) hydrate in water. The covalently attached ruthenium centre was retained on the carbon surface more effectively than an analogous ruthenium complex bound to the surface by adsorption through a pendant aromatic ligand.



Scheme 4

In addition to the functionalization of carbon surfaces by heating in air or by exposure to oxygen plasmas, the coupling yield of reagents onto carbon surfaces can be enhanced by argon plasma treatment[76] or mechanical abrasion[77] in order to produce 'oxide-free' carbon. Anson and co-workers exposed a carbon surface to an argon plasma and then to amine gases.[76] After carbodiimide coupling with nicotinic acid, the 'carbon pyridine surface' was subsequently coupled with $Ru(NH_3)_5(OH_2)^{3+}$. This argon plasma treatment procedure permits immediate exposure to the attaching reagent without surface functionalization; however, the approach produces a low coverage of reactive functionality. Yacynych and Kuwana reported the surface attachment of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) to a pyrolytic graphite surface which offers a potentially general linking group for coupling with nucleophilic electroactive materials (Scheme 5).[78] These workers demonstrated the utility of this linking agent by the immobilization of hydroxymethylferrocene to the electrode surface. Similarly, Itaya and Bard reported the use of poly(methacryl chloride) attached to an electrode surface to provide a high density of reactive surface functionality and also successfully



Scheme 5

immobilized hydroxymethylferrocene to the electrode surface.[79]

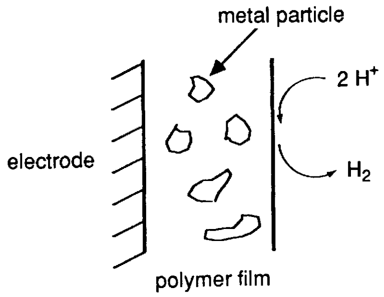
Polymer Films on Electrodes

Numerous investigators have pursued the formation of platinum particles on carbon supports, primarily because of their potential for use as a fuel-cell electrode.[80–84] The deposition of platinum particles on the surface of glassy carbon electrodes has been accomplished by many methods, including the chemical reduction of platinum salts,[85] vapour deposition of platinum metal,[86] and the electroreduction of K_2PtCl_6.[87] Many reports have focused on the production and study of polymeric coatings on electrodes because polymer films often exhibit greater stability than deposited clusters or adsorbed or covalently attached molecules. The polymer adheres to the electrode by a combination of surface adsorption and low solubility of the polymer in the contacting solvent or, in a few cases, by covalent attachment to the electrode surface.

Polymers have been coated on electrodes by adsorption or precipitation from solution,[88–90] electrochemical polymerization,[45,91–100] and plasma-discharge polymerization.[77] One approach to the preparation of thin films on glassy carbon electrodes utilizes redox polymers. These polymers contain the electroactive centre as a part of the polymer backbone, or the electroactive centre may be coupled to a functionalized polymer before or after the polymer is applied to the electrode. A wide variety of these polymers have been applied to electrode surfaces, in some instances with metal complexes or particles, including poly(4-nitrostyrene),[89] poly(acrylic acid),[101] dopamine-containing polymers,[102] poly(4-vinylpyridine),[77,103–105] Nafion,[106,107] poly(pyrrole),[94,96,97,108] poly(vinylferrocene),[109] and poly(aniline).[110,111]

Several investigators have reported the electrooxidative formation of polymeric tetraphenylporphyrin films.[44,45,93,98,99,112,113] Films of tetra(2-aminophenyl) porphyrinatocobalt(III), electrooxidatively polymerized from acetonitrile solution onto glassy carbon electrodes, exhibited a reversible $Co^{III/II}$ couple and also catalysed dioxygen reduction in both 0.5 mol dm^{-3} H_2SO_4 (with moderate stability) and 1 mol dm^{-3} NaOH (with high stability) aqueous solutions[45] and in the absence of liquid electrolyte when coated with a film of an ionically conducting polymer.[44] Anson and co-workers reported the incorporation of metalloporphyrins in a polymer film by copolymerization of a porphyrin functionalized with a methacrylamide group with a hydrophilic monomer, 1-vinyl-2-pyrrolidone.[41] The resultant polymer, which swelled on contact with aqueous solutions effectively exposing a greater portion of the films interior to solution, was metallated with iron and effectively mediated the electroreduction of dioxygen. Buttry and Anson reported the incorporation of *meso*-tetraphenylporphyrin into Nafion films under strongly acidic conditions followed by metallation with $Co(NO_3)_2$.[40] These workers reported that the addition of $Ru(NH_3)_6^{2+}$ provided a rapidly diffusing redox agent which allowed the slowly diffusing cobalt porphyrin molecules to effectively promote the reduction of dioxygen.

Metal particles can be introduced in polymer films coated on electrodes by the electroreduction of solutions of metal salts contained in porous polymer coatings. This approach presents several potential advantages compared with chemisorption or covalent attachment of catalysts to electrode surfaces including that the catalyst loading can be controlled; the size and distribution of metal particles could be controlled rather than the attachment of single metal centres to the surface; and that different combinations of metals or metal alloys could be deposited for specific purposes.



Murray and co-workers reported the electrodeposition of copper, silver, cobalt and nickel particles in poly[$Ru(bpy)_2$(4-vinylpyridine)] (bpy = bipyridine) coated on a platinum electrode.[104] These workers found that it was possible to effect deposition of the metal primarily on the surface of the polymer and not on the electrode surface as evidenced by X-ray photoelectron spectroscopic and cyclic voltammetry studies. Kao and Kuwana reported that the electroreduction of platinum(IV) in a film of poly(vinyl acetate) coated on a glassy carbon electrode (PVA–GC), gave a dispersion of 10–100 nm diameter platinum(0) particles with a surface loading level between 0.2 and 50 μg cm^{-2}.[114] The same procedure was used to electrodeposit palladium, silver, nickel, cadmium and a mixture of palladium and platinum in PVA–GC.[115] These electrodes were effective for the catalytic generation of hydrogen in acidic solution with overpotentials on platinum-PVA–GC for H^+ reduction similar to that observed on a smooth platinum electrode. The stability of the coating of the polymer on the electrode was tested by sonication for 15 min and the polymer was retained on the glassy carbon surface. Kuwana and co-workers also reported the electrodeposition of platinum microparticles in polyaniline films[111] and the electrodeposition of platinum, palladium, iridium, and ruthenium microparticles in poly(4-vinylpyridine) films[116,117] coated on glassy carbon electrodes. The platinum–polyaniline–GC electrodes, containing 13–51 μg(Pt) cm^{-2} loadings, exhibited catalytic activity for the oxidation of methanol and the reductive formation of hydrogen from acidic solution.

