

Section I

Synthesis

CHAPTER 1

Covalent Methods for Functional Carbons' Synthesis

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1.1 Towards a Molecular Understanding of the Reactivity of Carbon Surfaces

1.1.1 Role of Curvature and Topological Defects on Surface Reactivity

The unique chemico-physical properties of carbon-based materials in their various allotropic forms have made them valuable candidates for application in many catalytic processes. Traditionally, carbon materials have been employed as supports for metal-based multi-phase catalysts in heterogeneous processes although their role (innocent or non-innocent)

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in the catalytic performance remains largely questionable. The last few years have witnessed a *technological renaissance* that has boosted the exploitation of carbon-based nanomaterials for running a number of key industrial transformations with good to excellent catalytic outcomes. This renaissance is in line with seminal papers published in the 1960s by Donnet, Boehm, and Coughlin,^{1–3} who showed that the catalytic performance (activity and selectivity) of carbon catalysts is related to two largely interconnected features: the chemistry and electronic properties of their outer surfaces.

Many efforts in the scientific community have been devoted to the understanding of molecular-level phenomena that govern carbon material reactivity. The discovery of well-defined carbon nanomaterials in the 1980s and 1990s, namely fullerene and carbon nanotubes, offered unprecedented opportunities to advance our understanding of carbon materials' rich chemistry. Works on defect-free fullerenes and single-walled carbon nanotubes (SWCNTs) revealed notable connections between the curvature and the reactivity of carbon surfaces. For instance, for fullerenes, the reactivity of sp^2 hybridized carbons was demonstrated to be a result of the strain induced by the curvature.⁴ Indeed, any C- sp^2 carbon atom within a high curvature environment (radius of curvature from 5 to 10 Å) will undergo a strain-induced pyramidalization of its orbitals. This pyramidalization strongly facilitates addition reactions, thus breaking C=C bonds and inducing atoms' relaxation due to rehybridization to C- sp^3 .⁵ Chirality ordinarily present in SWCNTs creates additional strain on C=C bonds due to the "twisting" of the rolled graphene sheet that leads to a misalignment of the p_z orbitals.^{6,7} The high reactivity of strained carbon surfaces is not limited to well-defined nanocarbons like fullerene and SWCNTs, but it actually occurs on any site with a high local curvature. In the case of Stone–Wales defects (Figure 1.1), the presence of C_5 and C_7 rings would induce curvature in the carbon materials.^{4,8–11}

1.1.2 Surface Modification through Heteroatom Insertion

Typically, topological defects are reactive sites and their interaction with oxygen leads to modification of surface properties. Their oxidation generates a variety of oxygen-containing functional groups (carboxylic acid, anhydride, hydroxyl, lactone, ether), which alter both the polarity and acid–base properties of the carbon surface. Deep oxidation eventually results in the formation of CO_2 and the creation of a vacancy. This reactivity explains why carbons present a quilted surface consisting of defect-free graphitic domains interconnected by regions with amorphous carbon (sp^3), point defects, and vacancies. The interaction of defects with oxygen also introduces oxygen-doping functionalities on the surface of carbon materials, for example around vacancies as well as at the edge/prismatic plane carbon atoms as these sites are far more reactive towards oxidation than that of basal plane carbons.^{12–15} For instance, carbon atoms on the edges

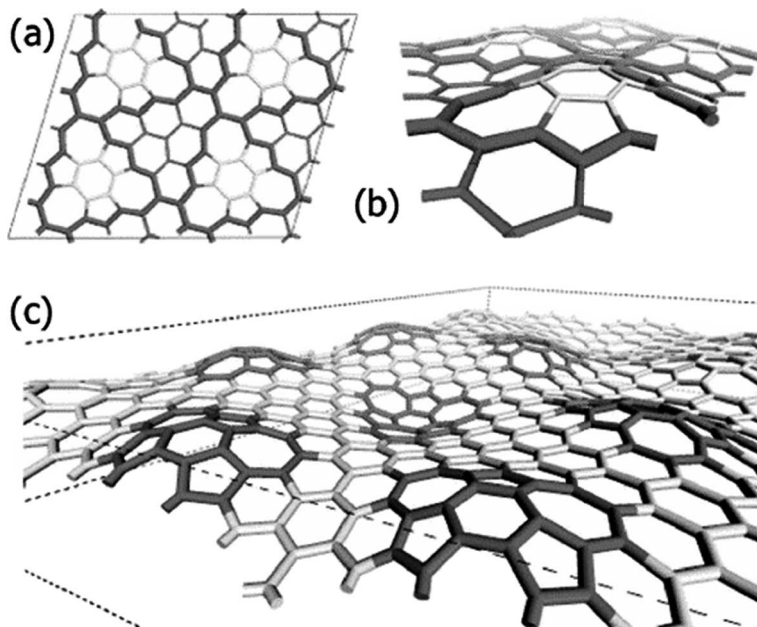


Figure 1.1 Top (a) and side views (b, c) of a graphene sheet presenting regions with high local curvature induced by C_5 and C_7 rings. Reprinted figure with permission from M. T. Lusk and L. D. Carr, *Phys. Rev. Lett.*, **100**, 175503, 2008. Copyright (2008) by the American Physical Society.⁸

of graphene can lead to activation of O_2 to form epoxides that migrate or hop on the surface of the basal plane.^{16,17} Therefore, the presence of edges or defects is essential for introducing heteroatoms in the basal plane of carbons.

Defects are generally introduced in carbon materials during synthesis as a result of fast reaction kinetics compared to the thermodynamically-favored formation of a defect-free honeycomb structure.¹⁸ Alternatively, the post-synthetic introduction of new defects typically relies on the use of strong oxidants able to disrupt carbon-carbon double bonds, such as the mixture of nitric acid and potassium chlorate as proposed by B. C. Brodie in 1859 for the oxidation of graphite.¹⁹ Similarly, the works of Staudenmaier, Hummers, and Offeman utilized potassium permanganate and sulfuric acid for further improving the process of graphene oxide (GO) synthesis.^{20,21} The introduction of defects and heteroatoms disrupts the delocalized electron cloud and alters the electronic properties of the surfaces, allowing the grafting of functional groups on the surface of nanocarbons.

In recent years, the heteroatom-doping (N, B, P, S) of carbon nanomaterials has emerged as an effective way to manipulate the electronic properties of nanocarbons. The inclusion of hetero-elements in the honeycomb carbon structure induces a deep redistribution of the electronic properties. An ever-growing number of light hetero-doped carbons (preferentially

containing nitrogen) are nowadays employed with success as metal-free catalysts. Selected systems from this series can offer higher catalytic activity and long-term operational stability than those measured with benchmark state-of-the-art metal-based systems.^{22–24} Post-synthetic chemical and thermal treatments (typically with strong and oxidizing acids or bases) have also been used to tune the materials' surface chemistry. The control of porosity and defect-sites' surface density along with the introduction of dangling (acidic or basic) functional groups is the new contemporary approach to prepare a family of new powerful catalysts.^{25–29} However, both heteroatom-doping and post-synthetic treatments generally suffer from moderate control on the nature of the chemical surface groups. Therefore, many efforts have been made to identify the active functionalities for a specific catalytic transformation and establish clear-cut structure-composition–reactivity relationships.

