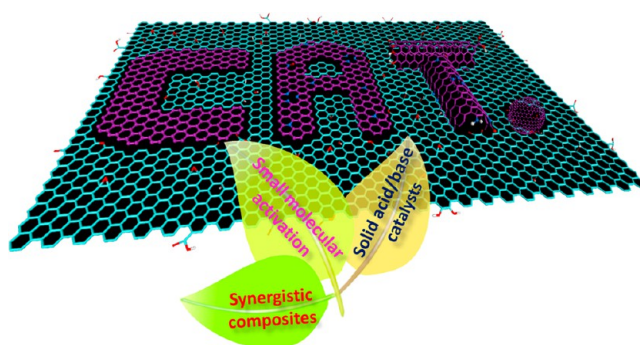# Carbocatalysts: Graphene Oxide and Its Derivatives

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CONSPECTUS

Graphene oxide (GO) sheets are emerging as a new class of carbocatalysts. Conventionally, researchers exfoliate graphite oxide into submicrometer-sized, water-dispersible flakes to produce these sheets. The presence of oxygen functional groups on the aromatic scaffold of GO allows these sheets to mediate ionic and nonionic interactions with a wide range of molecules. GO shows remarkable catalytic properties on its own and when hybridized with a second material. It is a perfect platform for molecular engineering.

This Account examines the different classes of synthetic transformations catalyzed by GO and correlates its reactivity with chemical properties. First, we raise the question of whether GO behaves as a reactant or catalyst during oxidation. Due to its myriad oxygen atoms, GO can function as an oxidant during anaerobic oxidation and become reduced at the end of the first catalytic cycle. However, partially reduced GO can continue to activate molecular oxygen during aerobic oxidation. Most importantly, we can enhance the conversion and selectivity by engineering the morphology and functionalities on the G/GO scaffold. GO can also be hybridized with organic dyes or organocatalysts. The photosensitization by dyes and facile charge transfer across the graphene interface produce synergistic effects that enhance catalytic conversion.

Using GO as a building block in supramolecular chemistry, we can extend the scope of functionalities in GO hybrids. The presence of epoxy and hydroxyl functional groups on either side of the GO sheet imparts bifunctional properties that allow it to act as a structural node within metal−organic frameworks (MOFs). For example, known homogeneous molecular catalysts can be anchored on the GO surface by employing them as scaffolds linking organometallic nodes. We have demonstrated that porphyrin building blocks with GO can lead to facile four-electron oxygen transfer reactions. We have also evaluated the advantages and disadvantages of GO as a catalytic material relative to other types of catalysts, both metallic and nonmetallic. Researchers would like to increase the potency of GO catalysts because many catalytic reactions currently require high loading of GO. Further research is also needed to identify a low-cost and environmentally friendly method for the synthesis of GO.

1. Introduction

Voices clamoring for environmental protection are becoming increasingly cogent today due to increasing environmental pressures from expanding economic activities and rising world population.[1] There are large classes of industrial liquid-phase reactions developed at the turn of the century that focus on economic benefits at the expense of environmental impact. With increasingly tight legislation on the control of chemical effluents, there is a need to invent chemical processes that can minimize the production of wastes and achieve optimal economic viability. In line with this, extensive research efforts have been devoted
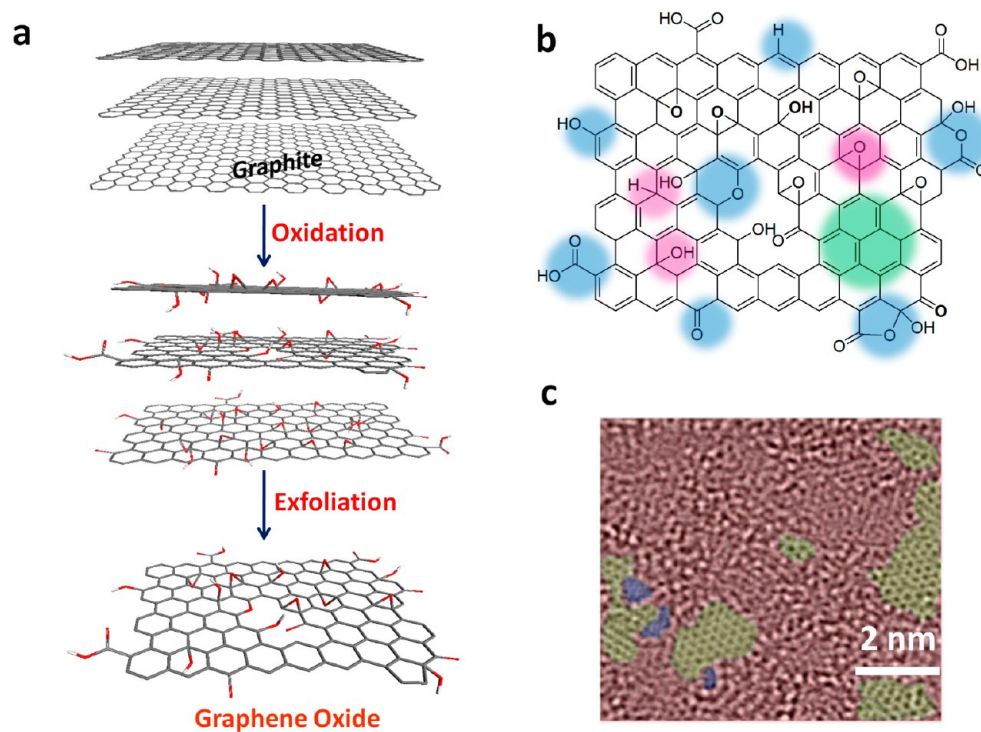
FIGURE 1. (a) Preparation of GO. (b) Proposed structure of GO based on the Lerf–Klinowski model. Hydroxyls and epoxide groups (pink) are the dominant functionalities on the basal plane. The edge defects are unique sites for some oxygen functionalities (blue), which are not found on the basal planes. (c) HR-TEM spectrum of GO. Panel c adapted with permission from ref 11. Copyright 2010 WILEY-VCH.