This general approach of electrodeposition of metal particles in polymer films coated on electrodes has also been used with some success by other investigators including the incorporation of platinum particles in Nafion films,[118–122] in Nafion with the addition of a cobalt porphyrin,[48] in Nafion with glucose oxidase immobilized on the polymer surface used for the detection of glucose,[123] and in polypyrrole.[94,96,108] In an effort to reduce mass transfer of substrates through a polymer film on an electrode, Fujihira and Poosittisak electrodeposited platinum particles in a Langmuir–Blodgett film.[124] The film was composed of a viologen surfactant giving an estimated thickness of *ca.* 10 nm on glassy carbon. Of the platinum particles that formed in the film or on the surface of the electrode, *ca.* 1/3 were catalytically active for the hydrogen evolution reaction and dioxygen reduction. The formation of platinum particles in a metal oxide matrix on an electrode surface was accomplished by the co-reduction of tungsten oxide ($WO_3 \cdot xH_2O$) and K_2PtCl_6 with a graphite or glassy carbon electrode giving platinum microparticles throughout the $W^{VI,V}$ oxide matrix.[125]

Shaw and Creasy have prepared composite electrodes by radical copolymerization of vinylferrocene and styrene in the presence of carbon black.[21] The poly(vinylferrocene)–polystyrene composite electrode was used as a working electrode in a solution containing 0.5 mmol dm^{-3} methyl viologen solution and had the same behaviour that glassy carbon electrodes exhibited. Similarly, the preparation of composite electrodes containing alumina, layered double hydroxides, and zeolites gave materials which could be polished to renew electrochemical activity[126] and a composite containing carbon particles and a viologen-based polymer behaved as though the carbon particles effectively increased the surface area of the polymer film.[19] A composite electrode prepared with methyl viologen, zeolites (A and Y), and carbon paste exhibited dioxygen reduction which was enhanced by the presence of the zeolite support.[127]

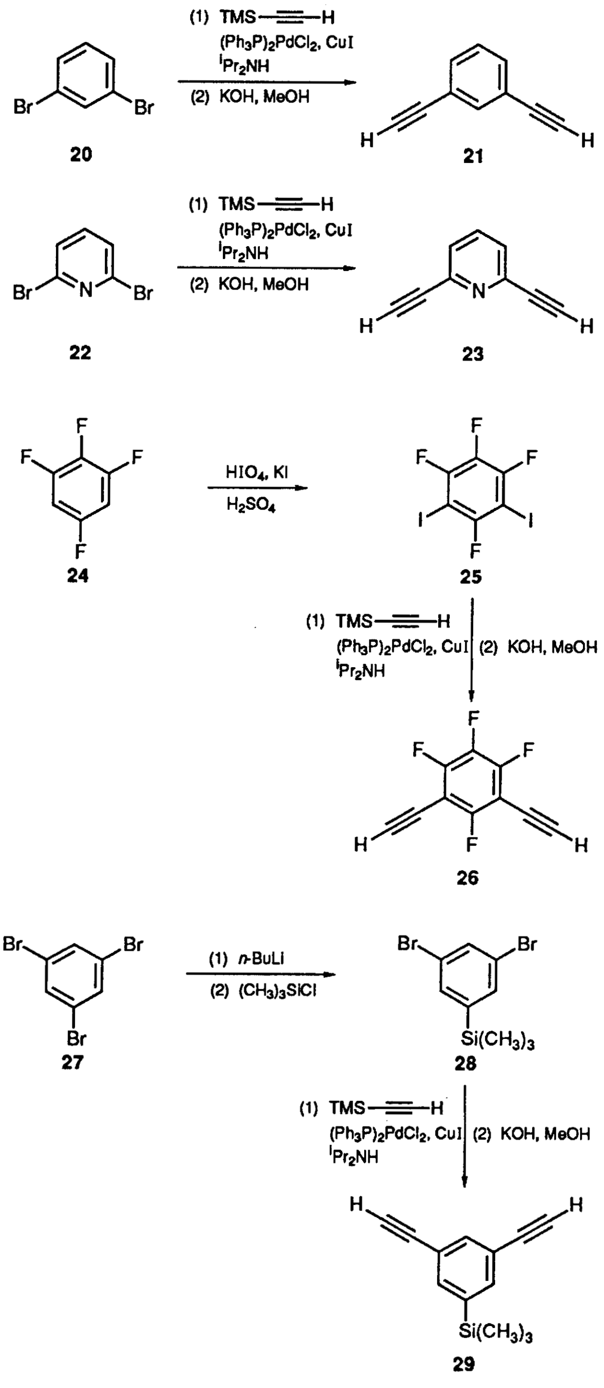
All of the methodologies described above for the modification of glassy carbon electrodes suffer from the disadvantage that the improvement in catalytic activity is rarely permanent. Indeed, many of these surface coatings offer improved catalytic properties for only small numbers of turnovers after which time the surface must be reactivated. The modification process is often quite complex and time-consuming. An alternative approach to the preparation of modified carbon electrodes, which we have pioneered, involves the homogeneous modification of carbon materials rather than the surface modification of the electrode.

Doped Glassy Carbon Materials

As was described briefly above, we have recently discovered a novel synthesis of glassy carbon which requires relatively low (<600 °C) thermal treatment for its preparation. This low-temperature synthesis allows, for the first time, the preparation of homogeneously doped glassy carbon (DGC) materials. The synthesis of DGC materials involves the preparation of diacetylenic oligomer or polymer precursors, moulding of the powder to form a disc, or alternatively casting as a film, and thermal treatment to form glassy carbon.[23,24] The key development to our success was the recognition that the thermal transformation of these highly unsaturated macromolecules could be carried out at relatively low temperatures, allowing for the production of glassy carbons containing substantial (>20% by weight) amounts of heteroatoms. In conventional glassy carbon syntheses, the extreme temperatures used (typically 1800–3000 °C) result in the production of glassy carbon containing less than 0.5% of any element other than carbon, regardless of the starting material used.

