Cite This: ACS Nano 2018, 12, 6089–6099

www.acsnano.org

The Role of Water in Mediating Interfacial Adhesion and Shear Strength in Graphene Oxide

Rafael A. Soler-Crespo,[†] Wei Gao,^{‡,§} Lily Mao,^{||} Hoang T. Nguyen,[†] Michael R. Roenbeck,[‡] Jeffrey T. Paci,^{||,⊥}[®] Jiaxing Huang,^{*,#}[®] SonBinh T. Nguyen,^{*,||®} and Horacio D. Espinosa^{*,†,‡}

[†]Theoretical and Applied Mechanics Program, [‡]Department of Mechanical Engineering, ^{||}Department of Chemistry, and "Department of Materials Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[§]Department of Mechanical Engineering, University of Texas at San Antonio, San Antonio, Texas 78249, United States ¹Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3 V6, Canada

Supporting Information

ABSTRACT: Graphene oxide (GO), whose highly tunable surface chemistry enables the formation of strong interfacial hydrogen-bond networks, has garnered increasing interest in the design of devices that operate in the presence of water. For instance, previous studies have suggested that controlling GO's surface chemistry leads to enhancements in interfacial shear strength, allowing engineers to manage deformation pathways and control failure mechanisms. However, these previous reports have not explored the role of ambient humidity and only offer extensive chemical modifications to GO's surface as the main pathway to control GO's interfacial properties. Herein, through atomic force microscopy experiments on GO-GO interfaces, the adhesion energy and interfacial shear strength of GO were measured as a function of ambient humidity. Experimental evidence shows that adhesion energy and interfacial shear strength can be improved by a factor of 2-3 when GO is exposed to moderate (~30% water weight) water content. Furthermore, complementary molecular dynamics simulations uncovered the mechanisms by which these nanomaterial interfaces achieve their properties. They reveal that the strengthening



mechanism arises from the formation of strongly interacting hydrogen-bond networks, driven by the chemistry of the GO basal plane and intercalated water molecules between two GO surfaces. In summary, the methodology and findings here reported provide pathways to simultaneously optimize GO's interfacial and in-plane mechanical properties, by tailoring the chemistry of GO and accounting for water content, in engineering applications such as sensors, filtration membranes, wearable electronics, and structural materials.

KEYWORDS: graphene oxide, adhesion energy, interfacial shear strength, surface roughness, water content

wo-dimensional materials (2D), such as graphene, have garnered significant interest as candidate building blocks in the design of nanomaterials-based devices,¹ sensors,³ filtration membranes,⁴ wearable electronics,⁵ and structural materials.⁶ However, the poor interlayer cohesion present in these materials, which often leads to lubricating behavior⁷ and shear-driven failure,⁸⁻¹⁰ has impeded their application in devices that require multilayer films.¹¹ For instance, graphene has been shown to possess very poor interlayer shear strengths (<1 MPa) which lead to facile interlayer sliding.^{7,11,12} Thus, it is not surprising that the functionalized variants of 2D materials, which can be made using facile syntheses that lead to tunable chemistry,¹³ have acquired significant interest for such applications.^{1,4,13-17} For instance, the tunable surface chemistry present in graphene oxide (GO), an oxidized variant of graphene,¹³ allows it to form

strongly interacting and dense hydrogen-bond networks,^{15,18} which provide fascinating opportunities to tailor interfacial interactions and enhance resistance to shear failure. Indeed, recent studies have demonstrated the utilization of such 2D constituents to maximize packing efficiency and load transfer in nanocomposites, for instance, in GO-based nanocomposites.¹⁹ Other theoretical studies have shown that improving interfacial shear strength between nanoscale constituents delivers commensurate enhancements in mechanical strength for carbon nanotube yarns.²⁰ As analogous improvements in mechanical properties would enhance the lifetime and

Received: March 29, 2018 Accepted: June 5, 2018 Published: June 5, 2018



Figure 1. (a) Schematic of the experimental setup in which a GO-coated SiO₂ sphere contacts a substrate-supported GO surface, providing interfacial information when subjected to different loading conditions (F_{normal} and F_{shear}). Gray, blue, silver, and yellow colors represent GO, SiO₂, Si, and gold surfaces, respectively. (b) Schematic of hydrogen bonding in GO, through GO–GO and GO–water–GO hydrogen bonds. Gray, red, and green beads represent carbon, oxygen, and hydrogen atoms, respectively. (c) Scanning electron microscopy post-testing inspection of AFM cantilever with a ~6 μ m diameter spherical tip. The integrity and presence of GO flakes in the bead apex is confirmed by Raman spectroscopy both pre- and post-testing (see Supporting Information, section S2). (d) AFM scan of a GO film deposited on a SiO₂ surface *via* the Langmuir–Blodgett process. The red box is used to determine thickness and surface roughness.

operating capabilities of GO-based devices, the practical realization of such enhancements would have significant implications in materials design and development and propose directions to engineer GO-based materials.

To improve the interfacial properties of GO-based systems, one must carefully consider surface roughness, chemistry, and operating environmental conditions. Researchers have recently proposed that by increasing the relative amount of hydroxyl functional groups on GO's surface, the hydrogen-bonding energy at the GO-GO interface can be increased, leading to enhanced interfacial shear strength.¹⁸ However, the experimental verification of such a hypothesis was limited because the effects of surface roughness and environmental humidity, which have been shown to greatly influence observable interfacial properties,²¹⁻²⁴ were not accounted for. Moreover, we recently demonstrated that hydroxyl-rich GO monolayers possess poorer ductility when compared to that of their epoxide-rich counterparts.^{25,26} Therefore, it is highly desirable to identify synthesis routes and operational conditions (water content) that leverage the reactive surface chemistry of GO to improve interlayer cohesion. In this light, the acceptor-donor behavior of water,¹⁵ its propensity to form hydrogen bonds,¹⁵ and pathways to control relative water content in certain applications make it attractive as a means to enhance the interfacial properties of GO.

Herein, we report a comprehensive experimental-computational study of the interfacial properties for relatively smooth

(*i.e.*, ~1 nm roughness, as opposed to ~8 nm by Daly *et al.*¹⁸), nanoscale, epoxide-rich GO-GO interfaces, over a broad range of humidity levels. We present an estimate of the intrinsic adhesion energy of GO, which is a key parameter of interest in device pull-off related failure modes, and its variation with water content. By carefully controlling the relative environmental humidity, we demonstrate that the interfacial shear strength for GO is at least 300% higher than that of graphene, reinforcing the positioning of GO as a promising candidate 2D material for device fabrication. Finally, experimental measurements are correlated with molecular dynamics simulations to elucidate the mechanisms that govern interfacial interactions under pull-off and sliding deformation modes. Our results demonstrate the beneficial role of water, which mediates adhesion and shear interactions at the nanoscale through improved hydrogen bonding across GO interfaces, providing a complementary tuning mechanism to the reported chemical strategies for modifying the surface properties of GO.¹³ Most importantly, these findings provide a set of benchmarks that should be considered in the characterization of nanoscale interfaces and the extraction of effective interfacial properties, both of which will be of enormous importance in guiding the design of engineered materials.

RESULTS AND DISCUSSION

Characterization of GO-Coated Surfaces. The adhesion energy (*G*) and interfacial shear strength (τ_0) of GO-GO

interfaces were quantified, as a function of humidity, *via* atomic force microscopy (AFM) to elucidate the role of water in mediating interfacial interactions (Figure 1a,b). GO-coated spheres were fabricated by dip-coating 6 μ m diameter SiO₂ spherical AFM tips in a solution containing a suspension of GO nanosheets (Figure 1c). To serve as the contact substrate, GO nanosheets were also transferred to a SiO₂-coated Si wafer (Figure 1d) *via* Langmuir–Blodgett deposition.²⁷ The GO-coated sphere and substrate were made to contact under varying normal applied loads (F_{normal} , Figure 1a) within a custom-designed humidity control AFM chamber, and friction (sliding) tests were conducted to probe the interfacial behavior between GO nanosheets by measuring shear load responses (F_{sheart} Figure 1a).

