Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Modification of Mechanical Properties of Vertical Graphene Sheets via Fluorination

Keivan Davami[1,2]*, Yijie Jiang[1], Chen Lin[1], John Cortes[1], Jeremy T. Robinson[3], Kevin T. Turner[1], Igor Bargatin[1]*

[1]Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

[2]Department of Mechanical Engineering, Widener University, One University Place, Chester, PA 19013, USA

[3]Naval Research Laboratory, Washington, D.C. 20375

*Corresponding authors: kdavami@seas.upenn.edu & bargatin@seas.upenn.edu

1. Raman Spectra of the VG Sheets

The Raman spectra of pristine VG sheets show four main peaks: D (~1330 cm^{-1}), G (~1580 cm^{-1}), D' (~1620 cm^{-1}) and 2D (~2660 cm^{-1}). It should be noted that a strong D peak is common in VG sheets due to the large number of edges, small crystallite size, and the dense structure of the VG sheets [1]. Figure S1 shows that the D peak (attributed to atomic scale defects) becomes wider and stronger with increasing fluorine content, indicating a higher degree of structural disorder. In Figure S1, the D/G ratio is 2.2 for pristine samples, but decreases to 2.0 for the 200 and 500 cycle-fluorinated samples. It should be noted that there are two different stages (Stage I and Stage II) associated with increasing defect concentration in sp^2 carbon. In Stage I the D/G peak ratio increases, and then in Stage II it decreases as the material becomes more nanocrystalline [2]. The full-width at half-maximum (FWHM) of the D peak is ~38 cm^{-1} for the pristine sample, increasing to ~46 cm^{-1} and ~48 cm^{-1} for the 200 and 500 cycle-fluorinated samples, respectively. For the highest fluorination exposure (500 cycles), similar to that reported previously for horizontal graphene [3], the G, D, and 2D peaks all become weaker, indicating a significant reduction in the quantity of sp^2-hybridized carbon [4].

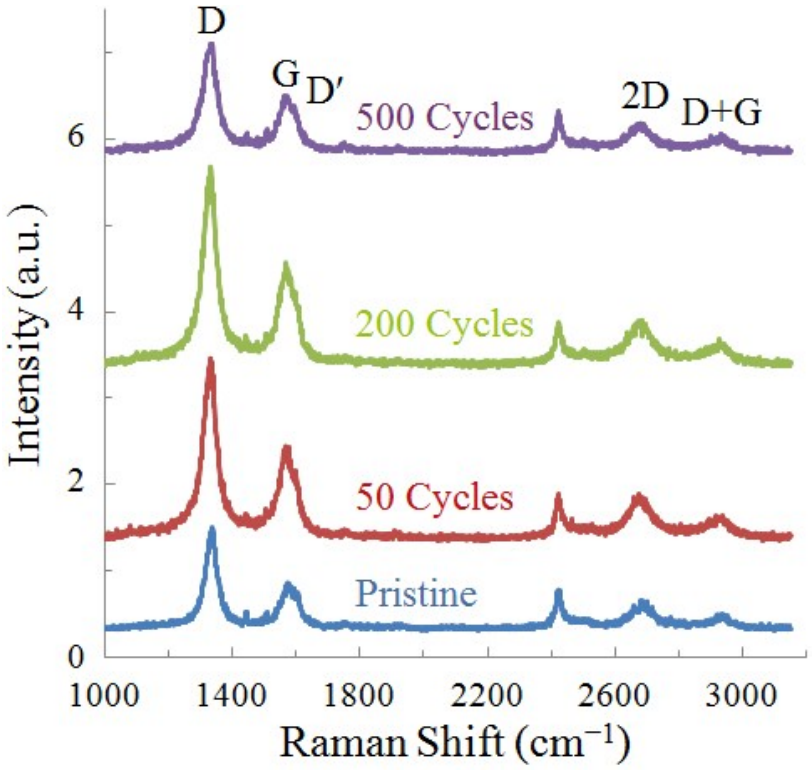
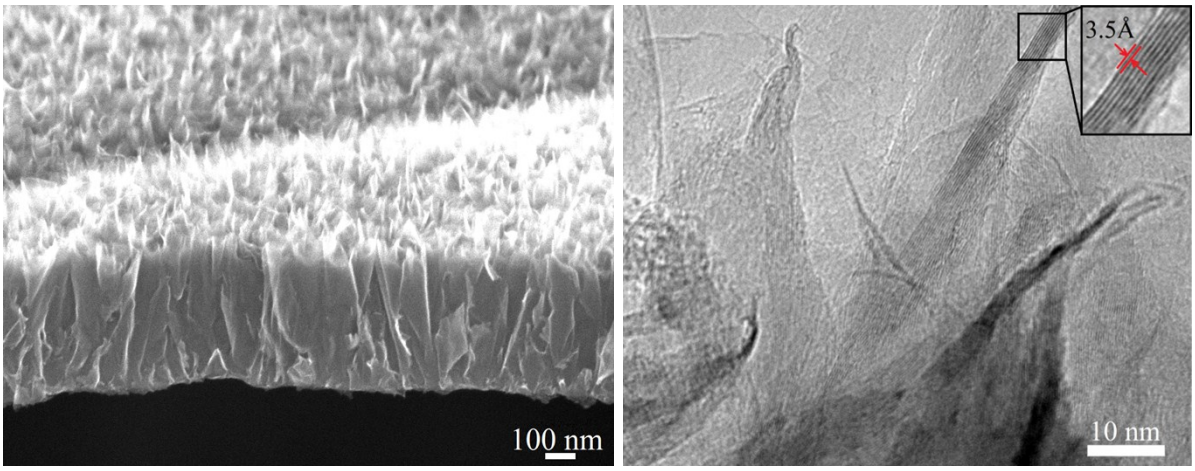


Figure S1. Raman spectra of pure and functionalized graphene, measured each time under the same Raman conditions. The successive spectra are offset for clarity.

2. Micrographs of a Pristine VG Sample



(a) (b)

Figure S2. (a) A cross-sectional SEM image of the VG sheets on a copper substrate. The tilt angle is slightly less than 90°. The scale bar is 100 nm. (b) A high-magnification TEM image of several VG sheets with inset showing distance between carbon layers. An interlayer distance of 0.35 nm is similar to that of graphite. The scale bar is 10 nm.

3. Energy-Dispersive X-ray Spectroscopy (EDS) Analysis

Table S1. Atomic percentages of carbon and fluorine for different samples.

Cycles of functionalization	Average atomic percent of fluorine content (%)	Average atomic percent of carbon content (%)
50	0.8	99.2
100	2.35	97.65
200	3.4	96.6
300	3.5	96.5
400	3.5	96.5
500	3.7	96.3

4. Selection, Characterization, and an SEM Image of the Tip

Given that the effective Young's modulus of VG sheets ranged from ~5 to 30 MPa, a tip with a stiffness of 2.5 N/m was chosen in accordance with the Bruker PeakForce QNM User Guide (Table S2). The spring constant was measured 6 times using the thermal tune method and calculated by the Bruker AFM built-in software. Tip radius was determined from the SEM image of the tip shown in Figure S2.

Table S2. Suggested cantilever spring constant in QNM User Guide.

Sample Modulus (E)	Nominal Spring Constant (k)
1 MPa < E < 20 MPa	0.5 N/m
5 MPa < E < 500 MPa	5 N/m

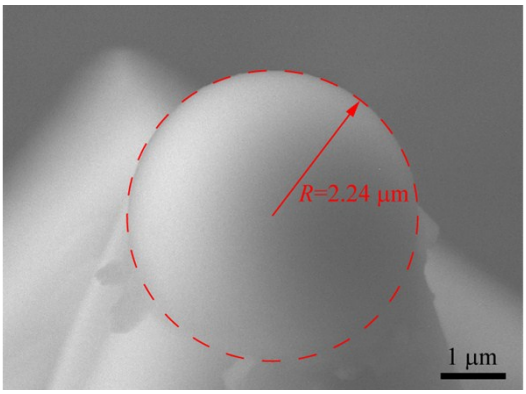


Figure S3. An SEM image of the tip.

