

Supporting Information

Wrinkling and Periodic Folding of Graphene Oxide Monolayers by Langmuir-Blodgett Compression

Gregory J. Silverberg[†] and Chad D. Vecitis^{†,*}

[†]Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

*Corresponding author: 120 Pierce Hall, 29 Oxford Street, Cambridge, MA 02138, (617) 496-1458
vecitis@seas.harvard.edu

Keywords. graphene oxide; wrinkling; electrode; Langmuir-Blodgett; energy storage

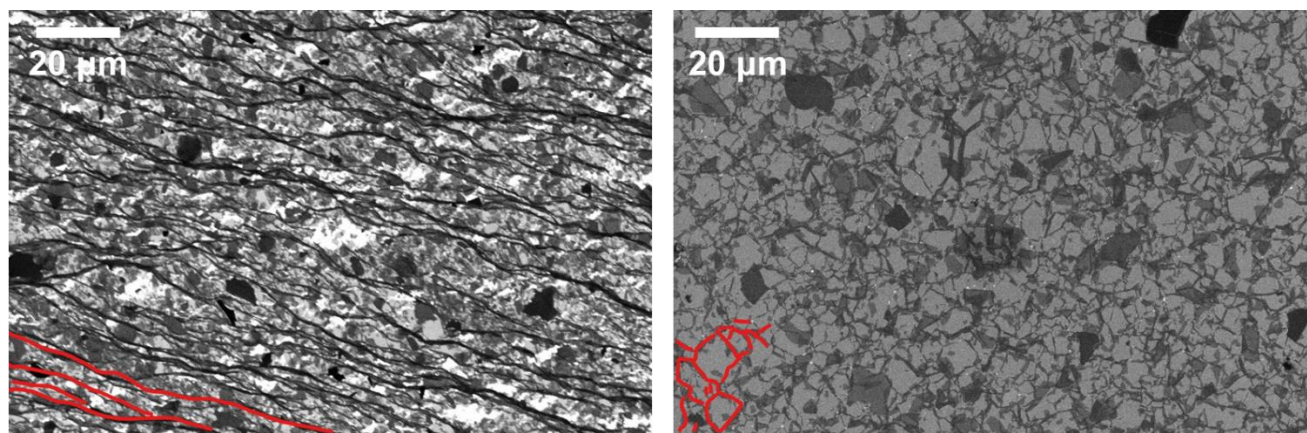


Figure S1. SEM images of wrinkling and crumpling behavior. **A)** GO-CTAB compressed to $R_C = 2$ shows semi-parallel and periodic folds. Some typical folds have been highlighted in red. **B)** GO alone occasionally displays crumpling behavior during which the edges of the sheets crumple randomly. Some typical crumples have been highlighted in red. This type of behavior is much less frequently observed than stacking behavior and depends on the surface potential of the GO sheets.

Estimating relative surface area of GO and CTAB. Surface area for GO and CTAB at the air-water interface are quite difficult to calculate accurately. When GO is dispensed on the water surface, a large amount enters the subphase because of hydrophilicity and the miscibility of ethanol. The area of GO for a typical experiment can be estimated using the mass of GO dispensed at the interface and the theoretical specific surface area of graphene ($2630 \text{ m}^2/\text{g}$). It is found to be $\sim 160,000 \text{ mm}^2$, which is not possible given the initial area of the trough is $\sim 5000 \text{ mm}^2$ and SEM images of deposited GO films have revealed a sub-monolayer. The same issue exists for CTAB. Assuming the cross-sectional area of CTAB is 0.2 nm^2 , the area provided by CTAB is $\sim 15,000 \text{ mm}^2$ which is not possible given the behavior of the surface pressure isotherms in Figure S6. These back of the envelope calculations do indicate a

much higher surface area of GO than CTAB, but the authors do not believe much more can be inferred from them.

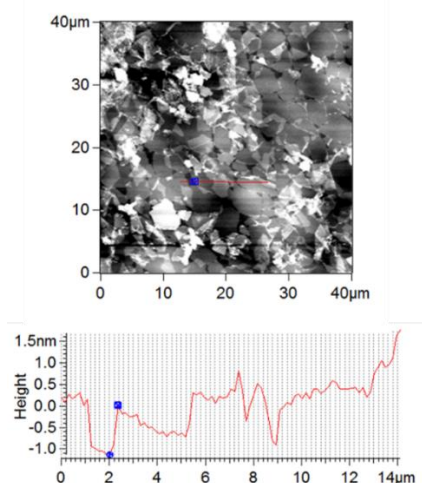


Figure S2. AFM micrograph of graphene oxide material. **Top:** AFM image of monolayer GO. **Bottom:** Cross-sectional height data displays the GO-to-substrate distance is ~ 1.1 nm and the GO is nearly completely exfoliated.