Synthesis of Doped Glassy Carbon Precursors

In our initial studies,[23,24] 1,3-diethynylbenzene (**21**), 2,6-diethynylpyridine (**23**), 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (**26**),[128] 1,3-diethynyl-5-trimethylsilylbenzene (**29**) (Scheme 6) were prepared by the palladium and copper catalysed reaction of the appropriate dihalogenoaromatic compound (**20, 22, 25, 28**) with trimethylsilylacetylene,[129] followed by removal of the protecting trimethylsilyl groups by treatment with dilute potassium hydroxide in methanol (Scheme 6). The diacetylene aromatics were either purified by vacuum distillation or by chromatographic separation.† We chose these four DGC precursor diethynyl aromatics in order to determine the sensitivity of the formation of glassy carbon at low temperatures to heteroatom doping and also to demonstrate the versatility of our approach to modified glassy carbon materials. We expected that the properties of carbon solids prepared from these diethynyl aromatics would be markedly different. The non-doped system based on **21** was expected to most closely resemble conventional glassy carbon while the incorporation of a pyridine group, as in **23** in a DGC precursor might serve as a potential binding site in glassy carbon for metal complexes. The incorporation of fluorine, as in **26**, was expected ultimately to generate a fluorinated glassy carbon surface and the addition of a trimethylsilyl group, as in **29**, was expected to serve as a probe of the sensitivity of the thermal conversion reaction to an alkyl side chain.



Scheme 6

The oligomerization of 1,3-diethynylbenzene (**23**) to form poly(buta-1,3-diynyl-1,3-phenylene) (**31**) was accomplished by a Glaser-type oxidative coupling, under conditions analogous to those first described by Hay,[130] using copper chloride as catalyst in 2-dichlorobenzene. In order to maintain solubility, ethynylbenzene (**30**) was added as an end-capping agent to the polymerization mixture to limit the molecular weight of the oligomers formed. Oligomers **33, 35**, and **36** were prepared in a similar manner using ethynylpyridine (**35**), 1-ethynyl-2,3,4,5,6-pentafluorobenzene (**34**), and ethynylbenzene (**30**) as end-capping groups, respectively. The ratio of diethynyl aro-

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† Compound **21** and all other volatile polyethynyl aromatics should be distilled at high vacuum at $T < 60\,^{\circ}\mathrm{C}$ in well shielded equipment. Only limited quantities should be distilled, stored or manipulated as pure (undiluted) material.

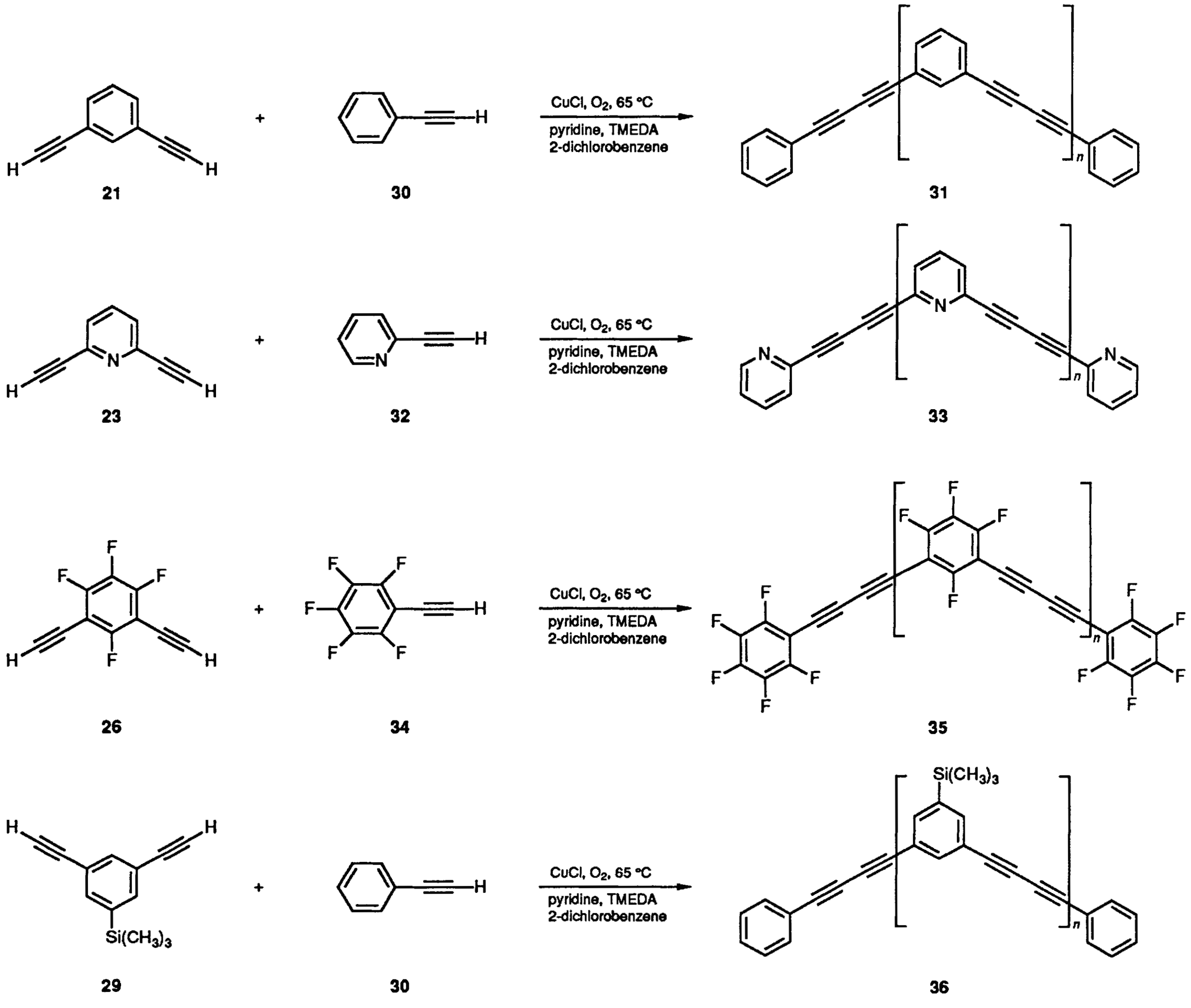
matic to monoethynyl aromatic in the polymerization reaction clearly has a dramatic effect on the molecular weight of the resulting oligomers. We varied the ratio of the diynyl aromatic : end-capping group from 3 : 1 to 10 : 1 to determine if the physical properties (especially solubility and film-forming properties) were influenced by the molecular weight of the oligomeric precursor. In general, it was found that the oligomers of lower molecular weights (*i.e.* resulting from a diynyl : monoynyl ratio of 3 : 1) provided materials with optimal solubility and film-forming behaviour and that both materials formed glassy carbon solids.