1.2 Strategies for the Synthesis of Functional Carbon Catalysts

1.2.1 Catalytic Chemical Vapor Deposition

The post-synthetic chemical functionalization of carbon materials typically requires multiple steps, making it a tedious process. In the case of carbon nanotubes (CNTs), many efforts have, therefore, focused on the introduction of heteroatoms directly during the synthesis of the nanocarbon using modified catalytic chemical vapor deposition (CCVD) techniques.^{30–32} Typically, the CCVD process consists of a hydrocarbon gas source that is heated in the presence of a transition metal catalyst (Fe, Co, Ni).¹⁸ This technique allows an easy incorporation of heteroatoms in the structure by altering the reaction mixture using precursors such as ammonia,³³ aniline,³⁴ phthalocyanine,^{30,35} melanine,³² acetonitrile,³⁶ pyridine,^{32,36} triazine,³² among others. N-doped CNTs have shown promising results in the high temperature (400 °C) oxidative dehydrogenation (ODH) of propane.³⁴ Graphene containing N-atoms synthesized by adding ammonia gas in the CCVD process has also been used for applications in oxygen reduction reactions (ORR) as a metal-free electrocatalyst.³⁷ The electrocatalytic applications demonstrated by the N-doped carbon nanomaterials in ORR and fuel cells are due to the modification of electronic properties caused by the electron donating/withdrawing nature of the heteroatoms which induce charge redistribution on the surface.^{35,37,38}

In addition to nitrogen, other heteroatoms such as phosphorus and silicon, can also be doped in nanocarbons using precursors such as triphenylphosphine^{39,40} and methoxytrimethylsilane.³⁹ Boron and phosphorus atoms have also been added in the CNT structure using CVD in the presence of triphenylborane,³⁸ triethylborate,⁴¹ diborane,⁴² and triphenylphosphine.⁴¹ The as-prepared materials showed promising results in ORR and the oxidation of cyclohexane.

Nanoporous graphene materials co-doped with sulfur and nitrogen using pyridine and thiophene have recently shown activity for the hydrogen evolution reaction (HER) comparable to 2D MoS₂, recognized as the best Pt-free HER catalyst.⁴³ The key reason for the performance of the catalyst in the HER was demonstrated to be the alteration of its electronic properties and, thereby, of the Gibbs free energy of hydrogen binding, a key descriptor for this reaction. These examples provide evidence that the electronic properties of nanocarbons can be tuned using heteroatom doping and, thereby, their performance can be varied by altering the heteroatom amount, its nature, and chemical environment.

While being an efficient strategy for introducing heteroatoms in the carbon backbone, CCVD suffers from several drawbacks. Notably, the high temperatures required for growing nanocarbons do not offer opportunities to control the nature of the inserted moieties. For instance, in the case of nitrogen, high temperatures favor the formation of pyridinic and quaternary nitrogen moieties, thus limiting the applications of these materials for reactions catalyzed by strong Brønsted bases. It should also be noted that the heteroatoms are typically distributed throughout the nanomaterial, meaning that only a fraction of the inserted heteroatoms are present on the surface and actively participate in catalytic reactions. Finally, it has also been shown that the addition of heteroatom-containing precursors in the gas feed during synthesis alters the growth process. For example, the addition of ammonia in the feed yielded bamboo-shaped CNTs instead of multiwalled carbon nanotubes (MWCNTs). The added arches close the inner channels, leading to a significant decrease in surface area and pore volume compared to undoped MWCNTs.

1.2.2 Post-synthetic Functionalization

The vast majority of covalently functionalized carbons are produced through post-synthetic treatments. The methods employed are typically derived from organic chemistry techniques and consist of tethering heteroatom-containing moieties to the carbon surface through oxidation and coupling reactions.

In the case of oxidations, the key challenges of the post-treatment techniques are the changes in the morphological and textural properties of carbons due to harsh conditions and the lack of control of the nature of active groups introduced on the surface. In the case of GO synthesis from graphite, the use of harsh oxidants leads to highly defective, wrinkled, graphene oxide sheets with difficult-to-control morphology and textural properties. However, modifications of the thermochemical procedures facilitate the introduction of functional groups without altering the structural integrity of carbons. For instance, the gas-phase oxidation of CNTs using HNO₃ vapors reported by Xia *et al.* introduced oxygen functionalities on their surface without deteriorating the material morphology.⁴⁴ The challenges associated with the control of the amount and nature of O-containing groups were addressed by partial defunctionalization methods. The knowledge of the thermal decomposition

of specific functional groups provided an excellent handle on the tunability of carbon's surface chemistry.⁴⁵ The control of surface functionalization was utilized for developing carbocatalysts, for instance by tuning the diketone and quinone groups for the ODH of ethyl benzene.⁴⁶

Apart from tuning the catalytic performance of carbons by controlling the surface O-functionalities, strategies were implemented for introducing other heteroatoms such as nitrogen. Treating oxidized CNTs or graphene with ammonia at elevated temperatures, among various other techniques, facilitated the introduction of nitrogen functional groups and control of acid/base properties of carbons.^{47–49} Boron could also be inserted in the carbon matrix by thermally annealing oxidized CNTs or GO in the presence of elemental boron and boron oxide.^{50,51} Sulfonate moieties can be incorporated in CNTs and graphite by treatment with oleum.^{52,53} The addition of heteroatoms such as boron and nitrogen have been reported to play a role in enhancing carbocatalysts' activity and selectivity for ODH and oxidation reactions in general.^{54,55} The doped carbon materials have demonstrated better catalytic performance than noble-metal-based catalysts for oxygen reduction reactions (ORR) along with better control of activity, selectivity and stability by tuning the dopant concentration.⁵⁶

Nitrogen incorporation is also possible using hydrothermal synthesis with melamine as a precursor.⁵⁷ Hydrothermal techniques open possibilities related to the use of multiple dopants in the same carbocatalyst. For example, boron and nitrogen doped graphene quantum dots deposited on GO using hydrothermal techniques (Figure 1.2) result in carbocatalysts that demonstrate better ORR activity than the benchmark Pt/C.⁵⁸ Further, nitrogen-doped graphene on CNTs, synthesized *via* hydrothermal techniques, successfully performed the metal-free electrocatalytic ORR.⁵⁹ The assembly of graphitic C₃N₄ on graphene using hydrothermal techniques also showed a promising performance for the HER reaction, comparable to those of metal catalysts.⁶⁰

