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Graphene Oxide as Catalyst: Application of Carbon Materials beyond Nanotechnology**

*Jeffrey Pyun**

carbocatalysis · graphene · graphene oxide ·
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Since the seminal report by Geim and co-workers, research on graphene and other two-dimensional sp^2-hybridized carbon nanomaterials has tremendously impacted the areas of modern chemistry, physics, and materials science and engineering.[1] The significant attraction of these materials can be attributed to the outstanding electrical, optical, electrochemical, and mechanical properties of graphene materials, especially in comparison to other carbon materials.[2] Although early routes to these materials were challenging, significant advances in synthetic and processing methods (e.g., synthetic "wet chemistry", micromechanical exfoliation, oxidation/reduction protocols, epitaxial growth, and vapor deposition) have enabled access to high-quality graphene or chemically modified graphenes (CMGs) in appreciable quantities.[3]

Beyond the applications described above, the use of graphene and CMGs as catalysts for facilitating synthetic transformations is a relatively new area with outstanding potential. The use of nanostructured carbon materials (see Figure 1) as both supports and metal-free catalysts has been investigated previously with 1D, 2D, and 3D carbonaceous materials. For example, Su and co-workers elegantly demonstrated that partially oxidized carbon nanotubes (CNTs) were able to catalytically dehydrogenate *n*-butane to 1-butene, albeit with modest conversion ($<15\,\%$ after 100 h).[4] Other forms of carbon, including carbon molecular sieves (CMSs), have also been employed in catalytic oxidation reactions, although harsh conditions (200+ °C and high pressures) were typically required for reasonable conversion.[5] Likewise, natural flake graphite has been shown to catalyze the reduction of a variety of substituted nitrobenzenes to the corresponding anilines (with hydrazine as the terminal reductant).[6]

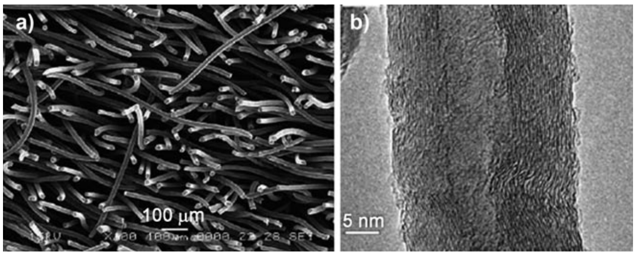

Figure 1. Examples of nanostructured carbon materials for applications in catalysis: a) SEM image of mesoporous graphite microfibers of a felt;[7a] b) TEM image of multiwalled carbon nanotubes.[7b]

Until now, however, the catalytic application of graphene and CMGs has focused primarily on the use of these materials as supports for catalytically active transition metals. In one such example, Mülhaupt and co-workers demonstrated that palladium nanoparticles dispersed on graphite oxide were able to catalyze Suzuki–Miyaura coupling reactions (see Figure 2).[8] Although the catalytic activity of this material was high (turnover frequencies in excess of $39\,000\,h^{-1}$ were reported), the supported metal was the active catalyst, not the carbon.

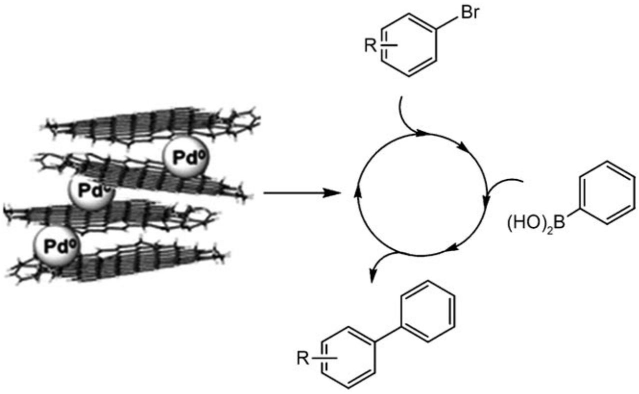

Figure 2. Graphene impregnated with Pd nanoparticles facilitated the Suzuki–Miyaura coupling of aryl halides with boronic acids (adapted from Ref. [8]).