Preparation of Doped Glassy Carbon Materials

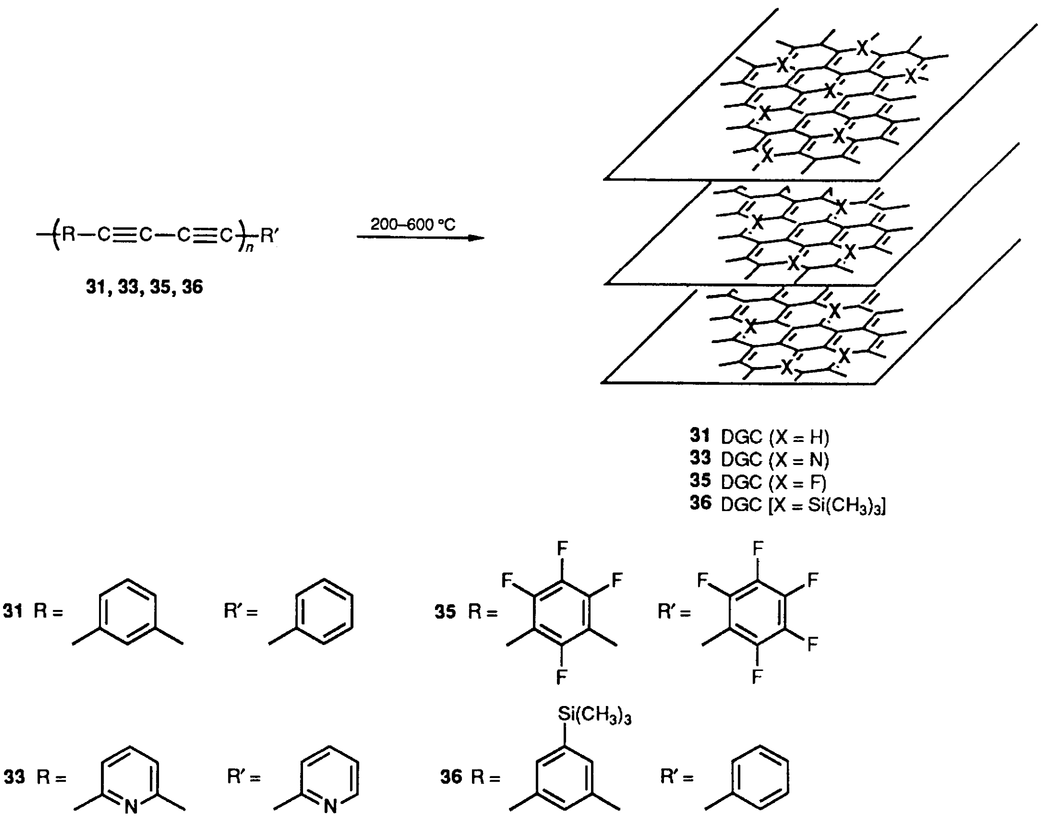
Interest in the thermal treatment of poly(buta-1,3-diynyl-1,3-phenylene) materials for the preparation of carbon materials dates from the 1960s when Hay showed that oxidative coupling of 1,3-diethynylbenzene yielded a soluble polymer which could be further processed at temperatures of 150–300 °C to yield carbon solids.[130,131] More recently, in their search for thin-film dielectrics, researchers have developed related materials based upon the oxidative coupling of 1,3,5-triethynylbenzene, followed by thermolysis of the resulting oligomers.[132]

We have found that oligomeric materials, **31**, **33**, **35**, and **36**, with limited molecular weights ($n \approx 10$) are soluble in organic solvents including methylene chloride, tetrahydrofuran, toluene, *etc.*, and form continuous films on a variety of substrates. Thermal treatment of **31**, **33**, **35**, or **36** as films on conventional glassy carbon at 600 °C gives the DGC materials (Scheme 8). When desirable, powders of **31**, **33**, **35**, or **36** can be moulded and subsequently thermally treated to give discs of doped glassy carbon. We have investigated the conversion of **31**, **33**, **35**, and **36** to the corresponding glassy carbon materials by thermal analysis, Raman spectroscopy, determination of the physical properties of the DGC solids, and by examination of the electrocatalytic behaviour of these materials.

Analysis of the oligomers **31**, **33**, **35**, and **36** by differential scanning calorimetry (DSC) found that they underwent a highly exothermic reaction on thermal treatment. The cure onset temperature ranged from *ca.* 150 to 200 °C (Table 1) and the cure energies ranged from 90 to 230 cal g^{-1}. Further analysis by DSC at temperatures up to 800 °C failed to detect any further reaction in the solid, although there are distinctive physical changes in the solid after thermal treatment through the exotherms listed in Table 1. The oligomers **31**, **33**, **35**, and **36** are typically yellow–tan powders. After thermal treatment, the materials have been converted into black, shiny, brittle solids which are completely insoluble in all organic solvents. The use of solid-state ^{13}C NMR spectroscopy is limited by



Scheme 7



Scheme 8

Table 1 Thermal analysis of materials **31**, **33**, **35** and **36**[a]

	TG[b]				DSC[c]		
	nitrogen		air				
sample	$T_{10\%}$/°C	$T_{50\%}$/°C	$T_{10\%}$/°C	$T_{50\%}$/°C	T_{onset}/°C	T_{max}/°C	cure energy /cal g^{-1}
31	1100	(10%)[d]	410	420	171	221	160
33	480	(21%)[d]	380	470	150	162	228
35	620	(38%)[d]	450	540	192	210	93
36	635	(13%)[d]	495	546	204	253	133

