

Harnessing the chemistry of graphene oxide

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Our understanding of the fundamental structure and bonding of graphene oxide (GO) as well as the scope of its utility have grown tremendously over the past decade. As a result, the pace of research efforts directed toward this carbon material continues to increase. Contemporary application now intersects a variety of disciplines and includes heterogeneous catalysis, flow reactor technologies, biomedicine and biotechnology, polymer composites, energy storage, and chemical sensors. Advances in these areas have been buoyed by improvements in the methods used to synthesize and characterize GO, as well as functionalized derivatives thereof. While the diverse uses of GO have been reviewed previously, herein we provide an overview of some of the most recent and significant developments in the field. A brief overview of GO's synthesis and characterization is also provided as well as several recently proposed structural models. The inherent reactivity of GO is described in the context of catalysis, and the utilization of GO's reactive oxygen groups and carbon framework to prepare functionalized derivatives is also discussed. Finally, we provide an outlook of potential areas where GO, its derivatives, and related materials may be expected to find utility or opportunity for further growth and study.

Introduction

Since Geim and Novoselov's seminal report on the electronic properties of monolayer graphene in 2004,¹ interest in graphene and related materials has escalated sharply.² At the outset, much of the interest focused on the material's unique electronic features, particularly its high carrier mobility and lack of a band gap. Since that time, however, the scope of applications that graphene has been used for has grown significantly,³ largely as a result of its unique structure and properties. For example, graphene and related materials possess a high surface area monolayer and can be chemically modified (both covalently and non-covalently) in ways that allow for new functionalities or conjugates to be introduced.^{4,5}

One of the materials that has played a prominent role in the development of graphene and its derivatives is graphene oxide (GO).⁶ As the nomenclature indicates, graphene oxide is related to graphene in that both are carbon nanomaterials and, in their pristine, isolated forms, true monolayers. Beyond these basic similarities, however, graphene oxide and graphene are very different. While graphene is composed of only sp²-hybridized carbon atoms, graphene oxide has a carbon structure that is

interrupted by a range of oxygen functional groups (imparting a substantial degree of sp³ hybridization), whose structure will be explored more fully below. Such functionalization has a profound impact on the properties of the material, particularly when compared to its graphene parent. For example, while graphene exhibits extraordinarily high conductivity with carrier mobilities that can exceed 200 000 cm² V⁻¹ s⁻¹,⁷ GO is an insulator.

In view of GO's broad and growing utility in a variety of areas, it is worthwhile to consider the fundamental chemical properties of the material and how various applications might be influenced by those chemical features. We and others have previously presented comprehensive overviews of this topic,^{3,5,6,8} and so herein we aim to provide an update of the most recent and, in our opinion, broadly applicable and significant advances in the field. As will be apparent from the discussion below, GO is a remarkable material and, in many ways, unlike any other, with a large range of potential applications.

Refining the structural models of GO

The structure of GO has been the subject of debate for many years (see Fig. 1 for a summary of several structural models that have been proposed).⁶ Though the Lerf-Klinowski model, which will be described in greater detail below, has been most widely adopted, agreement on this topic is far from unanimous. Perhaps either reflecting from or causing this ambiguity, there are multiple routes for preparing GO. Including the Staudenmaier,⁹

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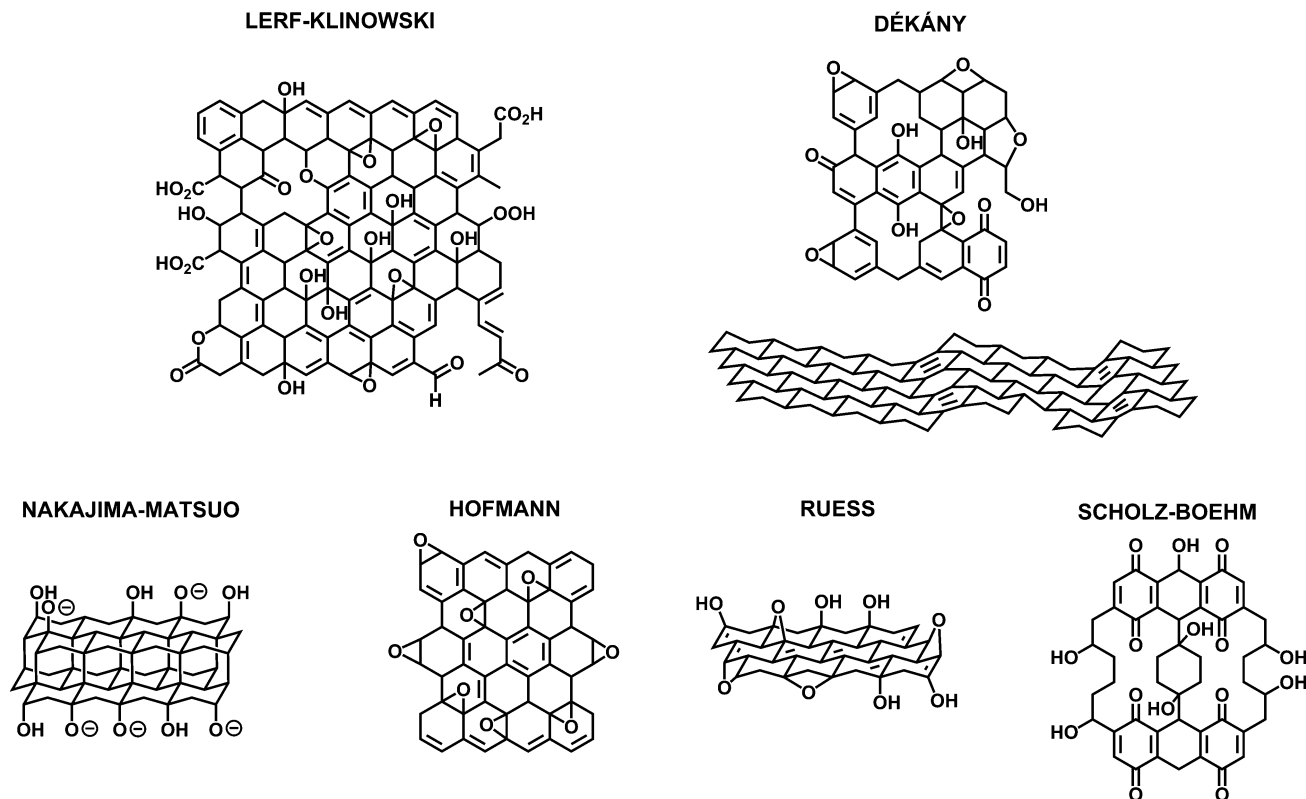


Fig. 1 Summary of structural models of GO that have been proposed, including modern examples (top; Lerf–Klinowski and Dékány models) as well as earlier examples (bottom; Nakajima–Matsuo, Hofmann, Ruess, and Scholz–Boehm models).^{6,20}

Table 1 Summary of synthetic methods used to prepare GO

Method	Oxidant	Reaction media	Carbon-to-oxygen ratio ^a	Raman spectral I_D/I_G ratio ^a	Charge-transfer resistance (R_{CT}) ^a (kΩ)	Notes
Staudenmaier ⁹	KClO ₃	Fuming HNO ₃	1.17	0.89	1.74	—
Brodie ¹⁰	KClO ₃	HNO ₃ + H ₂ SO ₄	—	—	—	KClO ₃ added stepwise rather than in a single bolus
Hofmann ¹¹	KClO ₃	Non-fuming HNO ₃	1.15	0.87	1.68	—
Hummers ¹²	KMnO ₄ + NaNO ₃	Conc. H ₂ SO ₄	0.84	0.87	1.98	Modifications can eliminate the need for NaNO ₃
Tour ¹³	KMnO ₄	H ₂ SO ₄ + H ₃ PO ₄	0.74	0.85	2.15	—

^a Reproduced from a previously reported comparison of the various preparation methods.¹⁴

Brodie,¹⁰ Hofmann,¹¹ Hummers,¹² and Tour methods,¹³ at least five different approaches for synthesizing GO have been described (see Table 1). Moreover, it has been shown that the structure of GO varies depending on the oxidation conditions¹⁴ and the starting graphite material employed.¹⁵ Thus, GO may be thought of as a family of materials, rather than as a single composition, and therefore must be properly and sufficiently described (*e.g.*, *via* carbon-to-oxygen ratio, conductivity, particle size, spectroscopic features, *etc.*).¹⁶ Moreover, adequate characterization and nomenclature are essential to limit reproducibility problems and batch-to-batch variations.

