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 micro-molecular surfaces is widely used for the precise structural and/or electrical manipulation of bulk materials.[1] In particular, atomically thin graphitic molecules such as fullerene, 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. Because of these attributes, numerous prepared graphitic derivatives have been utilized in a variety of academic and industrial applications.[3]

Unfortunately, few synthetic methods currently exist to covalently functionalize the surface of graphene.[4] This deficiency is due to both the use of meta-stable 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 to 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 carbonyls 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 to 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) DMDA′s chemospecificity for alcohol functional groups, 3) only thermal treatment of DMDA is necessary to affect the vinyl group transfer, and 4) the formation of quaternary carbon-carbon bonds is well established using the Eschenmoser-Claisen variant.[9]

We began the investigations into the proposed transformation by mixing graphite oxide with DMDA (~2 equivalents per oxygen on GO, see 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. After prolonged standing at room temperature significant sedimentation could be observed. The insoluble product was then subjected to repeated centrifugation, washing cycles and drying. Analysis of the graphite 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 Supporting Information).[12] GO is unstable with regard to reductive partial deoxygenation and some non-specific 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 epoxides is absent in the product)[13] a new carbonyl stretching-mode at 1635 cm$^{-1}$ emerges suggesting amide incorporation (Figure 1a).

X-ray powder diffraction (XRD) pattern analysis of G1 (Figure 1b) revealed an increase in distance within the intersheet gallery from 0.84 nm in GO to 0.93 nm in the product, which is a qualitative indicator of the installation of additional functionality on the surface of the basal plane of graphene.[14][15][16] It is important to note that simple reductive deoxygenation of GO leads to a decrease in the intersheet spacing.

**Scheme 1. Allylic oxygen to carbon bond transposition on graphite oxide (additional substrate oxygenation removed for clarity). For the Eschenmoser-Claisen rearrangement variant R = N(CH$_3$)$_2$.

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[2] This work was supported by the IC Postdoctoral Research Fellowship Program and the Army Research Office through the Institute for Soldier Nanotechnologies. This project cooperated within the Foundation for Polish Science MPD>Programme co-financed by the EU European Regional Development Fund. We thank Jason Cox for assistance with AFM measurements and Jan Schnorr and Libby Shaw with XPS measurements.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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Figure 1. a) FTIR spectrum of graphite oxide (red) and G1 (blue). b) XRD patterns of graphite (red), graphite oxide (light blue), and G1 (dark blue).
The quantitative evaluation of the product was accomplished through both thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The TGA 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). 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. The relatively high temperature at which this decomposition occurs suggests that covalent functionalization is occurring in this reaction and is not simply a physical adsorption process.

![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).](image)

High-resolution XPS analysis of G1 conclusively demonstrated that nitrogen incorporation occurred during the Eshenmoser-Claisen rearrangement (Table 1, entry 1; for spectra see Supporting Information). Through XPS it was determined that G1 contained 1.4% nitrogen. A single, amide N(1s) signal was found at 399.9 eV indicating 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 diacylamide functional groups covalently bound to the surface of activated carbon. 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 was occurring during the reaction. In effect, the atomic percent for oxygen content decreased from 27.7% found in the graphite oxide starting material to 19.6% in the product.

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 re-run in two higher boiling solvents: dioxane at 100 °C, and bis(2-methoxyethylether)ether [diglyme] at 150 °C. Nitrogen containing solvents were intentionally avoided so as to not complicate the analysis of the products. 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 of the C-O functionality occurred as indicated by an additional drop 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 amide N(1s) incorporation increased to a total of 3.1% in G3, while the oxygen atomic percent 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 carbons, 1 oxygen) this data corresponds to a functional group density of 1 amide per 23 carbons in G3 (1 functional group for 1.25 nm² of graphitic area).

Due to the fact that 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 1-3,7). 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. Thus, the DMDA is serving as both the vinyl transfer reagent in the Claisen reaction and as a reducing agent for GO.