[a] Measurements were obtained on a Perkin-Elmer TGS-2 thermogravimetric analyser interfaced with a System 4 microprocessor for temperature programming and a TADS Model 3700 data station for data acquisition and operational control. The heating rate was 5 °C min^{-1} for DSC and 10 °C min^{-1} for the TG. $T_{10\%}$ is the temperature at which the sample has lost 10% of mass at this heating rate; $T_{50\%}$ is the corresponding temperature for loss of 50% of the sample mass. [b] Measurements on samples thermally treated at 600 °C. [c] Measurements on oligomeric materials. [d] For these cases, $T_{50\%}$ exceeded the upper temperature limit of the thermal analyser (1100 °C). The values reported are the % mass of the sample lost at 1000 °C.

the broad range of the bands observed and by the fact that the materials begin to show some conductivity at cure temperatures of *ca.* 400 °C. Fortunately, Raman spectroscopy is ideally suited for the examination of carbons, allowing a probe of the microcrystalline structure of the solid. Fig. 1 shows the Raman spectra of highly ordered pyrolytic graphite (HOPG) and conventional glassy carbon prepared at 2000 °C. The HOPG spectrum shows the E_{2g} fundamental at 1582 cm^{-1} and lacks the disorder (D) mode at 1360 cm^{-1}. In contrast, glassy carbon exhibits the D mode and there are changes in the second-order region between 2600 and 3300 cm^{-1}. The 1300–1600 cm^{-1} region is diagnostic for carbon microstructure and the two peaks at 1360 and 1582 cm^{-1} indicate an extended sp^2-hybridized carbon lattice.

The Raman spectrum of **31**-DGC thermally treated at 200 °C (*i.e.* after the material has passed through the initial exotherm) shows the characteristic glassy carbon bands, albeit highly disordered (Fig. 2). Further thermal treatment at 400

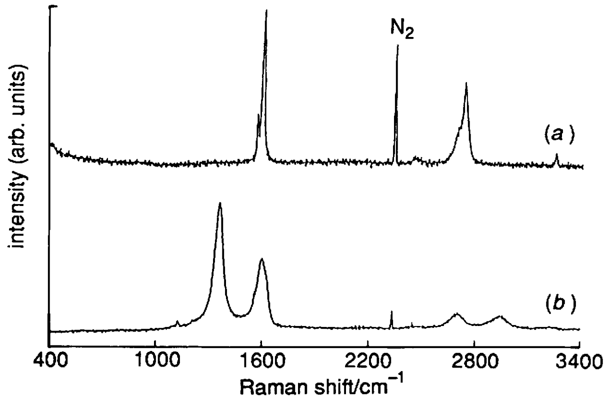


Fig. 1 Raman spectra of (*a*) highly ordered pyrolytic graphite (basal plane) and (*b*) glassy carbon prepared by thermal treatment at 2000 °C

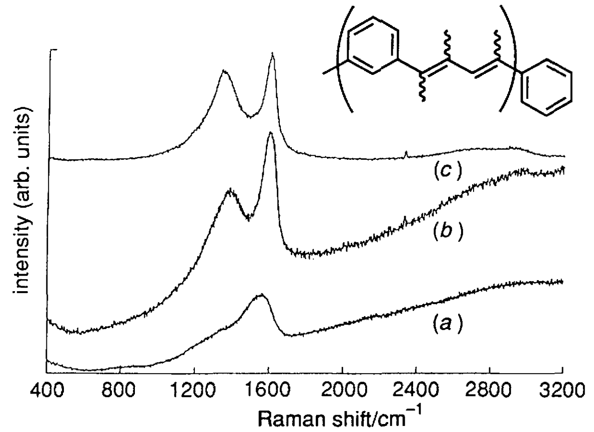


Fig. 2 Raman spectra of **31**-DGC, thermally treated at (*a*) 200, (*b*) 400 and (*c*) 600 °C (1 °C min^{-1} ramp rate to the ultimate temperature which was held for 6 h). Inset drawing does not represent the cross-linked structure of **31**-DGC

and 600 °C dramatically improves the resolution and intensity of the bands. The improved resolution of the bands indicates an increase in the L_a and L_c lattice parameters by an annealing process. These spectra provide unambiguous evidence that a glassy carbon matrix is being formed at temperatures as low as 200–600 °C. Thermal treatment of the remaining oligomers **33**, **35**, and **36** resulted in the formation of the doped glassy carbons **33**-DGC, **35**-DGC and **36**-DGC, respectively. X-Ray photoelectron spectroscopic analysis of **33**-DGC, **35**-DGC and **36**-DGC confirmed the retention of nitrogen, fluorine and silicon, respectively. The density, elastic modulus, shear modulus, and Poisson's ratio of the undoped solid, **31**-DGC, is strikingly similar to glassy carbon prepared by conventional high-temperature means (see Table 2). It is important to note, however, that the Young's moduli of **33**-DGC, **35**-DGC and **36**-DGC are less than half that observed for **31**-DGC illustrating clearly that the presence of dopants affects the elasticity of the carbon solids.

A critically important property of the DGC materials is low electrical resistivity to allow their use as an electrode. Thermal treatment of **31**, **33**, **35** and **36** heated to 200 °C for 6 h gave only insulating materials. However, the electrical conductivity of the organic materials increased dramatically with final heat treatment temperature. The increase in electrical conductivity with increasing thermal processing is shown in Fig. 3 for **31**-DGC. Thermal treatment of **31** at 400 °C for 6 h resulted in a conductivity of *ca.* 10^{-7} S cm^{-1}. Further thermal treatment to 600 °C for 6 h gave a material with a conductivity of *ca.* 1 S cm^{-1}, which is high enough for use as an electrode. Further thermal treatment to 800 °C gave a glassy carbon solid with a conductivity of 250 S cm^{-1}. The glassy carbons **33**-DGC, **35**-DGC and **36**-DGC gave similar results. The high conductivity attainable with **35**-DGC is particularly interesting given that this material contains >30% fluorine by weight.

