Electronic Supporting Information

Graphite Oxide as a Carbocatalyst for the Preparation of Fullerene-Reinforced Polyester and Polyamide Nanocomposites

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General Considerations. Unless otherwise noted, all reactions were performed under ambient conditions. All reagents were purchased from Bay Carbon, Inc., Fisher Scientific, Acros Organics, or Alfa Aesar. ε-Caprolactone and δ-valerolactone were distilled under reduced pressure prior to use, and ε-caprolactam was recrystallized from acetone prior to use. All other commercial reagents were used without further purification. Solution state ^{1}H and ^{13}C NMR spectra were collected on a Varian Mercury 400 MHz spectrometer. Chemical shifts (δ) are referenced downfield from $(CH_3)_4Si$ using the residual solvent peak as an internal standard ($CDCl_3$, 7.24 ppm for ^{1}H NMR; 77.0 ppm for ^{13}NMR). FT-IR analysis was performed using a Thermo Scientific Nicolet iS5 with a single bounce Ge ATR accessory. Raman spectra were recorded on a WiTec Alpha300 system with an incident wavelength of 532 nm. BET surface area measurements were performed by nitrogen adsorption on a Quantachrome NOVA 2200 surface analyzer. XRD data were collected on a Philips X'Pert PRO multipurpose X-ray diffractometer with an incident wavelength of 1.54 Å. Dynamic mechanical analysis was performed using a TA Instruments Q800. The samples were heated from -50 °C to their melting point (T_m) at a rate of 1 °C min^{-1} while oscillating at a constant amplitude of 50 μm and a frequency of 1 Hz. In order to maintain a minimum applied force of 0.1 N, above the T_m, increasingly large amplitudes were required until the point of sample failure. All DMA measurements were performed in triplicate and the reported errors represent 1 standard deviation from the mean. Tensile tests were performed after isotherming at 25 °C for 5 min, with a preload force of 0.01 N and a stress ramp rate of 2.0 N min^{-1}. Melting points (T_m) were determined by calculating the loss onset of the elastic modulus (E') measured *via* DMA. Thermogravimetric analysis was performed using a Mettler Toledo TGA/SDTA 851 at a heating rate of 10 °C min^{-1}. Elemental analyses were performed by Midwest Microlabs, LLC (Indianapolis, IN). Gel

permeation chromatography (GPC) was performed on a Viscotek HPLC system consisting of two Viscotek I-series columns (1 × MBHMW-3078 and 1 × MBMMW-3078) arranged in series and thermostated to 24 °C, a Viscotek 2001 GPCmax solvent/sample module, a Viscotek 270 dual detector, and a Viscotek 3580 refractive index (RI) detector. Molecular weight and polydispersity data determined by GPC are reported relative to polystyrene standards in tetrahydrofuran (THF). Viscosity average molecular weights (M_v) were obtained by dilute solution viscometry (DSV) obtained using an Ubbelohde viscometer (Cannon Instruments, size 0C) in the concentration range of 0.2–1.0 g dl^{-1}. High resolution transmission electron microscopy (HRTEM) was performed on a JEOL 2010F field emission transmission electron microscope.

Preparation of Graphite Oxide (GO). GO was prepared using a modified Hummers method.[1] A 250 mL reaction flask was charged with natural flake graphite (4.09 g; SP-1, Bay Carbon, Inc.), concentrated sulfuric acid (125 mL), and a magnetic stir bar, and then cooled on an ice bath. The flask was then slowly charged with $KMnO_4$ (9.05 g) over 3 h which afforded a dark colored mixture. After stirring at 0 °C for 1 h (relative humidity: 40–70%), the mixture was stirred for an additional 2 h at room temperature and then at 35 °C for 3 h. The flask was then cooled to room temperature and the resulting viscous dispersion was poured into 2 L of deionized water. A 30% aqueous solution of H_2O_2 (10 mL) was then added slowly to the aqueous mixture, concomitant with gas evolution. The resulting vibrant yellow mixture was then filtered through a coarse fritted funnel, and the isolated material was washed with additional 6 N HCl (1 L) and deionized water (2 L). The filtered solids were collected and dried under high vacuum to afford the desired product (8.18 g) as a dark brown powder.

Preparation of Basified Graphite Oxide (b-GO). A 20 mL scintillation vial was charged with graphite oxide (0.51 g), triethylamine (20 mL), and a magnetic stir bar. The reaction mixture was vigorously stirred at room temperature for 30 min. The product was then recovered by vacuum filtration and washed with additional triethylamine (3 × 20 mL). The filtered solid was collected and dried under high vacuum to afford the desired product (0.51 g) as a dark brown powder.

General Procedure Used to Prepare the PCL-GO Composites. A 30 mL vial was charged with ε-caprolactone (3.0 g), GO (2.5–20 wt%), and a magnetic stir bar. The vial was sealed with a Teflon-lined cap under ambient atmosphere and the resulting heterogeneous mixture was stirred (300 rpm) at 60 °C for 14 h. The reaction was then cooled to room temperature, at which point the polymer melt solidified. The polymer composite was isolated as a black solid in quantitative yield, requiring no further purification. The carbon and polymer were separated by dissolving the polymer in 30 mL of dichloromethane, followed by filtration and washing of the solid carbon with 3 × 30 mL with dichloromethane. Residual solvents were removed from both components under vacuum (10^{-3} Torr). ^{1}H NMR (400 MHz, $CDCl_3$): 3.97–4.03 (m, 80H), 3.55–3.58 (m, 2H), 2.21–2.29 (m, 80H), 1.49–1.61 (m, 160H), 1.27–1.37 (m, 80H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.5, 64.0, 34.0, 28.2, 25.4, 24.4.

General Procedure Used to Prepare the PVL-GO Composites. A 30 mL vial was charged with δ-valerolactone (3.0 g), GO (2.5 wt%), and a magnetic stir bar. The vial was sealed with a Teflon-lined cap under ambient atmosphere and the resulting heterogeneous mixture was stirred

(300 rpm) at 60 °C for 14 h. The reaction was then cooled to room temperature, at which point the crude mixture solidified. The carbon and polymer were separated by dissolving the polymer in 30 mL of tetrahydrofuran, followed by filtration and washing of the solid carbon with 3 × 30 mL with tetrahydrofuran. The polymer was then precipitated into deionized water to remove unreacted monomer, separated by vacuum filtration, and isolated as a white solid (2.6 g, 86%). Residual solvents were removed from both components under vacuum (10^{-3} Torr).

General Procedure Used to Prepare the Nylon 6-GO Composites. A 30 mL vial was charged with ε-caprolactam (3.0 g), b-GO (5.0 wt%), and a magnetic stir bar. The vial was purged with nitrogen and sealed with a Teflon-lined cap. The resulting heterogeneous mixture was stirred (300 rpm) at 300 °C for 14 h. The reaction was then cooled to room temperature, at which point the polymer melt solidified. The carbon and polymer were separated by dissolving the polymer in 30 mL of formic acid (88% aq.), followed by filtration and washing of the solid carbon with 3 × 30 mL with formic acid. Residual solvents were removed from both components under vacuum (10^{-3} Torr). The formic acid solution containing the polymer was precipitated into deionized water (1 L), recovered by vacuum filtration, and dried under vacuum, affording the target product as a white solid (2.4 g, 80%).

Molecular Weight Determinations. Due to the polymer's limited solubility, the molecular weights of the nylon 6 samples prepared by reaction of ε-caprolactam (3.0 g) with basified graphite oxide (b-GO) (5.0 or 10.0 wt%) or water (0.15 g, 5.0 wt%) were characterized by dilute solution viscometry (DSV). The polymers were isolated by dissolution in formic acid (88% aq.) (30 mL), precipitation into deionized water (1 L), and recovery by vacuum filtration. A series of five samples (ranging from 0.2–1.0 g dl^{-1}) was prepared and their relative viscosities analyzed in triplicate using an Ubbelodhe viscometer (size 0C) isothermed to 25 °C in a water bath. The reduced (η_{red}) and inherent (η_{inh}) viscosities were computed and plotted as a function of the sample concentration (see Figures S1–S3). The y-intercepts of the linear fits correspond to the intrinsic viscosities ($[\eta]$) of the samples. The intrinsic viscosity was then applied to the Mark Houwink equation (Eq. 1), and the viscosity average molecular weight (M_v) determined using previously reported Mark Houwink parameters (K, a) for nylon 6 in formic acid at 25 °C.[2]