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[*] Prof. J. Pyun
Department of Chemistry and Biochemistry
The University of Arizona
1308 East University Boulevard, Tucson, AZ 85721 (USA)
and
World Class University Program for Chemical Convergence for Energy and Environment
Department of Chemical and Biological Engineering
Seoul National University, Seoul 151-744 (Korea)
E-mail: jpyun@email.arizona.edu

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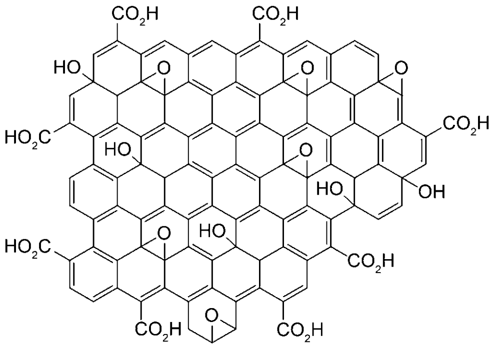
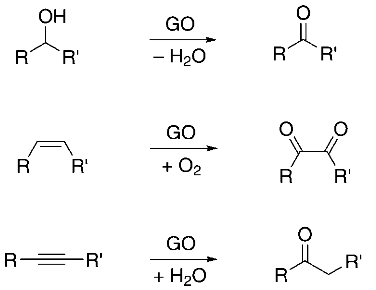
From a broader perspective, the unique properties inherent to well-defined 2D nanomaterials, such as graphene and graphene oxide (GO), are suitable for facilitating a wide range of transformations and may offer extraordinary potential in the design of novel catalytic systems. For example, it has long been recognized that materials such as GO (Scheme 1) possess interesting and potentially useful reactivity, such as their capacity to function as oxidants and/or acids.[9] However, the application of GO and other CMGs as catalysts in synthetic chemistry remains essentially unexplored.



Scheme 1. Simplified structure of a single layer of graphene oxide (GO).

Recently, in a seminal report, Bielawski and co-workers revealed the potential of harnessing the reactivity of GO for various synthetic reactions.[10] Capitalizing on the unique chemistry inherent to CMGs, the authors demonstrated the efficient oxidation of benzyl alcohol to benzaldehyde (conversion $>90\%$, Scheme 2) in the presence of GO as a heterogeneous catalyst. Overoxidation to benzoic acid was observed in only minimal amounts (7%) and only under certain conditions (e.g. at elevated temperatures). Interestingly, this and other oxidation reactions of alcohols were performed under ambient conditions and did not proceed under a nitrogen-blanketed atmosphere, which suggests that oxygen may be functioning as the terminal oxidant. Their results highlight the unique role that large-area, functionalized carbon materials, such as GO, may find in the activation of small molecules, such as O_2, for catalysis. This study is a compelling demonstration of the new concept of using large-area (metal-free) carbon materials as catalysts, aptly coined "carbocatalysis" by the authors.



Scheme 2. GO catalyzes the oxidation of alcohols and alkenes, as well as the hydration of alkynes. The reactions shown were generally performed at 100 °C under neat conditions. R, R′ = aryl, alkyl, H.

The study by Bielawski and co-workers also demonstrated that the scope of GO catalysis extends beyond simple oxidation reactions of alcohols. For example, the successful oxidation of *cis*-stilbene to benzil indicates that GO may find a role in the Wacker process, which currently requires the use of metal-based catalysts.[11] Additionally, a variety of alkynes were found to react with GO, although the products obtained were not the (dione) oxidation products that might be expected. Instead, the respective hydration products were isolated cleanly, which strongly suggests that the scope of the reactivity of GO may be quite broad. Several advantages were demonstrated in these oxygenation reactions, including the use of a simple and inexpensive catalyst, metal-free reactivity, and facile recovery of the GO from the reaction media by filtration.

The use of GO for "carbocatalysis" is a truly novel application of graphene-based nanomaterials and opens a host of possibilities for chemical synthesis. With dwindling supplies of the precious metals used in common catalysts, the prospect of replacing these metals with inexpensive carbon materials is extremely attractive and timely. Furthermore, it is likely that the scope of reactivity demonstrated by Bielawski and co-workers can be expanded to other methodologies by the exploitation of surface modifications and edge defects of GO. Hence, opportunity abounds, and the concept of "carbocatalysis" will undoubtedly be an intriguing new direction in chemistry and materials science.

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