The stoichiometry of GO's constituent oxygen functionality can vary as a function of the graphite precursor, oxidation conditions, and workup treatments. As a result, identifying and quantifying the various functional groups present in GO has proved to be

remarkably challenging. A broad array of analytical tools has been brought to bear on this problem, and several key features can be identified. The most widely accepted structural model of GO is the Lerf–Klinowski model (see Fig. 1)¹⁷ and is defined by two distinct regions in the GO structure: one of lightly functionalized, predominately sp²-hybridized carbon (graphene-like) atoms and a second of highly oxygenated predominately sp³-hybridized carbon atoms. In this model, hydroxyl and epoxide functional groups are proposed to decorate the basal plane which are segregated into islands among the lightly oxidized, graphene-like regions, while carboxylic acids or carboxylates, depending on the pH of the solution, are present on the edges of the sheets. Additionally, the harsh oxidizing conditions are known to “shred” the graphite into smaller particles. This effect is believed to occur in a step-wise process *via* the progressive oxidation of epoxides, defects, or other

functionality on the carbon surface, resulting in the formation of holes in the plane, smaller flake sizes, and highly oxidized species (e.g., carboxylic acids) on the periphery of the sheets.^{5,18,19} The resulting GO material is both oxidizing and acidic, properties which have found utility in GO's use as a catalyst for a variety of chemical reactions as will be described below. Other models of GO, such as those shown in Fig. 1, vary primarily with respect to the extent of sp^2 -hybridization of the carbon, the presence of 1,2- (i.e., epoxides) versus 1,3-ethers, and the presence of carboxylic acids versus quinones or other carbonyl species.^{6,20}

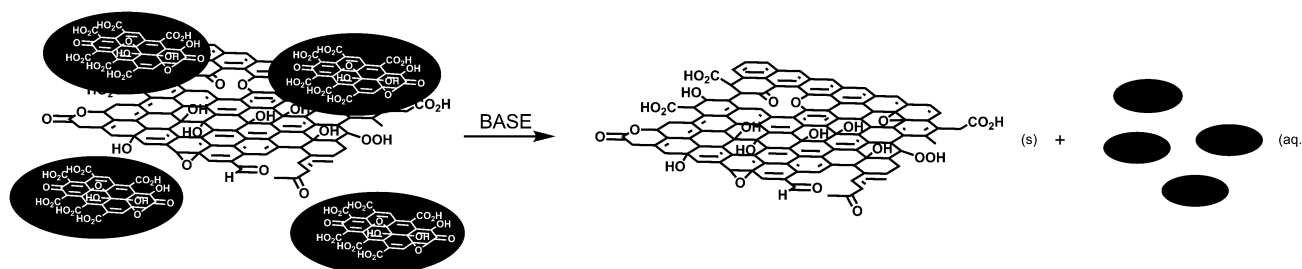
A thorough, comparative study of the synthetic oxidation methods used to access GO was recently reported by Pumera and co-workers.¹⁴ Briefly, the authors of this study found that permanganate-based oxidations (such as the Hummers and Tour methods) introduced a greater amount of oxygen functionality and a higher proportion of carbonyl and carboxylic acid groups than methods that utilize chlorate-based oxidants, as determined by XPS, elemental analysis, NMR spectroscopy, and FT-IR spectroscopy (see Table 1). Perhaps reflective of the relatively harsh reaction conditions and the greater extent of oxidation, the materials prepared using the former methods displayed a wider variety of electrochemical properties (e.g., electron-charge transfer resistance and electron transfer rate). In contrast, the chlorate-based oxidations (such as the Staudenmaier, the Brodie, and the Hofmann methods) were found to typically afford materials with less extensive but more uniform functionality, even when variations in the reaction conditions were explored.

Among the most significant changes in our understanding of GO's structure that have emerged over the last several years relate to the detection and elucidation of smaller scale atomic and molecular features. One significant contribution in this area has been the identification of so-called oxidative debris on the presence of GO's surface. First described in a seminal 2011 report by Rourke, Wilson, and co-workers,²¹ and followed by other subsequent studies,^{22,23} oxidative debris can be thought of as small, humic acid-like fragments of oxidized hydrocarbons that are generated during the oxidation of graphite. Though much smaller in size than the graphite flake from which they originated, the debris particles were sufficiently large to be insoluble and adhered strongly to the underlying graphitic surface (see Scheme 1). Harsh treatment with aqueous NaOH was necessary to solubilize and remove the adhered particles. Additionally, the authors discovered that these smaller fragments bore the majority of the oxygen functional groups found in bulk GO, and that the

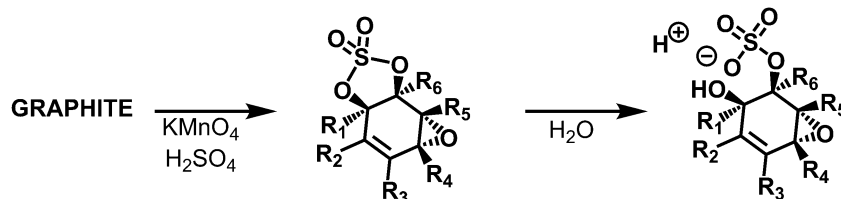
underlying basal plane was less oxidized, as evidenced by changes in solubility, oxygen content, and other key metrics following base treatment. While GO is known to be weakly fluorescent (albeit with a low quantum yield of approximately 0.02%), the aforementioned group found that much of the fluorescent properties may be attributable to the oxidative debris fragments²⁴ as the underlying graphene-like sheets typically have a strong fluorescence quenching effect.^{25,26}

Another significant advance in our understanding of GO's structure relates to the presence of sulfur functionality. Some of the methods for preparing GO utilize sulfur-containing reagents (e.g., H_2SO_4) as solvents, notably the Hummers and Tour methods.^{12,13} As a result, appreciable amounts of sulfur can be introduced into the GO product. Though it was known that GO prepared *via* the Hummers method often contains sulfur, these heteroatomic components did not receive much attention in the early models proposed (or, for that matter, in consideration of its properties); this viewpoint has recently changed. In 2013, Eigler and co-workers described a study that was specifically designed to understand how sulfur influences the structural, bonding, and physicochemical properties of GO.²⁷ As part of this analysis, it was found that extensive washing with aqueous media did not remove sulfur species from the GO, indicating that sulfur may be covalently bound to the surface. Upon characterizing these bound species, it was proposed that the Hummers method of oxidation resulted in the formation of cyclic organosulfates, which are susceptible to hydrolysis during the aqueous workup (see Scheme 2). These sulfate groups (estimated to be present at approximately one sulfate per twenty carbon atoms²⁷) are believed to be the source of GO's acidity (pK_a 3–4 in water), which is appreciably lower than what would be expected for carboxylates or other simple carbon–oxygen acidic species.^{28–30}

