The Role of Intercalated Water in Multilayered Graphene Oxide

Muge Acik,† Cecilia Mattevi,‡,§ Cheng Gong,† Geunsk Lee,† Kyeongjae Cho,† Manish Chhowalla,‡,§ and Yves J. Chabal†, *

†Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States, and ‡Rutgers University, Materials Science and Engineering, Piscataway, New Jersey 08854, United States. §Present address: Department of Materials, Imperial College, London, U.K. SW7 2AZ.

Graphene oxide (GO) has been considered for a number of applications involving tunable optoelectronic properties through reduction in the form of thin films1 or as a bulk powder material2 for high capacity chemical storage applications.3 Graphite oxide is synthesized by strong acid/base treatments4–6 of graphite resulting in the incorporation of oxygen in many forms, such as out of plane epoxide and hydroxyl species, edge functionalization (carboxyls, carbonyls, hydroxyls) and in-plane structures (ether-like species),7 and can be further exfoliated into separate GO sheets.8–10 GO is a nonstoichiometric,11 highly hygroscopic34 compound that is electrically insulating. The key to some electronic applications with graphene oxide is therefore efficient reduction toward graphene.

Theoretical and experimental studies have focused on understanding the structure and chemistry of single layer GO, both in as-synthesized12 and reduced forms13 as well as the evolution of structure at different degrees of reduction.14,15 Thermal reduction of GO for instance has been shown to involve the removal of epoxide and hydroxyl groups by formation of H₂O, H₂, O₂ (oxygen elimination), and also CO and CO₂ (carbon elimination) thus creating defects in the form of etch holes within the graphene basal plane.16,17 There is however little understanding of the behavior of multiple GO sheets that are stacked together in the form of thin films or as bulk materials for various energy applications.18 The interactions along the c-axis perpendicular to the GO sheets in the multilayered material have been mostly ignored. The multilayered structure assembled from exfoliated GO sheets is different from that of graphite oxide in that there is little or no commensurate stacking among the layers.19 Thus interactions among layers in multilayered GO are not strictly defined by the π–π interactions as in graphite but are dominated by hydrogen bonding of functional groups and trapped molecules between the layers.20 More specifically, reference to the presence of water and to strong interactions between GO planes has been made,21 but little is known about the nature and role of water trapped within the ~1 nm22,23 spacing between the sheets at the interface, and the chemistry it can foster especially during the reduction process. Yet, control of 3D multilayered GO structures is important for a number of applications, including electrolytes within supercapacitors and hybrid capacitors24 and batteries (ionic transport),25 mechanical actuators26 that convert external stimuli such as thermal, light, electrical27,28 or chemical energy to mechanical energy.29 For instance, in electro-mechanical resonators, the actuation depends on the variation of humidity and/or temperature.30 In supercapacitors, the ion transport is controlled by the size of openings (i.e., holes in GO layers) as well as the

**ABSTRACT** A detailed in situ infrared spectroscopy analysis of single layer and multilayered graphene oxide (GO) thin films reveals that the normalized infrared absorption in the carbonyl region is substantially higher in multilayered GO upon mild annealing. These results highlight the fact that the reduction chemistry of multilayered GO is dramatically different from the single layer GO due to the presence of water molecules confined in the ~1 nm spacing between sheets. IR spectroscopy, XPS analysis, and DFT calculations all confirm that the water molecules play a significant role interacting with basal plane etch holes through passivation, via evolution of CO₂ leading to the formation of ketone and ester carbonyl groups. Displacement of water from intersheet spacing with alcohol significantly changes the chemistry of carbonyl formation with temperature.

**KEYWORDS:** graphene oxide · water chemistry · ketones · infrared spectroscopy · intercalation

*Address correspondence to chabal@utdallas.edu.

Received for review July 30, 2010 and accepted September 24, 2010.

Published online October 1, 2010.

10.1021/nn101844t © 2010 American Chemical Society

www.acsnano.org VOL. 4 • NO. 10 • 5861–5868 • 2010 5861
paper-like composites are controlled by network of intersheet spacing.\textsuperscript{31} Mechanical properties of GO (three-layer and multilayers) thin films in transmission are shown in Figure 1 and Supporting Information, respectively. Several distinct vibrational modes are shown in Figure 1 and Supporting Information, respectively. Although the initial spectra are similar, the intensity increase takes place at lower temperatures in multilayered GO (GO-ML) due to trapped water in interlayer nanospacings,\textsuperscript{35} as a result of a high hydroxyl concentration as well as stronger hydrogen bonding interactions between OH and other oxygen functionalities in close proximity.