Electrodes could be easily fabricated from oligomers **31**, **33**, **35** and **36** by formation of a thin film on conventional glassy carbon followed by thermal treatment or by compressing the materials in powder form into 1 cm diameter pellets followed by thermal treatment to form doped glassy carbon. The electrodes fabricated by these techniques functioned as practical electrodes. Fig. 4 shows the voltammetry of the iron(II)/iron(III) cyanide $[Fe(CN_6)^{3-/4-}]$ couple on glassy carbon prepared at 2000 °C ($\Delta E_p = 74$ mV, $k° = 0.017$ cm s^{-1}) and

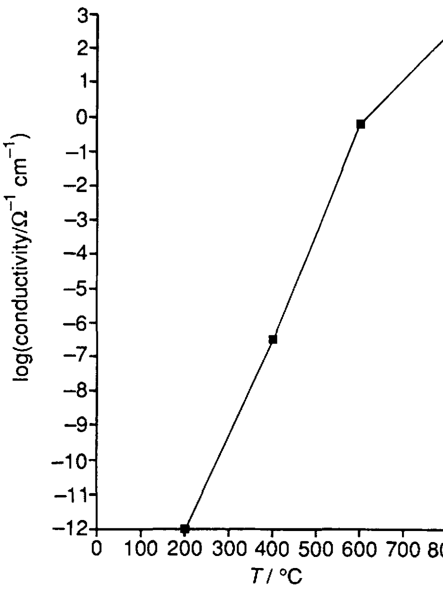


Fig. 3 Conductivity of **31**-DGC with thermal treatment. All conductivity measurements taken at ambient temperature

Table 2 Density (ρ), Young's Modulus (*E*),[a] Shear Modulus (*S*),[a] and Poisson's Ratio (υ)[a] of doped glassy carbon materials, graphitic carbon and diamond

entry	sample	T/°C	ρ/g cm^{-3}	E/MN m^{-2}	S/MN m^{-2}	υ
1	**31**-DGC	200	1.35	20 000	8040	0.241
2		400	1.35	22 500	9200	0.223
3		600	1.50	28 500	10 800	0.326
4	**33**-DGC	200	1.27	11 900	5000	0.192
5		400	1.64	12 300	5310	0.160
6		600	—	—	—	—
7	**35**-DGC	200	1.37	10 100	4000	0.288
8		400	1.32	6000	2300	0.306
9		600	1.55	12 200	4550	0.336
10	**36**-DGC	200	1.11	10 000	4700	0.200
11		400	1.01	5900	2300	0.256
12		600	1.29	12 600	4950	0.272
13	glassy carbon[b]	—	1.46	29 400	12 000	0.233
14	graphitic carbon[c]	—	1.89	13 900	5860	0.185
15	diamond	—	3.51	10 50 000	437 000	*ca.* 0.200

[a] The modulus measurements were determined by an ultrasonic method. Uncertainty in the measurement is <5%. [b] V10, Atomergic Company. [c] Carbon P03, Pure Carbon Company, St. Mary's, PA.

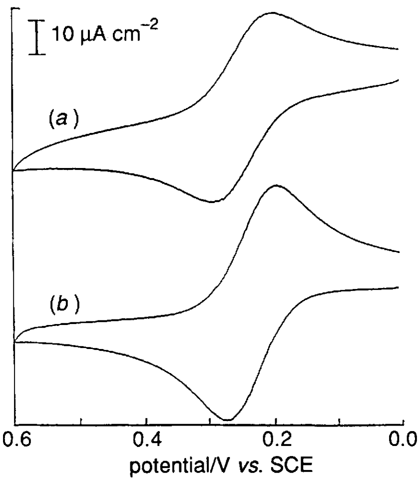


Fig. 4 Cyclic voltammograms of 0.1 mol dm^{-3} $Fe(CN)_6^{3-/4-}$ *vs.* Ag/AgCl (3 mol dm^{-3}). (*a*) **31**-DGC, 600 °C thermal treatment; (*b*) GC20, 2000 °C thermal treatment

31-DGC prepared at 600 °C as a solid disc ($\Delta E_p = 91$ mV, $k^\circ = 0.0075$ cm s^{-1}). The electrochemical response of the two glassy carbon electrodes are remarkably similar and establish clearly that materials prepared by this method could be of use as electrode materials and as matrix supports for electrocatalytic species. We have found that the DGC materials behave quite differently with respect to their electrochemical response as a function of the heteroatom dopant.[133]

Microcrystalline Platinum Doped Glassy Carbon

As was described above, platinum is known to be a catalyst for many important chemical reactions including dioxygen reduction and dihydrogen oxidation. The economic incentive for finding an effective, inexpensive means for reducing oxygen and hydrogen to water is truly enormous. An efficient oxygen–hydrogen or methanol–oxygen fuel cell based on an alternative to the use of high levels of platinum would provide an attractive source of energy.[134] Since fuel cells are not heat engines, they are not limited to the efficiency of a Carnot cycle. Therefore, they have high efficiency for the conversion of chemical energy to electricity. Unfortunately, the available effective oxygen electrodes use dispersions of platinum on carbon and the expense necessary for the high loadings of platinum is too great for widespread application.

Our initial experiments designed to incorporate platinum in glassy carbon involved the dispersion of commercially available platinum(IV) oxide in the parent carrier polymer. Poly(buta-1,3-diynyl-1,3-phenylene) (**31**) was mixed with 0.25 and 1 atom% of platinum(IV) oxide. The intimate mixture was pressed and thermally treated to 600 °C under the same conditions previously described for the thermal treatment of **31**, to form pellets of glassy carbon. X-Ray photoelectron spectroscopic analysis of these pellets carried out on a Physical Electronics Model 550 spectrometer, confirmed the incorporation of platinum as a dopant in the glassy carbon solid (PtO_2–GC). A study of the binding energy of the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ electrons found that there was a mixture of different oxidation states of platinum [Pt^{IV}, Pt^{II}, Pt^0]. The partial reduction of the platinum(IV) oxide to lower oxidation states is not surprising given the fact that a relatively labile oxide is being heated in a strongly reducing atmosphere during the formation of the glassy carbon matrix. Fig. 5 illustrates the current *vs.* potential response for the reduction of protons to dihydrogen on glassy carbon, platinum, and platinum DGC (0.25 and 1 atom%) electrodes. In contrast with non-doped glassy carbon electrodes where no response was recorded upon the application of a reducing potential, the immobilization of 0.25 and 1 atom% of platinum in glassy carbon led to efficient hydrogen evolution. These platinum DGC electrodes exhibited excellent stability and no evidence of degradation was found after several thousand reduction cycles. However, an overpotential of 50–100 mV, in comparison with a bulk platinum electrode, was found for the reduction.

