

[Supporting Information (SI) to accompany]

## Chemically Active Reduced Graphene Oxide with Tunable C/O Ratios

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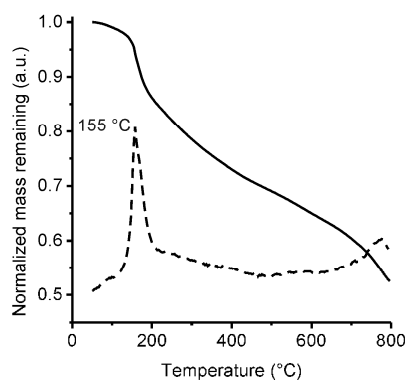
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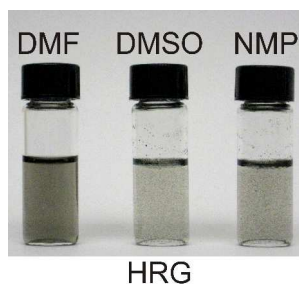
**Experimental details for the preparation of graphene oxide dispersions.** SP-1 graphite powder (5 g) was subjected to a pre-oxidation treatment by stirring vigorously for 6 h at 80 °C in a mixture of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 g), P<sub>2</sub>O<sub>5</sub> (10 g), and H<sub>2</sub>SO<sub>4</sub> (15 mL). The pre-oxidized graphite powder was dried overnight before further oxidative treatment by stirring for 2 days at 35 °C in a mixture of KMnO<sub>4</sub> (17 g) and H<sub>2</sub>SO<sub>4</sub> (125 mL). This GO suspension was then diluted to 250 mL with water and stirred for 5 min before treatment with aqueous H<sub>2</sub>O<sub>2</sub> (7 mL of a 30 wt% solution). The freshly prepared GO was purified by five cycles of centrifugation (30 min at 8,200 g) and washing with aqueous HCl (30 mL of a 1:9 v/v dilution of concentrated aqueous HCl), followed by five additional cycles of washing with ultrapure deionized water (30 mL). After this process, the GO was centrifuged down to a pellet and the supernatant was decanted away. An aqueous graphene oxide dispersion was prepared by suspending the wet GO pellet in water and sonicating for 30 min (30% amplitude, 10-s pulses alternating with 10-s rest periods). This dispersion was purified *via* five cycles of centrifugation (1 h at 8,200 g) with the supernatant retained and the precipitate discarded to remove unexfoliated particles. Residual ions were removed by dialysis in ultrapure deionized water (4 × 2 L over a period of 2 days).

**Polystyrene-CARGO nanocomposite hot-pressing.** After vacuum drying, the composite powder was pressed under vacuum at 11,000 N cm<sup>-2</sup> into a 3.175 cm diameter disc using a hand-operated hydraulic pump (SPEX SamplePrep, LLC, Metuchen, NJ). The disc was placed between two brass plates (~0.65 cm thick) separated by two thin pieces of copper (~0.25 cm thick), serving as spacers. A Kapton® polyimide film (Argon Masking, Inc., Monrovia, CA), resistant to heat degradation up to 400 °C, was placed between the disc and each brass plate to prevent adhesion after hot-pressing. In this configuration, the disc was compressed into a thin film by a AutoFour/30, P Type hydraulic press (Carver, Inc. Wabash, IN) at 130 °C and 7,000 N cm<sup>-2</sup> for 1 h, then cold-pressed at that same pressure for an additional hour after the platens were cooled to room temperature with circulating water.

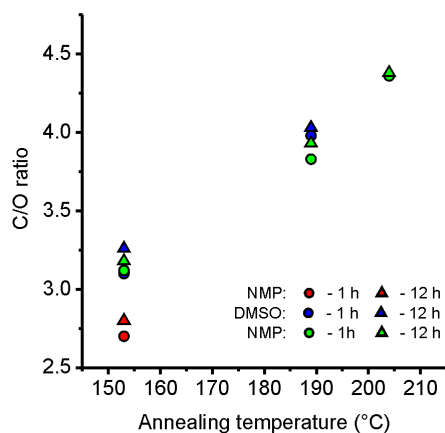
**Author contributions.** O.C.C. and S.T.N. conceived the experiments. O.C.C. and B.J. synthesized CARGO dispersions, fabricated CARGO papers, and analyzed TGA, FT-IR, XRD, and XPS data. O.C.C. fabricated nanocomposite samples, collected SEM images, and took digital photographs. D.A.D. collected and analyzed electrical conductivity measurements. A.A. prepared coin cell batteries and analyzed electrochemical data. O.C.C. and S.T.N. prepared the manuscript with advice from D.A.D. and A.A. S.T.N. and K.A. supervised the project.



