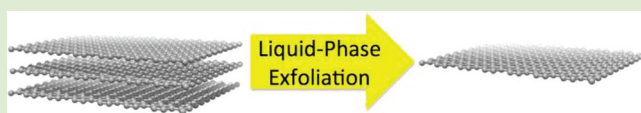


# Functional Graphene: Top-Down Chemistry of the $\pi$ -Surface

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**ABSTRACT:** A perspective on selected recent advances in graphene functionalization is offered. The activation of graphite as a means to create exfoliated sheets is highlighted as an important approach to achieve dispersions of individual graphene sheets.



Nanocarbon chemistry, the reactions and manipulation of fullerenes, carbon nanotubes, and graphene, are here to stay and will be a critical ingredient in emerging materials systems.<sup>1</sup> This transition is not without some necessary cultural shifts in the mindset of the modern polymer/materials chemist. We are comfortable with our traditional “pure” chemistry approach wherein materials’ structure and properties are controlled by a precise bottom-up synthesis wherein small fragments are connected to produce a material. We may do some cross-linking at the last stage of our synthesis, but in the end we are generally able to characterize our materials using conventional chemical analytical methods. As attractive as this approach is, it is not currently possible, or likely to be cost-effective, for the formation of advanced nanocarbon materials. As a result, new top-down functionalization schemes are needed to create stable dispersions with chemical functionality in carbon nanotubes and graphenes. The attractiveness of graphene’s compliant durable nature (Figure 1) and electronic

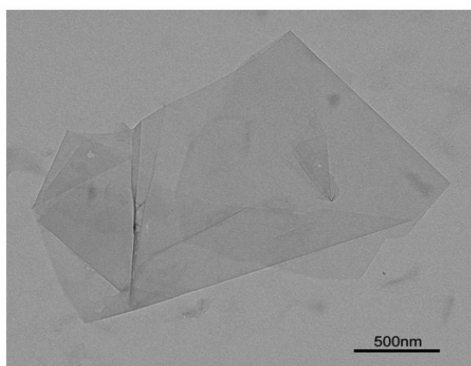


Figure 1. TEM image of a folded sheet of graphene.

properties has ignited a flurry of interest in its chemistry. Fortunately, the learning curve has been shortened by leveraging the lessons from the chemistry of carbon nanotubes. The familiarity of chemists with these cylindrical-shape persistent cousins of graphene has technically and conceptually taught us much about working with challenging, often metastable, dispersions. The chemistry of  $\pi$ -surfaces is now becoming a subarea of chemistry, rich with opportunity, and it

has set the stage for a hyper-rapid maturation cycle for applications of graphene.

As a result of its high sheet-to-sheet surface area, the exfoliation of graphite into individually dispersed graphene sheets requires much more aggressive chemistries than those used to unbundle carbon nanotubes. Specifically, relatively stable dispersions and bioconjugates of carbon nanotubes can be achieved using noncovalent functionalization;<sup>2</sup> however, it has yet to be demonstrated that equivalent methods are adequate to prevent reassembly of graphene sheets back into graphite stacks. Presently we must resort to methods that form strong chemical bonds to graphene’s  $\pi$ -surface. The classical approach to the activation of graphite is referred to as Hummer’s method and involves the aggressive oxidation of graphite to create dispersed sheets of graphene oxide (GO) materials with C/O ratios in the range of 2–3.<sup>3</sup> This complicated and highly irregular material has highly oxidized edges with abundant carbonyl functionalities, and the surfaces are decorated with hydroxyl and epoxide groups. Hummer’s conditions necessarily cause some bulk decomposition of the graphene sheets, and it has been recently demonstrated that this can give rise to small molecular fragments, called oxidative debris, in addition to the GO.<sup>4</sup> At the highest oxidation levels the material’s  $\pi$ -systems are heavily interrupted, and the aqueous dispersions are bright yellow in color. The reactivity of GO is significant, and functionalization is generally accompanied by unavoidable reduction. This is illustrated by the fact that even simple alcohols are highly effective at reducing GO.<sup>5</sup> Similarly, treatment with an aqueous base or mild heating can also cause GO to be reduced to give dark black solutions. The highly reactive nature of GO has been exploited in the functionalization and reaction with benzyl alcohol and has recently been shown to produce polymer grafts from the graphene surface.<sup>6</sup> Other approaches have focused on reactions with the oxygen functionality, and an early example includes the reaction with isocyanates to give surface urethane groups.<sup>7</sup>