$$[\eta] = KM_v^a \qquad \text{Eq. 1}$$

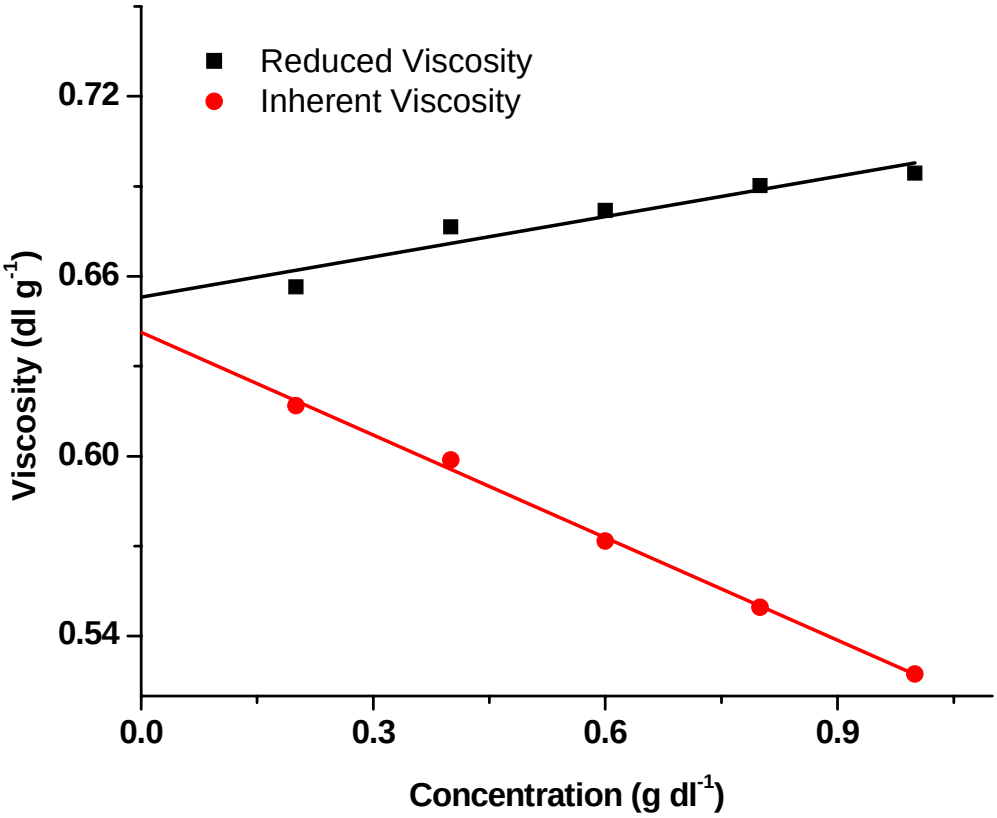

Figure S1. Huggins-Kraemer plot of nylon 6 prepared *via* the hydrolytic polymerization of ε-caprolactam (5.0 wt% water).

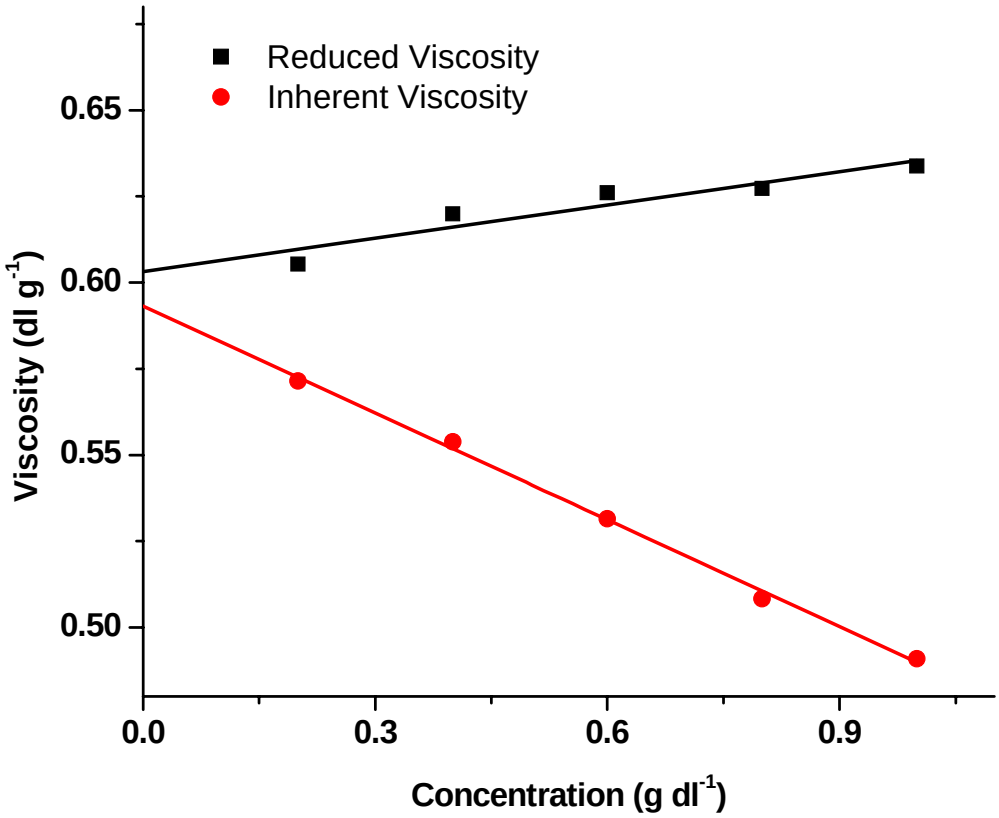

Figure S2. Huggins-Kraemer plot of nylon 6 prepared using 5.0 wt% basified graphite oxide (b-GO) for the polymerization of ε-caprolactam.

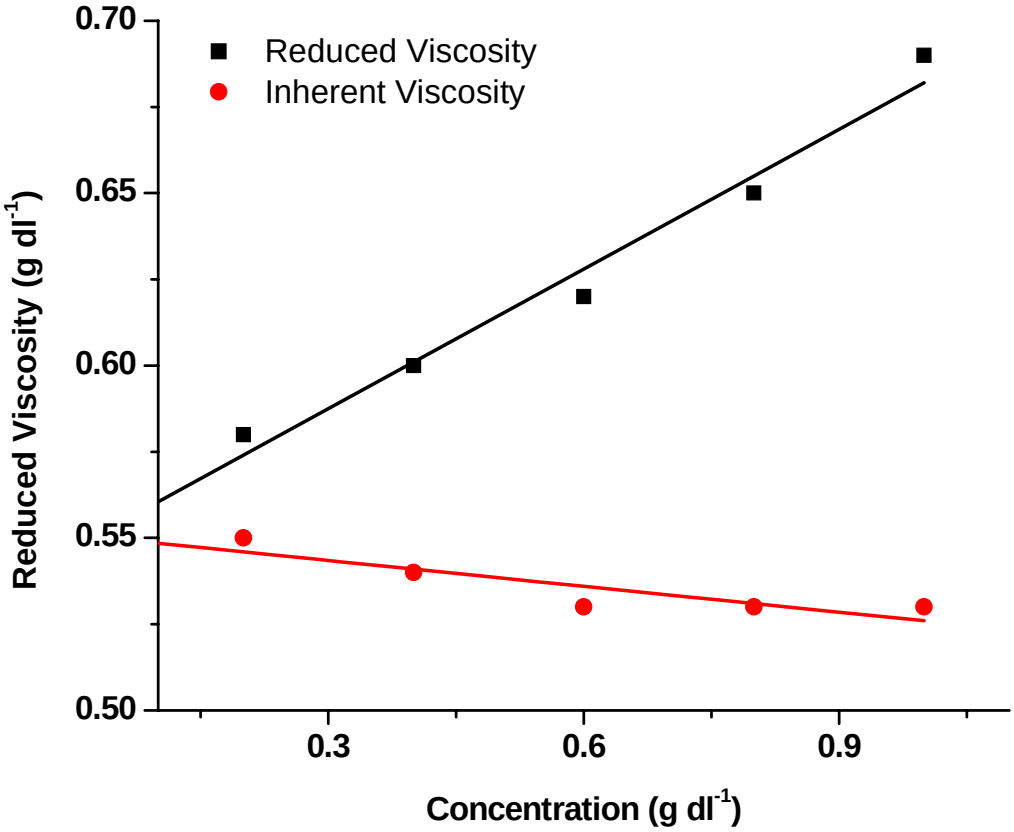

Figure S3. Huggins-Kraemer plot of nylon 6 prepared using 10.0 wt% basified graphite oxide (b-GO) for the polymerization of ε-caprolactam.