The reactivity of GO with water has been the subject of study as well, with a particular focus on the stability of GO under ambient conditions and changes that may occur in its structure over time.^{31,32} A seminal report by Tour and co-workers in 2012 revealed that GO prepared in the absence of aqueous purification (termed “pristine GO”) possessed a very different structure than GO prepared using a more typical aqueous workup.³³ Indeed, when organic media, such as methanol or trifluoroacetic acid, were used for purification, as opposed to the conventional aqueous media used to remove the acids and salts present in the oxidation, the diagnostic spectroscopic and morphological



Scheme 1 Schematic of oxidative debris (encircled) believed to be present on the as-prepared GO surface. Oxidative debris can be removed by treatment of crude GO with base, rendering the debris soluble. The GO sheet and oxidative debris are not shown to scale.



Scheme 2 Organosulfates present in GO prepared *via* the Hummers method have been shown to be susceptible to hydrolysis, leading to the formation of acidic sulfate species in the final product.

properties of GO, and even the color of the bulk material (an off-white or tan color, as opposed to brown or black), were different. Pristine GO was found to contain significantly less water in its structure, as determined by thermogravimetric analysis (TGA), and tended to decompose at elevated temperatures when compared to water-treated GO.

The spectroscopic characteristics of the pristine GO were also compared to those of the water-treated analogue. The former did not display significant UV-vis absorption in the range of 400–800 nm, which likely reflects the presence of smaller aromatic domains in the basal plane. Conversely, absorption was stronger in the latter at all wavelengths studied (200–800 nm) under otherwise identical conditions. The enhanced absorption was attributed to a greater number of conjugated, sp^2 -hybridized carbons in the water-treated GO, as determined by solid state ^{13}C NMR spectroscopy. Additionally, the IR spectrum recorded for the pristine GO displayed signals that were assigned to sulfate esters; analogous signals were not observed in IR spectra recorded for the water-treated sample. Upon exposure of the pristine GO to water, the intense brown coloration typically seen in GO samples returned. The authors attributed the aforementioned spectroscopic and chemical differences to the hydrolysis of metastable functional groups (see Scheme 3), including organosulfates, as well as the water-mediated rearrangement of oxygen functional groups on the GO surface. Collectively, the findings of these studies indicate that the functional groups introduced during the oxidation of graphite may be susceptible to further reaction under ambient conditions, particularly with water. Such reactivity may have implications on the materials' ultimate properties and functions, including catalytic activity, the structure of graphene produced from GO, and GO's reinforcing effects in polymer composites.

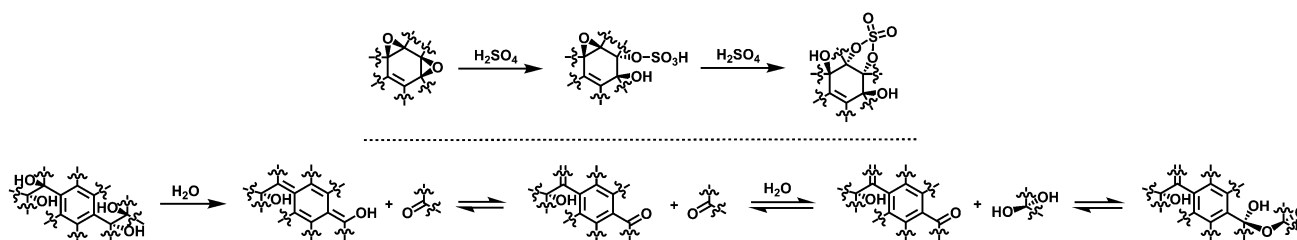
Characterization methodology

The characterization of GO is often directed toward understanding two fundamental properties of the material: the extent and identity of the chemical functionality present, and the

physical morphology of the nanomaterial (*e.g.*, particle size, surface area and porosity, lattice defects, stacking behavior, *etc.*). To analyze the chemical functionality, standard techniques such as FT-IR spectroscopy,³⁴ X-ray photoelectron spectroscopy (XPS),³⁵ solid state NMR spectroscopy,³⁶ various electrochemical methods,¹⁴ and a range of chemical reactivity tests have been used to qualitatively and quantitatively ascertain the surface functionality.^{17,37} The total oxygen content is a critical metric for understanding the extent of oxidation in any of the aforementioned synthetic protocols and can be readily quantified using either elemental combustion analysis or XPS. Additionally, it is also worth mentioning that unlike most other carbon nanomaterials, GO is readily dispersible in water or polar organic media. This useful property has enabled additional methods such as solution state UV-vis spectroscopy, although the solution state NMR spectra of GO have not been reported to date to the best of our knowledge; at present, solid state NMR techniques appear to be the preferred methods.

The suitability of various physical characterization methods depends on the form of the GO material. For example, particle size may be characterized in solution using DLS or other laser scattering methods,³⁸ or solid state techniques such as TEM^{39,40} or AFM.⁴¹ Given the dynamic, flexible nature of GO's lamellar morphology, differing particle sizes may be determined depending on the chosen method. Indeed, molecular dynamic simulations have shown that both pristine and functionalized graphene monolayers exhibit considerable structural flexibility^{42,43} which, in turn, influences the sheets' ability to interact with small molecules or biological agents (*e.g.*, proteins, enzymes, *etc.*) or be dispersed in solvents, polymers, and other nanomaterials.

Other properties of GO have also been evaluated in solution as well as in the solid state. For example, GO's surface area is most commonly measured using isothermal nitrogen sorption (the so-called BET method⁴⁴), although quantitative spectrophotometric techniques that involve measuring the adsorption of methylene blue in aqueous dispersions of the carbon material



Scheme 3 Proposed transformations that occur upon reaction of H_2SO_4 (top) or water (bottom) with so-called pristine GO lead to the conventional material that is commonly isolated and used.³³

have also been used.⁴⁵ While raw GO powder prepared *via* the Hummers method typically has a very low surface area ($< 5 \text{ m}^2 \text{ g}^{-1}$) due to its tightly stacked structure as well as the intercalation of water into the interlamellar region,⁴⁶ aqueous dispersions of GO exhibit surface areas in excess of $700 \text{ m}^2 \text{ g}^{-1}$ as a result of the material's extensive exfoliation in an aqueous environment.⁴⁵ Moreover, modifying the purification procedure or using expanded graphite in lieu of natural flake graphite as the starting material was shown to afford large sheets of GO (approximately $100\text{--}500 \text{ }\mu\text{m}$).^{47–50} Such sheets of GO were found to exhibit lyotropic liquid crystallinity in both aqueous and organic media, and thus are poised to induce advanced, higher order structures in fibers and polymer composites.^{51–53} Regardless, the interlayer spacing in the powdered GO material is often determined *via* powder X-ray diffraction,⁵⁴ and the extent of defects present in the lattice as well as the number of layers in the stacked structure can be measured using spectroscopic (*e.g.*, *via* Raman spectroscopy⁵⁵) or microscopic techniques (*e.g.*, *via* TEM,⁵⁶ SEM,⁵⁷ or AFM⁴¹). While the aforementioned methods provide information about the basic physicochemical properties of GO, more specialized techniques for characterizing or evaluating other properties of GO, such as cellular assays for determining GO's biocompatibility⁵⁸ or mouse models for determining biodistribution,⁵⁹ have been employed as needed.

