Graphene

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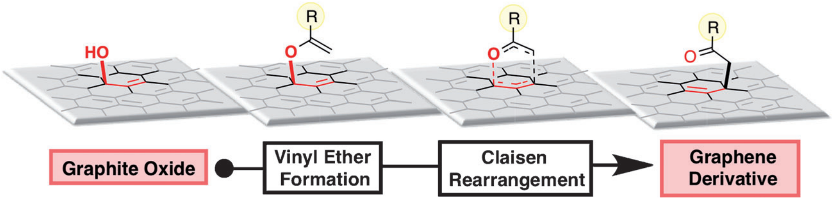
Claisen Rearrangement of Graphite Oxide: A Route to Covalently Functionalized Graphenes**

*William R. Collins, Wiktor Lewandowski, Ezequiel Schmois, Joseph Walish, and Timothy M. Swager**

The chemical modification of nano- or micromolecular surfaces is widely used for the precise structural and/or electrical manipulation of bulk materials.[1] In particular, atomically thin graphitic molecules such as fullerenes, carbon nanotubes, and graphene display pronounced physicochemical and electronic changes after synthetic derivatization of their surfaces.[2] In many cases these graphitic substrates can be imbued with a wide range of desirable attributes such as increased solubility in a specific solvent, enhanced mechanical properties, chemosensing, and conductance changes. As a consequence of these attributes, numerous graphitic derivatives have been utilized in a variety of academic and industrial applications.[3]



Scheme 1. Allylic oxygen to carbon bond transposition on graphite oxide (additional substrate oxygen groups have been removed for clarity). For the Eschenmoser–Claisen rearrangement variant, $R=N(CH_3)_2$.

Unfortunately, few synthetic methods currently exist to covalently functionalize the surface of graphene.[4] This deficiency is due to both the use of metastable colloidal suspensions of reduced graphite oxide (GO) as the starting material for many transformations,[5] as well as the decreased chemical reactivity of graphene in comparison to the more strained fullerene or carbon nanotubes.[6,7] Herein we report the covalent functionalization of soluble, exfoliated graphite oxide through a Claisen rearrangement (Scheme 1). Specifically, the allylic alcohol functional groups found on the surface of GO[8] are converted in situ into vinyl allyl ethers, and allylically transposed in a sigmatropic-type fashion to form new carbon–carbon bonds. As a direct result of this transformation, robust carbonyl groups are installed on the surface, which can undergo subsequent synthetic manipulations.

The Eschenmoser–Claisen rearrangement variant was chosen as the proof of principle test reaction on GO (Scheme 1, where $R=N(CH_3)_2$). In this reaction, allylic alcohols are converted into γ,δ-unsaturated *N*,*N*-dimethylamides through the use of the vinyl transfer reagent *N*,*N*-dimethylacetamide dimethyl acetal (DMDA). This reaction was chosen specifically for the following reasons: 1) the ability to quantitatively evaluate the efficacy of the transformation through nitrogen incorporation, 2) the chemospecificity of DMDA for alcohol functional groups, 3) only thermal treatment of DMDA is necessary to effect transfer of the vinyl group, and 4) the formation of bonds between quaternary carbon atoms is well established using the Eschenmoser–Claisen variant.[9]

We began the investigations into the proposed transformation by mixing graphite oxide with DMDA (ca. 2 equivalents per oxygen atom on GO, see the Supporting Information)[10] in THF at 60 °C for 24 h.[11] As the reaction progressed, the transparent GO/THF solution darkened to an opaque, black suspension. Significant sedimentation could be observed after prolonged standing of the mixture at room temperature. The insoluble product was then subjected to repeated centrifugation, washing cycles, and drying. Analysis of the graphitic material (**G1**) by UV/Vis and FTIR spectroscopy indicated that partial reconjugation of the π network had occurred, as evidenced by a bathochromic shift of the absorbance maximum from 240 nm in the starting material to 262 nm in the product (see the Supporting Information).[12] Graphene oxide is unstable with regard to reductive partial deoxygenation, and some nonspecific reduction was expected. In addition to a decrease in the IR frequencies associated with the C–O bonds in GO (the 1053 cm^{-1} peak ascribed to surface-bound epoxide moieties is absent in the product),[13] a new carbonyl stretching mode at 1635 cm^{-1} emerges, which suggests amide incorporation (Figure 1 a).