Thermal synthesis is another technique by which heteroatoms can be incorporated into nanocarbon materials. This method includes the decomposition of precursors such as melamine⁶¹ or dicyandiamide⁶² on the surface of nanocarbons. Recent studies have also utilized food-grade components as starting materials (*i.e.* glucose, citric acid, and ammonium carbonate) as aqueous solutions or physical mixtures for preparing highly N-rich carbon composites in the form of either film coatings for a variety of organic and inorganic macroscopic supports^{63,64} or 3D self-standing and shape-controllable open-cell mesoporous C-based foams (Figure 1.3).⁶⁵ These materials were successfully applied as metal-free catalysts for the electrochemical ORR, H₂S partial oxidation and direct dehydrogenation (DDH) of ethylbenzene to styrene. Another bottom-up synthesis technique comprised the annealing glucose, urea, and phosphoric acid together to obtain dual-doped nanoporous graphene, which depicted high catalytic activity for the hydrogen evolution reaction (HER), comparable to traditional metallic catalysts.⁶⁶

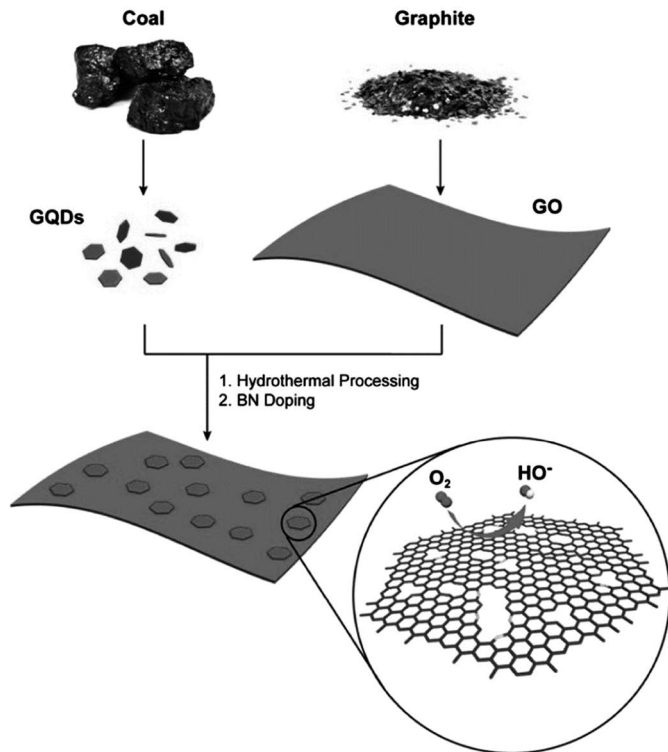


Figure 1.2 Illustration of the preparation procedure for the BN-GQD/G nanocomposite. Reprinted with permission from H. Fei, R. Ye, G. Ye, Y. Gong, Z. Peng, X. Fan, E. L. G. Samuel, P. M. Ajayan and J. M. Tour, *ACS Nano*, 2014, 8, 10837–10843.⁵⁸ Copyright (2014) American Chemical Society.

In addition to the application of carbocatalysts in ODH, ORR, and oxidation reactions in general, these materials also demonstrated activity for hydrogenation reactions when creating frustrated Lewis pairs (FLPs) on the carbon surface. FLPs consist of a Lewis acid and a base moiety in organic molecules, separated by an appropriate distance to maintain the interaction without being neutralized. In general, FLPs have been reported to be capable of hydrogen activation.^{67–69} Similar reaction mechanisms have been proposed for the FLP-driven hydrogenation of acetylene and alkene on graphene consisting of oxygen, phosphorus, sulfur, and nitrogen functionalities.⁷⁰ GO and reduced graphene oxide (rGO) synthesized by the pyrolysis of alginate have also demonstrated hydrogenation activity for various nitro compounds.⁷¹ Recent work by Sun *et al.* further provided theoretical evidence for the use of boron and nitrogen co-doped bilayer graphene and a graphene nanoribbon for hydrogen activation due to the presence of FLPs.⁷² This evidence for the capabilities of carbocatalysts as metal-free hydrogenation catalysts provides new opportunities for the development of sustainable and greener routes for the synthesis of specialty and fine chemicals.

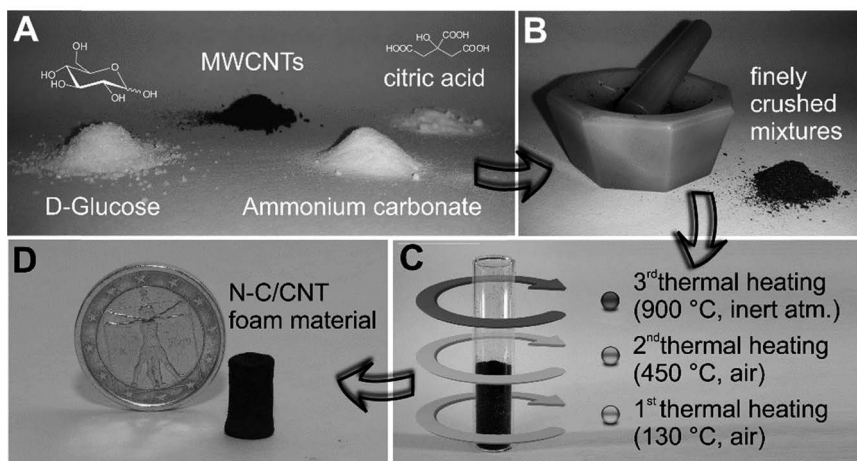
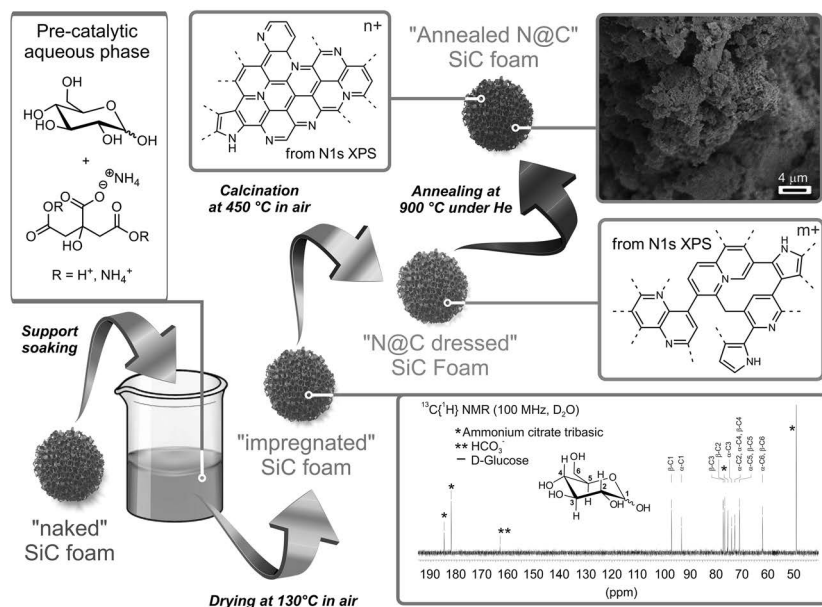