The GO sheets in this study were synthesized using a modified Hummer's method,²⁷ and representative GO monolayers were characterized via X-ray photoelectron spectroscopy (XPS) (see Materials and Methods for further details). XPS has been successfully employed to probe the surface chemistry of 2D monolayers in several works.^{13,28-32} Based on peak decomposition analysis of the collected XPS spectra, a functionalization (i.e., surface coverage) of ~70% was measured for the GO sheets at an epoxide/hydroxyl ratio of 4:1 (see Supporting Information, section S1, for further details). Our XPS analysis of GO composition was crucial to qualitatively understand the obtained measurements from a chemistry standpoint and to construct meaningful MD representations to explore the mechanistic behavior of adhesion and friction in water-mediated GO-GO interfaces. To further confirm the detected composition, the C 1s spectrum of the GO used in this study was compared to reported XPS data for highly functionalized, epoxide-rich GO^{32} and lightly oxidized GO functionalized primarily by hydroxyl functional groups.³¹ The composition and C 1s spectrum of the GO sheets in this study are comparable to the signatures for the spectra of highly functionalized and epoxide-rich GO-supporting the findings of peak decomposition analysis. Raman spectroscopy was performed on the sliding contact points of the GO-coated sphere and substrate to ensure the presence and adherence the GO nanosheets pre- and post-AFM friction measurements (see Supporting Information, section S2, for further details). Analysis of the Raman spectra confirmed the presence of the D (\sim 1340 cm⁻¹) and G (\sim 1600 cm⁻¹) peaks, which are characteristic of the structure of GO.33 In addition, the adherence of GO was qualitatively inspected via post-testing scanning electron microscopy characterization (Figure 1c).

Given the atomic interactions between GO-coated surfaces in AFM friction experiments, it is to be expected that nanoscale roughness^{18,21,23,34} poses significant challenges in accurately quantifying adhesion energy and interfacial shear strength. Indeed, previous studies on the effect of nanoscale asperities in the surface of platelet-like systems (e.g., diamond and mica) have shown their impact on effective interfacial properties due to dramatic increases in contact area.^{21–23,35} Daly et al. recently reported a very low interfacial shear strengths (5.3 \pm 3.2 MPa for 20% oxidized hydroxyl-rich GO), using an AFM methodology similar to the one reported herein, for drop-casted GO presenting an arithmetic average substrate roughness of $R_a \sim 8$ nm. In addition to chemical differences between the studied GO archetypes, Daly et al. did not account for the roughness of the surfaces or the effects of humidity,¹⁸ which undoubtedly affected their interfacial measurements. By comparison, the root-mean-square roughness of the GO-coated substrates ($R_{q} \approx$

0.15 nm) and spheres employed in this study ($R_q \approx 1.1$ nm) suggests much smoother contacts closer to GO's intrinsic roughness (see Supporting Information, section S3, for further details). In this light, the smoother and chemically well-characterized surfaces employed in this study closely represent the intrinsic properties of GO–GO interfaces, which, in turn, permits better comparison to interfacial properties derived from molecular dynamics (MD) simulations.

Experimental Analysis of Adhesion Energy and Interfacial Shear Strength. Adhesion energy and interfacial shear strength were extracted employing the Carpick–Ogletree–Salmeron (COS) data analysis procedure³⁶ based on Maugis–Dugdale contact theory.³⁷ In this approach, a normal load is applied *via* the GO-coated sphere to the GO-coated substrate followed by lateral sliding between the sphere and the substrate. The resulting shear load response is measured through friction loops (Figure 2a) and directly



Figure 2. (a) Representative shear load (F_{shear}) voltage measurement, as directly obtained from lateral force microscopy measurements, for a given applied normal load (F_{normal}) . (b) Representative shear load-applied normal load fits to extract interfacial properties, according to Carpick–Ogletree–Salmeron formulation of Maugis–Dugdale theory. All measured data are shown and fit according to second derivative criterion (see text). Dashed lines are extrapolations of model fit to predicted pull-off force. (c,d) Roughness-corrected (G') adhesion energy (c) and interfacial shear strength (d) for GO–GO interfaces as a function of relative humidity. Error bars correspond to mean value \pm standard deviation for 10 measurements.

correlated with the applied normal load using the COS procedure. Representative shear loads measured experimentally are shown in Figure 2b as a function of applied normal load and relative humidity. The results closely follow the behavior predicted by the COS framework of the Maugis–Dugdale model at positive (compressive) applied normal loads (*i.e.*, when the GO-coated sphere is compressed against the GO-coated substrate) but deviate considerably from this theory under *strongly* negative (tensile) applied normal loads (*i.e.*, when the GO-coated sphere is attracted toward the GO-coated substrate despite a counteracting normal force exerted by the

cantilever). Clearly, the sharp transition in the shear response in the latter regime suggests that sliding under strongly negative applied normal loads induces distinct mechanical behavior that appears not well described by adhesive contact mechanics theory.

A plausible interpretation of this distinct mechanical behavior under strongly negative applied normal loads is the potential intermittent loss of contact across the GO-GO interface. For instance, when the cantilever supporting the GO-coated sphere is subjected to negative applied loads during sliding, the sphere (which possesses finite, nanoscale roughness) would be more likely to experience occasional disruptions in shear load transfer than it would under compressive conditions. This complicates analysis of friction loops and, thus, prevents reliable interpretation of shear forces. It should likewise be noted that a previous AFM-based friction study of GO only considered frictional behavior in the compressive regime.¹⁸ It is known that under purely compressive loads, strong coupling between adhesive and shear deformations can lead to artifacts in the determination of interfacial properties. This can be accounted for, within the COS framework, by fitting interfacial interactions over attractive and compressive regimes. To aid in detecting applied loads for which intermittent loss of contact occurred, we calculated the second derivative of the shear load with respect to applied normal load (*i.e.*, $d^2F_{\text{shear}}/dF_{\text{normal}}^2$) and identified the inflection point at which this distinct mechanical behavior is observed. Data below this critical applied normal load are excluded from consideration during fitting.

To extract adhesion energy, *G*, and average interfacial shear strength, τ_{0} , we fit the experimental shear load, as a function of applied normal load, and leave the pull-off force, $F_{pull-off}$ the transition parameter, α , that describes the range of surface forces, and the shear force at zero applied normal load, F_0 , as free parameters determined from the model fit (see Supporting Information, sections S4 and S5, for details). With this strategy, it is possible to predict adhesion energy and interfacial shear strength using the following equations:

$$G = \frac{F_{\text{pull-off}}}{\pi R \hat{L}_{c}}; \ \hat{L}_{c} = \hat{L}_{c}[\lambda(\alpha)]$$
(1)

$$\tau_0 = \frac{F_0}{\pi a_0^2}; \ a_0 = a_0[\lambda(\alpha)]$$
(2)

where R is the radius of the indenting sphere, a_0 is the contact radius at zero applied normal load, and \hat{L}_c and λ are nondimensional constants related to α .³⁶ It is noteworthy that, in fitting the data, we consistently found $\alpha \approx 0$, corresponding to the traditional Derjaguin-Muller-Toporov contact mechanics limit, which is to be expected for stiff, nanoscale contacts such as those used herein.^{34,36,38} It is worth mentioning that while our contact surfaces are relatively smooth, any comparison to atomistic calculations, or estimation of intrinsic interfacial properties, requires the contact of surfaces whose roughness is comparable to GO's intrinsic roughness. Thus, to address the effects of roughness in our measurements, we augmented roughness correction models from previous work reported in the literature^{16,23} to account for the intrinsic roughness of surfaces and estimate the area of true interfacial contact in adhesion, yielding an estimate of intrinsic adhesion energy G' (see Supporting Information, section S6, for details).^{21,22} Analogous corrections for interfacial shear strength do not exist in the literature, as current continuumbased models cannot describe the dynamic nature of nanoscale contacts,^{34,36,39} thereby illustrating the importance of attaining atomically smooth surfaces to experimentally extract intrinsic shear properties.