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent/ temp (°C)</th>
<th>atomic (%)</th>
<th>amide / C/O</th>
<th>C/O Ratio</th>
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<tr>
<td>1[^a]</td>
<td>THF / 60</td>
<td>79.0</td>
<td>19.6</td>
<td>1.4/52</td>
</tr>
<tr>
<td>2[^b]</td>
<td>Dioxane / 100</td>
<td>85.5</td>
<td>12.4</td>
<td>1.37/52</td>
</tr>
<tr>
<td>3[^b]</td>
<td>Diglyme / 150</td>
<td>85.8</td>
<td>11.1</td>
<td>1/23</td>
</tr>
<tr>
<td>4[^c]</td>
<td>THF / 60</td>
<td>74.0</td>
<td>26.0</td>
<td>--</td>
</tr>
<tr>
<td>5[^c]</td>
<td>Dioxane / 100</td>
<td>75.5</td>
<td>24.5</td>
<td>--</td>
</tr>
<tr>
<td>6[^c]</td>
<td>Diglyme / 150</td>
<td>80.1</td>
<td>19.9</td>
<td>--</td>
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<tr>
<td>7[^d]</td>
<td>--</td>
<td>72.3</td>
<td>27.7</td>
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</table>

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

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 (See 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. As expected, from its increased interlayer spacing as well as covalently bound amide groups disrupting the graphene sheet’s conjugation, G3 displays a lower conductivity than reduced GO (with comparable C/O ratios) produced by hydrazine, anionic- or thermally-based deoxygenation.

We next determined whether the newly installed amide groups could be chemically converted into alternate functionality. It has been documented that the carboxylate groups on the edges of graphene can electrostatically stabilize colloidal dispersions of exfoliated graphene for short periods of time. It was therefore postulated that by increasing the carboxylate functional group density 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 (refluxing KOH/H₂O/ethanol) to saponify the amide groups. Aliquots were removed during the reaction timecourse at 12 h increments and the surface charge (zeta potential) of the graphene substrate was monitored (See Supporting Information). From the resulting measurements it was determined...
that the weakly charged (-19 mV) starting material G3 increasingly developed 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 washings, centrifugations, and dryings, the resulting graphene derivative’s (G4) chemical composition 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 Supporting Information for spectrum). This data translates to an amide functional group density drop to 1 group per ca. 80 graphitic carbons. In conjunction with the abovementioned 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 graphene derivative’s solubility profile in aqueous environments proved to be highly dependant upon the pH of the solution (Figure 3a). In aqueous, acidic solutions below pH 5, G4 proved to be largely insoluble in water. Under pH neutral or basic solutions G4 readily formed a homogeneous colloidal dispersion. Relatively high concentrations of up to 5 mg/mL 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 pH water show that the graphene sheets in these solutions are largely exfoliated in nature and not composed of higher-order graphitic aggregates (Figure 3b).

![Figure 3](image_url)

**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 of the aqueous environment and the solubility profile of G4. This was accomplished by measuring UV-Vis absorbance spectra over a pH ranging from 7.26 to 3.5. Within the pH range of 7.26 to 6 only small changes occur in the UV-Vis absorbance intensity. A much larger drop in the absorbance begins near or at pH 5. This spectral change is matched by the beginning of a noticeable flocculation of the graphene sheets in solution. Below pH 5 the absorbance dramatically decreases due to the aggregation and subsequent sedimentation of the graphene sheets in solution (Figure 4).

![Figure 4](image_url)

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

Zeta potential measurements performed over the same pH range correlate well with what is observed in the UV-Vis turbidity analysis (see Supporting Information). By lowering the pH below 7.26 the surface charge correspondingly decreases from the initial -68 mV. Between pH 6.3 and 4.6 a significant drop to -15 mV is observed. 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 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 of the aqueous solution is above the pKa of the surface bound carboxylic acid groups the resulting anionic surface charge acts to effectively disperse the sheets. Alternately, when the pH 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 the sigmatropic-type transformation on a graphitic surface. Utilizing the Eschenmoser-Claisen rearrangement on graphite oxide, the allylic alcohol surface functional groups were directly converted to 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 to the corresponding carboxylates, which have been shown to dramatically increase the solubility of the graphene derivative in aqueous environments without the need of co-solvents 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.

Received: (will be filled in by the editorial staff)
Published online on (will be filled in by the editorial staff)

**Keywords:** graphene · Claisen rearrangement · surface functionalization · electrostatic stabilization · water solubility


A one-pot, oxygen to carbon bond allylic transposition reaction and chemical reduction of graphite oxide has been demonstrated. Utilizing N,N-dimethylacetamide dimethylacetal, the basal plane allylic alcohol functionality of graphite oxide can be converted to N,N-dimethylamide groups through an Eschenmoser-Claisen sigmatropic-type rearrangement. These groups can be subsequently saponified to the carboxylic acid, which, when deprotonated, electrostatically stabilizes the graphene sheets in an aqueous environment.
Supporting Information