to the development of heterogeneous catalysts, which are easier to separate and reuse compared with homogeneous catalysts.[2,3] Replacing environmentally hazardous liquid Brønsted and Lewis acid catalysts with solid heterogeneous catalysts, which are environmentally benign, is currently an active area of research. Along this line, the emerging application of carbon materials as metal-free catalysts is increasingly attractive in the imminent "Carbon Age".[3−6] The rich polytypes of carbon, which include fullerene, nanodiamond, carbon nanotube, and graphene, present a rich class of solid-state materials that are nonpolluting and reusable. This Account will focus on the recent advances in the use of graphene oxide (GO) and its derivatives in catalysis. The classes of reactions that can be catalyzed by these materials, as well as the outlook for green and sustainable catalysis, will be discussed.
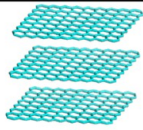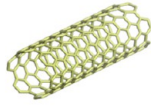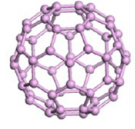
2. The Features of Graphene Oxide

Present day GO chemistry is largely inherited from Brodie's pioneering work on graphite oxide in the 18th century.[7] Solution-dispersible, substochiometrically oxidized graphene sheets called GO can be derived from the chemical exfoliation of graphite oxide (Figure 1a). The coverage of the oxygen-containing functional groups on GO varies widely

with these different synthetic procedures. The generally accepted models of GO structure[8−10] depict hydroxyl and epoxide groups as dominant functionalities residing mainly on the basal plane. Hole defects are found throughout of the scaffold,[11] which accommodate groups like carboxylic acids, ketones, phenols, lactols, and lactones. Small (2−3 nm) aromatic domains are isolated within the sp^3 C−O matrix (Figure 1b,c). Together, these complex cocktails of functionalities may act in concert during catalysis via hydrogen bonding, ionic complexation, radical stabilization, etc.

GO presents chemists with the opportunity to explore the solid-state analog of a polycondensed, conjugated molecule. Since it can be derived chemically from graphite, it is an abundant and inexpensive natural source of carbocatalyst.[6] Several unique features define this type of material in terms of its reactivity. First, the presence of oxygen-containing functional groups allows GO to function as a green oxidant or solid acid. The presence of defects like nanovoids and vacancies engendered in this material during its preparation endow it with unpaired spins, which can aid in the activation of small molecules by spin flip process. In addition, the aromatic scaffold provides a template to anchor active species such as organocatalysts or photocatalysts, and synergistic interactions between these and GO can result in

TABLE 1. Representative Reactions Catalysed by Pristine Carbons

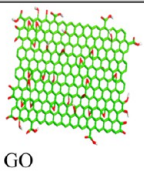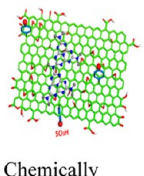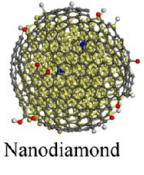| Pristine carbons	Catalyzed reactions	Substrates	Probable active species	Ref.
Graphite (3D)	Friedel-Crafts	Acyl Halides	π-System	13
	Friedel-Crafts	Alkyl Halides	π-System	14
	Oxidation	4-chlorophenol (H_2O_2)	π-System	15
	Reduction	Nitrobenzenes ($N_2H_4 \cdot H_2O$)	π-System	16
	Cycloaddition	(+)-Citronellal	Thermal conductivity	17
	Cycloaddition	Anthracene	Thermal conductivity	18
CNT (1D)	Oxidation	Cyclohexane	π-System	19
	Oxidative dehydrogenation (ODH)	9,10-Dihydroanthrac-ene (O_2)	π-System	20
Fullerene (0D)	Photocatalytic oxidation	Alkenes (O_2)	$C_{60} \underset{^1O_2 \quad ^3O_2}{\overset{h\upsilon}{\rightleftharpoons}} {}^3C_{60}{}^*$ **Energy transfer**	21
	Photocatalytic oxidation	Iminodiacetic Ester (O_2)		22
	Photocatalytic Reduction	Nitrobenzenes (H_2)	Unclear	23
	Thermal Reduction (C_{60}^-)	Nitrobenzenes (H_2)	Metal impurities in C_{60}^-	23, 24

enhanced yield. Graphene may also manifest in the form of a fullerenic-like shell surrounding a core consisting of an sp^3 phase such as nanodiamond. This can be produced when nanodiamond particles are partially graphitized at high temperature. In this case, the outer shell resembles strained graphene sheets, which can have enhanced chemical reactivity.[12] All these "imperfections" help to mediate the catalytic properties of graphene derivatives in a wide range of synthetic transformation.