The experimentally measured adhesion energy and interfacial shear strength for GO-GO surfaces, as a function of relative humidity, are reported in Table 1 and Figure 2c,d. In the

Table 1. Adhesion Energy and Interfacial Shear Strength as a Function of Relative Humidity for GO–GO Interfaces (10 Experiments Performed at Each Humidity Level)^a

relative humidity (%)	bulk water content (wt %)	uncorrected adhesion energy (J/m ²)	roughness- corrected adhesion energy (J/m ²)	interfacial shear strength (MPa)
13 ± 4	13 ± 3	0.016 ± 0.003	0.11 ± 0.02	28 ± 1
30 ± 1	18.1 ± 0.1	0.026 ± 0.002	0.17 ± 0.01	38 ± 6
45.9 ± 0.7	19.3 ± 0.1	0.031 ± 0.01	0.20 ± 0.07	44 ± 5
61.2 ± 0.5	23.7 ± 0.3	0.032 ± 0.008	0.21 ± 0.05	63 ± 30
^{<i>a</i>} Data are presented as mean value \pm standard deviation.				

experiments, the roughness-corrected adhesion energy (G')varies from 0.11 \pm 0.02 J m⁻² (mean value \pm standard deviation) at ~10% relative humidity to 0.21 \pm 0.05 J m⁻² at \sim 60% relative humidity. Noteworthy is the correction factor of \sim 6 that must be applied to account for roughness effects in the indenter-substrate contact at zero applied normal load, even when the roughness of the surfaces used in this study are well below previous and comparable reports.¹⁸ This adhesion energy correction factor agrees well with previous reports in the literature for contact surfaces of similar roughness.²¹ Notably, the variability in the measurements becomes more significant as humidity increases. As the MD simulations discussed in the next section reveal, local variations in GO chemistry have a larger impact on adhesion energy and interfacial shear strength as water content increases. Furthermore, variations in the contact region (*i.e.*, roughness and the area fraction of graphitic versus oxidized GO regions) can lead to deviations in experimental conditions and contribute to measurement fluctuations due to the chemical nature of the material. These observations serve as indicators of the sensitive nature of adhesive processes in molecular interfaces, where the effective (*i.e.*, measured) adhesion energy can fall well below molecular dynamics estimates. Indeed, this study and others highlight the need to carefully control and characterize contacting surfaces, as miniscule variations in roughness²¹ and local chemical environment¹⁸ can lead to significant changes in effective interfacial behavior.

The measured interfacial shear strength of 70% oxidized GO with a 4:1 epoxide/hydroxyl functional group ratio ranges from 28 ± 1 to 63 ± 30 MPa as a function of humidity, closely resembling the corresponding trends in adhesion energy. Importantly, because both adhesion energy and interfacial shear strength are directly proportional to the relative humidity in the experiments, the degree of interfacial hydrogen bonding across 70% oxidized epoxide-rich GO is expected to increase through water-mediated interfacial interactions. Notably, and similar to how the in-plane mechanical properties of GO can be tuned by controlling its chemistry,^{25,26} the experimental findings reported here show that GO–GO interfacial properties can be modified by manipulating the functionalization and intercalated water content. Remarkably, our findings suggest that GO-based device resilience can be enhanced by tuning

adhesion energy to decrease the likelihood of failure due to cleavage, associated with out-of-plane deformations, during device operation. In a similar fashion, the onset of lateral sheet pull-off (*i.e.*, from wrinkling in wearable electronics) can be prevented by tuning constituent interfacial shear strengths in devices. Similar concepts have been explored for carbon nanotube yarns and directly reflect the link between constituent shear strength and device failure strength in composites.²⁰

In this light, and from a structural materials or device perspective, graphene oxide, which is easily synthesized and contains intrinsic chemistry capable of interacting with itself and ambient water molecules,¹³ greatly benefits from the presence of functional groups which form strong hydrogenbonding interactions. These interactions, in turn, improve GO's interfacial shear strength (28-63 MPa) orders of magnitude beyond those of graphene (0.04 MPa),⁷ its less chemically functionalized counterpart, as graphene cannot benefit from significant interfacial interaction mechanisms such as those between GO and water. Indeed, previous studies on the interfacial properties of graphene have shown that graphene interactions are dominated by van der Waals forces,⁴⁰ which can be expected to force water outward from its gallery spacing, therefore making graphene-water systems much less attractive than its GO counterparts. In combination, thus, these functional chemistries make GO an excellent candidate building block for the next generation of engineered devices and demonstrate the potential of the material in engineering nanocomposites with optimized load transfer.^{19,26}

Mechanistic Understanding of Adhesion and Shear in GO-GO Interfaces. Understanding the mechanisms that enhance GO's interfacial properties as a function of water content will enable exploiting this feature during device design and provide knowledge to scientists that will suggest potential chemical modifications to analogous 2D systems (i.e., functionalized 2D piezoelectric materials). Here, we discuss simulations performed with the ReaxFF force field to gain a mechanistic understanding of the experimental findings. In the simulations, we probe the key mechanisms that arise during GO-GO pulloff and sliding (i.e., shearing) and extract adhesion energy and interfacial shear strength trends that can be compared to experimentally obtained interfacial properties to assess the role of roughness and humidity (see Materials and Methods for further details). In particular, we chose boundary conditions for the simulations that provide estimates of intrinsic interfacial properties. Furthermore, we measured the water content within bulk GO papers to relate water content (measured in MD) and relative humidity (measured experimentally). See Supporting Information, section S7, for further details.

Based on XPS measurements, we generated 70% oxidized GO MD configurations with a 4:1 epoxide/hydroxyl functional group ratio employing a configurational bias Monte Carlo sampling scheme which has been shown to reproduce experimentally and theoretically observed features in GO.²⁶ To further elucidate the effects of chemistry, we constructed specific 70% oxidized, 1:1 and 1:4 epoxide/hydroxyl functional group ratio GO MD representations, as well. After generating the nanosheets, a GO–GO bilayer with a variable quantity of intercalated water was configured to extract traction–separation curves. We achieved this by tracking traction in the system as the top GO layer was pulled off with controlled displacements. The obtained traction–separation curves (Figure 3a) were then numerically integrated to quantify adhesion energy (Figure 3b). Based on simulation results, adhesion energy improves with



Figure 3. (a) Traction-separation behavior predicted by ReaxFF MD simulations as a function of water content. (b) Adhesion energy as a function of water content. Water content levels between 10 and 23 wt %, representative of experimental conditions, are highlighted.

water content (G = 0.17 - 0.76 J m⁻²), in agreement with the overall trend observed in experiments for 4:1 epoxide/hydroxyl GO. Due to the higher density of donor-acceptor hydroxyl groups in 1:1 and 1:4 epoxide/hydroxyl GO, we observed adhesion values at 15% water weight ($G = 0.69 - 0.96 \text{ Jm}^{-2}$) that were significantly higher than those of GO with donor-only epoxide molecules ($G = 0.45 \text{ Jm}^{-2}$). Notably, although adhesion measurements were corrected for surface roughness effects, the adhesion energies predicted by MD are larger than those measured experimentally. In understanding these quantitative differences, we note that MD simulations are performed on GO sheets exhibiting surface roughness arising from thermal fluctuations but not those on the scale measured in the GO surface attached to the SiO₂ sphere. Similarly, rate effects can affect interfacial quantitative behavior even when capturing the correct mechanisms.⁴³ We also found that ReaxFF, which was parametrized to accurately model GO's behavior,44 overpredicts cohesive interactions between bulk water molecules, as reflected by bulk modulus and cavitation stress comparisons (see Supporting Information, section S8, for details). Unfortunately, force fields whose representation of water is more appropriate (i.e., optimized potential for liquid simulations) do not accurately capture the microstructure and chemistry of GO. Despite these caveats, the MD simulations herein reported were found to reveal key interfacial mechanisms and further confirm the beneficial role of functional groups in GO's surface, improving surface interfacial interactions beyond those present in graphene.