Figure 1.3 Top: synthesis of a highly N-doped carbon-based coating (N@C) on a model macroscopically shaped host matrix (SiC foam) (reproduced from ref. 63 with permission from the Royal Society of Chemistry). Bottom: sequential steps (A → D) for the preparation of N-doped 3D self-standing composites (N-C/CNT) (D), from a physical mixture (wt/wt) of commercially available food-grade components and pristine MWCNTs (reprinted with permission from H. Ba, Y. Liu, L. Truong-Phuoc, C. Duong-Viet, J.-M. Nhut, D. L. Nguyen, O. Ersen, G. Tuci, G. Giambastiani and C. Pham-Huu, *ACS Catal.*, 2016, 6, 1408–1419.⁶⁵ Copyright (2016) American Chemical Society).

1.2.3 Tethering Discrete Active Sites Through Nanomaterials' Surface Functionalization

The covalent grafting of well-defined (organic) functionalities or molecular entities at the nanomaterial surface is of growing interest.^{73,74} For many years, functionalization protocols have been optimized considering their foundational character in organic chemistry and material science.^{75,76} One of the main tasks driving this optimization is the improvement of the carbon nanomaterial dispersion/deaggregation in liquid media or in polymeric matrices to achieve an easier processing in composites production.⁷⁷ Recent findings in the field have demonstrated that chemical functionalization holds huge potential for a rational bottom-up design of complex carbon nanostructures with tailored chemical and electronic surface characteristics. Indeed, functional groups at the nanomaterial surface play a key role in specific catalytic processes, offering at the same time unique tools for the comprehension of their mechanism of action as metal-free systems. There is a huge number of original research papers and review articles dealing with the covalent functionalization of carbon nanomaterials. In the following sections, we will review the most representative studies in relation to their direct contribution to the catalytic performance of the nanomaterial as a metal-free catalyst.

1.3 Oxidized Carbon Nanomaterials in Catalysis

Oxidation is certainly the most widely employed methodology for nanomaterial surface grafting with a variety of O-containing groups (carboxyls, epoxides and hydroxyls). Variable distributions and loadings of oxygenated functionalities can be obtained depending on the oxidative protocol. The harsher the oxidation conditions, the higher the functionalization degree. High oxidative degrees typically translate into materials with better processability and dispersibility in various media but they also determine a progressive loss of their inherent electrical conductivity, a fundamental pre-requisite for the samples' exploitation as electrocatalysts.⁷⁸

Recent literature findings have demonstrated the impressive flexibility and performance of oxidized carbon nanomaterials within a very wide variety of catalytic processes. The interest in the sustainable development of single-phase catalysts that replace classical metal or noble-metal-based systems is shown by the number of papers that appeared on the topic. In some cases, controlled oxidation protocols together with a precise surface characterization offer an unambiguous explanation of the role played by O-containing functional groups and surface defects. For all processes outlined below, catalyst recovery and re-use are commonly claimed to be feasible, without appreciable loss of performance. Table 1.1 summarizes all the main catalytic transformations mediated by oxidized carbon nanomaterials and afterwards discussed in Sections 1.3.1–1.3.4.

Table 1.1 Class of reactions catalyzed by variably oxidized carbon nanomaterials.

Class of metal-free catalyzed reaction	Catalyst/co-catalyst or reagent	Reference
Oxidation of alcohols to aldehydes/ ketones	GO/O ₂	79
Hydration of alkynes to ketones	GO/O ₂	79
Electrochemical oxidation of alcohols	ox-CB or ox-MWCNTs	80 and 81
Benzene oxidation to phenol	CMG/H ₂ O ₂	82
Oxidative coupling of amine to imine	GO	83
Oxidative desulfurization (from thiophenes to aromatic sulfones)	rGO/O ₂	84
Oxidative alkane dehydrogenation (ODH)	ox-MWCNTs/O ₂	85 and 86
Catalytic wet air oxidation (CWAO)	GO, ox-(MWCNTs, CNFs)/O ₂	87 and 88
Oxygen evolution reaction (OER)	ox-MWCNTs	89 and 90
Nitroarene reduction to anilines	rGO or H ₂ O ₂ oxidized CNTs/H ₂ N-NH ₂	91–93
Photocatalytic water splitting (H ₂ production)	GO	94
Hydrogen evolution reaction (HER)	Activated CNTs, ox-MWCNTs	90 and 95
Oxygen reduction reaction (ORR)	ox-MWCNTs	90, 96, 97
Friedel–Crafts alkylation reactions	GO, fullereneol	98–100
Michael and aza-Michael reaction	GO, fullereneol	100–102
Aldol reaction	Fullereneol	100
C–H arylation of benzene	GO	103
CO ₂ cycloaddition reaction to propylene oxide	GO/R ₄ N ⁺ X ⁻ , fullereneol/KI	104–106
Ring-opening polymerization (ROP) and olefin polymerization	GO	107 and 108
Electrochemical polymerization	rGO	109
Epoxide ring opening	GO	110

1.3.1 Oxidation Reactions

This is probably one of the main application areas of oxidized nanocarbons in catalysis. Alkanes, alkenes, alcohols, aromatic compounds and amines are common substrates chosen to demonstrate the ability of variably oxidized carbon nanomaterials to convert them into their oxidized counterparts.

In 2010, Bielawski and co-workers have pioneered research in the field of liquid-phase reactions for the oxidation of alcohol by metal-free, carbon-based catalysts. They have shown that the oxygen-group-rich graphene oxide (GO) can selectively catalyze the oxidation of various alcohols to aldehydes and *cis*-stilbene to the corresponding dione. GO has also been proven to be effective in the hydration of various alkynes to their corresponding ketones at ambient conditions (in air).⁷⁹ More recently, the Australian team of Zhao and co-workers has reported on oxidized carbon-black (CB)⁸⁰ and oxidized MWCNTs⁸¹ as valuable electrocatalysts for alcohol oxidation reactions (AOR of R–OH; R = Me, Et, ^tPr) in alkaline media. Surface-oxidized carbon (*e.g.* ketonic groups) are claimed by these authors to enhance the material's

electrocatalytic performance significantly, both in terms of current density (j) and alcohol oxidation onset potentials (E_{on}). Ma *et al.* have recently demonstrated how chemically modified graphene (CMG),^{111,112} a variety of rGO, in combination with H_2O_2 as an oxidizing agent, promotes the challenging one-step conversion of benzene into phenol with good activity and excellent selectivity (up to 99%).⁸² Although the catalytic role of O-containing surface species in CMG is unclear, the benzene adsorption to the CMG conjugated network and simultaneous H_2O_2 activation by its surface functionalities make this oxidized material an outstanding catalyst for the process.