3. Pristine Carbons as Catalysts

To appreciate the role that graphene can play in catalysis, it is useful to review the reported catalytic performance of other graphitic carbons, from graphite to fullerenes and carbon nanotubes (CNT). Table 1 summarizes the classes of reactions that were reported to be catalyzed by graphite,[13−18] CNTs,[19,20] and fullerene.[21−24] It must be pointed out that most carbocatalysts (i.e., graphite, CNT, GO, etc.) can be contaminated by naturally occurring metals or treatment processes that typically require metal catalysts or metal-containing agents. Thus the role of these metal impurities in catalysis cannot be ruled out unless careful control studies have been carried out. For example, to exclude the role of

residual manganese in catalysis, Bao and co-workers[25] compared the catalytic activities of washed and unwashed rGO and found that no decrease of catalytic activity was observed for washed rGO, which had a much lower content of manganese (from 0.47 wt % to 0.0090 wt %). Pure graphite does not have a sufficient number of reactive sites to be a viable catalyst for wide-ranging reactions. Nonetheless, the noncovalent binding interactions of graphite or CNTs with the target molecules, along with the fast charge transfer and resonance stabilization of intermediate states by these aromatic platforms, have often been cited to play catalytic roles in reactions. For example, graphite can function as a Lewis base to stabilize electrophilic species as well as cation intermediates in Friedel−Crafts-type reactions.[13,14] van der Waals interaction of the aromatic scaffold in graphite with the target molecules as well as its high electron conductivity is believed to facilitate the reduction of nitroarenes by hydrazine.[16,26] In addition, the high thermal conductivity (19.1 W cm^{-1} K^{-1} at 300 K[27]) of graphite helps to promote thermal cycloadditions[17] and ene reaction.[18] In principle, most of the reactions that can be catalyzed by graphite or CNTs will be expected to work at least equally well with graphene, due to its larger surface area,

TABLE 2. Graphene Derivatives as Carbocatalysts and the Types of Reactions Catalyzed

Modified carbo-catalysts	Catalyzed reactions	Substrates	Probable active species	Ref.
GO	Hydration	Alkynes	Acidic groups	33
	Michael-type Friedel-Crafts	Indoles with Michael-acceptors	Acidic groups	35
	Aza-Michael addition	Amines with Michael-acceptors	Acidic groups	36
	Polymerization	Cyclic-lactones, lactams or alcohols	Acidic groups	37
	Oxidation	Alcohols (O_2)	Unclear	33
	Photo-oxidation (co-catalyst)	Tertiary amines (O_2)	Unclear	43
Chemically modified GO	Reduction (rGO)	Nitrobenzenes ($N_2H_4 \cdot H_2O$)	Zigzag edges	25
	Oxidation (*N*-doped Graphene)	Benzyl alcohols (O_2)	Nitrogen species	31
	Hydrolysis (Sulfonated-rGO)	Ester	Acidic groups	38
	Oxidation (rGO/*g*-C_3N_4)	Hydrocarbons (O_2)	π-π^* or charge-transfer interactions	40
	Oxidation (GO/P3HT)	Tertiary amines (O_2)	Charge-transfer interactions	41
Nanodiamond	Gas-phase ODH (OLC)	Ethyl benzene (O_2)	Di-ketonic groups	47
	Gas-phase DH (UDD)	Ethyl benzene (He)	Di-ketonic groups	49
	Gas-phase ODH (UDD)	*n*-butane	Di-ketonic groups	50

readily functionalizable properties, and good dispersion properties.

4. Graphene Oxide and Its Derivatives as Carbocatalysts

Graphene is an ideal playground for introducing a wide range of functionalities through covalent modification or noncovalent interaction.[8] This offers extraordinary potential in the invention of new sustainable catalytic systems. As shown in Table 2, the rather limited range of reactions that can be catalyzed by pristine graphene/graphite can be expanded by chemically modifying graphene. Figure 2 summarizes the potential active sites that can be introduced onto the graphene scaffold. In the case of GO, oxygen functionalities can be introduced onto the aromatic backbone by chemical oxidation.[9] The acidic and oxidative nature of these oxygen functionalities allows it to function as a solid acid or green oxidant. Carboxylic acids, quinones, and aromatic C−H, as well as the spin electrons, can be found at the edges or defect sites in GO. The quinone and diol redox sites
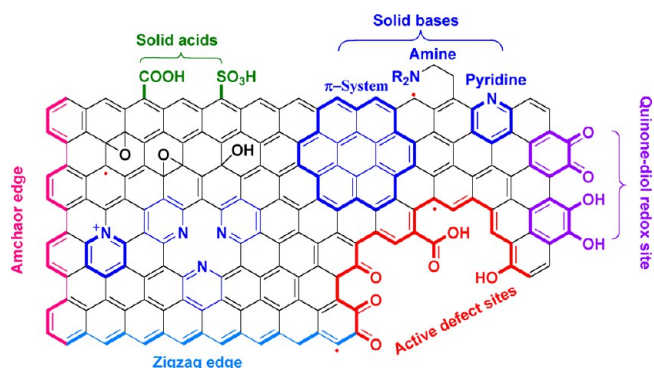

FIGURE 2. Schematic showing active catalytic sites in the graphene domain due to incorporation of heteroatoms.

have been identified in the past as active sites in carbon materials for oxygen-activation reactions.[4] In addition, the amphiphilic character of GO[28,29] should be advantageous, since it can act as a phase-transfer catalyst in oil−water biphasic systems.