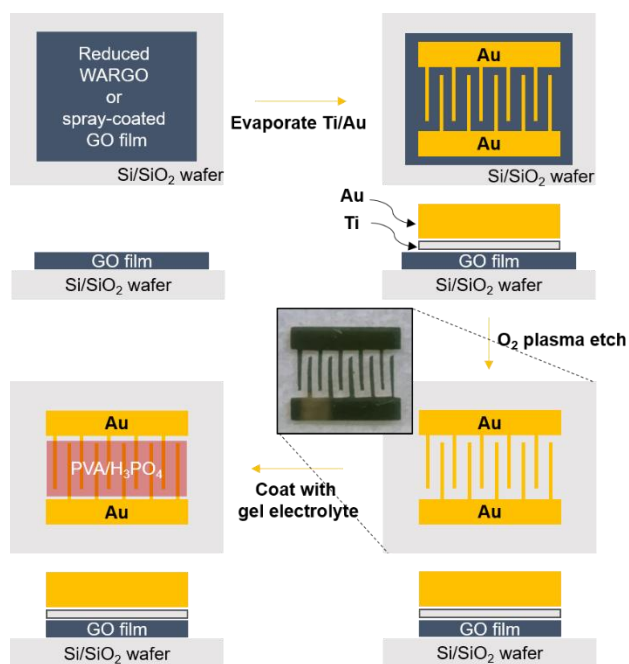


Figure S1. Schematic of device construction process. Beginning with a reduced GO film (upper left), a thin Ti/Au current conductor is evaporated through an acrylic interdigital mask (upper right). Subsequently, the reduced GO film that lies between the Ti/Au digits is etched away by oxygen plasma (lower right) and the polymer gel PVA/H₃PO₄ electrolyte is spread over the Ti/Au digits (lower left). Inset: a photograph of a finished device prior to the spreading of electrolyte.

Volumetric capacitance was calculated by:

$$C_{vol} = \frac{2I\Delta t}{V\Delta E} \quad (S1)$$

where I is the current (A), Δt is the discharge time (s), ΔE is the voltage change during discharge (V), and V is the volume of one electrode in the device (m^3). A factor of 2 is used in the numerator because the capacitance measured for the entire device is one-half of the capacitance for one electrode because the device is effectively two double-layer capacitors in series.

Energy (S2) and power density (S3) were calculated by:

$$E_{device} = \frac{1}{2} \frac{C_{vol}}{4} \Delta E^2 \quad (S2)$$

$$P_{device} = E_{device} / \Delta t \quad (S3)$$

Estimating electrode mass. The mass of the NF-GOS electrodes ($0.6 \mu g$) was estimated by assuming a nanofolded bilayer was deposited with each NF-GOS layer. Thus, the area of the electrodes ($0.25 cm^2$) was converted to mass by multiplying it by twice the number of layers deposited ($2 \times 15 = 30$ layers) and the specific surface area of graphene ($2630 m^2/g$). Mass of S-GOS electrodes ($0.5 \mu g$) was estimated by dividing the thickness after reduction ($19 nm$) by the expected thickness of a reduced GO monolayer ($0.5 nm/layer$) and multiplying by the specific surface area of graphene ($2630 m^2/g$).