**General Experimental:** Graphite powder was received from Alfa Aesar (natural, microcrystal grade, APS 2-15 micron, lot #C04U006) and used without further purification. N,N-dimethylacetamide dimethyl acetal (90% purity) was purchased from Sigma Aldrich and used without further purification. The reaction solvent THF (Fisher, spectroscopic grade) was dried by passage through two columns of neutral alumina in a solvent dispensing system. Dioxane (Aldrich, spectroscopic grade) and bis(2-methoxyethyl)ether [diglyme] (Aldrich, ACS grade) were dried over 3 angstrom molecular sieves for 24 h followed by drying with potassium hydroxide for 24 h and then passed through a column filled with activated alumina. Potassium hydroxide (Aldrich), ethanol (Fisher, ACS grade), dichloromethane (Aldrich, spectroscopic grade), N,N-dimethylacetamide (Aldrich), and acetone (Aldrich, spectroscopic grade) were purchased from commercial sources and used as received. Graphite oxide was synthesized utilizing a slightly modified Hummer’s oxidation procedure in which the sodium nitrate is excluded.

**General Instrumentation:** Fourier transform infrared (FT-IR) spectroscopy was performed on a Perkin-Elmar model 2000 FT-IR spectrophotometer using the Spectrum v. 2.00 software package. The spectra in the UV-Vis range were obtained using an Agilent 8453 UV-visible spectrophotometer. Raman spectra were measured on a Horiba LabRAM HR Raman Spectrometer using the excitation wavelength of 532 nm. TGA analyses were performed with a TGA Q50 apparatus (TA instruments). TGA experiments were carried out under a helium atmosphere. Samples were heated at 10 °C/min from 50 °C to 800 °C. The thickness of thin films was measured using a Dektak 6M stylus profilier by Vecco and their conductivities were measured utilizing a Signatone four point probe with a 1.27 mm spacing connected to a Keithley 2400 source meter. XPS spectra were recorded on a Kratos AXIS Ultra X-ray Photoelectron Spectrometer. XPS samples were prepared by drop-casting solutions onto silicon wafers. X-ray data was collected using an Inel CPS 120 position sensitive detector using an XRG 2000
generator (Cu Ka) and a Minco CT 137 temperature controller. XRD samples were prepared by
dropcasting concentrated solutions of the graphene derivative onto silicon wafers. Tapping-mode AFM
images were recorded on a Nanoscope V with dimension 3100 with the AFM samples prepared by drop-
casting onto freshly cleaved mica substrates. Zeta potential measurements and phase analysis light
scattering measurements were determined with a Brookhaven instruments Zeta PALS, zeta potential
analyzer. TEM images were acquired with a JEOL 2010 FEG Analytical Electron Microscope, and the
samples were prepared by drop-casting directly onto Quantfoil 200 M Cu holey carbon. All synthetic
manipulations were carried out under an argon atmosphere using standard Schlenk techniques.

**Synthesis of amide-functionalized graphene derivative G1:** To a flame-dried, 1 L round bottom
flask fitted with a stirbar, reflux condensor, soxlet extractor (filled with 4 angstrom molecular sieves)
and an argon inlet adaptor was added graphite oxide (350 mg) and THF (350 mL). The heterogeneous
 suspension was sonicated for 1 h in a bath sonicator to achieve a homogenous dispersion. The solution
was then brought to 60 °C in an oil bath and the N,N-dimethylacetamide dimethyl acetal (2.4 mL, 15.7
mmol, 2 times the molar mass of oxygen content of graphite oxide [XPS analysis: 72.3 C/ 27.7 O]) was
added in one portion. The mixture was refluxed for 24 h and then cooled to room temperature. During
the reaction the solution gradually darkened to an opaque black dispersion. After cooling, this dispersion
was filtered through an anodesic membrane (0.2 micron pore diameter, Milipore) with suction to obtain
a filter cake. The material was then washed with copious amounts of acetone, followed by sonication in
20 mL of acetone for 1 h in a cooled bath sonicator. The slurry was centrifuged at 14,500 rpm to obtain
a black sediment. Sonicative dispersion in acetone with subsequent centrifugation was repeated 3 times
with acetone, 2 times with water, and again 2 times with acetone. The supernatant was discarded each
time. The final sediment was dried under high vacuum (0.1 mm Hg) at 40 °C over a KOH desiccant for
24 h. See figures S1-S6 for TGA, XPS, FT-IR, XRD and UV-Vis characterization data.