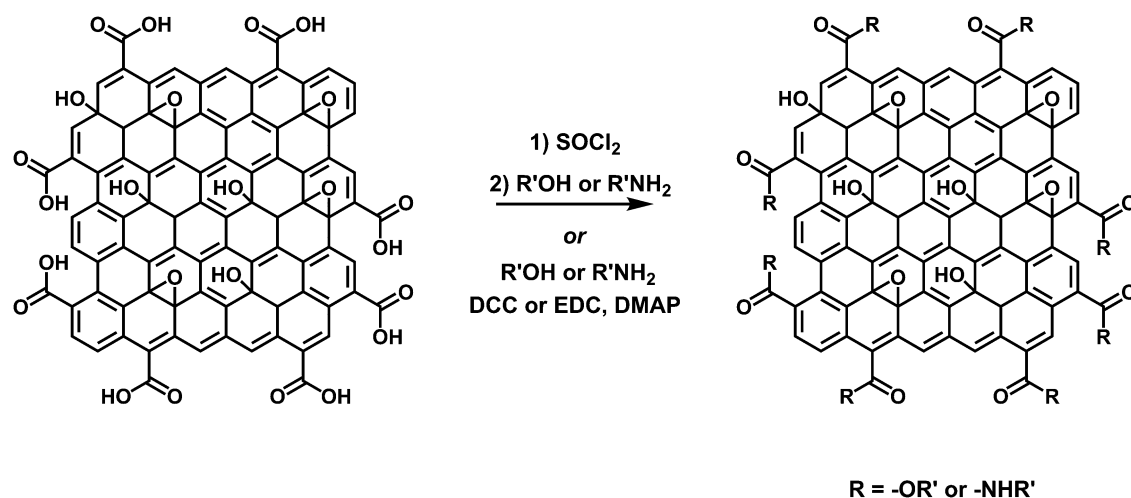
Functionalized derivatives of GO

It is well established that the densely functionalized surface of GO has provided unique opportunities for chemical modification *via* classic organic transformations to finely tune the material's chemical and physical properties. The methods used to derivatize GO are highly dependent on the desired application and properties such as electrical and thermal conductivity, hydrophilicity, and mechanical reinforcement. Oftentimes, functionalized derivatives of GO exhibit physical properties not found in as-synthesized GO. For example, in polymer composite processing, GO can be made

dispersible in organic solvents *via* functionalization with hydrophobic groups that also often influence interfacial interactions with the polymer. Moreover, functionalized derivatives of GO can also be reduced to obtain an electrically or thermally conductive material. In the broadest sense, the functionalization of GO can be divided into two categories: peripheral functionalization and basal plane functionalization. Modifications of the periphery of GO typically utilize the reactivity of the carboxylic acid groups whereas basal plane modification has traditionally harnessed the reactivity of the resident hydroxyl and epoxide groups. Notably, many of these functionalization routes have assumed, either explicitly or implicitly, the Lerf–Klinowski structural model, and because of their success have provided additional support for understanding GO's structure and bonding.

Functionalization of the carboxylic acids on graphite oxide

Generally, the peripheral carboxylic groups of GO may be activated by either pre-treatment with SOCl_2 followed by condensation with a nucleophile or through carbodiimide couplings with alcohols or amines (see Scheme 4). In the route that utilizes SOCl_2 , GO is typically exfoliated in THF or other relatively non-nucleophilic solvents and then refluxed with a large excess of the chlorinating agent, followed by the addition of a nucleophile. In the aforementioned carbodiimide coupling chemistry, GO is first exfoliated in a polar solvent (typically DMF or NMP) and then treated with a catalytic amount of *N,N*-dimethylaminopyridine (DMAP), *N*-hydroxysuccinimide (NHS), or another carboxylic acid activator. A mixture of the coupling agent (*e.g.*, dicyclohexyl carbodiimide [DCC] or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide [EDC]) and nucleophile are then added in excess and the reaction is allowed to proceed for a desired amount time. Isolation of the resultant modified GO obtained from either of the aforementioned methods is typically accomplished *via* filtration or centrifugation. Such methodology is not limited to small molecule nucleophiles; oligomeric and polymeric species can also be employed.^{60–64} For example, GO was



Scheme 4 Activation of GO's peripheral carboxylic acid groups with either SOCl_2 or a carbodiimide, and subsequent condensation with an alcohol or an amine.

activated with EDC and then functionalized with chitosan ($M_n = 3$ kDa). The resulting water-dispersible chitosan-GO composites were then used as a system to deliver a water-insoluble drug (camptothecin).⁶⁰ In another example, the carboxylic acid groups of GO were converted to the acyl halides using SOCl_2 and then subsequently treated with hydroxyl-terminated poly-(3-hexylthiophene) (P3HT) to form the corresponding esters. Blending P3HT-GO composites with C_{60} has been shown to afford photovoltaic devices that exhibit improved power conversion efficiencies with respect to analogous materials that lack GO.⁶⁴

Functionalization at the hydroxyl groups of GO

Similar to GO's carboxylic acid groups, the hydroxyl groups may be functionalized using carbodiimide coupling chemistry. In this case, a surface-bound hydroxyl group on GO serves as the nucleophile and condenses with an exogenous carboxylic acid. For example, Zhang and coworkers demonstrated that the hydroxyl groups of GO could be capped with *S*-1-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDMAT), a known chain transfer agent (CTA), through carbodiimide coupling.⁶⁵ Poly(*N*-vinylcarbazole) was then grafted in a controlled manner from the CTA-functionalized GO surface to yield materials that displayed electrical switching and memory effects when fabricated into an optoelectronic device. Alternatively, the hydroxyl groups readily react with trialkoxysilanes^{66–68} or alkyltrichlorosilanes⁶⁹ to afford siloxy linkages. One advantage of using silane reagents is that the byproducts (*e.g.*, ethanol or HCl) can be removed more conveniently than the urea byproducts generated during carbodiimide-mediated couplings.

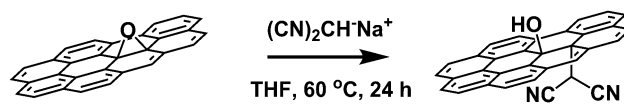
Another method of functionalization that initially utilizes the reactivity of the hydroxyl groups is through the reaction of *N,N*-dimethylacetamide dimethyl acetal (DMDA) with GO, as shown in Scheme 5.⁷⁰ In this approach, the hydroxyl group condenses with DMDA to form a vinyl ether intermediate which then undergoes an Eschenmoser–Claisen [3,3] sigmatropic rearrangement with a surface carbon to ultimately afford a C–C bond. Such C–C bond forming transformations are relatively rare for GO, and are of great importance and utility in the field of functionalized graphenes (see below for another example using malononitrile as a carbanionic nucleophile). Carbon–carbon bonds may be expected to be more stable than other linkages (*e.g.*, esters and amides are susceptible to hydrolysis), and thus it is likely that similar chemistry may be applied directly to functionalized graphite or graphene produced *via* other methods, bypassing the need to use GO as an intermediate. Regardless, evidence for the aforementioned sigmatropic rearrangement was confirmed through

the identification of an amide stretching frequency in the FTIR spectrum of the DMDA-treated GO. As an extension of the aforementioned methodology, the same group also utilized the Johnson–Claisen rearrangement to directly functionalize the sp^2 -hybridized, planar graphitic carbon. Triethyl orthoacetate was condensed with a surface hydroxyl group and subsequent rearrangement led to the formation of a basal γ,δ -ester. Furthermore, the resultant esters were hydrolyzed to afford basal carboxylic acids, which could be further modified using the carboxylic acid functionalization procedures described above.⁷¹