Powder X-Ray Diffraction. Powder X-ray diffraction (PXRD) was performed at room temperature (24 °C) at a relative humidity of approximately 45% on graphite, graphite oxide (GO), the carbon recovered after reaction of ε-caprolactone with GO, basified GO (b-GO), and the carbon recovered after reaction of ε-caprolactam with b-GO (see Figures S4 and S5). The former recovered carbon was obtained after reacting 3.0 g ε-caprolactone with 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. Basified graphite oxide was prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. The latter recovered carbon was obtained after heating 3.0 g of ε-caprolactam with 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

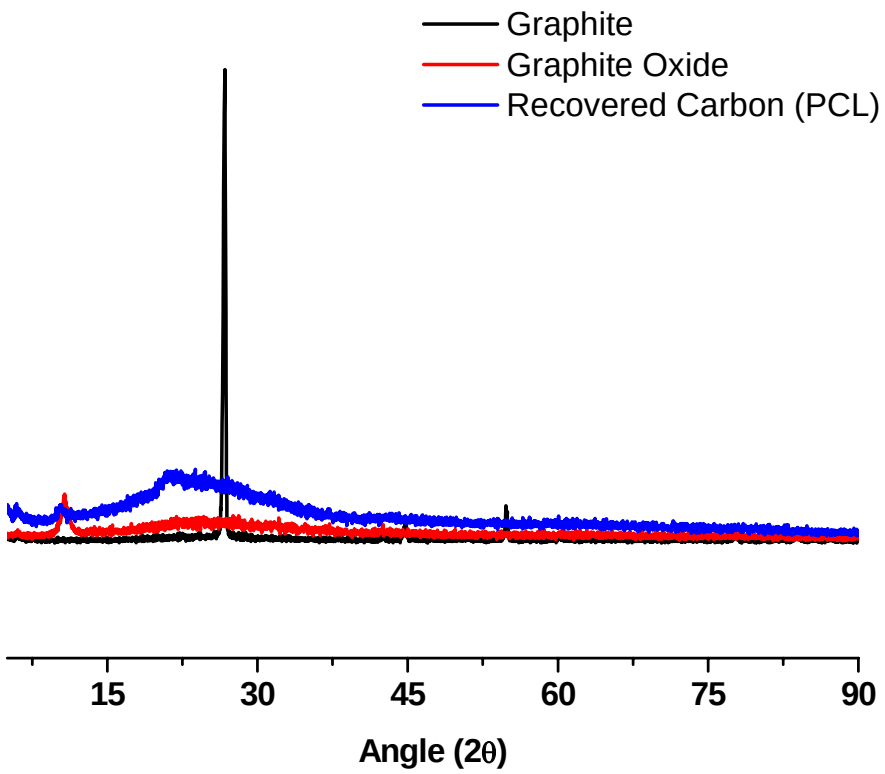

Figure S4. Powder X-ray diffraction plots for graphite, graphite oxide (GO), and the carbon recovered after reaction of ε-caprolactone with GO.

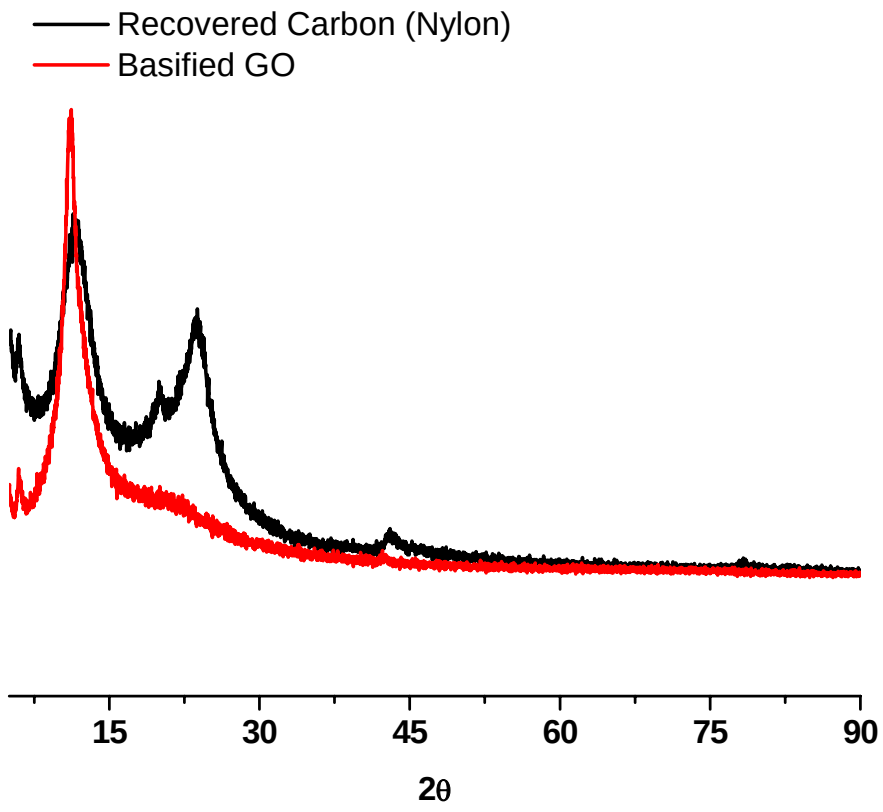

Figure S5. Powder X-ray diffraction plots for basified graphite oxide (b-GO) and the carbon recovered after reaction of ε-caprolactam with b-GO.

Elemental Combustion Analysis. Elemental combustion analyses were performed on graphite oxide (GO), the carbon recovered after reaction of GO with ε-caprolactone, basified graphite oxide (b-GO), and the carbon recovered after reaction of GO with ε-caprolactam (see Table S1). The former recovered carbon was obtained after reacting 3.0 g ε-caprolactone with 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. Basified graphite oxide was prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. The latter recovered carbon was obtained after heating 3.0 g of ε-caprolactam with 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

Table S1. Summary of combustion analysis data.

	Starting GO[a]	**Recovered Carbon**[b]	**b-GO**[c]	**Recovered Carbon**[d]
Carbon	54.08	70.37	53.94	76.79
Hydrogen	1.84	3.68	3.19	4.29
Nitrogen	none found	none found	0.66	5.49
Oxygen	40.74	24.65	37.25	11.14
Sulfur	-	1.30	1.43	0.39
Chlorine	-	none found	2.75	1.69
TOTAL	98.60	100.00	99.22	99.79
C:O Ratio	1.77	3.81	1.93	9.19

[a] Prepared *via* the Hummers method. [b] Material recovered after heating 3.0 g of ε-caprolactone in 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. [c] Prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. [d] Material recovered after heating 3.0 g of ε-caprolactam in 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

FT-IR Spectroscopy. FT-IR spectra were collected on graphite oxide (GO), the carbon recovered after reacting ε-caprolactone with GO, basified GO (b-GO), and the carbon recovered after reacting ε-caprolactam with b-GO (see Figures 5 and S6). The former recovered carbon was obtained after reacting 3.0 g ε-caprolactone with 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. Basified graphite oxide was prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. The latter recovered carbon was obtained after heating 3.0 g of ε-caprolactam with 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