To obtain a systematic understanding of the behavior of the system beyond the observed trends with water content, we further inspected the shape and change in traction separation

ACS Nano

behavior (Figure 3a) and the evolution of molecular deformations as hydrogen-bond networks form and rupture throughout the pull-off process. The traction-separation response obtained from MD pull-off simulations (Figure 3a) reveals two interesting mechanisms, which act synergistically to improve adhesion energy with increasing water content. First, as water content increases, the maximum traction (*i.e.*, the magnitude of the peak) increases. The maxima of these peaks correspond to strong GO–GO surface interactions, mediated through water hydrogen bonding, when the surfaces are in intimate contact (Figure 4a). As the surfaces begin to separate,



Figure 4. (a) Initial configuration and applied displacements during MD simulations of GO–GO interfacial pull-off. (b) Formation of water clusters (bridges) during GO–GO interfacial pull-off. The water clusters are wrapped with a transparent, blue surface of radius 0.1 nm around each water molecule to show the extent of hydrogen-bonding interactions. (c) Collapse of water clusters during GO–GO interfacial pull-off. For all shown atomistic visualizations, gray, red, and green beads represent carbon, oxygen, and hydrogen atoms, respectively, and blue particles represent water molecules. Water molecules have been given a uniform color herein for clarity. All visualizations are acquired from a 20% water weight ratio MD simulation.

increased water content enhances intersurface interactions through breaking and reforming of hydrogen-bond networks. Second, our simulations show that increasing water content leads to a significantly different softening response, with increasing water content, which increases the effective range of nonzero adhesive interactions. To explain these nonzero interactions, it is worth noting that, as separation continues, strongly cohesive water clusters, anchored along different regions on each surface (Figure 4b), maintain interactions across the GO-GO interface. As more water percolates between the surfaces, larger water clusters span across the interface and result in interfacial interactions through water menisci,45 until water achieves a cavitation stress which is sufficient to break the bridging water clusters (Figure 4c). Although we observe more significant clustering of water molecules in 1:1 and 1:4 epoxide/hydroxyl functional group ratio GOs due to differences in hydrogen-bonding donoracceptor behavior (see Supporting Information, section S9, for details), the overall trends and mechanistic response of the system remain unchanged. Therefore, these results clearly show that increasing water content in GO–GO interfaces improves the magnitude of adhesion energy, not only by increasing the overall number of interfacial interactions but also by providing long-ranged water-mediated interactions.

In order to estimate the interfacial shear strength of GO-GO interfaces (Figure 5a,b), the top GO sheet in a bilayer GO system was intercalated with a variable amount of water molecules (Figure 6a) in a manner similar to the adhesion simulations. Upon equilibration, the simulation supercell was subjected to a lateral sliding motion, with a sliding velocity of 10 m/s, whereas the lateral linear momentum of the bottom sheet was set to zero. Using this procedure, it was possible to extract interfacial shear loads and interfacial shear strength (defined here as average interfacial shear stress during sliding, Figure 5a), as a function of water content ($\tau_0 = 99-234$ MPa). MD predictions of interfacial shear strength, as a function of water content, are shown in Figure 5b. As with our analysis of adhesion, we observe that 1:1 and 1:4 epoxide/hydroxyl functional group ratio GOs show interfacial responses (τ_0 = 332-439 MPa) markedly stronger than those of 4:1 epoxide/ hydroxyl GO (τ_0 = 212 MPa) due to the donor-acceptor nature of hydroxyl groups, which allows for stronger interactions with water molecules. Notably, the observed trends agree with those captured experimentally, but MD quantitative predictions are larger in magnitude. After an initial sharp enhancement in interfacial shear strength from the dry condition, the rate of increase in interfacial shear strength with respect to water content drops (Figure 5b) and tends to saturate as water begins to lubricate the interface.^{15,46} One interpretation of this finding is that as GO contains a finite number of hydrogen-bonding functional groups, the number of interfacial hydrogen bonds-arising directly between functional groups or mediated through water-must saturate at higher water contents. Past the onset of saturation, any additional water molecules would not lead to further intersheet hydrogen bonding due to a dearth of unpaired functional groups along the graphitic backbone. Rather, these excess water molecules establish a self-interacting hydrogen-bond network, as in liquid water, which reduced load transfer efficiency *through* the gallery space of GO.

The quantitative differences between the experimentally measured and computationally predicted interfacial shear strengths can be rationalized by simplifications used in the analysis of the experiments. First, the sliding velocity employed in the MD simulations (10 m/s) is orders of magnitude higher than those in the experiment. Indeed, it is well documented in the literature the role of rate effects on predictions of interfacial shear strengths.⁴³ Second, the contact mechanics model used in analyzing the data computes the average shear stress as the ratio between lateral force and projected contact area without accounting for roughness effects. This issue is not easily addressed due to the lack of roughness corrections, at the continuum level, for shear strength predictions given the dynamic nature of interfacial sliding. Both of these factors are difficult to address given current limitations in computational power.

To elucidate the role of water in mediating interfacial load transfer, which leads to improvements in interfacial shear strength, we analyzed the evolution of molecular structures in the system. Atomistic snapshots of the sliding deformation



Figure 5. (a) Interfacial shear stress as a function of sliding distance and water content, as extracted from representative MD simulations. The selected curves are exemplary and do not represent all tested conditions. Dashed lines capture mean stress levels for each set of sliding conditions. (b) Interfacial shear strength as a function of water content based on average interfacial shear stress from MD calculations. Water content levels between 10 and 23 wt %, representative of experimental conditions, are highlighted. (c) Hydrogen bond (HB) analysis for GO–GO sliding calculations, as a function of water content.



Figure 6. (a) Initial contact and applied boundary conditions during MD simulation of GO–GO interfacial sliding. (b) Visualization of GO–GO interface during stable sliding, to illustrate the relative moment of water molecules. (c) Inset of dashed box in panel (b), illustrating the relative motion of water molecules. For all shown atomistic visualizations, the atomistic coloring scheme for GO and water has been simplified for increased clarity (all atoms belonging to a particular molecule are given uniform colors). Here, gray and purple colors represent GO sheets, and blue and red colors represent water molecules. All simulated atoms are shown in the visualizations, and all visualizations are acquired from a 20% water weight ratio MD simulation. (d,e) Close-up on unit volume for (d) 5% and (e) 20% water weight ratio MD simulations showing the formation and breaking of a (d) single hydrogen-bond bridge between two epoxide functional groups in adjacent GO sheets (12.5 fs elapse between each snapshot) and (e) formation and rupture of a GO–water–water–GO hydrogen-bond bridge (80 fs elapse between each snapshot). Here, gray, red, and green atoms represent carbon, oxygen, and hydrogen atoms, respectively, in GO. All atoms for water molecules are colored blue. A dashed, black envelope is drawn around atoms participating in hydrogen bonds.

process are illustrated in Figure 6a-e. Examination of these images reveals that water molecules adhere and bridge GO surfaces during sliding, thus enabling strong interactions to be maintained across the interface through a self-healing process of rupture and reformation of hydrogen bonds. As such, visualization of the interfacial deformation process yields direct insight into the fundamental mechanisms leading to improvements in interfacial shear strength with increasing water content. In particular, we observe significant bonding and debonding as the GO sheets slide relative to each other, and water molecules form GO-water-GO hydrogen-bond networks (Figure 6d,e). Importantly, we observe that water molecules form hydrogen bonds through single water molecules (i.e., GO-water-GO, such as in Figure 6d) or through collective networks (e.g., GO-water-water-GO hydrogen bonds, such as in Figure 6e). Notably, this effect

becomes more dramatic and synergistic as water content increases, which agrees with our trends in interfacial shear strength. To further reveal the role of water-mediated hydrogen bonding in GO interfacial shear, we classified and quantified different types of hydrogen bonds within the system (see Supporting Information, section S10, for details). Specifically, we analyze trends in the number of GO-GO, GO-water-GO, and effective number of interfacial hydrogen bonds as a function of water content (Figure 5c). See also Figure 1b and Supporting Information, section S10, for specific definitions. In these studies, as water content increases, a commensurate decrease in the number of GO-GO hydrogen bonds is observed (Figure 5c). These GO-GO hydrogen bonds are replaced by GO-water-GO bonds, which form from the intercalated water. The diffusivity of water permits rapid percolation and diffusion between GO surfaces,47 which facilitates the cleavage and reconstruction of the existing hydrogen-bond network. The distribution and saturation of hydrogen bonds varies with different types of GO (oxidation level and functional group type), as it is presumably related to the coverage of GO surface functionalities. It should be noted that the relative improvements in interfacial shear strength observed in experiments and simulations correlate well with the total number of hydrogen bonds that are effective in load transfer at different water contents, further emphasizing the critical role that hydrogen bonding, both through tunable chemistry and water molecules, plays on interfacial interactions of GO sheets. It is worth mentioning that the presence of high temperatures in the system leads to facile water intercalation, in turn reducing adhesion energy and interfacial shear strength of GO interfaces mediated by water molecules, similar to the behavior in hydrophilic polymers.⁴⁸ Nevertheless, these results have important implications for tuning the properties of GO-GO interfaces and, consequently, the use of the material for engineering applications.

