Graphene Oxide as an Electrophile for Carbon Nucleophiles

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General Experimental: Graphite powder was received from Alfa Aeser (natural, microcrystal grade, APS 2-15 micron, lot #C04U006) 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. Sodium hydride (dry 95%, Aldrich), malononitrile (Aldrich), acetyl chloride (Aldrich), 1-iodohexadecane (Aldrich), 1,3-propane sultone (Aldrich), methanol (Fisher, reagent grade), acetone (Aldrich, reagent grade), dichloromethane (Aldrich, reagent grade), dimethylformamide (Aldrich, reagent grade) and sodium bicarbonate (Fisher) were purchased from commercial sources and used as received. Graphite oxide¹ 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. TGA analyses were performed with a TGA Q50 apparatus (TA instruments). TGA experiments were carried out under a nitrogen 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 profiler 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 concentrated solutions of the graphene derivative onto silicon wafers. X-ray data was collected using an Inel CPS 120 position

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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. Zeta potential measurements and phase analysis light scattering measurements were determined with a Brookhaven instruments Zeta PALS, zeta potential analyzer. The zeta potential was taken as an average over 10 measurements [at 7.2 pH]. All synthetic manipulations were carried out under an argon atmosphere using standard Schlenk techniques.

Synthesis of acetylated graphite oxide: To a 100 mL, sealable Schlenk tube fitted with a stirbar was added graphite oxide (200 mg, [XPS analysis: 72.3 C/ 27.7 O]), acetyl chloride (50 mL) and sodium bicarbonate (100 mg). After sealing the pressure tube, the heterogeneous suspension was brought to 60 °C in an oil bath and heated for 24 h. After cooling, this dispersion was quenched dropwise with a cold solution of satd. sodium bicarbonate in methanol. The dispersion was then centrifuged at 10,000 rpm for 10 minutes to obtain a black sediment. Sonicative dispersion with subsequent centrifugation was repeated 3 times with water, 2 times with methanol, 2 times with dichloromethane, and again 2 times with acetone. The supernatant was discarded each time. The final sediment was dried under high vacuum (0.1 mm Hg) for 1 h. See figure S1 for FT-IR characterization data.

Synthesis of malononitrile-functionalized graphene derivatives (G1): To a 100 mL round bottom flask fitted with a stirbar and an argon inlet adaptor was added sodium hydride (82 mg, 3.41 mmol) and THF (30 mL). The solution was then brought to 0 °C in an ice bath and the malononitrile (220 mg, 3.33 mmol) was added in one portion. The mixture was stirred for 10 minutes. To another 100 mL round bottom flask fitted with a stirbar was added graphite oxide (40 mg, [XPS analysis: 72.3 C/ 27.7 O]) and THF (10 mL). The heterogeneous suspension was sonicated for 30 minutes in a bath sonicator to achieve a homogenous dispersion. The malononitrile solution was then added dropwise to the graphite oxide suspension at room temperature. The combined reaction mixture was then brought to 60 °C in an oil bath for 24 h.² During the reaction timecourse the solution gradually darkened to an opaque black dispersion. After cooling, this dispersion was centrifuged at 10,000 rpm for 10 minutes to obtain a black sediment. Sonicative dispersion with subsequent centrifugation at 14,500 rpm was repeated 3 times with

water, 2 times with methanol, and 2 times with acetone. The supernatant was discarded each time. The final sediment was dried under high vacuum (0.1 mm Hg) for 1 h. See figures S2-S6 and table S1 for FT-IR, XPS, high-resolution XPS, TGA, DTGA and XRD characterization data.

Synthesis of hexadecane/malononitrile-functionalized graphene derivatives (G2):³ To a 50 mL round bottom flask fitted with a stirbar and an argon inlet adaptor was added (1) (20 mg) and 2.5 mL anhydrous DMF. The black suspension was sonicated for 5 minutes to achieve a fine dispersion. To this suspension was added sodium hydride (40 mg, 1.66 mmol) and then 5minutes later 1-iodohexadecane (584 mg, 1.66 mmol) in one portion. The mixture was stirred for 16 hours at room temperature. To the reaction was then added 5 mL of water to quench the remaining NaH. An additional 40 mL of water was then added and the hetereogeneous dispersion was then centrifuged at 10,000 rpm for 10 minutes to obtain a black/grey sediment. Sonicative dispersion with subsequent centrifugation at 5,000 rpm was repeated 3 times with water, 3 times with acetone, and 3 times with THF. The supernatant was discarded each time. The final black sediment was dried under high vacuum (0.1 mm Hg) for 1 h. See figure S7-S9 for FT-IR, XPS and solubility characterization data.