The presence of \textit{physisorbed} water\textsuperscript{34} is observed on single layer GO (GO-1 L) surfaces, as evidenced by both OH stretching (ca. 3000–3500 cm\textsuperscript{-1}) and scissor (1600–1650 cm\textsuperscript{-1}) modes of H\textsubscript{2}O that are broadened through hydrogen interactions with C–OH (O–H stretch at 3000–3700 cm\textsuperscript{-1}) and COOH (OH stretch at ca. 3700 cm\textsuperscript{-1}) modes of various types of oxygen functionalities can be readily identified, namely, epoxides (C–O–C, 1280–1320 and \~{}850 cm\textsuperscript{-1}), edge carboxyl groups (COOH, 1650–1750 cm\textsuperscript{-1}) with C–OH modes at ca. 3000–3700 cm\textsuperscript{-1}, carbonyls (C=O and O–C=O, 1750–1850 and 1500–1750 cm\textsuperscript{-1}, respectively), and asymmetrical vibrational stretching of sp\textsuperscript{3}-hybridized C=C (1500–1600 cm\textsuperscript{-1}). These oxygen functionalities are common to all multilayered and single-layer GO films (Supporting Information, Figure S2) although the absolute intensities scale with the amount of material on the substrate. More specifically, various ketone and ester carboxyls are initially present as summarized in Supporting Information Table S1. With support from theoretical calculations, it is established that these chemical species have spectral contributions consisting of bending and stretching vibrational modes that overlap in \(\alpha\), \(\beta\), and \(\gamma\) regions highlighted in Figure 1.
These observations indicate that, for a given number of oxygen functionalities, a larger relative concentration of ketone and ester carbonyl derivatives (ca. 1500–1850 cm\(^{-1}\)) is produced in GO-ML than on GO-1 L. Correlated with these observations is an intensity loss of OH related vibrational modes.

Figure 3 quantifies the findings described above by showing the dependence of the integrated intensities of the H\(_2\)O and OH (C–OH, COOH) stretching modes (ca. 3000–3700 cm\(^{-1}\)) in Figure 3i and the normalized concentration of carbonyls (1100–1850 cm\(^{-1}\)) as a function of annealing temperatures in Figure 3ii. Figure 3i highlights the fact that a substantial amount of water is trapped between layers of multilayered GO and that there is a precipitous drop in water concentration at \(\sim 150 \, ^\circ\text{C}\). In contrast, single layer GO is characterized by OH stretch region primarily arising from carboxyls and hydroxyls with relatively insignificant contribution from physisorbed H\(_2\)O. Consequently, there is no sharp loss of OH stretch intensity at \(\sim 150 \, ^\circ\text{C}\) in GO-1 L.

In Figure 3ii, the integrated area associated with carbonyl formation is normalized to the total area of all oxygen functionalities prior to annealing. While there are marked variations in dipole moments, using this overall integrated area provides an excellent average measure of the total number of oxygen present in the sample and avoids uncertainties related to the degrees of surface coverage. The results clearly show that (1) the formation of carbonyls starts at lower temperatures (\(\sim 125 \, ^\circ\text{C}\)) in three-layered or multilayered GO than in single layer GO (\(\sim 150 \, ^\circ\text{C}\)), and (2) the amount of carbonyl formed is \(\sim 4\) times larger, for an identical initial oxy-
gen concentration (in all the functional forms), for GO-3 L than for GO-1 L (110% increase instead of 30% shown in Figure 3ii). A further proof for a larger carbonyl formation during annealing of multilayered GO is provided by XPS measurements. The deconvolution of the O 1s peak (Supporting Information, Figure S4a) at ca. 25–350 °C in multilayered GO shows an increase of C==O component along with a loss of C—O at 150–200 °C, which are larger than for GO-1 L (Supporting Information, Figure S4b). The effect of the presence of carbonyl groups on the total carbon to oxygen ratio in multilayered GO with respect to GO-1 L can be seen in Supporting Information, Figure S5. Taking into account the extra carbonyl groups, the carbon-to-oxygen ratio is calculated with (Supporting Information Figure S5a) and without (Supporting Information Figure S5b) C==O component as a function of annealing temperatures.

