# **Supplementary Information**

SI Important Acronyms Guide			
GO	Graphene Oxide		
EIS	Electrochemical Impedance Spectroscopy		
SEM	Scanning Electron Microscopy		
USANS	Ultra-Small-Angle Neutron Scattering		
DREAM	Differential Evolution Adaptive Metropolis		
EDX	Energy Dispersive X-ray		
DLS	Dynamic Light Scattering		

# **Graphene Oxide Synthesis**

An aqueous dispersion of chemically derived graphene sheets was created by a modified Hummers method as described in the literature.<sup>1</sup> All chemical and materials used in the synthesis of graphene oxide were in pure lab grade form purchased from chemical distributors such as Sigma-Aldrich, St. Louis, MO and Thermo Scientific, Waltham, MA. Graphite oxide was first synthesized from the chemical oxidation of natural graphite flakes (Sigma-Aldrich, St. Louis, MO).<sup>1,2</sup> 5.0 g of natural graphite flakes is combined with 100 mL of 18 M H<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich, ACS reagent, 95.0-98.0 % assay purity) and 2.5 g of NaNO<sub>3</sub> (Sigma-Aldrich, ACS reagent,  $\geq$  99.0 % assay purity) under stirring in an ice bath. Upon cooling the reaction mixture, 9.0 g of KMnO<sub>4</sub> (Sigma-Aldrich, ACS reagent,  $\geq$  99.0 % assay purity) was added during stirring at 35 °C for 2 hours. Finally, 150 mL of DI (deionized) water was slowly added while heating and an additional 500 mL of DI water was added to the reaction mixture before cooling to room temperature. While cooling under stirring, 15 mL of  $H_2O_2$  (30 % w/w in H<sub>2</sub>O, Sigma-Aldrich, 29.0-32.0 % assay purity) was added drop wise to the reaction mixture and left stirring for 12 hours until the reaction is complete. To purify the synthesized graphene oxide, it was filtered and washed with HCl (30 mL of 18 M HCl (Sigma-Aldrich, ACS reagent, 37 % assay purity), 270 mL DI water), and then washed again with 15 mL of DI water. DI water was then added to disperse the GO, and the mixture was left in dialysis tubing (Thermo Scientific<sup>™</sup> SnakeSkin<sup>™</sup> Dialysis Tubing with 3.5K MWCO, Waltham, MA) for 2 days.

We then sonicated the mixture for 2 hours and centrifuged in a Heraeus Pico 17 Microcentrifuge (Thermo Fisher Scientific, Waltham, MA) the GO at 4000 for 20 minutes. The graphene oxide dispersion was filtered through hydrophilic MilliporeSigma™ Durapore™ Membrane Filters (0.22 µm, MilliporeSigma, Burlington, MA) to result in a solid residue of graphene oxide. Finally, the solid GO was readily suspended in water to form a stable and light yellow-brown dispersion. To conduct a chemical reduction of the GO, 10 mL of GO suspension (0.2 mg/mL) is mixed with 10 mL of water, 10 µL of hydrazine monohydrate and 40 µL of ammonia dispersion (28 vol % in water), and the reaction mixture is heated in an oil bath (~95 °C) for 1 h. After the completion of the reduction reaction, excess hydrazine in the resulting suspension was removed by dialysis to produce a stable graphene suspension. Unreduced GO was used for all material, rheological, SANS,

and rheo-conductivity experiments presented in this study as a baseline for future studies to be conducted with reduced GO.

# Synthesis of GO Suspensions

To create a suspension of graphene oxide in heavy water  $(D_2O)$ , the GO dispersion is ultracentrifuged at 500 g for 15 minutes to sediment large particles at the bottom of the centrifuge tube. The resulting precipitate is the 500g sample. The supernatant suspension from the top was removed via pipette and then centrifuged again in a different tube with higher G-force (for example, 1000 g). This will precipitate, second, large particles again but the resulting graphene oxide sheets will be smaller in size than the first iteration. The dispersion was then centrifuged at increasing G-force for 15 minutes at a time to precipitate the graphene oxide with decreasing particle sizes. The precipitate was collected using a micropipette to extract the suspension from the top of the centrifuge tube without agitating the precipitate just after centrifugation from each G-force to separately disperse them in different dispersions for characterization.