The aromatic domain in GO can be readily functionalized via $\pi-\pi$ stacking or covalent C−C coupling reactions like
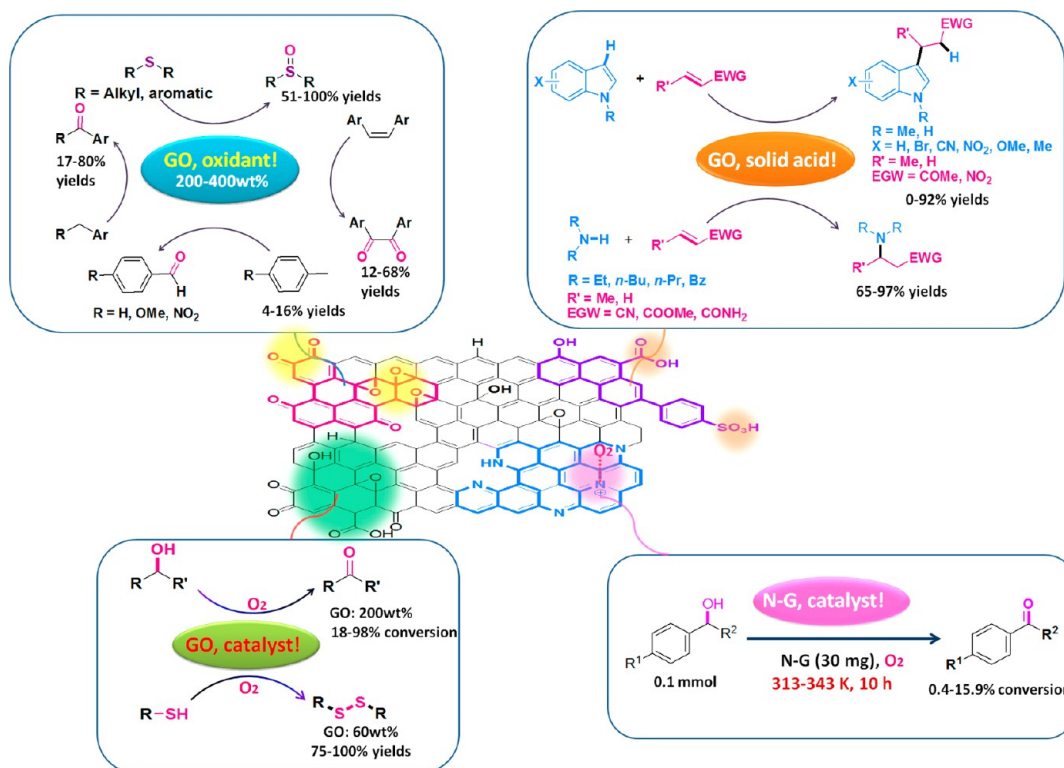
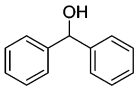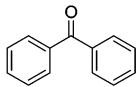**FIGURE 3.** Chemically modified GO as a heterogeneous catalyst/reagent.
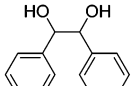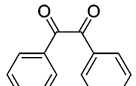
diazonium chemistry. Chemical doping is another important approach to tailor the properties of graphene. For example, the incorporation of nitrogen in graphene, especially in the form of the pyridinium moieties, has been shown to enhance the electrocatalytic activity for oxygen reduction reactions (ORR).[30] This improved catalytic performance is attributed to the electron-accepting ability of the nitrogen atoms, which polarize the adjacent carbon atom to enhance their bonding affinity with adsorbed oxygen species. N-doped graphene has also been applied successfully for the aerobic selective oxidation of benzylic alcohols.[31] Kinetic analysis showed that N-doped graphene-catalyzed aerobic oxidation has moderate activation energy close to that of Ru/Al$_2$O$_3$ catalyst.

4.1. Chemically Modified GO as Carbocatalysts. The use of GO as a metal-free catalyst/reagent for facilitating synthetic transformations is fascinating (Figure 3).[6,32] First, GO can be considered as a mild oxidant. Bielawski et al.[33,34] applied GO as a green oxidant to oxidize substituted *cis*-stilbenes to their corresponding diketones in 12−68% yields, using relatively high GO loading (400 wt %) at 100 °C for 24 h. The potential of GO in the oxidation of sp^3-hybridized C−H bonds was also tested. A variety of diarylmethanes were successfully converted into their corresponding ketones with the yields up to 80%. However its

widespread application is hindered by GO catalyst loading (200−400 wt %) and relatively harsh conditions. Bielawski and co-workers[33] also harnessed the acidic property of GO (200 wt %) for the hydration of alkynes, furnishing ketones in as high as 98% conversion. Since then, the catalytic applications of GO as a solid acid have been extensively explored; these included Michael-type Friedel−Crafts reaction,[35] aza-Michael additions,[36] and ring-opening polymerization.[37] Sulfonated groups can also be added[38] onto GO to produce a water-tolerant solid acid catalyst with strongly acidic sites (2.0 mmol g^{-1}). Multirun experiments show that the catalytic activity of the sulfonated graphene was unchanged with an average hydrolysis rate of 64.0% at 343 K for 6 h, which was a better performance than NR50, a well-known commercial solid acid for hydrolysis of ethyl acetate.