CONCLUSIONS

Using atomic force microscopy, the roughness-corrected adhesion energy ($G' = 0.11-0.21 \text{ Jm}^{-2}$) and interfacial shear strength ($\tau_0 = 28-63 \text{ MPa}$) of nanoscale interfaces composed of 70% oxidized GO with a 4:1 epoxide/hydroxyl functional group ratio were measured as a function of ambient humidity. Monotonic improvements in adhesion energy and interfacial shear strength, with increasing water content, were identified, revealing an important pathway through which the mechanical properties of GO–GO interfaces may be altered for a given GO chemistry.

Previously, we showed that the mechanical properties of GO are strongly dependent on the chemical composition of the material (*i.e.*, the ratio of functional groups and their coverage over the graphitic basal plane).²⁵ More specifically, we showed that the in-plane mechanical properties of GO (e.g., elastic moduli and strength) degrade as the material becomes more functionalized. In contrast, this study demonstrates that GO's adhesion and interfacial shear strength improve with interfacial hydrogen-bonding energy resulting from GO-water-GO hydrogen bonds. This points at a competition between inplane and out-of-plane properties in GO-based systems. For instance, whereas hydroxyl groups greatly weaken the in-plane mechanical properties of GO, they generally lead to strong enhancements in adhesion energy and interfacial shear strength. Conversely, epoxide functional groups maintain GO's structural integrity and lead to ductile failure but do not enhance the previously mentioned interfacial properties as dramatically, owing to their donor-only behavior with respect to hydrogen bonding. In this regard, our previous and current studies provide a pathway to simultaneously optimize GO's interfacial and in-plane mechanical properties by tailoring the chemistry of GO and its environment (i.e., humidity levels). Another implication from the study is that water content control, as opposed to GO's chemistry, leads to accessible tunability pathways that do not involve the more complex chemical reactions used in modifying GO's chemistry¹³ and, therefore, may facilitate the adoption of the material in engineering applications such as sensors and devices.

This study also reveals important gaps in the analysis of nanoscale experiments, which need to be addressed in future research. For instance, interpretation of AFM adhesion and interfacial shear experiments are indirect and as such they require the use of continuum and atomistic models for extracting the properties of interest. Accounting for surface roughness effects on atomic interactions remains challenging, leading to uncertainties in measured properties. Likewise, MD simulations are based on force fields parametrized for a class of atomic environments that for some heterogeneous materials systems do not appear general enough. As shown in this study, popular force fields such as ReaxFF, although excelling at the description of the energetics of GO sheets, appear to overpredict the cohesion imparted by water bridges. Moreover, the computational cost associated with large-scale atomistic simulations imposes constraints on domain size and deformation rates, which make direct comparison with experiments challenging.

In closing, we are confident that the methodology and findings reported here will provide future directions in the design of optimal GO–GO interfaces and reveal potential design strategies that can aid in controlling the interfacial behavior of contacting surfaces in emergent 2D materials systems.

MATERIALS AND METHODS

Materials and Instrumentation. Unless otherwise stated, all reagents were used as received. Graphite powder (grade 2139) was purchased from Asbury Carbons (Asbury, NJ). Sodium nitrate, potassium permanganate, absolute ethanol, acetone, and concentrated hydrochloric acid were purchased from Sigma-Aldrich Co. LLC (Milwaukee, WI). Concentrated sulfuric acid and methanol were purchased from VWR International LLC (Radnor, PA). Hydrogen peroxide (30 wt % in water) was purchased from Sigma-Aldrich Co. LLC (Milwaukee, WI) and refrigerated during storage. Ultrapure deionized water (resistivity 18.2 M Ω cm) was obtained from a Milli-Q Biocel A10 system (Millipore Inc., Billerica, MA). Silicon wafers (4 in. diameter, N-type) with a 285 nm thick surface oxide were purchased from Graphene Supermarket (Calverton, NY). For preparation of AFM cantilevers, tipless AFM cantilevers were purchased (catalog number: TL-FM-20, NanoSensors, Neuchâtel, Switzerland), and 6 µm SiO₂ spheres (catalog number: SS06N/10096, Bangs Laboratories, Fishers, IN) were glued using standard epoxy.

Scanning electron microscopy images were taken using a FEI NovaNano 600 scanning electron microscope (FEI, Hillsboro, OR). Atomic force microscopy images of flakes deposited on the substrates were obtained in tapping mode using a Park XE-120 AFM system (Park Systems, South Korea), and lateral force microscopy AFM experiments were conducted in a Veeco Dimension 3100 AFM system (Plainview, NY). Samples which required plasma cleaning were processed in a South Bay Technology PC-2000 plasma cleaner (San Clemente, CA). X-ray photoelectron spectroscopy was performed using a Thermo Scientific ESCALAB 250Xi (Al K α radiation, $h\nu$ = 1486.6 eV) (Thermo Fisher Scientific Inc., West Palm Beach, FL) equipped with an electron flood gun. XPS data were analyzed using Thermo Scientific Avantage Data System software (version 5.923), and a Smart background was subtracted prior to peak deconvolution and integration. Raman analysis was conducted using a using a commercial Raman system (LabRAM HR-800, Horiba Jobin Yvon) to identify the presence of GO flakes on the apex of the GO-coated SiO₂ spheres, that is, one of the contact points for the GO-GO interface. For the Raman spectrum acquisition, a solid-state green laser (average power <1 mW and wavelength ~532 nm) was focused to a spot size of less than 1 μ m using a 50× (NA = 0.8) objective. The reflected and scattered light was collected by the same objective and passed through a Rayleigh filter (efficient to <100 cm⁻¹) followed by a motorized Czerny-Turner spectrograph (1800 grooves/mm) coupled to a Peltier-cooled EMCCD (Andor Newton). The spectral resolution of the spectrograph is <1 cm⁻¹, and the accuracy of the peak locations can be further improved through Lorentzian line shape fitting. CHN elemental analysis by combustion and O elemental analysis by

pyrolysis were performed by Micro Analysis, Inc. (Wilmington, DE), with samples dried at 80 $^{\circ}$ C under vacuum for 4 h. Water content was measured by Karl Fischer titration using a C20 Compact Karl Fischer coulometer (Mettler-Toledo International Inc., Columbus, OH) on films dried at 80 $^{\circ}$ C under vacuum for 4 h and bath sonicated for 5 min in dry MeOH in a sealed vial. To measure water content in GO, the GO films were first equilibrated overnight at the desired humidity and then bath sonicated for 5 min in dry MeOH in a sealed vial (see below for further details).