X-ray powder-diffraction (XRD) pattern analysis of **G1** (Figure 1 b) revealed an increase in the distance within the intersheet gallery from 0.84 nm in GO to 0.93 nm in the

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[*] Dr. W. R. Collins, W. Lewandowski, E. Schmois, Dr. J. Walish, Prof. Dr. T. M. Swager
Department of Chemistry and
The Institute for Soldier Nanotechnologies
Massachusetts Institute of Technology
Cambridge, MA 02139 (USA)
E-mail: tswager@mit.edu

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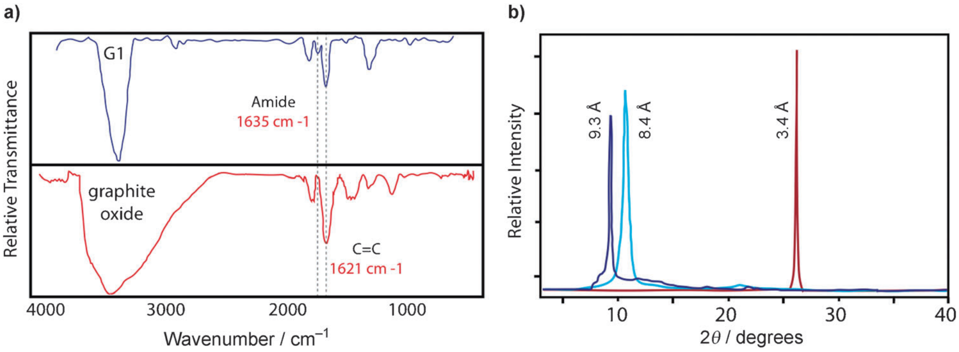

Figure 1. a) FTIR spectra of graphite oxide (red) and **G1** (blue). b) XRD patterns of graphite (red), graphite oxide (light blue), and **G1** (dark blue).

product, which is a qualitative indicator of the installation of additional functionality on the surface of the basal plane of graphene.[14–16] It is important to note that simple reductive deoxygenation of GO leads to a decrease in the intersheet spacing.

The quantitative evaluation of the product was accomplished through both thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). TGA analysis of **G1** showed a large decrease in the surface C–O functionality (epoxides and tertiary alcohols), as evidenced by a reduced mass change at 190–210 °C (Figure 2, thermograms A and B).[17] Additionally, a new thermal decomposition is observed between 290–310 °C, which could potentially be ascribed to amide groups found on the surface of **G1**.[18] The relatively high temperature at which this decomposition occurs suggests that covalent functionalization occurs in this reaction and is not simply a physical adsorption process.

High-resolution XPS analysis of **G1** conclusively demonstrated that nitrogen incorporation occurred during the Eshenmoser–Claisen rearrangement (Table 1, entry 1; for spectra see the Supporting Information).[19] Through XPS it was determined that **G1** contained 1.4 % nitrogen. A single, amide N(1s) signal was found at 399.9 eV, which indicates that all of the starting DMDA material was either consumed in the reaction or removed during the work-up. Importantly, the high-resolution N(1s) signal exactly corresponds to that of known XPS spectra of dialkylamide functional groups covalently bound to the surface of activated carbon.[20] The high-resolution C(1s) spectrum (between 284–288 eV) of **G1** further confirmed the previous observations that deoxygenation of the C–O functional groups occurs during the reaction. In effect, the atomic percentage of the oxygen content decreased from 27.7 % in the graphite oxide starting material to 19.6 % in the product.