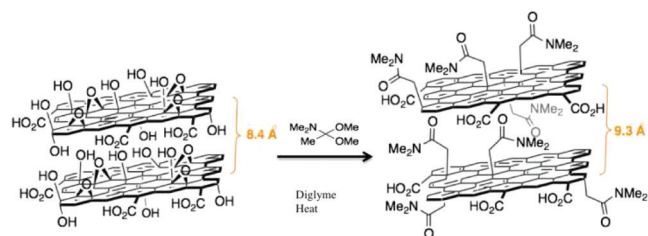
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GO's high reactivity stems from the fact that the lattice carbons are not able to achieve an optimal tetrahedral geometry and the higher electronegativity (good leaving group) nature of the oxygen functionality gives rise to facile heterolysis reactions. Therefore, a transformation that converts the graphene–oxygen bonds into graphene–carbon bonds that are not prone to heterolytic cleavage should produce more stable compositions. Simultaneous reduction and reaction with aryl diazonium groups is one route to these types of materials.<sup>8</sup> Another such transformation we recently developed makes use of the fact that all of the surface hydroxyls in GO are necessarily allylic. As a result, transformation of the allylic graphene–OH groups into allylic graphene–O–CR=CH<sub>2</sub> groups produces reactive intermediates that undergo rapid Claisen rearrangements.<sup>9</sup> As shown in Scheme 1, this transformation is accompanied by an expansion of the layer spacing of the solid material.

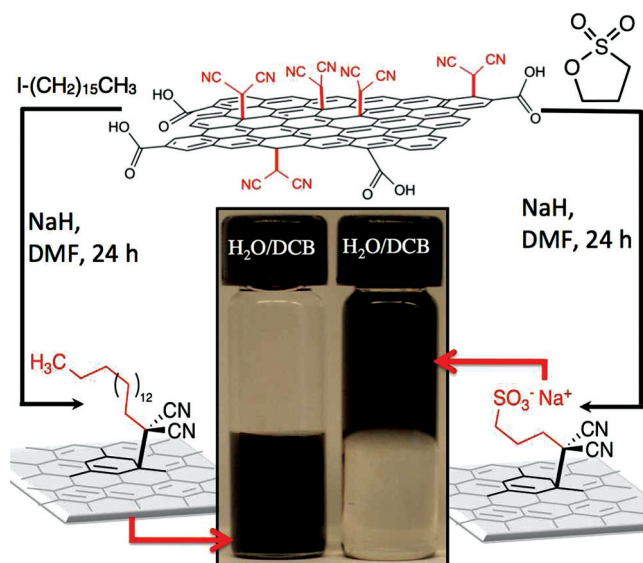
**Scheme 1. Conversion of GO to Amide-Functionalized Graphene**



The high stability of the resultant species is exemplified by the fact that graphene-bound amides can be quantitatively transformed to carboxylates by refluxing in EtOH/H<sub>2</sub>O/KOH for 36 h. The resultant polyelectrolyte graphene displays outstanding solution properties, and its high zeta potential (−68 mV) ensures that the material is dispersed as single sheets. The resulting sheets are conductive and can be repeatedly precipitated by acidification (pH < 5) and redissolved without need of sonication by raising the pH above 7.

Another obvious method for the conversion of the graphene–oxygen bonds into graphene–carbon bonds is to directly displace the oxygen groups with carbon nucleophiles. In considering this prospect, we surveyed a number of possible candidates and found that simple reduction of the GO dominated in most cases. We did find, though, that the nucleophile generated by deprotonating malononitrile ( $pK_a = 11.1$  in H<sub>2</sub>O) has only modest reducing power, rendering it to be a good choice for the reaction with GO. Another benefit of this reactant is that it contains diagnostic CN groups for XPS and IR characterization.<sup>10</sup> The reaction with the conjugate base of malononitrile leads to covalent attachment of CH(CN)<sub>2</sub> groups and an expansion of the graphene layer spacing to 9.5 Å in solid samples. However, significant reductive deoxygenation accompanies this functionalization, and the resultant materials have 1 malononitrile per 46 graphene carbons. Clearly the reaction of this  $\pi$ -surface need not proceed through a classical S<sub>N</sub>2 transition state but could involve S<sub>N</sub>2' or electron transfer processes, followed by radical recombination. In spite of the limited functional group density available by this method, there is considerable power in this method for the creation of a diversity of graphene functionality. Specifically, the graphene–malononitrile groups can be further transformed by classic

substitution reactions. As shown in Figure 2, deprotonation of the CH(CN)<sub>2</sub> groups followed by reaction with either 1-



**Figure 2.** Illustration of how a malononitrile-functionalized graphene sheet can be converted into polyelectrolytes readily dispersible in water or hydrocarbon-appended materials that can be dispersed in *o*-dichlorobenzene (DCB).

iodohexadecane or 1,3-propane sultone creates respective organic or water-soluble products.

Although GO offers inexpensive routes to many types of functional and dispersible graphene, the degradation of the carbon lattice during Hummer's conditions is extensive. The graphene pieces have been oxidatively eroded to create GO with irregular edges and potentially even random holes in the sheets. As a result, there is a need for other graphite exfoliation methods that are not prone to excising carbons from the graphene lattice. One method that has been used to great effect is to react highly reduced graphite with organic electrophiles. Graphite is known to form intercalation compounds wherein groups (often cations or anions) are placed between the graphene sheets.<sup>11</sup> A stage 1 graphite intercalation compound indicates that there are intercalation groups (ions) between every graphene layer. Stage 2 indicates that there are two graphene layers between intercalation groups, and so on. Obviously, stage 1 graphite would be expected to be most reactive. An early example of reactions with highly reduced (stage 1) graphite, KC<sub>8</sub>, was demonstrated by the “highly exothermic” reaction with ethanol, which resulted in exfoliation and ultimate relaxation of the graphite/graphene sheets into structures wherein the sheets are rolled up in a fashion similar to a paper scroll.<sup>12</sup> Other researchers developed covalent reactions by the reductive alkylation of graphite using the reaction of KC<sub>8</sub> with alkyl halides.<sup>13</sup>

The reductive activation approach has recently been shown to have great utility to create bulk functionalized graphene.<sup>14</sup> The more aggressive functionalization conditions included the reaction of potassium staged graphite with aryl-diazonium ions. The reaction is understood to proceed via an electron transfer mechanism starting with reduction of the diazonium ion to create a highly reactive aryl-radical species that reacts with unsaturated carbons.

There are many other possibilities for reactions with the  $\pi$ -surfaces of graphite and graphene. A natural possibility is reactions with alkenes, alkynes, and benzynes that could give rise to Diels–Alder or 2 + 2 products. The Diels–Alder reactivity of graphite/graphene surfaces has been recently described.<sup>15</sup> In this study the authors conclude that graphene exhibits both dienophile and diene reactivity. Reactions with benzynes have also been demonstrated to be highly effective at the formation of solvent dispersible graphenes.<sup>16</sup> It is natural to assume that 1,3-dipolar cycloadditions, carbene, and nitrene additions can also be effective in the functionalization of graphite to give dispersible graphenes.

It should be clear to the reader that the chemistry of the  $\pi$ -surfaces offers great diversity. There are many challenges that need to be addressed. For example, how can we create graphenes with completely different functional groups on each side? Such a material would be ideal to organize at interfaces or to create chemical domains that are completely separated but only angstroms apart. Creating printable forms of graphenes for high performance electronic devices is also a challenge worth the effort. Major opportunities lie in the construction of complex, multicomponent functional materials systems containing precise structures of graphenes, carbon nanotubes, fullerenes, proteins, and/or nanoparticles. It is clear that the field is moving fast. There is no speed limit on this  $\pi$ -way!

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### Notes

The authors declare no competing financial interest.

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