The role of confined water in altering the chemistry of multilayered GO upon mild annealing can be further elucidated by understanding the mechanisms of carbonyl formation at ~125 °C, which is accompanied by the evolution of CO2 (Supporting Information Figure S6a). The detection of CO2 molecules indicates the formation of defects in the graphene basal plane. Such defects occur in the form of holes and have been predicted by MD simulations and observed by high-resolution transmission electron microscopy. The mechanism for void formation by CO2 production is believed to be based on the reaction of dissociative oxygen (from the gas or water phase) with oxygen-
functionalized basal plane sites and possibly epoxide migration to the edges. It has also been proposed that carbon bonds below an epoxy group relax when aligned one dimensionally, resulting in the introduction of cracks upon reduction. Simultaneous decomposition of epoxides with carbonyl formation during annealing indicates that one source of basal plane defects is the epoxide removal (ring-opening), similar to the case of fullerenes via nucleophilic attack but can also exist intrinsic upon oxidation. In all proposed mechanisms, the presence of water molecules in close proximity to the reactants is essential for facilitating the reaction.

There are other mechanisms, such as edge interactions, which can lead to quinone-like carbonyl formation in both single and multilayered GO, as described in Supporting Information Figure S7. While these contribute to the process, they only contribute to a small fraction of the observed carbonyls.

To explain the large formation of these carbonyl species at ~175 °C, DFT calculations have been performed using a defective GO model with a localized etch hole, as illustrated in the lower left inset of Figure 4i. This model etch hole involves three carbon vacancies and is used to calculate how H$_2$O molecules can react with one or more dangling bonds, created via CO$_2$ production during the hole formation. The bottom of Figure 4 shows several possible reaction products with the formation energy associated with each reaction. One plausible path for carbonyl formation is an exothermic reaction lowering the energy of the system by 1.0 eV with a release of a H$_2$ shown in Figure 4iii that can happen when only one dangling bond exists. Another reaction path is through an exothermic reaction of a hydroxyl and C–H formation at two carbon dangling bonds which are formed reacting with a water molecule without a barrier and lower the energy by 3.9 eV as shown in Figure 4ii-a. Figure 4ii also shows a reaction process leading a carbonyl formation (Figure 4ii-e) with the same formation energy of 3.9 eV. This process has a small activation barrier (0.1 eV) and is likely to happen when more than one carbon dangling bond exist. The latter reaction path is the most likely route with the largest decrease in energy (3.9 eV), that is, leading to thermodynamically most stable products. These carbonyl groups subsequently react with residual epoxide groups which would migrate toward the etch hole, and such reactions will remove the carbonyl groups in the form of CO$_2$. Small activation barriers (0.1 and 0.129 eV) in Figure 4ii-a also confirm that hydroxyls and carbonyls are easily reversible at the etch holes. The fact that OH and C–O formation energies are the same indicates that these reactions are reversible and consistent.
with the commonly known keto-enol tautomerism.45 The incorporation of an oxygen in the basal plane through the C—O—C bond formation at two carbon dangling bond sites (resulting in cyclic ether formation along with a release of H2) is also energetically favorable (Figure 4iv) with a formation energy of 3.0 eV. The reaction energy calculations also show that a cyclic ether and a carbonyl can form in an etch hole when two H2O molecules react with two carbon dangling bonds releasing two H2 (Figure 4v) and the formation energy (3.8 eV) is reduced from the sum (1.0 eV + 3.0 eV) due to the repulsive coulomb interaction between the oxygen atoms.

To verify the role of water chemistry and the mechanism of ketone and ester carbonyl formation in multilayered GO, we sought to displace the water by alcohol intercalation in the nanoscopically confined space between the GO sheets.46 Intercalation of ethyl alcohol was achieved by immersion at room temperature for 4 days, as confirmed by an increase of interlayer spacing measured with XRD (Supporting Information, Figure S8). Spectroscopically, the IR data are consistent with the weakening of the H-bond network (less total hydrogen bonding, Supporting Information Figure S9) as a result of H-bond distortion once ethyl alcohol is introduced.

The behavior upon annealing is best described by the differential IR spectra of multilayered GO containing water with and without ethyl alcohol shown in Figures 5i,ii. The enhancement in C—O formation upon annealing can be readily observed in the multilayered GO in the presence of water, while no carbonyl formation is observed with ethyl alcohol (Figure 5ii), as a result of water displacement by alcohol. The absence of carbonyl formation in alcohol-intercalated multilayered GO is attributed to the lower intercalated water concentration,47 which minimizes the formation of etch holes and also the formation of carbonyls. The inactivity of intercalated alcohol upon annealing is shown in Supporting Information, Figure S9, where the integrated areas of OH stretch related modes do not change markedly over the 75—200 °C annealing range in sharp contrast to what is observed with water only (Figure 3i). The intercalation of alcohol therefore confirms the critical role played by water.