Synthesis of sulfonate/malononitrile-functionalized graphene derivatives (G3):³ To a 50 mL round bottom flask fitted with a stirbar and an argon inlet adaptor was added (1) (20 mg) and 2.5 mL anhydrous DMF. The black suspension was sonicated for 5 minutes to achieve a fine dispersion. To this suspension was added sodium hydride (40 mg, 1.66 mmol) and then 5 hours later 1,3-propane sultone (202 mg, 1.66 mmol) in one portion. The mixture was stirred for 16 hours at room temperature. To the reaction was then added 5 mL of water to quench the remaining NaH. An additional 40 mL of water was then added and the black homogeneous solution was then centrifuged at 14,500 rpm for 1 h to obtain a black sediment. The supernatant was carefully decanted and the remaining amount of water was removed by lyophilization for 24 h. Stable suspensions of G3 in pH 7 water could be formed for up to 12 h before significant sedimentation occurred. See figure S10-S11 for FT-IR and XPS characterization data.

General procedure for the determination of conductivities of (G1): A graphene derivative was sonicated in acetone for 30 min. Subsequently, 100 μ L 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 μ A 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

$$\sigma = I / (V \cdot t \cdot CF) \text{ (for t/s < 0.4)}$$
(1)

where I is the current, V is the voltage, t is the sample thickness, CF is the sheet resistance correction factor,⁴ and s is the four point probe spacing.

Conductivity of G1: The conductivity of a drop-cast film of malononitrile-functionalized graphene was determined to be ~0.01 S m⁻¹ (average of three films and four measurements each).

Conductivity of G1 (thermally treated): The conductivity of malononitrile -functionalized graphene annealed at 250 °C was determined to be 14.8 S m⁻¹ (average of two films and three measurements each).



Figure S1. Baseline corrected FTIR of acetylated graphite oxide (blue) and graphite oxide (red)

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Figure S2. baseline corrected FT-IR spectra of graphite oxide (red) and malononitrile functionalized graphene (G1, blue)



Figure S3. XPS survey spectrum of graphite oxide (red) and amide functionalized graphene (G1, blue)⁴

Peak	Position BE (eV)	Raw area (CPS)	Atomic Mass	Atomic Conc. % ^b
C 1s	284	1085251.9	12.011	81.52
O 1s	531	797064.4	15.999	15.10
N 1s	398	95545.0	14.007	3.38

Table S1. Atomic composition of chemically modified graphite oxide (G1) by X-ray photoelectron spectroscopy⁵

[a] Calculated by integration of diagnostic XPS signals. [b] Sensitivity factors: C(1s) 0.278, O(1s) 0.780, N(1s) 0.477

Atomic composition ratios:

■ Functional group density of 1 malononitrile per 46 graphitic carbon calculated by: (([C%][N%])-1)*2, wherein one carbon is removed due to its incorporation in the malononitrile structure, and the sum multiplied by 2 to account for 2 nitrogen atoms being incorporated for each malononitrile.

• C/O ratio of 5.40 calculated by: ([C%]/[O%])



Figure S4. High-resolution XPS spectra of C(1s) and N(1s) regions of G1 and graphite oxide



Figure S5. TGA and differential TGA thermograms of malononitrile functionalized graphene (**G1**, blue) and graphite oxide (red)



Figure S6. XRD patterns of malononitrile functionalized graphene (G1, blue), and graphite oxide (red), and graphite (green)

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Figure S7. baseline corrected FT-IR spectra of malononitrile functionalized graphene (G1, blue) and hexadecane/malononitrile functionalized graphene (G2, red)



Figure S8. XPS survey spectrum of hexadecane graphene (**G2**, red), atomic % composition [89.7% C/8.7% O/1.7% N]



Figure S9. solubility profile of G2 (1 mg/mL) and G1 (1 mg/mL) in various solvents. Solutions were hand shaken for 30 seconds and allowed to sit for 5 minutes (no sonication).



Figure S10. baseline corrected FT-IR spectra of malononitrile functionalized graphene (G1, blue) and sulfonate/malononitrile functionalized graphene (G3, red)



Figure S11. XPS survey spectrum of sulfonate graphene (G3, red), atomic % composition [78% C/18.8% O/1.9% N/1.3% S]

Citations:

- 1 W. S. Hummers, R. E. Offeman, J. Amer. Chem. Soc. 1958, 80, 1339-1340.
- 2 Further attempts to increase the malononitrile functional group density by changing the reaction solvent and increasing the reaction temperature were unsuccessful. It is known that anionic malononitrile can begin to form oligomers or polymeric species at or above 130 °C. This undesireable polymerization was observed experimentally in reactions of GO with anionic malononitrile at 150 °C in diglyme (as determined by ~35% nitrogen incorporation by XPS).
- 3. Control reactions were performed by reacting GO with either 1-iodo hexadecane or the 1,3propane sultone in the presence of sodium hydride in THF at room temperature. After 24 h the reactions were cooled and the graphitic material completely sedimented. No noticeable changes occurred by FTIR and no improvements in solubility were observed in organic solvents for the hexadecane reaction, or in water for the sulfonate reaction.
- 3. L. J. Swartzendruber, *National Bureau of Standards*, **1964**, Technical Note 199.
- 4. Attempts to completely remove the remaining sodium ions with additional washings had only a marginal effect (as determined by XPS analysis). The complete XPS report with sodium analysis is shown here: C(1s) 79.25, O(1s) 14.68, N(1s) 3.29, Na(1s) 2.79.