Synthesis of Graphene Oxide. Graphite oxide was prepared using a modified Hummer's method.²⁷ Briefly, graphite (3 g), sodium nitrate (3 g), and concentrated H₂SO₄ (138 mL) were stirred together and chilled to 0 °C using an ice bath. Potassium permanganate (18 g) was slowly added to this mixture, taking care to keep the temperature below 10 °C. The reaction mixture was then transferred to a 35 °C water bath and stirred for 1 h. Next, ultrapure deionized water (240 mL) was slowly added, and the solution was stirred for 30 min while increasing the temperature to 90 °C. Additional ultrapure deionized water (500 mL) was then added, followed by the addition of H_2O_2 (18 mL of a 30 wt % solution) until the solution became orange brown. The resulting graphite oxide was filtered and washed with HCl (2 L of a 3.7 wt % solution) over a PTFE membrane (Omnipore, 5 μ m pore size, Millipore Inc., Billerica, MA) overnight. The GO filter cake was dispersed in acetone (500 mL), filtered, and washed with acetone (2 L) over a PTFE membrane overnight. This final GO filter cake was dispersed in ultrapure deionized water, with the dispersion stirred overnight. Any residual unexfoliated graphite oxide was removed by centrifuging at 8228 rcf for 5 min $(2\times)$ with the precipitate discarded. The final dispersions contained ~2.5 mg/mL of GO, with a C/O ratio determined by elemental analysis to be 1.42. Accounting for a water content of 10 wt % results in a C/O ratio of 1.79. GO films for XPS analysis were prepared by drop-casting GO solution onto silicon wafers, followed by drying at 60 °C. XPS results are shown in Supporting Information, section S1, confirming that the composition of our GO was similar to moderately oxidized, epoxide-rich GO samples reported previously.^{26,32}

Preparation of GO-Coated SiO₂ Substrates and Spheres. To deposit GO films in the GO-coated substrates used for lateral force microscopy (LFM) experiments, the Langmuir-Blodgett assembly method was employed.²⁷ The as-prepared aqueous GO dispersion was diluted with MeOH to a mixture of 5:1 v/v MeOH/GO dispersion. The Nima technology (Espoo, Finland) model 116 trough was cleaned with acetone and filled with ultrapure deionized water. Generally, GO solution (480 μ L) was spread onto the water surface dropwise at a rate of 100 μ L/min using a glass syringe, forming a monolayer film on the surface. The surface pressure was monitored using a tensiometer attached to a Wilhelmy plate. The film was allowed to equilibrate for at least 20 min after the spreading and then compressed by barriers at a speed of 100 cm²/min. Prior to GO deposition, silicon substrates with a ~300 nm thick oxide layer were cleaned with acetone and treated with O_2 plasma (5 min at 80 W and ~200 mTorr O_2) in a South Bay Technology, Inc. (San Clemente, CA) model PC-2000 plasma cleaner. The GO films were transferred near the onset of the surface pressure increase by vertically dipping the substrate into the trough and slowly pulling it up at a rate of 2 mm/min. It is important to note that the GO flakes deposited on the SiO₂ substrate were readily visible in optical microscopy, which was crucial for flake identification during AFM analysis.

GO-coated spheres were prepared by dip-coating 6 μ m SiO₂ spheres in a diluted GO solution. Briefly, the SiO₂ spheres (catalog number: SS06N/10096, Bangs Laboratories, Fishers, IN) were glued onto tipless Si cantilevers (catalog number: TL-FM-20, NanoSensors, Neuchâtel, Switzerland) with epoxy using a custom-built micromanipulation stage within an optical microscope setup. Then, the glued SiO₂ sphere and cantilever were plasma cleaned for 5 min to activate the SiO₂ sphere surface and maximize the potential for GO adhesion to the spheres, according to previous findings.²⁶ Plasma cleaning was performed in a South Bay Technology PC-2000 plasma cleaner (San Clemente, CA) with an applied power of 80 kW and a reflected power of 16–20 kW, under an oxygen pressure of ~200

mTorr. Finally, the cantilever with the glued and activated SiO₂ sphere was immersed in 10 μ L of a diluted GO solution (2.5 mg/mL solution of GO further diluted with 100 mL of DI water) for 20 s, with slight agitation.

Lateral Force Microscopy AFM Experimental Procedure. LFM measurements were taken in a Veeco Dimension 3100 AFM (Plainview, NY). To obtain friction load-applied normal load estimates, it is necessary to measure the instrument electrical measurement (voltage) sensitivities and cantilever stiffnesses for different deformation modes. Estimates for stiffness values are discussed in the Supporting Information, section S4. The lateral electrical measurement sensitivity of the AFM was calibrated by horizontally pushing the midpoint of a SiO₂ sphere against the side wall of a Si substrate to acquire the lateral deflection response versus the lateral displacement signal from the cantilever, as discussed elsewhere.49 The bending sensitivity of the AFM was measured by plotting bending deflection versus imposed displacement against a rigid Si substrate to quantify bending electrical measurement sensitivity. It is noteworthy to mention that the measured in-plane bending properties take into account bending and torsional cantilever motion components, as established elsewhere.49

To acquire experimental measurements, GO flakes whose roughness and thickness had been characterized independently using a Park XE-120 AFM system (Park Systems, South Korea) were located using an optical microscope setup within the Veeco Dimension 3100 AFM. Then, sliding tests were performed at a 0° scan angle with a scan rate of 1 Hz (raster velocity of 250 nm/s), while varying both relative humidity level and applied normal load. Ten independent LFM experiments were conducted for each relative humidity level. Humidity levels were controlled by mixing inert, hydrated nitrogen and dry nitrogen using mixing valves and stabilizing the system for 1 h prior to the start of experimentation.

Quantification of Water Content Intercalated in GO Interfaces. Water content was measured by Karl Fischer titration using a C20 Compact Karl Fischer coulometer (Mettler-Toledo International Inc., Columbus, OH). To determine the carbon-to-oxygen (C/O) ratio of the bulk GO, measurements were done on multilayer films dried at 80 °C under vacuum for 4 h. Due to the small size of the GO–GO interfaces used in the adhesion and shear experiments, Karl Fischer titration of these samples was not feasible. To evaluate the water content of these GO–GO interfaces, measurements were instead done on lyophilized GO samples that were first equilibrated for 2 h at various humidity levels, including those used in AFM experiments.

To measure water content, GO samples were placed in a tared, capped vial and weighed. The capped vial was tared again, anhydrous methanol (\sim 3 mL) was added, and the vial was weighed to obtain the mass of the MeOH. Anhydrous methanol was obtained from a Dow-Grubbs solvent system installed by Glass Contours, Inc. (now SG Waters USA, Nashua, NH). GO samples were bath sonicated for at least 30 min to completely disperse the GO in the methanol. A control sample of anhydrous methanol (\sim 3 mL) was sonicated along with the GO samples. After sonication, the methanol sample was first injected into the Karl Fischer coulometer to measure the background water content of the solvent. GO samples were then injected into the Karl Fischer coulometer to measure their water content. Postprocessing of the obtained results is further discussed in the Supporting Information, section S7.

Molecular Dynamics Simulation Methodology. The largescale atomic/molecular massively parallel simulator (LAMMPS) software package was employed to carry out all-atom MD simulations.⁵⁰ The ReaxFF force field,⁴⁴ as parametrized for simulations with hydrocarbons systems, was employed for all simulations described. GO models were generated according to a configurational bias Monte Carlo sampling method, as described elsewhere.^{25,26} A time step of 0.25 fs was employed for all simulations described herein to account for the vibrational frequency of H atoms present in GO functional groups. For all simulations described below, the system was first equilibrated in an isothermal–isobaric (NPT) ensemble at a temperature of 300 K and zero external pressure for 1 ns. Periodic boundary conditions were enforced for all dimensions of the MD supercell. The time constants for temperature and pressure relaxation were chosen to be 2.5 and 25 fs, respectively. The total energy of the system was monitored until convergence was achieved during equilibration, before equilibrated structures were subjected to different loading conditions. All simulations were visualized with the VMD software.⁵¹

Three GO compositions were utilized: 4:1, 1:1, and 1:4 epoxide/ hydroxyl functional group ratio GOs with a total 70% oxidation. The first case (4:1) corresponds to XPS measurements for the GO utilized experimentally, whereas the remaining two compositions are used to computationally examine the effect of chemistry in interfacial behavior. The simulation domain for GO-GO pull-off calculations consisted of a single $6 \times 6 \text{ nm}^2$ GO monolayer coated by a variable amount of water molecules on both sides of the graphitic backbone. When periodic boundary conditions are employed, the designed system replicates an infinitely layered stack of GO monolayers intercalated with water molecules in the gallery spacing. The amount of water molecules was varied to achieve the desired water content, measured as a weight percentage. The simulation box was deformed in the outof-plane direction at a constant engineering strain rate of 1×10^6 s⁻¹ within the canonical (NVT) ensemble, which is equivalent to pull-off between GO sheets by separating adjacent GO sheets. Stress in MD simulations is reported using the virial formulation as implemented in LAMMPS, and stress measurements were recorded as a function of box displacement to extract traction-separation behavior.

The simulation of GO–GO sliding was performed using the same supercell size, ensemble, and boundary conditions. For sliding experiments, a GO bilayer system with a variable amount of water molecules coating both GO flakes on both sides of the graphitic backbone was programmed into the supercell. The upper GO layer in the stack was pulled laterally using the steered molecular dynamics method⁵² within a canonical (NVT) ensemble. In this approach, a virtual spring is pulled in a predefined direction at a constant velocity (10 m/s for our simulations), which causes a virtual force to be distributed on a selected group of atoms. The pulling force exerted on the top GO layer was recorded as a function of relative sheet sliding and the contact area of the domain was used to determine the interfacial shear stresses.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b02373.

XPS characterization of as-synthesized GO monolayers, Raman spectrum analysis for experimental surfaces, roughness characterization for experimental surfaces, characterization of AFM cantilever properties, experimental frictional force fitting procedure, analytical model for surface roughness correction in adhesion, quantification of water content in experimental measurements, analysis of bulk water behavior in MD simulations, and hydrogen-bond counting scheme (PDF)

AUTHOR INFORMATION

Corresponding Authors

- *E-mail: espinosa@northwestern.edu.
- *E-mail: stn@northwestern.edu.
- *E-mail: jiaxing-huang@northwestern.edu.

ORCID 0

Jeffrey T. Paci: 0000-0003-4341-752X

Jiaxing Huang: 0000-0001-9176-8901

- SonBinh T. Nguyen: 0000-0002-6977-3445
- Horacio D. Espinosa: 0000-0002-1907-3213

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the support of NSF through DMREF Award No. CMMI-1235480 and the ARO through MURI Award No. W911NF-08-1-0541. Material characterization used the Keck-II facility (NUANCE Center-Northwestern University). This work used the Extreme Science and Engineering Discovery Environment (XSEDE), under Award No. TG-MSS140028, which is supported by National Science Foundation Award No. ACI-1053575. The authors acknowledge the Texas Advanced Computing Center (TACC) at the University of Texas at Austin for providing HPC resources that have contributed to the research results reported within this paper. The authors also acknowledge S. Shiva P. Nathamgari for the assistance in the acquisition of Raman spectra for the GO-coated surfaces. R.A.S.-C. acknowledges support from NSF through the Graduate Research Fellowships Program (GRFP). M.R.R. acknowledges partial support from the Department of Defense (DoD) through the National Defense Science and Engineering Graduate Fellowship (NDSEG) Program. R.A.S.-C. and M.R.R. acknowledge partial support from the Northwestern University Ryan Fellowship & International Institute for Nanotechnology, and partial support from Northwestern University through Royal Cabell Terminal Year Fellowships. The authors thank Xu Zhang, Matthew Daly, and David Restrepo for insightful discussions.

REFERENCES

(1) Borini, S.; White, R.; Wei, D.; Astley, M.; Haque, S.; Spigone, E.; Harris, N.; Kivioja, J.; Ryhanen, T. Ultrafast Graphene Oxide Humidity Sensors. *ACS Nano* **2013**, *7*, 11166–11173.

(2) Zhang, Y.; Zhang, L.; Zhou, C. Review of Chemical Vapor Deposition of Graphene and Related Applications. *Acc. Chem. Res.* **2013**, *46*, 2329–2339.

(3) Yuan, W.; Shi, G. Graphene-Based Gas Sensors. J. Mater. Chem. A 2013, 1, 10078–10091.

(4) Hu, M.; Mi, B. Enabling Graphene Oxide Nanosheets as Water Separation Membranes. *Environ. Sci. Technol.* **2013**, *47*, 3715–3723.

(5) Meng, Y.; Zhao, Y.; Hu, C.; Cheng, H.; Hu, Y.; Zhang, Z.; Shi, G.; Qu, L. All-Graphene Core-Sheath Microfibers for All-Solid-State, Stretchable Fibriform Supercapacitors and Wearable Electronic Textiles. *Adv. Mater.* **2013**, *25*, 2326–2331.

(6) Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-Based Composites. *Chem. Soc. Rev.* 2012, 41, 666–686.

(7) Wang, G.; Dai, Z.; Wang, Y.; Tan, P.; Liu, L.; Xu, Z.; Wei, Y.; Huang, R.; Zhang, Z. Measuring Interlayer Shear Stress in Bilayer Graphene. *Phys. Rev. Lett.* **2017**, *119*, 036101.

(8) Ruiz, L.; Xia, W.; Meng, Z.; Keten, S. A Coarse-Grained Model for the Mechanical Behavior of Multi-Layer Graphene. *Carbon* **2015**, 82, 103–115.

(9) Xia, W.; Ruiz, L.; Pugno, N. M.; Keten, S. Critical Length Scales and Strain Localization Govern the Mechanical Performance of Multi-Layer Graphene Assemblies. *Nanoscale* **2016**, *8*, 6456–6462.

(10) Filleter, T.; Bernal, R.; Li, S.; Espinosa, H. Ultrahigh Strength and Stiffness in Cross-Linked Hierarchical Carbon Nanotube Bundles. *Adv. Mater.* **2011**, *23*, 2855–2860.

(11) Young, R. J.; Kinloch, I. A.; Gong, L.; Novoselov, K. S. The Mechanics of Graphene Nanocomposites: A Review. *Compos. Sci. Technol.* **2012**, *72*, 1459–1476.

(12) Gong, L.; Young, R. J.; Kinloch, I. A.; Riaz, I.; Jalil, R.; Novoselov, K. S. Optimizing the Reinforcement of Polymer-Based Nanocomposites by Graphene. *ACS Nano* **2012**, *6*, 2086–2095.

(13) Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. The Chemistry of Graphene Oxide. *Chem. Soc. Rev.* 2010, 39, 228-240.

(14) Bi, H.; Yin, K.; Xie, X.; Ji, J.; Wan, S.; Sun, L.; Terrones, M.; Dresselhaus, M. S. Ultrahigh Humidity Sensitivity of Graphene Oxide. *Sci. Rep.* **2013**, 3, 02714.

(15) Compton, O. C.; Cranford, S. W.; Putz, K. W.; An, Z.; Brinson, L. C.; Buehler, M. J.; Nguyen, S. T. Tuning the Mechanical Properties of Graphene Oxide Paper and Its Associated Polymer Nanocomposites by Controlling Cooperative Intersheet Hydrogen Bonding. *ACS Nano* **2012**, *6*, 2008–2019.

(16) Joshi, R.; Carbone, P.; Wang, F.-C.; Kravets, V. G.; Su, Y.; Grigorieva, I. V.; Wu, H.; Geim, A. K.; Nair, R. R. Precise and Ultrafast Molecular Sieving through Graphene Oxide Membranes. *Science* **2014**, *343*, 752–754.

(17) Li, H.; Song, Z.; Zhang, X.; Huang, Y.; Li, S.; Mao, Y.; Ploehn, H. J.; Bao, Y.; Yu, M. Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation. *Science* **2013**, *342*, 95–98.

(18) Daly, M.; Cao, C.; Sun, H.; Sun, Y.; Filleter, T.; Singh, C. V. Interfacial Shear Strength of Multilayer Graphene Oxide Films. *ACS Nano* **2016**, *10*, 1939–1947.

(19) Li, Z.; Kinloch, I. A.; Young, R. J. The Role of Interlayer Adhesion in Graphene Oxide Upon Its Reinforcement of Nanocomposites. *Philos. Trans. R. Soc., A* **2016**, 374, 20150283.

(20) Beese, A. M.; Wei, X.; Sarkar, S.; Ramachandramoorthy, R.; Roenbeck, M. R.; Moravsky, A.; Ford, M.; Yavari, F.; Keane, D. T.; Loutfy, R. O.; et al. Key Factors Limiting Carbon Nanotube Yarn Strength: Exploring Processing-Structure-Property Relationships. *ACS Nano* **2014**, *8*, 11454–11466.