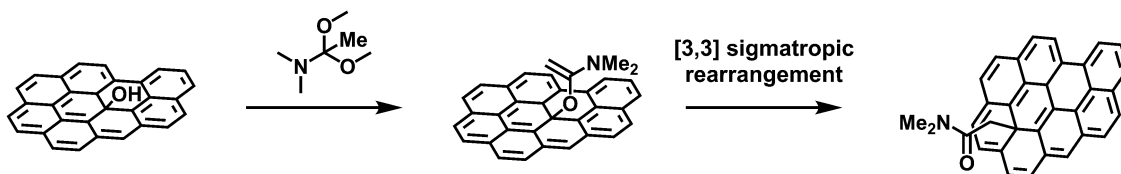
Functionalization *via* epoxide ring opening

Another route to derivatize the basal carbon surface of GO is through the ring opening of the epoxide groups. The nucleophile of choice is typically an amine, including aliphatic, aromatic, and polymeric variants. Generally, the amine is heated in the presence of exfoliated GO in a polar solvent and purification/isolation involves either filtration or centrifugation. Beyond heteroatomic nucleophiles, carbanions have also been used in the same manner to open the epoxide groups.⁷² For example, Swager and coworkers demonstrated that the sodium salt of malononitrile could form a C–C bond with the sp^2 -hybridized graphitic carbon (see Scheme 6).

To attenuate adventitious acid/base reactivity associated with the carboxylic acid groups present on GO, a large excess (5.5 mass equivalents) of the malononitrile salt was employed to ensure adequate functionalization. The presence of the malononitrile group was confirmed through FTIR, XPS and powder XRD analyses, with the $\text{C}\equiv\text{N}$ groups providing diagnostic spectroscopic handles. Moreover, it was shown that the surface-appended malononitrile group could be deprotonated with NaH, and subsequently alkylated with hydrophobic (*e.g.*, 1-iodohexadecane) or hydrophilic (*e.g.*, 1,3-propanesultone) groups to influence the solvent compatibility of the respective GO derivatives. Other carbon-based nucleophiles were tested (*i.e.*, organolithium and organocuprate reagents); however, both proved to be incompatible with GO. The basicity of the aforementioned carbon nucleophiles was found to be problematic due to the generation of strong alkaline solutions, which can lead to the reduction/deoxygenation of GO. As previously mentioned, such chemistry could occur through stripping



Scheme 6 The reaction of the sodium salt of malononitrile with the epoxide groups on the basal plane of GO.



Scheme 5 General strategy used to functionalize GO *via* condensation followed by Eschenmoser–Claisen [3,3] sigmatropic rearrangements.

of the oxidative debris present on the GO surface²¹ rather than through deoxygenation of the basal plane itself.

Reactive intermediate functionalization of GO

The use of reactive intermediates (*e.g.*, aryl diazonium salts,^{73,74} carbenes,^{75,76} and nitrenes^{77,78}) to directly functionalize the sp^2 -hybridized basal plane have typically been reserved for reduced forms of GO (*e.g.*, chemically-reduced GO). Recently, however, Liu and coworkers demonstrated that unmodified or “as-synthesized” GO was compatible with carbethoxycarbene.⁷⁹ As summarized in Scheme 7, following dispersing GO in THF and adding ethyl diazoacetate, the resulting mixture was subjected to microwave irradiation to generate the carbene *in situ*. Functionalization was confirmed by the appearance of alkyl stretching frequencies in the FTIR spectrum. One advantage of the aforementioned cyclopropanation methodology is that the majority of the oxygen functionality remains unaltered, which could allow for further modification.

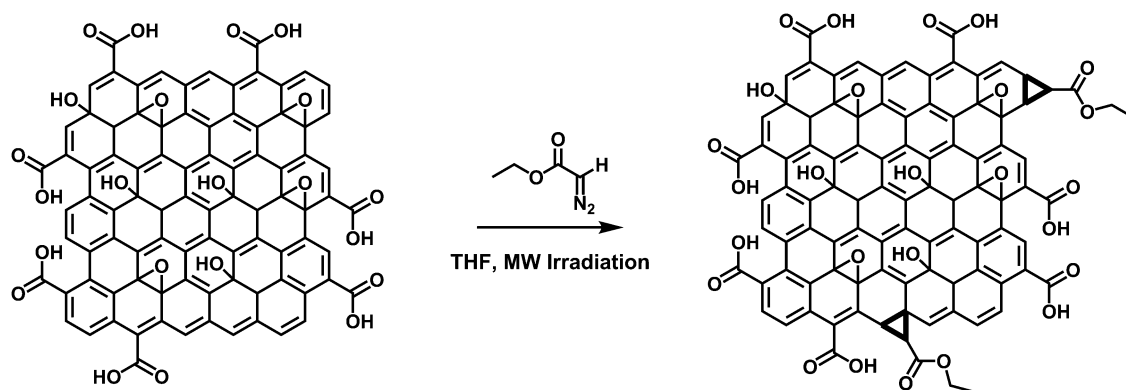
The functionalization of GO *via* the aforementioned routes has led to complex architectures with diverse properties such as increased hydrophilicity or hydrophobicity as well as enhanced thermal stability and mechanical robustness. As such, functionalized derivatives of GO have found applications in polymer composites, drug delivery systems, analyte sensing, and electrochemical devices.⁸⁰ One aspect of GO functionalization that remains challenging is control over chemoselectivity and regioselectivity. For instance, when GO's carboxylic acid groups are amidated using $SOCl_2$ or carbodiimide coupling chemistry, the exogenous amine can simultaneously functionalize the basal plane *via* ring opening of the epoxide group. As such, careful consideration should be given to the reaction conditions when modifying the functional groups of GO. Regardless, modifying GO to achieve desired chemical and physical properties will continue to be an important objective for the development and progression of the chemistry of GO.

Covalent and non-covalent approaches to GO-based polymer composites

Polymer composites represent another area that frequently capitalizes on GO's reactivity and ability to modify the carbon

material's functional groups. GO-based polymer composites are attractive materials in that they often possess enhanced thermal and/or mechanical stability when compared to the filler-free polymer.^{81–83} Ultimately, as with all nanocomposite materials, the final properties of the composite are dictated by the filler's dispersion and the polymer–filler interfacial interaction. Chemical modification of GO's functional groups can maximize both of the aforementioned properties. For example, using a grafting-to approach, carboxylic acids present on GO were esterified with poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS, $M_n = 170$ kDa).⁸⁴ The resulting polymer functionalized-GO was solution blended in THF with poly(styrene) (PS) to form composites (carbon loadings at 0.5, 1.0, and 2.0 wt%) that showed an increase up to 78% in the tensile strength and 73% in the Young's modulus when compared to unmodified PS. Furthermore, PS blended with 2.5 wt% of the polymer functionalized-GO showed a 26 °C difference in the temperature at which 10% of the mass of the material is lost, as determined *via* thermogravimetric analysis (TGA) under an atmosphere of air, when compared to the carbon-free polymer. The increased mechanical and thermal robustness of the composites was a result of uniformly distributed SEBS functionalized-GO within the PS matrix which ultimately led to maximized interfacial interaction. A variety of other similar grafting-to approaches have been used, with similar results, and polymer-functionalized GO materials have likewise been synthesized using grafting-from methods, wherein the polymers are grown from initiators covalently bound to the GO surface.^{85,86}

In contrast to covalently modifying GO's functional groups for polymer composite applications, there are examples where as-synthesized GO enhanced the physical properties of various polymer matrices *via* non-covalent interactions. Non-covalent approaches for composite fabrication take advantage of hydrogen bonding and van der Waals' interactions between the polymer and GO to enhance the polymer's physical properties. For example, there was a 76% increase in the tensile strength and a 62% increase in the Young's modulus of poly(vinyl alcohol) when GO was incorporated into the polymer at 0.7 wt% when compared to GO-free PVA.⁸⁷ The improvement in mechanical properties was attributed to the hydrogen bonding between the hydroxyl groups of PVA and GO's functional groups



Scheme 7 Cyclopropanation of as-synthesized GO using carbethoxycarbene under microwave irradiation (adapted from ref. 79). The bonds comprising the cyclopropane rings were emboldened to improve clarity.