Table 1: List of the atomic composition of chemically/thermally modified graphite oxide by XPS.[a]

Entry	Solvent/*T* [°C]	Atomic [%] C	O	N	Amide/C[e]	C/O ratio
1[b]	THF/60	79.0	19.6	1.4	1:52	4.03:1
2[b]	dioxane/100	85.5	12.4	2.1	1:37	6.90:1
3[b]	diglyme/150	85.8	11.1	3.1	1:23	7.73:1
4[c]	THF/60	74.0	26.0	–	–	2.85:1
5[c]	dioxane/100	75.5	24.5	–	–	3.08:1
6[c]	diglyme/150	80.1	19.9	–	–	4.03:1
7[d]	–	72.3	27.7	–	–	2.61:1

[a] Calculated by integration of diagnostic XPS signals. [b] Reaction performed with 2 equiv DMDA per GO oxygen atom. [c] Thermal reduction performed without DMDA. [d] Unchanged GO starting material. [e] Ratio = [(C %)/(N %)]−4.

With evidence in hand for a successful Claisen rearrangement of graphite oxide, we next attempted to improve the efficacy of the transformation by increasing the reaction temperature. The rearrangement was thus rerun in two higher boiling solvents: dioxane at 100 °C, and bis(2-methoxymethylether)ether (diglyme) at 150 °C. Nitrogen-containing solvents were intentionally avoided so as to not complicate the analysis of the products.[21] In both reactions, as observed before, the solution rapidly turned black. TGA analysis of the isolated products **G2** (from dioxane) and **G3** (from diglyme) showed that in both cases a further decrease in the C–O functionality occurred, as indicated by an additional decrease in the mass loss at 190–210 °C. Importantly, a concomitant increase in the functional groups that fragment at higher temperatures was also observed in both cases (Figure 2, thermograms C and D).

The XPS data for **G2** and **G3** correlated well with the observed trends in the TGA thermograms. The incorporation of amide N(1s) increased to a total of 3.1 % in **G3**, while the percentage of atomic oxygen decreased to 11.1 % in **G3** (Table 1, entries 1–3). When the carbon and oxygen atoms within the appended amide molecule are taken into account (4 carbon atoms, 1 oxygen atom), these data correspond to a functional

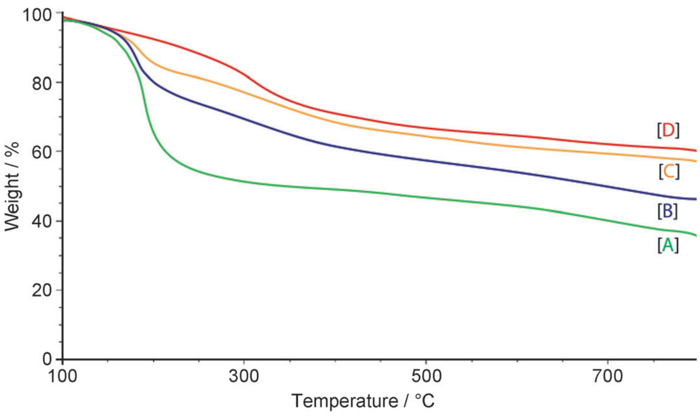

Figure 2. TGA thermograms of GO (A, green), THF rearrangement product **G1** (B, dark blue), dioxane rearrangement product **G2** (C, yellow), and diglyme rearrangement product **G3** (D, red).

group density of 1 amide per 23 carbon atoms in **G3** (1 functional group for 1.25 nm^2 of graphitic area).

Since the oxygen content decreased in all three transformations, we were interested in whether the deoxygenation of the GO was a sole function of prolonged exposure to high reaction temperatures or whether the DMDA was acting in some capacity as a reducing agent. Therefore, we re-ran the three reactions without the addition of DMDA and evaluated the products by XPS analysis (Table 1, entries 4–6, compare to entries 1–3, and 7). It can be seen that in all three cases a small to moderate amount of thermal deoxygenation occurs, but that this process alone cannot account for the extensive reduction that is observed.[22] Thus, the DMDA serves as both the vinyl transfer reagent in the Claisen reaction and as a reducing agent for GO.

Four-point probe measurements on thin films of **G3** revealed that the DMDA reduction process sufficiently re-established conjugation within the graphene sheet to produce a moderate level of conductivity of 1.7 S m^{-1} (see the Supporting Information). Annealing the sample at 250 °C for 24 h (below the temperature at which the amide groups are thermally eliminated) resulted in a further increase in the conductivity to 538 S m^{-1}. As expected, from its increased intersheet spacing as well as covalently bound amide groups disrupting the conjugation of the graphene sheet, **G3** displays a lower conductivity than reduced GO (with comparable C/O ratios) produced by hydrazine, anionic, or thermal deoxygenation.[23]

We next determined whether the newly installed amide groups could be chemically converted into alternative functionality. It has been documented that the carboxylate groups on the edges of graphene can stabilize colloidal dispersions of exfoliated graphene electrostatically for short periods of time.[12] It was, therefore, postulated that by increasing the density of carboxylate functional groups through saponification of the surface-bound amide groups, the resulting graphene derivatives could exist as stable colloidal solutions for prolonged periods of time. To this end, we treated **G3** under strongly basic conditions (KOH/H$_2$O/ethanol at reflux) to saponify the amide groups. Aliquots were removed during the reaction at 12 h increments and the surface charge (zeta potential) of the graphene substrate was monitored (see the Supporting Information). From the resulting measurements it was determined that the weakly charged (−19 mV) starting material **G3** developed an increasing surface charge as the reaction progressed, with the zeta potential reaching a maximum of −68 mV at 36 h.

After acidification of the reaction solution, the resulting graphene derivative could be precipitated and isolated. Following successive washing, centrifugation, and drying, the chemical composition of the resulting graphene derivative (**G4**) could be quantitatively assessed. XPS analysis showed that the atomic weight percent of nitrogen had decreased from 3.1 % in the starting material to 0.6 % (see the Supporting Information for spectrum). These data translate to a drop in the density of amide functional groups to 1 group per approximately 80 graphitic carbon atoms. In conjunction with the above-mentioned zeta potential measurements, the loss of the amide N(1s) signal suggested that extensive saponification had in fact occurred on the graphene surface.

Visual observations of the solubility of **G4** provided additional support for the existence of surface-bound carboxylate groups. Specifically, the solubility profile of the graphene derivative in aqueous environments proved to be highly dependant upon the pH value of the solution (Figure 3 a). **G4** proved to be largely insoluble in aqueous, acidic solutions below pH 5. Under neutral or basic solutions, **G4** readily formed a homogeneous colloidal dispersion. Relatively high concentrations of up to 5 mg mL^{-1} of **G4** in neutral pH water have been generated and shown to be stable for over 3 months without sedimentation. Tapping-mode atomic force microscopy (AFM) images of drop-cast solutions of **G4** in neutral water show that the graphene sheets in these solutions are largely exfoliated in nature and not composed of higher-order graphitic aggregates (Figure 3 b).

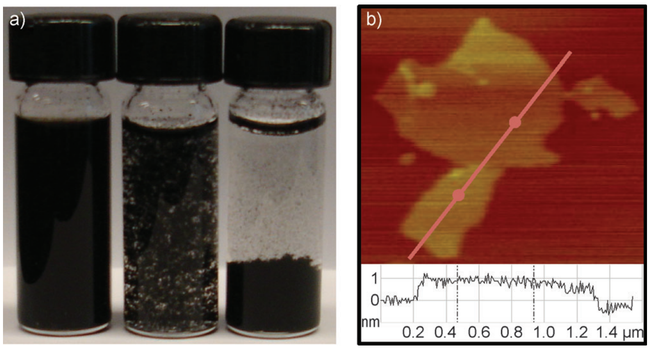

Figure 3. a) Solubility profile of **G4** in water at pH 7.2, 5.2, and 3.3. b) Tapping-mode AFM image of **G4** with a height profile taken across the red line. The imaged sample was prepared by drop-casting a 0.01 M solution of **G4** in neutral water onto mica followed by evaporative drying of the sample.