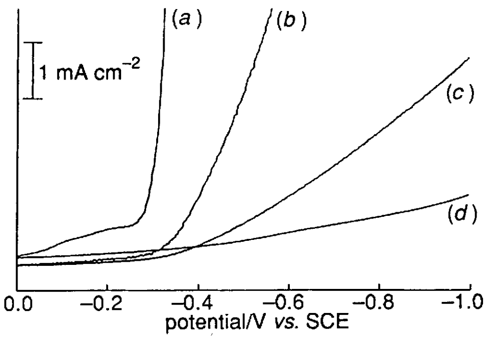


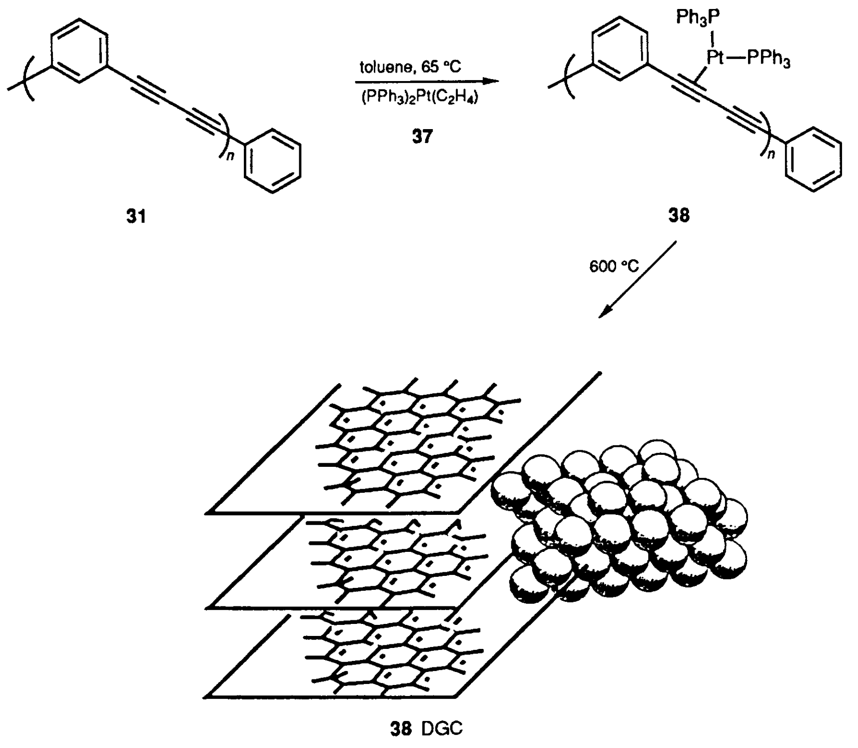
Fig. 5 Reduction of 1 mol dm^{-3} perchloric acid *vs.* Ag/AgCl (3 mol dm^{-3}) on (*a*) platinum, (*b*) 1.0 atom% PtO_2-DGC, (*c*) 0.5 atom% PtO_2-DGC and (*d*) **31**-DGC

Synthesis of Nanoscale Clusters of Platinum in Glassy Carbon

In an effort to prepare glassy carbons with a more intimate platinum–carbon relationship, we sought chemistries that would allow the dispersion of platinum species at the atomic level in glassy carbon precursors. Coordination of platinum to the carbon–carbon triple bond of poly(buta-1,3-diynyl-1,3-phenylene) offered a convenient method of dispersing platinum at an atomic level along the glassy carbon precursor, and, under the most optimistic of scenarios, offered a method of dispersing platinum at the atomic level in the glassy carbon solid itself. Scheme 9 shows the synthetic strategy for the preparation of *catena*-[poly(buta-1,3-diynyl-1,3-phenylene)]-bis(triphenylphosphine)platinum(0) (**38**). The synthesis makes use of the known lability of alkene ligands coordinated to platinum towards displacement by acetylenes.[135] We chose ethylene bis(triphenylphosphine)platinum(0) (**37**)[136] as the precursor to **38** because the presence of triphenylphosphine ligands was expected to enhance the solubility of the resulting polymer platinum complex, and because the use of triphenylphosphine as a ligand provides a convenient way to prepare platinum in its zerovalent state. Reaction of ethylene bis(triphenylphosphine)platinum (**37**) with poly(buta-1,3-diynyl-1,3-phenylene) (**31**) in toluene at 65 °C under argon for 6 h resulted in the consumption of **37** and formation of a red–brown solution. Precipitation of the reaction solution on addition to an excess of petroleum ether gave a green–yellow solid (**38**) in 69% yield. This solid was air-stable and soluble in toluene and benzene. Prolonged reaction for 3 days under similar conditions resulted in the formation of intractable solid presumably resulting from displacement of triphenylphosphine ligands from platinum by acetylenes on other diacetylenic polymer chains.

Conversion of the platinum-containing oligomers to platinum-doped glassy carbon (**38**-DGC) at 600 °C was accomplished as described as either a film on conventional glassy carbon or in the form of a disc. The conversion of **38** to a material containing a microcrystalline structure similar to glassy carbon was confirmed by Raman spectroscopy. X-Ray photoelectron spectroscopic and microprobe analyses of the materials confirmed the incorporation of *ca.* 0.5–1 atom% of platinum(0) in glassy carbon, with no evidence for the presence of other oxidation states of platinum.

We examined **38**-DGC by transmission electron microscopy



Scheme 9

(TEM) to determine the size of the platinum species formed in the carbon matrices as we anticipated that the platinum atoms would undergo some degree of aggregation in the carbonization process. TEM analysis of thin films of the platinum-doped glassy carbon found a narrow size distribution of clusters of platinum, with an average diameter of *ca.* 16 Å, consistent with the formation of clusters of *ca.* 100 platinum atoms (Fig. 6). The small size of the platinum clusters contained in **38**-DGC is remarkable, particularly when compared with platinum clusters prepared by electroreduction methodology which results in the formation of platinum clusters with average diameters that are rarely smaller than 600 Å.