(*e.g.*, hydroxyl, carbonyl, epoxides). Another example of using non-covalent interactions to form GO-based composites was illustrated by Tsukruk and coworkers who fabricated fibroin-GO composites using a layer-by-layer deposition technique with varying ratios of GO (*e.g.*, 3.0, 6.0, 9.0, 11.5 and 23.5 vol%).⁸⁸ Fibroin, a protein with exceptional mechanical properties found in silk,⁸⁹ contains both hydrophilic and hydrophobic regions. After processing, the resulting composites displayed significant improvements in mechanical properties when compared the unmodified fibroin. For example, at 23.5 vol% of GO (relative to fibroin), the Young's modulus of the composite was 145 GPa whereas the GO-free fibroin displayed a Young's modulus of 10 GPa. The improvement in mechanical properties was attributed to hydrogen bonding between the amide functionality of the fibroin and the oxygen functionality of the GO, and hydrophobic interactions between the fibroin and aromatic regions of the GO. Collectively, the synergy of multiple non-covalent interactions between the fibroin and GO produced a mechanically robust synthetic and bioderived composite.

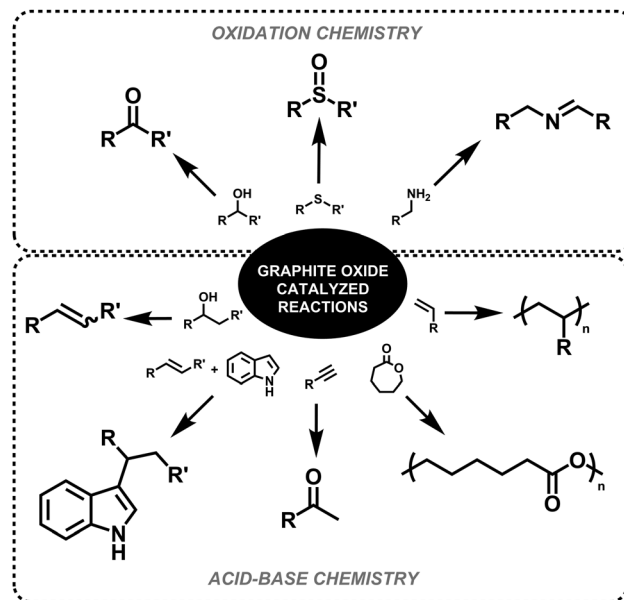


Fig. 2 Examples of various transformations facilitated by GO.

Catalytic applications

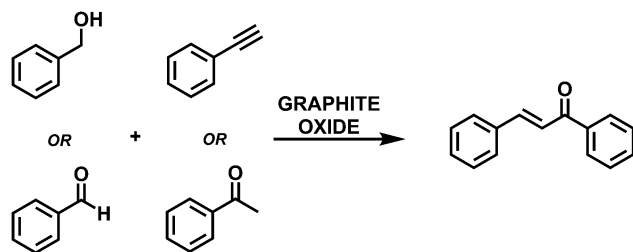
GO's intrinsic reactivity

As a result of GO's remarkable physicochemical structure and properties (such as its high surface area upon exfoliation), the material has found broad utility as a component in synthetic reactions. Since at least 1962 it has been recognized that GO has "rather strong oxidizing properties,"⁹⁰ but only recently has this property been utilized to drive chemical reactions. Our own work in this field began with studies exploring GO's utility in alcohol oxidations and alkyne hydrations.^{46,91} Several key observations were made. First, while GO facilitated the aforementioned transformations, reduced GO (prepared by reacting GO with hydrazine hydrate) and graphite did not, indicating that oxygen functionality appeared to be a crucial component of the reaction process(es). Second, performing the alcohol oxidations under an inert atmosphere of nitrogen resulted in minimal conversion, as did performing the reaction in the presence of a radical inhibitor (*e.g.*, butylated hydroxytoluene; BHT), both consistent with a radical-based process that incorporated molecular oxygen as the stoichiometric oxidant. Third, the GO was recovered and reused in multiple oxidation cycles. Collectively, these findings suggested to us that GO acted as a catalyst rather than a stoichiometric reagent. It should be noted, however, that in our studies relatively high mass loadings of the GO were required. While such a level of loading might be indicative of stoichiometric reactivity, it is critical to note that at this point the active site is not well understood (though computational work suggests that epoxides present on the GO surface may be active in some of these reactions⁹²), and its concentration in the as-prepared GO material could be low. Moreover, a dependence on both an oxygenated catalyst surface and molecular oxygen in the gas phase is consistent with a Mars-van Krevelen-type mechanism,⁹³ wherein surface groups on the catalyst are consumed during the reaction and then are regenerated (in this case by O₂), completing the catalytic cycle.

Following these initial studies, a wide variety of reactions have been reported incorporating GO in various roles,⁹⁴ expanding the field of so-called "carbocatalysis" (*i.e.*, the use of heterogeneous, metal-free carbon materials in synthesis^{95–97}). Broadly speaking, the various reactions take advantage of either GO's acidity or oxidation potential (see Fig. 2), or both.

GO's utility as a solid state acid catalyst stems from its high acidity (pK_a 3–4 in water^{28–30}), potentially as a result of the sulfate or sulfonic acid groups present on its surface, as described previously. These acidic characteristics have been used to facilitate the Friedel-Crafts addition of α,β -unsaturated ketones to indoles,⁹⁸ the conversion of polysaccharides (*e.g.*, fructose, sucrose, and inulin) to 5-ethoxymethylfurfural (proposed as a potential biofuel with an energy density of 30.3 MJ L⁻¹),⁹⁹ and various dehydrative or cationic addition polymerizations.^{28,29,100} GO's acidity can also be promoted when combined with other heterogeneous materials, such as zeolites. These composite materials have been shown to be highly active in the dehydration of secondary and tertiary alcohols to their corresponding olefins.¹⁰¹ Derivatives of GO functionalized with basic moieties have also been shown to exhibit bifunctional acid-base behavior,¹⁰² and GO has even been used as a phase transfer catalyst to improve the organic solubility of inorganic salts such as KOH.¹⁰³

The utility of GO in oxidations is similarly broad and improvements continue to be made. Of note is the exceptional scope of organic molecules that can be oxidized by GO. As previously mentioned, alcohols can be oxidized to the corresponding aldehydes or acids (typically exhibiting high selectivity for the aldehyde over the acid),^{46,91,104} alkanes to the corresponding olefins,^{105–107} thiols to the corresponding disulfides,¹⁰⁸ organic sulfides to the corresponding sulfoxides,¹⁰⁸ aqueous sulfide anions to polysulfides,¹⁰⁹ and amines to the corresponding imines.^{110,111} The latter of these (amine-to-imine oxidation) is becoming a standard reaction used for the purpose