# **Electrochemical Impedance Spectroscopy Background**

An RLC equivalent circuit model from EIS data is a representation of the impedance as resistors, inductors, and capacitors in series or parallel. Table S1 references how each internal circuit is ideally calculated given the component value and frequency. By keeping the applied potential or current constant and varying the frequency, the impedance value of each component can be obtained as shown in Table S1 below. By plotting the imaginary component of the resistance versus real resistance at each frequency measured, the resulting spectroscopy can be analyzed for the effects of pure resistance contributions and how frequency impacts capacitance and inductance values within RLC model circuit.

 Table S1. Impedance calculations for basic circuit components.

Element	Impedanc e
Resistor (R)	Z
Capacitor (C)	$\overline{2\pi fC}$
Inductor (L)	2πfC

By identifying the frequency in the circuit where only the impedance contribution of the circuit occurs from ohmic resistance, the imaginary impedance contributions from any inductor or capacitor components in the circuit are muted. This also occurs where the impedance spectroscopy intersects the x-axis. Isolating this ohmic resistance value is necessary to solve for the conductivity of the GO where conductivity is the inverse of resistivity ( $\rho$ ) [ $\Omega$ -cm]. This occurs because the only ohmic resistance contribution in the circuit comes from GO and all other factors that depend on frequency have no imaginary

impedance contributions to the circuit. Resistance of GO is calculated by the following equation where I is the length of the bob (cm), A is the cross-sectional area of the bob (cm<sup>2</sup>), and R is the recorded resistance in ohms ( $\Omega$ ).



Figure S1. ImageJ image processing steps for particle distribution analysis.

Figure S2. (a) SANS measurements of graphene oxide suspended in different deuterated solvent mixtures, corresponding to H2O/D2O v/v ratios of 80/20 (orange hexagons), 60/40 (green down-triangles), 40/60 (red up-triangles), 20/80 (blue squares), and 0/100 (black circles). Horizontal dashed lines show the incoherent background scattering in each solvent mixture. (b) Coherent neutron scattering intensity after background subtraction. Dashed line shows a  $I(q) \sim q^{-2}$  expected for flat, sheet-like objects. (c) The summed coherent scattering as a function of calculated solvent scattering length density (SLD). Assuming a twocomponent system, the match-point corresponds to when the linear fit (dashed line) intercepts the x-axis, giving a particle SLD of as  $\rho_{p}$  = 8.3±0.4 x 10<sup>-6</sup> Å<sup>-2</sup>.



**RSC Advances** 

Parameter name	Symbol	Best fit value	Uncertainty (95%)	Units
A_scale	CA	8.2E-02	7.9E-03	-
A_lorentz_scale	LA	8.2E+06	7.0E+05	-
A_porod_scale	PA	3.0E-06	5.8E-07	-
A_cor_length	ξ	5.4E+03	1.2E+02	Å
A_porod_exp	n	3.2E+00	1.4E-02	-
A_lorentz_exp	m <sub>q</sub>	3.6E+00	3.5E-02	-
B_scale	Св	7.0E-04	8.7E-05	-
B_thickness	δ	1.1E+01	1.1E+00	Å
B_sld*	ρ <sub>p</sub>	8.3E-06	-	Å-2
B_sld_solvent*	ρs	-5.6E-07	-	Å-2

Figure S3. Combining slit-smeared Ultra-small-angle neutron scattering

(USANS) data (red triangles) with pin-hole-smeared SANS data (orange

squares). The incoherent background at high-q (B = 1.169 cm<sup>-1</sup>) is shown as the horizontal dashed line. The de-smeared USANS is combined with SANS data after subtracting the incoherent background (blue circles). The model fit across the full q-range is shown as the solid black line.

Table S2. Best fit parameters and 95% uncertainty intervals for the summed lamellar correlation model. \*Denotes a fixed parameter.

(S2) 
$$I(q) = C_A I_A(q) + C_B I_B(q) + B$$

(S3)

(S4)

$$I_B(q) = \frac{4(\rho_p - \rho_s)^2}{q^2} \sin^2\left(\frac{q\delta}{2}\right)$$

 $I_A(q) = \frac{P_A}{q^n} + \frac{L_A}{1 + (q\xi)^{m_q}}$ 

### **Small-Angle Neutron Scattering Analysis**

The above model was created using the "model editor" feature in SasView.<sup>3</sup> The scale parameter in SasView was fixed ("scale" = 1) and the incoherent background was fixed "background" = 0), as the incoherent background  $(B=1.169 \text{ cm}^{-1})$  was subtracted from the data before fitting. Due to the overall goodness of fit ( $\chi^2/N = 3.9$ ), no polydispersity was applied to the relevant parameters. Physically realistic minimum and maximum constraints were applied to each fit parameter, to constrain the DREAM random sampling and initializations. Details of the DRFAM algorithm found in can be SasView documentation.<sup>3</sup>

Note, that the Lorentz exponent ( $m_q$ =3.6) in the model fit is an overestimate of the apparent slope determined with a simple power-law fit in a similar q-range ( $m_{q=3.2}$ ). This discrepancy between scaling exponents is likely due to the simplifying assumption of independent (uncoupled) scattering models. By neglecting cross-terms (i.e. C<sub>AB</sub>) that would otherwise couple the lamellar and correlation length model parameters, a broad range of surface fractal exponents ( $m_q$  = -3.2 to -3.6) could be possible in this intermediate q-range. Nevertheless, the surface fractal dimension determined in either model is sufficiently distinct and resides somewhere between a perfectly smooth surface ( $m_q = -4$ ) and a perfectly roughened surface smooth surface ( $m_{q} = -3$ ).

For any two-phase or two-component system, the Dynamic Light Scattering of Graphene Oxide scattering invariant (Q\*) can be calculated by

$$Q^* = \int_0^\infty q^2 I(q) dq \tag{S5}$$

The accuracy of this discrete sum or integration (weighted area under the scattering curve) is dependent on the range and extrapolation of intensity as a function of q. The scattering invariant is particularly sensitive to scattering at high q given the weighting of  $q^2$  in the integral. Given the broad range of measured q-values, no extrapolation in high-q was used. In this case,  $Q^* = 2.3 \times 10^{-4} \text{ cm}^{-1} \text{ Å}^{-3}$ . The invariant of a two-phase system is also related to the volume fraction of scatterers and the difference in scattering length densities, given by

$$Q^{*} = 2\pi^{2} (\Delta \rho)^{2} \phi (1 - \phi)$$
 (S6)

By rearranging and solving the guadratic equation, the volume fraction ( $\phi$ ) of the minority phase is given by

$$\phi = \frac{1 - (1 - 4A)^{0.5}}{2} \tag{S7}$$

$$A = \frac{Q^*}{2\pi^2 (\Delta \rho)^2} \tag{58}$$

Here, the scattering length density difference between particle and solvent is  $\Delta \rho = \rho_P - \rho_{H20}$  was determined to be 8.86 x 10<sup>-6</sup> Å<sup>-2</sup> from contrast variation measurements. The resulting estimate for the volume fraction of graphene oxide particles is  $\phi = 0.15\%$  by volume GO in H<sub>2</sub>O.

The Porod constant  $(C_P)$  can be determined in the limit of high q to estimate the total specific surface area of scatterers (per unit volume of scattering centers). From a linear fit of  $q^4 I(q)$  as a function of  $q^4$  in the range 0.4 < q < 0.53, the Porod constant and uncertainty was determined to be  $C_P = 2.9 \pm 1.8 \times 10^{-4} \text{ cm}^{-1} \text{ Å}^{-4}$ . Given this Porod constant and SLD difference, the specific surface area is estimated by

$$S\mathbb{Z}_{v} = C\mathbb{Z}_{p}(2\pi)^{-1}(\Delta\rho)^{-2}$$
(S9)

which is estimated in this case to be  $S_v = 5.8\pm3.7 \times 10^{-3} \text{ Å}^{-1}$ . The specific surface area here is defined by the particle surface area per particle volume. An assumed GO particle density of 0.26 g cm<sup>-3</sup> is used to convert to customary units for specific surface area (m<sup>2</sup> g<sup>-1</sup>), which gives a result equivalent to  $S_v = 220 \pm 140 \text{ m}^2 \text{ g}^{-1}$ .



Figure S4. Size distribution of 500g GO as a function of intensity (%).

DLS was conducted on the 500g GO suspension where the highest scattered light intensity at 420.2 nm peak indicates maximum size distribution of monodispered the aggregates and the most prevalent GO particle size within the suspension. The size range of particles is from a minimum of 310.7 nm to a maximum of 568.3 nm indication of the presence of co-existing polydispersed GO with variable size of aggregates in suspension.



	D Band Intensity (cts/s)	G Band Intensity (cts/s)	2D Band Intensity (cts/s)	I <sub>D</sub> /I <sub>G</sub>	I <sub>2D</sub> /I <sub>G</sub>
This Study	16164.1	17357.2	1193.9	0.94	0.07
Literatures				0.80-1.404-12	0.08-0.354-6

Figure S5. Raman spectra of GO thin films after ambient drying.

Raman spectroscopy of GO after chemical exfoliation using Hummer's method was conducted using a Horiba XploRA Plus Raman Microscope spectrometer (XploRA, HORIBA Scientific, France). A 532 nm excitation laser was focused on the sample with a 50x magnification objective lens (0.55 NA, 20 mm working distance).

Raman spectroscopy of the graphene oxide was conducted after chemical exfoliation via Hummer's method. After synthesis, the resulting GO slurry in solution was ambiently dried onto a glass microscope slide for characterization. Figures S5 shows the most representative Raman spectrum and S6 show the Raman Spectroscopy results of 4 different GO thin films after ambient drying with characteristic D-Band, G-Band, and 2D-Band within ranges of 1349-1392 cm<sup>-1</sup>, 1602-1618 cm<sup>-1</sup>, and 2436-2709 cm<sup>-1</sup>, respectively. The intensity ratios of the D-band to the G-band correspond to the number of defects on graphene oxide resulting from the oxygenated functional groups on the edge and basal plane developed during the modified Hummer's synthesis method. The intensity ratios of the 2D-Band to the G-Band indicates the thickness or number of layers in the graphene material. The lower the intensity ratio of the 2D/G, the more layers of graphene present.<sup>13</sup> The most representative Raman Spectrum was added as Figure S5 with a corresponding table with the average D-Band, G-Band, 2D-Band,  $I_D/I_G$ , and  $I_{2D}/I_G$  values determined from the Raman Spectra of the 4 different GO thin films.

There were increased D/G intensity ratios (almost 1:1) across all four GO films confirms the chemical exfoliation of graphene to produce graphene oxide from the oxygen containing functional groups. Moreover, the average 2D/G ratio of 0.066 indicates the presence of multi-layer graphene likely from the self-stacking and aggregation of



sheets during the ambient drying process.

**Figure S6.** Raman Spectra of the four thin films of GO formed from ambient drying after modified Hummer's Method. The legend from each spectra contains the GO film number and the multiple locations of GO films.

As seen in Table S3, the increased D/G intensity ratios (almost 1:1) across all four GO films confirms the chemical exfoliation of graphene to produce graphene oxide from the oxygen containing functional groups. Moreover, the average 2D/G ratio of 0.066 indicates the presence of multi-layer graphene likely from the self-stacking and aggregation of sheets during the ambient drying process.

 Table S3.
 Raman Spectroscopy results values of D-Band, G-Band, and 2D-Band intensities as well as the intensity ratios of D/G and 2D/G for the

Raman Spectroscopy - GO Sample# (Spectrum for sample)	D Band Intensity (cts/s)	G Band Intensity (cts/s)	2D Band Intensity (cts/s)	lơ/la	l <sub>2D</sub> /l <sub>G</sub>
GO1 (A)	14146.100	14567.200	712.678	0.971	0.049
GO1 (B)	14163.300	14724.500	264.397	0.962	0.018
GO1 (C)	14869.100	14918.000	596.616	0.997	0.040
GO2 (A)	11395.600	12093.500	1391.720	0.942	0.115
GO2 (B)	16417.500	17936.200	3541.390	0.915	0.197
GO2 (C)	12074.100	12484.500	781.477	0.967	0.063
GO3 (A)	11752.100	12895.400	647.708	0.911	0.050
GO3 (B)	30572.700	37846.400	3521.410	0.808	0.093
GO3 (C)	21745.200	22063.900	723.867	0.986	0.033
GO3 (D)	20156.500	21276.000	692.191	0.947	0.033
GO4 (A)	13762.500	14278.400	748.159	0.964	0.052
GO4 (B)	12914.500	13202.200	704.924	0.978	0.053
AVERAGE	16164.1	17357.18333	1193.878083	0.945717692	0.066366576

spectra shown in Figure S6.

Scanning Electron Microscopy and Energy Dispersive X-



**Ray of Graphene Oxide Sheets** 

**Figure S7** SEM from GO films from ambient drying of GO produced through Modified Hummer's Method.

Figure S8. EDX of GO conducted on the ambiently dried films.





Figure S9. SEM images of GO sheets from heated drying at 80°C.

Since our study was focused on investigating the properties of graphene oxide in aqueous solutions at atmospheric and room temperature conditions, so we did not investigate the impact of temperature and pressure on the governing materials, rheological, and electrochemical properties. However, studies on the morphology of resulting GO thin films comparing ambient drying to heated drying at 80°C was conducted to characterize the resulting GO sheets that form onto a substrate. A 1 mL aliquot of the 500g centrifuged GO solution was drop casted onto a clean Si wafer and placed into a heating oven set at 80°C until the films appeared dry. As seen in the SEM images in Figure S9, heated drying of the GO solution after drop casting led to films with less prevalence of "clustering" or aggregation of GO sheets onto the Si wafer. The non-uniform distribution of GO sheets on the Si wafer was likely due to the impact temperature during the vaporization process of the solution. However, this was not the case for ambiently dried films as seen in the SEM images included in Figure S8 of SI which shows more distribution of GO sheets onto the Si wafer. The authors acknowledge the impacts of temperature and pressure on the GO sheets and based on our preliminary experiments of heated drying there should be more future studies on the impact of temperature and pressure on the properties of GO sheets in suspension.



6





Min: 0.426 Max: 35.863 Mode: 0.426 (27) Bin Width: 3.544

Units in um, um<sup>2</sup>

Graphene Oxide Particle Distribution Sample: Drop Casted Graphene Oxide (500g) Ambiently Dried

# Image Processing with ImageJ Maximized contrast with Brightness/Contrast



#### Units in µm, µm<sup>4</sup>

Graphene Oxide Particle Distribution Sample: Drop Casted Graphene Oxide (500g) Ambiently Dried

- Image Processing with ImageJ Maximized contrast with Brightness/Contrast Convet to Binary Binary/Fill Holes Binary/Frode (to reduce pixel noise) Divided ROI26 overlapping sheets with drawing tool Analyze Particles (with a min threshold size of 0.5µm<sup>2</sup>)











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Table S4. Reported electronic conductivity of GO from literatures.

Material Tested	Experimental Method	Electronic Conductivity (S/cm)	
GO Pellets	Dielectric Spectroscopy	{10 <sup>-6</sup> to 10 <sup>-5</sup> } <sup>14</sup>	
GO Nanofluid	Conductivity Probe	$\{2.3 \times 10^{-4} \text{ to } 2.4 \times 10^{-4}\}$	
GO Paper	Dielectric Spectroscopy	{10 <sup>-5</sup> to 10 <sup>-4</sup> } <sup>16</sup>	
GO Pellet with Gold Electrodes	Dielectric Spectroscopy	{10 <sup>-6</sup> to 10 <sup>-4</sup> } <sup>17</sup>	
Reduced GO Paper in Organic Solutions	Conductivity Probe	{2.0 to 6.9} <sup>18</sup>	

# **SI Notes and References**

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