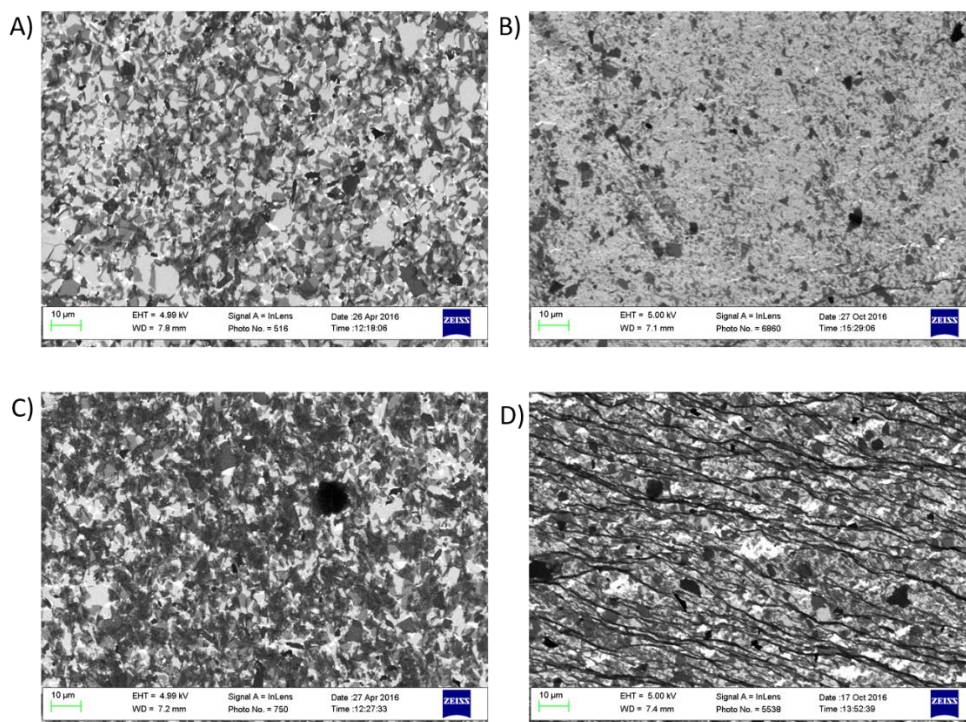


Figure S2. SEM images display that CTAB enhances the uniformity of GO films. A) GO film (0.05 mL of 0.25 mg/mL GO) compressed to $R_c=2.1$ shows substantial overlap (i.e., darker regions indicate multilayer GO). **B)** GO-CTAB film (0.1 mL of 1 mM CTAB, 0.1 mL of 0.25 mg/mL GO) compressed to $R_c=1.7$ shows limited overlap and enhanced uniformity (i.e., minimal contrast) due to

2D aggregation of GO-CTAB flakes. **C)** More compressed GO film (0.075 mL of 0.25 mg/mL GO) compressed to $R_c=3.8$ shows more overlap than in panel A. **D)** More compressed GO-CTAB film (0.1 mL of 1 mM CTAB, 0.1 mL of 0.25 mg/mL GO) compressed to $R_c=2$ shows nanofolding behavior.

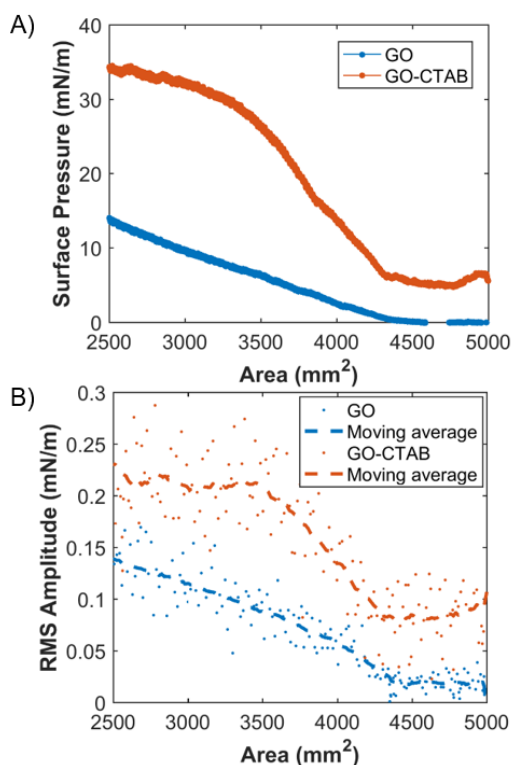


Figure S5. Surface pressure and periodic pulsing compression (PPC) for GO (0.25 mL of 0.25 mg/mL GO deposited) **and GO-CTAB** (0.1 mL of 1 mM CTAB and 0.1 mL of 0.25 mg/mL GO deposited). **A)** Typical surface pressure-area isotherms show linear behavior for GO and plateauing behavior for GO-CTAB. In the viscous dominant regime, the slope of the isotherm is much steeper for GO-CTAB than for GO, indicative of more in-plane rigidity. The plateau in the GO-CTAB isotherm indicates wrinkling behavior. **B)** Typical RMS amplitude during PPC show only viscous-dominant behavior for GO with no transition to elastic-dominant behavior. GO-CTAB films show a clear transition (i.e., plateau) to elastic-dominant (i.e., jamming) behavior which is indicative of the onset of wrinkling.

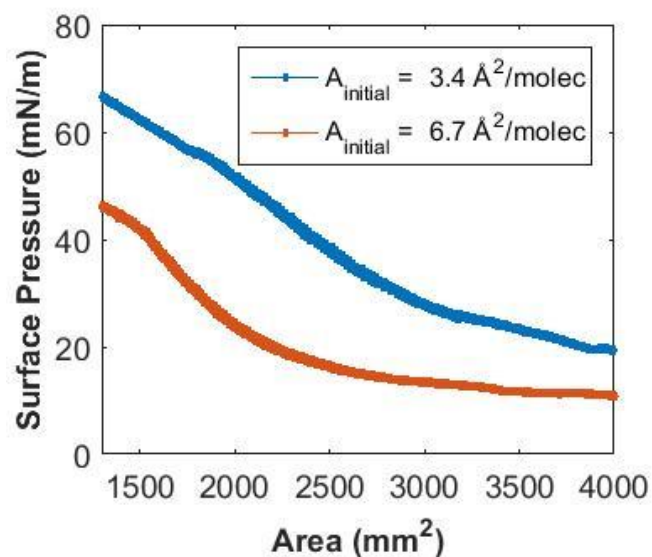


Figure S6. Surface pressure versus area isotherms for CTAB alone. The isotherm with initial molecular surface area of $6.7 \text{ \AA}^2/\text{molecule}$ is the same concentration used in the GO-CTAB isotherms in Figure 1. Even at much higher compression ($< 1500 \text{ mm}^2$) and higher concentration ($3.4 \text{ \AA}^2/\text{molecule}$), a plateau in surface pressure is not observed as it is in the GO-CTAB isotherms.