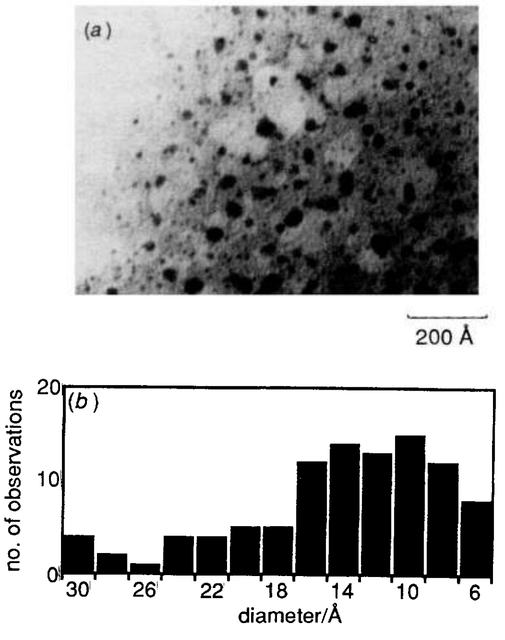


Fig. 6 (*a*) Transmission electron micrograph of the edge of a film of **38**-DGC which was deposited onto a sodium chloride pellet then lifted onto a copper microgrid. The dark spots represent platinum clusters. (*b*) Cluster diameter distribution measured from (*a*) Eighteen observations were recorded above 30 Å and due to the limit of resolution of the microscope, observations below 6 Å were not included in the calculation of average diameter

The electrolytic activity of the platinum-doped glassy carbon materials was evaluated with respect to both H^+ and O_2 reduction. Fig. 7 shows the electrochemical response of Pt-DGC [curve (*a*)], polycrystalline platinum [curve (*b*)], 1 atom% PtO_2-DGC [curve (*c*)], 0.5 atom% PtO_2-DGC [curve (*d*)] and glassy carbon [curve (*e*)] in 1 mol dm^{-3} $HClO_4$ solution. It is clear that Pt-DGC has, within experimental error, the same overpotential for H^+ reduction as that found for polycrystalline platinum, and offers a considerable improvement over the PtO_2-DGC described earlier. A remarkable result is that the Pt-DGC materials are significantly more stable under the reaction conditions than bulk platinum. The current density for H^+ reduction with the Pt-DGC sample decays by less than 20% after 1 h of electrolysis. In contrast, polycrystalline platinum electrodes mounted in glass, decayed by 75% over the same period, to current

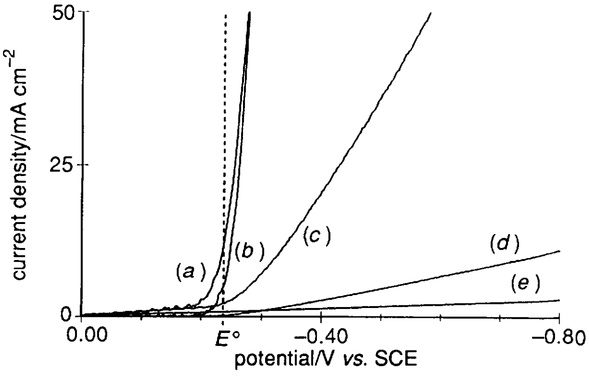


Fig. 7 Reduction of 1 mol dm^{-3} perchloric acid *vs.* Ag/AgCl (3 mol dm^{-3}) on (*a*) Pt-DGC; (*b*) polycrystalline platinum; (*c*) 1.0 atom% PtO_2-DGC; (*d*) 0.5 atom% PtO_2-DGC and (*e*) **31**-DGC

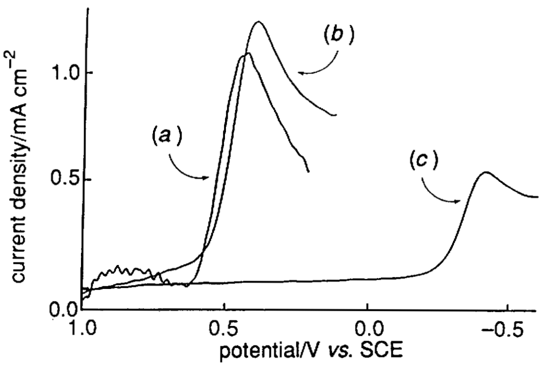


Fig. 8 Voltammograms for O_2 saturated 1 mol dm^{-3} $HClO_4$ buffer, 50 mV s^{-1} scan rate for (*a*) **38**-DGC thin film on conventional glassy carbon; (*b*) polycrystalline platinum mounted in a Kel-F holder; (*c*) conventional GC

densities lower than those of the Pt-DGC samples despite the low atomic percentage of platinum present in the Pt-DGC materials.

Dioxygen reduction with the Pt-DGC was studied with similarly exciting results. Fig. 8 shows a comparison between conventional glassy carbon [curve (*c*)], bulk polycrystalline Pt [curve (*b*)], and a 1 atom% Pt-DGC thin film coated on conventional glassy carbon [curve (*a*)]. At both pH 0 and 7, the Pt-DGC reduced the overpotential for O_2 reduction by *ca.* 800 mV and resulted in a voltammetric response similar to that of pure platinum.

The greatly enhanced catalytic activity of Pt-DGC materials, for both H^+ and O_2 reduction may arise from a number of factors. Of particular significance is the fact that our synthetic methodology allows us to prepare very small clusters in a rigid conducting matrix, which presumably does not allow further aggregation of the clusters once they are formed. The matrix itself may also be a benefit for the catalytic activity of the platinum clusters because of the ability of the carbon to adsorb potential platinum poisons.

Summary

We have described a new approach to the synthesis of doped glassy carbon materials by the low-temperature thermal treatment of acetylenic oligomeric materials. These materials represent the first homogeneously modified glassy carbon materials. Incorporation of platinum into the glassy carbon matrix allows for the preparation of new electrocatalysts that are useful for the reduction of both H^+ and O_2. Our approach for the preparation of modified glassy carbon electrodes offers potential for the construction of new electrolytic processes, electrochemical sensors, and for the development of efficient fuel cells.

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