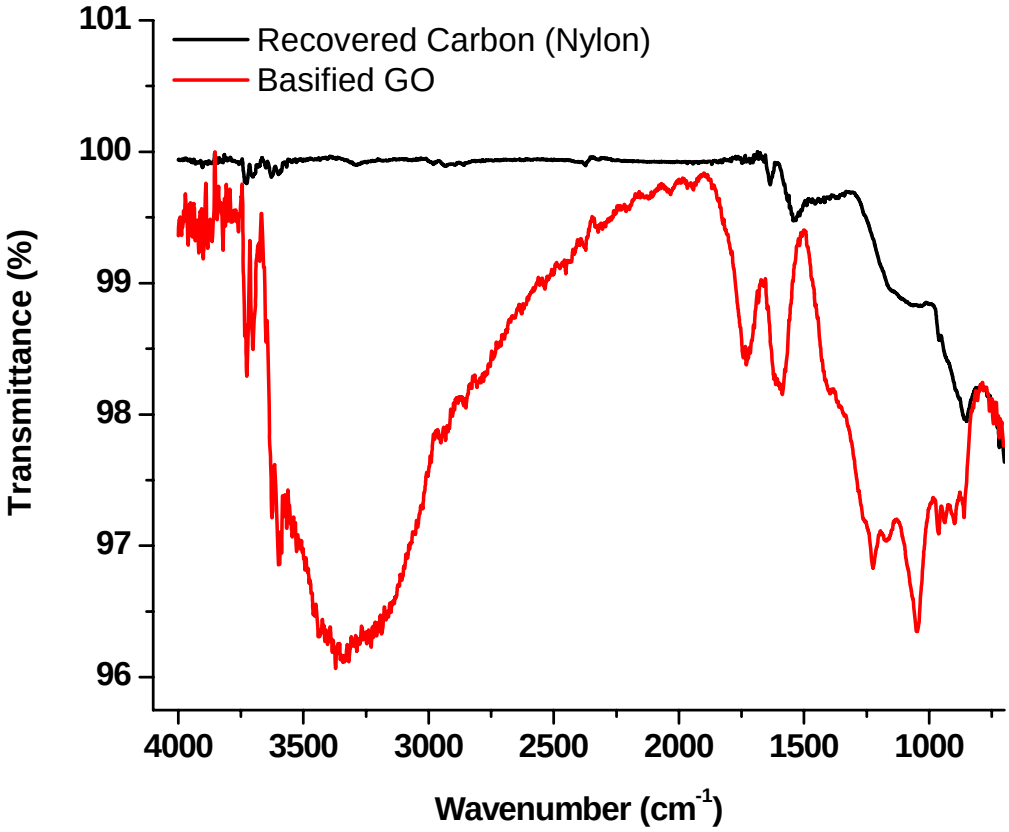

Figure S6. FT-IR spectra of basified graphite oxide (b-GO) (black) and the carbon recovered after reacting ε-caprolactam with b-GO (red).

Raman Spectroscopy. Raman spectra were collected on graphite, graphite oxide (GO), the carbon recovered after reacting ε-caprolactone with GO, basified GO (b-GO), and the carbon recovered after reacting ε-caprolactam with b-GO (see Figures S7–S11). The former recovered carbon was obtained after reacting 3.0 g ε-caprolactone with 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. Basified graphite oxide was prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. The latter recovered carbon was obtained after heating 3.0 g of ε-caprolactam with 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

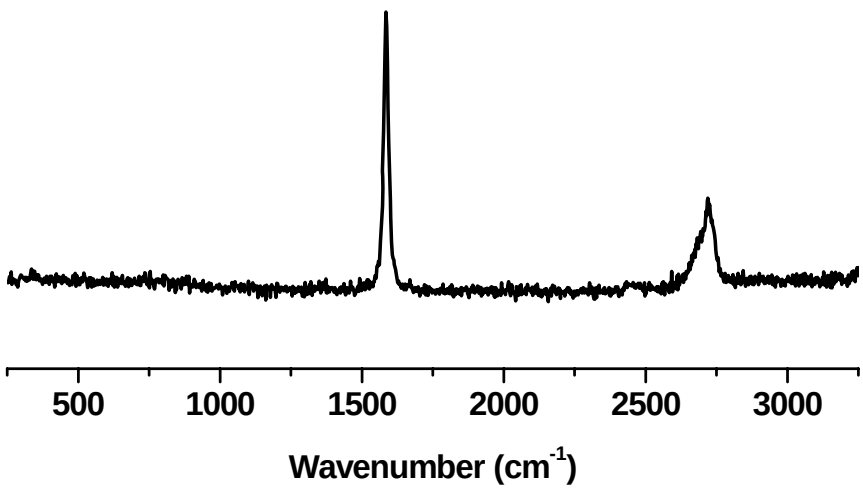

Figure S7. Raman spectrum of SP-1 graphite.

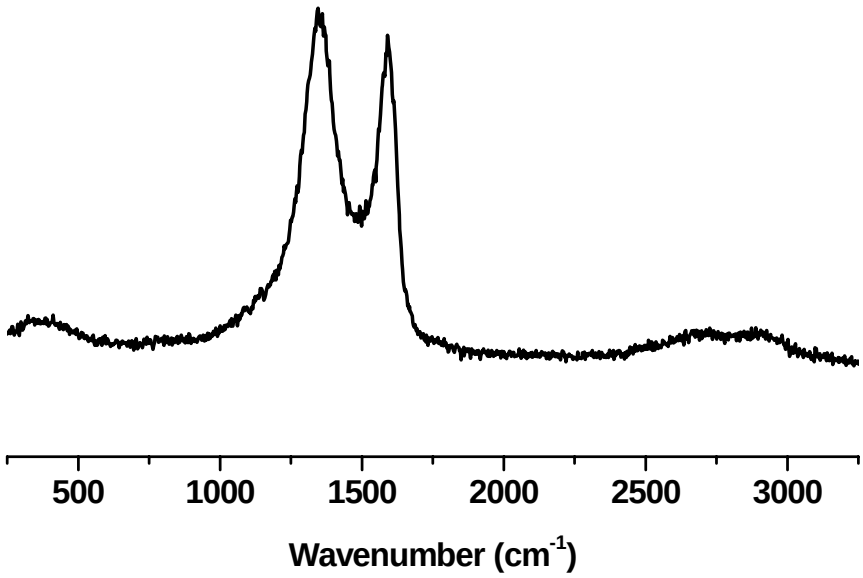

Figure S8. Raman spectrum of graphite oxide (GO).

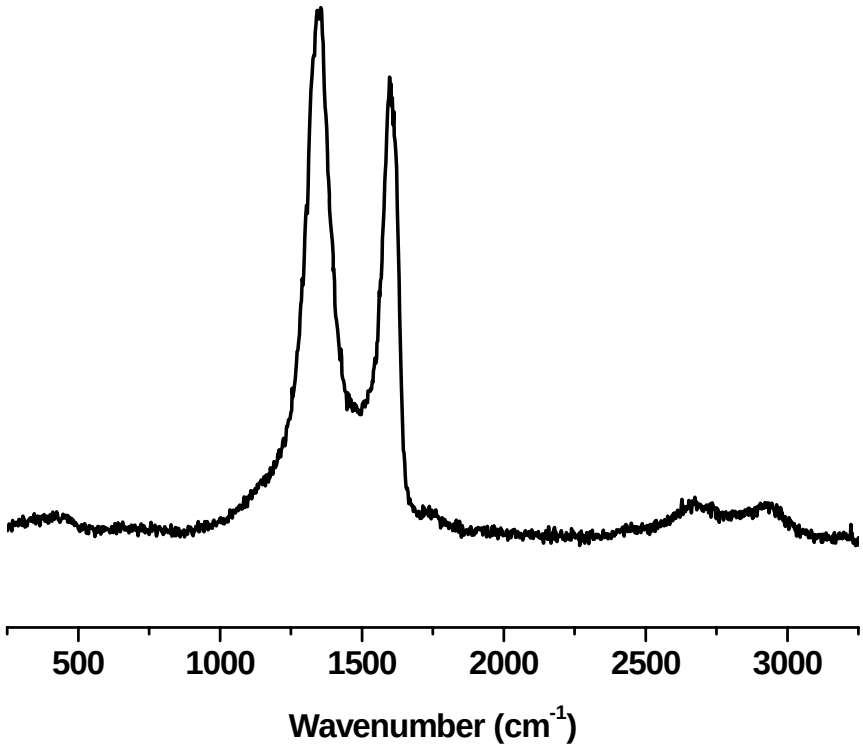

Figure S9. Raman spectrum of carbon recovered after reaction of GO with ε-caprolactone.

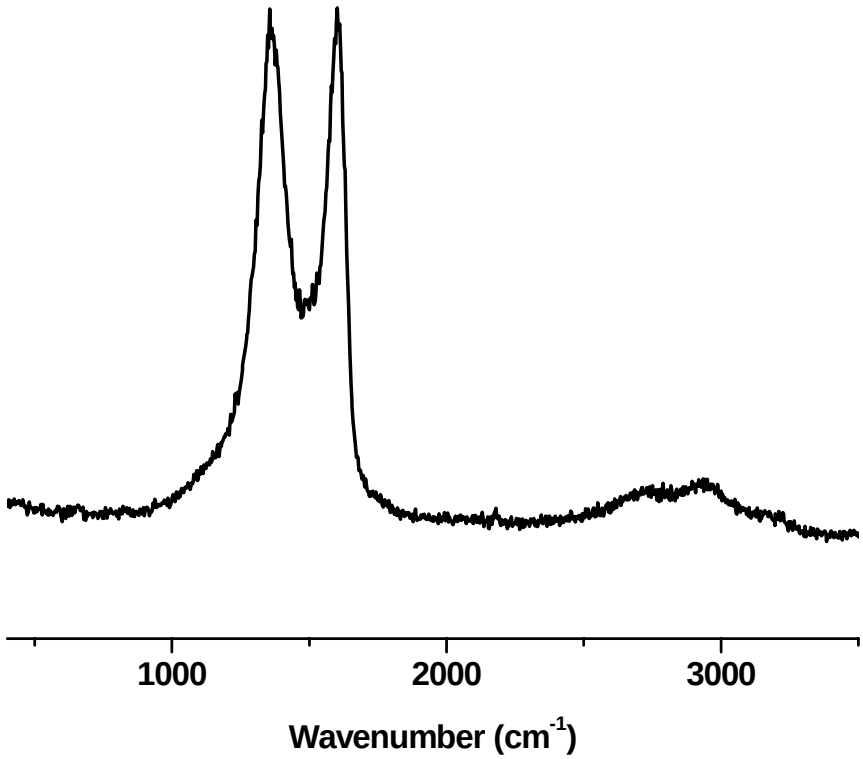

Figure S10. Raman spectrum of basified graphite oxide (b-GO).