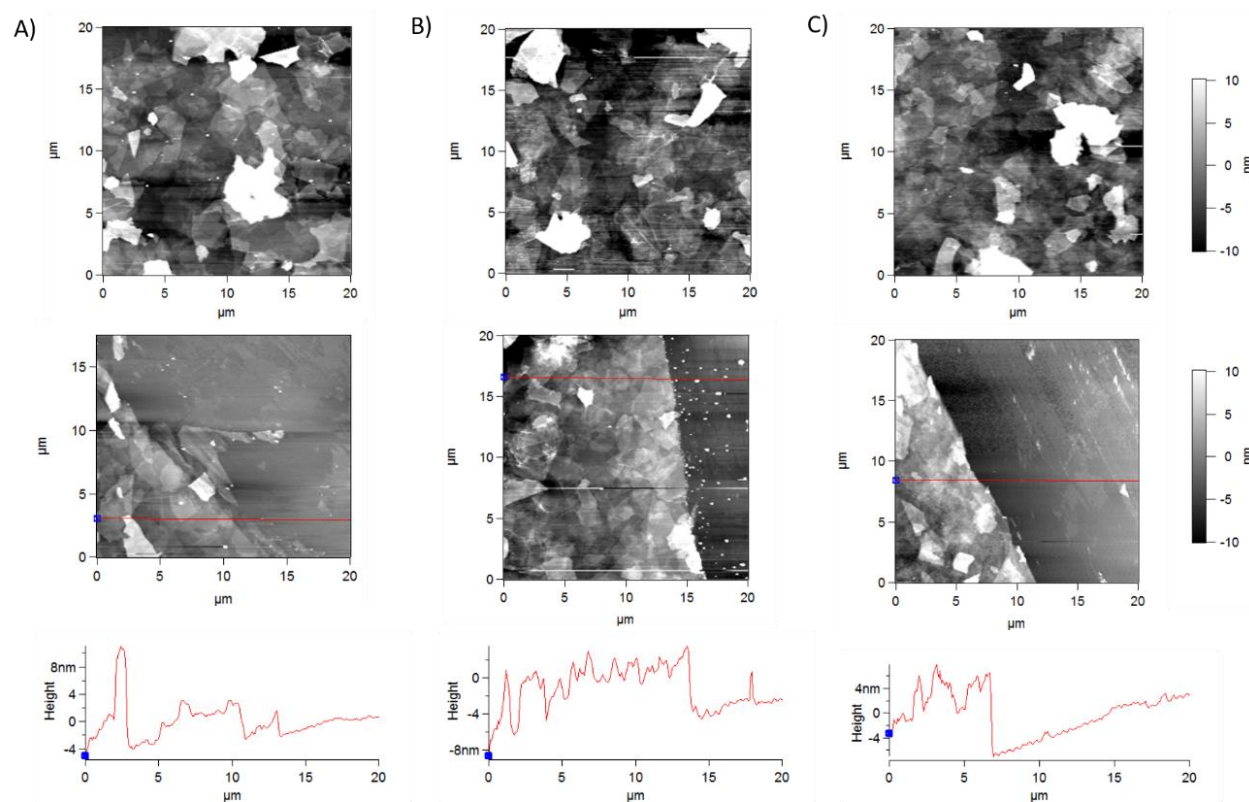
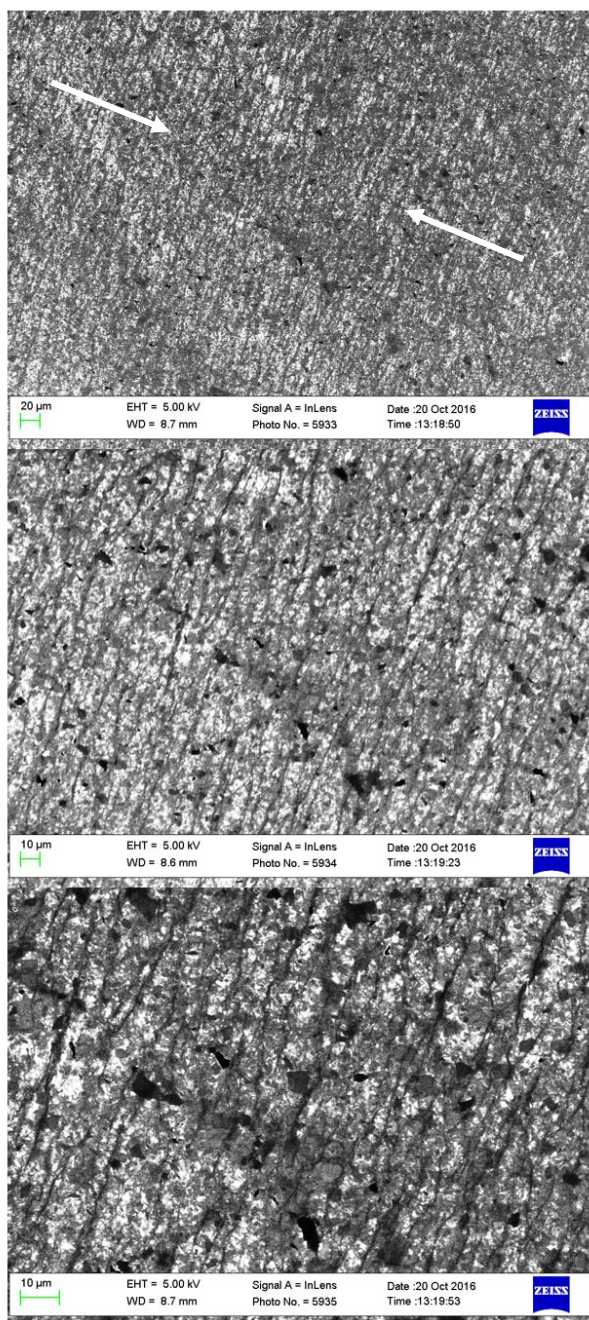


Figure S7. AFM images (top, center) and cross-sectional height data (bottom) for three-layer pure GO films with increasing volume of deposited GO. A) Three-layer GO film made from 0.3 mL of 0.25 mg/mL GO deposited per layer was denoted with $R_c=1$ (due to thickness corresponding to three monolayers of GO at ~ 4.5 nm). **B)** Three-layer GO film made from 0.5 mL of 0.25 mg/mL GO deposited per layer was denoted $R_c=1.7$. **C)** Three-layer GO film made from 0.7 mL of 0.25 mg/mL GO deposited per layer was denoted $R_c=2.3$. Bottom three AFM images and line scans include regions of both coated and uncoated substrate.

A)



B)

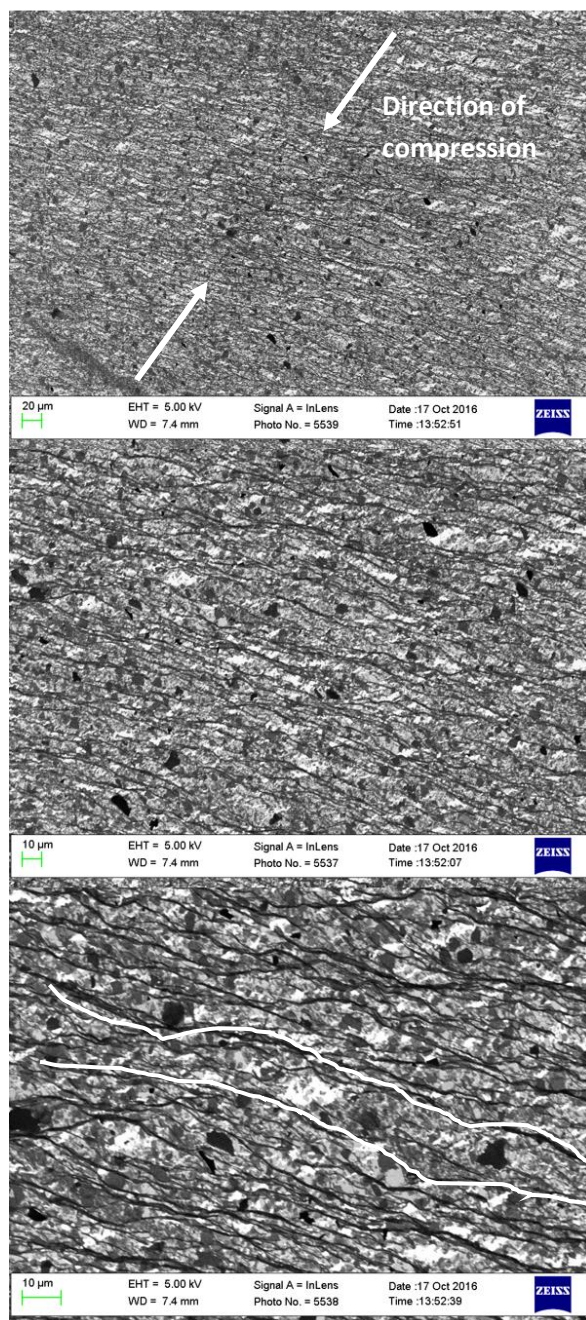


Figure S8. SEM of two samples of nanofolded GO-CTAB at different magnifications (top: 500X, middle: 1000X, bottom: 2000X, arrows indicate direction of compression). A) GO-CTAB nanofolded film prepared by injecting 50 μL of CTAB followed by 100 μL of GO and compressing to $R_c = 2$. B) GO-CTAB nanofolded film prepared by injecting 100 μL of CTAB followed by 100 μL of GO and compressing to $R_c = 2$. Two wrinkles are outlined for clarity in the bottom image.

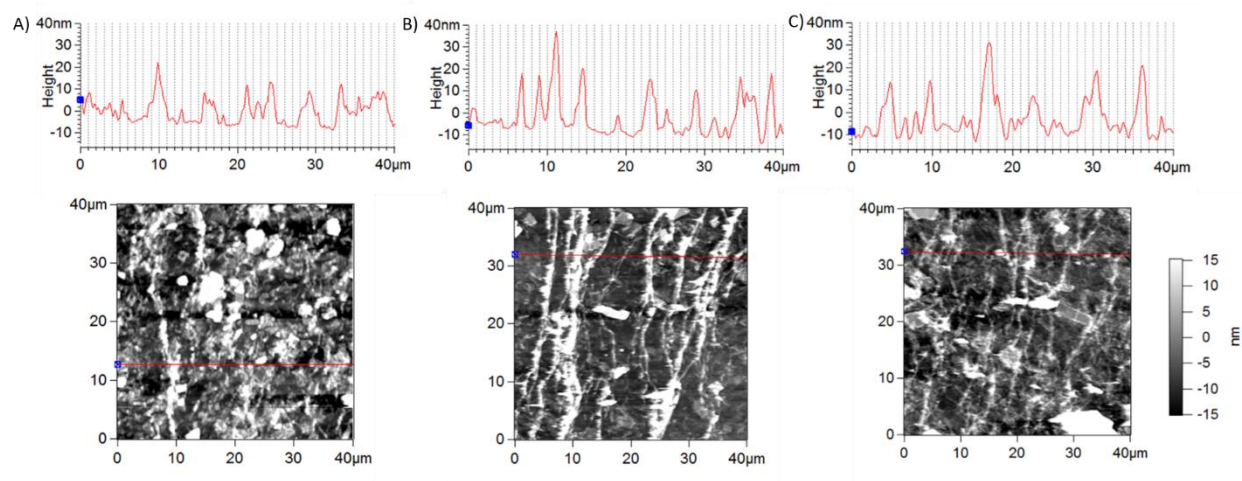


Figure S9. AFM of NF-GOS with increasing compression ratio. **A)** Line scan (top) and AFM image (bottom) of nanofolded GO-CTAB film at $R_c = 1.4$. **B)** Line scan (top) and AFM image (bottom) of nanofolded GO-CTAB film at $R_c = 2.0$. **C)** Line scan (top) and AFM image (bottom) of nanofolded GO-CTAB film at $R_c = 3.3$.

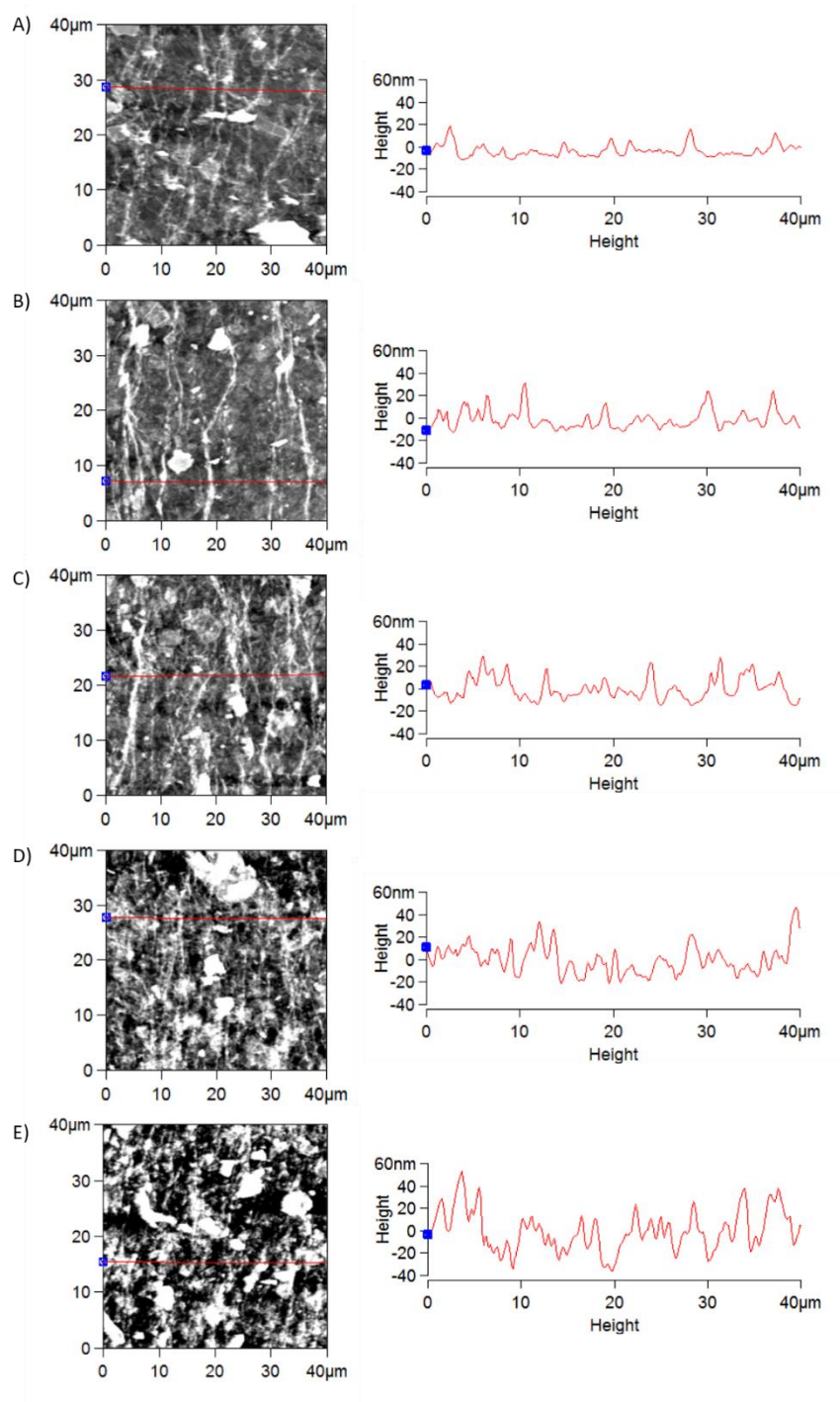


Figure S10. AFM of NF-GO with increasing number of layers deposited. A) AFM image (left) and line scan (right) of one layer nanofolded GO-CTAB film. **B)** AFM image (left) and section (right) of three-layer nanofolded GO-CTAB film. **C)** AFM image (left) and line scan (right) of six-layer nanofolded GO-CTAB film. **D)** AFM image (left) and line scan (right) of nine-layer nanofolded GO-CTAB film. **E)** AFM image (left) and line scan (right) of fifteen-layer nanofolded GO-CTAB film.

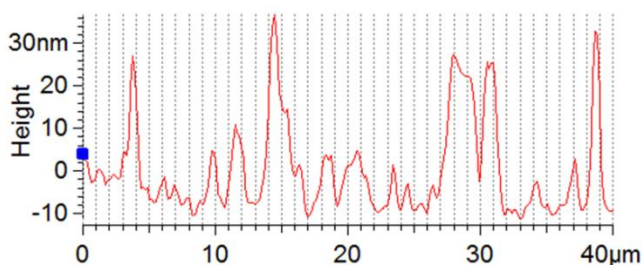


Figure S11. Sample AFM cross-sectional height profile of single-layer nanofolded GO-CTAB displaying typical nanofolded height (20-30 nm), width (1-3 μm), and separation ($\sim 10\text{-}15\ \mu\text{m}$).

XPS data shows O:C ratios for S-GOS (0.18 ± 0.01) and NF-GOS (0.23 ± 0.05) films are similar O:C ratios. Although samples were thoroughly rinsed after reduction in fuming hydroiodic acid, there remained $\sim 0.26\%$ residual iodine in NF-GOS and $\sim 0.10\%$ residual iodine in S-GOS. Iodine concentration in NF-GOS is slightly higher probably due to larger exposed surface area for adsorption. However, uncertainty in iodine atomic percentage is significant ($\sim 0.1\ \text{at.}\%$). Although this difference in iodine atomic percentage ($\sim 2.5\times$) could contribute in minor additional pseudocapacitance for NF-GOS devices, it could not account for the large differences ($>5\times$) in capacitance between NF-GOS and S-GOS at high scan rates ($>1\ \text{Hz}$) where kinetics of iodine redox are too slow.^[1]

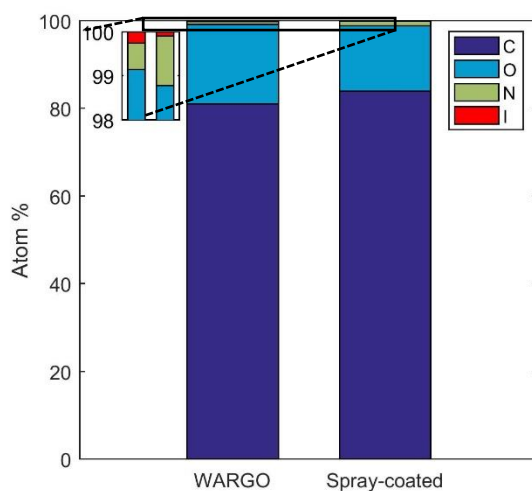


Figure S12. XPS data of reduced NF-GOS and S-GOS films.

Table S1. Atomic percentages of major constituents in reduced and unreduced NF-GOS and S-GOS films. Unreduced NF-GOS has a significantly lower O:C ratio than unreduced S-GOS because of partial reduction during low-temperature adhesion steps between each deposited GO-CTAB layer.

	C (at. %)	O (at. %)	O:C	N (at %)	I (at %)
Unreduced NF-GOS	77.9	19.5	0.25 ± 0.02	2.6	0.00
Reduced NF-GOS	81.0	18.1	0.23 ± 0.05	0.6	0.26 ± 0.08
Unreduced S-GOS	47.2	18.0	0.40 ± 0.07	1.2	0.01 ± 0.02
Reduced S-GOS	84.0	14.8	0.18 ± 0.01	1.1	0.10 ± 0.02

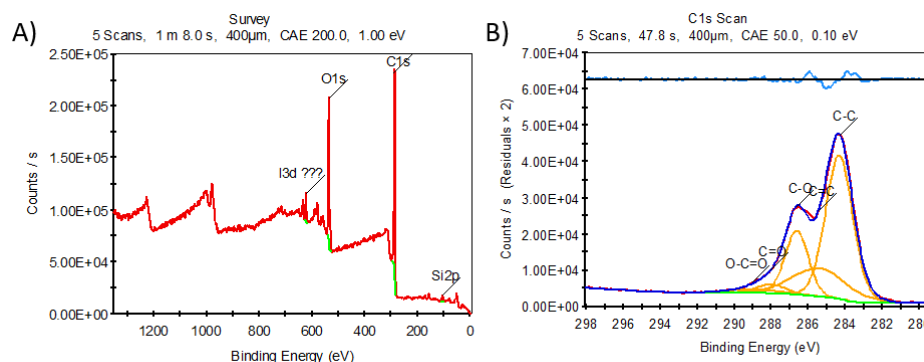


Figure S13. Sample XPS scans of NF-GOS. **A)** Sample survey scan of reduced NF-GOS. **B)** Sample deconvoluted high-resolution C1s peak of unreduced NF-GOS used to estimate the carboxylate concentration.

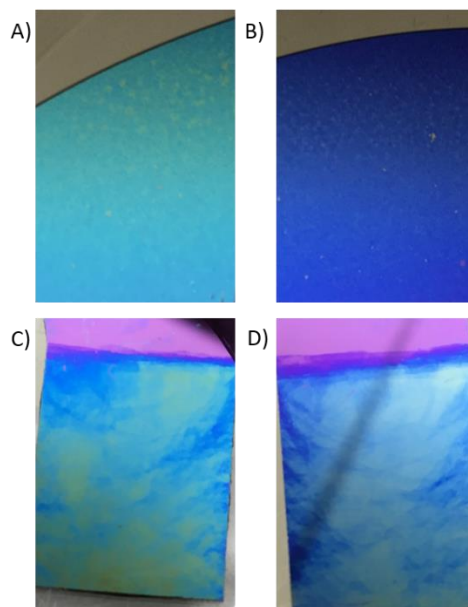


Figure S14. Images of S-GOS and NF-GOS films before and after reduction. **A)** Unreduced S-GOS film is a yellowish color. **B)** Reduced S-GOS is significantly darker. **C)** Unreduced NF-GOS film is a yellowish-brown color. **D)** Reduced NF-GOS film remains approximately the same color. It should be noted that unreduced films are approximately the same thickness (~50 nm).

EIS data modeling. Frequency-dependent capacitance was estimated based on the conventional RC equivalent circuit (**Figure S2**) using:



Figure S15. Schematic of RC equivalent circuit.

$$C = \frac{1}{2\pi f Z''} \quad (\text{S4})$$

where Z'' is the imaginary component of the impedance and f is the frequency (Hz). Although using an RC equivalent circuit is convenient for calculating the capacitance, it is not realistic because of the higher mass transfer resistance of the NF-GOS electrode. Thus, although capacitance trends observed in **Figure 3B** are likely accurate, the raw capacitance values are likely not accurate.

A Warburg impedance element was incorporated by using the Randle's equivalent circuit (**Figure S14**). The parameters for each component of the Randle's circuit were fitted to the EIS data using CH Instruments AC-impedance modeling software.

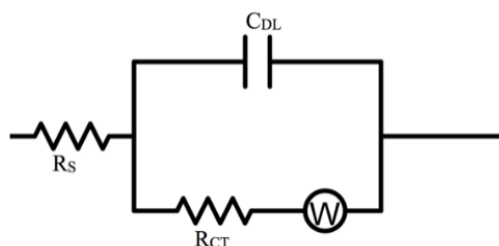


Figure S16. Schematic of Randle's equivalent circuit where R_s is the equivalent series resistance (including electrode resistance, solution resistance, and contact resistance), C_{DL} is the double-layer capacitance, R_{CT} is the charge transfer resistance, and W is the Warburg impedance.

References.

1. G. Lota, E. Frackowiak, Striking capacitance of carbon/iodide interface. *Electrochem. Commun.* **2009**, *11* (1), 87-90.