Scheme 8 A GO-facilitated synthesis of a chalcone via an auto-tandem reaction.

of catalyst comparison owing to its widely demonstrated success, ease of product characterization, and high selectivity for the imine product. Mechanistically, much remains to be learned; for example, Loh and co-workers recently showed that treatment of GO with aqueous NaOH afforded a material with substantially improved activity toward amine oxidation.¹¹¹ It was proposed that this was a result of increased defect concentration (*i.e.*, “holes”) in the GO basal plane, and that these defects functioned as active sites in the aforementioned oxidation. EPR spectroscopy indicated the presence of unpaired electrons in the catalyst structure, which are believed to be concentrated at these defect sites, consistent with a radical-based oxidation process. With its improved activity, the catalyst loadings employed in the reaction were lowered to as little as 5 wt% of the catalyst under solvent-free, ambient air conditions, while still affording greater than 90% isolated yield of the desired product.

There are not many examples of materials (either nanomaterials such as GO or small molecule homogeneous catalysts) that have such broad reactivity. While this breadth presents challenges with respect to the selectivity of a reaction for any one product, particularly with multifunctional molecules (*e.g.*, natural products), GO's extensive reactivity has been employed toward performing multiple mechanistically distinct reactions in a single vessel in what are known as tandem reactions.¹¹² Tandem reactions that use a single catalyst (referred to as “auto-tandem reactions”) may be performed through the sequential addition of reagents, or with all of the necessary reagents present at the start of the reaction, resulting in simple routes for generating relatively sophisticated molecules. We have previously demonstrated that GO can function in such a manner by combining its oxidizing and acidic properties to generate chalcones from various mixtures of alcohols or aldehydes and alkynes or methyl ketones (see Scheme 8).⁹¹ No changes to the GO itself or to the reaction conditions were necessary in order to drive the independent oxidation, hydration, and condensation reactions. It is likely that other similar tandem or auto-tandem reactions may be catalyzed using GO, and would underscore the diverse and useful properties of such carbocatalysts.

Platform for supported heterogeneous catalysis

In addition to its inherent reactivity, GO has also been used as a support for exogenous metal catalysts. Carbon materials have long been used in this role,⁹⁷ primarily due to their high surface area which increases catalyst exposure, as well as their chemical

and thermal stability. Thus, as GO's place in the field of carbon nanomaterials has grown, it too has been explored as a catalyst support. It should be noted that most examples of GO's use as a support utilize thermally or otherwise exfoliated material. Raw GO has a low surface area (typically $<5\text{ m}^2\text{ g}^{-1}$) in the solid state, making it unfavorable for heterogeneous catalyst applications, and may be unstable to reaction conditions wherein the deposited catalyst would be used, especially if elevated temperatures ($>100\text{ }^\circ\text{C}$) are required.

Exfoliated GO provides several key distinctions and advantages over other carbon supports. While retaining high surface area, the material provides an abundance of surface functionality that provide anchor points for electrophilic metals such as Pd (shown to be useful in C–C coupling reactions^{113,114}), Pt (shown to be useful in the electrocatalytic reduction of oxygen in fuel cells^{113,115,116}), and many others.^{117–122} Metals deposited on exfoliated GO are strongly bound to the surface, and it has been demonstrated that Pd nanoparticles exhibit minimal surface migration at temperatures up to $700\text{ }^\circ\text{C}$.¹²³ As a result of the strong link between the metal and the GO, catalyst leaching and degradation of catalyst activity would be expected to be less problematic than might be observed when other carbon supports are used.

In addition to its role as a high surface area, functionalized platform, GO can also provide synergistic reactivity with the deposited catalyst. This property has been particularly useful in areas where proton transfer or buffering plays a role in the reaction mechanism. In one example by Ren, Qu, and co-workers, gold nanoparticles were deposited onto the surface of GO and the resulting composite material displayed peroxidase-like activity in the reduction of H_2O_2 or 3,3',5,5'-tetramethylbenzidine (TMB).¹²⁴ While the deposited metal was shown to be responsible for the observed reaction, the gold catalyst was reactive over a considerably broader pH range than the gold nanoparticle on its own. The catalytic constant (k_{cat}) of the deposited gold catalyst was reduced only from 236 to 196.8 s^{-1} when the pH was raised from 4.0 to 7.0, while the k_{cat} of the free gold catalyst fell from 260 to 4.3 s^{-1} upon a similar increase in pH. For comparison, horseradish peroxidase (HRP), a naturally occurring peroxidase, exhibited a k_{cat} of 4000 s^{-1} at pH = 4.0 and 204.5 s^{-1} at pH = 7.0. The authors proposed that the observed preservation of reactivity of the gold catalyst at elevated pH was due to modulation of the deposited gold centers' reactivity,¹²⁴ though it is also possible that the GO acted as a buffer creating a locally acidic environment that would favor the peroxidase-like reaction. Indeed, similar influence of GO on Brønsted acid–base chemistry has been shown in alcohol dehydrations wherein neutral zeolites blended with acidic GO were used to catalyze the reaction, as previously described.¹⁰¹ Shorter reaction times and lower catalyst loadings were needed to effect the desired reaction when the zeolite–GO blend was used to catalyze the reaction, as compared to GO alone, and higher yields and selectivities were typically achieved. It is believed that this was a result of localized proton transfer that activates the otherwise dormant zeolite toward participation in the reaction.

In addition to small molecule reactions, such as those previously described, GO-supported metal catalysts have been

applied toward polymerizations and the formation of GO-reinforced polymer composites. Several recent reports describe the deposition of Zr,¹²⁵ Cr,¹²⁶ or Ti catalysts¹²⁷ on the surface of exfoliated GO, and the subsequent polymerization of ethylene or propylene using the metal-carbon composite material. Incorporation of GO, graphene, or other carbon nanomaterials into pre-formed hydrophobic polyolefins such as polyethylene and polypropylene has been particularly challenging due to the phase incompatibility of the polymer and the carbon.¹²⁸ The aforementioned one-step routes for converting monomers to carbon-reinforced composites using GO-supported polymerization catalysts offer potential solutions to such problem. Indeed, the carbon in the aforementioned composites did not adversely affect the reactivity of the deposited catalyst, and the polymeric products were of high molecular weights and displayed improved mechanical properties (particularly Young's moduli) as well as appreciable electrical conductivity.