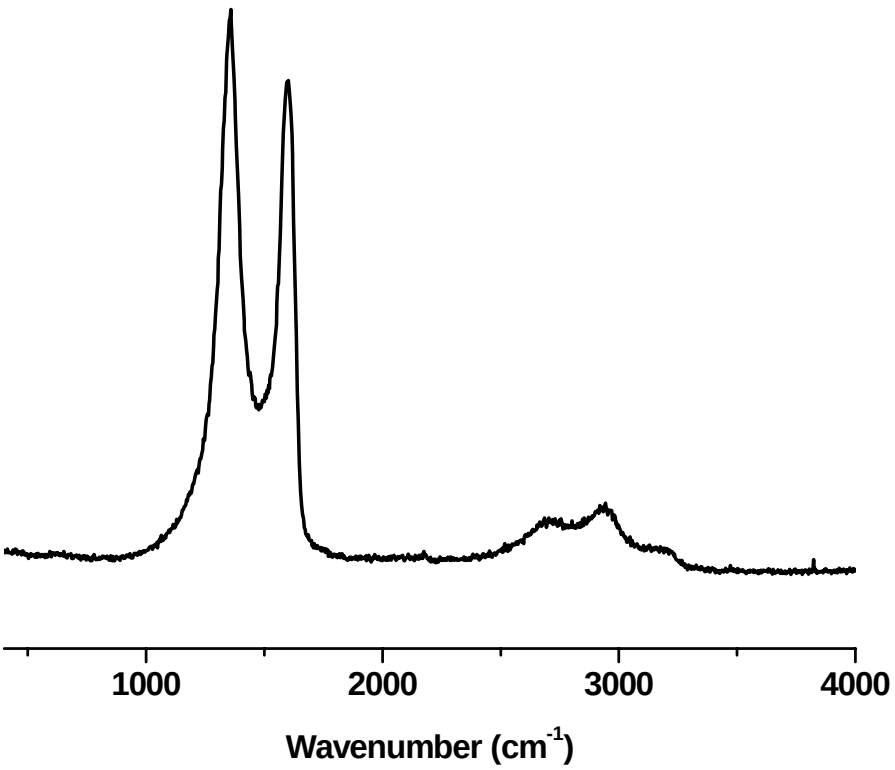

Figure S11. Raman spectrum of carbon recovered after reaction of b-GO with ε-caprolactam.

BET Surface Analysis. The surface areas for graphite oxide (GO), the carbon recovered after reacting ε-caprolactone with GO, basified GO (b-GO), and the carbon recovered after reacting ε-caprolactam with b-GO.[3] Specific surface areas (in $m^2\ g^{-1}$) were determined by converting the isotherms of these measurements into BET plots (see Figures S12–S15). These surface areas were determined by determining the slope of a line of best fit to Eq. 2 (the BET equation), where W and W_m are the quantities of adsorbed gas and monolayer quantity of adsorbed gas, respectively; P and P_0 are the equilibrium and the saturation pressure of adsorbates; c is the BET constant. The results are summarized in Table S2.

$$\frac{1}{W[(P-P_o)-1]} = \frac{c-1}{W_m c}\left(\frac{P}{P_o}\right) + \frac{1}{W_m c} \qquad \text{Eq. 2}$$

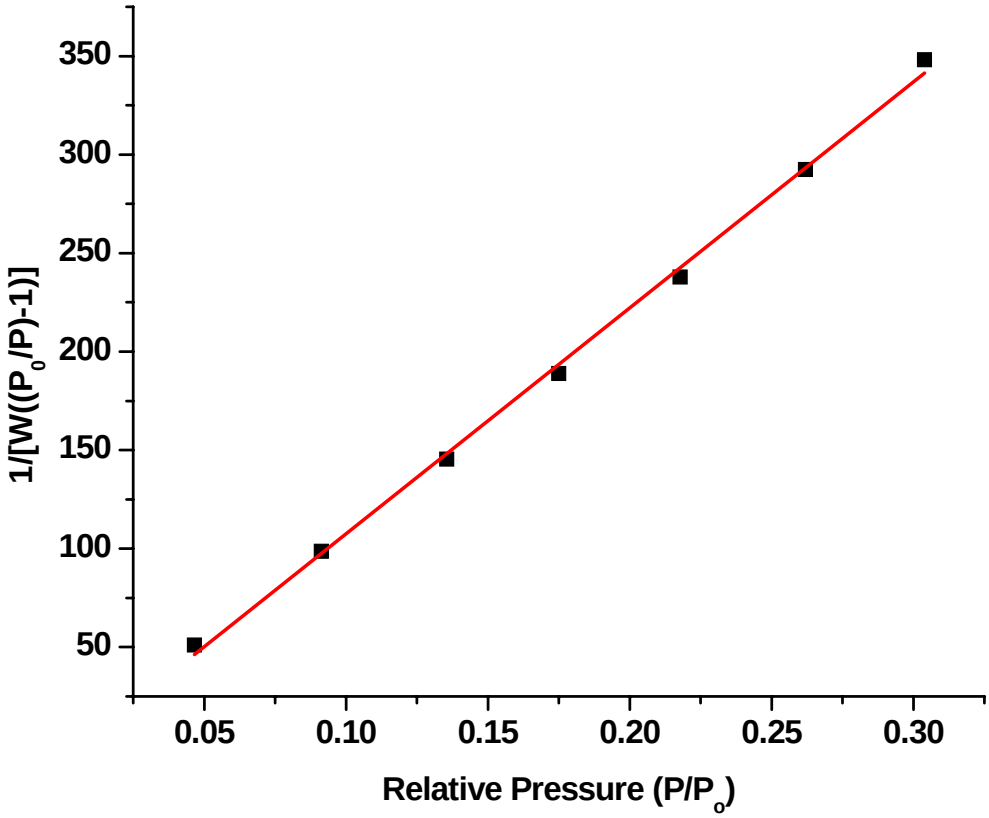

Figure S12. BET plot of graphite oxide (GO).

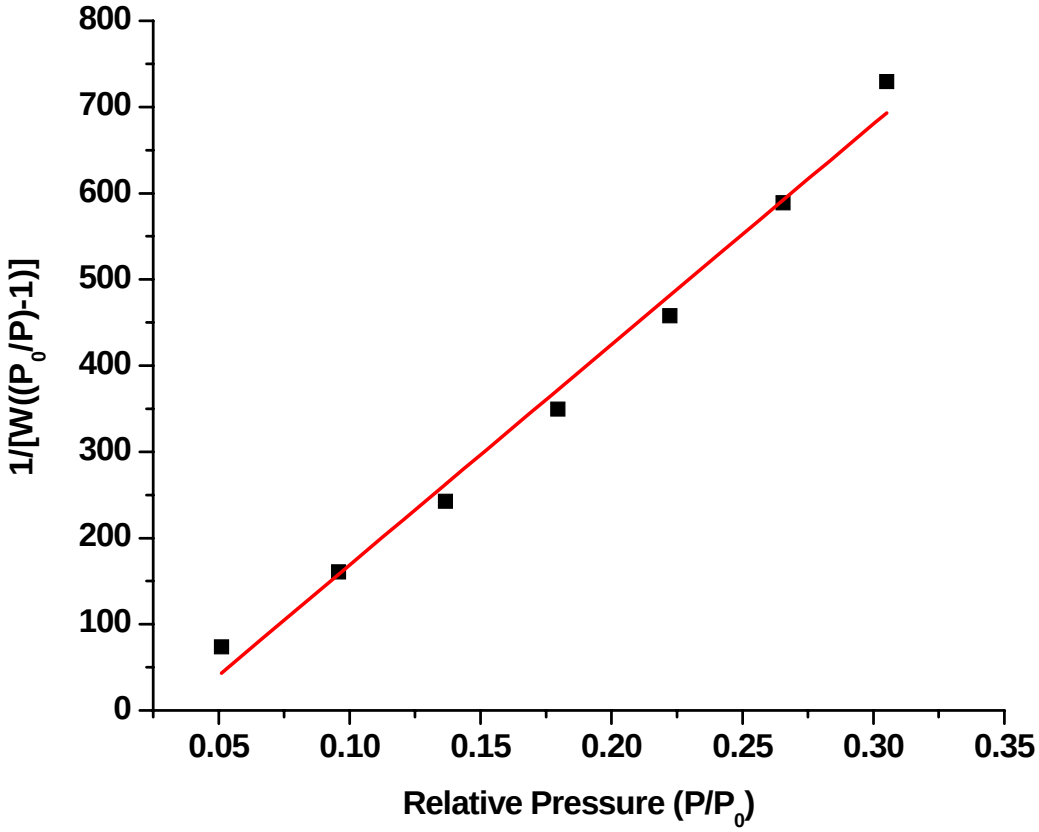

Figure S13. BET plot of carbon recovered after reaction of GO with ε-caprolactone.