Chemical, electrochemical, or thermal post-treatments of classically prepared oxidized nanocarbons can change their inherent catalytic behavior. Loh and co-workers have reported on the oxidative coupling of amines to imines catalyzed by GO under aerobic oxidative conditions. The authors have demonstrated how the GO performance can be dramatically enhanced by a sequential basic and acidic treatment.⁸³

The chemical processing redraws the material surface chemistry and generates carboxylic groups at the edges of surface defects along with localized unpaired electrons. They work synergistically to trap amines and molecular oxygen with beneficial effects on the catalyst performance (Figure 1.4).

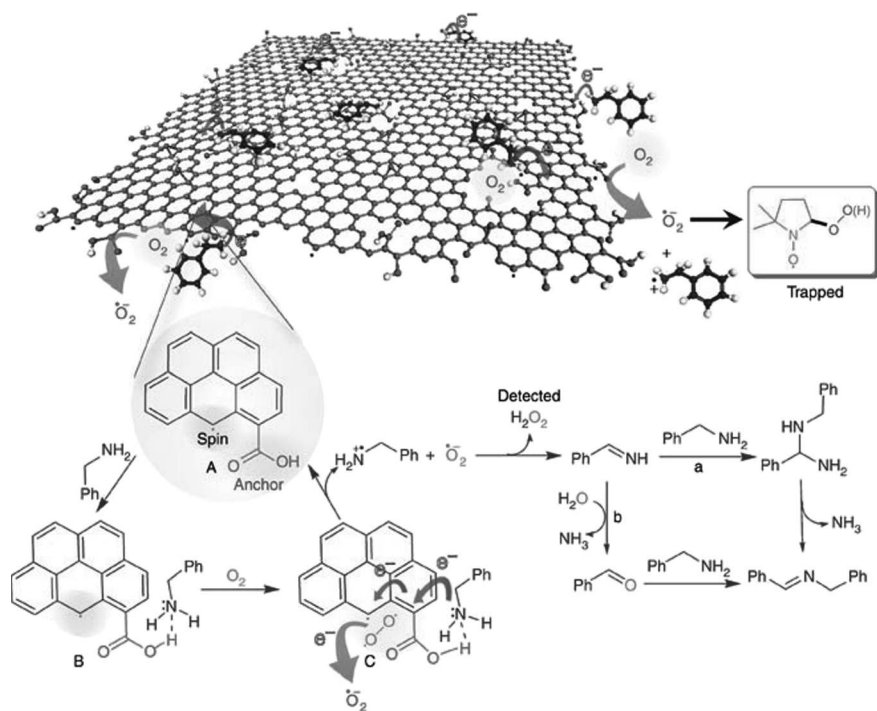


Figure 1.4 Mechanism of the GO-catalyzed oxidative coupling of primary amines. Reprinted by permission from Macmillan Publishers Ltd: *Nature Communications* (ref. 83), copyright (2012).

The combined action of O-containing functional groups (specifically carbonyl) and electronic properties of neighboring carbon sites are also claimed to drive the aerobic oxidative desulfurization of a broad range of sulfur-containing compounds from fuel. Su and co-workers have reported on a variety of reduced graphene oxides and their gas oxidation treatment as a valuable material process for the improvement of the rGO catalytic activity in the process.⁸⁴ The same authors have also shown that ketonic carbonyl groups are key functionalities in the nanocarbon-catalyzed oxidative dehydrogenation (ODH) of alkanes to alkenes.^{85,113} Recent findings from this team have elegantly contributed to elucidating the catalytic mechanism of action of oxidized nanocarbon in the ODH process by means of conjugated polymers containing ketonic functionalities as model catalysts.⁸⁶ Carbon-based materials have also received a great deal of attention as catalysts in industrial wastewater treatment. In the catalytic wet air oxidation (CWAO) of organic pollutants from water, surface functional groups are known to play a pivotal role on the final performance of these metal-free systems. Yang *et al.*⁸⁷ and Wang *et al.*⁸⁸ have reported on various oxidized carbon samples (GO, rGO, ox-MWCNTs and ox-carbon nanofibers) as excellent metal-free catalysts for the CWAO of phenol in aqueous media. Carboxylic groups at the surface of these materials are claimed to drive the catalyst performance while promoting the production of active radical species throughout the oxidation process.

Oxidized nanocarbons have also answered to the most urgent needs of a clean and sustainable production of energy. In this regard, hydrogen/oxygen production by electrochemical water splitting represents one of the most promising reactions to satisfy the steadily increasing global energy demand.⁸⁹ As for oxidation processes, Zhao and collaborators have shown that chemically oxidized MWCNTs followed by controlled hydrothermal and electrochemical activation treatments generate metal-free systems with unprecedented activity in the electrochemical oxygen evolution reaction (OER) in alkaline media.^{90,114} The observed OER performance is ascribed to the presence of ketonic groups that activate neighboring carbon surface sites, making them suitable acceptors of water oxidation intermediates.

1.3.2 Reduction Reactions

Chemical reduction processes promoted by oxidized carbon nanomaterials are almost exclusively limited to the activation and conversion of selected aromatic substituents. Ma and Bao have pioneered this research area.⁹¹ In 2011, they showed for the first time that the hydrogenation of nitrobenzene to aniline can be carried out with very high activity and selectivity over rGO at room temperature using hydrazine as the hydrogen source. In this seminal contribution, the authors proposed that carbon atoms at the zig-zag edges of rGO are the active sites for the activation and conversion of the nitro group. Later, Su and co-workers demonstrated that a controlled (and mild) oxidation of carbon nanomaterials by H_2O_2 provides valuable

catalytic systems for the process.⁹² Experimental evidence suggested that highly oxidized carbon sites at the nanomaterial surface (*i.e.* carboxylic group and anhydride) had only detrimental effects on nitroarene reduction. On the other hand, carbonyl groups seemed to favor the process by fostering hydrazine activation.⁹³

Recent studies have shown that oxygen-containing surface groups in nanocarbons hold key roles in reductive photochemical¹¹⁵ and electrochemical¹¹⁶ processes at the heart of renewable energy technology,⁷⁸ such as the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). Under UV or visible light irradiation, GO with an appropriate oxidation level can serve as a photocatalyst for water splitting and H₂ production without employing any charge separation co-catalyst.⁹⁴ Chemically activated CNTs *via* acidic oxidation followed by a cathodic electrochemical pre-treatment generate an outstanding class of acid stable metal-free HER electrocatalyst.⁹⁵ A hydrothermal method to improve the electrochemical properties of surface-oxidized MWCNTs without reducing their initial oxygen content has recently been proposed by Zhao and collaborators.⁹⁰ Such a post-oxidation treatment is found to improve the materials' hydrophilicity, induce transformation of oxygen functional groups and enhance the samples' electrical conductivity. The higher electrocatalytic performance of the hydrothermally treated materials in HER is mainly ascribed to the increased amount of surface groups with stronger electron withdrawing abilities (*i.e.* ketone and carboxylic groups). These authors have also shown that ORR kinetics on MWCNTs are strongly affected by the graphitic structure and surface oxygen functional groups available in the oxidized samples.⁹⁰ Similar to carbon samples for HER, hydrothermally treated oxidized MWCNTs offer better electrochemical performance in ORR than their simply oxidized counterparts. Wang's team has demonstrated that oxygen-containing functional groups (*i.e.* C–O and C=O) at the surface of carbon nanomaterials cause similar electronic effects to those observed in nitrogen doped systems.⁹⁶ Their surface grafting increases the number of defective carbon atoms and re-draws the material's electronic surface properties. The latter point is claimed to enhance the material oxygen adsorption properties. Lastly, surface functionalities improve the material wettability and lead to a better electrolyte diffusion.⁹⁶ As a matter of fact, hydrophilic moieties like carboxylic groups are claimed to impart beneficial effects to the nanomaterials' electrochemical performance in ORR.⁹⁷

1.3.3 C–C and C–N Bond Forming Reactions

Oxidized nanocarbons as metal-free systems catalyze C–C and C–N bond forming reactions, acting as stable and long-term re-usable solid materials. Classically prepared and carefully purified GO was proposed to efficiently catalyze the Friedel–Crafts reaction of indoles with various electron-rich and electron-deficient α,β -unsaturated ketones, giving the corresponding adducts with good yields and without by-products.⁹⁸ Song and co-workers have demonstrated that C₆₀ fulleranol (a poly-hydroxylated fullerene

prepared through a hydrogen peroxide heating method)¹¹⁷ is an active catalyst for promoting Friedel–Crafts reactions as well as other important C–C bond forming reactions such as Michael addition, Henry reaction, and aldol addition.¹⁰⁰ Among challenging C–C bond forming reactions, Szostak and co-workers have proposed a highly efficient and stereoselective protocol for the coupling reaction between styrenes and alcohols catalyzed by graphene oxides.⁹⁹ Mechanistic studies suggest that the reaction proceeds *via tandem* catalysis (Figure 1.5) with both reactants transiently activated at the GO functionalities and properly positioned for a concerted C–C bond forming step. GO is also employed as a simple and efficient phase transfer catalyst for Michael addition reactions in biphasic media, showing similar behavior to that of more classical crown-ethers in the process. Its highly hydrophilic surface along with the hydrophobic nature of the carbon network, make GO a valuable phase transfer candidate for driving potassium cations through two immiscible phases (aqueous and organic).¹⁰¹ Jain and Khatri found that GO can be a highly efficient, re-usable and cost-effective organocatalyst for the aza-Michael reaction between various amines and electron deficient olefins.¹⁰² These reactions proceed under mild conditions and afford C–N coupling products with excellent yields within short reaction times. The highly hydrophilic character of GO finally makes its separation and re-use after each catalytic run easy by means of simple extractions of the reaction mixture with dichloromethane.

More recently, Ma and co-workers have reported on the GO-catalyzed direct C–H arylation of benzene with various aryl iodides as a heterogeneous, cheap and environmentally friendly metal-free protocol enabling the formation of biaryl compounds.¹⁰³ The direct correlation between oxygen content in GO and yield of biaryl compounds has been demonstrated; the specific role of edge- or basal-plane O-containing groups has been clarified by means of oxygenated model molecular catalysts. According to the authors' conclusions, the combination of local charge densities induced by various C–O bond

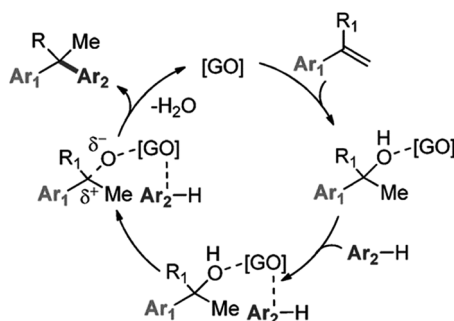


Figure 1.5 Mechanism for the GO-catalyzed alkylation of arenes. Reprinted with permission from F. Hu, M. Patel, F. Luo, C. Flach, R. Mendelsohn, E. Garfunkel, H. He and M. Szostak, *J. Am. Chem. Soc.*, 2015, **137**, 14473.⁹⁹ Copyright (2015) American Chemical Society.

polarizations and GO surface topological defects triggers the C-C coupling catalysis.

1.3.4 Cycloaddition and Polymerization Reactions

With the inter- and intra-molecular assistance of ammonium halides, GO also exhibits excellent catalytic performance in the CO_2 cycloaddition to propylene oxide (PO) thus giving the corresponding cyclic carbonate (propylene carbonate, PC) with high yield and selectivity under mild conditions. The reaction can be generalized in terms of epoxides' ring opening *via* CO_2 cycloaddition to provide cyclic carbonates as products. In 2014, Yin and co-workers have shown that GO hydroxyl groups foster the cycloaddition process by activating PO to undergo ammonium-halide (co-catalyst) mediated epoxide ring opening and CO_2 insertion.¹⁰⁴ Later on, the same group has reported on the superior catalytic activity of a properly synthesized multi-functional GO material (containing silanol groups, quaternary ammonium salts and amines) in the cycloaddition process (Figure 1.6).¹⁰⁵

The authors claim that covalently linked amines act as adsorption sites and activators for CO_2 , whereas silanol groups provide activation sites for PO and stabilize the ring opened oxirane before the intramolecular CO_2 addition and subsequent cyclization steps. C_{60} fullereneol was also found to be a highly

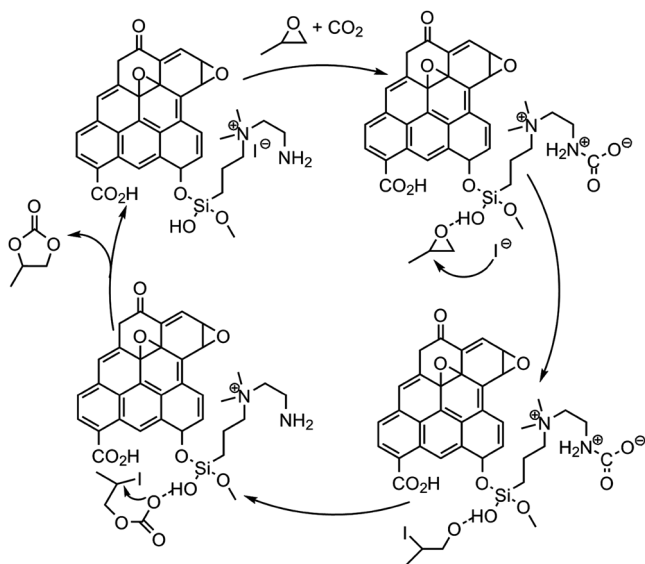


Figure 1.6 Possible reaction mechanism for the CO_2 cycloaddition to PO catalyzed by multifunctional GO. Reprinted from *Carbon*, **93**, D-H. Lan, L. Chen, C.-T. Au, S.-F. Yin, One-pot synthesized multi-functional graphene oxide as a water-tolerant and efficient metal-free heterogeneous catalyst for cycloaddition reaction, 22–31, copyright (2015), with permission from Elsevier.¹⁰⁵