**Synthesis of amide-functionalized graphene derivatives G2/G3:** To a flame-dried, 1 L round
bottom flask fitted with a stirbar and an argon inlet adaptor was added graphite oxide (350 mg) and
dioxane (350 mL) or diglyme (350 mL). The heterogeneous suspension was sonicated for 1 h in a bath
sonicator to achieve a fine dispersion. The solution was then brought to 100 °C or 150 °C in an oil bath and the N,N-dimethylacetamide dimethyl acetal (2.4 mL, 15.7 mmol, 2 times the molar mass of oxygen content of graphite oxide [XPS analysis: 72.3 C/ 27.7 O]) was added in one portion. The dispersion was heated for 24 h and then cooled to room temperature. During the reaction the solution darkened to an opaque black dispersion. After cooling, this dispersion was filtered through an anodesic membrane (0.2 micron pore diameter, Milipore) with suction to obtain a filter cake. The material was then washed with copious amounts of acetone, followed by sonication in 20 mL of acetone for 1 h in a cooled bath sonicator. The slurry was centrifuged at 14,500 rpm to obtain a black sediment. Sonicative dispersion in acetone with subsequent centrifugation was repeated 3 times with acetone, 2 times with water, and again 2 times with acetone. The supernatant was discarded each time. The final sediment was dried under high vacuum (0.1 mm Hg) at 40 °C over a KOH desiccant for 24 h. See figures S7-S12 for TGA, HRTEM/EFTEM, Raman and XPS characterization data.

**Synthesis of G4:** To a flame-dried 100 mL round bottom flask fitted with a stir bar, reflux condensor and an argon inlet adaptor was added G3 (25 mg) and ethanol (25 mL). To this mixture was added an aqueous potassium hydroxide solution (25 mL, 11 M) and the resulting dispersion was sonicated for 1 h in a bath sonicator. The mixture was then heated to reflux (85 °C) for 36 h. At 12 h increments 0.5 mL aliquots were removed and the graphene particle’s zeta potential was analyzed (See figure S13). After 36 h the reaction mixture was cooled to room temperature and centrifuged at 14,500 rpm for 30 min. The supernatant was discarded. The black sediment was re-dispersed in 100 mL pH neutral water (MilliQ water). The resulting solution was acidified to pH 3 upon which the graphene precipitated out of solution. The supernatant was discarded and the graphite derivative was sonicatively dispersed and centrifuged twice in 20 mL dichloromethane, twice in acetone, twice in water and then twice in acetone again. In all cases the supernatant was discarded. The final sediment was dried under high vacuum (0.1 mm Hg) at 40 °C for 24 h. See figures S13-S19 for XPS, FTIR, XRD, Raman, UV-Vis, HRTEM/EFTEM and zeta potential characterization data.
Control reactions for G1/G2/G3: To a flame-dried, 50 mL round bottom flask fitted with a stirbar and an argon inlet adaptor was added graphite oxide (35 mg) and THF (35 mL) or dioxane (35 mL) or diglyme (35 mL). The heterogeneous suspension was sonicated for 1 h in a bath sonicator to achieve a fine dispersion. The solution was then brought to 60 °C or 100 °C or 150 °C in an oil bath and the N,N-dimethylacetamide (0.146 mL, 1.57 mmol, 2 times the molar mass of oxygen content of graphite oxide [XPS analysis: 72.3 C/ 27.7 O]) followed by MeOH (0.126 mL, 3.14 mmol, 4 times the molar mass of oxygen content of graphite oxide) was added in one portion. The dispersion was heated for 24 h and then cooled to room temperature. During the reaction the solution darkened to an opaque black dispersion (although in each case to a much less extent than when DMDA was added). After cooling, this dispersion was filtered through an anodesic membrane (0.2 micron pore diameter, Milipore) with suction to obtain a filter cake. The material was then washed with copious amounts of acetone, followed by sonication in 20 mL of acetone for 1 h in a cooled bath sonicator. The slurry was centrifuged at 14,500 rpm to obtain a black sediment. Sonication dispersion in acetone with subsequent centrifugation was repeated 3 times with acetone, 2 times with water, and again 2 times with acetone. The supernatant was discarded each time. The final sediment was dried under high vacuum (0.1 mm Hg) at 40 °C over a KOH desiccant for 24 h. In no case was nitrogen incorporation observed. See figures S20-S22 XPS characterization data.