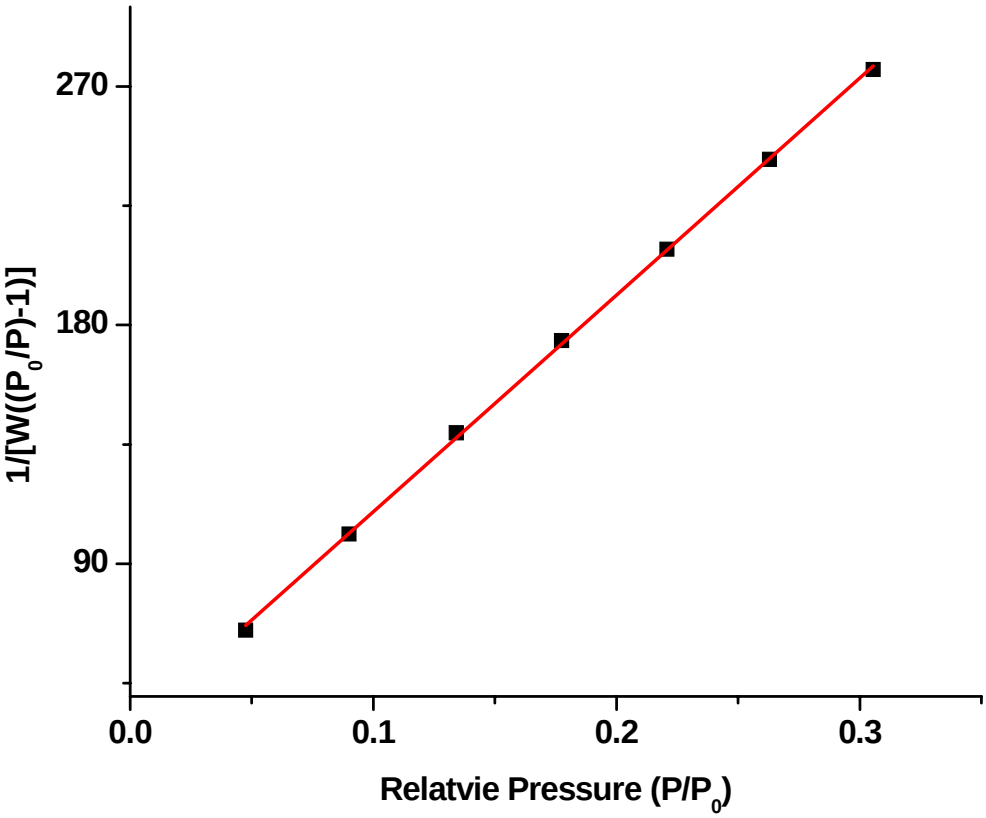

Figure S14. BET plot of basified GO (b-GO).

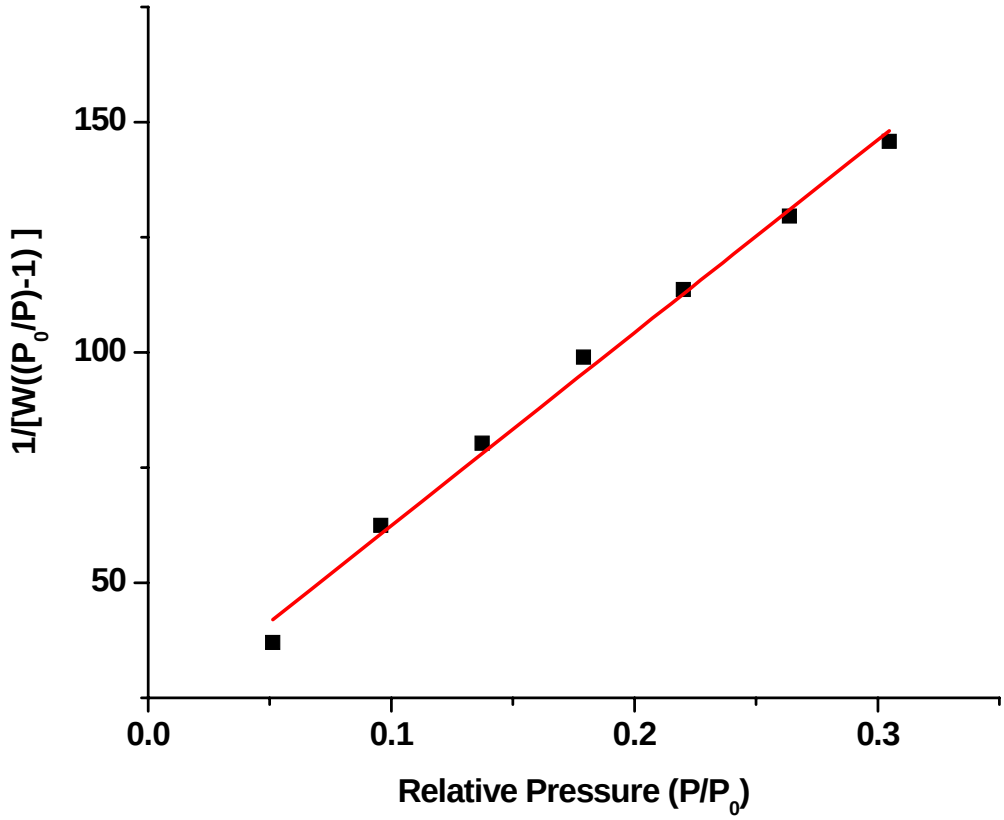

Figure S15. BET plot of carbon recovered after reaction of basified GO (b-GO) with ε-caprolactam.

Table S2. Summary of BET data.

	GO[a]	Recovered Carbon[b]	b-GO[c]	Recovered Carbon[d]
Area (m^2 g^{-1})	3.06	1.41	4.12	7.93
Best Fit Line Slope	1146.4	2557.7	817.1	419.0
Y-Intercept	-7.13	-87.1	27.9	20.5
Corr. Coefficient	0.9991	0.9944	0.9999	0.9970
BET constant (*c*)	-159.8	-28.4	30.3	21.4

[a] Prepared *via* the Hummers method. [b] Material recovered after heating 3.0 g of ε-caprolactone in 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. [c] Prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. [d] Material recovered after heating 3.0 g of ε-caprolactam in 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

Thermogravimetric Analysis. Thermogravimetric analysis was performed on graphite oxide (GO), the carbon recovered after reaction of GO with ε-caprolactone, basified graphite oxide (b-GO), and the carbon recovered after reaction of GO with ε-caprolactam (see Figure S16). The former recovered carbon was obtained after reacting 3.0 g ε-caprolactone with 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. Basified graphite oxide was prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. The latter recovered carbon was obtained after heating 3.0 g of ε-caprolactam with 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