Harnessing the chemistry of GO: new frontiers and outstanding challenges

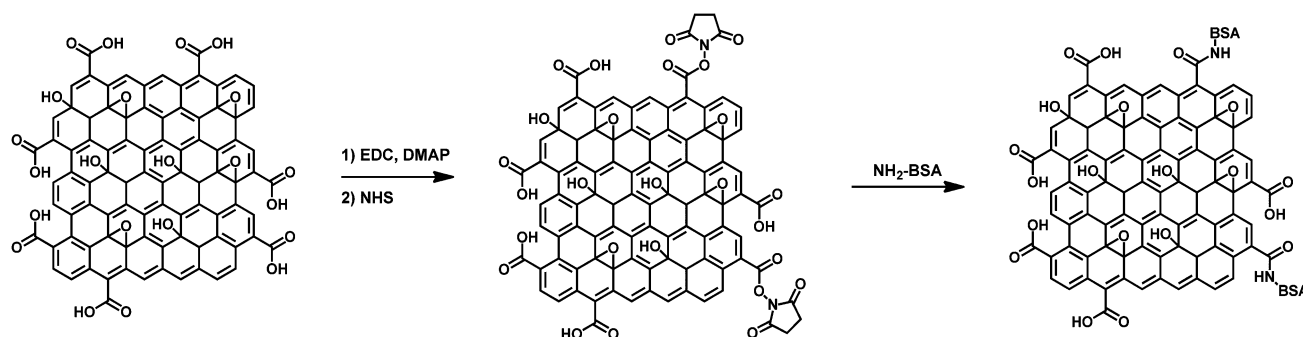
Beyond GO's use as a catalyst support, a filler in polymer composites, and a catalyst itself, the material has started to find increasing utility in various biomedical applications. It comes as no surprise that the oxygen functionality of GO can be modified with various compounds that increase its biocompatibility and/or biofunctionality. Biomolecule-functionalized GO derivatives have a diverse set of applications ranging from chemical sensing to drug and gene delivery systems.^{129–131} GO forms a stable dispersion at physiological pH values in aqueous media, though it does not tolerate high ionic strength solutions such as PBS, and functionalization with PEG or other solubilizers is needed for these types of media.¹³² Collectively, these attributes render GO an ideal carbon-based material for many therapeutic and biomedical applications. Proteins,¹³³ DNA,^{134,135} and antibodies or antigens¹³⁶ may be covalently attached to the surface, albeit using modified functionalization procedures to avoid denaturation of the conjugated biomolecule. For example, bovine serum albumin (BSA) was attached to the surface of GO using carbodiimide coupling chemistry wherein the carboxylic acid groups were first primed with *N*-hydroxysuccinimide (NHS) to allow for milder coupling conditions (see Scheme 9).¹³³ The installed NHS group was subsequently

displaced by exposed lysine residues on the BSA protein under mild conditions (pH 6.1 and room temperature). This method, first demonstrated by Ye and coworkers,¹³³ has become a widely accepted route to covalently link proteins to the surface of GO due to its convenience and robustness.

With the expanding use of GO in biomedical applications, a broader understanding of its toxicology is imperative. Recently, several *in vitro* and *in vivo* studies that examined the toxicity of GO have been disclosed.^{58,129,137–144} While the initial results have been generally inconclusive, the majority of studies revealed that GO possesses dose-dependent toxicities toward multiple cells lines and live subjects. Furthermore, in a study by Pumera and coworkers, the toxicity of GO was variable depending on the method used for its synthesis (*i.e.*, Hummers, Brodie, Staudemeir, and Tour).¹⁴⁵ Regardless, more studies are needed to reveal the complete toxicological and biodistribution profiles of GO and its derivatives.

Another major challenge that remains for GO is the development of an industrially viable process for its synthesis. If widespread implementation of GO-based materials is desired, a large-scale, environmentally tolerable process is needed, and to the best of our knowledge one does not currently exist. The methods described herein and elsewhere are frequently performed on the scale of grams to tens of grams, and such quantities are typically suitable for most academic or small scale projects. However, for the purposes of commercial utility, these quantities are likely too small. Moreover, the reagents used in the reactions present formidable safety challenges due to the formation of highly reactive intermediates or byproducts (*e.g.*, Mn₂O₇, in the case of permanganate-based oxidations, or Cl₂ or ClO₂ in chlorate-based methods) as well as the tendency of the graphite oxidation reaction to violently exotherm. Additionally, GO is susceptible to photocatalyzed decomposition when exposed to UV or visible light of sufficient intensity (typically under reactive atmospheres such as H₂ or ethanol),^{146,147} presenting additional challenges with respect to preparation and handling. Without scalable synthetic and purification methods, the implementation of GO in any high volume commercial application may not be possible.

One method that could prove viable is the bottom up synthesis from low cost starting materials. For example, Tang and coworkers demonstrated the synthesis of GO nanoplatelets using glucose as the initial carbon source.¹⁴⁸ A key feature of



Scheme 9 Functionalization of GO with bovine serum albumin (BSA) using an *N*-hydroxysuccinimide-activated ester.

their technique was that the layer thickness could be tuned by modifying the glucose concentration, annealing temperature, and duration of annealing. In their process, 1 nm thick sheets of GO were obtained when a 0.5 M aqueous glucose solution was heated at 160 °C for 70 minutes. Conversely, a material with a thickness of 1500 nm was synthesized when an identical glucose solution was heated at 180 °C for 11 hours. XPS analysis showed that the functional groups present were consistent with those found in samples GO prepared using the aforementioned methods, including hydroxyls, carboxylic acids, and epoxides.

Another area that may benefit from further study, particularly in the area of catalytic applications of GO and related materials, is the development of well-defined small molecule analogues of GO. The complexity of GO's structure affords it a remarkable breadth of reactivity, as previously described, but renders the task of separating the active groups from the spectator groups difficult. Taking GO's ability to function as an oxidation catalyst as an example, the presence of a broad distribution of functional groups challenges the determination of a reaction mechanism and subsequent optimization of its structure and reactivity. Such a task would be greatly simplified if small molecule analogues, with well-defined and distinct functionalities and reactivities, could be substituted.

Conclusions

While GO and related materials have been known for more than 150 years, they continue to be chemical curiosities and remain the primary foci of many fundamental and applied studies. Herein, we have endeavored to discuss only the most recent advances, particularly as they relate to our basic understanding of GO's chemical structure, reactivity, and properties. In particular, newly proposed small scale structural features, including the presence of so-called oxidative debris as well as sulfur-containing functionality, have been discussed. Additionally, new routes for functionalization, including various C–C bond forming reactions with the sp²-hybridized graphitic carbons, have been described, as well as the use of GO's reactivity in various chemical reactions (both small molecule transformations and polymerizations).

Several key themes emerge from a survey of the literature related to GO's chemistry. First, GO has multiple levels of structure, including atomic (*i.e.*, specific functional groups), molecular (*i.e.*, oxidative debris decorating the surface), and macromolecular (*i.e.*, morphology of particles and sheets) that vary with the conditions and starting materials used for its preparation. Rigorous analytical characterization (*e.g.*, electrical conductivity, elemental analysis, pH in various solvents, and onset of thermal decomposition) and exactness of nomenclature and terminology are essential when describing new compositions. While its precise atomic structure can vary, many of its bulk properties, as previously noted, are relatively straightforward to determine and can serve as good indicators of the extent and nature of its functionalization. Second, GO is a highly reactive material. This has been exploited in a number of useful ways for

the purposes of functionalization as well as catalysis. The broad reactivity of GO presents challenges with respect to selectivity, and passivation of undesirable reactive sites may be necessary to finely tune and optimize its properties and functions. Third, while GO and other graphene-related materials are related, the differences between them are stark. As a result, it is of value to study them independently, and the application of GO should not be confined to what have been perceived to be the limits of application of graphene (*e.g.*, electronics and optoelectronics, electrode materials, *etc.*) Fortunately, this has largely not been the case as GO has come into its own and been developed independently in recent years, but it is worth mentioning if only to encourage this further. It is our hope that this review will catalyze the realization of ideas for new applications for GO and related materials. As with many contemporary breakthroughs, substantive advances are likely to be multidisciplinary in nature and occur at the interfaces of chemistry and other disciplines. We believe that a basic knowledge of GO's fundamental chemistry will better position the field for further breakthroughs.

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