In summary, we have shown that intercalated water changes the entire interlayer chemistry in multilayered GO as compared with single layer GO. By using alcohol intercalation, we confirm that both defect (hole) formation and carbonyl formation is driven by intercalated water. First principles calculations further quantify the thermodynamic drive for carbonyl formation from water. The present work also suggests that multilayered GO is an interesting system to address issues related to water and other molecules in confined nanoscopic environments,48 and should therefore stimulate further studies, such as 2D-IR Echo spectroscopy,49 related to the role of confined molecules in carbon chemistry.

**EXPERIMENTAL METHODS**

**Sample Preparation.** GO was prepared using NaNO3 and KMnO4 in H2SO4 by the modified Hummers’ method.4 The GO thin films (1, 3, and 7 layers) were deposited from a suspension (0.18 mg/L) using amounts of 15, 45, and 105 mL and a vacuumfiltration method on a mixed cellulose ester membrane with 220 nm (Millipore). Further drying was performed for 12 h. Then the membrane was cut into sizes comparable to the substrate dimensions, slightly wetted with deionized water, and the upside was pressed against the substrate surface. The membrane with the GO film was allowed to dry and adhere to the substrate at room temperature under a 1 kg weight for 12 h. The weight was then removed and the membrane was dissolved using acetone without removing the GO films from the substrate. The samples...
were then immersed in pure acetone for 5 min at 60 °C. The samples were subsequently rinsed with methanol and dried with a nitrogen flow. The air-dried GO samples on each substrate were then characterized using Raman spectroscopy and AFM prior to annealing.22

The GO-ML samples were also prepared from a GO solution (0.18 mg/mL) taking in this case only 0.05 μL and drop casting this amount directly on clean SiO2/Si substrates. Intercalation of multilayered GO was studied after drying the samples on the substrate in air. Each sample was soaked into 40 mL of ethanol alcohol (95%, 190 proof, 5 v/v % of water) in a centrifuge tube and kept closed. The ethyl alcohol solution was replaced with a fresh alcohol solution every day without disturbance of GO thin film. After blowing with nitrogen, each intercalated sample on the substrate was directly transferred into the annealing chamber in less than a minute within a laboratory humidity content of 35–40% (dew point of 8.0–11.0) and kept in vacuum during annealing.

Analytical Characterization. All substrates (Si/SiO2, f=100, double-sided polished) were cleaned mechanically using ethyl acetate, ethyl alcohol and distilled water (18 MΩ, Millipore) and then chemically in piranha solution [a mixture of H2SO4 and H2O2 (2:1, v/v)] by heating at 90 °C for 20 min to remove the organic residues from the surface. Each sample was transferred on these clean surfaces either using membrane dissolution or direct drop-casting methods for thermal annealing.

Thermal annealing of GO samples on Si/SiO2 substrates supported between tantalum-made clips was performed in situ (in vacuum) in an annealing chamber placed in an IR sample compartment with IR beam aligned at Brewster’s angle of 70° for direct transmission. Therefore, no sample transfer was required between the spectrometer and the annealing chamber. Each temperature was monitored by a k-type thermocouple attached to the sample edge. The errors in each thermocouple reading calibrated using a pyrometer are systematic so that the relative measurements are accurate and reproducible. FTIR measurements for each specific temperature were performed at 60 °C within 5 min of annealing. The total annealing time per sample was ~18 h. The analysis of each sample was repeated twice to determine and quantify the reproducibility and consistency of the IR data.

UHV-XPS spectra were acquired in normal emission geometry using a conventional Mg X-ray source (hv = 1253.6 eV), pass energy at 20 eV, and with hemispherical electrostatic analyzer and a five channeltron detector.

Theoretical Methods. The DFT calculations were performed using the Vienna ab initio simulation package (VASP),29 where the projector-augmented wave (PAW) method within local density approximation (LDA) was employed.

In discussing the main experimental results, K.C. proposed the critical role of water molecules confined between graphene layers and stimulated the subsequent modeling and additional experiments that validated this prediction. J.Y.C., M.C. and K.C. directed and supervised the experimental and theoretical research, respectively.

Supporting Information Available: Supportive FTIR, XPS, XRD data and corresponding simulated IR frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