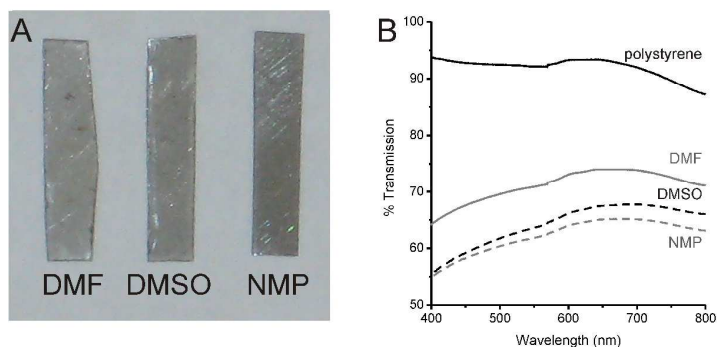
**Figure S1.** TGA profile of graphene oxide (solid line) and the corresponding first-derivative curve (dashed line) illustrating the temperature (155 °C) at which the first mass loss feature initiates.



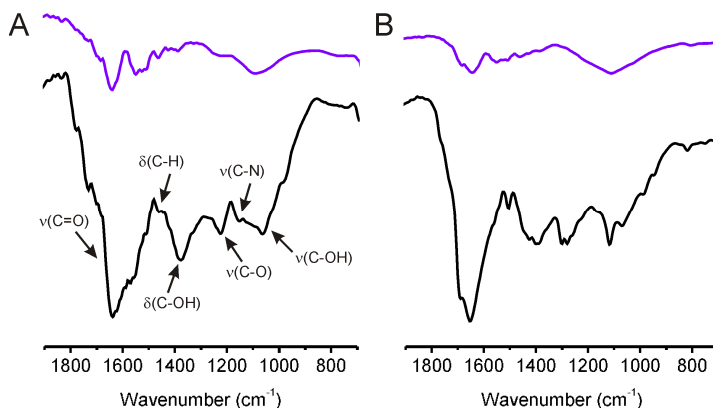
**Figure S2.** Digital image of highly reduced graphene oxide (HRG) prepared *via* hydrazine reduction in DMF, DMSO, and NMP. We note that the aggregates formed in DMSO and NMP are not present in thermally reduced CARGO (see Figure 1 in main text).



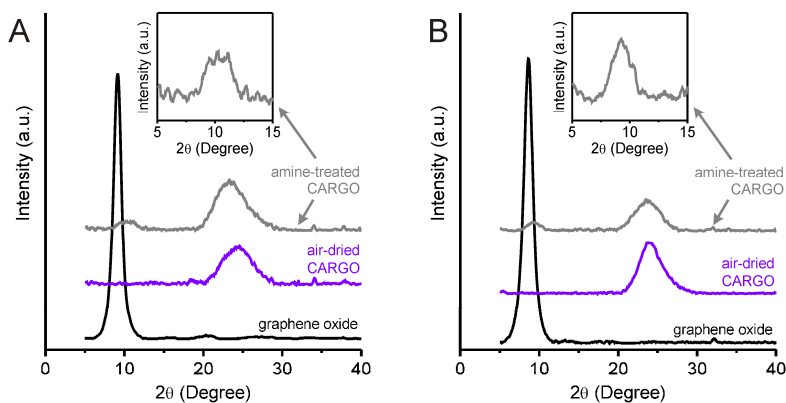
**Figure S3.** Plot of the C/O ratios of chemically active reduced graphene oxide (CARGO) samples prepared in different solvent three different reflux temperatures. The dependence of C/O ratios on temperature shows a linear relationship ( $R^2 = 0.94$  for 1-h reflux and  $R^2 = 0.93$  for 12-h reflux).



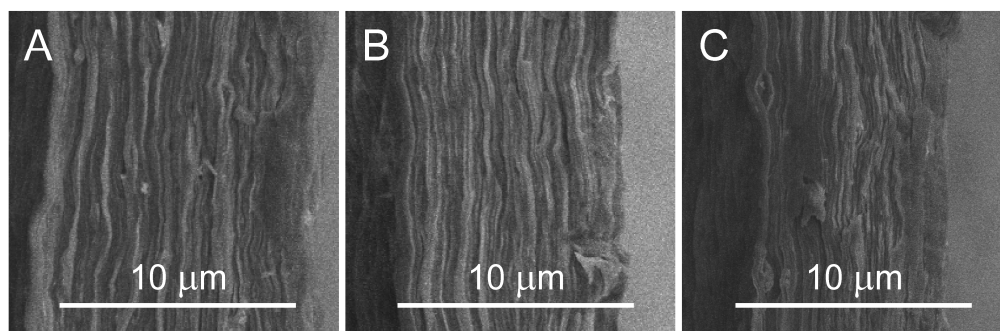
**Figure S4.** (A) Digital image of CARGO-polystyrene nanocomposite thin films containing 0.025 wt% of CARGO as nanofiller. The solvents used to prepare the CARGO nanosheets are noted at the bottom of each thin film. Aggregates are clearly visible in the sample containing DMF-prepared CARGO, illustrating the poor dispersion of this more-hydrophilic nanofiller. (B) Corresponding transmission spectra of the nanocomposite samples shown in (A). A spectrum for pristine polystyrene is included as a reference, since the polymer matrix is responsible for some light scattering.



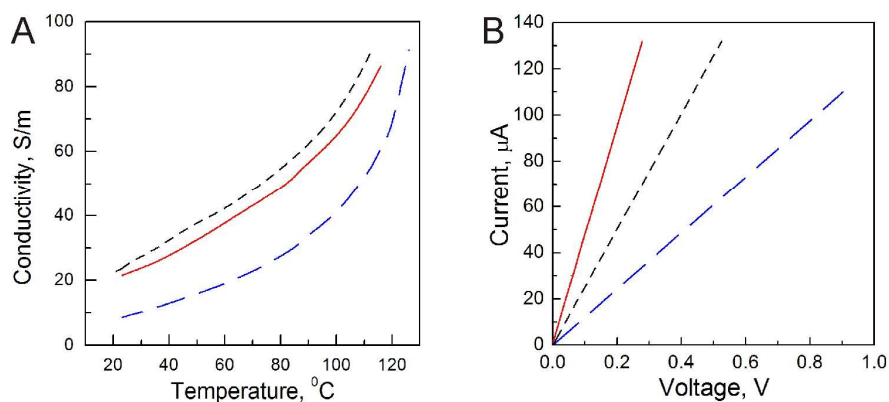
**Figure S5.** FT-IR spectra of graphene oxide and CARGO (black and purple lines, respectively) samples prepared in DMF (A) and NMP (B). Spectra for the samples prepared in DMSO can be found in Figure 5 of the main text. The peaks for  $\delta(\text{C-H})$  and  $\nu(\text{C-N})$  should be attributed to residual solvent in the sample.



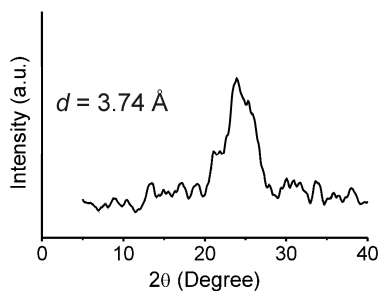
**Figure S6.** XRD patterns of graphene oxide paper (black lines) and CARGO paper before and after reaction with hexylamine (purple and gray lines, respectively) samples prepared from DMF (A) and NMP (B). Inset: Magnified plot of the diffraction peak near  $2\theta = 10^\circ$ . Patterns for the papers prepared from DMSO can be found in Figure 6 of the main text.



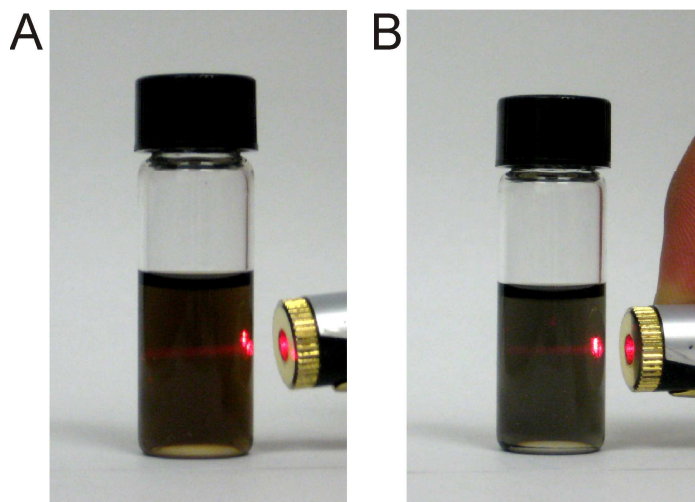
**Figure S7.** SEM images of CARGO papers prepared from (A) DMF, (B) DMSO, and (C) NMP. The thickness of each sample, used in the calculation of conductivity values, was determined from these and similar images taken along the fracture edge of the papers at several locations.



**Figure S8.** (A) Plots of conductivity for CARGO papers as a function of temperature, showing the different profiles for CARGO prepared in DMF (blue, dashed), DMSO (red, solid), and NMP (black, dotted). (B) Plots of current through the aforementioned CARGO paper samples as a function of voltage, demonstrating the linear relation between these values at low voltage bias.



**Figure S9.** XRD pattern of 4-chlorophenyl isocyanate-functionalized CARGO paper, exhibiting a slight increase in intersheet spacing afforded by the functional group in the intersheet gallery.



**Figure S10.** Digital images demonstrating the Tyndall effect in DMSO dispersions of graphene oxide (A) and CARGO (B), which both effectively scatter laser light.

**Calculation of C/O and C/functional group ratios.** The elemental composition of graphene oxide and CARGO samples were obtained from combustion analysis by Atlantic Microlab (Norcross, GA) as wt% of each element. Ratios for C/O, C/amine, and C/isocyanate were calculated from these data according to the following procedure:

- 1) The wt% of each element was converted to an “atom count” by dividing the reported wt% by the atomic mass of the given element (*e.g.*, C = 12.01, N = 14.01, O = 16.00, etc.).
- 2) The number of functional groups in the sample was assumed to be equivalent to the number of Cl atoms (for 4-chlorophenyl isocyanate and 4-chlorobenzylamine functionalization).
- 3) The number of additional atoms present in the functional groups were next discounted from the total atom count for each element (obtained in step 1) according to their stoichiometric ratio with respect to Cl. The molecular formulas for the functional groups in this study are: a)  $C_7H_4NCl$  for 4-chlorobenzylamine and b)  $C_7H_8NOCl$  for 4-chlorophenyl isocyanate. If the sample was not functionalized, this step was skipped.
- 4) The atoms present in residual solvent molecules were then discounted from the total atom count according to their stoichiometric ratio with respect to the unique atom (N or S) that is not present on graphene oxide. The molecular formulas for the solvents in this study are: a)  $C_3H_7NO$  for DMF, b)  $C_2H_6OS$  for DMSO, and c)  $C_5H_9NO$  for NMP. For samples prepared from DMF and NMP, the remaining number of N atoms, after subtraction of those from the functional groups in step 3, were utilized for this step.
- 5) Final total atom counts of C, O, amine (Cl), and isocyanate (Cl) (see last column in Table S1 for an example) are used to calculate the appropriate ratios shown in Table 1 in the main text.

**Table S1.** Example calculations from experimental data for a sample of CARGO prepared in NMP ( $C_5H_9NO$ ) and functionalized with 4-chlorophenyl isocyanate ( $C_7H_8NOCl$ )

	wt% (reported data)	atom count (step 1)	atom count after discounting the functional group (step 3)	atom count after discounting the residual solvent ( <i>i.e.</i> , from the CARGO samples alone) (step 4)
C	66.13	5.51	5.42	4.19
H	2.71	2.69	2.64	0.43
N	3.61	0.26	0.25	0.00
O	19.63	1.23	1.22	0.97
S	0	0.00	0.00	0.00
Cl	0.42	0.01 <sup>a</sup>	0.00	0.00

<sup>a</sup> In step 2, the number of functional groups was treated as 0.012 since two significant digits were reported in the wt% data.

**Table S2.** Mass increase in graphene oxide paper after hexylamine treatment

dispersing solvent from which paper was fabricated	mass before treatment (mg)	mass after treatment (mg)	increase in mass (%)
DMF	5.13	5.84	13.8
DMSO	4.88	5.54	13.5
NMP	5.59	6.32	13.1