5. Maps of Different Properties Provided by the PeakForce QNM® Method

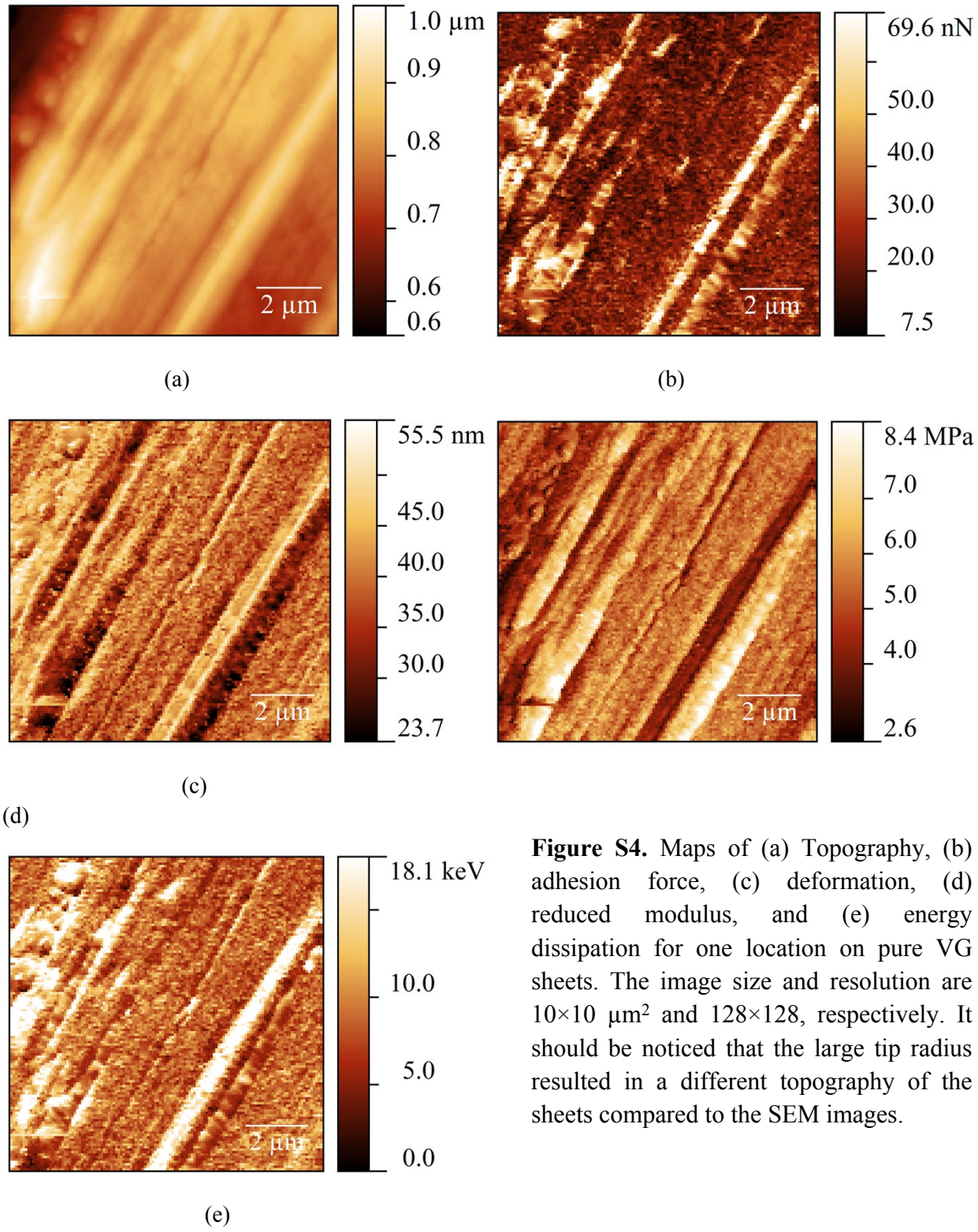


Figure S4. Maps of (a) Topography, (b) adhesion force, (c) deformation, (d) reduced modulus, and (e) energy dissipation for one location on pure VG sheets. The image size and resolution are 10×10 µm^2 and 128×128, respectively. It should be noticed that the large tip radius resulted in a different topography of the sheets compared to the SEM images.

6. Verification of the Results with a Second Probe

Table S3. A comparison of the results obtained with two different probes.

# of Cycles		Reduced Modulus (MPa)	Peak Force (nN)	Adhesion (nN)	Deformation (nm)	Dissipation (keV)
500.0	**Tip 1**	32.7	101.6	12.2	17.5	1.5
	Tip 2	30.1	90.2	10.6	17.1	1.8
400.0	**Tip 1**	30.4	97.9	12.1	18.2	1.9
	Tip 2	26.7	99.7	10.5	19.9	3.4
300.0	**Tip 1**	22.9	100.5	19.0	20.1	5.1
	Tip 2	25.4	105.7	19.5	23.7	4.2
200.0	**Tip 1**	17.1	97.5	14.0	24.3	6.5
	Tip 2	19.6	96.4	11.0	23.5	2.6
100.0	**Tip 1**	17.5	99.1	13.8	31.6	9.5
	Tip 2	12.5	102.0	12.8	31.6	6.4
50.0	**Tip 1**	8.4	97.8	12.1	31.3	8.4
	Tip 2	8.6	91.5	11.0	36.3	6.2

References

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4. Robinson, J. T.; Burgess, J. S.; Junkermeier, C. E.; Badescu, S. C.; Reinecke, T. L.; Perkins, F. K.; Zalalutdniov, M. K.; Baldwin, J. W.; Culbertson, J. C.; Sheehan, P. E.; Snow, E. S., Properties of Fluorinated Graphene Films. *Nano Letters* **2010,** 10, (8), 3001-3005.