In the tradition of carbon-based catalysts like activated carbon, GO can also be used for the activation of O$_2$ for the selective oxidation of alcohols (Table 3).[33] At present, the morphology and functionalities of GO need to be engineered to improve its efficiency, since high loading of the material (200 wt %) is often employed to ensure good conversion (18% to >98%), keeping in mind that for noble metals such as Ru/Al$_2$O$_3$, low catalyst loading (2.5−10 mol %) can result in high conversion (71% to >99%) and selectivity (mostly >95%).[39] Molecular oxygen is usually ascribed as

TABLE 3. Oxidation of Various Alcohols[a]

Entry	Alcohol	Product	Conversion (%)
1			>98[b]
2			>98
3			96
4			26
5			>98
6[c]			18

[a]Conditions: 200 wt % GO, 100 °C, 24 h. [b]Aldehyde/acid = 92:7. [c]Conditions: 50 wt % GO, 75 °C, 24 h.

the terminal oxidant. However we like to point out that the oxidative role of GO cannot be ignored because GO becomes inevitably reduced after participating in the oxidative reactions. To address the role of GO as an oxidant (anaerobic) versus a catalysts for O_2 activation (aerobic), we carried out the reaction of GO (200 wt %) with benzyl alcohol in a glovebox with oxygen level less than 0.2 ppm to fully exclude the contribution from oxygen. Indeed, GO can act as a "reactant" and provides 33% gas-chromatography yield under anaerobic conditions. The depleted oxygen functionalities cannot be regenerated by exposure to O_2 (Figure 4). Bielawski and co-workers found that in the presence of O_2, the catalytic reactivity of GO can be sustained up to 10 cycles[33] even though it becomes reduced after the first run; this suggests that the "real catalyst" might be partially reduced GO rather than GO itself. A clear picture of the nature of the active oxygen functional groups participating in the reaction and the mechanism of catalytic cycle is currently lacking, and it needs to be further investigated.

The reduction of GO is necessary to restore its π-network and convert it to a semimetal. However, chemical and thermal treatments involved in the synthesis and reduction of GO can be destructive in nature.[11] Nanovoids are created in the basal plane of GO due to the loss of carbon atoms in the form of CO or CO_2. The presence of such defect sites can be advantageous in catalysis because molecular species can
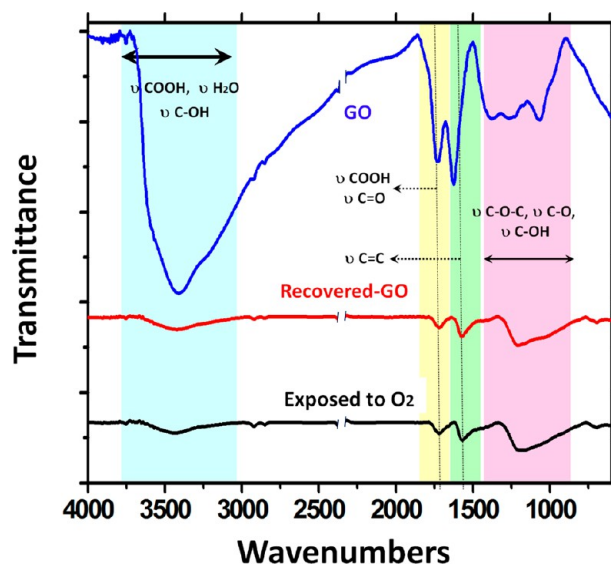

FIGURE 4. The FTIR spectra of GO (blue), recovered GO (red line, recovered from anaerobic conditions), and recovered GO exposed to aerobic conditions (black), carried out using 50 mg of recovered GO in the presence of oxygen (1 atm) at 100 °C for 12 h.

be trapped and activated at these defects. Recently, reduced GO (rGO) has been found to be a reusable and efficient catalyst for the hydrogenation of nitrobenzene.[25] In this case, rGO (2 wt %, 94.2%) shows comparable reactivity to noble metal (1% Pt/SiO_2, 96.0%) under reflux conditions in hydrazine hydrate. When the reaction was performed at room temperature, rGO (10 wt %) exhibits 97.4% yield, whereas GO (18.5%) and natural graphite (0.4%) show much lower reactivity. The zigzag edges of rGO are suggested to be the catalytically active sites, judging from the observations that graphene with fewer defects gave much lower performance in catalysis and the yield scaled with increased density of defects created by further treatment with HNO_3. Mechanistic insights from DFT calculations suggest that interaction between carbon atoms at the zigzag edges and terminal oxygen atoms of nitrobenzene weakens the N–O bond.

4.2. GO Composites as Synergistic Catalysts. The greatest value proposition for graphene (including G, GO, rGO) as a catalyst material lies in the synergistic interaction it can have with enzyme, organocatalyst, electrocatalyst, and photocatalyst.[40−43] Here, we select several examples of our work to show the synergistic interactions of GO with conjugated polymer, organometallic catalyst, or organic dye. The physical binding between GO and these material ranges from covalent binding or noncovalent binding to long-range interactions in solutions. In all cases, enhanced conversion and yield were obtained compared with the controlled tests where GO was absent.
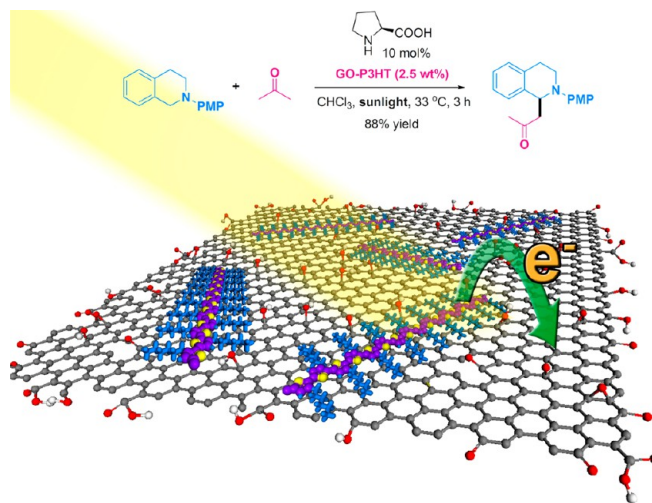
FIGURE 5. $\pi-\pi$ interactions: GO/P3HT hybrid as a synergistic photocatalyst. Figure adapted with permission from ref 41. Copyright 2012 American Chemical Society.

4.2.1. Noncovanetly Bonded GO−Polymer Hybrid as a Synergistic Catalyst.
The work function of GO falls within the band gap of polymers like poly(3-hexylthiophene-2, 5-diyl) (P3HT). This suggests that GO can be hybridized with P3HT to form a charge transfer complex. Hybrid GO/P3HT sheets are assembled via $\pi-\pi$ interaction and carefully isolated from the nonreacted precursors. We have studied the photocatalytic performance of the hybrid in Mannich reaction (Figure 5).[41] The catalytic yield of GO−P3HT (2.5 wt %) is 93% (same weight P3HT, 65%), which is markedly superior to TiO$_2$ (P25) ($\sim$33.5 wt %, 58%), a well-known commercial photocatalyst.[44] Under sunlight, the reaction can be finished in as short as 3 h (88%); this is also better than the Au-catalyzed process, which requires $\sim$9.6 wt % catalyst loading at 60 °C for 2 h to give 78%.[45] Transient photoabsorption studies were carried out to probe the charge transfer dynamics between P3HT and GO. It was observed that the GO−P3HT hybrid exhibits a photoinduced absorption signal with two ultrafast decay time scales ($\tau = 1.4$ ps, $\tau = 38.5$ ps), which can be attributed to the ultrafast charge dissociation of P3HT excitons at the P3HT/GO interface followed by its rapid injection into GO. The cooperative interaction allows the P3HT/GO to function as a dyad in photocatalysis. The reaction is initiated by photoexcited electron and hole pairs of P3HT. The tertiary amine is oxidized by the positive hole on the HOMO of P3HT via single electron transfer to form the radical cation. At the same time, the excited electron is injected from the LUMO of P3HT into GO, which is then used to activate molecular oxygen to form the dioxygen radical anion, the latter can be stabilized by the aromatic

scaffold in GO. Considering that the chemical potential of GO can be readily tuned by molecular engineering, the GO scaffold can potentially act as an efficient electron relay for photoexcited holes generated in a wide range of organic dyes.

4.2.2. Covalently Functionalized GO Composites as a Synergistic Electrocatalyst.
GO composite can be synthesized by using GO sheets, which are covalently functionalized on either side by linkers, for example, decorating with either carboxylic or pyridine groups on either side of the sheets, analogous to pillar connectors such as 1, 4-benzenedicarboxylic acids or 4,4-bipyridine used in MOF synthesis.[42,46] We have applied functionalized GO to synthesize a GO−metalloporphyrin hybrid with electrocatalytic properties (Figure 6).[42] We tested the electrocatalytic reactivity of this GO−metalloporphyrin hybrid in oxygen reduction reaction (ORR), one of the key reactions occurring at the cathode in methanol fuel cells. The ORR kinetics is very sluggish and usually Pt-based catalysts, although costly, are employed. Iron porphyrin is known to facilitate ORR via four-electron reaction to water. Although rGO can be used in ORR on its own, the electrocatalytic activity is not efficient. The synergistic interactions can be seen from the improvement of the electrocatalytic current when a higher loading of GO is used in the metalloporphyrin composite. The overpotential for ORR in the GO−metalloporphyrin is shifted positively by 120 mV compared with GO, and the ORR current density of the composite is higher than that of either GO or MOF constructed from porphyrin alone. These improvements in catalytic activities can be explained by the synergistic effects of framework porosity, a larger bond polarity due to nitrogen ligand in the pyridinium-terminated GO and the catalytically active iron-porphyrin in the hybrid MOF. In addition it was also found that methanol cross over reaction is minimized due to the inactivity of the hybrid MOF for methanol oxidation.

4.2.3. Long Range Interactions: GO and Rose Bengal as a Synergistic Photocatalyst.
In another approach, the organic dye was not intentionally coupled onto graphene via covalent or noncovalent interactions. Rather, GO at 50 wt % was simply mixed with Rose Bengal (RB) and used for the visible light induced oxidative C−H functionalization of tertiary amines (Figure 7).[43] This reaction avoided the use of metal catalyst and stoichiometric amounts of peroxy compounds as terminal oxidants. This reaction is useful for trialkyl amines including chiral tertiary amines. We showed that both cyanide and trifluoromethyl nucleophiles participate in this reaction, providing α-cyano- and α-trifluoromethylated tertiary amines. The improved yield and chemoselectivity when RB and GO were present together
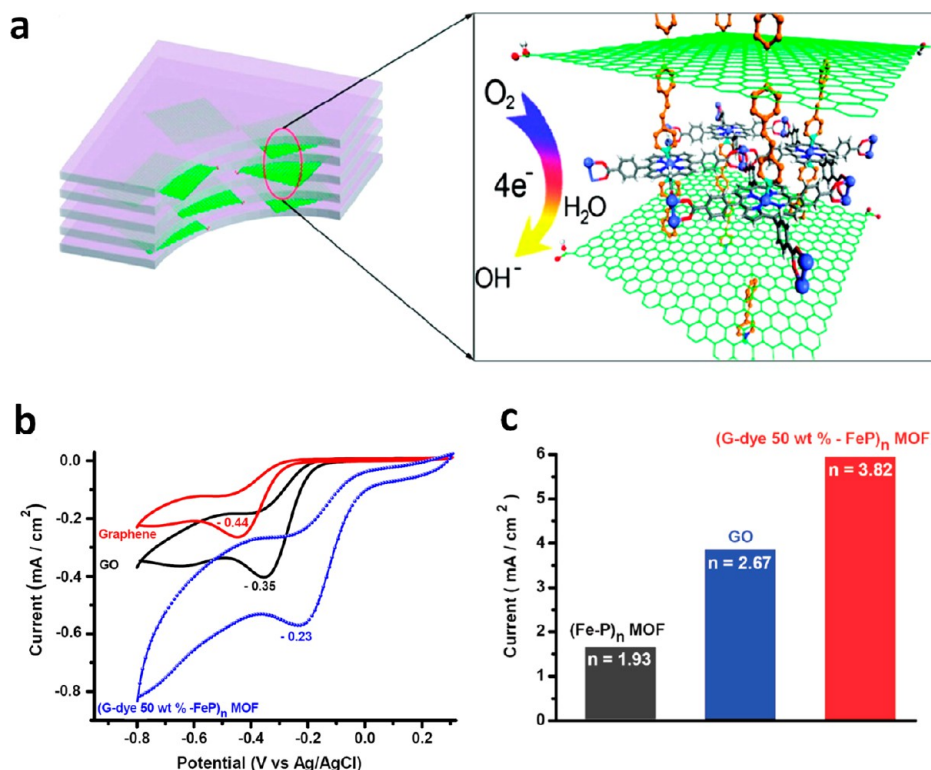
FIGURE 6. Covalent interaction: GO−porphyrin MOF composites for ORR. (a) Schematic of the chemical structures of $(G\text{-}dye\text{-}FeP)_n$ MOF. (b) Cyclic voltammograms of oxygen reduction on exfoliated graphene, GO, and $(G\text{-}dye\ 50\ wt\ \%\text{-}FeP)_n$ MOF. (c) Electrochemical activity given as diffusion-limited current density (J_K) at -0.65 V for $(FeP)_n$ MOF, $(G\text{-}dye\ 50\ wt\ \%\text{-}FeP)_n$ MOF, and GO. Figures adapted with permission from ref 42. Copyright 2012 American Chemical Society.
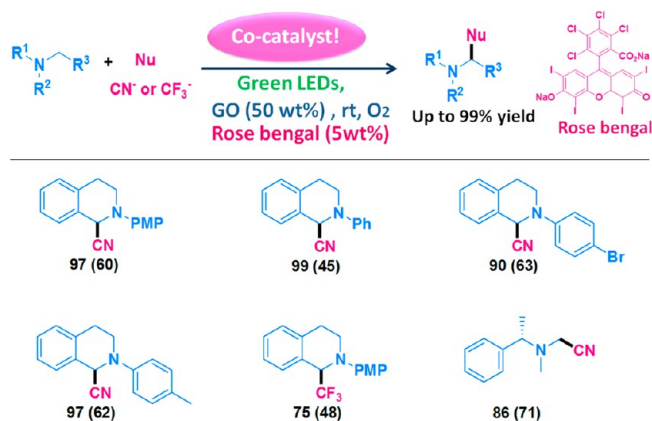

FIGURE 7. Long range interaction: GO and Rose Bengal as a cocatalyst for C−H functionalization of tertiary amines using visible light. Reaction was performed using 0.1 mmol of tertiary amines and 0.25 mmol of $TMSCN$ or $TMSCF_3$ in 1.0 mL of CH_3CN. Number in bracket is the yield without GO.

in the solution was evident. Controlled tests showed that in the absence of GO, the yield was obviously reduced. At present, the role of GO in this photocatalytic reaction is not clear. UV/visible absorption and fluorescence quenching studies revealed that there was no strong $\pi-\pi$ interactions between RB and GO, due to the electrostatic repulsion between RB anion and the negatively charged oxygen functional groups of GO. Even though there was no direct physical interaction between RB and GO, it can be appreciated that the stabilization of the imminium intermediate by slightly acidic GO and the intrinsic high surface area of GO could contribute to rate enhancement.

4.3. Graphitic Nanocarbons in Gas Phase Reactions. Gas phase reactions are usually carried out at higher temperature than liquid phase reaction and thus demand structural stability of the carbon scaffold. Nanocarbon with strained graphitic structure has shown unprecedented performance in the gas phase production of styrene, which is a very important precursor for the production of polystyrene.[4] Styrene is mainly produced by catalytic dehydrogenation of ethylbenzene. One main disadvantage of the current industrial process is coke formation on the metal oxide-based catalyst; this problem is alleviated by using steam as a protection agent to avoid coking, thus keeping the catalysts active. The steam generation consumes massive amounts of energy. The endothermic nature of the reaction ($\Delta H = 129.4$ kJ/mol) and equilibrium-limited yield are the main disadvantages that limit the energy efficiency and yield.
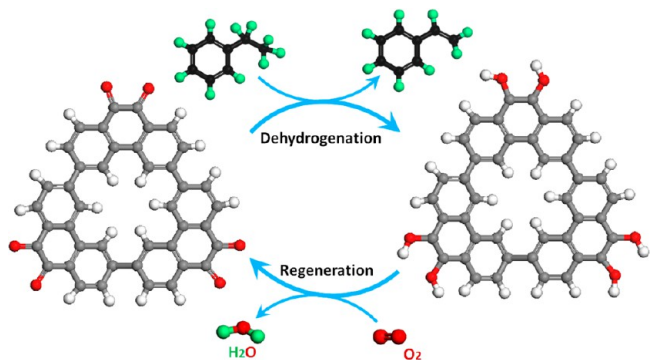
FIGURE 8. Molecular macrocyclic trimer is used as a model to study the ODH reaction, confirming the hypothesis that diketone-like groups can serve as active sites.