active, selective and stable catalyst for CO₂ cycloaddition to epoxides to give a variety of cyclic carbonates with excellent yields.¹⁰⁶ The authors propose a solid/liquid interfacial hydrogen-bond assistance of the hydroxyl groups in the cycloaddition mechanism. They act as weak acids for the activation of epoxides; ring opening by a I⁻ anion followed by CO₂ insertion/cyclization leads to cyclic carbonates. The typical (Brønsted) acidic surface properties of oxidized nanocarbons make them ideal candidates to catalyze acid-mediated transformations. Bielawski's team discovered that GO (pK_a ~ 3 in water) catalyzes the efficient ring opening polymerization of various cyclic lactones and lactams to the corresponding polyesters and polyamides, respectively.¹⁰⁷ It can also act as a solid-state initiator for a broader range of acid-catalyzed olefins' polymerization.¹⁰⁸ The excellent activity of GO as an acid catalyst has been also proven by Garcia *et al.* in the ring opening of epoxides using methanol as a solvent and nucleophile at room temperature.¹¹⁰ On the other hand, rGO seems to be the best candidate to increase the electrochemical polymerization rate of 3-aminophenylboronic acid (ABA). Tan and Feng have systematically compared GO and its reduced counterpart in the ABA electrochemical polymerization, showing that stronger π - π interactions between the monomer and the larger graphitic network in rGO foster the electron transfer from the catalytic material to the adsorbed monomer.¹⁰⁹

1.4 Tuning Chemical and Electronic Surface Properties of Carbon Nanomaterials in Catalysis via Tailored Chemical Functionalization Protocols

Despite the huge versatility of simply oxidized nanocarbons in catalysis and the impressive number of catalytic processes they can promote as metal-free systems, other protocols have been recently applied to the development of covalently functionalized systems with tailored surface groups.

The use of well-defined functionalization procedures meets two fundamental needs: (a) to improve the catalytic performance of the metal-free systems, maximizing the amount of surface functionalities and (b) to provide new insights on the complex structure–reactivity relationship that controls their catalytic performance. Table 1.2 lists all the catalytic transformations promoted by covalently-decorated carbon nanomaterials as metal-free catalysts and afterwards discussed in Sections 1.4.1–1.4.2.

1.4.1 Acid- and Base-catalyzed Reactions with Functionalized Nanocarbons

One of the most relevant applications of chemically functionalized nanocarbons in metal-free catalysis refers to the acidic or basic character of their outer surface. Feng and co-workers have pioneered this research area with the

Table 1.2 Reactions catalyzed by functionalized carbon nanomaterials.

Class of metal-free catalyzed reaction	Covalently linked surface groups	Dominant surface properties	Reference
Esterification and hydrolyses reactions	Aryl sulfonic acids	Acid groups	118–121
Hydroquinone alkylation with ^t Bu-OH	Poly(styrene sulfonic acid)		122
Transesterification reactions	Tertiary aliphatic amines	Basic groups	123–125
Knoevenagel condensation	Aliphatic amines		126 and 127
Oxygen reduction reaction (ORR)	Poly(diallyldimethylammonium chloride) (PDDA)	Electronic control	128
	Aziridines		127
	Pyridines		129–131
	Pyroles		129

development of aryl sulfonic acids chemically grafted to the surface of ordered mesoporous carbons.¹¹⁸ The authors have demonstrated the effective use and recycling of these solid and highly porous materials as acid catalysts in esterification reactions for biodiesel production.¹¹⁹ Following these seminal contributions, other related functionalization protocols for the chemical grafting of aryl sulfonic acids have been accomplished with the aim of preparing acidic materials for catalysis. Poly(styrene sulfonic acid)-grafted carbon nanotubes have been presented in 2010 as acidic catalysts for the model alkylation of hydroquinone with *tert*-butanol.¹²² Fan and co-workers have also prepared a graphene-based catalyst by direct anchoring of sulfonic acid aryl radicals to reduced graphene.¹²⁰ Graphene surfaces undergo irreversible destruction upon direct treatment with sulfuric acid. In addition, the sulfonation reaction normally provides low yields. For these reasons, the use of aryl radicals to decorate graphene with phenyl sulfonic groups has provided an alternative and valuable approach for the preparation of the same kinds of samples. Later, Bitter's group has described a similar functionalization protocol for the surface decoration of carbon nanofibers with aryl sulfonic groups *via* aryl-diazonium salt chemistry.¹²¹ The authors have demonstrated the remarkable catalytic performance of the as-prepared solid acid materials in the transesterification of triolein and they have also shown how this functionalization approach provides samples that outperform benchmark acid catalysts for the same process.

For nanomaterial surface decoration with basic functionalities, Tessonier *et al.* have proposed the direct alkylation of MWCNTs with tertiary aliphatic amines for application in catalytic biomass conversion. At odds with more traditional and multi-step functionalization paths (*i.e.* MWCNTs' oxidation followed by activation of carboxylic acids as acyl chlorides and amine

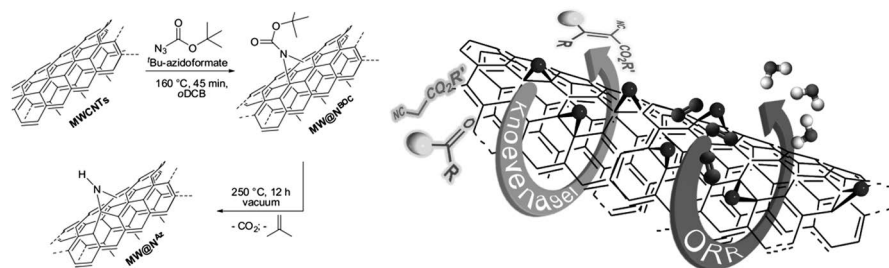


Figure 1.7 Left: [2+1] cycloaddition of *t*-Bu-azidoformate followed by BOC thermal decomposition for the synthesis of aziridine functionalized MWCNTs. Right: aziridine decorated MWCNTs as a versatile catalytic platform for the Knoevenagel condensation and electrochemical oxygen reduction reaction (ORR). Reprinted with permission from G. Tuci, L. Luconi, A. Rossin, E. Berretti, H. Ba, M. Innocenti, D. Yakhvarov, S. Caporali, C. Pham-Huu and G. Giambastiani, *ACS Appl. Mater. Interfaces*, 2016, **8**, 30099.¹²⁷ Copyright (2016) American Chemical Society.