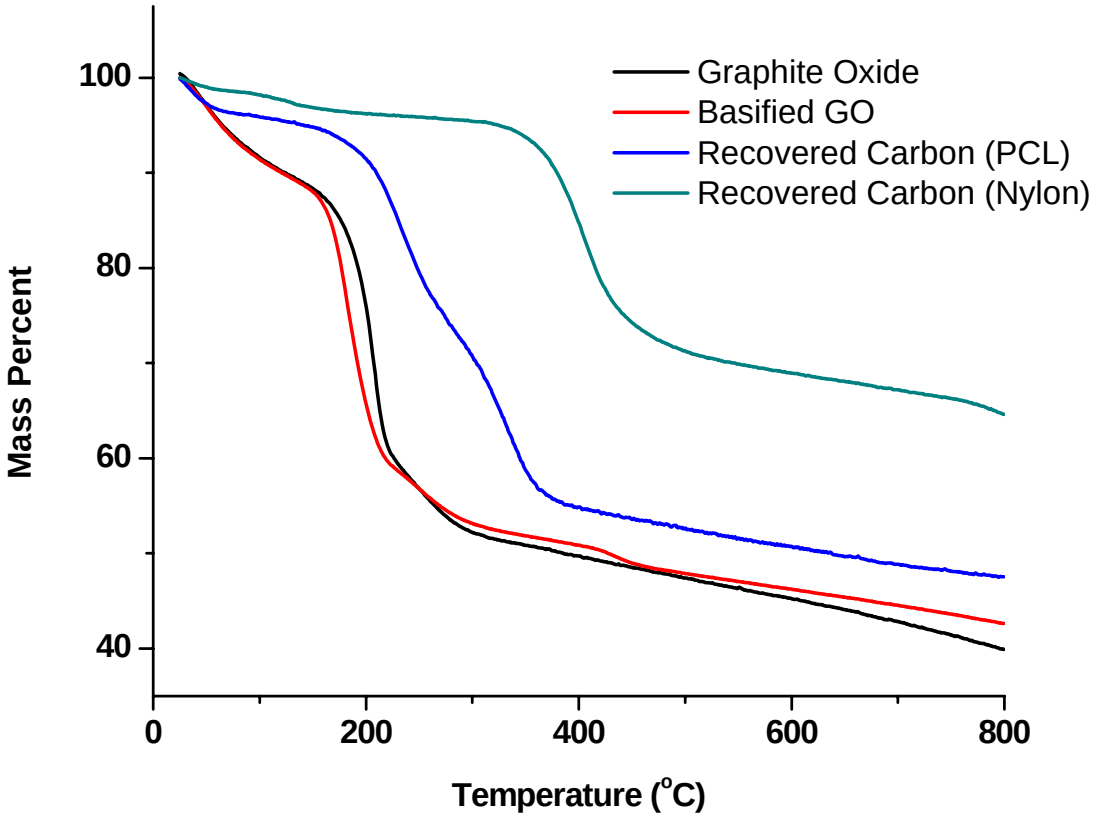

Figure S16. Thermogravigrams of graphite oxide (GO) (black), basified graphite oxide (b-GO) (red), the carbon recovered after reaction of GO with ε-caprolactone (blue), and the carbon recovered after reaction of b-GO with ε-caprolactam (gray).

Powder Conductivity. The electrical conductivities of graphite oxide (GO), the carbon recovered after reaction of GO with ε-caprolactone, basified graphite oxide (b-GO), and the carbon recovered after reaction of GO with ε-caprolactam (see Figure S17–S20) were determined by fitting the observed powder conductivity experimental data (see below) to Eq. 3 with the assumption that the conductivity of the low-conductive phase (air) is zero.[4,5] Briefly, a given quantity of powder (50–100 mg) was poured into a poly(ethylene) tube (ID = 5 mm). The powder was manually compressed between two steel plungers that closely matched the tube's ID. A 5.5 digit Keithley multimeter was connected to the plungers and was used to measure DC resistance by a two-probe method. The plungers were compressed and the resistance was recorded at multiple compression steps (ϕ shown in Eq. 3 below). A digital micrometer was used to measure the height of the powder column at each compression step, allowing for conversion of the measured resistances to conductivities (σ_c in Eq. 3).

$$\sigma_c = \sigma_h \left[\frac{\phi - \phi_c}{1 - \phi_c}\right]^k \qquad \text{Eq. 3}$$

where σ_c is the conductivity of the composite medium, σ_h and ϕ are the conductivity of the conductive phase (graphite oxide or recovered carbon) and their volume fractions respectively, ϕ_c is the percolation threshold, and k is a critical exponent related to the percolation threshold and to the shape of the particles.

The percolation threshold, ϕ_c, is determined as a ratio of the apparent powder density before compression, d_p, and the apparent density of the particles, d_g. The bulk density of graphite (2.2 g cm^{-3}) was used[3] as a value for d_g. The constants σ_c and ϕ_c were calculated from the parent volume of the reduced graphite oxide powders and the resistance of the powders as measured by a multi-meter. Figures S19 and S20 show σ_c values as a function of ϕ during the

compression for GO and the recovered carbon, respectively. The results are summarized in Table S3.

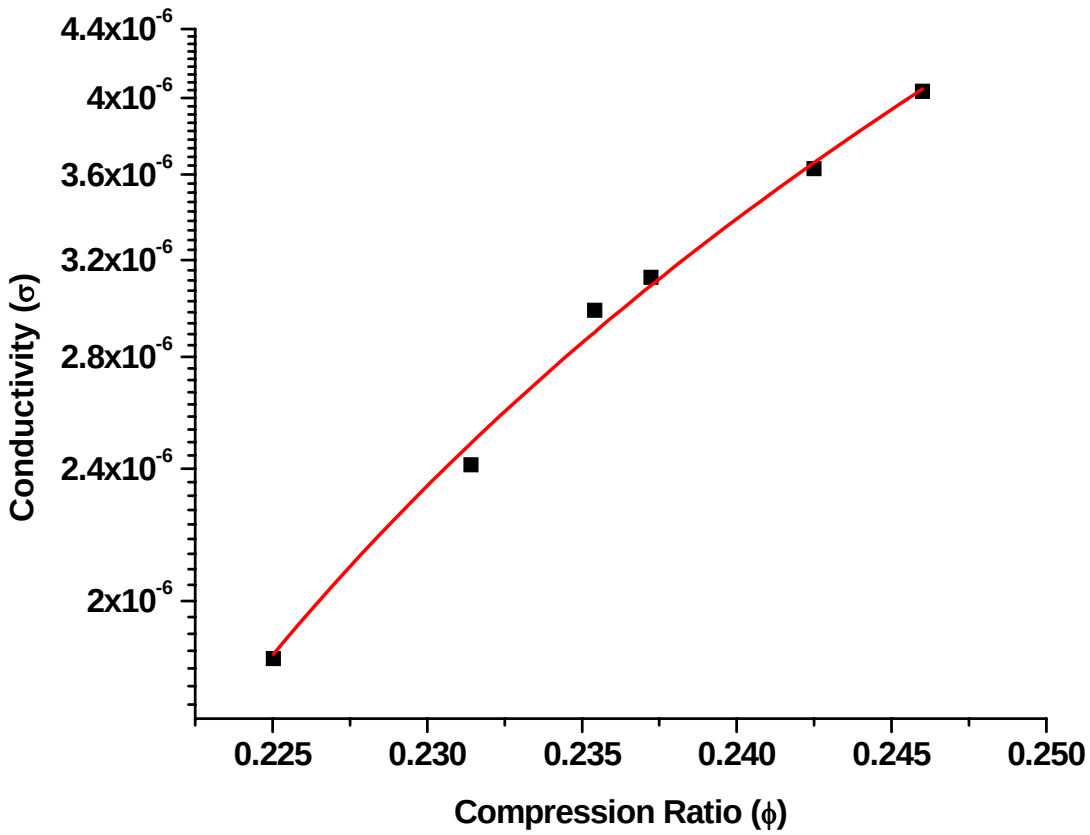

Figure S17. Powder conductivity plot of graphite oxide (GO).