A turbidity analysis was undertaken to determine the precise correlation between the pH value of the aqueous environment and the solubility profile of **G4**. This was accomplished by measuring UV/Vis absorbance spectra over a pH range of 7.26 to 3.5. Only small changes occur in the UV/Vis absorbance intensity between pH 7.26 and 6. A much larger drop in the absorbance begins near or at pH 5. This spectroscopic change is matched by the beginning of a noticeable flocculation of the graphene sheets in solution. Below pH 5, the absorbance dramatically decreases because of the aggregation and subsequent sedimentation of the graphene sheets in solution (Figure 4).

Measurement of the zeta potential over the same pH range correlates well with what is observed in the UV/Vis turbidity analysis (see the Supporting Information). Lowering the pH value below 7.26 results in a decrease in the surface charge from the initial −68 mV. A significant drop to −15 mV is observed between pH 6.3 and 4.6. At pH 3, most of the anionic functionality on the sheet has been protonated, as indicated by a near-neutral zeta potential.

Taken together, the turbidity analysis, zeta potential measurements, and visual observations all suggest that the

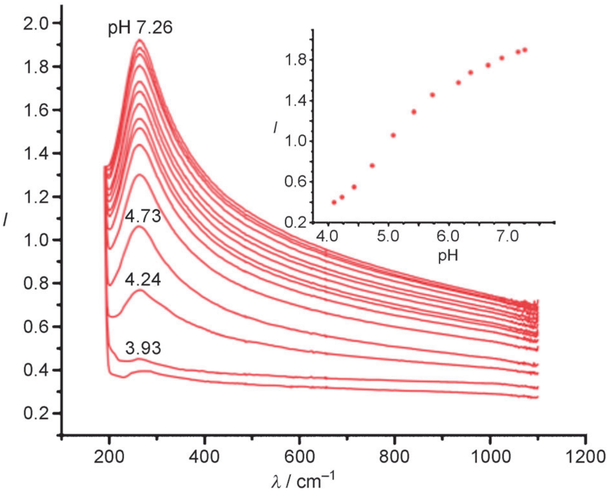

Figure 4. UV/Vis absorbance of **G4** in an aqueous solution with the pH value ranging from 7.26 to 3.5. (Inset: UV/Vis maximum absorbance of **G4** at 262 nm plotted against the pH range of the aqueous solution.)

carboxylate functionality is not only present on the surface of **G4** but that these groups play an important role in electrostatically stabilizing the graphene sheets in aqueous environments. In particular, when the pH value of the aqueous solution is above the pK_a value of the surface-bound carboxylic acid groups, the resulting anionic surface charge acts to effectively disperse the sheets. Alternately, when the pH value is reduced to pH 5 or below, the carboxylate functional groups are protonated, the electrostatic charge is lost, and the sheets hydrophobically aggregate and begin to sediment.[24,25]

In summary, this study reports a sigmatropic-type transformation on a graphitic surface. By utilizing the Eschenmoser–Claisen rearrangement on graphite oxide, the surface allylic alcohol functional groups were directly converted into carbon-bound *N*,*N*-dimethylamide groups through the use of the reagent DMDA.[25] These amide groups, when saponified under strongly basic conditions, were converted into the corresponding carboxylates, which have been shown to dramatically increase the solubility of the graphene derivative in aqueous environments without the need for cosolvents or additives.[26] Current efforts are underway to expand the scope and application of this transformation and to investigate the possibility of additional Claisen rearrangements on graphitic substrates.

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