In contrast, oxidative dehydrogenation (ODH) of ethylbenzene is an exothermic reaction ($\Delta H = -116$ kJ/mol) and is more efficient energetically for the industrial production of styrene. Conventional activated carbon has been applied extensively as catalyst in the ODH reaction; however the fast destruction of its disordered structure limits its use. Interests have focused on CNT, carbon fibers, and diamonds, because higher activity can be maintained over a longer period than that with activated carbon.[4]

Ultradisperse diamond (UDD) nanoparticles, which are produced by detonation synthesis, consist of diamond cores partially coated by curved graphitic shells. At high temperature (2140 K), most of the sp^3-carbon in nanodiamond will be transformed into onion-like sp^2 carbon. Graphitized UDD provides the highest conversion (90%) and yield (65%) of styrene in comparison with other carbon forms.[4,47] Diketonic C=O groups on onion-like carbon are suggested to activate the alkane part of ethylbenzene to produce styrene and hydroxyl groups (C−OH) as intermediates. The catalytic cycle is achieved by the oxidization of C−OH by gas phase oxygen to C=O and water, which is thermodynamically favorable. The active role of diketone-like groups in catalysis has been confirmed by a small molecule mimetic study (Figure 8).[48]

An oxygen-free dehydrogenation process was also investigated to find a solution to the unsatisfactory selectivity of the ODH reaction. The reactivity (>20.5% yield, 97.3% selectivity) and stability of graphite-coated nanodiamond in oxygen-free dehydrogenation exceeds commercial K-promoted Fe catalyst, in which the reactivity dropped rapidly from 20.2% to 9.2% and stayed at about 7.1%.[49] Importantly, the reactivity of nanodiamond can be fully recovered by air exposure of the catalyst at 400 °C. Similar to ODH reactions of ethylbenzene, the catalytic turnover is controlled by the surface C=O and C−OH groups; in this case, the regeneration of the active site is achieved by thermal dehydrogenation instead of oxidation of C−OH. The superior performance of the graphitized nanodiamond hybrid has also been demonstrated in the activation of alkanes to alkenes.[50]

At present, the production of nanodiamond and solution-processed graphene is entering the first phase of commercialization. The large scale production of nanodiamond is based on detonation synthesis from energetic molecules, which provide a source of both carbon and energy.[51] The estimated cost of detonation soot based on the price of explosive materials, the charge preparation, and blasting in the reactor is around $96−555/kg, depending on the weight of the charge used in the synthesis. The detonation soot needs to be purified by hazardous liquid acid, which contributes up to 40% to the product cost. Alternatively, oxidation in air is robust, cost-effective, and relatively benign in terms of environmental footprint. The commercial price for detonation soot and UDD is around $550−1100/kg and $1500−3000/kg, respectively.[52]

Although graphite, the raw material for producing solution processed graphene, is cheap (90% C, ~$1275−1700/ton) and abundant, the subsequent processing needed to produce solution-processable graphene can be costly and environmentally unfriendly when copious quantities of sulfuric acids, nitric acids, or oxidizing agents have to be used during the exfoliation process. For example, the estimated cost of GO based only on the price of raw materials used in Hummer's methods[53] can be more than 10−20 times that of graphite. Therefore to ensure compliance with the objectives of green catalysis, green and economical methods for tonnage scale production of graphene flakes must be developed. Several routes for the high-yield synthesis of GO or exfoliated graphene have been developed.[54−56] Jeon et al.[55] reported high yield production of edge-selectively carboxylated graphite via the ball milling of graphite with dry ice. The resultant material is solution-processable and can be exfoliated into single- and few-layer graphene sheets in a variety of solvents. Lau and co-workers[56] invented an attractive process for the mass preparation of GO from renewable bioderived feedstock (e.g., glucose) via intermolecular polymerization under hydrothermal conditions. Related to this, functionalized amorphous carbon derived from biomass is a promising class of carbon-solid acids in terms of its low cost of production and environmental sustainability.[57]

5. Conclusion and Outlook

Historically, nanostructured carbons have functioned primarily as heterogeneous supports for metal catalysts. The latter are the main actors in the catalysis play, with carbon material assuming the supporting role. Here, we present an overview of graphene derivatives as main players in catalysis. GO can be readily functionalized, which renders it useful in a wide range of synthetic transformations and catalyses. In terms of challenges, one issue is the industrial scalability and economic viability of these carbocatalysts. An affordable method of producing carbocatalysts at industrial scale is needed before they can be applied for large scale catalytic application. Chemists are now making efforts for the green and sustainable synthesis of these carbocatalysts. It is envisaged that the number of new carbocatalyzed transformations will continue to grow and new forms of carbon-related materials, with engineered morphology or functionalities, will emerge as powerful catalysts for mediating synthetic transformations.

BIOGRAPHICAL INFORMATION

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Professor Kian Ping Loh received his Ph.D. in 1996 from the Physical and Theoretical Chemistry Laboratory in the University of Oxford. He is one of the key founding members of Graphene Research Centre in Singapore and leads the chemistry and materials growth effort there. His research activities encompass physical as well as chemical aspects of diamond and graphene, ranging from molecular science at the atomic domains to chemical vapor deposition, optoelectronics, solar cells, and catalysis. He is the winner of the University Outstanding Researcher award in 2012.

FOOTNOTES

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The authors declare no competing financial interest.

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