(21) Jacobs, T. D.; Ryan, K. E.; Keating, P. L.; Grierson, D. S.; Lefever, J. A.; Turner, K. T.; Harrison, J. A.; Carpick, R. W. The Effect of Atomic-Scale Roughness on the Adhesion of Nanoscale Asperities: A Combined Simulation and Experimental Investigation. *Tribol. Lett.* **2013**, *50*, 81–93.

(22) Rabinovich, Y. I.; Adler, J. J.; Ata, A.; Singh, R. K.; Moudgil, B. M. Adhesion between Nanoscale Rough Surfaces: I. Role of Asperity Geometry. *J. Colloid Interface Sci.* **2000**, 232, 10–16.

(23) Rabinovich, Y. I.; Adler, J. J.; Ata, A.; Singh, R. K.; Moudgil, B. M. Adhesion between Nanoscale Rough Surfaces: Ii. Measurement and Comparison with Theory. J. Colloid Interface Sci. 2000, 232, 17–24.

(24) Christenson, H. Adhesion and Surface Energy of Mica in Air and Water. J. Phys. Chem. 1993, 97, 12034–12041.

(25) Soler-Crespo, R. A.; Gao, W.; Xiao, P.; Wei, X.; Paci, J. T.; Henkelman, G.; Espinosa, H. D. Engineering the Mechanical Properties of Monolayer Graphene Oxide at the Atomic Level. *J. Phys. Chem. Lett.* **2016**, *7*, 2702–2707.

(26) Wei, X.; Mao, L.; Soler-Crespo, R. A.; Paci, J. T.; Huang, J.; Nguyen, S. T.; Espinosa, H. D. Plasticity and Ductility in Graphene Oxide through a Mechanochemically Induced Damage Tolerance Mechanism. *Nat. Commun.* **2015**, *6*, 8029.

(27) Cote, L. J.; Kim, F.; Huang, J. Langmuir– Blodgett Assembly of Graphite Oxide Single Layers. J. Am. Chem. Soc. 2009, 131, 1043–1049.

(28) Ganguly, A.; Sharma, S.; Papakonstantinou, P.; Hamilton, J. Probing the Thermal Deoxygenation of Graphene Oxide Using High-Resolution in Situ X-Ray-Based Spectroscopies. *J. Phys. Chem. C* 2011, *115*, 17009–17019.

(29) Pulido, A.; Concepción, P.; Boronat, M.; Botas, C.; Alvarez, P.; Menendez, R.; Corma, A. Reconstruction of the Carbon sp^2 Network in Graphene Oxide by Low-Temperature Reaction with Co. *J. Mater. Chem.* **2012**, 22, 51–56.

(30) Koinuma, M.; Tateishi, H.; Hatakeyama, K.; Miyamoto, S.; Ogata, C.; Funatsu, A.; Taniguchi, T.; Matsumoto, Y. Analysis of Reduced Graphene Oxides by X-Ray Photoelectron Spectroscopy and Electrochemical Capacitance. *Chem. Lett.* **2013**, *42*, 924–926.

(31) Cao, C.; Daly, M.; Singh, C. V.; Sun, Y.; Filleter, T. High Strength Measurement of Monolayer Graphene Oxide. *Carbon* **2015**, *81*, 497–504.

(32) Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. ACS Nano **2010**, *4*, 4806–4814.

(33) King, A. A.; Davies, B. R.; Noorbehesht, N.; Newman, P.; Church, T. L.; Harris, A. T.; Razal, J. M.; Minett, A. I. A New Raman Metric for the Characterisation of Graphene Oxide and Its Derivatives. *Sci. Rep.* **2016**, *6*, 19491.

(34) Grierson, D.; Flater, E.; Carpick, R. Accounting for the JKR– DMT Transition in Adhesion and Friction Measurements with Atomic Force Microscopy. J. Adhes. Sci. Technol. **2005**, 19, 291–311.

(35) Zappone, B.; Rosenberg, K. J.; Israelachvili, J. Role of Nanometer Roughness on the Adhesion and Friction of a Rough Polymer Surface and a Molecularly Smooth Mica Surface. *Tribol. Lett.* **2007**, *26*, 191.

(36) Carpick, R. W.; Ogletree, D. F.; Salmeron, M. A General Equation for Fitting Contact Area and Friction Vs Load Measurements. *J. Colloid Interface Sci.* **1999**, *211*, 395–400.

(37) Maugis, D. Adhesion of Spheres: The JKR-DMT Transition Using a Dugdale Model. J. Colloid Interface Sci. **1992**, 150, 243–269.

(38) Derjaguin, B. V.; Muller, V. M.; Toporov, Y. P. Effect of Contact Deformations on the Adhesion of Particles. *J. Colloid Interface Sci.* **1975**, 53, 314–326.

(39) Mo, Y.; Turner, K. T.; Szlufarska, I. Friction Laws at the Nanoscale. *Nature* **2009**, 457, 1116–1119.

(40) Roenbeck, M. R.; Furmanchuk, A. o.; An, Z.; Paci, J. T.; Wei, X.; Nguyen, S. T.; Schatz, G. C.; Espinosa, H. D. Molecular-Level Engineering of Adhesion in Carbon Nanomaterial Interfaces. *Nano Lett.* **2015**, *15*, 4504–4516.

(41) Filleter, T.; Yockel, S.; Naraghi, M.; Paci, J. T.; Compton, O. C.; Mayes, M. L.; Nguyen, S. T.; Schatz, G. C.; Espinosa, H. D. Experimental-Computational Study of Shear Interactions within Double-Walled Carbon Nanotube Bundles. *Nano Lett.* **2012**, *12*, 732–742.

(42) Roenbeck, M. R.; Wei, X.; Beese, A. M.; Naraghi, M.; Furmanchuk, A.; Paci, J. T.; Schatz, G. C.; Espinosa, H. D. In Situ Scanning Electron Microscope Peeling to Quantify Surface Energy between Multiwalled Carbon Nanotubes and Graphene. *ACS Nano* **2014**, *8*, 124–138.

(43) Li, Q.; Dong, Y.; Perez, D.; Martini, A.; Carpick, R. W. Speed Dependence of Atomic Stick-Slip Friction in Optimally Matched Experiments and Molecular Dynamics Simulations. *Phys. Rev. Lett.* **2011**, *106*, 126101.

(44) Chenoweth, K.; Van Duin, A. C.; Goddard, W. A. ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. J. Phys. Chem. A **2008**, 112, 1040–1053.

(45) Devanathan, R.; Chase-Woods, D.; Shin, Y.; Gotthold, D. W. Molecular Dynamics Simulations Reveal That Water Diffusion between Graphene Oxide Layers Is Slow. *Sci. Rep.* **2016**, *6*, 29484.

(46) Medhekar, N. V.; Ramasubramaniam, A.; Ruoff, R. S.; Shenoy, V. B. Hydrogen Bond Networks in Graphene Oxide Composite Paper: Structure and Mechanical Properties. *ACS Nano* 2010, *4*, 2300–2306.
(47) Rezania, B.; Severin, N.; Talyzin, A. V.; Rabe, J. P. Hydration of

Bilayered Graphene Oxide. Nano Lett. 2014, 14, 3993-3998. (48) Heydari, G.; Tyrode, E.; Visnevskij, C.; Makuska, R.; Claesson,

 P. M. Temperature-Dependent Deicing Properties of Electrostatically Anchored Branched Brush Layers of Poly (Ethylene Oxide). *Langmuir* 2016, 32, 4194–4202.

(49) Cannara, R. J.; Eglin, M.; Carpick, R. W. Lateral Force Calibration in Atomic Force Microscopy: A New Lateral Force Calibration Method and General Guidelines for Optimization. *Rev. Sci. Instrum.* **2006**, *77*, 053701.

(50) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comput. Phys. **1995**, 117, 1–19.

(51) Humphrey, W.; Dalke, A.; Schulten, K. Vmd: Visual Molecular Dynamics. J. Mol. Graphics 1996, 14, 33–38.

(52) Park, S.; Khalili-Araghi, F.; Tajkhorshid, E.; Schulten, K. Free Energy Calculation from Steered Molecular Dynamics Simulations Using Jarzynski's Equality. *J. Chem. Phys.* **2003**, *119*, 3559–3566.