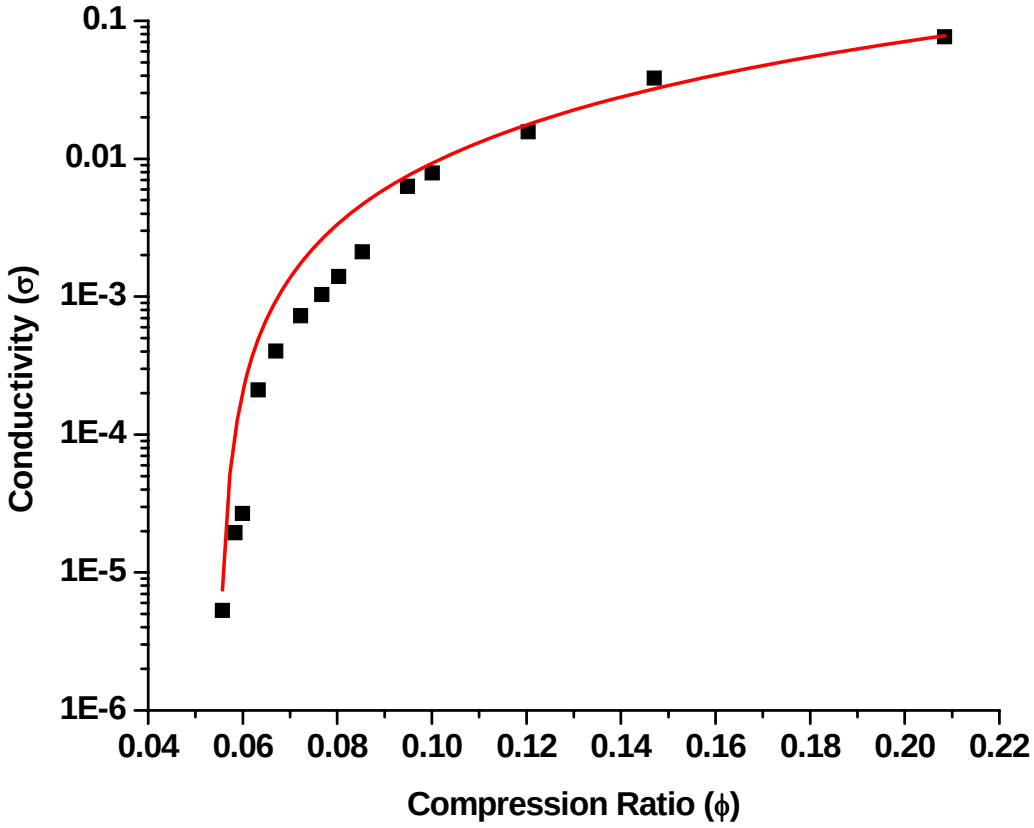

Figure S18. Powder conductivity plot of carbon recovered after reacting GO with ε-caprolactone.

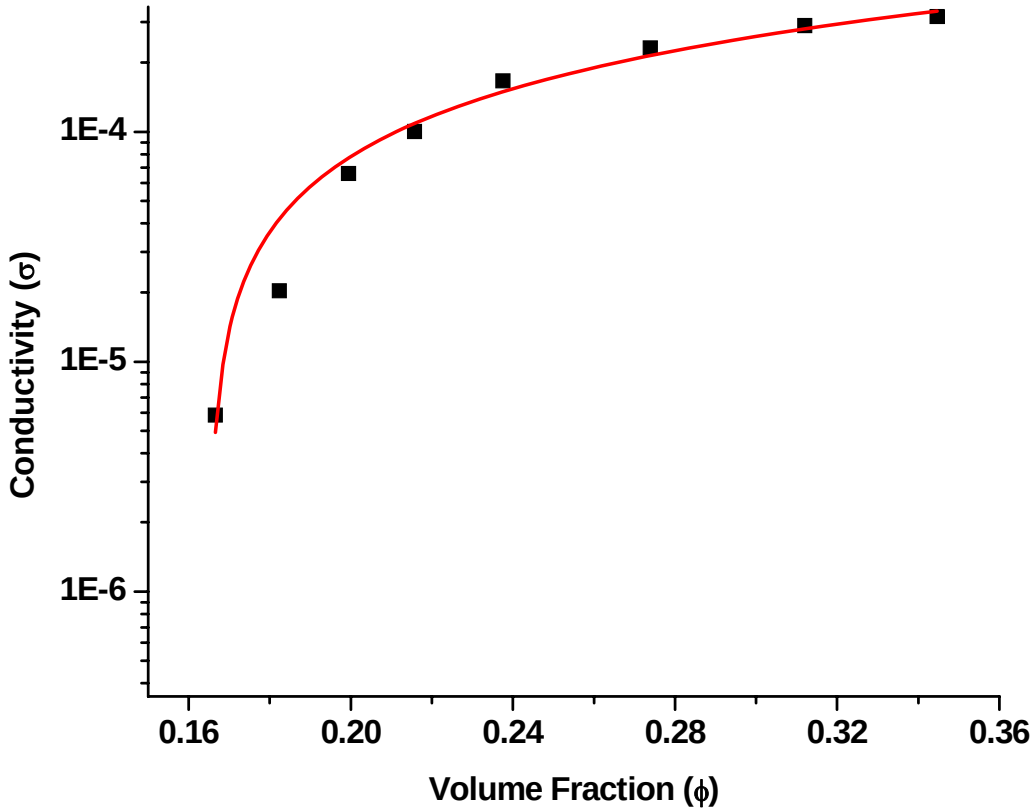

Figure S19. Powder conductivity plot of basified graphite oxide (b-GO).

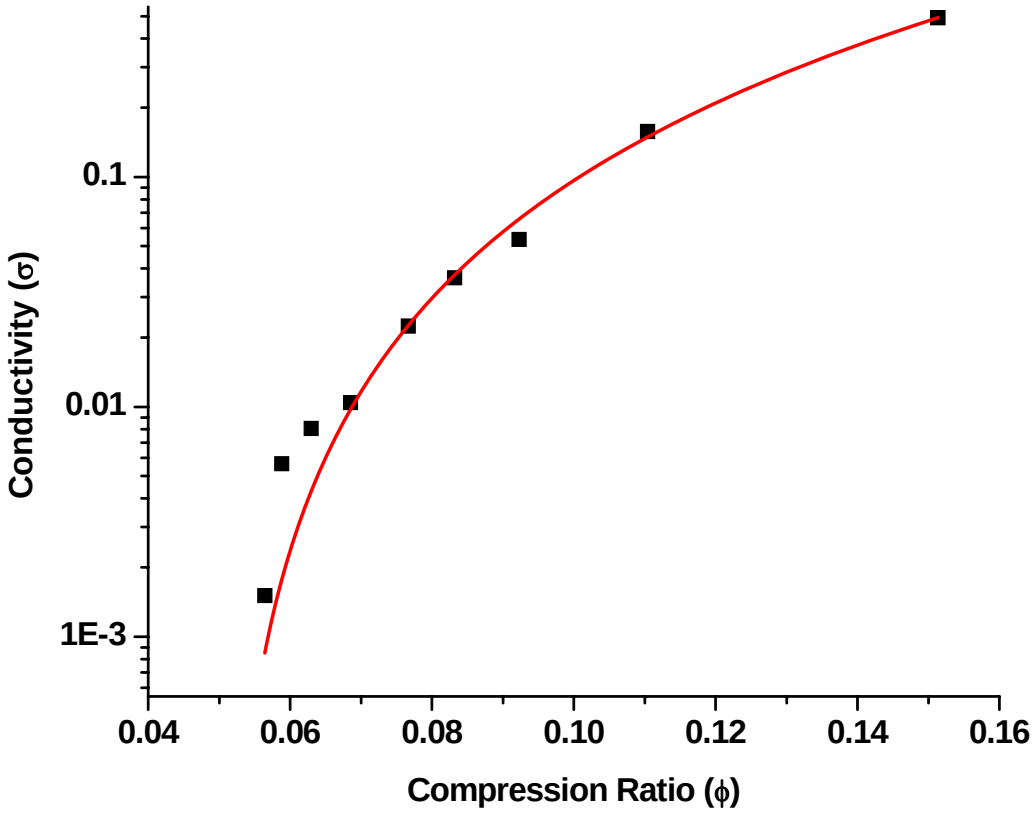

Figure S20. Powder conductivity plot of carbon recovered after reacting b-GO with ε-caprolactam.

Table S3. Summary of powder conductivity data.

	Powder Conductivity (σ_h; S m^{-1})[a]	Critical exponent (k)[a]
GO[b]	1.57×10^{-4}	1.28
Recovered Carbon[c]	1.84	1.74
b-GO[d]	1.32×10^{-3}	0.89
Recovered Carbon[e]	86.39	2.31

[a] Powder conductivity (σ_h) and critical exponent (k) were determined by measuring conductivity (σ_c) as a function of a volume compression (Φ) and fitting a line of best fit using Eq. 3. [b] Prepared *via* the Hummers method. [c] Material recovered after heating 3.0 g of ε-caprolactone in 0.075 g (2.5 wt%) of GO at 60 °C for 14 h, followed by dissolution of the polymer in dichloromethane and isolation of the carbon product by filtration. [d] Prepared by reacting GO (0.5 g) with triethylamine (20 mL) at 25 °C for 30 min. [e] Material recovered after heating 3.0 g of ε-caprolactam in 0.15 g (5.0 wt%) of GO at 300 °C for 14 h, followed by dissolution of the polymer in formic acid (88% aq.) and isolation of the carbon product by filtration.

References

1. Hummers Jr., W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

2. Brandrup, J.; Immergut, E. H.; Grulke, E. A. In *Polymer Handbook*; 4th ed.; Wiley: New York, 1999, p VII-68.

3. Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.

4. Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon*, **2007**, *45*, 1558–1565.

5. Zhu, Y.; Murali, S.; Stoller, M. D.; Velamakanni, A.; Piner, R. D.; Ruoff, R. S. *Carbon*, **2010**, *48*, 2118–2122.