nucleophilic substitution), the authors have proposed an elegant and faster nanotube deprotonation followed by direct amine grafting. The as-prepared metal-free catalyst has been tested with satisfactory outcomes in the transesterification of glyceryl tributyrates with methanol as a model reaction for biodiesel production.^{123–125}

Later, Cao and Song have reported on the amination reaction of the highly reactive fullerene (C₆₀) using organic amines.¹²⁶ The C₆₀-amine functionalized samples have been employed as stable and re-usable solid base catalysts for the Knoevenagel condensation, to give α,β -unsaturated compounds from the reaction between carbon acid compounds and a variety of aliphatic or aromatic carbonyls. Aziridine functionalized MWCNTs offer higher catalytic performance in the Knoevenagel process. Giambastiani *et al.* have proposed a two-step functionalization protocol for nanotube decoration with selected secondary (NH) aziridine groups (Figure 1.7).¹²⁷ The [2+1] nitrene cycloaddition of *tert*-butyl azidoformate, followed by a controlled thermal decomposition of the BOC protecting groups, led to the isolation of a highly basic, solid, and re-usable material for the Knoevenagel condensation with superior activity to that of related state-of-the-art N-doped and N-decorated carbon nanomaterials. Besides their basic character, the adopted functionalization protocol has also been used to modulate the surface electronic distribution thus imparting multimodality in catalysis to the as-synthesized samples. Indeed, the close proximity of the N-dopant to the sp² C-network creates high energy C-sites that activate small molecules for their conversion under appropriate conditions. The authors have demonstrated that aziridine functionalized MWCNTs act as excellent metal-free electrocatalysts under an alkaline environment for dioxygen activation and subsequent O₂ bond breaking within a prevalent 4e⁻ reduction process.

1.4.2 Chemically Decorated Nanocarbons with Tailored Functional Groups for the Electrochemical Oxygen Reduction Reaction (ORR)

Nitrogen-doped 1D and 2D carbon nanomaterials are known to act as valuable metal-free electrocatalysts for promoting ORR, a fundamental process at the heart of renewable energy technology.^{132,133} A relatively high number of N-doped carbon nanostructures with remarkable catalytic performance in ORR have been prepared through classical *in situ* nanomaterial doping (*i.e.* chemical vapor deposition technique).¹³⁴ Much less work, though, has been done for the design of catalytically active N-decorated samples by means of *ex situ* (exohedral) organic functionalization techniques.

Dai and co-workers have discovered in 2011 that functionalization of CNTs with polyelectrolyte chains containing positively charged nitrogen moieties creates net positive charges on CNT-carbon atoms *via* intermolecular charge transfer. Such an effect was found to remarkably improve the electrocatalytic activity of the functionalized systems in the ORR, providing metal-free systems with comparable, or higher, electrocatalytic activity and long-term stability to those of commercially available Pt/C electrodes.¹²⁸ More recently, Giambastiani and collaborators have proposed the grafting of tailored N-containing heterocycles through an aryl-radical attachment (Tour functionalization protocol) to the surface of purified MWCNTs.¹²⁹ This alternative approach offers a unique model system for the elucidation of the role of different N-configurations (pyridinic, pyrrolic, quaternary nitrogen) and that of their electronic surroundings on the O₂ activation mechanism.¹³⁰ Giambastiani and Pham-Huu have also demonstrated the existence of a rational trend (coherent with Sabatier's principle) between the electronic charge density distribution at the grafted N-heterocycles and their final control on the overpotential value at which the ORR starts.¹³¹ This trend is conveniently summarized with a volcano plot representation for a quick visual identification of the most suitable N-containing group for the process (Figure 1.8).

Finally, the same group has described the use of a [2+1] nitrene cycloaddition for the preparation of aziridine-decorated carbon-based systems as effective metal-free electrocatalysts for the ORR in an alkaline environment (Section 1.4.1).¹²⁷

1.5 Conclusion

We have provided a snapshot of covalent synthesis techniques for metal-free hetero-doped carbocatalysts. Post-synthetic modifications of graphene, fullerene, and carbon nanotubes using scalable liquid and gas phase techniques have given access to a range of materials active for traditional petrochemical reactions (oxidative dehydrogenation, desulfurization, *etc.*), fine chemicals synthesis (nitroarene reduction, Michael and Friedel–Crafts reactions, *etc.*), and electrocatalysis (OER, ORR). The grafting of desired moieties

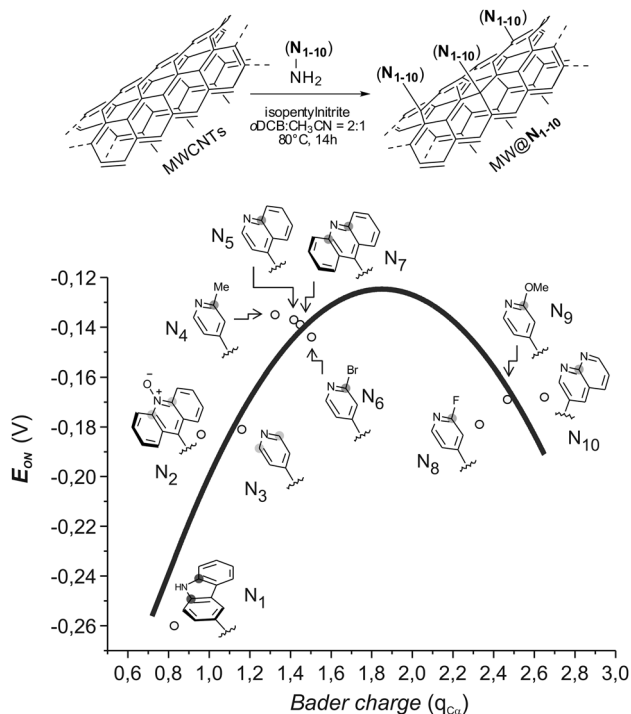


Figure 1.8 Top: MWCNT N-decoration *via* aryldiazonium salt (Tour) protocol.^{129,131} Bottom: a volcano plot representation for the "just right" interaction between O₂ and tailored N-groups at the outer surface of chemically decorated MWCNTs engaged in the ORR in an alkaline environment. Reproduced with permission from *CHIMIA*, 2017, 71, 568.¹³⁵ Copyright Swiss Chemical Society.

using C–C coupling reactions has allowed a better understanding of the nature of the active species, notably for electrocatalysis. Future advances in the field will rely on progress in controlling the nature, concentration, and distribution of heteroatom-containing moieties on carbon surfaces using scalable synthesis techniques. The deviation of carbo-catalyzed processes from conventional transition metal- and metal oxide-based catalysis will also require new insights from theory to understand the fundamental steps involved in these new conversions.

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