Procedure for turbidity analysis/zeta potential analysis of G4: In a quartz cuvette fitted with a micro-stir bar was added 0.75 mL of the carboxylate graphene derivative (G4) solution [0.0001 M] in pH 7.26 MilliQ water. The UV-Vis spectrum, particle size (average over ten measurements: 876 nm – uses spherical particle assumptions) and zeta potential (average of ten measurements) were initially taken. To this solution, with vigorous stirring, was added 10 µL increments of a 0.01 N HCl solution. Between each addition of acid, the pH of the solution was measured in duplicate, and the UV-Vis spectrum and zeta potential (average of ten measurements) were obtained. Visually, small amounts of flocculation could be observed as early as pH 5.9. Severe heterogeneity was observed at pH 5 and below (See figure S23).
General procedure for the determination of conductivities of G3 and G4: A graphene derivative was sonicated in NMP (G3) for 30 min. Subsequently, 100 µL of the suspension was drop-cast onto a glass slide and air-dried to create a thin film. Using a four-point probe setup, the electric potential was measured at a current of 2,4, and 6 µA for each film. The film was then annealed in a vacuum oven at 250 °C for 24 h and the electric potential was re-measured. Subsequently, the thickness of the film was measured using a profilometer and the conductivity was calculated using equation 1

\[ \sigma = \frac{I}{V \cdot t \cdot CF} \] (for \( t/s < 0.4 \))

where \( I \) is the current, \( V \) is the voltage, \( t \) is the sample thickness, \( CF \) is the sheet resistance correction factor, and \( s \) is the four point probe spacing.

Conductivity of G3: The conductivity of a drop-cast film of amide-functionalized graphene was determined to be 1.7 S m\(^{-1}\) (average of two films and three measurements each).

Conductivity of G3 (thermally treated): The conductivity of amide-functionalized graphene annealed at 250 °C was determined to be 538 S m\(^{-1}\) (average of two films and three measurements each).

**Figure S1.** TGA of amide functionalized graphene (G1, blue, [B]) and graphite oxide (green, [A])
**Figure S2.** XPS survey spectrum of graphite oxide (red) and amide functionalized graphene (G1, blue).

**Figure S3.** High-resolution XPS spectra of C(1s) and N(1s) regions of G1 and graphite oxide.
Figure S4. baseline corrected FT-IR spectra of graphite oxide (red) and G1 (blue)

Figure S5. XRD patterns of (G1, dark blue), graphite oxide (light blue) and graphite (red)
**Figure S6.** UV-Vis spectra of graphite oxide (red) and amide functionalized graphene G1 (blue)

**Figure S7.** TGA of amide functionalized graphene (G2, yellow, [C]) and graphite oxide (green, [A])
Figure S8. XPS survey spectrum of graphite oxide (red) and amide functionalized graphene (G2, blue)

Figure S9. TGA of amide functionalized graphene (G3, red, [D]) and graphite oxide (green, [A])
**Figure S10.** XPS survey spectrum of graphite oxide (red) and amide functionalized graphene (G3, blue)

**Figure S11.** Overlayed energy filtering TEM (EFTEM) images of the basal plane of (G3). The green coloration is carbon atoms and the red nitrogen atoms. HRTEM image of (G3)
Figure S12. Raman spectrum of graphite oxide (red) and amide functionalized graphene (G3, blue)

Figure S13. XPS survey spectrum of graphite oxide (red) and carboxylate graphene (G4, blue)
Figure S14. baseline corrected FT-IR spectra of graphite oxide (red) and carboxylate G4 (blue)

Figure S15. Raman spectrum of graphite oxide (red) and amide functionalized graphene (G3, blue)
Figure S16. XRD patterns of (G4, green), G3 (dark blue), graphite oxide (light blue) and graphite (red)

Figure S17. overlayed energy filtering TEM (EFTEM) images of the basal plane of (G4). The green coloration is carbon atoms and the red nitrogen atoms. HRTEM image of (G4)
Figure S18. Zeta potential of (G3) converting to (G4) as a function of reaction time

Figure S19. Zeta potential of (G4) in an aqueous solution with varying pH
Figure S20. XPS survey spectrum of graphite oxide (red), $\textbf{G1}$ (blue) and control reaction for $\textbf{G1}$ (green)

Figure S21. XPS survey spectrum of graphite oxide (red), $\textbf{G2}$ (blue) and control reaction for $\textbf{G2}$ (green)
Figure S22. XPS survey spectrum of graphite oxide (red), G3 (blue) and control reaction for G3 (green)

Figure S23. UV-Vis absorbance intensity of (G4) in an aqueous solution with varying pH

Citations/Footnotes:
